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Rates and Mechanism of Fluoride and Water Exchange in $UO_2F_5^{3-}$ and $[UO_2F_4(H_2O)]^{2-}$ Studied by NMR Spectroscopy and Wave Function Based Methods

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The reaction mechanism for the exchange of fluoride in $UO_2F_5^{3-}$ and $UO_2F_4(H_2O)^{2-}$ has been investigated experimentally using ^{19}F NMR spectroscopy at –5 °C, by studying the line broadening of the free fluoride, $UO_2F_4^{2-}(aq)$ and $UO_2F_5^{3-}$, and theoretically using quantum chemical methods to calculate the activation energy for different pathways. The new experimental data allowed us to make a more detailed study of chemical equilibria and exchange mechanisms than in previous studies. From the integrals of the different individual peaks in the new NMR spectra, we obtained the stepwise stability constant $K_5 = 0.60 \pm 0.05$ M^{-1} for $UO_2F_5^{3-}$. The theoretical results indicate that the fluoride exchange pathway of lowest activation energy, 71 kJ/mol, in $UO_2F_5^{3-}$ is water assisted. The pure dissociative pathway has an activation energy of 75 kJ/mol, while the associative mechanism can be excluded as there is no stable $UO_2F_6^{4-}$ intermediate. The quantum chemical calculations have been made at the SCF/MP2 levels, using a conductor-like polarizable continuum model (CPCM) to describe the solvent. The effects of different model assumptions on the activation energy have been studied. The activation energy is not strongly dependent on the cavity size or on interactions between the complex and Na^+ counterions. However, the solvation of the complex and the leaving fluoride results in substantial changes in the activation energy. The mechanism for water exchange in $UO_2F_4(H_2O)^{2-}$ has also been studied. We could eliminate the associative mechanism, the dissociative mechanism had the lowest activation energy, 39 kJ/mol, while the interchange mechanism has an activation energy that is approximately 50 kJ/mol higher.

Introduction

In a previous paper[1] we have discussed the mechanism of water exchange in $[UO_2(H_2O)_5]^{2+}$ and $[UO_2(oxalate)_2(H_2O)]^{2-}$ by using information on the activation energy and the geometry along the reaction coordinate, obtained by quantum chemical methods. We tested various exchange pathways both in the gas phase and in the aqueous solvent described by a conductor-like polarizable continuum model (CPCM) using a shape-adapted cavity. We concluded that the water exchange in $[UO_2(H_2O)_5]^{2+}$ follows an interchange (I) mechanism, while the water exchange in $[UO_2(oxalate)_2(H_2O)]^{2-}$ is best described by an associative (A) mechanism. We also suggested that the rate and mechanism of water exchange might depend on the geometry of the first coordination sphere, in particular the uranium−ligand bond distance. In this study we have pursued these ideas and investigated the mechanism of water exchange in $[UO_2F_4(H_2O)]^{2-}$, where the first coordination sphere is more crowded than in the other two complexes because of the short, 2.26 Å, uranium−fluoride distances. From these results, we are able to predict the nature of the exchange mechanism and draw some more general conclusions on mechanisms for water exchange in uranyl(VI) complexes.

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We have also explored the dynamics of fluoride exchange reactions in the uranium(VI)−fluoride system both from the experimental and theoretical points of view. We have extended earlier ^{19}F NMR studies[2,3] on the equilibrium dynamics of the ligand exchange reactions in the uranium(VI)−fluoride system to cover a much larger fluoride concentration range and, by using a better NMR spectrometer and software, to obtain more precise information on the exchange dynamics/mechanisms for $UO_2F_4^{2-}$ and $UO_2F_5^{3-}$. This information is necessary for comparisons between experiment and theory. By combining theoretical findings on both the fluoride and water exchange mechanisms, we have proposed a reaction pathway for the fluoride exchange between $UO_2F_5^{3-}$ and $UO_2F_4(H_2O)^{2-}$. The only previous theoretical study of intimate exchange mechanisms involving negatively charged ligands seems to be a study by Rotzinger and Benoit[4] of the isomerization reaction

$$Co(NH)_3SCN^{2+} \rightleftharpoons Co(NH)_3NCS^{2+}$$

Experimental Part: NMR Methods and Results

NMR Measurements. The NMR spectra were recorded on a Bruker DMX500 spectrometer at 470.5 MHz in 5 mm tubes at −5 °C, using 5% D_2O to get a locked mode. The temperature was checked using the chemical shift of methanol and controlled as described previously.[5] The reference was an aqueous alkaline solution of 0.01 M NaF in 1 M $NaClO_4$ at 25 °C. The line widths were determined by fitting a Lorentzian curve to the experimental signal using the WIN NMR software.[6]

The total concentration of fluoride was varied between 0.2 and 1 M using NaF in an ionic medium with $[Na^+] = 1$ M. For each fluoride concentration, test solutions with different total concentration of uranium(VI) (5−100 mM) were investigated. All experiments were made at pH > 8, to avoid exchange with HF that will result in additional ^{19}F line broadening. The dominant uranium species in the fluoride concentration range investigated are $UO_2F_4^{2-}$ and $UO_2F_5^{3-}$, with $UO_2F_3^-$ present as a minor component at the lowest fluoride concentration. The formation of hydrolytic species is negligible at pH < 9.

Results. In one of our previous studies,[6] we used an older NMR instrument, which made it difficult to obtain a precise baseline correction for the $UO_2F_5^{3-}$ peak, mainly due to the "back-folded" high-intensity signal from the bulk fluoride. Hence, we could not use this peak to obtain kinetic information. The peak integral also turned out to be affected by large systematic errors, resulting in an overestimation of the equilibrium constant for the complex. Recent developments, e.g. digital filtering, made it possible to reduce these errors, even at large spectral windows.

From the integrals of the different individual peaks in the new NMR spectra, we obtained the equilibrium constant $K_5 = 0.60 \pm 0.05$ M^{-1} for the reaction

$$UO_2F_4(H_2O)^{2-} + F^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} UO_2F_5^{3-} \qquad (1)$$

This value is much smaller than that previously determined,[7] $K_5 = 3.0$ M^{-1}, for reasons given above. The new value of K_5 is approximately the same as that[8] for the formation of $[UO_2(OH)_5]^{3-}$.

The complex $UO_2F_5^{3-}$ gives one broad ^{19}F signal with a line width that is independent of the concentration of $UO_2F_4^{2-}$ and free fluoride (cf. Figure S1). This observation conclusively shows that the exchange does not take place in an associative mechanism involving free fluoride but rather via the dissociation of fluoride in the reverse reaction in eq 1.

The rate of dissociation of the fluoride is then

$$-d[UO_2F_5^{3-}]/dt = k_{-1}[UO_2F_5^{3-}] \qquad (2)$$

and from the line width of $UO_2F_5^{3-}$ we obtain the first-order rate constant[2]

$$k(\text{obs})_1 = \pi\Delta\upsilon(UO_2F_5^{3-}) = \text{rate}/[UO_2F_5^{3-}] = k_{-1} = (6.5 \pm 0.5) \times 10^3\ \text{s}^{-1} \qquad (3)$$

At higher total fluoride concentrations the fluoride exchange will depend on three components, $UO_2F_4(H_2O)^{2-}$, $UO_2F_5^{3-}$, and free fluoride. Our experiments show that the line width of the free fluoride signal is a linear function of $[UO_2F_4(H_2O)^{2-}]$.

$$k(\text{obs})_2 = \pi\Delta\upsilon(F^-) = c_1[UO_2F_4(H_2O)^{2-}] \qquad (4)$$

A linear regression of the data (Supporting Informaton, Figure S2) results in a zero intercept and a slope $c_1 = (3.65 \pm 0.10) \times 10^3$ M^{-1} s^{-1}. This value is close to that ($k_1 \approx 3.9 \times 10^3$ M^{-1} s^{-1}) calculated for the forward reaction in eq 1, using k_{-1} and K_5. This indicates that the line width of the free fluoride signal does not depend on additional exchange reactions but more important that the self-exchange[2]

$$UO_2F_4(H_2O)^{2-} + {}^*F^- \rightleftharpoons UO_2{}^*F_4(H_2O)^{2-} + F^- \qquad (5)$$

is not an elementary reaction. It involves as the first step the rate-determining formation of $UO_2F_5^{3-}$, as for reaction 1, followed by the faster fluoride dissociation and water coordination.

The rate constant k_1 is smaller than that published in our previous paper[2] $(8.50 \pm 0.10) \times 10^3$, which was based on a higher value of K_5 (3 M^{-1}). Moreover, the least-squares fitting in that study was more prone to errors than the direct determination used here.

The rate of ligand exchange has also been investigated using the line width of $UO_2F_4(H_2O)^{2-}$. By varying the total concentration of fluoride when keeping that of uranium

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[7] Ferri, D.; Salvatore, F.; Vasca, E.; Glaser, J.; Grenthe, I. *Acta Chem. Scand.* **1993**, *47*, 855.
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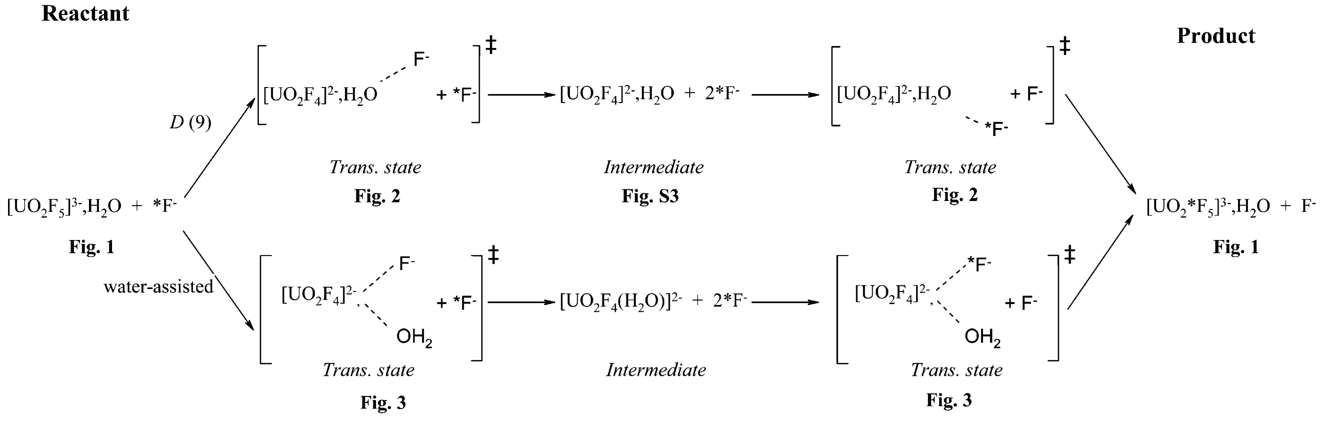
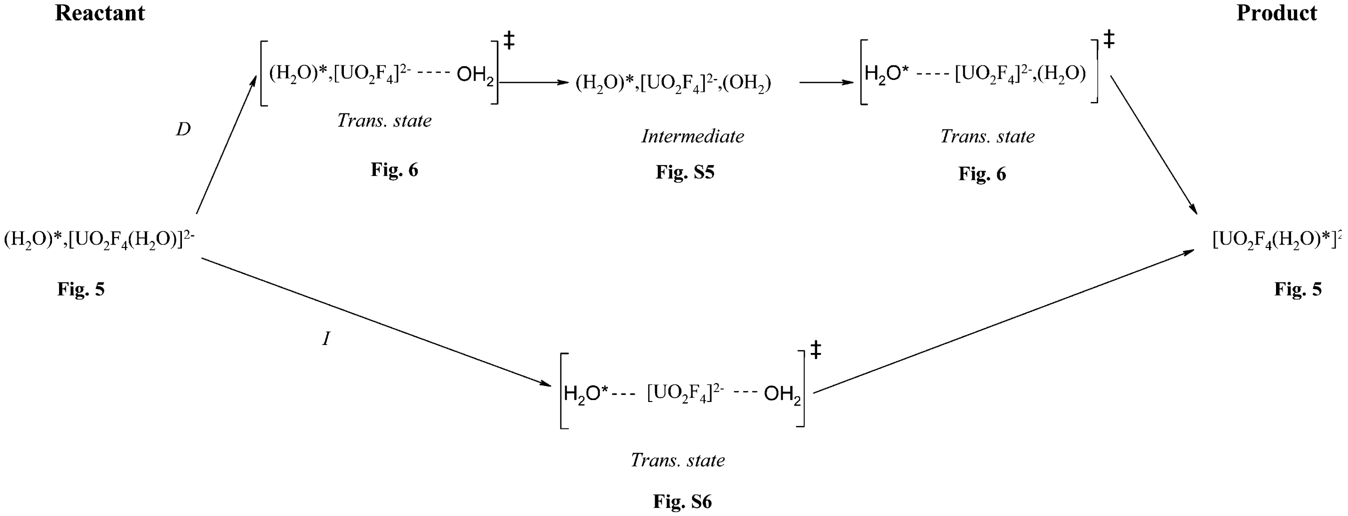
Scheme 1



Scheme 2



constant, we found that the line width of the complex was mainly determined by the concentration of the free fluoride. There was also an additional line broadening due to the concentration of $\mathrm{UO_2F_4(H_2O)^{2-}}$. The pseudo-first-order rate constant is thus the sum of two terms

$$k(\mathrm{obs})_3 = \pi\Delta\upsilon(\mathrm{UO_2F_4(H_2O)^{2-}}) = c_2[\mathrm{F^-}] + c_3[\mathrm{UO_2F_4\,(H_2O)^{2-}}] \quad (6)$$

where c_2 is equal to the previously determined rate constant $k_1 = (3.65 \pm 0.10) \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$ for the exchange between $\mathrm{UO_2F_4(H_2O)^{2-}}$ and free $\mathrm{F^-}$. From the function $k(\mathrm{obs})_4$ (eq 7) calculated from the known concentrations of $\mathrm{F^-}$ and $\mathrm{UO_2F_4(H_2O)^{2-}}$, we determined the second-order rate constant c_3 by linear regression and found $c_3 = (8.2 \pm 0.3) \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$. The available experimental information does not permit any conclusion about the intimate mechanism of the reaction that gives rise to the second term in eq 6.

$$k(\mathrm{obs})_4 = \pi\Delta\upsilon(\mathrm{UO_2F_4(H_2O)^{2-}}) - c_2[\mathrm{F^-}] = c_3[\mathrm{UO_2F_4\,(H_2O)^{2-}}] \quad (7)$$

It is not possible to measure the activation parameters for reaction 1 because the peaks for $\mathrm{UO_2F_4^{2-}}$ and $\mathrm{UO_2F_5^{3-}}$ merge and disappear into the baseline with an increase of temperature by 10 °C, resulting in a very large experimental error in the activation enthalpy. As $\mathrm{UO_2F_4(H_2O)^{2-}}$ is always present, even at the highest fluoride concentrations, the contribution of reaction 5 to the fluoride exchange cannot be eliminated.

An estimate of the activation parameters for the fluoride may be obtained from the data for ternary complexes given in ref 9, as mentioned in the Discussion. There is no experimental information available on the rate of exchange of water between $[\mathrm{UO_2F_4(H_2O)}]^{2-}$ and the water solvent, only on the fluoride exchange.

Quantum Chemical Calculations: Methods and Results. Model Reactions. The exchange between free and coordinated fluoride in $\mathrm{UO_2F_5^{3-}}$ was studied both in gas phase and in solvent. The reaction may follow dissociative (D), interchange (I), or associative (A) pathways,[10] with or without participation of a solvent molecule. We have explored all three possibilities including the water-assisted pathway using a single water molecule hydrogen-bonded in the second coordination sphere; cf. Scheme 1. The water exchange in the five-coordinated complex $\mathrm{UO_2F_4(H_2O)^{2-}}$, Scheme 2, could only be studied in the CPCM solvent

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[9] Szabó, Z.; Grenthe, I. *Inorg. Chem.* **1998**, *37*, 6214.

[10] Langford, C. H.; Gray, H. B. *Ligand Substitution Dynamics*; Benjamin: New York, 1965.

because it is not the ground-state configuration in the gas phase, as discussed in a previous study.[11] $[UO_2F_4(H_2O)]^{2-}\cdot H_2O$ was used as the reactant in the study of the water exchange mechanism. The entering water molecule is located in the second hydration sphere either in a cis- or trans-position to the coordinated water. The identification of the preferred mechanism for reaction 1 is based both on the geometry of the transition/ intermediate states and on the computed activation energy.

Computational Details. The calculations have been carried out both in the gas phase and using the CPCM solvent model,[12] at the Hartree−Fock level for the geometry optimizations, and at the MP2 level for energies, using Gaussian98.[13] The CPCM solvent model describes the solvent as a uniform dielectric continuum medium of permittivity $\epsilon_r = 80$ and uses a shape-adapted cavity, which is appropriate to estimate hydration effects on nonspherical systems, as we discussed previously in ref 11. The geometry of the complexes was optimized without symmetry constraints. The transition states were identified as explained in a previous study.[1] The quantum chemical methods used are described in more detail in our two previous communications[1,11] on uranium(VI) fluoride complexes.

The results of the theoretical calculations are presented in Tables 1−4 and Figures 1−6 and discussed below.For information we also report the activation volume $\Delta V^\ddagger$, estimated from the volume change of the CPCM cavity.

Fluoride Exchange Mechanisms in $UO_2F_5^{3-}$. (a) Associative and Interchange Mechanisms. The A mechanism requires the existence of a six-coordinated intermediate $UO_2F_6^{4-}$

$$UO_2F_5^{3-} + {}^*F^- \rightarrow UO_2{}^*F_6^{4-} \rightarrow UO_2{}^*F_5^{3-} + F^- \quad (8)$$

However, according to our calculations $UO_2F_6^{4-}$ is not a stable complex either in the gas phase or in the solvent. This is due to the strong electrostatic repulsion between the six fluoride ligands in the first coordination sphere. We can therefore rule out both the A and I mechanisms. This is in agreement with the experimental data where the rate of exchange was found to be independent of the fluoride concentration.

(b) Dissociative Mechanism. The D mechanism involves a four-coordinated intermediate $[UO_2F_4]^{2-}$. We explored this pathway starting from $[UO_2F_5]^{3-}\cdot H_2O$ with a hydrogen-bonded water in the second coordination sphere, cf. Figure 1, by stretching one of the U−F bonds.

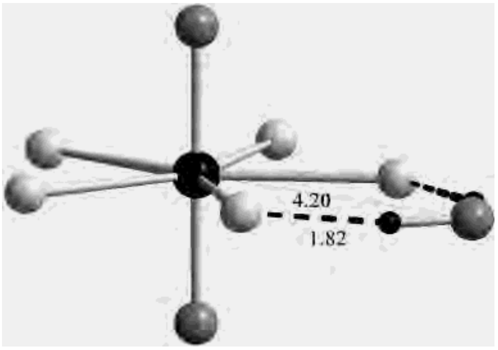

Figure 1. Uranium(VI) pentafluoride $[UO_2F_5]^{3-}\cdot H_2O$ reactant in the A, D, and I mechanisms in water (CPCM). The uranium atom and the hydrogen atoms are black; the fluoride atoms are light gray, and the oxygen atom is medium gray. The thin line denotes the distance between nonbonded atoms, and the dark dashed lines denote hydrogen-bond interactions. Distances are in Å.

$$[UO_2F_5]^{3-}\cdot H_2O \rightarrow \{[UO_2F_4\cdots F]^{3-}\cdot H_2O\}^\ddagger \rightarrow [UO_2F_4]^{2-}\cdot H_2O + F^- \quad (9)$$

where $\{[UO_2F_4\cdots F]^{3-}\cdot H_2O\}^\ddagger$ is a transition state with a square bipyramid geometry. It has one imaginary frequency that corresponds to the translation of the leaving fluoride. The spectator ligands have square-planar geometry in the equatorial plane with bond distances close to those in the ground state, while the leaving fluoride is hydrogen bonded to the outer-sphere water molecule at a distance from uranium of 3.19 and 3.56 Å, in the gas phase and the solvent, respectively; cf. Table 1 and Figure 2. The calculated activation energy $\Delta U^\ddagger$ is 28 kJ/mol in gas phase and 75 kJ/mol in the solvent. We have repeated the calculations in a model without hydrogen-bonded water in the second coordination sphere,

$$[UO_2F_5]^{3-} \rightarrow \{[UO_2F_4\cdots F]^{3-}\}^\ddagger \rightarrow [UO_2F_4]^{2-} + F^- \quad (10)$$

The distance to the leaving fluoride is in this case longer (3.80 Å; cf. Table 1 and Figure S4 in the Supporting Information) and the activation energy 18 kJ/mol higher than for eq 9; cf. Table 2.

(c) Water-Assisted Fluoride Exchange Mechanisms. From the experimental NMR data it is not possible to draw any conclusions about possible water participation in the dissociation of fluoride. We have therefore considered this possibility for associative and interchange mechanisms starting from $[UO_2F_5]^{3-}\cdot H_2O$. It was not possible to identify a six-coordinated intermediate $[UO_2F_5(H_2O)]^{3-}$, presumably as a result of the very crowded first coordination sphere due to the short U−F distances; this excludes a solvent-assisted associative exchange mechanism. However, an interchange pathway was identified, with the transition state $\{[UO_2F_4\cdots F\cdots(H_2O)]^{3-}\}^\ddagger$, shown in Figure 3; the entering water molecule ($U{-}OH_2 = 3.09$ Å) and the leaving fluoride ($U{-}F = 3.20$ Å) are located in a cis-position above and below the equatorial plane, with an angle O−U−F of 47°. Because of the long U−F distance the mechanism is best

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(12) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995.

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Table 1. Calculated Bond Distances for the Species Participating in the Exchange Reaction between $UO_2F_5^{3-}$ and Free Fluoride[a]

chem species	sym	Figure No.	method	U−F (Å)	$U-OH_2$ (Å)
$[UO_2F_5]^{3-}\cdot H_2O$	C_{2v}		SCF gas phase	2.32, 2.32, 2.32, 2.39, 2.39	4.25
	C_{2v}	1	SCF + CPCM	2.29, 2.29, 2.29, 2.31, 2.31	4.20
$\{[UO_2F_4\cdots F]^{3-}\cdot H_2O\}^{\ddagger}$ (D)	C_1		SCF gas phase	2.26, 2.29, 2.29, 2.30, 3.19	4.50
	C_1	2	SCF + CPCM	2.23, 2.24, 2.24, 2.25, 3.56	4.55
$[UO_2F_4]^{2-}\cdot H_2O)\cdot F^-$	C_1	S3	SCF + CPCM	2.23, 2.23, 2.24, 2.24, 3.94	4.62
$\{[UO_2F_4\cdots F\cdots H_2O]^{3-}\}^{\ddagger}$ (I)	C_1	3	SCF + CPCM	2.25, 2.26, 2.26, 2.26, 3.20	3.09
$UO_2F_5^{3-}$	D_{5h}		SCF gas phase	2.35 × 5	
	D_{5h}		SCF + CPCM	2.29 × 5	
$\{UO_2F_4\cdots F^{3-}\}^{\ddagger}$ (D)	C_{2v}		SCF gas phase	2.26, 2.26, 2.31, 2.31, 3.26	
	C_1	S4	SCF + CPCM	2.23, 2.23, 2.24, 2.243.80	
$UO_2F_4^{2-} + F^-$	D_{4h}		SCF gas phase	2.249 × 4, ∞	
	D_{4h}		SCF + CPCM	2.232 × 4	
$[UO_2F_5]^{3-}\cdot 2H_2O$	C_{2v}		SCF + CPCM	2.28, 2.28, 2.29, 2.29, 2.34	4.44, 4.44
$\{[UO_2F_4\cdots F]^{3-}\cdot 2H_2O\}^{\ddagger}$ (D)	C_1	S8	SCF + CPCM	2.23, 2.24, 2.25, 2.25, 3.50	4.12, 5.70

[a] All structures were optimized at the Hartree−Fock level in the gas phase and in the solvent (CPCM model).

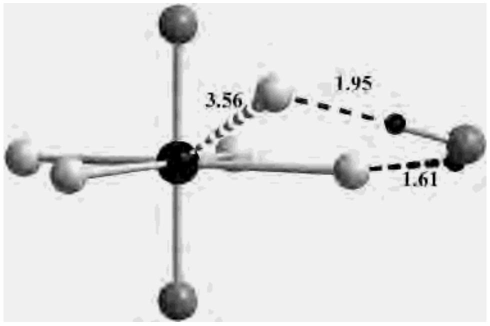

Figure 2. Dissociative transition state $\{[UO_2F_4\cdots F]^{3-}\cdot H_2O\}^{\ddagger}$ with a water molecule in the second hydration sphere optimized in solvent (CPCM). The uranium atom and the hydrogen atoms are black; the fluoride atoms are light gray, and the oxygen atom is medium gray. The dark dashed lines denote hydrogen-bond interactions, and the light dashed bond denotes the distance to the leaving fluoride atom. Distances are in Å.

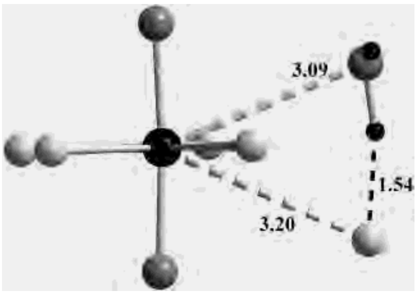

Figure 3. Interchange transition state $[UO_2F_4\cdots F\cdot\cdot H_2O]^{3-}$ in solvent. The uranium atom and the hydrogen atoms are black; the fluoride atoms are light gray, and the oxygen atom is medium gray. The dark dashed lines denote hydrogen-bond interactions, and the light dashed bonds, the distances to the exchanging ligands. Distances are in Å.

described as a dissociative interchange, with an activation energy $\Delta U^{\ddagger}$ equal to 71 kJ/mol. The small difference between this value and the one obtained for the pure D pathway, 75 kJ/mol, cf. Table 2, does not allow us to distinguish between the D and I_d mechanisms on the basis of the theoretical results. The key point is the observation that both mechanisms have a dissociative character, presumably as a result of the shorter U(VI)−ligand bonds in the fluoride complexes. Despite the somewhat lower activation energy for the water-assisted reaction, we prefer the D mechanism for the fluoride exchange because it results in the formation of the same intermediate as the one identified in the water exchange reaction for $UO_2F_4(H_2O)^{2-}$; vide infra.

Water Exchange in $[UO_2F_4(H_2O)]^{2-}$. The water exchange refers to the reaction

$$[UO_2F_4(H_2O)]^{2-}(aq) + H_2O^* \rightleftharpoons [UO_2F_4(H_2O^*)]^{2-}(aq) + H_2O \quad (11)$$

for which there are no experimental data available, and we therefore had to rely on quantum chemical methods to explore the D, I, and A mechanisms as outlined in Scheme 2. We used $[UO_2F_4(H_2O)]^{2-}\cdot H_2O$ as reactant with a water in the second coordination sphere, hydrogen bonded to one of the fluoride atoms, either in a cis- (cf. Figure 4) or in a trans-position (cf. Figure 5).

We were not able to identify a transition state or stable intermediate for the cis-exchange reactions. The six-coordinated intermediate *trans*-$[UO_2F_4(H_2O)_2]^{2-}$ is not a stable species, which eliminates the associative mechanism. The feasability of a D mechanism was shown by the transition state $\{$*trans*-$[UO_2F_4\cdots(H_2O)]^{2-}\cdot H_2O\}^{\ddagger}$ and the intermediate *trans*-$[UO_2F_4]^{2-}\cdot 2H_2O$; cf. Figure 6 and Figure S5 in the Supporting Information. The spectator ligands are in both cases located in the plane perpendicular to the "yl"-axis, at the same distance as in the reactant. The leaving water molecule is at a distance of 3.50 Å from uranium; the activation energy is 39 kJ/mol. The *trans*-$[UO_2F_4]^{2-}\cdot 2H_2O$ intermediate has a square bipyramid geometry. The energy barrier between the intermediate and the transition state is $\Delta U_I^{\ddagger} = 22.3$ kJ/mol.

We also identified a transition state for the interchange mechanism, where the long $U-OH_2$ distance, 3.30 Å, indicates that it is of I_d-type; cf. Figure S6. The activation energy is about 50 kJ/mol, higher than that for the pure D mechanism, indicating that the latter is the preferred pathway. To conclude, the water exchange mechanism in $UO_2F_4(H_2O)^{2-}$ is dissociative.

The simplified dissociative model without a second coordination sphere yielded a shorter $U-OH_2$ distance (3.25 Å; cf. Table 3) in the transition state (cf. Figure S7 in the Supporting Information) and a lower activation barrier (26 kJ/mol; cf. Table 4).

Discussion

Experimental Conclusions. The following discussion is based both on experimental findings and quantum chemical

Table 2. Relative Energy in kJ/mol for the Formation of Transition State Species (TS) and Intermediate in the Gas Phase and Solvent for the Fluoride Exchange in $UO_2F_5^{3-}$

		gas phase		solvent		
chem species	class	ΔU(SCF) (kJ/mol)	ΔU(MP2) (kJ/mol)	ΔU(SCF) (kJ/mol)	ΔU(MP2) (kJ/mol)	ΔV (cm^3/ mol)
$[UO_2F_5]^{3-}\cdot H_2O$	reactant	0.00	0.0	0.0	0.0	0.0
$\{[UO_2F_4\cdots F]^{3-}\cdot H_2O\}^{\ddagger}$	D-TS	22.9	27.7	66.9	74.9	4.0
$[UO_2F_4]^{2-}\cdot H_2O\cdot F^-$	D-intermed			61.7	69.2	5.1
$\{[UO_2F_4\cdots F\cdots H_2O]^{3-}\}^{\ddagger}$	I-TS			72.9	70.5	1.0
$UO_2F_5^{3-}$	reactant	0.0	0.0	0.0	0.0	0.0
$\{UO_2F_4\cdots F^{3-}\}^{\ddagger}$	D-TS	34.9	43.1	81.8	93.1	5.6
$UO_2F_4^{2-} + F^-$	D-intermed	−555.0	−542.8	16.2	41.1	2.3
$[UO_2F_5]^{3-}\cdot 2H_2O$	reactant			0.0	0.0	0.0
$\{[UO_2F_4\cdots F]^{3-}\cdot 2H_2O\}^{\ddagger}$	D-TS			64.2	73.1	4.0

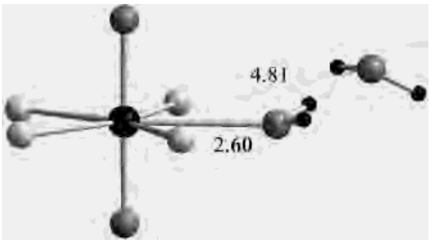

Figure 4. Perspective view of the reactant *cis*-$[UO_2F_4\cdot H_2O]^{2-}\cdot H_2O$ in the D mechanism in solvent. The uranium atom and the hydrogen atoms are black; the fluoride atoms are light gray, and the oxygen atom is medium gray. The thin line denotes the distance to the water in the second coordination sphere. Distances are in Å.

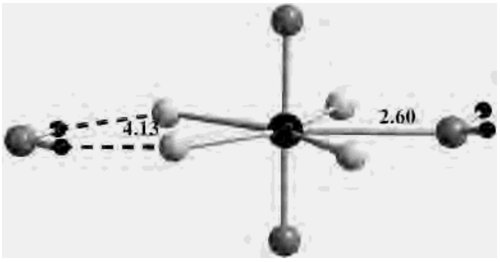

Figure 5. Perspective view of the reactant *trans*-$[UO_2F_4\cdot H_2O]^{2-}\cdot H_2O$ in the D mechanism in solvent. The uranium atom and the hydrogen atoms are black; the fluoride atoms are light gray, and the oxygen atom is medium gray. The thin line denotes the distance to the water in the second coordination sphere, and the dark dashed lines denote hydrogen-bond interactions. Distances are in Å.

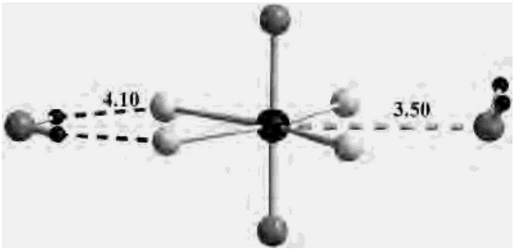

Figure 6. Perspective view of the D transition state $\{$*trans*-$[UO_2F_4\cdots H_2O]^{2-}\cdot H_2O\}^{\ddagger}$ in solvent. The uranium atom and the hydrogen atoms are black; the fluoride atoms are light gray, and the oxygen atom is medium gray. The thin lines denote the distance to the water in the second coordination sphere. The dark dashed lines denote hydrogen-bond interactions, and the light dashed line denotes the distance to the leaving water molecule. Distances are in Å.

calculations. Harada et al.[3] calculated the equilibrium constant $K_5 = 1.1$ M^{-1} at 0 °C. The difference from our value measured at −5 °C cannot be explained by the temperature difference. We believe that our value is more precise because it is calculated from the peak integrals of $UO_2F_4^{2-}$ and $UO_2F_5^{3-}$, while Harada's value is based on a nonlinear fitting using the peak integrals of the coordinated and free fluoride and the equilibrium constant for the formation of $UO_2F_4^{2-}$ determined at 25 °C. The intensity of the signals used in their calculation differ very much; hence, a small error in the integration could result a large error for K_5.

Harada et al.[3] suggested an associative or associative interchange mechanism for the fluoride exchange reaction between $UO_2F_5^{3-}$ and free fluoride (eq 12), based on the activation parameters and the results of exchange reactions studied under laser irradiation.

We do not agree with this interpretation; using the rate constants of Harada et al.,[3] we find that the contribution of this reaction to the observed rate of exchange is at most 1%. The experimental error in the determination of k_{obs} is much larger than this; hence, we suspect that the reported rate constant is an artifact arising from an erroneous parameter fitting.

$$UO_2F_5^{\ 3-} + {}^*F^- \rightleftharpoons UO_2{}^*F_5^{\ 3-} + F^- \tag{12}$$

Accuracy of the Theoretical Approach. The exchange of F^- results in a change in charge between reactants, transition states, and products; we will therefore discuss the accuracy of quantum chemical approaches in this particular case by exploring some of the simplifications in the models used to estimate activation energies.

The first point of concern is the influence of the interaction between the negatively charged complexes and the counterion, Na^+, which is present in high concentration in the NMR samples. The counterions are presumably located outside the second coordination shell, at a long distance to the coordinated fluoride. We have estimated the counterions effect by using a simple model where two sodium atoms are directly bonded to the fluoride ligands at about 2.10 Å. We found only a marginal change in the U−F distances and in the dissociation energy, 5 kJ/mol, for the reaction

$$[UO_2F_5]^{3-}\cdot 2Na^+ \rightleftharpoons [UO_2F_4]^{2-}\cdot 2Na^+ + F^- \tag{13}$$

It is reasonable to assume a similar small counterion effect also on the transition state, suggesting that counterions have a negligible influence on the activation energy.

The solvation of the leaving fluoride results in a decrease of the activation energy, from 93 to 75 kJ/mol for eqs 10 and 9, respectively. The activation energy is somewhat smaller, 73 kJ/mol, if we add a second hydrogen bonded water molecule to the leaving fluoride; cf. Figure S8 in the

Table 3. Calculated Bond Distances for the Species Participating in the Water Exchange Reaction in $[UO_2F_4(H_2O)]^{2-}$ [a]

chem species	sym	Figure No.	method	U−F (Å)	U−O (Å)
trans-$[UO_2F_4(H_2O)]^{2-}\cdot H_2O$	C_{2v}	5	SCF + CPCM	2.26, 2.26, 2.27, 2.27	2.60, 4.13
{*trans*-$[UO_2F_4\cdots H_2O)]^{2-}\cdot H_2O\}^{\ddagger}$ (D)	C_1	6	SCF + CPCM	2.23, 2.23, 2.25, 2.25	3.50, 4.10
trans-$[UO_2F_4]^{2-}\cdot 2H_2O$ (D)	C_1	S5	SCF + CPCM	4 × 2.24	4.01
{*trans*-$[UO_2F_4\cdots 2H_2O]^{2-}\}^{\ddagger}$ (I)	C_2	S6	SCF + CPCM	4 × 2.26	3.30
$[UO_2F_4(H_2O)]^{2-}$	C_{2v}		SCF + CPCM	2.26, 2.26, 2.27, 2.27	2.61
$\{[UO_2F_4\cdots H_2O]^{2-}\}^{\ddagger}$ (D)	C_s	S7	SCF + CPCM	2.23, 2.23, 2.25, 2.25	3.25
$[UO_2F_4]^{2-}\cdot H_2O$	C_{2v}		SCF + CPCM	2.22, 2.22, 2.25, 2.25	3.99

[a] All structures were optimized at the Hartree−Fock level in the solvent (CPCM model).

Table 4. Relative Energy in kJ/mol for the Formation of Transition State Species and Intermediate in the Gas Phase and Solvent for the Water Exchange in $[UO_2F_4(H_2O)]^{2-}$

chem species	class	ΔU(SCF) (kJ/mol)	ΔU(MP2) (kJ/mol)	ΔV (cm^3/ mol)
trans-$[UO_2F_4\cdot H_2O]^{2-}\cdot H_2O$	reactant	0.0	0.0	0.0
{*trans*-$[UO_2F_4\cdots H_2O]^{2-}\cdot H_2O\}^{\ddagger}$	D	27.6	39.2	4.7
trans-$[UO_2F_4]^{2-}\cdot 2H_2O$	D-intermed	1.3	16.9	4.0
{*trans*-$[UO_2F_4\cdots 2H_2O]^{2-}\}^{\ddagger}$	I	50.8	49.5	0.5
$[UO_2F_4\cdot H_2O]^{2-}$	reactant	0.0	0.0	0.0
$\{[UO_2F_4\cdots H_2O]^{2-}\}^{\ddagger}$	D	27.6	26.1	1.8
$[UO_2F_4]^{2-}\cdot H_2O$	D-intermed	1.9	12.4	3.4

Supporting Information. It is obviously important to consider solvation when comparing experimental activation enthalpies and calculated activation energies. However, a more complete hydration model accounting for both of the solvation of the leaving and the coordinated ligands would require a large number of explicitly treated water molecules to be included in the calculations.

There may also be some shortcomings in the CPCM model itself; the value for the radius of the metal ion used to build up the cavity around the solute is usually optimized to reproduce the experimental hydration energy. As no data are available for the uranyl ion, we have varied the radius of uranium and calculated the resulting change in energy. The effect turned out to be less than 2 kJ/mol for a 5% variation in the ionic radius, suggesting that it is not important for the accuracy of the activation energy.

In previous studies,[1,11] we have tested the CPCM model on charged ions, by comparing the energy with that obtained using a mixed model with a discrete second hydration shell. The results indicate that the CPCM model describes solute−solvent interactions reasonably well when the total charge of the species is constant. When there is a change of charge, the model appears less precise as indicated by the computed energy changes for the following stepwise equilibria

$$[UO_2F_n(H_2O)_{5-n}]^{2-n} + H_2O \rightleftharpoons [UO_2F_{n-1}(H_2O)_{5-n+1}]^{2-n+1} + F^- \quad n = 1-5 \quad (14)$$

that are different from the experimental Gibbs energies of reaction taken from ref 14; cf. Table S1. In the fluoride exchange reactions there is an extensive delocalization of charge between the ground and transition states that may contribute to this problem.

Rotzinger and Benoit[4] reported good agreement of the calculated activation energy with experimental data for the isomerization of the positively charged thiocyanatopentaaminecobalt(III) ion in water using a self-consistent reaction field model for geometry and PCM model for the energy. However, they only present barriers calculated at the SCF level, arguing that since the SCF results agreed well with experiment it was not necessary to use correlated methods. They did investigate the effect of correlation on the computed geometries, but it would have been interesting also to see the corresponding effects on the computed barriers. We have found in the present study that the contribution of correlation to the activation barrier barriers is of the order of 10 kJ/mol (see Tables 2 and 4), which is significant but not large.

Experimental and Theoretical Study of the Activation Parameters for Fluoride Exchange Reactions. There are no experimental activation parameters for the fluoride dissociation from $UO_2F_5^{3-}$; the only experimental activation enthalpies refer to the *inter*molecular exchange[9] reactions, e.g.

$$UO_2LF_3 + {}^*F^- \rightleftharpoons UO_2L^*F_3 + F^- \quad (15)$$

where L = CO_3^{2-}, picolinate, 4-nitropicolinate, 4-(3-pentyl)-picolinate, or oxalate (charges have been omitted for simplicity). All have nearly the same value, $\Delta H^{\ddagger} = 59 \pm 4$ kJ/mol, close to the calculated activation energy for the water-assisted pathway in $UO_2F_5^{3-}$, 70 kJ/mol. This might indicate similar exchange mechanisms in the UO_2LF_3 complexes and in $UO_2F_5^{3-}$. To corroborate this we made a theoretical investigation of the exchange (15) for the oxalate system but without taking second sphere solvent molecules into account. The preliminary results give an activation energy in the CPCM solvent of 138 kJ/mol, to be compared with 93 kJ/mol for the exchange in $UO_2F_5^{3-}$ using the same solvation model. By including explicit water molecules, we thus expect the oxalate value to decrease with about 20 kJ/mol, but it will still be about a factor of 2 larger than the experimental value. Our conclusion is that also the activation energy for the fluoride exchange in $UO_2F_5^{3-}$ is overestimated by approximately a factor of 2. However, this should be a systematic error that does not affect the identification of the reaction pathway with lowest activation energy.

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(14) Grenthe, I.; Fuger, J.; Konings, R. J. M.; Lemire, R. J.; Muller, A. B.; Nguyen-Trung, C.; Wanner, H. *Chemical Thermodynamics of Uranium*; North-Holland: Amsterdam, 1992.

Water Exchange in $UO_2F_4(H_2O)^{2-}$. The dissociative pathway has by far the lowest activation energy, and the corresponding intermediate $[UO_2F_4]^{2-}$ is identical with the one formed when a fluoride dissociates from $UO_2F_5^{3-}$ along a D pathway. The activation energy $\Delta U^{\ddagger}$ is 39 kJ/mol, close to the value of the values found for the water exchange in $UO_2(H_2O)_5^{2+}$ and $UO_2(oxalate)_2(H_2O)^{2-}$.

Intimate Mechanism for the Fluoride Exchange in $UO_2F_5^{3-}$ and $UO_2F_4(H_2O)^{2-}$. In a previous paper[2] we have discussed the intimate mechanism for exchange reactions of the type

$$UO_2F_p(H_2O)_{5-p}{}^{2-p} + F^- \rightleftharpoons UO_2F_{p+1}(H_2O)_{4-p}{}^{1-p} \quad p = 3, 4 \tag{16}$$

in terms of an Eigen−Wilkins mechanism. However, the experimental rate laws do not provide any information on the timing of the water bond breaking and fluoride bond formation. The theoretical data discussed above indicate that the water bond breaking takes place before fluoride bond formation in the forward direction of reaction 1, while uranium−fluoride bond breaking takes place before water bond formation for the reverse reaction.

Water Exchange in Uranyl(VI) Complexes. We have studied the water exchanges in $[UO_2(H_2O)_5]^{2+}$ and $[UO_2(ox)_2(H_2O)]^{2-}$ previously and suggested that they follow the A or I pathway, while the water exchange in $[UO_2F_4(H_2O)]^{2-}$ follows a D mechanism. The observed changes in the mechanism may be explained by the different geometry of the first coordination sphere. For geometrical reasons we expect the associative pathway to be less favored the shorter the bond distance between uranium and the spectator ligands is. In the two systems investigated previously this distance is around 2.40 Å, as compared to 2.25 Å in the fluoride system. We have previously studied the rate and mechanism of ligand exchange reactions including the exchange of water[5] in $[UO_2(oxalate)F_2(H_2O)]^{2-}$, where it is approximately 2 orders of magnitude smaller than in the aqua ion. In view of the findings discussed previously, we may speculate that this is a result of a change of exchange mechanism; there is no room for an entering water molecule to form an A/I transition state in the crowded $[UO_2(oxalate)F_2(H_2O)]^{2-}$ complex. Hence, the water exchange follows a D mechanism with a larger activation energy and slower rate of exchange.

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Supporting Information Available: Fluoride NMR spectra for $UO_2F_4^{2-}$(aq) and $UO_2F_5^{3-}$ (Figure S1), a plot of the pseudo-first-order rate constants calculated from the line width of the free fluoride signal against the equilibrium concentration of $UO_2F_4^{2-}$ (Figure S2), all the structures not presented in the text (Figures S3−S8), energy change for the stepwise formation of $[UO_2F_n(H_2O)_{5-n}]^{2-n}$ (Table S1), and all coordinates of the computed structures (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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