Electronic Structure and Volatility of Group-8 Oxides MO₄, where M = Ru, Os, and Element 108, Hs

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The discovery [1] of a relatively long-lived isotope of element 108, Hs, makes it now possible to design chemical experiments studying its chemical properties. Hs is expected to be a member of group 8 of the Periodic Table and, thus, a homolog of Ru and Os. If the chemical properties of Hs are comparable to those of Ru and Os, it should form a very volatile tetroxide, HsO₄. Several experimental groups including one from Mainz/GSI are, therefore, preparing gas-phase experiments on studying volatility of OsO_4 and its holomogs, RuO₄ and OsO_4 .

In the current report, we present results of the fully relativistic electronic structure calculations for group 8 gasphase tetroxides, RuO_4 , OsO_4 , and HsO_4 , and predict their volatility as an adsorption enthalpy with respect to the particular experimental conditions. The electronic structure calculations of MO_4 (M = Ru, Os, and Hs) including the geometry optimization were performed using the fully relativistic *ab initio* Density-Functional method in the GGA approximation for the exchange-correlation potential [2]. The calculated bond lengths, bond strengths, effective charges and covalence effects (OP) of these molecules are shown in Table 1. They indicate that HsO₄ is the most stable and the most covalent compound in the row.

The adsorption enthalpy of MO_4 on the quartz surface of the chromatography column was calculated using the following model of a molecule-slab interaction

$$E(x)_{\text{molecule-slab}} = -(\pi/6)NC_1/x^3, \tag{1}$$

where N is the number of atoms per cm^3 and x is the moleculesurface interaction distance. In the case of the dispersion interaction of a polarizable molecule with an inert surface consisting of molecular units

$$C_{1} = \frac{3}{2} \frac{\alpha_{1} \alpha_{2}}{\left(\frac{1}{h \nu_{1}} + \frac{1}{h \nu_{2}}\right)}$$
(2)

where hv_1 and hv_2 denote roughly ionization energies, and α_1 and α_2 - polarizabilities of the molecule (1) and the surface (2), respectively. Using the relation between polarizability of the surface and its dielectric constant, eqs. (1) and (2) transform into

$$E(x) = -\frac{3}{16} \left(\frac{\varepsilon - 1}{\varepsilon + 2} \right) \frac{\alpha_{mol}}{\left(\frac{1}{hv_{slab}} + \frac{1}{hv_{mol}} \right) x^3}$$
(3)

where $\varepsilon = 3.81$ is taken for the highest quartz modification - glass.

Table 1. Calculated bond lengths R_e (in Å), bond strengths D_e (in eV), ionization potentials IP (in eV), polarizabilities α (in a.u.), effective charges Q_M and overlap populations (OP) of MO₄ (M = Ru, Os, and Hs)

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Property	RuO_4	OsO_4	HsO ₄
R_e (calc.)	1.73	1.75	1.81
R_{e} (exp.) [3]	1.706	1.711	-
D_e (calc.)	27.48	27.71	28.44
α (calc.)	43.73	40.22	42.24
IP (calc.)	12.25	12.35	12.28
IP (exp.) [4]	12.19	12.35	-
Q_M	1.45	1.46	1.39
OP	1.92	1.94	2.17

By putting the experimental, when available, or calculated parameters into eq. (3), interaction energies E(x) were calculated as shown in Table 2. In the case when the SiO₂ surface is covered with adsorbed O₂, or has an effective charge (*Q*=-0.4), models similar to that of eqs. (1-3) were used giving the interaction energies listed in Table 2 as well.

Table 2. Contributions to the interaction energies E(x) between the neutral MO₄ (M = Ru, Os, and Hs) molecules and a) pure quartz surface; b) surface covered with O₂; c) surface with effective charge Qe (Q = -0.4)

Molecule	α - α (SiO ₂) E10 ²⁴ x ³	$\alpha - \alpha(O_2)$ E10 ²⁴ x ³	α -Qe E10 ³² x ⁴
	$(eV cm^3)$	$(eV cm^3)$	$(eV cm^4)$
RuO_4	4.73	6.28	10.01
OsO_4	4.48	6.01	9.41
HsO_4	4.64	6.16	9.73

The unknown distance *x* (of 2.25 Å for OsO₄ in the case "a") was deduced from the experimental $\Delta H_{ads}(OsO_4)$ by setting *E*(*x*) equal to -38 ± 1.5 kJ/mol. Taking *x*=2.25 Å as a benchmark and assuming that the molecule-surface distance is directly related to the size of the interacting molecules, the adsorption enthalpies for RuO₄ and HsO₄ were calculated using the data of Table 2. The obtained ΔH_{ads} for RuO₄ and HsO₄ (independently of the model) are larger and smaller than $\Delta H_{ads}(OsO_4)$ by about 2 kJ/mol, respectively. Thus, the volatility has the trend RuO₄ < OsO₄ < HsO₄, with the differences between the species being almost within the experimental uncertainties.

References

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