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On the Mechanism of Oxygen Exchange Between Uranyl(VI) Oxygen and Water in Strongly Alkaline Solution as Studied by ^{17}O NMR Magnetization Transfer

Zoltán Szabó* and Ingmar Grenthe

School of Chemical Science and Engineering, Department of Chemistry, Royal Institute of Technology (KTH), S-10044 Stockholm, Sweden

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The mechanism, rate constant, and activation parameters for the exchange between uranyl(VI) oxygen and water oxygen in tetramethyl ammonium hydroxide solution, TMA−OH, have been determined using ^{17}O NMR magnetization transfer technique. In the concentration range investigated, the predominant complex is $UO_2(OH)_4{}^{2-}$. The experimental rate equation, rate = $k_{ex}[TMA{-}OH]_{free}[U(VI)]^2_{total}$ indicates that the exchange takes place via a binuclear complex or transition state with the stoichiometry $[(UO_2(OH)_4{}^{2-})(UO_2(OH)_5{}^{3-}]$. The rate-determining step most likely takes place between the axial “yl” oxygens and the equatorial hydroxides. The experimental Gibbs energy of activation, $\Delta G^{\ddagger} = 60.8 \pm 2.4$ kJ/mol is in good agreement with the value, $\Delta A^{\ddagger} \approx \Delta G^{\ddagger} = 52.3 \pm 5.4$ kJ/mol, found by Bühl and Schreckenbach in a recent Car−Parrinello molecular dynamics study, indicating that their proposed “shuttle” mechanism may be applicable also on the proposed binuclear transition state.

Introduction

We have previously studied the exchange between uranyl(VI) oxygen and water oxygen in acid solution[1a] and deduced rate constants, the mechanism and activation parameters for the reaction; in this study, we also investigated the exchange in 3.5 M tetramethyl ammonium hydroxide (TMA−OH), repeating a previous study by Clark et al.[1b] Our conclusion from the latter study, based on the observation that the uranyl ^{17}O NMR signal which did not change with time, was that there was no exchange in this system. This interpretation was erroneous because we did not analyze the enrichment in the uranyl oxygen peak—in fact the test solution we used was in isotope equilibrium with the solvent, and accordingly, there was no change in the ^{17}O signal with time. With this communication we want to correct this mistake, at the same time, we will broaden the study by determining the stoichiometric reaction mechanism, the rate constants, and the activation parameters for the exchange reaction. This information is not available from the study by Clark et al., as their exchange experiments were made at a single total concentration of U(VI) and TMA−OH. We studied the “yl” exchange over a range of U(VI) and TMA−OH concentrations by using ^{17}O NMR inversion−transfer experiments. This was done by selective inversion of the ^{17}O water peak, as described in the Experimental Section. This ^{17}O NMR technique does not seem to have been used previously because of limitations due to the fast longitudinal relaxation of the quadrupolar oxygen.

The constitution and structure of the hydroxide complex in strongly alkaline solution has been studied since 1998 using different experimental and quantum chemical methods[1] and is of key importance for the interpretation of the kinetic data in the present study. Extended X-ray absorption fine structure (EXAFS)[1b−d] has been used to suggest the stoichiometry of the complex in solution, but despite very similar results for the U − OH bond length, the groups involved have drawn different conclusions on the constitution; Clark et al.[1b] suggest $UO_2(OH)_5{}^{3-}$ based on additional information on the hydroxide concentration dependence of UV−vis and luminescence spectra, but they also suggested the formation of an additional complex at lower temperature. The authors of refs 1a, 1c, and 1e suggest the stoichiometry $UO_2(OH)_4{}^{2-}$, based on comparison of the solution EXAFS with solid-state data[1b] and additional quantum chemical information.[1c,e,f]

Moll et al.[1d] studied the constitution of the complexes formed in a mixed water/methanol solvent in 1 and 3 M TMA−OH using ^{17}O NMR spectroscopy and noted the appearance of a new peak at the higher TMA−OH. Using peak deconvolution, they estimated an equilibrium

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*Corresponding author. E-mail: zoltan@kth.se.

[1] (a) Szabó, Z.; Grenthe, I. *Inorg. Chem.* **2007**, *46*, 9372–9378. (b) Clark, D. L.; Conradson, S. D; Donohoe, R. J.; Keogh, D. W.; Morris, D. E.; Palmer, P. D.; Rogers, R. D.; Tait, C. D. *Inorg. Chem.* **1999**, *38*, 1456–1466. (c) Wahlgren, U.; Moll, H.; Grenthe, I.; Schimmelpfennig, B.; Maron, L.; Vallet, V.; Gropen, O. *J. Phys. Chem. A* **1999**, *103*, 8257–8264. (d) Moll, H.; Reich, T.; Szabó, Z. *Radiochim. Acta* **2000**, *88*, 411–415. (e) Vallet, V.; Wahlgren, U.; Schimmelpfennig, B.; Moll, H.; Szabó., Z.; Grenthe, I. *Inorg. Chem.* **2001**, *40*, 3516–3525. (f) Schreckenbach, G.; Hay, P. J.; Martin, R. L. *Inorg. Chem.* **1998**, *37*, 4442–4451.

Table 1. Measured and Calculated Kinetic Data, Temperatures, and Chemical Composition of the Test Solution Used

sample	$[UO_2^{2+}]_{tot}$ [M]	$[TMA-OH]_{tot}$ [M]	$[TMA-OH]_{free}$[a] [M]	temp [K]	line width UO_2^{2+} [Hz]	line width water [Hz]	$k_{(obs)}$[b] $[s^{-1}]$	$k_{(obs)}$[c] $[s^{-1}]$	k[d] $[M^{-2}s^{-1}]$	$1/T_1$ water $[s^{-1}]$
A	0.0315	2.91	2.78	298	17	157	22	32	251	365.5
				308	20	130	38	42	433	275.1
				318	26	105	60	60	684	205.2
				328	36	83	95	92	1083	161.8
				338	51	66	145	139	1653	128.6
B/1	0.0355	1.15	1.00	328	16	66	35	29	978	94.6
B/2	0.0305	1.81	1.68	328	21	65	55	45	1068	113.5
B/3	0.0314	2.38	2.25	328	32	76	75	79	1059	139.4
B/4	0.0315	2.91	2.78	328	36	83	95	92	1083	161.8
C/1	0.0314	2.38	2.25	328	22	72	75	48	1059	152.7
C/2	0.0784	2.38	2.06	328	59	105	160	164	987	151.0
C/3	0.0986	2.38	1.98	328	69	119	210	196	1072	151.4
C/4	0.120	2.38	1.89	328	82	135	255	236	1113	151.1
1 M HNO_3	0.126	–	–	328	6.7	26	–	–	–	75.5 (water) 2.97 (uranyl)
3.5 M TMA–OH	0	3.5	3.5	328	–	64	–	–	–	192.3

[a] Calculated by the assumption that $UO_2(OH)_4^{2-}$ is the dominating species in the test solutions. [b] Calculated from the inversion–transfer experiments. [c] Calculated from the line width of the uranyl signal (assuming a 6.7 Hz line width for the uranyl signal in the absence of chemical exchange in all experiments). [d] Calculated by using the $k_{(obs)}$ values from the inversion–transfer experiments.

constant, *K*, for reaction 1 to 0.4 M^{-1} in the mixed solvent at 258 K.

$$UO_2(OH)_4^{2-} + OH^- \rightleftarrows UO_2(OH)_5^{3-} \qquad (1)$$

As this experiment was made at a single total concentration of uranium(VI), they could not determine the nuclearity of the complex formed and assumed that it was mononuclear. The equilibrium constant must be much lower than this in the pure water solvent in order to be consistent with the EXAFS data. This seems likely as equilibrium constants in mixed water/methanol media are usually larger than in pure water.

Since the stoichiometry of the complex at high TMA–OH concentration is of key importance for the mechanistic interpretation of the "yl" exchange reaction, we redetermined the value of *K* for reaction 1 in a mixed water/methanol medium at three different uranium concentrations in 3 M TMA–OH at 258 K in order to clarify the constitution of the complexes formed.

Experimental Section

Chemicals and Sample Preparation. All test solutions were prepared using double-distilled water from $UO_2(NO_3)_2 \cdot 6\,H_2O$ (from Merck) and $(CH_3)_4N-OH \cdot 5H_2O$, tetra-methyl ammonium hydroxide (from Aldrich). A 1.55 M ^{17}O-enriched uranyl(VI) nitrate stock solution was prepared by dissolving 0.1995 g of uranyl(VI) nitrate in 0.2018 g of ^{17}O-enriched water (29 atom % enrichment, from ISOTEC), followed by UV irradiation overnight. This resulted in an isotope enrichment of 22.6% in the stock solution.

The equilibrium constant *K* was determined in test solutions using three different total concentration of uranium(VI) 50, 100, and 150 mM, all at a total concentration of TMA–OH equal to 3.0 M. The experiments were made as described in ref 1d at 258 K using a methanol solvent with 5% deuterated methanol for lock signal. As the solid TMA–OH contained five waters of crystallization, the test solutions had a water concentration of 15 M.

The exchange experiments were made in water using three sets of test solutions, denoted A, B, and C in Table 1. From previous experience we knew that an isotope enrichment of 2–4% resulted in a satisfactory signal-to-noise ratio within reasonable experimental time for uranyl concentrations about 30 mM, in the investigated temperature range. All the test solutions were prepared to satisfy this requirement. The various test solutions were prepared as follows: the uranium(VI) concentration was changed, either by using the ^{17}O enriched uranium–nitrate stock solution or by adding solid uranyl–nitrate. The TMA–OH concentration was changed, either by adding solid TMA–OH to the sample or by adding water (with or without ^{17}O enrichment). In this way we could keep the total uranyl concentration in test solution B and the TMA–OH concentration in test solution C approximately constant.

NMR Measurements. The ^{17}O NMR spectra were recorded on Bruker Avance-500 (67.8 MHz) and DRX-400 (54.2 MHz) spectrometers in 10 mm NMR tubes in H_2O without lock, using normal broadband probe heads. We measured the samples without any D_2O in order to avoid any isotope effects. The signal of tap water measured at 298 K was used as chemical shift reference. The probe temperature was measured by a calibrated Pt-100 resistance thermometer and adjusted using a Bruker Eurotherm variable temperature control unit. The selective magnetization transfer experiments were performed in two-dimensional (2D) fashion using a home-written pulse program. Selective inversion of the water signal was performed using 0.5 (DRX-400) or 1 ms (Avance-500) Gaussian pulses. The delays between the 180° selective pulse and the 90° hard pulse were varied 18–22 times between 0.5 ms and 0.2 s. A relaxation delay of 0.6 s was used. In order to obtain a satisfactory signal-to-noise ratio within one series of the experiment, we varied the number of collected scans in accordance with the ^{17}O enrichment and the total uranyl ion concentration of the test solutions. Usually 760–2600 and 16–64 scans were collected for the uranyl and the water signals, respectively. This resulted in total experimental times of 3.5–13 h and 10–40 min, respectively. In order to make the experimental data comparable, we normalized all spectra to the signal intensity from 1024 collected scans. We noticed a significant transfer of magnetization on the uranyl signal at 328 K, therefore, this temperature was used to study the concentration dependence of the rate of exchange.

Inversion–Transfer Experiments and Data Treatment. One-dimensional (1D) inversion–transfer experiments[2] provide information on the exchanging system if the rate is too slow to

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[2] (a) Orrell, K. G.; Šik, V.; Stephenson, D. *Prog. Nucl. Magn. Reson. Spectrosc.* **1990**, *22*, 141. (b) Sandström, J.; *Dynamic NMR Spectroscopy*; Academic Press: London, 1982. (c) Forsén, S.; Hoffman, R. A. *J. Chem. Phys.* **1963**, *39*, 2892.

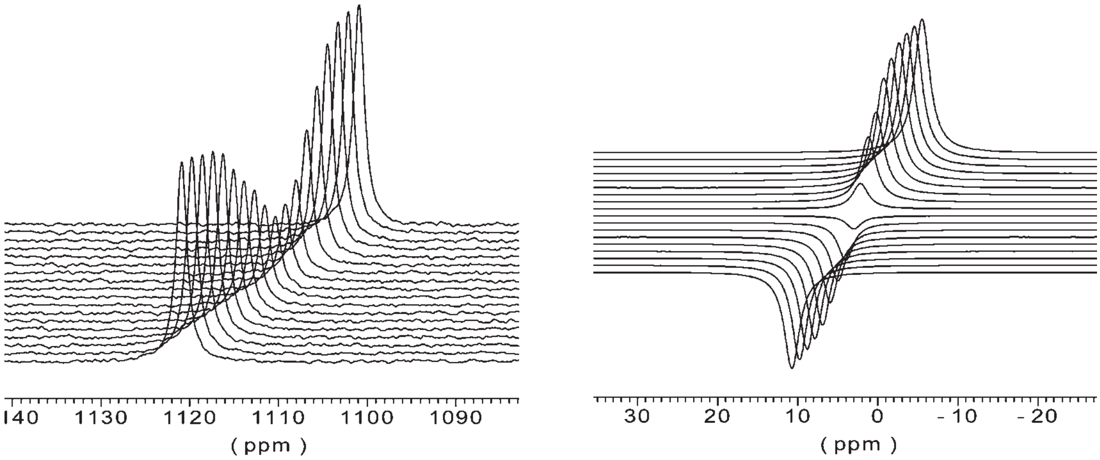

Figure 1. Stacked plots of the ^{17}O NMR spectra of the uranyl "yl" oxygen (left) and water (right) after selective inversion of the water signal as a function of increasing delays between the selective inversion pulse and the nonselective observation pulse ($[\mathrm{UO_2}^{2+}]_{\mathrm{total}}$ = 78.4 mM, $[\mathrm{TMA{-}OH}]_{\mathrm{total}}$ = 2.38 M, 328 K, test solution C/2). We used 2600 and 64 scans for the uranyl and water signals, respectively, with 18 delays incremented between 0.0005 and 0.2 s, which resulted in ca. 13 h and 20 min experimental times, respectively.

affect the line shape (but comparable with the reciprocal value of the longitudinal relaxation time, $1/T_1$, of the exchanging species). In this type of experiment, inverting one of the peaks using a 180° selective pulse (inversion−transfer) and then observing all of the peaks by a delayed (t) 90° hard pulse, the intensities of the signals depend on the longitudinal relaxation rate ($1/T_1$) of the exchanging species, on the exchange rates between the sites, and on the variable delay (t) value. The desired kinetic information can be calculated from the time dependence of the signal intensities by a nonlinear fitting procedure using a MATLAB[3] program written for the purpose, using the Bloch−McConnell equations, modified for the transfer of magnetization by chemical exchange,[4], eq 2:

$$d[M_{i(t)} - M_{i(\infty)}]/\mathrm{dt} = \mathbf{R}[M_{i(t)} - M_{i(\infty)}] \qquad (2)$$

where $M_{i(t)}$ and $M_{i(\infty)}$ are the z-magnetization of site i at time t and at equilibrium, respectively. **R** is the rate matrix with the exchange rates $k_{i,j}$, ($i \neq j$) as off-diagonal elements and the sum of the exchange rates $k_{j,i}$ and the relaxation rates $(1/T_1)_i$ ($j \neq i$) as the diagonal elements. For exchange between more than two sites, eq 1 is written as

$$M_{i(t)} = M_{i(\infty)} + \exp(Rt)[M_{i(t)} - M_{i(\infty)}] \qquad (3)$$

The solution after diagonalization of **R** by means of $\mathbf{R} = \mathbf{X\Lambda X}^{-1}$, (**X** is the eigen-vector matrix, $\mathbf{X}^{-1}$ its inverse, and $\mathbf{\Lambda}$ the diagonal eigen-value matrix), is

$$M_{i(t)} = M_{i(\infty)} + \sum_{j=1}^{n} c_{ij} \exp(-\lambda_j t) \qquad (4)$$

where

$$c_{ij} = \mathbf{X}_{ij} \sum_{k=1}^{n} (\mathbf{X}^{-1})_{jk}[M_{k(0)} - M_{k(\infty)}] \qquad (5)$$

λ_j are the elements of $\mathbf{\Lambda}$, and $M_{i(0)}$ is the initial magnetization of the site i.

We have previously used ^{1}H-, ^{19}F-NMR inversion−transfer experiments to study both intra- and intermolecular ligand exchange reactions in various uranium(VI) systems.[5] As detailed above, this method can only be applied if the exchange rate(s) and the longitudinal relaxation rates ($1/T_1$) of the exchanging nuclei have the same order of magnitude. Since preliminary experiments indicated very fast oxygen exchange, we expected that ^{17}O NMR inversion−transfer experiments could be applied in the present system, where the longitudinal relaxation is fast due to the quadrupolar ^{17}O nucleus. To the best of our knowledge this is the first selective ^{17}O NMR inversion−transfer experiment reported.

In order to avoid distortion of the spectra due to the very large chemical shift difference between the uranyl and the water signals (ca. 1110 ppm, depending on the temperature and the composition of the test solutions), two series of experiments were performed using a 100 ppm spectral window around the investigated signals. By inverting the water signal in both experiments, we observed the uranyl signal in the first experiment and the water signal in the second as shown in Figure 1.

In some of the inversion−transfer experiments we also inverted the uranyl signal. However, due to the very large differences in the intensity of the exchanging sites (the ratio varied from 400 to 900 between the different experiments), the inversion of the uranyl signal had no observable effect on the water signals. The change in the absolute values of the intensity of the uranyl signal, in comparison to absolute value of the water signal, is very small, cf. Figure 2. Because of this small intensity change, the exchange rate cannot be treated as variable and cannot be calculated by our computer program. We had instead to use the exchange rate as a constant in the rate matrix that was varied in several steps until the agreement between observed and calculated data were judged to be satisfactory, cf. Figure 2.

The additional variables used in this fitting procedure were the initial and the equilibrium magnetizations and the longitudinal relaxation rate ($1/T_1$) for water. The pseudo-first-order rate constants ($k_{\mathrm{(obs)}}$) resulting from the best fit and the calculated values for the latter are listed in Table 1. For comparison, we measured the corresponding relaxation rates in 1 M $\mathrm{HNO_3}$ and 3.5 M TMA−OH. The experiments show that the longitudinal relaxation rate of water increases with the TMA−OH concentration and decreases with temperature, however, there is no change with the uranyl concentration in the concentration range studied.

Since the exchange between the two sites was slow on the actual ^{17}O chemical shift time scale, we also calculated the

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[3] *MATLAB for Windows*; 4.2c ed.; Mathworks, Inc.: Natick, MA, 1994.

[4] Led, J. J.; Gesmar, J. *J. Magn. Reson.* **1982**, *49*, 444.

[5] (a) Szabó, Z.; Glaser, J.; Grenthe, I. *Inorg. Chem.* **1996**, *35*, 2036–2044. (b) Szabó, Z.; Aas, W.; Grenthe, I. *Inorg. Chem.* **1997**, *36*, 5369–5375. (c) Aas, W.; Szabó, Z.; Grenthe, I. *J. Chem. Soc., Dalton Trans.* **1999**, 1311–1317. (d) Szabó, Z. *J. Chem. Soc., Dalton Trans.* **2002**, 4242–4247.

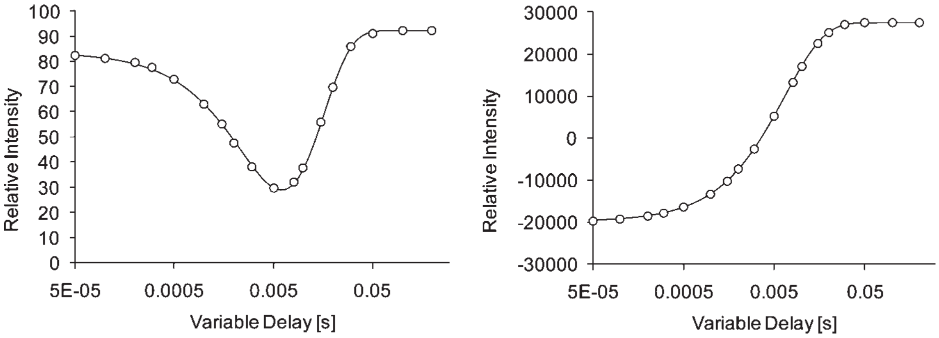

Figure 2. Plots of peak intensities of the inverted water (right) and the uranyl signal (left) against the variable delays from the ^{17}O NMR magnetization transfer experiments shown in Figure 1. The solid lines are generated by a nonlinear fitting procedure of the experimental data as detailed in the text.

pseudo-first-order rate constants ($k_{(obs)}$) from the line width of the uranyl signal using eq 6:

$$k_{(obs)} = \pi(\Delta\nu_{1/2} - \Delta\nu^{o}_{1/2}) \qquad (6)$$

in which $\Delta\nu_{1/2}$ is the half-width of the exchange broadened uranyl signal, and $\Delta\nu^{o}_{1/2}$ is the half-width of the uranyl signal in the absence of chemical exchange. The latter depends on the transverse-relaxation rate ($1/T_2$) and the field inhomogeneity. The calculated values are given in Table 1, and a comparison with the values from inversion−transfer experiments is shown as Supporting Information, Figure S3. These figures clearly demonstrate that the inversion−transfer experiments resulted in the kinetic parameters with much higher accuracy. Therefore, the following discussion and further calculations are based on these data.

Results and Discussion

Two preliminary ^{17}O NMR experiments were performed using test solutions of 37.8 mM uranyl−nitrate in 3.5 M TMA−OH and 1 M HNO_3, respectively, prepared using the ^{17}O isotope-enriched uranyl stock solution. A comparison of the integrals of the uranyl "yl" oxygen signals in the two solutions unambiguously showed that the isotope exchange in 3.5 M TMA−OH is very fast, resulting in isotope equilibrium shorter than the time between the sample preparation and the time for recording the spectrum (ca. 30 min). The isotope equilibrium in 3.5 M TMA−OH was confirmed by the measured ratio between the water and the "yl" oxygen signals, 548, for an isotope enrichment of 0.7%, which agrees well with the calculated value of 594 from the mol ratio between uranyl oxygen and water. After these preliminary measurements, experiments were performed to determine how the rate depended on the uranium and hydroxide concentrations. This was made by using test solutions where the hydroxide concentration was varied at constant uranium concentration, test solution B, and where the uranium concentration was varied at constant hydroxide concentration, test solution C. The composition of the test solutions, the experimental details, and the calculated kinetic parameters are given in Table 1. The experimental results from test solutions B and C are shown in Figures 3 and 4.

The pseudo-first-order rate constants in test solutions B and C are given by eqs 7 and 8:

$$k_{\text{obs}} = \frac{1}{[U_{\text{tot}}]} \times \frac{d[U_{\text{tot}}]}{\text{d}t} = k_{\text{B}}[\text{TMA}-\text{OH}]_{\text{free}} \qquad (7)$$

$$k_{\text{obs}} = \frac{1}{[U_{\text{tot}}]} \times \frac{d[U_{\text{tot}}]}{\text{d}t} = k_{\text{C}}[U_{\text{tot}}] \qquad (8)$$

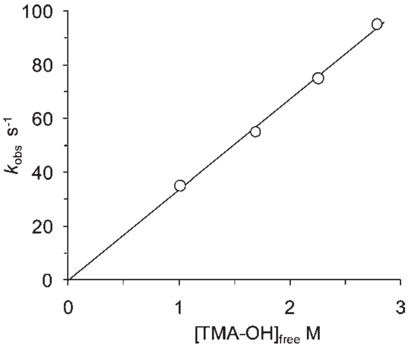

Figure 3. Plot of the experimental pseudo-first-order rate constant (k_{obs}) for the exchange between the uranyl "yl" oxygen and water against the equilibrium concentration of TMA−OH measured at 328 K. Linear regression of the data resulted in a slope of 33.8 ± 1.4 M^{-1} s^{-1} and an intercept of −0.3 ± 2.8 s^{-1} (see text for experimental details).

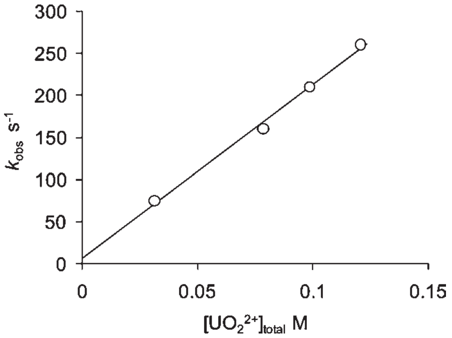

Figure 4. Plot of the experimental pseudo-first-order rate constant (k_{obs}) for the exchange between the uranyl "yl" oxygens and water against the total concentration of uranyl ion measured at 328 K. Linear regression of the data resulted in a slope of 2067 ± 108 M^{-1} s^{-1} and an intercept of 6.2 ± 9.6 s^{-1} (see text for experimental details).

The experimental slopes k_B and k_C are 33.8 ± 1.4 and 2067 ± 108 M^{-1} s^{-1}, respectively. The uncertainty is equal to the standard error in the linear regression using EXCEL.

The combination of eqs 7 and 8 gives the concentration dependence of the pseudo-first-order rate constant, eq 9:

$$k_{\text{obs}} = \frac{1}{[U_{\text{tot}}]} \times \frac{d[U_{\text{tot}}]}{\text{d}t} = k[\text{TMA}-\text{OH}]_{\text{free}}[U_{\text{tot}}] \qquad (9)$$

This gives $k_B = k[U_{\text{tot}}]$ and $k_C = k[\text{TMA}-\text{OH}]_{\text{free}}$, the k values for each experiment can be calculated and are given in Table 1, their average is 1055 ± 77 $M^{-2}s^{-1}$, where the uncertainty represents the largest deviation from the mean.

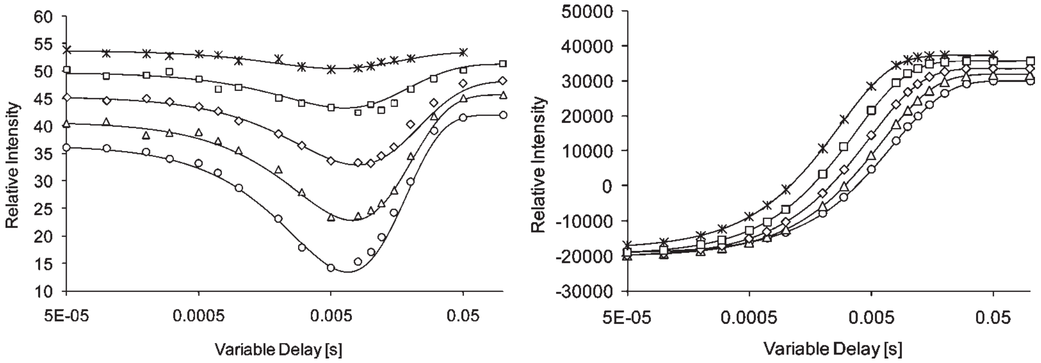

Figure 5. Plots of peak intensities against the variable delays from ^{17}O NMR magnetization transfer experiments measured at various temperatures to determine the activation parameters for the oxygen exchange between the uranyl "yl" oxygens and water. The curves show the intensity change of the inverted water (right) and the uranyl (left) signals. The temperatures from top to bottom are 298, 308, 318, 328, and 338 K. The intensities are given in arbitrary units that reflect the relative ratio of the exchanging sites. The solid lines are generated by a nonlinear fitting procedure of the experimental data, as detailed in the text ($[UO_2^{2+}]_{total}$ = 0.0315 M, $[TMA-OH]_{total}$ = 2.91 M).

Deduction of a Possible Stoichiometric Reaction Mechanism for the Exchange Reaction. The test solutions may contain two complexes, $UO_2(OH)_4^{2-}$ and $UO_2(OH)_5^{3-}$ that are in fast equilibrium with the equilibrium constant *K*, see eq 1.

Previous experimental data (EXAFS and spectroscopic data) indicate that the *K* is small and that $[UO_2(OH)_4^{2-}]$ is the predominant complex in the test solutions, hence $U_{tot} = [UO_2(OH)_4^{2-}]$.

The experimental rate equation is then:

$$\frac{d[U_{tot}]}{dt} = \frac{d[UO_2(OH)_4^{2-}]}{dt} = k[TMA-OH]_{free}[U_{tot}]^2 = k[TMA-OH]_{free}[UO_2(OH)_4{}^{2-}]^2 \qquad (10)$$

The hydroxide reaction order in the experimental rate equation shows that only eq 11, obtained by using eq 1, is consistent with the experimental observations.

$$\frac{d[U_{tot}]}{dt} = \frac{d[UO_2(OH)_4^{2-}]}{dt} = k[TMA-OH]_{free}[U_{tot}]^2 = k[UO_2(OH)_4{}^{2-}][UO_2(OH)_5{}^{3-}]/K \qquad (11)$$

This rate equation suggests the following stoichiometric mechanism:

$$UO^*{}_2(OH)_4{}^{2-} + OH^- \rightleftarrows UO^*{}_2(OH)_5{}^{3-} \qquad (12)$$

that is followed by the rate determining step:

$$(UO^*{}_2(OH)_4{}^{2-})(UO^*{}_2(OH)_5{}^{3-}) + H_2O \rightleftarrows (UO_2(OH)_4{}^{2-})(UO_2(OH)_5{}^{3-}) + H_2O^* \qquad (13)$$

where the star indicates the ^{17}O-enriched sites. As eq 12 is very fast, we can assume that the rate determining reaction is the exchange between the "yl" oxygen and the coordinated oxygen in the equatorial plane, which in turn are in fast exchange with water.

We will discuss if $(UO_2(OH)_4{}^{2-})(UO_2(OH)_5{}^{3-})$ is a binuclear complex or a transition state in the following section.

Determination of the Stoichiometry and Equilibrium Constant for the Complex Formed at High Hydroxide Concentration in a Mixed Methanol/Water Solvent. It was necessary to work at low temperature in order to "freeze out" the equilibrium between the different species known to exist in the test solutions, hence the use of methanol/water as a solvent; here we observed two peaks at 258 K, (see Supporting Information, Figure S4). As the water concentration is high (15 M), we have assumed that we have a very similar chemistry in the water and methanol/water solvents. We varied the total uranium concentration in order to decide if one of the peaks should be assigned to a binuclear complex, or not. The two peaks were deconvoluted, and their intensity ratio was determined to 43(3)/57(3), where the values within parentheses denote the deviation from the mean in the three experiments. This ratio corresponds to an equilibrium constant of 0.30 ± 0.05 M^{-1}, independent of the total concentration of uranium. The equilibrium constant agrees with the estimate by Moll et al.[1d] The fact that the equilibrium constant does not vary with the concentration of uranium(VI) shows that it refers to an equilibrium between two mononuclear complexes and that there is no evidence for the formation of significant amounts of a binuclear complex, consequently there only is a single transition state, $[UO^*{}_2(OH)_4{}^{2-})(UO^*{}_2(OH)_5{}^{3-}]^{\ddagger}$, along the energy–reaction coordinate pathway.

Determination of Activation Parameters. Test solution A was used to determine the temperature variation of the rates. As the equilibrium constant *K* is small, it is reasonable to assume that the predominant complex is $UO_2(OH)_4^{2-}$ in the temperature range used. The experimental rate data at the different temperatures are shown in Figure 5.

From the Eyring plot in Figure 6 we obtain $\Delta H_{ex}{}^{\ddagger} = 36.6 \pm 0.4$ kJ/mol and $\Delta S_{ex}{}^{\ddagger} = -75.8 \pm 1.2$ J/K·mol; the uncertainty corresponds to the standard error in the linear regression analysis using EXCEL. The activation parameters are composite quantities $\Delta H_{ex}{}^{\ddagger} = \Delta H(1) + \Delta H(12)^{\ddagger}$ and $\Delta S_{ex}{}^{\ddagger} = \Delta S(1) + \Delta S(12)^{\ddagger}$, where $\Delta H(1)$ and $\Delta S(1)$ refer to the equilibrium eq 12.

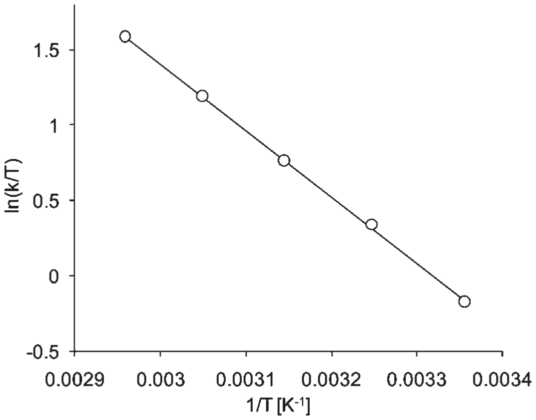

Figure 6. Eyring plot for the oxygen exchange between the uranyl "yl" oxygens and water measured at $[UO_2^{2+}]_{total}$ = 0.0315 M and $[TMA-OH]_{total}$ = 2.91 M. Linear fit of the data resulted in: $\Delta H_{ex}^{\ddagger}$ = 36.6 ± 0.4 kJ/mol and $\Delta S_{ex}^{\ddagger} = -75.8 \pm 1.2$ J/K·mol, where the errors are calculated from the linear regression.

Comparison with Previous Experimental and Theoretical Data. As mentioned in the introduction, there are three sets of EXAFS data, all of which agree with the U−OH bond distance: 2.22 ± 0.01 Å (Clark et al.);[1b] 2.24 ± 0.01 Å (Wahlgren et al.);[1c] 2.26_5 ± 0.01 Å (Moll et al.).[1d] The number of coordinated hydroxide ligands is very uncertain, 4.5 ± 0.5, and the authors give different suggestions for the stoichiometry of the predominant complex at high concentrations of TMA−OH. Clark et al.[1b] suggest $UO_2(OH)_5^{3-}$ based on the common five coordination in the equatorial plane, while Wahlgren et al.[1c] and Moll et al.[1d] suggest $UO_2(OH)_4^{2-}$ based on good agreement between the bond distances in the solid complex containing $UO_2(OH)_4^{2-}$ and the solution EXAFS data. In addition, the quantum chemical calculations by Wahlgren et al.[1c,e] suggest four-coordinated oxygen in the equatorial plane based on bond distances calculated for both the five-coordinated $UO_2(OH)_4(OH_2)^{2-}$ and $UO_2(OH)_5^{3-}$, the distances for the latter deviated significantly from the experimental values. The calculation in ref 1c refers to the SCF level in a gas phase and those in ref 1e to SCF values in a CPCM solvent. Clark et al.[1b] noted that room temperature UV−vis spectra change with the concentration of TMA−OH, however, they point out "there is no evidence in these absorption spectra for isosbestic points", as expected for an equilibrium between two species. Clark et al.[1b] also investigated emission spectra at liquid nitrogen temperatures of samples at different TMA−OH concentrations. They observed that the peak at 490 nm increased by approximately a factor of three for an increase in the TMA−OH concentration by a factor of three, indicating equilibrium between two emitting species at low temperature. The increase in intensity must be due to the formation of $UO_2(OH)_5^{3-}$, and we can use the intensity change as a measure of the ratio $[UO_2(OH)_5^{3-}]/[UO_2(OH)_4^{2-}]$ and the concentration of TMA−OH to estimate the equilibrium constant at liquid nitrogen temperature to approximately 1 M^{-1}. As there was no evidence for an equilibrium at room temperature from the UV−vis spectra, the equilibrium constant must increase with decreasing temperature, that is the reaction enthalpy $\Delta H(1)$ is negative. An equilibrium constant $K \approx 1$ at liquid nitrogen temperature and an enthalpy of reaction $\Delta H(1) \approx -4$ kJ/mol corresponds to an equilibrium constant at room temperature of 10^{-2} M^{-1}, consistent with the absence of an isosbestic point in the UV−vis spectra. At 258 K, the temperature used by Moll et al. and in the present study, the equilibrium constant is $\approx 10^{-1}$ M^{-1}, in fair agreement with the experimental observations. The activation parameters determined from the magnetization transfer experiments, $\Delta H_{ex}^{\ddagger}$ = 36.6 ± 0.4 kJ/mol and $\Delta S_{ex}^{\ddagger} = -75.8 \pm 1.2$ J/K·mol, are in good agreement with those determined by Clark et al.,[1b] $\Delta H_{ex}^{\ddagger}$ = 41 ± 1 kJ/mol and $\Delta S_{ex}^{\ddagger} = -75 \pm 17$ J/K·mol. The determination of K at different total concentrations of U(VI) shows that there is no experimental support for the formation of a binuclear complex $[(UO_2(OH)_4)(UO_2(OH)_5)]^{5-}$, such a complex is conceivable from a coordination chemical point of view, containing one bridging and eight terminal hydroxide ligands, resulting in the same pentagonal bipyramid geometry around the two uranium atoms. Macroscopic kinetics cannot provide the microscopic details about how the exchange takes place, however, an exchange between axial "yl" and equatorial OH^- ligands seems most reasonable. Bühl and Schreckenbach[6] have discussed the intimate mechanism of the exchange of oxygen between uranyl complexes in strongly alkaline solution and in solvent water, using Car−Parrinello molecular dynamics. Their mechanistic model, given as Scheme 1 in ref 6, discusses details in this type of exchange. This is based on exchange involving only the complex $UO_2(OH)_5^{3-}$ and with no evidence for a contribution from $UO_2(OH)_4^{2-}$. One should note that this modeling is based on an "infinite" dilute system, while our experimental data refer to moderately high concentrations. The studies are, therefore, not directly comparable, however it is of interest to note that their calculated Gibbs energy of activation at 320 K is $\Delta A^{\ddagger} \approx \Delta G^{\ddagger}$ = 52.3 ± 5.4 kJ/mol is in fair agreement with our value $\Delta G^{\ddagger}$ = 60.8 ± 2.4 kJ/mol calculated at the same temperature. Their proposed proton shuttle mechanism might, therefore, be applicable to a transition state with a "binuclear" stoichiometry. It is of interest to note that the "yl" exchange in acid solution takes place via a binuclear complex that is present in significant amounts in the test solutions studied. It would be of interest to explore if theory can be used to explore the details of this reaction.

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Supporting Information Available: Plots of peak intensities against the variable delays from ^{17}O NMR magnetization transfer experiments measured at various TMA−OH and uranium(VI) concentrations at 328 K (Figures S1 and S2). Plots of the experimental pseudo-first-order rate constant (k_{obs}) measured for the exchange between the uranyl "yl" oxygens and water against the equilibrium concentration of TMA−OH and the total concentration of uranyl ion (Figure S3). ^{17}O NMR peaks for the uranyl "yl" oxygens measured at various total uranium(VI) concentrations in 3 M TMA−OH in methanol at 258 K (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org

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