

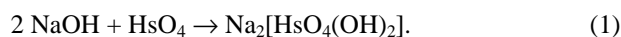
Theoretical Investigations of the Reactivity of MO_4 and the Electronic Structure of $\text{Na}_2[\text{MO}_4(\text{OH})_2]$, where $\text{M} = \text{Ru}, \text{Os},$ and Hs (element 108)

V. Pershina* and J. V. Kratz**

*GSI, Darmstadt

**Institut für Kernchemie, Universität Mainz

Recent experiments on the chemical identification of element 108, Hs, have delivered straightforward evidence that it belongs to group 8 of the Periodic Table [1]. In the presence of oxygen, Hs formed HsO_4 which was deposited in a gas-phase chromatography column at a temperature somewhat higher than that of OsO_4 , thus confirming its chemical similarity with the latter and the high volatility. In more recent experiments [2] with volatile tetroxides, HsO_4 was shown to react with moisturized NaOH forming very probably the sodium hassate (VIII), $\text{Na}_2[\text{HsO}_4(\text{OH})_2]$, by analogy with $\text{Na}_2[\text{OsO}_4(\text{OH})_2]$ according to the reaction



In the present work, we study the reactivity of RuO_4 , OsO_4 , and HsO_4 with NaOH on the basis of results of the fully relativistic calculations for the components of the reaction of type (1) using the 4-component Density-Functional Theory method [3]. A model [4] was used to determine the free energy change ΔG^f of a reaction via changes in the ionic (ΔE^C) and covalent (ΔE^{OP}) contributions to the total binding energy. The latter are calculated using Mulliken effective charges Q_M and overlap populations, OP. It was shown that relative values of ΔG^f could be reliably predicted via the ΔE^C . The bond lengths (R_e) of the Os complex were taken from the experiment [5], and those of the Ru and Hs complexes were estimated using R_e for RuO_4 and HsO_4 with respect to $R_e(\text{OsO}_4)$ [6].

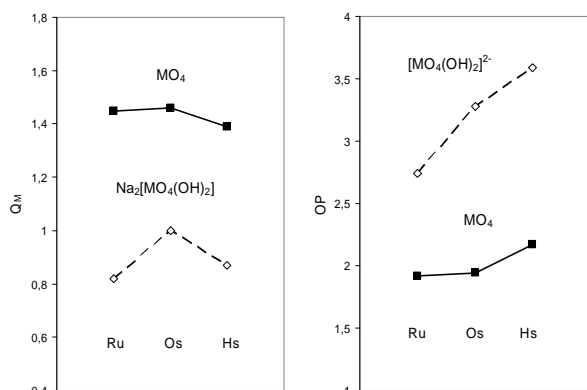


Fig. 1. Effective metal charges, Q_M , and overlap populations, OP, in MO_4 [6] and $[\text{MO}_4(\text{OH})_2]^{2-}$ [this work] ($\text{M} = \text{Ru}, \text{Os},$ and Hs).

The values of Q_M and OP obtained for $[\text{MO}_4(\text{OH})_2]^{2-}$ and MO_4 are depicted in Fig. 1. They show $[\text{HsO}_4(\text{OH})_2]^{2-}$ to be more covalent than the Os homolog, similarly to MO_4 . Both Q_M and OP in $[\text{RuO}_4(\text{OH})_2]^{2-}$ are significantly smaller than Q_M and OP of the Os and Hs anions, which is indicative for

the fact that the Ru anion is not stable due to the weak ionic and covalent constituents of the bond strength. This is not the case with MO_4 , where Q_M and OP of RuO_4 are very similar to those of OsO_4 (Fig. 1).

Table 1. Coulomb binding energies, E^C , for complexes of Ru, Os, and Hs and their differences, ΔE^C (in eV), for reactions of the complex formation

Complex/reaction	Ru	Os	Hs	Ref.
$E^C: \text{MO}_4$	-13.74	-13.86	-12.04	6
$E^C: [\text{MO}_4(\text{OH})_2]^{2-}$	-3.58	-7.64	-5.26	this
$E^C: \text{Na}_2[\text{MO}_4(\text{OH})_2]$	-5.70	-8.77	-6.41	this
$\Delta E^C: \text{MO}_4 \Leftrightarrow [\text{MO}_4(\text{OH})_2]^{2-}$	10.16	6.23	6.78	this
$\Delta E^C: \text{MO}_4 \Leftrightarrow \text{Na}_2[\text{MO}_4(\text{OH})_2]$	8.04	5.09	5.63	this

The obtained E^C for the species and ΔE^C for the complex formation reactions are given in Table 1. The values are similar for reactions of HsO_4 and OsO_4 : HsO_4 should be slightly less reactive than OsO_4 . We can give the upper limit of the difference in ΔG^f between HsO_4 and OsO_4 of 52 kJ/mol defined by the difference in their ΔE^C . (The slightly larger $\Delta \text{OP}=1.42$ for the Hs reaction than $\Delta \text{OP}=1.34$ for the Os reaction should slightly decrease this value). The values of ΔE^C for the reactions of RuO_4 are about 300 kJ/mol more positive than ΔE^C of the OsO_4 and HsO_4 reactions. The reason for that is the too low stability of the Ru complex anion manifested in its low E^C (low Q_M) and low E^{OP} (low OP) (Fig. 1). Thus, the so much more positive ΔG^f of the complex formation reaction of Ru compared to those of Os and Hs explains why $[\text{RuO}_4(\text{OH})_2]^{2-}$ is not known. Finally, on the basis of these calculations, we predict the following trend for the formation of $[\text{MO}_4(\text{OH})_2]^{2-}$, or $\text{Na}_2[\text{MO}_4(\text{OH})_2]$ in group 8:



The predicted slightly lower reactivity of HsO_4 as compared to that of OsO_4 has so far not clearly been revealed experimentally [2].

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