

The Mechanism of Water Exchange in $\text{AmO}_2(\text{H}_2\text{O})_5^{2+}$ and in the Isoelectronic $\text{UO}_2(\text{H}_2\text{O})_5^+$ and $\text{NpO}_2(\text{H}_2\text{O})_5^{2+}$ Complexes as Studied by Quantum Chemical Methods

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The structure and thermodynamics of the linear actinyl aqua ions $\text{MO}_2(\text{H}_2\text{O})_5^{2+}$ and $\text{MO}_2(\text{H}_2\text{O})_5^+$ have been studied both by experimental and quantum chemical methods.^{1–3} However, the information on the dynamics, and in particular the reaction mechanisms, is scarce and often contradictory.³ In previous studies, we have discussed the mechanism of water exchange between the uranyl(VI) aqua ion $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ and the water solvent,² based on both experimental data and a quantum chemical analysis, and also the effect of systematic errors on estimates of thermodynamic quantities.⁴ In this communication, we have studied water exchange of $\text{AmO}_2(\text{H}_2\text{O})_5^{2+}$ and the isoelectronic ions $\text{UO}_2(\text{H}_2\text{O})_5^+$ and $\text{NpO}_2(\text{H}_2\text{O})_5^{2+}$ in water solution, using the mechanistic schemes and the quantum chemical methods and basis sets described in ref 2, p 12001. We have not considered the QM/MM method because of the instabilities of geometry optimization when two solvation shells are treated at the QM level,⁵ and in addition this method may not easily be used to estimate activation parameters. By comparing the activation energy of the dissociative (*D*), associative (*A*), and interchange (*I*) mechanisms for the uranyl(VI) and neptunyl(VI) aqua ions and the *D* and *A* intermediates for the corresponding americyl(VI) ion, we suggest that the reaction mechanism for the water exchange is the same for the different actinyl(VI) ions. We have also studied the influence of the formal charge of the actinide on the activation energy and the reaction mechanism for $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ and $\text{UO}_2(\text{H}_2\text{O})_5^+$. The calculated thermodynamic data for the various reactions in a PCM solvent using geometries optimized in the gas phase or in solvent are given in Table 1; coordinates, bond distances, and the energy in atomic units are described in Tables S1 and S2 of the Supporting Information. There is no change in the electronic state between precursor, transition state, and intermediate in the open shell systems (Table 2), indicating that spin–orbit effects are negligible.

The change in bond distances between the metal and the water in the optimized structures is in general less than 0.05 Å. For $\text{UO}_2(\text{H}_2\text{O})_5^+$, it was only possible to identify an intermediate for the dissociative mechanism, and the possibility of an associative reaction could therefore be eliminated. This makes the interchange mechanism less likely; in fact, no transition state was identified for this pathway. Structures for the precursor, the *D* transition state, and intermediate are shown in Figure 1. They differ noticeably from the corresponding species in the dissociative pathway for $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$; the U–water bond distances are longer and there is a hydrogen bond interaction between the outer-sphere water molecule and the UO_2^+ “yl” oxygen that is absent in the uranyl(VI) species

Table 1. Activation Energies and Energies of the Intermediates for the *D*, *I*, and *A* Water Exchange Mechanisms^a

complex	<i>D</i>		<i>A</i>		<i>I</i>
	ΔE^\ddagger	ΔE_1	ΔE^\ddagger	ΔE_1	ΔE^\ddagger
$[\text{UO}_2(\text{VI})(\text{H}_2\text{O})_5]^{2+}$	70.1	65.8	<i>18.7</i>	<i>15.8</i>	21.2
$[\text{UO}_2(\text{V})(\text{H}_2\text{O})_5]^+$	36.4	27.0			
$[\text{NpO}_2(\text{VI})(\text{H}_2\text{O})_5]^{2+}$	62.6	58.1	<i>30.0</i>	28.5	30.4
$[\text{AmO}_2(\text{VI})(\text{H}_2\text{O})_5]^{2+}$		67.7		22.6	

^a Values in italic refer to calculations using geometries optimized in the solvent. ΔE^\ddagger and ΔE_1 are the activation energy and the energy of the intermediate relative to the precursor, respectively.

Table 2. Electronic Configuration and Mulliken Atomic Charges on the Actinide Center and on the O_{yl} in Different Actinyl Species

conf.	U(VI)O_2^{2+} 5f ⁰	U(V)O_2^+ 5f ¹	Np(VI)O_2^{2+} 5f ⁰	Am(VI)O_2^{2+} 5f ⁰ 5f ₆ ²
	Naked			
An	2.43	1.94	2.32	2.31
O _{yl}	−0.21	−0.47	−0.16	
	Penta Aqua Ion			
An	2.43	2.19	2.36	2.31
O _{yl}	−0.43	−0.66	−0.40	−0.33

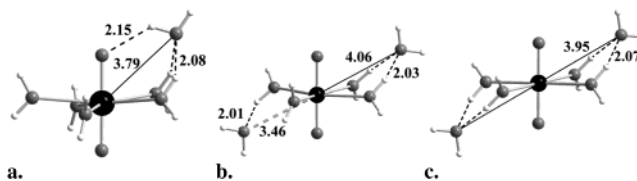


Figure 1. Perspective views of the reactant (a), transition state (b), and intermediate (c) of the *D* mechanism for uranyl(V) system.

(cf. ref 2 and Figures 1a and 2a). We ascribe this difference to the change in charge of the central uranium atom and the “yl” oxygens (the latter within parentheses) that are 2.43 (−0.43) and 2.19 (−0.66) for UO_2^{2+} and UO_2^+ , respectively (cf. Table 2). The large negative charge on the uranyl(V) oxygen atoms makes them much stronger hydrogen bond acceptors than the uranyl(VI) oxygens; the larger negative charge also suggests an explanation for the ability of UO_2^+ (and other actinyl(V) ions) to form cation–cation complexes.^{6,7}

The additional 5f electron in UO_2^+ occupies a nonbonding 5f₀ orbital (Figure 3a and Table 2) and induces a weakening of both axial and equatorial bonds as reflected by the increase of 0.10 and 0.09 Å in the U–O_{yl} and U–water bond distances, as compared to those in UO_2^{2+} .

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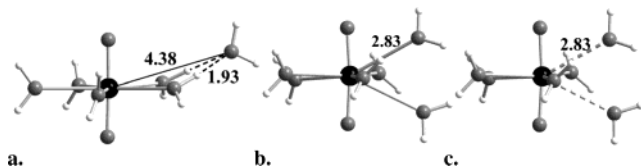


Figure 2. Perspective views of the reactant (a) and the intermediate (b) for the *A* mechanism and transition state (c) for the *I* mechanism for neptunyl(VI) system.

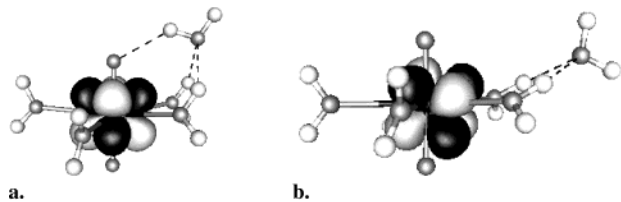


Figure 3. Contour plot of the singly occupied $5f_5$ orbital in $[\text{UO}_2(\text{H}_2\text{O})_5]$, $(\text{H}_2\text{O})^+$ (a) and $[\text{NpO}_2(\text{H}_2\text{O})_5]$, $(\text{H}_2\text{O})^{2+}$ (b) displayed with gopenmol.

For the water exchange in $\text{UO}_2(\text{H}_2\text{O})_5^+$, we find a difference of 27 kJ/mol in electronic energy between the precursor and the intermediate; the electronic activation energy is 36 kJ/mol, as compared to 70 kJ/mol in the corresponding uranyl(VI) reaction, in both cases referring to single-point calculations within the CPCM solvent, using the gas-phase geometry. The activation energy for the *D* pathway in $\text{UO}_2(\text{H}_2\text{O})_5^+$ is approximately 20 kJ/mol higher than that for the *A/I* pathway in $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$, but this does not necessarily result in a smaller rate constant for the uranyl(V) water exchange. This is not determined by the electronic energy, but by the activation free energy, ΔG^\ddagger , even if the former contains a solvent free energy contribution when using the PCM model. An estimate of ΔG^\ddagger requires information of the vibration frequencies of the molecular part of the system, and this is not available to us. However, experimental data show that the activation entropy is always larger for a dissociative than for the alternative associative mechanism, and an entropy difference of 50 J/K·mol is not uncommon in experimental studies (ref 8, p 202) and will result in a rate constant at 25 °C that is about the same for both $\text{UO}_2(\text{H}_2\text{O})_5^+$ and $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$.

The geometry and bond distances for the precursor, transition states, and intermediates for the different reaction pathways in the $\text{NpO}_2(\text{H}_2\text{O})_5^{2+}$ and $\text{AmO}_2(\text{H}_2\text{O})_5^{2+}$ systems (Table S1) are very close to those of the corresponding UO_2^{2+} system. However, we note a shortening of the actinyl M–O bond by 0.024 (Np) and 0.036 (Am) Å, and of the M–water bond by 0.005 (Np) and 0.01 (Am) Å, respectively, from those in the uranyl(VI) aqua ion. This is presumably a result of a contraction of the 5f orbitals with increased nuclear charge. The 5f orbitals do not participate in the bonding as efficiently in Np and Am as in U. This is the explanation for the smaller charge on Am(VI) and Np(VI), 2.31 and 2.36 as compared to 2.43 for U(VI) (cf. Table 2).

In the $\text{NpO}_2(\text{H}_2\text{O})_5^{2+}$ and $\text{AmO}_2(\text{H}_2\text{O})_5^{2+}$ systems, we have identified the four- and one six-coordinated intermediates for the *D* and *A* mechanisms, respectively; the latter is only stable in the solvent. The electronic energy for the *D* and *A* intermediates is 68 and 29 kJ/mol higher than that in the precursor for Np(VI) and 68 and 23 kJ/mol higher than that in the precursor for Am(VI), as compared to 62 and 16 kJ/mol for $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$. This demonstrates a preferred hydration number of five, consistent with NMR data of Bardin et al.⁹ For Np(VI), the structure of the six-coordinated intermediate is nearly identical with that of the

I-transition state (cf. Figure 2b,c). The distance from the neptunium center to the two water molecules located above and below the equatorial plane in a symmetric manner is significantly longer (0.18 Å) than that reported² for $[\text{UO}_2(\text{H}_2\text{O})_6]^{2+}$. The distance to the leaving water molecule in the *D* transition state is slightly shorter (0.09 Å) than in the uranyl(VI) system. There is no significant difference between the activation energy and the structure of the activated complex in the *A* and *I* pathways; the activation energy, 30 kJ/mol, is slightly larger than that in the uranyl(VI) system. The energy difference ΔE_1^\ddagger between the associative transition state and the intermediate is very small, 1.5 kJ/mol, less than the thermal energy at 25 °C, and the water exchange is therefore best described as an *I_a* mechanism. The *D* activation energy, 70 kJ/mol, is slightly lower in the neptunyl(VI) than in the uranyl(VI) system; however, the *I_a* mechanism is still the one of lowest energy, as in the uranyl(VI) system.

The results obtained in the present and a previous study² indicate that the increased nuclear charge and decreasing ionic radius of the actinide in $\text{MO}_2(\text{H}_2\text{O})_5^{2+}$ complexes result in an increase in the activation energy for the *A/I* pathway; this is in contradiction to the observation by Bardin et al.,⁹ who reported a decrease of the activation enthalpy of about 10 kJ/mol between UO_2^{2+} and NpO_2^{2+} . However, this study was made in a mixed water/acetone medium, and both experimental rate constants and the activation parameters varied substantially with the composition of the solvent.

The significant difference between the dissociative activation energies for the uranyl(V) and actinyl(VI) ions can be understood in terms of a charge-dipole interaction; the smaller the charge on the metal center, the weaker the metal–water interaction.

There are no experimental data on rates and mechanism for ligand substitution reactions in uranyl(V) complexes; however, such data exist for neptunium(V). If the ligand exchange reactions follow the Eigen–Wilkins mechanism, it might be possible to make some statements about the rate of water exchange (cf. ref 10, p 2042). However, as the literature data^{3,11} refer to ligand exchange in systems where the ligands are multidentate weak acids, it is virtually impossible to draw any mechanistic conclusions from the experimental data.

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Supporting Information Available: Geometries (Table S1, Figures S1–S4) and coordinates (Table S2) of these species discussed in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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