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Rates and Mechanisms of Water Exchange of UO_2^{2+}(aq) and UO_2(oxalate)$F(H_2O)_2^-$: A Variable-Temperature ^{17}O and ^{19}F NMR Study

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This study consists of two parts: The first part comprised an experimental determination of the kinetic parameters for the exchange of water between $UO_2(H_2O)_5^{2+}$ and bulk water, including an ab initio study at the SCF and MP2 levels of the geometry of $UO_2(H_2O)_5^{2+}$, $UO_2(H_2O)_4^{2+}$, and $UO_2(H_2O)_6^{2+}$ and the thermodynamics of their reactions with water. In the second part we made an experimental study of the rate of water exchange in uranyl complexes and investigated how this might depend on *inter*- and *intra*molecular hydrogen bond interactions. The experimental studies, made by using ^{17}O NMR, with Tb^{3+} as a chemical shift reagent, gave the following kinetic parameters at 25 °C: $k_{ex} = (1.30 \pm 0.05) \times 10^6\ s^{-1}$; $\Delta H^{\ddagger} = 26._1 \pm 1._4$ kJ/mol; $\Delta S^{\ddagger} = -40 \pm 5$ J/(K mol). Additional mechanistic indicators were obtained from the known coordination geometry of U(VI) complexes with unidentate ligands and from the theoretical calculations. A survey of the literature shows that there are no known isolated complexes of UO_2^{2+} with unidentate ligands which have a coordination number larger than 5. This was corroborated by quantum chemical calculations which showed that the energy gains by binding an additional water to $UO_2(H_2O)_4^{2+}$ and $UO_2(H_2O)_5^{2+}$ are 29.8 and −2.4 kcal/mol, respectively. A comparison of the change in ΔU for the reactions $UO_2(H_2O)_5^{2+} \rightarrow UO_2(H_2O)_4^{2+} + H_2O$ and $UO_2(H_2O)_5^{2+} + H_2O \rightarrow UO_2(H_2O)_6^{2+}$ indicates that the thermodynamics favors the second (associative) reaction in gas phase at 0 K, while the thermodynamics of water transfer between the first and second coordination spheres, $UO_2(H_2O)_5^{2+} \rightarrow UO_2(H_2O)_4(H_2O)^{2+}$ and $UO_2(H_2O)_5(H_2O)^{2+} \rightarrow UO_2(H_2O)_6^{2+}$, favors the first (dissociative) reaction. The energy difference between the associative and dissociative reactions is small, and solvation has to be included in ab initio models in order to allow quantitative comparisons between experimental data and theory. Theoretical calculations of the activation energy were not possible because of the excessive computing time required. On the basis of theoretical and experimental studies, we suggest that the water exchange in $UO_2(H_2O)_5^{2+}$ follows a dissociative interchange mechanism. The rates of exchange of water in UO_2(oxalate)$F(H_2O)_2^-$ (and UO_2(oxalate)$F_2(H_2O)^{2-}$ studied previously) are much slower than in the aqua ion, $k_{ex} = 1.6 \times 10^4\ s^{-1}$, an effect which we assign to hydrogen bonding involving coordinated water and fluoride. The kinetic parameters for the exchange of water in $UO_2(H_2O)_5^{2+}$ and quenching of photo excited $^*UO_2(H_2O)_5^{2+}$ are very near the same, indicating similar mechanisms.

Introduction

The rate and mechanism of the exchange between coordinated and free solvent provide important information for the deduction of the intimate mechanisms of many ligand substitution reactions in metal complexes. The most direct experimental route to study these reactions is offered by isotope substitution and NMR methods. The rate of solvent exchange may also be inferred indirectly; the classical example is the Eigen−Wilkins mechanism, in combination with the Fouss equation,[1] for the estimation of the outer sphere equilibrium constant between the reactants.

The variations in the rate of exchange of water between the first and second coordination spheres have been discussed in terms of differences in electronic structure and size of the metal ion and ion−dipole interactions between the central ion and coordinated water.[2−4] The charge to ionic radius ratio seems to exert a large influence on these variations for the main group metal ions, while the electron configuration seems to be a key factor for the d-transition elements.

In previous papers[5−8] we have described rates and mechanisms of ligand exchange reactions in various binary and ternary U(VI) complexes and discussed if and how water is involved in these reactions. The present study is an attempt to measure the rate of water exchange and to obtain additional information on the intimate mechanism of the water exchange in $UO_2(H_2O)_5^{2+}$ and UO_2(oxalate)$F(H_2O)_2^-$.

There are four possible mechanisms for the water exchange: two limiting mechanisms, D and A, with the intermediates UO_2-

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$(H_2O)_4^{2+}$ and $UO_2(H_2O)_6^{2+}$, and two interchange mechanisms, I_d and I_a. As intermediates could not be identified, we have made ab initio calculations in order to obtain information on the thermodynamics for their formation for the (hypothetical) D and A reactions. In the two interchange mechanisms $\Delta G = 0$ and the potential function describing the reaction along the reaction coordinate must therefore be symmetric; the only difference between them is that the distance uranium–leaving and entering water is longer at the transition state for I_d than for I_a. A choice between them might therefore be made using either an experimental determination of the change in activation volume $\Delta V^{\ddagger}$ or by a theoretical calculation of the reaction energy profile and activation energy. The experimental tools for determination of $\Delta V^{\ddagger}$ are not available to us. Theoretical calculations of the reaction energy profile require the inclusion of both the first and second coordination spheres, and such calculations are at present too large for systems containing actinides. Hence, the information required for a detailed mechanistic discussion is incomplete and this will by necessity be provisional.

The water exchange was studied using ^{17}O NMR relaxation, where the transverse and longitudinal relaxation rates of the bulk water signal contain information on the exchange rate. The theory and practice of this technique for paramagnetic metal ions are well established.[9−13] In the fast exchange regime two methods, either a relaxation or a chemical shift reagent, may be used, as summarized by Bleuzen et al.[14] and used to study the water exchange in Mg^{2+}. The magnitude of the rate constant, $k = 6.7 \times 10^5\ s^{-1}$, encouraged us to use the method for the diamagnetic UO_2^{2+} ion, which we expected to have a similar rate.

Experimental Section

Preparation of Stock Solutions. *$UO_2(ClO_4)_2$ solutions* were prepared from $UO_2(NO_3)_2{\cdot}H_2O$, which was thermally decomposed to U_3O_8 and then dissolved with HIO_3 in $HClO_4$ solution.[15] The uranyl concentration was determined by gravimetry using 8-hydroxyquinoline[15] and checked from time to time using spectrophotometry. *$Tb(ClO_4)_3$ solutions* were prepared by dissolving terbium oxide in warm perchloric acid using moderate heating, followed by EDTA titration using a hexamethylenetetramine buffer and xylenol orange as indicator.[16]

NMR Sample Preparations. The ionic medium had a constant perchlorate concentration of 4 mol/kg; the concentrations of the cations Na^+, H^+, Tb^{3+}, and UO_2^{2+} varied as described in the Supporting Information. The hydrogen ion concentration was adjusted with $HClO_4$. The samples contained 5% $H_2{}^{17}O$ (36% enrichment). The test solutions were prepared by weight, and their concentrations are given in mol/kg of water (m). The uranyl stock solution used to study isotope effects on the solvent exchange was prepared by evaporating the water carefully and replacing it by weighed amounts of D_2O.

The ternary uranium–oxalate–fluoride system was studied in a 1.00 M $NaClO_4$ ionic medium, using the equilibrium constants described in a recent paper.[17] The test solution contained 0.020 M U(VI), 0.020 M oxalate, and 0.010 M fluoride at pH = 3.6, where the dominant species is $UO_2(ox)F(H_2O)_2^-$. The equilibrium distribution of the solutions was calculated and graphically presented using the MEDUSA program.[18]

NMR Measurements. The ^{17}O NMR spectra were obtained with Bruker Avance-800 (18.8 T) and Bruker DMX-500 (11.7 T) spectrometers, using 5 mm tubes, in the case of Tb^{3+} using solutions without lock. The temperature was varied using the Bruker Eurotherm variable-temperature control unit, and the temperature scale was calibrated using methanol.[19] Shimming was made at 270 K and controlled by measuring the line width of the methanol methyl signal at the other temperatures studied. There was only a marginal increase in the line broadening, 1 Hz, at $T > 305$ K for the 18.8 T data. The line broadening was larger, 5 Hz, for the 11.7 T data. The longitudinal relaxation rates were measured by the inversion recovery method. The transverse relaxation rates were obtained from the line width, in case of broad signals determined by Lorentzian fitting of the peaks. The chemical shifts are given relative to that of water in the corresponding ionic medium. The temperature dependence of these parameters was used to obtain the activation parameters for the water exchange reactions. The ^{19}F NMR spectra were recorded on a Bruker DMX 500 spectrometer using 5% D_2O solution in the locked mode. They were referenced to an aqueous solution of 0.010 M NaF in 1 M $NaClO_4$ (pH = 12) at 25 °C.

Data Treatment. $Tb^{3+}(aq)$ was used as a chemical shift agent to determine the rate constant for the water exchange in the uranyl(2+) ion using the "paramagnetic solvent" concept from Bleuzen et al.[14] A concise description of the effect of paramagnetic species in small population on the longitudinal and transverse relaxation rates and the chemical shift of bulk water in the case of *fast exchange* has been given by Powell and Merbach.[13] The rate constants were obtained from the experimental values of $1/T_1$ and $1/T_2$ using eqs 1 and 2; for notation

$$Y = \frac{1}{T_2} - \frac{1}{T_1} - P_{Tb^{3+}} \frac{{\Delta\omega_{rTb^{3+}}}^2}{k_{exTb^{3+}}} = P_{UO_2^{2+}} \frac{k_{exUO_2^{2+}}(P_{Tb^{3+}}\Delta\omega_{rTb^{3+}})^2}{k_{exUO_2^{2+}} + (P_{Tb^{3+}}\Delta\omega_{rTb^{3+}})^2} \tag{1}$$

$$\Delta\omega = P_{Tb^{3+}}\Delta\omega_{rTb^{3+}} \tag{2}$$

compare refs 13 and 14. The assumption of extreme narrowing for water was tested by measuring T_{1A} and T_{2A}. Their difference was 3−4 Hz at $T > 305$ K, indicating either the error in the extreme narrowing approximation or an inhomogeneity contribution to T_{2A}. We prefer the latter explanation.

The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined from the experimental rate constants using eq 3.

$$k_{ex} = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}\right) \tag{3}$$

The experimental quantity Y (cf. eq 1) increases with decreasing temperature. Hence, systematic errors are expected to be larger at higher temperature. For the 11.7 T data we estimate the inhomogeneity error to 12 Hz at high and 3 Hz at low temperature. The resulting error in $k_{exUO_2^{2+}}$ varies between 3 and 30% between 260 and 325 K. For the 18.8 T data the corresponding errors are 3 and 1 Hz, at respectively 325 and 270 K. The corresponding error in $k_{exUO_2^{2+}}$, varies between 4% at high and 1% at low temperature. This error estimation indicates that individual weights of the various measurements should be used in the data interpretation. We made four different evaluations: using each series of measurements separately; treating all series together using weighted data; assigning equal relative weights to all experimental points. The individual weight for an experimental point, i, is $w_i = 1/\sigma_i^2$; σ_i is the estimated uncertainty. The experimental data with their uncertainty are given in Supporting Information. The kinetic results are given in Table 1. The parameter values obtained when using equal relative and individual weights were the same, but the standard deviation for the latter was lower. By giving zero weight to the experimental

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Table 1. Kinetic Data for Tb^{3+}(aq), UO_2^{2+}(aq) and UO_2(ox)F$(H_2O)_2^-$

ion	k_{ex}/s^{-1} at 298 K	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	$-(A/h)/10^5$ rad/s
${}^{a}UO_2^{2+}\ {}^{a}$	$(1.6 \pm 0.06) \times 10^6$	28.4 ± 1	-31 ± 3	
${}^{b}UO_2^{2+}\ {}^{b}$	$(1.3 \pm 0.04) \times 10^6$	24.6 ± 1.1	-45 ± 4	
${}^{c}UO_2^{2+}\ {}^{c}$	$(1.4 \pm 0.2) \times 10^6$	32 ± 3	-20 ± 10	
${}^{d}UO_2^{2+}\ {}^{d}$	$(1.3 \pm 0.05) \times 10^6$	26.1 ± 1.4	-40 ± 5	
${}^{e}UO_2^{2+}\ {}^{e}$	1.4×10^6	38 ± 2	-12 ± 1	
${}^{a}Tb^{3+}\ {}^{a}$	$(2.73 \pm 0.27) \times 10^8$	17.5 ± 3.5	-25 ± 12	5.44 ± 0.02
${}^{b}Tb^{3+}\ {}^{b}$	$(3.00 \pm 0.1) \times 10^8$	12.8 ± 1.5	-40 ± 5	5.23 ± 0.06
${}^{c}Tb^{3+}\ {}^{c}$	$(2.31 \pm 0.1) \times 10^8$	10.4 ± 1	-50 ± 4	5.51 ± 0.06
${}^{f}Tb^{3+}\ {}^{f}$	$(5.58 \pm 0.1) \times 10^8$	12.1 ± 0.5	-36.9 ± 1.6	6.96 ± 0.02
${}^{g}Tb^{3+}\ {}^{g}$	$(7.3 \pm 0.1) \times 10^8$	14.3 ± 0.4		7.305 ± 0.001
$UO_2(ox)F(H_2O)_2^-$	$(1.8 \pm 0.05) \times 10^4$	45.4 ± 3.8	-11.3 ± 0.5	

[a–c] Result for fitting data obtained for the sample with ${}^{a}[UO_2^{2+}] = 0.67$ m for $T < 304$ K at 11.7 T, ${}^{b}[UO_2^{2+}] = 0.67$ m at 18.8 T, and ${}^{c}[UO_2^{2+}] = 0.42$ m for $T < 304$ K at 11.7 T. [d] All data at 18.8 T and low-temperature data at 11.7 T together. [e] Reference 5. [f] Reference 12 recalculated to 8 coordination. [g] Reference 14. The errors are given as 2 SDs.

data above 304 K, we also obtained the same rate constants and activation parameters but with standard deviations that are 20% larger than when all data are used. The coordination numbers used were 5 for UO_2^{2+}(aq) and 8 for Tb^{3+}(aq).[14]

Bleuzen et al.[14] used ^{17}O-enriched nitromethane as an inner standard to determine the kinetic parameters for Tb^{3+}; these are therefore well-known. We checked the reliability of our data and experimental technique by comparing them with those of Bleuzen et al. We made a redetermination of hyperfine coupling constant (*A/h*) and the dynamics of the water exchange of the Tb^{3+} aquo ion both at 18.8 and 11.7 T from the temperature dependence of $\Delta\omega_{rTb^{3+}}$ using eq 4, where B is

$$\Delta\omega_{rTb^{3+}} = \frac{2\pi B g_L (g_L - 1) J(J+1)\mu_B}{3k_B T}\left(\frac{A}{h}\right) \qquad (4)$$

the static magnetic field, g_L the isotropic Landé factor (1.5 for Tb^{3+}), J the electron spin angular momentum quantum number (6 for Tb^{3+}), and μ_B the Bohr magneton.

Ab Initio Computational Details. All theoretical calculations were carried out using the Molcas-4 program package.[20] Scalar relativistic effects were described using the Douglas−Kroll transformation.[21,22] The size of the computational problem was reduced using the AIMP method,[23,24] determined for the ground state of neutral uranium. Geometry optimizations were done at the SCF level using gradient techniques, with symmetry constraints. The final energies for the various configurations were calculated at the MP2 level at the optimized SCF geometry. Additional details, including the basis set, are given in one of our previous communications.[25]

Results

NMR Investigations. The kinetic parameters for the exchange between UO_2^{2+}(aq) and Tb^{3+}(aq) and bulk water are given in Table 1. The values for the Tb^{3+}(aq) system differ somewhat from the results obtained by Cossy, Helm, and Merbach[12] and by Bleuzen et al.,[14] indicating that the precision in measurements of this type is larger than their accuracy.

The rate constant for the water exchange in UO_2^{2+} is rather precise, while the activation parameters are more uncertain. The activation parameters obtained at 11.7 T from two different samples are in good agreement. The data at 18.8 T are expected to be the more precise but differ slightly from those in the other two experimental series. The standard deviations, but not the absolute values, of the kinetic parameters for the water exchange in UO_2^{2+}(aq) are dependent on the weighting of the data. The result of fitting all the data together is $k_{ex}(298\text{ K}) = (1.30 \pm 0.05) \times 10^6$ s^{-1}, $\Delta H^{\ddagger} = 26._1 \pm 1._4$ kJ/mol, and $\Delta S^{\ddagger} = -40 \pm 5$ J/(mol K), where the uncertainty is twice the estimated standard deviations, when all data are assigned individual weights. As we used the same terbium solutions for the measurements with and without uranyl, the error in the rate of exchange of water in UO_2^{2+}(aq) is not affected by an error in the rate of water exchange in Tb^{3+}(aq).

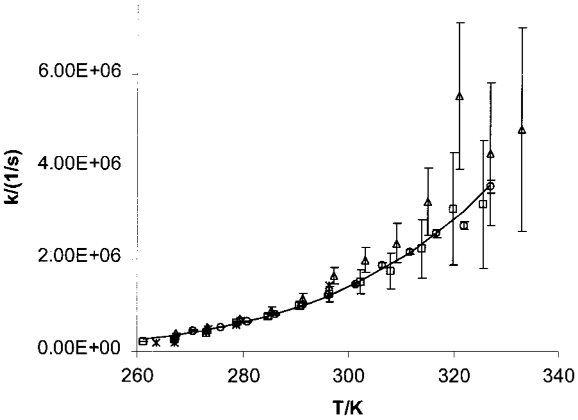

Figure 1. Temperature dependence of the exchange rate constant in acidic UO_2^{2+} solutions in the presence of Tb^{3+}. Data measured at 18.8 T in a solution containing $[UO_2^{2+}] = 0.67$ m, $[Tb^{3+}] = 0.55$ m, $[H^+] = 0.90$ m, and $[ClO_4^-] = 4.3$ m are shown as ○. The data for the solution measured at 11.7 T are shown as △. Data measured at 11.7 T in a solution containing $[UO_2^{2+}] = 0.42$ m, $[Tb^{3+}] = 0.53$ m, $[H^+] = 0.95$ m, and $[ClO_4^-] = 4.0$ m are shown as □. The full-drawn curve is the result of fitting all the data measured at 18.8 T and the low-temperature data at 11.7 T together. The experimental data measured in D_2O are shown as ∗.

The experimental data, together with the rate constants calculated from the "best" parameter set (full-drawn curve), are shown in Figure 1. The rate of exchange is the same in ordinary and heavy water, indicating that there is no measurable isotope effect on the water exchange; the situation is different for the proton-catalyzed exchange of fluoride and carbonate.[5,6]

Water Exchange in Ternary Dioxouranium(VI) Complexes. In a previous study[6] we have identified isomers of the ternary complexes $UO_2(ox)F_2(H_2O)^{2-}$ and $UO_2(ox)F(H_2O)_2^-$ by ^{19}F NMR spectroscopy and shown that the exchange between the isomers takes place through exchange between coordinated and solvent water. In this study we have determined the

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Table 2. Bond Distances and Total Water Binding Energies ΔU for Various UO_2^{2+} Aqua Ions[a]

chem species	$U-O_{calcd}$, Å	$U-H_2O$, Å	ΔU(MP2), kcal/mol
UO_2^{2+}	1.633		
D_{4h} $UO_2(H_2O)_4^{2+}$	1.668	2.52	−214.04
D_{5h}, perpendicular $UO_2(H_2O)_5^{2+}$	1.675	2.57	−243.83
D_{5h}, planar $UO_2(H_2O)_5^{2+}$ 25	1.664	2.59[b]	−221.82[c]
C_{5h}, planar, hydrogen bonded $UO_2(H_2O)_5^{2+}$	(1.675)[d]	(2.53)[d]	−74.03[d]
$UO_2(H_2O)_6^{2+}$	1.670	2.70	−241.44

[a] The theoretical calculations have been made using ab initio methods, SCF and MP2. The total energies of UO_2^{2+} and H_2O at the MP2 level are −621.366 319 and −76.319 242 au, respectively. The calculated bond distances in the uranyl unit are approximately 0.1 Å shorter than the experimental value 1.78 Å, while the equatorial bond distances are longer than the experimental value 2.42 Å. The reasons for this systematic difference are discussed by Wahlgren et al.[25] [b] An O basis without diffuse functions was used in this geometry optimization. [c] Estimated from the rotational barriers calculated in ref 25. [d] Approximate, not optimized geometry; see text.

activation parameters for the water exchange from the temperature dependence of the line widths of the ^{19}F NMR signals from the two isomers for $UO_2(ox)F(H_2O)_2^-$; for details compare ref 6, p 5374. These measurements were made in the temperature region where the *inter*molecular oxalate and fluoride exchange is negligible. The activation enthalpy and entropy from an Eyring plot are given in Table 1. The kinetic parameters at 25 °C are $k_{ex} = 1.8 \times 10^4$ s^{-1}, $\Delta H^{\ddagger} = 45._4 \pm 3._8$ kJ/mol, and $\Delta S^{\ddagger} = -11.3 \pm 0.5$ J/(K mol); i.e., the rate of water exchange in the ternary complex is 2 orders of magnitude slower than in the aqua ion. (The equilibrium diagram of the investigated solution, the isomers and their ^{19}F spectra measured at different temperature and the Eyring plot are shown in the Supporting Information.)

Quantum Chemical Calculations. The coordination geometry of different aqua ions, $UO_2(H_2O)_n^{2+}$, and the relative energy of the hypothetical intermediates $UO_2(H_2O)_4^{2+}$ and $UO_2(H_2O)_6^{2+}$ can only be studied using computational chemistry. The quantum chemical methods used, ab initio calculations at the SCF and MP2 levels, have been calibrated using $UO_2(H_2O)_5^{2+}$ and $UO_2(OH)_4^{2-}$, where the bond distances are well-known; cf. ref 25 for details.

The total energy, U_{tot}, for the reaction

$$UO_2^{2+}(g, 0\ K) + nH_2O(g, 0\ K) \rightarrow UO_2(H_2O)_n^{2+}(g, 0\ K) \quad n = 4, 5, 6 \quad (5)$$

and the energy difference $\Delta U(6)$ for the reaction

$$UO_2(H_2O)_{n-1}^{2+}(g, 0\ K) + H_2O(g, 0\ K) \rightarrow UO_2(H_2O)_n^{2+}(g, 0\ K) \quad n = 5, 6 \quad (6)$$

were calculated in order to obtain information on the thermodynamics of the uranium(VI)−water system, i.e. how the bonding energy of water varies with n, and thereby of the preferred coordination number. In addition, these data provide information on the thermodynamics of the bonding and dissociation of water in $UO_2(H_2O)_5^{2+}$ in the gas phase at 0 K. The calculations are computer intensive, and it was not feasible to include a second coordination sphere in the calculations or to calculate potential surfaces for the reactions.

$UO_2(H_2O)_5^{2+}$. A comparison between calculated and experimental bond distances is given in Table 2. These data are discussed in detail in a previous study.[25] We also calculated the energy differences for different orientations of the water molecules in $UO_2(H_2O)_5^{2+}$. In the most stable configuration four water molecules have their planes perpendicular to the coordination plane and one its plane coinciding with this. The configuration with all five water planes perpendicular to the coordination plane and the one with three water perpendicular and two in the plane is 0.36 and 1.30 kcal/mol, respectively, higher in energy. The configuration where the planes of all water molecules coincide with the coordination plane has the highest energy, 22.4 kcal/mol above the ground state; cf. Figure 2a,b. Hence, the rotational barrier for a water in the first coordination sphere is small. Internal hydrogen bonding, as depicted in Figure 2c, does not represent a stable configuration, and its geometry

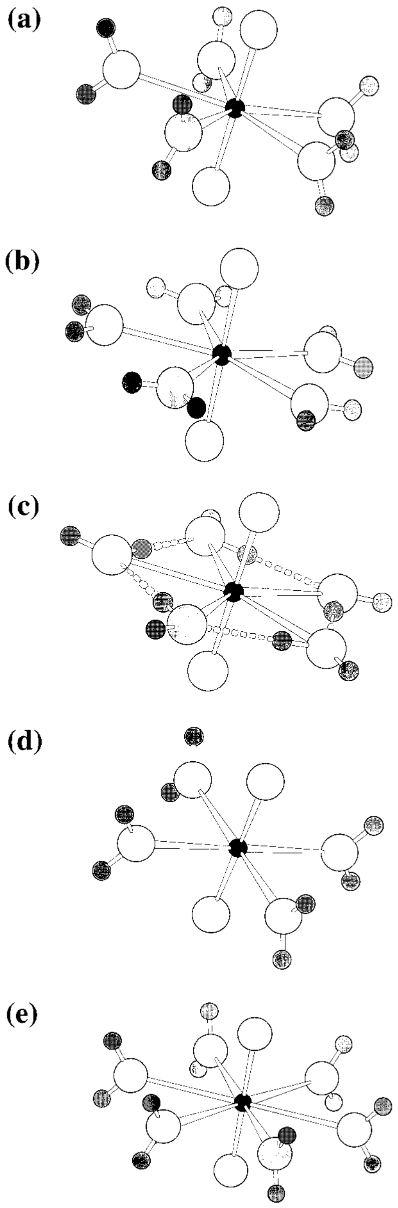

Figure 2. Different coordination geometries of UO_2^{2+}(aq) ions. (a) and (b) show two different orientations of the water molecules in $UO_2(H_2O)_5^{2+}$, where (b) is 22.0 kcal/mol higher in energy than (a). (c) shows the optimum coordination geometry for the formation of intramolecular hydrogen bonding in $UO_2(H_2O)_5^{2+}$; this has an energy that is approximately 140 kcal higher than the ground-state geometry. However, the configuration does not represent a stable geometry as discussed in the text. (d) and (e) show the coordination geometry of $UO_2(H_2O)_4^{2+}$ and $UO_2(H_2O)_6^{2+}$.

cannot be optimized; it converged in all cases to the planar D_{5h}. The energy at a very approximate geometry is about 140 kcal/mol higher than the ground-state configuration. These findings are in agreement with the available experimental structure data; cf. the Discussion.

$UO_2(H_2O)_6^{2+}$. The most stable configuration has all water molecules oriented perpendicular to the coordination plane, with a uranium−oxygen distance 0.13 Å longer than in the pentaaqua ion; cf. Figure 2d.

$UO_2(H_2O)_4^{2+}$. The most stable geometry is shown in Figure 2e, where the uranium−oxygen bond distances are 0.05 Å shorter than in the pentaaqua ion.

The values of ΔU given in Table 2 show a decrease in the bonding energy of 2.4 kcal/mol when one water is added to the pentaaqua complex, an indication of preferred five-coordination. Similar observations have been made by Siegbahn et al. in aqua complexes of Be^{2+}, Mg^{2+}, Ca^{2+}, and Zn^{2+}.[26]

For the reactions 7 and 8, which may be used to describe the thermodynamics of the D and A mechanisms, we obtain at the

$$UO_2(H_2O)_5^{2+}(g, 0\ K) \rightarrow UO_2(H_2O)_4^{2+}(g\ 0\ K) + H_2O(g, 0\ K) \quad (7)$$

$$UO_2(H_2O)_5^{2+}(g, 0\ K) + H_2O(g, 0\ K) \rightarrow UO_2(H_2O)_6^{2+}(g, 0\ K) \quad (8)$$

SCF and MP2 levels $\Delta U(7) = 25.3$ and 29.8 kcal/mol and $\Delta U(8) = 4.0$ and 2.4 kcal/mol, respectively; i.e., the associative reaction is thermodynamically favored.

However, the experimental water exchange refers to reactions between water in the first and second coordination spheres at 25 °C. As we could not include a second coordination sphere in the ab initio calculations, we used the results of Siegbahn et al.[26] They found that the change in ΔU for the addition of one water molecule from gas phase to the outer-sphere of the various aqua ions of Mg^{2+}, Ca^{2+}, and Zn^{2+} was nearly constant, with an average value of 20 kcal/mol. The binding energy to the second solvation shell can also be estimated by simple electrostatics. An estimate of ΔU for reaction 9 can be made by

$$UO_2(H_2O)_n^{2+}(g, 0\ K) + H_2O(g, 0\ K) \rightarrow UO_2(H_2O)_n^{2+}(H_2O)(g, 0\ K) \quad n = 4, 5 \quad (9)$$

assuming a dipole of 1 au for water located at a distance of 4.1 Å from the central ion in the second hydration shell (2.4 Å to the first shell, a water−water distance of 2.6 Å, and a U−O−O angle of 109°). This results in a binding energy estimate of 21 kcal/mol. Using the ab initio value 20 kcal/mol, we obtain

$$UO_2(H_2O)_5^{2+}(g, 0\ K) \rightarrow UO_2(H_2O)_4^{2+}(H_2O)\ (g, 0\ K) \quad \Delta U(10) = 9.8\ \text{kcal/mol (MP2)} \quad (10)$$

$$UO_2(H_2O)_5^{2+}(H_2O)(g, 0\ K) \rightarrow UO_2(H_2O)_6^{2+}(g, 0\ K) \quad \Delta U(11) = 22.4\ \text{kcal/mol (MP2)} \quad (11)$$

i.e. the dissociative reaction is now thermodynamically favored. However, both reactions are less favored than the interchange reactions for which $\Delta U = 0$.

The thermodynamics for reactions 10 and 11 in water solution and 298 K can be estimated from the heat capacities and heats of solution of the various reactants and products. These have the same charge and approximately the same size, indicating that the difference in their solvation energy is small. We also expect that the rotation and vibration modes of reactants and products are sufficiently similar to result in only a small difference in entropy and heat capacity between them. Hence, the thermodynamics of the gas-phase reactions at 0 K may be a reasonable estimate also of the thermodynamics in solution. The energy difference between the associative and dissociative pathways is small. In this context one may note that the solvent exchange in some nonaqueous UO_2^{2+} systems follows two parallel pathways, one solvent dependent and the other solvent independent.[2]

The hydration of UO_2^{2+} and PuO_2^{2+} has recently been studied by Spencer et al.[27] using DFT methods. The resulting coordination geometries for $UO_2(H_2O)_n^{2+}$, $n = 4-6$, are very similar to the results obtained here. It is interesting to note that Spencer et al. also find the same reversal in stability between the complexes with $n = 4$ and 6 when going from gas phase to solution as we observe. However, the model they used to describe the solution is totally different.

Discussion

Mechanistic Characteristics of Water Exchange Reactions. The experimental rate equation does not provide enough information to decide the mechanism for water exchange. There is no experimental evidence for the formation of intermediates. As it is not possible to calculate the reaction energy profile as in a number of studies by Rotzinger,[28] we have to rely on simplifications, which means that the mechanistic assignment is provisional. The activation entropy and the activation volume provide information about the intimate mechanism. The activation entropy is a good indicator only if it has a large positive (I_d) or negative value (I_a); the value is fairly small in this study. As we do not have the experimental tools to determine activation volumes, we must rely on other criteria as discussed in the following.

Structure Characteristics of the First and Second Coordination Spheres of Dioxouranium(VI) Complexes. UO_2^{2+} complexes with small unidentate ligands are predominantly five-coordinated, with all exchangeable ligands placed in, or close to, the plane through uranium and perpendicular to the linear UO_2 axis.[5] The only exceptions are the six coordination found in $UO_2F_2(s)$[29,30] and α-$UO_2(OH)_2$[31] and four coordination in $UO_2(OH)_4^{2-}$, both in the solid state[32] and in solution.[25,32,33] Six coordination is only known for chelating ligands with a short ligand bite, such as carbonate[31] and acetate.[31] Oxalate is a special case; in the tris(oxalato) complex, two oxalate ligands form chelates using both carboxylate groups while the third ligand forms a chelate using one carboxylate group, resulting in six coordination with two different sets of ligand bites.[34]

The coordination geometry of $UO_2(H_2O)_5^{2+}$ has been determined both in the solid state[34] using single-crystal X-ray diffraction and in solution using large-angle X-ray scattering[35] and EXAFS.[25] All methods indicate the same pentagonal

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bipyramid coordination geometry with the water molecules in, or very close to, the plane perpendicular to the linear UO_2 group. The strong preference for five coordination is also seen from the magnitude of the binding energy of water as obtained from the quantum chemical calculations; cf. Table 2. The orientation of the water molecules cannot be determined directly from most of the experimental structure data. However, the hydrogen bond scheme deduced from the single-crystal X-ray and neutron diffraction studies[29,36,37] indicates that their planes are tilted with respect to the coordination plane. Tilting is also found in the $UO_2(ox)_2(H_2O)^{2-}$ present in uranyl oxalate trihydrate.[38] The predominance of five coordination and the relative energies of the hypothetical intermediates $UO_2(H_2O)_4^{2+}$ and $UO_2(H_2O)_6^{2+}$ indicates that a dissociative (I_d) mechanism is more plausible than an associative (I_a) for the water exchange in UO_2^{2+}(aq).

The water exchange in UO_2^{2+}(aq) and UO_2(oxalate)$F(H_2O)_2^-$ takes place between the first and second coordination spheres. Hence, the preferred ground-state coordination geometry and the hydrogen bond interactions between the two coordination spheres may provide additional mechanistic indications. The second coordination spheres are very different in the two ions; in UO_2^{2+}(aq) the water protons in the first coordination sphere are hydrogen bond donors to water oxygen acceptors in the second coordination sphere, while in $UO_2(ox)F(H_2O)_2^-$ the oxalate and fluoride ligands are strong hydrogen bond acceptors. The importance of hydrogen bond interactions is illustrated in the crystal structure of $[(CH_3)_4N]_2[UO_2F_4(H_2O)]\cdot 2H_2O$,[39] where the coordinated water molecule (O(2)) has a very short bond distance, 2.11 ± 0.02 Å, to uranium; the distance O(2)−F(1) and its symmetry equivalent at $(-x, y, -z)$ is 2.72 Å, indicating the possible formation of a bent *intra*molecular hydrogen bond, O(2)−H- - -F(1), where the estimated H−F(1) distance is 2.1 Å; for notation cf. ref 39. As a result the plane of the water coincides with that of the coordination plane; i.e., we have a very different water orientation from that found in $UO_2(ox)_2(H_2O)$,[38] where two planes are perpendicular and the distance between uranium and water is 2.44 Å. Both inter- and intramolecular hydrogen bonding of a coordinated water might be expected to change its rate of exchange with bulk water, particularly as the rate of exchange of bonded fluoride is known to be slow.

Kinetic Data. There are three previous determinations of the kinetic parameters for the water exchange. Tomiyasu et al.[40] report $k_{ex} = (7.8 \pm 0.3) \times 10^5$ s^{-1}, $\Delta H^{\ddagger} = 41 \pm 2$ kJ/mol, and $\Delta S^{\ddagger} = 8 \pm 8$ J/mol K extrapolated to 25 °C from a mixed water/acetone solvent. Bardin et al. [41] have also measured the kinetics in mixed water−acetone media but report different kinetic parameters, which seem to be dependent on the magnetic field. The experimental data are not published, and it is therefore difficult to assess these results. Szabó et al.[5] deduced kinetic parameters for water exchange from ligand exchange data in the binary uranyl−fluoride system. They assumed an Eigen-Wilkins mechanism with the outer-sphere equilibrium constant estimated by the Fuoss equation and report $k_{ex} = 1.4 \times 10^6$ s^{-1}, $\Delta H^{\ddagger} = 37._7 \pm 2$ kJ/mol, and $\Delta S^{\ddagger} = -11._8 \pm 1._2$ J/(mol K), at 25 °C, where the uncertainties are equal to 2σ. There is an approximate linear (isokinetic) relationship between $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$, cf. Figure 3, indicating that the exchange reactions follow the same (I_d) mechanism. The activation parameters for the quenching of the photochemically excited state of UO_2^{2+}(aq), vide infra, are also close to this line.

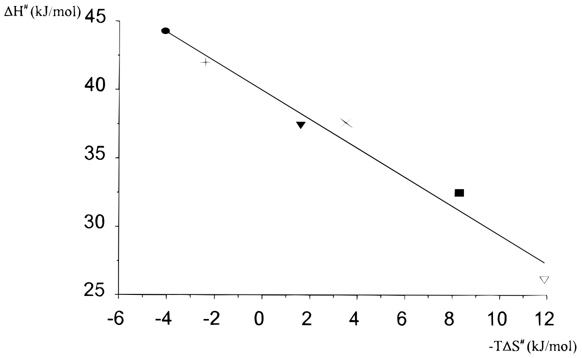

Figure 3. Isokinetic plot $\Delta H^{\ddagger}$ vs $-T\Delta S^{\ddagger}$ for different water exchange reactions and for quenching reactions of $^*UO_2^{2+}$ and $^*UO_2F^+$. The different symbols refer to the following data: Ikeda et al.,[40] +; Szabo et al.,[5] ×; Nagaishi et al.,[42] ▼ in pure H_2O, ■ in mixed H_2O/D_2O, $X_{H_2O} = 0.1$; Tomiyasu et al.,[43] ●; the present study, ▽.

The rate of water exchange in $UO_2(ox)F(H_2O)_2^-$ and $UO_2(ox)F_2(H_2O)^{2-}$ is about 2 orders of magnitude slower than in the aqua ion. It is only when the leaving water ligand returns to a different site that isomerization occurs; cf. Figure 6 in ref 6. The geometrical restrictions for an increase in coordination number in complexes such as $UO_2(ox)F(H_2O)_2^-$ containing a chelate are more severe than in the pentaaqua ion, which should favor a dissociative water exchange mechanism. The rates of exchange is not only determined by geometrical constraints, as indicated by the rate constants for water exchange in $UO_2(ac)_2(H_2O)$ and $UO_2(ox)_2(H_2O)^{2-}$, which are 6.7×10^5 s^{-1}, and 2.9×10^7 s^{-1}, respectively at 25 °C, estimated by assuming an Eigen−Wilkins mechanism.[5] The slow rate of water exchange in both $UO_2(ox)F(H_2O)_2^-$ and $UO_2(ox)F_2(H_2O)^{2-}$ may be due to hydrogen bond interactions as discussed above.

To conclude, the theoretical calculations indicate a strong preference for five coordination in the aqua complexes of dioxouranium(VI). They also allow an estimate of the thermodynamics of the dissociative and associative pathways, which shows that the dissociative pathway is preferred over the associative when it takes place between the first and second coordination spheres. However, the thermodynamics for both these reactions are less favored than that for interchange reactions for which $\Delta G = 0$. There is no experimental evidence for the formation of intermediates in the water exchange reactions, and they are therefore classified as interchange reactions. On the basis of theoretical estimates and the preferred five coordination of dioxouranium(VI) complexes, we suggest that a dissociative interchange mechanism is more plausible than an associative, because it results in smaller ligand−ligand repulsion in the transition state. The large variations in the lability of coordinated water in the complexes studied might be due to different hydrogen bond interactions between the first and second coordination spheres.

Implications for the Photochemical Quenching of Uranium(VI) Complexes in Water. Nagaishi et al.[42] studied the isotope and temperature effects of photochemical reactions of UO_2^{2+} in H_2O-D_2O mixtures and pointed out the large

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differences between the quenching of uranium(VI) and trivalent lanthanides and actinides. For the latter two the rate of quenching is nearly independent of temperature, but there is a strong H/D isotope effect. For uranium(VI) the rate of quenching is strongly temperature dependent, while the isotope effect is much smaller than for the trivalent ions. These facts indicate that the quenching of uranium(VI) is strongly dependent on collision mechanisms rather than vibration energy transfer from coordinated water, the established mechanism for quenching of the trivalent ions. This interpretation is supported by the close similarity of rate constants and activation parameters for quenching and water exchange, which fall on the same isokinetic plot; cf. Figure 3. The collision quenching is also supported by data from fluoride containing solutions. Tomiyasu et al.[43] determined kinetic parameters for the quenching of both photoexcited $^*UO_2^{2+}$ and $^*UO_2F^+$. The observed lifetimes are 1.7 and 207 μs, respectively. Their ratio is in fair agreement with the ratio 52 ± 15 between the observed rate constants for the exchange of water in UO_2^{2+} and for the exchange reaction $UO_2^{2+} + UO_2F^+ \leftrightarrow UO_2^{2+} + UO_2F^+$ studied by Szabó et al.,[5] indicating similar mechanisms.

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Supporting Information Available: Listings of primary ^{17}O NMR data as a function of temperature at two different magnetic fields, 11.7 and 18.8 T, temperature-dependent ^{19}F NMR spectra and structural isomers for $UO_2(ox)F(H_2O)_2^-$, an equilibrium fluoride distribution diagram as a function of pH, and the Eyring plot of the rate constants between the isomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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