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Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species

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Abstract. This article, the second in the series, presents kinetic and photochemical data evaluated by the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. It covers the gas phase and photochemical reactions of Organic species, which were last published in 1999, and were updated on the IUPAC website in late 2002, and subsequently during the preparation of this article. The article consists of a summary table of the recommended rate coefficients, containing the recommended kinetic parameters for the evaluated reactions, and eight appendices containing the data sheets, which provide information upon which the recommendations are made.

1 Introduction

In the mid 1970s it was appreciated that there was a need for the establishment of an international panel to produce a set of critically evaluated rate parameters for reactions of interest for atmospheric chemistry. To this end the CODATA Task Group on Chemical Kinetics, under the auspices of the International Council of Scientific Unions (ICSU), was constituted in 1977, and tasked to produce an evaluation of relevant, available kinetic and photochemical data. The first evaluation by this international committee was published in J. Phys. Chem. Ref. Data in 1980 (Baulch et al., 1980), followed by Supplements in 1982 (Baulch et al., 1982) and 1984 (Baulch et al., 1984). In 1986 the IUPAC Subcommittee on Data Evaluation superseded the original CODATA Task Group for Atmospheric Chemistry, and the Subcommittee has continued its data evaluation program with Supplements published in 1989 (Atkinson et al., 1989), 1992 (Atkinson et al., 1992), 1997 (Atkinson et al., 1997a), 1997 (Atkinson et al., 1997b), 1999 (Atkinson et al., 1999), and 2000 (Atkinson et al., 2000). Following the last of these reports, Supplement VIII (Atkinson et al., 2000), the evaluation has continued to be updated and published on the worldwide web (http://www.iupac-kinetic.ch.cam.ac.uk/). The IUPAC website hosts an interactive data base with a search facility and implemented hyperlinks between the summary table and the data sheets, both of which can be downloaded as individual PDF files. In order to further enhance the accessibility of this updated material to the scientific community, the evaluation is being published as a series of articles in *Atmospheric Chemistry and Physics*. This article is the second of the series, Volume II.

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2 Table of the summary of recommended rate coefficients for organic reactions

The ordering of families in the summary table of the recommended rate coefficients is O(^{3}P) and O(^{1}D) atom reactions, HO radical reactions, RO reactions, RO_2 reactions, O_3 reactions, halogen atom reactions and photochemical reactions. Reactions are numbered sequentially in each family. Chemical reactions are listed as first reactant (usually an atom or radical) + second reactant (usually a molecule). Each datasheet has a unique identifier: 'Volume: Appendix number: reaction number'. For example, the first reaction in the summary sheet below refers to Datasheet 'II.A1.1'.

reaction number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta \log k^a_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)/K^a$
O atom Reactions based on data sheets in Appendix A1							
1	O + CH_3 → products	1.3×10^{-10}		±0.1	1.3×10^{-10}	290–900	±100
2	O(^{1}D) + CH_4 → HO + CH_3	1.05×10^{-10}			1.05×10^{-10}	200–350	
	→ CH_3O or CH_2OH + H	3.45×10^{-11}			3.45×10^{-11}	200–350	
	→ HCHO + H_2	7.50×10^{-12}			7.50×10^{-12}	200–350	
	overall	1.50×10^{-10}		±0.10	1.50×10^{-10}	200–350	±100
HO Reactions based on data sheets in Appendix A2							
3	HO + CH_4 → H_2O + CH_3	6.4×10^{-15}		±0.08	$1.85 \times 10^{-12}\exp(-1690/T)$	200–300	±100
4	HO + C_2H_2 + M → C_2H_2OH + M	$5 \times 10^{-30}[N_2]$	(k_0)	±0.1	$5 \times 10^{-30}(T/300)^{-1.5}[N_2]$	300–800	Δn=±1.5
		1.0×10^{-12}	(k_∞)	±0.3			
		7.8×10^{-13}(1 bar air)		±0.15			
		$F_c = 0.37$					
5	HO + C_2H_4 + M → C_2H_4OH + M	$8.6 \times 10^{-29}[N_2]$	(k_0)	±0.3	$8.6 \times 10^{-29}(T/300)^{-3.1}[N_2]$	200–300	Δn=±2
		7.9×10^{-12}(1 bar air)		±0.1			
		9.0×10^{-12}	(k_∞)	±0.3	$9 \times 10^{-12}(T/300)^{-0.85}$	100–500	Δn=±0.3
		$F_c = 0.48$					
6	HO + C_2H_6 → H_2O + C_2H_5	2.4×10^{-13}		±0.08	$6.9 \times 10^{-12}\exp(-1000/T)$	200–300	±100
7	HO + C_3H_6 + M → C_3H_6OH + M	$8 \times 10^{-27}[N_2]$	(k_0)	±0.5	$8 \times 10^{-27}(T/300)^{-3.5}[N_2]$	200–300	Δn=±1
		2.9×10^{-11} (1 bar air)		±0.1			
		3.0×10^{-11}	(k_∞)	±0.1	$3.0 \times 10^{-11}(T/300)^{-1}$	200–300	Δn=±1
		$F_c = 0.5$					
8	HO + C_3H_8 → H_2O + C_3H_7	1.1×10^{-12}		±0.08	$7.6 \times 10^{-12}\exp(-585/T)$	200–300	±100
9	HO + $CH_3CH_2CH_2CH_3$ → products	2.3×10^{-12}		±0.10	$9.1 \times 10^{-12}\exp(-405/T)$	230–300	±150
10	HO + CH_2=C(CH_3)CH=CH_2 (isoprene) → products	1.0×10^{-10}		±0.10	$2.7 \times 10^{-11}\exp(390/T)$	240–430	±100
11	HO + α-Pinene → products	5.3×10^{-11}		± 0.15	$1.2 \times 10^{-11}\exp(440/T)$	290–430	±200
12	HO + CO → H + CO_2	$1.44 \times 10^{-13}(1 + [N_2]/4.2 \times 10^{19}$ molecule cm^{-3})		±0.05	1.3×10^{-13}(1 + 0.6 P/bar)	200–300	Δ log k±0.2
	HO + CO + M → HOCO + M	see data sheeet for OH + CO + M					
13	HO + HCHO → H_2O + HCO	8.5×10^{-12}		±0.08	$5.4 \times 10^{-12}\exp(135/T)$	200–300	±100
14	HO + CH_3CHO → H_2O + CH_3CO	1.5×10^{-11}		±0.08	$4.4 \times 10^{-12}\exp(365/T)$	200–350	±100
15	HO + C_2H_5CHO → products	2.0×10^{-11}		±0.1	$5.1 \times 10^{-12}\exp(405/T)$	240–380	±200
16	HO + $CH_3CH_2CH_2CHO$ → products	2.4×10^{-11}		±0.1	$6.0 \times 10^{-12}\exp(410/T)$	250–430	±250
17	HO + CH_2=C(CH_3)CHO → products	2.9×10^{-11}		±0.10	$8.0 \times 10^{-12}\exp(380/T)$	230–380	±200
18	HO + Pinonaldehyde → products	4.2×10^{-11}		±0.25			
19	HO + $(CHO)_2$ → H_2O +CH(O)CO	1.1×10^{-11}		±0.3			
20	HO + $HOCH_2CHO$ → H_2O +$HOCH_2CO$	8.8×10^{-12}		±0.15			
	→ H_2O +HOCHCHO	2.2×10^{-12}					
	overall	1.1×10^{-11}		±0.15			
21	HO + $CH_3C(O)CHO$ → H_2O + $CH_3C(O)CO$	1.5×10^{-11}		±0.2			
22	HO + $CH_3C(O)CH_3$ → H_2O + $CH_2C(O)CH_3$	1.8×10^{-13}		±0.08	$8.8 \times 10^{-12}\exp(-1320/T)$ + $1.7 \times 10^{-14}\exp(423/T)$	195–440	Δlog k = ±0.08
23	HO + $CH_3C(O)CH_2CH_3$ → products	1.2×10^{-12}		±0.15	$1.3 \times 10^{-12}\exp(-25/T)$	240–300	±200
24	HO + CH_2=CHC(O)CH_3 → products	2.0×10^{-11}		±0.10	$2.6 \times 10^{-12}\exp(610/T)$	230–380	±200
25	HO + CH_3OH → H_2O + CH_2OH	7.65×10^{-13}					
	→ H_2O + CH_3O	1.35×10^{-13}					
	overall	9.0×10^{-13}		±0.08	$2.85 \times 10^{-12}\exp(-345/T)$	210–300	±150
26	HO + C_2H_5OH → H_2O + CH_2CH_2OH	1.6×10^{-13}					
	→ H_2O + CH_3CHOH	2.9×10^{-12}					
	→ H_2O + CH_3CH_2O	1.6×10^{-13}					
	overall	3.2×10^{-12}		±0.08	$3.0 \times 10^{-12}\exp(20/T)$	210–300	±150

reaction number	Reaction	k_{298} cm^3 $molecule^{-1}$ s^{-1}	$\Delta\log k_{298}^a$	Temp. dependence of k/cm^3 $molecule^{-1}$ s^{-1}	Temp. range/K	$\Delta(E/R)/K^a$
27	$HO + CH_3CH_2CH_2OH \rightarrow$ products	5.8×10^{-12}	±0.10	$4.6 \times 10^{-12}\exp(70/T)$	260–380	±100
28	$HO + CH_3CH(OH)CH_3 \rightarrow$ products	5.1×10^{-12}	±0.08	$2.6 \times 10^{-12}\exp(200/T)$	250–360	±100
29	$HO + CH_3CH_2CH_2CH_2OH \rightarrow$ products	8.5×10^{-12}	±0.15	$5.3 \times 10^{-12}\exp(140/T)$	260–380	±200
30	$HO + CH_3CH(OH)CH_2CH_3 \rightarrow$ products	8.7×10^{-12}	±0.15			
31	$HO + (CH_3)_2C(OH)CH{=}CH_2 \rightarrow$ products	6.4×10^{-11}	± 0.15	$8.2 \times 10^{-12}\exp(610/T)$	230–300	± 200
32	$HO + CH_3OCH_3 \rightarrow H_2O + CH_3OCH_2$	2.8×10^{-12}	±0.08	$5.7 \times 10^{-12}\exp(-215/T)$	230–300	±100
33	HO + 3-methylfuran → products	9.3×10^{-11}	±0.3			
34	$HO + CH_3C(O)CH_2OH \rightarrow$ products	3.0×10^{-12}	±0.15			
35	$HO + (CH_3)_2C(OH)CHO \rightarrow$ products	1.5×10^{-11}	± 0.3			
36	$HO + CH_3OOH \rightarrow H_2O + CH_2OOH$	1.9×10^{-12}				
	$\rightarrow H_2O + CH_3OO$	3.6×10^{-12}				
	overall	5.5×10^{-12}	±0.2	$2.9 \times 10^{-12}\exp(190/T)$	220–430	± 150
37	$HO + HC(O)OH \rightarrow$ products	4.5×10^{-13}	± 0.15	4.5×10^{-13}	290–450	±250
38	$HO + CH_3C(O)OH \rightarrow$ products	7.4×10^{-13}	±0.15	$4.2 \times 10^{-14}\exp(855/T)$	220-300	± 400
39	$HO + C_2H_5C(O)OH \rightarrow$ products	1.2×10^{-12}	±0.2	1.2×10^{-12}	290–450	± 300
40	$HO + CH_3ONO_2 \rightarrow$ products	2.3×10^{-14}	$^{+0.5}_{-0.2}$	$4.0 \times 10^{-13}\exp(-845/T)$	220–300	±400
41	$HO + C_2H_5ONO_2 \rightarrow$ products	1.8×10^{-13}	±0.3	$6.7 \times 10^{-13}\exp(-395/T)$	230–300	±400
42	$HO + 1\text{-}C_3H_7ONO_2 \rightarrow$ products	5.8×10^{-13}(1 bar air)	±0.3			
43	$HO + 2\text{-}C_3H_7ONO_2 \rightarrow$ products	2.9×10^{-13}	±0.2	$6.2 \times 10^{-13}\exp(-230/T)$	230–300	±300
44	$HO + 1\text{-}C_4H_9ONO_2 \rightarrow$ products	1.6×10^{-12}	±0.2			
45	$HO + 2\text{-}C_4H_9ONO_2 \rightarrow$ products	8.6×10^{-13}	±0.3			
46	$HO + CH_3C(O)OONO_2 \rightarrow$ products	$<3 \times 10^{-14}$				
47	$HO + CH_3C(O)CH_2ONO_2 \rightarrow$ products	$<1 \times 10^{-12}$				
48	$HO + CH_3CH_2C(O)CH_2ONO_2 \rightarrow$ products	8.2×10^{-13}	±0.3			
49	$HO + CH_3CH(ONO_2)C(O)CH_3 \rightarrow$ products	1.2×10^{-12}	±0.3			
50	$HO + CH_2{=}C(CH_3)C(O)OONO_2 \rightarrow$ products	2.9×10^{-11}	$^{+0.2}_{-0.5}$			
51	$HO + HCN \rightarrow$ products	3.0×10^{-14} (1 bar)	±0.5	$1.2 \times 10^{-13}(-400/T)$ (1 bar)	290–440	± 300
52	$HO + CH_3CN \rightarrow$ products	2.2×10^{-14} (1 bar)	±0.15	$8.1 \times 10^{-13}(-1080/T)$	250–390	±200
HO_2 Reactions – based on data sheets in Appendix A2a						
53	$HO_2 + CH_3O_2 \rightarrow O_2 + CH_3OOH$	5.2×10^{-12}	± 0.3	$3.8 \times 10^{-13}\exp(780/T)$	225–580	± 500
54	$HO_2 + HOCH_2O_2 \rightarrow O_2 + HOCH_2OOH$					
	$\rightarrow O_2 + HCOOH + H_2O$					
	overall	1.2×10^{-11}	± 0.3	$5.6 \times 10^{-15}\exp(2300/T)$	275–335	± 1500
55	$HO_2 + C_2H_5O_2 \rightarrow O_2 + C_2H_5OOH$	7.8×10^{-12}	±0.2	$3.8 \times 10^{-13}\exp(900/T)$	200–500	± 400
56	$HO_2 + CH_3CO_3 \rightarrow O_2 + CH_3C(O)OOH$	1.1×10^{-11}				
	$\rightarrow O_3 + CH_3C(O)OH$	2.8×10^{-12}				
	overall	1.4×10^{-11}	±0.3	$5.2 \times 10^{-13}\exp(980/T)$	250–400	± 500
57	$HO_2 + HOCH_2CH_2O_2 \rightarrow$ products	1.2×10^{-11}	± 0.3			
58	$HO_2 + CH_3OCH_2O_2$	See data sheet				
	$\rightarrow O_2 + CH_3OCH_2OOH$					
	$\rightarrow O_2 + CH_3OCHO + H_2O$					
59	$HO_2 + CH_3COCH_2O_2$					
	$\rightarrow O_2 + CH_3COCH_2OOH$	9.0×10^{-12}	± 0.3			
60	$HO_2 + HCHO \rightarrow HOCH_2OO$	7.9×10^{-14}	± 0.3	$9.7 \times 10^{-15}\exp(625/T)$	275–333	± 600
61	$HOCH_2OO \rightarrow HO_2 + HCHO$	1.5×10^{2} (k/s^{-1})	± 0.3	$2.4 \times 10^{12}\exp(-7000/T)$	275–330	± 2000
NO_3 Reactions – based on data sheets in Appendix A3						
62	$NO_3 + CH_4 \rightarrow HNO_3 + CH_3$	$<1 \times 10^{-18}$				
63	$NO_3 + C_2H_2 \rightarrow$ products	$<1 \times 10^{-16}$				
64	$NO_3 + C_2H_4 \rightarrow$ products	2.1×10^{-16}	± 0.2	$3.3 \times 10^{-12}\exp(-2880/T)$	270–340	± 500
65	$NO_3 + C_2H_6 \rightarrow HNO_3 + C_2H_5$	$<1 \times 10^{-17}$				
66	$NO_3 + C_3H_6 \rightarrow$ products	9.5×10^{-15}	± 0.2	$4.6 \times 10^{-13}\exp(-1155/T)$	290–430	± 300
67	$NO_3 + C_3H_8 \rightarrow HNO_3 + C_3H_7$	$<7 \times 10^{-17}$				
68	$NO_3 + n\text{-}C_4H_{10} \rightarrow$ products	4.6×10^{-17}	± 0.2	$2.8 \times 10^{-12}\exp(-3280/T)$	290–430	± 400
69	$NO_3 + CH_2{=}C(CH_3)CH{=}CH_2$(isoprene) → products	7.0×10^{-13}	± 0.2	$3.15 \times 10^{-12}\exp(-450/T)$	250–390	± 200
70	$NO_3 + \alpha$-Pinene → products	6.2×10^{-12}	± 0.1	$1.2 \times 10^{-12}\exp(490/T)$	260–390	± 300
71	$NO_3 + HCHO \rightarrow HNO_3 + HCO$	5.6×10^{-16}	± 0.3			
72	$NO_3 + CH_3CHO \rightarrow HNO_3 + CH_3CO$	2.7×10^{-15}	± 0.2	$1.4 \times 10^{-12}\exp(-1860/T)$	260–380	± 500
73	$NO_3 + C_2H_5CHO \rightarrow$ products	6.4×10^{-15}	± 0.2			
74	$NO_3 + C_3H_7CHO \rightarrow$ products	1.1×10^{-14}	± 0.15	$1.7 \times 10^{-12}\exp(-1500/T)$	260–340	± 500
75	$NO_3 + CH_2{=}C(CH_3)CHO \rightarrow$ products	3.4×10^{-15}	± 0.15			

reaction number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}^a$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
76	$NO_3 + CH_3C(O)CH{=}CH_2 \rightarrow$ products	$<6.0 \times 10^{-16}$					
77	NO_3 + Pinonaldehyde → products	2.0×10^{-14}		± 0.25			
78	$NO_3 + CH_3C(O)CH_3 \rightarrow HNO_3 + CH_3COCH_2$	$<3 \times 10^{-17}$					
79	NO_3 + 3-methylfuran → products	1.9×10^{-11}		± 0.5			
80	$NO_3 + CH_2{=}C(CH_3)C(O)OONO_2 \rightarrow$ products	1.6×10^{-16}		± 0.7			
81	$NO_3 + CH_3OH \rightarrow$ products	1.3×10^{-16}		± 0.5	$9.4 \times 10^{-13}\exp(-2650/T)$	250–370	± 700
82	$NO_3 + C_2H_5OH \rightarrow$ products	$<2 \times 10^{-15}$					
83	$NO_3 + CH_3CH(OH)CH_3 \rightarrow$ products	1.4×10^{-15}		± 0.3			
84	$NO_3 + CH_3CH(OH)CH_2CH_3 \rightarrow$ products	2.0×10^{-15}		±0.3			
85	$NO_3 + (CH_3)_2C(OH)CH{=}CH_2 \rightarrow$ products	1.2×10^{-14}		±0.2	$4.6 \times 10^{-14}\exp(-400)/T)$	260–400	± 200
Carbon Radical Reactions – based on data sheets in Appendix A4							
86	$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	$1.0 \times 10^{-30}[N_2]$	(k_0)	± 0.2	$1.0 \times 10^{-30}(T/300)^{-3.3}[N_2]$	200–300	$\Delta n = \pm 1$
		1.8×10^{-12}	(k_∞)	± 0.3	$1.8 \times 10^{-12}(T/300)^{1.1}$	200–300	$\Delta n = \pm 1$
		$F_c = 0.27$					
87	$CH_3 + O_3 \rightarrow$ products	2.3×10^{-12}		± 0.3	$4.7 \times 10^{-12}\exp(-210/T)$	240–400	± 200
88	$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$	3.8×10^{-15}	(1 bar air)	± 0.5			
		1.9×10^{-14}	(0.133 bar air)	± 0.5			
89	$C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$	$5.9 \times 10^{-29}[N_2]$	(k_0)	± 0.3	$5.9 \times 10^{-29}(T/300)^{-3.8}[N_2]$	200–300	$\Delta n = \pm 1$
		7.8×10^{-12}	(k_∞)	± 0.2	7.8×10^{-12}	200–300	
					$F_c = 0.58\exp(-T/1250)$	200–300	
					$+ 0.42\exp(-T/183)$	200–300	
90	$n\text{-}C_3H_7 + O_2 + M \rightarrow n\text{-}C_3H_7O_2 + M$	8.0×10^{-12}	(k_∞)	± 0.2	8.0×10^{-12}	200–300	
91	$i\text{-}C_3H_7 + O_2 + M \rightarrow i\text{-}C_3H_7O_2 + M$	1.1×10^{-11}	(k_∞)	± 0.3	1.1×10^{-11}	200–300	
92	$1\text{-}C_4H_9 + O_2 + M \rightarrow 1\text{-}C_4H_9O_2 + M$	7.5×10^{-12}	(k_∞)	± 0.5			
93	$2\text{-}C_4H_9 + O_2 + M \rightarrow 2\text{-}C_4H_9O_2 + M$	1.7×10^{-11}	(k_∞)	± 0.5			
94	$CH_3C(O)CH_2 + O_2 + M \rightarrow CH_3C(O)CH_2O_2 + M$	1.5×10^{-12}	(k_∞)	±0.5			
95	$HCO + O_2 \rightarrow CO + HO_2$	5.1×10^{-12}		±0.15	5.1×10^{-12}	200–300	
96	$CH_3CO + O_2 + M \rightarrow CH_3C(O)O_2 + M$	5.1×10^{-12}	(k_∞)	±0.2	5.1×10^{-12}	220–300	
97	$CH_2OH + O_2 \rightarrow HCHO + HO_2$	9.7×10^{-12}		±0.12			
98	$CH_3CHOH + O_2 \rightarrow CH_3CHO + HO_2$	1.9×10^{-11}		±0.3			
99	$CH_2CH_2OH + O_2 \rightarrow$ products	3.0×10^{-12}		±0.3			
RO Radical Reactions – based on data sheets in Appendix A5							
100	$CH_3O + O_2 \rightarrow HCHO + HO_2$	1.9×10^{-15}		±0.2	$7.2 \times 10^{-14}\exp(-1080/T)$	290–610	±300
101	$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$	8.1×10^{-15}		±0.2	$2.4 \times 10^{-14}\exp(-325/T)$	295–355	±300
102	$1\text{-}C_3H_7O + O_2 \rightarrow C_2H_5CHO + HO_2$	1.0×10^{-14}		±0.2	$2.6 \times 10^{-14}\exp(-253/T)$	220–380	±500
103	$2\text{-}C_3H_7O + O_2 \rightarrow CH_3COCH_3 + HO_2$	7.0×10^{-15}		±0.2	$1.5 \times 10^{-14}\exp(-230/T)$	210–390	±200
104	$CH_3CH_2CH_2CH_2O + O_2 \rightarrow CH_3\ CH_2\ CH_2CHO + HO_2$	1.4×10^{-14}		±0.3	$8.9 \times 10^{-14}\exp(-550/T)$	270-340	± 300
105	$CH_3CH_2CH_2CH_2O + M \rightarrow CH_2CH_2CH_2CH_2OH + M$	2.9×10^{5}	(s^{-1})(1 bar)	±0.2	$4.6 \times 10^{10}\exp(-3570/T)$(1 bar)	250–350	± 300
106	$CH_3OCH_2O + O_2 \rightarrow CH_3OCHO + HO_2$	see data sheet					
	$CH_3OCH_2O + M \rightarrow CH_3OCHO + H + M$	for CH_3OCH_2O radical					
107	$CH_3C(O)CH_2O + O_2 \rightarrow CH_3C(O)CHO + HO_2$	see data sheet					
	$CH_3C(O)CH_2O + M \rightarrow CH_3CO + HCHO + M$	for $CH_3C(O)CH_2O$ radical					
108	$CH_3CH(O)CH_2CH_3 + O_2 \rightarrow CH_3C(O)CH_2CH_3 + HO_2$	7.6×10^{-15}		± 0.3	$1.5 \times 10^{-14}\ \exp(-200/T)$	250-350	± 300
109	$CH_3CH(O)CH_2CH_3 + M \rightarrow CH_3CHO + C_2H_5 + M$	2.0×10^{4}	(s^{-1})(1bar)	±0.3	$7.2 \times 10^{12}\exp(-5780/T)$(1 bar)	240–340	±500
110	$CH_3O + NO + M \rightarrow CH_3ONO + M$	$2.6 \times 10^{-29}[N_2]$	(k_0)	±0.1	$2.6 \times 10^{-29}(T/300)^{-2.8}[N_2]$	200–400	$\Delta n = \pm 0.5$
		3.3×10^{-11}	(k_∞)	±0.5	$3.3 \times 10^{-11}(T/300)^{-0.6}$	200–400	$\Delta n = \pm 0.5$
					$F_c = \exp(-T/900)$		
	$CH_3O + NO \rightarrow HCHO + HNO$	see data sheet					
111	$C_2H_5O + NO + M \rightarrow C_2H_5ONO + M$	$2.2 \times 10^{-28}[N_2]$	(k_0)	± 0.3			
		4.4×10^{-11}	(k_∞)	± 0.3	4.4×10^{-11}	200–400	
		$F_c{=}0.6$					
	$C_2H_5O + NO \rightarrow CH_3CHO + HNO$	see data sheet					
112	$n\text{-}C_3H_7O + NO + M \rightarrow n\text{-}C_3H_7ONO + M$	3.8×10^{-11}	(k_∞)	± 0.3			
113	$i\text{-}C_3H_7O + NO + M \rightarrow i\text{-}C_3H_7ONO + M$	3.4×10^{-11}	(k_∞)	± 0.3			
114	$(CH_3)_3CO + NO + M \rightarrow (CH_3)_3CONO + M$	2.6×10^{-11}		± 0.3	$2.6 \times 10^{-11}(T/300)^{-1.4}$	200–400	$\Delta n = \pm 0.5$
115	$2\text{-}C_4H_9O + NO + M \rightarrow 2\text{-}C_4H_9ONO + M$	2.5×10^{-11}		± 0.5			
116	$CH_3O + NO_2 + M \rightarrow CH_3ONO_2 + M$	$8.1 \times 10^{-29}[N_2]$	(k_0)	± 0.3	$8.1 \times 10^{-29}(T/300)^{-4.5}[N_2]$	200–400	$\Delta n = \pm 1$
		2.1×10^{-11}	(k_∞)	± 0.3	2.1×10^{-11}	200–400	$\Delta n = \pm 0.5$
		$F_c{=}0.44$					
	$CH_3O + NO_2 \rightarrow HCHO + HONO$	see data sheet					
117	$C_2H_5O + NO_2 + M \rightarrow C_2H_5ONO_2 + M$	2.8×10^{-11}	(k_∞)	± 0.3	2.8×10^{-11}	200–300	$\Delta n = \pm 0.5$
	$C_2H_5O + NO_2 \rightarrow CH_3CHO + HONO$	see data sheet					
118	$1\text{-}C_3H_7O + NO_2 + M \rightarrow 1\text{-}C_3H_7ONO_2 + M$	3.6×10^{-11}	(k_∞)	±0.3			
119	$2\text{-}C_3H_7O + NO_2 + M \rightarrow 2\text{-}C_3H_7ONO_2 + M$	3.4×10^{-11}	(k_∞)	± 0.2	3.4×10^{-11}	200–300	

reaction number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}^a$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
RO_2 Reactions – based on data sheets in Appendix A6							
120	$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	7.7×10^{-12}		±0.05	$2.3 \times 10^{-12}\exp(360/T)$	200–430	± 100
121	$C_2H_5O_2 + NO \rightarrow$ products	9.2×10^{-12}		± 0.1	$2.6 \times 10^{-12}\exp(380/T)$	200–410	± 50
122	$HOCH_2CH_2O_2 + NO \rightarrow HOCH_2CH_2O + NO_2$	9×10^{-12}		± 0.5			
123	n-$C_3H_7O_2 + NO \rightarrow$ products	9.4×10^{-12}		± 0.2	$2.9 \times 10^{-12}\exp(350/T)$	200–410	± 100
124	i-$C_3H_7O_2 + NO \rightarrow$ products	9.0×10^{-12}		± 0.1	$2.7 \times 10^{-12}\exp(360/T)$	200–410	± 100
125	$CH_3C(O)CH_2O_2 + NO$ $\rightarrow CH_3C(O)CH_2O + NO_2$	8×10^{-12}		± 0.3			
126	$CH_3C(O)O_2 + NO \rightarrow CH_3C(O)O + NO_2$	2.0×10^{-11}		± 0.15	$7.5 \times 10^{-12}\exp(290/T)$	200–350	± 250
127	$C_2H_5C(O)O_2 + NO \rightarrow C_2H_5C(O)O + NO_2$	2.1×10^{-11}		± 0.15	$6.7 \times 10^{-12}\exp(340/T)$	220–410	± 200
128	$CH_3O_2 + NO_2 + M \rightarrow CH_3O_2NO_2 + M$	$2.5 \times 10^{-30}[N_2]$	(k_0)	±0.3	$2.5 \times 10^{-30}(T/300)^{-5.5}[N_2]$	250–350	Δn=± 1
		1.8×10^{-11}	(k_∞)	±0.3	1.8×10^{-11}	250–350	Δn=± 0.5
		F_c =0.36					
129	$CH_3O_2NO_2 + M \rightarrow CH_3O_2 + NO_2 + M$	$6.8 \times 10^{-19}[N_2]$	(k_0/s^{-1})	±0.3	$9 \times 10^{-5}\exp(-9690/T)[N_2]$	250–300	±500
		4.5	(k_∞/s^{-1})	±0.3	$1.1 \times 10^{16}\exp(-10560/T)$	250–300	±500
		F_c = 0.6					
130	$C_2H_5O_2 + NO_2 + M \rightarrow C_2\ H_5O_2NO_2 + M$	$1.3 \times 10^{-29}[N_2]$	(k_0)	±0.3	$1.3 \times 10^{-29}(T/300)^{-6.2}[N_2]$	200–300	Δn =± 1
		8.8×10^{-12}	(k_∞)	±0.3	8.8×10^{-12}	200–300	$\Delta\log k$=± 0.3
		F_c = 0.31					200–300
131	$C_2H_5O_2NO_2 + M \rightarrow C_2H_5O_2 + NO_2 + M$	$1.4 \times 10^{-17}[N_2]$	(k_0/s^{-1})	±0.5	$4.8 \times 10^{-4}\exp(-9285/T)[N_2]$	250–300	±1000
		5.4	(k_∞/s^{-1})	±0.5	$8.8 \times 10^{15}\exp(-10440/T)$	250–300	±1000
		F_c = 0.31					250–300
132	$CH_3C(O)O_2 + NO_2 + M \rightarrow CH_3C(O)O_2NO_2 + M$	$2.7 \times 10^{-28}[N_2]$	(k_0)	±0.4	$2.7 \times 10^{-28}(T/300)^{-7.1}[N_2]$	250–300	Δn =± 2
		1.2×10^{-11}	(k_∞)	±0.2	$1.2 \times 10^{-11}(T/300)^{-0.9}$	250–300	Δn =± 1
		F_c = 0.3					
133	$CH_3C(O)O_2NO_2 + M \rightarrow CH_3C(O)O_2 + NO_2 + M$	$1.1 \times 10^{-20}[N_2]$	(k_0/s^{-1})	±0.3	$4.9 \times 10^{-3}\exp(-12100/T)[N_2]$	300–330	±1000
		3.8×10^{-4}	(k_∞/s^{-1})	±0.3	$5.4 \times 10^{16}\exp(-13830/T)$	300–330	±300
		F_c = 0.3					
134	$C_2H_5C(O)O_2NO_2 + M \rightarrow C_2H_5C(O)O_2 + NO_2 + M$	$6.2 \times 10^{-20}[N_2]$	(k_0/s^{-1})	±0.5	$1.7 \times 10^{-3}\exp(-11280/T)[N_2]$	290–320	±2000
		4.0×10^{-4}	(k_∞/s^{-1})	±0.2	$8.3 \times 10^{16}\exp(-13940/T)$	290–320	±1000
		F_c = 0.36					
135	$CH_3C(O)CH_2O_2NO_2 + M \rightarrow$ $CH_3C(O)CH_2O_2 + NO_2 + M$		(k_∞/s^{-1})	± 0.3	$1.4 \times 10^{16}\exp(-10730/T)$(1 bar)	240–260	±200
136	$CH_2{=}C(CH_3)C(O)OONO_2 + M \rightarrow$ $CH_2{=}C(CH_3)C(O)OO + NO_2$	3.5×10^{-4}	(s^{-1})(1 bar)	±0.3	$1.6 \times 10^{16}\exp(-13500/T)$(1 bar)	290–330	±1000
137	$CH_3O_2 + NO_3 \rightarrow CH_3O + NO_2 + O_2$	1.3×10^{-12}		±0.3			
138	$C_2H_5O_2 + NO_3 \rightarrow C_2H_5O + NO_2 + O_2$	2.3×10^{-12}		±0.2			
139	$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2$						
	$\rightarrow 2\ CH_3O + O_2$	1.3×10^{-13}		±0.15	$7.4 \times 10^{-13}\exp(-520/T)$	220–330	±300
	$\rightarrow CH_3OOCH_3 + O_2$						
	overall	3.5×10^{-13}		± 0.12	$1.0 \times 10^{-13}\exp(365/T)$	200–400	±200
140	$CH_3O_2 + CH_3C(O)O_2$						
	$\rightarrow CH_3O + CH_3CO_2 + O_2$	9.9×10^{-12}					
	$\rightarrow CH_3COOH + HCHO + O_2$	1.1×10^{-12}					
	overall	1.1×10^{-11}		±0.15	$2.0 \times 10^{-12}\exp(500/T)$	200–350	± 250
141	$CH_3O_2 + CH_3C(O)CH_2O_2$						
	$\rightarrow CH_3OH + CH_3C(O)CHO + O_2$	1.9×10^{-12}					
	$\rightarrow HCHO + CH_3C(O)CH_2OH + O_2$	7.6×10^{-13}					
	$\rightarrow CH_3O + CH_3C(O)CH_2O + O_2$	1.1×10^{-12}					
	overall	3.8×10^{-12}		±0.3			
142	$HOCH_2O_2 + HOCH_2O_2$						
	$\rightarrow HC(O)OH + CH_2(OH)_2 + O_2$	7.0×10^{-13}		±0.3	$5.7 \times 10^{-14}\exp(750/T)$	270–330	±750
	$\rightarrow 2\ HOCH_2O + O_2$	5.5×10^{-12}		±0.3			
143	$C_2H_5O_2 + C_2H_5O_2 \rightarrow C_2H_5OH + CH_3CHO + O_2$	2.4×10^{-14}					
	$\rightarrow 2\ C_2H_5O + O_2$	4.0×10^{-14}					
	overall	6.4×10^{-14}		±0.12	6.4×10^{-14}	250–450	$^{+300}_{-100}$
144	$C_2H_5O_2 + CH_3C(O)O_2$						
	$\rightarrow C_2H_5O + CH_3C(O)O + O_2$						
	$\rightarrow CH_3CHO + CH_3C(O)OH + O_2$						
	overall	1.6×10^{-11}		±0.5	$4.4 \times 10^{-13}\exp(1070/T)$	220–440	±500
145	$CH_3OCH_2O_2 + CH_3OCH_2O_2$						
	$\rightarrow CH_3OCH_2OH + CH_3OCHO + O_2$						
	$\rightarrow 2\ CH_3OCH_2O + O_2$	1.4×10^{-12}					
	overall	2.1×10^{-12}		±0.3			

reaction number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}^a$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
146	$CH_3C(O)O_2 + CH_3C(O)O_2 \rightarrow 2\ CH_3C(O)O + O_2$	1.6×10^{-11}		±0.1	$2.9 \times 10^{-12}\ \exp(500/T)$	200–370	±200
147	$CH_3CO_3 + CH_3C(O)CH_2O_2$						
	$\rightarrow CH_3C(O)OH + CH_3C(O)CHO + O_2$						
	$\rightarrow CH_3CO_2 + CH_3C(O)CH_2O + O_2$	2.5×10^{-12}					
	overall	5.0×10^{-12}		±0.3			
148	$HOCH_2CH_2O_2 + HOCH_2CH_2O_2$						
	$\rightarrow HOCH_2CH_2OH + HOCH_2CHO + O_2$	1.1×10^{-12}					
	$\rightarrow 2\ HOCH_2CH_2O + O_2$	1.1×10^{-12}					
	overall	2.2×10^{-12}		±0.1	$7.8 \times 10^{-14}\exp(1000/T)$	250–450	±300
149	$n\text{-}C_3H_7O_2 + n\text{-}C_3H_7O_2 \rightarrow n\text{-}C_3H_7OH + C_2H_5CHO + O_2$						
	$\rightarrow 2\ n\text{-}C_3H_7O + O_2$						
	overall	3.0×10^{-13}		±0.5			
150	$i\text{-}C_3H_7O_2 + i\text{-}C_3H_7O_2 \rightarrow i\text{-}C_3H_7OH + CH_3C(O)CH_3 + O_2$	4.4×10^{-16}					
	$\rightarrow 2\ i\text{-}C_3H_7O + O_2$	5.6×10^{-16}					
	overall	1.0×10^{-15}		±0.3	$1.6 \times 10^{-12}\exp(-2200/T)$	300–400	±300
151	$CH_3C(O)CH_2O_2 + CH_3C(O)CH_2O_2$						
	$\rightarrow CH_3C(O)CH_2OH + CH_3C(O)CHO + O_2$	2.0×10^{-12}					
	$\rightarrow 2\ CH_3C(O)CH_2O + O_2$	6.0×10^{-12}					
	overall	8.0×10^{-12}		±0.3			
152	$RCHOO + O_3 \rightarrow RCHO + 2O_2$						
	$RCHOO + H_2O \rightarrow$ products						
	$RCHOO + CO \rightarrow$ products						
	$RCHOO + HCHO \rightarrow$ products						
	$RCHOO + C_2H_4 \rightarrow$ products	No recommendations					
	$RCHOO + NO \rightarrow RCHO + NO_2$	(see data sheet)					
	$RCHOO + NO_2 \rightarrow RCHO + NO_3$						
	$RCHOO + SO_2 \rightarrow$ products						
	$RCHOO + HC(O)OH \rightarrow$ products						
	$RCHOO + CH_3CHO \rightarrow$ secondary ozonide						
	$RCHOO \rightarrow$ products						
	$RRCOO \rightarrow$ products						
O_3 Reactions – based on data sheets in Appendix A1							
153	O_3 + alkene $\rightarrow$ HO + products	see data sheet					
154	$O_3 + C_2H_2 \rightarrow$ products	1.0×10^{-20}		±1.0			
155	$O_3 + C_2H_4 \rightarrow$ products	1.6×10^{-18}		±0.1	$9.1 \times 10^{-15}\exp(-2580/T)$	180–360	±100
156	$O_3 + C_3H_6 \rightarrow$ products	1.0×10^{-17}		±0.1	$5.5 \times 10^{-15}\exp(-1880/T)$	230–370	±200
157	$O_3 + CH_2{=}C(CH_3)CH{=}CH_2 \rightarrow$ products	1.27×10^{-17}		± 0.1	$1.03 \times 10^{-14}\exp(-1995/T)$	240–360	± 200
158	$O_3 + \alpha$-Pinene $\rightarrow$ products	9.0×10^{-17}		± 0.2	$6.3 \times 10^{-16}\ \exp\ (-580/T)$	270–370	± 300
159	$O_3 + CH_2{=}C(CH_3)CHO \rightarrow$ products	1.2×10^{-18}		±0.2	$1.4 \times 10^{-15}\exp(-2100/T)$	240–330	±300
160	$O_3 + CH_2{=}CHC(O)CH_3 \rightarrow$ products	5.2×10^{-18}		±0.2	$8.5 \times 10^{-16}\exp(-1520/T)$	240–330	±200
161	O_3 + 3-methylfuran $\rightarrow$ products	2.0×10^{-17}		±0.3			
162	$O_3 + CH_2{=}C(CH_3)C(O)OONO_2 \rightarrow$ products	8.2×10^{-18}		±0.3			
163	O_3 + Pinonaldehyde $\rightarrow$ products	$< 2 \times 10^{-20}$					
164	$O_3 + (CH_3)_2C(OH)CH{=}CH_2 \rightarrow$ products	1.0×10^{-17}		±0.2			
Halogen atom Reactions – based on data sheets in Appendix A7							
165	$F + CH_4 \rightarrow HF + CH_3$	6.3×10^{-11}		± 0.15	$1.3 \times 10^{-10}\exp(-215/T)$	180–410	±200
166	$Cl + CH_4 \rightarrow HCl + CH_3$	1.0×10^{-13}		± 0.06	$6.6 \times 10^{-12}\exp(-1240/T)$	200–300	±200
167	$Cl + C_2H_2 + M \rightarrow C_2H_2Cl + M$	$6.1 \times 10^{-30}[N_2]$	(k_0)	±0.3	$6.1 \times 10^{-30}(T/300)^{-3}[N_2]$	200–300	$\Delta n = \pm 1$
		2.0×10^{-10}	(k_∞)	±0.3	2.0×10^{-10}	200–400	$\Delta n = \pm 1$
		F_c=0.6					
168	$Cl + C_2H_4 + M \rightarrow C_2H_4Cl + M$	1.85×10^{-29}[air]	(k_0)	±0.5	$1.85 \times 10^{-29}(T/300)^{-3.3}$[air]	250–300	$\Delta n = \pm 1$
		6×10^{-10}[air]	(k_∞)	±0.3	6×10^{-10}	250–300	$\Delta n = \pm 1$
		F_c=0.4					
169	$Cl + C_2H_6 \rightarrow HCl + C_2H_5$	5.9×10^{-11}		±0.06	$8.3 \times 10^{-11}\exp(-100/T)$	220–600	±100
170	$Cl + C_3H_6 + M \rightarrow C_3H_6Cl + M$	$4.0 \times 10^{-28}[N_2]$	(k_0)	±0.5			
		2.8×10^{-10}	(k_∞)	±0.3			
171	$Cl + C_3H_8 \rightarrow HCl + C_3H_7$	1.4×10^{-10}		±0.06	1.4×10^{-10}	200–700	± 100
172	$Cl + n\text{-}C_4H_{10} \rightarrow HCl + C_4H_9$	2.05×10^{-10}		±0.06	2.05×10^{-10}	290–600	±100
173	$Cl + HCHO \rightarrow HCl + HCO$	7.2×10^{-11}		±0.06	$8.1 \times 10^{-11}\exp(-34/T)$	200–500	±100
174	$Cl + CH_3CHO \rightarrow HCl + CH_3CO$	8.0×10^{-11}		±0.07	8.0×10^{-11}	210–340	±300
175	$Cl + C_2H_5CHO \rightarrow$ products	1.3×10^{-10}		±0.2			
176	$Cl + CH_3C(O)CH_3 \rightarrow HCl + CH_3C(O)CH_2$	2.1×10^{-12}		±0.15	$3.2 \times 10^{-11}\exp(-815/T)$	215–300	±300
177	$Cl + CH_3C(O)C_2H_5 \rightarrow$ products	3.6×10^{-11}		±0.15			
178	$Cl + CH_3OH \rightarrow HCl + CH_2OH$	5.5×10^{-11}		±0.07	5.5×10^{-11}	200–500	±200
179	$Cl + C_2H_5OH \rightarrow$ products	1.0×10^{-10}		±0.08	$8.6 \times 10^{-11}\exp(45/T)$	295–600	±100

reaction number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta \log k_{298}^a$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
180	$Cl + n\text{-}C_3H_7OH \rightarrow$ products	1.6×10^{-10}		± 0.15	$2.5 \times 10^{-10}\exp(-130/T)$	270–350	± 100
181	$Cl + i\text{-}C_3H_7OH \rightarrow$ products	8.6×10^{-11}		± 0.1			
182	$Cl + CH_3OOH \rightarrow$ products	5.9×10^{-11}		± 0.5			
183	$Cl + HC(O)OH \rightarrow$ products	1.9×10^{-13}		± 0.15			
184	$Cl + CH_3C(O)OH \rightarrow$ products	2.65×10^{-14}		$\pm$ 0.2			
185	$Cl + CH_3ONO_2 \rightarrow$ products	2.4×10^{-13}		± 0.15			
186	$Cl + C_2H_5ONO_2 \rightarrow$ products	4.7×10^{-12}		± 0.2			
187	$Cl + n\text{-}C_3H_7ONO_2 \rightarrow$ products	2.2×10^{-11}		± 0.2			
188	$Cl + i\text{-}C_3H_7ONO_2 \rightarrow$ products	3.8×10^{-12}		± 0.3			
189	$Cl + 1\text{-}C_4H_9ONO_2 \rightarrow$ products	8.5×10^{-11}		± 0.3			
190	$Cl + CH_3C(O)OONO_2 \rightarrow$ products	$<2 \times 10^{-14}$					
191	$Cl + CH_3CN \rightarrow$ products	1.2×10^{-14}		± 0.3	$1.6 \times 10^{-11}\exp(-2140/T)$	270–350	± 300
192	$Br + C_2H_2 \rightarrow$ products	2.6×10^{-14}	(1 bar air)	± 0.2	$6.35 \times 10^{-15}\exp(440/T)$	230–300	$\pm$ 200
193	$Br + C_2H_4 \rightarrow$ products	1.3×10^{-13}	(1 bar air)	± 0.15	$2.80 \times 10^{-13}\exp(224/T)B/(B + 8.5 \times 10^{12}\exp(-3200/T))$ $B = 7.5 \times 10^{-12}[O_2]s^{-1}$	240–300	
194	$Br + C_3H_6 \rightarrow$ products	3.6×10^{-12}	(1 bar air)	± 0.2			
195	$Br + HCHO \rightarrow HBr + HCO$	1.1×10^{-12}		± 0.15	$7.7 \times 10^{-12}\exp(-580/T)$	220–300	± 200
196	$Br + CH_3CHO \rightarrow HBr + CH_3CO$	3.9×10^{-12}		± 0.2	$1.8 \times 10^{-11}\exp(-460/T)$	250–400	± 200

Data for the following Photochemical Reactions are based on data sheets in Appendix A8

197	$HCHO + h\nu \rightarrow$ products
198	$CH_3CHO + h\nu \rightarrow$ products
199	$C_2H_5CHO + h\nu \rightarrow$ products
200	pinonaldehyde^a + $h\nu \rightarrow$ products
201	$(CHO)_2 + h\nu \rightarrow$ products
202	$HOCH_2CHO + h\nu \rightarrow$ products
203	$CH_3C(O)CHO + h\nu \rightarrow$ products
204	$CH_3C(O)CH_3 + h\nu \rightarrow$ products
205	$CH_3C(O)C_2H_5 + h\nu \rightarrow$ products
206	$CH_2{=}C(CH_3)CHO + h\nu \rightarrow$ products
207	$CH_3C(O)CH{=}CH_2 + h\nu \rightarrow$ products
208	$n\text{-}C_3H_7CHO + h\nu \rightarrow$ products
209	$CH_3OOH + h\nu \rightarrow$ products
210	$HOCH_2OOH + h\nu \rightarrow$ products
211	$CH_3ONO_2 + h\nu \rightarrow$ products
212	$C_2H_5ONO_2 + h\nu \rightarrow$ products
213	$n\text{-}C_3H_7ONO_2 + h\nu \rightarrow$ products
214	$i\text{-}C_3H_7ONO_2 + h\nu \rightarrow$ products
215	$i\text{-}C_4H_9ONO_2 + h\nu \rightarrow$ products
216	$2\text{-}C_4H_9ONO_2 + h\nu \rightarrow$ products
217	$CH_3O_2NO_2 + h\nu \rightarrow$ products
218	$CH_3C(O)OONO_2 + h\nu \rightarrow$ products

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[a] The cited uncertainty is an expanded uncertainty corresponding approximately to a 95% confidence limit.

3 Guide to the data sheets

The data sheets are principally of two types: (i) those for individual thermal reactions and (ii) those for the individual photochemical reactions.

3.1 Thermal reactions

The data sheets begin with a statement of the reactions including all pathways which are considered feasible. This is followed by the corresponding enthalpy changes at 298 K, calculated from the enthalpies of formation summarized in the Thermodynamics Data summary.

The available kinetic data on the reactions are summarized under two headings: (i) Absolute Rate Coefficients, and (ii) Relative Rate Coefficients. Under these headings, we include new data which have been published since the last published IUPAC evaluation as well as the data used in deriving the preferred values. Under both of the headings above, the data are presented as absolute rate coefficients. If the temperature coefficient has been measured, the results are given in a temperature dependent form over a stated temperature range. For bimolecular reactions, the temperature dependence is usually expressed in the normal Arrhenius form, $k{=}A\ \exp(-B/T)$, where $B{=}E/R$. For a few bimolecular reactions, we have listed temperature dependences in the alternative form, $k{=}A'T^n$ or $CT^n\ \exp(-D/T)$, where the original authors have found this to give a better fit to the data. For pressure dependent combination and dissociation reactions, the non-Arrhenius temperature dependence is used. This is discussed more fully in a subsequent section of this Introduction.

Single temperature data are presented as such and wherever possible the rate coefficient at, or close to, 298 K is quoted directly as measured by the original authors. This means that the listed rate coefficient at 298 K may differ slightly from that calculated from the Arrhenius parameters determined by the same authors. Rate coefficients at 298 K marked with an asterisk indicate that the value was calculated by extrapolation of a measured temperature range which did not include 298 K. The tables of data are supplemented by a series of comments summarizing the experimental details. The following list of abbreviations, relating to experimental techniques, is used in the Techniques and Comments sections:

A – absorption
AS – absorption spectroscopy
CCD – charge coupled detector
CIMS – chemical ionization mass spectroscopy/spectrometric
CL – chemiluminescence
CRDS – cavity ring-down spectroscopy
DF – discharge flow
EPR – electron paramagnetic resonance
F – flow system
FP – flash photolysis
FTIR – Fourier transform infrared
FTS – Fourier transform spectroscopy
GC – gas chromatography/gas chromatographic
HPLC – high-performance liquid chromatography
IR – infrared
LIF – laser induced fluorescence
LMR – laser magnetic resonance
LP – laser photolysis
MM – molecular modulation
MS – mass spectrometry/mass spectrometric
P – steady state photolysis
PLP – pulsed laser photolysis
PR – pulse radiolysis
RA – resonance absorption
RF – resonance fluorescence
RR – relative rate
S – static system
TDLS – tunable diode laser spectroscopy
UV – ultraviolet
UVA – ultraviolet absorption
VUVA – vacuum ultraviolet absorption

For measurements of relative rate coefficients, wherever possible the comments contain the actual measured ratio of rate coefficients together with the rate coefficient of the reference reaction used to calculate the absolute rate coefficient listed in the data table. The absolute value of the rate coefficient given in the table may be different from that reported by the original author owing to a different choice of rate coefficient of the reference reaction. Whenever possible the reference rate data are those preferred in the present evaluation.

The preferred rate coefficients are presented (i) at a temperature of 298 K and (ii) in temperature dependent form over a stated temperature range. This is followed by a statement of the uncertainty limits in log k at 298 K and the uncertainty limits either in (E/R) or in n, for the mean temperature in the range. Some comments on the assignment of uncertainties are given later in this introduction.

The "Comments on Preferred Values" describe how the selection was made and give any other relevant information. The extent of the comments depends upon the present state of our knowledge of the particular reaction in question. The data sheets are concluded with a list of the relevant references.

3.2 Conventions concerning rate coefficients

All of the reactions in the table are elementary processes. Thus the rate expression is derived from a statement of the reaction, e.g.

$$\mathrm{A} + \mathrm{A} \rightarrow \mathrm{B} + \mathrm{C}$$

$$-\frac{1}{2}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = k[\mathrm{A}]^2.$$

Note that the stoichiometric coefficient for A, i.e. 2, appears in the denominator before the rate of change of [A] (which is equal to $2k[\mathrm{A}]^2$) and as a power on the right-hand side.

Representations of k as a function of temperature characterize simple "direct" bimolecular reactions. Sometimes it is found that k also depends on the pressure and the nature of the bath gas. This may be an indication of complex formation during the course of the bimolecular reaction, which is always the case in combination reactions. In the following sections the representations of k which are adopted in these cases are explained.

3.3 Treatment of combination and dissociation reactions

Unlike simple bimolecular reactions such as those considered in Sect. 1.2, combination reactions

$$\mathrm{A} + \mathrm{B} + \mathrm{M} \rightarrow \mathrm{AB} + \mathrm{M}$$

and the reverse dissociation reactions

$$\mathrm{AB} + \mathrm{M} \rightarrow \mathrm{A} + \mathrm{B} + \mathrm{M}$$

are composed of sequences of different types of physical and chemical elementary processes. Their rate coefficients reflect the more complicated sequential mechanism and depend on the temperature, T, and the nature and concentration of the third body, [M]. In this evaluation, the combination reactions are described by a formal second order rate law:

$$\frac{\mathrm{d}[\mathrm{AB}]}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{B}]$$

while dissociation reactions are described by a formal first-order rate law:

$$\frac{-\mathrm{d}[\mathrm{AB}]}{\mathrm{d}t} = k[\mathrm{AB}]$$

In both cases, k depends on the temperature and on [M].

In order to rationalize the representations of the rate coefficients used in this evaluation, we first consider the Lindemann-Hinshelwood reaction scheme. The combination reactions follow an elementary mechanism of the form,

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB}^* \quad (1)$$

$$\mathrm{AB}^* \rightarrow \mathrm{A} + \mathrm{B} \quad (\text{-}1)$$

$$\mathrm{AB}^* + \mathrm{M} \rightarrow \mathrm{AB} + \mathrm{M} \quad (2)$$

while the dissociation reactions are characterized by:

$$\mathrm{AB} + \mathrm{M} \rightarrow \mathrm{AB}^* + \mathrm{M} \quad (\text{-}2)$$

$$\mathrm{AB}^* + \mathrm{M} \rightarrow \mathrm{AB} + \mathrm{M} \quad (2)$$

$$\mathrm{AB}^* \rightarrow \mathrm{A} + \mathrm{B} \quad (\text{-}1)$$

Assuming quasi-stationary concentrations for the highly excited unstable species AB^* (i.e. that $\mathrm{d}[\mathrm{AB}^*]/\mathrm{d}t \sim 0$), it follows that the rate coefficient for the combination reaction is given by:

$$k = k_1 \left(\frac{k_2[\mathrm{M}]}{k_{-1} + k_2[\mathrm{M}]} \right)$$

while that for the dissociation reaction is given by:

$$k = k_{-2}[\mathrm{M}] \left(\frac{k_{-1}}{k_{-1} + k_2[\mathrm{M}]} \right)$$

In these equations the expressions before the parentheses represent the rate coefficients of the process initiating the reaction, whereas the expressions within the parentheses denote the fraction of reaction events which, after initiation, complete the reaction to products.

In the low pressure limit ([M]→0) the rate coefficients are proportional to [M]; in the high pressure limit ([M]→∞) they are independent of [M]. It is useful to express k in terms of the limiting low pressure and high pressure rate coefficients,

$$k_0 = \lim_{[\mathrm{M}] \rightarrow 0} k([\mathrm{M}]) \quad \text{and,} \quad k_\infty = \lim_{[\mathrm{M}] \rightarrow \infty} k([\mathrm{M}])$$

respectively. From this convention, the Lindemann-Hinshelwood equation is obtained

$$k = \frac{k_o k_\infty}{k_o + k_\infty}$$

It follows that for combination reactions, $k_0 = k_1 k_2[\mathrm{M}]/k_{-1}$ and $k_\infty = k_1$, while for dissociation reactions, $k_0 = k_{-2}[\mathrm{M}]$ and $k_\infty = k_{-1}k_{-2}/k_2$. Since detailed balancing applies, the ratio of the rate coefficients for combination and dissociation at a fixed T and [M] is given by the equilibrium constant $K_c = k_1 k_2/k_{-1}k_{-2}$.

Starting from the high-pressure limit, the rate coefficients fall-off with decreasing third body concentration [M] and the corresponding representation of k as a function of [M] is termed the "falloff curve" of the reaction. In practice, the above Lindemann-Hinshelwood expressions do not suffice to characterize the falloff curves completely. Because of the multistep character of the collisional deactivation (k_2[M]) and activation (k_{-2}[M]) processes, and energy- and angular momentum-dependencies of the association (k_1) and dissociation (k_{-1}) steps, as well as other phenomena, the falloff expressions have to be modified. This can be done by including a broadening factor F to the Lindemann-Hinshelwood expression (Troe, 1979):

$$k = \frac{k_o k_\infty}{k_o + k_\infty} F = k_o \left(\frac{1}{1 + \frac{k_o}{k_\infty}} \right) F = k_\infty \left(\frac{\frac{k_o}{k_\infty}}{1 + \frac{k_o}{k_\infty}} \right) F$$

The broadening factor F depends on the ratio k_0/k_∞, which is proportional to [M], and can be used as a measure of "reduced pressure". The first factors on the right-hand side represent the Lindemann-Hinshelwood expression and the additional broadening factor F, at not too high temperatures, is approximately given by (Troe, 1979):

$$\log F \cong \frac{\log F_c}{1 + [\log(k_0/k_\infty)/N]^2}$$

where log=$\log_{10}$ and N=[0.75$-$1.27 log F_c]. In this way the three quantities k_0, k_∞, and F_c characterise the falloff curve for the present application.

The given approximate expression for the broadening factor F was obtained from statistical unimolecular rate theory in its simplest form (Troe, 1979). More rigorous representations require detailed information on the potential energy surfaces and on the collisional energy transfer step of the reaction. If this information is not available, one may assume typical behaviour and rely on the theoretical analysis given by Cobos and Troe (2003). For T=200–300 K and the collider M=N_2 (with a collision efficiency $\beta_c \approx 0.3$), this treatment predicts $F_c \approx 0.49$, 0.44, 0.39, and 0.35, if the reactants A and B in total have r=3, 4, 5, or 6 rotational degrees of freedom, respectively (e.g. for the reaction HO+NO_2, one would have r=5 and hence $F_c \approx 0.39$). It is also predicted that F_c, for the present applications, should be nearly temperature independent. Finally, more rigorous expressions for the broadening factors F are given in Cobos and Troe (2003) which, in general do not differ from the above formula by more than about 10 percent. Since the special properties of each reaction system may lead to some deviations from the given values of F_c, these should only be used for a first orientation. Larger deviations of experimentally fitted F_c-values from the given "standard values", however, may be an indication for inadequate falloff extrapolations to k_0 and k_∞. In this case, the apparent values for F_c, k_0, and k_∞ obtained by fitting still can provide a satisfactory representation of the considered experimental data, in spite of the fact that inadequate values of k_0 and k_∞ are obtained by extrapolation.

If a given falloff curve is fitted in different ways, changes in F_c require changes in the limiting k_0 and k_∞ values. For the purpose of this evaluation, this is irrelevant if the preferred k_0 and k_∞ are used consistently together with the preferred F_c values. If the selected F_c value is too large, the values of k_0 and k_∞ obtained by fitting the falloff expression to the experimental data are underestimated. If F_c is too small, k_0 and k_∞ are overestimated. However uncertainties in F_c influence the fitted k_0 and k_∞ in different ways. A simpler policy of fitting falloff was chosen by the NASA/JPL panel (Sander et al., 2003) in putting F=0.6 and N=1. This generally leads to different values of the fitted k_0 and k_∞ and their temperature dependencies than derived here, although experimental data over the range of atmospheric interest can generally be reproduced equally well. However the derived k_0 and k_∞ may differ from the true limiting rate coefficients and thus should be interpreted by theory only with caution.

In the present evaluation, we generally follow the experimentally fitted values for F_c, k_0, and k_∞, provided F_c does not differ too much from the values given above. If large deviations are encountered, the experimental data are re-evaluated using the F_c-values given above.

Besides the energy-transfer mechanism, i.e. Reactions (1), (-1), and (2), a second mechanism appears to be relevant for some reactions considered here. This is the radical-complex (or chaperon) mechanism

$$\mathrm{A + M \rightarrow AM} \tag{3}$$

$$\mathrm{AM \rightarrow A + M} \tag{-3}$$

$$\mathrm{B + AM \rightarrow AB + M} \tag{4}$$

which, in the low pressure range, leads to

$$k_0 = (k_3/k_{-3})k_4[\mathrm{M}].$$

For some tri- and tetra-atomic adducts AB, this value of k_0 may exceed that from the energy-transfer mechanism and show stronger temperature dependencies. This mechanism may also influence high pressure experiments when k_0 from the radical-complex mechanism exceeds k_∞ from the energy-transfer mechanism (Oum et al., 2003). In this case falloff over wide pressure ranges cannot be represented by contributions from the energy-transfer mechanism alone, in particular when measurements at pressures above about 10 bar are taken into consideration.

The dependence of k_0 and k_∞ on the temperature T is represented in the form $k \propto T^{-n}$ except for cases with an established energy barrier in the potential. We have used this form of temperature dependence because it usually gives a better fit to the data over a wider range of temperature than does the Arrhenius expression. It should be emphasised that the chosen form of the temperature dependence is often only adequate over limited temperature ranges such as 200–300 K. Obviously, the relevant values of n are different for k_0 and k_∞. In this evaluation, values of k_0 are given for selected examples of third bodies M, and if possible for M=N_2, O_2 or air.

3.4 Treatment of complex-forming bimolecular reactions

Bimolecular reactions may follow the "direct" pathway

$$\mathrm{A + B \rightarrow C + D}$$

and/or involve complex formation,

$$\begin{array}{l} \mathrm{A + B \Leftrightarrow AB^* \rightarrow C + D} \\ \qquad\quad\ \downarrow \mathrm{M} \\ \qquad\quad\ \mathrm{AB} \end{array}$$

We designate the rate coefficients of the individual steps as in Sect. 1.3, above:

$$\mathrm{A + B \rightarrow AB^*} \tag{1}$$

$$\mathrm{AB^* \rightarrow A + B} \tag{-1}$$

$$AB^* + M \rightarrow AB + M \qquad (2)$$

$$AB^* \rightarrow C + D \qquad (3)$$

Assuming quasi-stationary concentrations of AB^* (i.e. $d[AB^*]/dt \sim 0$), a Lindemann-Hinshelwood type of analysis leads to,

$$\frac{d[AB]}{dt} = k_S[A][B]$$

$$\frac{d[C]}{dt} = k_D[A][B]$$

$$\frac{d[A]}{dt} = (k_S + k_D)[A][B]$$

where

$$k_S = k_1\left(\frac{k_2}{k_{-1} + k_2 + k_3}\right)$$

$$k_D = k_1\left(\frac{k_3}{k_{-1} + k_2 + k_3}\right)$$

Note that since k_2 is proportional to [M], k_S and k_D are dependent on the nature and concentration of the third body M, in addition to their temperature dependence. In reality, as for the combination and dissociation reactions, the given expressions for k_S and k_D have to be extended by suitable broadening factors F in order to account for the multistep character of process (2) and the energy dependencies of processes (1), (-1) and (3). These broadening factors, however, differ from those for combination and dissociation reactions. For simplicity, they are ignored in this evaluation such that k_D at high pressure approaches

$$k_D \rightarrow k_1 k_3 / k_2$$

which is inversely proportional to [M]. k_D may also be expressed by

$$k_D \approx k_{D0} k_S / k_{S0}$$

where k_{D0} and k_{S0} are the respective limiting low-pressure rate coefficients for the formation of C+D or A+B at the considered [M]. When it is established that complex-formation is involved, this equation is used to characterize the increasing suppression of C+D formation with increasing [M].

3.5 Photochemical reactions

The data sheets begin with a list of feasible primary photochemical transitions for wavelengths usually down to 170 nm, along with the corresponding enthalpy changes at 0 K where possible or alternatively at 298 K, calculated from the data in the Thermodynamic Data summary. Calculated threshold wavelengths corresponding to these enthalpy changes are also listed, bearing in mind that the values calculated from the enthalpy changes at 298 K are not true “threshold values”.

This is followed by tables which summarise the available experimental data for: (i) absorption cross-sections and (ii) quantum yields. These data are supplemented by a series of comments.

The next table lists the preferred absorption cross-section data and the preferred quantum yields at appropriate wavelength intervals. For absorption cross-sections the intervals are usually 1 nm, 5 nm or 10 nm. Any temperature dependence of the absorption cross-sections is also given where possible. The aim in presenting these preferred data is to provide a basis for calculating atmospheric photolysis rates. For absorption continua the temperature dependence is often represented by Sulzer-Wieland type expressions (Astholz et al., 1981). Alternately a simple empirical expression of the form: $\log_{10}(\sigma_{T1}/\sigma_{T2})=B(T_1 - T_2)$ is used.

The comments again describe how the preferred data were selected and include other relevant points. The photochemical data sheets are also concluded with a list of references.

3.6 Conventions concerning absorption cross-sections

These are presented in the data sheets as “absorption cross-sections per molecule, base e”. They are defined according to the equations:

$$I/I_0 = \exp(-\sigma[N]l),$$

$$\sigma = \{1/([N]l)\}\ln(I_0/I),$$

where I_0 and I are the incident and transmitted light intensities, σ is the absorption cross-section per molecule (expressed in this paper in units of cm^2), [N] is the number concentration of absorber (expressed in molecule cm^{-3}), and l is the path length (expressed in cm). Other definitions and units are frequently quoted. The closely related quantities “absorption coefficient” and “extinction coefficient” are often used, but care must be taken to avoid confusion in their definition. It is always necessary to know the units of concentration and of path length and the type of logarithm (base e or base 10) corresponding to the definition. To convert an absorption cross-section to the equivalent Naperian (base e) absorption coefficient (expressed in cm^{-1}) of a gas at a pressure of one standard atmosphere and temperature of 273 K, multiply the value of σ in cm^2 by 2.69×10^{19}.

3.7 Assignment of uncertainties

Under the heading “reliability,” estimates have been made of the absolute accuracies of the preferred values of k at 298 K and of the preferred values of E/R over the quoted temperature range. The accuracy of the preferred rate coefficient at 298 K is quoted as the term $\Delta\log k$, where $\Delta\log k = D$ and D is defined by the equation, $\log_{10} k = C \pm D$. This is equivalent to the statement that k is uncertain to a factor of F, where $D = \log_{10} F$. The accuracy of the preferred value of

E/R is quoted as the term $\Delta(E/R)$, where $\Delta(E/R)=G$ and G is defined by the equation $E/R=H\pm G$. D and G are expanded uncertainties corresponding approximately to a 95% confidence limit.

For second-order rate coefficients listed in this evaluation, an estimate of the uncertainty at any given temperature within the recommended temperature range may be obtained from the equation:

$$\Delta \log k(T) = \Delta \log k(298\,\mathrm{K}) + 0.4343\{\Delta E/R(1/T - 1/298)\}$$

The assignment of these absolute uncertainties in k and E/R is a subjective assessment of the evaluators. They are not determined by a rigorous, statistical analysis of the database, which is generally too limited to permit such an analysis. Rather, the uncertainties are based on a knowledge of the techniques, the difficulties of the experimental measurements, the potential for systematic errors, and the number of studies conducted and their agreement or lack thereof. Experience shows that for rate measurements of atomic and free radical reactions in the gas phase, the precision of the measurement, i.e. the reproducibility, is usually good. Thus, for single studies of a particular reaction involving one technique, standard deviations, or even 90% confidence limits, of ±10% or less are frequently reported in the literature. Unfortunately, when evaluators come to compare data for the same reaction studied by more than one group of investigators and involving different techniques, the rate coefficients often differ by a factor of 2 or even more. This can only mean that one or more of the studies has involved large systematic uncertainty which is difficult to detect. This is hardly surprising since, unlike molecular reactions, it is not always possible to study atomic and free radical reactions in isolation, and consequently mechanistic and other difficulties frequently arise.

The arbitrary assignment of uncertainties made here is based mainly on our state of knowledge of a particular reaction which is dependent upon factors such as the number of independent investigations carried out and the number of different techniques used. On the whole, our assessment of uncertainty limits tends towards the cautious side. Thus, in the case where a rate coefficient has been measured by a single investigation using one particular technique and is unconfirmed by independent work, we suggest that minimum uncertainty limits of a factor of 2 are appropriate.

In contrast to the usual situation for the rate coefficients of thermal reactions, where intercomparison of results of a number of independent studies permits a realistic assessment of reliability, for many photochemical processes there is a scarcity of apparently reliable data. Thus, we do not feel justified at present in assigning uncertainty limits to the parameters reported for the photochemical reactions.

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APPENDIX A1
Data Sheets for $O(^3P)$ and $O(^1D)$ atom, and O_3 reactions

APPENDIX A2
Data Sheets for HO and HO_2 radical reactions

APPENDIX A3
Data Sheets for NO_3 reactions

APPENDIX A4
Carbon radical reactions

APPENDIX A5
Data sheets for RO radical reactions

APPENDIX A6
Data Sheets for RO_2 reactions

APPENDIX A7
Halogen atom reactions

APPENDIX A8
Photochemical reactions

Appendix A1: O_x + VOC reactions

II.A1.1

$$\begin{aligned} \mathbf{O + CH_3} &\rightarrow \mathbf{HCHO + H} && \mathbf{(1)} \\ &\rightarrow \mathbf{HCO + H_2} && \mathbf{(2)} \\ &\rightarrow \mathbf{CO + H_2 + H} && \mathbf{(3)} \end{aligned}$$

$\Delta H°(1) = -286.2$ kJ·mol^{-1}
$\Delta H°(2) = -352.5$ kJ·mol^{-1}
$\Delta H°(3) = -288.1$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2+k_3)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.2 \pm 0.17) \times 10^{-10}$	1700–2300	Bhaskaran et al., 1979	SH-RA (a)
$(1.14 \pm 0.29) \times 10^{-10}$	295	Plumb and Ryan, 1982	DF-MS (b)
$(1.4 \pm 0.3) \times 10^{-10}$	294–900	Slagle et al., 1987	F-MS (c)
$k_1 = (1.1 \pm 0.4) \times 10^{-10}$	298	Zellner et al., 1988	LP-LIF (d)
$(1.3 \pm 0.2) \times 10^{-10}$	300	Oser et al., 1991	DF-MS (e)
$(9.4 \pm 3.0) \times 10^{-11}$	~298	Seakins and Leone, 1992	PLP-FTIR (f)
$(1.4 \pm 0.3) \times 10^{-10}$	1609–2002	Lim and Michael, 1993	SH-RA (g)
$(1.7 \pm 0.3) \times 10^{-10}$	299	Fockenberg et al., 1999	PLP-MS (h)
Branching Ratios			
$k_1/k > 0.85$	300	Niki et al., 1968	DF-MS (i)
$k_2/k \leq 0.2$	300	Hoyermann and Sievert, 1979	F-MS (j)
$k_1/k = 0.84 \pm 0.15$	299	Fockenberg et al., 1999	PLP-MS (h)
$k_3/k = 0.17 \pm 0.11$	299		
$k_3/k = 0.18 \pm 0.04$	296	Preses et al., 2000	PLP-IRA (k)

Comments

(a) Decomposition of C_2H_6-O_2 mixtures in a shock tube. k was derived from computer simulation of [O] and [H] profiles determined by RA.

(b) Discharge flow system with MS detection of O and CH_3, k was determined from the decay of [CH_3] with [O] $\gg$ [CH_3].

(c) Flow system with generation of CH_3 radicals and O(^{3}P) atoms from simultaneous in situ photolysis of $CH_3C(O)CH_3$ and SO_2, and determination of [CH_3] and [O] by photoionization MS. Experiments were performed under conditions such that [O]/[CH_3]>20, and rate coefficients were determined from the decay of CH_3 radicals. The rate coefficient k was found to be independent of pressure over the range 1.3 mbar to 15 mbar (1 Torr to 11 Torr), and its value was confirmed by measurement of the rate of formation of HCHO. HCO and CH_2 were not detected as products but the analytical system could not detect CO or H_2.

(d) Laser photolysis at 193 nm of flowing mixtures of N_2-N_2O-$(CH_3)_2N_2$. k was determined from the rate of formation of HCHO (using LIF) with [O]>[CH_3]. Mass balance estimates indicated that channel (1) predominates.

(e) Discharge flow system with generation of CH_3 from F+CH_4 in He-O_2 mixtures at pressures of 0.25 mbar to 1.0 mbar (0.17 Torr to 0.78 Torr). k was determined from the decay of [CH_3] by MS with [O]/[CH_3]>10.

(f) Obtained from the rate of formation of HCHO product by monitoring the C-H stretch emission by FTIR spectroscopy.

(g) Shock heating of CH_3Cl in Ar coupled with laser photolysis of SO_2. k was determined from computer simulation of [O] profiles measured by RA.

(h) Pulsed laser photolysis at 193 nm of mixtures of $CH_3C(O)CH_3$, CH_3Br and SO_2 at 1.3 mbar pressure. Product analysis by time-of-flight mass spectrometry.

(i) DF-MS study of $O+C_2H_4$ reaction in which CH_3 is a product. HCHO assumed to arise from channel (1).

(j) Discharge flow system with CH_3 being generated from $F+CH_4$ and O from a microwave discharge. Electron impact MS analysis of HCO and HCHO. No evidence found for channel (2).

(k) Pulsed laser photolysis at 193 nm of mixtures of CH_3COCH_3, SO_2, and Ar at 6.6 mbar pressure. Product analysis by tunable infrared diode laser absorption.

Preferred Values

$k = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290–900 K.
$k_1/k = 0.83$ at 298 K.
$k_3/k = 0.17$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 100$ K.
$\Delta k_1/k = \pm 0.15$ at 298 K.
$\Delta k_3/k = \pm 0.11$ at 298 K.

Comments on Preferred Values

The recommended value of k is the mean of the results of Plumb and Ryan (1982), Slagle et al. (1987), Zellner et al. (1988), Oser et al. (1991), Seakins and Leone (1992) and Fockenberg et al. (1999) which are in good agreement. The data of Bhaskaran et al. (1980) and Lim and Michael (1993) indicate that the rate coefficient is independent of temperature up to at least 2300 K.

The preferred branching ratios are based on the studies of Fockenberg et al. (1999) and Preses et al. (2000). The values of the branching ratio k_3/k reported in these studies, using completely different detection methods, are in excellent agreement. These results are consistent with earlier results reported in Niki et al. (1968), Hoyermann and Sievert (1979) and Seakins and Leone (1992). Seakins and Leone (1992) found CO to be a primary product, and they also estimated the overall branching ratio for CO formation to be 0.40±0.10. Fockenberg et al. (1999) and Preses et al. (2000) suggest that the overall branching ratio for CO formation estimated in Seakins and Leone (1992) includes CO formed in an oxidation chain beginning with HCHO.

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II.A1.2

$$\begin{aligned} \mathbf{O(^1D) + CH_4} \quad & \rightarrow \mathbf{HO + CH_3} && \mathbf{(1)} \\ & \rightarrow \mathbf{CH_3O} \text{ or } \mathbf{CH_2OH + H} && \mathbf{(2)} \\ & \rightarrow \mathbf{HCHO + H_2} && \mathbf{(3)} \end{aligned}$$

$\Delta H°(1) = -180.5$ kJ·mol^{-1}
$\Delta H°(2) = -128.9$ or -163.0 kJ·mol^{-1}
$\Delta H°(3) = -472.7$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2+k_3)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.3 \pm 0.2) \times 10^{-10}$	298	Davidson et al., 1976	PLP (a)
$(1.4 \pm 0.4) \times 10^{-10}$	200–350	Davidson et al., 1977	PLP (a)
$(1.57 \pm 0.13) \times 10^{-10}$	295	Amimoto et al., 1979	PLP-RA (b)
Branching Ratios			
$k_1/k = 0.9$	295	Lin and DeMore, 1973	P-GC (c)
$k_3/k = 0.09$	295		
$k_1/k = 0.90 \pm 0.02$	298	Jayanty et al., 1976	P-GC (d)
$k_3/k = 0.11 \pm 0.02$	298		
$k_1/k = 0.8$	293	Addison et al., 1979	FP-AS (e)
$k_3/k_2 < 0.25$	–	Casavecchia et al., 1980	(f)
$k_1/k = 0.75 \pm 0.08$	–	Sataypal et al., 1989	PLP-LIF (g)
$k_2/k = 0.25 \pm 0.08$	–		
$k_2/k = 0.15 \pm 0.03$	–	Matsumi et al., 1993	PLP-LIF
$k_1/k = 0.90^{+0.1}_{-0.2}$	298	Hack and Thiesemann, 1995	PLP-LIF
$k_2/k = 0.30 \pm 0.11$	298	Brownsword et al., 1998	PLP-LIF
$k_1/k = 0.71 \pm 0.05$	298	Ausfelder et al., 2000	PLP-LIF

Comments

(a) Pulsed laser photolysis of O_2 at 266 nm. O(^{1}D) atoms were monitored by time-resolved emission from the transition O(^{1}D) → O(^{3}P) at 630 nm.

(b) Pulsed laser photolysis at 248 nm of O_3-CH_4-He mixtures with time-resolved measurement of O(^{3}P) atoms by resonance absorption.

(c) Photolysis of N_2O-CH_4 mixtures at 184.9 nm with end-product analysis by GC.

(d) Photolysis of N_2O-CH_4-O_2 mixtures at 216 nm with measurement of H_2 by GC.

(e) Flash photolysis of O_3 at 200 nm to 300 nm with [OH] monitored by absorption at 308.15 nm.

(f) Molecular beam study with MS detection of CH_3O or CH_2OH. Experimental temperature not stated.

(g) Pulsed laser photolysis of O_3 at 248.4 nm with LIF determination of [H]. Experimental temperature not stated.

Preferred Values (k=k_1+k_2+k_3)

$k = 1.5\times10^{-10}$ cm^3 molecule^{-1} s^{-1} independent of temperature over the range 200–350 K.
$k_1/k = 0.70$ at 298 K.
$k_2/k = 0.23$ at 298 K.
$k_3/k = 0.05$ at 298 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta k_1/k = \pm 0.15$ at 298 K.
$\Delta k_2/k = \pm 0.07$ at 298 K.
$\Delta k_3/k = \pm 0.05$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred value of k at 298 K is the mean of the results of Davidson et al. (1977) and Amimoto et al. (1979), and the temperature dependence is that from Davidson et al. (1977).

The preferred branching ratios are based on the critical review by Lee and co-workers (1999) of the results of Hack and Thiesemann (1995), Brownsword et al. (1998), Satayapal et al. (1989) and their own crossed-beam experiments (Casavecchia et al., 1980; Lin et al., 1998, 1999). Reaction channel (2) has been shown by Lee and co-workers (Lin et al., 1998, 1999, 2000) to produce mainly CH_2OH+H, and the production of CH_3O+H is at most a minor channel. In addition, the experiments of Wine and Ravishankara (1982), Matsumi et al. (1993) and Takahashi et al. (1996) have shown that the yield of $O(^3P)$ atoms is small or zero. The 248 nm pulsed laser photolysis study of Aker et al. (1986), of O_3-CH_4 mixtures with low-pressure FTIR emission spectroscopy to monitor the HO^* product, has provided evidence that the partitioning of energy in the vibrationally excited HO radical (up to n=4, the maximum allowable based on the energetics of the reaction) is non-statistical.

A discussion of kinetic isotope effects in this reaction can be found in the publication of Saueressig et al. (2001) and references cited therein.

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O_3 Reactions – Appendix A1

II.A1.153

$$O_3 + R_1R_2C{=}CR_3R_4 \rightarrow HO + products \qquad (1)$$

(R=H or CH_3)

Product yield data

Alkene	Criegee Intermediate(s)	HO Yield (1 bar) (Δ[HO]/Δ[$R_1R_2C{=}CR_3R_4$])	Reference	Technique Comments
Ethene	CH_2OO	0.18 ± 0.06	Paulson et al., 1999a	Tracer (a)
Ethene	CH_2OO	0.14 ± 0.07	Rickard et al., 1999	Tracer (b)
Ethene	CH_2OO	0.20 ± 0.02	Mihelcic et al., 1999	MI-ESR (c)
Ethene	CH_2OO	(ca. 0.14)	Kroll et al., 2001a	Low pressure LIF see comment (d)
Propene	CH_2OO, CH_3CHOO	0.35 ± 0.07	Paulson et al., 1999a	Tracer (a)
Propene	CH_2OO, CH_3CHOO	0.32 ± 0.08	Rickard et al., 1999	Tracer (b)
Propene	CH_2OO, CH_3CHOO	$0.34^{+0.03}_{-0.06}$	Neeb and Moorgat, 1999	Kinetic/ Scavenger (e)
Z-2-butene	CH_3CHOO	0.33 ± 0.07	McGill et al., 1999	Tracer (b)
Z-2-butene	CH_3CHOO	0.33 ± 0.05	Orzechowska and Paulson, 2002	Tracer (a)
E-2-butene	CH_3CHOO	0.61 ± 0.28	Fenske et al., 2000	Tracer (a)
E-2-butene	CH_3CHOO	0.64 ± 0.12	Orzechowska and Paulson, 2002	Tracer (a)
E-2-butene	CH_3CHOO	0.54 ± 0.11	McGill et al., 2000	Tracer (b)
E-2-butene	CH_3CHOO	ca. 0.60	Kroll et al., 2001a	Low pressure LIF see comment (d)
E-2-butene	CH_3CHOO	0.75 ± 0.19	Siese et al., 2001	LIF (f)
2-Methyl -propene	CH_2OO, $(CH_3)_2COO$	0.72 ± 0.12	Paulson et al., 1999b	Tracer (a)
2-Methylpropene	CH_2OO, $(CH_3)_2COO$	0.60 ±0.15	Rickard et al., 1999	Tracer (b)
2-Methylpropene	CH_2OO, $(CH_3)_2COO$	$0.60^{+0.05}_{-0.02}$	Neeb and Moortgat, 1999	Kinetic/ Scavenger (e)
Z-2-Pentene	CH_3CHOO, CH_3CH_2CHOO	0.29 ± 0.06	Orzechowska and Paulson, 2002	Tracer (a)
Z-2-Pentene	CH_3CHOO, CH_3CH_2CHOO	0.27 ± 0.07	Orzechowska and Paulson, 2002	Scavenger (g)
E-2-Pentene	CH_3CHOO, CH_3CH_2CHOO	0.46 ± 0.08	Orzechowska and Paulson, 2002	Tracer (a)
2-Methyl-2-butene	CH_3CHOO, $(CH_3)_2COO$	0.93 ± 0.14	Chew and Atkinson, 1996	Scavenger (g)
2-Methyl-2-butene	CH_3CHOO, $(CH_3)_2COO$	0.81 ± 0.16	McGill et al., 1999	Tracer (b)
2-Methyl-2-butene	CH_3CHOO, $(CH_3)_2COO$	(ca. 0.6)	Kroll et al., 2001a	Low pressure LIF see comment (d)
2-Methyl-2-butene	CH_3CHOO, $(CH_3)_2COO$	0.89 ± 0.22	Siese et al., 2001	LIF (f)
2-Methyl-2-butene	CH_3CHOO, $(CH_3)_2COO$	0.98 ± 0.24	Orzechowska and Paulson, 2002	Tracer (a)
2-Methyl-2-butene	CH_3CHOO, $(CH_3)_2COO$	0.80 ± 0.12	Orzechowska and Paulson, 2002	Scavenger (a)
2,3-Dimethyl-2 -butene	$(CH_3)_2COO$	0.80 ± 0.12	Chew and Atkinson, 1996	Scavenger (g)

Alkene	Criegee Intermediate(s)	HO Yield (1 bar) (Δ[HO]/Δ [$R_1R_2C{=}CR_3R_4$])	Reference	Technique Comments
2,3-Dimethyl-2-butene	$(CH_3)_2COO$	0.89 ± 0.22	Rickard et al., 1999	Tracer (b)
2,3-Dimethyl-2-butene	$(CH_3)_2COO$	(ca. 1.00)	Kroll et al., 2001	Low pressure LIF see comment (d)
2,3-Dimethyl-2-butene	$(CH_3)_2COO$	1.00 ± 0.25	Siese et al., 2001	LIF (f)
2,3-Dimethyl-2–butene	$(CH_3)_2COO$	0.91 ± 0.14	Orzechowska and Paulson, 2002	Scavenger (a)
Isoprene (2-methyl-1,3-butadiene)	H_2COO, $H_2C{=}C(CH_3)CHOO$, $OOC(CH_3)CH{=}CH_2$	0.25 ± 0.06	Paulson et al., 1998	Tracer (a)
Isoprene (2-methyl-1,3-butadiene)	H_2COO, $H_2C{=}C(CH_3)CHOO$, $OOC(CH_3)CH{=}CH_2$	$0.26^{+0.03}_{-0.06}$	Neeb and Moortgat, 1999	Kinetic/ Scavenger (e)
Isoprene (2-methyl-1,3-butadiene)	H_2COO, $H_2C{=}C(CH_3)CHOO$, $OOC(CH_3)CH{=}CH_2$	(ca. 0.25)	Kroll et al., 2001a	Low pressure LIF see comment (d)
Methylvinyl ketone	H_2COO, $CH_3C(O)CHOO$	0.16 ± 0.08	Aschmann et al., 1996	Scavenger (g)
Methylvinyl ketone	H_2COO, $CH_3C(O)CHOO$	0.16 ± 0.05	Paulson et al., 1998	Tracer (a)
Methacrolein	H_2COO, $HC(O)C(CH_3)OO$	$0.20^{+0.10}_{-0.13}$	Aschmann et al., 1996	Scavenger (g)
α-Pinene	R_1CHOO, R_2R_3COO	0.76 ± 0.11	Chew and Atkinson, 1996	Scavenger (g)
α-Pinene	R_1CHOO, R_2R_3COO	0.70 ± 0.17	Paulson et al., 1998	Tracer (a)
α-Pinene	R_1CHOO, R_2R_3COO	1.00	Pfeiffer et al., 1998	Absorption detection of HO (h)
α-Pinene	R_1CHOO, R_2R_3COO	0.83 ± 0.21	Rickard et al., 1999	Tracer (b)
α-Pinene	R_1CHOO, R_2R_3COO	0.91 ± 0.23	Siese et al., 2001	LIF (f)
β-Pinene	H_2COO, R_1R_2COO	0.24 ± 0.06	Rickard et al., 1999	Tracer (b)
Sabinene	H_2COO, R_1R_2COO	0.33 ± 0.06	Chew and Atkinson, 1996	Scavenger (g)

Comments

(a) Small quantities of a tracer compound (1,3,5-trimethylbenzene, *m*-xylene and di-*n*-butyl ether), that react rapidly with HO and very slowly with ozone, were added to the ozone/alkene reaction mixture. HO yields were determined from the diminution in concentration of the added tracer.

(b) Similar study to comment (b) using 1,3,5-trimethylbenzene as an HO tracer compound.

(c) Matrix Isolation Electron Spin Resonance (MI-ESR) study in which HO_2 was quantitatively detected. HO was converted to HO_2 by reaction with CO.

(d) Steady-state HO concentrations in a flow-tube were measured directly by laser induced fluorescence (LIF). The reported HO yields correspond to prompt HO production over short time-scales (within ca. 30 ms) at total pressures of a few Torr. Although prompt HO yields were seen to decrease rapidly with increasing pressure, the HO yield for 2,3-dimethyl-2-butene at atmospheric pressure was seen to approach the prompt, low-pressure yield over much longer time-scales. Thus although the reported yields are for prompt HO production, it is assumed that the long-time-scale yields of HO due to thermal decomposition of the carbonyl oxide are the same.

(e) The rate of alkene consumption was observed under pseudo-first order conditions with an excess concentration of ozone. The decrease in observed rate in the presence of excess cyclohexane (to scavenge any HO formed) was used to derive HO formation yields.

(f) HO detected by LIF in the EUPHORE outdoor simulation chamber in Valencia. Time-dependent HO and O_3 concentration data were numerically simulated to obtain HO yields.

(g) Ozonolysis reactions carried out in the presence of sufficient 2-butanol to scavenge ≥95% of all adventitiously formed HO. HO yields derived from the amount of 2-butanone formed. This method superseded earlier experiments in the laboratory of Atkinson and co-workers in which ozonolysis reactions were carried out in the presence of excess cyclohexane, and from which HO formation efficiencies were derived from measured yields of cyclohexanol and cyclohexanone (Atkinson et al., 1992; Atkinson and Aschmann, 1993). However, due to the complex peroxy radical chemistry giving rise to these observed products, an uncertainty of around a factor of 1.5 was estimated for the HO yields determined from these studies.

Preferred Values

Alkene	$k_{ozone+alkene}$ (298 K) /cm^3 molecule^{-1} s^{-1}	Preferred HO Yield	References
Ethene	1.6×10^{-18}	0.16	Paulson et al., 1999a Rickard et al., 1999
Propene	1.0×10^{-17}	0.34	Paulson et al., 1999a Rickard et al., 1999 Neeb and Moortgat, 1999
Z-2-butene	1.3×10^{-16}	0.33	McGill et al., 1999 Orzechowska and Paulson, 2002
E-2-butene	1.9×10^{-16}	0.64	McGill et al., 1999 Orzechowska and Paulson, 2002 Fenske et al., 2000 Siese et al., 2001
2-Methylpropene	1.1×10^{-17}	0.62	Rickard et al., 1999 Neeb and Moortgat, 1999 Paulson et al., 1999
2-Methyl-2-butene	4.1×10^{-16}	0.88	McGill et al., 1999 Orzechowska and Paulson, 2002 Siese et al., 2001 Chew and Atkinson, 1996
2,3-Dimethyl-2-butene	1.1×10^{-15}	0.90	Rickard et al., 1999 Orzechowska and Paulson, 2002 Siese et al., 2001 Chew and Atkinson, 1996
Isoprene	1.27×10^{-17}	0.25	Neeb and Moortgat, 1999 Paulson et al., 1998
α-Pinene	9.0×10^{-17}	0.80	Rickard et al., 1999 Siese et al., 2001 Chew and Atkinson, 1996 Paulson et al., 1998

Δlog(yield) = 0.15

[a] Rate coefficients taken from Atkinson (1997)

Comments on Preferred Values

The currently accepted mechanism of HO production from ozone-alkene reactions involves the following steps:

$O_3 + R_1R_2C{=}R_3R_4 \rightarrow R_1R_2C(OOO)R_3R_4$ (primary ozonide) (1a)
$R_1R_2C(OOO)R_3R_4 \rightarrow R_1R_2COO + R_3C(O)R_4$ (1b)
$R_1R_2C(OOO)R_3R_4 \rightarrow R_1C(O)R_2 + R_3R_4COO$ (1c)
R_1R_2COO (and R_3R_4COO) $\rightarrow$ HO + products (1d)
R_1R_2COO (and R_3R_4COO) $\rightarrow$ other products (1e)

Until recently it was generally accepted that HO radicals were produced as a decomposition product of vibrationally excited carbonyl oxide (Criegee) intermediates. In the case of methyl-substituted Criegee intermediates (methylcarbonyl oxide and dimethylcarbonyl oxide) the HO yield varies with the number of methyl-groups in a manner that is consistent with isomerisation of the Criegee intermediate to a hydroperoxide intermediate followed by decomposition and HO release (Rickard et al., 1999; Niki et al., 1987; Martinez and Herron, 1988, Kroll et al., 2001b). However, experimental studies by Kroll et al. (2001a) looked directly at the formation of HO by LIF over short-timescales, as a function of pressure. As the pressure was increased from a few Torr to around atmospheric pressure, the yields of prompt HO (i.e. that formed within 30 ms or so) were seen to decrease to essentially zero. It was concluded that the majority of HO production reported in previous experimental studies of ozone-alkene reactions was due to the thermal decomposition of stabilised Criegee intermediates. This assertion was supported by further LIF studies in which HO production in the ozonolysis of 2,3-dimethyl-2-butene, at one atmosphere of pressure, was seen to increase over significantly longer time-scales (Kroll et al., 2001b). A study by Johnson et al. (2001) looked at the HO production efficiency of the reaction of ozone with 2-methyl-2-butene in the presence of relatively high concentrations of scavenger species believed to react with Criegee intermediates. Under the conditions of these latter experiments (with concentrations of scavenger species in excess of those that would be encountered in the troposphere), no effect upon the yield of HO was observed. Thus, it is concluded that, the bimolecular reactions of stabilised Criegee intermediates produced in the ozonolysis of 2-methyl-2-butene (methylcarbonyl oxide and dimethylcarbonyl oxide) will not under atmospheric conditions compete with the formation of HO due to their thermal decomposition. It is further concluded that the HO yield measurements summarised above are applicable to the chemistry of the troposphere. The preferred HO yield data listed above are the average values of the measurements for each individual compound.

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II.A1.154

$O_3 + C_2H_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(7.8 \pm 1.2) \times 10^{-21}$	294	Atkinson and Aschmann, 1984	S-CL (a)

Comments

(a) Static system, with $[O_3]$ being monitored by chemiluminescence in large excess of C_2H_2 at a total pressure of 980 mbar.

Preferred Values

$k = 1 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 1.0$ at 298 K.

Comments on Preferred Values

The literature data at room temperature (Atkinson and Aschmann, 1984; Cadle and Schadt, 1953; DeMore, 1969, 1971; Pate et al., 1976; Stedman and Niki, 1973) exhibit a large degree of scatter covering the range $k = (0.78\text{–}7.8) \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} at 298 K. The preferred value at 298 K is based upon the value obtained by Atkinson and Aschmann (1984). This is the most recent study; it gives the lowest of the values so far obtained and is likely to be the most accurate (any impurities are likely to lead to higher values).

There has been one study of the temperature dependence of the rate coefficient (DeMore, 1969) giving a value of E/R=5435 K over the temperature range 243–283 K. However, in view of the difficulties in studying this reaction and the small temperature range covered, no recommendation is made concerning the temperature dependence of this rate coefficient. A large uncertainty is assigned to the preferred value at 298 K to encompass the wide scatter in the results.

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II.A1.155

$O_3 + C_2H_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
3.3×10^{-15} exp[-(2365 ± 101)/T]	178–233	DeMore, 1969	S-UVA (a)
1.18×10^{-18}	298*		
$(1.55 \pm 0.15) \times 10^{-18}$	299	Stedman et al., 1973	S-CL (b)
9.00×10^{-15} exp[-(2557 ± 167)/T]	235–362	Herron and Huie, 1974	(c)
1.69×10^{-18}	298		
$(1.9 \pm 0.1) \times 10^{-18}$	299	Japar et al., 1974	S-CL (b)
$(1.9 \pm 0.1) \times 10^{-18}$	299	Japar et al., 1976	S-CL (b)
$(1.69 \pm 0.13) \times 10^{-18}$	303	Toby et al., 1976	S-UVA (a)
$(1.43 \pm 0.19) \times 10^{-18}$	296	Atkinson et al., 1982	S-CL (b)
7.72×10^{-15} exp[-(2557 ± 30)/T]	232–298	Bahta et al., 1984	S-UVA (a)
$(1.45 \pm 0.10) \times 10^{-18}$	298		
5.1×10^{-15} exp[-(2446 ± 91)/T]	240–324	Treacy et al., 1992	S-CL (b)
$(1.37 \pm 0.08) \times 10^{-18}$	298		

Comments

(a) Static system, with UV absorption detection of O_3 at 253.7 nm.

(b) Static system with chemiluminescence detection of O_3.

(c) Stopped flow system with MS detection of O_3. Carried out at a total pressure of ~5 mbar but with sufficient O_2 present to minimize the occurrence of secondary reactions removing O_3.

Preferred Values

$k = 1.6 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 9.1 \times 10^{-15} \exp(-2580/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 180–360 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The temperature dependent kinetic studies of Bahta et al. (1984) and Treacy et al. (1992) are in good agreement. These two studies result in rate coefficients (Bahta et al., 1984; Treacy et al., 1992) which are somewhat lower than many of the previous determinations, including those of Su et al. (1980) and Kan et al. (1981) which are not used in this evaluation. Since Treacy et al. (1992) did not tabulate the individual rate coefficients at the various temperatures studied, only their 298 K value can be used in the evaluation of the rate coefficient for this reaction. The preferred values are obtained from a least-squares analysis of the rate coefficients of DeMore (1969), Stedman et al. (1973), Herron and Huie (1974), Japar et al. (1974, 1976), Toby et al. (1976), Atkinson et al. (1982), Bahta et al. (1984) (averaging the rate coefficients at each of the four temperatures studied) and the 298 K rate coefficient of Treacy et al. (1992).

As discussed by Atkinson (1997), the initial reaction forms the energy-rich ‘primary ozonide’ which rapidly decomposes (see Fig. 1a) to yield HCHO and the energy-rich Criegee intermediate $[CH_2OO]^*$. Grosjean and Grosjean (1996) and Grosjean et al. (1996) have measured a formation yield of HCHO of unity at atmospheric pressure of air.

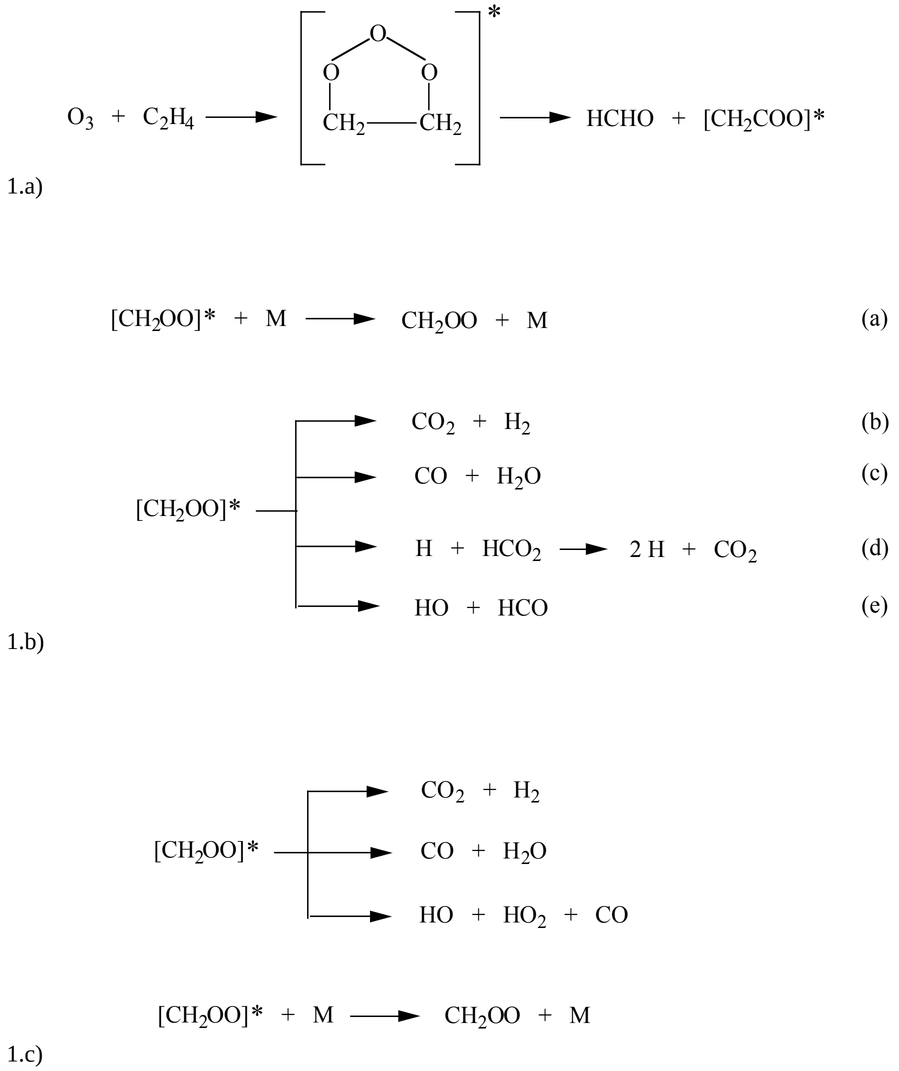

Fig. 1. See text.

The energy-rich Criegee intermediate can either be stabilized or decompose, with the decomposition channels (b) through (e) having been postulated (see Fig. 1b).

There have been a number of determinations of the yield of the stabilized Criegee intermediate. The values obtained at room temperature and atmospheric pressure by Su et al. (1980) (35±5%), Kan et al. (1981) (37±2%), Niki et al. (1981) (35±5%), Hatakeyama et al. (1984, 1986) (39.0±5.3%) and Hasson et al. (2001) (39±11%) are in good agreement (with an average yield of 37%) and are preferred to the slightly higher value of 47% obtained by Horie and Moortgat (1991). The yield of stabilized Criegee intermediate appears to be pressure dependent although a significant fraction have been reported to be formed thermally "cold" at low pressures; by extrapolation of measurements over the range 13 mbar to 1.5 bar, Hatakeyama et al. (1986) found this fraction to be 20±3% at zero pressure.

The formation of HO radicals has been observed from the reaction of O_3 with ethene at atmospheric pressure of air, with the measured HO radical yield being in the range 12–18% (Atkinson et al., 1992; Paulson et al., 1999; Rickard et al., 1999) (see the data sheet in this article on the reactions of $O_3+R_1R_2C=CR_3R_4 \rightarrow HO+products$). This observed formation of HO radicals (Atkinson et al., 1992; Paulson et al., 1999; Rickard et al., 1999), presumably via pathway (e), suggests that pathway (d) does not occur, since the low pressure study of Herron and Huie (1977) which invoked pathway (d) could not differentiate between formation of H atoms and HO radicals (any H atoms formed would rapidly react with O_3 in the reaction system used by Herron and Huie (1977) to produce HO radicals). Hence a possible reaction sequence at atmospheric pressure of air is depicted in Fig. 1c.

Under typical lower tropospheric conditions, the stabilized Criegee intermediate CH_2OO is expected to react with water vapor to form hydroxymethyl hydroperoxide, $HOCH_2OOH$ (Neeb et al., 1996; Hasson et al., 2001),

$$CH_2OO + H_2O \rightarrow HOCH_2OOH$$

which may decompose on surfaces to formic acid plus water vapor (Neeb et al., 1996; Hasson et al., 2001).

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II.A1.156

$O_3 + C_3H_6 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
6.14×10^{-15} exp[-(1897 ± 109)/T]	235–362	Herron and Huie, 1974	(a)
1.06×10^{-17}	298		
4.9×10^{-15} exp[-(1858 ± 70)/T]	240–324	Treacy et al., 1992	S-CL (b)
$(9.4 \pm 0.4) \times 10^{-18}$	298		

Comments

(a) Stopped flow system, with MS detection of O_3. Carried out at a total pressure of ~5 mbar, but with sufficient O_2 present to minimize the occurrence of secondary reactions removing O_3. Due to a typographical error, the lowest temperature studied was 235.0 K and not 250.0 K as originally stated (Herron and Huie, 1974).

(b) Static system, with chemiluminescence detection of O_3. C_3H_6 in large excess over O_3.

Preferred Values

$k = 1.0 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.5 \times 10^{-15}$ exp(-1880/T) cm^3 molecule^{-1} s^{-1} over the temperature range 230–370 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute rate coefficients of Herron and Huie (1974) (note that the lowest temperature studied was 235.0 K and not 250.0 K as given by Herron and Huie, 1974) and Treacy et al. (1992) are in excellent agreement for propene, 1-butene, *cis*- and *trans*-2-butene, 2-methylpropene and 2-methyl-2-butene over the temperature ranges common to both studies. Accordingly, the 298 K rate coefficients and temperature dependencies of Herron and Huie (1974) and Treacy et al. (1992) have been averaged to yield the preferred Arrhenius expression (note that the individual rate coefficients at the various temperatures studied by Treacy et al. (1992) were not tabulated).

The reaction proceeds via the initial formation of the ‘primary ozonide’ (Atkinson, 1997), which rapidly decomposes to two sets of ‘primary’ carbonyl plus Criegee intermediate (see Fig. 2a).

For 1-alkenes measured product yields suggest that the rate coefficient ratio $k_b/(k_a+k_b)$ is in the range 0.65–0.50 at room temperature (Atkinson, 1997; Grosjean et al., 1996; Tuazon et al., 1997; Rickard et al., 1999). For propene, yields of CH_3CHO have been measured in the presence of an HO radical scavenger (see below) by Grosjean et al. (1996) (0.520±0.026 at 55±10% relative humidity), Tuazon et al. (1997) (0.446±0.092 at ~5% relative humidity) and Rickard et al. (1999) (0.34±0.01 in dry air). Higher yields of HCHO were obtained by Grosjean et al. (1996) and Tuazon et al. (1997), but these include any formation of HCHO from subsequent reactions of the $[CH_3CHOO]^*$ intermediates. The energy-rich Criegee intermediates are believed to be carbonyl oxides, and the Criegee intermediate $[CH_3CHOO]^*$ can exist in the *anti*- or *syn*-configuration (Fenske et al., 2000a) (see Fig. 2b).

It is assumed (in the absence of other information; Rickard et al., 1999) that the reactions of the energy-rich Criegee intermediate $[CH_2OO]^*$ formed from propene are similar to those for $[CH_2OO]^*$ formed from ethene. Hence, as for the O_3+C_2H_4 reaction at room temperature and 1 bar of air, the reactions are as shown in Fig. 2c.

Less data are available concerning the stabilization and decomposition reactions of the $[CH_3CHOO]^*$ intermediate. Based upon the SO_2 to H_2SO_4 conversion yield in an O_3 + propene reaction system, Hatakeyama et al. (1984) determined an overall

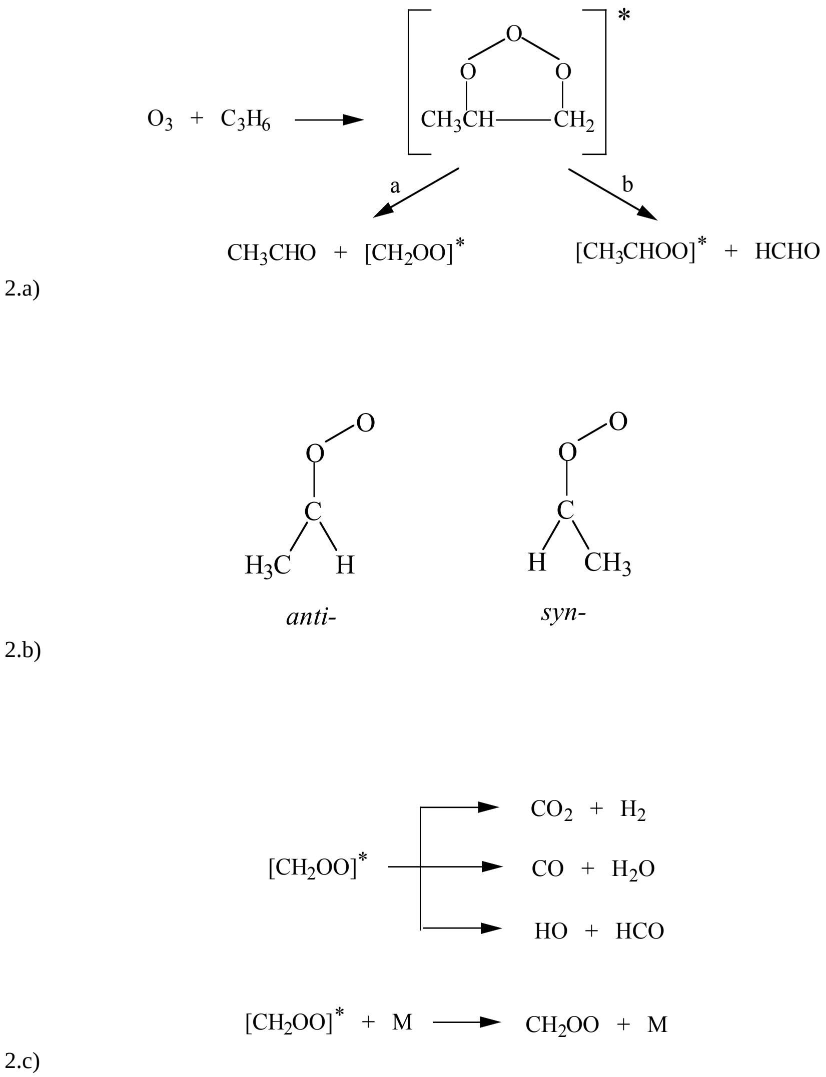

Fig. 2. **(a)**, **(b)** and **(c)** – see text.

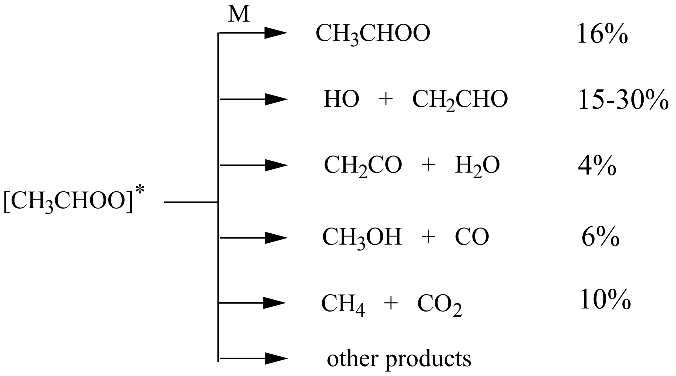

Fig. 3. See text.

stabilized Criegee intermediate [CH_2OO+CH_3CHOO] yield of 0.254±0.023 at room temperature and atmospheric pressure, while Horie and Moortgat (1991) obtained a stabilized Criegee intermediate yield of 0.44. Rickard et al. (1999) measured the acetaldehyde yield in the presence and absence of 0.002 bar SO_2 and ascribed the observed increase in the acetaldehyde yield to the reaction $SO_2+CH_3CHOO \rightarrow SO_3+CH_3CHO$ (similar to the assumptions made by Hatakeyama et al., 1984) which corresponds to a yield of stabilized CH_3CHOO of 0.12–0.16 for rate coefficient ratios $k_b/(k_a+k_b)$ of 0.65–0.50. For rate coefficient ratios $k_b/(k_a+k_b)$ of 0.65–0.50 and asuming that the $[CH_2OO]^*$ stabilization yield is 0.37, the data of Hatakeyama et al. (1984) lead to a fraction of the $[CH_3CHOO]^*$ intermediate which is stabilized at ~298 K and 1 bar of air of 0.14–0.19, reasonably consistent with the study of Rickard et al. (1999). While the stabilization/decomposition yields are expected to depend on the individual alkene reacting with O_3 (and on the total pressure and temperature), this fraction of $[CH_3CHOO]^*$ biradicals which are stabilized at 298 K and 1 bar of air (0.12–0.19) is similar to the measured yields of stabilized CH_3CHOO from *trans*-2-butene of 0.185 (Hatakeyama et al., 1984) and 0.13 (Rickard et al., 1999) and from *cis*-2-butene of 0.18 (Niki et al., 1977) and 0.19 (Rickard et al., 1999). A yield of stabilized CH_3CHOO from $[CH_3CHOO]^*$ of 0.16 at 298 K and 1 bar of air is recommended, with it being likely that this stabilized CH_3CHOO intermediate is *anti*-CH_3CHOO.

The $[CH_3CHOO]^*$ decomposition pathways include the formation of HO radicals through the 'hydroperoxide' channel (see the data sheet on the reactions of $O_3+R_1R_2C=CR_3R_4 \rightarrow HO$ + products).

$$[CH_3CHOO] \rightarrow [CH_2{=}CHOOH] \rightarrow CH_2CHO + HO$$

and this reaction pathway is believed to occur for the initially energy-rich Criegee intermediate and possibly for the stabilized *syn*-CH_3CHOO intermediate (Fenske et al., 2000a; Kroll et al., 2001). At atmospheric pressure, the measured HO radical formation yield is in the range 0.32–0.37 (Atkinson and Aschmann, 1993; Neeb and Moortgat, 1999; Paulson et al., 1999; Rickard et al., 1999; Fenske et al., 2000b). Other decomposition pathways include (Atkinson, 1997; Tuazon et al., 1997):

$$\begin{array}{lcl} [CH_3CHOO]^* & \rightarrow & CH_4 + CO_2 \\ [CH_3CHOO]^* & \rightarrow & CH_3OH + CO \\ [CH_3CHOO]^* & \rightarrow & CH_2CO + H_2O \end{array}$$

with measured methane, methanol and ketene yields at atmospheric pressure (in the presence of an HO radical scavenger) of 0.096±0.010 (Tuazon et al., 1997), 0.055±0.007 (Tuazon et al., 1997) and 0.036±0.008 (Tuazon et al., 1997), respectively. Considering that subsequent reaction of the vinoxy (CH_2CHO) radical in air may lead to the formation of HO radicals (Atkinson, 1997), then a possible overall reaction sequence involves the initial formation of 35–40% ($[CH_2OO]^*$+CH_3CHO) and 65–60% ($[CH_3CHOO]^*$+HCHO), followed by the reactions of the $[CH_2OO]^*$ intermediate shown above (leading to an HO radical yield, relative to the propene reacted, of ~0.05) and the following reactions of the $[CH_3CHOO]^*$ intermediate (the yields are given relative to the propene reacted, and that for the HO+CH_2CHO pathway depends on the amount of HO radicals formed from subsequent reactions of the vinoxy radical) (see Fig. 3).

Under lower tropospheric conditions, the stabilized Criegee intermediate CH_3CHOO (expected to be in the *anti*-configuration) is anticipated to react with water vapor to form the hydroxyhydroperoxide (Neeb et al., 1999; Sauer et al., 1999; Baker et al., 2002).

$$CH_3CHOO + H_2O \rightarrow CH_3CH(OH)OOH$$

This hydroxyhydroperoxide may decompose (possibly heterogeneously) to $CH_3C(O)OH+H_2O$ or to $CH_3CHO+H_2O_2$ (Neeb et al., 1999; Sauer et al., 1999).

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II.A1.157

$O_3 + CH_2{=}C(CH_3)CH{=}CH_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.27×10^{-17}	295 ± 1	Arnts and Gay, 1979	S-CL/GC (a)
7.0×10^{-18}	260±2	Adeniji et al., 1981	S-CL
1.65×10^{-17}	294 ± 2		
1.1×10^{-17}	291	Kamens et al., 1982	(b)
$1.54 \times 10^{-14} \exp[-(2153 \pm 430)/T]$	278–323	Atkinson, et al., 1982	S-CL
$(1.17 \pm 0.19) \times 10^{-17}$	296 ± 2		
$7.8 \times 10^{-15} \exp[-(1913 \pm 139)/T]$	242–323	Treacy et al., 1992	S-UVA
$(1.28 \pm 0.12) \times 10^{-17}$	298		
$(8.95 \pm 0.25) \times 10^{-18}$	293 ± 2	Grosjean et al., 1993	S-UVA
$(1.13 \pm 0.32) \times 10^{-17}$	291 ± 2	Grosjean and Grosjean, 1996	S-UVA
Relative Rate Coefficients			
$(1.16 \pm 0.02) \times 10^{-17}$	296 ± 2	Greene and Atkinson, 1992	RR (c)
$9.21 \times 10^{-15} \exp[-(1955 \pm 42)/T]$	242–324	Khamaganov and Hites, 2001	RR (d,e)
$(1.29 \pm 0.08) \times 10^{-17}$	298		
$1.62 \times 10^{-14} \exp[-(2078 \pm 120)/T]$	242–324	Khamaganov and Hites, 2001	RR (d,f)
$(1.50 \pm 0.13) \times 10^{-17}$	298		
$1.24 \times 10^{-14} \exp[-(2050 \pm 87)/T]$	257–324	Khamaganov and Hites, 2001	RR (d,g)
$(1.26 \pm 0.07) \times 10^{-17}$	298		
$9.45 \times 10^{-15} \exp[-(1963 \pm 72)/T]$	258–324	Khamaganov and Hites, 2001	RR (d,h)
$(1.35 \pm 0.08) \times 10^{-17}$	298		
$1.36 \times 10^{-14} \exp[-(2015 \pm 149)/T]$	278–353	Avzianova and Ariya, 2002	RR (i)
$(1.22 \pm 0.03) \times 10^{-17}$	298		

Comments

(a) Carried out in one atmosphere of air in 330 liter volume reaction chambers. The O_3 and isoprene concentrations were measured by chemiluminescence and GC, respectively.

(b) Carried out at atmospheric pressure of air in a large outdoor chamber at night. O_3 was introduced continually over a period of 1.4 h to an isoprene-air mixture. The isoprene and O_3 concentrations were monitored by GC and chemiluminescence, respectively, and the rate coefficient obtained by fitting the measured isoprene and O_3 concentrations to a computer model.

(c) Relative rate study, with n-octane being present to scavenge the OH radicals formed from the O_3 reactions. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(O_3\text{+isoprene})/k(O_3\text{+propene})=1.21\pm0.02$ is placed on an absolute basis by use of a rate coefficient of $k(O_3\text{+propene})=9.6\times10^{-18}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recomendation).

(d) Relative rate method carried out at 760 Torr (1.013 bar) of helium diluent in a 192 cm^3 volume cylindrical quartz reactor, with ethanol or acetaldehyde being present to scavenge the OH radicals formed. The concentrations of isoprene and the reference compound were monitored by MS.

(e) With 2-methylpropene as the reference compound. The measured rate coefficient ratios $k(O_3\text{+isoprene})/k(O_3\text{+2-methylpropene})$ are placed on an absolute basis by use of a rate coefficient of $k(O_3\text{+2-methylpropene})=2.70\times10^{-15}$ $\exp(-1632/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 1997).

(f) With *cis*-2-butene as the reference compound. The measured rate coefficient ratios $k(O_3\text{+isoprene})/k(O_3+\textit{cis}\text{-2-butene})$ are placed on an absolute basis by use of a rate coefficient of $k(O_3+\textit{cis}\text{-2-butene})=3.22\times10^{-15}\exp(-968/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 1997).

(g) With 1-butene as the reference compound. The measured rate coefficient ratios $k(O_3\text{+isoprene})/k(O_3\text{+1-butene})$ are placed on an absolute basis by use of a rate coefficient of $k(O_3\text{+1-butene})=3.36\times10^{-15}\exp(-1744/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 1997).

(h) With 2,3-dimethyl-1,3-butadiene as the reference compound. The measured rate coefficient ratios $k(O_3\text{+isoprene})/k(O_3\text{+2,3-dimethyl-1,3-butadiene})$ are placed on an absolute basis by use of a rate coefficient of $k(O_3\text{+2,3-dimethyl-1,3-butadiene})=6.9\times10^{-15}\exp(-1668/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 1997).

(i) Relative rate method carried out at 760 Torr (1.013 bar) of air diluent in a 3 liter volume Pyrex reactor, with 1,3,5-trimethylbenzene being present to scavenge the OH radicals formed. The concentrations of isoprene and propene (the reference compound) were monitored by GC. The measured rate coefficient ratios $k(O_3\text{+isoprene})/k(O_3\text{+propene})$ are placed on an absolute basis by use of a rate coefficient of $k(O_3\text{+propene})=5.5\times10^{-15}\exp(-1880/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recomendation). Note that the 298 K rate coefficient calculated from the Arrhenius expression is 1.57×10^{-17} cm^3 molecule^{-1} s^{-1}, 29% higher than the measured value (see table).

Preferred Values

$k = 1.27 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.03 \times 10^{-14}\exp(-1995/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–360 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The measured room temperature rate coefficients (Arnts and Gay, 1979; Adeniji et al., 1981; Atkinson et al., 1982; Kamens et al., 1982; Greene and Atkinson, 1992; Treacy et al., 1992; Grosjean et al., 1993; Grosjean and Grosjean, 1996; Khamaganov and Hites, 2001; Avzianova and Ariya, 2002) and temperature dependencies (Atkinson et al., 1982; Treacy et al., 1992; Khamaganov and Hites, 2001; Avzianova and Ariya, 2002) are in good agreement. The preferred temperature dependence is the average of those determined by Treacy et al. (1992), Khamaganov and Hites (2001) and Avzianova and Ariya (2002). The preferred 298 K rate coefficient is the average of the rate coefficients of Atkinson et al. (1982), Greene and Atkinson (1992), Treacy et al. (1992), Grosjean et al. (1993), Grosjean and Grosjean (1996), Khamaganov and Hites (2001) and Avzianova and Ariya (2002) adjusted to 298 K where necessary (Atkinson et al., 1982; Greene and Atkinson, 1992; Grosjean et al., 1993; Grosjean and Grosjean, 1996) using the preferred temperature dependence. The preferred temperature dependence is combined with the preferred rate coefficient at 298 K to obtain the pre-exponential factor.

The reaction proceeds by initial addition of O_3 to the C=C bonds to form one of two primary ozonides, which rapidly decompose to form four possible sets of carbonyl + Criegee intermediate (see data sheets on the reactions of O_3 with ethene and propene). Methacrolein, methyl vinyl ketone and formaldehyde are significant products of this reaction, with measured formation yields of 39–44%, 16–17%, and 90%, respectively (Atkinson, 1997). HO radicals are also formed from the reaction of O_3 with isoprene, in 25% yield (see the data sheet on the $O_3+R_1R_2C{=}CR_3R_4 \rightarrow HO$ + products reaction).

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II.A1.158

O_3 + α-Pinene → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.6×10^{-16}	294	Ripperton et al., 1972	S-CL
1.45×10^{-16}	295 ± 1	Grimsrud et al., 1975	F-CL
$(3.3 \pm 0.3) \times 10^{-16}$	298	Japar et al., 1974	S-CL
9.4×10^{-16} exp[-(731 ± 173)T]	276–324	Atkinson et al., 1982	S-CL
$(8.4 \pm 1.9)\times 10^{-17}$	296 ± 2		
$(9.71 \pm 1.06) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990	S-CL (a)
Relative Rate Coefficients			
$(8.20 \pm 1.24)\times 10^{-17}$	297 ± 2	Nolting et al., 1988	RR (b)
5.7×10^{-16} exp[-(584 ± 87)T]	288–363	Khamaganov and Hites, 2001	RR (c,d)
$(9.05 \pm 0.45)\times 10^{-17}$	298		
3.5×10^{-16} exp[-(429 ± 303)T]	288–343	Khamaganov and Hites, 2001	RR (c,e)
$(8.11 \pm 0.33)\times 10^{-17}$	298		
$(1.06 \pm 0.09)\times 10^{-16}$	295 ± 0.5	Witter et al., 2002	RR (f)

Comments

(a) From measurements of the absolute rate coefficient for the reaction of O_3 with sabinene and the rate coefficient ratio k(O_3+α-pinene)/k(O_3+sabinene), a rate coefficient of k(O_3+α-pinene)=$(7.99\pm1.20)\times10^{-17}$ cm^3 molecule^{-1} s^{-1} was also derived.

(b) The concentrations of a series of alkenes (including α-pinene and *cis*-2-butene, the reference compound) were monitored by GC in a 520 L Pyrex chamber at ∼1 bar pressure of purified air in the presence of O_3. The measured rate coefficient ratio k(O_3+α-pinene)/k(O_3+*cis*-2-butene) is placed on an absolute basis by use of a rate coefficient at 297 K of k(O_3+*cis*-2-butene)=1.24×10^{-16} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003a). Details concerning the reactant mixtures and the presence or absence of an HO radical scavenger were not reported.

(c) The concentrations of α-pinene and 1-butene or 2-methylpropene (the reference compounds) were monitored by MS in reacting O_3 – α-pinene – 1-butene (or 2-methylpropene) – acetaldehyde (or ethanol) [HO radical scavengers] – He mixtures in a 192 cm^3 volume quartz vessel at ∼1 bar pressure. The measured rate coefficient ratios k(O_3+α-pinene)/k(O_3+1-butene)=0.17 exp[(1190±87)/T] and k(O_3+α-pinene)/k(O_3+2-methylpropene)=0.13 exp[(1203±303)/T] are placed on an absolute basis by use of rate coefficients of k(O_3+1-butene)=3.36×10^{-15} exp(-1774/T) cm^3 molecule^{-1} s^{-1} and k(O_3+2-methylpropene)=2.70×10^{-15} exp(-1632/T) cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003a). The combined data lead to the Arrhenius expression k(O_3+α-pinene)=4.8×10^{-16} exp[-(530 ± 150)/T) cm^3 molecule^{-1} s^{-1} over the temperature range 288–363 K and k(O_3+α-pinene)=$(8.41\pm0.74)\times10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K (Khamaganov and Hites, 2001).

(d) Relative to k(O_3+1-butene).

(e) Relative to k(O_3+2-methylpropene).

(f) The concentrations of α-pinene and 2-methyl-2-butene (the reference compounds) were monitored by GC in reacting O_3 – α-pinene – 2-methyl-2-butene – *m*-xylene (the HO radical scavenger) – air mixtures in a flow system at 1.00 bar pressure. The measured rate coefficient ratio of k(O_3+α-pinene)/k(O_3+2-methyl-2-butene)=0.270±0.022 is placed on an absolute basis by use of a rate coefficient at 295 K of k(O_3+2-methyl-2-butene)=3.92×10^{-16} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003a).

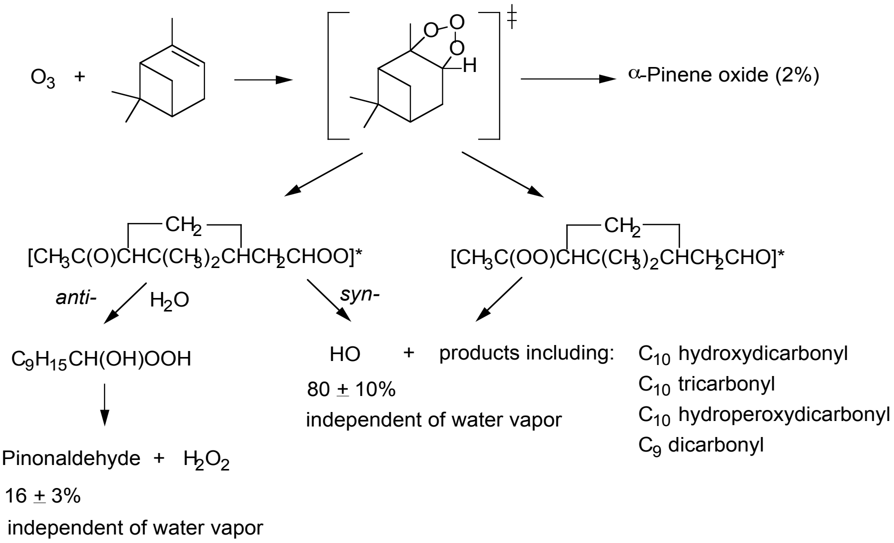

Fig. 4. See text.

Preferred Values

$k = 9.0 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.3 \times 10^{-16} \exp(-580/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–370 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The room temperature rate coefficients reported by Ripperton et al. (1972), Grimsrud et al. (1975) and Japar et al. (1974) are significantly higher than the more recent measurements of Atkinson et al. (1982, 1990), Nolting et al. (1988), Khamaganov and Hites (2001) and Witter et al. (2002), although there is still a significant amount of scatter between the room temperature rate coefficients of Atkinson et al. (1982, 1990), Nolting et al. (1988), Khamaganov and Hites (2001) and Witter et al. (2002). The preferred temperature dependence is obtained from a simple average of the temperature dependencies obtained by Atkinson et al. (1982) and Khamaganov and Hites (2001). The preferred 298 K rate coefficient is an average of those of Atkinson et al. (1982, 1990), Nolting et al. (1988), Khamaganov and Hites (2001) and Witter et al. (2002), corrected to 298 K where necessary using the preferred temperature dependence. The pre-exponential factor is adjusted to fit the 298 K preferred value.

The reaction proceeds by initial addition of O_3 to the C=C bond to form a ‘primary ozonide’ which rapidly decomposes to two Criegee intermediates. Subsequent reactions of these lead to pinonaldehyde, HO radicals, formaldehyde, acetone, α-pinene oxide and a number of other products. A schematic reaction scheme is shown below (Fig. 4), noting that the pinonaldehyde yield shown is derived from product studies employing GC analyses (see Atkinson and Arey, 2003a, b).

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II.A1.159

O_3 + CH_2=C(CH_3)CHO → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.12 \pm 0.13) \times 10^{-18}$	296 ± 2	Atkinson et al., 1981	S-CL
1.1×10^{-18}	∼294	Kamens et al., 1982	S-CL/GC (a)
1.3×10^{-15} exp[-(2112 ± 131)/T]	240–324	Treacy et al., 1992	S-UVA
$(1.1 \pm 0.2) \times 10^{-18}$	298		
$(1.02 \pm 0.05) \times 10^{-18}$	291 ± 2	Grosjean et al., 1993	S-UVA
$(1.08 \pm 0.20) \times 10^{-18}$	290 ± 1	Grosjean and Grosjean, 1998	S-UVA
$(1.3 \pm 0.14) \times 10^{-18}$	296 ± 2	Neeb et al., 1998	S-FTIR (b)

Comments

(a) Carried out at atmospheric pressure of air in a large outdoor chamber at night. O_3 was introduced continually over a period of ∼5 h to a methacrolein-air mixture. The methacrolein and O_3 concentrations were monitored by GC and chemiluminescence, respectively, and the rate coefficient obtained by fitting the measured methacrolein and O_3 concentrations to a computer model.

(b) The decays of methacrolein were measured in the presence of excess concentrations of O_3, with cyclohexane also being present as an HO radical scavenger.

Preferred Values

$k = 1.2 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.4 \times 10^{-15}$ exp(-2100/T) cm^3 molecule^{-1} s^{-1} over the temperature range 240–330 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The measured room temperature rate coefficients (Atkinson et al., 1981; Kamens et al., 1982; Treacy et al., 1992; Grosjean et al., 1993; Grosjean and Grosjean, 1998; Neeb et al., 1998) are in good agreement. The preferred 298 K rate coefficient is the average of all of the measured rate coefficients (Atkinson et al., 1981; Kamens et al., 1982; Treacy et al., 1992; Grosjean et al., 1993; Grosjean and Grosjean, 1998; Neeb et al., 1998), adjusted to 298 K where necessary (Atkinson et al., 1981; Kamens et al., 1982; Grosjean et al., 1993; Grosjean and Grosjean, 1998; Neeb et al., 1998) using the temperature dependence of Treacy et al. (1992). The temperature dependence measured by Treacy et al. (1992) is accepted, and is combined with the 298 K preferred value to obtain the pre-exponential factor.

The reaction proceeds by initial addition of O_3 to the C=C bond to form a primary ozonide which rapidly decomposes to methylglyoxal + $[CH_2OO]^*$ or to formaldehyde + $[CH_3C(OO)CHO]^*$ (see data sheets on the reactions of O_3 with ethene and propene). Methylglyoxal and formaldehyde have been observed as significant products of this reaction, with formation yields of 52–64% and 9–15%, respectively (Grosjean et al., 1993), indicating that formation of methylglyoxal + $[CH_2OO]^*$ dominates. HO radicals are also formed, with a reported yield of 20^{+10}_{-13}% (Aschmann et al., 1996).

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II.A1.160

$O_3 + CH_3C(O)CH{=}CH_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.77 \pm 0.59) \times 10^{-18}$	296 ± 2	Atkinson et al., 1981	S-CL
4.0×10^{-18}	~294	Kamens et al., 1982	S-CL/GC (a)
6.9×10^{-16} exp[-(1521 ± 78)/T]	240–324	Treacy et al., 1992	S-UVA
$(4.2 \pm 0.4) \times 10^{-18}$	298		
$(4.72 \pm 0.09) \times 10^{-18}$	291 ± 2	Grosjean et al., 1993	S-UVA
$(5.84 \pm 0.39) \times 10^{-18}$	291 ± 1	Grosjean and Grosjean, 1998	S-UVA
$(5.4 \pm 0.6) \times 10^{-18}$	296 ± 2	Neeb et al., 1998	S-FTIR (b)

Comments

(a) Carried out at atmospheric pressure of air in a large outdoor chamber at night. O_3 was introduced continually over a period of ~5 h to a methyl vinyl ketone-air mixture. The methyl vinyl ketone and O_3 concentrations were monitored by GC and chemiluminescence, respectively, and the rate coefficient obtained by fitting the measured methyl vinyl ketone and O_3 concentrations to a computer model.

(b) The decays of methyl vinyl ketone were measured in the presence of excess concentrations of O_3, with cyclohexane also being present as an HO radical scavenger.

Preferred Values

$k = 5.2 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.5 \times 10^{-16}$ exp(-1520/T) cm^3 molecule^{-1} s^{-1} over the temperature range 240–330 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The measured room temperature rate coefficients (Atkinson et al., 1981; Kamens et al., 1982; Treacy et al., 1992; Grosjean et al., 1993; Grosjean and Grosjean, 1998; Neeb et al., 1998) range over a factor of 1.5, with the temperature dependent study of Treacy et al. (1992) having the lowest measured rate coefficient (taking into account the actual value of room temperature in the various studies). The preferred 298 K rate coefficient is the average of all of the measured rate coefficients (Atkinson et al., 1981; Kamens et al., 1982; Treacy et al., 1992; Grosjean et al., 1993; Grosjean and Grosjean, 1998; Neeb et al., 1998), adjusted to 298 K where necessary (Atkinson et al., 1981; Kamens et al., 1982; Grosjean et al., 1993; Grosjean and Grosjean, 1998; Neeb et al., 1998) using the temperature dependence of Treacy et al. (1992). The temperature dependence measured by Treacy et al. (1992) is accepted, and is combined with the 298 K preferred value to obtain the pre-exponential factor.

The reaction proceeds by initial addition of O_3 to the C=C bond to form a primary ozonide which rapidly decomposes to methylglyoxal + $[CH_2OO]^*$ or to formaldehyde + $[CH_3C(O)CHOO]^*$ (see data sheets on the reactions of O_3 with ethene and propene). Methylglyoxal has been observed as a major product of this reaction, with a formation yield of 82–92% (Grosjean et al., 1993), indicating that formation of methylglyoxal + $[CH_2OO]^*$ dominates. HO radicals are also formed, with measured yields of 16±8% (Aschmann et al, 1996) and 16±5% (Paulson et al., 1998).

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II.A1.161

O_3 + 3-methylfuran → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.04 \pm 0.08) \times 10^{-17}$	296 ± 2	Alvarado et al., 1996	RR (a)

Comments

(a) Relative rate method carried out at atmospheric pressure of air. The concentrations of 3-methylfuran and propene (the reference compound) were measured by GC, and cyclohexane was added to the reactant mixtures to scavenge the HO radicals formed (Atkinson, 1997). The measured rate coefficient ratio of $k(O_3$ + 3-methylfuran)/$k(O_3$ + propene) = 2.12 ± 0.08 is placed on an absolute basis by use of a rate coefficient of $k(O_3$ + propene) = 9.6×10^{-18} cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation).

Preferred Values

$k = 2.0 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the sole study of this reaction by Alvarado et al. (1996). The reaction proceeds by initial addition of O_3 to the C=C bonds. HO radicals were observed to be formed from the reaction of O_3 with 3-methylfuran, in ∼60% yield (Alvarado et al., 1996).

References

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IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2005.

II.A1.162

O_3 + CH_2=C(CH_3)C(O)OONO$_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
(8.2 ± 2.0) × 10^{-18}	295 ± 5	Grosjean et al., 1993	(a)

Comments

(a) Experiments were carried out at atmospheric pressure of air, by monitoring the decay rates of CH_2=C(CH_3)C(O)OONO$_2$ (MPAN) in the presence of known excess concentrations of O_3. Cyclohexane was added to the reactant mixtures to scavenge any OH radicals present. MPAN concentrations were measured by GC with electron capture detection.

Preferred Values

$k = 8.2 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the sole study of this reaction by Grosjean et al. (1993). The rate coefficient for this reaction is similar in magnitude to those for the reactions of O_3 with propene (Atkinson, 1997; IUPAC, current recommendation) and 2-methylpropene (Atkinson, 1997) and a factor of 5 higher than that for the reaction of O_3 with ethene (Atkinson, 1997; IUPAC, current recommendation). This reactivity of MPAN towards O_3 is consistent with the recommended rate coefficient for the reaction of MPAN with HO radicals (IUPAC, current recommendation). The reaction of O_3 with MPAN proceeds by initial addition of O_3 to the C=C bond, and formaldehyde has been observed as a reaction product with a formation yield of 60 ±10% (Grosjean et al., 1993).

References

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IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2005.

II.A1.163

O_3 + Pinonaldehyde → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.9 \pm 1.3) \times 10^{-20}$	300 ± 5	Glasius et al., 1997	S-FTIR (a,b)
$<2 \times 10^{-20}$	296 ± 2	Alvarado et al., 1998	S-GC (a,c)

Comments

(a) Decays of pinonaldehyde monitored in the presence of an excess concentration of O_3 in the presence of ∼1 bar of air.

(b) Pinonaldehyde was observed to decay to the 480 L reaction chamber walls in the absence of O_3, and these measured dark decays were taken into account in the data analysis.

(c) No decays of pinonaldehyde (<5%) were observed in the 7000 L Teflon chamber used.

Preferred Values

$k < 2 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit to the 298 K rate coefficient is based on the study of Alvarado et al. (1998) carried out in a large volume Teflon chamber in which no wall losses of pinonaldehyde were observed.

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II.A1.164

O_3 + $(CH_3)_2C(OH)CH{=}CH_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.00 \pm 0.3) \times 10^{-17}$	291 ± 1	Grosjean and Grosjean, 1994	S-UV
Relative Rate Coefficients			
9×10^{-18}	298 ± 2	Fantechi et al., 1998a	RR (a)

Comments

(a) O_3 was reacted with 2-methyl-3-buten-2-ol and propene or 2-methylpropene (the reference compounds) in the presence of propane as an OH radical scavenger. The concentrations of 2-methyl-3-buten-2-ol and propene or 2-methylpropene were monitored by FTIR spectroscopy. The measured rate coefficient ratios (which were not reported) were placed on an absolute basis by use of rate coefficients at 298 K of $k(O_3$ + propene) = 1.2×10^{-17} cm^3 molecule^{-1} s^{-1} (Atkinson et al., 1992) and $k(O_3$ + 2-methylpropene) = 1.13×10^{-17} cm^3 molecule^{-1} s^{-1} (Atkinson, 1997). The reference compound corresponding to each of the two reported rate coefficients of $k(O_3$ + 2-methyl-3-buten-2-ol) = $(1.15\pm0.22) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} and $(8.0 \pm 1.0) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} was not reported; however, using the currently recommended rate coefficients at 298 K of $k(O_3$ + propene) = 1.01×10^{-17} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003a; IUPAC, current recommendation) and $k(O_3$ + 2-methylpropene) = 1.13×10^{-17} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003a) results in the approximate average rate coefficient cited in the table.

Preferred Values

$k = 1.0 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The rate coefficients of Grosjean and Grosjean (1994) at 291±1 K and of Fantechi et al. (1998a) at 298±2 K are in reasonable agreement. However, as noted in comment (a), the lack of detail in the Fantechi et al. (1998a) publication makes re-evaluation of their data somewhat uncertain, especially the derivation of the associated uncertainty. Assuming that the reaction of O_3 with 2-methyl-3-buten-2-ol has a similar temperature dependence to the reactions of O_3 with propene and 2-methylpropene (which have similar room temperature rate coefficients as noted in comment (a)), then the Grosjean and Grosjean (1994) rate coefficient corresponds to a 298 K rate coefficient of $\sim1.16\times10^{-17}$ cm^3 molecule^{-1} s^{-1}. The preferred value is an average of the 298 K rate coefficients obtained from the studies of Grosjean and Grosjean (1994) and Fantechi et al. (1998a).

The reaction proceeds by initial addition of O_3 across the C=C bond to form a 'primary ozonide' which rapidly decomposes to $(CH_3)_2C(OH)CHO + [CH_2OO]^*$ and to HCHO + $[(CH_3)_2C(OH)CHOO]^*$ (Grosjean and Grosjean, 1995; Fantechi et al., 1998b; Alvarado et al., 1999). Product studies of this reaction have been carried out by Grosjean and Grosjean (1995), Fantechi et al. (1998b) and Alvarado et al. (1999) (see also Atkinson and Arey, 2003b), and the observed products are HCHO, $(CH_3)_2C(OH)CHO$ (2-hydroxy-2-methylpropanal), acetone, formic acid, and HO radicals. There are significant discrepancies in the measured yields of formaldehyde, 2-hydroxy-2-methylpropanal and acetone (Grosjean and Grosjean, 1995; Fantechi et al., 1998b; Alvarado et al., 1999; Atkinson and Arey, 2003b), with the most recent and extensive study of Alvarado et al. (1999) reporting molar formation yields of: HCHO, 29±3%; $(CH_3)_2C(OH)CHO$, ∼47%; acetone, initially ∼15% and apparently increasing with the extent of reaction; and HO radicals, 19^{+10}_{-7}%. As discussed by Grosjean and Grosjean (1995) and Alvarado et al. (1999), acetone is presumably formed from the $[(CH_3)_2C(OH)CHOO]^*$ Criegee intermediate, and this may account for the variable yields reported (Grosjean and Grosjean, 1995; Fantechi et al., 1998b; Alvarado et al., 1999; Atkinson and Arey, 2003b) and for the observation of Alvarado et al. (1999) of an increasing yield with extent of reaction. Note that the reported yields of 2-hydroxy-2-methylpropanal (Grosjean and Grosjean, 1995; Alvarado et al., 1999) are likely to be lower limits because of the difficulties in quantitatively analyzing this hydroxyaldehyde, which is not commercially available and does not elute from GC columns without prior derivatization.

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Appendix A2: HO_x + VOC reactions

II.A2.3

$$HO + CH_4 \rightarrow H_2O + CH_3$$

$\Delta H^\circ = -57.8 \mathrm{kJ} \cdot \mathrm{mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.3 \pm 0.9) \times 10^{-12}$	1234±15	Bott and Cohen, 1989	SH-RA
$1.59 \times 10^{-20}\ T^{2.84} \exp(-978/T)$	223–420	Vaghjiana and	PLP-LIF
6.35×10^{-15}	298	Ravishankara, 1991	
$4.0 \times 10^{-12} \exp[-(1994 \pm 114)/T]$	278–378	Finlayson-Pitts et al., 1992	DF-RF
5.87×10^{-15}	298		
$9.65 \times 10^{-20}\ T^{2.58} \exp(-1082/T)$	293–800	Dunlop and Tully, 1993	PLP-LIF (a)
$(5.62 \pm 0.43) \times 10^{-15}$	293		
$2.56 \times 10^{-12} \exp[-(1765 \pm 146)/T]$	233–343	Mellouki et al., 1994	PLP-LIF
$(6.34 \pm 0.88) \times 10^{-15}$	298		
$1.85 \times 10^{-20}\ T^{+2.82} \exp[-(987 \pm 6)/T]$	195–296	Gierczak et al., 1997	PLP-LIF
$(6.40 \pm 0.38) \times 10^{-15}$	298		FP-LIF (b)
$5.65 \times 10^{-21}\ T^{3.01} \exp[-(959 \pm 36)/T]$	295–668	Bonard et al., 2002	PLP-LIF
$(6.23 \pm 0.20) \times 10^{-15}$	295		

Comments

(a) The temperature-dependent expression cited is that for the rate coefficients of Dunlop and Tully (1993) (T=293–800 K) combined with those of Vaghjiani and Ravishankara (1991) (T=223–420 K) and as such covers the temperature range 223–800 K.

(b) The temperature-dependent expression cited is that for the rate coefficients of Gierczak et al. (1997) (T=195–296 K) combined with those of Vaghjiani and Ravishankara (1991) (T=223–420 K) obtained using a similar technique, and therefore covers the temperature range 195–420 K.

Preferred Values

$k = 6.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.85 \times 10^{-12} \exp(-1690/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The absolute rate coefficients of Vaghjiani and Ravishankara (1991), Finlayson-Pitts et al. (1992), Dunlop and Tully (1993), Mellouki et al. (1994), Gierczak et al. (1997) and Bonard et al. (2002) are in good agreement. However, over the temperature range ∼250–420 K these rate coefficients of Vaghjiani and Ravishankara (1991), Finlayson-Pitts et al. (1992), Dunlop and Tully (1993), Mellouki et al. (1994), Gierczak et al. (1997) and Bonard et al. (2002) are ∼20% lower than most of the previously reported absolute rate coefficients (Atkinson, 1994).

The preferred values are derived from the absolute rate coefficient data of Vaghjiani and Ravishankara (1991) and Gierczak et al. (1997), both conducted over significant and overlapping temperature ranges. The temperature-dependent expression obtained by Gierczak et al. (1997) from a fit of their data and those of Vaghjiani and Ravishankara (1991) to the three-parameter equation k=CT^n exp(-D/T) is accepted, of k=1.85×10^{-20} $T^{2.82}$ exp(-987/T) cm^3 molecule^{-1} s^{-1} over the temperature range 195–420 K (Gierczak et al., 1997). The preferred Arrhenius expression, k=A exp(-B/T), is centered at 250 K and is derived from the three-parameter equation with A=Ce^n T^n and B=$D + nT$. The recommended three-parameter expression leads to calculated rate coefficients at 800 K and 1234 K which are within 12% and 3%, respectively of the values measured by Dunlop and Tully (1993) at 800 K and Bott and Cohen (1989) at 1234 K, and agrees to within 8% with the rate coefficients measured by Bonard et al. (2002) over the temperature range 295–668 K.

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II.A2.4

$$\mathbf{HO + C_2H_2 + M \rightarrow C_2H_2OH + M}$$

$\Delta H^\circ = -145\text{kJ} \cdot \text{mol}^{-1}$

Low-pressure Rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3\pm1) \times 10^{-30}(T/300)^{1.0}$ [Ar]	297–429	Perry and Williamson, 1982	FP-RF (a)
$(6\pm3) \times 10^{-30}$ [He]	298	Hack et al., 1983	DF-EPR (b)
$(2.5\pm0.3) \times 10^{-30}$[Ar]	295	Schmidt et al., 1985	PLP-LIF (c)
5×10^{-30} [N_2]	298	Wahner and Zetzsch, 1985	PLP-A (d)
$(4.1\pm1.6) \times 10^{-30}$ [N_2]	298	Bohn et al., 1996	PLP-A (e)
4.3×10^{-29} $(T/300)^{-3.1}$exp (-910/T)[He]	300–814	Fulle et al., 1997	PLP-LIF (f)
2.1×10^{-30}[He]	298		
Absolute Rate Coefficients			
$(2.92\pm0.55) \times 10^{-30}$[air]	296	Sørenson et al., 2003	RR (g)

Comments

(a) Photolysis of H_2O-C_2H_2 mixtures at 26-530 mbar Ar diluent. Pressure dependence observed is in agreement with earlier work (Perry et al., 1977; Michael et al., 1980). Evaluation of the falloff curve with F_c=0.5.

(b) Pressures of 2.0-2.6 mbar were used. By the use of data from Perry and Williamson (1982) and F_c=0.5, a falloff analysis of the measured k leads to the given k_0 value.

(c) Experiments in He, Ar and N_2 at pressures between 1 mbar and 1000 mbar (in Ar). Construction of falloff curve with F_c=0.6 leads to $k_\infty=(8.3\pm0.8) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(d) Experiments in N_2 over the range 20 mbar to 1000 mbar. Falloff curve constructed with F_c=0.6 leading to $k_\infty=9\times10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(e) Experiments with M=N_2, O_2 and synthetic air at pressures from 15 mbar to 1 bar. Falloff extrapolation with F_c=0.6. Effective rate coefficients for HO radical removal in O_2 and synthetic air were markedly lower than in N_2 due to HO radical regeneration by the reaction $C_2H_2OH+O_2 \rightarrow HO$ + products, which shows evidence for an influence of the extent of vibrational de-excitation of C_2H_2OH.

(f) Pressure range 2 mbar to 130 bar of He. Combined with the data of (Schmidt et al., 1985), falloff curves were constructed using a calculated F_c = [0.17 exp(-51/T) + exp(-T/204)], i.e., F_c(298 K) = 0.37. From a third-law analysis of the equilibrium constant, the value $\Delta H^\circ(0\,\text{K}) = -(146\pm10)$ kJ mol^{-1} was derived. The equilibrium constant obtained at temperatures above 700 K is given by $K_c=5.4\times10^{-2}\ T^{-1.7}$ exp(17 560/T) bar^{-1}.

(g) HO radicals were generated by the photolysis of CH_3ONO in air. The concentrations of C_2H_2 and dimethyl ether or propane (the reference compounds) were monitored by in situ FTIR spectroscopy or GC-FID, respectively. The measured rate coefficient ratios k(HO + C2H2)/k(HO + dimethyl ether) and k(HO + C_2H_2)/k(HO + propane) were placed on an absolute basis using rate coefficients of k(HO + dimethyl ether) = 2.98×10^{-12} cm^3 molecule^{-1} s^{-1} and k(HO + propane) = 1.11×10^{-12} cm^3 molecule^{-1} s^{-1} (Sørensen et al., 2003). Experiments were carried out over the pressure range 25–750 Torr (33–1000 mbar) of air or O_2 with analysis by FTIR spectroscopy and dimethyl ether as the reference compound, and over the pressure range 25–7905 Torr (33 mbar to 10.5 bar) of O_2–N_2 diluent, with propane as the reference organic. Falloff curve was constructed with F_c=0.6. Use of F_c=0.4 led to $k_0 = (7.00 \pm 1.30) \times 10^{-30}$ [air] cm^3 molecule^{-1} s^{-1} and $k_\infty = (1.06 \pm 0.034) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k_0 = 5 \times 10^{-30} (T/300)^{-1.5} [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 300–800 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.
$\Delta n = \pm 1.5$.

Comments on Preferred Values

The preferred rate coefficient at 298 K is based on the experimental data of Schmidt et al. (1985), Wahner and Zetzsch (1985) and Bohn et al. (1996) and the theoretical analysis of Smith et al. (1984). The temperature dependence is based on the data of Perry et al. (1977), Michael et al. (1980) and Perry and Williamson (1982) as discussed and evaluated by Atkinson (1989). At temperatures above ∼500 K another component of the rate coefficient with a much stronger temperature dependence also has to be taken into account (Atkinson, 1989). The preferred values should be used in connection with the calculated F_c values from Fulle et al. (1997) such as given in comment (f) of k_0 (F_c = 0.37 at 298 K).

A comparison of the data of Perry et al. (1977), Michael et al. (1980), Perry and Williamson (1982), Hack et al. (1983), Atkinson and Aschmann (1984), Schmidt et al. (1985), Wahner and Zetzsch (1985), Hatakeyama et al. (1986), Liu et al. (1988), Arnts et al. (1989) and Bohn et al. (1996) at pressures between 0.01–1 bar with the results from Fulle et al. (1997) at 2–80 bar shows considerable discrepancies, with the data of Fulle et al. (1997) leading to k_∞ considerably higher than the lower pressure data. This influences the construction of falloff curves and the extrapolation to k_0. The recent study of Sørensen et al. (2003) confirms the earlier data of Perry et al. (1977), Michael et al. (1980), Perry and Williamson (1982), Hack et al. (1983), Atkinson and Aschmann (1984), Schmidt et al. (1985), Wahner and Zetzsch (1985), Hatakeyama et al. (1986), Liu et al. (1988), Arnts et al. (1989) and Bohn et al. (1996) [see below].

High-pressure Rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.91\pm0.90) \times 10^{-13}$	297	Perry and Williamson, 1982	FP-RF (a)
$(8.3\pm0.8) \times 10^{-13}$	295	Schmidt et al., 1985	PLP-LIF (b)
9×10^{-13}	298	Wahner and Zetzsch, 1985	PLP-A (c)
$(8.5\pm0.6) \times 10^{-13}$	298	Bohn et al., 1996	PLP-A (d)
$8.5 \times 10^{-12} \exp(-705/T)$	333–1273	Liu et al., 1988	PR-RA (e)
8.0×10^{-13}	298*		
$3.8 \times 10^{-11} \exp(-910/T)$	300–814	Fulle et al., 1997	PLP-LIF (f)
1.8×10^{-12}	298*		
Relative Rate Coefficients			
$(8.1\pm1.3) \times 10^{-13}$ (1 bar air)	298	Atkinson and Aschmann, 1984	RR (g)
$(8.1\pm1.8) \times 10^{-13}$ (1 bar air)	297±2	Hatakeyama et al., 1986	RR (h)
$(7.0\pm0.7) \times 10^{-13}$ (1 bar air)	297 ± 2	Arnts et al., 1989	RR (i)
$(9.69\pm0.30) \times 10^{-13}$	296	Sørensen et al., 2003	RR (j)
$(7.67\pm0.06) \times 10^{-13}$ (1 bar air)	296	Sørensen et al., 2003	RR (k,l)
$(8.2\pm1.0) \times 10^{-13}$ (1 bar N_2-O_2)	296	Sørensen et al., 2003	RR (k,m)

Comments

(a) See comment (a) for k_0.

(b) See comment (c) for k_0.

(c) See comment (d) for k_0.

(d) See comment (e) for k_0.

(e) Measurements were conducted at 1 bar of Ar.

(f) See comment (e) for k_0.

(g) HO radicals were generated by the photolysis of CH_3ONO in CH_3ONO-NO-C_2H_2-cyclohexane-air mixtures at 1 bar total pressure. The concentrations of acetylene and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane)=6.97×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 1997).

(h) HO radicals were generated by photolysis of H_2O_2 in air at 254 nm. The concentrations of acetylene and cyclohexane (the reference compound) were monitored by FTIR spectrometry. Measurements were carried out at 1 bar pressure in air. The measured rate coefficient ratio $k(HO+C_2H_2)/k$(HO + cyclohexane) = 0.116 ± 0.025 is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane)=6.95×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 2003).

(i) HO radicals were generated by the photolysis of CH_3ONO in air at 1 bar pressure. The concentrations of acetylene and ethane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(HO+C_2H_2)/k$(HO + ethane) = 2.84 ± 0.26 (two standard deviations) is placed on an absolute basis by use of a rate coefficient of k(HO + ethane) = 2.45×10^{-13} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2005).

(j) See comment (g) for k_0.

(k) HO radicals were generated by the photolysis of CH_3ONO in air at 928–1013 mbar of O_2-N_2 diluent. The concentrations of C_2H_2 and dimethyl ether or propane (the reference compounds) were monitored by in situ FTIR spectroscopy or GC-FID, respectively. The measured rate coefficient ratios $k(HO + C_2H_2)/k$(HO + dimethyl ether) = 0.276 ± 0.021 and $k(HO + C_2H_2)/k$(HO + propane) = 0.761 ± 0.09 were placed on an absolute basis using rate coefficients of k(HO + dimethyl ether) = 2.78×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2005) and k(HO + propane) = 1.08×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2005).

(l) Relative to dimethyl ether.

(m) Relative to propane.

Preferred Values

$k = 7.8\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K and 1 bar of air.
$k_\infty = 1.0\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 1 bar air and 298 K.
$\Delta \log k_\infty = \pm 0.3$ at 298 K.

Comments on Preferred Values

The recent study of Sørensen et al. (2003) confirms the earlier data of Perry et al. (1977), Michael et al. (1980), Perry and Williamson (1982), Atkinson and Aschmann (1984), Schmidt et al. (1985), Wahner and Zetzsch (1985), Hatakeyama et al. (1986), Liu et al. (1988), Arnts et al. (1989) and Bohn et al. (1996), all of which indicate a rate coefficient at room temperature and 1 bar of air or N_2 of $\sim 8\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} and a value of $k_\infty \sim 1.0\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. These data are, however, inconsistent with those from the study of Fulle et al. (1997), for reasons which are presently not understood (at 298 K and 1 bar of He, the data of Fulle et al. (1997) lead to $k = 1.12\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, with $k_\infty = 1.8\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K).

The preferred values are based on the data of Perry and Williamson (1982), Atkinson and Aschmann (1984), Schmidt et al. (1985), Wahner and Zetzsch (1985), Hatakeyama et al. (1986), Liu et al. (1988), Arnts et al. (1989), Bohn et al. (1996) and Sørensen et al. (2003) and are applicable to room temperature only.

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II.A2.5

$HO + C_2H_4 + M \rightarrow C_2H_4OH + M$

$\Delta H^\circ = -23 \text{kJ} \cdot \text{mol}^{-1}$

Low-pressure Rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
5.5×10^{-29} [Ar]	296	Zellner and Lorenz, 1984	PLP-RF (a)
$(6.1\pm1.2) \times 10^{-29}$ [N_2]	300	Kuo and Lee, 1991	DF-RF (b)
$(5.2\pm1.1) \times 10^{-29}$ [O_2]	300		
$4.1 \times 10^{-29} (T/300)^{-3.4}$ [He]	300–800	Fulle et al., 1997	PLP-LIF (c)
$(2.8\pm0.1) \times 10^{-29} (T/300)^{-3.5}$ [He]	300–423	Chuong and Stevens, 2000	DF-LIF (d)
$(11.6\pm1.8) \times 10^{-29}$ [N_2]	296	Vakhtin et al., 2003	PLP-LIF (e)
Relative Rate Coefficients			
$(9.5^{+3.2}_{-2.4}) \times 10^{-29}$ [air]	295	Klein et al., 1984	RR (f)
$(5.9^{+3.0}_{-1.0}) \times 10^{-29}$ [Ar]	295		

Comments

(a) Pressure range 4 mbar to 130 mbar, temperature range 296 K to 524 K. Falloff extrapolation using F_c=0.8.

(b) Pressure range 0.4 mbar to 66 mbar. HO radicals were generated by reaction of H atoms with excess NO_2. Data extrapolated using F_c=0.7.

(c) The pressure was varied between 1 mbar and 150 bar. Falloff curves were also constructed using earlier rate data with a calculated F_c=0.21 exp(-220/T)+exp(-T/305) and F_c (300)=0.47. The value ΔH° (0 K)=−(123±6) kJ mol^{-1} was derived from a third-law analysis of the equilibrium constant K_c for which $K_c=2.1\times10^{-2}\ T^{-0.95}$ exp(14 780/T) bar^{-1} was obtained from measurements performed at 646–803 K and He pressures up to 140 bar.

(d) Pressure range 2.6 mbar to 8 mbar. Falloff extrapolation using F_c=0.6 and $k_\infty=1.96\times10^{-12}$ exp(438/T) cm^3 molecule^{-1} s^{-1} from Klein et al. (1984). Differences to the results from Fulle et al. (1997) due to the use of a larger F_c.

(e) Experiments with pulsed Laval nozzle supersonic expansion over the range $2 \times 10^{16} \leq [N_2] \leq 3 \times 10^{18}$ cm^3 molecule^{-1} s^{-1} at 296 K. Single experiments at (2–3) × 10^{16} cm^3 molecule^{-1} s^{-1} also at 96, 110, and 165 K. Falloff extrapolation with F_c = 0.65 and k_∞ (296 K) = 7.5×10^{-12} cm^3 molecule^{-1} s^{-1}.

(f) HO_2NO_2-NO system used as source of HO radicals. Reaction of HO radicals with C_2H_4 was studied in 420 L glass reactor relative to HO + n-hexane where the latter reaction was calibrated against absolute measurements of the reaction HO + n-butane [k(295 K)=2.53×10^{-12} cm^3 molecule^{-1} s^{-1}]. Pressure range 1.3–1000 mbar, falloff curves constructed with F_c=0.7.

Preferred Values

$k_0 = 8.6 \times 10^{-29} (T/300)^{-3.1} [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 2$.

Comments on Preferred Values

Preferred values are based on an average of the data from Zellner and Lorenz (1984), Kuo and Lee (1991), Fulle et al. (1997), Chuong and Stevens (2000), Klein et al. (1984), Atkinson (1994), Tully (1983), Davis et al. (1975), Howard (1976), Greiner (1970), Morris et al. (1971), Overend and Paraskevopoulos (1977), Atkinson et al. (1977), Lloyd et al. (1976), Cox (1975) and Vakhtin et al. (2003), where the latter work showed the lowest scatter and, therefore, is given the highest weight. Falloff curves are constructed with the calculated F_c=0.48 from Fulle et al. (1997).

High-pressure Rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.47\pm0.24) \times 10^{-12}$	291	Tully, 1993	PLP-LIF (a)
$3.3 \times 10^{-12} \exp[(320 \pm 150)/T]$	296–524	Zellner and Lorenz, 1984	PLP-RF (b)
9.7×10^{-12}	298		
$(9.4\pm1.6) \times 10^{-12}$	298	Nielsen et al., 1990	(c)
$(7.7\pm1.0) \times 10^{-12}$	298	Becker et al., 1991	PLP-LIF (d)
1.0×10^{-11}	300–800	Fulle et al., 1997	PLP-LIF (e)
$(8.7 \pm 0.7) \times 10^{-12} (T/300)^{-0.85}$	96–296	Vakhtin et al., 2003	PLP-LIF (f)
Relative Rate Coefficients			
$(7.84\pm0.35) \times 10^{-12}$	299±2	Atkinson et al., 1982	RR (g)
$(8.5 \pm0.6) \times 10^{-12}$	295	Klein et al., 1984	RR (h)

Comments

(a) Higher end of falloff curve at 66 mbar to 790 mbar; temperature range 291–591 K.

(b) See comment (a) for k_0.

(c) Pulse radiolysis of H_2O-Ar mixtures. HO monitored by UV absorption at 309 nm. Rate coefficient determined at a total pressure of 1 bar.

(d) Experiments were carried out at a total pressure of 1 bar of synthetic air. Numerical simulation with a mechanism of 12 reactions.

(e) See comment (c) for k_0.

(f) See comment (e) for k_0.

(g) HO radicals were generated by photolysis of CH_3ONO in presence of air containing NO. Concentrations of ethene and cyclohexane (the reference compound) were measured by GC. The rate coefficient ratio of k(HO + ethene)/k(HO + cyclohexane) = 1.12±0.05 is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 7.00 $\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson, 2003).

(h) See comment (e) for k_0.

Preferred Values

$k = 7.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.
$k_\infty = 9.0 \times 10^{-12} (T/300)^{-0.85}$ cm^3 molecule^{-1} s^{-1} over the temperature range 100–500 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.3$.

Comments on Preferred Values

The preferred value is from Vakhtin et al. (2003), being similar to those selected in Fulle et al. (1997), Lloyd et al. (1976) and Nielsen et al. (1990). Falloff curves should be calculated with the theoretical expression for F_0= 0.48 which probably applies to M = He as well as N_2 and is practically constant over the indicated temperature range.

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II.A2.6

$HO + C_2H_6 \rightarrow H_2O + C_2H_5$

$\Delta H^\circ = -74.1 \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.90 \pm 0.60) \times 10^{-13}$	296	Howard and Evenson, 1976	DF-LMR
$(2.6 \pm 0.4) \times 10^{-13}$	298	Leu, 1979	DF-RF
8.0×10^{-14}	238	Margitan amd Watson, 1982	PLP-RF
$1.43 \times 10^{-14}\ T^{1.05}\exp(-911/T)$	297–800	Tully et al., 1983	FP-RF
$(2.59 \pm 0.21) \times 10^{-13}$	297		
$1.80 \times 10^{-11}\ \exp[-(1240 \pm 110)T]$	240–295	Smith et al., 1984	FP-RF
$(2.63 \pm 0.10) \times 10^{-13}$	295		
2.75×10^{-13}	295	Devolder et al., 1984	DF-RF
$(2.67 \pm 0.40) \times 10^{-13}$	295±2	Baulch et al., 1985	DF-RF
$8.51 \times 10^{-18} T^{2.06}\exp(-430/T)$	293–705	Tully et al., 1986	PLP-LIF
$(2.39 \pm 0.10) \times 10^{-13}$	292.5		
$(1.27 \pm 0.08) \times 10^{-13}$	248	Stachnik et al., 1986	PLP-RA
$(1.29 \pm 0.09) \times 10^{-13}$	248		
$(2.51 \pm 0.06) \times 10^{-13}$	297		
$(2.50 \pm 0.06) \times 10^{-13}$	297		
$(2.77 \pm 0.3) \times 10^{-13}$	296 ± 2	Bourmada et al., 1987	DF-RF
$8.4 \times 10^{-12}\exp[-(1050 \pm 100)T]$	226–363	Wallington et al., 1987	FP-RF
$(2.30 \pm 0.26) \times 10^{-13}$	296		
$(2.61 \pm 0.13) \times 10^{-13}$	296	Zabarnick et al., 1988	PLP-LIF
$(2.38 \pm 0.16) \times 10^{-13}$	297±2	Abbatt et al., 1990	DF-LIF
$(1.54 \pm 0.24) \times 10^{-11}$	1225±16	Bolt and Cohen, 1991	SH-RA
$1.03 \times 10^{-11}\exp[-(1108 \pm 40)/T]$	231–377	Talukdar et al., 1994	PLP-LIF
$(2.43 \pm 0.13) \times 10^{-13}$	298		
8.37×10^{-12}	974±16	Koffend and Cohen, 1996	SH-RA
$(2.55 \pm 0.3) \times 10^{-13}$	300	Donahue et al., 1996	DF-LIF
$(2.59 \pm 0.08) \times 10^{-13}$	300	Donahue et al., 1998	DF-LIF
$(3.55 \pm 0.11) \times 10^{-13}$	325		
$(3.90 \pm 0.12) \times 10^{-13}$	340		
$(4.38 \pm 0.23) \times 10^{-13}$	360		
$(5.61 \pm 0.17) \times 10^{-13}$	375		
$(6.04 \pm 0.18) \times 10^{-13}$	390		
$(2.69 \pm 0.27) \times 10^{-14}$	180	Clarke et al., 1998	DF-LIF
$(3.77 \pm 0.04) \times 10^{-14}$	190		
$(4.54 \pm 0.25) \times 10^{-14}$	200		
$(6.51 \pm 0.07) \times 10^{-14}$	213		
$(8.08 \pm 0.12) \times 10^{-14}$	225		
$(9.67 \pm 0.18) \times 10^{-14}$	238		
$(1.251 \pm 0.014) \times 10^{-13}$	250		
$(1.640 \pm 0.018) \times 10^{-13}$	265		
$(2.081 \pm 0.016) \times 10^{-13}$	280		
$(2.515 \pm 0.021) \times 10^{-13}$	295		
$(2.953 \pm 0.050) \times 10^{-13}$	310		
$(3.464 \pm 0.037) \times 10^{-13}$	325		
$(3.744 \pm 0.038) \times 10^{-13}$	340		
$(4.637 \pm 0.164) \times 10^{-13}$	360		

Preferred Values

$k = 2.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.9 \times 10^{-12}$ exp(-1000/T) cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred values were obtained by using the absolute rate coefficient data of Smith et al. (1984), Tully et al. (1986) (this study being judged to supersede that of Tully et al., 1983), Stachnick et al. (1986), Wallington et al. (1987), Abbatt et al. (1990), Bott and Cohen (1991), Talukdar et al. (1994), Koffend and Cohen (1996), Donahue et al. (1996, 1998) and Clarke et al. (1998). The absolute rate coefficients used in the evaluation (Smith et al., 1984; Tully et al., 1986; Stachnik et al., 1986; Wallington et al., 1987; Abbatt et al., 1990; Bott and Cohen, 1991; Talukdar et al., 1994; Koffend and Cohen, 1996; Donahue et al., 1996, 1998; Clarke et al., 1998) were fitted to the three-parameter equation k=CT^2 exp(-D/T), resulting in k=1.49×10$^{-17}T^2$ exp(-499/T) cm^3 molecule^{-1} s^{-1} over the temperature range 180–1230 K. The preferred Arrhenius expression, $k = A$ exp(-B/T), is centered at 250 K and is derived from the three-parameter equation with $A = Ce^2T^2$ and $B = D + 2T$. The preferred Arrhenius expression predicts rate coefficients at 180 K and 190 K which agree to within 6% with those measured by Clarke et al. (1998).

The absolute rate coefficients of Howard and Evenson (1976), Leu (1979), Margitan and Watson (1982), Devolder et al. (1984), Baulch et al. (1985), Bourmada et al. (1987), Zabarnick et al. (1988) and Schiffman et al. (1991) (at room temperature, the precise temperature not being specified), which are not used in the evaluation of the rate coefficient, are in good agreement with the preferred values, as are the relative rate coefficients of Baulch et al. (1983), Edney et al. (1986) and Finlayson-Pitts et al. (1993).

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II.A2.7

HO + C_3H_6 + M → C_3H_6OH + M

$\Delta H^\circ = -134 \text{kJ} \cdot \text{mol}^{-1}$

Low-pressure Rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
8×10^{-28}[Ar]	298	Zellner and Lorenz, 1983	PLP-RF (a)
9×10^{-27}[N_2]	298	Vakhtin et al., 2003	PLP-LIF (b)
Relative Rate Coefficients			
8×10^{-27}[Ar]	298	Klein et al., 1984	(c)
8×10^{-27}[air]			

Comments

(a) Pressure range 1.3 mbar to 170 mbar. Falloff behavior detected, and evaluated with F_c=0.8. Rough estimate of k_0 because of the only limited extent of observed falloff.

(b) Experiments with pulsed Laval nozzle supersonic expansion over the range $2 \times 10^{-16} \leq [N_2] \leq 3 \times 10^{18}$ molecule cm^{-3} at 296 K. Single experiments at (2–3) $\times 10^{16}$ molecule cm^{-3} of N_2 were also carried out at 96, 103, and 165 K. Rough estimate of k_0 because of limited extent of observed falloff. Falloff curves constructed with F_c = 0.5 and k_∞ (296 K) = 2.6×10^{-11} cm^3 molecule^{-1} s^{-1} . See also comment (d) for k_∞.

(c) HO_2NO_2-NO system used as source of HO radicals. Reaction studied relative to HO + *n*-hexane, with the latter reaction calibrated against absolute measurements of the reaction HO + *n*-butane (k=2.53×10^{-12} cm^3 molecule^{-1} s^{-1} at 295 K). Pressure range 1.3 mbar to 1000 mbar; falloff effects could be detected. Evaluation with F_c=0.5 gives the present k_0 value. Rough estimate of k_0 because of the only limited extent of observed falloff.

Preferred Values

$k_0 = 8 \times 10^{-27} (T/300)^{-3.5} [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 1.0$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The uncertainty of the extrapolated k_0 is large, because the reaction is close to the high-pressure limit at the pressures studied. The preferred values follow the falloff extrapolation from Klein et al. (1984) which shows the smallest scatter. Falloff extrapolations are made using F_c=0.5 at 300 K. The temperature coefficient of k_0 is estimated by analogy to the reaction $HO+C_2H_4+M \rightarrow C_2H_4OH+M$.

High-pressure Rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.0\pm0.5)\times10^{-11}$	298	Zellner and Lorenz, 1984	PLP-RF (a)
$(8.1\pm1.8)\times10^{-11}$	103	Vakhtin et al., 2001	(b)
$(2.95\pm0.10)\times10^{-11}\ (T/300)^{-1.06}$	96-296	Vakhtin et al., 2003	PLP-LIF (c)
Relative Rate Coefficients			
$(3.0\pm0.2)\times10^{-11}$	295	Klein et al., 1984	(d)

Comments

(a) See comment (a) for k_0.

(b) Pulsed Laval nozzle supersonic expansion of nitrogen with admixed reactants. HO generated by photolysis of H_2O_2 $[N_2]=2.1\times10^{16}$ molecule cm^{-3}. Reaction observed very close to the high pressure limit.

(c) See comment (b) for k_0.

(d) See comment (c) for k_0.

Preferred Values

$k = 2.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.
$k_\infty = 3.0\times10^{-11}\ (T/300)^{-1}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm\ 0.1$ over the temperature range 200–300 K.
$\Delta n = \pm\ 1$.

Comments on Preferred Values

The preferred values are based on Zellner and Lorenz (1984), Klein et al. (1984), Vakhtin et al. (2003), Nielsen et al. (1990) and Tully and Goldsmith (1985). There is an uncertainty about the extent of falloff at temperatures above 300 K and there is the possibility of a small activation barrier, such as observed in the reaction $HO+C_2H_2+M\rightarrow C_2H_2OH+M$. The preferred temperature dependence is derived by combining the results from Zellner and Lorenz (1984), Klein et al. (1984) and Vakhtin et al. (2003), confirming the suggestions from Atkinson (1994) and Tsang (1991). F_c=0.5 serves for estimating the extent of falloff.

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II.A2.8

$$\begin{aligned} \textbf{HO + C}_3\textbf{H}_8 \quad &\rightarrow \textbf{H}_2\textbf{O + CH}_3\textbf{CH}_2\textbf{CH}_2 \quad \textbf{(1)} \\ &\rightarrow \textbf{H}_2\textbf{O + CH}_3\textbf{CHCH}_3 \quad \textbf{(2)} \end{aligned}$$

$\Delta H^0\,(1) = -73.7\,\text{kJ}\cdot\text{mol}^{-1}$

$\Delta H^0\,(2) = -87.9\,\text{kJ}\cdot\text{mol}^{-1}$

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
(2.62±0.67) × 10^{-11}	1220 ± 15	Bott and Cohen, 1984	SH-RA
(2.19±0.60) × 10^{-11}	1074	Smith et al., 1985	LH-LIF
(1.20±0.18) × 10^{-12}	295 ± 2	Baulch et al., 1985	DF-RF
1.04 × $10^{-16}T^{1.72}$exp(-145/T)	293–854	Droege and Tully, 1986	PLP-LIF
(1.10±0.04) × 10^{-12}	293		
(1.21±0.10) × 10^{-12}	297 ± 2	Abbatt et al., 1990	DF-LIF
(1.22±0.08) × 10^{-12}	298	Mac Leod et al., 1990	PLP-LIF
9.81 × 10^{-12}exp[-(650± 30)/T]	233–363	Mellouki et al., 1994	PLP-LIF
(1.05±0.09) × 10^{-12}	295		
1.01 × 10^{-11}exp[-(657± 46)/T]	233–376	Talukdar et al., 1994	PLP-LIF
(1.11±0.04) × 10^{-12}	298		
(1.09±0.03) × 10^{-12}	300	Donahue et al., 1998	DF-LIF
(1.37±0.04) × 10^{-12}	325		
(1.46±0.04) × 10^{-12}	340		
(1.60±0.09) × 10^{-12}	360		
(1.85±0.06) × 10^{-12}	375		
(1.83±0.10) × 10^{-12}	390		
(3.626±0.247) × 10^{-13}	190	Clarke et al., 1998	DF-LIF
(4.136±0.127) × 10^{-13}	200		
(4.864±0.095) × 10^{-13}	213		
(5.602±0.063) × 10^{-13}	225		
(6.475±0.053) × 10^{-13}	238		
(7.532±0.051) × 10^{-13}	250		
(8.691±0.147) × 10^{-13}	265		
(1.129±0.0159) × 10^{-12}	295		
(1.276±0.0182) × 10^{-12}	310		
(1.356±0.0140) × 10^{-12}	325		
(1.480±0.0136) × 10^{-12}	340		
(1.640±0.0229) × 10^{-12}	360		
(1.15±0.1) × 10^{-12}	298	Carl and Crowley, 2001	PLP-RF
(1.17±0.1) × 10^{-12}	298		
5.81 × $10^{-12}T^{1.83}$ exp(-167/T)	210–480	Kozlov et al., 2003	FP-RF
(1.13±0.02) × 10^{-12}	298		

Preferred Values

k = 1.1 × 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 7.6 × 10^{-12} exp(-585/T) cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

Δ log k = $\pm$ 0.08 at 298 K.
Δ (E/R) = $\pm$ 100 K.

Comments on Preferred Values

The absolute rate coefficient data of Bott and Cohen (1984), Smith et al. (1985), Droege and Tully (1986), Abbatt et al. (1990), Mac Leod et al. (1990), Mellouki et al. (1994), Talukdar et al. (1994), Donahue et al. (1998) and Clarke et al. (1998) were used to derive the preferred value. These data were fitted to the three-parameter equation k=CT^2 exp(-D/T), resulting in k=1.65$\times$10^{-17}T^2 exp(-87/T) cm^3 molecule^{-1} s^{-1} over the temperature range 190–1220 K. The rate coefficients recently measured by Kozlov et al. (2003) are in agreement with the preferred value to within 5% over the entire temperature range studied (210–480 K). The preferred Arrhenius expression, k=A exp($-B/T$), is centered at 250 K, and is derived from the three-parameter equation with A=Ce^2T^2 and $B = D + 2T$. The preferred Arrhenius expression predicts a rate coefficient at 190 K which is within 4% of that measured by Clarke et al. (1998). The relative rate coefficients of Atkinson et al. (1982), Baulch et al. (1983), Edney et al. (1986), Nielsen et al. (1991), Finlayson-Pitts et al. (1993) and DeMore and Bayes (1999) are in good agreement with the recommended expression, as are the absolute rate coefficients of Tully et al. (1983) (judged to be superseded by the study of Droege and Tully, 1986), Baulch et al. (1985), Schiffman et al. (1991) and Carl and Crowley (2001).

Droege and Tully (1986) also measured rate coefficients for the reaction of the HO radical with fully and partially deuterated propanes, and derived a value of k_1/k_2=226 $T^{-0.64}$ exp(-816/T), leading to k_1=3.0$\times$10^{-13} cm^3 molecule $^{-1}$ s^{-1} at 298 K and k_2=8.0$\times$10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K.

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II.A2.9

$$\mathbf{HO + CH_3CH_2CH_2CH_3} \begin{array}{ll} \rightarrow \mathbf{H_2O + CH_2CH_2CH_2CH_3} & \mathbf{(1)} \\ \rightarrow \mathbf{H_2O + CH_3CHCH_2CH_3} & \mathbf{(2)} \end{array}$$

$\Delta H^0\,(1) = -72.4\,\mathrm{kJ \cdot mol^{-1}}$

$\Delta H^0\,(2) = -86.6\,\mathrm{kJ \cdot mol^{-1}}$

Rate coefficient data (*k*=*k_1*+*k_2*)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.41 \times 10^{-11}\exp[-(524\pm93)/T]$	298–495	Greiner, 1970	FP-AS
$(2.56\pm0.08) \times 10^{-12}$	298		
$(2.35\pm0.35) \times 10^{-12}$	298	Stuhl, 1973	FP-RF
$(4.22\pm0.17) \times 10^{-12}$	298	Gordon and Mulac, 1975	PR-RA
$(4.15\pm0.17) \times 10^{-12}$	381		
$(4.98\pm0.17) \times 10^{-12}$	416		
$1.76 \times 10^{-11}\exp[-(559\pm151)/T]$	298–420	Perry et al., 1976	FP-RF
$(2.72\pm0.27) \times 10^{-12}$	298		
$(2.67\pm0.22) \times 10^{-12}$	297±2	Paraskevopoulos and Nip, 1980	FP-RA
$(2.3\pm0.3) \times 10^{-12}$	295	Schmidt et al., 1985	PLP-LIF
$2.34 \times 10^{-17}T^{1.95}\exp(134/T)$	294–509	Droege and Tully, 1986	PLP-LIF
$(2.42\pm0.10) \times 10^{-12}$	294		
$(2.25\pm0.10) \times 10^{-12}$	297 ± 2	Abbatt et al., 1990	DF-LIF
$(2.32\pm0.08) \times 10^{-12}$	∼298	Schiffman et al., 1991	PLP-IR
$2.04 \times 10^{-17}T^{2}\exp[(85\pm8)/T]$	231–378	Talukdar et al., 1994	PLP-LIF
$(2.459\pm0.018) \times 10^{-12}$	299		
$(2.43\pm0.07) \times 10^{-12}$	300	Donahue et al., 1998	DF-LIF
$(2.74\pm0.08) \times 10^{-12}$	325		
$(2.87\pm0.09) \times 10^{-12}$	340		
$(3.48\pm0.10) \times 10^{-12}$	375		
$(3.54\pm0.11) \times 10^{-12}$	390		
$(2.6 \pm 0.5) \times 10^{-12}$	300	Chuong and Stevens, 2002	DF-LIF
$(2.6 \pm 0.2) \times 10^{-12}$	300		
Relative Rate Coefficients			
9.9×10^{-12}	753	Baker et al., 1970; Baldwin and Walker, 1979	RR (a)
$(9.3\pm0.8) \times 10^{-12}$	653	Hucknell et al., 1975	RR (b)
$(2.52\pm0.25) \times 10^{-12}$	299±2	Atkinson et al., 1981	RR (c)
$(2.71\pm0.32) \times 10^{-12}$	295±1	Atkinson and Aschmann, 1984	RR (c)
$(2.70\pm0.34) \times 10^{-12}$	300±2	Barnes et al., 1986	RR (d)
$(2.36\pm0.04) \times 10^{-12}$	300±2	Behnke et al., 1988	RR (e)
$1.39 \times 10^{-11}\exp(-526/T)$	235–361	DeMore and Bayes, 1999	RR (f)
2.33×10^{-12}	298		

Comments

(a) Derived from the effects of the addition of small amounts of n-butane to slowly reacting mixtures of H_2+O_2. The loss of H_2 was followed by monitoring the pressure change due to the reaction $2H_2+O_2 \rightarrow 2H_2O$, and the loss of n-butane was measured by GC. The rate coefficient ratio k(HO + n-butane)/k(HO + H_2) = 13.2 is placed on an absolute basis by use of a rate coefficient of k(HO+H_2)=7.87×10^{-13} cm^3 molecule^{-1} s^{-1} at 753 K (Atkinson, 2003).

(b) HO radicals were generated by the decomposition of H_2O_2 in a boric acid-coated reaction vessel, and the concentrations of n-butane and propane (the reference compound) were measured by GC. The measured rate coefficient ratios of k(HO + n-butane)/k(HO + propane) = 1.54 ± 0.13 is placed on an absolute value using a rate coefficient of k(HO + propane) = 6.16×10^{-12} cm^3 molecule^{-1} s^{-1} at 653 K (IUPAC, 2005).

(c) HO radicals were generated by the photolysis of CH_3ONO in one atmosphere of air. The concentrations of n-butane and propene (the reference compound) were measured by GC. The measured rate coefficient ratios of k(HO + n-butane)/k(HO + propene) = 0.0962±0.0093 at 299±2 K (Atkinson et al., 1981) and 0.101±0.012 at 295±1 K (Atkinson and Aschmann, 1984) are placed on an absolute value using a rate coefficient of k(HO + propene) = 4.85×10^{-12} exp(504/T) cm^3 molecule^{-1} s^{-1} at atmospheric pressure of air (Atkinson, 1997).

(d) HO radicals were generated by the photolysis of H_2O_2 in air at atmospheric pressure, and the concentrations of n-butane and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + n-butane)/ k(HO + ethene) = 0.32±0.04 is placed on an absolute basis by use of a rate coefficient of k(HO + ethene) = 8.44×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K and atmospheric pressure of air (Atkinson, 1997).

(e) HO radicals were generated by the photolysis of NO_x-organic-air mixtures at atmospheric pressure. The concentrations of n-butane and n-octane (the reference compound) were measured by GC, and the measured rate coefficient ratio of k(HO + n-butane)/k(HO + n-octane) is placed on an absolute basis by use of a rate coefficient of k(HO + n-octane) = 8.15×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K (Atkinson, 2003).

(f) HO radicals were generated by the photolysis of H_2O at 185 nm or, at low temperatures, by the photolysis of N_2O at 185 nm in the presence of H_2. The concentrations of n-butane and propane (the reference compound) were measured by GC. The measured rate coefficient ratios k(HO + n-butane)/k(HO + propane) are placed on an absolute basis using a rate coefficient of k(HO + propane) = 1.65×10^{-17} T^2 exp(-87/T) cm^3 molecule^{-1} s^{-1} (IUPAC, 2005).

Preferred Values

k = 2.3 × 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 9.1 × 10^{-12} exp(-405/T) cm^3 molecule^{-1} s^{-1} over the temperature range 230–300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta (E/R) = \pm 150$ K.

Comments on Preferred Values

The preferred values are based on the absolute rate coefficients of Droege and Tully (1986), Abbatt et al. (1990), Talukdar et al. (1994) and Donahue et al. (1998) and the relative rate coefficients of Baker et al. (1970) (as re-evaluated by Baldwin and Walker, 1979), Hucknall et al. (1975) and DeMore and Bayes (1999). The rate coefficients from these studies (Droege and Tully, 1986; Abbatt et al., 1990; Talukdar et al., 1994; Donahue et al., 1998; Baker et al., 1970; Baldwin and Walker, 1979; Hucknall et al., 1975; DeMore and Bayes, 1999) are fitted to the three parameter expression, $k=CT^2$ exp($-D/T$), resulting in k=1.81×10^{-17} T^2 exp(114/T) cm^3 molecule^{-1} s^{-1} over the temperature range 230–760 K. The preferred Arrhenius expression, k=A exp($-B/T$), is centered at 260 K and is derived from the three parameter expression with $A = Ce^2T^2$ and $B = D + 2T$. The preferred values are in good agreement with the room temperature absolute and relative rate coefficients of Greiner (1970), Stuhl (1973), Perry et al. (1976), Paraskevopoulos and Nip (1980), Schmidt et al. (1985), Schiffman et al. (1991), Atkinson et al. (1981), Atkinson and Aschmann (1984), Barnes et al. (1986), Behnke et al. (1988) and Chuong and Stevens (2002), which were not used in the evaluation of the rate coefficient.

Droege and Tully (1986) also measured rate coefficients for the reaction of the HO radical with n-butane-d$_{10}$, and derived a value of k_1/k_2=1.035 exp(-536/T), leading to k_1=3.4×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K and k_2=2.00×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.

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II.A2.10

HO + CH_2=C(CH_3)CH=CH_2 → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.36 \times 10^{-11}\exp[(409\pm28)/T]$	299–422	Kleindienst et al., 1982	FP-RF
$(9.26\pm1.5) \times 10^{-11}$	299		
$9.7 \times 10^{-11}(T/298)^{-1.36}$	249–348	Siese et al., 1994	FP-RF
9.7×10^{-11}	298		
$(1.10\pm0.05) \times 10^{-10}$	298	Stevens et al., 1999	DF-LIF
$2.70 \times 10^{-11}\exp[(336\pm74)/T]$	251–341	Campuzano-Jost et al., 2000	PLP-LIF (a)
$(8.56\pm0.26) \times 10^{-11}$	297		
$(1.10 \pm 0.04) \times 10^{-10}$	300	Chuong and Stevens, 2000	DF-LIF (b)
$(9.6 \pm 0.5) \times 10^{-11}$	295	McGivern et al., 2000	PLP-LIF (c)
$(1.01 \pm 0.08) \times 10^{-10}$	298 ± 2	Zhang et al., 2000	DF-CIMS (d)
9.1×10^{-11}	298 ± 2	Zhang et al., 2001	DF-CIMS (e)
$(1.08 \pm 0.05) \times 10^{-10}$	300	Chuong and Stevens, 2002	DF-LIF (f)
Relative Rate Coefficients			
7.8×10^{-11}	300	Cox et al., 1980	RR (g)
$(9.98 \pm 0.45) \times 10^{-11}$	299 ± 2	Atkinson et al., 1982	RR (h)
$(9.90 \pm 0.27) \times 10^{-11}$	297 ± 2	Ohta, 1983	RR (i)
$(1.02 \pm 0.04) \times 10^{-10}$	295 ± 1	Atkinson and Aschmann, 1984	RR (j)
$(1.01 \pm 0.02) \times 10^{-10}$	297 ± 1	Edney et al., 1986	RR (k)
$(1.11 \pm 0.23) \times 10^{-10}$	298	McQuaid et al., 2002	RR (l)
$2.56 \times 10^{-11}\exp[(408\pm42)/T]$	298–363	Gill and Hites, 2002	RR (m)
$(1.01\pm0.05) \times 10^{-10}$	298		

Comments

(a) Rate coefficients for the reactions of HO radicals with isoprene-d_6 and DO radicals with isoprene were also measured at 297 K, these being $(8.31\pm0.10)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} and $(8.27\pm0.10)\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively.

(b) Carried out at total pressures of 2–6 Torr (2.7–8.0 mbar) of helium diluent. No pressure dependence of the rate coefficient was observed at 300 K. However, at higher temperatures (321–423 K) the rate coefficient increased with increasing total pressure, with the effect being more pronounced at higher temperature.

(c) Carried out at total pressures of 0.5–20 Torr (0.7–27 mbar) of argon diluent. The rate coefficient was observed to be pressure dependent below 10 Torr total pressure; the value cited in the table is that measured at 20 Torr total pressure.

(d) Carried out at total pressures of 72.7–112.7 Torr (97–150 mbar) of N_2 diluent. The measured rate coefficient was independent of pressure over this range.

(e) Based on a very limited kinetic study carried out at a total pressure of 1.9 Torr (2.5 mbar) of helium diluent (the focus of the study was on formation of HO-isoprene adducts and their subsequent reactions).

(f) Carried out at total pressures of argon diluent of 100 Torr (133 mbar) and 150 Torr (200 mbar). The measured rate coefficient was independent of total pressure over this range.

(g) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of HONO at wavelengths >300 nm. The concentrations of isoprene and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio k(HO + isoprene)/k(HO + ethene) is placed on an absolute basis by use of a rate coefficient of k(HO + ethene) = 8.44×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 300 K and atmospheric pressure of air (Atkinson, 1997).

(h) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO at wavelengths $>$300 nm. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + isoprene)/k(HO + propene) = 3.81±0.17 is placed on an absolute basis by use of a rate coefficient of k(HO + propene) = 2.62×10^{-11} cm^3 $molecule^{-1}s^{-1}$ at 299 K and atmospheric pressure of air (Atkinson, 1997).

(i) Relative rate method carried out at atmospheric pressure of N_2+O_2. HO radicals were generated by photolysis of H_2O_2 at 253.7 nm. The concentrations of isoprene and 1,3-butadiene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + isoprene)/k(HO + 1,3-butadiene) = 1.48±0.04 is placed on an absolute basis by use of a rate coefficient of k(HO + 1,3-butadiene) = 6.69×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 297 K and atmospheric pressure of air (Atkinson, 1997).

(j) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO at wavelengths $>$300 nm. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + isoprene)/k(HO + propene) = 3.81±0.15 is placed on an absolute basis by use of a rate coefficient of k(HO + propene) = 2.68×10^{-11} cm^3 $molecule^{-1}s^{-1}$ at 295 K and atmospheric pressure of air (Atkinson, 1997).

(k) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO at wavelengths $>$300 nm. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + isoprene)/k(HO + propene) is placed on an absolute basis by use of a rate coefficient of k(HO + propene) = 2.65×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 297 K and atmospheric pressure of air (Atkinson, 1997).

(l) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO. The concentrations of isoprene and *trans*-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + isoprene)/k(HO + *trans*-butene) = 1.74±0.14 is placed on an absolute basis by use of a rate coefficient of k(HO + *trans*-2-butene) = 6.40×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K and atmospheric pressure of air (Atkinson, 1997). The cited error limits are the 95% confidence intervals (McQuaid et al., 2002).

(m) Relative rate method carried out in a 192 cm^3 volume quartz reaction vessel at atmospheric pressure of helium diluent. HO radicals were generated by photolysis of H_2O_2. The concentrations of isoprene and 2-methylpropene (the reference compound) were measured by MS. The measured rate coefficient ratios of k(HO + isoprene)/k(HO + 2-methylpropene) are placed on an absolute basis by use of a rate coefficient of k(HO + 2-methylpropene) = 9.47×10^{-12} exp($504/T$) cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 1997). The error limits for the 298 K rate coefficient cited in the table are based on those associated with the rate coefficient ratio (Gill and Hites, 2002).

Preferred Values

$k = 1.0 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k = 2.7 \times 10^{-11}$ exp($390/T$) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 240–430 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The measured room temperature rate coefficients (Kleindienst et al., 1982; Siese et al., 1994; Stevens et al., 1999; Campuzano-Jost et al., 2000; Chuong and Stevens, 2000, 2002; McGivern et al., 2000; Zhang et al., 2000, 2001; Cox et al., 1980; Atkinson et al., 1982; Ohta, 1983; Atkinson and Aschmann, 1984; Edney et al., 1986; McQuaid et al., 2002; Gill and Hites, 2002) and temperature dependencies (Kleindienst et al., 1982; Siese et al., 1994; Campuzano-Jost et al., 2000; Gill and Hites, 2002) are good agreement (the temperature dependence measured by Siese et al. (1994) corresponds to E/R =

-400 K over the temperature range 249–349 K). The preferred 298 K rate coefficient is an average of the room temperature rate coefficients of Kleindienst et al.(1982), Siese et al. (1994), Stevens et al. (1999), Campuzano-Jost et al. (2000), Chuong and Stevens (2000, 2002), McGivern et al. (2000), Zhang et al. (2000), Atkinson et al. (1982), Ohta (1983), Atkinson and Aschmann (1984), Edney et al. (1986), McQuaid et al. (2002), and Gill and Hites (2002). The preferred temperature dependence is an average of those obtained from the four temperature dependent studies (Kleindienst et al., 1982; Siese et al., 1994; Campuzano-Jost et al., 2000; Gill and Hites, 2002). The pre-exponential factor is calculated from the preferred 298 K rate coefficient and the preferred temperature dependence.

The reaction proceeds by initial addition of the HO radical to the two C=C bonds, followed by addition of O_2 to form six possible hydroxyalkyl radicals (Atkinson, 1997). The subsequent chemistry of these radicals in the atmosphere and the products observed is discussed by Atkinson (1997) and Calvert et al. (2000). In the presence of NO (so that organic peroxy radicals react dominantly with NO) the products observed (Atkinson, 1997; Atkinson et al., 1989; Tuazon and Atkinson, 1990; Paulson et al., 1992; Miyoshi et al., 1994; Kwok et al., 1995; Chen et al., 1998) are methyl vinyl ketone (33%), methacrolein (23%), formaldehyde (60%), 3-methylfuran (4.8%), hydroxynitrates such as $HOCH_2C(CH_3)=CHCH_2ONO_2$ (and isomers) (4.4%), and the hydroxycarbonyls $HOCH_2C(CH_3)=CHCHO$ and/or $HOCH_2CH=C(CH_3)CHO$.

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II.A2.11

HO + α-Pinene → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.37 \times 10^{-11}\exp[(446\pm76)/T]$	298–422	Kleindienst et al., 1982	FP-RF
$(6.01\pm0.82) \times 10^{-11}$	298		
$1.63 \times 10^{-12} \exp[(1080\pm50)/T]$	300–435	Chuong et al., 2002	DF-RF (a)
$(6.08\pm0.24) \times 10^{-11}$	300		
Relative Rate Coefficients			
$(5.6\pm1.7) \times 10^{-11}$	305±2	Winer et al., 1976	RR (b)
$(5.35\pm0.31) \times 10^{-11}$	294±1	Atkinson et al., 1986	RR (c)
$1.17 \times 10^{-11} \exp[(436\pm53)/T]$	295–364	Gill and Hites, 2002	RR (d)
$(5.05\pm1.23) \times 10^{-11}$	298		

Comments

(a) Experiments carried out at 5 Torr (6.7 mbar) of He or 90% He+10% O_2.

(b) HO radicals were generated by the photolysis of NO_x-organic-air mixtures in a 5870 L chamber at ∼1 bar pressure. The concentrations of α-pinene and 2-methylpropene (the reference compound) were analyzed by GC during the experiments. The measured rate coefficient ratio k(HO + α-pinene)/k(HO + 2-methylpropene) = 1.14 (±30%) is placed on an absolute basis by use of a rate coefficient at 305 K of k(HO + 2-methylpropene) = 4.94×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003a).

(c) HO radicals were generated by the photolysis of CH_3ONO in air at wavelengths >300 nm in a 6400 L Teflon chamber at ∼980 mbar pressure. The concentrations of α-pinene and 2,3-dimethyl-2-butene (the reference compound) were analyzed by GC during the CH_3ONO-NO-α-pinene-2,3-dimethyl-2-butene-air irradiations. The measured rate coefficient ratio k(HO + α-pinene)/k(HO + 2,3-dimethyl-2-butene) = 0.487 ± 0.028 is placed on an absolute basis by use of a rate coefficient at 294 K of k(HO + 2,3-dimethyl-2-butene) = 1.10×10^{-10} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003a).

(d) HO radicals were generated by the photolysis of H_2O_2 in helium diluent in a 192 cm^3 volume quartz vessel. The concentrations of α-pinene and 1-butene, 2-methylpropene or *trans*-2-butene (the reference compounds) were analyzed by MS during the experiments. The measured rate coefficient ratios k(HO + α-pinene)/k(HO + 1-butene), k(HO + α-pinene)/k(HO + 2-methylpropene) and k(HO + α-pinene)/k(HO + *trans*-2-butene) are placed placed on an absolute basis by use of rate coefficients of k(HO + 1-butene) = $6.55\times10^{-12}\exp(467/T)$ cm^3 molecule^{-1} s^{-1}, k(HO + 2-methylpropene) = $9.47\times10^{-12}\exp(504/T)$ cm^3 molecule^{-1} s^{-1} and k(HO + *trans*-2-butene) = $1.01\times 10^{-11}\exp(550/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003a).

Preferred Values

$k = 1.2 \times 10^{-11} \exp(440/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–430 K.
$k = 5.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

At room temperature, the rate coefficients of Winer et al. (1976), Kleindienst et al. (1982), Atkinson et al. (1986), Gill and Hites (2002) and Chuong et al. (2002) are in good agremeent, as are the temperature dependencies obtained by Kleindienst et al. (1982) and Gill and Hites (2002). The temperature dependence obtained by Chuong et al. (2002) at 6.7 mbar pressure is significantly higher than those of Kleindienst et al. (1982) and Gill and Hites (2002), possibly because of fall-off effects above 300 K (although no evidence was obtained to support this conclusion). The preferred temperature dependence is based on those obtained by Kleindienst et al. (1982) and Gill and Hites (2002), and the preferred 298 K rate coefficient is the average of the measurements of Kleindienst et al. (1982), Atkinson et al. (1986) (corrected to 298 K using the preferred temperature dependence) and Gill and Hites (2002). The pre-exponential factor is adjusted to fit the 298 K preferred value.

A number of product studies have been carried out at room temperature and atmospheric pressure of air (see Atkinson and Arey, 2003b, and references therein). The reaction proceeds mainly by initial addition of the HO radical to the C=C bond, resulting in two hydroxyalkyl radicals which then add O_2 to form two 1,2-hydroxyalkyl peroxy radicals. H-atom abstraction almost certainly occurs to a minor extent, with acetone (Aschmann et al., 1998; Reissell et al., 1999; Nozière et al., 1999; Orlando et al., 2000) being one of the likely products. Subsequent reactions of these 1,2-hydroxyalkyl peroxy radicals with NO, NO_2, HO_2 radicals, organic peroxy radicals and NO_3 radicals will lead to the products formed in the atmosphere. In the presence of NO such that organic peroxy radicals react dominantly with NO, the products observed (and their reported yields) are: pinonaldehyde, 28±5% to 87±20% (Arey et al., 1990; Hatakeyama et al., 1991; Hakola et al., 1994; Nozière et al., 1999; Wisthaler et al., 2001; Aschmann et al., 2002) with the lower yields being obtained by GC analyses (Arey et al., 1990; Hakola et al., 1994; Aschmann et al., 2002) and by proton-transfer mass spectrometry (Wisthaler et al., 2001) and the higher values by in situ FTIR spectroscopy (Hatakeyama et al., 1991; Nozière et al., 1999); acetone, 5–11% (Aschmann et al., 1998; Reissell et al., 1999; Nozière et al., 1999; Orlando et al., 2000), formic acid, 7% (Orlando et al., 2000); organic nitrates, 18±9% (Nozière et al., 1999); a molecular weight 184 dihydroxycarbonyl, ∼19% (Aschmann et al., 2002); a molecular weight 200 product, ∼11% (Aschmann et al., 2002), and molecular weight 215 C_{10}-hydroxynitrates and molecular weight 231 C_{10}-dihydroxynitrates (Aschmann et al., 1998, 2002).

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II.A2.12

$$\mathbf{HO + CO \rightarrow H + CO_2 \quad (1)}$$
$$\mathbf{HO + CO + M \rightarrow HOCO + M \quad (2)}$$

$\Delta H^0\,(1) = -102.3\,\mathrm{kJ \cdot mol^{-1}}$

$\Delta H^0\,(2) = -114.6\,\mathrm{kJ \cdot mol^{-1}}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k(P \rightarrow 0)$			
1.37×10^{-13}	300	Greiner, 1969	FP-RA (a,c)
1.35×10^{-13}	300	Stuhl and Niki, 1972	FP-RF
1.66×10^{-13}	300	Mulcahy and Smith, 1971	DF-MS
1.33×10^{-13}	298	Westenberg and deHaas, 1973	DF-EPR
1.39×10^{-13}	298	Smith and Zellner, 1973	FP-RA (a,c)
1.58×10^{-13}	298	Davis et al., 1974	FP-RF
1.56×10^{-13}	296	Howard and Evenson, 1974	DF-LMR
1.20×10^{-13}	298	Trainor and von Rosenberg, 1974	FP-RA (a,c)
0.90×10^{-13}	298	Gordon and Mulac, 1975	PR-RA (b,d)
1.54×10^{-13}	299	Atkinson et al., 1977	FP-RF (e)
1.63×10^{-13}	296	Overend and Paraskevopoulos, 1977	FP-RA (b,f)
1.41×10^{-13}	299	Perry et al., 1977	FP-RF (g)
1.46×10^{-13}	300	Biermann et al., 1978	FP-RA (h)
1.50×10^{-13}	298	Dreier and Wolfrum, 1981	DF (i)
1.46×10^{-13}	298	Husain et al., 1982	FP-RF
1.28×10^{-13}	298	Ravishankara and Thompson, 1983	FP-RF (j)
1.50×10^{-13}	298	Paraskevopoulos and Irwin, 1984	FP-RA
1.58×10^{-13}	298	Hofzumahaus and Stuhl, 1984	FP-RA (k)
1.23×10^{-13}	298	Jonah et al., 1984	PR-RA (l)
0.88×10^{-13}	298	Beno et al., 1985	PR-RA (l)
1.47×10^{-13}	299	Hynes et al., 1986	PLP-LIF
1.50×10^{-13}	298	Stacknik and Molina, 1988	PLP-RA
1.26×10^{-13}	298	Wahner and Zetsch, 1988	PLP-A (m)
1.49×10^{-13}	298	Brunning et al., 1988	FP-LIF (n)
1.30×10^{-13}	298	Forster et al., 1995	PLP-LIF
1.53×10^{-13}	298	Golden et al., 1998	PLP-LIF
1.57×10^{-13}	220–400	McCabe et al., 2001	PLP-LIF
$k/k(P \rightarrow 0)$ with $[N_2]$ in molecule cm^{-3}			
$1 + [N_2]/5.4 \times 10^{19}$	298	Paraskevopoulos and Irwin, 1984	FP-RA
$1 + [N_2]/4.1 \times 10^{19}$	298	Hofzumahaus and Stuhl, 1984	FP-RA (o)
$1 + [N_2]/4.8 \times 10^{19}$	298	Hynes et al., 1986	PLP-LIF
$1 + [N_2]/4.6 \times 10^{19}$	298	Wahner and Zetsch, 1988	PLP-A (m)
$1 + [N_2]/4.4 \times 10^{19}$	220–400	McCabe et al., 2001	PLP-LIF
$1 + [N_2]/4.0 \times 10^{19}$	200–300	Fulle et al., 1996	PLP-LIF (p)

Comments

(a) Extrapolation for P→0 with pressure dependence from Golden et al. (1998).

(b) Extrapolation for P→0 with pressure dependence from Paraskevopoulos and Irwin (1984).

(c) Measurements at 100 Torr of He giving k=1.43×10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

(d) Measurements at 760 Torr of Ar giving k=1.54×10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

(e) No pressure dependence detected between 25 and 650 Torr of Ar. Value taken as indicated.

(f) Measurements at 50 Torr of He giving k=1.66×10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

(g) Measurements at 25 Torr of SF_6 giving k=1.53×10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

(h) Measurements at 25 Torr of N_2 giving k=1.51×10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

(i) Measurements of CO_2 yields accounting for loss of HO by other reactions.

(j) Measurements at 100 Torr of Ar giving k=1.4×10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

(k) Measurements at 760 Torr of N_2 giving k=2.3×10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

(l) Measurements at 760 Torr of Ar giving k=2.1×10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

(m) Measurements at 760 Torr of N_2 giving k=2.15×10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

(n) Measurements at 25 Torr of Ar giving k=1.53×10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

(o) Referred to k_0=1.44×10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

(p) Measurements up to 700 bar of He with data representation between 90 and 3000 K. Conversion to the bath gas N_2 with efficiency relative to He at 298 K, see comments on preferred values. Temperature dependence from theoretical modelling of the experimental results, see Troe (1998).

Preferred Values

$k = 1.44 \times 10^{-13} (1 + [N_2]/4.2 \times 10^{19}$ molecule $cm^{-3})$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 200–300 K and the pressure range 0–1 bar of N_2.

Reliability

$\Delta \log k = \pm 0.05$ at 298 K.
$\Delta \log k = \pm 0.1$ over the temperature range 200–300 K and the pressure range 0–1 bar.

Comments on Preferred Values

The preferred values at P→0 represent a weighted average of all low pressure data excluding pulse radiolysis results which show larger scatter. The preferred values at P=1 bar of N_2 correspond to an average over those results for which $k/k(P \rightarrow 0)$ is given in the table (except the results from Fulle et al., 1996, which were obtained in the bath gas He).

The preferred values for k cannot be used over larger pressure and temperature ranges where more complicated expressions have to be employed. One may, e.g. take the representation $k_1=k_{1,0}$ $[1-[x/(x+1)]F_c^{1/[1+(\log x)^2]}]$, $k_2=k_{2,0}$ $[1+y/(1+x)]F_c^{1/[1+(\log x)^2]}]$ with $x=k_{2,0}/(k_{2,\infty}-k_{1.0})$ and $y=k_{1,0}/(k_{2,\infty}-k_{1.0})$, $F_c \approx 0.7$, $k_{1,0}=1.8\times10^{-12}$ exp(-2720/T) + 1.6×10^{-13} exp(-60/T), $k_{2,0}$=[He] 2.0×10^{-32} $(T/300)^{-2.7}$ exp(-490/T) and $k_{2,\infty}=1.8\times10^{-11}$ exp(-1850/T) + 1.5×10^{-12} exp(-130/T), see Fulle et al. (1996) and Troe (1998). For N_2 instead of He, $k_{2,0}$ should be increased by a factor of 1.6. These expressions also give the partitioning of k into k_1 and k_2. For the limited temperature and pressure range of the present evaluation, the simplified model from the introduction for complex-forming bimolecular reactions can be used. At low pressures this gives a relative HOCO yield of approximately $[k-k(P\rightarrow0)]/[k(P\rightarrow\infty)-k(P\rightarrow0)]$ which at 298 K and 1 bar of N_2 corresponds to about 12% (Troe, 1998). As HOCO under excess of O_2 rapidly reacts to HO_2+CO_2 (Miyoshi et al., 1994) and as other reactions of HOCO presumably proceed similarly as reactions of H, k probably in effect can be used as if it would correspond to Reaction (1) alone. At higher temperatures, thermal decomposition of HOCO would occur which would lead to more complex kinetic rate laws, see Forster et al. (1996). This can be neglected at temperatures below 300 K.

The present evaluation was based on absolute rate coefficients only, neglecting relative rate measurements and measurements in other bath gases such as H_2O. Reference to this work is found in the given literature. Since the reaction has been studied very extensively, the present evaluation also cannot be exhaustive. The thermochemistry of HOCO is based on the new determination by Feller et al. (2003). There is extensive modelling of the reaction, see Golden et al. (1998) and Troe (1998), which provide excellent representations of the experimental data with empirically fitted potential parameters. Increasingly reliable quantum-chemical determinations of the HOCO potential (see e.g. Yu et al., 2001 and Lakin et al., 2003) allows also for more basic treatments of the dynamics, see e.g. Medvedev et al. (2004), He et al. (2004), Valero and Kroes (2002), Valero et al. (2004). However, this work does not yet replace the experiments on which this evaluation is based.

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II.A2.13

HO + HCHO → H_2O + HCO

$\Delta H^\circ = -127.3 \mathrm{kJ} \cdot \mathrm{mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.25 \times 10^{-11} \exp[-(88\pm151)/T]$	299–426	Atkinson and Pitts, 1978	FP-RF
$(9.4\pm1.0) \times 10^{-12}$	299		
$(1.05\pm0.11) \times 10^{-11}$	228–362	Stief et al., 1980	FP-RF
$(9.86\pm1.13) \times 10^{-12}$	298		
$(8.1\pm1.7) \times 10^{-12}$	296	Temps and Wagner, 1984	DF-LMR
$1.66 \times 10^{-11} \exp[-(86\pm40)/T]$	296–576	Zabarnick et al., 1988	PLP-LIF
$(1.25\pm0.11) \times 10^{-11}$	298±3		
$(7.95^{+2.04}_{-1.44}) \times 10^{-12}$	298	Yetter et al., 1989	DF-RF
$(1.94\pm0.30) \times 10^{-11}$	1205±16	Bott and Cohen, 1991	SH-RA
$9.52 \times 10^{-18}\, T^{2.03} \exp(636/T)$	202–399	Sivakumaran et al., 2003	PLP-LIF (a)
$(8.46\pm0.5) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(8.40\pm0.51) \times 10^{-12}$	299±2	Niki et al., 1984	RR (b)

Comments

(a) The authors combined their data with previous room temperature data of Atkinson and Pitts (1978), Stief et al. (1980), Temps and Wagner (1984), Niki et al. (1984), Zabarnick et al. (1988) and Yetter et al. (1989) to obtain a 298 K rate coefficient of $k=8.6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} and a temperature-dependent expression of $k=9.65\times10^{-18}\, T^{2.03}$ exp(636/T) cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K. Using resonance fluorescence detection of H atoms, an upper limit of 4% was determined for the production of H atoms at 298 K.

(a) HO radicals were generated by the photolysis of methyl or ethyl nitrite in air, and the concentration of $^{13}CH_2O$ and ethene (the reference compound) were measured by FTIR absorption spectroscopy during the experiments. The measured rate coefficient ratio of k(HO+$^{13}CH_2O$)/k(HO + ethene) = 0.99±0.06 is placed on an absolute basis by use of a rate coefficient of k(HO + ethene) = 8.48×10^{-12} cm^3 molecule^{-1} s^{-1} at 299 K and atmospheric pressure (Atkinson and Arey, 2003).

Preferred Values

$k = 8.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.4 \times 10^{-12} \exp(135/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The absolute rate coefficients of Atkinson and Pitts (1978), Stief et al. (1980), Temps and Wagner (1984), Yetter et al. (1989) and Sivakumaran et al. (2003) and the relative rate coefficient of Niki et al. (1984) at 299±2 K are in good agreement (to within ∼20% or better at any given temperature) over the temperature range common to two or more of these studies (228–399 K).

The absolute rate coefficients of Zabarnick et al. (1988) over the temperature range 296–378 K are consistently higher than those of Atkinson and Pitts (1978), Stief et al. (1980), Temps and Wagner (1984), Niki et al. (1984), Yetter et al. (1989) and Sivakumaran et al. (2003), and are not used in the evaluation.

The absolute rate coefficients of Atkinson and Pitts (1978), Stief et al. (1980), Temps and Wagner (1984), Yetter et al. (1989) and Sivakumaran et al. (2003), and the relative rate coefficient of Niki et al. (1984) for formaldehyde-^{13}C, have been fitted to the three parameter expression $k=CT^2 \exp(-D/T)$, resulting in $k=1.25\times10^{-17}\ T^2 \exp(615/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 202–426 K. This expression yields rate coefficients which are within 3% of those calculated from the three parameter expression recommended by Sivakumaran et al. (2003) for the temperature range 200–430 K (see comment (a) above) and predicts a rate coefficient at 1205 K a factor of 1.56 higher that that measured by Bott and Cohen (1991). The preferred Arrhenius expression, $k=A \exp(-B/T)$, is centered at 240 K and is derived from the three parameter expression with $A = C\ e^2\ T^2$ and $B = D + 2T$. Note that the preferred Arrhenius expression should not be used outside of the specified temperature range (200–300 K); rather the full three parameter expression should be used.

The product data of Temps and Wagner (1984), Niki et al. (1984) and Sivakumaran et al. (2003) and the kinetic/modeling results of Yetter et al. (1989) show that at 298 K this reaction yields H_2O+HCO, as also concluded by Butkovskaya and Setser (1998) from an infrared chemiluminescence study of the reaction at 0.67–1.3 mbar.

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II.A2.14

$HO + CH_3CHO \rightarrow H_2O + CH_3CO$

$\Delta H^\circ = -123.2\text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.55\pm0.39) \times 10^{-11}$	300	Morris et al., 1971	DF-MS
$6.87 \times 10^{-12}\exp[(257\pm151)/T]$	299–426	Atkinson and Pitts, 1978	FP-RF
$(1.60\pm0.16) \times 10^{-11}$	299		
$7.1 \times 10^{-12}\exp[(165\pm91)/T]$	253–424	Semmes et al., 1985	FP-RF
$(1.22\pm0.27) \times 10^{-11}$	298		
$5.52 \times 10^{-12}\exp[(307\pm52)/T]$	244–528	Michael et al., 1985	DF-RF
$(1.47\pm0.28) \times 10^{-11}$	298		
$8.6 \times 10^{-12}\exp[(200\pm60)/T]$	297–517	Dóbé et al., 1989	DF-RF/LIF
$(1.69\pm0.34) \times 10^{-11}$	298±2		
$(1.7\pm0.3) \times 10^{-11}$	298	Balestra-Garcia et al., 1992	PLP-RF
$(1.44\pm0.25) \times 10^{-11}$	298	Tyndall et al., 1995	DF-LIF
$4.31 \times 10^{-12}\exp[(309\pm19)/T]$	295–550	Taylor et al., 1996	PLP-LIF
1.23×10^{-11}	295		
$4.4 \times 10^{-12}\exp[(366\pm30)/T]$	202–348	Sivakumaran and Crowley, 2003	PLP-LIF
1.50×10^{-11}	298		
Relative Rate Coefficients			
$(1.62\pm0.18) \times 10^{-11}$	298±2	Niki et al., 1978	RR (a)
$(1.28\pm0.43) \times 10^{-11}$	298±4	Kerr and Sheppard, 1981	RR (b)
$(1.62\pm0.10) \times 10^{-11}$	298±2	Scollard et al., 1993	RR (c)
$(1.44\pm0.08) \times 10^{-11}$	298±2	D'Anna et al., 2001	RR (d)

Comments

(a) HO radicals were generated by the photolysis of HONO in air, and the concentrations of CH_3CHO and ethene (the reference compound) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of k(HO + CH_3CHO)/k(HO + ethene) = 1.9±0.2 is placed on an absolute basis by use of a rate coefficient of k(HO + ethene) = 8.52×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure (Atkinson, 1997).

(b) HO radicals were generated by the photolysis of HONO in air, and the concentrations of CH_3CHO and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + CH_3CHO)/k(HO + ethene) = 1.50±0.50 is placed on an absolute basis by use of a rate coefficient of k(HO + ethene) = 8.52×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure (Atkinson, 1997).

(c) HO radicals were generated from the photolysis of CH_3ONO in air, and the concentrations of CH_3CHO and ethene (the reference compound) were measured during the experiments by GC. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of k(HO + ethene) = 8.52×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure (Atkinson, 1997).

(d) HO radicals were generated by the photolysis of an organic nitrite in air and the concentrations of acetaldehyde and 1-butene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of k(HO + CH_3CHO)/k(HO + 1-butene) = 0.458±0.024 is placed on an absolute basis by use of a rate coefficient of k(HO + 1-butene) = 3.14×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure of air (Atkinson, 1997).

Preferred Values

$k = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.4 \times 10^{-12} \exp(365/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–350 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The room temperature rate coefficients range from $(1.2–1.7)\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, with the absolute rate coefficients of Atkinson and Pitts (1978), Michael et al. (1985), Tyndall et al. (1995) and Sivakumaran and Crowley (2003) being in reasonably good agreement. The temperature dependences of Michael et al. (1985), Taylor et al. (1996) and Sivakumaran and Crowley (2003) are in excellent agreement and also agree well with the temperature dependence measured over a smaller temperature range by Atkinson and Pitts (1978). The extensive study of Sivakumaran and Crowley (2003), which extends to significantly lower temperatures than the other temperature-dependent studies (Atkinson and Pitts, 1978; Semmes et al., 1985; Michael et al., 1985; Dóbé et al., 1989; Taylor et al., 1996), is used as the basis for the preferred values. The data of Semmes et al. (1985) are lower than the preferred values by up to ∼20%, possibly because of the reported difficulties in accurately determining the acetaldehyde concentrations (Semmes et al., 1985). While the absolute rate coefficients measured by Dóbé et al. (1989) for CH_3CHO are in good agreement with the preferred values, their measured rate coefficients for the reactions of the HO radical with the higher aldehydes $(CH_3)_2CHCHO$ and $(CH_3)_3CCHO$ are significantly higher, by factors of ∼1.5 to 2.3, than the rate coefficients of Kerr and Sheppard (1981) and Semmes et al. (1985) (which are in good agreement).

Cameron et al. (2002) have investigated the products of this reaction, using absorption spectroscopy to detect CH_3 and CH_3CO radicals and resonance fluorescence to detect H atoms. Upper limits for the formation of CH_3+HC(O)OH (<3% at 296 K) and H+CH_3C(O)OH (<2% over the temperature range 237–296 K) were obtained, and the major reaction pathway was determined to be formation of CH_3CO+H_2O, with a measured yield of 93±18% at 296 K (Cameron et al., 2002). H-atom abstraction from the CH_3 group therefore accounts for <25% of the overall reaction at room temperature.

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II.A2.15

HO + C_2H_5CHO → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.71\pm0.24) \times 10^{-11}$	298	Semmes et al., 1985	FP-RF
$5.3 \times 10^{-11}\exp[(405\pm30)/T]$	240–372	Thévenet et al., 2000	PLP-LIF
$(2.0\pm0.3) \times 10^{-11}$	298		
Relative Rate Coefficients			
$(2.22\pm0.09) \times 10^{-11}$	298±2	Niki et al., 1978	RR (a)
$(1.94\pm0.15) \times 10^{-11}$	298±4	Kerr and Sheppard, 1981	RR (b)
$(2.00\pm0.14) \times 10^{-11}$	296±2	Papagni et al., 2000	RR (c)
$(1.89\pm0.16) \times 10^{-11}$	298±2	D'Anna et al., 2001	RR (d)

Comments

(a) HO radicals were generated by the photolysis of HONO in air and the concentrations of propanal and ethene (the reference compound) were measured by FTIR absorption spectroscopy during the experiments. The measured rate coefficient ratio of k(HO + propanal)/k(HO + ethene) = 2.6±0.1 is placed on an absolute basis by use of a rate coefficient of k(HO + ethene) = 8.52×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure (Atkinson, 1997).

(b) HO radicals were generated by the photolysis of HONO in air and the concentrations of propanal and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + propanal)/k(HO + ethene) = 2.28±0.17 is placed on an absolute basis by use of a rate coefficient of k(HO + ethene) = 8.52×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure (Atkinson, 1997).

(c) HO radicals were generated by the photolysis of CH_3ONO in air and the concentrations of propanal and methyl vinyl ketone (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + propanal)/k(HO + methyl vinyl ketone) = 0.982±0.065 is placed on an absolute basis by use of a rate coefficient of k(HO + methyl vinyl ketone) = 2.04×10^{-11} cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation).

(d) HO radicals were generated by the photolysis of an organic nitrite in air and the concentrations of propanal and propene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of k(HO + propanal)/k(HO + propene) = 0.72±0.06 is placed on an absolute basis by use of a rate coefficient of k(HO + propene) = 2.63×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure of air (Atkinson, 1997).

Preferred Values

$k = 2.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.1 \times 10^{-12} \exp(405/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–380 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is derived from the mean of the room temperature absolute rate coefficients of Semmes et al. (1985) and Thévenet et al. (2000) and the relative rate coefficients of Niki et al. (1978), Kerr and Sheppard (1981), Papagni et al. (2000) and D'Anna et al. (2001). The temperature dependence is that measured by Thévenet et al. (2000) and the pre-exponential factor is adjusted to fit the 298 K preferred value. The relative rate coefficient of Audley et al. (1981) was not used in the evaluation, due to questions concerning the applicability of the experimental technique used (Semmes et al., 1985; Atkinson, 1989).

The major reaction channel is expected to be H-atom abstraction from the -CHO group to form $H_2O+C_2H_5CO$.

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II.A2.16

$HO + CH_3CH_2CH_2CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$5.7 \times 10^{-12}\exp[(411\pm164)/T]$	258–422	Semmes et al., 1985	FP-RF
$(2.06\pm0.30) \times 10^{-11}$	298		
Relative Rate Coefficients			
$(2.52\pm0.06) \times 10^{-11}$	298±4	Kerr and Sheppard, 1981	RR (a)
$(2.45\pm0.15) \times 10^{-11}$	296±2	Papagni et al., 2000	RR (b)
$(2.39\pm0.16) \times 10^{-11}$	298±2	D'Anna et al., 2001	RR (c)

Comments

(a) HO radicals were generated by the photolysis of HONO in air and the concentrations of butanal and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + butanal)/k(HO + ethene) = 2.96 ± 0.07 is placed on an absolute basis by use of a rate coefficient of k(HO + ethene) = 8.52×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure (Atkinson, 1997).

(b) HO radicals were generated by the photolysis of CH_3ONO in air and the concentrations of butanal and methyl vinyl ketone (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + butanal)/ k(HO + methyl vinyl ketone) = 1.20 ± 0.07 is placed on an absolute basis by use of a rate coefficient of k(HO + methyl vinyl ketone) = 2.04×10^{-11} cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation).

(c) HO radicals were generated by the photolysis of an organic nitrite in air and the concentrations of butanal and 1-butene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of k(HO + butanal)/k(HO + 1-butene) = 0.76 ± 0.05 is placed on an absolute basis by use of a rate coefficient of k(HO + 1-butene) = 3.14×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure of air (Atkinson, 1997).

Preferred Values

$k = 2.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.0 \times 10^{-12} \exp(410/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–430 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta (E/R) = \pm 250$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the mean of the room temperature absolute rate coefficient of Semmes et al. (1985) and the relative rate coefficients of Kerr and Sheppard (1981), Papagni et al. (2000) and D'Anna et al. (2001). The temperature dependence is that measured by Semmes et al. (1985), with the pre-exponential factor being adjusted to fit the 298 K preferred value. The relative rate coefficient of Audley et al. (1981) has not been used in the evaluation because, while it is in good agreement with the preferred 298 K rate coefficient, the rate coefficients of Audley et al. (1981) for 2-methyl-1-propanal, 1-pentanal and 2, 2-dimethyl-1-propanal are significantly lower than the values of Semmes et al. (1985) and Kerr and Sheppard (1981). At room temperature and below, the reaction is expected to proceed primarily by H-atom abstraction from the -CHO group.

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II.A2.17

$HO + CH_2{=}C(CH_3)CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.77 \times 10^{-11}\exp[(175\pm52)/T]$	300–423	Kleindienst et al., 1982	FP-RF
$(3.14\pm0.49) \times 10^{-11}$	300		
$7.73 \times 10^{-12}\exp[(379\pm46)/T]$	234–373	Gierczak et al., 1997	PLP-LIF
$(2.79\pm0.12) \times 10^{-11}$	298		
$9.8 \times 10^{-13}\exp[(1050\pm120)/T]$	300-422	Chuong and Stevens, 2003	DF-RF/LIF (a)
$(3.23\pm0.36) \times 10^{-11}$	300		
$(3.22\pm0.10) \times 10^{-11}$	300	Chuong and Stevens, 2004	DF-LIF (b)
Relative Rate Coefficients			
$(2.96\pm0.24) \times 10^{-11}$	299±2	Atkinson et al., 1983	RR (c)
$(3.90\pm0.31) \times 10^{-11}$	298±2	Edney et al., 1986	RR (d)

Comments

(a) No variation in the rate coefficient was observed over the pressure range 2.7–6.7 mbar (2–5 Torr) of He diluent at any of the temperatures studied (300–422 K). The cited temperature-dependent rate expression uses data at 6.7 mbar pressure of He (Chuong and Stevens, 2003). Problems ascribed to reversible wall adsorption of methacrolein and heterogeneous wall reactions were observed; these were avoided or minimized by addition of ∼10% O_2 or by conditioning the reactor with high F atom concentrations

(b) At 133 mbar (100 Torr) of N_2 diluent, using a turbulent flow reactor.

(c) Relative rate study carried out at atmospheric pressure of air. The concentrations of methacrolein and propene (the reference compound) were measured by GC. The measured rate coefficient ratio k(HO + methacrolein)/k(HO + propene) = 1.13 ± 0.09 is placed on an absolute basis by using a rate coefficient of k(HO + propene) = 2.62×10^{-11} cm^3 molecule^{-1} s^{-1} at 299 K and atmospheric pressure of air (Atkinson, 1997).

(d) Relative rate study carried out at atmospheric pressure of air. The concentrations of methacrolein and propene and trans-2-butene (the reference compounds) were measured by GC. The measured rate coefficient ratios are placed on an absolute basis by using rate coefficients of k(HO + propene) = 2.63×10^{-11} cm^3 molecule^{-1} s^{-1} and k(HO + trans-2-butene) = 6.40×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure of air (Atkinson, 1997). The indicated uncertainty is one standard deviation (Edney et al., 1986).

Preferred Values

$k = 2.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.0 \times 10^{-12} \exp(380/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–380 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The room temperature rate coefficients of Kleindienst et al. (1982), Atkinson et al. (1983), Gierczak et al. (1997) and Chuong and Stevens (2003, 2004) are in good agreement, with the relative rate measurement of Edney et al. (1986) being ∼20 ∼30% higher. The temperature dependence obtained by Kleindienst et al. (1982) [300–423 K] and Chuong and Stevens (2003) [300-422 K] are respectively lower and higher than that determined by Gierczak et al. (1997) over the wider temperature range of 234–373 K. In the Chuong and Stevens (2003) study, the rate coefficients at 300, 328 and 361 K are in good agreement with the rate expression of Gierczak et al. (1997); those 390 and 422 K (Chuong and Stevens, 2003) are lower than predicted from the Arrhenius expression of Gierczak et al. (1997). Because of the wider temperature range used by Gierczak et al. (1997) and the fact that it extends below room temperature, the temperature dependence of Gierczak et al. (1997) is accepted. The preferred 298 K rate coefficient is based on the room temperature rate coefficients of Atkinson et al. (1983) and Gierczak et al. (1997), and the pre-exponential factor is calculated from the preferred 298 K rate coefficient and the temperature dependence.

The products of the reaction of HO radicals with methacrolein in the presence of NO have been investigated by Tuazon and Atkinson (1990) and Orlando and Tyndall (1999). The reaction proceeds by two pathways: H-atom abstraction from the CHO group, and initial addition of the HO radical to the carbon atoms of the C=C bond. H-atom abstraction from the CHO group accounts for 50–55% of the overall reaction at room temperature (Tuazon and Atkinson, 1990; Orlando and Tyndall, 1999), forming the acyl radical $CH_2{=}C(CH_3)CO$ which then adds O_2 to form the acyl peroxy radical $CH_2{=}C(CH_3)C(O)OO$. This acyl peroxy radical reacts with NO_2, to form the peroxyacyl nitrate $CH_2{=}C(CH_3)C(O)OONO_2$ (MPAN), or with NO (Tuazon and Atkinson, 1990; Orlando and Tyndall, 1999).

$$\begin{aligned} CH_2{=}C(CH_3)C(O)OO + NO_2 &\rightarrow CH_2{=}C(CH_3)C(O)OONO_2 \\ CH_2{=}C(CH_3)C(O)OO + NO &\rightarrow CH_2{=}CCH_3 + CO_2 + NO_2 \end{aligned}$$

The $CH_2{=}CCH_3$ radical reacts to form HCHO, CO and CO_2 (Orlando and Tyndall, 1999).

Initial HO radical addition to the C=C bond leads (in the presence of NO) to the intermediate hydroxyalkoxy radicals $HOCH_2C(O)(CH_3)CHO$ and $OCH_2C(OH)(CH_3)CHO$, which decompose by the pathways (Tuazon and Atkinson, 1990; Orlando and Tyndall, 1999):

$$\begin{aligned} HOCH_2C(O)(CH_3)CHO &\rightarrow CH_3C(O)CHO + CH_2OH \\ HOCH_2C(O)(CH_3)CHO &\rightarrow HOCH_2C(O)CH_3 + HCO \\ \text{and} & \\ OCH_2C(OH)(CH_3)CHO &\rightarrow HCHO + CH_3C(OH)CHO \end{aligned}$$

followed by reactions of CH_2OH and $CH_3C(OH)CHO$ radicals with O_2 to form $HCHO{+}HO_2$ and $CH_3C(O)CHO{+}HO_2$, respectively. The HO radical addition reaction appears to be in the high-pressure region above ∼2.7 mbar (2 Torr) pressure (Gierczak et al., 1997; Chuong and Stevens, 2003). The first generation products from the HO radical addition pathways are therefore HCHO + $CH_3C(O)CHO$ and $HOCH_2C(O)CH_3$ + CO (the CO arising from reaction of HCO with O_2). The studies of Tuazon and Atkinson (1990) and Orlando and Tyndall (1999) measured formation yields of methylglyoxal and hydroxyacetone of 8.4% and 44%, respectively, showing that initial HO radical addition occurs mainly at the terminal CH_2 moiety (Tuazon and Atkinson, 1990).

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II.A2.18

OH + Pinonaldehyde → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(8.72 \pm 1.14) \times 10^{-11}$	298 ± 2	Hallquist et al., 1997	RR (a)
$(8.9 \pm 2.6) \times 10^{-11}$	300 ± 5	Glasius et al., 1997	RR (b,c)
$(9.0 \pm 1.3) \times 10^{-11}$	300 ± 5	Glasius et al., 1997	RR (b,d)
$(4.5 \pm 0.8) \times 10^{-11}$	296 ± 2	Alvarado et al., 1998	RR (e,f)
$(4.9 \pm 1.1) \times 10^{-11}$	296 ± 2	Alvarado et al., 1998	RR (e,g)
$(5.4 \pm 0.9) \times 10^{-11}$	296 ± 2	Alvarado et al., 1998	RR (e,h)
$(3.0 \pm 0.8) \times 10^{-11}$	295 ± 3	Nozière et al., 1999	RR (c,i)
$(5.5 \pm 1.5) \times 10^{-11}$	295 ± 3	Nozière et al., 1999	RR (d,i)
$(4.7 \pm 0.6) \times 10^{-11}$	295 ± 3		
$(2.8 \pm 1.0) \times 10^{-11}$	295 ± 3		
$(2.7 \pm 0.6) \times 10^{-11}$	295 ± 3	Nozière et al., 1999	RR (i,j)
$(3.3 \pm 0.3) \times 10^{-11}$	295 ± 3		
$(2.8 \pm 0.3) \times 10^{-11}$	295 ± 3		
$(3.9 \pm 0.4) \times 10^{-11}$	295 ± 3		
$(3.7 \pm 1.1) \times 10^{-11}$	299 ± 2	Nozière et al., 1999	RR (j,k)
$(4.2 \pm 1.1) \times 10^{-11}$	290 ± 2		
$(3.8 \pm 1.5) \times 10^{-11}$	288 ± 1		
$(4.4 \pm 0.8) \times 10^{-11}$	287 ± 1		
$(4.4 \pm 1.0) \times 10^{-11}$	289 ± 2		

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures at 1013±5 mbar pressure. The concentrations of pinonaldehyde and propene (the reference compound) were measured by FTIR spectroscopy. Wall losses of pinonaldehyde in the 153 L chamber were observed and measured in separate experiments and taken into account in the data analysis. The measured rate coefficient ratio of k(HO + pinonaldehyde)/k(HO + propene) is placed on an absolute basis by use of a rate coefficient at 298 K and atmospheric pressure of air of k(HO + propene) = 2.63×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(b) HO radicals were generated by the photolysis of CH_3ONO-NO-air or H_2O_2-air mixtures at 987±7 mbar pressure. The concentrations of pinonaldehyde and isoprene or 1,3-butadiene (the reference compounds) were measured by FTIR spectroscopy. Decays of pinonaldehyde in the dark and due to photolysis were observed in the 480 L reaction chamber used and were taken into account in the data analysis. The measured rate coefficient ratios of k(HO + pinonaldehyde)/k(HO + isoprene) = 0.896±0.260 and k(HO + pinonaldehyde)/k(HO + 1,3-butadiene) = 1.37±0.19 are placed on an absolute basis by use of rate coefficients at 300 K of k(HO + isoprene) = 9.91×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation) and k(HO + 1,3-butadiene) = 6.59×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(c) Relative to k(HO + isoprene).

(d) Relative to k(HO + 1,3-butadiene).

(e) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures at 987 mbar pressure. The concentrations of pinonaldehyde and propene, 1-butene or *m*-xylene (the reference compounds) were measured by GC. No measurable decays (<5%) of pinonaldehyde were observed due to dark decays to the walls of the 7000 L Teflon chamber used or due to photolysis at wavelengths >300 nm. The measured rate coefficient ratios of k(HO + pinonaldehyde)/k(HO + propene) = 1.70±0.29, k(HO + pinonaldehyde)/k(HO + 1-butene) = 1.56±0.33 and k(HO + pinonaldehyde)/k(HO + *m*-xylene)

= 2.35±0.35 are placed on an absolute basis by use of rate coefficients at 296 K and atmospheric pressure of air of k(HO + propene) = 2.66×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, k(HO + 1-butene) = 3.17×10^{-11} cm^3 $molecule^{-1}$ s^{-1} and k(HO + *m*-xylene) = 2.31×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003).

(f) Relative to k(HO + propene).

(g) Relative to k(HO + 1-butene).

(h) Relative to k(HO + *m*-xylene).

(i) HO radicals were generated by the photolysis of CH_3ONO-NO-air or H_2O_2-air mixtures at 1013 mbar pressure. The concentrations of pinonaldehyde and reference compound (isoprene, 1,3-butadiene or cyclohexane) were measured by FTIR spectroscopy. Wall losses and photolysis was observed in the various chambers used (ranging from 405 to 1080 L volume) and were taken into account in the data analysis. The measured rate coefficient ratios of k(HO + pinonaldehyde)/k(HO + isoprene), k(HO + pinonaldehyde)/k(HO + 1,3-butadiene) and
k(HO + pinonaldehyde)/k(HO + cyclohexane) are placed on an absolute basis by use of rate coefficients at 295 K of k(HO + isoprene) = 1.01×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, current recommendation), k(HO + 1,3-butadiene) = 6.76×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003) and k(HO + cyclohexane) = 6.90×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 2003; Atkinson and Arey, 2003).

(j) Relative to k(HO + cyclohexane).

(k) Experiments carried out in the ∼180 000 L volume EUPHORE chamber with HO radicals being generated by the dark reaction of ozone with 2,3-dimethyl-2-butene in air at ∼1 bar pressure. The concentrations of pinonaldehyde and cyclohexane were monitored during the experiments by FTIR spectroscopy (pinonaldehyde and cyclohexane) and also by HPLC after derivatization for pinonaldehyde and by GC for cyclohexane. The measured rate coefficient ratios of k(HO + pinonaldehyde)/k(HO + cyclohexane) are placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 3.26×10^{-17} T^2 exp(262/T) cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 2003; Atkinson and Arey, 2003).

Preferred Values

$k = 4.2 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.25$ at 298 K.

Comments on Preferred Values

Pinonaldehyde is a low volatility product of the atmospheric reactions of α-pinene which is prone to wall losses, making measurement of its reaction rate coefficients difficult. The available rate coefficients are all from relative rate studies carried out at around room temperature, and range over a factor of ∼3 (Hallquist et al., 1997; Glasius et al., 1997; Alvarado et al., 1998; Nozière et al., 1999). The rate coefficients measured by Hallquist et al. (1997) and Glasius et al. (1997) are a factor of ∼2 higher than those of Alvarado et al. (1998) and Nozière et al. (1999), possibly because of unresolved wall adsorption problems. The preferred values are based on the study of Alvarado et al. (1998) carried out in a large volume Teflon chamber and the extensive study of Nozière et al. (1999) carried out in various chambers of volume ranging from 405 L to ∼180 000 L. The rate coefficients measured by Alvarado et al. (1998) have been aggregated into an average rate coefficient of 4.9×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, and those measured by Nozière et al. (1999) have been aggregated into an average rate coefficient from the indoor chambers with photolytic production of HO radicals of 3.6×10^{-11} cm^3 $molecule^{-1}$ s^{-1} and an average rate coefficient from the EUPHORE chamber study (with dark production of HO radicals) of 4.1×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. A simple average of these three rate coefficients, which are in agreement within their large experimental uncertainties, leads to the preferred 298 K rate coefficient.

The reaction proceeds by H-atom abstraction from the various C-H bonds, including from the -CHO group.

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II.A2.19

$HO + (CHO)_2 \rightarrow H_2O + HC(O)CO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.06 \pm 0.04) \times 10^{-11}$	298±2	Plum et al., 1983	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of glyoxal and cyclohexane (the reference compound) were measured by differential optical absorption spectroscopy and GC, respectively. The measured rate coefficient ratio of k(HO + glyoxal)/k(HO + cyclohexane) = 1.52 ± 0.05 is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 6.97×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

Preferred Values

$k = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred rate coefficient is based on the study of Plum et al. (1983), with increased uncertainty limits. The rate coefficient at 298 K is similar to those for other aldehydes. A close to zero temperature dependence is expected at around 298 K. The reaction is assumed to proceed via overall H-atom abstraction to yield H_2O + HC(O)CO. Niki et al. (1985) and Orlando and Tyndall (2001) have shown, from product studies of the Cl atom- and HO radical-initiated reactions of glyoxal using FTIR spectroscopy, that the HC(O)CO radical reacts by the pathways:

$$HC(O)CO \rightarrow HCO + CO \qquad (a)$$
$$HC(O)CO + O_2 \rightarrow HC(O)C(O)OO \qquad (b)$$
$$HC(O)CO + O_2 \rightarrow 2CO + HO_2 \qquad (c)$$

Niki et al. (1985) determined that at 298 K and 933 mbar (700 Torr) total pressure, $k_b \sim k_c$ and $k_a/k_b = 3.5 \times 10^{18}$ molecule cm^3. More recently, Orlando and Tyndall (2001) measured the rate coefficient ratio k_c/k_b to be $k_c/k_b = 1.0 \pm 0.2$, independent of temperature over the range 224–317 K at 933 mbar (700 Torr) total pressure, in good agreement with the earlier measurement of Niki et al. (1985). Assuming an temperature-independent rate coefficient of k_b (=k_c) = 5×10^{-12} cm^3 molecule^{-1} s^{-1}, Orlando and Tyndall (2001) also derived a rate coefficient at 933 mbar pressure for the HC(O)CO decomposition of $k_a = 1.4 \times 10^{-12} \exp[-(3160 \pm 500)/T]$ s^{-1}. This results in a rate coefficient ratio k_a/k_b at 298 K a factor of 2 higher than that derived by Niki et al. (1985).

In the presence of NO_2, Orlando and Tyndall (2001) observed no evidence for the formation of the PAN-type compound $HC(O)C(O)OONO_2$, even at 224 K. Based on the observed formation of CO, CO_2, HO_2NO_2 and N_2O_5, Orlando and Tyndall (2001) postulated that the HC(O)C(O)OO radical reacts with NO_2 as follows,

$$HC(O)C(O)OO + NO_2 (+ M) \rightarrow HCO + CO_2 + NO_3 (+ M)$$

with subsequent reactions of HCO with O_2 to form HO_2 + CO, of HO_2 with NO_2 to form HO_2NO_2, and of NO_3 with NO_2 to form N_2O_5 leading to the observed products.

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II.A2.20

$$\mathbf{HO + HOCH_2CHO \rightarrow H_2O + HOCH_2CO \quad (1)}$$
$$\mathbf{\rightarrow H_2O + HOCHCHO \quad (2)}$$

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(9.4\pm0.9) \times 10^{-12}$	298±2	Niki et al., 1987	RR (a)
$(1.24\pm0.16) \times 10^{-11}$	298	Bacher et al., 2001	RR (a,b)
$(1.03\pm0.07) \times 10^{-11}$	298	Bacher et al., 2001	RR (b,c)
$(1.22\pm0.20) \times 10^{-11}$	296 ± 2	Baker et al., 2004	RR (d,e)
$(8.0\pm1.7) \times 10^{-12}$	296 ± 2	Baker et al., 2004	RR (d,f)
$(1.08\pm0.08) \times 10^{-11}$	298 ± 3	Magneron et al., 2005	RR (g,h)
$(1.33\pm0.15) \times 10^{-11}$	298 ± 3	Magneron et al., 2005	RR (g,i)
$(1.09\pm0.09) \times 10^{-11}$	298 ± 3	Magneron et al., 2005	RR (g,j)
$(1.38\pm0.17) \times 10^{-11}$	298 ± 3	Magneron et al., 2005	RR (g,k)
Branching Ratios			
$k_1/k = 0.80$	298±2	Niki et al., 1987	(l)
$k_2/k = 0.20$	298±2	Niki et al., 1987	(l)
$k_2/k = 0.22 \pm 0.06$	~298	Magneron et al., 2005	(m)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in air and the concentrations of $HOCH_2CHO$ and acetaldehyde (the reference compound) measured by FTIR absorption spectroscopy. The measured rate coefficient ratios of $k(HO + CH_3CHO)/k(HO + HOCH_2CHO) = 1.6\pm0.15$ (Niki et al., 1987) and $k(HO + HOCH_2CHO)/k(HO + CH_3CHO) = 1.03\pm0.13$ (Bacher et al., 2001) are placed on an absolute basis by use of a rate constant of $k(HO + CH_3CHO) = 1.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(b) Wall losses were estimated (Bacher et al., 2001) to have led to a ~20% overestimation of the HO radical reaction rate coefficients. The rate coefficients cited in the table are the rate coefficients calculated from the measured rate coefficient ratios, reduced by 20%.

(c) HO radicals were generated by the photolysis of CH_3ONO in air and the concentrations of $HOCH_2CHO$ and propene (the reference compound) measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(HO + HOCH_2CHO)/k(HO + \text{propene}) = 0.49 \pm 0.03$ is placed on an absolute basis by use of a rate coefficient of $k(HO + \text{propene}) = 2.63 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure of air (Atkinson, 1997).

(d) HO radicals were generated by the photolysis of CH_3ONO in air. $HOCH_2CHO$ was generated in situ from the OH radical-initiated reaction of 1,2-butanediol or 2-methyl-3-buten-2-ol, and the concentrations of $HOCH_2CHO$ and its precursor measured by GC. From comparison of the measured time-concentration behavior of $HOCH_2CHO$ and its precursor with calculations, rate coefficient ratios of $k(HO + HOCH_2CHO)/k(HO + \text{1,2-butanediol}) = 0.485 \pm 0.073$ and $k(HO + HOCH_2CHO)/k(HO + \text{2-methyl-3-buten-2-ol}) = 0.124 \pm 0.025$ were derived. These rate coefficient ratios are placed on an absolute basis by use of rate coefficients at 296 K of $k(HO + \text{1,2-butanediol}) = (2.51 \pm 0.13) \times10^{-11}$ cm^3 molecule^{-1} s^{-1} (Baker et al., 2004) and $k(HO + \text{2-methyl-3-buten-2-ol}) = 6.44 \times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(e) Relative to 1,2-butanediol.

(f) Relative to 2-methyl-3-buten-2-ol.

(g) HO radicals were generated by the photolysis of HONO in air and the concentrations of $HOCH_2CHO$ and diisopropyl ether, diethyl ether, 1,3-dioxolane or acetaldehyde (the reference compounds) measured by FTIR absorption spectroscopy. The measured rate coefficient ratios of k(HO + $HOCH_2CHO$)/k(HO + diisopropyl ether) = 1.06 ± 0.07, k(HO + $HOCH_2CHO$)/k(HO + diethyl ether) = 0.98 ± 0.11, k(HO + $HOCH_2CHO$)/k(HO + 1,3-dioxolane) = 0.98 ± 0.08 and k(HO + $HOCH_2CHO$)/k(HO + acetaldehyde) = 0.92 ± 0.11 are placed on an absolute basis by use of rate coefficients at 298 K of k(HO + diisopropyl ether) = 1.02×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Magneron et al., 2005), k(HO + diethyl ether) = 1.36×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Magneron et al., 2005), k(HO + 1,3-dioxolane) = 1.11×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Magneron et al., 2005) and k(HO + acetaldehyde) = 1.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, current recommendation).

(h) Relative to diisopropyl ether.

(i) Relative to diethyl ether.

(j) Relative to 1,3-dioxolane.

(k) Relative to acetaldehyde.

(l) HO radicals were generated by the photolysis of ethyl nitrite in air, and $HOCH_2CHO$ and products [$(CHO)_2$, CO_2 and HCHO] were measured by FTIR absorption spectroscopy. Product formation yields of $(CHO)_2$, 21.1 ± 2.4%; CO_2, 81.3 ± 3.2%; and HCHO, 82.4 ± 4.6% were obtained, leading to branching ratios of $k_1/k = 0.80$ and $k_2/k = 0.20$.

(m) HO radicals were generated by photolysis of HONO in air in the EUPHORE chamber, and $HOCH_2CHO$ and products [HCHO, CO and $(CHO)_2$] monitored by FTIR spectroscopy. The measured glyoxal yield of 22 ± 6% was attributed to channel (2). The initial HCHO yield was 64 ± 5%.

Preferred Values

$k = 1.1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k_1/k = 0.80$ at 298 K.
$k_2/k = 0.20$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (k_1/k) = \Delta (k_2/k) \pm 0.10$ at 298 K.

Comments on Preferred Values

All the reported rate coefficients are from relative rate studies conducted at room temperature, and as evident from the table there is a substantial amount of scatter in the rate coefficients obtained. The preferred 298 K rate coefficient is the mean of the room temperature rate coefficients of Niki et al. (1987), Bacher et al. (2001), Baker et al. (2004) and Magneron et al. (2005). The branching ratios k_1/k and k_2/k are taken from the studies of Niki et al. (1987) and Magneron et al. (2005), which are in good agreement.

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II.A2.21

$HO + CH_3C(O)CHO \rightarrow H_2O + CH_3C(O)CO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(7.1\pm1.6) \times 10^{-12}$	297±2	Kleindienst et al., 1982	FP-RF
$8.4 \times 10^{-13}\exp[(830\pm300)/T]$	260–333	Tyndall et al., 1995	DF-LIF
$(1.32 \pm 0.30) \times 10^{-11}$	298		
Relative Rate Coefficients			
$(1.60 \pm 0.12) \times 10^{-11}$	298±2	Plum et al., 1983	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in air. The concentrations of $CH_3C(O)CHO$ and cyclohexane (the reference compound) were measured by differential optical absorption spectroscopy and GC, respectively. The measured rate coefficient ratio of $k(HO + CH_3C(O)CHO)/k(HO + \text{cyclohexane}) = 2.29\pm0.16$ is placed on an absolute basis by use of a rate coefficient $k(HO + \text{cyclohexane}) = 6.97\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

Preferred Values

$k = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is an average of the relative rate coefficient of Plum et al. (1983) and the absolute rate coefficient of Tyndall et al. (1995). The absolute rate coefficient measured by Kleindienst et al. (1982) may have been low due to the presence of significant levels of low reactivity impurities in the methylglyoxal samples used. The data of Tyndall et al. (1995) indicate a significant negative temperature dependence; while no recommendation is made concerning the temperature dependence of this reaction a negative temperature dependence is expected at around room temperature (see, for example, the $HO+CH_3CHO$ reaction (IUPAC, this evaluation). The reaction is assumed to proceed via H-atom abstraction to form $H_2O+CH_3C(O)CO$. Green et al. (1990) have shown that the dominant fate of the $CH_3C(O)CO$ radical under atmospheric conditions is decomposition to form CH_3CO+CO.

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II.A2.22

$HO + CH_3C(O)CH_3 \rightarrow H_2O + CH_2C(O)CH_3$

$\Delta H^\circ = -87.8 \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.7 \times 10^{-12}\exp[-(600 \pm 75)/T]$	240–440	Wallington and Kurylo, 1987	FP-RF
$(2.16\pm0.16) \times 10^{-13}$	296		
$(8.80\pm1.32) \times 10^{-12}$	1217	Bott and Cohen, 1991	SH-RA
$1.25 \times 10^{-12}\exp[-(561\pm57)/T]$	243–372	Le Calvé et al., 1998	PLP-LIF
$(1.84\pm0.24) \times 10^{-13}$	298		
$8.8 \times 10^{-12}\exp[-(1320\pm163)/T]$	202–395	Wollenhaupt et al., 2000	PLP-LIF/RF
$+ 1.7 \times 10^{-14}\exp[(423\pm109)/T]$			
$(1.73\pm0.09) \times 10^{-13}$	298		
$(1.73\pm0.05) \times 10^{-13}$	298	Vasvári et al., 2001	DF-RF
$1.38 \times 10^{-13} + 3.86 \times 10^{-11} \exp[-1997/T]$	199-383	Gierczak et al., 2003	PLP-LIF/DF-CIMS (a)
$(1.77\pm0.18) \times 10^{-13}$	298		
$3.99 \times 10^{-24}\ T^{4.00} \exp[(453 \pm 44)/T]$	298-832	Yamama et al., 2003	PLP-LIF
$(1.56 \pm 0.08) \times 10^{-13}$	298		
$4.90 \times 10^{-11} \exp[-2297/T]$	982-1300	Vasudevan et al., 2005	SH-RA (b)
Relative Rate Coefficients			
$(2.7\pm0.1) \times 10^{-13}$	303±2	Kerr and Stocker, 1986	RR (c)
$1.39 \times 10^{-12} \exp[-(604 \pm 44)/T]$	253-373	Raff et al., 2005	RR (d)
1.83×10^{-13}	298		

Comments

(a) Rate coefficients for the reaction of HO radicals with acetone were shown to be independent of pressure over the range 1.1 Torr (1.5 mbar) of He diluent to 490 Torr (653 mbar) of SF6 diluent. Rate coefficients were also measured for the reactions $HO + CD_3C(O)CD_3$ (211-383 K), $DO + CD_3C(O)CD_3$ (213-324 K), $H^{18}O + CH_3C(O)CH_3$ (240-296 K) and $DO + CH_3C(O)CH_3$ (223-296 K) over the indicated temperature ranges. The measured H/D isotope effect, $k(HO + CH_3C(O)CH_3)/k(HO + CD_3C(O)CD_3)$, increased from 5.9 ± 0.9 at 298 K to 8.6 ± 0.8 at 212 K.

(b) HO radicals were generated by shock-heating of tert-butyl hydroperoxide and monitored by laser absorption at 306.7 nm. A fit of the absolute rate data of Wallington and Kurylo (1987), Bott and Cohen (1991), Le Calvé et al. (1998), Wollenhaupt et al. (2000), Gierczak et al. (2003) and Vasudevan et al. (2005) and the relative rate data of Tranter et al. (2001) to a multi-parameter expression yielded $k = \{1.33 \times 10^{-13} + 1.01 \times 10^{-15}\ T^{1.41} \exp(-1289/T)\}$ cm^3 molecule^{-1} s^{-1} over the temperature range 199-1300 K.

(c) HO radicals were generated by the photolysis of HONO in air, and the concentrations of acetone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + acetone)/k(HO + ethene) = 0.032 ± 0.001 is placed on an absolute basis by use of a rate coefficient of k(HO + ethene) = 8.32×10^{-12} cm^3 molecule^{-1} s^{-1} at 303 K and atmospheric pressure (Atkinson, 1997).

(d) HO radicals were generated by the photolysis at <315 nm of O_3-O_2-H_2O-He mixtures at 735–750 Torr (980–1000 mbar) total pressure in 0.16 or 0.50 L quartz reaction vessels. The concentrations of acetone and CH_3CHF_2 (the reference compound) were measured by MS. The measured rate coefficient ratios of k(HO + acetone)/$k(HO + CH_3CHF_2)$ are placed on an absolute basis by use of a rate coefficient of $k(HO + CH_3CHF_2) = 2.80 \times 10^{-18}\ T^2 \exp(-580/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2005). Rate coefficients were also measured for the reaction of HO radicals with $CD_3C(O)CD_3$, relative to those for CH_2F_3, over the temperature range 293–373 K. Use of $k(HO + CH_2F_2) = 4.80 \times 10^{-18} T^2 \exp(-1080/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2005) leads to $k(HO + CD_3C(O)CD_3) = 5.06 \times 10^{-13} \exp(-819/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 293–373 K. Acetic acid was observed as a product of the reaction of HO radicals with $CH_3C(O)CH_3$, but was attributed mainly or wholly to secondary chemistry.

Preferred Values

$k = 1.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = \{8.8 \times 10^{-12} \exp(-1320/T) + 1.7 \times 10^{-14} \exp(423/T)\}$ cm^3 molecule^{-1} s^{-1} over the temperature range 195–440 K.

Reliability

$\Delta \log k = \pm 0.08$ over the temperature range 200–400 K.

Comments on Preferred Values

The absolute rate studies of Wallington and Kurylo (1987), Bott and Cohen (1991), Le Calvé et al. (1998), Wollenhaupt et al. (2000), Vasvári et al. (2001), Gierczak et al. (2003), Yamada et al. (2003) and Vasudevan et al. (2005) lead to a generally consistent temperature-dependent set of rate coefficients for the reaction of HO radicals with acetone over the range 199-1300 K, and the relative rate coefficients measured by Raff et al. (2005) over the temperature range 253–373 are also in good agreement with these absolute studies. In particular, the rate coefficients of Wollenhaupt et al. (2000) and Gierczak et al. (2003) are in excellent agreement over the temperature range common to both studies (202–383 K), and the low temperature ($<$240 K) data of Wollenhaupt et al. (2000) have been confirmed by Gierczak et al. (2003). In these studies of Wollenhaupt et al. (2000) and Gierczak et al. (2003), the concentration of acetone in the flow stream was measured by UV absorption. The preferred rate expression uses the non-linear least-squares analysis presented by Wollenhaupt et al. (2000), which leads to a generally excellent fit of the rate coefficients of Wallington and Kurylo (1987), Le Calvé et al. (1998), Wollenhaupt et al. (2000) and Gierczak et al. (2003) over the range 199–440 K. Note that the temperature-dependence of the rate coefficient for this reaction at $\leq$200 K is not well established, and the preferred expression should not be used below 195 K.

The measured deuterium isotope effect, $k(HO + CH_3C(O)CH_3)/k(HO + CD_3C(O)CD_3)$, is substantial, being 5.9 ± 0.9 (Gierczak et al., 2003), 6.8 ± 1.0 (Yamada et al., 2003) and 5.65 (Raff et al., 2005) at 298 K, increasing to 8.6 ± 0.8 at 212 K (Gierczak et al., 2003). The magnitude of this deuterium isotope effect indicates that the rate-determining step involves C-H (or C-D) bond breakage.

Products of this reaction have been investigated by Wollenhaupt and Crowley (2000), Vasvári et al. (2001), Vandenberk et al. (2002), Tyndall et al. (2002), Turpin et al. (2003) and Talukdar et al. (2003), with conflicting results in some cases. Wollenhaupt and Crowley (2000) measured the amount of CH_3 radicals formed in the pathway

$$HO + CH_3C(O)CH_3 \rightarrow CH_3C(O)OH + CH_3$$

by converting methyl radicals to methoxy radicals by reaction with NO_2 and monitoring CH_3O by LIF, and concluded that the channel forming $CH_3C(O)OH + CH_3$ accounted for $\sim$50% of the overall reaction at 298 K and $\sim$30% at 233 K. Vasvári et al. (2001) used a DF system with LIF detection of HO radicals and $CH_3C(O)CH_2$ radicals to obtain a branching ratio for the H-atom abstraction pathway of 0.50 ± 0.04 at 298 K, apparently consistent with the data of Wollenhaupt and Crowley (2000). However, Vandenberk et al. (2002), Tyndall et al. (2002) and Talukdar et al. (2003) measured upper limits to acetic acid formation of $<$5% at 298 K (Vandenberk et al., 2002), $<$10% at 296 K and 251 K (Tyndall et al., 2002), and $<$1% over the range 237–353 K (Talukdar et al., 2003). Furthermore, Talukdar et al. (2003) and Turpin et al. (2003) measured yields of $CH_3C(O)CH_2$ radicals of 96 ± 11%, independent of temperature over the range 242–350 K, and 90 ± 10% at 298 K, respectively. The results of these recent product studies of Vandenberk et al. (2002), Tyndall et al. (2002), Turpin et al. (2003) and Talukdar et al. (2003), together with the large deuterium isotope effect observed by Gierczak et al. (2003), Yamada et al. (2003) and Raff et al. (2005) and the lack of a pressure dependence (Gierczak et al., 2003), indicate that the reaction proceeds by H-atom abstraction.

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II.A2.23

HO + $CH_3C(O)CH_2CH_3$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.3×10^{-12}exp[-(170 ±120)/T]	240–440	Wallington and Kurylo, 1987	FP-RF
$(1.15\pm0.10) \times 10^{-12}$	296		
1.51×10^{-12} exp[-(60±61)/T]	243–372	Le Calvé et al., 1998	PLP-LIF
$(1.19\pm0.18) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(3.5\pm1.0) \times 10^{-12}$	305±2	Winer et al., 1976	RR (a)
2.74×10^{-12}	300	Cox et al., 1980	RR (b)
$(9.5\pm0.9) \times 10^{-13}$	295±2	Cox et al., 1981	RR (b)
$(9.1\pm1.6) \times 10^{-13}$	297	Edney et al., 1986	RR (c)

Comments

(a) HO radicals were generated by the photolysis of NO_x-organic-air mixtures, and the concentrations of 2-butanone and 2-methylpropene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + 2-butanone)/k(HO + 2-methylpropene) = 0.07 (±30%) is placed on an absolute basis by use of a rate coefficient of k(HO + 2-methylpropene) = 4.94×10^{-11} cm^3 molecule^{-1} s^{-1} at 305 K (Atkinson, 1997).

(b) HO radicals were generated by the photolysis of HONO in air, and the concentrations of 2-butanone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratios k(HO + 2-butanone)/k(HO + ethene) are placed on an absolute basis by use of rate coefficients at atmospheric pressure of k(HO + ethene) = 8.44×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K and 8.65×10^{-12} cm^3 molecule^{-1} s^{-1} at 295 K (Atkinson, 1997).

(c) HO radicals were generated from the photolysis of CH_3ONO in air, and the concentrations of 2-butanone and propane (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + 2-butanone)/k(HO + propane) is placed on an absolute basis by use of a rate coefficient of k(HO + propane) = 1.07×10^{-12} cm^3 molecule^{-1} s^{-1} at 297 K (IUPAC, current recommendation).

Preferred Values

$k = 1.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.3 \times 10^{-12}$ exp(-25/T) cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

Photolysis of 2-butanone may have contributed to the measured 2-butanone loss rates in the relative rate studies of Winer et al. (1976) and Cox et al. (1980). A unit-weighted least-squares analysis of the absolute rate coefficients of Wallington et al. (1987) and Le Calvé et al. (1998), using the three-parameter expression $k=CT^2 \exp(-D/T)$, results in $k=2.53\times10^{-18}\ T^2$ exp(503/T) cm^3 molecule^{-1} s^{-1} over the temperature range 240–440 K. The preferred Arrhenius expression, $k=A \exp(-B/T)$, is centered at 265 K and is derived from the above three-parameter expression with $A=C\ e^2T^2$ and $B=D+2T$.

Cox et al. (1981) observed acetaldehyde as a product of the HO radical reaction with 2-butanone, with a formation yield of 0.62±0.02. Acetaldehyde is expected to arise from 2-butanone after H-atom abstraction from the CH_2 group, and hence the fraction of the overall HO radical reaction with 2-butanone proceeding via

$$HO + CH_3C(O)CH_2CH_3 \rightarrow H_2O + CH_3C(O)CHCH_3$$

is ∼0.62.

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II.A2.24

HO + $CH_3C(O)CH=CH_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$3.85 \times 10^{-12}\exp[(456 \pm 73)/T]$	298–424	Kleindienst et al., 1982	FP-RF
$(1.79 \pm 0.28) \times 10^{-11}$	298		
$2.67 \times 10^{-12} \exp[(612 \pm 49)/T]$	232–378	Gierczak et al., 1997	PLP-LIF
$(2.03 \pm 0.17) \times 10^{-11}$	298		
$(1.73 \pm 0.21) \times 10^{-11}$	300	Chuong and Stevens, 2003	DF-RF/LIF (a)
$(1.78 \pm 0.08) \times 10^{-11}$	300	Chuong and Stevens, 2004	DF-LF (b)
$(1.86 \pm 0.12) \times 10^{-11}$	298 ± 2	Holloway et al.,, 2005	PLP-LIF (c)
Relative Rate Coefficients			
1.48×10^{-11}	300	Cox et al., 1980	RR (d)
$(1.96 \pm 0.15) \times 10^{-11}$	299±2	Atkinson et al., 1983	RR (e)

Comments

(a) At 300 K no measurable variation in the rate coefficient was observed over the pressure range 2.7–6.7 mbar (2–5 Torr) of He diluent; the cited rate coefficient is that obtained at 6.7 mbar (5 Torr) of He diluent. However, at the other temperatures studied (328, 361, 390 and 422 K) the measured rate coefficients increased with increasing pressure over the range 2.7–6.7 mbar of He, showing that the reaction was in the fall-off regime under these temperature and pressure conditions. Problems ascribed to reversible wall adsorption of methyl vinyl ketone and heterogeneous wall reactions were observed; these were avoided or minimized by addition of ∼10% O_2 or by conditioning the reactor with high F atom concentrations

(b) At 133 mbar (100 Torr) of N_2 diluent, using a turbulent flow reactor.

(c) The pulsed laser photolysis of 3-methyl-2,4-dione at 248 nm was used to generate HO radicals.

(d) Relative rate study carried out at atmospheric pressure of air. The concentrations of methyl vinyl ketone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio is placed on an absolute basis by using a rate coefficient of k(HO + ethene) = 8.44×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K and atmospheric pressure of air (Atkinson, 1997).

(e) Relative rate study carried out at atmospheric pressure of air. The concentrations of methyl vinyl ketone and propene (the reference compound) were measured by GC. The measured rate coefficient ratio k(HO + methyl vinyl ketone)/k(HO + propene) = 0.747 ± 0.055 is placed on an absolute basis by using a rate coefficient of k(HO + propene) = 2.62×10^{-11} cm^3 molecule^{-1} s^{-1} at 299 K and atmospheric pressure of air (Atkinson, 1997).

Preferred Values

$k = 2.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.6 \times 10^{-12} \exp(610/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–380 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The room temperature rate coefficients of Kleindienst et al. (1982), Atkinson et al. (1983), Gierczak et al. (1997), Chuong and Stevens (2003, 2004) and Holloway et al. (2005) are in good agreement, but are higher by ∼20-35% than the earlier relative rate measurement of Cox et al. (1980). The preferred 298 K rate coefficient is based on the room temperature rate coefficients of Atkinson et al. (1983), Gierczak et al. (1997) and Holloway et al. (2005). The temperature dependence measured by Gierczak et al. (1997) is accepted and the pre-exponential factor is calculated from the preferred 298 K rate coefficient and the temperature dependence.

The products of the reaction of HO radicals with methyl vinyl ketone in the presence of NO have been investigated by Tuazon and Atkinson (1989). The reaction proceeds by initial addition of the HO radical to the carbon atoms of the C=C bond, forming (in the presence of NO) the intermediate hydroxyalkoxy radicals $CH_3C(O)CH(O)CH_2OH$ and $CH_3C(O)CH(OH)CH_2O$, which decompose by the pathways:

$$\begin{aligned} CH_3C(O)CH(O)CH_2OH &\rightarrow CH_3C(O)CHO + CH_2OH \\ CH_3C(O)CH(O)CH_2OH &\rightarrow CH_3CO + HOCH_2CHO \end{aligned}$$

and

$$CH_3C(O)CH(OH)CH_2O \rightarrow HCHO + CH_3C(O)CHOH$$

followed by reactions of CH_2OH and $CH_3C(O)CHOH$ radicals with O_2 to form HCHO + HO_2 and $CH_3C(O)CHO$ + HO_2, respectively. The first generation products are therefore HCHO + $CH_3C(O)CHO$ and $HOCH_2CHO$ + CH_3CO (with the acetyl radical reacting to form peroxyacetyl nitrate [$CH_3C(O)OONO_2$; PAN] or HCHO (Tuazon and Atkinson, 1989; IUPAC, 2005). Tuazon and Atkinson (1989) measured formation yields of methylglyoxal and glycolaldehyde of 25 ± 8% and 64 ± 16%, respectively, showing that initial HO radical addition occurs mainly at the terminal CH_2 group (Tuazon and Atkinson, 1989).

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II.A2.25

$$\begin{aligned} \mathbf{HO + CH_3OH} &\rightarrow \mathbf{H_2O + CH_2OH} \quad (1) \\ &\rightarrow \mathbf{H_2O + CH_3O} \quad (2) \end{aligned}$$

$\Delta H^\circ(1) = -95.2 \mathrm{kJ \cdot mol^{-1}}$

$\Delta H^\circ(2) = -60.2 \mathrm{kJ \cdot mol^{-1}}$

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.06\pm0.10) \times 10^{-12}$	296±2	Overend and Paraskevopoulos, 1978	FP-RA
$(1.00\pm0.10) \times 10^{-12}$	298	Ravishankara and Davis, 1978	FP-RF
$4.8 \times 10^{-12} \exp[-(480 \pm 70)/T]$	240–440	Wallington and Kurylo, 1987	FP-RF
$(8.61\pm0.47) \times 10^{-13}$	296		
$(1.01\pm0.10) \times 10^{-12}$	298±2	McCaulley et al., 1989	DF-LIF
$5.89 \times 10^{-20} T^{2.65} \exp(444/T)$	294–866	Hess and Tully, 1989	PLP-LIF
$(9.34\pm0.41) \times 10^{-13}$	294		
$(9.0\pm0.9) \times 10^{-13}$	298 ±2	Nelson et al., 1990	PR-RA
$(8.64\pm1.30) \times 10^{-12}$	1205±16	Bott and Cohen, 1991	SH-RA
$3.6 \times 10^{-12} \exp[-(415 \pm 70/T)]$	235-360	Jiménez et al. 2003	PLP-LIF
$(9.3\pm1.1) \times 10^{-13}$	298		
$6.67 \times 10^{-18} T^2 \exp[(140 \pm 14/T)]$	210-351	Dillon et al. 2005	PLP-LIF
$(9.3\pm0.7) \times 10^{-13}$	298 ± 1		
Relative Rate Coefficients			
$(9.0\pm0.7) \times 10^{-13}$	300±3	Tuazon et al., 1983	RR (a)
$(9.3\pm2.2) \times 10^{-13}$	298±2	Nelson et al., 1990	RR (b)
$(8.6\pm0.8) \times 10^{-13}$	298±4	Picquet et al., 1998	RR (c)
$(9.6\pm1.0) \times 10^{-13}$	298±2	Oh and Andino, 2001	RR (d)
$(8.4\pm0.7) \times 10^{-13}$	298±2	Oh and Andino, 2001	RR (b)
$(7.88\pm0.47) \times 10^{-13}$	296±2	Sørensen et al., 2002	RR (e,f)
$(8.18\pm0.52) \times 10^{-13}$	296±2	Sørensen et al., 2002	RR (e,g)
Branching Ratios			
k_2/k = 0.15±0.08	298±2	McCaulley et al., 1989	(h)

Comments

(a) HO radicals were generated by the dark reaction of hydrazine with O_3 in air. The concentrations of methanol and dimethyl ether (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of k(HO + methanol)/k(HO + dimethyl ether) = 0.314±0.024 is placed on an absolute basis using the rate coefficient k(HO + dimethyl ether) = 2.86×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K (IUPAC, current recommendation).

(b) HO radicals were generated by the photolysis of CH_3ONO in air at >300 nm. The concentrations of methanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + methanol)/k(HO + cyclohexane) is placed on an absolute basis using a rate coefficient of k(HO + cyclohexane) = 6.97×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

(c) HO radicals were generated by the photolysis of H_2O_2 in air at 254 and 310 nm. The concentrations of methanol and n-pentane (the reference compound) were measured by GC. The measured rate coefficient ratio, k(HO + methanol)/k(HO

+*n*-pentane), is placed on an absolute basis using a rate coefficient of k(HO + *n*-pentane) = 3.80×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

(d) HO radicals were generated by the photolysis of CH_3ONO in air at $>$300 nm. The concentrations of methanol and ethanol (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + methanol)/k(HO + ethanol) = 0.30±0.03 is placed on an absolute basis using a rate coefficient of k(HO + ethanol) = 3.2×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(e) HO radicals were generated by the photolysis of CH_3ONO in air at 1.0 bar (750 Torr). The concentrations of methanol and acetylene or ethene (the reference compounds) were measured by in situ FTIR spectroscopy. The measured rate coefficient ratios of k(HO + methanol)/k(HO + acetylene) = 1.01 ± 0.06 and k(HO + methanol)/k(HO + ethene) = 0.095 ± 0.006 are placed on an absolute basis using rate coefficients of k(HO + acetylene) = 7.8 $\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 750 Torr pressure of air or O_2 and 296 ± 2 K (Sørensen et al., 2003) and k(HO + ethene) = 8.61 $\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 296 K and atmospheric pressure of air (Atkinson, 1997). No effect of the presence of NaCl or NH_4NO_3 aerosol was observed.

(f) Relative to acetylene.

(g) Relative to ethene.

(h) Derived from measurements of the rate coefficients for the reactions of the HO radical with CH_3OH, CD_3OH and CD_3OD and of the DO radical with CH_3OH, CH_3OD, CD_3OH and CD_3OD, assuming that secondary kinetic isotope effects are negligible.

Preferred Values

k = 9.0 × 10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 2.85 × 10^{-12} exp(-345/T) cm^3 molecule^{-1} s^{-1} over the temperature range 210–300 K.
k_2/k = 0.15 at 298 K.

Reliability

Δ log k = ± 0.08 at 298 K.
Δ (*E/R*) = ± 150 K.
Δ k_2/k = ± 0.10 at 298 K.

Comments on Preferred Values

The preferred rate coefficient is obtained by fitting the absolute rate coefficients of Wallington and Kurylo (1987), Hess and Tully (1989), Jiménez et al. (2003) and Dillon et al. (2005) to the three parameter expression $k = CT^2$ exp($-D/T$). This results in k = 6.38 × 10^{-18} T^2 exp(144/T) cm^3 molecule^{-1} s^{-1} over the temperature range 210-866 K. The preferred Arrhenius expression, k=A exp($-B/T$), is centered at 245 K, and is derived from the three parameter equation with A=Ce^2T^2 and B=$D+2T$. Note that the Arrhenius expression should not be used outside of the stated temperature range (210–300 K); rather the three-parameter expression k = 6.38 × 10^{-18} T^2 exp(144/T) cm^3 molecule^{-1} s^{-1} should be employed. The absolute room temperature rate coefficients of Overend and Paraskevopoulos (1978), Ravishankara et al. (1978), McCaulley et al. (1989) and Nelson et al. (1990) are in good agreement with the preferred values, as are the room temperature relative rate coefficients of Tuazon et al. (1983), Nelson et al. (1990), Picquet et al. (1998), Oh and Andino (2001) and Sørensen et al. (2002).

The kinetic (McCaulley et al., 1989) and product (Hägele et al., 1983; Meier et al., 1984) studies show that the reaction proceeds mainly by channel(1) at room temperature, as expected from the thermochemistry of the reaction pathways (1) and (2).

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II.A2.26

$$\begin{aligned} \mathbf{HO + C_2H_5OH} &\rightarrow \mathbf{H_2O + CH_2CH_2OH} \quad &\mathbf{(1)} \\ &\rightarrow \mathbf{H_2O + CH_3CHOH} \quad &\mathbf{(2)} \\ &\rightarrow \mathbf{H_2O + CH_3CH_2O} \quad &\mathbf{(3)} \end{aligned}$$

$\Delta H^\circ(1) = -67\text{kJ} \cdot \text{mol}^{-1}$

$\Delta H^\circ(2) = -95.8\text{kJ} \cdot \text{mol}^{-1}$

$\Delta H^\circ(3) = -59.7\text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data (k=k_1+k_2+k_3)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.25×10^{-11} exp[-(360±52)/T]	255–459	Greenhill and O'Grady, 1986	FP-RA
$(3.40\pm0.17) \times 10^{-12}$	293		
7.4×10^{-12}exp[-(240±110)/T]	240–440	Wallington and Kurylo, 1987	FP-RF
$(3.33\pm0.23) \times 10^{-12}$	296		
$(3.26\pm0.14) \times 10^{-12}$	293	Hess and Tully, 1988	PLP-LIF (a,b)
$(3.33\pm0.14) \times 10^{-12}$	326.5		
$(3.63\pm0.15) \times 10^{-12}$	380		
$(3.94\pm0.16) \times 10^{-12}$	441		
$(3.32\pm0.16) \times 10^{-12}$	295	Hess and Tully, 1988	PLP-LIF (b,c)
$(5.47\pm0.34) \times 10^{-12}$	599		
$(3.04\pm0.25) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	PR-RA
k_2+ k_3 = $(8.80\pm1.32) \times 10^{-12}$	1204±16	Bott and Cohen, 1991	SH-RA (d)
4.3×10^{-12} exp[-(85 ± 35)/T]	227-360	Jiménez et al., 2003	PLP-LIF
$(3.1 \pm 0.4) \times 10^{-12}$	298		
4.0×10^{-12} exp[-(42 ± 10)/T]	216-368	Dillon et al., 2005	PLP-LIF
$(3.35 \pm 0.17) \times 10^{-12}$	298 ± 2		
Relative Rate Coefficients			
$(3.22\pm0.49) \times 10^{-12}$	298±2	Nelson et al., 1990	RR (e)
$(3.64\pm0.11) \times 10^{-12}$	298±4	Picquet et al., 1998	RR (f)
$(2.79\pm0.28) \times 10^{-12}$	298±2	Oh and Andino, 2001	RR (e)
$(2.72\pm0.25) \times 10^{-12}$	298±2	Oh and Andino, 2001	RR (g)
$(3.39\pm0.24) \times 10^{-12}$	296±2	Sørensen et al. , 2002	RR (h,i)
$(3.36\pm0.35) \times 10^{-12}$	296±2	Sørensen et al., 2002	RR (h,j)
$(3.37\pm0.25) \times 10^{-12}$	295±2	Wu et al., , 2003	RR (k)

Comments

(a) Reaction of $H^{16}O$ radicals.

(b) Thermal decomposition of the $H^{16}OCH_2CH_2$ radical formed by H-atom abstraction from the -CH_3 group to regenerate $H^{16}O$ radicals occurs at temperatures >500 K, and hence the $H^{16}O$ rate coefficient data do not yield the rate coefficient k=(k_1+k_2+k_3) above ~500 K. Since thermal decomposition of the $H^{16}OCH_2CH_2$ radical does not lead to regeneration of the $H^{18}O$ radical, the $H^{18}O$ rate coefficient data yield the overall reaction rate coefficient, k=(k_1+k_2+k_3).

(c) Rate coefficients for reaction of the $H^{18}O$ radical. $H^{18}O$ radicals were generated from pulsed laser photolysis of $H_2{}^{18}O$, with $H^{18}O$ radicals being detected by LIF.

(d) HO radicals were generated by the thermal decomposition of *t*-butyl hydroperoxide in a shock tube, with detection by resonance absorption at 309 nm. The measured rate coefficient corresponds to (k_2+k_3) because of the rapid thermal decomposition of the CH_2CH_2OH radical formed in reaction channel (1) [this is the same radical as formed from the addition of HO radicals to ethene].

(e) HO radicals were generated by photolysis of CH_3ONO in air. The ethanol and cyclohexane (the reference organic) concentrations were measured by GC. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 6.97×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson, 2003).

(f) HO radicals were generated by the photolysis of H_2O_2 in air at 254 and 310 nm. The concentrations of ethanol and *n*-hexane (the reference compound) were measured by GC. The measured rate coefficient ratio, k(HO + ethanol)/k(HO + *n*-hexane), is placed on an absolute basis using a rate coefficient of k(HO + *n*-hexane) =5.20×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

(g) HO radicals were generated by photolysis of CH_3ONO in air. The ethanol and *p*-xylene (the reference organic) concentrations were measured by GC. The measured rate coefficient ratio of k(HO + ethanol)/k(HO + *p*-xylene) = 0.19±0.01 is placed on an absolute basis by use of a rate coefficient of k(HO + *p*-xylene) = 1.43×10^{-11} cm^3 molecule^{-1} s^{-1} (Calvert et al., 2002).

(h) HO radicals were generated by the photolysis of CH_3ONO in air at 1.0 bar (750 Torr). The concentrations of ethanol and acetylene or ethene (the reference compounds) were measured by in situ FTIR spectroscopy. The measured rate coefficient ratios of k(HO + ethanol)/k(HO + acetylene) = 4.35 ± 0.30 and k(HO + ethanol)/k(HO + ethene) = 0.39 ± 0.04 are placed on an absolute basis using rate coefficients of k(HO + acetylene) = 7.8×10^{-13} cm^3 molecule^{-1} s^{-1} at 750 Torr pressure of air or O_2 and 296 ± 2 K (Sørensen et al., 2003) and k(HO + ethene) = 8.61×10^{-12} cm^3 molecule^{-1} s^{-1} at 296 K and atmospheric pressure of air (Atkinson, 1997). No effect of the presence of NaCl or NH_4NO_3 aerosol was observed.

(i) Relative to acetylene.

(j) Relative to ethene.

(k) HO radicals were generated by the photolysis of H_2O_2 in 1 atmosphere of air at 254 nm. The concentrations of ethanol and propane (the reference compound) were measured by GC. The measured rate coefficient ratio, k(HO + ethanol)/k(HO + propane), is placed on an absolute basis using a rate coefficient of k(HO + propane) = 1.07×10^{-12} cm^3 molecule^{-1} s^{-1} at 295 K (Atkinson, 2003; IUPAC, current recommendation).

Preferred Values

k = 3.2×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 3.0×10^{-12} exp(20/T) cm^3 molecule^{-1} s^{-1} over the temperature range 210–300 K.
k_1/k= 0.05 at 298 K.
k_3/k = 0.05 at 298 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta (E/R) = \pm 150$ K.
$\Delta k_1/k = ^{+0.10}_{-0.05}$ at 298 K.
$\Delta k_3/k = ^{+0.10}_{-0.05}$ at 298 K.

Comments on Preferred Values

There is substantial scatter in the room temperature rate coefficients measured to date. The most definitive absolute rate studies are those of Wallington and Kurylo (1987), Hess and Tully (1988), Jiménez et al. (2003) and Dillon et al. (2005). The preferred rate coefficient is derived from fitting the $H^{18}O$ and (for temperatures <500 K) the $H^{16}O$ rate coefficients of Hess and Tully (1988) and the absolute rate constants determined by Wallington and Kurylo (1987), Jiménez et al. (2003) and Dillon et al. (2005) to the three parameter expression $k = CT^2 \exp(-D/T)$. This results in $k = 6.70\times10^{-18}\ T^2 \exp(511/T)$ cm^3

molecule^{-1} s^{-1} over the temperature range 216–599 K. The preferred Arrhenius expression, $k = A$ exp($-B/T$) is centered at 245 K and is derived from this three parameter expression with $A = Ce^2T^2$ and $B = D + 2T$. Note that the Arrhenius expression should not be used outside of the stated temperature range (210-300 K); rather the three-parameter expression k = 6.70 $\times 10^{-18}$ T^2 exp($511/T$) cm^3 molecule^{-1} s^{-1} should be employed. The rate coefficient calculated from the preferred Arrhenius expression at 255 K is 14% higher than the lowest temperature rate coefficient reported by Greenhill and O'Grady (1986). The preferred 298 K rate coefficient is in good agreement with the absolute and relative rate coefficients of Nelson et al. (1990), Picquet et al. (1998), Sørensen et al. (2002) and Wu et al. (2003), but is ∼15% higher than the relative rate data of Oh and Andino (2001). The rate coefficient measured by Bott and Cohen (1991) at 1204 K, and ascribed to (k_2+k_3), is consistent with the value of (k_1+k_2+k_3) calculated from the recommended three parameter expression and with the rate coefficient k_1 at 1204 K estimated using the procedure of Kwok and Atkinson (1987).

Meier et al. (1985) determined that at room temperature the reaction proceeds mainly (75±15%) via formation of the CH_3CHOH radical, consistent with the thermochemistry of the reaction steps. The kinetic data of Hess and Tully (1988) for the reactions of the $H^{16}O$ and $H^{18}O$ radicals with ethanol indicate that channel (1) accounts for ∼15% of the overall reaction at 600 K, in agreement with the calculated value of 17% from the estimation procedure of Kwok and Atkinson (1995). This agreement allows a rate coefficient ratio of k_1/k = 0.05 at 298 K to be estimated. Assuming that H-atom abstraction from the -OH group in ethanol [channel (3)] has a similar rate coefficient to the analogous channel for methanol (IUPAC, current evaluation) allows k_3/k = 0.05 at 298 K to be estimated. The resulting value of k_2/k = 0.90 at 298 K is just consistent with the product data of Meier et al. (1985).

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II.A2.27

$HO + CH_3CH_2CH_2OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.33\pm0.54) \times 10^{-12}$	296±2	Overend and Paraskevopoulos, 1978	FP-RA
$(5.34 \pm 0.39) \times 10^{-12}$	296	Wallington and Kurylo, 1987	FP-RF
$(5.64\pm0.48) \times 10^{-12}$	298±2	Nelson et al., 1990	PR-RA
$4.68 \times 10^{-12} \exp[(68\pm41)/T]$	263–372	Yujing and Mellouki, 2001	PLP-LIF
$(5.83\pm0.18) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(3.7\pm0.6) \times 10^{-12}$	292	Campbell et al., 1976	RR (a)
$(5.12\pm0.41) \times 10^{-12}$	298±2	Nelson et al., 1990	RR (b)
$(4.42\pm0.26) \times 10^{-12}$	298±2	Oh and Andino, 2000	RR (c,d)
$(6.44\pm0.43) \times 10^{-12}$	298±2	Oh and Andino, 2000	RR (c,e)
$(5.11\pm0.19) \times 10^{-12}$	273	Cheema et al., 2002	RR (f)
$(5.50\pm0.17) \times 10^{-12}$	298		
$(5.74\pm0.33) \times 10^{-12}$	313		
$(6.20\pm0.17) \times 10^{-12}$	343		

Comments

(a) HO radicals were generated by the dark reaction of H_2O_2-NO_2 mixtures in the presence of CO and an organic compound. From sequential experiments using n-butane and 1-propanol, a rate coefficient ratio of k(HO + 1-propanol)/k(HO + n-butane) = 1.67±0.27 (two standard deviations) was derived. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of k(HO + n-butane) = 2.22×10^{-12} cm^3 molecule^{-1} s^{-1} at 292 K (IUPAC, current recommendation).

(b) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 1-propanol and cyclohexane (the reference compound) were measured by GC The measured rate coefficient ratio k(HO + 1-propanol)/k(HO + cyclohexane) is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 6.97×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

(c) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 1-propanol and n-hexane and p-xylene (the reference compounds) were measured by GC. The measured rate coefficient ratios of k(HO + 1-propanol)/k(HO + n-hexane) = 0.85±0.05 and k(HO + 1-propanol)/k(HO + p-xylene) = 0.45±0.03 are placed on an absolute basis by use of rate coefficients at 298 K of k(HO + n-hexane) = 5.20×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson, 2003) and k(HO + p-xylene) = 1.43×10^{-11} cm^3 molecule^{-1} s^{-1} (Calvert et al., 2002).

(d) Relative to HO + n-hexane.

(e) Relative to HO + p-xylene.

(f) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 1-propanol and 2,3-dimethylbutane (the reference compound) were measured by GC. The measured rate coefficient ratios of k(HO + 1-propanol)/k(HO + 2,3-dimethylbutane) are placed on an absolute basis by use of a rate coefficient of k(HO + 2,3-dimethylbutane) = $1.66\times10^{-17}\ T^2 \exp(407/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 2003).

Preferred Values

$k = 5.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.6 \times 10^{-12} \exp(70/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–380 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred values are based on the temperature-dependent absolute rate study of Yujing and Mellouki (2001). At room temperature, the rate coefficients measured by Yujing and Mellouki (2001) are in good agreement with the absolute rate coefficients of Overend and Paraskevopoulos (1976), Wallington and Kurylo (1987) and Nelson et al. (1990), and with the relative rate constant of Nelson et al. (1990). The experimental technique of Campbell et al. (1976) was possibly prone to unrecognized problems, and the relative rate constants of Oh and Andino (2000) measured relative to n-hexane and p-xylene are respectively 25% higher and 11% lower than the preferred value. The rate coefficients determined by Cheema et al. (2002) relative to that for 2,3-dimethylbutane are in good agreement with the preferred values (to within 15%), although the Cheema et al. (2002) data indicate a positive temperature dependence in contrast to that observed by Yujing and Mellouki (2001) and used as the basis for the preferred values.

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$$
\begin{array}{lll}
\mathbf{HO + CH_3CH(OH)CH_3} & \mathbf{\rightarrow H_2O + (CH_3)_2CHO} & \mathbf{(1)} \\
 & \mathbf{\rightarrow H_2O + CH_3C(OH)CH_3} & \mathbf{(2)} \\
 & \mathbf{\rightarrow H_2O + CH_3CH(OH)CH_2} & \mathbf{(3)}
\end{array}
$$

$\Delta H^\circ(1) = -58.8 \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data (k=k_1+k_2+k_3)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.48\pm0.55) \times 10^{-12}$	296±2	Overend and Paraskevopoulos, 1978	FP-RA
5.8×10^{-12} exp[-(30±90)/T]	240–440	Wallington and Kurylo, 1987	FP-RF
$(5.81\pm0.34) \times 10^{-12}$	296		
$(5.69\pm1.09) \times 10^{-12}$	298±2	Nelson et al., 1990	PR-RA
1.044×10^{-17} $T^{1.86}$ exp(736/T)	293–587	Dunlop and Tully, 1993	PLP-LIF (a)
$(5.10\pm0.21) \times 10^{-12}$	293		
2.80×10^{-12} exp[(184±40)/T]	253–372	Yujing and Mellouki, 2001	PLP-LIF
$(5.17\pm0.23) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(5.38\pm0.70) \times 10^{-12}$	298±2	Nelson et al., 1990	RR (b)

Comments

(a) The reactions of $H^{16}O$ radicals were studied over the temperature range 293 K to 745 K and the reactions of $H^{18}O$ radicals were studied at 548 K and 587 K. Non-exponential decays of $H^{16}O$ radicals were observed over the temperature range 504 K to 600 K and, while exponential $H^{16}O$ radical decays were observed above 600 K, the rate coefficients were significantly lower than expected from extrapolation of the lower temperature data. These observations are consistent with thermal decomposition of the $CH_3CH(OH)CH_2$ radical formed in reaction channel (3) [the same radical as formed from HO radical addition to propene] at temperatures $>$500 K. Hence using $H^{16}O$ radicals, values of (k_1+k_2+k_3) were measured at temperatures $\leq$500 K and (k_1+k_2) at temperatures $>$600 K. No regeneration of $H^{18}O$ radicals from thermal decomposition of the $CH_3CH(^{16}OH)CH_2$ radical can occur, and hence the measured $H^{18}O$ rate coefficients are those for (k_1+k_2+k_3).

(b) HO radicals were generated by the photolysis of CH_3ONO in air. The concentrations of 2-propanol and cyclohexane (the reference organic) were measured by GC. The measured rate coefficient ratio k(HO + 2-propanol)/k(HO + cyclohexane) is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 6.97×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

Preferred Values

$k = 5.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.6 \times 10^{-12}$ exp(200/T) cm^3 molecule^{-1} s^{-1} over the temperature range 250–360 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The absolute rate coefficients measured by Dunlop and Tully (1993) and Yujing and Mellouki (2001) are in excellent agreement over the temperature range common to both studies (293–378 K), and the preferred rate coefficients are derived from these two studies (Dunlop and Tully, 1993; Yujing and Melloui, 2001). The $H^{18}O$ rate coefficients at 548 K and 587 K and the $H^{16}O$ rate coefficients at $\leq$502 K obtained by Dunlop and Tully (1993) and the rate coefficients of Yujing and Mellouki (2001) (253–372 K) were fitted to the three parameter expression k=CT^2 exp(-D/T), resulting in k=4.03×10^{-18} T^2 exp(792/T) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 253–587 K. The preferred Arrhenius expression, k=A exp(-B/T), is centered at 295 K and is derived from the three parameter expression with A=Ce^2T^2 and B=$D + 2T$. The preferred rate coefficients are within 15% of those measured by Wallington and Kurylo (1987) over the temperature range 250 K to 360 K and are in agreement within the cited error limits with the room temperature absolute and relative rate coefficients of Overend and Paraskevopoulos (1978) and Nelson et al. (1990).

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II.A2.29

$HO + CH_3CH_2CH_2CH_2OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.31\pm0.63) \times 10^{-12}$	296	Wallington and Kurylo, 1987	FP-RA
$(7.80\pm0.20) \times 10^{-12}$	298±2	Nelson et al., 1990	PR-RA
$5.30 \times 10^{-12} \exp[(146 \pm 92)/T]$	263–372	Yujing and Mellouki, 2001	PLP-LIF
$(8.47 \pm 0.34) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(6.7\pm1.3) \times 10^{-12}$	292	Campbell et al., 1976	RR (a)
$(7.97\pm0.66) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	RR (b)
$(1.03\pm0.05) \times 10^{-11}$	298 ± 2	Oh and Andino, 2001	RR (c)

Comments

(a) HO radicals were generated by the dark reaction of H_2O_2-NO_2 mixtures in the presence of CO and an organic compound. From sequential experiments using *n*-butane and 1-butanol, a rate coefficient ratio of k(HO + 1-butanol)/k(HO + *n*-butane) = 3.00±0.56 (two standard deviations) was derived. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of k(HO + *n*-butane) = 2.22×10^{-12} cm^3 molecule^{-1} s^{-1} at 292 K (IUPAC, current recommendation).

(b) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 1-butanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio k(HO + 1-butanol)/k(HO + cyclohexane) is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 6.97×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

(c) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 1-butanol and *p*-xylene (the reference compound) were measured by GC. The measured rate coefficient ratio k(HO + 1-butanol)/k(HO + *p*-xylene) = 0.72±0.03 is placed on an absolute basis by use of a rate coefficient of k(HO + *p*-xylene) = 1.43×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K (Calvert et al., 2002).

Preferred Values

$k = 8.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.3 \times 10^{-12} \exp(140/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–380 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute rate study of Yujing and Mellouki (2001), the sole temperature-dependence study, is used to derive the preferred values. The 298 K coefficient from the study of Yujing and Mellouki (2001) is in good agreement with the room temperature absolute and relative rate coefficients of Wallington and Kurylo (1987) and Nelson et al. (1990), but is 18% lower than the relative rate coefficient of Oh and Andino (2001). The experimental technique of Campbell et al. (1976) was possibly prone to unrecognized problems.

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II.A2.30

HO + $CH_3CH(OH)CH_2CH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(8.58 \pm 0.49) \times 10^{-12}$	296 ±2	Chew and Atkinson, 1996	RR (a)
$(8.80 \pm 0.14) \times 10^{-12}$	297±3	Baxley and Wells, 1998	RR (b,c)
$(7.57 \pm 0.44) \times 10^{-12}$	297±3	Baxley and Wells, 1998	RR (b,d)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 2-butanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + 2-butanol)/k(HO + cyclohexane) = 1.24±0.07 is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 6.92×10^{-12} cm^3 molecule^{-1} s^{-1} at 296 K (Atkinson, 2003).

(b) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 2-butanol and n-nonane and dodecane (the reference compounds) were measured by GC. The measured rate coefficient ratios of k(HO + 2-butanol)/k(HO + n-nonane) and k(HO + 2-butanol)/k(HO + dodecane) are placed on an absolute basis by use of rate coefficients at 297 K of k(HO + n-nonane) = 9.69×10^{-12} cm^3 molecule^{-1} s^{-1} and k(HO + dodecane) = 1.32×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson, 2003).

(c) Relative to HO + n-nonane.

(d) Relative to HO + dodecane.

Preferred Values

$k = 8.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

Comments on Preferred Values

The preferred value is based on the relative rate coefficient of Chew and Atkinson (1996) and that of Baxley and Wells (1998) relative to HO + n-nonane, which are in excellent agreement. The rate coefficient of Baxley and Wells (1998) measured relative to that for HO + dodecane, while in agreement with the other two rate coefficients (Chew and Atkinson, 1996; Baxley and Wells, 1998), is more uncertain because of the small data-base for HO + dodecane, and hence this rate coefficient is not used in the evaluation.

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II.A2.31

$OH + (CH_3)_2C(OH)CH{=}CH_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$8.2 \times 10^{-12}\exp[(610 \pm 50)/T]$	231–300	Rudich et al., 1995	PLP-LIF (a)
$(6.4 \pm 0.6) \times 10^{-11}$	298		
Relatve Rate Coefficients			
$(3.81 \pm 0.80)\times 10^{-11}$	298 ± 2	Fantechi et al., 1998a	RR (b,c)
$(4.27 \pm 1.80)\times 10^{-11}$	298 ± 2	Fantechi et al., 1998a	RR (b,d)
$(6.43 \pm 0.54)\times 10^{-11}$	295 ± 1	Ferronato et al., 1998	RR (e,f)
$(7.35 \pm 0.78)\times 10^{-11}$	295 ± 1	Ferronato et al., 1998	RR (e,g)
$(5.64 \pm 0.13)\times 10^{-11}$	296 ± 2	Papagni et al., 2001	RR (h)

Comments

(a) Rate coefficients for the reactions of HO, $H^{18}O$ and DO radicals with 2-methyl-3-buten-2-ol were measured, in the presence and absence of O_2 (up to 13.5 Torr (18 mbar) O_2 in the case of the HO radical reaction), over the temperature range 231–410 K. Above ∼350 K the rate coefficients decreased with increasing temperature faster than predicted based on extrapolation of the lower temperature data. For the HO radical reaction, the rate coefficients in the presence of 2–13.5 Torr of O_2 were up to 15–20% higher than in the absence of O_2, while the measured rate coefficients for the DO radical reaction were invariant to the presence or absence of O_2. HO radicals were observed to be formed in the DO radical reaction, and the rate coefficients of the DO radical and $H^{18}O$ radical reactions were essentially identical to those for the HO radical reactions in the presence of O_2. These data indicated that the measured rate coefficients from the HO radical reaction in the absence of O_2 are low because of HO radical regeneration, whereas $H^{18}O$ and DO radical regeneration does not occur from reactions of $H^{18}O$ and DO radicals with 2-methyl-3-buten-2-ol (HO radicals being formed by elimination of the -OH group in the 2-methyl-3-buten-2-ol in the absence of O_2). The rate coefficient cited is derived (Rudich et al., 1995) from the rate coefficients measured for the HO and DO radical reactions in the presence of O_2 over the temperature range 230–300 K, and is expected to be applicable to atmospheric conditions.

(b) HO radicals were generated by the photolysis of H_2O_2 at 253.7 nm in air at 987±7 mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and isoprene (or propene) [the reference compounds] were measured during the experiments by FTIR spectroscopy. The measured rate coefficient ratios k(HO + 2-methyl-3-buten-2-ol)/k(HO + isoprene) and k(HO + 2-methyl-3-buten-2-ol)/k(HO + propene) are placed on an absolute basis by use of rate coefficients at 298 K and atmospheric pressure of k(HO + isoprene) = 1.00×10^{-10} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003; IUPAC, current recommendation) and k(HO + propene) = 2.63×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(c) Relative to k(HO + isoprene).

(d) Relative to k(HO + propene).

(e) HO radicals were generated by the photolysis of $^{13}CH_3ONO$-NO- $(CH_3)_2C(OH)CH{=}CH_2$-propene (or ethene) [the reference compounds]-air mixtures at 933 mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and propene (or ethene) were measured by FTIR spectroscopy. The measured rate coefficient ratios of k(HO + 2-methyl-3-buten-2-ol)/k(HO + propene) = 2.4±0.2 and k(HO + 2-methyl-3-buten-2-ol)/k(HO + ethene) = 8.5±0.9 are placed on an absolute basis by use of rate coefficients at 295 K and atmospheric pressure of air of k(HO + propene) = 2.68×10^{-11} cm^3 molecule^{-1} s^{-1} and k(HO + ethene) = 8.65×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(f) Relative to k(HO + propene).

(g) Relative to k(HO + ethene).

(h) HO radicals were generated by the photolysis of CH_3ONO-NO- $(CH_3)_2C(OH)CH{=}CH_2$-1,3,5-trimethylbenzene (the reference compound)-air mixtures at 987 mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and 1,3,5-trimethylbenzene were measured by GC. The measured rate coefficient ratio of k(HO + 2-methyl-3-buten-2-ol)/k(HO + 1,3,5-trimethylbenzene) = 0.995±0.022 is placed on an absolute basis by use of a rate coefficient at 296 K of k(HO + 1,3,5-trimethylbenzene) = 5.67×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003).

Preferred Values

$k = 8.2 \times 10^{-12} \exp(610/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 230–300 K.
$k = 6.4 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The room temperature rate coefficients of Rudich et al. (1995), Ferronato et al. (1998) and Papagni et al. (2001) are in reasonable agreement, although the rate coefficient of Ferronato et al. (1998) relative to ethene is somewhat higher than those of Rudich et al. (1995) and Papagni et al. (2001) and that of Ferronato et al. (1998) relative to propene. The two relative rate coefficients of Fantechi et al. (1998a) are significantly lower than the values measured by Rudich et al. (1995), Ferronato et al. (1998) and Papagni et al. (2001). The preferred 298 K rate coefficient is the average of the absolute and relative rate coefficients of Rudich et al. (1995), Ferronato et al. (1998) and Papagni et al. (2001), and is identical to the 298 K absolute rate coefficient cited by Rudich et al. (1995). The preferred temperature dependence is that reported by Rudich et al. (1995).

The reaction proceeds almost totally by initial addition of HO to the C=C bond (Fantechi et al., 1998b; Ferronato et al., 1998; Alvarado et al., 1999; Spaulding et al., 2002; Reisen et al., 2003). In the presence of NO at atmospheric pressure of air the observed products are formaldehyde, acetone, glycolaldehyde, 2-hydroxy-2-methylpropanal [$(CH_3)_2C(OH)CHO$], and dihydroxynitrates [presumed to be $(CH_3)_2C(OH)CH(OH)CH_2ONO_2$ and $(CH_3)_2C(OH)CH(ONO_2)CH_2OH$] (Fantechi et al., 1998b; Ferronato et al., 1998; Alvarado et al., 1999; Spaulding et al., 2002; Reisen et al., 2003). Based on the product studies of Ferronato et al. (1998), Alvarado et al. (1999) and Reisen et al. (2003) carried out in the presence of NO, the product yields are: formaldehyde, 35±4% (Ferronato et al., 1998) and 29±3% (Alvarado et al., 1999); acetone, 52±5% (Ferronato et al., 1998) and 58±4% (Alvarado et al., 1999); glycolaldehyde, 50±5% (Ferronato et al., 1998) and 61±9% (Alvarado et al., 1999); 2-hydroxy-2-methylpropanal, 31±4% (Reisen et al., 2003); and dihydroxynitrates, 5±2% (Alvarado et al., 1999). The reaction mechanism is discussed in detail in Alvarado et al. (1999). Reactions of the $(CH_3)_2C(OH)CH(OH)CH_2OO$ and $(CH_3)_2C(OH)CH(OO)CH_2OH$ peroxy radicals (formed after addition of O_2 to the initially formed $(CH_3)_2C(OH)CH(OH)CH_2$ and $(CH_3)_2C(OH)CHCH_2OH$ radicals) with NO lead to the formation predominantly of the dinitrates $(CH_3)_2C(OH)CH(OH)CH_2ONO_2$ and $(CH_3)_2C(OH)CH(ONO_2)CH_2OH$ or NO_2 plus the dihydroxyalkoxy radicals $(CH_3)_2C(OH)CH(OH)CH_2O$ and $(CH_3)_2C(OH)CH(O)CH_2OH$. These dihydroxyalkoxy radicals appear to dominantly decompose at room temperature and atmospheric pressure:

$$\begin{array}{lll} \mathrm{(CH_3)_2C(OH)CH(OH)CH_2O} & \rightarrow & \mathrm{HCHO + (CH_3)_2C(OH)CHOH} \\ & & \qquad\qquad\quad \downarrow \mathrm{O_2} \\ & & \mathrm{(CH_3)_2C(OH)CHO + HO_2} \end{array}$$

$$\begin{array}{lll} \mathrm{(CH_3)_2C(OH)CH(O)CH_2OH} & \rightarrow & \mathrm{(CH_3)_2C(OH)CHO + CH_2OH} \\ & & \qquad\qquad\quad \downarrow \mathrm{O_2} \\ & & \qquad\quad \mathrm{HCHO + HO_2} \end{array}$$

and/or

$$\begin{array}{lll} \mathrm{(CH_3)_2C(OH)CH(O)CH_2OH} & \rightarrow & \mathrm{(CH_3)_2COH + HOCH_2CHO} \\ & & \qquad\qquad \downarrow \mathrm{O_2} \\ & & \quad \mathrm{CH_3C(O)CH_3 + HO_2} \end{array}$$

Hence, as observed, the yield of HCHO equals that of $(CH_3)_2C(OH)CHO$, and the yield of $HOCH_2CHO$ equals that of $CH_3C(O)CH_3$ (Ferronato et al., 1998; Alvarado et al., 1999; Reisen et al., 2003).

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II.A2.32

$HO + CH_3OCH_3 \rightarrow H_2O + CH_3OCH_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.29 \times 10^{-11} \exp[-(388 \pm 151)/T]$	299–424	Perry et al., 1977	FP-RF
$(3.50 \pm 0.35) \times 10^{-12}$	299		
$1.04 \times 10^{-11} \exp[-(372 \pm 34)/T]$	295–442	Tully and Droege, 1987	PLP-LIF
$(2.95 \pm 0.12) \times 10^{-12}$	295		
$6.7 \times 10^{-12} \exp[-(300 \pm 70)/T]$	240–440	Wallington et al., 1988	FP-RF
$(2.49 \pm 0.22) \times 10^{-12}$	296		
$(2.35 \pm 0.24) \times 10^{-12}$	298±2	Nelson et al., 1990	PR-RA
$6.38 \times 10^{-12} \exp[-(234 \pm 34)/T]$	230–372	Mellouki et al., 1995	PLP-LIF
$(2.82 \pm 0.21) \times 10^{-12}$	295		
$3.39 \times 10^{-24} T^{4.11} \exp[(1221 \pm 252)/T]$	295–650	Arif et al., 1997	PLP-LIF
$(2.95 \pm 0.21) \times 10^{-12}$	295		
$3.02 \times 10^{-20}\, T^{2.85} \exp[(618 \pm 13)/T]$	295–618	Bonard et al., 2002	PLP-LIF
$(2.67 \pm 0.07) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(2.11 \pm 0.21) \times 10^{-12}$	295±3	Wallington et al., 1989	RR (a)
$(2.97 \pm 0.66) \times 10^{-12}$	298±2	Nelson et al., 1990	RR (b)
2.41×10^{-12}	263	DeMore and Bayes, 1999	RR (c,d)
2.47×10^{-12}	273		
2.70×10^{-12}	293		
2.72×10^{-12}	298		
3.03×10^{-12}	313		
3.23×10^{-12}	333		
3.39×10^{-12}	351		
3.04×10^{-12}	295	DeMore and Bayes, 1999	RR (c,e)
3.25×10^{-12}	305		
3.16×10^{-12}	318		
3.42×10^{-12}	328		
3.81×10^{-12}	336		
3.62×10^{-12}	345		
3.86×10^{-12}	364		
3.18×10^{-12}	306	DeMore and Bayes, 1999	RR (c,f)
3.33×10^{-12}	324		
3.62×10^{-12}	351		
3.82×10^{-12}	361		

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures at atmospheric pressure. The concentrations of dimethyl ether and n-butane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(CH_3OCH_3)/k(n\text{-butane}) = 0.918 \pm 0.090$ is placed on an absolute basis by using a rate coefficient of $k(n\text{-butane}) = 2.30 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures at atmospheric pressure. The concentrations of dimethyl ether and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio $k(CH_3OCH_3)/k$(cyclohexane) is placed on an absolute basis by use of a rate coefficient of k(cyclohexane) = 6.97×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K (Atkinson, 2003).

(c) HO radicals were generated by the photolysis of O_3 at 254 nm in the presence of water vapor. The concentrations of dimethyl ether and the reference compound were measured by GC.

(d) Relative to k(HO + n-butane). The measured rate coefficient ratios k(HO + dimethyl ether)/k(HO + n-butane) are placed on an absolute basis by use of a rate coefficient of k(HO + n-butane) = $1.81\times10^{-17}T^2$ exp(114/T) cm^3 $molecule^{-1}$ s^{-1} (IUPAC, current recommendation).

(e) Relative to k(HO + n-pentane). The measured rate coefficient ratios k(HO + dimethyl ether)/k(HO + n-pentane) are placed on an absolute basis by use of a rate coefficient of k(HO + n-pentane) = $2.52\times10^{-17}T^2$ exp(158/T) cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 2003).

(f) Relative to k(HO + cyclohexane). The measured rate coefficient ratios k(HO + dimethyl ether)/k(HO + cyclohexane) are placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = $3.26\times10^{-17}T^2$ exp(262/T) cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 2003).

Preferred Values

$k = 2.8 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k = 5.7 \times 10^{-12}$ exp(-215/T) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 230–300 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The reported room temperature absolute (Perry et al., 1977; Tully and Droege, 1987; Wallington et al., 1988; Nelson et al., 1990; Mellouki et al., 1995; Arif et al., 1997; Bonard et al., 2002) and relative (Nelson et al., 1990; Wallington et al., 1989; DeMore and Bayes, 1999) rate coefficients exhibit appreciable scatter, covering a range of a factor of 1.6. The measured temperature dependencies (Perry et al., 1977; Tully and Droege, 1987; Wallington et al., 1988; Mellouki et al., 1995; Arif et al., 1997; Bonard et al., 2002; DeMore and Bayes, 1999) are in reasonable agreement. The preferred values are based on the absolute rate coefficient studies of Tully and Droege (1987), Mellouki et al. (1995), Arif et al. (1997) and Bonard et al. (2002), the rate coefficients of which are in good agreement and which are between those of the other two absolute temperature-dependent studies of Perry et al. (1977) and Wallington et al. (1988).

Because Arrhenius plots of the data of Mellouki et al. (1995), Arif et al. (1997) and Bonard et al. (2002) show curvature, the rate coefficients of Tully and Droege (1987), Mellouki et al. (1995), Arif et al. (1997) and Bonard et al. (2002) have been fitted to the expression k=CT^2 exp(-D/T), resulting in k=1.14×10^{-17} T^2 exp(303/T) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 230–650 K. The preferred Arrhenius expression k=A exp(-B/T) is centered at 260 K and is derived from the three-parameter expression with $A=C\ e^2T^2$ and $B=D+2T$. The rate coefficients determined by DeMore and Bayes (1999) relative to that for the reaction of HO radicals with n-butane are in excellent agreement with the recommendation; however the rate coefficients determined by DeMore and Bayes (1999) relative to those for the reactions of HO radicals with n-pentane and cyclohexane are uniformly ∼10% higher than the preferred values.

The significant deuterium isotope effect observed by Tully and Droege (1987) indicates that reaction proceeds by initial H-atom abstraction.

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II.A2.33

HO + 3-Methylfuran → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
(9.26±0.24) × 10^{-11}	296±2	Atkinson et al., 1989	RR (a)

Comments

(a) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by the photolysis of methyl nitrite-NO-air mixtures, and the concentrations of 3-methylfuran and 2,3-dimethyl-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + 3-methylfuran)/k(HO + 2,3-dimethyl-2-butene) = 0.842±0.021 is placed on an absolute basis by use of a rate coefficient of k(HO + 2,3-dimethyl-2-butene) = 1.10×10^{-10} cm^3 molecule^{-1} s^{-1} at 296 K (Atkinson, 1997).

Preferred Values

$k = 9.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the sole study of this reaction by Atkinson et al. (1989). The reaction of HO radicals with 3-methylfuran is expected to proceed almost exclusively by initial HO radical addition to the C=C bonds (Atkinson et al., 1989).

References

Atkinson, R., Aschmann, S. M., Tuazon, E. C., Arey, J., and Zielinska, B.: Int. J. Chem. Kinet., 21, 593, 1989.
Atkinson, R.: J. Phys. Chem. Ref. Data, 26, 215, 1997.

II.A2.34

$HO + CH_3C(O)CH_2OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.0\pm0.3) \times 10^{-12}$	298	Dagaut et al., 1989	FP-RF
$(2.8\pm0.2) \times 10^{-12}$	~298	Chowhury et al., 2001	PLP-LIF (a)
Relative Rate Coefficients			
$(2.52\pm0.27) \times 10^{-12}$	298	Orlando et al., 1999	RR (b,c)
$(3.52\pm0.32) \times 10^{-12}$	298	Orlando et al., 1999	RR (b,d)

Comments

(a) HO radicals generated by the 193 nm photolysis of $CH_3C(O)CH_2OH$.

(b) HO radicals were generated by the photolysis of methyl nitrite in synthetic air at 1 bar total pressure. Hydroxyacetone and methanol and ethanol (the reference compounds) were monitored by FTIR spectroscopy. The measured rate coefficient ratios k(HO + hydroxyacetone)/k(HO + methanol) = 2.8±0.3 and k(HO + hydroxyacetone)/k(HO + ethanol) = 1.1±0.1 are placed on an absolute basis using rate coefficients of k(HO + methanol) = 9.0×10^{-13} cm^3 molecule^{-1} s^{-1}and k(HO + ethanol) = 3.2×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K, respectively (IUPAC, current recommendation).

(b) Relative to OH + methanol.

(c) Relative to OH + ethanol.

Preferred Values

$k = 3.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

Comments on Preferred Values

The preferred value is an average of the absolute and relative rate coefficients of Dagaut et al. (1989), Orlando et al. (1999) and Chowdhury et al. (2001) which are in reasonable agreement.

References

Chowdhury, P. K., Upadhyaya, H. P., Naik, P. D. and Mittal, J. P.: Chem. Phys. Lett. 351, 201, 2001.
Dagaut, P., Liu, R., Wallington, T. J., and Kurylo, M. J.: J. Phys. Chem., 93, 7838, 1989.
Orlando, J. J., Tyndall, G. S., Fracheboud, J.-M., Estupiñan, E. G., Haberkorn, S., and Zimmer, A.: Atmos. Environ., 33, 1621, 1999.

II.A2.35

OH + $(CH_3)_2C(OH)CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.51 \pm 0.22) \times 10^{-11}$	296 ± 2	Baker et al., 2004	RR(a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures at wavelengths >300 nm. $(CH_3)_2C(OH)CHO$ was generated in situ from the reaction of HO radicals with $(CH_3)_2C(OH)CH{=}CH_2$ and its concentration was measured during the reactions using solid phase microextraction fibers pre-coated with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine for on-fiber derivatization of carbonyl compounds, with subsequent GC analyses. From the time-concentration behavior of $(CH_3)_2C(OH)CHO$ during the reactions, the rate coefficient ratio $k(HO+(CH_3)_2C(OH)CHO)/kHO+(CH_3)_2C(OH)CH{=}CH_2)=0.234\pm0.033$ was derived. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient at 296 K of $k(HO+(CH_3)_2C(OH)CH{=}CH_2)=6.44\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the sole study of this reaction. The reaction is expected to proceed mainly by H-atom abstraction from the -CHO group (Baker et al., 2004).

References

Baker, J., Arey, J., and Atkinson, R.: J. Phys. Chem. A, 108, 7032, 2004.
IUPAC, http://www.iupac-kinetic.ch.cam.ac.uk/.

II.A2.36

$$\begin{aligned} \mathbf{HO + CH_3OOH} \quad &\rightarrow \mathbf{H_2O + CH_2OOH} \quad \mathbf{(1)} \\ &\rightarrow \mathbf{H_2O + CH_3OO} \quad \mathbf{(2)} \end{aligned}$$

$\Delta H^\circ(2) = -139\mathrm{kJ} \cdot \mathrm{mol}^{-1}$

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.93 \times 10^{-12} \exp[(190\pm14)/T]$	223–423	Vaghjiani and Ravishankara, 1989	(a)
5.54×10^{-12}	298		
$k_2 = 1.78 \times 10^{-12} \exp[(220\pm21)/T]$	203–348	Vaghjiani and Ravishankara, 1989	(a)
$k_2 = (3.85\pm0.23) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(1.02\pm0.08) \times 10^{-11}$	∼ 298	Niki et al., 1983	RR (b)
$(1.02\pm0.11) \times 10^{-11}$	∼ 298	Niki et al., 1983	RR (c)

Comments

(a) $H^{16}O$, $H^{18}O$ and DO radicals were generated by flash photolysis or pulsed laser photolysis of the following precursors: for $H^{16}O$, CH_3OOH, $H_2{}^{16}O$ and O_3-$H_2^{16}O$; for $H^{18}O$, $H_2{}^{18}O$ and O_3-$H_2^{18}O$; and for DO, D_2O, O_3-D_2O and O_3-D_2, and $H^{16}O$, $H^{18}O$ and DO radicals were monitored by LIF. Rate coefficients (k_1 + k_2) were obtained from measurements of the decay rates of $H^{18}O$ and DO radicals in the presence of excess CH_3OOH. Rate coefficients k_2 were obtained from the decay rates of $H^{16}O$ radicals in the presence of CH_3OOH. The CH_2OOH radical formed in reaction channel (1) rapidly decomposes to HO + HCHO, and hence the use of $H^{16}O$ allowed only the rate coefficient k_2 to be measured.

(b) HO radicals were generated by the photolysis of CH_3ONO or C_2H_5ONO in air. The concentrations of CH_3OOH and ethene (the reference compound) were measured by FTIR absorption spectroscopy. The measured rate coefficientratio of k(HO + CH_3OOH)/k(HO + ethene) = 1.20±0.09 is placed on an absolute basis by use of a rate coefficient of k(HO + ethene) = 8.52×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure of air (Atkinson, 1997).

(c) HO radicals were generated by the photolysis of CH_3ONO in air and the concentrations of CH_3OOH and CH_3CHO (the reference compound) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of k(HO + CH_3OOH)/k(HO + CH_3CHO) = 0.68±0.07 is placed on an absolute basis by use of a rate coefficient of k(HO + CH_3CHO) = 1.5×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

Preferred Values

$k = 5.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.9 \times 10^{-12} \exp(190/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–430 K.
$k_1/k = 0.35$ over the temperature range 220–430 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 150$ K.
$\Delta (k_1/k) = \pm 0.15$ at 298 K.

Comments on Preferred Values

The preferred values are those of Vaghjiani and Ravishankara (1989). The reasons for the factor of ∼2 discrepancy with the relative rate data of Niki et al. (1983) are not known (Vaghjiani and Ravishankara, 1989). The preferred branching ratio, also taken from the absolute rate coefficient study of Vaghjiani and Ravishankara (1989), is in reasonable agreement with the earlier measurement of Niki et al. (1983).

References

Atkinson, R.: J. Phys. Chem. Ref. Data, 26, 215, 1997.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/.
Niki, H., Maker, P. D., Savage, C. M., and Breitenbach, L. P.: J. Phys. Chem., 87, 2190, 1983.
Vaghjiani, G. L. and Ravishankara, A. R.: J. Phys. Chem., 93, 1948, 1989.

II.A2.37

HO + HC(O)OH → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.62\pm0.78) \times 10^{-13}$	298–430	Wine et al., 1985	FP/PLP-RF (a)
$(4.90\pm0.12) \times 10^{-13}$	296	Jolly et al., 1986	PLP-RA (b)
$2.91 \times 10^{-13} \exp[(102 \pm 194)/T]$	297–445	Singleton et al., 1988	PLP-RA
$(4.47\pm0.28) \times 10^{-13}$	297		
$(3.7\pm0.4) \times 10^{-13}$	298	Dagaut et al., 1988	FP-RF

Comments

(a) H atom formation was also measured by resonance fluorescence, and an H-atom formation yield of 0.75±0.25 measured. At 298 K, the measured rate coefficient for the reaction of the HO radical with DC(O)OH was identical to that for HO radical reaction with HC(O)OH.

(b) Experiments with added O_2 led to non-exponential and slower HO radical decays, indicating the formation of H atoms from the HO radical reaction with HC(O)OH.

Preferred Values

$k = 4.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290–450 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 250$ K.

Comments on Preferred Values

A major problem with the determination of the rate coefficient for this reaction concerns the ready dimerization of HC(O)OH. The studies of Wine et al. (1985), Jolly et al. (1986) and Singleton et al. (1988) monitored formic acid in the experimental systems used by UV absorption spectroscopy. The data from these studies (Wine et al., 1985; Jolly et al., 1986; Singleton et al., 1988) agree well, and are in reasonable agreement with the room temperature rate coefficient of Dagaut et al. (1988). The data of Wine et al. (1985) and Singleton et al. (1988) show that the temperature dependence of the rate coefficient is zero within the experimental uncertainties. The average of the rate coefficients of Wine et al. (1985), Jolly et al. (1986) and Singleton et al. (1988) has been used to derive the preferred rate coefficient.

The studies of Wine et al. (1985) and Jolly et al. (1986) showed that H atoms are produced in this reaction, with a yield of 0.75±0.25 (Wine et al., 1985). Furthermore, Wine et al. (1985) and Singleton et al. (1988) showed that within the experimental uncertainties the rate coefficient for the reaction of the HO radical with DC(O)OH is identical to that for HC(O)OH at 298 K. Also, the room temperature rate coefficients for the reactions of the DO radical with HC(O)OD and DC(O)OD are significantly lower than those for the reactions of the HO radical with HC(O)OH and DC(O)OH (Singleton et al., 1988). The reaction then appears to proceed by,

$$\begin{array}{lll} \mathrm{OH + HC(O)OH} & \rightarrow \mathrm{H_2O} + & \mathrm{HC(O)O} \\ & & \downarrow \\ & & \mathrm{H + CO_2} \end{array}$$

with overall abstraction of the H (or D) atom from the -OH (or -OD) group being the major pathway at room temperature.

References

Dagaut, P., Wallington, T. J., Liu, R., and Kurylo, M. J.: Int. J. Chem. Kinet., 20, 331, 1988.
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II.A2.38

HO + $CH_3C(O)OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.3 \times 10^{-12} \exp[-(170 \pm 20)/T]$	298–440	Dagaut et al., 1988	FP-RF (a)
$(7.4 \pm 0.6) \times 10^{-13}$	298		
$(8.67 \pm 0.65) \times 10^{-13}$	296.8	Singleton et al., 1989	PLP-RA
$(5.63 \pm 0.44) \times 10^{-13}$	326.2		
$(4.88 \pm 0.17) \times 10^{-13}$	356.4		
$(4.09 \pm 0.14) \times 10^{-13}$	396.8		
$(3.95 \pm 0.07) \times 10^{-13}$	446.2		
$2.2 \times 10^{-14} \exp[(1012 \pm 80)/T]$	229–300	Butkovskaya et al., 2004	DF-CIMS (b)
$(6.6 \pm 1.1) \times 10^{-13}$	300		

Comments

(a) Rate coefficient also measured at 240 K where the major species present was expected to be the dimer. Assuming that the monomer and dimer were equally reactive towards the HO radical (but see Butkovskaya et al., 2004), a rate coefficient of $(6.4 \pm 0.9) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 240 K. was obtained.

(b) Experiments were carried out in a turbulent flow system at ~200 Torr (267 mbar) pressure. Combined with the rate data of Singleton et al. (1989), the expression $k = 2.45 \times 10^{-16} (T/298)^{5.24} \exp(2358 \pm 189)/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 229-446 K was obtained. The CO_2 yield was measured by CIMS to be 64 ± 17%, independent of temperature over the range 249–298 K.

Preferred Values

$k = 7.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.2 \times 10^{-14} \exp(855/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$(E/R) = \pm 400$K.

Comments on Preferred Values

At room temperature, the rate coefficients of Dagaut et al. (1988), Singleton et al. (1989) and Butkovskaya et al., 2004 are in reasonable agreement. However, the measured temperature dependencies disagree significantly. At temperatures above 298 K, Dagaut et al. (1988) observed the rate coefficient to increase with increasing temperature, while Singleton et al. (1989) observed the rate coefficient to decrease in a non-Arrhenius manner with increasing temperature. The rate coefficients of Singleton et al. (1989) and Butkovskaya et al. (2004) are consistent in that the rate coefficient increases with decreasing temperature and exhibits a reasonably linear Arrhenius plot below 300 K. The rate coefficients of Singleton et al. (1989) and Butkovskaya et al. (2004) have been fitted to the three-parameter expression $k = CT^2 \exp(-D/T)$, resulting in $k = 8.60 \times 10^{-20}\ T^2 \exp(1363/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 229-446 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 255 K and is derived from the three-parameter equation with $A = Ce^2T^2$ and $B = D + 2T$. The three-parameter expression $k = 8.60 \times 10^{-20}\ T^2 \exp(1363/T)$ cm^3 molecule^{-1} s^{-1} and that reported by Butkovskaya et al. (2004), from combination of their data and those of Singleton et al. (1989), of $k = 2.45 \times 10^{-16} (T/298)^{5.24} \exp(1363/T)$ cm^3 molecule^{-1} s^{-1} result in rate coefficients which agree to within ~10% over the temperature range 229-446 K.

The rate coefficients of Singleton et al. (1989) for the reactions of the HO radical with $CH_3C(O)OH$, $CD_3C(O)OH$ and $CD_3C(O)OD$ indicate that at room temperature the major reaction channel involves overall H-atom abstraction from the -OH bond:

$$HO + CH_3C(O)OH \rightarrow H_2O + CH_3C(O)O$$

This is confirmed by the measured CO_2 yields of 64 ± 17% over the temperature range 249–298 K (Butkovskaya et al. (2004) and 64 ± 14% at 290 K (De Smedt et al., 2005), with the CO_2 arising from decomposition of the $CH_3C(O)O$ radical:

$$CH_3C(O)O \rightarrow CH_3 + CO_2$$

References

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Singleton, D. L., Paraskevopoulos, G. and Irwin, R. S.: J. Am. Chem. Soc. 111, 5248, 1989.

II.A2.39

HO + $C_2H_5C(O)OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.8 \times 10^{-12} \exp[-(120 \pm 30)/T]$	298–440	Dagaut et al., 1988	FP-RF
$(1.22 \pm 0.12) \times 10^{-12}$	298		
$(1.07 \pm 0.05) \times 10^{-12}$	298–445	Singleton et al., 1989	PLP-RA
$(1.02 \pm 0.55) \times 10^{-12}$	298		

Preferred Values

$k = 1.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290–450 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The rate coefficients measured by Dagaut et al. (1988) and Singleton et al. (1989) are in good agreement and indicate that the rate coefficient for this reaction is independent of temperature over the range 298–445 K. The preferred value is an average of all of the rate coefficients of Dagaut et al. (1988) and Singleton et al. (1989), combined with a zero temperature dependence. The reaction is expected to proceed by H-atom abstraction from the C-H bonds of the -CH_3 group and the O-H bond of the -C(O)OH group.

References

Dagaut, P., Wallington, T. J., Liu, R., and Kurylo, M. J.: Int. J. Chem. Kinet., 20, 331, 1988.
Singleton, D. L., Paraskevopoulos, G., and Irwin, R. S.: J. Am. Chem. Soc., 111, 5248, 1989.

II.A2.40

HO + $CH_3ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.4\pm 0.4) \times 10^{-14}$	298	Gaffney et al., 1986	DF-RF (a)
$8.8 \times 10^{-15} \exp[(1050 \pm 180)/T]$	298–393	Nielsen et al., 1991	PR-RA (b)
$(3.2\pm0.5) \times 10^{-13}$	298 ± 2		
$8.2 \times 10^{-13} \exp[-(1020\pm60)/T)$	221–414	Talukdar et al., 1997	PLP-LIF (c)
$(2.36\pm0.16) \times 10^{-14}$	298		
$4.1 \times 10^{-13} \exp[-(604\pm121)/T]$	298–423	Shallcross et al., 1997	DF-RF (d)
$(4.7\pm1.0) \times 10^{-14}$	298		
Relative Rate Coefficients			
$(3.8\pm1.0) \times 10^{-13}$	303 ± 2	Kerr and Stocker, 1986	RR (e)
$(3.1\pm0.7) \times 10^{-13}$	298±2	Nielsen et al., 1991	RR (f)
$(3.0\pm 0.7) \times 10^{-14}$	307±3	Kakesu et al., 1997	RR (g)

Comments

(a) Conducted at 2.6–4.2 mbar (2.0–3.2 Torr) of He.

(b) Conducted at 1 bar Ar.

(c) In addition to measuring rate coefficients for the reaction of the HO radical with CH_3ONO_2, rate coefficients were measured for the reactions of the HO radical with CD_3ONO_2 (298–409 K), the DO radical with CH_3ONO_2 (246–353 K) and the $H^{18}O$ radical with CH_3ONO_2 (253–298 K). HO, $H^{18}O$ and DO radicals were generated by the pulsed laser photolysis of HONO at 355 nm and of O_3-H_2O mixtures at 266 nm, photolysis of O_3-$H_2^{18}O$ mixtures at 266 nm, and photolysis of DONO at 355 nm and of O_3-D_2O mixtures at 266 nm, respectively. The diluent gas pressure was varied from 67 mbar (50 Torr) He plus 67 mbar (50 Torr) SF_6 to 133 mbar (100 Torr) He and to 400 mbar (300 Torr) SF_6, and up to 67 mbar (50 Torr) of O_2 was included in certain experiments. No effect of total pressure, nature of the diluent gas, or presence of O_2 on the measured rate coefficients was observed. The rate coefficients for the reactions of the $H^{18}O$ radical with CH_3ONO_2 were essentially identical to those for the corresponding HO radical reaction, while the measured rate coefficients for the DO radical reaction were ∼10–20% higher than the HO radical reaction. No evidence for formation of HO radicals was observed from these $H^{18}O$ and DO radical reactions. The rate coefficients for the reaction of the HO radical with CD_3ONO_2 were a factor of 3 to 4 lower than those for HO+CH_3ONO_2 over the temperature range studied (298–409 K).

(d) The rate coefficient at 298 K was measured over the pressure range 2.7–27 mbar (2–20 Torr) of He, with no effect of pressure being observed. Rate coefficients at 333–423 K were measured over the pressure range 1.3–4.0 mbar (1–3 Torr) of He.

(e) HO radicals were generated from the photolysis of HONO-air mixtures at atmospheric pressure. The concentrations of methyl nitrate and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + methyl nitrate)/k(HO + ethene) = 0.046±0.011 placed on an absolute basis by use of k(HO + ethene) = 8.32×10^{-12} cm^3 molecule^{-1} s^{-1} at 303 K and one atmosphere of air (Atkinson, 1997).

(f) HO radicals generated by the photolysis of CH_3ONO-NO-air mixtures at atmospheric pressure. The decays of CH_3ONO_2 and $(CH_3)_3CH$ (the reference compound) were measured by GC. The rate coefficient ratio was placed on an absolute basis by use of k(HO+$(CH_3)_3$CH)=2.12×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson, 2003).

(g) HO radicals were generated by photolysis of O_3-H_2O-O_2 mixtures at atmospheric pressure at ∼290–310 nm. Methyl nitrate and the reference compounds (methane, ethane and HFC-152a) were monitored by GC. The measured rate coefficient ratios are placed on an absolute basis by use of rate coefficients of $k(HO+CH_4)=1.85\times10^{-12}\exp(-1690/T)$ cm^3 molecule^{-1} s^{-1}, $k(HO+C_2H_6)=6.9\times10^{-12}\exp(-1000/T)$ cm^3 molecule^{-1} s^{-1} and $k(HO+CH_3CHF_2)=1.0\times10^{-12}\exp(-990/T)$ cm^3 molecule $^{-1}$ s^{-1} (IPUPAC, current recommendation). The cited rate coefficient is the unweighted average, with a two standard deviation error limit.

Preferred Values

$k = 2.3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.0 \times 10^{-13}\exp(-845/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–300 K.

Reliability

$\Delta \log k = ^{+0.5}_{-0.2}$ at 298 K.
$\Delta (E/R) = \pm$ 400 K.

Comments on Preferred Values

There are serious discrepancies between the room temperature rate coefficients of Gaffney et al. (1986), Talukdar et al. (1997) and Kakesu et al. (1997) and those of Kerr and Stocker (1986) and Nielsen et al. (1991), of a factor of ∼10. Additionally, the temperature dependencies of Nielsen et al. (1991) and Talukdar et al. (1997) differ by ∼2000 K. The positive temperature-dependence observed by Talukdar et al. (1997) is supported, qualitatively, by the low-pressure absolute rate study of Shallcross et al. (1997), although the rate coefficients of Shallcross et al. (1997) are a factor of ∼1.3–2.0 higher than those of Talukdar et al. (1997) over the temperature range 298–423 K. The reasons for these various discrepancies are not presently known, but we favor the results of the Talukdar et al. (1997) study which are consistent with H- (or D-) atom abstraction to form H_2O+CH_2ONO. The extensive absolute study of Talukdar et al. (1997) shows no effect of the measured rate coefficient on pressure or diluent gas (133 mbar He to 400 mbar SF_6) nor on the presence or absence of up to 67 mbar of O_2. The experiments of Talukdar et al. (1997) on the reactions $HO+CH_3ONO_2$, $H^{18}O+CH_3ONO_2$, $DO+CH_3ONO_2$ and $HO+CH_3ONO$ show no formation of HO radicals from the $H^{18}O$ and DO radical reactions with CH_3ONO, and the deuterium isotope effect of k_H/k_D ∼4 at 298 K is totally consistent with H- (or D-) atom abstraction.

The preferred values are obtained from a unit-weighted least-squares analysis of the 221–298 K rate coefficients of Talukdar et al. (1997). Because of the significant discrepancies between the various studies (Gaffney et al., 1986; Kakesu et al., 1997; Kerr and Stocker, 1986; Nielsen et al., 1991; Shallcross et al., 1997; Talakdur et al., 1997), large uncertainty limits are assigned to the 298 K rate coefficient and the temperature dependence. Clearly, further absolute rate studies at atmospheric pressure of air are needed.

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Talukdar, R. K., Herndon, S. C., Burkholder, J. B., Roberts, J. M., and Ravishankara, A. R.: J. Chem. Soc. Faraday Trans., 93, 2787, 1997.

II.A2.41

HO + $C_2H_5ONO_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.7 \times 10^{-14} \exp[(716\pm138)/T]$	298–373	Nielsen et al., 1991	PR-RA (a)
$(5.3\pm0.6) \times 10^{-13}$	298±2		
$3.68 \times 10^{-12} \exp[-(1077/T)]$	223–394	Talukdar et al., 1997	PLP-LIF (b)
$+ 5.32 \times 10^{-14} \exp(126/T)$			
$(1.80\pm0.12) \times 10^{-13}$	298		
$3.30 \times 10^{-12} \exp[-(699\pm140)/T]$	298–373	Shallcross et al., 1997	DF-RF (c)
$(3.30\pm0.68) \times 10^{-13}$	298		
Relative Rate Coefficients			
$(4.9\pm2.1) \times 10^{-13}$	303±2	Kerr and Stocker, 1986	RR (d)
$(4.2\pm0.3) \times 10^{-13}$	298±2	Nielsen et al., 1991	RR (e)
$(2.2\pm0.8) \times 10^{-13}$	304±6	Kakesu et al., 1997	RR (f)

Comments

(a) Conducted at 1 bar Ar.

(b) Extensive study of the reactions of ethyl nitrate with HO radicals (223–394 K), $H^{18}O$ radicals (300 K) and DO radicals (229–378 K). HO, $H^{18}O$ and DO radicals were produced from the pulsed laser photolysis of HONO at 355 nm, of O_3-$H_2^{18}O$ mixtures at 248 nm, and of DONO at 355 nm, respectively. The diluent gas and total pressures were He [67–400 mbar (50–300 Torr)], N_2 [400 mbar (300 Torr)], SF_6 [267 mbar (200 Torr)] or He-SF_6 [133–400 mbar (100–300 Torr)], and O_2 partial pressures of 67 mbar (50 Torr) were used in certain experiments. No effects on the measured rate coefficients were observed on varying the total pressure, the diluent gas, or the partial pressure of O_2. The measured rate coefficients for the reactions of the $H^{18}O$ and DO radicals with ethyl nitrate were 11–16% higher than that for the HO radical reaction, and no formation of HO radicals was observed in the $H^{18}O$ and DO radical reactions.

(c) The rate coefficient at 298 K was measured over the pressure range 5.7–27 mbar (4.3–19.9 Torr) of He, with no effect of pressure being observed. The rate coefficients at 313 K and 373 K were measured over the pressure range 1.3–4.0 mbar (1–3 Torr) of He.

(d) HO radicals generated by photolysis of HONO-air mixtures at atmospheric pressure. The concentrations of ethyl nitrate and ethene (the reference organic) were measured by GC. The measured rate coefficient ratio of k(HO + ethyl nitrate)/k(HO + ethene) = 0.059±0.025 is placed on an absolute basis by use of a rate coefficient k(HO + ethene) = 8.32×10^{-12} cm^3 molecule^{-1} s^{-1} at 303 K and atmospheric pressure of air (Atkinson, 1997).

(e) HO radicals were generated by photolysis of CH_3ONO-NO-air mixtures at atmospheric pressure. The concentrations of ethyl nitrate and 2-methylpropane (the reference organic) were measured by GC, and the measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of k(HO + 2-methylpropane) = 2.12×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson, 2003).

(f) Relative rate method. HO radicals were generated by the photolysis of O_3-H_2O-O_2 mixtures at atmospheric pressure at ∼290–310 nm. The concentrations of ethyl nitrate and the reference compounds ethane and 2-methylpropane were measured by GC. The measured rate coefficient ratios are placed on an absolute basis by use of rate coefficients of k(HO + ethane) = $6.9\times10^{-12} \exp(-1000/T)$ cm^3 molecule^{-1} s^{-1} and k(HO + 2-methylpropane) = $1.17\times10^{-17}\, T^2 \exp(213/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 2003; IUPAC, current recommendation). The cited rate coefficient is the unweighted average with a two standard deviation error limit.

Preferred Values

$k = 1.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.7 \times 10^{-13} \exp(-395/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–300 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

There are serious discrepancies between the absolute and relative rate studies of Kerr and Stocker (1986) and Nielsen et al. (1991) carried out at ∼1 bar total pressure and the absolute rate and the relative rate studies of Talukdar et al. (1997) and Kakesu et al. (1997), respectively, in both the room temperature rate coefficient (Nielsen et al., 1991; Talukdar et al., 1997; Kerr and Stocker, 1986; Kakesu et al., 1997) and the temperature dependence (Nielsen et al., 1991; Talukdar et al., 1997). The positive temperature-dependence observed by Talukdar et al. (1997) is supported, qualitatively, by the low-pressure absolute rate study of Shallcross et al. (1997), although the rate coefficients of Shallcross et al. (1997) are a factor of ∼1.8 higher than those of Talukdar et al. (1997). The reasons for these discrepancies are not known, but we favor the results of the extensive Talukdar et al. (1997) study which are consistent with H- (or D-) atom abstraction. The study of Talukdar et al. (1997) showed no effect of total pressure, diluent gas [ranging from 67 mbar (50 Torr) of He to 267 mb (200 Torr) of SF_6 or 400 mbar (300 Torr) N_2] or the presence or absence of O_2 at a partial pressure of 67 mbar (50 Torr) on the measured rate coefficients.

While the study of Talukdar et al. (1997) was not carried out in air at 1 bar pressure, the data obtained strongly suggest that the rate coefficient is consistent with an H-atom abstraction process and that the measured rate coefficients should be appropriate for atmospheric purposes. The Arrhenius plots of the HO and DO radical reactions exhibit significant curvature (Talukdar et al., 1997). The preferred values are based on a unit-weighted least-squares fit of the 233–298 K rate coefficients of Talukdar et al. (1997) to the Arrhenius expression, $k=A \exp(-B/T)$. Large uncertainty limits are assigned because of the discrepancies between the various studies (Kakesu et al., 1997; Kerr and Stocker, 1986; Nielsen et al., 1991; Shallcross et al., 1997; Talukdar et al., 1997) noted above. Further absolute rate studies conducted at atmospheric pressure of air are required.

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Talukdar, R. K., Herndon, S. C., Burkholder, S. B., Roberts, J. M., and Ravishankara, A. R.: J. Chem. Soc. Faraday Trans., 93, 2787, 1997.

II.A2.42

HO + 1-$C_3H_7ONO_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$5.0 \times 10^{-13} \exp[(140\pm144)/T]$	298–368	Nielsen et al., 1991	PR-RA (a)
$(8.2\pm0.8) \times 10^{-13}$	298±2		
Relative Rate Coefficients			
$(7.2\pm2.3) \times 10^{-13}$	303±2	Kerr and Stocker, 1986	RR (b)
$(5.8\pm1.0) \times 10^{-13}$	298±2	Atkinson and Aschmann, 1989	RR (c)
$(7.0\pm0.8) \times 10^{-13}$	298±2	Nielsen et al., 1991	RR (d)

Comments

(a) Carried out in 1 bar Ar.

(b) HO radicals were generated by the photolysis of HONO-air mixtures at atmospheric pressure. The decay rates of 1-propyl nitrate and ethene (the reference organic) were measured by GC and rate coefficient ratio k(HO + 1-propyl nitrate)/k(HO + ethene) = 0.086±0.027 is placed on an absolute basis by use of a rate coefficient of k(HO + ethene) = 8.32×10^{-12} cm^3 molecule^{-1} s^{-1} at 303 K and atmospheric pressure of air (Atkinson, 1997).

(c) HO radicals were generated by the photolysis of CH_3ONO at ∼1 bar air at >300 nm. Experiments were carried out in a 6400 liter Teflon chamber. The concentrations of 1-propyl nitrate and cyclohexane (the reference organic) were measured by GC, and irradiations in the absence of CH_3ONO allowed the photolysis of 1-propyl nitrate to be accurately taken into account in the data analysis. The measured rate coefficient ratio of k(HO + 1-propyl nitrate)/k(HO + cyclohexane) = 0.083±0.013 is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 6.97×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

(d) HO radicals were generated from the photolysis of CH_3ONO in 1 bar air at >290 nm. The concentrations of 1-propyl nitrate and 2-methylpropane (the reference organic) were measured by GC. The measured rate coefficient ratio k(HO + 1-propyl nitrate)/k(HO + 2-methylpropane) is placed on an absolute basis by use of a rate coefficient of k(HO + 2-methylpropane) = 2.12×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

Preferred Values

$k = 5.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar air.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The absolute and relative rate coefficients of Kerr and Stocker (1986), Atkinson and Aschmann (1989) and Nielsen et al. (1991) are in reasonable agreement at room temperature. All studies have been carried out at ∼1 bar pressure.

The absolute rate coefficient study of Talukdar et al. (1997) for the HO radical reactions with CH_3ONO_2 and $C_2H_5ONO_2$ is in serious disagreement (by a factor of 13–16 for CH_3ONO_2 and a factor of 2.3–2.9 for $C_2H_5ONO_2$) with the rate coefficients from the studies of Kerr and Stocker (1986) and Nielsen et al. (1991), while for 2-$C_3H_7ONO_2$ the 298 K rate coefficients of Talukdar et al. (1997) and Atkinson and Aschmann (1989) disagree by 33% (suggesting for one that the discrepancies decrease as the reactivity of the alkyl nitrate increases). Accordingly, the 298 K rate coefficient of Atkinson and Aschmann (1989) is used for the preferred value and no temperature dependence is recommended (note that by analogy with the reaction of the OH radical with 2-propyl nitrate (IUPAC, this evaluation), the temperature dependence of the rate coefficient is likely to be small). That 1-propyl nitrate is more reactive than 2-propyl nitrate is expected from structure-reactivity relationships (Atkinson and Aschmann, 1989) based on assuming that the reaction proceeds by H-atom abstraction, as concluded by Talukdar et al. (1997) for methyl nitrate, ethyl nitrate and 2-propyl nitrate.

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II.A2.43

HO + 2-$C_3H_7ONO_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
4.3×10^{-12} exp(-1250/T) + 2.5×10^{-13} exp(-32/T)	233–395	Talukdar et al., 1997	PLP-LIF (a)
$(2.88\pm0.19) \times 10^{-13}$	298		
Relative Rate Coefficients			
$(1.68\pm0.42) \times 10^{-13}$	299±2	Atkinson et al., 1982	RR (b)
$(5.3\pm2.1) \times 10^{-13}$	295±2	Becker and Wirtz, 1989	RR (c)
$(3.83\pm0.49) \times 10^{-13}$	298±2	Atkinson and Aschmann, 1989	RR (d)

Comments

(a) Experiments were carried out as a function of total pressure and with different diluent gases (133 mbar He to 400 mbar SF_6) and with up to 80 mbar O_2 present. No effect of pressure, diluent gas or presence or absence of O_2 on the measured rate coefficients was observed. Rate coefficients for the reactions of $H^{18}O$ and DO radicals with 2-propyl nitrate were also measured over the temperature ranges 233–298 K and 230–403 K, respectively, with 298 K rate coefficients of $(3.15\pm0.20)\times10^{-13}$ cm^3 molecule^{-1} s^{-1} and $(3.6\pm0.4)\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, respectively.

(b) HO radicals were generated from the photolysis of CH_3ONO in ∼1 bar air at >300 nm. Experiments were carried out in an ∼75 liter Teflon chamber and concurrent photolysis of 2-propyl nitrate was indicated from the data analysis. The concentrations of 2-propyl nitrate and cyclohexane (the reference organic) were measured by GC. The measured rate coefficient ratio of k(HO + 2-propyl nitrate/k(HO + cyclohexane) = 0.024±0.006 is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 7.00×10^{-12} cm^3 molecule^{-1} s^{-1} at 299 K (Atkinson, 2003).

(c) HO radicals were generated from the photolysis of CH_3ONO in 1 bar air at 280 nm to 450 nm. Experiments were carried out in a 36.5 liter quartz chamber, and photolysis of 2-propyl nitrate was indicated from the data analysis. The concentrations of 2-propyl nitrate and n-butane (the reference organic) were measured by GC-MS and GC, respectively. The measured rate coefficient ratio of k(HO + 2-propyl nitrate)/k(HO + n-butane) = 0.23±0.09 is placed on an absolute basis by use of a rate coefficient of k(HO + n-butane) = 2.30×10^{-12} cm^3 molecule^{-1} s^{-1} at 295 K (IUPAC, current recommendation).

(d) HO radicals were generated by the photolysis of CH_3ONO in ∼1 bar air at >300 nm. Experiments were carried out in a 6400 liter Teflon chamber. The concentrations of 2-propyl nitrate and cyclohexane (the reference organic) were measured by GC, and irradiations in the absence of CH_3ONO allowed the photolysis of 2-propyl nitrate to be accurately taken into account in the data analysis. The measured rate coefficient ratio of k(HO + 2-propyl nitrate)/k(HO + cyclohexane) = 0.055±0.007 is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 6.97×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003). This study supersedes the earlier study of Atkinson et al. (1982).

Preferred Values

$k = 2.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.2 \times 10^{-13}$ exp(-230/T) cm^3 molecule^{-1} s^{-1} over the temperature range 230–300 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values are based on the absolute 233–300 K rate coefficients of Talukdar et al. (1997). The extensive study of Talukdar et al. (1997) provided no evidence for the rate coefficient *k* to depend on total pressure, nature of the diluent gas, or the presence of O_2 at pressures up to 80 mbar (60 Torr). Additionally, the use of DO radicals showed no evidence for the formation of HO radicals as a reaction product. However, as noted in the data sheets for the reactions of the HO radical with CH_3ONO_2 and $C_2H_5ONO_2$, the experiments of Talukdar et al. (1997) were not actually carried out in air at 1 bar total pressure.

Arrhenius plots of the rate coefficients for the reactions of HO, $H^{18}O$ and DO radicals with 2-propyl nitrate exhibit significant curvature (especially pronounced for the DO radical reaction for which the measured rate coefficient was independent of temperature over the range 230–269 K). The measured temperature dependencies at around 298 K and below are quite small. The room temperature relative rate coefficient of Atkinson and Aschmann (1989) (which supersedes the earlier data of Atkinson et al., 1982) is 33% higher than the recommended 298 K rate coefficient, which may be considered reasonable agreement because of the low rate coefficient (on the low end of those reported by that research group) and hence small fraction of 2-propyl nitrate reacted during the experiments. The relative rate coefficient of Becker and Wirtz (1989) is almost a factor of 2 higher than the recommendations, but has high cited uncertainties.

We attach rather large uncertainties to the recommended values of the 298 K rate coefficient and *E/R* until the data of Talukdar et al. (1997) are confirmed by absolute techniques in air at 1 bar pressure.

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II.A2.44

HO + 1-$C_4H_9ONO_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.74\pm0.19) \times 10^{-12}$	298±2	Nielsen et al., 1991	PR-RA (a)
Relative Rate Coefficients			
$(1.31\pm0.10) \times 10^{-12}$	299±2	Atkinson et al., 1982	RR (b,c)
$(1.65\pm0.18) \times 10^{-12}$	298±2	Atkinson and Aschmann, 1989	RR (b,d)
$(1.47\pm0.08) \times 10^{-12}$	298±2	Nielsen et al., 1991	RR (b,e)

Comments

(a) Carried out at a total pressure of 1 bar Ar.

(b) HO radicals were generated by the photolysis of CH_3ONO in air at atmospheric pressure (0.97 bar to 1.0 bar). The concentrations of 1-butyl nitrate and the reference organic were measured by GC.

(c) The measured rate coefficient ratio of k(HO + 1-butyl nitrate)/k(HO + cyclohexane) = 0.187±0.014 is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 7.00×10^{-12} cm^3 molecule^{-1} s^{-1} at 299 K (Atkinson, 2003). Experiments were carried out in an ∼75 liter Teflon chamber, and the data were interpreted as involving concurrent photolysis of 1-butyl nitrate.

(d) Experiments were carried out in a 6400 liter Teflon chamber, and irradiations were also carried out in the absence of CH_3ONO, allowing the photolysis rate to be accurately allowed for in the data analysis. The measured rate coefficient ratio of k(HO + 1-butyl nitrate)/k(HO + cyclohexane) = 0.237±0.025 is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 6.97×10^{-12} cm^{-3} molecule^{-1} s^{-1} at 298 K (Atkinson, 2003). These data supersede those of Atkinson et al. (1982).

(e) The measured rate coefficient ratio k(HO + 1-butyl nitrate)/k(HO + 2-methylpropane) is placed on an absolute basis by use of a rate coefficient of k(HO + 2-methylpropane) = 2.12×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

Preferred Values

$k = 1.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The absolute and relative rate coefficients of Atkinson and Aschmann (1989) (which supersedes the earlier data of Atkinson, 1982) and Nielsen et al. (1991) are in good agreement. The preferred value is an average of the absolute and relative rate constants of Atkinson and Aschmann (1989) and Nielsen et al. (1991). By analogy with the reaction of the HO radical with 2-propyl nitrate (this evaluation), the temperature dependence of the rate coefficient at temperatures below 300 K is likely to be small.

References

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II.A2.45

HO + 2-$C_4H_9ONO_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(6.4\pm1.0) \times 10^{-13}$	299±2	Atkinson et al., 1982	RR (a,b)
$(8.6\pm1.5) \times 10^{-13}$	298±2	Atkinson and Aschmann, 1989	RR (a,c)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in one atmosphere of air. The concentrations of 2-butyl nitrate and the reference organic were measured by GC.

(b) Experiments were carried out in an ∼75 liter Teflon chamber, and the data were interpreted as involving concurrent photolysis of 2-butyl nitrate. The measured rate constant ratio of k(HO + 2-butyl nitrate)/k(HO + cyclohexane) = 0.091 ± 0.013 is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 7.00×10^{-12} cm^3 molecule^{-1} s^{-1} at 299 K (Atkinson, 2003).

(c) Experiments were carried out in a 6400 liter Teflon chamber, and irradiations were also carried out in the absence of CH_3 ONO allowing the photolysis rate to be accurately allowed for in the data analysis. The measured rate coefficient ratio of k(HO + 2-butyl nitrate)/k(HO + cyclohexane) = 0.123 ± 0.021 is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 6.97×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003). These data supersede those of Atkinson et al. (1982).

Preferred Values

$k = 8.6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the rate coefficient of Atkinson and Aschmann (1989), which supersedes the earlier study of Atkinson et al. (1982). By analogy with the reaction of the HO radical with 2-propyl nitrate (this evaluation), the temperature dependence of the rate coefficient at temperatures below 300 K is likely to be small.

References

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II.A2.46

$HO + CH_3C(O)OONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 1.7 \times 10^{-13}$	299±1	Winer et al., 1977	FP-RF
$1.23 \times 10^{-12}\exp[-(651 \pm 229)/T]$	273–297	Wallington et al., 1984	FP-RF
$(1.37\pm0.05) \times 10^{-13}$	297 ± 2		
$(7.5\pm1.4) \times 10^{-14}$	298 ± 2	Tsalkani et al., 1988	DF-EPR
$< 3.0 \times 10^{-14}$	298	Talukdar et al., 1995	FP/PLP-LIF (a)

Comments

(a) Experiments were carried out over the temperature range 253–298 K, using pulsed laser photolysis of HONO at 355 nm, pulsed laser photolysis of O_3-H_2O mixtures at 266 nm, or flash photolysis of H_2O at 165-185 nm to generate HO radicals. The measured HO radical decay rates corresponded to rate coefficients in the range $(0.82–2.50)\times10^{-14}$ cm^3 molecule^{-1} s^{-1} with no obvious dependence on temperature. The measured HO radical decay rates were attributed to the reaction of HO radicals with HCHO impurity, and a conservative upper limit to the rate coefficient k was cited (see table).

Preferred Values

$k < 3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit to the 298 K rate coefficient is the upper limit reported by Talukdar et al. (1995) from an extensive and careful study. The higher rate coefficients measured by Wallington et al. (1984) and Tsalkani et al. (1988) were almost certaintly due to the presence of reactive impurities.

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II.A2.47

HO + $CH_3C(O)CH_2ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$<4.0 \times 10^{-13}$	298±2	Zhu et al., 1991	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO-NO-N_2-O_2 mixtures at 1 bar pressure. The concentrations of $CH_3C(O)CH_2ONO_2$ and n-butane were measured during the experiments by GC, and the measured rate constant ratio of $k(HO + CH_3C(O)CH_2ONO_2)/k(HO + n\text{-butane}) < 0.17$ is placed on an absolute basis by use of a rate coefficient of k(HO + n-butane) = 2.3×10^{-12} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k < 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based on the sole study of Zhu et al. (1991), but with a higher upper limit to reflect additional uncertainties.

References

IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/.
Zhu, T., Barnes, I., and Becker, K. H.: J. Atmos. Chem., 13, 301, 1991.

II.A2.48

$HO + CH_3CH_2C(O)CH_2ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(8.21\pm1.38) \times 10^{-13}$	298±2	Zhu et al., 1991	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO-NO-N_2-O_2 mixtures at 1 bar pressure. The concentrations of $CH_3CH_2C(O)CH_2ONO_2$ and n-butane were measured during the experiments by GC, and the measured rate constant ratio of $k(HO + CH_3CH_2C(O)CH_2ONO_2)/k(HO + n\text{-butane}) = 0.357\pm0.060$ is placed on an absolute basis by use of a rate coefficient of $k(HO + n\text{-butane}) = 2.3\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 8.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the sole study of Zhu et al. (1991) but with a higher uncertainty.

References

IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/.
Zhu, T., Barnes, I., and Becker, K. H.: J. Atmos. Chem., 13, 301, 1991.

II.A2.49

$HO + CH_3CH(ONO_2)C(O)CH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.15 \pm 0.13) \times 10^{-12}$	298±2	Zhu et al., 1991	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO-NO-N_2-O_2 mixtures at 1 bar pressure. The concentrations of $CH_3CH(ONO_2)C(O)CH_3$ and n-butane were measured during the experiments by GC, and the measured rate constant ratio of $k(HO + CH_3CH(ONO_2)C(O)CH_3)/k(HO + n\text{-butane}) = 0.499 \pm 0.056$ is placed on an absolute basis by use of a rate coefficient of $k(HO + n\text{-butane}) = 2.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 1.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the sole study of Zhu et al. (1991) but with a higher uncertainty.

References

IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/.
Zhu, T., Barnes, I., and Becker, K. H.: J. Atmos. Chem., 13, 301, 1991.

II.A2.50

HO + CH_2=C(CH_3)C(O)OONO_2 (MPAN) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(3.33\pm0.40) \times 10^{-12}$	298±2	Grosjean et al., 1993	RR (a)
$(3.76\pm0.58) \times 10^{-11}$	275±3	Orlando et al., 2002	RR (b,c)
$(2.88\pm0.46) \times 10^{-11}$	275±3	Orlando et al., 2002	RR (b,d)

Comments

(a) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by the photolysis (using natural sunlight) of ethyl nitrite-air mixtures, and the concentrations of CH_2=C(CH_3)C(O)OONO_2 (MPAN) and 1-butyl nitrate (the reference compound) were measured by GC with electron capture detection. The measured rate coefficient ratio of k(HO + MPAN)/k(HO + 1-butyl nitrate) = 2.08±0.25 is placed on an absolute basis by use of a rate coefficient of k(HO + 1-butyl nitrate) = 1.6×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(b) Relative rate method carried out in synthetic air at 0.93–0.97 bar. HO radicals were generated by the photolysis of ethyl nitrite-NO-air mixtures, and the concentrations of CH_2=C(CH_3)C(O)OONO_2 (MPAN) and ethene and propene (the reference compounds) were measured by in situ FTIR spectroscopy. Experiments were carried out at 275±3 K to decrease the rate of thermal decomposition of MPAN (IUPAC, current recommendation) in the presence of NO. The measured rate coefficient ratios of k(HO + MPAN)/k(HO + ethene) = 3.9±0.6 and k(HO + MPAN)/k(HO + propene) = 0.95±0.15 are placed on an absolute basis by use of rate coefficients at 275 K and atmospheric pressure of air of k(HO + ethene) = 9.64×10^{-12} cm^3 molecule^{-1} s^{-1} and k(HO + propene) = 3.03×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson, 1997).

(c) Relative to HO + ethene.

(d) Relative to HO + propene.

Preferred Values

$k = 2.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = ^{+0.2}_{-0.5}$ at 298 K.

Comments on Preferred Values

The rate coefficients measured in the two studies of Grosjean et al. (1993) and Orlando et al. (2002) disagree by a factor of ∼10, for reasons which are not known. The reaction of HO radicals with CH_2=C(CH_3)C(O)OONO_2 is expected to proceed almost exclusively by initial HO radical addition to the C=C bond (Grosjean et al., 1993; Orlando et al., 2002), and is expected to have a small (and probably negative) temperature dependence at around room temperature. Support for the Orlando et al. (2002) study arises from the structurally similar compound CH_2=C(CH_3)C(O)OCH_3 having a rate coefficient for its HO radical reaction of $(2.6\pm0.5)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K (Saunders et al., 1994), which is similar to that measured by Orlando et al. (2002) for HO + MPAN. Accordingly, the preferred value is based on the rate coefficients measured by Orlando et al. (2002) at 275 K, adjusted to 298 K using the temperature dependence observed for HO + propene (Atkinson, 1997), and with appropriately large and asymmetric uncertainties. Formaldehyde and hydroxyacetone have been observed as products of this reaction (Grosjean et al., 1993; Orlando et al., 2002).

References

Atkinson, R.: J. Phys. Chem. Ref. Data, 26, 215, 1997.
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IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/.
Orlando, J. J., Tyndall, G. S., Bertman, S. B., Chen, W., and Burkholder, J. B.: Atmos. Environ., 36, 1895, 2002.
Saunders, S. M., Baulch, D. L., Cooke, K. M., Pilling, M. J., and Smurthwaite, P. I.: Int. J. Chem. Kinet., 26, 113, 1994.

II.A2.51

HO + HCN → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.2×10^{-13}exp(-400/T)	296–433	Fritz et al., 1984	FP-RA (a)
$(3.0 \pm 1.0) \times 10^{-14}$	298		

Comments

(a) The measured rate coefficients were observed to be pressure dependent over the range ∼13–600 mbar (∼10–450 Torr) of N_2 diluent. The cited rate coefficients are those extrapolated to the high-pressure limit (k_∞) using a simple Lindemann extrapolation.

Preferred Values

$k = 3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar.
$k = 1.2 \times 10^{-13}$ exp(-400/T) cm^3 molecule^{-1} s^{-1} over the temperature range 290–440 K at 1 bar.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values are those of Fritz et al. (1984) with wider error limits. The rate coefficient increases with increasing pressure over this temperature range, and the rate coefficients cited are those extrapolated by Fritz et al. (1984) to the high-pressure limit.

The reaction proceeds by HO radical addition over this temperature range. At higher temperatures the available rate coefficient data indicate a direct abstraction reaction (Atkinson, 1989).

References

Atkinson, R.: J. Phys. Chem. Ref. Data, Monograph, 1, 1, 1989.
Fritz, B., Lorenz, K., Steinert, W., and Zellner, R.: Oxid. Comm., 6, 363, 1984.

II.A2.52

HO + $CH_3CN \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.1\pm0.3) \times 10^{-14}$	295±2	Poulet et al., 1984	DF-EPR
$(8.6\pm1) \times 10^{-14}$	393		
$6.28 \times 10^{-13}\exp(-1030/T)$	250–363	Kurylo and Knable, 1984	FP-RF
$(1.94\pm0.37) \times 10^{-14}$	298		
$1.1 \times 10^{-12}\exp[-(1130\pm90)/T)]$	256–388	Hynes and Wine, 1991	PLP-LIF (a)
$(2.48\pm0.38) \times 10^{-14}$	298		

Comments

(a) No definitive evidence for a pressure dependence of the rate coefficient for the HO+CH_3CN reaction was observed over the pressure range 61–933 mbar (46–700 Torr) of N_2 diluent or 40–840 mbar (30–630 Torr) of He diluent. In the presence of O_2, the HO radical decays were non-exponential indicating regeneration of HO radicals.

Preferred Values

$k = 2.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K (1 bar).
$k = 8.1 \times 10^{-13} \exp(-1080/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–390 K at 1 bar.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is a unit-weighted average of the rate coefficients of Poulet et al. (1984), Kurylo and Knable (1984) and Hynes and Wine (1991). The temperature dependence is the mean of those determined by Kurylo and Knable (1984) and Hynes and Wine (1991). Hynes and Wine (1991) observed no definitive evidence for a pressure dependence of the rate coefficient for the HO+CH_3CN reaction in N_2 or He diluent over the pressure ranges 61–933 mbar (46–700 Torr) or 40–840 mbar (30–630 Torr), respectively. In the presence of O_2, the HO radical decays were non-exponential (Hynes and Wine, 1991), indicating regeneration of HO radicals. Combined with analogous data for the reactions of HO radicals with CD_3CN (for which the rate coefficient was pressure dependent over the pressure range 53–923 mbar (40–692 Torr) of N_2 diluent) (Hynes and Wine, 1991) and of DO radicals with CH_3CN and CD_3CN (Hynes and Wine, 1991), it appears that the initial HO radical reaction proceeds by H-atom abstraction from the CH_3 group and HO radical addition to the CN group (Hynes and Wine, 1991).

$$\begin{aligned} HO + CH_3CN &\rightarrow H_2O + CH_2CN \\ HO + CH_3CN &\rightarrow [CH_3CNOH]^{\ddagger} \end{aligned}$$

Subsequent reactions of the addition adduct in the presence of O_2 then lead to the regeneration of HO radicals. In view of the possibility of a pressure dependence of the 298 K rate coefficient at low total pressures (Hynes and Wine, 1991) ($\leq$0.1 bar), the preferred values are applicable to atmospheric conditions.

Tyndall et al. (2001) have observed the formation of formyl cyanide, HC(O)CN, from reaction of HO radicals with CH_3CN at atmospheric pressure of synthetic air using FTIR spectroscopy, and a formation yield of HC(O)CN of 40±20% was obtained. The details of the reaction mechanism, including that for formation of HC(O)CN, are presently not known.

References

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Kurylo, M. J. and Knable, G. L.: J. Phys. Chem., 88, 3305, 1984.
Poulet, G., Laverdet, G., Jourdain, J. L., and Le Bras, G.: J. Phys. Chem., 88, 6259, 1984.
Tyndall, G. S., Orlando, J. J., Wallington, T. J., and Hurley, M. D.: J. Phys. Chem. A, 105, 5380, 2001.

Appendix A2a: HOx + VOC continued reactions

II.A2a.53

$$\begin{aligned} \mathbf{HO_2 + CH_3O_2} \quad &\rightarrow \mathbf{O_2 + CH_3OOH} \qquad &\mathbf{(1)} \\ &\rightarrow \mathbf{O_2 + HCHO + H_2O} \qquad &\mathbf{(2)} \end{aligned}$$

$\Delta H^\circ(1) = -155\text{kJ} \cdot \text{mol}^{-1}$

$\Delta H^\circ(2) = -374\text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$7.7 \times 10^{-14}\exp[(1296 \pm 364)/T]$	274–338	Cox and Tyndall, 1980	MM-AS (a)
$(6.5\pm1.0) \times 10^{-12}$	298		
$(5.4\pm1.1) \times 10^{-12}$	300	Jenkin et al., 1988	MM-IR-AS (b)
$3.0 \times 10^{-13}\exp[(720\pm100)T]$	228–380	Dagaut et al., 1988	FP-AS (c)
$(2.9\pm0.4) \times 10^{-12}$	298		
$(4.8\pm0.2) \times 10^{-12}$	300	Moortgat et al., 1989	MM-IR-AS (d)
$4.4 \times 10^{-13}\exp[(780\pm55)/T]$	248–573	Lightfoot et al., 1990	FP-AS (e)
$(6.2\pm1.0) \times 10^{-12}$	298		
$2.9 \times 10^{-13}\exp(862\pm44)/T]$	248–700	Lightfoot et al., 1991	FP-AS (f)
$(5.13\pm0.55) \times 10^{-12}$	298	Boyd et al., 2003	PLP-AS (g)
Branching Ratios			
$k_1/k = 0.92 \pm 0.05$	295	Wallington and Japar, 1990; Wallington, 1991	P-FTIR (h)
$k_2/k = 1/[1 + 498 \exp(-1160/T)]$	218–298	Elrod et al., 2001	DF-CIMS (i)
$k_2/k = 0.11 \pm 0.02$	298		

Comments

(a) MM study of photolysis of Cl_2 in the presence of CH_4-H_2-O_2 mixtures at 1013 mbar (760 Torr) pressure. CH_3O_2 and HO_2 radicals were monitored by absorption at 250 nm and 210 nm, respectively.

(b) MM study of photolysis of Cl_2 in the presence of CH_4-H_2O_2-O_2 mixtures. HO_2 radicals were monitored by IR absorption with a tunable diode laser and CH_3O_2 monitored by UV absorption at 260 nm. $\sigma(CH_3O_2) = 3.53\times10^{-18}$ cm^2 molecule^{-1} was determined at 260 nm. k determined from observed perturbation of the second-order kinetics of the HO_2 radical self-reaction by the presence of CH_3O_2 in large excess. Experiments were carried out at a total pressure of 13 mbar (10 Torr). Similar experiments on mixtures of Cl_2-H_2-CH_4-O_2 were performed at 1013 mbar (760 Torr) total pressure and 303 K and yielded $k=(6.8\pm0.9)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, which was taken as confirmation of the value obtained at 13 mbar (10 Torr).

(c) FP-UV absorption study involving Cl_2-CH_3OH-CH_4-O_2-N_2 mixtures at total pressures of 133 mbar (100 Torr); $\sigma(HO_2)$ and $\sigma(CH_3O_2)$ were determined over the wavelength range 215 nm to 280 nm. At 250 nm $\sigma(CH_3O_2) = 3.3\times10^{-18}$ cm^2 molecule^{-1} was determined. First- or second-order kinetics conditions were not obtainable for either HO_2 or CH_3O_2 and k was determined from computer modeling of the absorption decay curves.

(d) Study of the photooxidation of CH_3CHO at 933 mbar (700 Torr), with double multipath spectrometer, combining both IR and UV absorption spectrometry for monitoring reactants and products, together with modulated photolysis for transient detection. Transient absorptions were assigned to peroxy radicals and the rate coefficient was obtained from kinetic analysis by computer simulation.

(e) FP-UV absorption study of Cl_2-CH_3OH-CH_4-O_2-N_2 mixtures at pressures of 160 mbar or 1013 mbar (120 Torr or 760 Torr). Revised cross-section data were used, $\sigma(HO_2)=5.3\times10^{-18}$ cm^2 molecule^{-1} at 210 nm and $\sigma(CH_3O_2)$ = 3.6×10^{-18} cm^2 molecule^{-1} at 260 nm.

(f) FP-UV absorption study of Cl_2-CH_3OH-CH_4-O_2-N_2 mixtures at 1013 mbar (760 Torr) and over the temperature range 600 K to 719 K. The temperature-dependent rate coefficient listed above was derived by the authors from a re-analysis of all of their data, including previous studies from flash photolysis experiments.

(g) PLP-UV absorption study of H_2O_2-CH_4-O_2-N_2 mixtures at 1013 mbar (760 Torr) and 298 K. Conditions were chosen such that HO_2 was in excess, with initial concentration ratios $[HO_2]/[CH_3O_2]$ in the range 4–10. k was determined from simulation of transient decay traces recorded at 270 nm and either 210 nm or 220 nm. The signal at 270 nm was dominated by CH_3O_2 absorption, with its decay being almost entirely due to the reaction with HO_2. The signal at 210 nm or 220 nm was mainly due to HO_2 absorption, with its self-reaction making the major contribution to its removal.

(h) Photolysis of F_2 in the presence of CH_4 and H_2 in synthetic air or O_2 at total pressures in the range 20 mbar (15 Torr) to 933 mbar (700 Torr). CH_3OOH, CH_4, and a number of minor products were monitored by FTIR.

(i) Turbulent fast-flow system operating at total pressures of 133 mbar (100 Torr). CH_3O_2 was produced by reaction of CH_4 with F atoms and subsequent addition of O_2. The CH_3O_2 was mixed with HO_2 produced by the H+O_2+M reaction. Concentrations of CH_3O_2, CH_3OOH, CH_2O, and HO_2 were monitored by time-resolved CIMS. Values of k_2 were derived by detailed modelling of the $[CH_2O]$ profile. Values of the branching ratio are based on the NASA expression for k (NASA Evaluation, 1997).

Preferred Values

$k = 5.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.8 \times 10^{-13} \exp(780/T)$ cm^{3}molecule^{-1} s^{-1} over the temperature range 225–580 K.
k_2/k = 0.1 at 298 K.
$k_2/k = 1/[1+ 498 \exp(-1160/T)]$ over the temperature range 220–300 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 500$ K.
$\Delta(k_2/k) = \pm 0.1$ at 298 K.
$\Delta(E_2/R–E/R) = \pm 500$ K.

Comments on Preferred Values

The discrepancies in the data for this reaction, due in part to the different values of the UV absorption cross sections used in various studies, remain unresolved.

The preferred rate coefficient at 298 K is the mean of the values of Cox and Tyndall (1980), Jenkin et al. (1988), Dagaut et al. (1988), Moortgat et al. (1989), Lightfoot et al. (1990) and Boyd et al. (2003). The recommended temperature coefficient is that reported by Lightfoot et al. (1991), selected on the basis of their wider range of temperatures than previous studies (Cox and Tyndall, 1980; Dagaut et al., 1988). The A-factor was then adjusted to fit the preferred value of k at 298 K.

The studies of Kurylo et al. (1987), Jenkin et al. (1988) and Lightfoot et al. (1990) show that the room temperature rate coefficient is independent of pressure over the range 13 mbar to 1013 mbar (10 Torr to 760 Torr).

The most direct studies of the branching ratio are those of Wallington and Japar (1990), Wallington (1991) and Elrod et al. (2001). These studies confirm that the contribution of channel (2) is small at 298 K ($k_2/k\approx0.1$), supporting the earlier findings of Jenkin et al. (1988), Moortgat et al. (1989) and Lightfoot et al. (1991). The only information on the temperature dependence of the branching ratio comes from the study of Elrod et al. (2001) and suggests that it increases significantly in going to lower temperatures, reaching a value of $k_2/k\approx0.31$ at 218 K. Provisionally the expression for k_2/k derived by Elrod et al. (2001) is accepted with substantial error limits until confirmatory studies on both the temperature and pressure dependence are available.

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II.A2a.54

$$\begin{array}{llr} \mathbf{HO_2 + HOCH_2O_2} & \mathbf{\rightarrow O_2 + HOCH_2O_2H} & \mathbf{(1)} \\ & \mathbf{\rightarrow O_2 + HC(O)OH + H_2O} & \mathbf{(2)} \end{array}$$

$\Delta H^\circ(2) = -473.1 \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$5.6 \times 10^{-15}\exp[(2300 \pm 1100)/T]$	275–333	Veyret et al., 1989	FP-AS (a)
$(1.2\pm0.4) \times 10^{-11}$	295		
$(1.2\pm0.3) \times 10^{-11}$	298	Burrows et al., 1989	MM-IR (b)
Branching Ratios			
k_2/k = 0.40±0.15	298	Burrows et al., 1989	MM-IR (c)

Comments

(a) Flash photolysis of Cl_2 in the presence of HCHO or CH_3OH and O_2 at total pressures of 110 mbar to 230 mbar (85 Torr to 170 Torr), with time-resolved absorption spectroscopy detection of HO_2 and $HOCH_2O_2$ radicals. The rate coefficient k was obtained from a computer simulation of the absorption profiles based on a mechanism of nine elementary reactions.

(b) MM study of Cl_2-HCHO-O_2 mixtures at total pressures of 930 mbar (700 Torr), with diode laser IR spectroscopy detection of HO_2 and $HOCH_2O_2$ radicals. The rate coefficient k was obtained from a computer simulation of [HO_2] absorption profiles based on a mechanism of eight elementary reactions.

(c) Same experimental system as for comment (b). The branching ratio was determined from a computer simulation of the quantum yields of HC(O)OH formation.

Preferred Values

$k = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.6 \times 10^{-15} \exp(2300/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 275–335 K.
k_2/k = 0.4 at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 1500$ K.
$\Delta(k_2/k) = 0.4$ at 298 K.

Comments on Preferred Values

The two studies (Veyret et al., 1989; Burrows et al., 1989) of the rate coefficient at 298 K are in good agreement and confirm that this reaction is fast compared with the HO_2 radical reactions with CH_3O_2 and $C_2H_5O_2$ radicals. The reaction is presumed to proceed via a six-membered cyclic intermediate, analogous to that proposed for the formation of HCHO, CH_3OH and O_2 from the interaction of CH_3O_2 radicals (Jenkin et al., 1988). Both the temperature dependence and the branching ratio require independent confirmation. In addition, there is the possibility that the rate coefficient could be both pressure and bath-gas dependent.

References

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II.A2a.55

$$\mathbf{HO_2 + C_2H_5O_2 \rightarrow O_2 + C_2H_5OOH}$$

$\Delta H^\circ = -159 \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.3 \pm 0.9) \times 10^{-12}$	295	Cattell et al., 1986	MM-IR-AS (a)
$5.6 \times 10^{-13} \exp[(650 \pm 125)/T]$	248–380	Dagaut et al., 1988	FP-AS (b)
$(5.3 \pm 1.0) \times 10^{-12}$	298		
$1.6 \times 10^{-13} \exp[(1260 \pm 130)/T]$	248–480	Fenter et al., 1993	FP-AS (c)
$(1.10 \pm 0.21) \times 10^{-11}$	298		
$6.9 \times 10^{-13} \exp[(702 \pm 69)/T]$	210–363	Maricq and Szente, 1994	FP-AS (d)
$(8.3 \pm 1.5) \times 10^{-12}$	295		
$(8.14 \pm 0.38) \times 10^{-12}$	298	Boyd et al., 2003	PLP-AS (e)

Comments

(a) MM spectrometry system with HO_2 and $C_2H_5O_2$ radicals generated simultaneously by photolysis of Cl_2 in the presence of C_2H_6-CH_3OH-O_2-N_2 mixtures at pressures of 3.2 mbar (2.4 Torr). HO_2 radicals were monitored by IR absorption with a tunable diode laser and $C_2H_5O_2$ radicals were monitored by UV absorption at 260 nm. The rate coefficient, k, was determined from the observed perturbation of the second-order kinetics of the HO_2 self-reaction when $C_2H_5O_2$ was present in large excess, and shown to be essentially independent of pressure over the range 3.2 mbar to 1013 mbar (2.4 Torr to 760 Torr).

(b) Flash photolysis of Cl_2 in the presence of C_2H_6-CH_3OH-O_2-N_2 mixtures at total pressures of 33 mbar to 533 mbar (25 Torr to 400 Torr). Composite transient absorption decay curves for HO_2 and $C_2H_5O_2$ radicals were measured at 230 nm, 250 nm and 280 nm. Kinetic analysis derived from computer modeling of experimental data.

(c) FP-UV absorption study of Cl_2-C_2H_6-O_2-N_2 mixtures at 1013 mbar (760 Torr) total pressure. Rate coefficients were derived from simultaneous computer analyses of several decay curves collected at different wavelengths.

(d) FP-UV absorption study of F_2-H_2-C_2H_6-O_2-N_2 mixtures at a total pressure of ∼270 mbar (∼ 200 Torr). Rate coefficients were derived from computer simulation of time-resolved decay curves.

(e) PLP-UV absorption study of H_2O_2-C_2H_6-O_2-N_2 mixtures at 1013 mbar (760 Torr) and 298 K. Conditions were chosen such that HO_2 was in excess, with initial concentration ratios $[HO_2]/[C_2H_5O_2]$ in the range 4–10. k was determined from simulation of transient decay traces recorded at 270 nm and either 210 nm or 220 nm. The signal at 270 nm was dominated by $C_2H_5O_2$ absorption, with its decay being almost entirely due to the reaction with HO_2. The signal at 210 nm or 220 nm was mainly due to HO_2 absorption, with its self-reaction making the major contribution to its removal.

Preferred Values

$k = 7.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.8 \times 10^{-13} \exp(900/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–500 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

The room temperature rate coefficients of Fenter et al. (1993), Maricq and Szente (1994) and Boyd et al. (2003) are in reasonable agreement with the previous direct studies of Cattell et al. (1986) and Dagaut et al. (1988). We have based our recommendations on the average value of k_{298} from these five studies. However, the temperature coefficient of Fenter et al. (1993) is almost a factor of two higher than those of Dagaut et al. (1988) and Maricq and Szente (1994), indicating a systematic error in one or more of the studies. The rate coefficients determined in all of these studies depend upon the values of σ (HO_2) and σ ($C_2H_5O_2$), the latter of which is not well established. Clearly more work is needed on this reaction and in the meantime we recommend an E/R value corresponding to the rounded-off mean of the three determinations (Dagaut et al., 1988; Fenter et al., 1993; Maricq and Szente, 1994), with relatively large error limits.

The FTIR spectroscopic product study of Wallington and Japar (1990) has shown that this reaction is dominated by a single channel at 298 K, to yield $C_2H_5OOH+O_2$. The results of Spittler et al. (2000) and Hasson et al. (2004) have confirmed this, with the former study demonstrating that this continues to be the case over the temperature range 284 K to 312 K.

References

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II.A2a.56

$$\begin{aligned} \mathbf{HO_2 + CH_3C(O)O_2} &\rightarrow \mathbf{O_2 + CH_3C(O)OOH} && \mathbf{(1)} \\ &\rightarrow \mathbf{O_3 + CH_3C(O)OH} && \mathbf{(2)} \\ &\rightarrow \mathbf{O_2 + OH + CH_3C(O)O} && \mathbf{(3)} \end{aligned}$$

$\Delta H^\circ(1) = -180 \text{kJ} \cdot \text{mol}^{-1}$

$\Delta H^\circ(2) = -132 \text{kJ} \cdot \text{mol}^{-1}$

$\Delta H^\circ(3) = -13 \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data (k=k_1+k_2+k_3)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.3 \times 10^{-13} \exp[(1040 \pm 100)/T]$	253–368	Moortgat et al., 1989	FP-AS (a)
$(1.3 \pm 0.3) \times 10^{-11}$	298		
$3.9 \times 10^{-13} \exp[(1350 \pm 250)/T]$	269–363	Crawford et al., 1999	PLP-IR-AS (b)
$(4.4 \pm 1.6) \times 10^{-11}$	297		
$6.4 \times 10^{-13} \exp[(925 \pm 120)/T]$	273–403	Tomas et al., 2001	FP-AS (c)
$(1.51 \pm 0.07) \times 10^{-11}$	293		
Branching Ratios			
$k_1/k \approx 0.75$	298	Niki et al., 1985	FTIR (d)
$k_2/k \approx 0.25$			
$k_2/k = 0.33 \pm 0.07$	253–368	Moortgat et al., 1989	FP-AS (e)
$k_1/k_2 = 3.3 \times 10^2 \exp[(-1430 \pm 480/T)]$	263–333	Horie and Moortgat, 1992	FTIR (f)
$k_1/k_2 = 2.7$	298		
$k_2/k = 0.12 \pm 0.04$	295	Crawford et al., 1999	PLP-FTIR (g)
$k_2/k = 0.20 \pm 0.02$	298–373	Tomas et al., 2001	FP-AS (h)
$k_1/k = 0.40 \pm 0.16$	298	Hasson et al., 2004	UVP-FTIR/HPLC (i)
$k_2/k = 0.20 \pm 0.08$	298		
$k_3/k = 0.40 \pm 0.16$	298		

Comments

(a) Flash photolysis of Cl_2 in the presence of CH_3CHO-CH_3OH-N_2 mixtures at total pressures of 800 mbar to 866 mbar (600 Torr to 650 Torr). [$CH_3C(O)O_2$] was monitored by UV absorption over the wavelength range 195 nm to 280 nm and the absorption cross-section measured relative to $\sigma(HO_2)=5.3 \times 10^{-18}$ cm^2 molecule^{-1} at 210 nm. Rate coefficients were derived from a computer simulation of absorption traces at a range of wavelengths, based on a mechanism including secondary removal of $CH_3C(O)O_2$. The mechanism assumed that the $CH_3C(O)O_2$+HO_2 reaction proceeds by channels (1) and (2).

(b) Pulsed laser photolysis of Cl_2-CH_3OH-CH_3CHO-O_2-N_2 mixtures at a total pressure of about 67 mbar (50 Torr). The progress of the reaction was followed by time-resolved UV absorption measurements over the range 200 nm to 300 nm and by monitoring [HO_2] by infrared laser diode absorption at 1117.5 cm^{-1}. Because of the difficulty of deconvoluting the UV spectra, values of k were determined from the infrared measurements by fitting the [HO_2] profiles using a detailed mechanism. The mechanism assumed that the $CH_3C(O)O_2$+HO_2 reaction proceeds by channels (1) and (2).

(c) Flash photolysis of Cl_2-CH_3CHO-CH_3OH-O_2-N_2 mixtures. The progress of the reaction was followed by time-resolved UV absorption measurements at 207 nm and 250 nm. Values of k were derived by simulation of the absorption measurements at 207 nm, using a detailed chemical mechanism. The mechanism assumed that the $CH_3C(O)O_2$+HO_2 reaction proceeds by channels (1) and (2).

(d) FTIR study of irradiated Cl_2-HCHO-CH_3CHO-O_2 mixtures. The branching ratio was based on the analysis of the products $CH_3C(O)OOH$, $CH_3C(O)OH$ and O_3, with the assumption that the reaction proceeds via channels (1) and (2).

(e) Derived from the same experiments as in Comment (a) by making allowance for absorption by O_3 product.

(f) FTIR study of irradiated $CH_3C(O)C(O)CH_3$ in the presence of Ar-O_2 mixtures at total pressures of 973 mbar to 1026 mbar (730 Torr to 770 Torr). The reaction products CO_2, CO, HCHO, HC(O)OH, $CH_3C(O)OH$, $CH_3C(O)OOH$, CH_3OH, H_2O_2 and O_3 were analyzed by matrix-isolation FTIR spectroscopy combined with a molecular-beam sampling technique. The branching ratio (k_1/k_2) was derived from the yields of $CH_3C(O)OH$ and O_3.

(g) UV irradiation of Cl_2-CH_3CHO-CH_3OH-air mixtures in a smog chamber fitted with an FTIR detection system. Branching ratios were derived from the yields of $CH_3C(O)OOH$ and $CH_3C(O)OH$ which gave k_2/k=0.10±0.02 at 295 K. Branching ratios were also derived from the O_3 yields determined from the kinetics traces at long reaction times in experiments performed to obtain the rate coefficient [see Comment (b)]. These experiments gave k_2/k=0.16±0.04 at 295 K. The value cited in the Table is a weighted mean of values from all the experiments. The O_3 yield measurements suggest only a small increase in k_2/k as temperature is lowered from 359 K to 265 K. The interpretation of the results assumed that the $CH_3C(O)O_2$+HO_2 reaction proceeds by channels (1) and (2).

(h) Branching ratios were derived from the O_3 yields at long reaction times in experiments described in Comment (c). There was no detectable change in k_2/k with change in temperature from 298 K to 373 K.

(i) Continuous photolysis of Cl_2 in the presence of CH_3CHO-CH_3OH-O_2-N_2 mixtures at a total pressure of 1066 mbar (800 Torr). Yields of CH_3OOH and $CH_3C(O)OOH$ (by HPLC) and CH_3OOH, $CH_3C(O)OOH$, $CH_3C(O)OH$ and CO_2 (by FTIR) were measured as a function of the initial concentration ratio $[CH_3OH]_0/[CH_3CHO]_0$ over the range 0 to 5, corresponding to conditions over which dominant removal of $CH_3C(O)O_2$ changes from its self reaction to the reaction with HO_2. The results were analysed by simulation using a detailed chemical mechanism taking account of the sequential formation of CH_3O_2 in the system.

Preferred Values

$k = 1.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.2 \times 10^{-13} \exp(980/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–400 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

Several studies have obtained evidence for the existence of reaction channels (1) and (2) (Niki et al., 1985; Moortgat et al., 1989; Horie and Moortgat, 1992; Crawford et al., 1999; Tomas et al., 2001), with reasonably consistent branching ratios being reported. However, the product yields measured in the recent study of Hasson et al. (2004), and their dependence on reagent conditions (see comment (i)), cannot be interpreted in terms of the reaction of $CH_3C(O)O_2$ with HO_2 proceeding via channels (1) and (2) alone. Hasson et al. (2004) interpreted their observations in terms of a major contribution to the reaction being made by the HO radical-forming channel (3), which also leads to subsequent formation of CH_3O_2. The results of the original product study of Niki et al. (1985) at high $[HO_2]/[CH_3C(O)O_2]$ (i.e. when $CH_3C(O)O_2$ is mainly removed via reaction with HO_2) also provide some support for this interpretation, through the reported observation of significant formation of CH_3OOH, and because the products of channels (1) and (2), $CH_3C(O)OH$ and $CH_3C(O)OOH$, only account for ≈50% of the loss of the $CH_3C(O)O_2$ precursor, CH_3CHO. The participation of channel (3) leads to potential errors in both the absolute and relative branching ratios in the majority of the earlier studies, through possible secondary formation of $CH_3C(O)OH$ from the reaction of CH_3O_2 with $CH_3C(O)O_2$, and the regeneration of both $CH_3C(O)O_2$ and HO_2 from reactions of HO. However, the relative branching ratio determination of Horie and Moortgat (1992) relied on the observed formation of $CH_3C(O)OOH$ and O_3, which are almost certainly specific products of reaction channels (1) and (2), respectively. The 298 K value of k_1/k_2=2.7 of Horie and Moortgat (1992) is in reasonable agreement with the value of 2 reported by Hasson et al. (2004). Independent verification of the participation of channel (3) is required.

There are substantial differences among the available kinetics measurements of k, which are also subject to further potential uncertainty because channel (3) was generally not taken into account in the analyses. Prior to recognition of this, Tyndall et al. (2001) have made a comparison of the studies of Moortgat et al. (1989) and Crawford et al. (1999) using updated absorption cross-sections and taking into account present understanding of the effects of the HO_2+CH_3CHO reaction. Their reanalysis of the [HO_2] decay traces published in these studies favours the values of k obtained by Moortgat et al. (1989). Tyndall et al. (2001) also point out that the values of k reported by Crawford et al. (1999) are high compared with those from analogous RO_2 + HO_2 reactions. Their conclusions are supported by the more recent study of Tomas et al. (2001) who used sufficiently low concentrations to avoid effects due to the HO_2+CH_3CHO reaction. Their results are in excellent agreement with those of Moortgat et al. (1989). Our preferred expression for k is therefore provisionally based on the mean of the values of E/R obtained by Moortgat et al. (1989) and Tomas et al. (2001), combined with an A-factor to give a value of k at 298 K which is the mean of the values obtained in the same two studies. It is recognised, however, that the likely regeneration of both $CH_3C(O)O_2$ and HO_2 from channel (3) under the experimental conditions employed in all the reported kinetics studies, leads to the possibility that the observed removal kinetics may underestimate the overall rate coefficient: although the extent of any underestimate could only be obtained from reanalysis of the original data. This is reflected in the uncertainty assigned to the preferred values.

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II.A2a.57

HO_2+ $HOCH_2CH_2O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate coefficients			
$(4.8\pm1.5) \times 10^{-12}$	298	Jenkin and Cox, 1991	MM-AS (a)
$\sim2.0 \times 10^{-11}$	298	Anastasi et al., 1991	PR-AS (b)
$(1.2\pm 0.3) \times 10^{-11}$	296	Murrells et al., 1991	PLP-AS (c)
$(1.17\pm 0.22) \times 10^{-11}$	298	Boyd et al., 2003	PLP-AS (d)

Comments

(a) MM study with $HOCH_2CH_2O_2$ radicals being generated from the photolysis of $HOCH_2CH_2I$ in the presence of O_2 and N_2 at total pressures of 13 mbar, 133 mbar and 1013 mbar (10 Torr, 100 Torr, and 760 Torr) in a slow flow system. The modulated absorption spectrum in the range 205 nm to 310 nm showed that additional transient species were absorbing, and these were ascribed to $HOCH_2CH_2OOI$ and HO_2. The rate coefficient was obtained from computer simulations of the time-resolved absorption waveforms at 220 nm to 310 nm for experiments at 13 mbar (10 Torr) pressure.

(b) Pulse radiolysis study, with $HOCH_2CH_2O_2$ radicals being generated from C_2H_4-O_2-H_2O-SF_6 and CH_3CH_2OH-O_2-SF_6 mixtures at total pressures of 1013 mbar (760 Torr). [$HOCH_2CH_2O_2$] was monitored by absorption at 230 nm and k derived from kinetic modelling of absorption profiles.

(c) Pulsed laser photolysis study, with $HOCH_2CH_2O_2$ radicals being generated from photolysis of $HOCH_2CH_2Cl$ in the presence of O_2 and N_2 at total pressures of 973 mbar (730 Torr). The rate coefficient was obtained by modelling the observed absorption profiles on the basis of a simplified mechanism of four reactions.

(d) PLP-UV absorption study of H_2O_2-C_2H_4-O_2-N_2 mixtures at 1013 mbar (760 Torr) and 298 K. Conditions were chosen such that HO_2 was in excess, with initial concentration ratios [HO_2]/[$HOCH_2CH_2O_2$] in the range 4–10. k was determined from simulation of transient decay traces recorded at 270 nm and either 210 nm or 220 nm. The signal at 270 nm was dominated by $HOCH_2CH_2O_2$ absorption, with its decay being almost entirely due to the reaction with HO_2. The signal at 210 nm or 220 nm was mainly due to HO_2 absorption, with its self-reaction making the major contribution to its removal.

Preferred Values

$k = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred value of k is based on the results of the pulsed laser photolysis studies of Murrells et al. (1991) and Boyd et al. (2003), which are in excellent agreement.

The earlier determinations of Jenkin and Cox (1991) and Anastasi et al. (1991) were subject to errors in the magnitude and shape of the $HOCH_2CH_2O_2$ absorption spectrum, respectively, which influenced the derived values of k. Murrells et al. (2001) demonstrated that cross-sections reported by Jenkin and Cox (1991), from molecular modulation studies of the photolysis of $HOCH_2CH_2I$, are low by a factor of approximately two. Jenkin and Cox (1991) made the assumption that the photolysis of $HOCH_2CH_2I$ in their system yielded entirely $HOCH_2CH_2O_2$ radicals, which was apparently not the case. Increasing $\sigma_{230}(HOCH_2CH_2O_2)$ by a factor of two in a re-interpretation (Murrells et al., 1991) of the data of Jenkin and Cox (1991) yielded a revised value of $k=(8.4\pm3.0)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 13 mbar pressure, in fair agreement with the current recommendation. The approximate value of k derived by Anastasi et al. (1991) from pulsed radiolysis experiments is almost a factor of two higher than our recommended value. We have not taken this value of Anastasi et al. (1991) into account, because of the differences in the absorption spectrum of the radical observed compared with the consistent spectra shapes reported by Jenkin and Cox (1991) and Murrells et al. (1991) (see the data sheet for the reaction: 2 $HOCH_2CH_2O_2 \rightarrow$ products).

References

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II.A2a.58

$$\begin{aligned} \mathbf{HO_2 + CH_3OCH_2O_2} &\rightarrow \mathbf{O_2 + CH_3OCH_2OOH} \quad \mathbf{(1)} \\ &\rightarrow \mathbf{O_2 + CH_3OCHO + H_2O} \quad \mathbf{(2)} \end{aligned}$$

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Branching Ratios			
k_1/k = 0.53±0.08	295	Wallington et al., 1993	P-FTIR (a)
k_2/k = 0.40±0.04			

Comments

(a) HO_2 and $CH_3OCH_2O_2$ radicals were generated from the steady-state photolysis of Cl_2 in the presence of CH_3OH-CH_3OCH_3-O_2 mixtures at a total pressure of 930 mbar (700 Torr). Branching ratios were derived from FTIR analyses of CH_3OCHO and CH_3OCH_2OOH products, which accounted for 93±12% of the CH_3OCH_3 loss.

Preferred Values

k_1/k = 0.60 at 298 K.
k_2/k = 0.40 at 298 K.

Reliability

$\Delta(k_1/k)$ = ±0.10 at 298 K.
$\Delta(k_2/k)$ = ±0.10 at 298 K.

Comments on Preferred Values

The reaction between HO_2 radicals and $CH_3OCH_2O_2$ radicals is analogous to that between HO_2 radicals and $HOCH_2O_2$ radicals in that there are two channels of nearly equal importance at room temperature producing (i) the hydroperoxide plus O_2 and (ii) a carbonyl product, H_2O and O_2. In contrast, the HO_2 reactions with unsubstituted alkyl peroxy radicals, RO_2, appear to have only a single channel, producing the alkyl hydroperoxide.

It has been proposed (Wallington et al., 1993) that the reaction between HO_2 and substituted RO_2 radicals yielding the carbonyl compounds proceeds through a six-member transition state similar to that suggested by Russell (1957) to explain the molecular products from the interactions of RO_2 radicals.

References

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Wallington, T. J., Hurley, M. D., Ball, J. C., and Jenkin, M. E.: Chem. Phys. Lett., 211, 41, 1993.

II.A2a.59

$$\begin{aligned} \mathbf{HO_2 + CH_3C(O)CH_2O_2} &\rightarrow \mathbf{O_2 + CH_3C(O)CH_2OOH} \quad &\mathbf{(1)} \\ &\rightarrow \mathbf{O_2 + HO + CH_3C(O)CH_2O} \quad &\mathbf{(2)} \end{aligned}$$

$\Delta H^\circ = -161 \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.0 \pm 1.0) \times 10^{-12}$	298	Bridier et al., 1993	FP-AS (a)
Branching Ratios			
$k_1/k = 0.33 \pm 0.10$	298	Hasson et al., 2004	UVP-FTIR/HPLC (b)
$k_2/k = 0.67 \pm 0.20$	298		

Comments

(a) Flash photolysis of Cl_2 in the presence of $CH_3C(O)CH_3$-CH_3OH-O_2-N_2 mixtures at a total pressure of 1013 mbar (760 Torr). The rate coefficient k was derived from a kinetic analysis of absorption-time profiles measured at 210 nm and 230 nm.

(b) Continuous photolysis of Cl_2 in the presence of $CH_3C(O)CH_3$-CH_3OH-O_2-N_2 mixtures at a total pressure of 1066 mbar (800 Torr). Yields of CH_3OOH, $CH_3C(O)OOH$ and $CH_3C(O)CH_2OOH$ (by HPLC) and $CH_3C(O)OOH$, HCHO, CO and CO_2 (by FTIR) were measured as a function of the initial concentration ratio $[CH_3OH]_0/[CH_3C(O)CH_3]_0$ over the range 0 to 0.5, corresponding to conditions over which dominant removal of $CH_3C(O)CH_2O_2$ changes from its self reaction to the reaction with HO_2. The results were analysed by simulation using a detailed chemical mechanism taking account of the sequential formation of $CH_3C(O)O_2$ and CH_3O_2 in the system.

Preferred Values

$k = 9.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value of k is provisionally based on the sole determination, reported by Bridier et al. (1993). Although this value seems reasonable in comparison with other $RO_2 + HO_2$ reactions, it has been obtained from the kinetic analysis of a complex chemical system, with only product channel (1) represented in the mechanism. The yields of $CH_3C(O)CH_2OOH$ measured in the recent product study of Hasson et al. (2004) suggest that other channels occur, with the best interpretation of the results obtained from inclusion of the HO radical-forming channel (2) as the main product channel. Under these circumstances, the likely regeneration of both $CH_3C(O)CH_2O_2$ and HO_2 under the experimental conditions employed by Bridier et al. (1993) leads to the possibility that the observed removal kinetics may underestimate the overall rate coefficient: although the extent of any underestimate could only be obtained from reanalysis of the original data. Independent verification of the participation of channel (2) is therefore required, in addition to further kinetics studies to reduce the uncertainty in the preferred value.

References

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II.A2a.60

HO_2 + HCHO → $HOCH_2OO$

$\Delta H^\circ = -68.1 \mathrm{kJ \cdot mol^{-1}}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.1 \pm 0.4) \times 10^{-13}$	273	Barnes et al., 1985	S-FTIR (a)
$7.7 \times 10^{-15} \exp[(625 \pm 550)/T]$	275–333	Veyret et al., 1989	FP-AS (b)
$(6.0 \pm 0.7) \times 10^{-14}$	295		

Comments

(a) FTIR spectroscopic study in a 420 L reaction chamber. HO_2 radicals were generated from the thermal decomposition of HO_2NO_2 in the presence of HCHO, NO_2 and synthetic air at a total pressure of 530 mbar (400 Torr). The rate coefficient, k, was obtained from a computer simulation of the rates of decay of HCHO and rates of formation of HC(O)OH and $HOCH_2O_2NO_2$, based on a reaction scheme consisting of nine elementary reactions.

(b) Flash photolysis of Cl_2 in the presence of HCHO or CH_3OH and O_2 with long-path absorption measurements of HO_2 and $HOCH_2O_2$ radicals at total pressures of 110 mbar to 230 mbar (85 Torr to 170 Torr). The rate coefficient, k, was obtained from a computer simulation of the absorption profiles based on a mechanism of five elementary reactions.

Preferred Values

$k = 7.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 9.7 \times 10^{-15} \exp(625/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 275–333 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 600$ K.

Comments on Preferred Values

The studies of Barnes et al. (1985) and of Veyret et al. (1989) are in excellent agreement regarding this rate coefficient, and both are in good agreement with the earlier data of Veyret et al. (1982). The preferred expression for the rate coefficient is derived by taking an average value of the rate coefficients of Barnes et al. (1985) [k(273 K)=1.1×10^{-13} cm^3 molecule^{-1} s^{-1}] and Veyret et al. (1989) [k(275 K)=8.0×10^{-14} cm^3 molecule^{-1} s^{-1}] together with the value of E/R determined by Veyret et al. (1989).

This reaction is believed to proceed via the initial formation of the adduct radical, HO_2CH_2O, which rapidly isomerizes to the product radical, $HOCH_2OO$ via H-atom transfer.

References

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II.A2a.61

$HOCH_2OO \rightarrow HO_2 + HCHO$

$\Delta H^\circ = 68.1\text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

k/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
20^{+20}_{-10}	273	Barnes et al., 1985	S-FTIR (a)
$2.0 \times 10^{12}\exp[-(7000 \pm 2000)/T]$	275–333	Veyret et al., 1989	FP-AS (b)
100±50	295		

Comments

(a) FTIR spectroscopic study in a 420 L reaction chamber. HO_2 radicals were generated from thermal decomposition of HO_2NO_2 in the presence of HCHO, NO_2 and synthetic air at a total pressure of 533 mbar (400 Torr). The rate coefficient, k, was derived from a computer simulation of the rates of decay of HCHO and rates of formation of HCOOH and $HOCH_2O_2NO_2$ based on a reaction scheme consisting of nine elementary reactions.

(b) Flash photolysis of Cl_2 in the presence of HCHO or CH_3OH and O_2 with long-path absorption measurements of $[HO_2]$ and $[HOCH_2O_2]$ at total pressures of 113 mbar to 227 mbar (85 Torr to 170 Torr). The rate coefficient, k, was obtained from a computer simulation of the absorption profiles based on a mechanism of five elementary reactions.

Preferred Values

$k = 1.5 \times 10^2\ \text{s}^{-1}$ at 298 K.
$k = 2.4 \times 10^{12} \exp(-7000/T)\ \text{s}^{-1}$ over the temperature range 275–330 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 2000$ K.

Comments on Preferred Values

The studies of Barnes et al. (1985) and of Veyret et al. (1989) are in good agreement regarding the rate coefficient of this reaction. The preferred rate equation has been obtained by taking the average of the rate coefficients at 273 K to 275 K from these studies together with the *E/R* determined by Veyret et al. (1989). It should be pointed out that the value of the equilibrium constant, K_1, for the reaction $HO_2+HCHO \rightleftharpoons HOCH_2O_2$ (1,-1), $K_1=5.0\times10^{-16}\ \text{cm}^3\ \text{molecule}^{-1}$ at 298 K, derived from the kinetic study of Veyret et al. (1989) (which is identical to the value obtained from our recommended data for k_1 and k_{-1}), is in excellent agreement with the value of $K_1=4.0\times10^{-16}\ \text{cm}^3\ \text{molecule}^{-1}$ at 298 K obtained independently by Burrows et al. (1989) from molecular modulation studies. The above value of K_1 is, however, considerably smaller than the value of $K_1=3.4\times10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}$ at 298 K reported by Zabel et al. (1987) from EPR spectroscopic measurements of the ratio of concentrations of HO_2 and $HOCH_2O_2$ radicals in the photolysis of HCHO-O_2 mixtures.

References

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Appendix A3: NO_3 + VOC

II.A3.62

$$\mathbf{NO_3 + CH_4 \rightarrow HNO_3 + CH_3}$$

$\Delta H° = 12.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<4 \times 10^{-16}$	298	Burrows et. al., 1985	(a)
$\leq 2 \times 10^{-17}$	298 ± 2	Wallington et. al., 1986	FP-A (b)
$\leq 8 \times 10^{-19}$	302	Boyd et. al., 1991	(c)
Relative Rate Coefficients			
$< 5 \times 10^{-21}$	~ 298	Cantrell et. al., 1987	(d)

Comments

(a) NO_3 radicals were generated by the modulated photolysis of Cl_2-$ClONO_2$-N_2 or F_2-HNO_3-N_2 mixtures and monitored by optical absorption at 662 nm.

(b) NO_3 radicals were generated by the flash photolysis of $ClONO_2$-He mixtures and detected by optical absorption at 662 nm.

(c) Stopped-flow system with optical absorption detection of NO_3 radicals at 662 nm. The occurrence of secondary reactions was expected to lead to a stoichiometry factor of ≥ 2, resulting in the upper limit to the rate coefficient cited in the table.

(d) Relative rate method. Upper limit to the rate coefficient was derived from the absence of observed CO and CO_2 formation after addition of CH_4 to N_2O_5-NO_3-NO_2-N_2 mixtures. An equilibrium constant for the $NO_2+NO_3 \leftrightarrow N_2O_5$ reactions of 2.90×10^{-11} cm^3 molecule^{-1} at 298 K (IUPAC, current recommendation) has been used to derive the rate coefficient cited.

Preferred Values

$k < 1 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based on the upper limits to the rate coefficients obtained by Cantrell et al. (1987) and Boyd et al. (1991), and is consistent with the higher upper limits reported by Burrows et al. (1985) and Wallington et al. (1986).

References

Boyd, A. A., Canosa-Mas, C. E., King, A. D., Wayne, R. P., and Wilson, M. R.: J. Chem. Soc. Faraday Trans., 87, 2913, 1991.
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Wallington, T. J., Atkinson, R., Winer, A. M., and Pitts Jr., J. N.: J. Phys. Chem., 90, 4640, 1986.

II.A3.63

$NO_3 + C_2H_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.9 \times 10^{-13} \exp[-(2742 \pm 542)/T]$	295–523	Canosa-Mas et al., 1988a, b	DF-A
$(5.1 \pm 3.5) \times 10^{-17}$	295 ± 2		
Relative Rate Coefficients			
$\leq 3.0 \times 10^{-17}$	298 ± 2	Atkinson et al., 1987	RR (a)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5. The concentrations of acetylene and ethene (the reference organic) were measured by GC. The measured rate coefficient ratio of $k(NO_3+C_2H_2)/k(NO_3+C_2H_4) \leq 0.14$ at 298 ± 2 K is placed on an absolute basis by use of a rate coefficient of $k(NO_3+C_2H_4) = 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k < 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The measurement of rate coefficients for low reactivity organics is complicated by the possibility of secondary reactions, leading to erroneously high measured rate coefficients. The relative rate measurements of Atkinson et al. (1987) show C_2H_2 to be significantly less reactive than C_2H_4. The preferred value of the upper limit to the rate coefficient is sufficiently high to be consistent with the data of Canosa-Mas et al. (1988a). Until there are confirmatory data for the reported temperature dependence of this rate coefficient (Canosa-Mas et al. (1988b), no temperature dependence is recommended.

References

Atkinson, R., Aschmann, S. M., and Goodman, M. A.: Int. J. Chem. Kinet., 19, 299, 1987.
Canosa-Mas, C., Smith, S. J., Toby, S., and Wayne, R. P.: J. Chem. Soc. Faraday Trans., 2, 84, 247, 1988a.
Canosa-Mas, C., Smith, S. J., Toby, S., and Wayne, R. P.: J. Chem. Soc. Faraday Trans., 2, 84, 263, 1988b.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/.

II.A3.64

$NO_3 + C_2H_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
6.29×10^{-12} exp[-(3103 ± 145)/T]	295–523	Canosa-Mas et al., 1988a, b	DF-A
$(1.85 \pm 0.24) \times 10^{-16}$	295 ± 2		
$(1.7 \pm 0.5) \times 10^{-16}$	300	Biggs et al., 1991; Boyd et al., 1991	(a)
Relative Rate Coefficients			
$(2.16 \pm 0.20) \times 10^{-16}$	296 ± 2	Atkinson et al., 1988	RR (b)

Comments

(a) Stopped-flow technique with optical absorption of the NO_3 radical at 662 nm. The influence of the reaction $NO_2+NO_3+He\rightarrow N_2O_5+He$ was taken into account by numerical modeling, leading to a stoichiometry factor for NO_3 radical decays of ∼1.9 and the cited rate coefficient for the elementary NO_3 + ethene reaction.

(b) NO_3 radicals were generated by the thermal decomposition of N_2O_5. A series of rate coefficient ratios were measured, with the concentrations of the organic compounds involved being measured by GC. Based on rate coefficient ratios for the sets of organic compounds ethene vs. 2,3-dimethylbutane, 2,3-dimethylbutane vs. tetrahydrofuran, tetrahydrofuran vs. propene, propene vs. thiophene, thiophene vs. bicyclo[2.2.2]-2-octene, and bicyclo[2.2.2]-2-octene vs. *trans*-2-butene, a rate coefficient ratio of k(NO_3 + ethene)/k(NO_3 + *trans*-2-butene) = 0.000554±0.000050 was obtained. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of k(NO_3 + *trans*-2-butene) = 3.89×10^{-13} cm^3 molecule^{-1} s^{-1} at 296 K (Atkinson, 1997).

Preferred Values

$k = 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.3 \times 10^{-12}$ exp(-2880/T) cm^3 molecule^{-1} s^{-1} over the temperature range 270–340 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred rate coefficient is derived using the absolute rate coefficient data of Canosa-Mas et al. (1988a, b) and the relative rate coefficient of Atkinson et al. (1988). These data were fitted to the three parameter expression $k=CT^2$ exp(-D/T), resulting in $k=4.88\times10^{-18}\ T^2$ exp(-2282/T) cm^3 molecule^{-1} s^{-1} over the temperature range 295–523 K. The preferred Arrhenius expression, $k=A$ exp(-B/T), is centered at 300 K and is derived from the three parameter expression with $A=C\ e^2T^2$ and $B=D+2T$.

The preferred rate coefficient is in agreement with the 300 K rate coefficient of Biggs et al. (1991) and Boyd et al. (1991).

References

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Canosa-Mas, C., Smith, S. J., Toby, S., and Wayne, R. P.: J. Chem. Soc. Faraday Trans., 2, 84, 263, 1988b.

II.A3.65

$$\mathbf{NO_3 + C_2H_6 \rightarrow HNO_3 + C_2H_5}$$

$\Delta H^\circ = -3.9\,\mathrm{kJ \cdot mol^{-1}}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 4 \times 10^{-18}$	298 ± 2	Wallington et al., 1986	FP-A (a)
$5.7 \times 10^{-12} \exp[-(4426 \pm 337)/T]$	453–553	Bagley et al., 1990	DF-A
2.0×10^{-18}	298*		
$\leq (2.7 \pm 0.2) \times 10^{-17}$	302	Boyd et al., 1991	(b)

Comments

(a) NO_3 radicals were generated by the flash photolysis of $ClONO_2$-He mixtures and detected by optical absorption at 662 nm.

(b) Stopped-flow system with optical absorption detection of the NO_3 radical at 662 nm. Secondary reactions were expected to lead to a stoichiometry factor of ≥2, leading to the upper limit to the rate coefficient cited in the table.

Preferred Values

$k < 1 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

Extrapolation of the absolute rate coefficients obtained by Bagley et al. (1990) over the temperature range 453–553 K to 298 K leads to a 298 K rate coefficient of 2×10^{-18} cm^3 molecule^{-1} s^{-1}, probably uncertain to at least a factor of 2 due to the long extrapolation and possible non-Arrhenius behavior of the rate coefficient for this reaction. The preferred upper limit is based on the upper limit of Wallington et al. (1986) and extrapolation to 298 K of the elevated temperature rate coefficients of Bagley et al. (1990).

References

Bagley, J. A., Canosa-Mas, C., Little, M. R., Parr, A. D., Smith, S. J., Waygood, S. J., and Wayne, R. P.: J. Chem. Soc. Faraday Trans., 86, 2109, 1990.
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Wallington, T. J., Atkinson, R., Winer, A. M., and Pitts Jr., J. N.: J. Phys. Chem., 90, 4640, 1986.

II.A3.66

$NO_3 + C_3H_6 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.74 \times 10^{-13} \exp[-(1171 \pm 66)/T]$	298–423	Canosa-Mas et al., 1991	DF-A
$(9.3 \pm 1.2) \times 10^{-15}$	298		
Relative Rate Coefficients			
$(5.4 \pm 1.4) \times 10^{-15}$	300	Morris and Niki, 1974	RR (a)
$(9.2 \pm 0.6) \times 10^{-15}$	300	Japar and Niki, 1975	RR (a)
$(6.4 \pm 1.3) \times 10^{-15}$	298 ± 1	Atkinson et al., 1984	RR (a)
$(7.4 \pm 2.0) \times 10^{-15}$	298 ± 1	Atkinson et al., 1984	RR (b)
$(9.45 \pm 0.47) \times 10^{-15}$	296 ± 2	Atkinson et al., 1988	RR (c)

Comments

(a) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The experimental data were relative to the equilibrium coefficient K for the $NO_3+NO_2 \leftrightarrow N_2O_5$ reactions, and are placed on an absolute basis by use of $K=2.90\times10^{-11}$ cm^3 molecule^{-1} at 298 K and 2.26×10^{-11} cm^3 molecule^{-1} at 300 K (IUPAC, current recommendation).

(b) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The concentrations of propene and *trans*-2-butene were measured by GC, and a rate coefficient ratio of k(NO_3 + propene)/k(NO_3 + *trans*-2-butene) = 0.019±0.005 obtained. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of k(NO_3 + *trans*-2-butene) = 3.90×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 1997).

(c) NO_3 radicals were generated by the thermal decomposition of N_2O_5. A series of rate coefficient ratios were measured, with the concentrations of the organic compounds involved being measured by GC. Based on rate coefficient ratios for the sets of organic compounds, propene vs. thiophene, thiophene vs. bicyclo[2.2.2]-2-octene, and bicyclo[2.2.2]-2-octene vs. *trans*-2-butene, a rate coefficient ratio of k(NO_3 + propene)/k(NO_3 + *trans*-2-butene) = 0.0243±0.0012 at 296±2 K was obtained. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of k(NO_3 + *trans*-2-butene) = 3.89×10^{-13} cm^3 molecule^{-1} s^{-1} at 296 K (Atkinson, 1997).

Preferred Values

$k = 9.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.6 \times 10^{-13} \exp(-1155/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–430 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values are derived using the room temperature relative rate coefficient of Atkinson et al. (1988) and the 298–423 K absolute rate coefficients of Canosa-Mas et al. (1991). The preferred 298 K rate coefficient is in reasonable agreement with the relative rate measurements of Morris and Niki (1974), Japar and Niki (1975) and Atkinson et al. (1984) when the differing values of the equilibrium constant used for the $N_2O_5 \leftrightarrow NO_3+NO_2$ reactions are taken into account, and considering the uncertainties in this equilibrium constant.

The NO_3 radical reaction with propene proceeds by initial addition, leading to the formation under simulated tropospheric conditions of HCHO, CH_3CHO and $CH_3C(O)CH_2ONO_2$ (Bandow et al., 1980; Shepson et al., 1985; Barnes et al., 1990; Hjorth et al., 1990; Atkinson, 1997).

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Atkinson, R.: J. Phys. Chem. Ref. Data, 26, 215, 1997.
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Shepson, P. B., Edney, E. O., Kleindienst, T. E., Pittman, J. H., Namie, G. R., and Cupitt, L. T.: Environ. Sci. Technol., 19, 849, 1985.

II.A3.67

$$\begin{aligned} \mathbf{NO_3 + C_3H_8} &\rightarrow \mathbf{HNO_3 + CH_3CH_2CH_2} \quad &\mathbf{(1)} \\ &\rightarrow \mathbf{HNO_3 + CH_3CHCH_3} \quad &\mathbf{(2)} \end{aligned}$$

ΔH^0 (1) = -3.5 kJ·mol^{-1}
ΔH^0 (2) = -17.7 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq(4.8 \pm 1.7) \times 10^{-17}$	298	Boyd et al., 1991	(a)

Comments

(a) Stopped-flow system with optical absorption detection of the NO_3 radical at 662 nm. The occurrence of secondary reactions is expected to lead to a stoichiometry factor of $\geq$2, resulting in the upper limit to the rate coefficient cited in the table.

Preferred Values

$k \leq 7 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based on the upper limit derived by Boyd et al. (1991).

References

Boyd, A., Canosa-Mas, C. E., King, A. D., Wayne, R. P., and Wilson, M. R.: J. Chem. Soc. Faraday Trans., 87, 2913, 1991.

II.A3.68

$NO_3 + n\text{-}C_4H_{10} \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 2 \times 10^{-17}$	298 ± 2	Wallington et al., 1986	FP-A (a)
$(4.5 \pm 0.6) \times 10^{-17}$	298	Bagley et al., 1990	DF-A
$(1.44 \pm 0.12) \times 10^{-16}$	333		
$(4.6 \pm 1.2) \times 10^{-16}$	373		
$(1.12 \pm 0.12) \times 10^{-15}$	423		
$(3.2 \pm 0.3) \times 10^{-15}$	473		
$(9.0 \pm 0.4) \times 10^{-15}$	523		
Absolute Rate Coefficients			
$(6.6 \pm 1.7) \times 10^{-17}$	296 ± 2	Atkinson et al., 1984	RR (b)

Comments

(a) NO_3 radicals were generated by the flash photolysis of $ClONO_2$ at wavelengths $>$180 nm and monitored by optical absorption at 662 nm.

(b) NO_3 radicals were produced by the thermal decomposition of N_2O_5, and the concentrations of n-butane and n-heptane (the reference organic) were measured by GC. A rate coefficient ratio of $k(NO_3 + n\text{-butane})/k(NO_3 + n\text{-heptane}) = 0.48 \pm 0.12$ was obtained and is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + n\text{-heptane}) = 1.37 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 296 K (Atkinson, 1991).

Preferred Values

$k = 4.6 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.8 \times 10^{-12} \exp(-3280/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–430 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

The preferred values are based on the absolute rate coefficients measured by Bagley et al. (1990) over the temperature range 298–423 K (at temperatures above 423 K the Arrhenius plot exhibits upward curvature, especially above 473 K). A least-squares analysis of the 298–423 K rate coefficients of Bagley et al. (1990) results in the preferred Arrhenius expression. The preferred rate coefficient at 298 K is at least a factor of 2 higher than the upper limit reported by Wallington et al. (1986), but is in agreement within the measurement uncertainties with the relative rate coefficient of Atkinson et al. (1984). At room temperature and below the reaction proceeds mainly by H-atom abstraction from the CH_2 groups (Bagley et al., 1990; Atkinson, 1991).

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Bagley, J. A., Canosa-Mas, C., Little, M. R., Parr, A. D., Smith, S. J., Waygood, S. J., and Wayne, R. P.: J. Chem. Soc. Faraday Trans., 86, 2109, 1990.
Wallington, T. J., Atkinson, R., Winer, A. M., and Pitts Jr., J. N.: J. Phys. Chem., 90, 4640, 1986.

II.A3.69

NO_3 + CH_2=C(CH_3)CH=CH_2 (isoprene) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.3 \pm 0.14) \times 10^{-12}$	298	Benter and Schindler, 1988	DF-MS
3.03×10^{-12} exp[-(450 ± 70)/T]	251–381	Dlugokencky and Howard, 1989	F-LIF (a)
$(6.52 \pm 0.78) \times 10^{-13}$	297		
$(7.30 \pm 0.44) \times 10^{-13}$	298	Wille et al., 1991	DF-MS
$(8.26 \pm 0.60) \times 10^{-13}$	298	Wille et al., 1991; Lancar et al., 1991	DF-MS
$(1.07 \pm 0.20) \times 10^{-12}$	295 ± 2	Ellermann et al., 1992	PR-A (b)
$(7.3 \pm 0.2) \times 10^{-13}$	298 ± 2	Suh et al., 2001	F-CIMS (c)
Relative Rate Coefficients			
$(5.94 \pm 0.16) \times 10^{-13}$	295 ± 1	Atkinson et al., 1984	RR (d)
$(1.21 \pm 0.20) \times 10^{-12}$	298 ± 2	Barnes et al., 1990	RR (e)
$(6.86 \pm 0.55) \times 10^{-13}$	298	Berndt and Böge, 1997	RR (f)

Comments

(a) NO_3 radicals were generated by thermal decomposition of N_2O_5 in a flow system at total pressures of 1.0–1.1 Torr (1.3–1.5 mbar), and monitored by LIF.

(b) NO_3 radicals were generated by pulse radiolysis of SF_6-HNO_3-isoprene mixtures at 1 bar total pressure, and monitored by optical absorption at 662 nm.

(c) NO_3 radicals were generated by thermal decomposition of N_2O_5 in a flow system at total pressures of 5.1–6.0 Torr (6.8–8.0 mbar), and monitored by CIMS using the reaction $NO_3+SF_6^- \rightarrow NO_3^-+SF_6$.

(d) Relative rate method carried out at atmospheric pressure of air. NO_3 radicals were generated by thermal decomposition of N_2O_5. The concentrations of isoprene and *trans*-2-butene (the reference compound) were measured by GC. Small corrections (2–4%) to the measured isoprene concentrations were made to take into account the gas-phase reaction of isoprene with NO_2 (Atkinson et al., 1984; Atkinson, 1997). The resulting rate coefficient ratio of k(NO_3 + isoprene)/k(NO_3 + *trans*-2-butene) = 1.53±0.04 is placed on an absolute basis by use of a rate coefficient of k(NO_3 + *trans*-2-butene) = 3.88×10^{-13} cm^3 molecule^{-1} s^{-1} at 295 K (Atkinson, 1997).

(e) Relative rate method carried out at atmospheric pressure of synthetic air. NO_3 radicals were generated by thermal decomposition of N_2O_5. The concentrations of isoprene and *trans*-2-butene (the reference compound) were measured by GC. No corrections for the reaction of isoprene with NO_2 were found to be necessary. The measured rate coefficient ratio of k(NO_3 + isoprene)/k(NO_3 + *trans*-2-butene) = 3.1±0.5 is placed on an absolute basis by use of a rate coefficient of k(NO_3 + *trans*-2-butene) = 3.90×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 1997).

(f) Relative rate method carried out in a flow system at a total pressure of 6.8 mbar (5.1 Torr) of N_2. NO_3 radicals were generated by thermal decomposition of N_2O_5. The concentrations of isoprene and *trans*-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(NO_3 + isoprene)/k(NO_3 + *trans*-2-butene) = 1.76±0.14 is placed on an absolute basis by use of a rate coefficient of k(NO_3 + *trans*-2-butene) = 3.90×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 1997).

Preferred Values

$k = 7.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.15 \times 10^{-12}$ exp(-450/T) cm^3 molecule^{-1} s^{-1} over the temperature range 250–390 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The measured room temperature rate coefficients range over a factor of 2.2, irrespective of whether absolute or relative rate methods were used. The study of Wille et al. (1991) is stated to supersede the earlier study of Benter and Schindler (1988) carried out over a more restricted range of conditions (and in which heterogeneous reactions between isoprene and F_2 could have occurred; Wille et al., 1991). The only temperature dependent measurements of the kinetics of this reaction are from Dlugokencky and Howard (1989). The preferred 298 K rate coefficient is an average of the room temperature absolute and relative rate coefficients of Dlugokencky and Howard (1989), Wille et al. (1991), Lancar et al. (1991), Suh et al. (2001), Atkinson et al. (1984) and Berndt and Böge (1997), which are in reasonably good agreement. The temperature dependence of Dlugokencky and Howard (1989) is accepted, and the pre-exponential factor is calculated from the 298 K preferred rate coefficient and the temperature dependence.

The reaction proceeds by initial addition of the NO_3 radical to the carbon-carbon double bonds (Atkinson, 1997). At low pressures the products are NO_2 plus an oxirane (Atkinson, 1997). The formation yield of the oxirane decreases with increasing total pressure and with increasing O_2 concentration (Atkinson, 1997), with oxirane formation at atmospheric pressure of air being of no importance (Atkinson, 1997; Skov et al., 1994). Using in situ FTIR spectroscopy, Skov et al. (1992) reported that the products formed at atmospheric pressure of air are $O_2NOCH_2C(CH_3)$=CHCHO as the major product, and with $O_2NOCH_2CH=C(CH_3)CHO$, $O_2NOCH_2C(O)C(CH_3)=CH_2$, $O_2NOCH_2CH(OH)C(CH_3)=CH_2$ and $O_2NOCH_2C(CH_3)=CHCH_2OH$ as minor products. Using atmospheric pressure ionization tandem mass spectrometry Kwok et al. (1996) observed $O_2NOCH_2C(CH_3)$=CHCHO (and isomers), $O_2NOCH_2C(CH_3)=CHCH_2OH$ (and isomers), $O_2NOCH_2C(CH_3)=CHCH_2OOH$ (and isomers), and $HOCH_2C(CH_3)$=CHCHO (and isomers) as products of the reaction (again at atmospheric pressure of air). Kwok et al. (1996) also observed the formation of methacrolein and methyl vinyl ketone, with measured formation yields of each of these α,β-unsaturated carbonyls being $3.5\pm1.4\%$.

The FTIR study of Skov et al. (1992) indicates that the NO_3 radical adds dominantly to the 1- and 4-positions, in a 3.5:1 ratio. At atmospheric pressure of air, the reaction then proceeds mainly by,

$$
\begin{array}{ll}
NO_3 + CH_2{=}C(CH_3)CH{=}CH_2 \rightarrow & O_2NOCH_2C(CH_3)CH{=}CH_2 \\
 & \qquad\qquad \updownarrow \\
 & O_2NOCH_2C(CH_3){=}CHCH_2
\end{array}
$$

followed by addition of O_2 to form the corresponding peroxy radicals $O_2NOCH_2C(OO)(CH_3)CH=CH_2$ and $O_2NOCH_2C(CH_3)CH=CH_2OO$. These peroxy radicals then react with NO, NO_2, HO_2 and organic peroxy radicals (Atkinson, 1997), depending on the concentrations of these species.

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II.A3.70

NO_3 + α-Pinene → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.19 \times 10^{-12} \exp[(490 \pm 70)/T]$	261–384	Dlugokencky and Howard, 1989	F-LIF(a)
$(6.18 \pm 0.74) \times 10^{-12}$	298		
$3.5 \times 10^{-13} \exp[(841 \pm 144)/T]$	298–423	Martínez et al., 1998	DF-LIF(b)
$(5.9 \pm 0.8) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(5.82 \pm 0.16) \times 10^{-12}$	295 ± 1	Atkinson et al., 1984	RR(c)
$(6.56 \pm 0.94) \times 10^{-12}$	298 ± 2	Barnes et al., 1990	RR(d)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 at ∼400 K. Experiments were carried out in a low-pressure flow tube at ∼1.3–1.4 mbar of He diluent. The NO_2 yield at 1.3 mbar He and 298 K was 67%.

(b) Carried out under conditions such that a second-order kinetic analysis was necessary.

(c) NO_3 radicals were generated by the thermal decomposition of N_2O_5. The concentrations of α-pinene and 2-methyl-2-butene (the reference compound) were monitored by GC in reacting N_2O_5-NO_2-α-pinene-2-methyl-2-butene-air mixtures at 980 mbar pressure in a ∼6400 L Teflon chamber. The measured rate coefficient ratio k(NO_3 + α-pinene)/k(NO_3 + 2-methyl-2-butene) = 0.621±0.017 is placed on an absolute basis by use of a rate coefficient at 295 K of k(NO_3 + 2-methyl-2-butene) = 9.37×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003a).

(d) NO_3 radicals were generated by the thermal decomposition of N_2O_5. The concentrations of α-pinene and 2-methyl-2-butene (the reference compound) were monitored by GC in reacting N_2O_5-α-pinene-2-methyl-2-butene-air mixtures at 1 bar pressure in a 420 L glass reaction vessel. The measured rate coefficient ratio k(NO_3 + α-pinene)/k(NO_3 + 2-methyl-2-butene) = 0.70±0.10 is placed on an absolute basis by use of a rate coefficient at 298 K of k(NO_3 + 2-methyl-2-butene) = 9.37×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003a).

Preferred Values

$k = 6.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.2 \times 10^{-12} \exp(490/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–390 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The room temperature relative rate coefficients of Atkinson et al. (1984) and Barnes et al. (1990) and the absolute rate coefficients of Dlugokencky and Howard (1989) and Martínez et al. (1998) are in excellent agreement. However, the temperature dependencies obtained by Dlugokencky and Howard (1989) and Martínez et al. (1998) differ significantly. Because the study of Dlugokency and Howard (1989) extends to lower temperatures representative of the troposphere, the data from the studies of Atkinson et al. (1984), Dlugokencky and Howard (1989) and Barnes et al. (1990) are used in the evaluation of the rate coefficient for this reaction. The preferred values are obtained from a least-squares fit of the rate coefficients of Atkinson et al. (1984), Dlugokencky and Howard (1989) and Barnes et al. (1990). The is no evidence for a pressure dependence of the rate coefficient over the range ∼1–1000 mbar, at least at room temperature.

The reaction proceeds by initial addition of NO_3 to the C=C bond. At low pressures or in the absence of O_2, the initially formed nitrooxyalkyl radicals eliminate NO_2 and form α-pinene oxide (Dlugokencky and Howard, 1989; Atkinson, 1991; Berndt and Böge, 1997). At atmospheric pressure of air, O_2 addition to the nitrooxyalkyl radicals forms two nitrooxyalkyl peroxy radicals, although some α-pinene oxide (3±0.5%) is still observed at 1 bar of air (Wängberg et al., 1997). The nitrooxyalkyl peroxy radicals then react with HO_2 radicals, organic peroxy radicals, NO, NO_2, and NO_3 radicals, leading to the observed products (Atkinson and Arey, 2003a, b). Under laboratory conditions, the observed products and their yields at atmospheric pressure of air are: pinonaldehyde, 62±4% (Wängberg et al., 1997) and 69% (Hallquist et al., 1999); 2-hydroxypinan-3-nitrate, 5±0.4% (Wängberg et al., 1997); 3-oxopinan-2-nitrate, 3±0.2% (Wängberg et al., 1997); and α-pinene oxide, 3±0.5% (Wängberg et al., 1997), with a total organic nitrate yield of 14–19% (Wängberg et al., 1997; Hallquist et al., 1999). Note that the products formed in the atmosphere, and their yields, may be different from those observed in laboratory studies, because of the differing concentrations (both absolute and relative) of HO_2, RO_2 and NO_3 radicals and NO and NO_2.

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II.A3.71

$NO_3 + HCHO \rightarrow HNO_3 + HCO$

$\Delta H° = -57.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
5.6×10^{-16}	298 ± 2	Cantrell et al., 1985	(a)
Relative Rate Coefficients			
$(5.01 \pm 0.41) \times 10^{-16}$	298 ± 1	Atkinson et al., 1984	(b,c)
$(8.4 \pm 1.5) \times 10^{-16}$	298 ± 2	Cantrell et al., 1985	(c,d)
$(1.21 \pm 0.25) \times 10^{-15}$	295 ± 2	Hjorth et al., 1988	(b,c,d,e)

Comments

(a) NO_3 radicals were generated in situ from the reaction $NO_2+O_3 \rightarrow NO_3+O_2$. NO_3 radical concentrations were measured by differential optical absorption spectroscopy (DOAS), and the rate coefficient derived from the concentrations of reactants and products measured by FTIR absorption spectroscopy and by DOAS (for the NO_3 radical and NO_2).

(b) NO_3 radicals were generated by the thermal decomposition of N_2O_5.

(c) Relative to the equilibrium coefficient K for the reactions $NO_2+NO_3 \leftrightarrow N_2O_5$. The experimental data are placed on an absolute basis by use of an equilibrium coefficient of $K=2.90\times10^{-11}$ cm^3 molecule^{-1} at 298 K and 4.22×10^{-11} cm^3 molecule^{-1} at 295 K (IUPAC, current recommendation).

(d) NO_3 radicals were generated in situ from the reaction $NO_2+O_3 \rightarrow NO_3+O_2$.

(e) Note that while the equilibrium coefficient used in the data analysis of Hjorth et al. (1988) was stated to be from Graham and Johnston (1978) (3.43×10^{-11} cm^3 molecule^{-1} at 295 K), the value used (Hjorth et al., 1988) was 1.88×10^{-11} cm^3 molecule^{-1}.

Preferred Values

$k = 5.6 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The relative rate coefficients measured by Atkinson et al. (1984), Cantrell et al. (1985) and Hjorth et al. (1988) disagree by a factor of ∼2.5 when a consistent temperature-dependent equilibrium coefficient for the $NO_2+NO_3 \leftrightarrow N_2O_5$ reactions is used to place the rate coefficients on an absolute basis. The rate coefficient obtained by Cantrell et al. (1985) from experiments in which NO_3 radicals were measured directly by DOAS (and hence derivation of the rate coefficient does not involve the equilibrium coefficient for the $NO_2+NO_3 \leftrightarrow N_2O_5$ reactions) falls within the range of these relative rate coefficients (Atkinson et al., 1984; Cantrell et al., 1985; Hjorth et al., 1988).

Accordingly, the preferred value of $k=5.6\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K is based on the absolute rate measurements of Cantrell et al. (1985), with the uncertainty limits reflecting the single absolute study. While no temperature dependence of the rate coefficient has been measured to date, by analogy with the NO_3 radical reaction with CH_3CHO a pre-exponential factor of $\sim2\times10^{-12}$ cm^3 molecule^{-1} s^{-1} is expected, and hence $k(NO_3+HCHO)\sim2\times10^{-12}\exp(-2440/T)$ cm^3 molecule^{-1}

s^{-1}. This reaction proceeds by H-atom abstraction.

$$NO_3 + HCHO \rightarrow HNO_3 + HCO$$

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IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/.

II.A3.72

$NO_3 + CH_3CHO \rightarrow HNO_3 + CH_3CO$

$\Delta H^\circ = -53.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.44 \times 10^{-12} \exp[-(1860 \pm 300)/T]$	264–374	Dlugokencky and Howard, 1989	F-LIF (a)
$(2.74 \pm 0.33) \times 10^{-15}$	298		
$6.2 \times 10^{-11} \exp[-(2826 \pm 866)/T]$	298–433	Cabañas et al., 2001	DF-LIF (b)
$(3.2 \pm 0.8) \times 10^{-15}$	298 ± 2		
Relative Rate Coefficients			
$(2.17 \pm 0.55) \times 10^{-15}$	300	Morris and Niki, 1974	RR (c)
$(2.08 \pm 0.52) \times 10^{-15}$	298 ± 1	Atkinson et al., 1984	RR (c)
$(2.69 \pm 0.52) \times 10^{-15}$	299 ± 1	Cantrell et al., 1986	RR (c)
$(2.62 \pm 0.29) \times 10^{-15}$	298 ± 2	D'Anna et al., 2001a, b	RR (d)

Comments

(a) NO_3 radicals were generated by the thermal dissociation of N_2O_5 in a flow system. Initial NO_3 radical concentrations were $(0.6\text{–}3.0)\times10^{10}$ molecule cm^{-3}.

(b) Initial NO_3 radical concentrations were $(0.6\text{–}3\ .0)\times10^{12}$ molecule cm^{-3}.

(c) The cited rate coefficients are relative to the equilibrium coefficient K for the reactions $NO_3 + NO_2 \leftrightarrow N_2O_5$, with values of $K=2.90\times10^{-11}$ cm^3 molecule^{-1} at 298 K, 2.56×10^{-11} cm^3 molecule^{-1} at 299 K and 2.26×10^{-11} cm^3 molecule^{-1} at 300 K being used (IUPAC, current recommendation) to place the measured rate coefficient ratios on an absolute basis.

(d) Relative rate method, with NO_3 radicals being generated by the thermal dissociation of N_2O_5. Experiments were carried out in 1 atmosphere of air with measurements of acetaldehyde and 1-butene (the reference compound) by FTIR spectroscopy. The measured rate coefficient ratio $k(NO_3$ + acetaldehyde$)/k(NO_3$ + 1-butene$) = 0.194\pm0.021$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3$ + 1-butene$) = 1.35\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 1997). Experiments with acetaldehyde-d$_1$ (CH_3CDO) yielded a rate coefficient ratio $k(NO_3 + CH_3CHO)/k(NO_3 + CH_3CDO) = 2.37\pm0.08$ at 298 ± 2 K (D'Anna et al., 2001b).

Preferred Values

$k = 2.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.4 \times 10^{-12} \exp(-1860/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–380 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The rate coefficients measured relative to the equilibrium coefficient for the reactions $NO_2+NO_3 \leftrightarrow N_2O_5$ are subject to significant uncertainties arising from uncertainties in the equilibrium coefficient for these reactions, and the relative rate coefficients of Morris and Niki (1974), Atkinson et al. (1984) and Cantrell et al. (1986) are therefore not used in the evaluation of the rate coefficient for this reaction (although they are in agreement with the absolute room temperature rate coefficient of Dlugokencky and Howard (1989)). The room temperature rate coefficient of D'Anna et al. (2001a, b), determined relative to that for the reaction of NO_3 radicals with 1-butene, is in excellent agreement with the absolute rate coefficient measured by Dlugokencky and Howard (1989). The absolute study of Cabañas et al. (2001) employed much higher initial NO_3 radical concentrations than did Dlugokencky and Howard (1989) (by a factor of $\sim$100) and the measured rate coefficients (Cabañas et al., 2001) are significantly less precise and show a significantly higher temperature dependence.

The preferred values are based upon the absolute rate coefficient study of Dlugokencky and Howard (1989). The significant deuterium isotope effect observed by D'Anna et al. (2001b) indicates that, as expected, the reaction proceeds by H- (or D-) atom abstraction from the -CHO (or -CDO) group.

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II.A3.73

$NO_3 + CH_3CH_2CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.7×10^{-11} exp[-(2250 ± 192)/T]	298–433	Cabañas et al., 2001	DF-LIF
$(6.0 \pm 0.6) \times 10^{-15}$	298 ± 2		
Relative Rate Coefficients			
$(5.80 \pm 0.48) \times 10^{-15}$	298 ± 2	D'Anna and Nielsen, 1997	RR (a)
$(7.28 \pm 0.41) \times 10^{-15}$	296 ± 2	Papagni et al., 2000	RR (b)
$(6.18 \pm 0.57) \times 10^{-15}$	298 ± 2	D'Anna et al., 2001	RR (a)

Comments

(a) Relative rate method, with NO_3 radicals being generated by the thermal dissociation of N_2O_5. Experiments were carried out in 1 atmosphere of air with measurements of propanal and propene (the reference compound) by FTIR spectroscopy. The measured rate coefficient ratios $k(NO_3 + \text{propanal})/k(NO_3 + \text{propene}) = 0.61 \pm 0.05$ (D'Anna and Nielsen, 1997) and 0.65 ± 0.06 (D'Anna et al., 2001) are placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{propene}) = 9.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(b) Relative rate method, with NO_3 radicals being generated by the thermal dissociation of N_2O_5. Experiments were carried out in 1 atmosphere of air with measurements of propanal and methacrolein (the reference compound) by GC. The measured rate coefficient ratio $k(NO_3 + \text{propanal})/k(NO_3 + \text{methacrolein}) = 2.14 \pm 0.12$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{methacrolein}) = 3.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation).

Preferred Values

$k = 6.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the room temperature relative rate coefficients of D'Anna et al. (1997, 2001) and Papagni et al. (2000), which are in reasonable agreement and which also agree with the absolute room temperature rate coefficient of Cabañas et al. (2001). Because of the higher temperature dependence obtained by Cabañas et al. (2001) for the reactions of NO_3 radicals with acetaldehyde and butanal than by other investigators (IUPAC, this evaluation) and because the rate coefficient at 298 K calculated from the Arrhenius expression of Cabañas et al. (2001) is 50% higher than their measured value, the Cabañas et al. (2001) data are not used in the evaluation of the rate coefficient for this reaction, and no recommendation is made concerning the temperature dependence for this reaction.

References

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II.A3.74

$NO_3 + CH_3CH_2CH_2CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.26×10^{-12} exp(-1478/T)	267–332	Ullerstam et al., 2000	DF-RA (a)
$(1.1 \pm 0.1) \times 10^{-14}$	296		
7.6×10^{-11} exp[-(2466 ± 505)/T]	298–433	Cabañas et al., 2001	DF-LIF
$(1.46 \pm 0.16) \times 10^{-14}$	298 ± 2		
Relative Rate Coefficients			
$(1.09 \pm 0.09) \times 10^{-14}$	298 ± 2	D'Anna and Nielsen, 1997	RR (b)
$(1.04 \pm 0.11) \times 10^{-14}$	297 ± 2	Ullerstam et al., 2000	RR (c)
$(1.15 \pm 0.06) \times 10^{-14}$	296 ± 2	Papagni et al., 2000	RR (d)
$(1.23 \pm 0.11) \times 10^{-14}$	298 ± 2	D'Anna et al., 2001	RR (b)

Comments

(a) Carried out in the presence of 20% O_2 in the diluent gas to minimize secondary reactions (experiments in the absence of O_2 yielded rate coefficents a factor of ∼3 higher (Ullerstam et al., 2000)). The Arrhenius expression cited in the table is obtained from a least-squares analysis of the measured rate coefficients at 267 K, 296 K and 332 K.

(b) Relative rate method, with NO_3 radicals being generated by the thermal dissociation of N_2O_5. Experiments were carried out in 1 atmosphere of air with measurements of butanal and 1-butene (the reference compound) by FTIR spectroscopy. The measured rate coefficient ratios $k(NO_3 + \text{butanal})/k(NO_3 + \text{1-butene}) = 0.81 \pm 0.06$ (D'Anna and Nielsen, 1997) and 0.91 ± 0.08 (D'Anna et al., 2001) are placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{1-butene}) = 1.35 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 1997).

(c) Relative rate method, with NO_3 radicals being generated by the thermal dissociation of N_2O_5. Experiments were carried out in 1 atmosphere of synthetic air or N_2 with measurements of butanal and propene (the reference compound) by FTIR spectroscopy. The measured rate coefficient ratios $k(NO_3 + \text{butanal})/k(NO_3 + \text{propene}) = 1.1 \pm 0.1$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{propene}) = 9.42 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 297 K (IUPAC, current recommendation). The rate coefficient ratio was independent of the presence or absence of O_2.

(d) Relative rate method, with NO_3 radicals being generated by the thermal dissociation of N_2O_5. Experiments were carried out in 1 atmosphere of air with measurements of butanal and methacrolein (the reference compound) by GC. The measured rate coefficient ratio $k(NO_3 + \text{butanal})/k(NO_3 + \text{methacrolein}) = 3.38 \pm 0.15$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{methacrolein}) = 3.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation).

Preferred Values

$k = 1.1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.7 \times 10^{-12}$ exp(-1500/T) cm^3 molecule^{-1} s^{-1} over the temperature range 260–340 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the room temperature relative rate coefficients of D'Anna and Nielsen (1977), D'Anna et al. (2001), Ullerstam et al. (2000) and Papagni et al. (2001) and the absolute rate coefficient of Ullerstam et al. (2000) (measured in the presence of O_2). The absolute rate coefficient measured at 298 K by Cabañas et al. (2001) is 20–40% higher than the other absolute and relative rate coefficients (D'Anna and Nielsen, 1997; D'Anna et al., 2001; Papagni et al., 2000; Ullerstam et al., 2000), possibly indicating the occurrence of secondary reactions. The two measurements of the temperature dependence (Cabañas et al., 2001; Ullerstam et al., 2000) disagree significantly, with the pre-exponential factor derived from the study of Cabañas et al. (2001) being within a factor of ∼5 of gas kinetic. The preferred temperature dependence is that obtained from the study of Ullerstam et al. (2000), with a high uncertainty.

References

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II.A3.75

NO_3 + CH_2=C(CH_3)CHO (methacrolein) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 8 \times 10^{-15}$	298	Rudich et al., 1996	F-A (a)
Relative Rate Coefficients			
$(4.46 \pm 0.58) \times 10^{-15}$	296 ± 2	Kwok et al., 1996	RR (b)
$(3.08 \pm 0.18) \times 10^{-15}$	298 ± 2	Chew et al., 1998	RR (c)
$(3.50 \pm 0.15) \times 10^{-15}$	298 ± 2	Chew et al., 1998	RR (d)
$(3.72 \pm 0.47) \times 10^{-15}$	296 ± 2	Canosa-Mas et al., 1999	RR (e)

Comments

(a) NO_3 radicals were generated by thermal decomposition of N_2O_5 in a flow system at total pressures of 1.5–3 Torr (2–4 mbar), and monitored by absorption at 661.9 nm.

(b) Relative rate method carried out at atmospheric pressure of air. NO_3 radicals were generated by thermal decomposition of N_2O_5. The concentrations of methacrolein and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(NO_3 + \text{methacrolein})/k(NO_3 + \text{propene}) = 0.48 \pm 0.06$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{propene}) = 9.29 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation).

(c) Relative rate method carried out at atmospheric pressure of air. NO_3 radicals were generated by thermal decomposition of N_2O_5. The concentrations of methacrolein and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(NO_3 + \text{methacrolein})/k(NO_3 + \text{propene}) = 0.324 \pm 0.017$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{propene}) = 9.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(d) Relative rate method carried out at atmospheric pressure of air. NO_3 radicals were generated by thermal decomposition of N_2O_5. The concentrations of methacrolein and 1-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(NO_3 + \text{methacrolein})/k(NO_3 + \text{1-butene}) = 0.259 \pm 0.011$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{1-butene}) = 1.35 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 1997).

(e) Relative rate method carried out at atmospheric pressure of N_2. NO_3 radicals were generated by thermal decomposition of N_2O_5. The concentrations of methacrolein and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(NO_3 + \text{methacrolein})/k(NO_3 + \text{propene}) = 0.40 \pm 0.05$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{propene}) = 9.29 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation). An absolute rate coefficient of $(9.6 \pm 2.0) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} was also measured at 300 ± 7 K using a discharge flow system with LIF detection of NO_3 radicals.

Preferred Values

$k = 3.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

Comments on Preferred Values

The 298 K preferred value is the average of the relative rate coefficients of Chew et al. (1998) (which supersedes the earlier and less extensive study of Kwok et al., 1996) and Canosa-Mas et al. (1999), which are in good agreement and are consistent with the upper limit reported by Rudich et al. (1996).

The room temperature rate coefficient is similar to that for reaction of NO_3 radicals with acetaldehyde (IUPAC, this evaluation), and the reaction is expected to proceed mainly by H-atom abstraction from the CHO group.

References

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II.A3.76

$NO_3 + CH_3C(O)CH{=}CH_2$ (methyl vinyl ketone) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 1.2 \times 10^{-16}$	298	Rudich et al., 1996	F-A (a)
Relative Rate Coefficients			
$< 6 \times 10^{-16}$	296 ± 2	Kwok et al., 1996	RR (b)
$(5.0 \pm 1.2) \times 10^{-16}$	296 ± 2	Canosa-Mas et al., 1999	RR (c)

Comments

(a) NO_3 radicals were generated by thermal decomposition of N_2O_5 in a flow system at total pressures of 1.5–3 Torr (2–4 mbar), and monitored by absorption at 661.9 nm. A rate coefficient of $(1.0 \pm 0.2) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} was measured but an upper limit cited because of the difficulty in measuring such low reaction rate coefficients (Rudich et al., 1996).

(b) Relative rate method carried out at atmospheric pressure of air. NO_3 radicals were generated by thermal decomposition of N_2O_5. The concentrations of methyl vinyl ketone and propene (the reference compound) were measured by GC. The measured upper limit to the rate coefficient ratio of $k(NO_3$ + methyl vinyl ketone$)/k(NO_3$ + propene$) < 0.06$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3$ + propene$) = 9.29 \times 10^{-15}$ cm^3 molecule^{-1} $^{-1}$ at 296 K (IUPAC, current recommendation).

(c) Relative rate method carried out at atmospheric pressure of N_2. NO_3 radicals were generated by thermal decomposition of N_2O_5. The concentrations of methyl vinyl ketone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(NO_3$ + methyl vinyl ketone$)/k(NO_3$ + ethene$) = 2.53 \pm 0.59$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3$ + ethene$) = 1.96 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation). An absolute rate coefficient of $(3.2 \pm 0.6) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} was also measured at 296 ± 1 K using a discharge flow system with LIF detection of NO_3 radicals.

Preferred Values

$k < 6 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The rate coefficient measured in the relative rate study of Canosa-Mas et al. (1999) is consistent with the upper limit obtained by Kwok et al. (1996) but not with the rate coefficient (or cited upper limit) determined in the absolute rate study of Rudich et al. (1996). Although Canosa-Mas et al. (1999) also obtained an absolute rate coefficient in reasonable agreement with their relative rate coefficient, the absolute rate coefficient must be viewed as an upper limit because of the potential for secondary reactions (as observed by Canosa-Mas et al. (1999) in the same study for the reactions of NO_3 radicals with acrolein and methacrolein).

The preferred upper limit to the rate coefficient is that measured by Kwok et al. (1996) and is sufficiently high to encompass the rate coefficients obtained by Canosa-Mas et al. (1999).

References

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II.A3.77

NO_3 + Pinonaldehyde → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.40 \pm 0.38) \times 10^{-14}$	299 ± 2	Hallquist et al., 1997	RR (a)
$(6.0 \pm 2.0) \times 10^{-14}$	300 ± 5	Glasius et al., 1997	RR (b)
$(1.99 \pm 0.52) \times 10^{-14}$	296 ± 2	Alvarado et al., 1998	RR (c,d)
$(2.16 \pm 0.53) \times 10^{-14}$	296 ± 2	Alvarado et al., 1998	RR (c,e)
$(1.93 \pm 0.44) \times 10^{-14}$	296 ± 2	Alvarado et al., 1998	RR (c,f)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in N_2O_5-pinonaldehyde-propene (the reference compound)-air mixtures at 1013±5 mbar pressure. The concentrations of pinonaldehyde and propene were measured by FTIR spectroscopy. Dark decays of pinonaldehyde in the 153 L chamber used were observed, and taken into account in the data analysis. The measured rate coefficient ratio $k(NO_3$ + pinonaldehyde$)/k(NO_3$ + propene) is placed on an absolute basis by use of a rate coefficient of $k(NO_3$ + propene) = 9.5×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(b) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in N_2O_5-pinonaldehyde-1-butene (the reference compound)-air mixtures at 987±7 mbar pressure. The concentrations of pinonaldehyde and 1-butene were measured by FTIR spectroscopy. Dark decays of pinonaldehyde in the 480 L chamber used were observed, and taken into account in the data analysis. The measured rate coefficient ratio $k(NO_3$ + pinonaldehyde$)/k(NO_3$ + 1-butene) is placed on an absolute basis by use of a rate coefficient of $k(NO_3$ + 1-butene) = 1.38×10^{-14} cm^3 molecule^{-1} s^{-1} at 300 K (Atkinson and Arey, 2003).

(c) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in N_2O_5-pinonaldehyde-reference compound (propene, 1-butene or thiophene)-air mixtures at 987 mbar pressure. The concentrations of pinonaldehyde, propene, 1-butene and thiophene were measured by GC. No dark decays of pinonaldehyde (<5%) were observed in the 7000 L Teflon chamber used. The measured rate coefficient ratios $k(NO_3$ + pinonaldehyde$)/k(NO_3$ + propene) = 2.09±0.54, $k(NO_3$ + pinonaldehyde$)/k(NO_3$ + 1-butene) = 1.64±0.40 and $k(NO_3$ + pinonaldehyde$)/k(NO_3$ + thiophene) = 0.49±0.11 are placed on an absolute basis by use of rate coefficients at 296 K of $k(NO_3$ + propene) = 9.5×10^{-15} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation), $k(NO_3$ + 1-butene) = 1.32×10^{-14} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003) and $k(NO_3$ + thiophene) = 3.93×10^{-14} cm^3 molecule^{-1} s^{-1} (Atkinson, 1991).

(d) Relative to $k(NO_3$ + propene).

(e) Relative to $k(NO_3$ + 1-butene).

(f) Relative to $k(NO_3$ + thiophene).

Preferred Values

$k = 2.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.25$ at 298 K.

Comments on Preferred Values

Pinonaldehyde is a low volatility product of the atmospheric reactions of α-pinene which is prone to wall losses, making measurement of its reaction rate coefficients difficult. The available rate coefficients are all from relative rate studies carried out at room temperature, and range over a factor of $\sim$3 (Hallquist et al., 1997; Glasius et al., 1997; Alvarado et al., 1998). The rate coefficient measured by Glasius et al. (1997) is a factor of $\sim$2.5–3 higher than those of Hallquist et al. (1997) and Alvarado et al. (1998), possibly because of unresolved wall adsorption problems. The preferred values are based on the study of Alvarado et al. (1998) carried out in a large volume Teflon chamber in which no wall losses of pinonaldehyde were observed.

References

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II.A3.78

$$\mathbf{NO_3 + CH_3C(O)CH_3 \rightarrow HNO_3 + CH_3C(O)CH_2}$$

$\Delta H^\circ = -15.5\ \mathrm{kJ \cdot mol^{-1}}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq(8.5 \pm 2.5) \times 10^{-18}$	302	Boyd et al., 1991	(a)

Comments

(a) Stopped flow system with detection of the NO_3 radical by optical absorption at 662 nm. Secondary reactions were believed to be important and a stoichiometry factor of ≥2 has been used to obtain the cited upper limit to the rate coefficient.

Preferred Values

$k < 3 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The upper limit to the preferred value is derived from the overall rate coefficient of $(1.7 \pm 0.5) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} measured by Boyd et al. (1991), with no account taken of the expected greater than unity stoichiometry.

References

Boyd, A., Canosa-Mas, C. E., King, A. D., Wayne, R. P., and Wilson, M. R.: J. Chem. Soc. Faraday Trans., 87, 2913, 1991.

II.A3.79

NO_3 + 3-methylfuran → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.31 \pm 0.02) \times 10^{-11}$	296 ± 2	Alvarado et al., 1996	RR (a)
$(2.86 \pm 0.06) \times 10^{-11}$	295 ± 2	Kind et al., 1996	RR (b)

Comments

(a) Relative rate method carried out at one atmosphere of air. NO_3 radicals were generated by thermal decomposition of N_2O_5. The concentrations of 3-methylfuran and 2-methyl-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(NO_3$ + 3-methylfuran)/$k(NO_3$ + 2-methyl-2-butene) = 1.40±0.02 is placed on an absolute basis by use of a rate coefficient of $k(NO_3$ + 2-methyl-2-butene) = 9.37×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson, 1997).

(b) Relative rate method carried out in a flow system at a total pressure of 6.8 mbar of N_2. NO_3 radicals were generated by thermal decomposition of N_2O_5. The concentrations of 3-methylfuran and 2,3-dimethyl-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(NO_3$ + 3-methylfuran)/$k(NO_3$ + 2,3-dimethyl-2-butene) = 0.50 ± 0.01 is placed on an absolute basis by use of a rate coefficient of $k(NO_3$ + 2,3-dimethyl-2-butene) = 5.72×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson, 1997). In the same study, the measured rate coefficient for the reaction of NO_3 radicals with furan was shown to be independent of total pressure (of N_2 diluent) over the range 6.8–200 mbar.

Preferred Values

$k = 1.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The rate coefficients measured in the relative rate studies of Alvarado et al. (1996) and Kind et al. (1996) disagree by a factor of 2.2, for unknown reasons. The preferred value is a simple average of the rate coefficients from these two studies (Alvarado et al., 1996; Kind et al., 1996), with a large uncertainty limit. The reaction of NO_3 radicals with 3-methylfuran proceeds by initial addition of the NO_3 radical to the C=C bonds (Kind et al., 1996).

References

Alvarado, A., Atkinson, R., and Arey, J.: Int. J. Chem. Kinet., 28, 905, 1996.
Atkinson, R.: J. Phys. Chem. Ref. Data, 26, 215, 1997.
Kind, I., Berndt, T., Böge, O., and Rolle, W.: Chem. Phys. Lett., 256, 679, 1996.

II.A3.80

NO_3 + CH_2=C(CH_3)C(O)OONO$_2$ (MPAN) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.6 \pm 0.6) \times 10^{-16}$	296 ± 2	Canosa-Mas et al., 1999	RR (a)

Comments

(a) Relative rate method carried out at one atmosphere of air. CH_2=CH(CH_3)C(O)OONO$_2$ (MPAN) was prepared in situ from the reaction of NO_3 radicals (generated from the thermal decomposition of N_2O_5) with methacrolein. After complete consumption of N_2O_5 and methacrolein, ethene (the reference compound) was added and several additions of N_2O_5 were made to the collapsible 56 L chamber. The concentrations of MPAN and ethene were measured during the experiments by FTIR spectroscopy. The measured rate coefficient ratio of $k(NO_3 + \text{MPAN})/k(NO_3 + \text{ethene}) = 0.79 \pm 0.28$ (two standard deviations) is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{ethene}) = 2.0 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation). Dark decays of MPAN and dilution due to successive additions of N_2O_5 to the chamber were taken into account in the data analysis.

Preferred Values

$k = 1.6 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.7$ at 298 K.

Comments on Preferred Values

The preferred value is based on the sole study of this reaction by Canosa-Mas et al. (1999), with large uncertainty limits because of the difficult nature of the experiments and the need for large dilution corrections (cited as being up to 40%). The reaction of NO_3 radicals with MPAN proceeds by initial addition of the NO_3 radical to the C=C bond (Canosa-Mas et al., 1999). On the basis of the recommended rate coefficients for the reactions of MPAN with HO radicals and O_3 and those for the reactions of ethene, propene and 2-methylpropene with HO and NO_3 radicals and O_3 (Atkinson, 1997; IUPAC, current recommendation), the rate coefficient for the reaction of NO_3 radicals with MPAN may be expected to be significantly higher than the measured value (i.e., $\sim 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K).

References

Atkinson, R.: J. Phys. Chem. Ref. Data, 26, 215, 1997.
Canosa-Mas, C. E., King, M. D., Shallcross, D. E., and Wayne, R. P.: Phys. Chem. Chem. Phys., 1, 2411, 1999.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/.

II.A3.81

$NO_3 + CH_3OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 6 \times 10^{-16}$	298 ± 2	Wallington et al., 1987	FP-A
1.25×10^{-12} exp[-(2562 ± 241)/T]	294–473	Canosa-Mas et al., 1989	DF-A
$(2.1 \pm 1.1) \times 10^{-16}$	294		
1.06×10^{-12} exp[-(2093 ± 803)/T]	258–367	Langer and Ljungström, 1995	DF-A (a)
$(1.32 \pm 0.24) \times 10^{-16}$	295		

Comments

(a) The cited Arrhenius expression leads to a rate coefficient at 295 K of 8.8×10^{-16} cm^3 molecule^{-1} s^{-1}, clearly in disagreement with the measured value. A unit-weighted least-squares analysis of the rate coefficients measured by Langer and Ljungström (1995) (Table 3 of Langer and Ljungström, 1995) leads to k=9.36×10^{-13} exp[-(2652±312)/T] cm^3 molecule^{-1} s^{-1}, where the indicated error is one standard deviation.

Preferred Values

$k = 1.3 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 9.4 \times 10^{-13}$ exp(-2650/T) cm^3 molecule^{-1} s^{-1} over the temperature range 250–370 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta (E/R) = \pm 700$ K.

Comments on Preferred Values

The reported rate coefficients of Canosa-Mas et al. (1989) are higher by factors of 1.6–2.1 than those of Langer and Ljungström (1995) over the temperature range common to both studies (294–373 K). Clearly there are systematic errors in one or both of these studies. Based on the observation that for the NO_3 radical reaction with 2-propanol the data of Langer and Ljungström (1995) may still be an upper limit to the rate coefficient, the preferred values were derived from the data of Langer and Ljungström (1995) using the Arrhenius parameters given in Comment (a). The preferred 298 K rate coefficient is calculated from the resulting Arrhenius expression. It is possible that the preferred values are still high because of the potential for secondary reactions in slowly reacting systems using absolute rate methods.

References

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Langer, S. and Ljungström, E.: J. Chem. Soc. Faraday Trans., 91, 405, 1995.
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II.A3.82

$NO_3 + C_2H_5OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 9 \times 10^{-16}$	298 ± 2	Wallington et. al., 1987	FP-A
6.99×10^{-13} exp [-(1815 ± 419)/T]	273–367	Langer and Ljungström, 1995	DF-A
$(1.81 \pm 0.26) \times 10^{-15}$	297		

Preferred Values

$k < 2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

By analogy with the data for the reaction of the NO_3 radical with 2-propanol, it is likely that the rate coefficients of Langer and Ljungstrm (1995) are high because of the occurrence of secondary reactions. The preferred value is based on the upper limit to the rate coefficient determined by Wallington et al. (1987), and is consistent with the 298 K rate coefficient of Langer and Ljungström (1995) calculated from their Arrhenius expression. No recommendation is made concerning the temperature dependence.

References

Langer, S. and Ljungström, E.: J. Chem. Soc. Faraday Trans., 91, 405, 1995.
Wallington, T. J., Atkinson, R., Winer, A. M., and Pitts Jr., J. N.: Int. J. Chem. Kinet., 19, 243, 1987.

II.A3.83

$$
\begin{aligned}
\mathbf{NO_3 + CH_3CH(OH)CH_3} &\rightarrow \mathbf{HNO_3 + CH_3C(OH)CH_3} \quad &\mathbf{(1)}\\
&\rightarrow \mathbf{HNO_3 + CH_2CH(OH)CH_3} \quad &\mathbf{(2)}
\end{aligned}
$$

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 2.3 \times 10^{-15}$	298 ± 2	Wallington et al., 1987	FP-A
1.54×10^{-12} exp[-(1743 ± 1009)/T]	273–364	Langer and Ljungström, 1995	DF-A
$(3.13 \pm 0.64) \times 10^{-15}$	295		
Relative Rate Coefficients			
$\leq (1.8 \pm 0.2) \times 10^{-15}$	298 ± 2	Chew et al., 1998	RR (a)
$k_1 = (1.4 \pm 0.3) \times 10^{-15}$	298 ± 2	Chew et al., 1998	RR (a)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in air at atmospheric pressure. Experiments were carried out in a ~7000 liter Teflon chamber, and the concentrations of 2-propanol and methacrolein (the reference organic) were measured by GC. Rate coefficient ratios k(NO_3 + 2-propanol)/k(NO_3 + methacrolein) were measured as a function of initially added NO_2 over the range $(0–2.4)\times10^{14}$ molecule cm^{-3} ($\sim2\times10^{16}$ molecule cm^{-3} of ethane were added when no NO_2 was initially added). The rate coefficient ratios were independent of initial NO_2 concentration in the range $(0–4.8)\times10^{13}$ molecule cm^{-3}, but increased for initial NO_2 concentrations $\geq9.6\times10^{13}$ molecule cm^{-3}. Acetone was observed as a reaction product, presumably from channel (1) followed by,

$$CH_3C(OH)CH_3 + O_2 \rightarrow CH_3C(O)CH_3 + HO_2$$

with a yield of ~0.76±0.09 at initial NO_2 concentrations of $(0–4.8)\times10^{13}$ molecule cm^{-3}, decreasing at higher initial NO_2 concentrations. The values of k(NO_3 + 2-propanol) (yield of acetone)/k(NO_3 + methacrolein) were independent of initial NO_2 concentration over the entire range studied ($(0–2.4)\times10^{14}$ molecule cm^{-3}), with an average value of 0.40±0.06 for experiments with initial NO_2 concentrations of $(0–4.8)\times10^{13}$ molecule cm^{-3}. The observed behavior is interpreted as involving a gas-phase reaction of 2-propanol with the NO_3 radical and a reaction (gas-phase or heterogeneous) of N_2O_5 with 2-propanol to form nitrates (Langer and Ljungström, 1995). The rate coefficient k is obtained from the rate coefficient ratio k(NO_3 + 2-propanol)/k(NO_3 + methacrolein) = 0.519±0.053 at low added NO_2 concentrations, combined with a rate coefficient ratio of k(NO_3 + methacrolein) = 3.4×10^{-15} cm^3 molecule^{-1} s^{-1} at 298±2 K (IUPAC, current recommendation). This overall rate coefficient could still be an upper limit, and the true rate coefficient may be the value obtained for k_1 obtained from the ratio k(NO_3 + 2-propanol)(yield of 2-acetone)/k_2 (NO_3 + methacrolein) = 0.40±0.06 and the rate coefficient of k(NO_3 + methacrolein) (IUPAC, current recommendation).

Preferred Values

$k = 1.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 1.0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_1/k) = \pm 0.3$ at 298 K.

Comments on Preferred Values

The room temperature values for the overall reaction rate coefficient k and for k_1 obtained by Chew et al. (1998) are consistent with the upper limit to the rate coefficient of Wallington et al. (1987), but are a factor of $\sim$2 lower than the absolute rate coefficient of Langer and Ljungström (1995). It is expected that the reaction of the NO_3 radical occurs almost entirely by H-atom abstraction from the tertiary C-H bond (and hence that $k_1/k\sim1.0$) (Atkinson, 1991). This expectation is consistent with the data of Chew et al. (1998). The 298 K preferred value is based on the value of k_1 obtained by Chew et al. (1998) with the expectation that $k_1/k=1.0$ (Atkinson, 1991). No temperature dependence is recommended.

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II.A3.84

$$\begin{array}{llr}
\mathbf{NO_3 + CH_3CH(OH)CH_2CH_3} & \mathbf{\rightarrow HNO_3 + CH_3C(OH)CH_2CH_3} & \mathbf{(1)} \\
 & \mathbf{\rightarrow HNO_3 + CH_2CH(OH)CH_2CH_3} & \mathbf{(2)} \\
 & \mathbf{\rightarrow HNO_3 + CH_3CH(OH)CHCH_3} & \mathbf{(3)} \\
 & \mathbf{\rightarrow HNO_3 + CH_3CH(OH)CH_2CH_2} & \mathbf{(4)}
\end{array}$$

Rate coefficient data (k=k_1+k_2+k_3+k_4)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$\leq(2.6 \pm 0.3) \times 10^{-15}$	298 ± 2	Chew et al., 1998	RR (a)
$k_1 = (2.0 \pm 0.3) \times 10^{-15}$	298 ± 2	Chew et al., 1998	RR (a)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in air at atmospheric pressure. Experiments were carried out in a ∼7000 liter Teflon chamber, and the concentrations of 2-butanol and methacrolein (the reference organic) were measured by GC. Rate coefficient ratios $k(NO_3$ + 2-butanol)/$k(NO_3$ + methacrolein) were measured as a function of initially added NO_2 over the range (0–2.4) × 10^{-14} molecule cm^3 (∼2×10^{16} molecule cm^{-3} of ethane were added when no NO_2 was initially added). The rate coefficient ratios were independent of initial NO_2 concentration in the range (0–4.8) × 10^{13} molecule cm^{-3}, but increased for initial NO_2 concentrations $\geq 9.6\times10^{13}$ molecule cm^{-3}. 2-Butanone was observed as a reaction product, presumably from channel (1) followed by,

$$CH_3C(OH)CH_2CH_3 + O_2 \rightarrow CH_3C(O)CH_2CH_3 + HO_2$$

with a yield of ∼0.79 ± 0.09 at initial NO_2 concentrations of $(0–4.8)\times10^{13}$ molecule cm^{-3}, and decreasing at higher initial NO_2 concentrations. The values of $k(NO_3$ + 2-butanol) (yield of 2-butanone)/$k(NO_3$ + methacrolein) were independent of initial NO_2 concentration over the entire range studied ($(0–2.4)\times10^{14}$ molecule cm^{-3}), with an average value of 0.60 ± 0.07 for experiments with initial NO_2 concentrations of (0–4.8) × 10^{13} molecule cm^{-3}. The observed behavior is interpreted as involving a gas-phase reaction of 2-butanol with the NO_3 radical and a reaction (gas-phase or heterogeneous) of N_2O_5 with 2-butanol to form nitrates (Langer and Ljungström, 1995). The rate coefficient k is obtained from the rate coefficient ratio $k(NO_3$ + 2-butanol)/$k(NO_3$ + methacrolein) = 0.754 ± 0.065 at low added NO_2 concentrations, combined with a rate coefficient ratio of $k(NO_3$ + methacrolein) = 3.4×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 ± 2 K (IUPAC, current recommendation). This overall rate coefficient could still be an upper limit, and the true-rate coefficient may be the value obtained for k_1 obtained from the ratio $k(NO_3$ + 2-butanol)(yield of 2-butanone)/k_2 (NO_3 + methacrolein) = 0.60 ± 0.07 and the rate coefficient $k(NO_3$ + methacrolein) (IUPAC, current recommendation).

Preferred Values

$k = 2.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 1.0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_1/k) = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred values are based on the sole study of Chew et al. (1998). In view of the magnitude of the rate coefficient compared to that for the reaction of the NO_3 radical with n-butane (IUPAC, current recommendation), the reaction is expected to occur almost totally at the tertiary C-H bond (i.e., k_1/k=1.0). The preferred value therefore uses the measured rate coefficient k_1 combined with the expectation that k_1/k=1.0.

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IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/.
Langer, S. and Ljungström, E.: J. Chem. Soc. Faraday Trans., 91, 405, 1995.

II.A3.85

NO_3 + $(CH_3)_2C(OH)CH{=}CH_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.6 \times 10^{-14}\exp[-(400 \pm 35)/T]$	267–400	Rudich et al., 1996	F-A (a)
$(1.21 \pm 0.09) \times 10^{-14}$	298		
$(2.1 \pm 0.3) \times 10^{-14}$	294	Hallquist et al., 1996	DF-A
Relative Rate Coefficients			
$(1.55 \pm 0.55) \times 10^{-14}$	294	Hallquist et al., 1996	RR (b)
$(8.7 \pm 3.0) \times 10^{-15}$	298 ± 2	Fantechi et al., 1998a	RR (c)
$(1.0 \pm 0.2) \times 10^{-14}$	297 ± 2	Noda et al., 2002	RR (d)
$(1.1 \pm 0.1) \times 10^{-14}$	297 ± 2	Noda et al., 2002	RR (e)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 at 400 K in a flow system, and NO_3 radical concentrations were measured by visible tunable diode laser absorption at 661.9 nm.

(b) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in N_2O_5-$(CH_3)_2C(OH)CH{=}CH_2$-propene (the reference compound)-diluent (not specified) mixtures at 1013 mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and propene were measured by FTIR spectroscopy, and the measured rate coefficient ratio $k(NO_3$ + 2-methyl-3-buten-2-ol)/$k(NO_3$ + propene) is placed on an absolute basis by use of a rate coefficient of $k(NO_3$ + propene) = 9.0×10^{-15} cm^3 molecule^{-1} s^{-1} at 294 K (IUPAC, current recommendation).

(c) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in N_2O_5-$(CH_3)_2C(OH)CH{=}CH_2$-propene (the reference compound)-air mixtures at 987±7 mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and propene were measured by FTIR spectroscopy, and the measured rate coefficient ratio $k(NO_3$ + 2-methyl-3-buten-2-ol)/$k(NO_3$ + propene) is placed on an absolute basis by use of a rate coefficient of $k(NO_3$ + propene) = 9.5×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(d) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in N_2O_5-$(CH_3)_2C(OH)CH{=}CH_2$-propene (the reference compound)-air (or N_2) mixtures at ~1.02 bar pressure. The concentrations of 2-methyl-3-buten-2-ol and propene were measured by FTIR spectroscopy, and the measured rate coefficient ratio $k(NO_3$ + 2-methyl-3-buten-2-ol)/$k(NO_3$ + propene) is placed on an absolute basis by use of a rate coefficient of $k(NO_3$ + propene) = 9.4×10^{-15} cm^3 molecule^{-1} s^{-1} at 297 K (IUPAC, current recommendation).

(e) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in N_2O_5-$(CH_3)_2C(OH)CH{=}CH_2$-butanal (the reference compound)-air (or N_2) mixtures at 1.01±0.01 bar pressure. The concentrations of 2-methyl-3-buten-2-ol and butanal were measured by collection onto solid phase microextraction fibers with GC analyses. The measured rate coefficient ratio $k(NO_3$ + 2-methyl-3-buten-2-ol)/$k(NO_3$ + butanal) is placed on an absolute basis by use of a rate coefficient of $k(NO_3$ + butanal) = 1.1×10^{-14} cm^3 molecule^{-1} s^{-1} at 297 K (IUPAC, current recommendation).

Preferred Values

$k = 1.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.6 \times 10^{-14} \exp(-400/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–400 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

At room temperature, the relative rate coefficients of Hallquist et al. (1996), Fantechi et al. (1998a) and Noda et al. (2002) are in agreement, within the combined error limits, with the absolute rate coefficient of Rudich et al. (1996). However, the absolute rate coefficient of Hallquist et al. (1996) is a factor of 1.7 higher than that of Rudich et al. (1996). The absolute data of Rudich et al. (1996) are the basis for the preferred values. The reaction proceeds by initial addition of NO_3 to the C=C bond (Fantechi et al., 1998b; Noda et al., 2000), forming (after addition of O_2) the peroxy radicals $(CH_3)_2C(OH)CH(ONO_2)CH_2OO$ and $(CH_3)_2C(OH)CH(OO)CH_2ONO_2$ (and mainly the $(CH_3)_2C(OH)CH(OO)CH_2ONO_2$ radical (see below)). Reactions of these peroxy radicals with HO_2 radicals, organic peroxy radicals, NO, NO_2, and NO_3 radicals will lead to the products observed in the atmosphere (Atkinson and Arey, 2003). Under laboratory conditions, the observed products at atmospheric pressure of air are acetone and O_2NOCH_2CHO, with measured molar yields of 68.7±7.1% (Fantechi et al., 1998b) and 63±6% (Noda et al., 2000) for acetone and 67±8% for 2-nitrooxyacetaldehyde (Noda et al., 2000). These observed products presumably arise from self-reaction of the $(CH_3)_2C(OH)CH(OO)CH_2ONO_2$ peroxy radical, followed by decomposition of the resulting $(CH_3)_2C(OH)CH(O)CH_2ONO_2$ radical:

$$2(CH_3)_2C(OH)CH(OO)CH_2ONO_2 \rightarrow 2(CH_3)_2C(OH)CH(O)CH_2ONO_2 + O_2$$

$$\begin{array}{ll} (CH_3)_2C(OH)CH(O)CH_2ONO_2 \rightarrow & (CH_3)_2COH + HC(O)CH_2ONO_2 \\ & \downarrow O_2 \\ & CH_3C(O)CH_3 + HO_2 \end{array}$$

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Appendix A4: Carbon radical Reactions

II.A4.86

$$\mathbf{CH_3 + O_2 + M \rightarrow CH_3O_2 + M}$$

$\Delta H^\circ = -136.0$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.6×10^{-31} [N_2]	298	Basco et al., 1972	FP-AS (a)
3.1×10^{-31} [N_2]	298	Parkes, 1977	MM-AS (b)
4.5×10^{-31} [N_2]	296	Selzer and Bayes, 1983	PLP-MS (c)
$(7.0 \pm 1.0) \times 10^{-31}$ [Ar]	298	Cobos et al., 1985	PLP-AS (d)
$(8.0 \pm 1.0) \times 10^{-31}$ [N_2]	298		
$(4.8 \pm 0.6) \times 10^{-31}$ [Ar]	298	Pilling and Smith, 1985	PLP-AS (e)
$(1.0 \pm 0.3) \times 10^{-30}$ $(T/300)^{-3.3}$[Ar]	334–582	Keiffer et al., 1987	PLP-AS (f)
Relative Rate Coefficients			
$6.1 \times 10^{-33}\exp(1000/T)$ [N_2]	259–339	Washida and Bayes, 1976	DF-MS (g)
1.8×10^{-31} [N_2]	298		
$8.0 \times 10^{-32}\exp(243/T)$ [Ar]	230–568	Pratt and Wood, 1984	(h)
1.8×10^{-31} [Ar]	298		
$(7.56 \pm 1.1) \times 10^{-31}$ $(T/300)^{-3.64}$[N2]	264–370	Kaiser, 1993	(i)

Comments

(a) Pressure range 40 mbar to 500 mbar. Lindemann-Hinshelwood plot was used for extrapolation to k_0 and k_∞

(b) Molecular modulation spectroscopy. Pressure range 25 mbar to 1000 mbar. Lindemann-Hinshelwood extrapolation to k_0 and k_∞.

(c) Pressure varied between 0.6 mbar and 8 mbar.

(d) Pressure of the bath gases N_2, Ar and O_2 varied between 0.2 mbar and 150 bar. Falloff curves were constructed with F_c=0.27, N=1.47 and k_∞=2.2×10^{-12} cm^3 molecule^{-1} s^{-1}. The low value of the theoretically modeled F_c leads to a high limiting value of k_0 extracted from the measurements.

(e) Pressures of bath gas Ar varied between 4.2 mbar and 645 mbar. Falloff curves constructed using F_c=0.57 (including strong and weak collision contributions).

(f) Measurements in the pressure range 25 mbar to 790 mbar. Falloff curves constructed with F_c=0.6. Various fitting procedures were applied and discussed.

(g) The rate coefficients $k(CH_3+O_2+M \rightarrow CH_3O_2+M)$ plus $k(CH_3+O_2 \rightarrow HCHO+HO)$ were measured relative to $k(O + CH_3 \rightarrow \text{products})$. Evaluation with $k(O+CH_3)=1.0\times10^{-10}$ cm^3 molecule^{-1} s^{-1}. Extrapolation to k_0.

(h) Discharge-flow system at pressures of 2.6 mbar to 13 mbar. CH_3 radicals were produced from the $H+C_2H_4$ reaction. Reaction rates were determined from the effect of added O_2 on the radical combination products. Falloff curves were constructed assuming that k_∞ and F_c are independent of temperature.

(i) Mixtures of Cl_2, CH_4, diluent (N_2, Ar, He, or SF_6) were irradiated with a fluorescent lamp. The CH_4 loss and CH_3Cl formation were measured by GC. Data were obtained (for N_2 or O_2) between 3 mbar and 13 bar at 297 K, 25 mbar and 2 bar at 370 K and 50 mbar and 15 bar at 264 K. The data were fitted using F_c=0.48 at 264 K, 0.46 at 297 K and 0.42 at 370 K.

Preferred Values

$k_0 = 1.0 \times 10^{-30} (T/300)^{-3.3}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The evaluation uses the results of Keiffer et al. (1987) and Kaiser (1993), although different values of F_c were employed. The temperature dependence of F_c applied in Keiffer et al. (1987) does not extend to temperatures below 300 K. The calculated values of F_c from Cobos et al. (1985) are preferred, i.e., F_c=0.27 at 300 K.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.8×10^{-12}	298	Van den Bergh and Callear, 1971	FP-AS (a)
5×10^{-13}	298	Basco et al., 1972	FP-AS (b)
1.2×10^{-12}	298	Parkes, 1977	FP-AS (c)
2.2×10^{-12}	295	Hochanadel et al., 1977	FP-AS (d)
$(2.2 \pm 0.3) \times 10^{-12} (T/300)^{0.94}$	200–400	Cobos et al., 1985	PLP-AS (e)
$(1.05 \pm 0.12) \times 10^{-12}$	298	Pilling and Smith, 1985	PLP-AS (f)
$(1.2 \pm 0.2) \times 10^{-12} (T/300)^{1.2}$	334–582	Keiffer et al., 1987	PLP-AS (g)
Relative Rate Coefficients			
1.7×10^{-12}	298	Laufer and Bass, 1975	FP-GC (i)
$(1.31 \pm 0.1) \times 10^{-12} (T/300)^{1.2}$	264–370	Kaiser, 1993	(j)

Comments

(a) Pressure range 40 mbar to 400 mbar of C_3H_8. RRKM extrapolation to k_∞.

(b) See comment (a) for k_0.

(c) See comment (b) for k_0.

(d) 12 percent falloff correction applied using the results of Basco et al. (1972).

(e) See comment (d) for k_0.

(f) See comment (e) for k_0.

(g) See comment (f) for k_0.

(h) See comment (g) for k_0.

(i) Pressure range 66 mbar to 920 mbar, RRKM extrapolation to k_∞. Rate measured relative to CH_3+CH_3 $\rightarrow C_2H_6$ and evaluated with $k(CH_3+CH_3 \rightarrow C_2H_6)=9.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1} from the same work.

(j) See comment (i) for k_0.

Preferred Values

$k = 9.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.
$k_\infty = 1.8 \times 10^{-12} \exp(T/300)^{1.1}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred value is an average of earlier results from Cobos et al. (1985) and Keiffer et al. (1987) and the more recent determination by Kaiser (1993).

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II.A4.87

$CH_3 + O_3 \rightarrow$ products

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$5.1 \times 10^{-12}\exp[-(210 \pm 84)/T]$	243–384	Ogryzlo et al., 1981;	FP-MS (a)
$(2.53 \pm 0.54) \times 10^{-12}$	298	Paltenghi et al., 1984	
$(2.2 \pm 0.3) \times 10^{-12}$	298	Albaladejo et al., 2002	PLP-LIF (b)

Comments

(a) Flash photolysis of CH_3NO_2 at 193 nm in a flow system with He carrier gas at pressures of ~2.7 mbar (~2 Torr). [CH_3] was monitored by photoionization MS under pseudo-first-order conditions; no product analyses. The original data of Ogryzlo et al. (1981) were revised by Paltenghi et al. (1984) on the basis of a correction for the pressure drop along the flow tube between the reaction vessel and the manometer.

(b) Pulsed laser photolysis of CH_3Br at 193 nm and 133 mbar (100 Torr) He coupled with laser-excited fluorescence detection of CH_3O at 292.4 nm in a slow-flow cell. The rate coefficient for total removal of CH_3 was determined by numerical analysis of the temporal profiles of the CH_3O signal. The calibration of the CH_3O concentration was performed by comparing LIF signals with those for the reaction $CH_3 + NO_2$ obtained under identical conditions. The CH_3O absolute yield from the $CH_3 + O_3$ reaction was measured to be 0.044 ± 0.013 and leads to $k=(9.68 \pm 1.10) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} for the reaction channel $CH_3+O_3 \rightarrow CH_3O+O_2$.

Preferred Values

$k = 2.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.7 \times 10^{-12} \exp(-210/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–400 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred values are based on the mean of the revised calculations by Paltenghi et al. (1984) of the earlier data of Ogryzlo et al. (1981) and of the data of Albaladejo et al. (2002).

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II.A4.88

$$\mathbf{C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2}$$

$\Delta H^\circ = -54.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.1 \pm 0.5) \times 10^{-13}$	295	Plumb and Ryan, 1981	(a)
$<10^{-13}$	1000	Wagner et al., 1990	PLP-MS (b)
Relative Rate Coefficients			
1.9×10^{-14} (133 mbar, air)	298	Kaiser et al., 1990	(c)
3.8×10^{-15} (1 bar, air)	298		
9.8×10^{-16} (8 bar, air)	298		

Comments

(a) Discharge flow system. C_2H_5 radicals were generated from the reaction $Cl+C_2H_6 \rightarrow HCl+C_2H_5$. C_2H_5 and C_2H_4 were measured directly by MS. The rate coefficient k was determined from the measured yields of C_2H_4. k found to be independent of pressure (0.8 mbar to 13 mbar).

(b) Experimental and theoretical study of the $C_2H_5+O_2$ reaction. Experiments were carried out in tubular flame reactor. C_2H_5 radicals were formed by laser photolysis of C_2H_5Br or CCl_4-C_2H_6 mixtures. Concentrations of C_2H_5 and C_2H_4 were monitored by photoionization MS.

(c) Study of the yields of C_2H_4 produced relative to the C_2H_6 consumed (GC analysis) in a system in which C_2H_5 radicals were generated from UV irradiation of Cl_2-C_2H_6-O_2-N_2 (or air) mixtures. Up to 8 bar the percentage of C_2H_4 produced, relative to the C_2H_6 consumed, decreased from 12% to 0.02%, following a $P^{-(0.8\pm0.1)}$ pressure dependence in air. The listed pressure-dependent k values are relative to values of $k(C_2H_5+O_2+M \rightarrow C_2H_5O_2+M)$ calculated from the recommended values of Baldwin et al. (1980).

Preferred Values

$k = 3.8 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.
$k = 1.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K and 0.133 bar of air.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The recommended pressure-dependent values of k_{298} are from the product study of Kaiser et al. (1990). Increasing the pressure, therefore, decreases the apparent rate coefficient of this reaction. At a given pressure, increasing the temperature leads to an increasing yield of C_2H_4.

For a full discussion of the mechanism of the $C_2H_5+O_2$ reaction see Wagner et al. (1990), Miller et al. (2000) and Miller and Klippenstein (2001). It is clear that for atmospheric conditions the interaction of C_2H_5 with O_2 to form $C_2H_5O_2$ radicals is by far the dominant pathway. The work of Kaiser (1995) provides information on the mechanism of C_2H_4 formation. According to this, the reaction proceeds via a rearrangement of the excited $C_2H_5O_2$ adduct with an energy barrier of (4.6±1.0) kJ·mol^{-1}.

References

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II.A4.89

$$\mathbf{C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M}$$

$\Delta H^\circ = -149.6\ \mathrm{kJ{\cdot}mol^{-1}}$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(7.5 \pm 2) \times 10^{-29}$ [He]	295	Plumb and Ryan, 1981	DF-MS (a)
7.5×10^{-29} [He]	298	Slagle et al., 1984	DF-MS (b)
$1.96 \times 10^{-5}\ T^{-8.24} \exp(-2150/T)$ [He]	296–850	Wagner et al., 1990	PLP-MS (c)
5.9×10^{-29} [He]	298		
Relative Rate Coefficients			
$(6.5 \times 2.0) \times 10^{-29}$ [He]	298	Kaiser et al., 1990	(d)

Comments

(a) Measurements at 2×10^{16} molecule cm^{-3} to 3.4×10^{17} molecule cm^{-3} of He, extrapolated to k_0 and k_∞ with F_c=0.85.

(b) Bath gas concentration varied between 1.6×10^{16} molecule cm^{-3} and 2.4×10^{17} molecule cm^{-3}. Data in agreement with values measured by Plumb and Ryan (1981).

(c) Experiments carried out in a heatable tubular reactor. He pressures from 0.7 mbar to 20 mbar were used.

(d) C_2H_5 radicals were produced by UV irradiation of mixtures of Cl_2-C_2H_6-O_2. The consumed C_2H_6 was determined by either FTIR or GC with flame ionization detection (which also allowed the amount of C_2H_5Cl formed to be measured). Rate coefficients were measured as a function of pressure (4 mbar to 2000 mbar) relative to that of the reaction $C_2H_5+Cl_2 \rightarrow C_2H_2Cl+Cl$, and placed on an absolute basis by use of a rate coefficient of $k(C_2H_5+Cl_2)=2.9\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 7 mbar.

Preferred Values

$k_0 = 5.9 \times 10^{-29}\ (T/300)^{-3.8}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

We prefer the extensive results from Wagner et al. (1990) because the falloff extrapolation k_0 was done with a careful theoretical analysis. Falloff extrapolations were made with theoretically derived (Wagner et al., 1990) values of F_c=0.64 at 200 K and 0.54 at 300 K.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.4 \pm 0.5) \times 10^{-12}$	295	Plumb and Ryan, 1981	DF-MS (a)
4.4×10^{-12}	300	Slagle et al., 1984	DF-MS (b)
$1.3 \times 10^{-12} \exp(420/T)$	298–400	Munk et al., 1986	(c)
5.3×10^{-12}	298		
$3.67 \times 10^{-14}\ T^{0.772} \exp(287/T)$	296–850	Wagner et al., 1990	PLP-MS (d)
7.8×10^{-12}	298		
Relative Rate Coefficients			
$(9.2 \pm 0.9) \times 10^{-12}$	298	Kaiser et al., 1990	(e)
$(8.1 \pm 0.3) \times 10^{-12}$	260–380	Kaiser, 1995	(f)
$2.9 \times 10^{-12}\exp(289/T)$	243–475	Dilger et al., 1996	(g)
7.6×10^{-12}	298		

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0.

(c) Pulse radiolysis in H_2 at 1 bar. C_2H_5 radicals were generated from the reaction of H + C_2H_4. $C_2H_5O_2$ radicals were monitored by absorption at 240 nm.

(d) See comment (c) for k_0.

(e) See comment (d) for k_0.

(f) Photolysis of Cl_2 in the presence of C_2H_6, O_2 and M=He or N_2 at a pressure of 773 mbar. k_∞ was measured relative to the reaction $C_2H_5 + Cl_2 \rightarrow C_2H_5Cl + Cl$ for which a rate coefficient of $1.04 \times 10^{-11} \exp(300/T)$ cm^3 molecule^{-1} s^{-1} was employed (Kaiser, 1990; Timonen and Gutman, 1986).

(g) Muon relaxation method in longitudinal magnetic fields. $MuCH_2CH_2$ radicals were generated by addition of muonium ($Mu=\mu^+ e^-$) to C_2H_4. Total pressures of N_2 varied between 1.5 bar and 60 bar.

Preferred Values

$k = 7.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.
$k_\infty = 7.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ over the temperature range 200–300 K.

Comments on Preferred Values

As for k_0, we prefer the extensive data from Wagner et al. (1990) because of the careful theoretical analysis. We assume a temperature independent rate coefficient k_∞ below 300 K. Falloff curves were fitted (Wagner et al., 1990) with an expression F_c=[0.58 exp (-T/1250)+0.42 exp(-T/183)] which leads to F_c=0.64 at 200 K and 0.54 at 300 K. Within the stated error limits, the available data all agree with the preferred values based on Wagner et al. (1990). QRRK calculations (Bozzelli and Dean, 1990) of the reaction are less realistic than the RRKM calculations of Wagner et al. (1990). The analysis of the reaction system is complicated because there is a coupling of the addition reaction with the reaction forming C_2H_4, i.e., $C_2H_5+O_2 \rightarrow C_2H_4+HO_2$ (see the analysis in Wagner et al., 1990; Miller et al., 2000; Miller and Klippenstein, 2001).

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II.A4.90

$$n\text{-}\mathbf{C_3H_7 + O_2 + M} \rightarrow n\text{-}\mathbf{C_3H_7O_2 + M}$$

High-pressure rate coefficients

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.5 \pm 0.9) \times 10^{-12}$	298	Ruiz and Bayes, 1984	FP-MS (a)
6×10^{-12}	297	Slagle et al., 1985	PLP-MS (b)

Comments

(a) No pressure dependence detected between 1.3 mbar and 5 mbar of He or N_2.

(b) n-C_3H_7 radicals were produced by CO_2 laser photolysis of $C_6F_5C_4H_9$. Only weak pressure dependences were observed over the range of He or N_2 pressures from 0.5 mbar to 9 mbar. The rate coefficient decreased from 6×10^{-12} cm^3 molecule^{-1} s^{-1} to 2.8×10^{-13} cm^3 molecule^{-1} s^{-1} over the temperature range 297 K to 635 K.

Preferred Values

$k = 6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 mbar to 10 mbar of air.
$k \approx k_\infty$ at 298 K and 1 bar of air.
$k_\infty = 8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ over the range 200–300 K.

Comments on Preferred Values

The available experimental data are consistent with each other (Ruiz and Bayes, 1984; Slagle et al., 1985). Because they were obtained at total pressures below 130 mbar, we estimate that some falloff corrections have to be applied and these are taken into account in the preferred values. These values are consistent with experiments for the reactions $C_2H_5+O_2+M \rightarrow C_2H_5O_2+M$ and i-$C_3H_7+O_2+M \rightarrow$ i-$C_3H_7O_2+M$ (see this evaluation).

References

Ruiz, R. P. and Bayes, K. D.: J. Phys. Chem., 88, 2592, 1984.
Slagle, I. R., Park, J.-Y., and Gutman, D.: 20th Int. Symp. on Combustion, Combustion Institute, Pittsburgh, pp. 733–741, 1985.

II.A4.91

$$\boldsymbol{i\text{-}C_3H_7 + O_2 + M \rightarrow i\text{-}C_3H_7O_2 + M}$$

$\Delta H^\circ = -158.9$ kJ·mol^{-1}

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.41 \pm 0.24) \times 10^{-11}$	298	Ruiz and Bayes, 1984	FP-MS (a)
8.3×10^{-12}	300	Munk et al., 1986	(b)

Comments

(a) No pressure dependence detected for He or N_2 pressures from 1.3 mbar to 5 mbar.

(b) Pulse radiolysis in H_2 at 1 bar. i-C_3H_7 radicals were generated by the addition of H atoms to C_3H_6 and i-$C_3H_7O_2$ detected by UV absorption at 253 nm. Absorption spectrum of i-C_3H_7 was also detected.

Preferred Values

$k \approx k_\infty$ at 298 K and 1 bar of air.
$k_\infty = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the range 200–300 K.

Comments on Preferred Values

The preferred values are the average of the results from Ruiz and Bayes (1984) and Munk et al. (1986). Falloff corrections are probably within the uncertainties of the average. The rate coefficient k_∞ for this reaction appears consistent with those for the reactions $C_2H_5+O_2+M \rightarrow C_2H_5O_2+M$ and n-$C_3H_7+O_2+M \rightarrow$ n-$C_3H_7O_2+M$ (see this evaluation).

References

Munk, J., Pagsberg, P., Ratajczak, E., and Sillesen, A.: Chem. Phys. Lett., 132, 417, 1986.
Ruiz, R. P. and Bayes, K. D.: J. Phys. Chem., 88, 2592, 1984.

II.A4.92

$$\mathbf{1\text{-}C_4H_9 + O_2 + M \rightarrow 1\text{-}C_4H_9O_2 + M}$$

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(7.5 \pm 1.4) \times 10^{-12}$	300	Lenhardt et al., 1980	FP-MS (a)

Comments

(a) 1-Butyl radicals were generated by the flash photolysis of 1-butyl iodide and detected by MS. No pressure dependence of the rate coefficients was observed over the range 1.3 mbar to 5.3 mbar of He.

Preferred Values

$k_\infty = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 298 K.

Comments on Preferred Values

The preferred value is based on the study of Lenhardt et al. (1980). Because this is the only study of this reaction, we assign large error limits. This reaction should be close to the high pressure limit at atmospheric pressure.

References

Lenhardt, T. M., McDade, C. E., and Bayes, K. D.: J. Chem. Phys., 72, 304, 1980.

II.A4.93

$$\mathbf{2\text{-}C_4H_9 + O_2 + M \rightarrow 2\text{-}C_4H_9O_2 + M}$$

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.66 \pm 0.22) \times 10^{-11}$	300	Lenhardt et al., 1980	FP-MS (a)

Comments

(a) 2-Butyl radicals were generated by the flash photolysis of 2-butyl iodide and detected by MS. No pressure dependence of the rate coefficients was observed over the range 1.3 mbar to 5.3 mbar of He.

Preferred Values

$k_\infty = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 298 K.

Comments on Preferred Values

The preferred value is based on the study of Lenhardt et al. (1980).

References

Lenhardt, T. M., McDade, C. E., and Bayes, K. D.: J. Chem. Phys., 72, 304, 1980.

II.A4.94

$$\mathbf{CH_3C(O)CH_2 + O_2 + M \rightarrow CH_3C(O)CH_2O_2 + M}$$

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.45×10^{-12}	298	Cox et al., 1990	(a)

Comments

(a) Pulse radiolysis of $CH_3C(O)CH_3$-O_2-SF_6 mixtures at 1 bar of SF_6. $CH_3C(O)CH_2$ radicals were formed from the reaction of F atoms with $CH_3C(O)CH_3$. At the monitoring wavelength of 310 nm both $CH_3C(O)CH_2$ and $CH_3C(O)CH_2O_2$ absorb, with the absorption cross-section of the peroxy radical being a factor of 1.7 greater than that of the $CH_3C(O)CH_2$ radical. The rate coefficient was evaluated by simulations of the above reaction together with the reaction $CH_3C(O)CH_2+CH_3C(O)CH_2O_2 \rightarrow 2\ CH_3C(O)CH_2O$.

Preferred Values

$k \approx k_\infty$ at 298 K and 1 bar of air.
$k_\infty = 1.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 298 K.

Comments on Preferred Values

The preferred values are based on the study of Cox et al. (1990). Because this is the only study of this reaction, we assign large error limits. Near atmospheric pressure this reaction should be close to the high pressure limit.

References

Cox, R. A., Munk, J., Nielsen, O. J., Pagsberg, P., and Ratajczak, E.: Chem. Phys. Lett., 173, 206, 1990.

II.A4.95

$HCO + O_2 \rightarrow CO + HO_2$

$\Delta H^\circ = -139.0\ \mathrm{kJ \cdot mol^{-1}}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.6 \pm 0.9) \times 10^{-12}$	300	Shibuya et al., 1977	FP-AS (a)
$5.5 \times 10^{-11} T^{-(0.4 \pm 0.3)}$	298–503	Veyret and Lesclaux, 1981	FP-AS (b)
$(5.6 \pm 0.6) \times 10^{-12}$	298		
$(4.65 \pm 0.6) \times 10^{-12}$	295	Langford and Moore, 1984	PLP-AS (c)
1.3×10^{-11} exp[-(204 ± 180)/T]	295–713	Timonen et al., 1988	PLP-MS (d)
6.2×10^{-12}	295		
3.2×10^{-12} exp(87/T)	200–398	Stief et al., 1990	DF-MS (e)
4.3×10^{-12}	298		
4.3×10^{-12}	298	Dóbé et al., 1995	DF-LMR (f)
$(2.2) \times 10^{-12}$exp[(170 ± 22)/T]	200–298	Nesbitt et al., 1999	DF-MS (g)
$(4.0 \pm 0.6) \times 10^{-12}$	298		
$(5.9 \pm 0.5) \times 10^{-12}$	295	Ninomiya et al., 2000	PLP-AS (h)
$(5.0 \pm 0.7) \times 10^{-12}$	294 ± 2	Hanoune et al., 2001	PLP-AS (i)
Relative Rate Coefficients			
$(5.7 \pm 1.2) \times 10^{-12}$	297	Washida et al., 1974	RR (j)
$(6.3 \pm 1.5) \times 10^{-12}$	295	Ninomiya et al., 2000	RR (k)

Comments

(a) Flash photolysis of CH_3CHO-O_2 mixtures; HCO monitored by time-resolved absorption at 613.8 nm. There was no pressure effect on k for pressures of up to 690 mbar (520 Torr) of He.

(b) Flash photolysis of HCHO and CH_3CHO; HCO was monitored by laser absorption at 614.5 nm at total pressures of 17 mbar to 660 mbar (13 Torr to 500 Torr).

(c) Pulsed laser photolysis of HCHO or $(CHO)_2$ with monitoring of HCO by absorption at total pressures of up to 1330 mbar (1000 Torr).

(d) Pulsed laser photolysis of CH_3CHO; HCO was monitored by photoionization MS at pressures of 0.69 mbar to 1.22 mbar (0.52 Torr to 0.92 Torr).

(e) Discharge-flow system. HCO radicals were generated from Cl + HCHO and monitored by photoionization MS.

(f) HCO radicals were generated by the reaction of F atoms with HCHO. The total pressure was 1.7 mbar of He. The yield of HO_2 radicals was measured relative to the formation yield of HO_2 radicals from the reaction of F atoms with H_2O_2, and determined to be 1.00 ± 0.05.

(g) Same experimental technique as in comment (e). The rate constant measured at 398 K seems to indicate a slight positive temperature dependence for $T > 300$ K in qualitative agreement with Timonen et al. (1988).

(h) Pulsed laser photolysis of CH_3CHO at 266 nm; HCO was monitored by cavity ring-down spectroscopy at 613.5 nm at total pressures of 5.32–13.3 mbar (4–10 Torr) of N_2.

(i) Pulsed laser photolysis of a mixture of H_2CO and Cl_2 at 355 nm with monitoring of the R5 or R6 transition in CO by tunable diode laser absorption in the range 6.4–62.0 mbar (4.8–46.5 Torr). Only data with $[O_2]>5\times10^{15}$ molecule cm^{-3} have been used in the analysis.

(j) Discharge flow system with HCO being monitored by photoionization MS. k measured relative to k(O + HCO → products) = 2.1×10^{-10} cm^3 $molecule^{-1}$ s^{-1} (measured in the same apparatus) by observing the effect of O_2 on [HCO] in a flowing mixture of O_2-C_2H_4; k/k(O + HCO)=(2.74 ± 0.21)$\times10^{-2}$.

(k) Based on the ratio of the rate coefficients k(HCO + O_2)/k(HCO + Cl_2)=0.85 ± 0.02 measured in a smog chamber coupled to FTIR detection. The absolute value of k(HCO + Cl_2) used to place the relative rate on an absolute basis was (7.4 ± 1.7)$\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

Preferred Values

$k = 5.1 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 150$ K.

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is the average of the room-temperature rate coefficients of Shibuya et al. (1977), Veyret and Lesclaux (1981), Langford and Moore (1984), Timonen et al. (1988), Stief et al. (1990), Dóbé et al. (1995), Nesbitt et al. (1999), Ninomiya et al. (2000) and Hanoune et al. (2001). Taken together, the temperature-dependent studies of Veyret and Lesclaux (1981), Timonen et al. (1988), Stief et al. (1990) and Nesbitt et al. (1999) suggest that the rate coefficient of this reaction has a slight negative temperature dependence over the range 200 to 298 K and possibly a small positive temperature dependence above 300 K. However, within the measurement uncertainties the rate coefficient can be considered to be independent of temperature over the range 200–400 K.

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II.A4.96

$$\mathbf{CH_3CO + O_2 + M \rightarrow CH_3C(O)O_2 + M}$$

$\Delta H^\circ = -162.0\ \mathrm{kJ \cdot mol^{-1}}$

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.0 \pm 0.4) \times 10^{-12}$	298	McDade et al., 1982	(a)
$(5.4 \pm 1.9) \times 10^{-12}$	296	Kaiser and Wallington, 1995	RR (b)
$(5.7 \pm 1.9) \times 10^{-12}$	295 ± 2	Tyndall et al., 1997	RR (c)
$(5.9 \pm 1.9) \times 10^{-12}$	228		
$(4.4 \pm 0.7) \times 10^{-12}$	295	Sehested et al., 1998	PR-AS (d)

Comments

(a) Flow system with CH_3CO generated from pulsed photolysis of $CH_3C(O)CH_3$ or $CH_3C(O)CH_2COCH_3$. [CH_3CO] was monitored by photoionization mass spectrometry and kinetics evaluated from pseudo-first-order decays of CH_3CO. The pressure range was 1.3 mbar to 5 mbar.

(b) Measurement of the rate coefficient ratio for $k(CH_3CO+Cl_2)/k(CH_3CO+O_2)=7.9\pm0.5$ at 930 mbar total pressure. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(CH_3CO+Cl_2)=(4.3\pm1.5)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (Tyndall et al., 1999).

(c) Measurement of the rate coefficient ratios $k(CH_3CO+Cl_2)/k(CH_3CO+O_2)$ at 228 K and 298 K over the pressure range 0.13 mbar to 1460 mbar. The rate constant k was observed to increase with increasing pressure, with the rate coefficient k approaching the high-pressure limit above ∼400 mbar. The rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(CH_3CO+Cl_2)=(4.3\pm1.5)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (Tyndall et al., 1999).

(d) Pulse radiolysis of a mixture of CH_3CHO and O_2 in 1 bar of SF_6 coupled with transient UV absorption spectroscopy of $CH_3C(O)O_2$ at 260 nm. Numerical modeling was used with a complex reaction mechanism.

Preferred Values

$k_\infty = 5.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 220–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ over the temperature range 220–300 K.

Comments on Preferred Values

The preferred values are based on the data of Sehested et al. (1998) and Tyndall et al. (1997) using the temperature-independent reference rate constant for CH_3CO+Cl_2 of Tyndall et al. (1999).

References

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Tyndall, G. S., Orlando, Kegley-Owen, C. S., Wallington, T. J., and Hurley, M. D.: Int. J. Chem. Kinet., 31, 776, 1999.

II.A4.97

$$CH_2OH + O_2 \rightarrow HCHO + HO_2$$

$\Delta H^\circ = -76.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.5 \pm 2.5) \times 10^{-12}$	298	Grotheer et al., 1985	DF-MS (a)
$(1.06 \pm 0.25) \times 10^{-11}$	296	Dóbé et al., 1985	DF-LMR (b)
$(1.05 \pm 0.47) \times 10^{-11}$	296		
$(8.6 \pm 2.0) \times 10^{-12}$	298	Payne et al., 1988	DF-MS (c)
$2.5 \times 10^{-9}\ T^{-1.0}$ + 4.0×10^{-10}exp(-2525/T)	370–684	Grotheer et al., 1988	DF-MS (d)
5.6×10^{-9} exp(-1700/T)	215–250	Nesbitt et al., 1988	DF-MS (e)
$(8.61 \pm 1.14) \times 10^{-12}$	300		
$(8.8 \pm 0.2) \times 10^{-12}$	298	Pagsberg et al., 1989	PR-AS (f)
$(1.17 \pm 0.12) \times 10^{-11}$	296	Miyoshi et al., 1990	PLP-MS (g)
$(1.00 \pm 0.14) \times 10^{-11}$	294	Hanoune et al., 2001	PLP-AS (h)

Comments

(a) CH_2OH was generated from Cl+CH_3OH at total pressures of 0.4 mbar to 1.2 mbar (0.3 Torr to 0.9 Torr). k was derived from the rate of disappearance of CH_2OH in excess O_2 by MS.

(b) CH_2OH was generated from F+CH_3OH at total pressures of 0.69 mbar to 6.5 mbar (0.52 Torr to 4.9 Torr). Two values of k were derived from the rate of disappearance of CH_2OH and of the appearance of HO_2, both monitored by LMR spectroscopy.

(c) CH_2OH was generated from Cl + CH_3OH at total pressures of ∼1.3 mbar (∼1 Torr). k was derived from the rate of disappearance of CH_2OH in excess O_2 by MS.

(d) As for comment (a) at pressures of ∼1.1 mbar (∼ 0.8 Torr).

(e) As for comment (c) at pressures of ∼1.3 mbar (∼ 1 Torr).

(f) CH_2OH was generated from F+CH_3OH at total pressures of 1 bar (760 Torr). k was derived from the rate of disappearance of CH_2OH in excess of O_2 by absorption at 285.5 nm.

(g) Pulsed laser photolysis of $CH_3C(O)CH_2OH$, with the decay of CH_2OH being monitored by photoionization MS, at total pressures of 1.7 mbar to 7.3 mbar (1.3 Torr to 5.5 Torr).

(h) Pulsed laser photolysis of a mixture of CH_3OH and Cl_2 at 355 nm with monitoring of HCHO at 1707.9 cm^{-1} by tunable diode laser absorption in the range 7.71–20.22 mbar (5.8–15.2 Torr). Only data with $[O_2] > 2 \times 10^{15}$ molecule cm^{-3} have been used in the analysis.

Preferred Values

$k = 9.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.12$ at 298 K.

Comments on Preferred Values

The rate coefficient at 298 K is now well established for this reaction, and our recommendation is the average of the results of Grotheer et al. (1985), Dóbé et al. (1985), Payne et al. (1988), Nesbitt et al. (1988), Pagsberg et al. (1989), Miyoshi et al. (1990) and Hanoune et al. (2001). The earlier data of Wang et al. (1984) and Radford (1980) are rejected on the basis that they involved high concentrations of radicals, leading to mechanistic complications (Radford, 1980). The two studies of the temperature dependence of this reaction (Grotheer et al., 1989, Nesbitt et al., 1988) indicate that the rate coefficient follows a complicated non-Arrhenius behavior over the range 200 K to 700 K. The existing data on the temperature dependence are difficult to explain and more work is needed to confirm the observed temperature dependence of this reaction before a recommendation can be made.

Grotheer et al. (1988) have carried out experiments replacing CH_3OH by CH_3OD and have observed no kinetic isotope effect for the CH_2OH/CH_2OD+O_2 reactions.

References

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Wang, W. C., Suto, M., and Lee, L. C.: J. Chem. Phys., 81, 31, 1984.

II.A4.98

$CH_3CHOH + O_2 \rightarrow CH_3CHO + HO_2$

$\Delta H^\circ = -87.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.4 \times 10^{-8} T^{-1.2}$ + 8.0×10^{-10} exp(-2525/T)	300–682	Grotheer et al., 1988	DF-MS (a)
1.56×10^{-11}	300		
$(1.3 \pm 0.2) \times 10^{-11}$	300	Anastasi et al., 1989	PR-AS (b)
$(2.8 \pm 0.2) \times 10^{-11}$	293	Miyoshi et al., 1989	PLP-MS (c)

Comments

(a) CH_3CHOH was generated from Cl+C_2H_5OH in the presence of a large excess of O_2 at total pressures of ∼1 mbar (∼0.8 Torr). The rate coefficient k was derived from the disappearance of CH_3CHOH, as monitored by low electron energy MS.

(b) Pulsed radiolysis of Ar-SF_6-HCl-C_2H_5OH-O_2 mixtures at total pressures of 1 bar (760 Torr) and with $[SF_6] \gg [HCl] \gg [C_2H_5OH] \gg [O_2]$. CH_3CHOH was generated from Cl+C_2H_5OH and monitored by UV absorption at 260 nm.

(c) Pulsed laser photolysis of $CH_3C(O)CH(OH)CH_3$ in a large excess of He at total pressures of 2.7 mbar to 9.3 mbar (2 Torr to 7 Torr). CH_3CHOH was monitored by photoionization MS in the presence of excess O_2.

Preferred Values

$k = 1.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value of k_{298} is the mean of the results of Grotheer et al. (1989), Anastasi et al. (1989) and Miyoshi et al. (1989). The rather large discrepancy between the data of Miyoshi et al. (1989) and the other two studies (Grotheer et al., 1989; Anastasi et al., 1989) could be due to the different sources of generation of the CH_3CHOH radical. CH_3CHOH radical generation involving Cl attack on C_2H_5OH (Grotheer et al., 1989; Anastasi et al., 1989) may not be as clean a source as is the photolysis of $CH_3C(O)CH(OH)CH_3$ (Miyoshi et al., 1989).

The temperature dependence of the rate coefficient determined by Grotheer et al. (1989) shows a marked non-Arrhenius behavior, but this needs to be confirmed before a recommendation can be made. Evidence for the reaction between CH_3CHOH and O_2 yielding CH_3CHO as a major product comes from the product study of the photooxidation of ethanol by Carter et al. (1979).

References

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Miyoshi, A., Matsui, H., and Washida, N.: Chem. Phys. Lett., 160, 291, 1989.

II.A4.99

$CH_2CH_2OH + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.0 \pm 0.4) \times 10^{-12}$	293	Miyoshi et al., 1989	PLP-MS (a)

Comments

(a) Pulsed laser photolysis of $ClCH_2CH_2OH$ and $BrCH_2CH_2OH$ in a large excess of He at total pressures of 2.7 mbar to 9.3 mbar (2 Torr to 7 Torr). CH_2CH_2OH radicals were monitored by photoionization MS in the presence of excess O_2.

Preferred Values

$k = 3.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The direct measurements of this rate coefficient (Miyoshi et al., 1989), from the pulsed laser photolysis of either $ClCH_2CH_2OH$ or $BrCH_2CH_2OH$ as the radical source, showed a good level of consistency. By analogy with the reactions $C_2H_5+O_2+M \rightarrow C_2H_5O_2+M$ and $CH_3CO+O_2+M \rightarrow CH_3CO_3+M$ (this evaluation), the rate coefficient for this reaction is expected to be close to the high-pressure limit under the experimental conditions employed. The UV absorption spectrum of the $HOCH_2CH_2O_2$ radical has been observed by pulse radiolysis of SF_6-H_2O mixtures (Anastasi et al., 1991) and pulsed laser photolysis of H_2O_2 in the presence of C_2H_4 and O_2 (Murrells et al., 1991). These observations indicate that the reaction between CH_2CH_2OH radicals and O_2 leads predominantly to the adduct peroxy radical.

References

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Murrells, T. P., Jenkin, M. E., Shalliker, S. J., and Hayman, G. D.: J. Chem. Soc. Faraday Trans., 87, 2351, 1991.

Appendix A5: R + O_2

II.A5.100

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$\Delta H^\circ = -111.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.05×10^{-13} exp(-1310/T)	413–628	Gutman et al., 1982	PLP-LIF (a)
1.3×10^{-15}	298		
5.5×10^{-14} exp(-1000/T)	298–450	Lorenz et al., 1985	PLP-LIF (b)
1.9×10^{-15}	298		
2.3×10^{-14} $(1000/T)^{-9.5}$ × exp(2768/T)	298–973	Wantuck et al., 1987	PLP-LIF (c)
2.1×10^{-15}	298		

Comments

(a) CH_3O generated from pulsed laser photolysis of CH_3ONO at 266 nm. [CH_3O] was monitored by LIF at a total pressure of 53 mbar (40 Torr).

(b) Pulsed laser photolysis of CH_3ONO with monitoring of CH_3O by LIF, at pressures of 100 mbar (75 Torr) of He. At 298 K the rate coefficient was shown to be independent of pressure over the range 10 mbar to 200 mbar (7.5 Torr to 150 Torr) of He.

(c) Pulsed laser photolysis of CH_3OH or CH_3ONO at 193 nm in the presence of O_2 plus 33 mbar (25 Torr) of Ar. CH_3O radicals were monitored by LIF. Non-Arrhenius behavior was observed over entire temperature range and fitted by the cited empirical equation. Rate coefficients combined with the data of Gutman et al. (1982) and Lorenz et al. (1985) were found to obey a double exponential expression, with k=(1.5×10^{-10} exp(-6028/T)+3.6×10^{-14} exp(-880/T)) cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k = 1.9 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.2 \times 10^{-14}$ exp(-1080/T) cm^{3}molecule^{-1} s^{-1} over the temperature range 290–610 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The direct measurements of the rate coefficients by Lorenz et al. (1985) (298 K to 450 K) and Wantuck et al. (1987) (298 K to 973 K) are in good agreement with the similar measurements of Gutman et al. (1982) (413 K to 608 K), where the temperature ranges overlap. The preferred values are derived from a least-squares analysis of these three sets of data (Gutman et al., 1982; Lorenz et al., 1985; Wantuck et al., 1987) over the temperature range 298 K to 608 K. The higher temperature measurements of Wantuck et al. (1987) give a clear indication of non-Arrhenius behavior over the extended temperature range. The anomalously low A-factor for a simple H-atom transfer reaction and the possibility of a more complicated mechanism have both been noted (NASA, 1997).

References

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Lorenz, K., Rhäsa, D., Zellner, R., and Fritz, B.: Ber. Bunsenges. Phys. Chem., 89, 341, 1985.
NASA Evaluation No. 12, 1997 (see references in Introduction).
Wantuck, P. J., Oldenborg, R. C., Baughcum, J. L., and Winn, K. R.: J. Phys. Chem., 91, 4653, 1987.

II.A5.101

$$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$$

$\Delta H° = -135.7$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
8.0×10^{-15}	296	Gutman et al., 1982	PLP-LIF (a)
9.8×10^{-15}	353		
7.1×10^{-14} exp[-(552 ± 64)/T]	295–411	Hartmann et al., 1990	PLP-LIF (b)
$(1.08 \pm 0.20) \times 10^{-14}$	295		
2.4×10^{-14} exp[-(325 ± 120)/T]	295–354	Fittschen et al., 1999	PLP-LIF (c)
8.1×10^{-15}	298		

Comments

(a) Pulsed laser photolysis of C_2H_5ONO at 266 nm, with C_2H_5O radicals being monitored by LIF at a total pressure of 53 mbar (40 Torr).

(b) Pulsed laser photolysis of C_2H_5ONO at 266 nm in C_2H_5ONO-O_2-He mixtures, with LIF monitoring of C_2H_5O radicals in the wavelength range 310 nm to 330 nm. Studies were carried out at a total pressure of 35 mbar (26 Torr).

(c) Pulsed laser photolysis of C_2H_5ONO at 248 nm in C_2H_5ONO-O_2-He mixtures at 133 mbar (100 Torr) with LIF detection of C_2H_5O radicals excited at 323 nm and fluorescence detection to the red of 375 nm. The upper temperature limit was set by the unimolecular decomposition rate of ethoxy radical.

Preferred Values

$k = 8.1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.4 \times 10^{-14}$ exp(-325/T) cm^{3}molecule^{-1} s^{-1} over the temperature range 295–354 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred rate constant at 298 K is that of Gutman et al. (1982) and Fittschen et al. (1999). Their temperature dependence over the common range 296–353 K is in excellent agreement and is therefore recommended here. The relative rate measurements of Zabarnick and Heicklen (1985) yield a value of k_{298} which is consistent with the preferred value within the recommended error limits.

It should be noted that the A-factor for the above reaction is very low, but in keeping with that for the analogous reaction $CH_3O+O_2 \rightarrow HCHO+HO_2$.

References

Fittschen, C., Frenzel, A., Imrik, K., and Devolder, P.: Int. J. Chem. Kin., 31, 860, 1999.
Gutman, D., Sanders, N., and Butler, J. E.: J. Phys. Chem., 86, 66, 1982.
Hartmann, D., Karthäuser, J., Sawerysyn, J. P., and Zellner, R.: Ber. Bunsenges. Phys. Chem., 94, 639, 1990.
Zabarnick, S. and Heicklen, J.: Int. J. Chem. Kinet., 17, 455, 1985.

II.A5.102

$1\text{-}C_3H_7O + O_2 \rightarrow C_2H_5CHO + HO_2$

$\Delta H^\circ = -131.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.4×10^{-14} exp[-(108 ± 61)/T]	223–303	Mund et al., 1998	PLP-LIF (a)
9.8×10^{-15}	298		
2.5×10^{-14} exp[-(240 ± 60)/T]	289–381	Fittschen et al., 1999	PLP-LIF (b)
1.1×10^{-14}	298		
Relative Rate Coefficients			
2.8×10^{-13} exp[-(879 ± 117)/T]	247–393	Zabarnick and Heicklen, 1985	RR (c)
1.5×10^{-14}	298		

Comments

(a) Pulsed laser photolysis of propyl nitrite at 351 nm with laser-induced fluorescence detection of n-propoxy radical in the range 6–110 mbar He.

(b) Pulsed laser photolysis of $1\text{-}C_3H_7ONO$ at 351 nm in $1\text{-}C_3H_7ONO\text{-}O_2\text{-}He$ mixtures in the range 40–133 mbar (30–100 Torr) with LIF detection of $1\text{-}C_3H_7O$ excited at 349 nm and fluorescence detection to the red of 375 nm. The upper temperature limit is set by the unimolecular decomposition rate of n-propoxy radical.

(c) Photolysis at 366 nm of $n\text{-}C_3H_7ONO$ in a static system in the presence of NO, O_2, and N_2 at total pressures of >200 mbar (>150 Torr). Rate data were based on the measured quantum yields of C_2H_5CHO product. The rate coefficient k was measured relative to $n\text{-}C_3H_7O\text{+}NO \rightarrow$ products with $k(n\text{-}C_3H_7O\text{+}O_2)/k(n\text{-}C_3H_7O\text{+}NO)=6.8\times10^{-3}$ exp(-879/T), and is placed on an absolute basis by use of $k(n\text{-}C_3H_7O\text{+}NO)=4.1\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature.

Preferred Values

$k = 1.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.6 \times 10^{-14}$ exp(-253/T) cm^3 molecule^{-1} s^{-1} over the temperature range 220–380 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values are based on the absolute rate study of Fittschen et al. (1999), which is in excellent agreement with that of Mund et al. (1998) in the overlapping temperature range. The temperature dependence is that of both data sets taking into account the A factor that differs by a factor of two. The rate coefficients derived from the relative rate study of Zabarnick and Heicklen (1985) are in significant disagreement with the absolute rate data (Mund et al., 1998; Fittschen et al., 1999).

References

Mund, Ch., Fockenberg, Ch., and Zellner, R.: Ber. Bunsenges. Phys. Chem., 102, 709, 1998.
Fittschen, C., Frenzel, A., Imrik, K., and Devolder, P.: Int. J. Chem. Kin., 31, 860, 1999.
Zabarnick, S. and Heicklen, J.: Int. J. Chem. Kinet., 17, 455, 1985.

II.A5.103

$$\mathbf{2\text{-}C_3H_7O + O_2 \rightarrow CH_3C(O)CH_3 + HO_2}$$

$\Delta H^\circ = -150.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.51×10^{-14} exp[-(200 ± 140/T)]	294–384	Balla et al., 1985	PLP-LIF (a)
7.72×10^{-15}	298		
1.4×10^{-14} exp[-(217 ± 49)/T]	288–313	Mund et al., 1998, 1999	PLP-LIF (b)
6.8×10^{-15}	298		
1.6×10^{-14} exp[-(265 ± 24)/T]	218–364	Fittschen et al., 1999	PLP-LIF (c)
6.6×10^{-15}	298		
$(8.7 \pm 2.5) \times 10^{-15}$	296	Deng et al., 2000	PLP-LIF (d)

Comments

(a) Pulsed laser photolysis of 2-propyl nitrite at 355 nm, with LIF detection of 2-C_3H_7O radicals. The pressure range was 1.3 mbar to 67 mbar (1 Torr to 50 Torr).

(b) Pulsed laser photolysis of 2-propyl nitrite at 351 nm with laser-induced fluorescence detection of i-propoxy radical in the range 6–110 mbar He.

(c) Pulsed laser photolysis of 2-C_3H_7ONO at 351 nm in 2-C_3H_7ONO-O_2-He mixtures in the range 67–267 mbar (50–200 Torr) with LIF detection of 2-C_3H_7O excited at 347 nm and fluorescence detection to the red of 375 nm. The upper temperature limit is set by the unimolecular decomposition rate of i-propoxy radical.

(d) Pulsed laser photolysis of 2-propyl nitrite at 355 nm with laser-induced fluorescence detection of i-propoxy radical.

Preferred Values

$k = 7.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.5 \times 10^{-14}$ exp(-230/T) cm^{3}molecule^{-1} s^{-1} over the temperature range 210–390 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The results of Balla et al. (1985), Mund et al. (1998, 1999) and Fittschen et al. (1999) are in excellent agreement. The preferred values are based on the temperature-dependent data of Balla et al. (1985), Mund et al. (1998, 1999) and Fittschen et al. (1999).

References

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Mund, Ch., Fockenberg, Ch., and Zellner, R.: Ber. Bunsenges. Phys. Chem., 102, 709, 1998.
Mund, Ch., Fockenberg, Ch., and Zellner, R.: Phys. Chem. Chem. Phys., 1, 2037, 1999.

II.A5.104

$$\mathbf{CH_3CH_2CH_2CH_2O + O_2 \rightarrow CH_3CH_2CH_2CHO + HO_2}$$

$\Delta H° = -127.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
7.7×10^{-15}	298	Hoffmann et al., 1992	PLP-LIF (a)
$(1.4 \pm 0.7) \times 10^{-14}$	293	Hein et al., 1999	PLP-AS/LIF (b)
Relative Rate Coefficients			
6.8×10^{-13} exp[-(1178 ± 176)/T]	265–393	Morabito and Heicklen, 1987	RR (c)
1.3×10^{-14}	298		

Comments

(a) Pulsed laser photolysis of Cl_2 in the presence of n-C_4H_{10}-O_2-NO mixtures in a flow system at total pressures of 10–50 mbar (6.7–37.5 Torr). Time-resolved monitoring of HO radicals was carried out by CW-laser absorption, and of NO_2 by LIF. The rate coefficient was derived from a computer simulation of HO radical and NO_2 temporal profiles.

(b) Pulsed laser photolysis at 248 nm of a mixture of 1-bromobutane, O_2 and NO in N_2 at 50 mbar total pressure in a slow-flow system. HO and NO_2 were monitored in real-time using laser long-path absorption at 308.417 nm and cw laser-excited fluorescence after excitation at 488 nm, respectively. The rate coefficient was derived from a computer simulation of the HO and NO_2 temporal concentration profiles.

(c) Photolysis of 1-butyl nitrite at 366 nm in the presence of NO and O_2. Rate data were derived from the quantum yields of product formation, and a rate coefficient ratio of $k(1\text{-}C_4H_9O+O_2)/k(1\text{-}C_4H_9O+NO)=1.67\times10^{-2}$ exp[-(1178±176)/T] was obtained. This rate coefficient ratio is placed on an absolute basis using a rate cofficient of $k(1\text{-}C_4H_9O+NO)=4.1\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature (see data sheet for 2-C_3H_7O + NO this evaluation).

Preferred Values

$k = 1.4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.9 \times 10^{-14}$ exp(-550/T) cm^3 molecule^{-1} s^{-1} over range 270–340 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm$ 300K.

Comments on Preferred Values

k(298 K) based on the indirect study of Hein et al. (1999), which is in good agreement with the relative rate technique by Morabito and Heicklen (1987) at 298 K. Temperature dependence adopts (E/R) estimated by Atkinson (1997), based on available data for smaller alkoxy radicals, and an A-factor to give the preferred value at 298 K.

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II.A5.105

$$CH_3CH_2CH_2CH_2O + M \rightarrow CH_2CH_2CH_2CH_2OH + M$$

$\Delta H^\circ = -14.7$ kJ·mol^{-1}

Rate coefficient data

k/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.5 \pm 2) \times 10^4$	293	Hein et al., 1999	PLP-AS/LIF (a)
Relative Rate Coefficients			
2.2×10^5	303	Carter et al., 1979	S-GC (b)
$(2.1 \pm 0.5) \times 10^5$	296	Cox et al., 1981	S-GC (c)
$(2.7 \pm 0.2) \times 10^5$	298	Niki et al., 1981	S-FTIR (d)
$9.5 \times 10^{10} \exp(-3864/T)$	265-393	Morabito and Heicklen, 1987	S-GC (e)
2.2×10^5			
$(2.7 \pm 0.9) \times 10^5$	298	Geiger et al., 2002	S-FTIR (f)
$1.8 \times 10^{10} \exp(-3270/T)$	250-318	Cassanelli et al., 2005	FR-GC (g) (h)
3.0×10^5	298		
$4.9 \times 10^{10} \exp(-3570/T)$	253-295	Cassanelli et al., 2006	S-FTIR (i) (h)
3.1×10^5	298		

Comments

(a) Pulsed laser photolysis at 248 nm of a mixture of 1-bromobutane, O_2 and NO in N_2 at 50 mbar total pressure in a slow-flow system. HO and NO_2 were monitored in real-time using laser long-path absorption at 308.417 nm and cw laser-excited fluorescence after excitation at 488 nm, respectively. The rate coefficient was derived from a computer simulation of the HO and NO_2 temporal concentration profiles and is believed to be in the fall-off range.

(b) Smog chamber photolysis of n-C_4H_{10}-NO_x-air mixtures at 1 bar pressure in a 5870 L chamber at wavelengths >300 nm. End-product analysis of C_3H_7CHO by GC. $k/k(1\text{-}C_4H_9O+O_2)=1.6\times10^{19}$ molecule cm^{-3} obtained from yields of C_3H_7CHO and the rate of disappearance of n-C_4H_{10}. The above value of k is calculated by using a rate coefficient of $k=1.4\times10^{-14}$ cm^3 molecule^{-1} s^{-1} for the reference reaction 1-C_4H_9O + O_2 → C_3H_7CHO + HO_2 at 298 K (this evaluation).

(c) Smog chamber photolysis of n-C_4H_{10}-HONO-air mixtures at 1 bar (760 Torr) pressure. End product analysis of C_3H_7CHO by GC. $k/k(1\text{-}C_4H_9O+O_2)=(1.5\pm 0.5)\times10^{19}$ molecule cm^{-3} was derived from the yields of C_3H_7CHO and the rate of disappearance of n-C_4H_{10} as a function of [O_2]. Above value of k was calculated by using a rate coefficient of $k=1.4\times10^{-14}$ cm^3 molecule^{-1} s^{-1} for the reference reaction, 1-C_4H_9O + O_2 → C_3H_7CHO + HO_2 at 298 K (this evaluation).

(d) Photolysis of 1-C_4H_9ONO-NO-O_2-N_2 mixtures at 930 mbar (700 Torr) pressure in an FTIR cell. $k/k(1\text{-}C_4H_9O+O_2)=(1.9\pm0.2)\times10^{19}$ molecule cm^{-3} was derived from yields of C_3H_7CHO and the rate of disappearance of 1-C_4H_9ONO measured by calibrated FTIR spectroscopy. Above value of k calculated using a rate coefficient of $k=1.4\times10^{-14}$ cm^3 molecule^{-1} s^{-1} for the reference reaction, 1-C_4H_9O+O_2 →C_3H_7CHO+HO_2 at 298 K (this evaluation).

(e) Photolysis of 1-C_4H_9ONO-air mixtures at 1013 mbar (760 Torr) pressure. Analysis by GC. $k/k(1\text{-}C_4H_9O + NO) = (2.5 \pm 0.2) \times 10^{-23}$ cm^3 molecule^{-1} s^{-1} was derived from [O_2]-dependence of yields of C_3H_7CHO and the rate of disappearance of 1-C_4H_9ONO. Above value of k calculated using a rate coefficient of $k = 2.3 \times 10^{-11} \exp(150/T)$ cm^3 molecule^{-1} s^{-1} for the reference reaction, 1-C_4H_9O + NO → C_4H_9ONO, recommended by Atkinson (1997).

(f) Photolysis of 1-C_4H_9I-NO-O_2-N_2 mixtures at 1013 mbar (760 Torr) pressure. k/k(1-C_4H_9O + O_2) = (1.8 ± 0.6) × 10^{19} molecule cm^{-3} was derived from yields of C_3H_7CHO and the rate of disappearance of 1-C_4H_9ONO measured by calibrated FTIR spectroscopy. The observed [O_2] dependence of this ratio was attributed to influence of 10-20% production of 'hot' 1-butoxy produced in the RO_2 + NO reaction. Cited value of the ratio k refers to the thermally relaxed 1-butoxy and k is calculated using a rate coefficient of k(1-C_4H_9O + O_2) = 1.4 × 10^{-14} cm^3 $molecule^{-1}$ s^{-1} for the reference reaction, 1-C_4H_9O + O_2 → C_3H_7CHO + HO_2 at 298 K (this evaluation).

(g) Photolysis of 1-C_4H_9ONO-NO-O_2-N_2 mixtures or n-C_4H_{10}-HONO (or CH_3ONO)-NO-O_2-N_2 mixtures at 1013 mbar (760 Torr) pressure. Analysis by GC. k/k(1-C_4H_9O + O_2) = (1.98 ± 0.50) × 10^{23} exp{-(2720 ± 470)/T} molecule cm^{-3} was derived from [O_2]-dependence of yields of C_3H_7CHO and the rate of disappearance of 1-C_4H_9ONO. Evidence for the influence of 10% production of 'hot' 1-butoxy produced in the photolysis of 1-C_4H_9ONO. Cited value of the ratio k refers to the thermally relaxed 1-butoxy.

(h) Above value of k calculated using a rate coefficient of k = 8.9 × 10^{-14} exp(-550/T) cm^3 $molecule^{-1}$ s^{-1} for the reference reaction, 1-C_4H_9O + O_2 → C_3H_7CHO + HO_2, based on k(298 K) = 1.4 × 10^{-14} cm^3 $molecule^{-1}$ s^{-1} from this evaluation, and the temperature dependence recommended by Atkinson (1997; 2000): E/R = 550 K.

(i) Photolysis of 1-C_4H_9ONO-air mixtures at 930 mbar (700 Torr) pressure. Analysis by FTIR. k/k(1-C_4H_9O + O_2) = 5.5 × 10^{23} exp{-(3020±110)/T} molecule cm^{-3} was derived from [O_2]-dependence of relative yields of C_3H_7CHO and HOC_3H_7CHO (the main product formed following isomerisation), adjusted to take account of secondary reactions.

Preferred Values

k = 4.6 × 10^{10} exp(-3570/T) s^{-1} at 298 K over the temperature range 250–350 K and 1 bar pressure.
k = 2.9 × 10^5 s^{-1} at 298 K and 1 bar pressure.

Reliability

Δ log k = ± 0.2 at 298 K.
Δ (E/R) = ± 300 K.

Comments on Preferred Values

The preferred rate coefficient at room temperature is the mean from the relative rate studies of Cassanelli et al. (2005; 2006) and Geiger et al. (2002), which both take into account influence of 'hot' 1-butoxy radicals. The studies of Carter et al. (1979), Cox et al. (1981), Niki et al. (1981), Morabito and Heicklen, (1987) all give similar results. The values of k are all calculated using a rate coefficient of k(1-C_4H_9O + O_2) = 8.9 × 10^{-14} exp(-550/T) cm^3 $molecule^{-1}$ s^{-1} for the reference reaction (this evaluation). The direct measurement of Hein et al. (1999) at 50 mbar total pressure shows that the reaction is in the fall-off region below 1 bar. The preferred value of E/R is a mean of the results from the 2 studies of Cassanelli et al. (2005; 2006) and that of Morabito and Heicklen, (1987), and the A-factor fitted to give the recommended k_{298}. The pre-exponential factor obtained is lower than estimated by Atkinson (1997), but is consistent with the theoretical calculations of Vereecken and Peters (2003) using a rigorous multirotamer TST treatment.

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II.A5.106

$$\begin{array}{llr} \mathbf{CH_3OCH_2O + O_2} & \rightarrow \mathbf{CH_3OCHO + HO_2} & \mathbf{(1)} \\ \mathbf{CH_3OCH_2O + M} & \rightarrow \mathbf{CH_3OCHO + H + M} & \mathbf{(2)} \end{array}$$

Rate coefficient data

$k_1.k_2^{-1}$/cm^3 molecule^{-1}	Temp./K	Reference	Technique/Comments
$k_1[O_2] \sim k_2$(1 bar, air)	295	Jenkin et al., 1993	RR (a)

Comments

(a) Steady-state photolysis of Cl_2-CH_3OCH_3-O_2-N_2 mixtures at pressures of 13.3 mbar to 1013 mbar (10 Torr to 760 Torr) with long-path FTIR analyses, and molecular modulation studies of similar reactant mixtures with UV absorption monitoring of $CH_3OCH_2O_2$ radicals. In both systems, kinetic treatments indicate that Reactions (1) and (2) were competing under the conditions of the experiments.

Preferred Values

No quantitative recommendations.

Comments on Preferred Values

Although the results listed above for the reactions of the CH_3OCH_2O radical are not quantitative, for the purposes of atmospheric modelling studies it is recommended that the above qualitative information on the ratios k_1/k_2 be used to decide if one or the other of the alkoxy radical reaction pathways predominates, or if both pathways should be considered.

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II.A5.107

$$\begin{aligned} \mathbf{CH_3C(O)CH_2O + O_2} &\rightarrow \mathbf{CH_3C(O)CHO + HO_2} \quad \mathbf{(1)} \\ \mathbf{CH_3C(O)CH_2O + M} &\rightarrow \mathbf{CH_3CO + HCHO + M} \quad \mathbf{(2)} \end{aligned}$$

Rate coefficient data

$k_1.k_2^{-1}$/cm^3 molecule^{-1}	Temp./K	Reference	Technique/Comments
$k_1[O_2] \ll k_2$ (1 bar, air)	298	Jenkin et al., 1993	RR (a)
$k_1[O_2] \ll k_2$ (1 bar, air)	298	Bridier et al., 1993	RR (b)
$k_1[O_2] \ll k_2$ (1 bar, O_2/N_2)	225–298	Orlando et al., 2000	S-FTIR (c)

Comments

(a) Steady-state photolysis of Cl_2-$CH_3C(O)CH_3$-O_2-N_2 mixtures at 930 mbar (700 Torr) with long-path FTIR and long-path UV visible diode array spectroscopy analyses of products. Data indicate that Reaction (2) predominated over Reaction (1) under the conditions of the experiments.

(b) Flash photolysis of Cl_2-$CH_3C(O)CH_3$-air mixtures at 1 bar pressure with UV absorption monitoring of $CH_3C(O)CH_2O_2$ radicals. Data indicate that Reaction (2) predominated over Reaction (1) under the conditions of the experiments.

(c) Mixtures of Cl_2-acetone-O_2 pressurised to 1 atm with N_2 with and without NO_x were irradiated in a static chamber using a filtered Xe-arc lamp. The diagnostic products HCHO and methylglyoxal ($CH_3C(O)CHO$) and others were monitored using in situ long pathlength FTIR absorption. The independence of HCHO and $CH_3C(O)CHO$ yields on the O_2 partial pressure varied from 66 to 865 mbar was taken as an indication of the predominance of (2) over (1) across the entire temperature range 225–298 K, even at 1 atm of O_2: $k_2/k_1 = 1.5\times10^{20}$ and 1.0×10^{20} molecule cm^{-3} at 298 and 225 K, respectively.

Preferred Values

No quantitative recommendations.

Comments on Preferred Values

Although the results listed above for the reactions of the $CH_3C(O)CH_2O$ radical are not quantitative, for the purposes of atmospheric modelling studies it is recommended that the above qualitative information on the ratios k_1/k_2 be used to decide if one or the other of the alkoxy radical reaction pathways predominates, or if both pathways should be considered. All three studies listed above point towards the predominance of the decomposition pathway under atmospheric conditions down to 225 K.

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II.A5.108

$$\mathbf{CH_3CH(O)CH_2CH_3 + O_2 \rightarrow CH_3C(O)CH_2CH_3 + HO_2}$$

ΔH° = -154.4 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.5 \pm 2.0) \times 10^{-15}$	293	Hein et al., 1999	PLP-AS/LIF (a)
$1.33 \times 10^{-15} \exp[(659 \pm 83)/T]$	223–311	Deng et al., 2000	PLP/LIF (b)
$(1.2 \pm 0.4) \times 10^{-14}$	298		
$1.2 \times 10^{-15} \exp[(553 \pm 193)/T]$	221–266	Deng et al., 2001	PLP/LIF (c)
7.7×10^{-15}	298*		
$(9 \pm 3) \times 10^{-15}$	295	Falgayrac et al., 2004	PLP/LIF (d)

Comments

(a) Pulsed laser photolysis at 248 nm of a mixture of 2-bromobutane, O_2 and NO in N_2 at 50 mbar total pressure in a slow-flow system. HO and NO_2 were monitored in real-time using laser long-path absorption at 308.417 nm and cw laser-excited fluorescence after excitation at 488 nm, respectively. The rate coefficient was derived from a computer simulation of the HO and NO_2 temporal concentration profiles.

(c) Laser photolysis (355 nm) of 2-C_4H_9ONO-N_2-O_2 mixtures; LIF detection of 2-butoxy radicals. No pressure dependence observed.

(c) Repeat study as in (b) but with improved experimental arrangement, giving less potential problems with secondary chemistry. k(298K) obtained by extrapolation.

(d) Laser photolysis (351 nm) of 2-C_4H_9ONO-He-O_2 mixtures; LIF detection of 2-butoxy radicals. The same value of k was obtained at 291 and 295 K but investigation over a larger temperature range was not possible due to experimental constraints. An uncertainty of ±30% was estimated for the rate coefficient.

Preferred Values

$k = 7.6 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.5 \times 10^{-14} \exp(-200/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250-350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm$ 300K.

Comments on Preferred Values

The measurements of Hein et al. (1999), Falgayrac et al. (2004) and Deng et al. (2001) are in reasonable agreement. The preferred value for k(298 K) is the mean of these values. The second study of Deng et al. (2001) suggests problems in their earlier study (Deng et al., 2001). Although Deng et al. (2000; 2001) report a negative temperature dependence, we prefer to adopt the temperature dependence estimated by Atkinson (1997), (E/R = 200 K), based on available data for smaller alkoxy radicals, and an A-factor adjusted to give the preferred value at 298 K.

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II.A5.109

$$\mathbf{CH_3CH(O)CH_2CH_3 + M \rightarrow CH_3CHO + C_2H_5 + M \quad (1)}$$
$$\mathbf{\rightarrow CH_3 + C_2H_5CHO + M \quad (2)}$$

$\Delta H°(1) = 24.6$ kJ·mol^{-1}
$\Delta H°(2) = 28.5$ kJ·mol^{-1}

Rate coefficient data

k/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_1 = (3.5 \pm 2) \times 10^3$	293	Hein et al., 1998	PLP-AS/LIF (a)
$k_\infty = 1.1 \times 10^{14} \exp(-6450/T)$	291–348	Falgayrac et al., 2004	PLP/LIF (b)
$k_0 = 3.2 \times 10^{-8} \exp(-4320/T)$[He]			
$k = 2.9 \times 10^4$ (1 bar N_2)	298		
Relative Rate Coefficients			
$k_1 = 6.3 \times 10^{14} \exp(-7700/T)$	440–471	Batt and McCulloch, 1976	S-GC (c)
$k_1 = 3.8 \times 10^3$	298		
$k_1 = 2.2 \times 10^4$	303	Carter et al., 1979	S-GC (d)
$k_1 = 1.95 \times 10^4$	296	Cox et al., 1981	S-GC (e)
$k_1 = 6.3 \times 10^{13} \exp(-7600/T)$	363–503	Heiss et al., 1991	F-TLC/
$k_1 = 5.3 \times 10^2$	298		HPLC (f)
$k_1 = 3.0 \times 10^{12} \exp(-5663/T)$	280-313	Libuda et al., 2002	S-FTIR (g) (h)
$k_1 = 2.2 \times 10^4$			
$k_1 = 2.2 \times 10^4$	298	Meunier et al., 2003	S-FTIR (i) (h)
$k_1 = 4.1 \times 10^{12} \exp(-5904/T)$	250-318	Cassanelli et al., 2005	FR-GC (j) (h)
$k_1 = 2.0 \times 10^4$			
Branching Ratios			
$k_1/k_2 = 0.59 \exp(1350/T)$	399–493	Drew et al., 1985	S-GC (k)
$k_1/k_2 = 55$	298		

Comments

(a) Pulsed laser photolysis at 193 or 248 nm of a mixture of 2-bromobutane, O_2 and NO in N_2 at 50 mbar total pressure in a slow-flow system. HO and NO_2 were monitored in real-time using laser long-path absorption at 308.417 nm and cw laser-excited fluorescence after excitation at 488 nm, respectively. The rate coefficient was derived from a computer simulation of the HO and NO_2 temporal concentration profiles and is in the fall-off region at the total pressure used.

(b) Laser photolysis (351 nm) of 2-C_4H_9ONO-He mixtures with LIF detection of 2-butoxy radicals. The temperature and pressure dependence of the unimolecular decomposition was measured at total pressures between $0.01 < p < 0.8$ bar of helium and at four temperatures between 291 and 348 K. The low and the high pressure limiting rate coefficients as well as the broadening factor F_{cent} have been extracted from a falloff analysis of the experimental results: $k_{3,0,He} = 3.2 \times 10^{-8} \exp(-35.9 \text{ kJ mol}^{-1}/RT)$ cm^3 s^{-1}, $k_\infty = 1.1 \times 10^{14} \exp(-53.6 \text{ kJ mol}^{-1}/RT)$ s^{-1}, and $F_{3,c} = 0.87 - T/870$ K. The rate coefficient at 1 bar, 298 K was calculated from these expressions. An uncertainty of ±30% was estimated for these rate coefficients.

(c) Pyrolysis of 2-butyl nitrite in the presence of NO at pressures of ∼1 bar (∼760 Torr) in a static system. End-product analysis of CH_3CHO by GC. Results were derived relative to the reaction $2\text{-}C_4H_9O + NO \rightarrow 2\text{-}C_4H_9ONO$ for which a value of $k = 4.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was taken, independent of temperature.

(d) Smog chamber photolysis of n-C_4H_{10}-NO_x-air mixtures at 1 bar pressure. End-product analysis of CH_3CHO and $CH_3C(O)C_2H_5$ by GC yielded $k_1/k_2(2\text{-}C_4H_9O + O_2) = 3.15 \times 10^{18}$ molecule cm^{-3}. The above value of k_1 was obtained taking $k = 7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} for the reference reaction $2\text{-}C_4H_9O + O_2 \rightarrow CH_3C(O)C_2H_5 + HO_2$ (see this evaluation).

(e) Similar experiments as in comment (b) with n-C_4H_{10}-HONO-air mixtures yielding k_1/k_2(2-$C_4H_9O+O_2$)=(2.60±0.35)×10^{18} molecule cm^{-3}. The above value of k_1 was obtained taking k=7.6 ×10^{-15} cm^3 $molecule^{-1}$ s^{-1} for the reference reaction 2-$C_4H_9O+O_2 \rightarrow CH_3C(O)C_2H_5+HO_2$ (see this evaluation).

(f) Pyrolysis of (2-$C_4H_7O)_2$ in a stream of O_2-N_2 with end-product analyses. Rate data derived from a computer simulation of yields of CH_3CHO and $CH_3C(O)C_2H_5$ and assuming that k=2.6×10^{-14} exp(-100/T) cm^3 $molecule^{-1}$ s^{-1} for the competing reaction 2-$C_4H_9O+O_2 \rightarrow CH_3C(O)C_2H_5+HO_2$.

(g) Photolysis of 2-C_4H_9I-NO-O_2-N_2 mixtures at 1013 mbar (760 Torr) pressure. k/k(2-C_4H_9O + O_2) = (2.0 ± 0.5) × 10^{26} exp(-5463/T) molecule cm^{-3} was derived from yields of C_3H_7CHO and CH_3CHO products, measured by calibrated FTIR spectroscopy. The observed [O_2] dependence of this ratio was attributed to influence of 6-10% production of 'hot' 2-butoxy produced in the RO_2 + NO reaction. Pressure dependence of a factor ~1.6 increase in the rate coefficient ratio was observed over range 100–1000 mbar.

(h) Cited value of the ratio k refers to the thermally relaxed 1-butoxy and k (1 bar) is calculated using a rate coefficient of k(2-C_4H_9O + O_2) = 1.5 × 10^{-14} exp(-200/T) cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 1997).

(i) Photolysis (420 nm) of 2-C_4H_9ONO-NO-O_2-N_2 mixtures or n-C_4H_{10}-HONO(or CH_3ONO)-NO-O_2-N_2 mixtures at 1013 mbar (760 Torr) pressure. Analysis by FTIR. k/k(1-C_4H_9O + O_2) = (2.9 ± 0.4) × 10^{18} molecule cm^{-3} was derived from [O_2]-dependence of yields of C_3H_7CHO and CH_3CHO products. No chemical activation observed at this photolysis wavelength.

(j) Photolysis (360 nm) of 2-C_4H_9ONO-NO-O_2-N_2 mixtures at 1013 mbar (760 Torr) pressure. Analysis by GC. k/k(2-C_4H_9O + O_2) = 5.4 × 10^{26} exp{-(5704 ± 350)/T} molecule cm^{-3} was derived from [O_2]-dependence of C_3H_7CHO and CH_3CHO products. Evidence for the influence of production of 'hot' 2-butoxy produced in the photolysis of 2-C_4H_9ONO (5% at 283 K; 9% at 298 K). Cited value of the ratio k refers to the thermally relaxed 2-butoxy.

(k) Static thermal generation of radicals from F+2-C_4H_9OH with end-product analysis of CH_3CHO and C_2H_5CHO by GC.

Preferred Values

k_1 = 7.2 × 10^{12} exp(-5780/T) s^{-1} over the temperature range 240–340 K and 1 bar pressure.
k_1 = 2 × 10^4 s^{-1} at 298 K and 1 bar pressure.

Reliability

$\Delta \log k_1 = \pm 0.3$ at 298 K.
$\Delta (E_1/R) = \pm 500$ K.

Comments on Preferred Values

The recent results of Libuda et al. (2002) and Cassenelli et al. (2005) for the temperature dependence of the relative rate coefficients agree well with the room temperature data of Carter et al. (1979), Cox et al. (1981 and Meunier et al. (2003), especially when the small effects of 'hot' 2-butoxy production are taken into account. The preferred 298 K value of k is a mean value based on the measured ratios of k/k(2-butoxy + O_2) of Libuda et al. (2002) and Cassanelli et al. (2005), using a rate coefficient of k(2-butoxy + O_2) = 1.5 × 10^{-14} exp(-200/T) cm^3 $molecule^{-1}$ s^{-1} recommended by Atkinson (1997) and IUPAC (current evaluation). The temperature-dependence is based on a mean activation energy from these two studies, and a pre-exponential factor adjusted to fit the recommended 298 K value.

The recent comprehensive temperature and pressure dependence study of Falgayrac et al. (2004) confirms the earlier indications from measurements of Hein et al (1998) and Libuda et al. (2002) that decomposition is in the fall-off region below 1 bar. The low and the high pressure limiting rate constants as well as the broadening factor F_{cent} extracted from a falloff analysis of their experimental results can be used to calculate rate constants at other pressures (Falgayrac et al. 2004). The absolute rate coefficient at 1 bar pressure and 298 K (= 2.9 × 10^4 s^{-1}) (Falgayrac et al. 2004) is consistent with the preferred value within experimental error. The results are in good agreement with predictions from several theoretical studies of this unimolecular decomposition (Somnitz and Zellner (2000), Mereau et al. (2000) and Fittschen et al. (2000)).

Although the branching ratio (k_1/(k_2) reported by Drew et al. (1985) seems reasonable, it requires further confirmation before a recommendation can be made. None of the other studies of the decomposition of the 2-C_4H_9O radicals has reported C_2H_5CHO as a product of the decomposition reaction.

References

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II.A5.110

$$\begin{array}{lll} \mathbf{CH_3O + NO + M} & \rightarrow \mathbf{CH_3ONO + M} & \mathbf{(1)} \\ \mathbf{CH_3O + NO} & \rightarrow \mathbf{HCHO + HNO} & \mathbf{(2)} \end{array}$$

$\Delta H°(1) = -172.7$ kJ·mol^{-1}
$\Delta H°(2) = -103.1$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_{01}/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.35×10^{-29} $(T/298)^{-3.8}$[Ar]	296–573	Frost and Smith, 1990	PLF-LIF (a)
1.8×10^{-29} $(T/300)^{-3.2}$ [Ar]	220–473	McCaulley et al., 1990	DF-LIF (b)
$k_2 = (4.8 \pm 0.4) \times 10^{-12}$	298	Daële et al., 1995	DF-LIF (c)
2.65×10^{-29} $(T/298)^{-2.8}$ [He, Ar]	248–473	Caralp et al., 1998	DF/PLP-LIF (d)
$k_2 = 1.25 \times 10^{-11}$ exp(-1015/T) $+ 1.92 \times 10^{-12}$ $(T/298)^{-2.56}$			

Comments

(a) Rate coefficients were measured up to 165 mbar of Ar or CF_4 diluent. Evaluation of the chemical activation system CH_3O+NO→CH_3ONO^*, CH_3ONO^*+M→CH_3ONO+M, and CH_3ONO^* →HCHO+HNO were carried out using an extended Lindemann-Hinshelwood mechanism. At low pressures the disproportionation reaction CH_3O+NO→HCHO+HNO dominates (k_2=5.0×10^{-12} $(T/298)^{-0.6}$ cm^3 molecule^{-1} s^{-1}). Assuming that Reactions (1) and (2) involve the same intermediate complex, k_2 is expected to decrease with increasing pressure following the relationship $k_2=k_{02}k_1/k_{01}$.

(b) Measurements were made over the pressure range 1 mbar to 6.6 mbar in He or Ar. The disproportionation reaction CH_3O+NO→HCHO+HNO was measured by molecular beam MS (k_2=1.3×10^{-12} exp(250/T) cm^3 molecule^{-1} s^{-1}).

(c) Analysis by LIF and mass spectrometry. Experiments at 298 K and 1.3 mbar of He.

(d) Two sets of experiments, using DF over the range 0.6–7 mbar and 248–473 K, or PLP over the range 39–658 mbar and 284–364 K. Results with the bath gases He (mostly used) and Ar (some experiments) essentially agreed. Extensive RRKM modelling allowed to separate k_1 and k_2. Falloff curves for k_1 evaluated with F_c=exp(-T/900). The overall rate constant is assumed to be of the form $k=k_1$ ([M])+k_2.

Preferred Values

$k_{01} = 2.6 \times 10^{-29}$ $(T/300)^{-2.8}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.
$k_2 = 2.3 \times 10^{-12}$ $(T/300)^{-0.7}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_{01} = \pm 0.1$ at 298 K.
$\Delta n = \pm 0.5$
$\Delta \log k_2 = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred values are based on the extensive work by Caralp et al. (1998) which includes and supersedes the earlier results from Frost and Smith (1990), McCaulley et al. (1990) and Daële et al. (1995) as well as by Ohmori et al. (1993) in the middle of the falloff curve. The results are represented in the form of k=k_1 ([M])+k_2, where k_1(M) is based on k_{01} such as preferred here, $k_{\infty 1}$ such as given below and F_c=exp(-T/900) for M=He, Ar and N_2. It remains to be investigated whether k_2 decreases with increasing pressure (common intermediate of Reactions (1) and (2)) or is pressure independent (direct Reaction (2)).

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.1×10^{-11}	440–473	Batt et al., 1977	(a)
$(2.08 \pm 0.12) \times 10^{-11}$	298	Sanders et al., 1980	(b)
1.4×10^{-11}	298	Zellner, 1987	PLP-AS (c)
3.6×10^{-11} $(T/298)^{-0.6}$	296–573	Frost and Smith, 1990	PLF-LIF (d)
$(2.45 \pm 0.31) \times 10^{-11}$	300	Dóbé et al., 1994	DF-LIF (e)
3.26×10^{-11} $(T/298)^{-0.6}$	248–473	Caralp et al., 1998	PLP-LIF (f)

Comments

(a) Thermal decomposition of methyl nitrite in the presence of NO and $(CH_3)_3CH$. Combination of these data with the equilibrium constant gives the value indicated. For the second channel, $k(CH_3O+NO \rightarrow CH_2O+HNO)/k_\infty(CH_3O+NO \rightarrow CH_3ONO)=0.17$ was estimated.

(b) Photolysis of methyl nitrite at 266 nm with CH_3O detection by LIF at He pressure of 13 mbar to 66 mbar. HNO as a reaction product was also detected by LIF; however, no absolute estimate of its yield could be made.

(c) Falloff curve was measured over the range 5 mbar to 500 mbar. Extrapolations carried out using F_c=0.6.

(d) See comment (a) for k_0.

(e) CH_3O radicals and HCHO from Reaction (2) detected by LIF. The branching ratio for HCHO formation varied between 0.84 and 0.26 over the pressure range 1 mbar to 11 mbar.

(f) See comment (d) for k_0.

Preferred Values

$k_{\infty 1} = 3.3 \times 10^{-11}$ $(T/300)^{-0.6}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k_{\infty 1} = \pm 0.5$ at 298 K.
$\Delta n = \pm 0.5$

Comments on Preferred Values

The recommended value is from the most extensive study by Caralp et al. (1998) which supersedes and includes earlier work. The results are in accord with an RRKM modelling of the chemical activation system. Batt (1987) cites a rate coefficient ratio of $k_2/k<0.05$ from a study at 433–473 K, consistent with our preferred values.

References

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II.A5.111

$$\begin{array}{llll} \mathbf{C_2H_5O + NO + M} & \rightarrow \mathbf{C_2H_5ONO + M} & \mathbf{(1)} \\ \mathbf{C_2H_5O + NO} & \rightarrow \mathbf{CH_3CHO + HNO} & \mathbf{(2)} \end{array}$$

$\Delta H^\circ(1) = -178.5$ kJ·mol^{-1}
$\Delta H^\circ(2) = -127.6$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_{01}/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.2 \pm 1.2) \times 10^{-28}$ [He]	298	Daële et al., 1995	DF-LIF/MS (a)

Comments

(a) C_2H_5O radicals were generated by the reaction of F atoms with C_2H_5OH. Measurements were carried out at 0.7 mbar, 1.3 mbar and 2.6 mbar. The rate coefficient k_{01} was obtained from a Lindemann-Hinshelwood analysis, assuming identical intermediates in Reactions (1) and (2); $k_2=(1.1\pm0.5)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} was derived.

Preferred Values

$k_{01} = 2.2 \times 10^{-28}$ [N$_2$] cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_{01} = \pm 0.3$ at 298 K.
$\Delta \log k_2 = \pm 0.5$ at 298 K.

Comments on Preferred Values

The preferred values are from Daële et al. (1995) assuming that Reactions (1) and (2) can be separated by Lindemann-Hinshelwood extrapolation and $k=k_1([M])+k_2$. We assume equal values of k_{01} for He and N$_2$ as third bodies. In contrast to the simple Lindemann-Hinshelwood evaluation of Daële et al. (1995) corresponding to F_c=1, we recommend to use F_c=0.6 for a construction of the falloff curve for k_1 ([M]).

High-pressure rate coefficients

Rate coefficient data

$k_{\infty1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.4 \pm 0.4) \times 10^{-11}$	298	Frost and Smith, 1990	PLP-LIF (a)
$(3.1 \pm 0.8) \times 10^{-11}$	298	Daële et al., 1995	DF-LIF/MS (b)
$(3.7 \pm 0.7) \times 10^{-11}$ $(T/300)^{0.2}$	286–388	Fittschen et al., 1999	PLP-LIF (c)

Comments

(a) The rate coefficient k_1 is found not to depend on the pressure between 20 mbar and 130 mbar of Ar.

(b) See comment (a) for k_0.

(c) Measurements over the range 39–658 mbar of He. Results assumed to be in the high pressure range. Values taken from table of results, not abstract.

Preferred Values

$k_{\infty 1} = 4.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k_{\infty 1} = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$

Comments on Preferred Values

The preferred value of $k_{\infty 1}$ is from Frost and Smith (1990), in close agreement with Fittschen et al. (1999). For the falloff curve of Reaction (1), F_c=0.6 is chosen. The value of k_2 derived in Daële et al. (1995) with the preferred $k_{\infty 1}$ is in good agreement with the ratio $k_2/k_{\infty 1} = 0.3$ observed in Baker and Shaw (1965).

References

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II.A5.112

$$n\text{-}C_3H_7O + NO + M \rightarrow n\text{-}C_3H_7ONO + M$$

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.8 \pm 0.1) \times 10^{-11}$ $(T/300)^{-1.2}$	289–380	Fittschen et al., 1999	PLP-LIF (a)

Comments

(a) Measurements over the range 40–133 mbar of He. Results assumed to be in the high pressure range. The observed temperature dependence may be the result of falloff effects.

Preferred Values

$k_\infty = 3.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.

Comments on Preferred Values

The only available measurement from Fittschen et al. (1999) gives similar results as for i-C_3H_7O+NO+M→ i-C_3H_7ONO+M. The apparent temperature dependence may be due to falloff effects (its origin needs to be clarified).

References

Fittschen, C., Frenzel, A., Imrik, K., and Devolder, P.: Int. J. Chem. Kinet., 31, 800, 1999.

II.A5.113

$$\begin{array}{lll} \boldsymbol{i}\textbf{-C}_3\textbf{H}_7\textbf{O + NO + M} & \rightarrow \boldsymbol{i}\textbf{-C}_3\textbf{H}_7\textbf{ONO + M} & \textbf{(1)} \\ \boldsymbol{i}\textbf{-C}_3\textbf{H}_7\textbf{O + NO} & \rightarrow \textbf{CH}_3\textbf{C(O)CH}_3\textbf{ + HNO} & \textbf{(2)} \end{array}$$

$\Delta H^\circ(2) = -142.2$ kJ·mol^{-1}

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
3.4×10^{-11}	298	Balla et al., 1985	PLP-LIF (a)
$(3.3 \pm 0.1) \times 10^{-11}$ $(T/300)^{-1.3}$	286–389	Fittschen et al., 1999	PLP-LIF (b)

Comments

(a) No pressure dependence of the rate coefficient was observed over the range 1.3–6 mbar. The small negative temperature dependence [$k = 1.2\times10^{-11}$ exp(310/T) cm^3 molecule^{-1} s^{-1}] observed over the range 298–383 K may be attributed to falloff effects.

(b) Measurements over the range 40–667 mbar of He. Results assumed to be in the high pressure range. The observed temperature dependence corresponding to $k_{\infty 1}=8.9\times10^{-12}$ exp (397/T) may be attributed to falloff effects.

Preferred Values

$k_{\infty 1}=3.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2=6.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 27–270 mbar pressure.

Reliability

$\Delta \log k_{\infty 1} = \pm\ 0.3$ at 298 K.
$\Delta \log k_2 = \pm\ 0.5$ at 298 K.

Comments on Preferred Values

The preferred value of $k_{\infty 1}$ is based on the studies of Balla et al. (1985) and Fittschen et al. (1999). The apparent temperature coefficient of $k_{\infty 1}$ differs from that of $k_{\infty 1}$ for C_2H_5O+NO+M. It remains to be clarified whether falloff effects are responsible for the different behavior. The value of k_2 is obtained from the preferred $k_{\infty 1}$ and the rate coefficient ratio $k_2/k_1=0.19\pm0.03$ (independent of temperature) cited in Batt and Milne (1977).

References

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Fittschen, C., Frenzel, A., Imrik, K., and Devolder, P.: Int. J. Chem. Kinet., 31, 800, 1999.

II.A5.114

$$(CH_3)_3CO + NO + M \rightarrow (CH_3)_3CONO + M$$

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.17 \pm 0.12) \times 10^{-11}$ $(T/200)^{-1.27}$	200–390	Blitz et al., 1999	LP-LIF (a)
$(2.74 \pm 0.5) \times 10^{-11}$ $(T/300)^{-1.52}$	223–304	Lotz and Zellner, 2000	LP-LIF (b)

Comments

(a) Pulsed excimer laser photolysis of *tert*-butyl nitrite at 351 nm with and without added NO, using LIF detection of *tert*-butoxy and NO. Experiments in 92–658 mbar of He showed no pressure dependence of the rate coefficient.

(b) Pulsed excimer laser photolysis of di-*tert*-butyl peroxide with added NO using LIF of *tert*-butoxy. No pressure dependence detected over the range 6.6–105 mbar of N_2.

Preferred Values

$k_\infty = 2.6 \times 10^{-11}$ $(T/300)^{-1.4}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

The studies of Blitz et al. (1999) and Lotz and Zellner (2000) using different sources of *tert*-butoxy radicals are in good agreement. The preferred values present the average of the two results.

References

Blitz, M., Pilling, M. J., Robertson, S. H., and Seakins, P. W.: Phys. Chem. Chem. Phys., 1, 73, 999.
Lotz, Ch. and Zellner, R.: Phys. Chem. Chem. Phys., 2, 2353, 2000.

II.A5.115

$2\text{-}C_4H_9O + NO + M \rightarrow 2\text{-}C_4H_9ONO + M$

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.48 \pm 0.5) \times 10^{-11}$ $(T/300)^{-1.2}$	223–311	Deng et al., 2000	PLP-LIF (a)

Comments

(a) Measurements over the range 66–230 mbar of N_2. Results assumed to be in the high pressure range. The observed temperature dependence may be the result of falloff effects.

Preferred Values

$k_\infty = 2.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 298 K.

Comments on Preferred Values

The only available measurement from Deng et al. (2000) gives similar results as for smaller alkoxy radicals reacting with NO. The apparent temperature coefficient may be due to falloff effects (its origin needs to be clarified).

References

Deng, W., Wang, C., Katz, D. R., Gawinski, G. G., Davis, A. J., and Dibble, T. S.: Chem. Phys. Lett., 330, 541, 2000.

II.A5.116

$$\begin{array}{llr} \mathbf{CH_3O + NO_2 + M} & \rightarrow \mathbf{CH_3ONO_2 + M} & \mathbf{(1)} \\ \mathbf{CH_3O + NO_2} & \rightarrow \mathbf{HCHO + HONO} & \mathbf{(2)} \end{array}$$

$\Delta H^\circ(1) = -171.5$ kJ·mol^{-1}
$\Delta H^\circ(2) = -238.5$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_{01}/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.6×10^{-29} $(T/300)^{-4.5}$ [He]	220–473	McCaulley et al., 1985	DF-LIF (a)
$(5.2 \pm 1.9) \times 10^{-29}$ [He]	298	Frost and Smith, 1990	PLP-LIF (b)
$(9.0 \pm 1.9) \times 10^{-29}$ [Ar]	298		
$(11 \pm 3) \times 10^{-29}$ [CF_4]	298		
$(4.9 \pm 1.2) \times 10^{-29}$ [Ar]	390		
$(5.3 \pm 0.2) \times 10^{-29}$ [He]	298	Biggs et al., 1993	DF-LIF (c)
$(5.3 \pm 0.3) \times 10^{-29}$ $(T/297)^{-4.4}$ [Ar]	233–356	Wollenhaupt and Crowley, 2000	PLP-LIF (d)
$(3.93 \pm 0.05) \times 10^{-29}$ $(T/300)^{-1.74}$ [He]	250–390	Martínez et al., 2000	PLP-LIF (e)

Comments

(a) CH_3O radicals were produced by IR laser dissociation of $C_6F_5OCH_3$ to yield CH_3, followed by $CH_3 + NO_2 \rightarrow CH_3O + NO$. Pressure range 0.8 mbar to 5 mbar. Direct measurements of the branching ratio k_1/k_2 were not possible. A separation was performed by assuming that Reaction (1) was in the low pressure limit. A value of $k_2 = 9.6 \times 10^{-12}$ exp(-1150/T) cm^3 molecule^{-1} s^{-1} (with relatively large error limits) was estimated.

(b) Pulsed laser photolysis of CH_3ONO-NO mixtures at 266 nm. Rate coefficients were measured over the pressure ranges 40 mbar to 130 mbar of He, 8 mbar to 130 mbar of Ar, and 40 mbar to 100 mbar of CF_4. Falloff curves were fitted to the experimental data using F_c values of 0.41, 0.44, and 0.48 for He, Ar, and CF_4, respectively. The recombination Reaction (1) appears to dominate over Reaction (2).

(c) Pressures of He varied from 1.3 mbar to 13 mbar. Extrapolations were performed using F_c=0.6, an RRKM analysis was also done. A value $k_{01} = 5.9 \times 10^{-29}$ [He] cm^3 molecule^{-1} s^{-1} was obtained.

(d) Pulsed laser photolysis of CH_3ONO. Rate coefficients were measured over the range 13–263 mbar of Ar. Falloff curves represented with temperature-independent F_c=0.6, alternatively temperature-dependent F_c between 0.66 at 223 K and 0.55 at 356 K was used. $k_2/k_1 \approx 0.1$ at 13 mbar and 356 K, whereas $k_2/k_1 < 0.01$ was derived at 13 mbar and 233 K.

(e) Measurements over the pressure range 66–789 mbar. Falloff extrapolation with F_c=0.6.

Preferred Values

$k_{01} = 8.1 \times 10^{-29}$ $(T/300)^{-4.5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.
$k_2 = 9.6 \times 10^{-12}$ exp(-1150/T) cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k_{01} = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.
$\Delta \log k_2 = \pm 0.5$ at 298 K.

Comments on Preferred Values

The agreement between the studies of Frost and Smith (1990, 1993), Biggs et al. (1993), Wollenhaupt and Crowley (2000) and Martínez et al. (2000) appears satisfactory, in particular if the different ways of treating the falloff curve are taken into account. We assume similar values of k_{01} for M=Ar and N_2. Falloff curves are constructed with F_c=0.44 at 300 K such as chosen in Frost and Smith (1990, 1993). The preferred value is average of the results from Frost and Smith (1990, 1993) and Wollenhaupt and Crowley (2000) after reevaluation of the data from Wollenhaupt and Crowley (2000) with F_c=0.44. Reaction (2) appears to play only a minor role at pressures above 10 mbar. The value of k_2 remains relatively uncertain.

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.0 \pm 0.4) \times 10^{-11}$	295	Frost and Smith, 1990	PLP-LIF (a)
$(1.86 \pm 0.05) \times 10^{-11} (T/297)^{-1.87}$	233–356	Wollenhaupt and Crowley, 2000	PLP-LIF (b)
$(2.40 \pm 0.02) \times 10^{-11} (T/300)^{-0.88}$	250–390	Martínez et al., 2000	PLP-LIF (c)
$(1.3 \pm 0.1) \times 10^{-11}$	300	Kukui et al., 2000	PLP-LIF (d)
Relative Rate Coefficients			
1.5×10^{-11}	298	Wiebe et al., 1973	(e)
$(1.0 \pm 0.5) \times 10^{-11}$	392–420	Batt and Rattray, 1979	(f)
$(1.4 \pm 0.1) \times 10^{-11}$	298	Biggs et al., 1993	DF-LIF (g)
Branching Ratios			
$k_1/k = 0.92 \pm 0.08$	298	Wiebe et al., 1973	(e)
$k_2/k_1 \leq 0.05$	384–424	Batt and Rattray, 1979	(f)

Comments

(a) See comment (b) for k_0.

(b) See comment (d) for k_0.

(c) See comment (e) for k_0.

(d) Photolysis of CH_3SSCH_3-NO_2 mixtures with LIF detection of CH_3O. Measurements over the range 16–805 mbar of He. The given value is for about 750 mbar. No falloff extrapolation.

(e) Steady-state photolysis of CH_3ONO in the presence of NO-O_2 and NO-NO_2-N_2 mixtures at 10 mbar to 500 mbar. Relative rate coefficients were derived from $\Phi(CH_3ONO_2)$, with $k(CH_3O + NO)/k$=1.3 at 298 K. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(CH_3O + NO \rightarrow CH_3ONO) = 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 200 K to 400 K.

(f) Static reaction vessel, CH_3O formed from pyrolysis of CH_3OOCH_3 in the presence of NO-NO_2-CF_4 at a total pressure of 675 mbar. Relative rate coefficients were determined from end-product analysis of CH_3ONO and CH_3ONO_2 by GC. $k(CH_3O + NO \rightarrow CH_3ONO)/k$=2.03 ± 0.47 was obtained over the range 392 K to 420 K. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(CH_3O + NO \rightarrow CH_3ONO)=2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 200 K to 400 K. k_1/k_2 was determined from pyrolysis of CH_3OOCH_3 in the presence of NO_2 and N_2 and shown to be pressure dependent.

(g) See comment (c) for k_0. An RRKM extrapolation leads to the value $k_\infty=2.1\times10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k_1 = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.
$k_{\infty 1} = 2.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$

Comments on Preferred Values

The preferred $k_{\infty 1}$ value is based on Frost and Smith (1990, 1993), Wollenhaupt and Crowley (2000), Martínez et al. (2000) and Kukui et al. (2000). Falloff curves are constructed with F_c=0.44 from Frost and Smith (1990, 1993). Reaction (2) appears to be only of minor importance. Differences in the apparent temperature dependences of $k_{\infty 1}$ in part are due to different F_c-values used in the falloff extrapolations.

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II.A5.117

$$\mathbf{C_2H_5O + NO_2 + M \rightarrow C_2H_5ONO_2 + M \quad (1)}$$
$$\mathbf{C_2H_5O + NO_2 \rightarrow CH_3CHO + HONO \quad (2)}$$

$\Delta H°(1) = -171.7$ kJ·mol^{-1}
$\Delta H°(2) = -263.2$ kJ·mol^{-1}

High-pressure rate coefficients

Rate coefficient data

$k_{\infty1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.8 \pm 0.3) \times 10^{-11}$	295	Frost and Smith, 1990	PLP-LIF (a)

Comments

(a) The same rate coefficients were measured in the presence of 2 mbar or 130 mbar of He.

Preferred Values

$k_{\infty1} = 2.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_{\infty1} = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$

Comments on Preferred Values

The value of $k_{\infty1}$ is based on the data of Frost and Smith (1990), being consistent with values for related reactions such as RO+NO+M→RONO+M (with M=CH_3, C_2H_5, and i-C_3H_7) or $CH_3O+NO_2+M \rightarrow CH_3ONO_2+M$. Reaction (2) appears to be of minor importance, with a rate coefficient ratio of $k_2/k_1=0.1\pm0.01$ at ~450 K being cited by Batt (1987).

References

Batt, L.: Int. Rev. Phys. Chem., 6, 53, 1987.
Frost, M. J. and Smith, I. W. M.: J. Chem. Soc. Faraday Trans., 86, 1751, 1990.

II.A5.118

$$\begin{array}{lll} \mathbf{1\text{-}C_3H_7O + NO_2 + M} & \rightarrow \mathbf{1\text{-}C_3H_7ONO_2 + M} & \mathbf{(1)} \\ \mathbf{1\text{-}C_3H_7O + NO_2} & \rightarrow \mathbf{CH_3CH_2CHO + HONO} & \mathbf{(2)} \end{array}$$

$\Delta H°(1) = -165.9$ kJ·mol^{-1}
$\Delta H°(2) = -258.7$ kJ·mol^{-1}

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.6 \pm 0.4) \times 10^{-11}$	296	Mund et al., 1998	PLP-LIF (a)

Comments

(a) The rate coefficient was observed to be independent of total pressure over the range 6.7 mbar to 53 mbar of He.

Preferred Values

$k_{\infty 1} = 3.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K .

Reliability

$\Delta \log k_{\infty 1} = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the sole study of Mund et al. (1998) with expanded uncertainty limits. The rate coefficient is of a similar magnitude to other RO+NO$_2$ reactions (see data sheets in this evaluation for CH_3O+NO_2, C_2H_5O+NO_2 and 2-C_3H_7O+NO_2).

Although no statement on the branching ratio k_1/k_2 may be made on the basis of this work, it is expected that $k_1/k_2>0.2$.

References

Mund, C., Fockenberg, Ch., and Zellner, R.: Ber. Bunsenges. Phys. Chem., 102, 709, 1998.

II.A5.119

$$\begin{array}{llr} \mathbf{2\text{-}C_3H_7O + NO_2 + M} & \rightarrow \mathbf{2\text{-}C_3H_7ONO_2 + M} & \mathbf{(1)} \\ \mathbf{2\text{-}C_3H_7O + NO_2} & \rightarrow \mathbf{CH_3C(O)CH_3 + HONO} & \mathbf{(2)} \end{array}$$

$\Delta H°(1) = -171.7$ kJ·mol^{-1}
$\Delta H°(2) = -277.6$ kJ·mol^{-1}

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
3.5×10^{-11}	298	Balla et al., 1985	PLP-LIF (a)
$(3.3 \pm 0.3) \times 10^{-11}$	296	Mund et al., 1998	PLP-LIF (b)

Comments

(a) By extrapolation to zero laser power, a rate coefficient of $k_{\infty 1}$=1.5×10^{-11} exp[(250±200)/T] cm^3 molecule^{-1} s^{-1} was derived from measurements over the temperature range 295 K to 384 K. No pressure dependence was observed between 1.3 mbar and 13 mbar.

(b) The measured rate coefficient was observed to be independent of total pressure over the range 6.7 mbar to 106 mbar of He.

Preferred Values

$k_{\infty 1} = 3.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_{\infty 1} = \pm 0.2$ at 298 K.

Comments on Preferred Values

The recommendation is based on the data of Balla et al. (1985) and Mund et al. (1998). The value of $k_{\infty 1}$ is consistent with other related reactions such as RO+NO+M → RONO+M and RO+NO_2+M→$RONO_2$+M (with R=CH_3, C_2H_5, i-C_3H_7, see this evaluation). It is estimated that $k_2/k_{\infty 1}$<0.2. Batt (1987) cites a rate coefficient ratio of k_2/k_1=0.027±0.006 at ∼450 K, indicating that reaction (2) is of negligible importance under atmospheric conditions.

References

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Appendix A6: RO_2 reactions

II.A6.120

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$\Delta H^\circ = -48.8$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.0 \pm 2.0) \times 10^{-12}$	295	Plumb et al., 1979	DF-MS (a)
$(3.0 \pm 1.7) \times 10^{-12}$	298	Adachi and Basco, 1979	FP-AS
$(7.1 \pm 1.4) \times 10^{-12}$	298	Sander and Watson, 1980	FP-AS (b)
$(6.5 \pm 2.0) \times 10^{-12}$	298	Cox and Tyndall, 1979, 1980	MMS-AS (c)
$(8.1 \pm 1.6) \times 10^{-12}$	240–339	Ravishankara et al., 1981	PLP-LIF (d)
$2.1 \times 10^{-12}\exp[(380 \pm 250)/T]$	218–365	Simonaitis and Heicklen, 1981	FP-AS (e)
$(7.7 \pm 0.9) \times 10^{-12}$	298		
$(8.6 \pm 2.0) \times 10^{-12}$	295	Plumb et al., 1981	DF-MS (f)
$(7 \pm 2) \times 10^{-12}$	298	Zellner et al., 1986	PLP-AS (g)
$(8.8 \pm 1.4) \times 10^{-12}$	295	Sehested et al., 1993	PR-UV (h)
$(11.2 \pm 1.4) \times 10^{-12}$	298	Masaki et al., 1994	PLP-MS (i)
$2.8 \times 10^{-12}\exp[(285 \pm 60)/T]$	199–429	Villalta et al., 1995	F-CIMS (j)
$(7.5 \pm 1.3) \times 10^{-12}$	298		
$(7.5 \pm 1.0) \times 10^{-12}$	298	Helleis et al., 1996	DF-MS (k)
$9.2 \times 10^{-13} \exp[(600 \pm 140)/T]$	203–295	Scholtens et al., 1999	F-CIMS (l)
$(7.8 \pm 2.2) \times 10^{-12}$	298		
$1.75 \times 10^{-12} \exp[(435 \pm 35)/T]$	193–300	Bacak et al., 2004	F-CIMS (m)
$(7.42 \pm 0.27) \times 10^{-12}$	298		
$(9.9 \pm 2.1) \times 10^{-12}$	298	Xing et al., 2004	LP-MS (n)

Comments

(a) Flow tube at 11±2.6 mbar He. Direct detection of CH_3O_2 (generated in $O+C_2H_4+O_2$) via electron impact mass spectrometry.

(b) Data obtained at 100, 467 and 933 mbar He, and 933 mbar N_2. CH_3O_2 formed by $Cl+CH_4+O_2$.

(c) Data obtained at 720 mbar N_2+O_2. CH_3O_2 formed by $Cl+CH_4+O_2$.

(d) CH_3O_2 generated by photolysis of $CH_3N_2CH_3$ in presence of O_2. Rate data obtained via LIF detection of NO_2.

(e) Pressures of 93 to 800 mbar CH_4. CH_3O_2 formed by $Cl+CH_4+O_2$.

(f) Flow tube at 7.7 mbar He, direct detection of CH_3O_2 (generated in $Cl+CH_4+O_2$) via electron impact mass spectrometry.

(g) Experiments conducted at 13.3 mbar He or N_2. CH_3O_2 generated by photolysisof $CH_3N_2CH_3$ in presence of O_2. Rate data obtained by measuring CH_3O_2 by absorption spectroscopy, LIF used to observe formation of CH_3O.

(h) Experiments conducted in 1013 mbar SF_6 and O_2. CH_3O_2 generated in $F+CH_4$ ($+O_2$) and NO_2 formation monitored to derive kinetic information.

(i) Experiments conducted in 4–8 mbar N_2+O_2. Mass spectrometry using photo-ionisation detection of CH_3O_2, which was formed in the 193 nm photo-dissociation of acetone in the presence of O_2.

(j) Experiments conducted in 2.7–7.3 mbar He. CH_3O_2 generated by thermal decomposition of CH_3CH_2ONO in the presence of O_2. Mass spectrometry using chemi-ionisation detection of CH_3^+ generated in O_2^++CH_3O_2.

(k) Experiments conducted in 2.3 mbar He, CH_3O_2 generated in F+CH_4 (+O_2). Electron impact detection of CH_3O_2 in excess NO. Measurements using deuterated methyl peroxy gave $k(CD_3O_2+NO)=(8.6\pm1.0)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

(l) Turbulent flow reactor at 133 mbar N_2 total pressure. CH_3O_2 generated in F+CH_4 (+O_2) and detected as $CH_3OOH^+(H_2O)_n$ following proton transfer from H_3O^+.

(m) Turbulent flow reactor at 133 mbar or 266 mbar N_2 total pressure. CH_3O_2 generated in F+CH_4 (+O_2) and detected as FO_2^- following reaction with SF_6^-. Yield of NO_2 was found to be 1.0 ± 0.1 at 298 K.

(n) CH_3O_2 generated by reaction of CH_3 with O_2, whereby CH_3 radicals were generated in the 193 mm photolysis of $CH_3C(O)CH_3$, or the 248 nm photolysis of CH_3I. The data obtained using CH_3I are reported to be more reliable. CH_3O_2 was detected as the negative parent ion following electron transfer from high Rydberg state rare gas atoms. The total pressure was 5.3 mbar of the diluent containing 2.7 mbar O_2.

Preferred Values

$k = 7.7 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k = 2.3 \times 10^{-12} \exp(360/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 200–430 K.

Reliability

$\Delta \log k = \pm 0.05$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

This reaction has been subject of intensive investigation using several different experimental techniques. With the exception of the data of Adachi and Basco (1979), Masaki et al. (1994) and Xing et al. (2004), the remaining datasets at room temperature are in good agreement. The recommended value of the rate coefficient at 298 K is the average of the results from Scholtens et al. (1999), Helleis et al. (1996), Villalta et al. (1995), Ravishankara et al. (1981) and Bacak et al. (2004). The temperature dependence of the rate coefficient is described by four sets of data which are in good agreement at temperatures above 230 K. At lower temperatures there is some deviation, with the datasets of Scholtens et al. (1999) and Simonaitis and Heicklen (1981) deviating from Arrhenius behaviour. These data sets were obtained at higher pressures than that of Villalta et al. (1995) and the possibility of a pressure dependence in the rate coefficient at low temperatures has been discussed (Scholtens et al., 1999). The latest data on this reaction (Bacak et al., 2004) do not, however, support this.

The datasets of Villalta et al. (1995) and Bacak et al., (2004) which cover the largest temperature range, provide the basis of the recommended temperature dependence, which has been adjusted for the average 298 K rate coefficient.

The formation of CH_3O and NO_2 products has been confirmed (Ravishankara et al., 1981; Zellner et al., 1986; Bacak et al, 2004), whereas the alternative reaction channel of the peroxy + NO reaction leading to the formation of alkyl nitrate has never been observed for CH_3O_2 and accounts for <1% of the overall reaction at room temperature and below. This is consistent with an upper limit of 0.3% for formation of CH_3ONO at 295 K and 100 Torr N_2 (Scholtens et al., 1999).

References

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II.A6.121

$$\begin{aligned} &\mathbf{C_2H_5O_2 + NO} &&\rightarrow \mathbf{C_2H_5O + NO_2} && \mathbf{(1)}\\ &\mathbf{C_2H_5O_2 + NO + M} &&\rightarrow \mathbf{C_2H_5ONO_2 + M} && \mathbf{(2)} \end{aligned}$$

$\Delta H^\circ(1) = -45.2$ kJ·mol^{-1}
$\Delta H^\circ(2) = -217.0$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.7 \pm 0.2) \times 10^{-12}$	298	Adachi and Basco, 1979	FP-AS
$(8.9 \pm 3.0) \times 10^{-12}$	295	Plumb et al., 1982	DF-MS
$(8.5 \pm 1.2) \times 10^{-12}$	298	Sehested et al., 1993	PR-AS
$(8.2 \pm 1.6) \times 10^{-12}$	295	Däele et al., 1995	DF-MS (a)
$2.6 \times 10^{-12} \exp[(380 \pm 70)/T]$	207–403	Eberhard and Howard, 1996	F-CIMS (b)
$(9.3 \pm 1.6) \times 10^{-12}$	298		
$3.1 \times 10^{-12} \exp[(330 \pm 110)/T]$	220–355	Maricq and Szente, 1996	PLP-AS (c)
$(10.0 \pm 1.5) \times 10^{-12}$	295		
$3.8 \times 10^{-12} \exp[(290 \pm 110)/T]$	213–299	Ranschaert et al., 2000	F-CIMS (d)
$(10.1 \pm 0.9) \times 10^{-12}$	299		
Branching Ratio			
$k_2/k \leq 0.014$ (1 bar)	299	Atkinson et al., 1982	(e)
$k_2/k = 1.2 \times 10^{-3} \exp(610/T)$	213–298	Ranschaert et al., 2000	(f)
$k_2/k = 0.006$ (133 mbar N_2)	298		
$k_2/k = 0.02$ (133 mbar N_2)	213		

Comments

(a) Conventional discharge flow system with LIF detection of C_2H_5O product. k determined by simulation of experimental C_2H_5O profiles.

(b) Ethylperoxy radicals formed by the thermal decomposition of n-propyl nitrite in the presence of O_2, or by RF discharge through C_2H_5I (also in the presence of O_2). Pseudo first order kinetics with excess NO and CIMS detection of $C_2H_5O_2$ as the ethyl peroxy negative ion.

(c) Excimer laser photolysis of Cl_2-C_2H_6-NO-O_2-N_2 mixtures. Time-resolved measurements of $C_2H_5O_2$ decay and C_2H_5ONO formation using diode array UV absorption spectroscopy, and of NO loss and NO_2 formation using diode laser absorption spectroscopy.

(d) Turbulent flow reactor at 100 Torr (133 mbar) N_2 total pressure. $C_2H_5O_2$ detected as $C_2H_5OOH^+(H_2O)_n$ and $C_2H_5ONO_2$ detected as $C_2H_5ONO_2H^+(H_2O)_n$ following proton transfer from H_3O^+.

(e) GC analysis of $C_2H_5ONO_2$ product from photo-oxidation of C_2H_6 in Cl_2-C_2H_6-NO-air mixtures.

(f) Ranschaert et al. (2000) also present temperature dependent values of the rate coefficient k_2=1.6×10^{-15} exp $(1160/T)$ for the temperature range 213 to 299 K and 100 Torr (133 mbar) N_2 pressure. The authors state that the branching ratios are associated with large errors as the measurements were conducted near the detection limit for $C_2H_5ONO_2$ and were complicated by secondary chemistry.

Preferred Values

$k = 9.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.6 \times 10^{-12} \exp(380/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–410 K.
$k_2/k \leq 0.014$ at 298 K and 1 bar pressure.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 50$ K.

Comments on Preferred Values

With the exception of the measurement of Adachi and Basco (1979), all measurements at room temperature are in excellent agreement. The preferred value of the rate coefficient at room temperature is an average of the data from Plumb et al. (1982), Sehested et al. (1993), Däele et al. (1995), Eberhard and Howard (1996), Maricq and Szente (1996) and Ranschaert et al. (2000). The temperature coefficients (*E/R*) from the three temperature dependent studies (Eberhard and Howard, 1996; Maricq and Szente, 1996; Ranschaert et al., 2000) also show good agreement. The preferred value was obtained from a weighted fit (using the authors estimated errors) to the data of all three studies, and reflects the higher precision of the Eberhard and Howard (1996) dataset. The two sets of data (Ranschaert et al., 2000; Atkinson et al., 1982) for the branching ratio for $C_2H_5ONO_2$ formation are self consistent at the common temperature of 298 K, and show that this channel is minor under atmospheric conditions.

References

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II.A6.122

$HOCH_2CH_2O_2 + NO \rightarrow HOCH_2CH_2O + NO_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9 \pm 4) \times 10^{-12}$	298	Becker et al., 1991	PLP-LIF (a)

Comments

(a) Pulsed laser photolysis of H_2O_2 in the presence of C_2H_4-O_2-NO mixtures at a total pressure of 1 bar [760±5 Torr]. Relative HO radical concentrations were determined as a function of time using LIF, and simulated by a mechanism consisting of 11 reactions, of which k of above reaction was the most sensitive.

Preferred Values

$k = 9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The rate coefficient reported by Becker et al. (1991), which is recommended, is consistent with the rate coefficients of the reactions of other peroxy radicals with NO. Independent confirmation is needed to reduce the error limits. The hydroxy-alkoxy product has been shown to be formed with sufficient internal energy that prompt dissociation can take place as well as thermal decomposition and reaction with O_2 of the collisionally stabilised radical (Orlando et al., 1998; Vereecken et al., 1999).

References

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II.A6.123

$$\begin{array}{llr} \textit{n}\text{-}\mathbf{C_3H_7O_2 + NO} & \rightarrow \textit{n}\text{-}\mathbf{C_3H_7O + NO_2} & \mathbf{(1)} \\ \textit{n}\text{-}\mathbf{C_3H_7O_2 + NO + M} & \rightarrow \textit{n}\text{-}\mathbf{C_3H_7ONO_2 + M} & \mathbf{(2)} \end{array}$$

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.9 \times 10^{-12} \exp[(350 \pm 60)/T]$	201–402	Eberhard and Howard, 1996	F-CIMS(a)
$(9.4 \pm 1.6) \times 10^{-12}$	298		
Branching Ratio			
$k_2/k = 0.020 \pm 0.009$ (1 bar)	299	Atkinson et al., 1982; Carter and Atkinson, 1989	(b)

Comments

(a) n-$C_3H_7O_2$ radicals were produced by pyrolysis of n-$C_3H_7ONO_2$ in the presence of O_2 and detected by CIMS. Pseudo-first order kinetics with excess NO.

(b) Based on yield of n-$C_3H_7ONO_2$ product from photo-oxidation of C_3H_8 in NO_x-air mixtures. Carter and Atkinson (1989) revised the analysis of original data to provide the value quoted.

Preferred Values

$k = 9.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.9 \times 10^{-12} \exp(350/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–410 K.
$k_2/k = 0.020$ at 298 K and 1 bar pressure.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 100$ K.
$\Delta \log k_2/k = \pm 0.02$ at 298 K and 1 bar pressure.

Comments on Preferred Values

The measurements of Eberhard and Howard (1996) provide the only experimental data on this rate coefficient. The value of k_{298} is in line with the most recent measurements for reactions of ethyl peroxy and 2-propyl peroxy radicals with NO. The negative temperature coefficient is also consistent with that observed for the rate coefficient for other RO_2+NO reactions. The recommendation accepts the Arrhenius expression of Eberhard and Howard (1996).

The preferred branching ratio for n-propyl nitrate formation is that measured by Atkinson et al. (1982), as revised by Carter and Atkinson (1989).

References

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II.A6.124

$$\begin{array}{lll} \boldsymbol{i\text{-}C_3H_7O_2 + NO} & \boldsymbol{\rightarrow i\text{-}C_3H_7O + NO_2} & \textbf{(1)} \\ \boldsymbol{i\text{-}C_3H_7O_2 + NO + M} & \boldsymbol{\rightarrow i\text{-}C_3H_7ONO_2 + M} & \textbf{(2)} \end{array}$$

$\Delta H°(1) = -40.5$ kJ·mol^{-1}
$\Delta H°(2) = -212.2$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.3) \times 10^{-12}$	298	Adachi and Basco, 1982	FP-AS
$(5.0 \pm 1.2) \times 10^{-12}$	290	Peeters et al., 1992	DF-MS (a)
$2.7 \pm 10^{-12} \exp[(360 \pm 60)/T]$	201–401	Eberhard et al., 1996	F-CIMS (b)
$(9.0 \pm 1.5) \times 10^{-12}$	298		
$(9.1 \pm 1.5) \times 10^{-12}$	298	Eberhard and Howard, 1996	F-CIMS (c)
$4.3 \times 10^{-12} \exp[(268 \pm 56)/T]$	213–298	Chow et al., 2003	F-CIMS (d)
$(1.05 \pm 0.14) \times 10^{-11}$	298		
$(8.0 \pm 1.5) \times 10^{-12}$	298	Xing et al., 2005	LP-MS (e)
Branching Ratio			
$k_2/k = 0.042 \pm 0.003$ (1 bar air)	299	Atkinson et al., 1982; Carter and Atkinson, 1989	(f)
$k_2/k = 1.815 \times 10^{-4} \exp(1020/T)$ (133 mb N_2)	213-298	Chow et al., 2003	F-CIMS (d)
$k_2/k = 0.005$ (133 mb N_2)	298		

Comments

(a) Low pressure flow tube at 2.7 mbar He. Rate constant derived from analysis of NO_2 growth profiles.

(b) i-$C_3H_7O_2$ radicals produced by reaction of O_2 with i-C_3H_7 radicals produced by thermal decomposition of isobutyl nitrate. i-$C_3H_7O_2$ was detected as its parent negative ion formed by reaction with O_2^-. k determined by pseudo-first order loss of i-$C_3H_7O_2$ in the presence of NO.

(c) i-$C_3H_7O_2$ produced by reaction of O_2 with i-C_3H_7 produced in a low frequency RF discharge through i-propyl iodide.

(d) Turbulent flow reactor at 133 mb N_2 total pressure. $C_3H_7O_2$ radicals were generated by the reaction of Cl atoms with C_3H_8 in the presence of O_2, thus both n- $C_3H_7O_2$ and i- $C_3H_7O_2$ were present and the rate coefficients measured are overall values for both isomers,which were detected as $CH_3H_7OOH^+(H_2O)_3$ following reaction with $H^+(H_2O)_4$ ions. For branching ratio measurements, i-$C_3H_7O_2$ was selectively generated from the reaction of H atoms with C_3H_6 in the presence of O_2. i-$C_3H_7ONO_2$ was detected using $H^+(H_2O)_4$ ions; NO_2 was detected as NO_2^- following electron transfer from SF_6^-.

(e) i-$C_3H_7O_2$ generated by reaction of i-C_3H_7 with O_2, whereby i-C_3H_7 radicals were generated in the 193 nm photolysis of i-C_3H_7Br, or the 248 photolysis of i-C_3H_7I. i-$C_3H_7O_2$ was detected as the negative parent ion following electron transfer from high Rydberg state Xe atoms. The bath gas was 4–5.3 mb of He. Owing to poor sensitivity, and resultant side/secondary reactions the rate coefficient was extracted by numerical modelling of a complx reaction scheme.

(f) Photolysis of CH_3ONO-NO-C_3H_8-air or Cl_2-NO-C_3H_8-air mixtures at a total pressure of 1 bar. The branching ratio was determined from the measured yields of i-$C_3H_7ONO_2$ and the consumption of C_3H_8. Carter and Atkinson (1989) have re-evaluated the branching ratio, cited above, from the original data (Atkinson et al., 1982) on the basis of revised data for the rate coefficients of the HO radical reactions with alkanes.

Preferred Values

$k = 9.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.7 \times 10^{-12} \exp(360/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–410 K.
k_2/k= 0.042 at 298 K and 1 bar pressure.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 100$ K.
$\Delta\log(k_2/k) = \pm 0.3$ at 298 K and 1 bar pressure.

Comments on Preferred Values

The data from Eberhard et al. (1996) give a rate coefficient at 298 K which is significantly larger than the values obtained by Adachi and Basco (1982) or Peeters et al. (1992), and is close to the value obtained for a range of alkyl peroxy radicals at 298 K. In addition, the data of Chow et al. (2003), who measured a weighted average value for n-$C_3H_7O_2$ and i-$C_3H_7O_2$ are in good agreement, which confirms that n-$C_3H_7O_2$ and i-$C_3H_7O_2$ have similar rate coefficients for reaction with NO. The rather indirect measurement of Xing et al., (2005) is also in broad agreement. The preferred value for k_{298} and the temperature dependence is that reported by Eberhard et al. (1996).

There are two studies of the branching ratio to i-$C_3H_7ONO_2$ formation. Chow et al., (2003) report values at 133 mbar N_2 that vary from $\approx$ 0.005 at room temperature to 0.02 at 213 K, whereas Carter and Atkinson (1989) report 0.042 at 298 K and 1 bar air. The differences in these results are a result of the pressure difference in the two experiments reported, implying that k_2 is in the third-order limit at 133 mbar N_2. For purpose of atmospheric modelling of the lower troposphere, the recommended branching ratio is that reported by Carter and Atkinson (1989). Chow et al. (2003) note that their temperature dependence is reproduced using a model based on C_3- C_8 hydrocarbons (Arey et al., 2001).

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II.A6.125

$$\mathbf{CH_3C(O)CH_2O_2 + NO \rightarrow CH_3C(O)CH_2O + NO_2}$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.0 \pm 2.0) \times 10^{-12}$	295	Sehested et al., 1998	PR-AS (a)

Comments

(a) $CH_3C(O)CH_2O_2$ was formed in the pulsed radiolysis of $CH_3C(O)CH_3$-SF_6-O_2 mixtures, and the kinetics of the title reaction followed by monitoring formation of NO_2 in real time by absorption spectroscopy. The influence of secondary chemistry on formation of NO_2 was estimated by numerical simulation of an assumed reaction scheme.

Preferred Values

$k = 8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The recommendation is based on the sole study of the reaction of Sehested et al. (1998), with appropriately expanded error limits. The value of the rate coefficient at room temperature is consistent with reactions of other unsubstituted peroxy radicals with NO. The temperature dependence of the rate coefficient is also expected to be consistent with other RO_2+NO reactions, and the expression: $k=2.8\times10^{-12} \exp(300/T)$ cm^3 molecule^{-1} s^{-1} has been recommended (Tyndall et al., 2001).

References

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II.A6.126

$$CH_3C(O)O_2 + NO \rightarrow CH_3C(O)O + NO_2$$

$\Delta H^\circ = -93$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.1 \times 10^{-12} \exp[(570 \pm 140)/T]$	228–354	Maricq and Szente, 1996	PLP-AS (a)
$(1.4 \pm 0.2) \times 10^{-11}$	298		
$8.1 \times 10^{-12} \exp[(270 \pm 60)/T]$	200–402	Villalta and Howard, 1996	F-CIMS (b)
$(2.0 \pm 0.3) \times 10^{-11}$	298		
$(2.0 \pm 0.3) \times 10^{-11}$	295	Sehested et al., 1998	PR-A (c)
$6.0 \times 10^{-12} \exp[(320 \pm 40)/T]$	218–370	Moise et al., 1999	F-CIMS (d)
$(2.0 \pm 0.3) \times 10^{-11}$	296		
Relative Rate Coefficients			
$8.9 \times 10^{-12} \exp[(312 \pm 46)/T]$(1 bar air)	247–298	Seefeld et al., 1997	(e)
$(2.5 \pm 0.4) \times 10^{-11}$ (1 bar air)	298		
$(2.17 \pm 0.23) \times 10^{-11}$ (0.93 bar)	295	Sehested et al., 1998	(f)

Comments

(a) Pulsed laser photolysis of Cl_2-CH_3CHO-O_2-NO mixtures at 351 nm. Time-resolved absorption spectroscopy using a gated diode array for $CH_3C(O)O_2$ in the UV and using a diode laser for NO and NO_2 in the IR. Correction to k required for competing reactions of $CH_3C(O)O_2$.

(b) $CH_3C(O)O_2$ produced by thermal decomposition of peroxyacetyl nitrate and detected by CIMS through its reaction with SF_6^-. NO_2, CH_3 and CO_2 were positively identified as products implying rapid decomposition of $CH_3C(O)O$ to CH_3 and CO_2. Experiments conducted at pressures of 1.2–6 Torr (1.6–8 mbar) He.

(c) Pulse radiolysis of CH_3CHO-O_2-CO_2-NO and CH_3CHO-O_2-SF_6-NO mixtures at 1 bar pressure. The rate coefficient was obtained from the formation of NO_2, measured by absorption at 400.5 nm.

(d) $CH_3C(O)O_2$ produced by thermal decomposition of peroxyacetyl nitrate and detected by CIMS through its reaction with SF_6^-. Experiments conducted at 2–5 Torr (2.7–6.7 mbar) He.

(e) $CH_3C(O)O_2$ produced by steady state photolysis of biacetyl in the presence of O_2. Yields of peroxyacetyl nitrate were measured as a function of the [NO]/[NO_2] ratio. Data gave $k/k(CH_3C(O)O_2+NO_2)=2.44\pm0.18$ at 1 bar, independent of temperature over the range 247 K to 298 K. The expression in the table is calculated using the recommended value for $k(CH_3C(O)O_2+NO_2)$ at 1 bar pressure (IUPAC, this evaluation).

(f) $CH_3C(O)O_2$ radicals were produced by photolysis of Cl_2-CH_3CHO-O_2 mixtures, and reactants and products monitored by FTIR spectroscopy. The measured rate coefficient ratio $k(CH_3C(O)O_2+NO)/k(CH_3C(O)O_2+NO_2)=2.07\pm0.21$ at 932 mbar N_2 is placed on an absolute basis using the recommended value of $k(CH_3C(O)O_2+NO_2)$ (IUPAC, this evaluation).

Preferred Values

$k = 2.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.5 \times 10^{-12} \exp(290/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–350 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 250$ K.

Comments on Preferred Values

The direct measurements at 298 K of Villalta and Howard (1996), Moise et al. (1999) and Sehested et al. (1998) are in excellent agreement, all obtaining values of 2×10^{-11} cm^3 molecule^{-1} s^{-1}, and provide the basis of the 298 K recommendation. Those of Maricq and Szente (1996) give a value of k(298) approximately 30% lower. Of the three temperature dependent data sets, those of Villalta and Howard (1996) and Moise et al. (1999) agree within the error limits and present a significantly weaker dependence than the more highly scattered data of Maricq and Szente (1996). The recommended temperature dependence was obtained by weighted least squares fitting to the data of Villalta and Howard (1996) and Moise et al. (1999).

The earlier data for k, obtained relative to $k(CH_3C(O)O_2+NO_2)$ (Cox et al., 1976; Cox and Roffey, 1977; Hendry and Kenley, 1977; Kirchner et al., 1990; Tuazon et al., 1991), are generally consistent with this recommendation.

References

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II.A6.127

$C_2H_5C(O)O_2 + NO \rightarrow C_2H_5C(O)O + NO_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.7 \pm 1.7) \times 10^{-12} \exp[(340 \pm 80)/T]$	226–406	Froyd and Lovejoy, 1999	F-CIMS(a)
$(2.1 \pm 0.2) \times 10^{-11}$	298		
Relative Rate Coefficients			
$1.25 \times 10^{-11} \exp(240/T)$	249–302	Seefeld and Kerr, 1997	RR(b)
$(2.8 \pm 0.4) \times 10^{-11}$	298		
$(2.3 \pm 0.2) \times 10^{-11}$	302	Kerr and Stocker, 1985	RR(c)

Comments

(a) Low pressure flow tube at 1.5 to 15 Torr (2–20 mbar) He or N_2. $C_2H_5C(O)O_2$ was formed by thermal decomposition of $C_2H_5C(O)ONO_2$ and detected as $C_2H_5C(O)O_2^-$ or $C_2H_5C(O)O^-$ following reaction with SF_6^- or I^-. Results at 15 Torr N_2 analysed to set an upper limit to the association reaction of k_0(298 K) $<1.9\times 10^{-30}$ cm^6 molecule^{-2} s^{-1}.

(b) Ratio $k/k(C_2H_5C(O)O_2+NO_2)=2.33\pm0.38$, independent of temperature over the range 249–302 K. $C_2H_5C(O)O_2$ produced by photolysis of $C_2H_5C(O)Cl$ in a flow system at 1 atm pressure with analysis of $C_2H_5C(O)O_2NO_2$ by GC, as a function of the [NO]/[NO_2] ratio. k calculated with $k(C_2H_5C(O)O_2+NO_2)=k(CH_3C(O)O_2+NO_2)$ from the present evaluation [in Arrhenius form, $k_\infty(CH_3C(O)O_2+NO_2)=5.4 \times 10^{-12} \exp(240/T)$ cm^3 molecule^{-1} s^{-1} over the range 250 K to 300 K (IUPAC, this evaluation)]. Also showed that the above rate constant ratio was 11% lower than the corresponding ratio for $CH_3C(O)O_2$, which is consistent with a higher rate coefficient for the RO_2+NO_2 (+M) reaction for the C_3 acylperoxy radical.

(c) Ratio $k/k(C_2H_5C(O)O_2 + NO_2) = 1.89\pm0.21$. k calculated with $k(C_2H_5C(O)O_2 + NO_2) = k_\infty(CH_3C(O)O_2 + NO_2)$ from the present evaluation (in Arrhenius form, $k_\infty(CH_3C(O)O_2+NO_2) = 5.4\times10^{-12} \exp(240/T)$ cm^3 molecule^{-1} s^{-1} over the range 250 K to 300 K (IUPAC, this evaluation)].

Preferred Values

$k = 2.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.7 \times 10^{-12} \exp(340/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–410 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred values are based on the absolute determination of Froyd and Lovejoy (1999). The relative rate measurements (Seefeld and Kerr, 1997; Kerr and Stocker, 1985) are in agreement with this number, but suffer from the lack of an absolute measurement for $k(C_2H_5C(O)O_2+NO_2)$, the reference reaction rate coefficient (see comments above).

References

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II.A6.128

$$\mathbf{CH_3O_2 + NO_2 + M \rightarrow CH_3O_2NO_2 + M}$$

$\Delta H^\circ = -92.7$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.33 \pm 0.08) \times 10^{-30}[N_2]$	298	Sander and Watson, 1980	FP-AS (a)
$2.2 \times 10^{-30} (T/300)^{-2.5}[N_2]$	253–353	Ravishankara et al., 1980	FP-AS (b)
$(1.46 \pm 0.50) \times 10^{-30}[SF_6]$	295	Wallington et al., 1999	PR-AS (c)

Comments

(a) Pressure range 70 mbar to 900 mbar for the bath gases He, N_2, and SF_6. Analysis of the falloff curve was carried out with a theoretical F_c value of 0.39, in good agreement with the fitted value of F_c=0.4±0.10.

(b) Pressure range 100 mbar to 950 mbar. Analyses of the falloff curves at 253 K, 298 K and 353 K were carried out with F_c=0.4 independent of temperature.

(c) Pulse radiolysis study in 0.5–14 bar of SF_6. Evaluating the falloff curve with F_c=0.40.

Preferred Values

$k_0 = 2.5 \times 10^{-30} (T/300)^{-5.5} [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–350 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the results from Sander and Watson (1980) and the theoretical analysis from Destriau and Troe (1990). These values are based on a theoretically determined value of F_c=0.36 at 300 K.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.0 \pm 1.0) \times 10^{-12}$	298	Sander and Watson, 1980	FP-AS (a)
$7 \times 10^{-12} (T/298)^{-3.5}$	253–353	Ravishankara et al., 1980	FP-AS (b)
$(1.8 \pm 0.25) \times 10^{-11}$	295	Wallington et al., 1999	PR-AS (c)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0. The large negative temperature coefficient is probably an artifact of the interpretation. If a larger negative temperature exponent for k_0 and a smaller F_c value at higher temperature are used, the large negative temperature exponent of k_∞ will decrease.

(c) See comment (c) for k_0.

Preferred Values

$k = 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.
$k_\infty = 1.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–350 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$

Comments on Preferred Values

The preferred values are based on the high pressure study from Wallington et al. (1999). An experimental value of F_c=0.36 at 298 K appears well established. Less complete information on the falloff range is obtained from the experiments by Cox and Tyndall (1980), who measured k=1.6×10^{-12} cm^3 molecule^{-1} s^{-1} at 700 mbar of N_2 and 1.2×10^{-12} cm^3 molecule^{-1} s^{-1} at 66 mbar of Ar at 275 K, and Bridier et al. (1992) who measured k=(4.4±0.4)×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K in 1 bar of air. The apparent observation of a pressure independent rate coefficient k over the range 66 mbar to 760 mbar of Ar reported by Adachi and Basco (1980) is not confirmed by Sander and Watson (1980) and Ravishankara et al. (1980). ΔH is taken from the equilibrium measurements of Bridier et al. (1992).

References

Adachi, H. and Basco, N.: Int. J. Chem. Kinet., 12, 1, 1980.
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Cox, R. A. and Tyndall, G. S.: J. Chem. Soc. Faraday Trans., 2, 76, 153, 1980.
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Ravishankara, A. R., Eisele, F. L., and Wine, P. H.: J. Chem. Phys., 73, 3743, 1980.
Sander, S. P. and Watson, R. T.: J. Phys. Chem., 84, 1664, 1980.
Wallington, T. J., Nielsen, O. J., and Sehested, K.: Chem. Phys. Lett., 313, 456, 1999.

II.A6.129

$$\mathbf{CH_3O_2NO_2 + M \rightarrow CH_3O_2 + NO_2 + M}$$

ΔH° = 92.7 kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
9.0×10^{-5} exp(-9694/T)[N_2]	248–273	Zabel et al., 1989	(a)
6.7×10^{-19} [N_2]	298*		

Comments

(a) Rate of decomposition of $CH_3O_2NO_2$ followed by FTIR spectroscopy after generation in a reaction chamber, with subsequent addition of NO to scavenge CH_3O_2 radicals. Falloff curves were fitted with F_c=0.4.

Preferred Values

$k_0 = 6.8 \times 10^{-19}$ [N_2] s^{-1} at 298 K.
$k_0 = 9 \times 10^{-5}$ exp(-9690/T) [N_2] s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm$ 0.3 at 298 K.
Δ (E/R) = ± 500 K.

Comments on Preferred Values

The preferred values correspond to the data and analysis from Zabel et al. (1989). A theoretical analysis of these data and those of the reverse reaction from Sander and Watson (1980) and Ravishankara et al. (1980) in Destriau and Troe (1990) gave an internally consistent picture (with ΔH° = 88.5 kJ mol^{-1}). Slightly lower limiting rate coefficients were obtained in Bridier et al. (1992) where a value of F_c=0.6 was used. Direct measurements of the equilibrium constant $K_c=k/k_1=2.73\times10^{-28}$ exp(10910/T) cm^3 molecule^{-1} from Bridier et al. (1992) lead to ΔH=92.7 kJ mol^{-1} and provide an indication for the internal consistency of the rate data.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.1×10^{16} exp(-10920/T)	256–268	Bahta et al., 1982	(a)
2.6	298*		
1.1×10^{16} exp(-10560/T)	248–273	Zabel et al., 1989	(b)
4.5	298*		

Comments

(a) $CH_3O_2NO_2$ generated by photolysis of Cl_2 in the presence of NO_2, CH_4 and O_2. Kinetics were monitored in the presence of NO by UV absorption at 250 nm. At 460 mbar, $k=6\times10^{15}\exp(-10620/T)$ s^{-1}. The given value of k_∞ is derived with F_c=0.6. The data depend to some extent on the rate coefficient for the reaction $CH_3O_2+NO\rightarrow CH_3O+NO_2$.

(b) See comment (a) for k_0.

Preferred Values

k = 1.8 s^{-1} at 298 K and 1 bar of air.
k_∞ = 4.5 s^{-1} at 298 K.
$k_\infty = 1.1 \times 10^{16}\exp(-10560/T)$ s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

See comments on preferred values of k_0.

References

Bahta, A., Simonaitis, R., and Heicklen, J.: J. Phys. Chem., 86, 1849, 1982.
Bridier, I., Lesclaux, R., and Veyret, B.: Chem. Phys. Lett., 191, 259, 1992.
Destriau, M. and Troe, J.: Int. J. Chem. Kinet., 22, 915, 1990.
Ravishankara, A. R., Eisele, F. L., and Wine, P. H..: J. Chem. Phys., 73, 3743. 1980.
Sander, S. P. and Watson, R. T.: J. Phys. Chem., 84, 1664, 1980.
Zabel, F., Reimer, A., Becker, K. H., and Fink, E. H.: J. Phys. Chem., 93, 5500, 1989.

II.A6.130

$$\mathbf{C_2H_5O_2 + NO_2 + M \rightarrow C_2H_5O_2NO_2 + M}$$

$\Delta H^\circ = -67.7$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.8 \times 10^{-29}[N_2]$	254	Elfers et al., 1990	(a)

Comments

(a) Thermal decomposition of $C_2H_5O_2NO_2$ in a glass reaction chamber in the presenceof differing initial $[NO_2]/NO$ ratios at total pressures of 10 mbar to 1000 mbar. $C_2H_5O_2NO_2$ was prepared in situ by the photolysis of Cl_2-C_2H_6-O_2-NO_2-N_2 mixtures. $C_2H_5O_2NO_2$, NO_2 and NO concentrations were monitored by longpath FTIR absorption and rate coefficient ratios for the reaction of $C_2H_5O_2$ with NO and NO_2 were obtained. The reported rate coefficient for $C_2H_5O_2$+NO_2 was derived using a rate coefficient of 8.9×10^{-12} cm^3 molecule^{-1} s^{-1} for the reaction $C_2H_5O_2+NO\rightarrow C_2H_5O+NO_2$. Falloff curves were constructed based on the theoretical analysis from Destriau and Troe (1990) with F_c=0.31 and k_∞=7.5×10^{-12} cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k_0 = 1.3 \times 10^{-29} (T/300)^{-6.2} [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the data from Elfers et al. (1990) and the analysis from Destriau and Troe (1990). The temperature dependence is from the theoretical analysis of Destriau and Troe (1990). Falloff extrapolations were made with F_c=0.31 at 250 K to 300 K such as given from the theoretical analysis of Destriau and Troe (1990).

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.0×10^{-11}	254	Elfers et al., 1990	(a)

Comments

(a) See comment (a) for k_0.

Preferred Values

k = 6.1 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K and 1 bar of air.
k_∞ = 8.8 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–300 K.

Comments on Preferred Values

See comments on k_0. The theoretical analysis in Destriau and Troe (1990) also includes information from studies of the reverse reaction measured in Zabel et al. (1989).

References

Destriau, M. and Troe, J.: Int. J. Chem. Kinet., 22, 915, 1990.
Elfers, F., Zabel, F., and Becker, K. H.: Chem. Phys. Lett., 168, 14, 1990.
Zabel, F., Reimer, A., Becker, K. H., and Fink, E. H.: J. Phys. Chem., 93, 5500, 1989.

II.A6.131

$C_2H_5O_2NO_2 + M \rightarrow C_2H_5O_2 + NO_2 + M$

$\Delta H^\circ = 67.7\ \text{kJ·mol}^{-1}$

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.8 \times 10^{-4}\exp(-9285/T)[N_2]$	245–273	Zabel et al., 1989	FTIR (a)

Comments

(a) Unimolecular decay of $C_2H_5O_2NO_2$ followed at total pressures ranging from 10 mbar to 800 mbar. Falloff extrapolation with F_c=0.3.

Preferred Values

$k_0 = 1.4 \times 10^{-17}\ [N_2]\ \text{s}^{-1}$ at 298 K.
$k_0 = 4.8 \times 10^{-4} \exp(-9285/T)\ [N_2]\ \text{s}^{-1}$ over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.
$\Delta (E/R) = \pm 1000$ K.

Comments on Preferred Values

The dissociation data are consistent with experimental recombination data from Elfers et al. (1989) and the theoretical analysis from Zabel et al. (1989) and Destriau and Troe (1990). Falloff curves are constructed with F_c=0.31 (over the range 250 K to 300 K).

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$8.8 \times 10^{15} \exp(-10440/T)$	245–273	Zabel et al., 1989	FTIR(a)

Comments

(a) See comment (a) for k_0.

Preferred Values

$k = 4.0\ \text{s}^{-1}$ at 298 K and 1 bar of air.
$k_\infty = 5.4\ \text{s}^{-1}$ at 298 K.
$k_\infty = 8.8 \times 10^{15} \exp(-10440/T)\ \text{s}^{-1}$ over the temperature range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 300 K.
$\Delta (E/R) = \pm 1000$ K.

Comments on Preferred Values

See comments on k_0.

References

Destriau, M. and Troe, J.: Int. J. Chem. Kinet., 22, 915, 1990.
Elfers, G., Zabel, F., and Becker, K. H.: Chem. Phys. Lett., 168, 14, 1990.
Zabel, F., Reimer, A., Becker, K. H., and Fink, E. H.: J. Phys. Chem., 93, 5500, 1989.

II.A6.132

$$\mathbf{CH_3C(O)O_2 + NO_2 + M \rightarrow CH_3C(O)O_2NO_2 + M}$$

$\Delta H^\circ = -119\ \text{kJ}\cdot\text{mol}^{-1}$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
5.1×10^{-29} [N$_2$]	298	Basco and Parmar, 1987	FP-AS (a)
$(2.7 \pm 1.5) \times 10^{-28}(T/298)^{-7.1}$[air]	248–393	Bridier et al., 1991	FP-AS (b)

Comments

(a) Photolysis of Cl_2-CH_3CHO-O_2-N_2 and NO_2 at total pressures of 100 mbar to 800 mbar. Extrapolation of falloff curve with theoretically modeled value of F_c=0.19.

(b) The falloff curves were fitted using F_c=0.30. The discrepancy with the data of Basco and Parmar (1987) is attributed to an oversimplified kinetic scheme used in Basco and Parmar (1987).

Preferred Values

$k_0 = 2.7 \times 10^{-28}\ (T/300)^{-7.1}\ [N_2]\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm\ 0.4$ at 298 K.
$\Delta n = \pm\ 2$.

Comments on Preferred Values

The data from Basco and Parmar (1987) and Addison et al. (1980) are a factor of 2–3 lower than those from Bridier et al. (1991). The more extensive and internally consistent study of $CH_3C(O)OONO_2$ (PAN) formation and dissociation in Bridier et al. (1991) is preferred. Falloff extrapolations were performed with a modeled value of F_c=0.3.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
6.1×10^{-12}	298	Basco and Parmar, 1987	FP-AS (a)
$(1.21 \pm 0.05) \times 10^{-11}(T/298)^{-0.9}$	248–393	Bridier et al., 1991	FP-AS (b)
$(1.0 \pm 0.2) \times 10^{-11}$ (0.93 bar)	295	Sehested et al., 1998	PR-A (c)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0.

(c) $CH_3C(O)O_2$ radicals were generated from the pulsed radiolysis of CH_3CHO-O_2-CO_2-NO_2 and CH_3CHO-SF_6-O_2-NO_2 mixtures and the disappearance rate of NO_2 monitored by absorption at 400.5 and 452 nm.

Preferred Values

$k = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.
$k_\infty = 1.2 \times 10^{-11}$ $(T/300)^{-0.9}$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

See comments on k_0 . The measurement of Sehested et al. (1998) is in very good agreement with the results from Bridier et al. (1991) which form the basis of the preferred value.

References

Addison, M. C., Burrows, J. P., Cox, R. A., and Patrick, R.: Chem. Phys. Lett., 73, 283, 1980.
Basco, N. and Parmar, S. S.: Int. J. Chem. Kinet., 19, 115, 1987.
Bridier, I., Caralp, F., Loirat, H., Lesclaux, R., Veyret, B., Becker, K. H., Reimer, A., and Zabel, F.: J. Phys. Chem., 95, 3594 , 1991.
Sehested, J., Christensen, L. K., Møgelberg, T., Nielsen, O. J., Wallington, T. J., Guschin, A., Orlando, J. J., and Tyndall, G. S.: J. Phys. Chem. A, 102, 1779, 1998.

II.A6.133

$$\mathbf{CH_3C(O)O_2NO_2 + M \rightarrow CH_3C(O)O_2 + NO_2 + M}$$

$\Delta H^\circ = 119\ \mathrm{kJ{\cdot}mol^{-1}}$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\mathrm{s^{-1}}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.9 \pm 0.3) \times 10^{-3}\ \exp(-12100/T)[N_2]$	300–330	Bridier et al., 1991	FTIR (a)
$1.1 \times 10^{-20}[N_2]$	298*		

Comments

(a) Rate of the thermal decomposition of $CH_3C(O)OONO_2$ (PAN) measured by FTIR absorption spectroscopy in the presence of an excess of NO to scavenge CH_3CO_3 radicals. Pressure range 10 mbar to 790 mbar of N_2. Falloff curves were analyzed with F_c=0.30.

Preferred Values

$k_0 = 1.1 \times 10^{-20}\ [N_2]\ \mathrm{s^{-1}}$ at 298 K.
$k_0 = 4.9 \times 10^{-3}\ \exp(-12100/T)\ [N_2]\ \mathrm{s^{-1}}$ over the temperature range 300–330 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 1000$ K.

Comments on Preferred Values

The data base of Bridier et al. (1991) is large enough to allow for a falloff extrapolation to k_0, in part because falloff curves for PAN dissociation and recombination were measured independently. Falloff extrapolations were made with a modeled value of F_c=0.3; see the evaluation of the data from Bridier et al. (1991) in Zabel (1995).

High-pressure rate coefficients

Rate coefficient data

$k_\infty/\mathrm{s^{-1}}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.3 \pm 0.2) \times 10^{-4}$	297	Niki et al., 1985	FTIR (a)
2.2×10^{-4}	298	Senum et al., 1986	FTIR (b)
$2.52 \times 10^{16}\ \exp(-13573/T)$	283–313	Tuazon et al., 1991	FTIR (c)
4.2×10^{-4}	298		
$(4.0 \pm 0.8) \times 10^{16}\ \exp(-13600)/T$	300–330	Bridier et al., 1991	(d)
6.1×10^{-4}	298*		
$2.5 \times 10^{17}\ \exp[-(14340 \pm 250)/T]$	302–323	Roberts and Bertman, 1992	GC (e)
3.2×10^{-4}	298*		
3.1×10^{-4}	298	Roumelis and Glavas, 1992	GC (f)
$1.6 \times 10^{16}\ \exp[-(13539 \pm 1060)/T]$	288–298	Grosjean et al., 1994	GC (g)
3.0×10^{-4}	298		

Comments

(a) Decay of $CH_3C(O)O_2{}^{15}NO_2$ in the presence of $^{14}NO_2$ at a total pressure of 900 mbar of N_2.

(b) Decay of $CH_3C(O)O_2NO_2$ (PAN) in the presence of NO at a total pressure of 16 mbar.

(c) Thermal decomposition of PAN in an environmental chamber in the presence of 970 mbar of synthetic air or N_2.

(d) See comment (a) for k_0.

(e) Thermal decomposition of PAN at 1 bar total pressure. PAN concentrations were measured by GC with electron capture detection.

(f) Thermal decomposition of PAN in N_2 as well as in the presence of O_2, NO_2 and NO at 1 bar total pressure. The products methyl nitrate and NO_2 in PAN-N_2 mixtures were measured by GC. In the presence of large amounts of O_2, no methyl nitrate was formed at 333 K, indicating that the decomposition of PAN to methyl nitrate and CO_2 does not occur. The data obtained were simulated with 23 reactions.

(g) Thermal decomposition of PAN in 1 bar of air. PAN was measured by GC with electron capture detection.

Preferred Values

$k = 3.3 \times 10^{-4}\ s^{-1}$ at 298 K and 1 bar of air.
$k_\infty = 3.8 \times 10^{-4}\ s^{-1}$ at 298 K.
$k_\infty = 5.4 \times 10^{16} \exp(-13830/T)\ s^{-1}$ over the temperature range 300–330 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The reported values from Bridier et al. (1991), Tuazon et al. (1991), Roberts and Bertman, (1992) and Roumelis and Glavas (1992) as well as the selected more recent measurements from Sehested et al. (1998) are all in very good agreement at 298 K and are preferred here. The direct PAN decompositions to methyl nitrate and CO_2 (Roumelis and Glavas, 1992; Orlando et al., 1992) or to $CH_3C(O)O$ and NO_3 (Orlando et al., 1992) are very slow compared to the decomposition to $CH_3C(O)O_2$+NO_2.

References

Bridier, I., Caralp, F., Loirat, H., Lesclaux, R., Veyret, B., Becker, K. H., Reimer, A., and Zabel, F.: J. Phys. Chem., 95, 3594, 1991.
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Senum, G. I., Fajer, R., and Gaffney, J. S.: J. Phys. Chem., 90, 152, 1986.
Tuazon, E. C., Carter, W. P. L., and Atkinson, R.: J. Phys. Chem., 95, 2434, 1991.
Zabel, F.: Z. Phys. Chem., 188, 119, 1995.

II.A6.134

$$\mathbf{C_2H_5C(O)O_2NO_2 + M \rightarrow C_2H_5C(O)O_2 + NO_2 + M}$$

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.7×10^{-3} exp(-11280/T) [N_2]	291–320	Kirchner et al., 1999	(a)

Comments

(a) Experiments in a 420 L reaction chamber with photolytic generation of radicals forming peroxynitrates. Decomposition of propionyl peroxynitrate followed in the dark by FTIR spectrometry. Experiments between 11.5 and 1013 mbar of N_2. Falloff extrapolations with F_c=0.36.

Preferred Values

$k_0 = 6.2 \times 10^{-20}$ [N_2] s^{-1} at 298 K.
$k_0 = 1.7 \times 10^{-3}$ exp(-11280/T) [N_2] s^{-1} over the temperature range 290–320 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.
$\Delta (E/R) = \pm 2000$ K.

Comments on Preferred Values

The only available low pressure data from Kirchner et al. (1999) appear consistent with the more extensive data base for the high-pressure range. The falloff curve is constructed with F_c=0.36.

High-pressure rate coefficients

Rate coefficient data

k_∞/ s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2×10^{15} exp (-12800/T)	300–315	Mineshos and Glavas, 1991	(a)
4.4×10^{-4}	298*		
8.3×10^{16} exp(-13940/T)	291–320	Kirchner et al., 1999	(b)
4.0×10^{-4}	298		

Comments

(a) Thermal decomposition of propionyl peroxynitrate (PPN) in a 4.5 liter glass flask in the presence of 1 bar of N_2. PPN and the products ethyl nitrate, NO_2, and methyl nitrate were analyzed by GC at 323 K. In the presence of NO, ethyl nitrate was the major product observed.

(b) See comment (a) for k_0. Limited data from earlier work are also considered.

Preferred Values

$k = 3.6 \times 10^{-4}$ s^{-1} at 298 K and 1 bar of air.
$k_\infty = 4.0 \times 10^{-4}$ s^{-1} at 298 K.
$k_\infty = 8.3 \times 10^{16} \exp(-13940/T)$ s^{-1} over the temperature range 290–320 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 1000$ K.

Comments on Preferred Values

The values from Kirchner et al. (1999) and Minoshos and Glavas (1991) are in good agreement.

References

Kirchner, F., Mayer-Figge, A., Zabel, F., and Becker, K. H.: Int. J. Chem. Kinet., 31, 127, 1999.
Mineshos, G. and Glavas, S : React. Kinet. Catal. Lett., 45, 30, 5, 1991.

II.A6.135

$$CH_3C(O)CH_2O_2NO_2 + M \rightarrow CH_3C(O)CH_2O_2 + NO_2 + M$$

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.9×10^{16}exp(-10830/T)	250–298	Sehested et al., 1998	(a)
~3	295		
1.0×10^{16}exp(-10630/T)	246–262	Kirchner et al., 1999	(b)

Comments

(a) Loss of $CH_3C(O)CH_2O_2NO_2$, which was produced by static photolysis in a 140 l pyrex reaction chamber at pressure of 933 mbar, was followed by long path FTIR. k at room temperature (295 K) obtained by fitting acetonyl peroxynitrate decay with a complex mechanism. Data for low temperature (250–275 K) were obtained directly from the decay of preformed $CH_3C(O)CH_2O_2NO_2$ after the addition of excess NO.

(b) Experiments in a 420 L reaction chamber with photolytic generation of radicals forming peroxynitrates. Decomposition of acetonyl peroxynitrate in the dark followed by FTIR spectrometry. Measurements in 10, 100, and 800 mbar of N_2. Rate coefficients at 10 mbar are about a factor of 2 smaller than at 800 mbar.

Preferred Values

$k_\infty = 1.4 \times 10^{16}$ exp(-10730/T) s^{-1} over the temperature range 240–260 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 250 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The results from the two experimental studies are essentially in agreement, and are consistent with data for related reactions. The preferred Arrhenius parameters are a simple mean of the reported experimental values. The measured rate coefficients are expected, by analogy with the corresponding PAN decomposition at 1 bar of air (IUPAC, this evaluation), to be very close to the high pressure limit.

References

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II.A6.136

$$\mathbf{CH_2{=}C(CH_3)C(O)OONO_2 + M \rightarrow CH_2{=}C(CH_3)CO_3 + NO_2 + M}$$

Rate coefficient data

k/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.58 \times 10^{16} \exp[-(13488 \pm 504)/T]$	302.25–323.55	Roberts and Bertman, 1992	(a)
3.5×10^{-4}	298*		

Comments

(a) The thermal decomposition of $CH_2{=}C(CH_3)C(O)OONO_2$ (MPAN) was studied in one atmosphere of air, with added NO to ensure that $CH_2{=}C(CH_3)C(O)OO$ radicals reacted with NO (to form $NO_2{+}CO_2{+}CH_2{=}CCH_3$) rather than reacting with NO_2 to reform MPAN. MPAN concentrations were measured by GC with electron capture detection.

Preferred Values

$k = 3.5 \times 10^{-4}$ s^{-1} at 298 K and 1 bar.
$k = 1.6 \times 10^{16} \exp(-13500/T)$ s^{-1} over the temperature range 290–330 K at 1 bar.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 1000$ K.

Comments on Preferred Values

The preferred values are based on the sole study of this reaction by Roberts and Bertman (1992). The preferred values for the decomposition of MPAN are very similar to those for the thermal decomposition of $CH_3C(O)OONO_2$ (PAN) (Roberts and Bertman, 1992; IUPAC, see also this evaluation). The rate coefficients measured by Roberts and Bertman (1992) are expected, by analogy with the corresponding PAN decomposition (IUPAC, this evaluation), to be very close to the high pressure limit at 1 bar of air.

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Roberts, J. M. and Bertman, S. B.: Int. J. Chem. Kinet., 24, 297, 1992.

II.A6.137

$$\mathbf{CH_3O_2 + NO_3} \begin{array}{ll} \rightarrow \mathbf{CH_3O + NO_2 + O_2} & \mathbf{(1)} \\ \rightarrow \mathbf{other\ products} & \mathbf{(2)} \end{array}$$

$\Delta H^\circ(1) = -32.3$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.3 \pm 0.7) \times 10^{-12}$	298	Crowley et al., 1990	MMS-AS (a)
$(1.0 \pm 0.6) \times 10^{-12}$	298	Biggs et al., 1994a, b	DF-LIF/AS (b)
$(1.2 \pm 0.6) \times 10^{-12}$	298	Daële et al., 1995	DF-LIF/MS (c)
$(1.3 \pm 0.2) \times 10^{-12}$	298	Helleis et al., 1996	DF-MS (d)
Branching Ratios			
$k_1/k > 0.9$	298	Kukui et al., 1995	DF-LIF/MS (e)

Comments

(a) Computer simulation of NO_3 absorption profiles formed in the modulated photolysis of HNO_3 in the presence of CH_4 and O_2.

(b) CH_3O product of Reaction (1) measured by LIF; NO_3 by visible absorption spectroscopy. Pressure = 3.5 mbar. Modelling of CH_3O time-dependence gave $k/k(CH_3O + NO_3)=0.43\pm0.09$. k calculated with $k(CH_3O+NO_3)=(2.3\pm0.7)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} obtained in a similar study in the same apparatus.

(c) CH_3O measured by LIF; NO_3 by titration with 2,3-dimethyl-2-butene. The rate coefficient was extracted by numerical simulation from the CH_3O+NO_3 reactant system.

(d) CD_3O_2 decay measured directly in excess NO_3. Numerical simulation to take into account the re-formation of CD_3O_2 from CD_3O+NO_3.

(e) Based on observations of DCDO formation from the CD_3O+NO_3 reaction and the relative rates of reactions of CD_3O and CD_3O_2 with NO_3.

Preferred Values

$k = 1.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

None of the experimental studies for this reaction can be described as definitive or direct. In the flow tube measurements, a quasi-equilibrium between CH_3O_2 and CH_3O radicals is established and concentrations and decay kinetics are influenced by reactions of both radicals. The ratio $k_1/k(CH_3O+NO_3)$ should be well determined but values of 0.43 (Biggs et al., 1994b), 0.66 (Biggs et al., 1994a) and 0.30 (Daële et al., 1995) were obtained. The quasi-equilibrium is avoided by using O_2 to scavenge CH_3O in the work of Crowley et al. (1990) but the need to simulate a complex reaction system, and the possible influence of a dark reaction (Crowley et al., 1993) that generated NO_3 reduce the reliability of these experiments.

The method used by Helleis et al. (1996) to determine k_1 is the most direct. Their analysis considers all of the available information on the secondary chemistry and their value is recommended with wide error limits. The value reported by Kukui et al. (1995) differs substantially from those of Biggs et al. (1994a, b), Daële et al. (1995) and Helleis et al. (1996) and was not included in the evaluation of the rate coefficient. Their work (Kukui et al., 1995) suggests channel (1) is the predominant pathway, with $k_2/k<0.10$.

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II.A6.138

$$\mathbf{C_2H_5O_2 + NO_3 \rightarrow C_2H_5O + NO_2 + O_2} \quad \mathbf{(1)}$$
$$\mathbf{\rightarrow \text{other products}} \quad \mathbf{(2)}$$

$\Delta H^\circ(1) = -28.7$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.5 \pm 1.5) \times 10^{-12}$	298	Biggs et al., 1995	DF-LIF/AS (a)
$(2.3 \pm 0.5) \times 10^{-12}$	298	Ray et al., 1996	DF-LIF/MS (b)

Comments

(a) LIF detection of C_2H_5O. Detection of NO_3 by absorption spectroscopy at 662 nm. k was derived by modelling the kinetics of $C_2H_5O_2$+NO_3 in systems using C_2H_5+O_2 and C_2H_5O+NO_3 to generate $C_2H_5O_2$. Pressure = 2.9 mbar of He.

(b) LIF detection of C_2H_5O. MS detection of NO_3. k was derived from a model simulation of system using $C_2H_5O_2$ as initial reactant, with NO_3 in excess.

Preferred Values

$k_1 = 2.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

Both studies of this reaction used basically the same technique and gave similar results (Biggs et al., 1995; Ray et al., 1996). Extraction of values for k relies on modelling of the reaction system because radical concentrations are controlled by coupling between the $C_2H_5O_2$+NO_3 reaction and the reaction of the product C_2H_5O with NO_3, which regenerates $C_2H_5O_2$. The study of Ray et al. (1996) gave better defined k values and is the basis of the recommendation. Channel (1) is most important, and Biggs et al. (1995) suggest that $k_1/k \approx 0.8$.

References

Biggs, P., Canosa-Mas, C. E., Fracheboud, J.-M., Shallcross, D. E., and Wayne, R. P.: J. Chem. Soc. Faraday Trans., 91, 817, 1995.
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II.A6.139

$$\begin{array}{lll} \mathbf{CH_3O_2 + CH_3O_2} & \rightarrow \mathbf{CH_3OH + HCHO + O_2} & \mathbf{(1)} \\ & \rightarrow \mathbf{2CH_3O + O_2} & \mathbf{(2)} \\ & \rightarrow \mathbf{CH_3OOCH_3 + O_2} & \mathbf{(3)} \end{array}$$

$\Delta H°(1) = -331.0$ kJ·mol^{-1}
$\Delta H°(2) = 13.6$ kJ·mol^{-1}
$\Delta H°(3) = -146.5$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2+k_3)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.2 \pm 0.9) \times 10^{-13}$	298	Cox and Tyndall, 1980	MM-UVAS (a,b)
$(3.7 \pm 0.7) \times 10^{-13}$	298	Sander and Watson, 1980	FP-UVAS (a,c)
$1.40 \times 10^{-13} \exp[(223 \pm 41)/T]$	250–420	Sander and Watson, 1981	FP-UVAS (a,d)
$(3.0 \pm 0.5) \times 10^{-13}$	298		
$(4.4 \pm 1.0) \times 10^{-13}$	298	McAdam et al., 1987	FP-UVAS (a,e)
$1.3 \times 10^{-13} \exp[(220 \pm 70/T)]$	228–380	Kurylo and Wallington, 1987	FP-UVAS (a,f)
$(2.7 \pm 0.45) \times 10^{-13}$	298		
$(3.5 \pm 0.5) \times 10^{-13}$	298	Jenkin et al., 1988	MM-UVAS (a,g)
$(3.6 \pm 0.55) \times 10^{-13}$	300	Simon et al., 1990	MM-UVAS (a,h)
$1.3 \times 10^{-13} \exp(365/T)$	248–573	Lightfoot et al., 1990	FP-UVAS (a,i)
$(4.1 \pm 0.9) \times 10^{-13}$	300		
Branching Ratios			
$k_2/k = 1/\{1 + \exp[(1131 \pm 30)/T]/(17 \pm 5)\}$	223–333	Horie et al., 1990	P-FTIR (j)
$k_2/k = 0.30$	298		
$k_2/k = 0.41 \pm 0.04$	296	Tyndall et al., 1998	P-FTIR (k)
$k_3/k < 0.06$	296		

Comments

(a) k is defined by $-d[CH_3O_2]/dt=2k[CH_3O_2]^2$ and was derived from the measured overall second-order decay of CH_3O_2 radicals k_{obs} by correcting for secondary removal of the CH_3O_2 radicals.

(b) $[CH_3O_2]$ determined by absorption at 250 nm in modulated photolysis of Cl_2-CH_4-O_2 mixtures. $k/\sigma(250\,\text{nm})=1.33\times10^5$ cm s^{-1}, $\sigma=3.9\times10^{-18}$ cm^2 molecule^{-1} at 250 nm.

(c) Flash-photolysis of $(CH_3)_2N_2$-O_2 and Cl_2-CH_4-O_2 mixtures. $[CH_3O_2]$ monitored by long path UV absorption giving $k/\sigma=(1.06\pm0.07)\times10^5$ cm s^{-1} at 245 nm and $(2.84\pm0.36)\times10^5$ cm s^{-1} at 270 nm. Value quoted is a mean value using σ values obtained by Hochanadel et al. (1977). Small effects of varying O_2 and adding CO are reported.

(d) Flash-photolysis of Cl_2-CH_4-O_2 mixtures. σ determined from absorption at t=0 extrapolated from decay curves and estimate of $[CH_3O_2]_0$ from change in Cl_2 concentration in flash. $\sigma(250\,\text{nm})=(2.5 \pm 0.4)\times10^{-18}$ cm^2 molecule^{-1} at 298 K, and k/σ (250 nm)$=(5.6\pm0.8)\times10^4 \exp[(223\pm41)/T]$ cm s^{-1} (250 K to 420 K) were obtained.

(e) Flash-photolysis of Cl_2 in the presence of CH_4 and O_2 over the pressure range 169 mbar to 530 mbar (120 Torr to 400 Torr). $[CH_3O_2]$ monitored by UV absorption. $k_{obs}/\sigma(250\,\text{nm}) = 1.34 \times 10^5$ cm s^{-1} and $\sigma(250\,\text{nm})=4.4\times10^{-18}$ cm^2 molecule^{-1} were obtained. k_{obs}/k taken to be 1.35.

(f) Flash-photolysis of Cl_2 in the presence of CH_4-O_2-N_2 mixtures at pressures between 67 mbar and 530 mbar (50 Torr and 400 Torr). k_{obs}=(1.7±0.4)×10^{-13} exp[(220 ± 70)/T] cm^3 molecule^{-1} s^{-1} determined from measured values of $k_{obs}/\sigma(250)$ by taking $\sigma(250)=3.30\times10^{-18}$ cm^2 molecule^{-1} as previously determined by same authors. Here we have taken k_{obs}/k=1.35 to calculate k. k_{obs} shown to be independent of pressure over the range 67 mbar to 530 mbar (50 Torr to 400 Torr) at 298 K.

(g) Modulated photolysis of Cl_2 in the presence of CH_4-O_2 mixtures at a total pressure of 1 bar (760 Torr). $k_{obs}/\sigma(250\,nm)=1.11\times10^5$ cm s^{-1} and $\sigma(250\,nm)=(4.25\pm0.5)\times10^{-18}$ cm^2 molecule^{-1} were obtained leading to k_{obs}=(4.7 ± 0.5)×10^{-13} cm^3 molecule^{-1} s^{-1}. Cited value of k obtained by taking k_{obs}/k = 1.35 to allow for secondary removal of CH_3O_2.

(h) Modulated photolysis of Cl_2 in the presence of CH_4-O_2 mixtures at pressures of 320 mbar (240 Torr). $k_{obs}/\sigma(250\,nm)$ = 1.16 × 10^5 cm s^{-1} and σ (250 nm)=4.14×10^{-18} cm^2 molecule^{-1} were obtained, leading to k_{obs}=(4.8±0.5)×10^{-13} cm^3 molecule^{-1} s^{-1}. The cited value of k was obtained by taking k_{obs}/k = 1.35 to allow for secondary removal of CH_3O_2.

(i) Flash-photolysis of Cl_2 in the presence of CH_4-O_2-N_2 mixtures over the pressure range 270 mbar to 930 mbar (200 Torr to 700 Torr). CH_3O_2 radicals were monitored by UV absorption. The values k_{obs}/σ (210 nm to 260 nm)=1.17×10^5 cm s^{-1} and $\sigma(250\,nm)=4.8\times10^{-18}$ cm^2 molecule^{-1} were obtained. k_{obs}/k taken to be 1.35. At temperatures >373 K, the second-order decays of CH_3O_2 were affected by HO_2 radical reactions. The branching ratio was obtained from the effect of [HO_2] on the CH_3O_2 decays.

(j) Study of the photooxidation of CH_4, initiated by Cl atoms generated from Cl_2, in a slow-flow system under steady-state illumination. Analysis of HCHO, CH_3OH and HC(O)OH products by FTIR spectroscopy.

(k) Photolysis of $CH_3N_2CH_3$-O_2 and Cl_2-CH_4-O_2 mixtures, with analyses of reactants and products by FTIR spectroscopy.

Preferred Values

k = 3.5 × 10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 1.03 × 10^{-13} exp(365/T) cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.
k_2 = 1.3 × 10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K.
k_2 = 7.4 × 10^{-13} exp(-520/T) cm^3 molecule^{-1} s^{-1} over the temperature range 220–330 K.

Reliability

$\Delta \log k = \pm 0.12$ at 298 K.
$\Delta (E/R) = \pm 200$ K.
$\Delta \log k_2 = \pm 0.15$ at 298 K.
$\Delta (E_2/R) = \pm 300$ K.

Comments on Preferred Values

The room temperature measurements of k_{obs}/σ of Cox and Tyndall (1980), Sander and Watson (1980, 1981), McAdam et al. (1987), Kurylo and Wallington (1987), Jenkin et al. (1988), Simon et al. (1988) and Lightfoot et al. (1990) are in excellent agreement and lead to the recommended value of $k_{obs}/\sigma(250\,nm)=1.24\times10^5$ cm s^{-1}. The measurements of the absorption cross-section by Simon et al. (1990) form the basis of our recommendation of $\sigma(250\,nm)=3.9\times10^{-18}$ cm^2 molecule^{-1}. Thus, we recommend k_{obs}=4.8×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K. Taking the branching ratio of k_2/k=0.37 at 298 K yields the value of k at 298 K given above.

The temperature dependence of k reported by Lightfoot et al. (1990) is in excellent agreement with the studies of Sander and Watson (1981), Kurylo and Wallington (1987) and Jenkin and Cox (1991). Here we have recommended the *E/R* value of Lightfoot et al. (1990) on the basis of their more extensive temperature range, and the temperature-dependent branching ratio k_2/k. The recommended Arrhenius equation follows from the recommended values of k_{298} and *E/R*.

There have been a number of measurements of the branching ratio, k_2/k, which have been carefully reanalysed by Tyndall et al. (1998). The values of k_2/k at 298 K range from 0.30 to 0.45. Tyndall et al. (1998) recommend the average of 0.37±0.06 which is also accepted in the review of Tyndall et al. (2001). This value is taken as our preferred value at 298 K, with enhanced error limits. The two studies (Lightfoot et al., 1990; Horie et al., 1990) of the temperature dependence of the branching ratio involve different temperature ranges. Here we have selected the results of Horie et al. (1990) over the more atmospherically relevant temperature range of 200 K to 330 K, modified to reproduce our recommended value of k_2/k at 298 K. This has been combined with our recommended expression for k to obtain the preferred expression for k_2. There is no convincing evidence for any contribution from channel (3) (Tyndall et al., 1998).

It should be noted that, from an analysis of their own data (Horie et al., 1990) together with the results of Lightfoot et al. (1990), Anastasi et al. (1978), Kan et al. (1980), Parkes (1977), Niki et al. (1981) and Weaver et al. (1975), the equation k_2/k=1/(1+[exp(1330/T)]/33) was obtained by Horie et al. (1990) for the more extensive temperature range 223 K to 573 K. This equation shows slight non-Arrhenius behavior. Lightfoot et al. (1990) observed no pressure dependence of the branching ratio, k_2/k, over the range 0.28 bar to 1 bar.

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II.A6.140

$$\mathbf{CH_3O_2 + CH_3C(O)O_2 \rightarrow CH_3O + CH_3C(O)O + O_2 \quad (1)}$$
$$\mathbf{\rightarrow CH_3C(O)OH + HCHO + O_2 \quad (2)}$$

$\Delta H°(1) = -27.3$ kJ·mol^{-1}
$\Delta H°(2) = -378$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_1 = (8.8 \pm 1.5) \times 10^{-12}$	298	Roehl et al., 1996	PLP-UVAS (a)
$k_2 = (1.0 \pm 0.5) \times 10^{-12}$	298		
$8.5 \times 10^{-13} \exp[(726 \pm 25)/T]$	209–358	Maricq and Szente, 1996	PLP-UVAS (b)
$(1.0 \pm 0.2) \times 10^{-11}$	298		
$(8.2 \pm 0.6) \times 10^{-12}$	298	Villenave and Lesclaux, 1996	FP-UVAS (c)

Comments

(a) Acetyl radicals were produced from the photolysis of Cl_2-CH_3CHO-O_2 mixtures. CH_3O_2 radicals were produced as secondary products, or through added CH_4. k depends on $\sigma[CH_3C(O)O_2]$ for which values of 3.21×10^{-18} cm^2 molecule^{-1} at 240 nm and 6.67×10^{-18} cm^2 molecule^{-1} at 207 nm were obtained, relative to the UV spectrum of $C_2H_5O_2$ [σ(240 nm)=4.36×10^{-18} cm^2 molecule^{-1}]. A value of k_1/k=0.9 was used in the data analysis.

(b) Technique as for (a) but with UV spectra recorded on a gated diode array spectrometer. $\sigma[CH_3C(O)O_2]=6.5\times10^{-18}$ cm^2 molecule^{-1} at 206 nm and 2.9×10^{-18} cm^2 molecule^{-1} at 250 nm. On the basis of the HCHO kinetics observed it was concluded that channel (2) was dominant over the entire temperature range covered (209 K to 358 K). A value of k_1/k=0 was used in the data analysis.

(c) CH_3O_2 radicals were generated simultaneously with $CH_3C(O)O_2$ radicals from the flash photolysis of Cl_2-CH_3CHO-CH_4-O_2 mixtures. In the derivation of k, the branching ratio, α_c(=k_1/k) was assumed to be 0.65 but k was found to vary by less than 15% upon varying α between 0.5 and 1.0. Overall uncertainty was estimated to be 42% from error propagation analysis. A value of k_1/k=0.65 was used in the data analysis.

Preferred Values

$k = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.0 \times 10^{-12} \exp(500/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–350 K.
$k_1/k = 0.9$ at 298 K.
$k_2/k = 0.1$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 250$ K.
$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The three cited studies, which all used UV spectroscopy with similar values of the relevant absorption cross-sections to monitor the progress of the reaction are, apparently, in good agreement. However, the values of k derived depend upon the value of k_1/k used in the data analysis and since the three studies used values ranging from 0 to 0.9 their close agreement must be, to some degree, fortuitous. Tyndall et al. (2001) show that, using our preferred value for k_1/k, the studies of Roehl et al. (1996), Maricq and Szente (1996) and Villenave and Lesclaux (1996), give values of k in the range (0.98–2)$\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. We accept the analysis of Tyndall et al. (2001) and take the value of k which they recommend, based on the studies of Villenave and Lesclaux (1996) and Roehl et al. (1996), as our preferred value at 298 K. The temperature dependence is based on that observed for analogous reactions.

There is conflicting evidence on the branching ratios. At 298 K Moortgat et al. (1989) estimate that k_1/k=0.5, whilst Roehl et al (1996) find that k_1/k=0.9 and Maricq and Szente (1996) conclude that, essentially, the reaction proceeds entirely by channel (2). Further information comes from a study of Crawford et al. (1999) on the HO_2+$CH_3C(O)O_2$ reaction in which the yields of the products $CH_3C(O)OOH$ and $CH_3C(O)OH$ were monitored. Tyndall et al. (2001) have re-analysed the results reported by Crawford et al. (1999) and have shown that the product yields observed require that the CH_3O_2+$CH_3C(O)O_2$ reaction, which could also contribute to the $CH_3C(O)OH$ in the experiments of Crawford et al. (1999), must occur with k_1/k close to unity. Based on the studies of Moortgat et al. (1989), Horie and Moortgat (1992) and Roehl et al. (1996), Tyndall et al. (2001) recommend values of k_1/k=0.9 and k_2/k=0.1 at 298 K. These are adopted as our preferred values for the branching ratios. Moortgat et al. (1989) have reported values for the temperature dependence of k_1 and k_2 but they imply a difference in activation energy for the two channels of 32 kJ mol^{-1} which is much greater than found for analogous peroxy radical reactions. No recommendation is made for the temperature dependence of the branching ratio at this stage.

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II.A6.141

$$
\begin{aligned}
\mathbf{CH_3O_2 + CH_3C(O)CH_2O_2} &\rightarrow \mathbf{CH_3OH + CH_3C(O)CHO + O_2} \quad &\mathbf{(1)}\\
&\rightarrow \mathbf{HCHO + CH_3C(O)CH_2OH + O_2} \quad &\mathbf{(2)}\\
&\rightarrow \mathbf{CH_3O + CH_3C(O)CH_2O + O_2} \quad &\mathbf{(3)}
\end{aligned}
$$

$\Delta H°(1) = -319.7$ kJ·mol^{-1}
$\Delta H°(2) = -322.6$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2+k_3)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.8 \pm 0.4) \times 10^{-12}$	298	Bridier et al., 1993	FP-UVA (a)
Branching Ratios			
$k_1/k = 0.5 \pm 0.1$	298	Jenkin et al., 1993	P-FTIR (b)
$k_2/k = 0.2 \pm 0.1$	298		
$k_3/k = 0.3 \pm 0.1$	298	Bridier et al., 1993	FP-UVA (c)

Comments

(a) Flash photolysis of Cl_2 in the presence of $CH_3C(O)CH_3$-O_2-CH_4-N_2 mixtures at a total pressure of 1 bar (760 Torr). The overall rate coefficient k was derived from a kinetic analysis of absorption-time profiles measured at 230 nm and 260 nm.

(b) Steady-state photolysis of Cl_2 in the presence of $CH_3C(O)CH_3$-N_2 mixtures at a total pressure of 930 mbar (700 Torr). Branching ratios were deduced from measurements of HCHO and $CH_3C(O)CHO$ products by long-path FTIR spectroscopy and long-path UV-VIS diode-array spectroscopy.

(c) Derived from a kinetic analysis of the time-profiles obtained in the experiments described in Comment (a).

Preferred Values

$k = 3.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.5$ at 298 K.
$k_2/k = 0.2$ at 298 K.
$k_3/k = 0.3$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_1/k) = \Delta (k_2/k) = \Delta (k_3/k) = \pm 0.15$ at 298 K.

Comments on Preferred Values

The preferred values of the rate coefficient and branching ratios are based on the measurements of Bridier et al. (1993) and Jenkin et al. (1993), and require independent confirmation to reduce the assigned error limits.

References

Bridier, I., Veyret, B., Lesclaux, R., and Jenkin, M. E.: J. Chem. Soc. Faraday Trans., 89, 2993, 1993.
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II.A6.142

$$\begin{aligned} \mathbf{HOCH_2O_2 + HOCH_2O_2} &\rightarrow \mathbf{HC(O)OH + CH_2(OH)_2 + O_2} \quad &\mathbf{(1)} \\ &\rightarrow \mathbf{2\ HOCH_2O + O_2} \quad &\mathbf{(2)} \end{aligned}$$

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_1 = 5.65 \times 10^{-14} \exp[(750 \pm 400)/T]$	275–323	Veyret et al., 1989	FP-UVA (a,b)
$k_1 = (7.0 \pm 2.1) \times 10^{-13}$	295		
$k_1 = (5.6 \pm 2.8) \times 10^{-13}$	298	Burrows et al., 1989	MM-IR-AS (a,c)
Relative Rate Coefficients			
$k_1 = (5.5 \pm 1.1) \times 10^{-12}$	298	Burrows et al., 1989	MM-IR-AS (a,c)

Comments

(a) k is defined by $-d[\mathrm{HOCH_2O_2}]/dt = 2k[\mathrm{HOCH_2O_2}]^2$.

(b) Flash photolysis of Cl_2 in the presence of HCHO or CH_3OH and O_2, with time-resolved absorption spectroscopy for the detection of HO_2 and $HOCH_2O_2$ radicals. The rate coefficient k_1 was obtained from a computer fit of the absorption profiles of $HOCH_2O_2$ radicals at 250 nm. Channel (2) leads to the regeneration of HO_2 radicals and was thus not observable in this system.

(c) Molecular modulation study of Cl_2-HCHO-O_2 mixtures with diode laser infrared spectroscopy for the detection of HO_2 radicals and UV spectroscopy for $HOCH_2O_2$ radicals. The rate coefficient, k_2, was obtained from a computer simulation of quantum yields for HC(O)OH formation.

Preferred Values

$k_1 = 7.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 5.7 \times 10^{-14} \exp(750/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–330 K.
$k_2 = 5.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_1 = \pm 0.3$ at 298 K.
$\Delta (E_1/R) = \pm 750$ K.
$\Delta \log k_2 = \pm 0.3$ at 298 K.

Comments on Preferred Values

The parallel studies of Veyret et al. (1989) and Burrows et al. (1989) confirm that the interaction of $HOCH_2O_2$ radicals involves two channels. The two reports (Burrows et al., 1989; Veyret et al., 1989) of the rate coefficient, k_1, at room temperature are in good agreement, and indicate that this channel is a factor of ~3 to 4 faster than that for the analogous interaction of CH_3O_2 radicals. The rate coefficient, k_2, is even larger than k_1, with a value ~50 times greater than that for the analogous reaction of CH_3O_2 radicals. Confirmation of the temperature coefficient of k_1 is needed, as well as a determination of the temperature coefficient of k_2.

References

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Veyret, B., Lesclaux, R., Rayez, M.-T., Rayez, J.-C., Cox, R. A., and Moortgat, G. K.: J. Phys. Chem., 93, 2368, 1989.

II.A6.143

$$\begin{aligned} \mathbf{C_2H_5O_2 + C_2H_5O_2} &\rightarrow \mathbf{C_2H_5OH + CH_3CHO + O_2} && \mathbf{(1)}\\ &\rightarrow \mathbf{2C_2H_5O + O_2} && \mathbf{(2)}\\ &\rightarrow \mathbf{C_2H_5OOC_2H_5 + O_2} && \mathbf{(3)} \end{aligned}$$

$\Delta H°(1) = -345.8$ kJ·mol^{-1}
$\Delta H°(2) = -23.8$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2+k_3)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.0 \pm 0.1) \times 10^{-13}$	298	Adachi et al., 1979	FP-UVA (a,b)
2.7×10^{-13} exp(-470/T)	302–373	Anastasi et al., 1983	MM-UVA (a,c)
5.6×10^{-14}	298		
8.1×10^{-14}	266–348	Cattell et al., 1986	MM-UVA (a,d)
8.5×10^{-14} exp[-(110 ± 40)/T]	228–380	Wallington et al., 1988	FP-UVA (a,e)
5.9×10^{-14}	298		
6.7×10^{-14} exp[(60 ± 40)/T]	248–460	Fenter et al., 1993	FP-UVA (a,f)
$(7.9 \pm 0.5) \times 10^{-14}$	298		
2.49×10^{-13} exp(-518/T) + 9.39×10^{-16}exp(960/T)	220–330	Bauer et al., 1992	MM-UVA (a,g)
6.7×10^{-14}	298		
$(7.3 \pm 2.4) \times 10^{-14}$	295	Atkinson and Hudgens, 1997	PLP-UVA (a,h)
Branching Ratios			
$k_1/k_2 = 0.76$	298	Niki et al., 1982	P-FTIR (i)
$k_1/k_2 = 0.60$	298	Anastasi et al., 1983	MM-GC (c)
$k_1/k_2 = 0.49$	298	Wallington et al., 1989	P-FTIR (j)

Comments

(a) k is defined by -d[$C_2H_5O_2$]/dt=2k[$C_2H_5O_5$]^2 and is obtained from the overall decay constant k_{obs} corrected for secondary removal of $C_2H_5O_2$ radicals.

(b) k determined by simulation of $C_2H_5O_2$ radical decay using complex mechanism accounting for secondary removal of $C_2H_5O_2$ radicals.

(c) Modulated photolysis of $(C_2H_5)_2N_2$ in the presence of O_2 at pressures of 7 mbar to 200 mbar (5 Torr to 150 Torr) and N_2 at pressures of 550 mbar to 730 mbar (410 Torr to 550 Torr). k/σ(240 nm) and σ(240 nm) were found to be temperature dependent. Branching ratios were determined from analysis of products, C_2H_5OH and CH_3CHO, by GC. The data cited are derived from the rate coefficients k_1 and k_2 given in Table 6 of Anastasi et al. (1983).

(d) Modulated photolysis of Cl_2-C_2H_6-O_2-N_2 mixtures at pressures of 3 mbar to 1000 mbar (2 Torr to 760 Torr). k_{obs}/σ(260 nm)=(4.07±0.04)×10^4 cm s^{-1} and σ(260 nm)=(3.20±0.38)×10^{-18} cm^2 molecule^{-1} were obtained, leading to k_{obs}=(1.30±0.16)×10^{-13} cm^3 molecule^{-1} s^{-1}. Cited value of k obtained by taking k_{obs}/k=1.6.

(e) k_{obs}=(1.41±0.19)×10^{-13} exp[-(110±40)/T] cm^3 molecule^{-1} s^{-1} was obtained based on temperature independent value of σ(250 nm) = (3.89±0.54)×10^{-18} cm^2 molecule^{-1} and k_{obs}/k=1.66.

(f) Flash photolysis-UV absorption study of Cl_2-C_2H_6-O_2-N_2 mixtures at 1 bar (760 Torr) total pressure. Rate coefficients were derived from simultaneous computer analyses of several decay curves collected at different wavelengths. The value of k_{obs}=(1.40 ± 0.11)×10^{-13} exp[-(20±40)/T] cm^3 molecule^{-1} s^{-1} was corrected at each temperature by dividing by (1+α), where $\alpha=\beta/(1+\beta)$ and β=10.2 exp(-533/T).

(g) Molecular modulation study. $C_2H_5O_2$ radicals were generated from the photolysis of flowing mixtures of Cl_2-C_2H_6-O_2-N_2 at a total pressure of 133 mbar (100 Torr) and monitored by UV absorption. Values of k/σ were determined at 220 nm, 250 nm and 280 nm, leading to values of k_{obs}. The expression for k was derived by fitting the function $k_{obs}=A_1\exp(B_1/T)+A_2\exp(B_2/T)=2k_1+k_2$ to the observed values of k_{obs} over the temperature range 220–330 K, forcing the fit to a value of k_2/k of 0.65 at 298 K. The expressions for k_1 and k_2 obtained in this way gave $k_1/k_2=3.8\times10^{-3}$ $\exp(1478/T)$.

(h) Pulsed laser photolysis of Cl_2-C_2H_6-O_2-Ar mixtures at 7.3±1.0 mbar (5.5 Torr) total pressure with $C_2H_5O_2$ radicals being monitored by UV cavity ring-down spectroscopy at 265 nm and 270 nm. The measured value of k_{obs} was corrected for secondary reactions by taking $k_{obs}/k=1.7$.

(i) Photolysis of $(C_2H_5)_2N_2$-O_2 mixtures and of Cl_2-C_2H_6-O_2-N_2 mixtures at a total pressure of 920 mbar (700 Torr). Products CH_3CHO, C_2H_5OH and C_2H_5OOH monitored by FTIR.

(j) Photolysis of Cl_2-C_2H_6 mixtures in 930 mbar (700 Torr) air. Products monitored by FTIR.

Preferred Values

$k = 6.4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–450 K.
$k_2/k = 0.62$ at 298 K.

Reliability

$\Delta\log k = \pm\ 0.12$ at 298 K.
$\Delta(E/R) = ^{+300}_{-100}$ K
$\Delta(k_2/k) = \pm\ 0.1$ at 298 K.

Comments on Preferred Values

The rate coefficients for this reaction have all been determined using UV absorption to monitor $C_2H_5O_2$, and hence the measured quantity is k/σ where σ is the absorption cross-section at the monitoring wavelength. The data for k_{298} are generally in good agreement. The most recent temperature coefficient reported by Fenter et al. (1993) ($E/R=-60$ K) agrees with the earlier data of Cattell et al. (1986) ($E/R \approx 0$ K) but less well with those of Anastasi et al. (1983) ($E/R=470$ K), Wallington et al. (1988) ($E/R=110$ K) or Bauer et al. (1992) ($E/R=-230$ K). In view of the small temperature coefficients reported in most of these studies, together with the relatively large associated error limits, we have selected a temperature-independent rate coefficient k based on k_{298}. Thus, from the data of Adachi et al. (1979), Anastasi et al. (1983), Cattell et al. (1986), Wallington et al. (1988), Bauer et al. (1992) and Fenter et al. (1993), the average value of $k_{obs}=1.03\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K is obtained. Taking $k_2/k=0.62$ at 298 K (the mean of the data of Niki et al. (1982), Anastasi et al. (1983) and Wallington et al. (1989)) yields the recommended value of $k_{298}=6.4\times10^{-14}$ cm^3 molecule^{-1} s^{-1}. The data of Wallington et al. (1989) show that $k_3/k\leq0.06$. The rate coefficient of Atkinson and Hudgens (1997) is in agreement with the recommendations.

The differences between the values of the branching ratios reported by Anastasi et al. (1983) and Bauer et al. (1992) require further study.

References

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II.A6.144

$$
\begin{aligned}
\mathbf{C_2H_5O_2 + CH_3C(O)O_2} &\rightarrow \mathbf{C_2H_5O + CH_3C(O)O + O_2} \qquad &\mathbf{(1)}\\
&\rightarrow \mathbf{CH_3CHO + CH_3C(O)OH + O_2} \qquad &\mathbf{(2)}
\end{aligned}
$$

$\Delta H^\circ(1) = -23.6$ kJ·mol^{-1}
$\Delta H^\circ(2) = -398.5$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.0 \pm 0.3) \times 10^{-11}$	298	Villenave and Lesclaux, 1996	FP-UVAS (a)
$5 \times 10^{-13} \exp[(1070 \pm 200)/T]$	220–440	Maricq and Szente, 2000	PLP-UVAS (b)
2.2×10^{-11}	295		

Comments

(a) Flash photolysis of Cl_2-C_2H_6-CH_3CHO-O_2 mixtures. $CH_3C(O)O_2$ and $C_2H_5O_2$ radical concentrations were determined by fitting absorption-time data at 207 nm and 240 nm, using cross-sections recommended in Lightfoot et al. (1992). Complex reaction mechanism with α_c(=k_1/k) assumed to be 0.82. The overall uncertainty was estimated as 54%.

(b) Pulsed laser photolysis at 351 nm of CH_3CHO-C_2H_6-Cl_2-O_2-N_2 mixtures at total pressures of 167 mbar to 192 mbar (125 Torr to 144 Torr). The reaction progress was monitored by time-resolved UV absorption over the range 200 nm to 300 nm. Values of k were derived by fitting the spectral profiles using a detailed model. The cross-sections for the principal absorbing radicals ($CH_3C(O)O_2$, $C_2H_5O_2$, and CH_3O_2) were taken from the studies of Maricq and Szente (1996) and Maricq and Wallington (1992). A satisfactory fit to the spectra could be obtained using values of α_c(=k_1/k) in the range 1.0–0.80.

Preferred Values

$k = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.4 \times 10^{-13} \exp(1070/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–400 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The two available experimental studies of this reaction report values of the rate coefficient at 298 K differing by a factor of 2. In both cases substantial error limits were assigned reflecting the difficulties in deconvoluting overlapping UV spectra and in accounting for complex secondary chemistry in deriving the rate coefficient. Villenave and Leclaux (1996) based their results on absorption measurements at only two wavelengths, whereas Maricq and Szente (2000) used spectra covering the range 200 nm to 300 nm but, until more definitive measurements are available, the preferred value at 298 K is taken as the mean of the studies of Villenave and Lesclaux (1996) and of Maricq and Szente (2000), with substantial error limits. The only determination of the temperature dependence of k is that of Maricq and Szente (2000) who obtained a value of E/R of -1070 K, which is consistent with values found for analogous reactions. The preferred expression for k is obtained by combining the temperature dependence found by Maricq and Szente (2000) with an A-factor chosen to fit the preferred value of k at 298 K. Channel (1) is likely to be the main reaction channel at 298 K.

References

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Maricq, M. M. and Wallington, T. J.: J. Phys. Chem., 96, 986, 1992.
Villenave, E. and Lesclaux, R.: J. Phys. Chem., 100, 14372, 1996.

II.A6.145

$$\mathbf{CH_3OCH_2O_2 + CH_3OCH_2O_2 \rightarrow CH_3OCH_2OH + CH_3OCHO + O_2 \quad (1)}$$
$$\mathbf{\rightarrow 2CH_3OCH_2O + O_2 \quad (2)}$$

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.1 \pm 0.3) \times 10^{-12}$	298	Jenkin et al., 1993	MM-AS (a,b)
Branching Ratios			
$k_2/k = 0.67 \pm 0.11$	295	Jenkin et al., 1993	P-FTIR (c)
$k_2/k = 0.67 \pm 0.13$	298	Jenkin et al., 1993	P-FTIR (d)

Comments

(a) k is defined by $-d[CH_3OCH_2O_2]/dt=2k[CH_3OCH_2O_2]^2$ and has beenderived from the measured overall second-order decay of $CH_3OCH_2O_2$ radicals (k_{obs}).

(b) Molecular modulation study of Cl_2-CH_3OCH_3-O_2-N_2 mixtures together with a pulsed radiolysis study of SF_6-CH_3OCH_3-O_2 mixtures. k_{obs} was found to be dependent on the total pressure over the range 23 mbar to 1013 mbar (17 Torr to 770 Torr) and on the composition of the reaction mixture. On the basis of a mechanism involving the generation of H atoms via the reaction CH_3OCH_2O+M → CH_3OCHO+H+M, it was possible to derive the cited pressure-independent value of k.

(c) FTIR spectroscopic study of the steady-state photolysis of Cl_2 in the presence of CH_3OCH_3-O_2-N_2 mixtures over the total pressure range 13 mbar to 930 mbar (10 Torr to 700 Torr). The branching ratio was determined from the yields of CH_3OCHO and CH_3OCH_2OOH. Minor amounts of CH_3OCH_2OH were also observed.

(d) Similar study to that described in Comment (c). The branching ratio and k were derived from a kinetic analysis of the effects of $[O_2]$ and $[Cl_2]$ on k_{obs}, based on a mechanism including the production of H atoms from the reaction CH_3OCH_2O+M → CH_3OCHO+H+M.

Preferred Values

$k = 2.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.67$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The apparent effect of total pressure on k, the first reported for this type of reaction (Dagaut et al., 1989), has been shown to be an artifact by the more recent experiments of Jenkin et al. (1993). This comprehensive study, on which the recommendation is based, has shown that the pressure effect was due to secondary chemistry involving H atoms which arise from the reaction CH_3OCH_2O+M→CH_3OCHO+H+M. A kinetic analysis of the molecular modulation system, allowing for secondary chemistry, yielded the preferred rate coefficient. At the same time the derived value of the branching ratio, k_2/k, is in excellent agreement with that obtained from a steady-state photolysis system with FTIR spectroscopic analyses (Jenkin et al., 1993).

References

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II.A6.146

$$\mathbf{CH_3C(O)O_2 + CH_3C(O)O_2 \rightarrow 2CH_3C(O)O + O_2}$$

$\Delta H^\circ = -71$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.8 \times 10^{-12} \exp[(530 \pm 100)/T]$	253–368	Moortgat et al., 1989	FP-UVAS (a,b)
$(1.6 \pm 0.3) \times 10^{-11}$	298		
$(1.36 \pm 0.19) \times 10^{-11}$	298	Roehl et al., 1996	PLP-UVAS (a,c)
$3.0 \times 10^{-12} \exp[(504 \pm 114)/T]$	209–358	Maricq and Szente, 1996	PLP-UVAS (a,d)
1.5×10^{-11}	298		

Comments

(a) k is defined by $-d[CH_3C(O)O_2]/dt=2k\,[CH_3C(O)O_2]^2$.

(b) k was determined using absorption cross-sections for $CH_3C(O)O_2$ and CH_3O_2 radicals approximately 20% higher than later consensus values. $CH_3C(O)O_2$ radicals were produced by photolysis of Cl_2-CH_3CHO-O_2 mixtures.

(c) k was determined using an absorption cross-section of $\sigma=6.67\times10^{-18}$ cm^2 molecule^{-1} at 207 nm for $CH_3C(O)O_2$. Source of $CH_3C(O)O_2$ radicals as in (b). Detailed analysis of secondary chemistry.

(d) Based on $\sigma(CH_3C(O)O_2)=6.5\times10^{-18}$ cm^2 molecule^{-1} at 206 nm. Source of $CH_3C(O)O_2$ radicals as in (b). Detailed analysis of secondary chemistry.

Preferred Values

$k = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.9 \times 10^{-12} \exp(500/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–370 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

All three studies (Moortgat et al., 1989; Roehl et al., 1996; Maricq and Szente, 1996), taking account of the complex secondary chemistry following recombination of $CH_3C(O)O_2$ radicals and of the magnitude and overlap of the UV absorptions due to acetylperoxy, methylperoxy and hydroperoxy radicals, now give results in good agreement for k and its temperature dependence. The recommendation is thus based on the data of Moortgat et al. (1989), Roehl et al. (1996) and Maricq and Szente (1996).

References

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II.A6.147

$$\mathbf{CH_3C(O)O_2 + CH_3C(O)CH_2O_2 \rightarrow CH_3C(O)OH + CH_3C(O)CHO + O_2 \quad (1)}$$
$$\mathbf{\rightarrow CH_3C(O)O + CH_3C(O)CH_2O + O_2 \quad (2)}$$

$\Delta H^\circ(1) = -369$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.0 \pm 2.0) \times 10^{-12}$	298	Bridier et al., 1993	FP-UVAS (a)
$k_1 \leq 4 \times 10^{-12}$	298		
Branching Ratios			
$k_2/k = 0.5 \pm 0.2$	298	Jenkin et al., 1993	P-FTIR-AS (b)

Comments

(a) Flash photolysis of Cl_2 in the presence of $CH_3C(O)CH_3$-CH_3CHO-N_2 mixtures at a total pressure of 1 bar (760 Torr). The rate coefficient k was derived from a kinetic analysis of absorption-time profiles measured at 210 nm, 220 nm, 230 nm and 245 nm, using the value of k_2/k=0.5 determined by Jenkin et al. (1993).

(b) Steady-state photolysis of Cl_2 in the presence of $CH_3C(O)CH_3$-N_2 mixtures at a total pressure of 930 mbar (700 Torr). The branching ratio was deduced from measurements of the concentrations of the HCHO and $CH_3C(O)CHO$ products by long-path FTIR spectroscopy and long-path UV-VIS diode-array spectroscopy.

Preferred Values

$k = 5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.5$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_2/k) = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred values of the rate coefficient and the branching ratio are from the studies of Bridier et al. (1993) and Jenkin et al. (1993), and require independent confirmation.

References

Bridier, I., Veyret, B., Lesclaux, R., and Jenkin, M. E.: J. Chem. Soc. Faraday Trans., 89, 2993, 1993.
Jenkin, M. E., Cox, R. A., Emrich, M., and Moortgat, G. K.: J. Chem. Soc. Faraday Trans., 89, 2983, 1993.

II.A6.148

$$\mathbf{HOCH_2CH_2O_2 + HOCH_2CH_2O_2 \rightarrow HOCH_2CH_2OH + HOCH_2CHO + O_2} \quad \mathbf{(1)}$$
$$\mathbf{\rightarrow 2\,HOCH_2CH_2O + O_2} \quad \mathbf{(2)}$$

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.2 \pm 0.3) \times 10^{-12}$	296	Murrells et al., 1991	PLP/MM-UVAS (a,b)
$(2.1 \pm 0.3) \times 10^{-12}$	298	Jenkin and Hayman, 1995	MM-UVAS (a,c)
$7.8 \times 10^{-14} \exp[(1000 \pm 80)/T]$	300–470	Boyd and Lesclaux, 1997	PLP-UVAS (a,d)
$(2.2 \pm 0.3) \times 10^{-12}$	298		
Branching Ratios			
$k_2/k = 0.5 \pm 0.1$	298	Barnes et al., 1993	P-FTIR (e)
$k_2/k = 0.55$	298	Boyd and Lesclaux, 1997	PLP-UVAS (f)

Comments

(a) k is defined by $-d[HOCH_2CH_2O_2]/dt=2k[HOCH_2CH_2O_2]^2$.

(b) Separate pulsed laser photolysis and molecular modulation studies using the photolysis of H_2O_2 to produce HO radicals in the presence of ethene and air at a pressure of 1 bar (760 Torr). $HOCH_2CH_2O_2$ radicals were monitored by UV absorption at 250 nm with $\sigma_{250}=4.7\times10^{-18}$ cm^2 molecule^{-1} (mean value). $k_{obs}/\sigma_{250}=6.7\times10^5$ cm s^{-1}. k was calculated from the laser photolysis experiments with k_2/k=0.36.

(c) Identical technique to that in Comment (a). $k_{obs}/\sigma_{250}=(7.1\pm0.6)\times10^5$ cm s^{-1}. k calculated using k_2/k=0.5 and, in addition, using data from Murrells et al. (1991).

(d) Pulsed laser photolysis of H_2O_2 at 248 nm in the presence of ethene and O_2. $HOCH_2CH_2O_2$ radicals were monitored by absorption at 250 nm.

(e) Analysis of products by FTIR in the photolysis of $HOCH_2CH_2I$ or H_2O_2-C_2H_4 mixtures in O_2+N_2. Pressure 150 mbar to 900 mbar (114 Torr to 680 Torr). Mean value given from both systems, which were in excellent agreement, and independent of total pressure or O_2 concentration.

(f) Based on HO_2 radical formation from the $HOCH_2CH_2O + O_2$ reaction, measured by UV absorption at 220 nm.

Preferred Values

$k = 2.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.8 \times 10^{-14} \exp(1000/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–450 K.
k_2/k = 0.5 at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 300$ K.
$\Delta(k_2/k) = \pm 0.5$ at 298 K.

Comments on Preferred Values

All the recent studies of this reaction provide consistent and seemingly reliable values for the rate coefficient and for the branching ratio (Murrells et al., 1991; Boyd and Lesclaux, 1997). The preferred value of k at 298 K is a mean of the values reported by Murrells et al. (1991), Jenkin and Hayman (1995) and Boyd and Lesclaux (1997), and for the branching ratio the value of Barnes et al. (1993) is accepted. The temperature dependence of k from the work of Boyd and Lesclaux (1997), is recommended but with wider error limits on E/R. A measurement of the temperature dependence of the branching ratio would be of value.

References

Barnes, I., Becker, K. H., and Ruppert, L.: Chem. Phys. Lett., 203, 295, 1993.
Boyd, A. A. and Lesclaux, R.: Int. J. Chem. Kinet., 29, 323, 1997.
Jenkin, M. E. and Hayman, G. D.: J. Chem. Soc. Faraday Trans., 91, 1911, 1995.
Murrells, T. P., Jenkin, M. E., Shalliker, S. J., and Hayman, G. D.: J. Chem. Soc. Faraday Trans., 87, 2351, 1991.

II.A6.149

$$\begin{aligned} \boldsymbol{n\text{-}C_3H_7O_2 + n\text{-}C_3H_7O_2} &\rightarrow \boldsymbol{n\text{-}C_3H_7OH + C_2H_5CHO + O_2} \quad \textbf{(1)} \\ &\rightarrow \boldsymbol{2\ n\text{-}C_3H_7O + O_2} \quad \textbf{(2)} \end{aligned}$$

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.3 \pm 0.3) \times 10^{-13}$	298	Adachi and Basco, 1982	FP-UVAS (a,b)

Comments

(a) k is defined by $-d[n\text{-}C_3H_7O_2]/dt = 2k[n\text{-}C_3H_7O_2]^2$ and has been derived from the measured overall second order decay of n-$C_3H_7O_2$ radicals (k_{obs}) by correcting for secondary removal of the n-$C_3H_7O_2$ radicals.

(b) The monitoring wavelength for n-$C_3H_7O_2$ radicals was 260 nm, with $\sigma=3.15\times10^{-18}$ cm^2 molecule^{-1}. The rate coefficient was derived from $k_{obs}=(3.84\pm0.33)\times10^{-13}$ cm^3 molecule^{-1} s^{-1} on the basis of a mechanism with 12 secondary reactions.

Preferred Values

$k = 3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The recommended rate coefficient is the rounded-off value from the study of Adachi and Basco (1982). The room temperature rate coefficient requires substantiation along with a determination of the temperature coefficient.

The recommended value of k_{298} is in line with the rate coefficients of the analogous reactions of the CH_3O_2 and $C_2H_5O_2$ radicals. On the other hand, our recommended rate coefficient for the self-reaction of the i-$C_3H_7O_2$ radical is considerably lower ($k_{298}=1.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1}) and that reported (Anastasi et al., 1978) for the t-$C_4H_9O_2$ radical is even lower still ($k_{298}=2.3\times10^{-17}$ cm^3 molecule^{-1} s^{-1}). This trend is in keeping with that observed in the liquid phase for the RO_2 radical interactions (Bennett et al., 1970), i.e., k(primary RO_2)>k (secondary RO_2)>k(tertiary RO_2).

References

Adachi, H. and Basco, N.: Int. J. Chem. Kinet., 14, 1125, 1982.
Anastasi, C., Smith, I. W. M., and Parkes, D. A.: J. Chem. Soc. Faraday Trans., 1, 74, 1693, 1978.
Bennett, J. E., Brown, D. M., and Mile, B.: Trans. Faraday Soc., 66, 386, 1970.

II.A6.150

$$
\begin{aligned}
\boldsymbol{i\text{-}C_3H_7O_2 + i\text{-}C_3H_7O_2} \quad &\rightarrow \boldsymbol{i\text{-}C_3H_7OH + CH_3C(O)CH_3 + O_2} \quad &\textbf{(1)}\\
&\rightarrow \boldsymbol{2\ i\text{-}C_3H_7O + O_2} \quad &\textbf{(2)}
\end{aligned}
$$

$\Delta H°(1) = -352.1$ kJ·mol^{-1}
$\Delta H°(2) = -33.0$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.43×10^{-12} exp[-(2243 ± 69)/T)	300–373	Kirsch et al., 1978	MM-UVAS (a,b)
8.10×10^{-16}	300		
$(1.3 \pm 0.4) \times 10^{-15}$	298	Adachi and Basco, 1989	FP-UVAS (a,c)
$(5.3 \pm 0.5) \times 10^{-14}$	298	Munk et al., 1986	PR-UVAS (a,d)
Branching Ratios			
$k_1/k_2 = 1.39 \pm 0.04$	302	Kirsch et al., 1979	P-GC (e)
k_2/k_1 = 56.3 exp(-1130/T)	302–372	Cowley et al., 1982	P-GC (f)

Comments

(a) k is defined by $-d[i\text{-}C_3H_7O_2]/dt=2k[i\text{-}C_3H_7O_2]^2$ and has been derived from the observed overall second-order decay of i-$C_3H_7O_2$ radicals (k_{obs}) by correcting for secondary removal of the i-$C_3H_7O_2$ radicals.

(b) Molecular modulation study of the photolysis of 2,2′-azopropane in the presence of O_2 and N_2 at total pressures up to 950 mbar (710 Torr). i-$C_3H_7O_2$ radicals were monitored by absorption at 265 nm. The rate coefficient, k, has been calculated from the experimental value of k_{obs}=(2.37±0.17)×10^{-12} exp[-(2243±60)T] cm^3 molecule^{-1} s^{-1} and the branching ratio k_2/k_1=1.39 at 302 K determined in the subsequent study (Kirsch et al. 1979).

(c) Flash photolysis of 2,2′-azopropane in the presence of O_2 and added N_2 at total pressures up to 960 mbar (720 Torr). i-$C_3H_7O_2$ radicals were monitored by absorption at 240 nm, for which σ(240 nm)=4.86×10^{-18} cm^2 molecule^{-1}. The rate coefficient, k, has been calculated from the experimental value of k_{obs}=(2.03±0.58)×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K, on the basis of a proposed mechanism of 12 elementary reactions including secondary consumption of i-$C_3H_7O_2$ radicals.

(d) Pulsed radiolysis of H_2 at 1 bar in the presence of C_3H_6; i-C_3H_7 radicals were generated from the reaction of H atoms with C_3H_6. The absorption spectrum of the i-$C_3H_7O_2$ radical was observed on the addition of O_2 and the decay of i-$C_3H_7O_2$ radicals monitored by UV absorption at 253 nm, and found to obey second-order kinetics. It is not clear if the reported value of the rate coefficient is k_{obs} or k.

(e) Steady-state photolysis of 2,2′-azopropane in the presence of O_2 and added N_2 at total pressures up to 670 mbar (500 Torr). Ratio of rate coefficients based on analyses of $CH_3C(O)CH_3$ and $(CH_3)_2CHOH$ by GC.

(f) Extension of the experiments by Kirsch et al. (1979), to obtain k_2/k_1 at 333 K and 372 K. The Arrhenius equation calculated from these data and a value of k_2/k_1 at 302 K was reported by Kirsch et al. (1979).

Preferred Values

$k = 1.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.6 \times 10^{-12}$ exp(-2200/T) cm^3 molecule^{-1} s^{-1} over the temperature range 300–400 K.
k_1/k = 0.44 at 298 K.

$k_1/k = 3.7 \times 10^{-2} \exp(740/T)$ over the temperature range 300–400 K.
$k_2/k = 0.56$ at 298 K.
$k_2/k = 2.0 \exp(-380/T)$ over the temperature range 300–400 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 300$ K.
$\Delta (k_1/k) = \Delta (k_2/k) = \pm 0.15$ at 298 K.

Comments on Preferred Values

The recommended rate coefficient, k, at 298 K is the average of the rate coefficients from the data of Kirsch et al. (1978) and Adachi and Basco (1982), which are in reasonable agreement. We have not taken into account the rate coefficient reported by Munk et al. (1986), for which experimental details are lacking. The recommended temperature dependence of k is based on the results of Kirsch et al. (1978), which have been rounded-off and adjusted to the recommended value of k_{298}.

The measurements of the branching ratio and its temperature dependence (Kirsch et al., 1979; Cowley et al., 1982) appear to be reliable and have been adopted here, but require further confirmation.

The value of k_{298} is considerably lower than that for the analogous reaction of the n-$C_3H_7O_2$ radical, which is consistent with the trend observed in studies of the interactions of alkylperoxy radicals in solution (Bennett et al., 1970) i.e., k (primary RO_2)>k(secondary RO_2)>k(tertiary RO_2).

References

Adachi, H. and Basco, N.: Int. J. Chem. Kinet., 14, 1125, 1982.
Bennett, J. E., Brown, D. M., and Mile, B.: Trans. Faraday Soc., 66, 386,1970.
Cowley, L. T., Waddington, D. J., and Woolley, A.: J. Chem. Soc. Faraday Trans., 1, 78, 2535 ,1982.
Kirsch, L. J., Parkes, D. A., Waddington, D. J., and Woolley, A.: J. Chem. Soc. Faraday. Trans., 1, 74, 2293, 1978.
Kirsch, L. J., Parkes, D. A., Waddington, D. J., and Woolley, A.: J. Chem. Soc. Faraday Trans., 1, 75, 2678, 1979.
Munk, J., Pagsberg, P., Ratajczak, E., and Sillesen, A.: Chem. Phys. Lett., 132, 417, 1986.

II.A6.151

$$\mathbf{CH_3C(O)CH_2O_2 + CH_3C(O)CH_2O_2}$$

$$\begin{aligned} &\rightarrow \mathbf{CH_3C(O)CH_2OH + CH_3C(O)CHO + O_2} && \mathbf{(1)} \\ &\rightarrow \mathbf{2\ CH_3C(O)CH_2O + O_2} && \mathbf{(2)} \end{aligned}$$

$\Delta H°(1) = -314$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 8.3 \times 10^{-12}$	298	Cox et al., 1990	PR-UVA (a,b)
$(8.0 \pm 0.2) \times 10^{-12}$	298	Bridier et al., 1993	FP-UVA (a,c)
Branching Ratios			
k_2/k= 0.75 ± 0.1	298	Bridier et al., 1993	FP-UVA (d)
k_2/k= 0.50 ± 0.05	298	Emrich and Warneck, 2003	UVP-GC (e)

Comments

(a) k is defined by $-d[CH_3C(O)CH_2O_2]/dt=2k[CH_3C(O)CH_2O_2]^2$.

(b) Derived value of k_{obs}=(8.3±1.6)×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K is an upper limit due to secondary reactions producing possible enhanced decay of $CH_3C(O)CH_2O_2$ radicals.

(c) Flash photolysis of Cl_2 in the presence of $CH_3C(O)CH_3$-O_2-N_2 mixtures at a total pressure of 1013 mbar (760 Torr). The rate coefficient, k, was derived from a kinetic analysis of absorption-time profiles at 230 nm and 260 nm, taking account of the information on the mechanism of the overall reaction obtained from the product study of Jenkin et al. (1993).

(d) Technique as in Comment (c). The branching ratio was obtained on the basis of absorption due to radicals formed in channel (2) and subsequent reactions.

(e) Continuous photolysis of Cl_2 at 330 nm, in the presence of $CH_3C(O)CH_3$-O_2-NO_2-N_2 mixtures at a total pressure of 1020 mbar (765 Torr). The branching ratio, k_2/k, was determined from the observed formation of peroxyacetyl nitrate (PAN), which is generated in the system from chemistry subsequent to the thermal decomposition of $CH_3C(O)CH_2O$, using simulations with an explicit chemical mechanism. PAN was measured by GC coupled with indirect analysis, which involved conversion to NO in a heated molybdenum catalytic converter, followed by detection of NO by its chemiluminescent reaction with O_3.

Preferred Values

$k = 8.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.63$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_2/k) = \pm 0.2$ at 298 K.

Comments on Preferred Values

The rate coefficients for $CH_3C(O)CH_2O_2$ radical decay obtained in the two studies (Cox et al., 1990; Bridier et al., 1993) are in good agreement, and the more rigorous analysis carried out by Bridier et al. (1993) on the basis of the product study of Jenkin et al. (1993) provides the basis for the preferred rate coefficient. The value of k_2/k reported more recently by Emrich and Warneck (2003) is somewhat lower than that derived by Bridier et al. (1993), but the two determinations are in reasonable agreement, given the complexity of the chemical systems and the indirect nature of the determinations. The preferred branching ratio is the mean of the values reported in those two studies. Further verification of the overall rate coefficient and branching ratio is required, as are studies as a function of temperature.

References

Bridier, I., Veyret, B., Lesclaux, R., and Jenkin, M. E.: J. Chem. Soc. Faraday Trans., 89, 2993, 1993.
Cox, R. A., Munk, J., Nielsen, O. J., Pagsberg, P., and Ratajczak, E.: Chem. Phys. Lett., 173, 206, 1990.
Emrich, M. and Warneck, P.: Z. Naturforsch., 58a, 429, 2003.
Jenkin, M. E., Cox, R. A., Emrich, M., and Moortgat, G. K.: J. Chem. Soc. Faraday Trans., 89, 2983, 1993.

II.A6.152

$\mathbf{RCHOO + O_3 \rightarrow RCHO + 2O_2}$	**(1)**
$\mathbf{RCHOO + H_2O \rightarrow}$ **products**	**(2)**
$\mathbf{RCHOO + CO \rightarrow}$ **products**	**(3)**
$\mathbf{RCHOO + HCHO \rightarrow}$ **products**	**(4)**
$\mathbf{RCHOO + C_2H_4 \rightarrow}$ **products**	**(5)**
$\mathbf{RCHOO + NO \rightarrow RCHO + NO_2}$	**(6)**
$\mathbf{RCHOO + NO_2 \rightarrow RCHO + NO_3}$	**(7)**
$\mathbf{RCHOO + SO_2 \rightarrow}$ **products**	**(8)**
$\mathbf{RCHOO + HC(O)OH \rightarrow}$ **products**	**(9)**
$\mathbf{RCHOO + CH_3CHO \rightarrow}$ **secondary ozonide**	**(10)**
$\mathbf{RCHOO \rightarrow}$ **products**	**(11)**
$\mathbf{RRCOO \rightarrow}$ **products**	**(12)**

R=H or $\mathbf{CH_3}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Criegee intermediate	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients				
$k_2/k_8 = (6.1 \pm 0.3) \times 10^{-5}$	CH_3CHOO	295	Calvert et al., 1978	(a)
k_1:k_3:k_4:k_5:$k_8 = 2.5 \times 10^{-3}$: 1.8×10^{-3}:2.5×10^{-1}: 2.5×10^{-3}:1.0	CH_2OO	296	Su et al., 1980	RR-FTIR (b)
$k_2/k_8 = (2.3 \pm 1) \times 10^{-4}$	CH_2OO	298	Suto et al., 1984	(c)
$k_7/k_8 = (1.4 \pm 0.4) \times 10^{-2}$	CH_2OO	298	Manzanares et al., 1987	(d)
$k_2/k_8 = (8.3 \pm 3.6) \times 10^{-4}$	CH_2OO	298	Becker et al., 1993	RR-FTIR/TDLS (e)
$k_2/k_8 = (4.1 \pm 2.2) \times 10^{-4}$	$(CH_3)_2COO$	298	Becker et al., 1993	RR-FTIR/TDLS (f)
$k_2/k_9 = 7.1 \times 10^{-5}$	CH_2OO	298	Neeb et al., 1997	RR-FTIR/HPLC (g)
Absolute Rate Coefficients				
$k_{10} = 1.0 \times 10^{-12}$	CH_3CHOO	∼298	Fenske et al., 2000	FT-FTIR (h)
$k_{11} = 76$ s^{-1}	CH_3CHOO	∼298	Fenske et al., 2000	(i)
$k_{12} = 6.4$ s^{-1} (measured at ∼ 130 mbar)	$(CH_3)_2COO$	298	Kroll et al., 2001	LIF (j)

Comments

(a) Derived from a re-analysis of the data of Cox and Penkett (1972) from a study of the aerosol formation from SO_2 in the presence of O_3-O_2-*cis*-2-C_4H_8 mixtures at atmospheric pressure. In this system the Criegee intermediate involved is believed to be CH_3CHOO.

(b) FTIR study of the C_2H_4-O_3 reaction in the presence of O_2-N_2 mixtures at a total pressure of 920 mbar and with added CO, HCHO, or SO_2. Relative rate coefficients derived from a computer simulation of reactant consumption and product formation, based on a mechanism of 20 elementary reactions.

(c) Flow system involving C_2H_4-O_3-SO_2-H_2O mixtures in which H_2SO_4 aerosol concentrations were monitored by scattered UV light. Relative rate coefficients obtained from the dependencies of the aerosol formation on the concentrations of O_3, SO_2 and H_2O.

(d) Similar study to that of Comment (c), with the inclusion of the effect of added NO_2 on the formation of the H_2SO_4 aerosol.

(e) Study of the C_2H_4-O_3 reaction in the presence of 1 bar of synthetic air with and without added SO_2; H_2O_2 yields were measured by tunable diode laser absorption spectroscopy or by FTIR spectroscopy.

(f) Same study as for Comment (e) with $(CH_3)_2C{=}C(CH_3)_2$ as the reactant.

(g) Reaction carried out in a 570 L spherical glass reactor. Hydroxymethyl hydroperoxide (HMHP) concentrations monitored by HPLC and formic acid concentration by FTIR. Formation of HC(O)OH from HMHP shown to be due, in part, to heterogeneous processes. k_2/k_9 was derived by fitting [HC(O)OH] and [HMHP] as a function of time to a reaction scheme and using values of $k(O_3{+}C_2H_4){=}1.6{\times}10^{-18}$ cm^3 molecule^{-1} s^{-1}, $k(CH_3OO{+}H_2O){=}1{\times}10^{-17}$ cm^3 molecule^{-1} s^{-1} and assuming that 47% of the Criegee biradicals are stabilized.

(h) Reaction studied in an atmospheric pressure flow-tube. An excess of acetaldehyde was added to the reaction mixture through a sliding injector such that all thermalised CH_3CHOO, post-injector, was converted to secondary ozonide (SOZ). SOZ was detected by FTIR. The temperature of the study was not reported.

(i) Unimolecular decomposition rate coefficient obtained relative to the reaction with acetaldehyde from a numerical analysis of the flow-tube data.

(j) HO observed by LIF in flow-tube experiments. The unimolecular rate coefficient was calculated by assuming that at 100 Torr pressure the observed formation of HO, over timescales of $\sim$ 100-1000 ms, is due to the thermal decomposition of stabilised dimethylcarbonyl oxide.

Preferred Values

No recommendation for rate data.

Comments on Preferred Values

Vibrationally excited Criegee intermediates, $[RCHOO]^{\ddagger}$, are produced from the reactions of O_3 with alkenes (Atkinson and Carter, 1984). These species decompose unimolecularly to give molecular or radical products or undergo collisional deactivation to yield thermally equilibrated Criegee intermediates, RCHOO. Here we consider the kinetic and other information relating to the bimolecular reactions that have been proposed for these thermally equilibrated Criegee intermediates.

Studies have been made of the reactions of RCHOO with aldehydes (Su et al., 1980; Fenske et al., 2000; Cox and Penkett, 1972; Hanst et al., 1958; Kan et al., 1981; Niki et al., 1975, 1981; Neeb et al., 1995), SO_2 (Calvert et al., 1978; Su et al., 1980, Cox and Penkett, 1972; Kerr and Calvert, 1984; Hatakeyama et al., 1986), H_2O (Cox and Penkett, 1972; Akimoto et al., 1979; Kan et al., 1981), carboxylic acids (Neeb et al., 1995; Neeb et al., 1996) and methanol (Neeb et al., 1996), but detailed kinetic data are often lacking. Relative rate coefficients have been derived by Calvert et al. (1978), Su et al. (1980) and Suto et al. (1985) based on experimental measurements of the rates of consumption of molecular reactants relative to consumption of SO_2 in systems involving RCHOO Criegee intermediates. The only compound, other than SO_2, common to any of these studies is H_2O, for which the derived relative rate coefficients differ by a factor of $\sim$4. Notwithstanding this discrepancy, these relative rate measurements are the only experimental basis on which to assess the rates of these reactions. It is apparent from these measurements that the reactions of the Criegee intermediates, RCHOO, with O_3, CO and alkenes are not important under atmospheric conditions. The reactions with H_2O, RCHO, NO_2 and SO_2 need to be considered, although for most tropospheric conditions the only effective reaction of the Criegee intermediates is likely to be that with H_2O.

Previous reviewers (Kerr and Calvert, 1984; Atkinson and Lloyd, 1984) have made the reasonable assumption that the reaction of RCHOO with NO could also be significant, based on estimates of the energetics of the proposed reaction pathway $RCHOO{+}NO{\rightarrow}RCHO{+}NO_2$. Unfortunately, there is no direct experimental evidence for this reaction and very little information upon which to base an estimate of its rate coefficient. Atkinson and Lloyd (1984) have estimated the relative rate coefficients for RCHOO reacting with NO and SO_2, corresponding to $k_6/k_8{=}10^2$, whereas Kerr and Calvert (1984) propose $k_6/k_8{=}1$. Experimental data on this ratio of rate coefficients are badly needed.

In the absence of direct kinetic measurements of the absolute rate coefficients for any of the RCHOO bimolecular reactions (excepting the recent measurement of Fenske et al. (2000) for CH_3CHOO + CH_3CHO which cannot be used with any of the relative-rate measurements made to date), both Atkinson and Lloyd (1984) and Kerr and Calvert (1984) have suggested that k_6 should be equated to the rate coefficient for the structurally analogous reactions, $RO_2{+}NO{\rightarrow}RO{+}NO_2$, with $k_6{=}7{\times}10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K. While this seems a reasonable proposition, it is desirable to obtain experimental verification. At present it is difficult to see how any direct measurements could be made with RCHOO systems involving

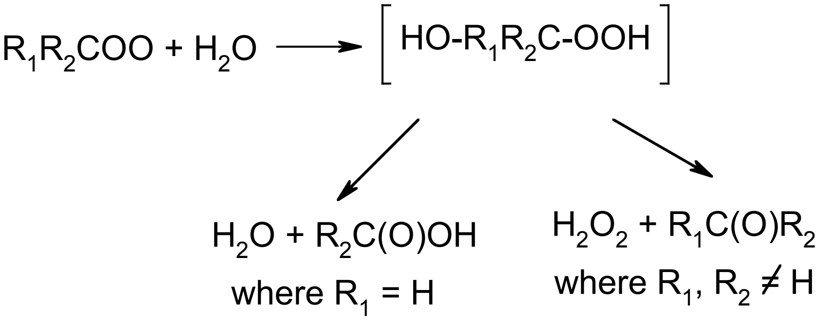

Fig. 5. See text.

O_3-alkene reactions owing to the complex chemistry involved. In this regard the study of Hatakeyama et al. (1981) involving the generation of CH_2OO Criegee intermediates from the reaction of $CH_2(^3B_1)$ with O_2 are of considerable interest.

In deriving the relative rate coefficients listed above, it has been necessary in some cases to compare data obtained from different O_3-alkene systems and to assume that all the RCHOO Criegee intermediates have equal reactivity, e.g., CH_2OO and CH_3CHOO. Again, while this seems to be a reasonable assumption, it requires experimental verification.

There is little direct experimental evidence on the products of the Reactions (1) to (9). Where the products are stated these have largely been suggested on the basis of analogy with related reactions.

Recent work of Neeb et al. (1997) shows that the reaction of the CH_2OO Criegee intermediate with H_2O leads initially to hydroxymethyl hydroperoxide ($HOCH_2OOH$). The $HOCH_2OOH$ may then decompose to HC(O)OH and H_2O but the extent to which this occurred by heterogeneous processes in the system used by Neeb et al. (1997) is uncertain. Hydroperoxides have been found in a number of other O_3-alkene studies (Simonaitis et al., 1991; Martinez et al., 1981; Winterhalter et al., 2000) and are suggested to arise in a similar way, by direct interaction of the Criegee intermediate with H_2O. In addition to the expected formation of carboxylic acids from the reactions of the Criegee intermediates with H_2O, recent studies of the reactions of O_3 with *trans*-2-butene (Becker et al., 1993; Simonaitis et al., 1991; Martinez et al., 1981), isoprene (Neeb et al., 1997; Simonaitis et al., 1991) and monoterpenes (Simonaitis et al., 1991; Martinez et al., 1981; Winterhalter et al., 2000) have reported varying amounts of H_2O_2 product. Since the yields of H_2O_2 were considerably enhanced by the presence of H_2O, it was proposed that H_2O_2 was formed in a direct reaction involving Criegee intermediates. Thus these observations may be rationalised in terms of the reactions depicted in Fig. 5. For the reaction of CH_2OO with H_2O, H_2O_2 formation is a minor pathway.

Reaction of R_1R_2COO Criegee intermediates with aldehydes leads to the formation of the corresponding ozonides (Fenske et al., 2000; Niki et al., 1977, 1983, 1987). However, the formation of ethene ozonide has not been observed in the reaction of CH_2OO with HCHO or in the O_3-ethene reaction (Su et al., 1980; Kan et al., 1981; Niki et al., 1981, 1983). The proposal that the reaction of the CH_2OO Criegee intermediate with HCHO leads to $HOCH_2OCHO$ (Su et al., 1980; Kan et al., 1981; Niki et al., 1981, 1983; Horie and Moortgat, 1991) has now been shown to be incorrect. The spectrum observed in the CH_2OO-HCHO reaction and assigned to $HOCH_2OCHO$ is now known to belong to $HOOCH_2OCHO$ (Neeb et al., 1995; Thamm et al., 1996), which is formed by the reaction of the CH_2OO Criegee intermediate with HC(O)OH.

Tobias and Zieman (2001) have determined rate coefficients for the reactions of the $CH_3(CH_2)_{11}CHOO$ Criegee intermediate with acids, aldehydes and alcohols relative to the reaction with H_2O. The following rate coefficient ratios were obtained (H_2O=1): methanol, 22; 2-propanol, 50; formaldehyde, 2700; and heptanoic acid, 17000.

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Appendix A7: X + VOC

II.A7.165

$$\mathbf{F + CH_4 \rightarrow HF + CH_3}$$

$\Delta H° = -131.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
5.5×10^{-10} exp[-(580 ± 150)/T]	250–350	Wagner et al., 1971	DF-MS
7.9×10^{-11}	298		
7.2×10^{-11}	298	Kompa and Wanner, 1972	(a)
$(6.0 \pm 6.0) \times 10^{-11}$	298	Clyne et al., 1973	DF-MS
$(5.72 \pm 0.30) \times 10^{-11}$	298	Fasano and Nogar, 1982	(b)
$(5.3 \pm 0.3) \times 10^{-11}$	294	Moore et al., 1994	(c)
Relative Rate Coefficients			
9.0×10^{-11} exp(-137/T)	253–348	Foon and Reid, 1971	RR (d)
5.7×10^{-11}	298		
1.3×10^{-10} exp(-215/T)	180–410	Persky, 1996	RR (e)
6.2×10^{-11}	298		

Comments

(a) Flash photolysis of WF_6. Overall rate coefficient was obtained by monitoring the decay of the HF chemical laser emission.

(b) Infrared multiphoton dissociation of SF_6 in a mixture of CH_4, D_2 and Ar. First-order decay of [F] was monitored by chemiluminescence from either HF or DF. Dependence of decay rate on mixture composition gave values for k and for k(F+D_2).

(c) Time-resolved vibrational chemiluminescence from HF monitored following the production of F atoms in the presence of CH_4 by pulsed laser photolysis of F_2 at 266 nm. Rate coefficient values were also reported at 218 K, 179 K and 139 K, with the values increasing at temperatures below about 200 K.

(d) Competitive fluorination-consumption technique. Value of k derived from measured ratio k/k(F+H_2)=0.82 exp(313/T) and k(F+H_2)=1.1×10^{-10} exp(-450/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current evaluation).

(e) Competitive study using DF-MS technique. Value of k derived from measured ratio k/k(F+D_2)=1.21 exp(420/T), the kinetic isotope effect k(F+H_2)/k(F+D_2)=1.04 exp(185/T) (Persky, 1973) and k(F+H_2)=1.1×10^{-10} exp(-450/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current evaluation).

Preferred Values

$k = 6.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.3 \times 10^{-10}$ exp(-215/T) cm^3 molecule^{-1} s^{-1} over the temperature range 180–410 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred value at room temperature is based on the room temperature values reported in Wagner et al. (1971), Kompa and Wanner (1972), Clyne et al. (1973), Fasano and Nogar (1982), Moore et al. (1994), Foon and Reid (1971) and Persky (1973). The preferred temperature dependence is that reported by Persky (1973). Results reported in this study are preferred over the temperature dependences reported in the much earlier studies of Wagner et al. (1971) and Foon and Reid (1971).

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II.A7.166

$Cl + CH_4 \rightarrow HCl + CH_3$

$\Delta H^\circ = 7.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$7.94 \times 10^{-12} \exp[-(1260 \pm 35)/T]$	218–401	Watson et al., 1976	FP-RF (a)
$(1.13 \pm 0.1) \times 10^{-13}$	298		
$7.93 \times 10^{-12} \exp[-(1272 \pm 51)/T]$	218–322	Manning and Kurylo, 1977	FP-RF
$(1.04 \pm 0.1) \times 10^{-13}$	296		
$6.51 \times 10^{-12} \exp[-(1229 \pm 27)/T]$	200–299	Whytock et al., 1977	FP-RF (b)
$(1.13 \pm 0.07) \times 10^{-13}$	299		
$(1.08 \pm 0.07) \times 10^{-13}$	298	Michael and Lee, 1977	DF-RF
$1.06 \times 10^{-11} \exp[-(1415 \pm 100)/T]$	268–423	Lin et al., 1978	DF-MS
$(9.6 \pm 0.9) \times 10^{-14}$	296		
$8.2 \times 10^{-12} \exp[-(1320 \pm 20/T]$	200–300	Zahniser et al., 1978	DF-RF (c)
$(9.9 \pm 1.5) \times 10^{-14}$	298		
$7.4 \times 10^{-12} \exp[-(1291 \pm 68)/T]$	220–298	Keyser, 1978	DF-RF (d)
$(1.01 \pm 0.02) \times 10^{-13}$	298		
$3.2 \times 10^{-12} \exp[-(1063 \pm 34)/T]$	221–298	Ravishankara and Wine, 1980	PLP-RF (e)
$(9.65 \pm 0.55) \times 10^{-14}$	298		
$8.06 \times 10^{-12} \exp[-(1300 \pm 113)/T]$	233–338	Heneghan et al., 1981	(f)
$(9.60 \pm 0.50) \times 10^{-14}$	298		
$(9.93 \pm 0.13) \times 10^{-14}$	298	Dobis and Benson, 1987	(f)
$(9.17 \pm 0.75) \times 10^{-14}$	294	Sawerysyn et al., 1987	DF-MS
$(9.40 \pm 0.40) \times 10^{-14}$	298	Beichert et al., 1995	DF-RF
$7.0 \times 10^{-12} \exp[-(1270 \pm 60)/T]$	181–291	Seeley et al., 1996	(g)
$(9.9 \pm 0.3) \times 10^{-14}$	298		
$(1.00 \pm 0.10) \times 10^{-13}$	298	Matsumi et al., 1997	PLP-LIF
$3.7 \times 10^{-13} (T/298)^{2.6} \exp(-385/T)$	292–800	Pilgrim et al., 1997	PLP (h)
$(9.3 \pm 0.9) \times 10^{-14}$	292		
$(1.07 \pm 0.03) \times 10^{-13}$	297	Mellouki, 1998	PLP-RF
$6.5 \times 10^{-12} \exp[-(1235 \pm 34)/T]$	218–298	Wang and Keyser, 1999	DF-RF
$(1.01 \pm 0.06) \times 10^{-13}$	298		

Comments

(a) These values were derived using the original data, but correcting for the presence of C_2H_6 (see Addenda to Watson, 1977).

(b) Non-linear Arrhenius behaviour was observed over the entire temperature range (200 K to 500 K) of measurements. Data for the temperature range 200 K to 299 K are well represented by the Arrhenius expression given in the table (Whytock et al., 1977).

(c) Non-linear Arrhenius behaviour was observed over the entire temperature range (200 K to 504 K) of measurements. Data for the temperature range 200 K to 300 K are well represented by the Arrhenius expression given in the table (Zahniser et al., 1978).

(d) Non-linear Arrhenius behaviour was observed over the entire temperature range (220 K to 423 K) of measurements. Data for the temperature range 220 K to 298 K are well represented by the Arrhenius expression given in the table (Keyser, 1978).

(e) Non-linear Arrhenius behaviour was observed. At temperatures at and below 240 K the apparent bimolecular rate constant was dependent upon the chemical composition of the reaction mixture. Ravishankara and Wine (1980) suggested that this was due to a non-equilibration of the $^2P_{1/2}$ and $^2P_{3/2}$ spin states of atomic chlorine at high values of the pseudo-first order rate constant, k', i.e., if the mixture did not contain an efficient spin equilibrator, e.g, Ar or CCl_4, the bimolecular rate constant decreased at high CH_4 concentrations, i.e., high values of k'. The Arrhenius expression for k between 221 K and 298 K was derived from the data shown in their Table II (excluding the high CH_4 concentration data in the He-Cl_2-CH_4 system).

(f) Very low pressure reactor system with MS detection of reactants and products.

(g) Turbulent flow tube technique at pressures near 80 mbar (60 Torr). The Cl atom decay was monitored by RF.

(h) Pulsed laser photolysis of CF_2Cl_2 at 193 nm. Time evolution of HCl product was monitored by continuous wave infrared long-path absorption at the R(3) line of the fundamental vibrational transition. Non-linear Arrhenius behavior was observed between 292 K and 800 K and was described by the modified Arrhenius expression given in the table.

Preferred Values

$k = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.6 \times 10^{-12} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred Arrhenius expression is derived from a least-squares fit to the experimental data between 200 K and 300 K reported in the studies of Watson et al. (1976), Manning and Kurylo (1977), Whytock et al. (1977), Michael and Lee (1977), Lin et al. (1978), Zahniser et al. (1978), Keyser (1978), Ravishankara and Wine (1980), Heneghan et al. (1981), Dobis and Benson (1987), Sawerysyn et al. (1987), Beichert et al. (1995), Seeley et al. (1996), Matsumi et al. (1997) and Pilgrim et al. (1997). The data used were restricted to the 200 K to 300 K temperature range because of the curvature in the Arrhenius plot at higher temperatures reported in the studies of Whytock et al. (1977), Zahniser et al. (1978), Keyser (1978), Ravishankara and Wine (1980) and Pilgrim et al. (1997). Therefore, for some studies only a subset of the data reported in the study was used. Results of the most recent studies of Mellouki et al. (1998) and Wang and Keyser (1999) are in excellent agreement with the preferred values. Results of relative rate studies were not used in this evaluation in the derivation of the preferred values. In general, the relative rate data (Lin et al., 1978; Watson, 1977; Pritchard et al., 1954; Pritchard et al., 1955; Knox, 1955) used in previous evaluations are in good agreement with the preferred values at room temperature, but are significantly lower than the preferred values at low temperatures.

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II.A7.167

$$\mathbf{Cl + C_2H_2 + M \rightarrow C_2H_2Cl + M}$$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.15 \pm 0.30) \times 10^{-21}\ T^{-3.5}$[Ar]	210–361	Brunning and Stief, 1985	FP-RF (a)
6.9×10^{-30} [Ar]	298		
Relative Rate Coefficients			
$(5.2 \pm 0.7) \times 10^{-30}$ [air]	295	Wallington et al., 1990	RR (b)
$5.4 \times 10^{-30}\ (T/300)^{-2.092}$[air]	252–370	Kaiser, 1992	RR (c)
$(6.1 \pm 0.2) \times 10^{-30}$ [air]	297	Kaiser and Wallington, 1996	RR (d)

Comments

(a) The concentration of the bath gas Ar was varied over the range $(2.7–120)\times10^{17}$ molecule cm^{-3}. Some experiments with N_2 were also conducted. Falloff extrapolations were made using F_c=0.6.

(b) Cl atoms were generated by photolysis of Cl_2 in the presence of C_2H_2 and C_2H_6 (or C_2H_5Cl). The decays of C_2H_2, C_2H_6 (or C_2H_5Cl) were followed by FTIR spectroscopy. The measured rate coefficient ratios have been placed on an absolute basis using a rate coefficient of $k(Cl+C_2H_6)=5.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. Measurements were conducted over the pressure range 0.013 mbar to 7.6 bar. Falloff extrapolations were made with F_c = 0.6.

(c) Mixtures of C_2H_2, C_2H_6, Cl_2 and diluent (air, N_2, or SF_6) were irradiated by a UV fluorescent lamp. C_2H_2 and C_2H_6 concentrations were determined by GC. The reaction was studied at pressures between 0.03 bar and 1.7 bar. The measured rate coefficient ratios are placed on an absolute basis using the rate coefficient 8.68×10^{-11} exp(-113/T) cm^3 molecule^{-1} s^{-1} for the reaction $Cl+C_2H_6 \rightarrow C_2H_5+HCl$. Falloff extrapolations were made with a temperature independent F_c=0.6.

(d) Mixtures of Cl_2, C_2H_2, CH_4, CH_3Cl, C_2H_6 and C_2H_5Cl and the diluent gases air and N_2 were irradiated with a UV fluorescent lamp. After irradiation C_2H_2, CH_4 and CH_3Cl were monitored by GC (0.4 mbar to 13 mbar). CH_3Cl, C_2H_6 and C_2H_5Cl were determined by FTIR (13 mbar to 920 mbar). The following values were used for the reference abstraction reactions: 1.0×10^{-13} cm^3 molecule^{-1} s^{-1} ($Cl+CH_4$), 4.9×10^{-13} cm^3 molecule^{-1} s^{-1} ($Cl+CH_3Cl$), 5.7×10^{-11} cm^3 molecule^{-1} s^{-1} ($Cl+C_2H_6$) and 8.05×10^{-12} cm^3 molecule^{-1} s^{-1} ($Cl+C_2H_5Cl$). The results were analyzed together with previous determinations performed between 0.13 bar and 7.9 bar and extrapolated with F_c=0.6 (Wallington et al., 1990).

Preferred Values

$k_0 = 6.1 \times 10^{-30}\ (T/300)^{-3}\ [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the room temperature measurements of Kaiser and Wallington (1996) which have been evaluated with F_c=0.6. The temperature dependence is a compromise of the results from Brunning and Stief (1985) and Kaiser (1992).

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.52 \pm 0.15) \times 10^{-4}\ T^{-2.63}$	210–361	Brunning and Stief, 1985	FP-RF (a)
4.7×10^{-11}	298		
Relative Rate Coefficients			
$(2.3 \pm 0.7) \times 10^{-10}$	295	Wallington et al., 1990	RR (b)
$2.13 \times 10^{-10}\ (T/300)^{-1.045}$	252–370	Kaiser, 1992	RR (c)
$(2.0 \pm 0.1) \times 10^{-10}$	297	Kaiser and Wallington, 1996	RR (d)

Comments

(a) to (d) See comments (a) to (d) for k_0.

Preferred Values

$k = 5.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.
$k_\infty = 2.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the data of Kaiser and Wallington (1996) which cover the broadest pressure range (0.13 bar to 7.9 bar). They have been evaluated with F_c=0.6. Relative rate coefficients near 1 bar from Lee and Rowland (1977), Atkinson and Aschmann (1985) and Wallington et al. (1988) are in good agreement with the preferred values. A branching ratio of 0.19 ± 0.05 for formation of *cis*- vs *trans*-isomers of the CHCl=CH adduct was determined by Zhu et al. (1994) around 1 bar of N_2 and 295 K.

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II.A7.168

$$\mathbf{Cl + C_2H_4 + M \rightarrow C_2H_4Cl + M}$$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.4 \pm 0.2) \times 10^{-29}$ $(T/298)^{-2.0}$[N$_2$]	218–297	Maricq et al., 1993	(a)
$(1.0 \pm 0.2) \times 10^{-29}$[He]	293	Stutz et al., 1997	(b)
Relative Rate Coefficients			
$(1.6^{+1}_{-0.3}) \times 10^{-29}$ [air]	295	Wallington et al., 1990	RR (c)
$(1.7 \pm 0.3) \times 10^{-29}$ $(T/298)^{-3.28}$[air]	297–383	Kaiser and Wallington, 1996	RR (d)
$(1.42 \pm 0.05) \times 10^{-29}$ [air]	297		
1.0×10^{-29} [He]	297	Kaiser and Wallington, 1998	RR (d,e)
1.85×10^{-29} [N$_2$]			

Comments

(a) IR absorption measurements of C_2H_4 and HCl after laser photolysis of Cl_2 in Cl_2-C_2H_4-O_2-N_2 mixtures. Measurements at 39 mbar of N_2, here evaluated without falloff corrections. k also measured at 170 mbar and 297 K.

(b) Fast-flow discharge study detecting Cl by resonance fluorescence at 135 nm. Similar results by relative rate measurements.

(c) Measurements of k performed by a relative rate technique. Cl atoms were generated by photolysis of Cl_2 in the presence of C_2H_4, and C_2H_6 (or C_2H_5Cl). Decay of C_2H_4, C_2H_6 (or C_2H_5Cl) monitored by FTIR spectroscopy. Using a value of 5.7×10^{-11} cm^3 molecule^{-1} s^{-1} for the rate coefficient for the $Cl+C_2H_6 \rightarrow C_2H_5+HCl$ reaction, the relative data were placed on an absolute basis. The reaction was studied over the pressure range 13 mbar to 4000 mbar and the measured rate coefficients fitted with F_c=0.6.

(d) Mixtures of Cl_2, C_2H_4, CH_4, CH_3Cl, CCl_3H, C_2H_6 and C_2H_5Cl and the diluent gases air and N_2 were irradiated with a UV fluorescent lamp. After irradiation, C_2H_4 and the above reference compounds were determined by GC or FTIR techniques. The experiments were performed at total pressures of 0.26 mbar to 130 mbar. The following values were used for the reference abstraction reactions: 1.0×10^{-13} cm^{-3} molecule^{-1} s^{-1} (Cl+CH_4), 4.9×10^{-13} cm^3 molecule^{-1} s^{-1} (Cl+CH_3Cl), 1.1×10^{-13} cm^3 molecule^{-1} s^{-1} (Cl+CCl_3H), 5.7×10^{-11} cm^3 molecule^{-1} s^{-1} (Cl+C_2H_6) and 8.05×10^{-12} cm^3 molecule^{-1} s^{-1} (Cl+C_2H_5Cl). The results were analyzed together with previous determinations conducted at 130 mbar to 4000 mbar of air (Wallington et al., 1990) and extrapolated with F_c=0.6.

(e) Falloff extrapolation with F_c=0.4.

Preferred Values

$k_0 = 1.85 \times 10^{-29}$ $(T/300)^{-3.3}$ [air] cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the most detailed results from Kaiser and Wallington (1996, 1998) which agree with the results from Maricq et al. (1993) and Stutz et al. (1997) (only for the bath gas He, but not N_2). The given value of k_0 corresponds to a falloff extrapolation with F_c=0.4.

High-pressure rate coefficients

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$3.05^{+2}_{-0.4}) \times 10^{-10}$	295	Wallington et al., 1990	RR (a)
$(3.2 \pm 0.15) \times 10^{-10}$	297	Kaiser and Wallington, 1996	RR (b)
5.7×10^{-10}	297	Kaiser and Wallington, 1998	RR (c)

Comments

(a) See comment (c) for k_0.

(b) See comment (d) for k_0.

(c) See comments (d) and (e) for k_0.

Preferred Values

$k = 1.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.
$k_\infty = 6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm\ 0.3$ at 298 K.
$\Delta n = \pm\ 1$.

Comments on Preferred Values

The falloff extrapolation of the data from Wallington et al. (1990) is consistent with results in the intermediate falloff range from Maricq et al. (1993), Lee and Rowland (1977), Iyer et al. (1983), Atkinson and Aschmann (1985), Atkinson and Aschmann (1987) and Wallington et al. (1988). Measurements of the reverse decomposition of C_2H_4Cl in the falloff range at 400–480 K have been reported by Knyazev et al. (1999).

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II.A7.169

$$\mathbf{Cl + C_2H_6 \rightarrow HCl + C_2H_5}$$

$\Delta H^\circ = -8.7$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(6.0 \pm 1.5) \times 10^{-11}$	298	Davis et al., 1970	FP-RF (a)
$7.29 \times 10^{-11} \exp[-(61 \pm 44)/T]$	222–322	Manning and Kurylo, 1977	FP-RF
$(5.93 \pm 0.44) \times 10^{-11}$	296		
$(5.95 \pm 0.28) \times 10^{-11}$	298	Ray et al., 1980	DF-MS
$9.01 \times 10^{-11} \exp[-(133 \pm 15)/T]$	220–604	Lewis et al., 1980	DF-RF
$(5.48 \pm 0.30) \times 10^{-11}$	298		
$8.20 \times 10^{-11} \exp[-(86 \pm 10)/T]$	203–343	Dobis and Benson, 1991	(b)
$(6.10 \pm 0.11) \times 10^{-11}$	298		
$(7.05 \pm 1.4) \times 10^{-11}$	298	Kaiser et al., 1992	PLP-IRA
$(5.9 \pm 0.6) \times 10^{-11}$	297	Stickel et al., 1992	PLP-TDLS
$(5.53 \pm 0.21) \times 10^{-11}$	298	Beichert et al., 1995	DF-RF
$(5.75 \pm 0.45) \times 10^{-11}$	298	Tyndall et al., 1997	FP-RF
$8.6 \times 10^{-11} \exp[-(135 \pm 26)]$	292–600	Pilgrim et al., 1997	PLP (c)
$(5.5 \pm 0.2) \times 10^{-11}$	292		
$(6.5 \pm 0.3) \times 10^{-11}$	297	Mellouki, 1998	PLP-RF
$(5.85 \pm 0.55) \times 10^{-11}$	298	Hitsuda et al., 2001	PLP-LIF
Relative Rate Coefficients			
$(6.0 \pm 1.3) \times 10^{-11}$	296	Hooshiyar and Niki, 1995	RR (d)
$(5.4 \pm 1.2) \times 10^{-11}$	298	Beichert et al., 1995	RR (e)
$(5.5 \pm 1.2) \times 10^{-11}$	297	Tyndall et al., 1997	RR (f)
$(5.7 \pm 0.5) \times 10^{-11}$	298	Finlayson-Pitts et al., 1999	RR (g)

Comments

(a) Reported value has been reduced by 10% as discussed previously (CODATA, 1980).

(b) Very low pressure reactor study. Cl atoms were generated by microwave discharge of Cl_2-He mixtures, with MS analysis of reactants and products.

(c) Cl atoms generated from pulsed laser photolysis of CF_2Cl_2 at 193 nm. Time evolution of HCl product was monitored by continuous wave infrared long-path absorpton at the R(3) line of the fundamental vibrational transition.

(d) Cl atoms generated by photolysis of Cl_2 in N_2 at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient rato $k/k(\mathrm{Cl}+n\text{-}C_4H_{10})=0.294\pm0.023$ is placed on an absolute basis by use of $k(\mathrm{Cl}+n\text{-}C_4H_{10})=2.05\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(e) Cl atoms generated by photolysis of Cl_2 in air at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(\mathrm{Cl}+n\text{-}C_4H_{10})=0.261\pm0.013$ is placed on absolute basis by use of $k(\mathrm{Cl} + n\text{-}C_4H_{10})=2.05\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(f) Cl atoms generated by photolysis of Cl_2 in air or N_2 at a total pressure of 156 mbar to 666 mbar (117–500 Torr). Relative disappearance rates of organics studied were measured by GC or FTIR. Rate coefficient ratio $k/k(\mathrm{Cl}+n\text{-}C_4H_{10})=0.267\pm0.037$ is placed on absolute basis by use of $k(\mathrm{Cl}+n\text{-}C_4H_{10})=2.05\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(g) Cl atoms generated by photolysis of Cl_2, $SOCl_2$, or CCl_3COCl in air or N_2 at 1 bar pressure. Rate coefficient ratio $k/k(Cl+n\text{-}C_4H_{10})$ = 0.277 ± 0.025 is placed on absolute basis by use of $k(Cl+n\text{-}C_4H_{10})=2.05\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, this evaluation).

Preferred Values

$k = 5.9 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k = 8.3 \times 10^{-11}$ exp(-100/T) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 220–600 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The 298 K rate coefficient is the average of the room temperature absolute rate coefficients of Davis et al. (1970), Manning and Kurylo (1977), Ray et al. (1980), Lewis et al. (1980), Dobis and Benson (1991), Kaiser et al. (1992), Stickel et al. (1992), Beichert et al. (1995), Tyndall et al. (1997), Pilgrim et al. (1997), Mellouki (1998) and Hitsuda et al. (2001). The temperature dependence is the average of those from the temperature-dependent studies of Manning and Kurylo (1977), Lewis et al. (1980), Dobis and Benson (1991) and Pilgrim et al. (1997). The room temperature relative rate values of Hooshiyar and Niki (1995), Beichert et al. (1995), Tyndall et al. (1997) and Finlayson-Pitts et al. (1999) are in good agreement with the preferred value, while those of Atkinson and Aschmann (1985) and Wallington et al. (1988) are 20% to 30% higher than the preferred value.

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II.A7.170

$Cl + C_3H_6 + M \rightarrow HCl + C_3H_6Cl + M$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(4.0 \pm 0.4) \times 10^{-28}$ [N_2]	298	Kaiser and Wallington, 1996	RR (a)

Comments

(a) Cl atoms were generated by photolysis of Cl_2 in the presence of C_3H_6 and C_2H_6 at 1 mbar to 900 mbar of N_2. C_3H_6 consumption was determined by FTIR or GC analysis, the major products being 3-chloropropene and 1,2-dichloropropane. At low pressure (below 12 mbar) 3-chloropropene is the major product indicating that abstraction of H by Cl from the CH_3 group in C_3H_6 is the dominant channel. At pressures higher than 12 mbar, the primary product observed is 1,2-dichloropropane, indicating that addition of a Cl atom to the double bond is the major channel. The limiting rate coefficients were obtained using F_c=0.6. A rate coefficient for the reference reaction $Cl+C_2H_6 \rightarrow C_2H_5+HCl$ of 5.9×10^{-11} cm^3 molecule^{-1} s^{-1} was employed (Kaiser and Wallington, 1996; this evaluation).

Preferred Values

$k_0 = 4.0 \times 10^{-28}$ [N_2] cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.

Comments on Preferred Values

The preferred value is based on the only value reported (Kaiser and Wallington, 1996). Due to this and to the uncertainty of the extrapolated k_0, a large error limit is assigned.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.54 \pm 0.09) \times 10^{-10}$	296	Atkinson and Aschmann, 1985	RR (a)
$(2.94 \pm 0.13) \times 10^{-10}$	295	Wallington et al., 1988	RR (b)
$(2.68 \pm 0.13) \times 10^{-10}$	298	Kaiser and Wallington, 1996	RR (c)

Comments

(a) Cl atoms generated by the photolysis of Cl_2-n-C_4H_{10}-C_3H_6-air at 1 bar. The reaction was studied relative to the reaction $Cl+n\text{-}C_4H_{10} \rightarrow$ products for which a rate coefficient 2.05×10^{-10} cm^3 molecule^{-1} s^{-1} is used (this evaluation). C_3H_6 and n-C_4H_{10} were analyzed by GC.

(b) Cl atoms were formed by photolysis of Cl_2 in the presence of C_3H_6 and n-C_4H_{10} at atmospheric pressure of synthetic air. The decay rate of C_3H_6 was measured relative to that of n-C_4H_{10} and placed on an absolute basis using rate coefficients of 2.05×10^{-10} cm^3 molecule^{-1} s^{-1} for the reference reactions (this evaluation).

(c) See comment (a) for k_0. Rate coefficient at 933 mbar (700 Torr) pressure of N_2 or air.

Preferred Values

$k = 2.7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.
$k_\infty = 2.8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value at 1 bar of air is an average of earlier results from Atkinson and Aschmann (1985) and Wallington et al. (1988), and the more recent determination by Kaiser and Wallington (1996). At room temperature and atmospheric pressure, the addition of Cl atoms to the double bond accounts for approximately 90% of the reaction (Kaiser and Wallington, 1996). The H atom abstraction occurs from the C-H bonds of the methyl group (Kaiser and Wallington, 1996).

References

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II.A7.171

$$\mathbf{Cl + C_3H_8 \rightarrow HCl + \mathit{n}\text{-}C_3H_7 \quad (1)}$$
$$\mathbf{\rightarrow HCl + \mathit{i}\text{-}C_3H_7 \quad (2)}$$

$\Delta H°(1) = -8.3$ kJ·mol^{-1}
$\Delta H°(2) = -22.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients (k)			
$1.36 \times 10^{-10} \exp[(44 \pm 25)/T]$	220–607	Lewis et al., 1980	DF-RF (a)
$(1.51 \pm 0.06) \times 10^{-10}$	298		
$(1.23 \pm 0.10) \times 10^{-10}$	298	Beichert et al., 1995	DF-RF (b)
$(1.38 \pm 0.03) \times 10^{-10}$	292–700	Pilgrim et al., 1997	PLP (c)
$(1.31 \pm 0.03) \times 10^{-10}$	297	Mellouki, 1998	PLP-RF (d)
$(1.33 \pm 0.03) \times 10^{-10}$	298	Hitsuda et al., 2001	PLP-LIF (e)
Relative Rate Coefficients (k)			
$(1.40 \pm 0.28) \times 10^{-10}$	296	Atkinson and Aschmann, 1985	RR (f)
$(1.45 \pm 0.28) \times 10^{-10}$	295	Wallington et al., 1988	RR (g)
$(1.34 \pm 0.28) \times 10^{-10}$	296	Hooshiyar and Niki, 1995	RR (h)
$(1.44 \pm 0.26) \times 10^{-10}$	298	Beichert et al., 1995	RR (i)
$(1.43 \pm 0.25) \times 10^{-10}$	297	Tyndall et al., 1997	RR (j)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients (k_1 and k_1)			
$k_1 = 7.0 \times 10^{-11} \exp[(-31 \pm 33)/T]$	299–468	Sarzynski and Sztuba, 2002	RR (k)
$(6.25 \pm 0.17) \times 10^{-11}$	299		
$k_2 = 5.2 \times 10^{-11} \exp[(118 \pm 25)/T]$	299–468		
$(7.73 \pm 0.14) \times 10^{-10}$	299		
Branching Ratios			
$k_1/k = (0.43 \pm 0.03)$	297	Tyndall et al., 1997	RR (j)
$k_2/k = (0.57 \pm 0.03)$			
$k_1/k = 0.59 \exp[-(87 \pm 58)/T]$	295-469	Sarzynski and Sztuba, 2002	RR (k)
$k_1/k = (0.45 \pm 0.02)$ 299			
$k_2/k = 0.43 \exp[(76 \pm 55)/T]$	295-469		
$k_2/k = (0.55 \pm 0.02)$	298		

Comments

(a) Rate constant was measured at three temperatures: 220 K, 298 K and 607 K. Within experimental uncertainty, the three values of k were the same. Authors gave as an alternative rate expression the simple mean of the three values: $k=(1.58\pm0.13)\times10^{-10}$ cm^3 molecule^{-1} s^{-1}.

(b) Both relative and absolute rate studies of reactions of Cl atoms with C_1-C_4 alkanes. Direct measurement of ratio $k/k(Cl+C_2H_6)$ is in good agreement with the ratio of the absolute values.

(c) Cl atoms were generated from pulsed laser photolysis of CF_2Cl_2 at 193 nm. Time evolution of HCl product was monitored by continuous wave infrared long-path absorption.

(d) Experiments carried out in 80 mbar He bath gas. O_2 added to prevent reformation of Cl atoms via $R+Cl_2$ which was used as Cl precursor (355 nm photolysis).

(e) 193 nm photolysis of HCl as Cl source. Detection of both $Cl(^2P_{1/2})$ and $Cl(^2P_{3/2})$ using VUV-LIF. The rate constants for $Cl(^2P_{1/2})$ were found to be ≈ 30% of those for the $Cl(^2P_{3/2})$ ground state. The rate constant for $Cl(^2P_{3/2})$ with fully deuterated propane was found to be 0.86×10^{-10} cm^3 $molecule^{-1}$ s^{-1}.

(f) Cl atoms were generated by photolysis of Cl_2 in air at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(Cl+n\text{-}C_4H_{10})=0.681\pm0.025$ is placed on absolute basis by use of $k(Cl+n\text{-}C_4H_{10})=2.05\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2005).

(g) Cl atoms were generated by photolysis of Cl_2 in air at 990 mbar (740 Torr) pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(Cl+n\text{-}C_4H_{10})=0.711\pm0.019$ is placed on absolute basis by use of $k(Cl+n\text{-}C_4H_{10})=2.05\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2005).

(h) Cl atoms were generated by photolysis of Cl_2 in N_2 at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(Cl+n\text{-}C_4H_{10})=0.656\pm0.009$ is placed on absolute basis by use of $k(Cl+n\text{-}C_4H_{10})=2.05\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2005).

(i) Cl atoms were generated by photolysis of Cl_2 in air at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(Cl+C_2H_6)=2.44\pm0.26$ is placed on absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2005).

(j) Cl atoms were generated by photolysis of Cl_2 in air or N_2 at a total pressure of 156 mbar to 666 mbar (117 Torr to 500 Torr). Relative disappearance rates of organics studied were measured by GC or FTIR. Rate coefficient ratio $k/k(Cl+C_2H_6)=2.42\pm0.10$ is placed on absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2005).

(k) Competitive photochlorination experiments with Cl atoms initially generated by the 420 nm photolysis of Cl_2 in N_2 at a total pressure of ≈ 133 mbar. Formation rates of CH_3CH_2CHCl (abstraction of primary H) and $CH_3CHClCH_3$ (Abstraction of secondary H) were measured relative CH_2H_5Cl (from reference compound ethane) by GC. The absolute rate coefficients reported in the table were derived by use of $k(Cl + CH_2H_6) = 8.3 \times 10^{-11} \exp(-100/T)$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2005).

Preferred Values

$k = 1.4 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, independent of temperature over the range 200–700 K.
$k_1/k = 0.59 \exp(-90/T)$
$k_2/k = 0.43 \exp(75/T)$

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred value of the overall rate coefficient, k, at room temperature is the mean of the absolute values reported by Lewis et al. (1980), Beichert et al. (1995), Pilgrim et al. (1997), Mellouki (1998) and Hitsuda et al. (2001) and the relative values reported by Atkinson and Aschmann (1985), Wallington et al. (1988), Hooshiyar and Niki (1995), Beichert et al. (1995), Tyndall et al. (1997) and Sarzynski and Sztuba (2002). Lewis et al. (1980) and Pilgrim et al. (1997) have shown that the overall rate coefficient is independent of temperature between 220 and 700 K. This is confirmed by the results of Sarzynski and Sztuba (2002) who showed that although k_1 and k_2 have weak temperature dependences, the sum of $k_1 + k_2$ is independent of temperature between 299 and 468 K. The branching ratios derived by Tyndall et al. (1997) and Sarzynski and Sztuba (2002) are in good agreement at 298 K. Temperature dependent branching ratios have only been determined by Sarzynski and Sztuba (2002), and their values are adopted.

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II.A7.172

$$\mathbf{Cl + \mathit{n}\text{-}C_4H_{10} \rightarrow HCl + 1\text{-}C_4H_9 \quad (1)}$$
$$\mathbf{Cl + \mathit{n}\text{-}C_4H_{10} \rightarrow HCl + 2\text{-}C_4H_9 \quad (2)}$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.15 \times 10^{-10} \exp[(12 \pm 26)/T]$	298–598	Lewis et al., 1980	DF-RF (a)
$(2.25 \pm 0.10) \times 10^{-10}$	298		
$(1.8 \pm 0.2) \times 10^{-10}$	298	Nesbitt and Leone, 1982	(b)
$(2.11 \pm 0.18) \times 10^{-10}$	298	Beichert et al., 1995	DF-RF (c)
$(2.15 \pm 0.15) \times 10^{-10}$	298	Tyndall et al., 1997	FP-RF (d)
$(1.91 \pm 0.10) \times 10^{-10}$	298	Qian et al., 2002	PLP-TDLS (e)
$(2.05 \pm 0.15) \times 10^{-10}$	298	Hitsuda et al., 2001	PLP-LIF (f)
Branching ratios			
$k_1/k = 0.29 \pm 0.02$	298	Tyndall et al., 1997	GC
$k_2/k = 0.71 \pm 0.02$	298	Tyndall et al., 1997	GC

Comments

(a) Rate constant was measured at three temperatures: 298 K, 422 K and 598 K. Within experimental uncertainty, these three values were the same. Authors gave as an alternative rate expression the simple mean of the three values: k=(2.20±0.10)×10^{-10} cm^3 molecule^{-1} s^{-1}.

(b) Laser photodissociation of Cl_2 with time-resolved monitoring of infrared emission of HCl (v=1) product.

(c) Both relative and absolute rate studies of reactions of Cl atoms with C_1 to C_4 alkanes. Direct measurement of ratio $k/k(Cl+C_2H_6)$ is in very good agreement with the ratio of the absolute values.

(d) Both relative and absolute rate studies of reactions of Cl atoms with C_2H_6, C_3H_8 and n-C_4H_{10}. Measurements of $k/k(Cl+C_2H_6)$ over the temperature range 298 K to 540 K support the essentially zero temperature dependence for k reported by Lewis et al. (1980). GC measurements at 298 K show that the reaction Cl+n-C_4H_{10} yields 29±2% 1-butyl radicals and 71±2% 2-butyl radicals.

(e) 193 nm Laser photolysis of $(ClOC)_2$ to form Cl. Kinetics of reaction derived from HCl formation profiles, measured using infrared diode laser absorption spectroscopy.

(f) 193 nm photolysis of HCl as Cl source. Detection of both Cl($^2P_{1/2}$) and Cl($^2P_{3/2}$) using VUV-LIF. The rate coefficient for Cl($^2P_{1/2}$) was found to be ≈30% of that for Cl($^2P_{3/2}$) ground state.

Preferred Values

$k = 2.05 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290–600 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred value at room temperature is the mean of the values reported by Beichert et al. (1995), Tyndall et al. (1997), Qian et al. (2002) and Hitsuda et al. (2001). The temperature independence is based on the results of Lewis et al. (1980) over the range 298 K to 598 K and is supported by the relative measurements of Tyndall et al. (1997) over the range 298 K to 540 K. Tyndall et al. (1997) studied the mechanism of the reaction at 298 K and reported the yield of 1-butyl radicals to be 29±2% and that of 2-butyl radicals to be 71±2%.

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II.A7.173

$Cl + HCHO \rightarrow HCl + HCO$

$\Delta H^\circ = -61.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(7.48 \pm 0.50) \times 10^{-11}$	200–500	Michael et al., 1979	FP-RF
$1.09 \times 10^{-10} \exp[-(131 \pm 98)/T]$	223–323	Anderson and Kurylo, 1979	FP-RF
$(7.18 \pm 0.61) \times 10^{-11}$	293		
$(7.40 \pm 0.7) \times 10^{-11}$	298	Fasano and Nogar, 1981	PLP-CL
$(6.98 \pm 0.69) \times 10^{-11}$	298	Seakins et al., 2004	LP-IR (a)
Relative Rate Coefficients			
$(7.6 \pm 0.6) \times 10^{-11}$	298	Niki et al., 1978	RR (a)
$(6.8 \pm 1.4) \times 10^{-11}$	295	Poulet et al., 1981	RR (b)

Comments

(a) Cl($^2P_{3/2}$ generated in 351 nm laser photolysis of Cl_2. Kinetic data obtained by monitoring the HCL product by IR emission spectroscopy.

(b) Competitive photo-chlorination between HCHO and C_2H_6 using FTIR. The measured rate coefficient ratio $k/k(Cl+C_2H_6)=1.3\pm0.1$ is placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2005).

(c) DF-MS study. Value of k derived from measured ratio of $k/k(Cl+C_2H_6)=1.16\pm0.12$ and $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2005).

Preferred Values

$k = 7.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.1 \times 10^{-11} \exp(-34/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–500 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred 298K rate coefficient is an unweighted average of all studies listed above, which are in good agreement. The preferred temperature dependence is based on a least-squares fit to the 200–500 K data of Michael et al. (1979) and the 223–323 K data of Anderson and Kurylo (1979), with the pre-exponential factor adjusted to reproduce the recommended rate coefficient at 298 K. The reaction generates vibrationally excited products, HCL and HCO (Dong et al., 2003), with ≈ (91 ± 14)% of HCL Formation as ν=1 (Seakins et al., 2004). Kinetic isotope effects have been determined in relative rate studies as k(Cl + HCHO)/k(Cl + DCDO) = 1.30, k(Cl + HCHO)/k(Cl + HCDO) = 1.201, k(Cl + HCHO)/k(Cl + HCH^{18}O)= 1.08 and k(Cl + H^{13}CHO)/k(Cl + DCDO) = 1.22 (Beukes et al., 2000; Feilberg et al., 2004).

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II.A7.174

$$\mathbf{Cl + CH_3CHO \rightarrow HCl + CH_3CO \quad (1)}$$
$$\mathbf{\rightarrow HCl + CH_2CHO \quad (2)}$$

$\Delta H^\circ(1) = -57.8$ kJ·mol^{-1}
$\Delta H^\circ(2) = -37.3$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.6 \pm 1.4) \times 10^{-11}$	210–343	Payne et al., 1990	FP-RF
$(7.3 \pm 0.7) \times 10^{-11}$	295	Tyndall et al., 1999	PLP-RF (a)
$(7.5 \pm 0.8) \times 10^{-11}$	298	Kegley-Owen et al., 1999	PLP-TDLAS (b)
Relative Rate Coefficients			
$(7.9 \pm 1.2) \times 10^{-11}$	298	Niki et al., 1985	RR (c)
$(8.1 \pm 0.8) \times 10^{-11}$	295 ± 2	Wallington et al., 1988	RR (d)
$(6.1 \pm 0.5) \times 10^{-11}$	298	Bartels et al., 1989	RR (e)
$(8.8 \pm 1.0) \times 10^{-11}$	298	Tyndall et al., 1999	RR (a)
Branching Ratios			
$k_2/k < 0.01$	298	Niki et al., 1985	(c)
$k_2/k < 0.07$	298	Bartels et al., 1989	(e)

Comments

(a) In the absolute study, Cl atoms were generated from the 308 nm photolysis of Cl_2. 1 Torr (1.3 mbar) of O_2 added to total pressure of 20–90 Torr (27–120 mbar) N_2 or He to scavenge CH_3CO and reduce regeneration of Cl, some correction was however still necessary. In the relative rate study, broad band irradiation of Cl_2 was the source of Cl atoms. Experiments were carried out in 700 Torr N_2, with analysis of CH_3CHO and reference compound (C_2H_6 and C_2H_4) with FTIR. $k(Cl+CH_3CHO)/k(Cl+C_2H_6)=1.49\pm0.1$, $k(Cl+CH_3CHO)/k(Cl+C_2H_4)=0.90\pm0.05$. The data have been placed on an absolute basis using $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(b) Cl atoms were generated from the 308 nm photolysis of Cl_2 at total pressures of 10-50 Torr (13–67 mbar) N_2. Kinetic parameters were derived by monitoring HCl formation (ν = 0) by infra-red tunable diode laser absorption spectroscopy. N_2O was added to quench vibrationally excited HCl, O_2 was added to reduce secondary regeneration of Cl via reaction of CH_3CO with Cl_2.

(c) Cl atoms were generated by photolysis of Cl_2 at 930 mbar (700 Torr) total pressure of N_2. Relative decay rates of CH_3CHO and C_2H_6 measured, and the measured rate coefficient ratio is placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation). The branching ratio was determined from FTIR spectroscopic product analysis.

(d) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-N_2-CH_3CHO-C_2H_6 mixtures and the relative decay rates of CH_3CHO and C_2H_6 measured. The measured rate coefficient ratio is placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(e) DF-MS study. Relative decay rates of CH_3CHO and C_2H_6 were monitored, and the measured rate coefficient ratio is placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation). The branching ratio was derived from the products observed by MS.

Preferred Values

$k = 8.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 210–340 K.
$k_2/k < 0.01$ at 298 K.

Reliability

$\Delta \log k = \pm 0.07$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the absolute rate coefficients of Tyndall et al. (1999) and Kegley Owen et al. (1999) and the relative rate coefficients of Niki et al. (1985), Wallington et al. (1988) and Tyndall et al. (1999). The lack of a temperature dependence of the rate coefficient is consistent with the data of Payne et al. (1990). The branching ratio is derived from the data of Niki et al. (1985). The relative rate measurement of Scollard et al. (1993) was carried out relative to $CH_3C(O)CH_3$, which is not considered sufficiently well defined to derive an accurate relative rate coefficient. Deuterium kinetic isotope effects were determined to be: $k(Cl+CH_3CHO)/k(Cl+CH_3CDO)=1.34\pm0.02$, $k(Cl+CH_3CHO)/k(Cl+CD_3CDO)=1.32\pm0.02$, $k(Cl+CD_3CHO)/k(Cl+CH_3CDO)=1.35\pm0.02$, $k(Cl+CD_3CHO)/k(Cl+CD_3CDO)=1.39\pm0.02$ (Beukes et al., 2000).

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II.A7.175

$Cl + C_2H_5CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.17 \pm 0.10) \times 10^{-10}$	295 ± 2	Wallington et al., 1988	RR (a)
$(1.45 \pm 0.08) \times 10^{-10}$	298 ± 3	Thévenet et al., 2000	RR(b)
$(1.20 \pm 0.07) \times 10^{-10}$	298 ± 3		(c)
$(1.25 \pm 0.06) \times 10^{-10}$	298 ± 3		(d)
$(1.41 \pm 0.10) \times 10^{-10}$	298 ± 3		(e)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-air mixtures, and the decay rates of C_2H_5CHO and C_2H_6 monitored by GC. The measured rate coefficient ratio is placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(b) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-air mixtures, and the decay rates of C_2H_5CHO and C_2H_6 monitored by GC. The measured rate coefficient ratio of $k(Cl+C_2H_5CHO)/k(Cl+C_2H_6)=2.46\pm0.08$ is placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(c) Method as (b) but C_3H_8 as reference gas. The measured rate coefficient ratio of $k(Cl+C_2H_5CHO)/k(Cl+C_3H_8)=0.85\pm0.05$ is placed on an absolute basis by use of $k(Cl+C_3H_8)=1.4\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(d) Method as (b) but n-C_4H_{10} as reference gas. The measured rate coefficient ratio of $k(Cl+C_2H_5CHO)/k(Cl+n\text{-}C_4H_{10})=0.61\pm0.03$ is placed on an absolute basis by use of $k(Cl+n\text{-}C_4H_{10})=2.05\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(e) Method as (b) but n-hexane as reference gas. The measured rate coefficient ratio of $k(Cl+C_2H_5CHO)/k(Cl+n\text{-hexane})=0.44\pm0.02$ is placed on an absolute basis by use of $k(Cl+n\text{-hexane})/k(Cl+n\text{-butane})=1.56$ (average value from Tyndall et al., 1997, and Hooshiyar and Niki, 1995) and $k(Cl+n\text{-butane})=2.05\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

Preferred Values

$k = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred value uses data from the relative rate studies of Wallington et al. (1988) and Thévenet et al. (2000), and is an average of the rate constants obtained in experiments in which, C_2H_6, C_3H_8 and n-C_4H_{10} were used as reference gases, which have well defined rate coefficients for reaction with Cl.

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II.A7.176

$Cl + CH_3C(O)CH_3 \rightarrow HCl + CH_3C(O)CH_2$

$\Delta H^\circ = -20.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.06 \pm 0.38) \times 10^{-12}$	298 ± 2	Notario et al., 2000	PLP-RF (a)
$(2.93 \pm 0.29) \times 10^{-12}$	298 ± 2	Albaladejo et al., 2003	PLP-RF (b)
Relative Rate Coefficients			
$(2.3 \pm 0.2) \times 10^{-12}$	295 ± 2	Wallington et al., 1990	RR (c)
$(1.7 \pm 0.3) \times 10^{-12}$	294 ± 1	Olsson et al., 1997	RR (d)
$3.1 \times 10^{-11} \exp[(815 \pm 150)/T]$	215–298	Orlando et al., 2000	RR (e)
$(2.0 \pm 0.3) \times 10^{-12}$	298		
$(2.07 \pm 0.12) \times 10^{-12}$	296	Christensen et al., 2000	RR (f)
$(2.25 \pm 0.08) \times 10^{-12}$	296	Christensen et al., 2000	RR (g)
$(2.15 \pm 0.04) \times 10^{-12}$	296	Christensen et al., 2000	RR (h)
$(2.22 \pm 0.14) \times 10^{-12}$	296	Christensen et al., 2000	RR (i)
$(2.00 \pm 0.09) \times 10^{-12}$	298	Sellevåg and Nielsen, 2003	RR (j)
$(2.12 \pm 0.05) \times 10^{-12}$	298	Carr et al., 2003	RR (k)

Comments

(a) Experiments carried out at pressures of 15 or 60 Torr (20 or 80 mbar) He using the 355 nm photolysis of Cl_2 as Cl-atom source. Addition of 0.4 Torr (0.53 mbar) O_2 (to scavenge organic radicals and prevent secondary formation of Cl) resulted in similar rate coefficients.

(b) Experiments carried out at pressures of 26.7, 80 and 267 mbar He using the 308 nm photolysis of Cl_2 as Cl-atom source.

(c) Cl atoms were generated by the photolysis of Cl_2-air (or N_2)-$CH_3C(O)CH_3$-C_2H_5Cl mixtures. From the relative decays of CH_3COCH_3 and C_2H_5Cl, a rate coefficient ratio of $k(Cl+CH_3C(O)CH_3)/k(Cl+C_2H_5Cl)=0.295\pm0.015$ was obtained. Absolute rate coefficient obtained using $k(Cl + C_2H_5Cl) = 7.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Wine et al, 1983; Bryukov et al., 2003).

(d) Cl atoms were generated by pulsed laser photolysis of Cl_2 at 355 nm followed by competition between the reactions $Cl+CH_3C(O)CH_3$ and $Cl+ClONO_2 \rightarrow Cl_2+NO_3$. The formation of NO_3 with and without acetone in the reaction mixture was monitored by TDLS at 661.8 nm. The value recommended in Yokelson et al. (1995) for the value of the rate constant of the reference reaction ($Cl+ClONO_2$) was used.

(e) Cl atoms were generated by the photolysis of Cl_2-$CH_3C(O)CH_3$-CH_2Cl_2 mixtures. From the relative decays of $CH_3C(O)CH_3$ and CH_2Cl_2, temperature dependent rate coefficient ratios of $k(Cl+CH_3C(O)CH_3)/k(Cl+CH_2Cl_2)=5.39$ (298 K), 5.83 (267 K), 6.26 (251 K), 6.69 (240 K), 7.21 (225 K) and 7.72 (215 K) were derived. These ratios were placed on an absolute basis using $k(Cl+CH_2Cl_2)=1.5\times10^{-11}\exp(-1100/T)$ cm^3 molecule^{-1} s^{-1} (Orlando, 1999).

(f) Cl atoms were generated by the broad band photolysis of Cl_2 in $O_2 + N_2$ at 933 mbar. Consumption of $CH_3C(O)CH_3$ measured relative to C_2H_5F to derive $k(Cl + CH_3C(O)CH_3) / k(Cl + C_2H_5F) = 0.288 \pm 0.017$. Rate coefficient in table calculated using $k(Cl + C_2H_5F) = 7.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2005).

(g) Cl atoms were generated by the broad band photolysis of Cl_2 in $O_2 + N_2$ at 933 mbar. Consumption of $CH_3C(O)CH_3$ measured relative to CH_3Cl to derive $k(Cl + CH_3C(O)CH_3) / k(Cl + CH_3Cl) = 4.69 \pm 0.16$. Rate coefficient in table calculated using $k(Cl + CH_3Cl) = 4.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2005).

(h) Cl atoms were generated by the broad band photolysis of Cl_2 in O_2 + N_2 at 933 mbar. Consumption of $CH_3C(O)CH_3$ measured relative to CH_3F to derive k(Cl + $CH_3C(O)CH_3$) / k(Cl + CH_3F) = 6.15 ± 0.26. Rate coefficient in table calculated using k(Cl + CH_3F) = 3.5×10^{-13} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2005).

(i) Cl atoms were generated by the broad band photolysis of Cl_2 in O_2 + N_2 at 933 mbar. Consumption of $CH_3C(O)CH_3$ measured relative to C_2H_5Cl to derive k(Cl + $CH_3C(O)CH_3$) / k(Cl + C_2H_5Cl) = 0.284 ± 0.018. Rate coefficient in table calculated using k(Cl + C_2H_5Cl) = 7.8×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Wine et al, 1983; Bryukov et al., 2003).

(j) Broad band photolysis (370 nm) of Cl_2 in presence of $CH_3C(O)CH_3$ and CH_2ClCH_2Cl. Relative decay rates of $CH_3C(O)CH_3$ and CH_2ClCH_2Cl measured using FTIR. Value of k(Cl + $CH_3C(O)CH_3$) / k(Cl + CH_2ClCH_2Cl) = 1.54 ± 0.06 was placed on an absolute basis using k(Cl + CH_2ClCH_2Cl) = 1.3×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Wallington et al., 1996).

(k) Cl atoms were generated by the broad band photolysis of Cl_2 in air or N_2 at 973–1013 mbar. Consumption of $CH_3C(O)CH_3$ measured relative to CH_3Cl to derive k(Cl + $CH_3C(O)CH_3$) / k(Cl + CH_3Cl) = 4.42 ± 0.11. Rate coefficient in table calculated using k(Cl + CH_3Cl) = 4.8×10^{-13} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2005).

Preferred Values

$k = 2.1 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k = 3.2 \times 10^{-11} \exp(-815/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 215-300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

Because of the potential for errors in the experimental technique of Olsson et al. (1997) (the assumption that Cl atoms only react with $ClONO_2$ and acetone, the need for absolute concentration measurements of acetone and the experimental approach of sequential experiments in the presence and absence of acetone) these data are not considered when making the recommendation. For room temperature, an average of all the relative rate coefficients is taken, as these show excellent agreement despite use of several different reference reactants. The temperature dependent expression adopts the value of E/R = 815 K from Orlando et al. (2000) with expanded error limits. The pre-exponential factor has been adjusted to yield the recommended rate coefficient at 298 K.

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II.A7.177

$Cl + CH_3C(O)CH_2CH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.24 \pm 0.38) \times 10^{-11}$	298 ± 2	Notario et al., 2000	LP-RF (a)
$(3.30 \pm 0.20) \times 10^{-11}$	298	Albaladejo et al., 2003	PLP-RF (b)
Relative Rate Coefficients			
$(4.28 \pm 0.59) \times 10^{-11}$	295	Wallington et al., 1990	RR (c)

Comments

(a) Experiments carried out at pressures of 15 or 60 Torr (20 or 80 mbar) He using the 355 nm photolysis of Cl_2 as Cl-atom source. Addition of 0.4 Torr (0.53 mbar) O_2 (to scavenge organic radicals and prevent secondary formation of Cl) resulted in similar rate coefficients.

(b) Cl generated in the 308 nm photolysis of Cl_2. Addition of 2×10^{16} molecule cm^{-3} of O_2 (scavenger of organic radicals) had no influence on the Cl decay kinetics.

(c) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-N_2-$CH_3C(O)C_2H_5$-C_2H_6 mixtures at 930 mbar (700 Torr) total pressure, and the $CH_3C(O)C_2H_5$ and C_2H_6 concentrations monitored by FTIR absorption spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2005).

Preferred Values

$k = 3.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

Comments on Preferred Values

The preferred value is an average result from the studies of Wallington et al. (1990), Notario et al. (2000) and Albaladejo et al. (2003). This result is supported by the value of $k=(3.8\pm0.3)\times10^{-11}$ cm^3 molecule^{-1} s $^{-1}$ quoted in Niki et al. (1987) as unpublished results from that laboratory.

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II.A7.178

$Cl + CH_3OH \rightarrow HCl + CH_2OH$

$\Delta H^\circ = -29.8$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.33 \pm 0.70) \times 10^{-11}$	200–500	Michael et al., 1979	FP-RF
$(5.1 \pm 1.0) \times 10^{-11}$	298	Payne et al., 1988	DF-MS (a)
$(6.14 \pm 0.67) \times 10^{-11}$	298 ± 2	Dóbé et al., 1993	DF-EPR
$(5.1 \pm 0.4) \times 10^{-11}$	295 ± 2	Tyndall et al., 1999	PLP-RF
Relative Rate Coefficients			
$(4.73 \pm 0.42) \times 10^{-11}$	295 ± 2	Wallington et al., 1988	RR (b)
$(5.0 \pm 0.34) \times 10^{-11}$	298 ± 2	Nelson et al., 1990	RR (c)
$(5.5 \pm 0.6) \times 10^{-11}$	295	Tyndall et al., 1999	RR (d)

Comments

(a) Reaction between Cl and CH_3OD was studied.

(b) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-CH_3OH-C_2H_6-air (N_2) mixtures at 1 bar total pressure. Concentrations of CH_3OH and C_2H_6 were monitored by GC and a rate coefficient ratio $k(Cl+CH_3OH)/k(Cl+C_2H_6)=0.802\pm0.071$ determined. This rate coefficient ratio is placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(c) Cl atoms were generated from the photolysis of Cl_2 or $C(O)Cl_2$ in Cl_2 (or $C(O)Cl_2$)-N_2 (or O_2)-CH_3OH-cyclohexane mixtures at 1 bar pressure. Concentrations of CH_3OH and cyclohexane were measured by GC, and the rate coefficient ratio is placed on an absolute basis by use of k(Cl+cyclohexane)/k(Cl+n-butane)=1.59 (Aschmann and Atkinson, 1995) and k(Cl+n-butane)$=2.05\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(d) Broad band irradiation of Cl_2 as source of Cl atoms. Experiments were carried out in 700 Torr N_2, with analysis of CH_3OH and reference compound (C_2H_6 and C_2H_4) with FTIR. $k(Cl+CH_3OH)/k(Cl+C_2H_6)=0.94\pm0.04$, $k(Cl+CH_3OH)/k(Cl+C_2H_4)=0.63\pm0.03$. The data have been place on an absolute basis using $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

Preferred Values

$k = 5.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–500 K.

Reliability

$\Delta \log k = \pm 0.07$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred 298 K value is the unweighted average of the absolute rate coefficients of Michael et al. (1979), Payne et al. (1988), Dóbé et al. (1993) and Tyndall et al. (1999), and the relative rate studies of Nelson et al. (1990) and Tyndall et al. (1999). The inclusion of the data of Payne et al. (1988) on Cl+CH_3OD is justified considering the strong body of evidence showing that the H-abstraction proceeds solely at the CH_2-group at room temperature (see Payne et al., 1988, Radford et al., 1981, Meier et al., 1984, Dóbé et al., 1994 and Jodkowski et al., 1998). The relative rate study of Wallington et al. (1988) has been superseded by a more recent study from the same group (Tyndall et al., 1999) and is not used in the evaluation. The zero temperature dependence is taken from the study of Michael et al. (1979) and is supported by time resolved measurement of relative HO_2 and CH_3O_2 concentrations formed in the photolysis of Cl_2 in the presence of CH_4 and CH_3OH and O_2 (Lightfoot et al., 1990).

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II.A7.179

$$\mathbf{Cl + CH_3CH_2OH \rightarrow HCl + CH_3CHOH \quad (1)}$$
$$\mathbf{Cl + CH_3CH_2OH \rightarrow HCl + CH_2CH_2OH \quad (2)}$$

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.4 \pm 1.4) \times 10^{-11} \exp[(45 \pm 32)/T]$	295–600	Taatjes et al., 1999	LP-IR (a)
$(1.09 \pm 0.9) \times 10^{-10}$	295		
Relative Rate Coefficients			
$(8.75 \pm 0.95) \times 10^{-11}$	295 ± 2	Wallington et al., 1988	RR (b)
$(1.06 \pm 0.06) \times 10^{-10}$	298 ± 2	Nelson et al., 1990	RR (c)
$(8.3 \pm 1.8) \times 10^{-11}$	295	Edelbüttel-Einhaus et al., 1992	RR (d)
$(9.4 \pm 0.8) \times 10^{-11}$	296 ± 2	Taatjes et al., 1999	RR (e)
Branching Ratios			
k_2/k_1 = 0.28 exp (-350/T)	295-600	Taatjes et al., 1999	(e)
k_1/k = 0.92	295		
k_2/k = 0.08	295		

Comments

(a) Cl atoms were generated by the 193 nm pulsed photolysis of CF_2Cl_2 or $CFCl_3$, and kinetic parameters were obtained by analysis of HCl product formation profiles using transient IR absorption spectroscopy. Bath gas was 10 Torr CO_2 to quench vibrationally excited HCl. Use of deuterated ethanol enabled site specific rate coefficients to be determined via measurement of HCl yields. Complementary FTIR product analysis confirmed the result.

(b) Cl atoms were generated by photolysis of Cl_2 in Cl_2-C_2H_5OH-C_2H_6-air (or N_2) mixtures at 1 bar total pressure. C_2H_5OH and C_2H_6 were monitored by GC and a rate coefficient ratio $k(Cl+C_2H_5OH)/k(Cl+C_2H_6)=1.483\pm0.160$ determined. Placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(c) Cl atoms were generated by photolysis of Cl_2 or $C(O)Cl_2$ in Cl_2 (or $C(O)Cl_2$)-N_2 (or O_2)-ethanol-cyclohexane mixtures at 1 bar pressure. Concentrations of ethanol and cyclohexane were measured by GC, and the rate coefficient ratio is placed on an absolute basis by use of k(Cl + cyclohexane)/ k(Cl + n-butane)=1.59 (Aschmann and Atkinson, 1995) and k(Cl + n-butane)=2.05×10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(d) Isothermal discharge flow reactor at 1 mbar pressure, with molecular beam sampling and analysis by mass spectrometry. $k/k(Cl+C_2H_6)$ measured to be 1.4±0.3. Placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation). Supersedes earlier value reported from same laboratory (Khatoon et al., 1989)

(e) Cl atoms were generated by the photolysis of Cl_2 in O_2 or N_2 bath gas. Loss of C_2H_5OH was measured relative to C_2H_6 using *in-situ* FTIR absorption spectroscopy. $k(Cl+C_2H_5OH)/k(Cl+C_2H_6)$ was measured to be 1.6±0.13 and is placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^{-3} molecule^{-1} s^{-1} (IUPAC, this evaluation). The branching ratios were derived by product analysis.

Preferred Values

$k = 1.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 8.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 0.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.6 \times 10^{-11} \exp(45/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 295–600 K.
k_2/k_1 = 0.28 exp(-350/T)

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the single absolute rate measurement of Taatjes et al. (1999) and the relative rate studies of Wallington et al. (1988), Nelson et al. (1990), Edelbüttel-Einhaus et al. (1992) and Taatjes et al. (1999), which are in good agreement. The slight temperature dependence is taken from Taatjes et al. (1999) as are temperature dependent values for the branching ratios for k_1 and k_2.

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II.A7.180

$$\begin{aligned} \mathbf{Cl + \textit{n}\text{-}C_3H_7OH} &\rightarrow \mathbf{CH_3CH_2CHOH + HCl} \quad \mathbf{(1)} \\ &\rightarrow \mathbf{CH_3CHCH_2OH + HCl} \quad \mathbf{(2)} \\ &\rightarrow \mathbf{CH_2CH_2CH_2OH + HCl} \quad \mathbf{(3)} \end{aligned}$$

Rate coefficient data (k=k_1+k_2+k_3)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.49 \pm 0.12) \times 10^{-10}$	295 ± 2	Wallington et al., 1988	RR (a)
$(1.53 \pm 0.07) \times 10^{-10}$	298 ± 2	Nelson et al., 1990	RR (b)
2.68×10^{-10} exp[-(128 ± 20)/T]	273–342	Cheema et al., 2002	RR (c)
$(1.69 \pm 0.20) \times 10^{-10}$	298		
Branching Ratios			
k_1/k = 0.56	298	Cheema et al., 2002	RR (c)
k_2/k = 0.30	298		
k_3/k = 0.14	298		

Comments

(a) Cl atoms were generated by photolysis of Cl_2 in Cl_2-n-C_3H_7OH-C_2H_6-air (or N_2) mixtures at 990 mbar (740 Torr) total pressure. n-C_3H_7OH and C_2H_6 were monitored by GC and a rate coefficient ratio k(Cl+n-C_3H_7OH)/k(Cl+C_2H_6)=2.518±0.202 determined. Placed on an absolute basis by use of k(Cl+C_2H_6)=5.9×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(b) Cl atoms were generated by the photolysis of Cl_2 or $C(O)Cl_2$ in Cl_2 (or $C(O)Cl_2$)-N_2 (or O_2)-n-propanol-cyclohexane mixtures at 1 bar pressure. Decay rates of n-propanol and cyclohexane were measured by GC, and the rate coefficient ratio placed on an absolute basis by use of k(Cl+cyclohexane)/k(Cl+n-butane)=1.59 (Aschmann and Atkinson, 1995) and k(Cl+n-butane)=2.05×10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(c) The reaction was initiated in 100, 250 or 1000 cm^3 Pyrex vessels by photolysis of Cl_2 in presence of O_2, NO, n-C_3H_7OH-C_2H_6 and N_2 mixtures at 700 Torr total pressure. n-C_3H_7OH and C_2H_6 were monitored by GC and rate coefficient ratios k(Cl+n-C_3H_7OH)/k(Cl+C_2H_6) determined at temperatures between 273 and 342 K. Placed on an absolute basis by use of k(Cl+C_2H_6)=8.3×10^{-11} exp(-100/T) cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation). Product analysis in separate FTIR experiments combined with an assumed reaction scheme to give branching ratios.

Preferred Values

$k = 1.6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.5 \times 10^{-10}$ exp(-130/T) cm^3 molecule^{-1} s^{-1} over the temperature range 270–350 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the data of Wallington et al. (1988), Nelson et al. (1990) and Cheema et al. (2002). The temperature dependence is taken from the single study (Cheema et al., 2002) that varied the temperature. The branching ratios are expected to be approximately independent of temperature over the atmospheric temperature range, but until this is confirmed, we make no recommendation.

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II.A7.181

$Cl + i\text{-}C_3H_7OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(8.80 \pm 0.35) \times 10^{-11}$	298 ± 2	Nelson et al., 1990	RR (a)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 or $C(O)Cl_2$ in isopropyl alcohol-cyclohexane-O_2 (or N_2) mixtures at 1 bar pressure. The decay rates of isopropyl alcohol and cyclohexane were measured, and rate coefficient ratio placed on an absolute basis by use of k(Cl + cyclohexane)/k(Cl+n-butane)=1.59 (Aschmann and Atkinson, 1995) and k(Cl+n-butane)=2.05×10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

Preferred Values

$k = 8.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

Comments on Preferred Values

Based on the sole study of Nelson et al. (1990).

References

Aschmann, S. M. and Atkinson, R.: Int. J. Chem. Kinet., 27, 613, 1995.
Nelson, L., Rattigan, O., Neavyn, R., Sidebottom, H., Treacy, J., and Nielsen, O. J.: Int. J. Chem. Kinet., 22, 1111, 1990.

II.A7.182

$$\mathbf{Cl + CH_3OOH \rightarrow HCl + CH_3O_2 \quad (1)}$$
$$\mathbf{\rightarrow HCl + CH_2OOH \quad (2)}$$

$\Delta H°(1) = -74$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(5.9 \pm 0.3) \times 10^{-11}$	295 ± 2	Wallington et al., 1990	RR (a)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-N_2-CH_3OOH-C_2H_6 mixtures at 930 mbar (700 Torr) total pressure, and the CH_3OOH and C_2H_6 concentrations monitored by FTIR absorption spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

Preferred Values

$k = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The sole study carried out to date is that of Wallington et al. (1990). The reaction may occur by the two pathways listed and the formation of HO radicals via decomposition of CH_2OOH may have led to secondary reactions involving HO radicals. Since the room temperature rate coefficient for the Cl atom reaction with H_2O_2 is two orders of magnitude lower than that for Cl+CH_3OOH (IUPAC, current recommendation), it is expected that channel (2) will dominate. Wallington et al. (1990) concluded that secondary reactions involving HO radicals did not contribute >15% to the observed CH_3OOH consumption. The cited uncertainty limits on the preferred values reflect this possibility.

References

IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/.
Wallington, T. J., Andino, J. M., Ball, J. C., and Japar, S. M.: J. Atmos. Chem., 10, 301, 1990.

II.A7.183

$$\begin{aligned} \mathbf{Cl + HC(O)OH} &\rightarrow \mathbf{HCl + HCO_2} \quad \mathbf{(1)} \\ &\rightarrow \mathbf{HCl + HOCO} \quad \mathbf{(2)} \end{aligned}$$

$\Delta H^\circ(2) = -52$ kJ·mol^{-1}

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.83 \pm 0.12) \times 10^{-13}$	295 ± 2	Li et al., 2000	FP-IR (a)
Relative Rate Coefficients			
$(2.15 \pm 0.12) \times 10^{-13}$	295 ± 2	Wallington et al., 1990	RR (b,c)
$(1.83 \pm 0.10) \times 10^{-13}$	295 ± 2	Wallington et al., 1990	RR (b,d)

Comments

(a) Cl-atoms made in the flash photolysis of Cl_2 in He at 10 Torr. O_2 was added to convert HOCO to CO_2, which was monitored by transient IR absorption spectroscopy to obtain kinetic data. A small correction (<10%) was applied to take HC(O)OH dimerisation into account.

(b) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-air-HC(O)OH-CH_3Cl (or CH_4) mixtures at 930 mbar (700 Torr) total pressure. HC(O)OH and CH_3Cl (or CH_4) were monitored by FTIR absorption spectroscopy during the experiments.

(c) Relative to k(Cl+CH_3Cl). Placed on an absolute basis by use of k(Cl+CH_3Cl)=4.9×10^{-13} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(d) Relative to k(Cl+CH_4). Placed on an absolute basis by use of k(Cl+CH_4)=9.9×10^{-14} cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

Preferred Values

$k = 1.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the absolute rate coefficient of Li et al. (2000) and the relative rate coefficients obtained by Wallington et al. (1990).

Tyndall et al. (1991) have observed that CO_2 is the sole carbon-containing product formed from this reaction in air or N_2 diluent, and conclude from comparison of the rate coefficients for the reactions of the Cl atom with HC(O)OH, $CH_3C(O)OH$ (Koch and Moortgat, 1990) and $CD_3C(O)OH$ (Koch and Moortgat, 1990) that reaction channel (2) dominates.

References

IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/.
Koch, S. and Moortgat, G. K.: Chem. Phys. Lett., 173, 531, 1990.
Li, Q., Osbourne, M. C., and Smith, I. W. M.: Int. J. Chem. Kinet., 32, 85, 2000.
Tyndall, G. S., Wallington, T. J., and Potts, A. R.: Chem. Phys. Lett., 186, 149, 1991.
Wallington, T. J., Andino, J. M., Ball, J. C., and Japar, S. M.: J. Atmos. Chem., 10, 301, 1990.

II.A7.184

$$\begin{aligned} \mathbf{Cl + CH_3C(O)OH} \quad &\rightarrow \mathbf{HCl + CH_2C(O)OH} \quad &\mathbf{(1)} \\ &\rightarrow \mathbf{HCl + CH_3C(O)O} \quad &\mathbf{(2)} \end{aligned}$$

$\Delta H^\circ(2) = 11\ \mathrm{kJ\cdot mol^{-1}}$

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.8 \pm 0.4) \times 10^{-14}$	298 ± 1	Koch and Moortgat, 1990	RR (a)
$(2.5 \pm 0.3) \times 10^{-14}$	295 ± 1	Crawford et al., 1999	RR (b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-$CH_3C(O)OH$-CH_4-N_2 mixtures at 1 bar total pressure. The concentrations of $CH_3C(O)OH$ and CH_4 were measured by IR absorption spectroscopy. The rate coefficient ratio $k(Cl+CH_3C(O)OH)/k(Cl+CH_4)=0.28\pm0.04$ is placed on an absolute basis by use of $k(Cl+CH_4)=1.0\times10^{-13}$ cm^3 molecule^{-1} s $^{-1}$(IUPAC, 2005). An analogous experiment using $CD_3C(O)OH$ yielded a rate coefficient of $k(Cl+CD_3C(O)OH)=(7.5\pm0.2)\times10^{-15}$ cm^3 molecule^{-1} s^{-1}, indicating that the reaction proceeds mainly by channel (1).

(b) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-$CH_3C(O)OH$-CH_4 mixtures in N_2 or air at 933 mbar total pressure. The concentrations of $CH_3C(O)OH$ and CH_4 were measured by IR absorption spectroscopy. The rate coefficient ratio $k(Cl + CH_3C(O)OH) / k(Cl + CH_4) = 0.25 \pm 0.03$ is placed on an absolute basis by use of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2005).

Preferred Values

$k = 2.65 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient an average of the similar studies of Koch and Moortgat (1990) and Crawford et al. (1999). The measured rate coefficient ratio of $k(Cl + CH_3C(O)OH)/k(Cl + CD_3C(O)OH) = 3.7$ at 298 ± 1 K indicates that channel (1) dominates at 298 K (Koch and Moortgat, 1990).

References

Crawford, M. A., Wallington, T. J., Szente, J. J., Maricq, M. M. and Francisco, J. S.: J. Phys. Chem. A 103, 365, 1999.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2005.
Koch, S. and Moortgat, G. K.: Chem. Phys. Lett., 173, 531, 1990.

II.A7.185

Cl + CH_3ONO_2 → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.42 \pm 0.02) \times 10^{-13}$	298 ± 2	Nielsen et al., 1991	RR (a)
$(2.40 \pm 0.20) \times 10^{-13}$	295 ± 2	Sokolov et al., 1999	RR (b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-CH_3ONO_2-C_2H_6-N_2 mixtures at 1 bar pressure. Concentrations of methyl nitrate and ethane were measured by GC and the rate coefficient ratio is placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(b) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-CH_3ONO_2-CH_3Cl or Cl_2-CH_3ONO_2-CH_4 mixtures at 700 Torr pressure of N_2. Concentrations of methyl nitrate and the reference compounds measured in situ using FTIR. Relative rates were $k(Cl+CH_3ONO_2)/k(Cl+CH_3Cl)=0.50\pm0.04$ and $k(Cl+CH_3ONO_2)/k(Cl+CH_4)=2.36\pm0.15$. The rate coefficient ratios were placed on an absolute basis by use of $k(Cl+CH_3Cl)=4.8\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation) and $k(Cl+CH_4)=9.9\times10^{-14}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation) and averaged to give the final number.

Preferred Values

$k = 2.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

Comments on Preferred Values

Based on the relative rate studies of Nielsen et al. (1991) and Sokolov et al. (1999). The reaction probably occurs via H-atom abstraction from the -CH_3 group (Nielsen et al., 1991).

References

IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/.
Nielsen, O. J., Sidebottom, H. W., Donlon, M., and Treacy, J.: Chem. Phys. Lett., 178, 163 1991.
Sokolov, O., Hurley, M. D., Ball, J. C., Wallington, T. J., Nelsen, W., Barnes, I., and Becker, K. H.: Int. J. Chem. Kinet., 31, 357, 1999.

II.A7.186

Cl + $C_2H_5ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(5.5 \pm 0.8) \times 10^{-12}$	295 ± 2	Wallington et al., 1990a	RR (a)
$(3.95 \pm 0.15) \times 10^{-12}$	298 ± 2	Nielsen et al., 1991	RR (b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-ethyl nitrate-C_2H_5Cl-air mixtures at 1 bar pressure. Ethyl nitrate and C_2H_5Cl were measured by GC, and a rate coefficient ratio of k(Cl + ethyl nitrate)/$k(Cl+C_2H_5Cl)=0.46\pm0.03$ determined. Combined with $k(Cl+C_2H_5Cl)/k(Cl+C_2H_6)=0.201\pm0.027$ (Wallington et al., 1990b) and $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation), the rate coefficient cited in the table is obtained.

(b) Cl atoms were generated by the photolysis of Cl_2-ethyl nitrate-C_2H_6-N_2 mixtures at atmospheric pressure. Concentrations of ethyl nitrate and ethane were measured by GC and the rate coefficient ratio placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

Preferred Values

$k = 4.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the data of Wallington et al. (1990a) and Nielsen et al. (1991). The reaction probably proceeds by H atom abstraction from the C-H bonds (Nielsen et al., 1991).

References

Nielsen, O. J., Sidebottom, H. W., Donlon, M., and Treacy, J.: Chem. Phys. Lett., 178, 163, 1991.
Wallington, T. J., Hinman, M. M., Andino, J. M., Siegl, W. O., and Japar, S. M.: Int. J. Chem. Kinet., 22, 665, 1990a.
Wallington, T. J., Andino, J. M., Ball, J. C., and Japar, S. M.: J. Atmos. Chem., 10, 301, 1990b.

II.A7.187

Cl + n-$C_3H_7ONO_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.1 \pm 0.13) \times 10^{-11}$	295 ± 2	Wallington et al., 1990a	RR (a)
$(2.28 \pm 0.14) \times 10^{-11}$	298 ± 2	Nielsen et al., 1991	RR (b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-n-propyl nitrate-C_2H_5Cl-air mixtures at 1 bar pressure. n-Propyl nitrate and C_2H_5Cl concentrations were measured by GC and a rate coefficient ratio of k(Cl+n-propyl nitrate)/k(Cl+C_2H_5Cl)=2.67±0.16 determined. Rate coefficient in table calculated using k(Cl + C_2H_5Cl) = 7.8×10^{-12} cm^3 molecule^{-1} s^{-1} (Wine et al, 1983; Bryukov et al., 2003).

(b) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-n-propyl nitrate-C_2H_6-N_2 mixtures at 1 bar pressure. Concentrations of n-propyl nitrate and C_2H_6 were measured by GC, and the rate coefficient ratio is placed on an absolute basis by use of k(Cl+C_2H_6)=5.9×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2005).

Preferred Values

$k = 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the data of Wallington et al. (1990a) and Nielsen et al. (1991). The reaction probably proceeds by H-atom abstraction from the C-H bonds (Nielsen et al., 1991).

References

Bryukov, M. G., Slagle, I. R., and Knyazev, V. D.: J. Phys. Chem. A 107, 6565, 2003.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2005.
Nielsen, O. J., Sidebottom, H. W., Donlon, M., and Treacy, J.: Chem. Phys. Lett., 178, 163, 1991.
Wallington, T. J., Hinman, M. M., Andino, J. M., Siegl, W. O., and Japar, S. M.: Int. J. Chem. Kinet., 22, 665, 1990a.
Wallington, T. J., Andino, J. M., Ball, J. C., and Japar, S. M.: J. Atmos. Chem., 10, 301, 1990b.
Wine, P. H., and Semmes, D. H.: J. Phys. Chem. 87, 3572, 1983.

II.A7.188

$Cl + i\text{-}C_3H_7ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(3.8 \pm 0.5) \times 10^{-12}$	295 ± 2	Wallington et al., 1990	RR (a)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-isopropyl nitrate-C_2H_5Cl-air mixtures at 1 bar pressure. Concentrations of isopropyl nitrate and C_2H_5Cl were measured by GC, and a rate coefficient ratio of k(Cl+isopropyl nitrate)/k(Cl+C_2H_5Cl)=0.49±0.06 determined. Rate coefficient in table calculated using $k(Cl + C_2H_5Cl) = 7.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Wine et al., 1983; Bryukov et al., 2003).

Preferred Values

$k = 3.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the sole study of Wallington et al. (1990).

References

Bryukov, M. G., Slagle, I. R. and Knyazev, V. D.: J. Phys. Chem. A 107, 6565, 2003.
Wallington, T. J., Hinman, M. M., Andino, J. M., Siegl, W. O. and Japar, S. M.: Int. J. Chem. Kinet., 22, 665, 1990.
Wine, P. H. and Semmes, D. H.: J. Phys. Chem. 87, 3572, 1983.

II.A7.189

$Cl + n\text{-}C_4H_9ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(8.54 \pm 0.20) \times 10^{-11}$	298	Nielsen et al., 1991	RR (a)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-n-butyl nitrate-C_2H_6-N_2 mixtures at 1 bar pressure. Concentrations of n-butyl nitrate and C_2H_6 were measured by GC, and the rate coefficient ratio placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

Preferred Values

$k = 8.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

Based on the sole study of Nielsen et al. (1991), with expanded uncertainty limits.

References

Nielsen, O. J., Sidebottom, H. W., Donlon, M., and Treacy, J.: Chem. Phys. Lett., 178, 163, 1991.

II.A7.190

$Cl + CH_3C(O)OONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.7 \pm 1.7) \times 10^{-13}$	298	Tsalkani et al., 1988	DF-EPR
Relative Rate Coefficients			
$<7 \times 10^{-15}$	295 ± 2	Wallington et al., 1990	RR (a)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-air-$CH_3C(O)OONO_2$-CH_4 mixtures at 930 mbar (700 Torr) total pressure, with the $CH_3C(O)OONO_2$ and CH_4 concentrations being monitored by FTIR absorption spectroscopy. Upper limit to relative rate coefficient ratio placed on an absolute basis by use of $k(Cl+CH_4)=9.9\times10^{-14}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

Preferred Values

$k < 2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based on the relative rate coefficient measurement of Wallington et al. (1990), in which no reaction of $CH_3C(O)OONO_2$ was observed in the presence of Cl atoms. In both the relative rate study of Wallington et al. (1990) and the absolute rate study of Tsalkani et al. (1988), the major impurity in the $CH_3C(O)OONO_2$ samples would be the C_{12} or C_{13} alkane solvent, respectively. While this was of no consequence in the relative rate study of Wallington et al. (1990), the presence of ∼0.1% tridecane in the $CH_3C(O)OONO_2$ sample used by Tsalkani et al. (1988) could account for the Cl reaction rate observed; their $CH_3C(O)OONO_2$ sample was >99% pure from IR measurements. The upper limit cited here is a factor of ∼3 higher than measured by Wallington et al. (1990) to allow for greater uncertainties.

References

Tsalkani, N., Mellouki, A., Poulet, G., Toupance, G., and Le Bras, G.: J. Atmos. Chem., 7, 409, 1988.
Wallington, T. J., Andino, J. M., Ball, J. C., and Japar, S. M.: J. Atmos. Chem., 10, 301, 1990.

II.A7.191

$Cl + CH_3CN \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 2.0 \times 10^{-15}$	298	Kurylo and Knable, 1984	FP-RF
3.46×10^{-11} exp[-(2785 ± 115)/T]	478–723	Poulet et al., 1984	DF-MS (a)
$(8.89 \pm 1.24) \times 10^{-15}$	295		
$(1.24 \pm 0.20) \times 10^{-14}$	296	Tyndall et al., 1996	PLP-RF
Relative Rate Coefficients			
7.2×10^{-12} exp(-2200/T)	370–413	Olbregts et al., 1984	RR (b)
1.7×10^{-11} exp[-(2140 ± 200)/T]	274–345	Tyndall et al., 1996	RR (c)
$(1.22 \pm 0.15) \times 10^{-14}$	296		

Comments

(a) Data were obtained over the range 295 K to 723 K, and a curved Arrhenius plot was observed.

(b) Relative formation rates of products were monitored in a competitive chlorination system between CH_3CN and $CHCl_3$. Placed on an absolute basis by use of $k(Cl+CHCl_3)=4.9\times10^{-12}$ exp(-1240/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(c) Relative decay rates of CH_3CN and the reference gas were monitored by FTIR. For the temperature dependent study the reference compound was CH_4. In a completely independent system, relative values at 296 K were also derived using as the reference compound CD_4, CF_3CCl_2H or CH_4. Based on three independent determinations by both absolute and relative rate methods the authors derived the value $k=(1.15\pm 0.20)\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 296 K and the Arrhenius expression $k=1.6\times10^{-11}$ exp[-(2140±200)/T] cm^3 molecule^{-1} s^{-1} over the temperature range 274–345 K.

Preferred Values

$k = 1.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.6 \times 10^{-11}$ exp(-2140/T) cm^3 molecule^{-1} s^{-1} over the temperature range 270–350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values are based on the results reported by Tyndall et al. (1996). The results of this study over a wide range of experimental conditions, using both relative and absolute rate methods, are preferred over results of earlier studies by Kurylo and Knable (1984), Poulet et al. (1984) and Olbregts et al. (1984). In the study of Tyndall et al. (1996), the room temperature rate coefficient was found to be independent of pressure over the range 7 mbar to 930 mbar (5 Torr to 700 Torr). Analysis of end products in smog-chamber experiments indicate that the reaction proceeds predominantly if not exclusively by H-abstraction (Tyndall et al., 1996, 2001). The atmospheric fate of the resultant CH_2CN radical is discussed by Tyndall et al. (2001).

References

IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/.
Kurylo, M. J. and Knable, G. L.: J. Phys. Chem., 88, 3305, 1984.
Olbregts, J., Brasseur, G., and Arijs, E.: J. Photochem., 24, 315, 1984.
Poulet, G., Laverdet, G., Jourdain, J. L., and Le Bras, G.: J. Phys. Chem., 88, 6259, 1984.
Tyndall, G. S., Orlando, J. J., Wallington, T. J., Sehested, J., and Nielsen, O. J.: J. Phys. Chem., 100, 660, 1996.
Tyndall, G. S., Orlando, J. J., Wallington, T. J., and Hurley, M. D.: J. Phys. Chem. A, 105, 5380, 2001.

II.A7.192

$Br + C_2H_2 + M \rightarrow BrC_2H_2 + M$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.0 \pm 0.8) \times 10^{-15}$	210–393	Payne et al., 1986	FP-RF (a)
Relative Rate Coefficients			
$(4.5 \pm 0.9) \times 10^{-15}$	295	Wallington et al., 1989	RR (b)
$(3.90 \pm 0.16) \times 10^{-14}$ (1013 mbar air)	298	Barnes et al., 1989	RR (c)
$(4.93 \pm 0.20) \times 10^{-14}$ (1013 mbar air)	298		RR (d)
$(3.51 \pm 0.18) \times 10^{-14}$ (1013 mbar air)	313		
$(2.44 \pm 0.10) \times 10^{-14}$ (1013 mbar air)	333		
$(1.78 \pm 0.06) \times 10^{-14}$ (1013 mbar air)	353		
$(3.94 \pm 0.28) \times 10^{-14}$ (940 mbar air)	239	Ramacher et al., 2001	RR (e)
$(3.59 \pm 0.25) \times 10^{-14}$ (940 mbar air)	249		
$(3.72 \pm 0.26) \times 10^{-14}$ (940 mbar air)	261		
$(3.24 \pm 0.23) \times 10^{-14}$ (940 mbar air)	280		
$(2.55 \pm 0.18) \times 10^{-14}$ (940 mbar air)	296		

Comments

(a) Flash photolysis of CH_3Br ($\lambda > 195$ nm) as Br source. Rate coefficient was independent of pressure between 20 and 133 mbar Ar.

(b) CW photolysis of Br_2 in the presence of C_2H_2 in 986 mbar (740 Torr) N_2 and 2-methylpropane as reference reactant. Depletion of reactants followed by GC to derive $k(Br+C_2H_2)/k$(Br + 2-methylpropane)=2.96±0.11. The rate coefficient was placed on an absolute basis using k(Br + 2-methylpropane)=1.52×10^{-15} cm^3 molecule^{-1} s^{-1} at 295 K (Russell et al., 1988).

(c) CW photolysis of Br_2 (300–500 nm) in the presence of C_2H_2 in 33–1013 mbar (25–760 Torr) N_2/O_2 bath gas and CH_3CHO as reference reactant. At 298 K and a total pressure of 760 Torr air, $k(Br+C_2H_2)/k(Br+CH_3CHO)=(1.0\pm0.04)\times10^{-2}$. Rate coefficient put on an absolute basis using $k(Br+CH_3CHO)=3.9\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(d) As (c) but using 2,2,4-trimethylpentane (TMP) as reference compound. Data put on absolute basis using $k(Br+TMP)=(4.16\pm0.33)\times10^{-12}\exp(-1820/T)$ (Barnes et al., 1989), which itself was measured relative to k(Br + 2-methylpropane)=$1.83\times10^{-10}\exp(-3452/T)$ cm^3 molecule^{-1} s^{-1} (Russell et al., 1988).

(e) Photolysis of Br_2 ($\lambda > 420$ nm) in presence of C_2H_2 in 933–946 mbar (700–710 Torr) air, and C_2H_4 as reference reactant. Depletion of reactants followed by FTIR absorption spectroscopy. $k(Br+C_2H_2)/k(Br+C_2H_4)=(6.9\pm0.5)\times10^{-2}$ at 239 K, $(7.9\pm0.5)\times10^{-2}$ at 249 K, $(9.6\pm0.7)\times10^{-2}$ at 261 K, $(13.5\pm0.9)\times10^{-2}$ at 280 K and $(19.3\pm1.4)\times10^{-2}$ at 296 K. Rate coefficients placed on an absolute basis using $k(Br+C_2H_4)=5.71\times10^{-13}$, 4.54×10^{-13}, 3.87×10^{-13}, 2.40×10^{-13} and 1.32×10^{-13} cm^3 molecule^{-1} s^{-1} at 239 K, 249 K, 261 K, 280 K and 296 K, respectively (see $Br+C_2H_4$ data sheet). The reference value for $k(Br+C_2H_4)$ at 261 K is the average of the values obtained using HCHO and CH_3CHO as reference reactants.

Preferred Values

$k = 2.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar air.
$k = 6.35 \times 10^{-15}\exp(440/T)$ cm^3 molecule^{-1} s^{-1} (for ∼1 bar air) over the temperature range 230–300 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The measured rate coefficients reveal a strong dependence on total pressure (Barnes et al., 1989), temperature (Barnes et al., 1989, Ramacher et al., 2001) and the O_2 partial pressure (Barnes et al., 1989). This has been taken to indicate (Barnes et al., 1989) that the mechanism involves formation of a Br-C_2H_2 adduct, which can dissociate to reactants or react with O_2 to form a peroxy radical. For this reason, the effective rate coefficient is significantly higher in air than in an oxygen free bath gas at total pressures of up to an atmosphere. There is insufficient data to describe the temperature, pressure and $[O_2]$ dependencies of the rate coefficient, and our recommendation is restricted to air as bath gas, and pressures close to 1 bar. The data presented by Ramacher et al. (2001) using C_2H_4 as reference reactant is preferred over measurements relative to 2,2,4-trimethylpentane for reasons discussed by these authors, and form the basis of our recommendation. The temperature dependence of the rate coefficient was derived by least squares fitting of the data listed. Further studies of the rate coefficient in air at low pressures and temperatures would be useful to aid modelling of the role of this reaction at high altitudes.

The formation of stable products when the reaction is initiated in air (in absence of NO_x) appears to be independent of temperature (Ramacher et al., 2001) and involves bimolecular reactions of the initially formed CHBr=CH radical with O_2 to form CO, HC(O)OH, HC(O)Br and CO_2 (for details see Barnes et al., 1989; Ramacher et al., 2001; Yarwood et al., 1991)

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II.A7.193

$Br + C_2H_4 + M \rightarrow BrC_2H_4 + M$

$\Delta H = -28$ kJ·mol^{-1} (Bedjanian et al., 1999)

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$3.0 \times 10^{-33} \exp[(730 \pm 220)/T]$ [He]	233–320	Bedjanian et al., 1999	DF-MS (a)
$(1.2 \pm 0.3) \times 10^{-15}$ (1.3 mbar He)	298		
Relative Rate Coefficients			
$< 2.5 \times 10^{-13}$	295	Wallington et al., 1989	RR (b)
1.69×10^{-13} (1013 mbar air)	298	Barnes et al., 1989	RR (c)
$(1.24 \pm 0.44) \times 10^{-14}$ (67 mbar air)	298		RR (d)
$(1.29 \pm 0.04) \times 10^{-13}$ (1013 mbar air)	313		
$(6.72 \pm 0.45) \times 10^{-14}$ (1013 mbar air)	333		
$(2.51 \pm 0.17) \times 10^{-14}$ (1013 mbar air)	353		
$(1.32 \pm 0.11) \times 10^{-13}$ (933 mbar air)	296	Yarwood et al., 1992	RR (e)
$(4.06 \pm 0.36) \times 10^{-13}$ (933 mbar air)	261	Ramacher et al., 2001	RR (f)
$(2.40 \pm 0.36) \times 10^{-13}$ (933 mbar air)	280		
$(1.22 \pm 0.18) \times 10^{-13}$ (933 mbar air)	296		
$(6.62 \pm 0.46) \times 10^{-13}$ (933 mbar air)	228	Ramacher et al., 2001	RR (g)
$(5.71 \pm 0.40) \times 10^{-13}$ (933 mbar air)	239		
$(4.54 \pm 0.32) \times 10^{-13}$ (933 mbar air)	249		
$(3.68 \pm 0.26) \times 10^{-13}$ (933 mbar air)	261		

Comments

(a) Experiments conducted at pressures of 0.7–2.7 mbar (0.5–2 Torr) He. Rate coefficient cited is at the low pressure limit, k=k_0. Br was detected as BrCl after titration with NOCl, and Br_2 was added to partly convert the BrC_2H_4 radical to BrC_2H_4Br, which was also detected. The kinetics of the title reaction were derived from fitting to an analytical expression that took loss of BrC_2H_4 by reaction with both Br_2 and Br into account.

(b) CW photolysis of Br_2 in the presence of C_2H_4 in 986 mbar (740 Torr) air and CH_3CHO as reference reactant. The depletion of reactants was followed by GC to derive $k(Br+C_2H_4)/k(Br+CH_3CHO)<0.067$. An absolute upper limit was calculated using $k(Br+CH_3CHO)=3.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 295 K (IUPAC, this evaluation).

(c) CW photolysis of Br_2 (300–500 nm) in the presence of C_2H_4 in 1013 mbar (760 Torr) N_2+O_2 bath gas and CH_3CHO as reference compound. Depletion of reactants monitored by GC. The tabulated rate coefficient in air was obtained by extrapolation of data obtained with O_2 partial pressures between 6.7 and 133 mbar (5 to 100 Torr) to 210 mbar O_2, and put on absolute basis using $k(Br+CH_3CHO)=3.9\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(d) CW photolysis of Br_2 (300–500 nm) in the presence of C_2H_4 in 33–1013 mbar (25–760 Torr) N_2+O_2 bath gas and 2,2,4-trimethylpenane (TMP) as reference compound. Depletion of reactants monitored by GC or FTIR spectroscopy. Data put on absolute basis using $k(Br+TMP)=(4.16\pm0.33)\times10^{-12}\exp(-1820/T)$ cm^3 molecule^{-1} s^{-1} (Barnes et al., 1989), which in turn was measured relative to $k(Br + 2\text{-methylpropane})=1.83\times10^{-10}\exp(-3452/T)$ cm^3 molecule^{-1} s^{-1} (Bierbach et al., 1996).

(e) CW photolysis ($\lambda>400$ nm) of Br_2 in presence of C_2H_4 and HCHO (reference reactant) in 933 mbar (700 Torr) air or N_2+O_2 bath gas. The depletion of reactants was monitored by FTIR spectroscopy. A rate coefficient ratio of $k(Br+C_2H_4)/k(Br+HCHO)=0.12\pm0.01$ was determined for 296 K and 933 mbar (700 Torr) air, and $k(Br+C_2H_4)$ was converted to an absolute value by use of $k(Br+HCHO)=1.1\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(f) CW photolysis ($\lambda > 420$ nm) of Br_2 in the presence of C_2H_4 and HCHO as reference reactant at total pressures of 933–946 (700–710 Torr) air. Depletion of reactants was monitored by FTIR spectroscopy. The following rate coefficient ratios were obtained: $k(Br+C_2H_4)/k(Br+HCHO)=0.487\pm0.073$ at 261 K, 0.247 ± 0.037 at 280 K and 0.112 ± 0.017 at 296 K. The tabulated absolute rate coefficients were derived using $k(Br+HCHO)=7.7\times10^{-12}$ exp (-580/T) cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(g) As (f) but using CH_3CHO as reference reactant. The following rate coefficient ratios were obtained: $k(Br+C_2H_4)/k(Br+CH_3CHO)=0.277\pm0.019$ at 228 K, 0.217 ± 0.015 at 239 K, 0.160 ± 0.011 at 249 K, and 0.119 ± 0.008 at 261 K. The absolute rate coefficients listed in the table were derived using $k(Br+CH_3CHO)=1.8\times10^{-11}$ exp (-460/T) cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

Preferred Values

$k = 1.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 296 K and 1 bar air.
$k = 2.80 \times 10^{-13}$ exp$(224/T) \times B/[B + 8.5 \times 10^{12}$ exp $(-3200/T)]$ cm^3 molecule^{-1} s^{-1} where $B = 7.5 \times 10^{-12}$ [O_2] s^{-1} and [O_2] is in molecules cm^{-3}. The temperature range is 240–300 K.

Reliability

$\Delta \log k = \pm\, 0.15$ at 298 K and 1 bar air.

Comments on Preferred Values

The measured rate coefficients reveal a strong dependence on total pressure (Barnes et al., 1989), temperature (Barnes et al., 1989; Ramacher et al., 2001) and the O_2 partial pressure (Barnes et al., 1989). This has been taken to indicate that the mechanism involves formation of a Br-C_2H_4 adduct, which can dissociate to reactants or react with O_2 to form a peroxy radical. For this reason, the effective rate coefficient is significantly higher in air than in an oxygen free bath gas at total pressures of up to an atmosphere. The 298 K recommendation is based on the average of the results of Yarwood et al. (1992) and Ramacher et al. (2001) which were both obtained relative to HCHO and which are in excellent agreement. As noted by both Barnes et al. (1989) and Ramacher et al. (2001) there is an inconsistency between the data sets of Barnes et al. (1989) obtained using CH_3CHO and 2,2,4-trimethylpentane/2-methylpropane as reference reactants, and the higher value of $k(298\,K)=1.69\times10^{-13}$ cm^3 molecule^{-1} s^{-1} obtained in that study is considered less reliable. The data of Ramacher et al. (2001) listed in the Table above, which yield consistent results with HCHO and CH_3CHO as reference compounds and also using C_2HCl_3 as secondary standard, are used to derive the temperature dependence of the rate coefficient in one atmosphere air bath gas. The expression given describes the temperature dependence of the effective rate coefficient in one atmosphere of air, and constrains the difference in the activation energies of the forward and reverse processes of adduct formation and dissociation according to Bedjanian et al. (1999) and assumes a temperature independent value of 7.5×10^{-12} cm^3 molecule^{-1} s^{-1} for the rate coefficient for the reaction of the Br-C_2H_4 adduct with O_2 at one atmosphere. Further details are given by Ramacher et al. (2001). Note that extrapolation to conditions very different from one atmosphere pressure air could lead to large errors, and is not recommended. Further studies of the rate coefficient in air at low pressures and temperatures would be useful to aid modelling of the role of this reaction at high altitudes.

Identification of brominated aldehydes, alcohols and acids in product studies provides evidence for the formation and subsequent reaction of the $BrC_2H_4O_2$ peroxy radical in air (Barnes et al., 1989; Yarwood et al., 1992).

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$$\begin{array}{llr} \mathbf{Br + C_3H_6} & \rightarrow \mathbf{HBr + C_3H_5} & \mathbf{(1)} \\ \mathbf{Br + C_3H_6 + M} & \rightarrow \mathbf{BrC_3H_6 + M} & \mathbf{(2)} \end{array}$$

$\Delta H(1) = -2.9$ kJ·mol^{-1} (Bedjanian et al., 1998)
$\Delta H(2) = -32.2$ kJ·mol^{-1} (Bedjanian et al., 1998)

Rate coefficient data (k=k_1+k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_1 = 8.3 \times 10^{-12}$ exp [-(2200 ± 300/T)]	263–363	Kondo et al., 1988	F-MS (a)
$k_1 = 8.15 \times 10^{-13}$ exp [-(1250 ± 160/T)]	233–320	Bedjanian et al., 1998	DF-MS (b)
$k_1 = 1.2 \times 10^{-14}$	298		
$k_2 = 3.8 \times 10^{-33}$ exp [(1200 ± 50)/T] [He]	233–320		
Relative Rate Coefficients			
$(4.2 \pm 0.5) \times 10^{-12}$	295	Wallington et al., 1989	RR (c)
$(2.9 \pm 0.3) \times 10^{-12}$	298	Barnes et al., 1989	RR (d)

Comments

(a) Very low pressure reactor at $\approx 1\times10^{-3}$ mbar with bromine atoms detected directly using a mass spectrometer. The Arrhenius expression was derived from a calculated pre-exponential factor associated with a bent transition state, combined with the most reliable rate coefficient, which was that obtained at 363 K.

(b) Experiments conducted at pressures of 0.7–2.7 mbar (0.5–2 Torr) He. Br was detected as BrCl after titration with NOCl. Consistent kinetic data for k_1 was derived by monitoring either Br, HBr or C_3H_5Br (formed in C_3H_5+Br). For determination of k_2, Br_2 was added to partly convert the BrC_3H_6 radical to BrC_3H_6Br, which could be detected, and to regenerate Br. Values of k_2 at pressures of 0.7 to 2.7 mbar (0.5 to 2 Torr) He and 233 to 308 K were then derived by fitting to an analytical expression assuming a steady state for Br. An approximately linear dependence on He pressure was observed indicating that the derived values of k_2 are close to the low-pressure limit.

(c) CW photolysis of Br_2 in the presence of C_3H_6 in 986 mbar (740 Torr) air and CH_3CHO as reference reactant. The depletion of reactants was followed by GC to derive $k(Br+C_3H_6)/k(Br+CH_3CHO)=1.10\pm0.12$. An absolute rate coefficient was calculated using $k(Br+CH_3CHO)=3.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 295 K (IUPAC, this evaluation).

(d) CW photolysis of Br_2 (300–500 nm) in the presence of C_3H_6 in 1013 mbar (760 Torr) N_2+O_2 bath gas and CH_3CHO as reference compound. Depletion of reactants monitored by FTIR to derive $k(Br+C_3H_6)/k(Br+CH_3CHO)=0.75\pm0.07$. An absolute rate coefficient was calculated using $k(Br+CH_3CHO)=3.9\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, this evaluation).

Preferred Values

$k_1 = 1.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 8.1 \times 10^{-13}$ exp(-1250/T) cm^3 molecule^{-1} s^{-1} over the temperature range 230–320 K.
$k = 3.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar air.

Reliability

$\Delta \log k_1 = \pm 0.2$ at 298 K.
$\Delta (E_1/R) = \pm 500$ K.
$\Delta \log k = \pm 0.2$ at 298 K and 1 bar air.

Comments on Preferred Values

The reaction proceeds via both direct abstraction (k_1) and via a termolecular channel (k_2) involving formation of a BrC_3H_6 adduct that can redissociate to products or react with O_2. The effective overall rate coefficient therefore displays a dependence on temperature, total pressure and the oxygen partial pressure (Barnes et al., 1989). The study of Bedjanian et al. (1998) is considered the more reliable measurement of k_1 as the work of Kondo et al. (1988) may have been influenced by the presence of excited states of Br. The recommended value for k_1 is therefore based on the work of Bedjanian et al. (1998), with expanded error limits.

In the absence of kinetic data for k_2 in the fall off regime it is not possible to derive a parameterisation of the rate coefficient for all atmospheric conditions. Instead, for the overall rate coefficient, we recommend an average of the results of the relative rate studies (Wallington et al., 1989; Barnes et al., 1989) at 298 K and note that the branching ratio to k_1 (i.e. to HBr formation) under atmospheric conditions is given by k_1/k. Pressure and temperature dependent studies in the fall-off regime are needed to model this reaction at high altitudes in the atmosphere where the pressure and temperature are lower. The structure of the radical product of the abstraction channel (1) is believed to be CH_2=$CHCH_2$ indicating that abstraction from the CH_3 group is most important (Kondo et al., 1988).

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$Br + HCHO \rightarrow HBr + HCO$

$\Delta H^\circ = 3.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.44 \times 10^{-11} \exp[-(750 \pm 112)/T]$	223–480	Nava et al., 1981	FP-RF (a)
$(1.08 \pm 0.10) \times 10^{-12}$	298		
$2.97 \times 10^{-11} \exp[-(1015 \pm 70)/T]$	295–480	Poulet et al., 1981	DF-MS
$(9.4 \pm 0.8) \times 10^{-13}$	295		
Relative Rate Coefficients			
$5.0 \times 10^{-12} \exp[-(460 \pm 200)/T]$	250–296	Ramacher et al., 2000	RR(b)
1.08×10^{-12}	296		

Comments

(a) There appears to be curvature in the Arrhenius plot above room temperature; using the low-temperature values at 223, 254, and 298 K gives E/R=584 K.

(b) Br atoms were generated by photolysis of Br_2 in the presence of HCHO and CH_3CHO in 1 bar N_2. Relative rates of decay of the two aldehydes were determined by an FTIR spectrometer system. The relative rates of decay were found to be independent of temperature over the range 250–296 K with the value $k(Br+CH_3CHO)/k(Br+HCHO)=3.60\pm0.29$. This temperature-independent rate coefficient ratio is placed on an absolute basis by the use of $k(Br+CH_3CHO)=1.8\times10^{-11} \exp[-(460)/T]$ cm^3 molecule^{-1} s^{-1} (this evaluation)

Preferred Values

$k = 1.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.7 \times 10^{-12} \exp(-580/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

In the derivation of the preferred rate expression only data at and below room temperature were used. The room temperature value is the average of the absolute rate coefficients reported by Nava et al. (1981) and Poulet et al. (1981), and is in excellent agreement with the derived value given in Ramacher et al. (2000). The temperature dependence is derived from the low temperature results of Nava et al. (1981) (E/R=584 K; see comment (a)), which is consistent with the relative rate data of Ramacher et al. (2000), and the A factor adjusted to yield the 298 K preferred values.

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Ramacher, B., Orlando, J. J., and Tyndall, G. S.: Int. J. Chem. Kinet., 32, 460, 2000.

II.A7.196

$Br + CH_3CHO \rightarrow HBr + CH_3CO$

$\Delta H° = 7.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.5) \times 10^{-12}$	300	Islam et al., 1984	(a)
$1.51 \times 10^{-11} \exp[-(364 \pm 41)/T]$	255–400	Nicovich et al., 1990	LP-RF
4.45×10^{-12}	298		
$(3.5 \pm 0.3) \times 10^{-12}$	298	Szilagyi et al., 1998	F-RF
Relative Rate Coefficients			
$(3.7 \pm 0.1) \times 10^{-12}$	298	Niki et al., 1985	RR (b)
$2.6 \times 10^{-11} \exp[-(580 \pm 200)/T]$	250–296	Ramacher et al., 2000	RR(c)
4.0×10^{-12}	296		

Comments

(a) Very low pressure reactor study. Br atoms were generated by microwave discharge of Br_2 in helium, with mass spectrometric detection of reactants and products.

(b) Br atoms were generated by photolysis of Br_2 at 350 nm to 600 nm in 930 mbar (700 Torr) total pressure of N_2. The rate coefficient was determined relative to that for the reaction of Br atoms with HCHO, with $k(Br+CH_3CHO)/k(Br+HCHO)=3.39\pm0.10$. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(Br+HCHO)=1.1\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (IUPAC, this evaluation).

(c) Br atoms were generated by photolysis of Br_2 in the presence of HCHO and CH_3CHO in 1 bar N_2. Relative rates of decay of the two aldehydes were determined by an FTIR spectrometer system. The relative rates of decay were found to be independent of temperature over the range 250–296 K with the value $k(Br+CH_3CHO)/k(Br+HCHO)=3.60\pm0.29$. This temperature-independent rate coefficient ratio is placed on an absolute basis by the use of $k(Br+HCHO)=7.7\times10^{-12}$ $\exp(-580/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation)

Preferred Values

$k = 3.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.8 \times 10^{-11} \exp(-460/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–400 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta E/R = \pm 200$ K.

Comments on Preferred Values

The room temperature value is the average of the rate coefficients reported by Islam et al. (1984), Nicovich et al. (1990), Szilagyi et al. (1998) and Niki et al. (1985), and is in excellent agreement with the relative rate value of Ramacher et al. (2000). The temperature dependence is derived from the results of Nicovich et al. (1990), which is consistent with the relative rate data of Ramacher et al. (2000), and the A factor adjusted to yield the 298 K preferred value. The preferred room temperature rate coefficient is consistent with the relative rate studies of Barnes et al. (1989) and Wallington et al. (1989) [which do not provide definitive data concerning the rate constant for the reaction of Br atoms with CH_3CHO].

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Appendix A8: Organic Photochemistry

II.A8.197

HCHO + hν → products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
HCHO + hν → H + HCO	(1)	369.7	324
→ H_2 + CO	(2)	−1.9	

Absorption cross-section data

Wavelength range/nm	Reference	Comments
240–360	Moortgat and Schneider, 1989	(a)
300–360	Cantrell et al., 1990	(b)
225–375	Meller and Moortgat, 2000	(c)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength range/nm	Reference	Comments
ϕ, ϕ_2/ϕ	253–353	Moortgat et al., 1983	(d)
ϕ_1	269–339	Smith et al., 2002	(e)

Comments

(a) Cross-sections measured at 220 K and 298 K at different concentrations of HCHO and extrapolated to zero concentration. This extrapolation procedure yielded virtually identical cross-sections with and without added N_2.

(b) High-resolution FT spectroscopy used to measure cross-sections as a function of temperature (223 to 293 K). Values at different concentrations of HCHO were extrapolated to zero concentration.

(c) Cross-section measurements with resolution of 0.025 nm at selected temperatures between 223–323 K. HCHO pressure kept below 0.65 mbar to avoid saturation effects. Error limits on $\sigma \pm$ 5% and on temperature coefficients <8%. Results compared in detail with earlier work.

(d) Quantum yields of CO and H_2 were measured as a function of wavelength for HCHO in low concentration in air. Previous results (Moortgat and Warneck, 1979) showing the pressure and temperature dependences of ϕ_1 and ϕ_2 were confirmed.

(e) The relative quantum yield for the production of radical products, H and HCO, measured directly using an NO-chemical amplification method, with subsequent detection of NO_2 by CIMS. All yields were measured at a pressure of 50 Torr (66 mbar) and were normalized to a quantum yield of ϕ_2=0.753 at 303.75 nm based on the recommendation of DeMore et al. (2000). The quantum yields were measured with sufficient wavelength resolution (±0.62 nm, fwhm), to observe structure which had not been previously reported.

Preferred Values

Absorption cross-sections at 298 and 223 K and Temperature Gradients of HCHO Averaged Over Intervals Used in Atmospheric Modelling

Wavelength λ/nm	Wavelength Range, λ/nm	$10^{20}\sigma(298\,\mathrm{K})\,\mathrm{cm}^2$	$10^{20}\sigma(223\,\mathrm{K})\,\mathrm{cm}^2$	$10^{24}\Gamma\,\mathrm{cm}^2\mathrm{K}^{-1}$
226.0	224.7–227.3	0.0165		
228.6	227.3–229.9	0.0181		
231.3	229.9–232.6	0.0302		
234.0	232.6–235.3	0.0315		
236.7	235.3–238.1	0.0625		
239.6	238.1–241.0	0.0705		
242.5	241.0–243.9	0.1268		
245.4	243.9–246.9	0.1390		
248.5	246.9–250.0	0.2537		
251.7	250.0–253.3	0.2699	0.2642	0.76
254.9	253.3–256.4	0.4560	0.4427	1.78
258.1	256.4–259.7	0.4768	0.4363	5.40
261.5	259.7–263.2	0.7034	0.6933	1.35
265.0	263.2–266.7	0.7379	0.7008	4.97
268.5	266.7–270.3	1.1287	1.1074	2.86
272.2	270.3–274.0	1.2922	1.2631	3.88
275.9	274.0–277.8	1.8442	1.8865	-5.64
279.8	277.8–281.7	1.8592	1.8874	-3.76
283.7	281.7–285.7	2.5555	2.7238	-22.43
287.8	285.7–289.9	2.3095	2.3613	-6.90
292.0	289.9–294.1	2.6653	2.9321	-35.58
296.3	294.1–298.5	3.2939	3.2524	5.54
300.8	298.5–303.0	1.6046	1.5854	2.55
305.4	303.0–307.7	4.3944	4.4061	-1.56
310.1	307.7–312.5	1.6318	1.6737	-5.58
315.0	312.5–317.5	4.0853	4.0230	8.30
320.0	317.5–322.5	1.5290	1.4679	8.15
325.0	322.5–327.5	2.7908	2.7612	3.94
330.0	327.5–332.5	1.9889	1.9094	10.59
335.0	332.5–337.5	0.1959	0.1831	1.71
340.0	337.5–342.5	2.3872	2.2729	15.24
345.0	342.5–347.5	0.7586	0.7547	0.51
350.0	347.5–352.5	0.1947	0.2204	-3.43
355.0	352.5–357.5	0.9604		
360.0	357.5–362.5	0.0139		
365.0	362.5–367.5	0.0100		
370.0	367.5–372.5	0.0368		

*Wavelengths are calibrated in air.

To calculate the UV absorption spectrum at a given temperature T, the following equation is used:
$\sigma(\lambda, T) = \sigma(\lambda, 298\mathrm{K}) + \Gamma(T - 298\ \mathrm{K})$

Absorption Cross-Sections at 298 K, σ (298 K), Averaged Over 1 nm Intervals Centered at the Cited Wavelength, λ.

λ/ nm*	$10^{21}\sigma$(298 K) cm^2	λ/ nm*	$10^{21}\sigma$(298 K) cm^2	λ/ nm*	$10^{21}\sigma$(298 K) cm^2
226	0.179	276	25.842	326	68.757
227	0.169	277	15.731	327	43.702
228	0.177	278	10.349	328	12.201
229	0.190	279	24.514	329	31.200
230	0.205	280	23.375	330	38.651
231	0.166	281	15.624	331	14.121
232	0.335	282	9.728	332	3.474
233	0.262	283	7.224	333	2.135
234	0.325	284	42.649	334	1.587
235	0.363	285	40.504	335	0.967
236	0.540	286	20.950	336	1.261
237	0.770	287	11.532	337	3.825
238	0.569	288	31.687	338	19.188
239	0.681	289	32.245	339	53.814
240	0.782	290	11.729	340	31.514
241	0.775	291	18.358	341	9.783
242	1.227	292	7.973	342	5.093
243	1.591	293	31.281	343	19.221
244	1.096	294	71.538	344	12.684
245	1.313	295	40.535	345	4.369
246	1.634	296	24.739	346	1.190
247	1.511	297	13.672	347	0.441
248	2.338	298	42.166	348	0.754
249	3.178	299	31.745	349	0.379
250	2.572	300	9.638	350	0.362
251	2.039	301	16.246	351	0.893
252	3.366	302	8.537	352	7.295
253	2.894	303	30.211	353	22.752
254	3.417	304	72.185	354	16.449
255	4.502	305	47.520	355	6.964
256	6.282	306	42.915	356	1.483
257	4.430	307	17.807	357	0.345
258	3.073	308	13.847	358	0.186
259	6.174	309	32.521	359	0.111
260	6.045	310	17.369	360	0.087
261	6.591	311	4.623	361	0.100
262	6.033	312	11.880	362	0.211
263	10.773	313	9.064	363	0.141
264	9.465	314	56.366	364	0.094
265	5.305	315	55.650	365	0.088
266	5.387	316	25.608	366	0.085
267	13.604	317	57.770	367	0.091
268	12.428	318	31.505	368	0.142
269	9.908	319	9.779	369	0.297
270	9.626	320	11.936	370	0.635
271	19.409	321	15.976	371	0.571
272	14.302	322	7.216	372	0.198
273	8.106	323	3.281	373	0.113
274	6.575	324	8.584	374	0.091
275	21.432	325	15.779	375	0.087

*Wavelengths are calibrated in air.

Quantum yields in air at 1 bar and 298 K*

λ/nm	ϕ_1	ϕ_2
240.00	0.270	0.490
250.00	0.290	0.490
260.00	0.300	0.490
268.75	0.425	0.385
278.75	0.570	0.320
283.75	0.673	0.247
288.75	0.746	0.214
293.75	0.694	0.286
298.75	0.642	0.348
301.25	0.725	0.275
303.75	0.780	0.220
306.25	0.684	0.316
308.75	0.735	0.265
311.25	0.704	0.296
313.75	0.715	0.285
316.25	0.673	0.327
321.25	0.663	0.337
326.25	0.528	0.452
328.75	0.373	0.577
331.25	0.476	0.424
333.75	0.311	0.489
336.25	0.072	0.627
338.75	0.041	0.559
340.00	0.00	0.560
350.00	0.00	0.210
360.00	0.00	0.030

*ϕ_1 values between 240–330 nm independent of temperature and pressure

Comments on Preferred Values

The new cross-section measurements by Meller and Moortgat (2000) provide for the first time high-resolution data over the complete UV absorption band with minimised systematic error. These are the basis of the preferred values. The measured cross sections are 5–10% higher than the values previously recommended by IUPAC, which were based on cross-sections reported by Moortgat and Schneider (1989) for $\lambda \leq 300$ nm and of Cantrell et al. (1990) for λ=301 nm to 356 nm. The temperature dependence over the range 250–356 nm reported by Meller and Moortgat (2000) exhibits the same general changes on band shape as previously recommended spectra, but differs in the shape of the individual rotational bands. Resolution should not exceed 1 nm to assure correct representation of the temperature dependent cross sections.

The recent quantum yield measurements of Smith et al. (2002) are in good agreement with those determined by Moortgat et al. (1983) upon which the earlier IUPAC recommended data for atmospheric pressure and 298 K was based, but show for the first time structure in the wavelength dependence of ϕ_1. These results are also consistent with earlier measurements of the quantum yields by Horowitz and Calvert (1978), Clark et al. (1978), Tang et al. (1979) and Moortgat et al. (1983)

The preferred values for ϕ_1 are calculated from the relative values of Smith et al. (2002), using the value of ϕ_1=0.78 at 302.5 nm. These values are independent of pressure and temperature in the atmospheric range. The values for ϕ_2 are obtained by the difference (ϕ_T–ϕ_1), where ϕ_T is the sum of the two channels (1) and (2) at 1 bar and 298 K, based on the data of Moortgat et al. (1983). Moortgat et al. (1979, 1983) show that for $\lambda > 330$ nm, the quantum yields of CO and H_2 production are pressure and temperature dependent; quenching parameters are given in Moortgat et al. (1983).

Photodissociation of HCHO involves both S^0 and T^1 excited states populated from the S^1 state produced initially by photo-excitation in the near UV. The structure observed by Smith et al. (2002) provides evidence for the complicated competition among the various dissociation pathways of singlet and triplet excited formaldehyde to give: H+HCO, H+H+CO and

H_2+CO, which has been diagnosed from numerous studies of the photo-dissociation dynamics of excited HCHO molecules. These studies reveal that several parallel unimolecular decomposition pathways exist, yielding the two sets of chemically distinct products: H+HCO (1) and H_2+CO (2) (Green et al., 1992). Reaction (1) can occur via both S^0 and T^1 states, while Reaction (2) occurs solely via S^0. Not only do the molecular and radical product channels compete, but distinct S^0 and T^1 pathways can lead to the same products, i.e. H + HCO (Chuang et al., 1987).

Recent experimental studies (Valachovic et al., 2000) of the radical channel have defined the energetics governing the competition between the S^0 and T^1 pathways, which are consistent with earlier experiments (Chuang et al., 1987) and with ab initio calculations (Yamaguchi et al., 1998). The T^1 route dominates at higher energies. For the molecular channel, the S^0 route, which is pressure quenched at energies below the radical threshold, may be replaced above the threshold by an 'abstraction' mechanism (v. Zee et al., 1993). This mechanism involves access to large H-HCO distances in the excited state just prior to bond breaking, which facilitate H-atom abstraction (Valachovic et al., 2000), producing H_2+CO. This may resolve some of the earlier discrepancies concerning the yields of molecular products at higher energies (Troe, 1984; Ho et al., 1982). Nevertheless, the branching ratios for $\lambda < 300$ nm should be treated with caution.

The new recommended quantum yields result in increases of at least 8% in the calculated H/HCO production rate from formaldehyde photolysis in the troposphere.

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II.A8.198

$CH_3CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CHO + h\nu$	$\rightarrow CH_4 + CO$	(1)	−19.5	
	$\rightarrow CH_3 + HCO$	(2)	355.3	337
	$\rightarrow CH_3CO + H$	(3)	373.8	320

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–365	Martinez et al., 1992	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement		Wavelength range/nm	Reference	Comments
ϕ_1	ϕ_2			
0.46	0.31	260	Meyrahn et al., 1982	(b)
0.42	0.32	265		
0.31	0.39	270		
0.16	0.51	275		
0.05	0.58	280		
0.02	0.57	285		
0.01	0.53	290		
0.005	0.48	295		
0.0	0.43	300		
0.0	0.37	305		
0.0	0.28	310		
0.0	0.10	320		
0.0	0.04	325		
0.0	0.00	330		

Comments

(a) Double beam spectrophotometric measurements with 10 cm path length. Data obtained at 0.1 nm intervals with 0.5 nm resolution. Argon-acetaldehyde mixtures used at a total pressure of 133 mbar and several acetaldehyde pressures in the range 1.3 mbar to 2.6 mbar. Cross-sections tabulated are averages over a 1 nm (λ>280 nm) or 4 nm (λ<280 nm) region centered on the corresponding wavelength (see Preferred Values).

(b) Quantum yields of CH_4 and CO determined from the photolysis of 100 ppm of CH_3CHO in air or N_2 at a total pressure of 1 bar. H_2 was found only in trace quantities and hence it was concluded that the photolytic channel giving CH_3CO+H ($\lambda_{threshold}$=320 nm) is negligible. Quantum yield data based on the assumption that $\phi_1+\phi_2+\phi_a=1$, where ϕ_a refers to the quenching process $CH_3CHO^* + M \rightarrow CH_3CHO + M$. Quantum yield data at 1 bar pressure were found to be independent of the diluent, N_2, or air. ϕ_{CO} both in N_2 and in air increased as the total pressure was lowered.

Preferred Values

Absorption Cross-Sections at 298 K

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
202	0.056	297	4.38	334	0.363
206	0.053	298	4.41	335	0.350
210	0.049	299	4.26	336	0.238
214	0.048	300	4.16	337	0.222
218	0.052	301	3.99	338	0.205
222	0.065	302	3.86	339	0.219
226	0.096	303	3.72	340	0.150
230	0.151	304	3.48	341	0.074
234	0.241	305	3.42	342	0.042
238	0.375	306	3.42	343	0.031
242	0.564	307	3.36	344	0.026
246	0.818	308	3.33	345	0.021
250	1.128	309	3.14	346	0.019
254	1.524	310	2.93	347	0.015
258	1.994	311	2.76	348	0.016
262	2.44	312	2.53	349	0.010
266	3.05	313	2.47	350	0.008
270	3.42	314	2.44	351	0.007
274	4.03	315	2.20	352	0.006
278	4.19	316	2.04	353	0.005
280	4.50	317	2.07	354	0.005
281	4.69	318	1.979	355	0.004
282	4.72	319	1.874	356	0.005
283	4.75	320	1.723	357	0.003
284	4.61	321	1.484	358	0.004
285	4.49	322	1.402	359	0.002
286	4.44	323	1.244	360	0.003
287	4.59	324	1.091	361	0.002
288	4.72	325	1.136	362	0.001
289	4.77	326	1.074	363	0.000
290	4.89	327	0.858	364	0.000
291	4.78	328	0.747	365	0.000
292	4.68	329	0.707		
293	4.53	330	0.688		
294	4.33	331	0.588		
295	4.27	332	0.530		
296	4.24	333	0.398		

Quantum yields in air at 1 bar and 298 K

λ/nm	ϕ_1	ϕ_2
260	0.46	0.31
270	0.31	0.39
280	0.05	0.58
290	0.01	0.53
295	0.00	0.48
300		0.43
305		0.37
310		0.29
315		0.17
320		0.10
325		0.04
330		0.00

Comments on Preferred Values

The preferred absorption cross-sections are from the extensive measurements of Martinez et al. (1992). Over the wavelength region 260 nm to 320 nm these cross-sections are within 5% of the data of Calvert and Pitts (1966) and Weaver et al. (1976).

The preferred values for the quantum yields are those obtained by Meyrahn et al. (1982). Atkinson and Lloyd (1984) have evaluated the quantum yield data of Meyrahn et al. (1982) and of Horowitz and Calvert (1982), and derive values in very close agreement with those recommended here.

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II.A8.199

$C_2H_5CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
C_2H_5CHO	$\rightarrow C_2H_5 + HCO$	(1)	351.4	340
	$\rightarrow C_2H_6 + CO$	(2)	−7.1	
	$\rightarrow C_2H_4 + HCHO$	(3)	131.0	913
	$\rightarrow CH_3 + CH_2CHO$	(4)	344.3	347

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–365	Martinez et al., 1992	(a)
280–330	Chen and Zhu, 2001	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4$)

Measurement	Wavelength range/nm	Reference	Comments
ϕ_1		Heicklen et al., 1986	(c)
0.89	294		
0.50	302		
0.26	325		
0.15	334		
ϕ_1		Chen and Zhu, 2001	(d)
0.85 ± 0.06	280		
1.01 ± 0.07	285		
0.95 ± 0.06	290		
0.98 ± 0.06	295		
0.92 ± 0.06	300		
0.95 ± 0.08	305		
0.98 ± 0.11	310		
0.91 ± 0.05	315		
1.08 ± 0.07	320		
1.07 ± 0.14	325		
0.84 ± 0.08	330		

Comments

(a) Absorption measurements as a function of C_2H_5CHO pressure using a diode array spectrometer. Cross-sections are the average cross-section over a 1 nm ($\lambda > 280$ nm) or 4 nm ($\lambda < 280$ nm) region centered at the corresponding wavelength (see Preferred Values).

(b) Cross-sections determined from transmission of UV light at 5 nm intervals from tunable dye laser, as a function of C_2H_5CHO pressure. Overall uncertainty estimated to be 5–10% at all wavelengths. Results agree with those from Martinez et al. (1992) except at 280 and 330 nm, where values are 20–30% higher.

(c) Laser flash photolysis of C_2H_5CHO in the presence of air and steady-state photolysis of C_2H_5CHO in the presence of O_2 at 263 K or 298 K, as a function of wavelength and of O_2 pressure. Quantum yields for radical channel from measurement of $C_2H_5O_2$ and HO_2 by UV absorption following laser photolysis. Quantum yields for CO and C_2H_6 were measured by GC. From the proposed mechanism it was deduced that ϕ_1=(ϕ_∞–ϕ[C_2H_6]). The values of ϕ quoted are for 1 bar air.

(d) Tunable dye laser photolysis of C_2H_5CHO with time resolved measurement of HCO concentration by cavity ring down spectroscopy at 613.8 nm. Absorbed flux was determined from photon fluence measurements using a calibrated Joulemeter. Absolute yields of HCO calculated from absorption cross sections, σ(HCO) determined in situ from either photodissociation of HCHO or Cl_2+HCHO mixtures (at 310–330 nm). A weak dependence of ϕ on $P_{C2H5CHO}$ was observed but no dependence of ϕ on N_2 up to 1 bar. The values of ϕ quoted are for zero pressure, but the same values apply at 1 bar N_2.

Preferred Values

Absorption Cross-Sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
202	0.049	295	5.57	330	0.575
206	0.049	296	5.37	331	0.494
210	0.057	297	5.16	332	0.466
214	0.069	298	5.02	333	0.430
218	0.080	299	5.02	334	0.373
222	0.091	300	5.04	335	0.325
226	0.115	301	5.09	336	0.280
230	0.163	302	5.07	337	0.230
234	0.257	303	4.94	338	0.185
238	0.407	304	4.69	339	0.166
242	0.622	305	4.32	340	0.155
246	0.909	306	4.04	341	0.119
250	1.287	307	3.81	342	0.076
254	1.745	308	3.65	343	0.045
258	2.25	309	3.62	344	0.031
262	2.88	310	3.60	345	0.025
266	3.43	311	3.53	346	0.019
270	4.12	312	3.50	347	0.016
274	4.59	313	3.32	348	0.014
278	5.17	314	3.06	349	0.013
280	5.16	315	2.77	350	0.010
281	5.21	316	2.43	351	0.008
282	5.35	317	2.18	352	0.007
283	5.57	318	2.00	353	0.005
284	5.78	319	1.864	354	0.004
285	5.86	320	1.831	355	0.002
286	5.82	321	1.777	356	0.001
287	5.72	322	1.662	357	0.001
288	5.59	323	1.577	358	0.000
289	5.52	324	1.488	359	0.000
290	5.56	325	1.300	360	0.000
291	5.68	326	1.129	361	0.000
292	5.81	327	0.996	362	0.000
293	5.88	328	0.828	363	0.000
294	5.80	329	0.685	364	0.000

Quantum yields in air at 1 bar and 298 K

λ/nm	ϕ_1
280	0.85
285	0.90
290	0.95
295	1.00
300	1.00
305	1.00
310	1.00

Preferred Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred absorption cross-sections are from the measurements of Martinez et al. (1992). Over the wavelength region 260 nm to 320 nm these cross-sections are within 5% of the earlier data of Calvert and Pitts (1966), and the less precise measurements of Chen and Zhu (2001).

The quantum yields, ϕ_1, reported by Chen and Zhu (2001) at wavelengths less than 310 nm and at 1 bar N_2, agree well with those obtained for 1 bar air in the less direct study of Heicklen et al. (1986). However at wavelengths $>$310 nm the results of Chen and Zhu (2001) do not show the fall off observed by Heicklen et al. (1986) in air. This could be due to quenching by O_2 of the excited triplet state, which is believed to dissociate to give radical products (channel 1), or to errors in the interpretation of the more complex chemistry in the presence of O_2. There are significant experimental uncertainties at the longer wavelengths associated with the weak absorption by propionaldehyde. Further work is needed to resolve this issue and we are unable to recommend values for ϕ_1 in this region.

References

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II.A8.200

pinonaldehyde^a + hν → products

Absorption cross-section data

Wavelength range/nm	Reference	Comments
275–345	Hallquist et al., 1997	(b)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
ϕ(average) = 0.14 ± 0.03	sunlight	RADICAL, 2002	(c)
ϕ(average) ≈ 0.4	sunlight	Jaoui and Kamens, 2003	(d)

Comments

(a) (3-acetyl-2,2-dimethyl-cyclobutyl)-acetaldehyde.

(b) The UV spectrum was determined from long path (39.1 m) absorption measurements in a 0.48 m^3 chamber. Measurements were made over the wavelength range 275–345 nm, at a resolution of 0.6 nm, using diode array spectroscopy. Cross sections were reported as averages over 5 nm intervals. Measurements were made at 300±1 K and low pressure ($<$0.1 mbar), and calibrated through measurement of the pressure change on admission of pinonaldehyde to the reaction vessel. Pinonaldehyde was synthesized from the ozonolysis of α-pinene. Its stated purity was 95%, based on GC-MS and NMR analyses.

(c) Natural sunlight photolysis of pinonaldehyde-cyclohexane-air mixtures in a 180 m^3 outdoor chamber (the European Photoreactor, EUPHORE). The photolysis rate of pinonaldehyde was determined from its measured decay (HPLC), following correction for its removal by wall loss and dilution (which accounted for ca. 60% of its removal). Cyclohexane was included in the reaction mixtures as an HO radical scavenger. An average photodissociation quantum yield was determined from the observed photolysis rate relative to a theoretical rate, which was calculated using the absorption cross sections of Hallquist et al. (1997), the measured actinic flux and the assumption of a unit quantum yield.

(d) Natural sunlight photolysis of pinonaldehyde-air and pinonaldehyde-cyclohexane-air mixtures in a 190 m^3 outdoor chamber, with GC-MS detection. The system was characterized by simulation using a detailed chemical mechanism, which also included pinonaldehyde removal by wall loss and dilution (which accounted for $\sim$ 70-80% of its removal). An average photodissociation quantum yield was derived from the simulations, based on light absorption described by the cross sections of Hallquist et al. (1997) and the measured actinic flux. More than nine products were identified or tentatively identified and quantified using GC-MS.

Preferred Values

Absorption Cross-Sections for pinonaldehyde at 300 K

λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$
277.5	12.19	312.5	6.84
282.5	12.96	317.5	4.90
287.5	13.48	322.5	3.07
292.5	12.94	327.5	1.72
297.5	12.17	332.5	0.72
302.5	10.62	337.5	0.29
307.5	8.94	342.5	0.08

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred absorption cross sections are from the study of Hallquist et al. (1997), which are the only measurements reported and appear to be reliable. As pointed out by Hallquist et al. (1997), the cross sections are consistent with additive contributions from the aldehyde and ketone groups in pinonaldehyde, based on cross sections reported for simple aldehydes and ketones.

The studies of RADICAL (2002) and Jaoui and Kamens (2003) are indicative of removal of pinonaldehyde through photolysis, with average quantum yields which are substantially below unity at wavelengths >290 nm. Large corrections for pinonaldehyde wall loss and dilution were required in both studies, such that no firm quantum yield recommendation is made. Jaoui and Kamens (2003) identified a series of products which provided evidence for photolysis via both molecular and radical-forming channels. Further studies of the quantum yield and photolysis product channels are required.

References

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Jaoui, M. and Kamens, R. M.: Atmos. Environ., 37, 1835, 2003.
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II.A8.201

$(CHO)_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$(CHO)_2 + h\nu$	$\rightarrow H_2 + 2CO$	(1)	−9.1	
	$\rightarrow 2HCO$	(2)	298.1	401
	$\rightarrow HCHO + CO$	(3)	−7.2	
	$\rightarrow H + CO + HCO$	(4)	362.5	330

Absorption cross-section data

Wavelength range/nm	Reference	Comments
230–462	Plum et al., 1983	(a)
210-450	Orlando and Tyndall, 2001	(b)
210-480	Horowitz et al., 2001	(c)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi = 0.029 \pm 0.018$	325–470	Plum et al., 1983	(d)
ϕ (HCO) = 0.8 ± 0.4	308	Langford and Moore, 1984	(e)
ϕ (HCO) = 0.42 ± 0.22	193	Zhu et al., 1996	(f)
ϕ (HCO) = 0.54 ± 0.24	248		
ϕ (HCO) = 0.70 ± 0.30	308		
ϕ (HCO) = 1.50 ± 0.6	351		

Comments

(a) Conventional spectrophotometric study (Cary 17-D) using glyoxal pressures of ∼4 mbar to 17 mbar.

(b) Diode array spectrometer with a spectral resolution of 0.6 nm. Glyoxal, prepared by heating glyoxal trimer dihydrate in the presence of P_2O_5, was used at pressures in the range $(1.5 – 10) \times 10^{16}$ molecule cm^3.

(c) Diode array spectrometer with a spectral resolution of 0.25 nm. Glyoxal, prepared as in (b), was used at a range of pressures but small deviations from Beer-Lambert law were found at partial pressures $> \sim 0.4$ mbar. Cross sections reported were determined in the linear region with bath gas up to 960 mbar.

(d) Rate of photolysis of glyoxal in air mixtures at atmospheric pressure measured in an environmental chamber. The quantum yield for the photodissociation of glyoxal was obtained by comparison of the measured rate of removal of glyoxal with the rate of photolysis of NO_2 under similar experimental conditions.

(e) Laser photolysis of 5.3 mbar glyoxal in 1.3 bar N_2 at 295 K. HCO product determined by time-resolved laser resonance absorption. Quantum yield determined by comparing the HCO radical absorption observed with the same signals following HCHO and $(CHO)_2$ photolyses.

(f) Excimer laser photolysis of flowing glyoxal-N_2 mixtures. [HCO] monitored by time-resolved cavity ring-down spectroscopy. Yields of HCO determined by comparison of absorption with signals from photolysis of formaldehyde-N_2 mixtures under similar conditions. Incident light intensities were measured by a Joulemeter calibrated by chemical actinometry. The HCO quantum yields were found to be independent of glyoxal pressure, total pressure (26 mbar to 470 mbar), and light intensity.

Preferred Values

Absorption Cross-Sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
210	1.46	298	3.87	384	1.81
212	1.16	300	3.80	386	1.81
214	0.94	302	3.59	388	2.83
216	0.79	304	3.20	390	3.30
218	0.66	306	3.09	392	3.35
220	0.57	308	2.99	394	3.17
222	0.52	310	3.01	396	3.47
224	0.49	312	3.18	398	3.88
226	0.47	314	2.93	400	3.92
228	0.46	316	2.40	402	5.70
230	0.48	318	2.09	404	5.73
232	0.52	320	1.74	406	4.28
234	0.54	322	1.69	408	3.59
236	0.58	324	1.57	410	5.21
238	0.66	326	1.55	412	6.99
240	0.71	328	1.76	414	9.49
242	0.76	330	1.47	416	7.65
244	0.83	332	0.97	418	7.18
246	0.95	334	0.85	420	6.76
248	1.03	336	0.59	422	7.34
250	1.09	338	0.58	424	9.50
252	1.19	340	0.54	426	13.30
254	1.34	342	0.49	428	16.06
256	1.44	344	0.56	430	6.70
258	1.50	346	0.66	432	5.86
260	1.61	348	0.54	434	6.39
262	1.77	350	0.37	436	10.21
264	1.92	352	0.39	438	10.77
266	2.03	354	0.38	440	17.34
268	2.10	356	0.41	442	8.97
270	2.24	358	0.44	444	12.39
272	2.41	360	0.49	446	6.58
274	2.65	362	0.58	448	4.66
276	2.76	364	0.57	450	9.76
278	2.85	366	0.65	452	20.37
280	2.89	368	0.87	454	34.09
282	3.08	370	1.01	456	9.66
284	3.27	372	1.05	458	1.60
286	3.52	374	1.18	460	1.13
288	3.57	376	1.26	462	0.47
290	3.52	378	1.42	464	0.32
292	3.43	380	1.81	466	0.41
29	3.53	382	2.00	468	0.09
296	3.62				

Comments on Preferred Values

Glyoxal exhibits two distinct absorption regions relevant for atmospheric photolysis. The first region consists of a series of discrete bands between 360 – 460 nm, super-imposed on a continuum. The second region shows a broad band with some structure with a maximum absorption near 300 nm. The preferred values for the absorption cross-sections are based on those determined by Horowitz et al. (2001), which, except at $\lambda < 240$ nm, are in excellent agreement with the data of Orlando and Tyndall (2001) and in satisfactory agreement with the earlier data of Plum et al. (1983). Zhu et al. (1996) have measured the cross-sections at 193 nm, 248 nm, 308 nm and 351 nm. Where comparison is possible there is good agreement with the recommended data at all wavelengths. The values given above are averaged over 2 nm and are taken from the compilation in http://www.atmosphere.mpg.de/enid/, which also contains data at other resolution.

There are insufficient data on quantum yields to recommend values as a function of wavelength under atmospheric conditions. The overall quantum efficiency in the first absorption region is low, but the results of Zhu et al. (1996) suggest that dissociation to 2 HCO radicals is significant at wavelengths less than the dissociation threshold (401 nm). The ”effective” quantum yield of ϕ= 0.029 reported by Plum et al. (1983) is valid only for the particular spectral distribution used in their study. They measured ($\phi\sigma$) integrated over the range 325 nm to 470 nm and this may be used to calculate the rate of photolysis of glyoxal under tropospheric conditions within that spectral region. Since the recommended σ values are ∼10% higher than reported by Plum et al. (1983) in this region, an ”effective” quantum yield of ϕ = 0.026 should be used. The validity of this calculation has been supported by chamber studies of Klotz et al. (2000). Both Zhu et al. (1996) and Langford and Moore (1984) obtain a value of $\phi_2 \approx 0.4$ at 308 nm. The fall off in ϕ(HCO) below 350 nm may be due to occurrence of molecular channels (1) and (3), which can now be rationalised theoretically.

References

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Plum, C. N., Sanhueza, E., Atkinson, R., Carter, W. P. L., and Pitts Jr., J. N.: Environ. Sci. Technol., 17, 479, 1983.
Zhu, L., Kellis, D., and Ding, C.-F.: Chem. Phys. Lett., 257, 487, 1996.

II.A8.202

$HOCH_2CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$HOCH_2CHO + h\nu$	$\rightarrow CH_3OH + CO$	(1)	−19.5	
	$\rightarrow HOCH_2 + HCO$	(2)	355.3	337
	$\rightarrow HOCH_2CO + H$	(3)	373.8	320

Absorption cross-sections

Wavelength range/nm	Reference	Comments
205–335	Bacher et al., 2001	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$0.5 < \phi < 1.0$	285 ± 25	Bacher et al., 2001	(b)

Comments

(a) Diode array spectrophotometric measurements with 90 cm pathlength. Data obtained with 1 nm resolution. Beer-Lambert plot linear over range of glycolaldehyde pressure of 0.04–0.6 mbar. Cross-sections tabulated at 1 nm intervals. Peak cross section at 277 nm was 5.49×10^{-20} cm^2 molecule^{-1} with an error of ±15%.

(b) Overall quantum yields for the photolysis of ∼100 ppm of $HOCH_2CHO$ in air at a total pressure of 1 bar, determined relative to a value of 0.3 determined for acetone in the same equipment. Products and mechanism of the steady state photolysis was deduced, which suggested that Reaction (2) was the main channel but with a significant contribution from Reaction (1).

Preferred Values

Absorption Cross-Sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
205	39.1	250	2.36	295	3.59
206	33.7	251	2.50	296	3.46
207	28.7	252	2.65	297	3.29
208	24.6	253	2.82	298	3.17
209	21.2	254	2.97	299	3.02
210	18.1	255	3.09	300	2.90
211	15.3	256	3.21	301	2.74
212	13.0	257	3.39	302	2.51
213	11.2	258	3.59	303	2.26
214	9.40	259	3.75	304	2.07
215	7.84	260	3.89	305	1.91
216	6.49	261	4.02	306	1.77
217	5.30	262	4.13	307	1.64

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
218	4.26	263	4.24	308	1.50
219	3.37	264	4.40	309	1.36
220	2.65	265	4.60	310	1.25
221	2.13	266	4.75	311	1.15
222	1.65	267	4.85	312	1.03
223	1.36	268	4.92	313	0.884
224	1.12	269	4.99	314	0.771
225	0.933	270	5.05	315	0.689
226	0.783	271	5.14	316	0.597
227	0.691	272	5.23	317	0.516
228	0.637	273	5.36	318	0.455
229	0.637	274	5.40	319	0.396
230	0.649	275	5.41	320	0.329
231	0.644	276	5.39	321	0.285
232	0.680	277	5.42	322	0.249
233	0.723	278	5.37	323	0.213
234	0.785	279	5.34	324	0.185
235	0.833	280	5.34	325	0.147
236	0.880	281	5.37	326	0.128
237	0.939	282	5.37	327	0.105
238	1.03	283	5.25	328	0.087
239	1.11	284	5.12	329	0.084
240	1.20	285	5.01	330	0.068
241	1.28	286	4.93	331	0.058
242	1.38	287	4.80	332	0.043
243	1.50	288	4.67	333	0.040
244	1.59	289	4.58	334	0.040
245	1.71	290	4.50	335	0.039
246	1.83	291	4.41		
247	1.95	292	4.19		
248	2.09	293	3.96		
249	2.22	294	3.76		

Quantum Yield: $\phi = 0.75 \pm 0.25$ for $\lambda = 260$–310 nm in 1 bar air

Comments on Preferred Values

The preferred absorption cross-sections are from the study of Bacher et al. (2001), which are the only measurements reported and appear to be reliable. The preferred value for the overall quantum yield is based on the work of Bacher et al. (2001). The value was determined relative to $\phi(CH_3C(O)CH_3)=0.3$ in 1 bar air for the wavelength region 260–310 nm, which is consistent with the work of Gierczak et al. (1998) which forms the basis of the current IUPAC evaluation. The most likely decomposition channel was shown to be HCO production in channel (2), but there is insufficient information to recommend a branching ratio.

References

Bacher, C., Tyndall, G. S., and Orlando, J. J.: J. Atm. Chem., 39, 171, 2001.
Gierczak, T., Burkholder, J. B., Bauerle, S., and Ravishankara, A. R.: Chem. Phys., 231, 229, 1998.

II.A8.203

$CH_3C(O)CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3C(O)CHO + h\nu$	$\rightarrow CH_4 + 2CO$	(1)	−24.7	
	$\rightarrow CH_3CO + HCO$	(2)	304.2	393
	$\rightarrow CH_3CHO + CO$	(3)	−5.2	

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220–480	Meller et al., 1991	(a)
205–480	Staffelbach et al., 1995	(b)
290–440	Chen et al., 2000	(c)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi(2)$			
0.14	240–420	Staffelbach et al., 1995	(d)
1.0	260–320	Koch and Moortgat, 1998	(e)
1.10 ± 0.14	380		
0.47 ± 0.09	400		
0.21 ± 0.06	420		
0.08 ± 0.02	440		
0.82 ± 0.06	290	Chen et al., 2000	(f)
0.89 ± 0.10	300		
0.97 ± 0.08	320		
0.92 ± 0.10	380		
0.56 ± 0.09	400		
0.27 ± 0.04	420		
0.17 ± 0.02	440		

Comments

(a) Measured over the range 220 nm to 480 nm by conventional UV spectroscopy in a cell of path length 63 cm. Light was detected by a diode array camera and the spectral resolution was 0.07 nm. As well as using methylglyoxal prepared external to the cell, methylglyoxal was generated in situ by the Cl atom-initiated modulated photo-oxidation of hydroxyacetone and the cross-sections were measured over the range 390 nm to 460 nm in these in situ studies.

(b) Cross-sections measured in a 90 cm cell using a diode array spectrometer. The spectral resolution was estimated to be 0.6 nm. Pressures in the range 0.13 mbar to 8.0 mbar were used and measurements were made at 248 K, 273 K and 298 K.

(c) Cross-sections determined from transmission of UV light at 5 nm intervals from tunable dye laser, as a function of $CH_3C(O)CHO$ pressure. Overall uncertainty estimated to be ∼10% at all wavelengths, except at 280 and 330 nm, where uncertainties are 20–30% higher.

(d) Low concentrations of methylglyoxal in an O_2 (20%)/N_2 (80%) mixture at 1 bar were photolysed with an Xe arc equipped with filters to isolate specific wavelength regions. Products (HCHO, $CH_3C(O)OH$, $CH_3C(O)O_2H$, CH_3OH, HC(O)OH, CO, CO_2) were monitored by FTIR. Light intensity calibrated by photolysis of Cl_2-CH_3OH-O_2-N_2 mixture. Quantum yields were derived by modeling product yields taking into account a number of important secondary reactions. Average ϕ value quoted.

(e) Static photolysis of $CH_3C(O)CHO$ in synthetic air. Quantum yields of molecular products CO and HCHO determined by GC. Pressure range 30–900 Torr (0.039–1.2 bar). For the short wavelength band ϕ was independent of pressure and wavelength; in the long wavelength band ϕ(CO) showed Stern-Volmer pressure quenching and ϕ(HCHO) increased with methylglyoxal pressure; zero pressure values of $CH_3C(O)CHO$ are quoted here. The primary process was attributed to Reaction (2) at all wavelengths.

(f) Tunable dye laser photolysis of $CH_3C(O)CHO$ with time resolved measurement of HCO concentration by cavity ring down spectroscopy at 613.8 nm. Absorbed flux was determined from photon fluence measurements using a calibrated Joulemeter. Absolute yields of HCO calculated from absorption cross sections, σ(HCO), determined by in situ calibration using either photo-dissociation of HCHO (at 290–310 nm) or Cl_2+HCHO mixtures (at 310–440 nm) to produce known amounts of HCO. A weak dependence of ϕ(HCO) on $P_{CH3COCHO}$ was observed and the values of ϕ quoted at selected wavelengths are for zero pressure, derived from Stern-Volmer plots. No dependence of ϕ(HCO) on N_2 pressure up to 520 mbar was observed in the 270–390 nm region. Pressure quenching by N_2 was observed in the long wavelength band (380–440 nm) and expressions were reported for the wavelength-dependent zero pressure quantum yield $\phi(HCO)_0=(3.63\pm0.32)\times10^{-7}$ [exp(-(5693±533)/λ (nm)] and Stern-Volmer quenching constant by N_2 (k_Q $(Torr^{-1})=(1.93\pm0.24)\times10^4$ [exp(-(5639±497)/λ (nm)]). Values of ϕ(2) for 1 bar air were obtained by extrapolation, and atmospheric photolysis rates were calculated.

Preferred Values

Absorption cross-sections at 298 K at 5 nm intervals between 225 nm and 410 nm

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
225	1.268	320	1.511
230	1.477	325	0.938
235	1.803	330	0.652
240	2.071	335	0.482
245	2.304	340	0.323
250	2.612	345	0.300
255	2.859	350	0.394
260	3.280	355	0.560
265	3.618	360	0.695
270	4.159	365	1.077
275	4.413	370	1.475
280	4.877	375	1.911
285	4.719	380	2.429
290	4.838	385	3.221
295	4.362	390	4.029
300	3.754	395	4.732
305	3.361	400	5.664
310	2.365	405	6.923
315	1.891	410	8.459

Absorption cross-sections at 298 K at 1 nm intervals between 401 nm and 475 nm

λ/nm	$10^{20}\sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\sigma/\mathrm{cm}^2$
401	5.90	439	11.01
402	6.07	440	9.94
403	6.35	441	10.39
404	6.54	442	10.20
405	6.91	443	10.17
406	7.20	444	11.17
407	7.58	445	9.61
408	7.94	446	8.90
409	8.12	447	9.84
410	8.52	448	9.18
411	8.63	449	10.13
412	9.07	450	8.67
413	9.37	451	6.34
414	9.62	452	6.33
415	9.68	453	6.08
416	9.71	454	4.46
417	10.04	455	3.69
418	10.07	456	3.08
419	10.12	457	2.46
420	10.21	458	1.81
421	10.34	459	1.28
422	10.51	460	0.914
423	10.45	461	0.795
424	10.15	462	0.642
425	10.34	463	0.479
426	10.24	464	0.332
427	9.84	465	0.268
428	10.01	466	0.227
429	9.94	467	0.187
430	10.41	468	0.160
431	10.53	469	0.133
432	9.79	470	0.108
433	10.64	471	0.099
434	10.54	472	0.089
435	10.81	473	0.077
436	11.13	474	0.067
437	9.99	475	0.062
438	10.59		

Quantum yields for zero pressure at 298 K

$\phi(2)_0 = (3.63 \pm 0.32) \times 10^{-7}$ [exp(5693 ± 533)/λ(nm)] for $380 < \lambda < 440$ nm

$\phi(2)_0 = 1.0$ for $280 < \lambda < 380$ nm

Comments on Preferred Values

The preferred values of the absorption cross-sections are taken from the work of Meller et al. (1991). The cross-sections of Staffelbach et al. (1995) and Chen et al. (2000) agree to within <10% with those of Meller et al. (1991) across the whole range of the three studies. Staffelbach et al. (1995) also studied the cross-sections at three different temperatures, 248 K, 273 K, and 298 K. They found little variation in the cross-sections ($\leq$10%) over this temperature range.

The recent studies of Koch and Moortgat (1998) and Chen et al. (2000) provide for the first time information on the wavelength-resolved quantum yields for methylglyoxal photolysis, and the latter study gives direct measurements of the initial product of photodissociation by Reaction (2), HCO. This demonstrates conclusively that Reaction (2) is the predominant dissociation channel over the wavelength range 280–440 nm. These results supercede the earlier work of Staffelbach et al. (1995), Raber and Moortgat (1997) and Plum et al. (1983), which used broad-band excitation.

The results of Koch and Moortgat (1998) and Chen et al. (2000) are in good agreement for the zero pressure quantum yields, and for the absence of pressure dependence of $\phi(2)$ at $\lambda<380$ nm. At the longer wavelengths ($380<\lambda<440$ nm) both studies observed a fall off in $\phi(2)$ with wavelength, and a complex pressure dependence. Koch and Moortgat (1998) interpret their HCHO yields using a mechanism with a reaction of excited methylglyoxal with the ground state. The quenching by N_2 observed by Chen et al. (2000) in the long wavelength band (380–440 nm) did not exhibit Stern-Volmer behaviour, indicating the involvement of more than one excited precursor for HCO. There is a difference of up to a factor of 4 in the extrapolated values for the quantum yields in the range λ=380–400 nm at atmospheric pressure reported from the two studies.

The preferred values are taken from Chen et al. (2000), since they were determined directly. The expression for the wavelength dependence of $\phi\,(2)_0$ (zero pressure) at $\lambda>380$ nm is taken from their work. Values at higher pressures (of air) can be calculated using the expression for the wavelength dependence of the quenching constant obtained by approximating to the Stern Volmer relationship:

$$1/\phi(2) = 1/\phi(2)_0 + k_Q\ P[N_2\ (\text{Torr})]$$

where k_Q (Torr^{-1})=$(1.93\pm0.24)\times10^4$ [exp(-(5639±497)/λ (nm)]. In view of the departure from linearity this leads to an estimated uncertainty up to ±50% in the overall quantum yield at 1 bar.

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$CH_3C(O)CH_3$ + hν → products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3C(O)CH_3$ + hν	→ $CH_3CO + CH_3$	(1)	353.6	338
	→ $2CH_3 + CO$	(2)	399.5	299

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–355	Martinez et al., 1992	(a)
260–360	Hynes et al., 1992	(b)
215–350	Gierczak et al., 1998	(c)
240–350	Yujing and Mellouki, 2000	(d)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength range/nm	Reference	Comments
ϕ_1 = 0.76–0.0033	250–330	Meyrahn et al., 1986	(e)
ϕ = 1.0–0.016	248–337	Gierczak et al., 1998	(f)
ϕ_1 = 1.0–0.062	280–330	Emrich and Warneck, 2000	(g)
ϕ_1 = 1.0, 0.28	248, 308	Emrich and Warneck, 2000	(h)
ϕ_1 = 1.0–0.01	279-327.5	Blitz et al., 2004	(i)
ϕ (CO) = 0.45 (20 mbar), 0.25 (900 mbar)	248	Somnitz et al., 2005	(j)

Comments

(a) Cross-sections are the average cross-section over a 1 nm (λ>280 nm) or 4 nm (λ<280 nm) region centered at the corresponding wavelength. σ_{max}=5.07×10^{-20} cm^2 molecule^{-1} at 278 nm.

(b) Cross-sections measured as a function of temperature over the range 260 K to 360 K. Data were presented in graphical form and show a marked decrease in cross-section with decreasing temperature at longer wavelengths.

(c) Measurements made using a diode array spectrometer with a D_2 lamp source and temperature controlled cell with 200 cm path-length. Resolution 0.5 nm. Temperature range 235–298 K. Modest temperature dependence at λ>300 nm. Tabulated cross sections at 1 nm intervals and parameterisation of temperature dependence given. σ_{max}=4.94×10^{-20} cm^2 molecule^{-1} (±5%) at 278 nm.

(d) Commercial diode array spectrometer with a D_2 lamp source and 200 cm pathlength cell at 298 K. Resolution 0.04 nm. Tabulated cross sections at 1 nm intervals given. σ_{max}=4.97×10^{-20} cm^2 molecule^{-1} (±5%) at 278 nm.

(e) Study of the quantum yield of formation of CO_2 and CO in the photolysis of dilute mixtures of acetone (0.13 mbar to 0.20 mbar) in air (990 mbar) at room temperature. In addition, the quantum yields of formation of peroxyacetyl nitrate (PAN) were measured when trace amounts of NO_2 (1.2×10^{-4} mbar) were added to the reactant mixtures. The listed values of ϕ_1 are the quantum yields of PAN, which were taken as a measure of the extent of primary process (1).

(f) Quantum yield determined using pulsed laser photolysis of static mixtures with measurement of the loss of acetone and formation of products. ϕ was determined as a function of pressure (30–1000 mbar air) and at nine discrete wavelengths in the stated range. At $\lambda > 270$ nm ϕ showed Stern-Volmer pressure quenching. The zero pressure quantum yield increased as wavelength decreased to a value of unity near 290 nm. At 308 nm ϕ was independent of temperature between 298 and 195 K. Expression given for the variation with pressure and wavelength of ϕ for 1 bar air.

(g) Quantum yields for peroxyacetyl nitrate (PAN) production from photodissociation of acetone (<1%) in air when trace amounts of NO_2 were added to the reactant mixtures. The quantum yields of PAN formation used to determine ϕ_1 at 10 nm intervals in the range given and at total pressures in the range 130–1000 mbar. Stern-Volmer pressure quenching observed at all wavelengths. Results interpreted in terms of the elementary processes involving the first excited singlet and triplet states of acetone, providing rate parameters for the competing processes as a function of excitation energy.

(h) Relative quantum yield for acetone photodissociation at the specified laser wavelengths with and without water present. At a total pressure of 133 mbar, H_2O up to 12 mbar suppressed the quantum yield, the effect being stronger at 308 nm.

(i) Quantum yields for CH_3CO formation determined as a function of temperature (218–295 K) and pressure (0.46–540 mbar, [He, N_2 or Air]) using time-resolved HO-photofragment spectroscopy to monitor acetyl radical production from PLP of acetone (0.006 mbar). HO produced from CH_3CO photolysis was monitored by LIF at 282 nm giving sensitivity of $< 10^8$ molecule cm^3. The total quantum yield $\phi_{total}(\lambda, p, T) = \phi_{CH3CO}(\lambda, p, T) + \phi_{CO}(\lambda, T) = \phi_1 + \phi_2$ was determined relative to the measured values of $\phi_{total} = 1$, $\phi_{CH3CO} = 0.65$ and $\phi_{CO} = 0.35$, at 248 nm and 295 K, at the pressure limit p = 0. Pressure dependence was represented by simple Stern-Volmer quenching at $\lambda < 302$ nm, but at longer wavelengths an extended form of Stern-Volmer expression was necessary to represent the data. A substantial decline in ϕ_{total} with decreasing temperature was observed at wavelengths above 310 nm. An empirical algorithm for the overall dissociation quantum yield, and for ϕ_{CH3CO} and ϕ_{CO} in air, as a function of wavelength, temperature and pressure is given.

(j) Quantum yields for CO formation determined as a function of pressure (20–900 mbar, [N_2]) at 298 K, using infrared diode laser absorption to monitor CO production from PLP of acetone at 248 nm. Results are interpreted to show CO production results exclusively from channel (1) via CH_3CO decomposition .

Preferred Values

Temperature dependent cross sections (215-349 nm)

λ/ (nm)	$10^{20}\sigma$ (cm^2)	10^3 A (K^{-1})	10^5 B (K^{-2})	10^8 C (K^{-3})	λ/ (nm)	$10^{20}\sigma$ (cm^2)	10^3 A (K^{-1})	10^5 B (K^{-2})	10^8 C (K^{-3})
215	0.167	-10.46	8.346	16.43	283	4.71	1.137	-1.350	3.272
216	0.180	-9.192	7.357	-14.51	284	4.62	0.8530	-1.158	2.943
217	0.196	-6.233	5.039	-10.0	285	4.54	0.6518	-1.023	2.714
218	0.212	-3.190	2.651	-5.359	286	4.44	0.4907	-0.9154	2.531
219	0.228	-1.002	0.9314	-2.003	287	4.36	0.3190	-0.7992	2.332
220	0.24	0.4104	-0.1807	0.1679	288	4.28	0.1109	0.6586	2.092
221	0.270	1.567	-1.090	1.93	289	4.15	-0.1230	-0.5036	1.833
222	0.294	2.962	-2.183	4.058	290	4.06	-0.3698	-0.3426	1.568
223	0.318	4.839	-3.651	6.909	291	3.95	-0.6430	-0.1615	1.265
224	0.346	6.940	-5.293	10.09	292	3.82	-0.9625	0.05796	0.8847
225	0.380	8.598	-6.588	12.60	293	3.71	-1.316	0.306	0.4472
226	0.419	9.380	-7.200	13.79	294	3.57	-1.650	0.535	0.0477
227	0.456	9.551	-7.336	14.06	295	3.42	-1.905	0.699	-0.2168
228	0.492	9.705	-7.462	14.31	296	3.26	-2.084	0.796	-0.3430
229	0.535	10.08	-7.761	14.89	297	3.11	-2.234	0.867	-0.4086
230	0.584	10.41	-8.023	15.41	298	2.98	-2.391	0.942	-0.4824
231	0.637	10.39	-8.002	15.36	299	2.82	-2.590	1.055	-0.6387
232	0.693	10.01	-7.707	14.79	300	2.67	-2.915	1.277	-1.020
233	0.750	9.534	-7.332	14.06	301	2.58	-3.421	1.649	-1.709
234	0.815	9.138	-7.022	13.46	302	2.45	-4.008	2.091	-2.543
235	0.885	8.851	-6.799	13.02	303	2.30	-4.508	2.465	-3.248

λ/ (nm)	$10^{20}\sigma$ (cm^2)	10^3 A (K^{-1})	10^5 B (K^{-2})	10^8 C (K^{-3})	λ/ (nm)	$10^{20}\sigma$ (cm^2)	10^3 A (K^{-1})	10^5 B (K^{-2})	10^8 C (K^{-3})
236	0.956	8.638	-6.634	12.70	304	2.18	-4.858	2.715	-3.699
237	1.03	8.471	-6.504	12.45	305	2.05	-5.120	2.880	-3.959
238	1.11	8.318	-6.385	12.22	306	1.89	-5.433	3.062	-4.219
239	1.21	8.125	-6.235	11.93	307	1.75	-6.010	3.429	-4.805
240	1.30	7.861	-6.031	11.53	308	1.61	-6.986	4.096	-5.954
241	1.40	7.554	-5.793	11.07	309	1.49	-8.135	4.899	-7.370
242	1.50	7.268	-5.571	10.64	310	1.36	-8.897	5.415	-8.255
243	1.60	7.035	-5.390	10.29	311	1.24	-8.923	5.378	-8.097
244	1.72	6.838	-5.237	9.994	312	1.14	-8.494	5.001	-7.305
245	1.83	6.649	-5.093	9.718	313	1.06	-8.228	4.754	-6.772
246	1.95	6.472	-4.960	9.464	314	0.944	-8.445	4.881	-6.959
247	2.07	6.326	-4.850	9.256	315	0.837	-8.966	5.240	-7.592
248	2.20	6.210	-4.763	9.091	316	0.760	-9.409	5.528	-8.076
249	2.33	6.099	-4.680	8.936	317	0.684	-9.584	5.588	-8.085
250	2.47	5.972	-4.587	8.763	318	0.598	-9.736	5.596	-7.946
251	2.60	5.832	-4.486	8.576	319	0.523	-10.39	5.958	-8.433
252	2.74	5.697	-4.389	8.399	320	0.455	-11.80	6.869	-9.933
253	2.87	5.581	-4.306	8.249	321	0.411	-13.48	7.962	-11.75
254	3.01	5.483	-4.235	8.120	322	0.348	-14.59	8.600	-12.67
255	3.15	5.385	-4.164	7.989	323	0.294	-14.98	8.670	-12.47
256	3.30	5.261	-4.075	7.825	324	0.248	-15.39	8.743	-12.27
257	3.44	5.101	-3.961	7.620	325	0.210	-16.28	9.187	-12.77
258	3.57	4.932	-3.843	7.410	326	0.174	-17.09	9.588	-13.21
259	3.69	4.802	-3.756	7.262	327	0.141	-17.21	9.471	-12.68
260	3.81	4.746	-3.723	7.215	328	0.113	-16.92	9.048	-11.58
261	3.94	4.744	-3.730	7.239	329	0.0913	-16.66	8.672	-10.62
262	4.07	4.734	-3.729	7.246	330	0.0740	-15.94	7.979	-9.099
263	4.20	4.651	-3.674	7.155	331	0.0586	-13.93	6.340	-5.829
264	4.32	4.482	-3.559	6.956	332	0.0465	-10.93	3.969	-1.214
265	4.41	4.271	-3.416	6.712	333	0.0375	-8.186	1.847	2.840
266	4.49	4.087	-3.296	6.513	334	0.0311	-6.530	0.6289	5.067
267	4.56	3.983	-3.234	6.420	335	0.0248	-5.692	0.1022	5.880
268	4.64	3.969	-3.235	6.440	336	0.0199	-4.656	-0.5382	6.860
269	4.72	4.009	-3.273	6.524	337	0.0162	-2.090	-2.355	10.09
270	4.79	4.025	-3.294	6.577	338	0.0135	3.113	-6.237	17.33
271	4.87	3.935	-3.240	6.494	339	0.0113	11.01	-12.26	28.77
272	4.91	3.704	-3.085	6.231	340	00912	20.02	-19.22	42.15
273	4.94	3.378	-2.861	5.845	341	00729	27.20	-24.83	53.03
274	4.94	3.061	-2.645	5.473	342	00583	29.63	-26.80	56.96
275	4.94	2.854	-2.508	5.243	343	00494	25.97	-24.04	51.78
276	4.93	2.790	-2.474	5.201	344	00365	16.35	-16.63	37.55
277	4.92	2.816	-2.505	5.276	345	0,0301	3.774	-6.858	18.72
278	4.94	2.82	-2,518	5.316	346	0.00235	-2.414	-1.987	9.304
279	4.92	2.692	-2.433	5.175	347	0.00158	7.880	-9.888	24.53
280	4.91	2.389	-2.222	4.803	348	0.00111	29.52	-26.61	56.78
281	4.86	1.963	-1.922	4.272	349	0.00107	41.03	-35.51	73.95
282	4.79	1.517	-1.612	3.726					

$\sigma(\lambda,T) = \sigma(\lambda,298\text{ K})[1 + \mathrm{A}(\lambda)T + \mathrm{B}(\lambda)T^2 + \mathrm{C}(\lambda)T^3]$.

Quantum Yields

$\boldsymbol{\phi_{\mathrm{total}}(\lambda, [\mathrm{M}], \mathrm{T}) = \phi_{\mathrm{CH3CO}}(\lambda, [\mathrm{M}], \mathrm{T}) + \phi_{\mathrm{CO}}(\lambda, \mathrm{T})}$

For λ = 279-327.5 nm

$$\phi_{\mathrm{CO}}(\lambda, \mathrm{T}) = \mathrm{i}/(1 + \mathrm{A}_0)$$

where $\mathrm{A}_0 = [\mathrm{a}_0/(1 - \mathrm{a}_0)] \exp[\mathrm{b}_0\{\lambda - 248\}]$
$\mathrm{a}_0 = (0.350 \pm 0.003)\ (\mathrm{T}/295)^{(-1.28\pm0.03)}$
$\mathrm{b}_0 = (0.068 \pm 0.002)\ (\mathrm{T}/295)^{(-2.65\pm0.20)}$

For λ = 279-302.5 nm

$$\phi_{\mathrm{CH3CO}}(\lambda, [\mathrm{M}], \mathrm{T}) = \{1-\phi_{\mathrm{CO}}(\lambda, \mathrm{T})\}/\{1+ \mathrm{A}_1[\mathrm{M}]\}$$

where $\mathrm{A}_1 = \mathrm{a}_1 \exp[-\mathrm{b}_1 \{(10^7/\lambda) - 33113\}]$
$\mathrm{a}_1 = (1.600 \pm 0.032) \times 10^{-19}\ (\mathrm{T}/295)^{(-2.38\pm0.08)}$
$\mathrm{b}_1 = (0.55 \pm 0.02) \times 10^{-3}\ (\mathrm{T}/295)^{(-3.19\pm0.13)}$

For λ = 302-327.5 nm

$$\phi_{\mathrm{CH3CO}}(\lambda, [\mathrm{M}], \mathrm{T}) = \{(1 + \mathrm{A}_4[\mathrm{M}] + \mathrm{A}_3)/[(1 + \mathrm{A}_2[\mathrm{M}] + \mathrm{A}_3)(1 + \mathrm{A}_4[\mathrm{M}])]\}\ \{1- \phi_{\mathrm{CO}}(\lambda, \mathrm{T})\}$$

where $\mathrm{A}_2 = \mathrm{a}_2 \exp[-\mathrm{b}_2\{(10^7/\lambda) - 30488\}]$
$\mathrm{a}_2 = (1.62 \pm 0.06) \times 10^{-17}\ (\mathrm{T}/295)^{(-10.03\pm0.20)}$
$\mathrm{b}_2 = (1.79 \pm 0.02) \times 10^{-3}\ (\mathrm{T}/295)^{(-1.364\pm0.036)}$
$\mathrm{A}_3 = \mathrm{a}_3 \exp[-\mathrm{b}_3\{(10^7/\lambda) - \mathrm{c}_3\}^2]$
$\mathrm{a}_3 = (26.29 \pm 0.88)\ (\mathrm{T}/295)^{(-6.59\pm0.23)}$
$\mathrm{b}_3 = (5.72 \pm 0.20) \times 10^{-7}\ (\mathrm{T}/295)^{(-2.93\pm0.09)}$
$\mathrm{c}_3 = (30006 \pm 41)\ (\mathrm{T}/295)^{(-0.064\pm0.004)}$
$\mathrm{A}_4 = \mathrm{a}_4 \exp[-\mathrm{b}_4 \{(10^7/\lambda) - 30488\}]$
$\mathrm{a}_4 = (1.67 \pm 0.14) \times 10^{-15}\ (\mathrm{T}/295)^{(-7.25\pm0.54)}$
$\mathrm{b}_4 = (2.08 \pm 0.02) \times 10^{-3}\ (\mathrm{T}/295)^{(-1.16\pm0.15)}$

In all cases [M] is in molecule cm^{-3}, λ in nm and T in K.

Comments on Preferred Values

The preferred absorption cross-sections are based on the measurements of Gierczak et al. (1998). They agree well with the room temperature measurements of Martinez et al. (1992) and Yujing and Mellouki (2000). Over the wavelength region 260 nm to 320 nm these cross-sections are within 5% of earlier recommendations based on the data of Calvert and Pitts (1966) and Meyrahn et al. (1986). The cross-sections reported by Hynes et al. (1992) at room temperature contain large error limits at 320 nm and 340 nm but are in reasonable agreement with those recommended here. The recommended temperature dependent cross sections for 1 nm intervals over the range 215 – 349 nm, are based on the expression derived by Burkholder (as cited in the NASA Evaluation No 15, 2005), obtained by using a cubic fit to the data of Gierczak et al. (1998).

The recent studies of the quantum yield for photodissociation of acetone [Gierczak et al., 1998; Emrich and Warneck, 2000; Blitz et al., 2005; Somnitz et al., 2005] have provided reliable wavelength and pressure dependence of ϕ and ϕ_1. The measured quantum yields and their pressure and wavelength dependence are essentially in agreement at wavelengths below 300 nm, where there is little temperature dependence. Both ϕ_{CH3CO} and ϕ_{CO} are quenched with pressure, and ϕ_{total} at 1 bar falls off with wavelength above 280 nm. The p = 0 limit value of ϕ_{total} is unity at 248 nm. At longer wavelengths (> 310 nm) the study of Blitz et al. (2004) gave values of ϕ_{CH3CO} substantially smaller than reported earlier, with a decrease of ϕ with temperature which becomes larger with increasing wavelength. This study provides a more precise measurement of the quantum yields, and the optimized parameterization of the quantum yields for the range 279–327.5 nm, temperature 218 to 295 K and pressure up to 1000 mbar, given by Blitz et al. (2005) is recommended in this evaluation. These equations can be used to calculate the quantum yields in the range 279–327 nm and 218–295 K. Arnold et al.(2004) have discussed application of these data for atmospheric photolysis of acetone, and also the photodissociation mechanism. Dissociation occurs exclusively from the excited singlet state with an increasing fraction of decomposition via channel (2) at wavelengths below the threshold for this process at 299 nm. The recent work of Somnitz et al. (2005) confirms that CO derives only from dissociation of excited $\mathrm{CH_3CO}$ and not by a direct/concerted channel from the excited singlet state of acetone.

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II.A8.205

$CH_3C(O)C_2H_5 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3C(O)C_2H_5 + h\nu$	$\rightarrow CH_3 + C_2H_5CO$	(1)	352.6	339
	$\rightarrow C_2H_5 + CH_3CO$	(2)	349.4	342
	$\rightarrow CH_3 + C_2H_5 + CO$	(3)	395.3	

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–355	Martinez et al., 1992	(a)
240–350	Yujing and Mellouki, 2000	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
ϕ_1 0.34 (1000 mbar) 0.89 (68 mbar)	275–380	Raber and Moortgat, 1987	(c)

Comments

(a) Conventional double-beam spectrophotometric measurements on mixtures of 2-butanone and argon at a resolution of 0.5 nm. The cross-sections are given as averages over a 1 nm (λ>280 nm) or 4 nm (λ<280 nm) region centered on the corresponding wavelength. $\sigma_{max}=5.77\times10^{-20}$ cm^2 molecule^{-1} at 278 nm.

(b) Diode array spectrometer measurements on pure 2-butanone at a resolution of 0.04 nm. The cross-sections are given over 1 nm intervals. Precision based on observed standard deviation was within ±5%. $\sigma_{max}=5.65\times10^{-20}$ cm^2 molecule^{-1} at 278 nm.

(c) 2-Butanone was photolyzed in synthetic air at several pressures in the range 68 mbar to 1 bar using a broad band radiation source (275 nm to 380 nm) and the product yields were monitored by FTIR. The quantum yield for photolysis of 2-butanone was found to be pressure dependent decreasing from 0.89 at 68 mbar to 0.34 at 1 bar. They also conclude that photolysis over the wavelength region used occurs to the extent of 80–90% by channel 2. These results were derived by modelling the secondary chemistry in the system.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\sigma/\mathrm{cm}^2$
202	1.412	292	4.60	324	0.229
206	0.192	293	4.42	325	0.189
210	0.160	294	4.24	326	0.156
214	0.183	295	4.08	327	0.129
218	0.225	296	3.93	328	0.105
222	0.290	297	3.79	329	0.085
226	0.391	298	3.65	330	0.067
230	0.534	299	3.48	331	0.054
234	0.742	300	3.30	332	0.042
238	1.029	301	3.10	333	0.033
242	1.410	302	2.89	334	0.025
246	1.886	303	2.69	335	0.020
250	2.45	304	2.50	336	0.014
254	3.09	305	2.33	337	0.011
258	3.74	306	2.17	338	0.008
262	4.39	307	2.02	339	0.007
266	4.96	308	1.876	340	0.005
270	5.40	309	1.727	341	0.005
274	5.68	310	1.575	342	0.003
278	5.77	311	1.423	343	0.003
280	5.74	312	1.276	344	0.002
281	5.72	313	1.136	345	0.001
282	5.68	314	1.009	346	0.001
283	5.62	315	0.896	347	0.000
284	5.54	316	0.794	348	0.001
285	5.44	317	0.697	349	0.000
286	5.35	318	0.611	350	0.000
287	5.26	319	0.531	351	0.000
288	5.17	320	0.457	352	0.001
289	5.06	321	0.389	353	0.000
290	4.94	322	0.328	354	0.000
291	4.78	323	0.276	355	0.000

Quantum Yields

$\phi = 0.34$ for $\lambda = 275$–380 nm at 1 bar

Comments on Preferrred Values

The preferred absorption cross-sections are taken from the measurements of Martinez et al. (1992) over the wavelength region 220 nm to 350 nm. The values at the band maximim are 5% higher than the recent data of Yujing and Mellouki (2000), but 5% lower than those of McMillan, reported by Calvert and Pitts (1966). Raber and Moortgat (1987) have also given a spectrum which is in good agreement with these cross-sections.

The only quantum yield measurements are those of Raber and Moortgat (1987), which forms the basis for the preferred quantum yield at 1 bar. This data needs further experimental support.

References

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II.A8.206

CH_2= $C(CH_3)CHO$ + hν → products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_2=C(CH_3)CHO + h\nu$	$\rightarrow CH_2=CCH_3 + HCO$	(1)	320.5	373.1
	$\rightarrow C_3H_6 + CO$	(2)	16.1	7428
	$\rightarrow H + CH_2=C(CH_3)CO$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
250–395	Gierczak et al., 1997	(a)
235–400	Raber and Moortgat., 1996	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength range/nm	Reference	Comments
ϕ = 0.008 (865 mbar)	308	Gierczak et al., 1997	(c)
ϕ = 0.005 (33 mbar)	308		
ϕ = 0.005 (865 mbar)	351		
ϕ = 0.003 (33 mbar)	351		
$\phi < 0.05$ at 1 bar	275–370	Raber and Moortgat, 1996	(d)

Comments

(a) Measurements made using a diode array spectrometer with a D_2 lamp source and temperature controlled cell with 200 cm path-length. Resolution 0.5 nm. Temperature range 250–298 K. Tabulated cross sections at 1 nm intervals. $\sigma_{max}=7.2\times10^{-20}$ cm^2 molecule^{-1} (±5%) at 331 nm and $\sigma=(2.21\pm0.03)\times10^{-17}$ cm^2 molecule^{-1} at 213.86 nm (Zn lamp source). Small increase with decreasing temperature at λ max.

(b) Measurements made at 298 K using a diode array spectrometer with a D_2 lamp source. $\sigma_{max}=7.64\times10^{-20}$ cm^2 molecule^{-1} (±5%) at 330.7 nm.

(c) Quantum yield determined using pulsed laser photolysis of static mixtures with measurement of the loss of $CH_2=C(CH_3)CHO$ (methacrolein) by GC. ϕ was determined at pressures of 25 and 650 Torr (33 and 865 mbar) air, and at 308 and 351 nm. ϕ increased with pressure by a factor of ∼2 over the range. Propene not observed as a product, in contrast to other studies.

(d) Broad band photolysis of static mixtures (bath gas is air) with measurement of the loss of $CH_2=C(CH_3)CHO$ and formation of products (C_2H_4, C_3H_6, C_2H_2, CO, CO_2, HCHO) by FTIR. Quantum yield from loss of $CH_2=C(CH_3)CHO$ and formation of CO. Indication of a weak pressure effect with ϕ (50 Torr)/ϕ (760 Torr) ∼2. No firm information on the relative importance of the photolysis channels could be obtained from the product yields.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
250	0.207	300	3.44	350	4.16
251	0.194	301	3.61	351	3.85
252	0.187	302	3.76	352	3.89
253	0.180	303	3.91	353	4.35
254	0.178	304	4.04	354	4.31
255	0.177	305	4.19	355	4.14
256	0.180	306	4.40	356	3.62
257	0.180	307	4.58	357	3.53
258	0.186	308	4.71	358	3.46
259	0.193	309	4.81	359	3.81
260	0.201	310	4.92	360	5.05
261	0.211	311	5.13	361	4.28
262	0.224	312	5.35	362	3.61
263	0.241	313	5.50	363	2.86
264	0.263	314	5.61	364	2.68
265	0.283	315	5.70	365	2.33
266	0.305	316	5.87	366	1.92
267	0.333	317	6.04	367	1.62
268	0.363	318	6.19	368	1.40
269	0.398	319	6.28	369	1.31
270	0.436	320	6.27	370	1.42
271	0.479	321	6.18	371	1.67
272	0.520	322	6.21	372	1.53
273	0.567	323	6.34	373	1.43
274	0.616	324	6.58	374	1.08
275	0.673	325	6.74	375	0.977
276	0.732	326	6.73	376	1.000
277	0.793	327	6.68	377	1.07
278	0.863	328	6.83	378	1.35
279	0.936	329	7.07	379	2.18
280	1.01	330	7.15	380	1.30
281	1.09	331	7.16	381	0.984
282	1.18	332	7.03	382	0.555
283	1.26	333	6.69	383	0.456
284	1.35	334	6.41	384	0.364
285	1.45	335	6.08	385	0.331
286	1.56	336	5.97	386	0.246
287	1.67	337	6.25	387	0.205
288	1.79	338	6.38	388	0.181
289	1.90	339	6.37	389	0.161
290	2.03	340	6.24	390	0.147
291	2.16	341	6.02	391	0.156
292	2.28	342	5.98	392	0.159
293	2.40	343	6.58	393	0.153
294	2.52	344	6.79	394	0.149
295	2.68	345	6.53	395	0.123
296	2.85	346	6.11		
297	2.99	347	5.63		
298	3.13	348	5.22		
299	3.26	349	4.55		

Quantum Yields

No recommendation

Comments on Preferred Values

The preferred absorption cross-sections are based on the measurements of Gierzak et al. (1997). The peak cross-section agrees within 10% with the measurements of Raber and Moortgat (1996).

The two studies (Gierczak et al., 1997; Raber and Moortgat, 1996) of the quantum yield for photodissociation of $CH_2=C(CH_3)CHO$ are not in good agreement, although both indicate very low quantum efficiencies with $\phi<0.05$. No firm recommendation can be given.

References

Gierczak, T., Burkholder, J. B., Talukdar, R. K., Mellouki, A., Barone, S. B., and Ravishankara, A. R.: J. Photochem. Photobiol. A: Chem., 110, 1, 1997.

Raber, W. H. and Moortgat, G. K.: in: 'Progress and Problems in Atmospheric Chemistry', edited by: Barker, J., pp. 318–373, World Scientific Publ. Co., Singapore, 1996.

II.A8.207

$CH_3C(O)CH=CH_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3C(O)CH=CH_2 + h\nu$	$\rightarrow CH_2=CHCO + CH_3$	(1)		
	$\rightarrow C_3H_6 + CO$	(2)	24.7	4842
	$\rightarrow C_2H_3 + CH_3CO$	(3)	405	295.3

Absorption cross-section data

Wavelength range/nm	Reference	Comments
250–395	Gierczak et al., 1997	(a)
235–400	Raber and Moortgat, 1996	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength range/nm	Reference	Comments
ϕ = 0.16 (33 mbar)	308	Gierczak et al., 1997	(c)
ϕ = 0.04 (33 mbar)	337		
ϕ = 0.01 (33 mbar)	351		
ϕ < 0.04 (1 bar)	275–370	Raber and Moortgat, 1996	(d)

Comments

(a) Measurements made using a diode array spectrometer with a D_2 lamp source and temperature controlled cell with 200 cm path-length. Resolution 0.5 nm. Temperature range 250–298 K. Tabulated cross sections at 1 nm intervals $\sigma_{max}=7.2\times10^{-20}$ cm^2 molecule^{-1} (±5%) at 331 nm and $\sigma=(6.6\pm0.35)\times10^{-18}$ cm^2 molecule^{-1} at 213.86 nm (Zn lamp source). Small temperature dependence at λ max (<2% increase at 250 K).

(b) Measurements made at 298 K using a diode array spectrometer with a D_2 lamp source. $\sigma_{max}=6.5\times10^{-20}$ cm^2 molecule^{-1} (±5%) at 330.7 nm.

(c) Quantum yield determined using pulsed laser photolysis of static mixtures with measurement of the loss of $CH_3C(O)CH=CH_2$ (methyl vinyl ketone) by GC. ϕ was determined at pressures of 25 and 650 Torr (33 and 850 mbar) air, and at 308, 337 and 351 nm. ϕ showed pressure quenching at 308 and 337 nm but not at 351 nm. Expression given for the variation with pressure (for air up to 1 bar) and wavelength of ϕ: $\phi_0(\lambda,P) < \exp[-0.055(\lambda-308)]/(5.5+9.2\times10^{-19}[M])$ where λ is in nm and M in molecule cm^{-3}.

(d) Broad band photolysis of static mixtures (bath gas is air) with measurement of the loss of $CH_3C(O)CH=CH_2$ and formation of products (C_3H_6, CO, HCHO with minor amounts of CO_2, HC(O)OH, CH_3OH, $CH_3(O)OH$ and $C_2H_3C(O)OH$) by FTIR. Quantum yield from loss of $CH_3C(O)CH=CH_2$ and formation of CO. Indication of a weak pressure effect with ϕ(50 Torr)/ϕ(760 Torr) ∼2. The relative importance of the photolysis channels could not be obtained accurately from the product yields.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
250	0.241	299	3.70	348	5.77
251	0.241	300	3.87	349	5.47
252	0.224	301	4.04	350	5.20
253	0.241	302	4.20	351	4.94
254	0.241	303	4.35	352	4.72
255	0.258	304	4.51	353	4.53
256	0.275	305	4.66	354	4.32
257	0.275	306	4.82	355	4.15
258	0.293	307	4.96	356	4.03
259	0.310	308	5.13	357	3.94
260	0.327	309	5.30	358	3.89
261	0.361	310	5.44	359	3.89
262	0.379	311	5.58	360	3.68
263	0.396	312	5.73	361	3.60
264	0.430	313	5.87	362	3.49
265	0.465	314	6.02	363	3.36
266	0.499	315	6.14	364	3.29
267	0.534	316	6.28	365	3.03
268	0.568	317	6.42	366	2.77
269	0.620	318	6.54	367	2.50
270	0.654	319	6.63	368	2.20
271	0.706	320	6.70	369	2.01
272	0.757	321	6.76	370	1.88
273	0.809	322	6.83	371	1.74
274	0.878	323	6.85	372	1.58
275	0.929	324	6.88	373	1.48
276	0.998	325	6.95	374	1.39
277	1.08	326	7.02	375	1.31
278	1.15	327	7.09	376	1.26
279	1.24	328	7.16	377	1.24
280	1.33	329	7.23	378	1.20
281	1.41	330	7.28	379	1.20
282	1.50	331	7.30	380	1.05
283	1.60	332	7.26	381	0.981
284	1.70	333	7.18	382	0.912
285	1.81	334	7.04	383	0.878
286	1.91	335	6.94	384	0.929
287	2.03	336	6.85	385	0.757
288	2.15	337	6.70	386	0.637
289	2.29	338	6.56	387	0.534
290	2.43	339	6.47	388	0.447
291	2.55	340	6.44	389	0.396
292	2.67	341	6.42	390	0.344
293	2.81	342	6.35	391	0.310
294	2.93	343	6.35	392	0.293
295	3.08	344	6.30	393	0.275
296	3.24	345	6.23	394	0.241
297	3.39	346	6.14	395	0.207
298	3.56	347	6.08		

Quantum Yields

$\phi_0(\lambda,P) = \exp[-0.055(\lambda-308)]/(5.5 + 9.2 \times 10^{-19}[M])$
where λ is in nm and M in molecule cm^{-3}.

Comments on Preferred Values

The preferred absorption cross-sections are based on the measurements of Gierczak et al. (1997). They agree well with the measurements of Raber and Moortgat (1996) within 10% over the range 290–365 nm.

The two studies (Gieczak et al., 1997; Raber and Moortgat, 1996) of the quantum yield for photodissociation of $CH_3C(O)CH{=}CH_2$ are essentially in agreement. Both show low efficiency for photolysis ($\phi<0.1$) and a weak pressure dependence in ϕ (ϕ decreases with increasing pressure between 25 Torr (33 mbar) and 760 Torr (1 bar)). Gierczak et al. (1997) also observe an increase at shorter wavelength. We recommend the empirical algorithm given by Gierczak et al. (1997) for the overall dissociation quantum yield in air as a function of wavelength and pressure, although this should be considered an upper limit. The results of Raber and Moortgat (1996) indicate that the photolysis channel leading to propene (channel 2) accounts for 60% of the $CH_3C(O)CH{=}CH_2$ loss, with the balance occurring by the two radical channels (1) and (3) with equal probability.

References

Gierczak, T., Burkholder, J. B., Talukdar, R. K., Mellouki, A., Barone, S. B., and Ravishankara, A. R.: J. Photochem. Photobiol. A: Chem., 110, 1, 1997.

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II.A8.208

n-C_3H_7CHO + hν → products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
n-C_3H_7CHO	→ n-C_3H_7 + HCO	(1)	355.7	336
	→ C_3H_8 + CO	(2)	−3.2	
	→ C_2H_4 + CH_2CHOH	(3)	∼136	880
	→ CH_3 + CH_2CH_2CHO	(4)		
	→ C_3H_6 + HCHO	(5)	123.4	969

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–365	Martinez et al., 1992	(a)
240–350	Tadic et al., 2001	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi = 0.48 \pm 0.02$ (100 Torr air)	275–380	Tadic et al., 2001	(c)
$\phi = 0.38 \pm 0.02$ (700 Torr air)	275–380		
$\phi_1 = 0.21$ (1 bar, air)	275–380		
$\phi_3 = 0.10$ (1 bar, air)	275–380		

Comments

(a) Absorption measurements as a function of C_3H_7CHO pressure using a diode array spectrometer. Cross-sections are the average cross-section over a 1 nm ($\lambda > 280$ nm) or 4 nm ($\lambda < 280$ nm) region centered at the corresponding wavelength.

(b) Cross-sections determined from absorption measurements as a function of C_3H_7CHO pressure using a diode array spectrometer, with resolution of 0.25 nm.

(c) Broad band (275–380 nm) steady-state photolysis of C_3H_7CHO in the presence of air at 298 K. Products measured by FTIR were CO, C_2H_4, CH_3CHO, CH_2CHOH and CO_2. Quantum yields of CO and C_2H_4 were measured as a function of wavelength and pressure, to provide values of ϕ_1 and ϕ_3. Overall quantum yields were pressure dependent over range 100–700 Torr, with the following Stern-Volmer expresssion: $1/\phi = 1.81 + (1.931 \times 10^{-3})$ P[Torr].

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
202	0.0178	295	6.03	330	0.868
206	0.0316	296	5.87	331	0.734
210	0.0475	297	5.69	332	0.647
214	0.0623	298	5.56	333	0.602
218	0.0771	299	5.46	334	0.554
222	0.0850	300	5.42	335	0.485
226	0.102	301	5.43	336	0.417
230	0.133	302	5.44	337	0.346
234	0.202	303	5.43	338	0.285
238	0.316	304	5.32	339	0.242
242	0.488	305	5.08	340	0.215
246	0.724	306	4.79	341	0.191
250	1.05	307	4.50	342	0.144
254	1.45	308	4.29	343	0.093
258	1.93	309	4.15	344	0.059
262	2.52	310	4.07	345	0.041
266	3.09	311	4.00	346	0.031
270	3.81	312	3.92	347	0.026
274	4.34	313	3.82	348	0.023
278	5.02	314	3.69	349	0.018
280	5.18	315	3.46	350	0.015
281	5.22	316	3.17	351	0.014
282	5.30	317	2.85	352	0.012
283	5.45	318	2.57	353	0.010
284	5.65	319	2.37	354	0.008
285	5.81	320	2.25	355	0.006
286	5.90	321	2.18	356	0.005
287	5.89	322	2.07	357	0.004
288	5.85	323	1.96	358	0.003
289	5.80	324	1.82	359	0.002
290	5.78	325	1.69	360	0.002
291	5.83	326	1.55	361	0.002
292	5.93	327	1.39	362	0.001
293	6.05	328	1.22	363	0.001
294	6.10	329	1.04	364	0.001

Quantum Yields

ϕ_3 = 0.10; ϕ_1 = 0.21 for 1 bar air, over the wavelength range 290–380 nm.

Comments on Preferred Values

The preferred absorption cross-sections are from the measurements of Martinez et al. (1992) The cross-section data of Tadic et al. (2001) are within 5% of the Martinez data over the wavelength region 260 nm to 350 nm.

The photolysis of long chain ($>C_4$) aldehydes undergo Norrish type I (ϕ_1) and Norrish type II (ϕ_3) dissociation in the first absorption band (260–340 nm). Channels 2, 4 and 5 are unimportant at wavelengths >280 nm. The indirect quantum yield measurements for the two channels, ϕ_1 and ϕ_3 reported by Tadic et al. (2001) for photolysis of n-C_3H_7CHO appear reliable and are recommended here. Quantum yield measurements for the channel producing HCO (ϕ_1) from n-pentanal, obtained in the same study, agree with direct measurements for n-pentanal obtained by Cronin and Zhu (1998) using cavity ring-down detection of HCO. Weak pressure quenching of reported by Tadic et al. (2001) for photolysis of n-C_3H_7CHO can be used to obtain quantum yields at lower atmospheric pressures, assuming constant branching ratio for channels 1 and 3.

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Martinez, R. D., Buitrago, A. A., Howell, N. W., Hearn, C. H., and Joens, J. A.: Atmos. Environ., 26A, 785, 1992.
Tadic, J., Juranic, I., and Moortgat, G. K.: J. Photchem. Photobiol. A: Chem., 143, 169, 2001.

II.A8.209

$CH_3OOH + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3OOH + h\nu$	$\rightarrow CH_3O + HO$	(1)	185	645
	$\rightarrow CH_3 + HO_2$	(2)	292	410
	$\rightarrow CH_3O_2 + H$	(3)	358	334

Absorption cross-section data

Wavelength range/nm	Reference	Comments
210–365	Vaghjiani and Ravishankara, 1989	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 = 1.00 \pm 0.18$	248	Vaghjiani and Ravishankara, 1990	(b)

Comments

(a) CH_3OOH prepared by methylation of H_2O_2 and shown by ^1H NMR to be >97% pure [major impurity $C_2H_5OC_2H_5$]. A diode-array spectrometer was used to make relative absorption measurements over the whole wavelength range and the results were put on an absolute basis by measurement of the cross-sections at 213.9 nm (Zn line), and at 298.1 nm, 326.1 nm, 340.4 nm and 361.1 nm using Cd lines. The CH_3OOH concentration was determined by trapping the vapor at 77 K and titrating with Fe^{2+} or I^-.

(b) Direct measurement of products, HO by LIF, and $O(^3P)$ and H atoms by resonance fluorescence. Quantum yields for the formation of $O(^3P)$ and H atoms of <0.007 and 0.038 ± 0.007, respectively, were obtained.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
210	31.2	290	0.691
215	20.9	295	0.551
220	15.4	300	0.413
225	12.2	305	0.313
230	9.62	310	0.239
235	7.61	315	0.182
240	6.05	320	0.137
245	4.88	325	0.105
250	3.98	330	0.079
255	3.23	335	0.061
260	2.56	340	0.047
265	2.11	345	0.035
270	1.70	350	0.027
275	1.39	355	0.021
280	1.09	360	0.016
285	0.863	365	0.012

Quantum Yields

$\phi_1 = 1.0$ for $\lambda > 290$ nm.

Comments on Preferred Values

The preferred absorption cross-section data are those of Vaghjiani and Ravishankara (1989), which are approximately 25% lower than the previously recommended data of Molina and Arguello (1979). The source of the discrepancy appears to lie in the determination of the concentrations of CH_3OOH in the absorption cell. Molina and Arguello (1979) used a bubbler containing Fe^{2+} solution, which Vaghjiani and Ravishankara (1989) showed does not give quantitative trapping.

On the basis of the results of Vaghjiani and Ravishankara (1990), who showed that $\phi_{OH} \sim 1.0$ at $\lambda = 248$ nm, we recommend that the atmospheric photolysis of CH_3OOH ϕ_1 be taken to be unity for wavelengths >290 nm.

References

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Vaghjiani, G. L. and Ravishankara, A. R.: J. Geophys. Res., 94, 3487, 1989.
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II.A8.210

$HOCH_2OOH + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$HOCH_2OOH + h\nu \rightarrow HOCH_2O + HO$	∼188	∼637

Absorption cross-section data

Wavelength range/nm	Reference	Comments
205–360	Bauerle and Moortgat, 1999	(a)

Quantum yield data

No data

Comments

(a) $HOCH_2OOH$ prepared by liquid phase reaction of HCHO with excess H_2O_2. A diode-array spectrometer was used to make relative absorption measurements over the whole wavelength range. The $HOCH_2OOH$ concentration was measured in situ by FTIR using a peak IR absorption coefficient of $\sigma=7.4\times10^{-19}$ cm^2 molecule^{-1} at 1049 cm^{-1}. This cross section was determined in the same system by quantitative measurement of the decomposition products of $HOCH_2OOH$ (HCOOH and HCHO) using the yields of these products. The decomposition channels were previously established by Neeb et al. (1997).

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
205	26.91	290	0.63
210	22.56	295	0.51
215	18.75	300	0.40
220	15.46	305	0.29
225	12.47	310	0.22
230	10.06	315	0.18
235	7.89	320	0.13
240	5.98	325	0.10
245	4.68	330	0.073
250	3.78	335	0.059
255	2.88	340	0.045
260	2.31	345	0.036
265	1.81	350	0.028
270	1.48	355	0.022
275	1.21	360	0.017
280	0.93	365	0.012
285	0.75		

Quantum Yields

ϕ_1 = 1.0 for $\lambda > 290$ nm.

Comments on Preferred Values

The preferred absorption cross-section data are those of Bauerle and Moortgat (1999) which are the only data reported for the absorption spectrum of $HOCH_2OOH$. The values are close to those recommended for CH_3OOH based on the measurements of Vaghjiani and Ravishankara (1990). The recommended quantum yields are based on an analogy with methyl hydroperoxide. Other channels may occur in photolysis at shorter wavelengths.

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Neeb, P., Sauer, F., Horie, O., and Moortgat, G. K.: Atmos. Environ., 31, 1417, 1997.
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II.A8.211

$CH_3ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3ONO_2 + h\nu$	$\rightarrow CH_3O + NO_2$	(1)	170.1	703
	$\rightarrow$ HCHO + HONO	(2)	−68.4	
	$\rightarrow CH_3ONO + O(^3P)$	(3)	303.6	394

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–315	Roberts and Fajer, 1989	(a)
220–335	Rattigan et al., 1992	(b)
236–344	Talukdar et al., 1997	(c)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 = 0.9 \pm 0.2$	248	Talukdar et al., 1997	(d)
$\phi_1 = 1.3 \pm 0.3$	248		(e)
$\phi_2 < 0.05$	248		(d)
$\phi_3 < 0.1$	248		(d)

Comments

(a) Absorption cross-sections were measured in a 10.2 cm pathlength cell, using a single-beam spectrometer with a photometric accuracy of ±0.5%. Numerical data for cross-sections are available from Roberts (1990).

(b) Cross-sections were measured with a dual-beam diode array spectrometer with a spectral resolution of 0.3 nm over the temperature range 238 K to 294 K. The temperature dependence of σ was found to obey the equation, $\ln\sigma(\lambda, T)=\ln\sigma(\lambda, 298\,K)+B(\lambda)(T-298)$.

(c) Absorption cross-sections were measured with a diode-array spectrometer. Absorbances were measured in 80 nm blocks, which were assembled to construct the spectrum. Cross-sections were measured at 298 K and 6 other temperatures in the range 240 K to 360 K. The temperature dependence of σ was found to obey the equation $\ln\sigma(\lambda, T)=\ln\sigma(\lambda, 298\,K)+B(\lambda)(T-298)$. The absorption cross-section at 213.86 nm (Zn line) was also measured. A value of $(1.67\pm0.08)\times10^{-18}$ cm^2 molecule^{-1} was obtained.

(d) Photolysis of methyl nitrate at 248 nm and 298 K in the presence of excess O_2 to scavenge radicals. Actinometry based on O_3 photolysis or N_2O photolysis in experiments carried out with 193 nm radiation. Yields of the products CH_3ONO, CH_2O, NO_2 and NO_3 were measured by UVA, NO_3 by time-resolved absorption at 662 nm, and H and O by resonance fluorescence. Channels leading to H, O, and NO_3 were found to make negligible contribution at 248 nm, but high yields of O were obtained at 193 nm. Small yields of HO observed were attributed to secondary reactions.

(e) Same technique as in (d), but NO was used to scavenge radicals instead of O_2.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
240	5.88	295	0.568
245	4.19	300	0.360
250	3.59	305	0.214
255	3.30	310	0.134
260	3.06	315	0.0633
265	2.77	320	0.0316
270	2.39	325	0.0144
275	2.00	330	0.00661
280	1.58	335	0.00274
285	1.19	340	0.00122
290	0.85		

Temperature dependence of the absorption cross-sections over the range 240 K to 330 K

λ/nm	$10^3 B/K^{-1}$	λ/nm	$10^3 B/K^{-1}$
240	3.48	290	4.04
245	3.29	295	4.47
250	2.96	300	4.94
255	2.82	305	5.56
260	2.83	310	6.33
265	2.92	315	7.34
270	3.08	320	8.74
275	3.28	325	9.97
280	3.51	330	13.6
285	3.78		

The tabulated values of B may be used to calculate $\sigma(\lambda, T)$ using the relationship $\ln \sigma(\lambda, T) = \ln \sigma(\lambda, 298\ K) + B\ (\lambda)(T - 298)$.

Quantum Yields

$\phi_1 = 1.0$ for $\lambda \geq 248$ nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are average values from the data of Roberts and Fajer (1989), Rattigan et al. (1992) and Talukdar et al. (1997), which are in excellent agreement over the whole wavelength range of the measurements. They are also in reasonable agreement with the absorption spectrum reported by Calvert and Pitts (1966) and with the cross-sections reported by Maria et al. (1973). The results of Taylor et al. (1980) are consistently higher than the values from the other studies (Roberts and Fajer, 1989; Rattigan et al., 1992; Talukar et al., 1997; Calvert and Pitts, 1966; Maria et al., 1973), by as much as a factor of two in the region 290 nm to 330 nm.

The two studies of the effect of temperature on the cross-sections are also in very good agreement with differences only appearing at wavelengths beyond 320 nm where the absorption cross-sections become very small and the precision of the measurements falls away. The preferred values of $B(\lambda)$ are those of Talukdar et al. (1997) averaged over 5 nm intervals around the given wavelength.

The preferred value of the quantum yield is based on the work of Talukdar et al. (1997) who concluded that the photodissociation of methyl nitrate at 248 nm produces NO_2 and CH_3O with a quantum yield of essentially unity. This is in accord with the general assumption (Roberts, 1990) that the lack of structure in the absorption spectrum of $RONO_2$ molecules indicates that the quantum yield for dissociation is unity, and is supported by the recently measured value for ethyl nitrate of $\phi_1 = 1.0 \pm 0.1$ at 308 nm (Zhu and Ding, 1997).

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II.A8.212

$C_2H_5ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$C_2H_5ONO_2 + h\nu$	$\rightarrow C_2H_5O + NO_2$	(1)	171.7	697
	$\rightarrow CH_3CHO + HONO$	(2)	−91.3	
	$\rightarrow C_2H_5ONO + O(^3P)$	(3)	299.4	400

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–315	Roberts and Fajer, 1989	(a)
185–330	Turberg et al., 1990	(b)
265–340	Zhu and Ding, 1997	(c)
265–340	Clemitshaw et al., 1997	(d)
265–340	Talukdar et al., 1997	(e)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 = 1.0 \pm 0.1$	308	Zhu and Ding, 1997	(f)

Comments

(a) Absorption cross-sections were measured in a 10.2 cm pathlength cell, using a single-beam spectrometer with a photometric accuracy of ±0.5%. Numerical data for cross-sections are available from Roberts (1990).

(b) Absorption cross-sections were measured in cells of 2 cm and 10 cm pathlengths with a range of pressures of $C_2H_5ONO_2$. The spectral resolution was not specified.

(c) Cross-sections measured at 10 nm intervals, between 238 K and 298 K, using cavity ring- down spectroscopy. Absorption cross-sections were obtained by measuring optical loss as a function of sample gas pressure (0.013 mbar to 18 mbar). The purity of ethyl nitrate was checked by FTIR and cavity ring-down spectroscopy.

(d) Absorption cross-sections were measured with a dual-beam diode array spectrometer, with a spectral resolution of approximately 0.6 nm, over the temperature range 233 K to 298 K. The purity of the ethyl nitrate was checked by NMR and FTIR.

(e) Absorption cross-sections were measured with a diode-array spectrometer at 298 K and six other temperatures in the range 240 K to 360 K. Absorbances were measured in 80 nm blocks which were assembled to construct the spectrum. Corrections were made for contributions to the spectrum from NO_2 present in the ethyl nitrate.

(f) Excimer laser used to photodissociate ethyl nitrate in a cavity ring-down spectrometer. Time-resolved spectra of products observed. Only NO_2 found as product, with undetectable yields of HONO and C_2H_5ONO. Quantum yield measurements were made at 278 K, 283 K, 288 K, 293 K and 298 K with ethyl nitrate pressures of 1.3 mbar to 13 mbar in a buffer gas of N_2 at total pressures of 16 mbar to 1 bar. ϕ_1 was found to be pressure and temperature independent.

Preferred Values

Absorption cross-sections at 298 K and their temperature dependence over the ranges 233 K to 360 K and 235 nm to 340 nm

λ/nm	$10^{20}\sigma/\mathrm{cm}^2$	$10^3 B/K^{-1}$	λ/nm	$10^{20}\sigma/\mathrm{cm}^2$	$10^3 B/K^{-1}$
185	1710		265	3.6	2.9
190	1710		270	3.1	3.1
195	1490		275	2.7	3.3
200	1140		280	2.2	3.6
205	738		285	1.7	3.8
210	400		290	1.2	4.2
215	195		295	0.85	4.7
220	91		300	0.55	5.1
225	45		305	0.33	5.8
230	24		310	0.19	6.7
235	11.9	1.4	315	0.10	7.9
240	7.7	2.8	320	0.051	8.6
245	5.4	2.9	325	0.026	10.4
250	4.5	2.8	330	0.012	12.9
255	4.1	2.6	335	0.0049	14.1
260	3.9	2.6	340	0.0025	15.6

The temperature variation of the absorption cross-section at a particular wavelength in the range 240 nm to 340 nm is expressed as $\ln\sigma(T)–\ln\sigma(298\ K) = B(T–298)$.

Quantum Yields

$\phi_1 = 1.0 \pm 0.1$ at 308 nm, independent of pressure over the temperature range 278–298 K.

Comments on Preferred Values

The preferred values of the cross-sections at 298 K are those obtained by Turberg et al. (1990) over the range 185 nm to 230 nm, where this is the only study, and for the range 235 nm to 340 nm averages are taken of the values from all of the five studies (Roberts and Fajer, 1989; Turberg et al., 1990; Zhu and Ding, 1997; Clemitshaw et al., 1997 and Talukdar et al., 1997) at the wavelengths where they overlap.

The temperature variation of the cross-sections has been studied by Zhu and Ding (1997), Clemitshaw et al. (1997) and Talukdar et al. (1997). These studies together cover the temperature range 233 K to 360 K and the wavelength range 235 nm to 340 nm. It is found in all of the studies that the temperature variation of σ can be expressed as $\ln\sigma(\lambda, T)–\ln\sigma(\lambda, 298\,\mathrm{K})=B(\lambda)(T–298)$. The results from the three studies (Zhu and Ding, 1997; Clemitshaw et al., 1997 and Talukdar et al., 1997) are in good agreement and the preferred values of B have been obtained by averaging values from the three studies (Zhu and Ding, 1997; Clemitshaw et al., 1997 and Talukdar et al., 1997).

The only direct measurement of the quantum yield is that of Zhu and Ding (1997). Their finding that at 308 nm the sole photodissociation channel was that leading to NO_2 production with a quantum yield of unity is accepted for our preferred value of the quantum yield. It is in accord with the studies of Luke et al. (1998, 1989) who concluded that the measured rates of NO_2 production from ethyl nitrate photolysis in sunlight could be accounted for by assuming that ϕ_1=1 throughout the region 290 nm to 340 nm. This is also supported by the measured value of unity for the same channel in the 248 nm photolysis of methyl nitrate (Talukdar et al., 1997).

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II.A8.213

n-$C_3H_7ONO_2$ + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
n-$C_3H_7ONO_2$ + $h\nu$	$\rightarrow$ n-C_3H_7O + NO_2	(1)	165.9	721
	$\rightarrow$ C_2H_5CHO + HONO	(2)	−92.8	
	$\rightarrow$ C_3H_7ONO + $O(^3P)$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–330	Roberts and Fajer, 1989	(a)
185–330	Turberg et al., 1990	(b)
220–340	Clemitshaw et al., 1997	(c)

Comments

(a) Absorption cross-sections were measured in a cell of 10.2 cm pathlength using a single-beam spectrometer with a photometric accuracy of ±0.5%. No NO_2 could be detected by FTIR in the n-propyl nitrate.

(b) Absorption cross-sections were measured in 2 cm and 10 cm pathlength cells with a range of pressures of n-$C_3H_7ONO_2$ at an unspecified spectral resolution.

(c) Absorption cross-sections were measured with a dual-beam diode array spectrometer, with a spectral resolution of approximately 0.6 nm. The purity of the n-propyl nitrate was checked by NMR and FTIR.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
185	1810	265	3.6
190	1800	270	3.2
195	1600	275	2.8
200	1260	280	2.3
205	855	285	1.8
210	489	290	1.3
215	244	295	0.95
220	105	300	0.57
225	50	305	0.34
230	27	310	0.19
235	15	315	0.10
240	8.9	320	0.053
245	6.0	325	0.031
250	4.8	330	0.022
255	4.4	335	0.018
260	4.0	340	0.016

Comments on Preferred Values

Clemitshaw et al. (1997) have measured the absorption cross-sections at 298 K over the range 220 nm to 340 nm. In the wavelength region where their measurements overlap with those of Roberts and Fajer (1989) (270 nm to 320 nm), the two studies are in excellent agreement. Agreement with the results of Turberg et al. (1990) is also very good in the range 220 nm to 295 nm, but the results of Turberg et al. (1990) deviate significantly from those of both Clemitshaw et al. (1997) and Roberts and Fajer (1989) at $\lambda > 295$ nm. This tendency to obtain higher values than others of the absorption cross-section at longer wavelengths is noticeable in the results of Turberg et al. (1990) in all of their studies of the higher nitrates and could be due to traces of NO_2 in their samples.

The preferred values of the absorption cross-section are those of Turberg et al. (1990) for the range 185 nm to 220 nm where theirs are the only measurements. Over the range 220 nm to 295 nm averages are taken of the results of Roberts and Fajer (1989), Turberg et al. (1990) and Clemitshaw et al. (1997) where their studies overlap, and over the range 295 nm to 340 nm the preferred values are based on the results of Roberts and Fajer (1989) and Clemitshaw et al. (1997).

There are no data on either the products of photodissociation or the quantum yields. However, the quantum yields for photodissociation of both ethyl and methyl nitrate to form NO_2 have been shown to be unity at 308 nm and 248 nm, respectively (see data sheets in this evaluation). Since the absorption spectra of organic nitrates are very similar, with structureless continua occurring in the same region of the spectrum, it seems likely that the photodissociation quantum yield for n-propyl nitrate will also be unity. Further support for this conclusion comes from direct measurements (Luke et al., 1989) of the rate of formation of NO_2 from the photolyses of n-$C_3H_7ONO_2$ in sunlight. These agreed well with the calculated rates of photolyses, based on measurements of the absorption cross-sections, solar irradiances, and an assumed value of $\phi_1=1$ throughout the wavelength region 290 nm to 340 nm (Luke et al., 1989).

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II.A8.214

i-$C_3H_7ONO_2$ + hν → products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
i-$C_3H_7ONO_2$ + hν	→ 2-C_3H_7O + NO_2	(1)	171.7	697
	→ $CH_3C(O)CH_3$ + HONO	(2)	−105.9	
	→ *i*-C_3H_7ONO + O	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–330	Roberts and Fajer, 1989	(a)
185–330	Turberg et al., 1990	(b)
220–340	Clemitshaw et al., 1997	(c)
240–360	Talukdar et al., 1997	(d)

Comments

(a) Absorption cross-sections were measured in a 10.2 cm pathlength cell using a single-beam spectrophotometer with a photometric accuracy of ±0.5%. Numerical data for cross-sections are available from Roberts (1990). Samples were checked by FTIR for the presence of NO_2, which was not found.

(b) Absorption cross-sections were measured in 2 cm and 10 cm pathlength cells, with a range of pressures of *i*-$C_3H_7ONO_2$, at a bandwidth of 1 nm.

(c) Absorption cross-sections were measured with a dual-beam diode array spectrometer, with a spectral resolution of approximately 0.6 nm. The purity of the *i*-propyl nitrate was checked by NMR and FTIR.

(d) Absorption cross-sections were measured with a diode-array spectrometer at 298 K and 6 other temperatures in the range 240 K to 360 K. Absorbances were measured in 80 nm blocks which were assembled to construct the spectrum.

Preferred Values

Absorption cross-sections at 298 K and their temperature dependence over the ranges 233 K to 360 K and 240 nm to 340 nm

λ/nm	$10^{20}\sigma$/cm^2	$10^3 B/K^{-1}$	$10^{20}\sigma$/cm^2	λ/nm	$10^3 B/K^{-1}$
185	1790		275	3.4	3.3
188	1810		280	2.8	3.6
190	1790		285	2.2	4.0
195	1610		290	1.6	4.4
200	1260		295	1.2	4.8
205	867		300	0.78	5.4
210	498		305	0.50	6.1
215	247		310	0.29	6.9
220	125		315	0.17	8.1
225	62		320	0.085	9.4
230	34		325	0.044	11.1
235	18		330	0.022	11.9
240	11	2.8	335	0.011	14.0
245	7.0	2.7	340	0.0053	13.9
250	5.4	2.5	345	0.0018	
255	4.9	2.5	350	0.00080	

λ/nm	$10^{20}\sigma/\text{cm}^2$	$10^3 B/K^{-1}$	λ/nm	$10^{20}\sigma/\text{cm}^2$	$10^3 B/K^{-1}$
260	4.6	2.6	355	0.00029	
265	4.3	2.8	360	0.00018	
270	3.9	3.1			

The temperature variation of the absorption cross-section at a particular wavelength in the range 240 nm to 340 nm is expressed as $\ln\sigma(T) - \ln\sigma(298\ K) = B(T-298)$.

Comments on Preferred Values

Clemitshaw et al. (1997) have measured the absorption cross-sections at 298 K over the range 220 nm to 340 nm and Talukdar et al. (1997) have measured both the cross-sections at 298 K over the range 240 nm to 360 nm and their temperature dependence at temperatures in the range 240 K to 360 K. The results of Clemitshaw et al. (1997) and of Talukdar et al. (1997) are in excellent agreement with the earlier results of Roberts and Fajer (1989) and Turberg et al. (1990) at wavelengths above where they overlap (in the range 220 nm to 330 nm), except for the results of Turberg et al. (1990) at wavelengths 310 nm which deviate increasingly from those of the other studies as the wavelength increases. This tendency, to obtain higher values than others, in this wavelength region, is noticeable in the results of Turberg et al. (1990) for all of the higher nitrates and could be due to traces of NO_2 present in their samples.

The preferred values of the absorption cross-sections at 298 K are those of Turberg et al. (1990) for the range 185 nm to 220 nm, where theirs are the only values. Over the range 220 nm to 305 nm averages are taken of the results of Roberts and Fajer (1989), Turberg et al. (1990), Clemitshaw et al. (1997), and Talukdar et al. (1997), where their studies overlap, and over the range 310 nm to 360 nm the preferred values are based on the results of Roberts and Fajer (1989), Clemitshaw et al. (1997) and Talukdar et al. (1997).

The preferred values of the constant B, which characterize the temperature dependence of the absorption cross-sections are those of Talukdar et al. (1997).

There are no data on either the products of photodissociation or the quantum yields. However, the quantum yields for the photodissociation of both ethyl and methyl nitrate to form NO_2 have been shown to be unity at 308 nm and 248 nm, respectively (see data sheets in this evaluation). Since the absorption spectra of organic nitrates are very similar structureless continua occurring at similar wavelengths, it seems likely that the photodissociation quantum yield for isopropyl nitrate will also be unity. Further support for this conclusion comes from measurements of the rate of formation of NO_2 from the photolyses of alkyl nitrates in sunlight (Luke et al., 1989). Thus the measured rate of formation of NO_2 matched well with calculated rates of photolyses based on measurements of the absorption cross-section, solar irradiances, and an assumed value of ϕ_1=1 throughout the wavelength region 290 nm to 330 nm (Luke et al., 1989).

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II.A8.215

1-$C_4H_9ONO_2$ + hν → products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
1-$C_4H_9ONO_2$ + hν	→ 1-C_4H_9O + NO_2	(1)		
	→ 1-C_3H_7CHO + HONO	(2)		
	→ i-C_4H_9ONO + O	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–315	Roberts and Fajer, 1989	(a)
185–320	Turberg et al., 1990	(b)
220–340	Clemitshaw et al., 1997	(c)

Comments

(a) Absorption cross-sections were measured in a 10.2 cm pathlength cell using a single-beam spectrophotometer with a photometric accuracy of ±0.5%. Data are presented graphically but an expression for σ as a function of λ is derived from a least squares fit to the data at $\lambda \geq 270$ nm. Purity of the butyl nitrate was checked by FTIR.

(b) Absorption cross-sections were measured in 2 cm and 10 cm pathlength cells in a Varian Carey 219 spectrophotometer using a bandwidth of 1 nm.

(c) Absorption cross-sections were measured with a dual-beam diode array spectrometer, with a spectral resolution of approximately 0.6 nm. The purity of the 1-butyl nitrate was checked by NMR and FTIR.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
185	1810	265	3.9
190	1810	270	3.4
195	1620	275	3.0
200	1300	280	2.4
205	889	285	1.9
210	518	290	1.4
215	263	295	0.89
220	111	300	0.57
225	58	305	0.34
230	30	310	0.19
235	17	315	0.10
240	9.8	320	0.051
245	6.3	325	0.031
250	5.3	330	0.021
255	4.6	335	0.016
260	4.3	340	0.013

Comments on Preferred Values

The results of Roberts and Fajer (1989), Turberg et al. (1990) and Clemitshaw et al. (1997) are in good agreement at wavelengths where the studies overlap (in the range 220 nm to 320 nm), except for the results of Turberg et al. (1990) at wavelengths $\geq$300 nm which deviate increasingly from those of the other studies as the wavelength increases. This tendency to obtain higher values than others, in this wavelength region, is noticeable in the results of Turberg et al. (1990) for all of the higher nitrates and could be due to traces of NO_2 present in their samples.

The preferred values of the absorption cross-sections are those of Turberg et al. (1990) for the range 185 nm to 220 nm, where theirs are the only values. Over the range 220 nm to 295 nm averages are taken of the results of Roberts and Fajer (1989), Turberg et al. (1990) and Clemitshaw et al. (1997), where their studies overlap, and over the range 300 nm to 400 nm the preferred values are based on the results of Roberts and Fajer and Clemitshaw et al. (1997).

There are no data on either the products of photodissociation or the quantum yields. However, the quantum yields for the photodissociation of both ethyl and methyl nitrates to form NO_2 have been shown to be unity at 308 nm and 248 nm, respectively (see data sheets in this evaluation). Since the absorption spectra of alkyl nitrates are very similar structureless continua occurring at similar wavelengths, it seems likely that the photodissociation quantum yield for 1-butyl nitrate will also be unity. Further support for this conclusion comes from measurements of the rate of formation of NO_2 from the photolyses of alkyl nitrates in sunlight (Luke et al., 1989). Thus the measured rate of formation of NO_2 matched well with calculated rates of photolyses based on measurements of the absorption cross-sections, solar irradiances, and an assumed value of $\phi_1 = 1$ throughout the wavelength region 290 nm to 330 nm (Luke et al., 1989).

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II.A8.216

$2\text{-}C_4H_9ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$2\text{-}C_4H_9ONO_2 + h\nu$	$\rightarrow 2\text{-}C_4H_9O + NO_2$	(1)		
	$\rightarrow CH_3C(O)C_2H_5 + HONO$	(2)		
	$\rightarrow 2\text{-}C_4H_9ONO + O$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
250–320	Roberts and Fajer, 1989	(a)

Comments

(a) Absorption cross-sections were measured in a cell of 10.2 cm pathlength using a single beam spectrophotometer with a photometric accuracy of ± 0.5%. The expression for σ as a function of λ was derived from a least-squares fit to the data at $\lambda \geq 270$ nm.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
250	6.5	290	1.8
255	5.6	295	1.3
260	5.2	300	0.74
265	4.8	305	0.50
270	4.2	310	0.29
275	3.7	315	0.15
280	3.1	320	0.08
285	2.4		

Values at $\lambda \leq 265$ nm are taken from graphs in Roberts and Fajer (1989)

Values at $\lambda \geq 270$ nm are calculated from the expression given in Roberts and Fajer (1989) based on a least-squares fit to the data.

Comments on Preferred Values

The only available measurements of the absorption cross-sections are those of Roberts and Fajer (1989). Their measurements of cross-sections for other alkyl nitrates have agreed well with other studies, and their values are accepted as the preferred values for 2-butyl nitrate.

There are no data on either the products of photodissociation or the quantum yields. However, the quantum yields for the photodissociation of both ethyl and methyl nitrates to form NO_2 have been shown to be unity at 308 nm and 248 nm, respectively (see data sheets in this evaluation). Since the absorption spectra of alkyl nitrates are very similar structureless continua occurring at similar wavelengths, it seems likely that the photodissociation quantum yield for 2-butyl nitrate will also be unity. Further support for this conclusion comes from measurements of the rate of formation of NO_2 from the photolyses of alkyl nitrates in sunlight (Luke et al., 1989). Thus the measured rate of formation of NO_2 matched well with the calculated rates of photolyses based on measurement of the absorption cross-sections, solar irradiances, and an assumed value of $\phi = 1$ throughout the wavelength region 290 nm to 330 nm (Luke et al., 1989).

References

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II.A8.217

$CH_3O_2NO_2$ + hν → products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3O_2NO_2$ + hν	→ $CH_3O_2 + NO_2$	(1)	86	1391
	→ $CH_3O + NO_3$	(2)	135	886

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–280	Bridier et al., 1992	(a)

Comments

(a) Flash photolysis of Cl_2 in the presence of CH_4-O_2-NO_2 mixtures at a total pressure of 1 bar, with UV absorption to monitor the concentrations of CH_3O_2 radicals and $CH_3O_2NO_2$.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
200	500	265	20.0
205	360	270	16.0
210	240	275	13.0
215	150	280	10.5
220	105	285	6.2
225	80	290	3.9
230	68	295	2.4
235	60	300	1.4
240	53	305	0.85
245	46	310	0.53
250	39	315	0.39
255	32	320	0.24
260	26	325	0.15

Comments on Preferred Values

In view of the thermal instability of $CH_3O_2NO_2$, the measurement of the cross-sections for $CH_3O_2NO_2$ presents considerable experimental problems. Nevertheless, the measurements of Bridier et al. (1992) are in moderately good agreement with previous data (Cox and Tyndall, 1979; Morel et al., 1980; Sander and Watson, 1980) at wavelengths <255 nm and are taken as the preferred values in the range 200 nm to 280 nm. At longer wavelengths the agreement is less good and the experimental data from Cox and Tyndall (1979), which are the only values extending into the wavelength region of importance for the atmosphere ($\lambda \geq 290$ nm), show large scatter. The preferred values given in the table for wavelengths >280 nm are based on a comparison with the spectrum of HO_2NO_2.

There are no data to indicate the relative importance of the two photodissociation channels, and neither can be precluded on energetic grounds in the absorbing wavelength region. By analogy with other molecules containing the -NO_2 chromophore (for example, HNO_3), it is likely that absorption around 270 nm is associated with an orbitally forbidden n-π^* transition which leads to dissociation of the molecule. Thus it is probable that $\phi_1+\phi_2=1$.

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II.A8.218

$CH_3C(O)OONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3C(O)OONO_2 + h\nu$	$\rightarrow CH_3C(O)O_2 + NO_2$	(1)	119	1004
	$\rightarrow CH_3CO_2 + NO_3$	(2)	124	963

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220–325	Libuda and Zabel, 1995	(a)
196–350	Talukdar et al., 1995	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi(NO_2)$	248	Mazely et al., 1995	(c)
$\phi(NO_3)$	248	Mazely et al., 1997	(d)
$\phi(NO_3)$	248, 308	Harwood et al., 2003	(e)

Comments

(a) Longpath (39.1 m) UV absorption cell with diode array detector used. The concentration of the $CH_3C(O)OONO_2$ (PAN) was determined by FTIR (pathlength = 51.6 m) in the same cell. The UV spectral resolution was 0.6 nm.

(b) Diode array spectrometer with a resolution of 0.2 nm used with temperature controlled (±1 K) absorption cells of pathlengths 100 cm and 25 cm. $CH_3C(O)OONO_2$ concentrations were determined by pressure measurements. Cross-sections were measured at 250 K, 273 K and 298 K.

(c) Pulsed laser photolysis of PAN with LIF detection of NO_2. The quantum yield for NO_2 formation was measured relative to the photodissociation of HNO_3 at 248 nm, assuming a value of $\phi(NO_2)$ from HNO_3 of unity at this wavelength (see HNO_3 photolysis data sheet http://www.iupac-kinetic.ch.cam.ac.uk/datasheets/photol/PNOx2_HONO2.pdf). A value of $\phi(NO_2)=0.83\pm0.09$ for the photolysis of PAN at 248 nm was obtained.

(d) Pulsed laser photolysis of PAN at 248 nm with LIF detection of NO_3. The quantum yield for NO_3 formation was determined by comparison to the photodissociation of N_2O_5, assuming a value of $\phi(NO_2)$ from HNO_3 of unity at this wavelength (see HNO_3 photolysis data sheet http://www.iupac-kinetic.ch.cam.ac.uk/datasheets/photol/PNOx2_HONO2.pdf). A value of $\phi(NO_3) = 0.3 \pm 0.1$ was obtained for PAN.

(e) Pulsed laser photolysis of PAN with LIF detection of NO_3. The quantum yield for NO_2 formation was measured relative to the photodissociation of HNO_3 at 248 nm, assuming a value of $\phi(NO_2)$ from HNO_3 of unity at this wavelength (see HNO_3 photolysis data sheet http://www.iupac-kinetic.ch.cam.ac.uk/datasheets/photol/PNOx2_HONO2.pdf). Values of $\phi(NO_3) = 0.19 \pm 0.04$ and $\phi(NO_3) = 0.41 \pm 0.10$ were obtained for the photolysis of PAN at 248 nm and 308 nm respectively.

Preferred Values

Absorption cross-sections at 298 K and the temperature coefficient B[a]

λ/nm	$10^{20}\sigma$/cm^2	$10^3 B/K^{-1}$	λ/nm	$10^{20}\sigma$/cm^2	$10^3 B/K^{-1}$
196	429	2.02	274	2.45	5.55
198	398	1.73	276	2.07	5.76
200	361	1.36	278	1.74	5.98
202	325	1.07	280	1.46	6.20
204	292	0.86	282	1.21	6.43
206	261	0.75	284	1.01	6.67
208	226	0.71	286	0.81	6.90
210	196	0.75	288	0.648	7.15
212	168	0.84	290	0.537	7.39
214	143	0.97	292	0.447	7.63
216	122	1.12	294	0.369	7.86
218	104	1.29	296	0.297	8.08
220	89.7	1.47	298	0.245	8.27
222	77.7	1.64	300	0.189	8.44
224	67.6	1.81	302	0.152	8.61
226	59.3	1.98	304	0.125	8.76
228	52.0	2.14	306	0.0998	8.87
230	45.8	2.30	308	0.0816	9.01
232	40.4	2.46	310	0.0666	9.13
234	35.5	2.63	312	0.0538	9.30
236	31.4	2.80	314	0.0462	9.46
238	27.9	2.96	316	0.0363	9.57
240	24.4	3.11	318	0.0300	9.75
242	21.5	3.25	320	0.0252	10.0
244	18.8	3.39	322	0.0199	10.2
246	16.6	3.52	324	0.0166	10.4
248	14.6	3.64	326	0.0140	10.6
250	12.9	3.76	328	0.0117	10.7
252	11.4	3.87	330	0.0106	10.9
254	10.0	3.98	332	0.00857	11.2
256	8.86	4.10	334	0.00676	11.5
258	7.8	4.23	336	0.00615	11.7
260	6.85	4.38	338	0.00526	11.9
262	6.01	4.53	340	0.00502	12.2
264	5.23	4.68	342	0.00360	12.4
266	4.54	4.82	344	0.00241	12.5
268	3.94	4.97	346	0.00231	
270	3.37	5.14	348	0.00247	
272	2.87	5.34	350	0.00165	

[a] Absorption cross-sections at temperatures in the range 250 K to 298 K are calculated using the equation $\ln[\sigma(T)/\sigma(298\ K)]=B(T-298)$.

Quantum Yields

ϕ_1 = 0.76 ; ϕ_2 = 0.24 at 248 nm
ϕ_1 = 0.61 ; ϕ_2 = 0.41 at 308 nm

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are based on the work of Libuda and Zabel (1995) and Talukdar et al. (1995), which agree to within a few percent at wavelengths below 290 nm and only slightly less well at longer wavelengths where the error limits on the measurements increase because of the difficulty of measuring the small cross-sections in that region of the spectrum.

Talukdar et al. (1995) have also measured the cross-sections at three temperatures and expressed their results in the form $\ln[\sigma(T)/\sigma(298\,\mathrm{K})]=B(T-298)$ where B is a constant at a particular wavelength. The values of B and $\sigma(298\,\mathrm{K})$ obtained by Talukdar et al. (1995) are listed as our preferred values.

Combination of the NO_2 and NO_3 formation quantum yields measured by Mazely et al. in their 1995 and 1997 studies suggests NO_2 and NO_3 are the sole N-containing photoproducts. at 248 nm. It is therefore suggested that $(\phi_1 + \phi_2) = 1$ following absorption in the UV region. The values of ϕ_2 from Harwood et al. (2003) and Mazely et al. (1997) are averaged for the recommended value at 248 nm, and ϕ_1 obtained by difference. The Harwood value for ϕ_2 at 308 nm is accepted and ϕ_1 obtained by difference.

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