

Solution Chemistry of Element 106: Hydrolysis of Group 6 Cations

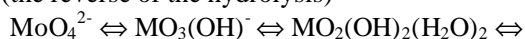
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The first chemical study of seaborgium in aqueous solution was its one-step elution as a neutral or anionic species in 0.1 M HNO₃/5×10⁻⁴ M HF from cation exchange columns [1]. These experiments showed the most stable oxidation state in aqueous solutions to be +6 as expected for a member of group 6 elements. The lighter homologs of Sg, Mo and W, are known to form under these conditions neutral or anionic oxo- or oxofluoro complexes. To exclude the influence of the strong complexing action of the F⁻ ions, another similar study [2] was performed in which the group 6 elements were eluted from cation exchange columns in 0.1 M HNO₃ without HF. In these later experiments, Sg was not eluted from the column in contrast to W, and this non-tungsten like behavior of Sg was tentatively attributed to its lower tendency to hydrolyze compared to that of tungsten. To render a theoretical assistance to those experiments, we have performed a study of hydrolysis of the group 6 elements using relativistic density-functional *ab initio* calculations of the hydrated and hydrolysed species of Mo, W and Sg.

The free energy changes for the following protonation processes (the reverse of the hydrolysis)



have been defined for Mo, W and Sg. For this purpose, a model has been used [3] which enables determination of the changes in the ionic and covalent contributions to the total binding energy separately using the Mulliken population analysis of the electronic density distribution. The latter was calculated using the fully relativistic *ab initio* Density-Functional method [4]. The geometry of the molecules was assumed based on experimental or extrapolated ionic radii.

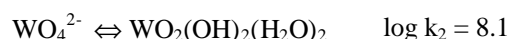
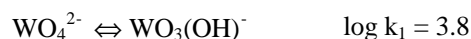
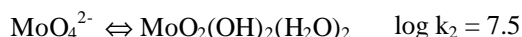
As a result of the calculations, the changes in the Coulomb part of the free energy for the protonation processes indicated above are presented in Table 1.

Table 1. Changes in the Coulomb part of the free energy ΔE^C (in eV) for the protonation reactions

Reaction	Mo	W	Sg
$\text{MO}_4^{2-} \rightleftharpoons \text{MO}_3(\text{OH})^-$	-13.18	-13.22	-13.45
$\text{MO}_3(\text{OH})^- \rightleftharpoons \text{MO}_2(\text{OH})_2(\text{H}_2\text{O})_2$	-20.86	-21.51	-20.92
$\text{MO}_2(\text{OH})_2(\text{H}_2\text{O})_2 \rightleftharpoons \text{MO}(\text{OH})_3(\text{H}_2\text{O})_2^+$	-4.96	-5.33	-5.53
$\text{MO}(\text{OH})_3(\text{H}_2\text{O})_2^+ \rightleftharpoons \text{M}(\text{OH})_4(\text{H}_2\text{O})_2^{2+}$	-0.61	-0.67	-1.12
$\text{M}(\text{OH})_4(\text{H}_2\text{O})_2^{2+} \rightleftharpoons \text{M}(\text{H}_2\text{O})_6^{6+}$	39.87	37.12	34.96



Comparisons of ΔE^C with the experimental equilibrium constants



have shown the former to correlate with k as it is seen from the following relations

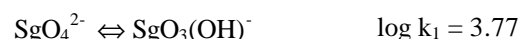
$$\log k_1(\text{Mo}) / \Delta E^C_1(\text{Mo}) = 3.7/13.18 = 0.28$$

$$\log k_1(\text{W}) / \Delta E^C_1(\text{W}) = 3.8/13.22 = 0.28$$

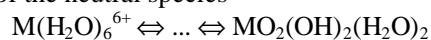
$$\log k_2(\text{Mo}) / \Delta E^C_2(\text{Mo}) = 7.50/34.01 = 0.22$$

$$\log k_2(\text{W}) / \Delta E^C_2(\text{W}) = 8.1/34.73 = 0.23$$

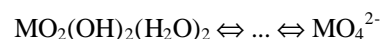
and to define trends in the changes in the free energy of the reactions and, hence, in hydrolysis. Using the relations between the k values and ΔE^C , the following equilibrium constants for the Sg reactions have been defined



Thus, the results of the calculations (Table 1) have shown hydrolysis of the cations in acid solutions with the final formation of the neutral species



to change in the following way $\text{Mo} > \text{W} > \text{Sg}$, while for the further hydrolysis in solutions of higher pH



the order is reversed $\text{Mo} \geq \text{Sg} > \text{W}$. The first predicted sequence of hydrolysis is in full agreement with that obtained experimentally for the acidic solutions with pH=1.

References

- [1] M. Schädel, *et al.*, *Nature* **388**, 55 (1997)
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[4] T. Bastug *et al.*, *Chem. Phys. Lett.* **211**, 119 (1993)