

## Electronic Structure and Volatility of Element 107 (Bh) Oxychloride

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First experiments on the chemical identification of element 107, bohrium, in the gas phase have recently been conducted [1]. They have successfully shown element 107 to form an oxychloride compound in the HCl/O<sub>2</sub> medium, probably of the type MO<sub>3</sub>Cl, similar to the lighter homologs in group 7, Tc and Re. In earlier test thermochromatography experiments [2] on volatility of Re and Tc compounds in the HCl/O<sub>2</sub> medium, the adsorption enthalpies and the boiling points were evaluated as -51 kJ/mol and -61 kJ/mol for TcO<sub>3</sub>Cl and ReO<sub>3</sub>Cl, respectively. In the current report, we present results of the electronic structure calculations for group 7 gas-phase compounds TcO<sub>3</sub>Cl, ReO<sub>3</sub>Cl and BhO<sub>3</sub>Cl, which were performed as predictions for the 107 experiments, and give estimates of volatility as an adsorption enthalpy with respect to the particular experimental conditions.

The calculations were performed using the fully relativistic *ab initio* Density-Functional method [3]. The frozen core approximation was used and the basis set included valence orbitals of the elements of interest. Mulliken population analysis was utilized for the electronic density distribution. In cases where the geometry was unknown it was assumed based on experimental or extrapolated ionic radii.

As a result, the following properties have been calculated: MO energies, ionization potentials (IP), electronic density distributions, effective charges (Q), overlap populations (OP), dipole moments ( $\mu$ ), and electric dipole polarizabilities ( $\alpha$ ) (Table 1). They show the closest analogy between the Re and Bh compounds.

Table 1. Effective charges ( $Q_M$ ), overlap populations (OP), Coulomb part of the binding energy ( $E^C$ ), dipole moments ( $\mu$ ), electric dipole polarizabilities ( $\alpha$ ) and ionization potentials (IP) for MO<sub>3</sub>Cl (M = Tc, Re and Bh)

Property	TcO <sub>3</sub> Cl	ReO <sub>3</sub> Cl	BhO <sub>3</sub> Cl
$Q_M$	1.28	1.21	1.13
OP	1.93	2.20	2.31
$E^C$ , eV	-10.03	-9.11	-7.74
$\mu$ , D	0.93	1.29	1.95
$\alpha$ , 10 <sup>24</sup> cm <sup>3</sup>	4.94	5.91	9.46
IP, eV	10.74	12.39	12.86

By using the calculated values and supposing that the interaction of the molecules with the SiO<sub>2</sub> surface takes place via the Cl atoms (with the charge  $Ze$ ) adsorbed on it, the energies of the following three types of the molecule - ionized surface interaction have been calculated:

1) Molecular dipole - charge ( $Ze$ )

$$\varepsilon(\mu, Ze) = -2\mu Ze/x^2,$$

2) Molecular polarizability - charge ( $Ze$ )

$$\varepsilon(\alpha, Ze) = -Z^2 e^2 \alpha / 2x^4$$

3) Dispersion interaction

$$e(\mathbf{a}, \mathbf{a}) = -\frac{3}{2} \frac{\mathbf{a}_1 \mathbf{a}_2}{x^6 \left( \frac{1}{h\mathbf{n}_1} + \frac{1}{h\mathbf{n}_2} \right)}$$

Here,  $h\mathbf{n}$  are roughly IP of the molecules and  $x$  is the molecule-surface distance. The Cl parameters  $\alpha$  and IP have been calculated as a dependence on its realistic effective charge. All the calculated contributions to the interaction energy (for  $Z = -0.4$  which is the most realistic value) are given in Table 2.

Table 2. Contributions to the interaction energies  $\varepsilon$  between neutral MO<sub>3</sub>Cl molecules (M = Tc, Re and Bh) and Cl<sup>Z</sup>(surface) ( $Z = -0.4$ )

Molecule	$\mu$ - $Ze$ $\varepsilon 10^{28} x^2$ (erg cm <sup>2</sup> )	$\alpha$ - $Ze$ $\varepsilon 10^{44} x^4$ (erg cm <sup>3</sup> )	$\alpha$ - $\alpha$ (Cl) $\varepsilon 10^{60} x^6$ (erg cm <sup>6</sup> )
TcO <sub>3</sub> Cl	3.59	9.12	576.88
ReO <sub>3</sub> Cl	4.96	10.91	729.87
BhO <sub>3</sub> Cl	7.49	17.46	1186.81

The unknown distance  $x$  has been deduced from the measured adsorption enthalpy for ReO<sub>3</sub>Cl by setting the expression for the interaction energy  $3.1/x^2 + 6.8/x^4 + 455.6/x^6$  (in eV) obtained using the terms from Table 2 to  $H_{\text{ads}} = -61 \pm 3$  kJ/mol (0.63 eV). This resulted in  $x = 3.38$  Å for ReO<sub>3</sub>Cl, which is related to the case when the adsorbate molecule and the Cl ion touch each other. Taking this as a benchmark and assuming that the molecule-surface distance is directly related to the size of the interacting molecules (which means  $x = 3.37$  Å for TcO<sub>3</sub>Cl and  $x = 3.44$  Å for BhO<sub>3</sub>Cl), we have calculated adsorption enthalpies for the other two oxychlorides using the data of Table 2. Thus, we obtained  $\Delta H_{\text{ads}} = -47$  kJ/mol and  $\Delta H_{\text{ads}} = -88$  kJ/mol for TcO<sub>3</sub>Cl and BhO<sub>3</sub>Cl, respectively. The experimental value of  $\Delta H_{\text{ads}} = -51 \pm 3$  kJ/mol for TcO<sub>3</sub>Cl is indicative of an adequate theoretical description of the process. Thus, the volatility of the group 7 oxychlorides was predicted to change in the following way TcO<sub>3</sub>Cl > ReO<sub>3</sub>Cl > BhO<sub>3</sub>Cl.

## References

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