2036 *Inorg. Chem.* **1996,** *35,* 2036−2044

Kinetics of Ligand Exchange Reactions for Uranyl(2+) Fluoride Complexes in Aqueous Solution

Zoltán Szabó,*,† Julius Glaser, and Ingmar Grenthe*

Inorganic Chemistry, Department of Chemistry, Royal Institute of Technology (KTH),
S-100 44 Stockholm, Sweden

Received August 29, 1995⊗

Rates and mechanisms of fluoride exchange reactions between various uranyl fluoro complexes $\{UO_2(H_2O)_{5-n}F_n^{2-n}\}$, and HF/F$^-$ have been studied in aqueous solution using ^{19}F and ^{17}O NMR line broadening technique. A group of 15 different exchange pathways has been identified, and their rate laws and rate constants have been determined. All reactions are first order with regard to the uranyl complex and second order overall. Two pathways dominate: fluoride exchange between two uranyl complexes, presumably through the formation of a fluoride bridging intermediate/transition state, e.g., $UO_2F^+ + UO_2{*}F_2 \rightleftharpoons UO_2F{*}F + UO_2F^+$ ($k_{1,2}$), and fluoride exchange between a uranyl complex and F$^-$/HF, e.g., $UO_2F^+ + H{*}F \rightleftharpoons UO_2{*}F^+ + HF$ ($k_{1,HF}$). The exchange between UO_2^{2+} and UO_2F^+ takes place mainly according to $UO_2^{2+} + HF \rightleftharpoons UO_2F^+ + H^+$ (forward, $k'_{0,HF}$; reverse, $k_{1,HF}$). Most of these reactions have rate constants, $k_{m,n} \approx 5 \times 10^4$ M^{-1} s^{-1}, at −5 °C. The exchange reactions seem to follow the Eigen−Wilkins mechanism, where the rate determining step is a ligand promoted dissociation of coordinated water. The exchanges involving $UO_2F_n^{2-n}$, $n = 4$ and 5, are much faster than the others, indicating mechanistic differences. The exchange rate was approximately 3 times faster for reactions involving DF than for HF. The activation parameters have been determined for two reaction pathways.

Introduction

The linear dioxoactinoid(VI) ions, e.g., UO_2^{2+}, have all their exchangeable ligands in a plane perpendicular to the linear axis. The "-yl" oxygens are substitution inert,[1] except in the case when the ion is excited by UV light.[2−4] This unusual coordination geometry indicates that the pathway for ligand substitution reactions might be located in, or close to, this plane, a very different situation from those encountered in most other coordination geometries. There are comparatively few investigations of the mechanisms for ligand substitutions in uranium(VI) complexes. Most studies have been made in nonaqueous systems, and these have been reviewed by Lincoln,[5] and Tomiyasu and Fukutomi.[6] Ligand exchange reactions in aqueous systems have been studied by Glaser et al.[7,8] and Tomiyasu et al.[9] In a previous paper[10] we have described the possibilities offered by 1D and 2D ^{19}F NMR methods for the study of the dynamics of fluoride complexes. Additional insight into the dynamics in the uranium(VI) fluoride system has been obtained from studies of luminescence lifetimes.[11,12]

Substitution mechanisms have been discussed,[5,6] and the experimental evidence seems to favor dissociative (D) or dissociative interchange (I_d) mechanisms. An exception is a recent study by Tomiyasu et al.,[9] interpreted in terms of an associative or associative interchange mechanism. The main indicators for this mechanism are a strongly negative activation entropy and that the rate of fluoride exchange is not influenced by irradiation at 488 nm, which is expected to increase the lability of the in-plane ligands. From the available literature information it is not possible to draw any clearcut mechanistic conclusions, and we have made the present study to try to resolve the conflicting mechanistic evidence. We have investigated the exchange reactions in the U(VI)−F$^-$ system over a very broad concentration range in order to obtain the rates and mechanisms of the exchange reactions between the various complexes $UO_2F_n^{2-n}$, $n = 1-5$, and between these and free F$^-$ and HF(aq). The experiments have been made in a 1.00 M NaClO$_4$ ionic medium, using the equilibrium constants previously determined by Ahrland and Kullberg,[13] the known analytical total concentrations of U(VI) and fluoride, and the measured hydrogen ion concentration to calculate the species distribution of the various test solutions investigated. The pH of the solutions was varied in the range 0 > pH > 6, where no hydroxo or mixed fluoro/hydroxo complexes are present.

Experimental Section

Solutions. An uranium(VI) perchlorate stock solution prepared by a method described earlier[14] and a NaF stock solution (from recrystallized NaF) were used to prepare the investigated solutions. The ionic medium was kept constant by NaClO$_4$ ([ClO$_4^-$] = 1 M). The free hydrogen ion concentration (−log[H$^+$]) was measured by a HF-resistant combined glass electrode (Ingold, HF-405-60-57/120; the inner solution

---

* Author to whom correspondence should be addressed.

† On leave from Alkaloida Chemical Co. Ltd., Tiszavasvári, H-4440, Hungary.

⊗ Abstract published in *Advance ACS Abstracts,* February 15, 1996.

(1) Gordon, G.; Taube, H. *J. Inorg. Nucl. Chem.* **1961**, *16*, 272.
(2) Jung, W.; Ikeda, Y.; Tomiyasu, H.; Fukutomi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2317.
(3) Kato, Y.; Fukutomi, H. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1323.
(4) Okuyama, K.; Ishikawa, Y.; Kato, Y.; Fukutomi, H. *Bull. Res. Lab. Nucl. React.* **1978**, *3*, 39.
(5) Lincoln, S. F. *Pure Appl. Chem.* **1979**, *51*, 2059.
(6) Tomiyasu, H.; Fukutomi, H. *Bull. Res. Lab. Nucl. React.* **1982**, *7*, 57.
(7) Brücher, E.; Glaser, J.; Tóth, I. *Inorg. Chem.* **1991**, *30*, 2239.
(8) Bányai, I.; Glaser, J.; Micskei, K.; Tóth, I.; Zekány, L. *Inorg. Chem.* **1995**, *34*, 3785.
(9) Harada, M.; Fujii, Y.; Sakamaki, S.; Tomiyasu, H. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3022.
(10) Szabó, Z.; Glaser, J. *Magn. Reson. Chem.* **1995**, *33*, 20.
(11) Park, Y.; Sakai, Y.; Abe, R.; Ishii, T.; Harada, M.; Kojima, T.; Tomiyasu, H. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 55.
(12) Moriyasu, M.; Yokoyama, Y.; Ikeda, S. *J. Inorg. Nucl. Chem.* **1977**, *39*, 2199.
(13) Ahrland, S.; Kullberg, L. *Acta Chem. Scand.* **1971**, *25*, 3457.
(14) Ciavatta, L.; Ferri, D.; Grenthe, I.; Salvatore, F. *Inorg. Chem.* **1981**, *20*, 463.

0020-1669/96/1335-2036$12.00/0

of KCl was replaced by 1 M NaCl solution in order to avoid precipitation of $KClO_4$ in the membrane between the electrode and the test solutions) connected to a pH meter (Radiometer PHM62). The hydrogen ion concentration was calculated from the measured pH using the method suggested by Irving et al.[15] pD in the pure D_2O solvent was calculated from glass electrode measurements using pD = pH + 0.4. ^{17}O NMR measurements were performed by using ^{17}O-enriched (about 4%) samples. The enrichment of the -yl oxygens of uranyl(2+) was accomplished by a procedure described previously[8] using $H_2{}^{17}O$ (12.3% ^{17}O, ISO-YEDA Co., Rehovot, Israel).

NMR Measurements. The NMR spectra have been recorded on a Bruker AM400 spectrometer in unlocked mode at −5 °C, or at variable temperature when determining activation parameters. The probe temperature was regulated using a Bruker Eurotherm variable temperature control unit and was measured by a calibrated Pt-100 resistance thermometer. Samples under investigation were kept in Teflon inserts within the standard 5 mm (for ^{19}F) or 10 mm (for ^{17}O measurements) sample tubes. Typical parameters for the NMR measurements are as follows: ^{19}F at 376.5 MHz; pulse width, 8 μs (∼70° pulse); relaxation delay, 2 s; spectral width, 80 000 Hz. The spectra are referenced to an aqueous solution of 0.01 M NaF in 1 M $NaClO_4$ (pH = 12); this corresponds to the chemical shift of the hydrated F^- ion in this medium. ^{17}O spectra were recorded at 54.2 MHz (pulse width, 15 μs (∼60° pulse); relaxation delay, 0.4 s; spectral width, 5500 Hz). The chemical shifts are given in ppm, using the signal of external tap water at 25 °C as the reference. The line widths were determined by fitting a Lorentzian curve to the experimental signal by using the standard Bruker software.

Results

Data Treatment. The choice of the optimal experimental technique in dynamic NMR spectroscopy depends on the characteristics of the exchange system. In systems which are in slow exchange on the time scale characterized by the chemical shift difference of the exchanging species, it is often possible to obtain kinetic information by using magnetization transfer experiments as detailed in the literature.[16,17] When the exchange is fast enough to affect the line shape, but slow on the actual chemical shift time scale, the desired kinetic parameters can be obtained by an analysis of exchange-broadened spectra. The observed separate Lorentzian peaks have a half-width equal to

$$\Delta\nu_{1/2}^{\text{obs}} = \frac{1}{\pi}\left(\frac{1}{T_2} + \frac{1}{T_{2(\text{inh})}} + \frac{1}{\tau_{(\text{ex})}}\right) \qquad (1)$$

which contains the transverse relaxation time, the field inhomogeneity, and the chemical exchange contributions. The pseudo-first-order rate constants can be calculated from the equation

$$\pi[(\Delta\nu_{1/2}^{\text{obs}}(m) - \Delta\overset{\circ}{\nu}_{1/2}(m))] = \pi\Delta\nu_{1/2}(m) = \sum_{n=0}^{n=5} k(\text{obs})_{m,n} \qquad (2)$$

where $\Delta\nu_{1/2}^{\text{obs}}$ (m) is the measured, and $\Delta\nu_{1/2}^{o}(m)$ is the nonexchange line width for the mth species, while $k(\text{obs})_{m,n}$ is the pseudo-first-order rate constant for the chemical exchange process from the mth site to the nth site. From the concentration dependence of the experimental $k(\text{obs})_{m,n}$ values the various stoichiometric rate constants in the experimental rate equations can be evaluated. Considering only the first-order terms, we have

$$\sum_{n=0}^{n=5} k(\text{obs})_{m,n} = k_0 + \sum_{n=0}^{n=5} k_{m,n}[UO_2F_n{}^{2-n}] + k_{m,\text{HF}}[\text{HF}] + k_{m,\text{F}^-}[\text{F}^-] + k_{m,\text{H}^+}[\text{H}^+] \qquad (3)$$

When the exchange is fast on the chemical shift time scale, only one peak can be observed in the spectrum. In this case the line shape can be described by creating a rate matrix using the formalism introduced by Reeves and Shaw.[18] The line width of the observed peak, with a chemical shift determined by the individual chemical shifts of all of the exchanging species and their relative concentrations, can then be compared to the line width calculated from the $k(\text{obs})_{m,n}$ values. The creation of a rate matrix using this formalism has been described in previous papers.[19,20] The calculated parameters are given in the following text with their standard deviations (1σ) or with their error limits (±values).

Determination of Empirical Rate Equations

^{19}F NMR Investigations. The line widths of different exchanging fluorine sites are very broad at room temperature. Depending on the composition of the solution, they can coalesce. At lower temperature and/or lower total concentration of uranyl(2+) ion, the exchange rates were slow enough on the ^{19}F NMR chemical shift scale to observe the different fluoride complexes separately. However, the exchange rate between the different fluorine sites within a given complex was fast. The equilibrium compositions of the investigated solutions were calculated using the stability constants determined in the same ionic medium by Ahrland and Kullberg.[13] These calculations showed that three or even more species may coexist in the solution, depending on the total concentrations of $UO_2{}^{2+}$ and $F^-$and on the pH; *cf.* Figure 1. We found it convenient to measure the line width of separate signals within a certain pH region at selected $R = [F^-]_{\text{tot.}}/[UO_2{}^{2+}]_{\text{tot.}}$ ratios. Preliminary experiments showed that it is essential to keep the number of exchanging sites to a minimum by a proper choice of R and to select a pH region in which the concentrations of the exchanging species are comparable. Their concentrations must also vary over a sufficiently wide range so that significant changes in the line widths could be observed. The equilibrium distributions of the investigated solutions at different $[F^-]_{\text{tot.}}/[UO_2{}^{2+}]_{\text{tot.}}$ ratios, R (Figure 1a−c), were used to select the pH regions where the first and the second complexes ($R = 3$), the second and the third complexes ($R = 4$), and the third and the fourth complexes ($R = 8$) are the only ones that give measurable contributions to the observed line width.

The experimental line width of the first complex, in solutions with $R = 3$, follows the empirical rate equation

$$\Delta\nu_{1/2}(1) = C_{1,\text{HF}}[\text{HF}] + C_{1,2}[UO_2F_2] \qquad (4)$$

By means of a least-squares fitting procedure, the following values of the constants were obtained: $C_{1,\text{HF}} = (1.7 \pm 0.2) \times 10^4$ M^{-1} s^{-1} and $C_{1,2} = (2.9 \pm 0.4) \times 10^4$ M^{-1} s^{-1}. The value

---

(15) Irving, H. M.; Miles, M. g.; Pettit, L. D. *Anal. Chim. Acta* **1967**, *38*, 475.

(16) Orrell, K. G.; Sik, V.; Stephenson, D. *Prog. Nucl. Magn. Reson. Spectrosc.* **1990**, *22*, 141.

(17) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.

(18) Reeves, L. W.; Shaw, K. N. *Can. J. Chem.* **1970**, *48*, 3641.

(19) Bányai, I.; Glaser. J *J. Am. Chem.Soc.* **1989**, *111*, 3186.

(20) Bányai, I.; Glaser. J *J. Am. Chem. Soc.* **1990**, *112*, 4703.

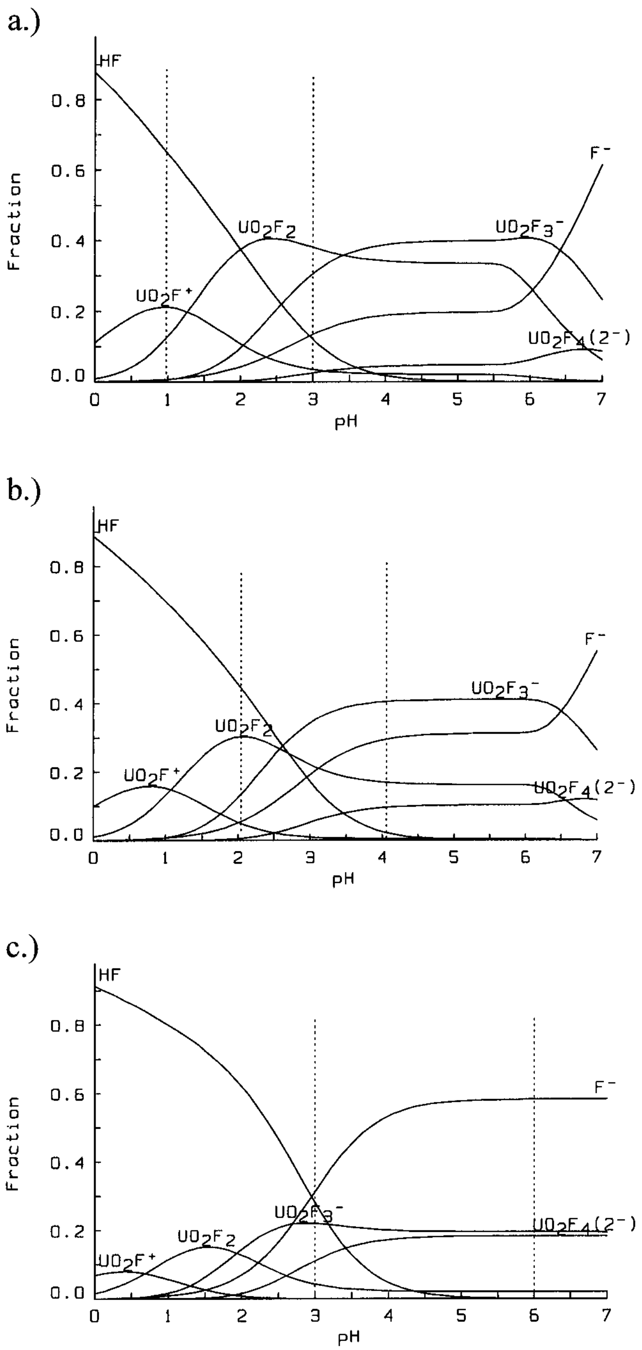

Figure 1. Distribution of uranyl(2+) fluoride complexes as a function of pH at different values of $R = [F]_{tot.}/[UO_2^{2+}]_{tot.}$, $[UO_2^{2+}]_{tot.} = 5$ mM: (a) $R = 3$, (b) $R = 4$, (c) $R = 8$. Dashed lines represent the investigated pH region.

of $C_{1,HF}$ refers to the following exchange reaction, without any net chemical exchange:

$$UO_2F^+ + H{*}F \underset{k_{1,HF}}{\overset{k_{1,HF}}{\rightleftharpoons}} UO_2{*}F^+ + HF \qquad (5)$$

The exchange rate between the different magnetic environments of the fluorine nuclei is

$$-d[UO_2F^+]/dt = 2k_{1,HF}[UO_2F^+][HF] \qquad (6)$$

where the factor of 2 takes the reverse reaction into account. From eqs 2, 4, and 6, we obtain $k_{1,HF} = \pi C_{1,HF}/2$. The calculated rate constants are given in Table 1. The dependence of the line width of the first complex on the HF concentration might also be influenced by the following exchange process:

$$UO_2F^+ + HF \underset{k_{2,H^+}}{\overset{k'_{1,HF}}{\rightleftharpoons}} UO_2F_2 + H^+ \qquad (7)$$

However, there was no experimental evidence for the reverse reaction in the line shape analysis of the second complex. This may be due to a small value of k_{2,H^+}, as discussed below. The parameter $C_{1,2}$ can then be assigned to the following exchange process only:

$$UO_2F^+ + UO_2{*}F_2 \underset{k_{1,2}}{\overset{k_{1,2}}{\rightleftharpoons}} UO_2F{*}F + UO_2F^+ \qquad (8)$$

for which $k_{1,2} = \pi C_{1,2}/2$.

The experimental line width of the second complex follows the rate equation:

$$\Delta\nu_{1/2}(2) = C_{0,2}[UO_2^{2+}] + C_{2,HF}[HF] + C_{2,1}[UO_2F^+] + C_{2,3}[UO_2F_3^-] \qquad (9)$$

where the parameters determined using a least-squares method were $C_{0,2} = (1.8 \pm 0.4) \times 10^4\ M^{-1}\ s^{-1}$, $C_{2,HF} = (2.3 \pm 0.3) \times 10^4\ M^{-1}\ s^{-1}$, $C_{2,3} = (8.2 \pm 0.5) \times 10^4\ M^{-1}\ s^{-1}$. The value of $C_{2,1}$ was fixed so that $C_{2,1} = C_{1,2}$. In this case $C_{0,2}$ can be attributed to the following process which leads to a net chemical change:

$$UO_2^{2+} + UO_2F_2 \underset{k_{1,1}}{\overset{k_{0,2}}{\rightleftharpoons}} 2UO_2F^+ \qquad (10)$$

The rate is

$$-d[UO_2F_2]/dt = k_{0,2}[UO_2^{2+}][UO_2F_2] \qquad (11)$$

with $k_{0,2} = \pi C_{0,2}$. The ratio between $k_{0,2}$ and $k_{1,1}$ can be obtained from the equilibrium constant, as follows:

$$\frac{k_{0,2}}{k_{1,1}} = \frac{[UO_2F^+]^2}{[UO_2^{2+}][UO_2F_2]} = \frac{\beta_1^{\,2}}{\beta_2} \qquad (12)$$

Using the data from the literature,[21] $\beta_1^2/\beta_2 \sim 13$. This means that the reverse of reaction 10 is approximately 1 order of magnitude slower than the forward reaction. Hence, it is understandable why this process did not make any measurable contribution to the line width of the first complex. In the same way, $C_{2,HF}$ and $C_{2,3}$ could be related to the following reactions:

$$UO_2F_2 + H{*}F \underset{k_{2,HF}}{\overset{k_{2,HF}}{\rightleftharpoons}} UO_2F{*}F + HF \qquad (13)$$

$$UO_2F_2 + UO_2{*}F_3^- \underset{k_{2,3}}{\overset{k_{2,3}}{\rightleftharpoons}} UO_2F_2{*}F^- + UO_2F_2 \qquad (14)$$

from which the values for $k_{2,HF}$ and $k_{2,3}$ could be calculated. The measured line widths of the complexes and the fitted curves using the rate constants given in Table 1 are shown in Figure 2a–c. Figure 1c shows that for $R = 8$ and pH = 6, the dominant species are $UO_2F_3^-$, $UO_2F_4^{2-}$, and F^-. The line broadening of the separate free fluoride signal was found to be determined only by the exchange processes:

$$UO_2F_3^- + {*}F^- \underset{k_{3,F^-}}{\overset{k_{3,F^-}}{\rightleftharpoons}} UO_2F_2{*}F^- + F^- \qquad (15)$$

$$UO_2F_4^{2-} + {*}F^- \underset{k_{4,F^-}}{\overset{k_{4,F^-}}{\rightleftharpoons}} UO_2F_3{*}F^{2-} + F^- \qquad (16)$$

---

[21] 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; Vol. 1.

Table 1. Rate Constants for Different Exchange Reactions at −5 °C (Calculated Standard Deviations (1σ) in Parentheses)

reacn type	rate constants ($M^{-1}\ s^{-1}$)	K_{os} (M)	K_{eq} (M) ($K_{os}n_{F^-}\ n_{H_2O}$)	k_{aq} (s^{-1}) ($k_{m,n}/K_{os}$)	k_{int} (s^{-1}) ($k_{m,n}/K_{eq}$)	$\Delta S^\ddagger$, $\Delta H^\ddagger$ (J mol^{-1} K^{-1}, kJ mol^{-1}]
$k_{0,1}$	$(5.5 \pm 0.5) \times 10^3$	0.018	0.09	3.0×10^5	6.1×10^4	−56, +31
$k_{0,2}$	$(5.6 \pm 0.6) \times 10^4$ [a]	0.3	3.0	1.8×10^5	1.8×10^4	
$k_{1,2}$	$(4.5 \pm 0.6) \times 10^4$,[a] $(3.6 \pm 0.6) \times 104$ [b]	0.3	2.4	1.5×10^5	1.8×10^4	
$k_{2,3}$	$(1.4 \pm 0.1) \times 10^5$,[a] $(1.3 \pm 0.1) \times 10^5$ [b]	0.3	2.7	4.6×10^5	5.1×10^4	
$k_{3,4}$	$(2.1 \pm 0.1) \times 10^5$,[a] $(2.2 \pm 0.1) \times 10^5$ [c]	0.018	0.144	1.2×10^7	1.5×10^6	
$k_{4,5}$	$(1.0 \pm 0.4) \times 10^6$ [c]	7.5×10^{-5}	3.75×10^{-4}	1.3×10^{10}	2.6×10^9	
$k'_{0,HF}$	$(5.7 \pm 0.6) \times 10^4$, $(1.8 \pm 0.2) \times 10^5$ [d]	0.3	1.5	1.9×10^5	3.8×10^4	−12, +38
$k_{1,HF}$	$(2.7 \pm 0.3) \times 10^4$ [a]	0.3	1.2	9.0×10^4	2.2×10^4	
$k_{2,HF}$	$(3.6 \pm 0.3) \times 10^4$,[a] $(2.8 \pm 0.5) \times 10^4$ [b]	0.3	0.9	1.2×10^5	4.0×10^4	
$k_{3,HF}$	$(9.4 \pm 0.5) \times 10^4$,[b] $(3.9 \pm 0.1) \times 10^5$,[e] $(1.1 \pm 0.1) \times 10^5$ [c]	0.3	0.6	3.1×10^5	1.5×10^5	
$k_{4,HF}$	$(3.9 \pm 0.2) \times 10^5$,[c] $(1.2 \pm 0.1) \times 10^6$ [e]	0.3	0.3	1.3×10^6	1.3×10^6	
$k_{5,HF}$	$>1 \times 10^6$	0.3		3.3×10^6		
k_{3,F^-}	$(4.7 \pm 1.3) \times 10^3$	0.074	0.148	6.3×10^4	3.2×10^4	
k_{4,F^-}	$(8.5 \pm 1.0) \times 10^3$	0.018	0.018	4.7×10^5	4.7×10^5	
k_{1,H^+}	$(1.5 \pm 0.1) \times 10^3$	0.074		2.0×10^4		

[a] Determined in solutions with $R = 3$. [b] $R = 4$. [c] $R = 8$. [d] In 80% D_2O. [e] In D_2O.

We determined the rate constants for these processes from the line width of the free fluoride signal in solutions with a total uranyl(2+) concentration of 5 mM, and a pH approximately constant at about 6. The concentrations of $UO_2F_3^-$ and $UO_2F_4^{2-}$ were varied by changing the total fluoride concentration between 50 and 100 mM. The calculated rate constants are $k_{3,F^-} = (4.7 \pm 1.3) \times 10^3\ M^{-1}\ s^{-1}$ and $k_{4,F^-} = (8.5 \pm 1.0) \times 10^3\ M^{-1}\ s^{-1}$.

The F^- line width is not affected by the concentrations of HF, UO_2F_2(aq), and $UO_2F_5^{3-}$. The concentration of HF is negligible at the pH studied, but the concentrations of the two complexes are higher, at most 5 and 14%, respectively, of the total uranyl(2+) concentration (see Supplementary Information). Assuming that the exchange rate between UO_2F_2(aq) and the free fluoride ion is of the same order of magnitude as those of $UO_2F_3^-$ and $UO_2F_4^{2-}$, and knowing that the rate constant, $k_{5,F^-} = 4.3 \times 10^1\ M^{-1}\ s^{-1}$,[9] is 2 orders of magnitude lower than k_{4,F^-}, we find that the contributions of UO_2F_2 and $UO_2F_5^{3-}$ to the line broadening of the F^- signal are negligible, in agreement with the experimental observations.

The exchange reactions involving the third and fourth complexes were determined from the concentration dependence of the line widths of all peaks measured in solutions with $R = 8$ (pH > 3.5). In addition to eqs 15 and 16, also the following four reactions contributed to the line broadening:

$$UO_2F_3^- + H{*}F \underset{k_{3,HF}}{\overset{k_{3,HF}}{\rightleftharpoons}} UO_2F_2{*}F^- + HF \tag{17}$$

$$UO_2F_3^- + UO_2{*}F_4^{2-} \underset{k_{3,4}}{\overset{k_{3,4}}{\rightleftharpoons}} UO_2F_3{*}F^{2-} + UO_2F_3^- \tag{18}$$

$$UO_2F_4^{2-} + H{*}F \underset{k_{4,HF}}{\overset{k_{4,HF}}{\rightleftharpoons}} UO_2F_3{*}F^{2-} + HF \tag{19}$$

$$UO_2F_4^{2-} + UO_2{*}F_5^{3-} \underset{k_{4,5}}{\overset{k_{4,5}}{\rightleftharpoons}} UO_2F_4{*}F^{3-} + UO_2F_4^{2-} \tag{20}$$

In order to facilitate the mechanistic deductions, we investigated if the exchange reactions showed any isotope effects by repeating the measurements for the third and the fourth complexes in deuterium oxide (*cf.* Figure 2c). No isotope effect was found for the exchange reactions between the various complexes ($k_{2,3}$, $k_{3,4}$, and $k_{4,5}$). However, there was a pronounced isotope effect, approximately three times *higher* exchange rates for DF than for HF, for the exchange reactions between HF and the third and fourth uranyl fluoride complexes ($k_{3,HF}$ and $k_{4,HF}$).

The fifth complex gave a very broad signal which was difficult to observe even at higher pH. Hence, it was impossible to get precise information on the exchange rate between the fifth complex and HF, at least in the slow-exchange region determined by the chemical shift difference of these species. However, the spectra measured at higher pH values indicate that this rate constant ($k_{5,HF}$) is larger than $1 \times 10^6\ M^{-1}\ s^{-1}$.

^{17}O NMR Investigations. The remaining exchange reactions between UO_2^{2+}, UO_2F^+, and HF were investigated by ^{17}O NMR technique, using ^{17}O-enrichment of the -yl oxygens. The chemical shift of the free uranyl(2+) ion was determined in a separate solution containing no fluoride. In solutions with the total concentrations of $[UO_2^{2+}] = 10$ mM and $[F^-] = 4$ mM, at −5 °C, we observed separate signals for the free uranyl(2+) ion and the first complex (see Supplementary Information). The observed chemical shifts did not change with the composition of the solution in the pH range 1−2, where the distribution of the uranyl varied between 60% UO_2^{2+}, 40% UO_2F^+, and 70% UO_2^{2+}, 30% UO_2F^+. This indicated that the exchange is slow on the time scale determined by the chemical shifts of the present species. In order to reduce the experimental time, and/or to improve the signal-to-noise ratio of the ^{17}O NMR experiments, the total concentration of uranyl(2+) was increased to 50 mM, where spectra with excellent signal-to-noise ratio were obtained within a short experimental time.

In order to deduce the experimental rate laws, we varied the total uranyl(2+) ion concentration between 10 and 50 mM at $R = 0.1$ and pH = 1.5−1.7, where the dominant species are UO_2^{2+} and UO_2F^+ and the equilibrium concentrations of HF and UO_2F_2 are very low. There is one dominant exchange path:

$${*}UO_2^{2+} + UO_2F^+ \underset{k_{0,1}}{\overset{k_{0,1}}{\rightleftharpoons}} {*}UO_2F^+ + UO_2^{2+} \tag{21}$$

At the high uranyl(2+) concentrations used, only one peak at approximately constant chemical shift was observed in the spectrum, because the small signal of UO_2F^+ was so exchange broadened that it disappeared in the base line (see Supplementary Information). The pseudo-first-order rate constant $k(\mathrm{obs})_{0,1}$, obtained by complete line shape analysis,[18] is equal to

$$k(\mathrm{obs})_{0,1} = 2k_{0,1}[UO_2F^+] \tag{22}$$

$k_{0,1}$ was determined from the slope of the straight line of $k(\mathrm{obs})_{0,1}$ vs $[UO_2F^+]$ (see Figure 3). At higher $[F^-]_{tot.}$ values the relationship is no longer linear, and an additional exchange path makes a contribution to the line broadening (*cf.* the following discussion).

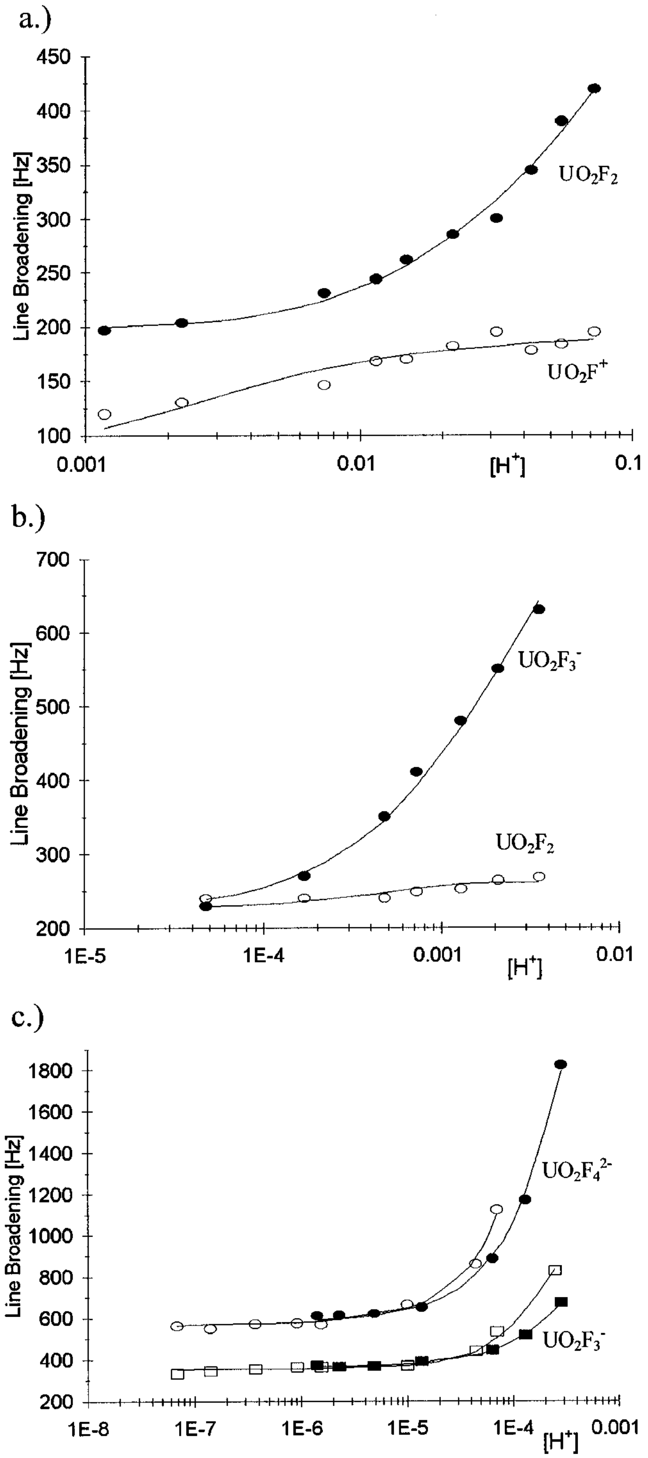

Figure 2. Line width dependence of ^{19}F NMR signals of uranyl(2+) fluoride complexes on pH, at different R values, $[UO_2^{2+}]_{tot.} = 5$ mM, $T = -5$ °C: (a) $R = 3$, (b) $R = 4$, and (c) $R = 8$ in H_2O (solid symbols) and in D_2O (empty symbols). Lines represent line widths calculated using rate constants in Table 1.

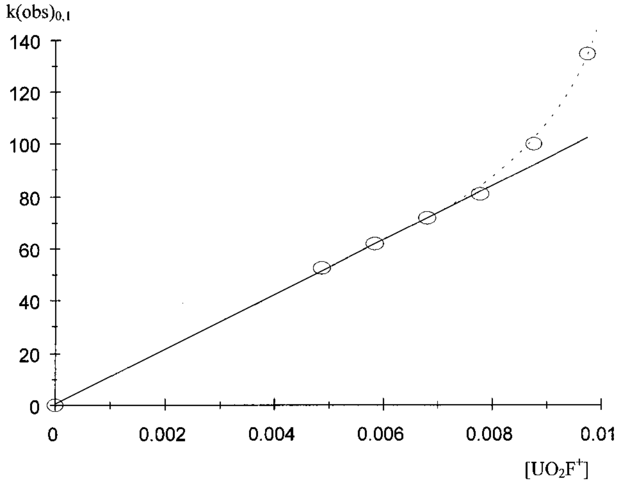

Figure 3. Dependence of $k(obs)_{0,1}$ on the equilibrium concentration of UO_2F^+ at $R = 0.1$, pH = 1.5, and $T = -5$ °C. The total concentration of uranyl(2+) ion was varied between 10 and 50 M.

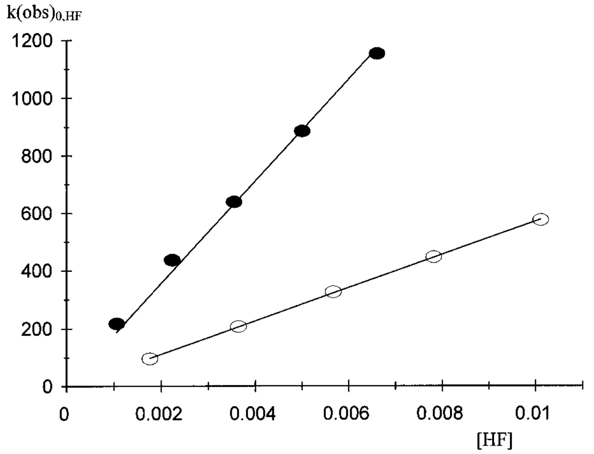

Figure 4. Dependence of $k(obs)_{0,HF}$ calculated by eq 25 on the equilibrium HF concentration: (○) in H_2O and (●) in 80% D_2O, $T = -5$ °C.

We have also studied the temperature dependence of exchange reactions 21 and 23, in order to obtain additional mechanistic indicators. These were the only reactions that could be studied without influence from parallel exchange pathways. For the other reactions it was not possible to interpret the temperature dependence of the exchange rates in terms of temperature dependent rate constants for the various parallel exchange pathways. By using a total fluoride concentration of 5 mM and $R = 0.1$ (where the HF dependent pathway gives a negligible contribution), we could determine the temperature dependence of $k_{0,1}$ and in this way calculate the corresponding activation parameters. The Eyring plots for $k_{0,1}$ between −5 and +70 °C are given in the Supporting Information. The activation parameters are $\Delta H^{\ddagger} = 31.2\ (1.4)$ kJ mol^{-1} and $\Delta S^{\ddagger} = -56.2\ (1.0)$ J mol^{-1} K^{-1}, where the value within parentheses is the computed standard deviation (1σ).

The influence of HF on the exchange between UO_2^{2+} and UO_2F^+ was studied by changing the total fluoride concentration between 5 and 25 mM in 1 M $HClO_4$. In these solutions, the total hydrogen ion concentration is constant and the concentration of UO_2F_2 negligible. The presence of HF results in a new exchange path, in addition to eq 21:

$$UO_2^{2+} + HF \underset{k_{1,H^+}}{\overset{k'_{0,HF}}{\rightleftharpoons}} UO_2F^+ + H^+ \qquad (23)$$

From eqs 22 and 23, the concentration dependence of the pseudo-first-order rate constant of the exchange process between UO_2^{2+} and UO_2F^+ can be written as

$$k(obs)_{0,1} = 2k_{0,1}[UO_2F^+] + k'_{0,HF}\,[HF] \qquad (24)$$

Using the known value of $k_{0,1}$, $k'_{0,HF}$ can be determined from the slope of the straight line of $k(obs)_{0,HF}$ vs [HF] (see Figure 4):

$$k(\text{obs})_{0,\text{HF}} = k(\text{obs})_{0,1} - 2k_{0,1}[\text{UO}_2\text{F}^+] = k'_{0,\text{HF}}\,[\text{HF}] \qquad (25)$$

These experiments were repeated in 80% D_2O in order to detect if there is any deuterium isotope effect (as previously observed for the reactions denoted by $k_{3,\text{HF}}$ and $k_{4,\text{HF}}$). The results showed that there is no isotope effect for the exchange between the free uranyl(2+) ion and the first complex, while there is a pronounced effect for reaction 23. From eq 25, the exchange rate in 80% D_2O was determined as described previously (Figure 4 and Supplementary Information). The rate constants are given in Table 1.

From Eyring plots for $k'_{0,\text{HF}}$ (see Supplementary Information) the following activation parameters were obtained: $\Delta H^‡ = 37.7$ (1.0) kJ mol^{-1} and $\Delta S^‡ = -11.8$ (0.6) J mol^{-1} K^{-1} (in H_2O) and $\Delta H^‡ = 38.7$ (1.1) kJ mol^{-1} and $\Delta S^‡ = 0.0$ (0.9) J mol^{-1} K^{-1} (in 80% D_2O).

Using the microscopic reversibility,

$$k(\text{obs})_{0,1}[\text{UO}_2^{\,2+}] = k(\text{obs})_{1,0}[\text{UO}_2\text{F}^+] \qquad (26)$$

we calculated the exchange rate of the reverse process in eq 23. The observed pseudo-first-order rate constant is equal to

$$k(\text{obs})_{1,0} = 2k_{0,1}[\text{UO}_2^{\,2+}] + k_{1,\text{H}^+}[\text{H}^+] \qquad (27)$$

from which

$$k(\text{obs})_{1,\text{H}^+} = k(\text{obs})_{1,0} - 2k_{0,1}[\text{UO}_2^{\,2+}] = k_{1,\text{H}^+}[\text{H}^+] \qquad (28)$$

Using these equations, the calculated rate constant k_{1,H^+} from the experiments (Figure 4) is 1430 ± 50 M^{-1} s^{-1} in H_2O, while the corresponding value in 80% D_2O is 2400 ± 200 M^{-1} s^{-1}. In addition, a direct determination of this rate constant was made in solutions where the total hydrogen ion concentration varied between 0.6 and 1 M, while $[\text{UO}_2]_{\text{tot.}}$ and $[\text{F}^-]_{\text{tot.}}$ were kept constant at 50 and 15 mM, respectively. In this region, the effect of UO_2F_2 on the exchange is negligible because of its very low concentration. Hence, k_{1,H^+} could be determined from the dependence of $k(\text{obs})_{1,\text{H}^+}$ on the total hydrogen ion concentration (see Supplementary Information). From the linear relationship we obtained $k_{1,\text{H}^+} = 1500 \pm 100$ M^{-1} s^{-1}, in good agreement with the value calculated above.

The ratio between $k'_{0,\text{HF}}$ and k_{1,H^+} is equal to the ratio between two equilibrium constants:

$$\frac{k'_{0,\text{HF}}}{k_{1,\text{H}^+}} = \frac{\beta_1}{K_{\text{HF}}} \qquad (29)$$

Literature data[22] on the equilibrium constants give $\beta_1/K_{\text{HF}} = 38.9$, which is an excellent agreement with our experimental ratio $k'_{0,\text{HF}}/k_{1,\text{H}^+} = 37$. The ratio $k'_{0,\text{DF}}/k_{1,\text{D}^+}$ is equal to 75. Using the experimental ratio $\log(K_{\text{HF}}/K_{\text{DF}}) = -0.31$, we find that the equilibrium constant for the formation of UO_2F^+ has approximately the same value in both solvents.

Using the solutions studied by ^{17}O NMR, it was possible to determine the exchange rate between UO_2F^+ and HF at higher hydrogen ion concentration by ^{19}F NMR . In these ^{19}F NMR experiments one also has to consider the exchange process given by eq 5 ($k_{1,\text{HF}}$). From the measured line width of UO_2F^+ the pseudo-first-order rate constant can be written as

$$k(\text{obs})_{1,\text{HF}} = \pi\Delta\nu_{1/2}(\text{UO}_2\text{F}^+) = k_{1,\text{H}^+}[\text{H}^+] + 2k_{1,\text{HF}}[\text{HF}] \qquad (30)$$

Using the value of $k_{1,\text{H}^+} = 1.5 \times 10^3$ M^{-1} s^{-1} from the previous experiment, we obtained $k_{1,\text{HF}}$ equal to (3.0 ± 0.5) × 10^4 M^{-1} s^{-1}, in good agreement with the value determined as detailed earlier. In another experiment, the total hydrogen ion concentration was kept constant ($[\text{H}^+] = 1$ M) and the total uranyl(2+) ion concentration was varied between 200 and 100 mM, at constant total fluoride concentration $[\text{F}^-]_{\text{tot.}} = 10$ mM. The line width of the UO_2F^+ signal was practically unchanged because of the low HF concentration. From eq 30, and with use of $k_{1,\text{HF}} = 2.7 \times 10^4$ M^{-1} s^{-1}, we calculated $k_{1,\text{H}+} = 1530 \pm 15$ M^{-1} s^{-1}, in good agreement with the value determined by the ^{17}O NMR experiments. The relatively low value of k_{1,H^+}, at least compared to $k_{1,\text{HF}}$, explains why this process could be observed only at higher hydrogen ion concentrations. At lower concentrations process 5, which is also an exchange path between HF and UO_2F^+, dominates.

If the reverse reaction in eq 7 (k_{2,H^+}) is slow, or at least much slower than the exchange process in eq 13 ($k_{2,\text{HF}}$), it will not influence the line shape of the second complex. This seems to be a possible explanation to why this reaction was not observed at the lower hydrogen ion concentration (see above).

From the published enthalpy data[22] it is obvious that the equilibrium constants in the uranium(VI) fluoride system do not change much with temperature. This is consistent with the observation that the ^{17}O chemical shift of the observed averaged signal of the exchanging species moves only slightly toward higher frequency with increasing temperature (Supplementary Information). A similar effect was previously observed in a solution containing only the free uranyl(2+) ion.[23] On the basis of these experiments, we have assumed that the chemical shift difference between the signal of free uranyl(2+) ion and the exchange broadened signal is approximately constant, independent of temperature. The values of the line width of the free uranyl(2+) signal decrease with increasing temperature (from 3 to 1 Hz between −5 and +70 °C). These changes were taken into account during the calculations of the temperature dependence data, although their effects on the resulting rate constants were almost negligible.

Discussion

The internal consistency of the experimental rate constants is satisfactory as judged by the agreement between independent determinations of the same rate constant(s). The agreement is also excellent between the rate constant ratio $k'_{0,\text{HF}}/k_{1,\text{H}^+}$ and β_1/K_{HF}, where the latter quantity is known from independent determinations of equilibrium constants. For a discussion of the NMR technical aspects of this study, the reader is referred to the previous paper.[10] The following discussion will be centered on mechanistic aspects of the various exchange reactions studied, using the following short-hand notation:

$$\text{A(aq)} + {}^*\text{F}{-}\text{X(aq)} \xrightleftharpoons{1} \text{A(aq)}\cdots{}^*\text{F}{-}\text{X(aq)} \xrightleftharpoons{2} \text{A}{-}{}^*\text{F}{-}\text{X(aq)} \xrightleftharpoons{3} \text{A}{-}{}^*\text{F} + \text{X(aq)} \qquad (31)$$

where A denotes $UO_2^{\,2+}$, or one of the fluoride acceptors $UO_2F_{n-1}^{\,2-(n-1)}$, and F−X one of the fluoride donors, $UO_2F_n^{\,2-n}$, or F^-/HF. Step 1 is a diffusion controlled formation of an outer-sphere ion pair, with the equilibrium constant K_{os}; this is an oversimplified description of the process, as will be discussed later on. Step 2 is the formation of a fluoride bridging intermediate/transition state (except in the exchange reactions involving F^-), and step 3 is the bond breaking between F and

---

[22] Ahrland, S.; Kullberg, L. *Acta Chem. Scand.* **1971**, *25*, 3471.

[23] Jung, W.; Tomiyasu, H.; Fukutomi, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 489.

X. We will base the mechanistic discussion on the following experimental observations: the second-order rate laws for the exchange pathways between two complexes (k_{mn}) and between the various complexes and F^- (k_{m,F^-}) and HF ($k_{m,HF}$); the slow rate of the direct exchange pathways between free fluoride and the various complexes in comparison with the other exchange reactions in the systems studied; the large H/D isotope effect for the pathways involving HF/DF (the rates increase ≈3 times in deuterated solutions) and the absence of a measurable isotope effect for the direct exchange reactions between the complexes and between the various complexes and F^-; the magnitude of the various rate constants differs fairly little from one another for most of the reactions studied; the size of the activation entropy for two of the studied reaction pathways, compared to the literature values for related reactions.

Before discussing the reaction mechanisms, we will consider the structure and coordination geometry of the uranyl(2+) ion. The structure of the complexed uranyl(2+) ion has been studied both in solution and in the solid state.[5,6,24,25] The axial (-yl) uranium−oxygen bonds are usually close to linear and kinetically inert.[1] The exchanging ligands are located in the plane perpendicular to the linear axis, and for the present purpose, only these ligands will be discussed. The coordination number in the equatorial plane can vary from four for bulky ligands with high donor numbers (e.g., HMPA[26]), through five for all known monodentate ligands,[6] to six for several bidentate ligands. (e.g., carbonate,[25] oxalate[27]). In the following discussion, it is assumed that all of the studied uranyl complexes are five-coordinated with the composition $UO_2F_n(OH_2)_{5-n}{}^{2-n}$.

The large number of possible exchange partners makes it difficult to determine rate laws, rate constants, and mechanisms. Fortunately, some kinetic information on this system is available from the literature. Ikeda et al.[28] have studied water exchange kinetics of hydrated uranyl complexes in mixed water/acetone solvent in the temperature range −60 to −90 °C and stated that this reaction is of the I_d type, with the breaking of the water−uranyl bond in the inner coordination sphere is the rate determining step. We have used the activation parameters determined in this study[28] to extrapolate the water exchange rate constant to the temperature used in the present study (−5 °C) and obtained $k_{aq} \approx 7 \times 10^5$ s^{-1}, recalculated to five coordination. There are two sources of error in this estimate: the first is the large difference between the two solvent systems used by Ikeda et al. and by us; the second is the large extrapolation from −60 to −5 °C. This value is compatible with the value estimated previously by Ekstrom and Johnson,[29] i.e., $k_{aq} > 10^5$ s^{-1} at room temperature.

The rate of exchange between HF and F^- has been studied experimentally, and the rate constant

$$HF \rightleftharpoons H^+ + F^- \qquad (32)$$

$k_{HF} \approx 6.7 \times 10^7$ s^{-1} at room temperature.[30] Recently, this value has been confirmed by a ^{19}F NMR study[31] ($k_{HF} = 3.4 \times 10^7$ s^{-1}, at +22 °C), which also showed that in the range $2 < \text{pH} < 4.5$ the averaged signal of HF/F^- is broadened due to chemical exchange in solutions of HF/F^- in water, with the line width maximum of about 16 Hz at pH ≈ 3. This proton exchange reaction is very fast compared to the rates determined in our study (see Table 1); hence, the chemical exchange between HF and F^- does not present an additional difficulty in the present study.

The following observations indicate that the exchange reaction pathways of the type $k_{n,HF}$ (e.g., eq 5) involve exchange between the uranyl complexes and HF, rather than a proton-catalyzed exchange of F^-: In the solution containing 5 mM total uranyl and 40 mM total fluoride, we varied the pH in the range $5 < \text{pH} < 6$ (see Figure 1c). As can be seen in the figure, the concentration of HF is small, and the concentrations of the main species (that is $UO_2F_3{}^-$, $UO_2F_4{}^{2-}$, and F^-) are practically constant, independent of the pH. If the exchange proceeds through a proton-catalyzed process between the uranyl complexes and F^-, we would expect a change of the exchange rate with pH. This is not the case, as can be seen in Figure 2c, which indicates that the line widths of the separate ^{19}F NMR signals (which are directly proportional to the overall exchange rates for these species) are essentially unchanged.

The first step in the mechanistic scheme is the formation of an outer-sphere ion pair, with an equilibrium constant, K_{os}, often estimated from the Fuoss equation. There is no reason to believe that this is a precise estimate in systems containing an ionic medium, with a concentration much higher than that of the reactants. However, the *relative* values of K_{os} for ions of different charge type in the same ionic medium might be more precise (they are *conditional* equilibrium constants, valid only in the given ionic medium). The estimated values of K_{os} are given in Table 1.

The second step involves the breaking of a water−uranium bond and the formation of a new uranium−fluoride bond. For uranium(VI) both associative and dissociative activation seems possible from a coordination chemical point of view.

The next step is the breaking of a uranium−fluoride bond, either in the bridge formed by the entering group or in the complex when the exchange involves F^-/HF.

There are four types of fluoride exchange reactions, exemplified by eqs 5, 8, 15, and 23. Most of the measured second-order rate constants have similar values, which may indicate a common rate determining step, either the rate of water dissociation in an Eigen−Wilkins type of mechanism or the rate of metal−fluoride bond breaking. Both of these possibilities will be discussed.

Eigen−Wilkins Mechanism. The exchange reactions involve encounters between the two reactants in a solvent cage—this is partly driven by electrostatic interactions and partly by the number of available donor sites, n_F, in $UO_2F_n{}^{2-n}$ and acceptor sites, n_{H2O}, in $UO_2F_{n-1}{}^{2-(n+1)}$. The Eigen−Wilkins mechanism has previously been discussed, e.g., by Hurwitz and Kustin[32] and by Ikeda et al.[28] for substitution reactions in uranyl(2+) complexes. The mechanism involves the following steps:

$$UO_2F_{n-1}(aq) + F{-}X(aq) \xrightarrow{k_I} UO_2F_{n-1}(H_2O)(H_2O)F{-}X \overset{K_{os}}{\rightleftharpoons} UO_2F_{n-1}(H_2O)F{-}X \xrightarrow{k_{aq}} F_{n-1}UO_2\cdots F\cdots X \rightarrow F_{n-1}UO_2{-}F + X(aq) \qquad (33)$$

k_I is determined by the rate of diffusion of the reactants in the medium, K_{os} is the outer-sphere equilibrium constant, and k_{aq} is the rate constant for the interchange between water and fluoride (largely independent on the entering ligand in a dissociative mechanism). The diffusion coefficients, and there-

---

(24) Wells, A. F. *Structural Inorganic Chemistry*, 5 ed.; Clarendon Press: Oxford, U.K., 1984.

(25) Åberg, M.; Ferri, D.; Glaser, J.; Grenthe, I. *Inorg. Chem.* **1983**, *22*, 3981.

(26) Honan, J. G.; Lincoln, S. F.; Williams, E. H. *Inorg. Chem.* **1978**, *17*, 1855.

(27) Alcock, N. W. *J. Chem. Soc., D* **1973**, 1610.

(28) Ikeda, Y.; Soya, S.; Fukutomi, H.; Tomiyasu, H. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1333.

(29) Ekstrom, A.; Johnson, D. A. *J. Inorg. Nucl. Chem.* **1974**, *69*, 2319.

(30) Eigen, M.; Hammes, G. G. *J. Am. Chem. Soc.* **1960**, *82*, 5952.

(31) Merbach, A. Private Communication.

(32) Hurwitz, P.; Kustin, K. *J. Phys. Chem.* **1967**, *71*, 324.

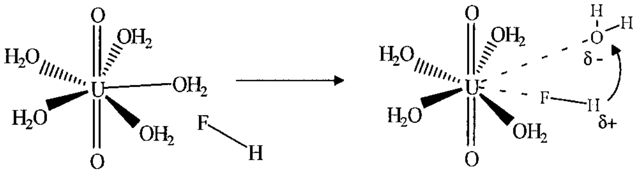

Figure 5. Mechanism for the exchange reaction between UO_2^{2+}(aq) and HF.

fore, k_I, are approximately 1.7 times smaller in deuterium oxide than in water,[33] while K_{os} calculated from the Fuoss equation is a few percent higher in D_2O than in H_2O.[34] Hence, this mechanism is expected to result in a slower rate of substitution in D_2O than in H_2O, as experimentally observed for Mg(II) and lanthanides.[33–35] In the Eigen–Wilkins mechanism $k_{mn} = K_{os}k_{aq}$, where the value of k_{aq} may be estimated from the experimental values of k_{mn} and the estimated values of K_{os}. These values of k_{aq} are given in Table 1 and are in fair agreement with that estimated by Ikeda et al.,[28] except for $k_{3,4}$ and $k_{4,5}$. This deviation might be due to a different mechanism or to erroneous estimates of K_{os}. The rate constants $k_{3,HF}$ and k_{3,F^-} (and $k_{4,HF}$ and k_{4,F^-}) show the variation depending on the charge of the entering ligand, as expected from an Eigen–Wilkins mechanism; c.f. Table 1. It must be pointed out that the numerical coincidence with the results of Ikeda et al.[28] may be accidental because of the large differences between the solvent systems. The values of k_{aq}, deduced from bimolecular rate constants for the formation of various uranyl(2+) complexes studied by Hurwitz and Kustin,[32] are much smaller than those observed here, except for acetate, where the rate constant for the formation of the first complex is equal to 10^3 M^{-1} s^{-1}. It has been suggested[30] that the small rate constants are due to the formation of $(UO_2)_2(OH)_2^{2+}$. The rate constants for the formation of uranium(VI)–diphosphonate complexes[36] are approximately 7×10^3 M^{-1} s^{-1}, i.e., closer to the values obtained in the fluoride system. Hence, there is some experimental information indicating that the rate of complex formation is not strongly dependent on the entering ligand, as expected from an Eigen–Wilkins mechanism.

The exchange reactions involving DF/HF are faster in D_2O than in H_2O, indicating that they involve bonding of HF/DF, as indicated in Figure 5. A proton transfer from $U\cdots F\cdots H^{\delta+}$ to $U\cdots OH_2$ (or $U\cdots F^-$) is consistent with a "reverse" isotope effect, because D_2O is a stronger base than H_2O (and F^- binding D^+ stronger than H^+). At the same time the difference in acid strength between the coordinated ("stretched") $F\cdots H$ and $F\cdots D$ is expected to be much smaller than in the ground state. This type of proton transfer is facilitated by the small size of HF, which brings the proton close to both the metal ion and the leaving group.

Mechanism Involving Uranyl–Fluoride Bond Breaking in the Rate Determining Step. We have estimated the influence of n_F and n_{H_2O} on the experimental rate constants from the following expression, assuming five exchangeable equatorial ligands and uranium–water bond breaking faster than for uranium–fluoride:

$$k_{int} = k_{mn}/(K_{os}n_F n_{H_2O}) \tag{34}$$

k_{int} is the "intrinsic" rate constant for the various exchange reactions, where the difference in electrostatic effects and the number of donor/acceptor sites have been corrected for. The values of k_{int} are given in Table 1. If the rate determining step is the dissociation of UO_2–F, rather than the dissociation of UO_2–OH_2, we have $k_f \approx (4 \times 10^4) \approx 4 \times 10^9$ M^{-1} s^{-1} for the bimolecular rate constant for the formation of UO_2F^+, which seems too large in comparison with the experimental values for other ligands. Hence, this mechanism is less plausible than the previous one.

Magnitude of $k_{3,4}$, $k_{4,5}$, $k_{4,HF}$, and $k_{5,HF}$. The rate constants $k_{3,4}$, $k_{4,5}$, $k_{4,HF}$, and $k_{5,HF}$ are much larger than expected for the proposed Eigen–Wilkins mechanism. These exchange reactions involves at least one reactant, containing no, or only one, coordinated water. The rate constant for the exchange reaction

$$UO_2F_4^{2-} + {}^*F^- \rightleftharpoons UO_2{}^*F_4^{2-} + F^- \tag{35}$$

is in good agreement with the value reported by Tomiyasu et al.,[9] $k_{4,F^-} = 6.96 \times 10^3$ M^{-1} s^{-1}. Tomiyasu et al. also discuss the exchange reaction

$$UO_2F_5^{3-} + {}^*F^- \rightleftharpoons UO_2{}^*F_5^{3-} + F^- \tag{36}$$

for which they report $k_{5,F^-} = 33.4$ M^{-1} s^{-1}. This value is about 500 times smaller than expected from our estimate of $k_{5,HF}$ and $K_{os} \approx 4.7 \times 10^{-3}$ M^{-1} if the reaction follows an Eigen–Wilkins mechanism. We are at the moment exploring how the number of coordinated water molecules are affecting the rate and mechanism of fluoride exchange, by studying reactions of the type

$$L{-}UO_2(H_2O)_nF_m + H^*F/{}^*F^- \rightleftharpoons L{-}UO_2(H_2O)_n{}^*F_m + HF/F^- \tag{37}$$

where L is a bi- or tridentate ligand, n varies between 0 and 3, and m varies between 1 and 3; the charges have been left out for simplicity.

Tomiyasu et al.[9] report $\Delta S^‡ = -128$ J mol^{-1} K^{-1} for reaction 36, postulate an associative mechanism, and cite as their main arguments the negative activation entropy and that the exchange rate is not influenced by laser irradiation (488 nm), which might be expected to labilize the equatorial ligands.

Activation Parameters for the Exchange Reactions. Complex formation reactions between hard donors and acceptors are in general accompanied by large and positive entropy changes, indicating substantial changes in the solvation between reactants and products. The available activation entropies for many reactions of this type are also large and positive, as exemplified by data for the beryllium(II)-,[37] aluminum(III)-,[38] and iron(III)[39] –fluoride systems; $\Delta S^‡ = 83$ J mol^{-1} K^{-1} for the formation of $Al(H_2O)_5F^{2+}$, indicating a transition state close to the product. The negative entropy of activation for reaction 21 is unexpected and indicates the formation of an intermediate that does not involve any substantial change of hydration between the reactants and the transition state. This is reasonable, since a coordinated fluoride should not interact strongly with the "bulk" water. A similar suggestion has previously been made by Pouli and Smith[39] to explain the lower activation entropy for the reaction $Fe^{3+} + HF \rightleftharpoons FeF^{2+} + H^+$, as compared to $Fe^{3+} + F^- \rightleftharpoons FeF^{2+}$. For reactions involving HF, e.g., eq 23, the activation entropy is less negative than for reaction 21. This is in agreement with the findings for other reactions involving hard

---

(33) Silber, H.; Wehner, P. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1025.

(34) Saar, D.; Macri, G.; Petrucci, S. *J. Inorg. Nucl. Chem.* **1971**, *33*, 4227.

(35) Silber, H. B.; Farina, R. D.; Swinehart, J. H. *Inorg. Chem.* **1969**, *8*, 819.

(36) Hines, M. A.; Sullivan, J. C.; Nash, K. L. *Inorg. Chem.* **1993**, *32*, 1820.

(37) Baldwin, W. G.; Stranks, D. R. *Aust. J. Chem.* **1968**, *21*, 2161.

(38) Plankey, B. J.; Patterson, H. H. *Inorg. Chem.* **1989**, *28*, 4331.

(39) Pouli, D.; Smith, MacF. W. *Can. J. Chem.* **1960**, *38*, 567.

acceptors, e.g., reactions between Fe(III) and HF or F^{-} [39] and between Be(II) and HF.[37]

Conclusions

A common reaction mechanism is proposed for all of the dominating ligand exchange pathways in the current system. The mechanism involves a nucleophilic attack of fluoride, either from F^-/HF or $UO_2F_n^{2-n}$, on another fluoride complex $UO_2F_{n-1}^{2-(n+1)}$, followed by the breaking of the uranium−fluoride bond of the leaving fluoride, in an I_d interchange mechanism. For reactions involving HF/DF the exchange reaction is accompanied by a proton transfer from the entering to the leaving group.

Exchange reactions involving a complex with no, or only one, coordinated water have much higher rate constants than expected from an Eigen−Wilkins mechanism.

An alternative mechanism, where the breaking of the uranium−fluoride bond is the rate determining step, was rejected because it results in an estimated value for the rate of formation of UO_2F^+ that is unexpectedly large ($k_f \approx 10^9$ M $^{-1}$ s^{-1}). This mechanism is also more difficult to reconcile with the observed H/D isotope effects.

Acknowledgment. The financial support of the Swedish Natural Science Research Council (NFR) is gratefully acknowledged. We also thank Professor André Merbach, University of Lausanne, for providing experimental data on HF prior to publication. We have had many fruitful discussions with our friends Imre Tóth and István Bányai, for which they are gratefully acknowledged.

Supporting Information Available: Figures with species distribution diagrams for the solutions used expansion of Figures 1c and 2c, Eyring plots of the temperature dependence of $k_{0,1}$ and $k'_{0,\mathrm{HF}}$, plot of the dependence of $k(\mathrm{obs})_{1,\mathrm{H}^+}$ on the total hydrogen ion concentration, ^{17}O NMR spectra at $R = 0.5$ and $U_{\mathrm{tot.}} = 50$ mM in 1 M $HClO_4$ as a function of temperature and ^{17}O NMR spectra (a) at $R = 0.4$ and $U_{\mathrm{tot.}} = 10$ mM and (b) at $R = 0.1$ and $U_{\mathrm{tot.}} = 50$ mM, $T = -5$ °C (12 pages). Ordering information is given on any current masthead page.

IC951140Q