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Inorganic Chemistry Article

Reactivity of the “yl”-Bond in Uranyl(VI) Complexes. 1. Rates and Mechanisms for the Exchange between the *trans*-dioxo Oxygen Atoms in $(UO_2)_2(OH)_2^{2+}$ and Mononuclear $UO_2(OH)_n^{2-n}$ Complexes with Solvent Water

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The stoichiometric mechanism, rate constant, and activation parameters for the exchange of the “yl”-oxygen atoms in the dioxo uranium(VI) ion with solvent water have been studied using ^{17}O NMR spectroscopy. The experimental rate equation, $\vec{v} = k_{2obs}[UO_2^{2+}]_{tot}^2/[H^+]^2$, is consistent with a mechanism where the first step is a rapid equilibrium $2U^{17}O_2^{2+} + 2H_2O \rightleftharpoons (U^{17}O_2)_2(OH)_2^{2+} + 2H^+$, followed by the rate-determining step $(U^{17}O_2)_2(OH)_2^{2+} + H_2O \rightleftharpoons (UO_2)_2(OH)_2^{2+} + H_2{}^{17}O$, where the back reaction can be neglected because the ^{17}O enrichment in the water is much lower than in the uranyl ion. This mechanism results in the following rate equation $\vec{v} = d[(UO_2)_2(OH)_2^{2+}]/dt = k_{2,2}[(UO_2)_2(OH)_2^{2+}] = k_{2,2}{}^*\beta_{2,2}[UO_2^{2+}]^2/[H^+]^2$; with $k_{2,2} = (1.88 \pm 0.22) \times 10^4\ h^{-1}$, corresponding to a half-life of 0.13 s, and the activation parameters $\Delta H^{\ddagger} = 119 \pm 13$ kJ mol^{-1} and $\Delta S^{\ddagger} = 81 \pm 44$ J mol^{-1} K^{-1}. $^*\beta_{2,2}$ is the equilibrium constant for the reaction $2UO_2^{2+} + 2H_2O \rightleftharpoons (UO_2)_2(OH)_2^{2+} + 2H^+$. The experimental data show that there is no measurable exchange of the “yl”-oxygen in UO_2^{2+}, $UO_2(OH)^+$, and $UO_2(OH)_4^{2-}$/ $UO_2(OH)_5^{3-}$, indicating that “yl”-exchange only takes place in polynuclear hydroxide complexes. There is no “yl”-exchange in the ternary complex $(UO_2)_2(\mu\text{-}OH)_2(F)_2(oxalate)_2^{4-}$, indicating that it is also necessary to have coordinated water in the first coordination sphere of the binuclear complex, for exchange to take place. The very large increase in lability of the “yl”-bonds in $(UO_2)_2(OH)_2^{2+}$ as compared to those of the other species is presumably a result of proton transfer from coordinated water to the “yl”-oxygen, followed by a rapid exchange of the resulting OH group with the water solvent. “Yl”-exchange through photochemical mediation is well-known for the uranyl(VI) aquo ion. We noted that there was no photochemical exchange in $UO_2(CO_3)_3^{4-}$, whereas there was a slow exchange or photo reduction in the $UO_2(OH)_4^{2-}$ / $UO_2(OH)_5^{3-}$ system that eventually led to the appearance of a black precipitate, presumably UO_2.

Introduction

The first experimental study that shed some light on the kinetic lability of the uranyl(VI) bond dates back to 1949 when Crandall[1] used the exchange reaction $UO_2^{2+} + H_2{}^{18}O \rightleftharpoons U^{18}O_2^{2+} + H_2O$ to prepare ^{18}O-enriched uranyl ions to determine its stoichiometry. At the time it was unclear if the composition was UO_2^{2+} or $U(OH)_4^{2+}$; he noted that there was no significant exchange between $H_2{}^{18}O$ and the uranyl oxygen atoms over a period of 48 h in 0.10 M HCl. Gordon and Taube[2,3] investigated the same reaction with ^{18}O-enriched water and determined the rate equation and rate constant for the exchange using mass spectrometry. They also made the important observation that the reactivity of the “yl”-bond in UO_2^+(aq) was much larger than that in UO_2^{2+}(aq), a factor of at least 10^7 in 0.08 M $HClO_4$ and 3×10^9 in 1 M $HClO_4$. Clark et al.[4] studied the “yl”-exchange between $U^{17}O_2(OH)_4^{2-}$ and water in 3.5 M tetra-methyl ammonium hydroxide and

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concluded that there was a fast exchange with a rate constant $k_{283} = 18 \pm 6$ s^{-1}. This study is commented on in the Discussion. They suggested that the high rate was a result of the weakening of the "yl"-bond, as indicated by the experimentally observed increase in the U$-$O$_{yl}$ bond length between $UO_2(OH_2)_5^{2+}$ and $UO_2(OH)_4^{2-}$. Clark et al.[4] speculated on the electronic origin of this weakening and suggested that it might be partially due to the strong σ-donating ability of hydroxide ligands and also as a result of the competing participation of uranium 6d orbitals in both the U$-$O$_{yl}$ and U$-$OH π bonds. This theme has recently been explored by Ingram et al.; [5] a comparison of the energy-level diagrams of the uranyl orbitals and a population analysis in complexes with an increasing number of coordinated hydroxide ions reveals that, of the two effects invoked by Clark et al., only the σ-donating ability of the hydroxide ligands can explain the weakening of the "yl" bond. Burns et al.[6] have discussed how the basicity and lability of the uranyl oxo ligands are affected by the coordination of other strong donors in the equatorial plane of the uranyl(VI) complexes.

Additional information on "yl"-exchange was provided by Moll et al.[7] by noting that the ^{17}O NMR signal in test solutions containing ^{17}O-enriched uranyl(VI) was lost within 10 min in the pH range where uranyl hydroxide complexes are formed. A significantly slower loss in the signal was observed in the range where ternary polynuclear OH^-/SO_4^{2-} complexes were predominant; there was no loss of signal intensity in test solutions containing only binary sulfate complexes.

The rate equation for the exchange between "yl"-oxygen and water deduced in the study of Gordon and Taube,[2,3] (eq 1), indicates that the exchange between "yl"-oxygen and the water solvent takes place in the complex $UO_2(OH)^+$ and that there is no significant contribution to the exchange involving $UO_2(OH_2)_5^{2+}$, as shown by the rate equation:

$$\vec{v} = \frac{k_{obs}[UO_2^{\ 2+}]_{tot}}{[H^+]} \tag{1}$$

In a more recent study, Mashirov et al.[8] report a different rate equation (eq 2) for the exchange between ^{18}O-enriched uranyl and water:

$$\vec{v} = \frac{k_{2\mathrm{obs}}[UO_2^{\ 2+}]_{\mathrm{tot}}^{\ 2}}{[H^+]^2} + \sum_n \frac{k_{n,\mathrm{obs}}[UO_2^{\ 2+}]_{\mathrm{tot}}^{\ 2}}{[H^+]^m} \tag{2}$$

They suggest that the predominant exchange pathway in the pH range 1$-$3 involves the binuclear complex $(UO_2)_2(OH)_2^{2+}$ with some contribution from$(UO_2)_2(OH)_3^+$, whereas there is no measurable contribution from $UO_2(OH_2)_5^{2+}$. At higher pH, other polynuclear hydroxide complexes, for example, $(UO_2)_3(OH)_5^+ \equiv (UO_2)_2(O)(OH)_3^{2+}$ are formed[9] that might give a contribution to the rate of exchange.[8] Neither the study by Gordon and Taube nor the one by Mashirov et al. has discussed the mechanism of the exchange reaction.

We have previously used ^{17}O-enriched uranyl(VI) in combination with NMR spectroscopy to study equatorial ligand substitution reactions in uranyl(VI) systems with the ligands fluoride,[10] picolinate,[11] α-hydroxy-carboxylates,[12] amino-carboxylates[12] and glyphosate.[13] In these studies, we found no evidence for "yl"-exchange with the solvent within a time scale of 48 h. The test solutions used in these studies did not contain hydroxide complexes, suggesting that "yl"-exchange requires the presence of terminal and/or bridging hydroxide groups in the equatorial plane of the uranyl(VI) ion.

"Yl"-exchange can also be achieved photochemically[14] using UV irradiation of an acid aqueous solution of $U^{17}O_2^{2+}/H_2O$ or $UO_2^{2+}/H_2^{17}O$. Photochemical excitation may involve protonation of the "yl"-oxygen, forming $U^{17}OOH^{2+}$ through hydrogen abstraction from the water solvent[15] that could result in weakening of the "yl"-bond, facilitating the exchange with water. We have investigated if this is also the case in test solutions containing the complexes $U^{17}O_2(CO_3)_3^{4-}$ and $U^{17}O_2(OH)_4^{2-}/U^{17}O_2(OH)_5^{3-}$.

In the present study, we have measured rate constants and activation parameters for the "yl"-exchange in the $-\log[H^+]$ range 1$-$2 and on the basis of these data suggested a rate equation and a stoichiometric mechanism for the exchange. The exchange reaction can formally be described using eq (3)

$$\text{“}U^{17}O_2(aq)\text{”} + H_2O \rightleftharpoons \text{“}UO_2(aq)\text{”} + H_2{}^{17}O \tag{3}$$

"$U^{17}O_2(aq)$" denotes the sum of the various uranyl(VI) species present in the test solutions studied; the dominant species in the $-\log[H^+]$ range 1$-$2 is the aquo ion UO_2^{2+}. In our experiments, the back reaction in eq (3) can be neglected as the ^{17}O enrichment in the uranyl ion is much larger than that in the water solvent.

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Table 1. Experimental Data for the Exchange Reaction “$U^{17}O_2$” + $H_2O \rightleftharpoons$ “UO_2” + $H_2{}^{17}O$; Where “$U^{17}O_2$” Is the Total Concentration of Uranyl(VI) Species, $[UO_2{}^{2+}]_{tot}$[a]

$[UO_2{}^{2+}]_{tot}$ (M)	-log[H^+]	k_{obs} (h^{-1})	Temp (K)
0.0297	1.48	$(5.83 \pm 0.25) \times 10^{-3}$	298
	1.56	$(1.99 \pm 0.16) \times 10^{-2}$	
	1.90	$(1.78 \pm 0.04) \times 10^{-1}$	
	2.04	$(2.20 \pm 0.02) \times 10^{-1}$	
	2.64	(1.09 ± 0.03)	
0.0424	1.67	$(9.65 \pm 0.18) \times 10^{-2}$	298
	1.82	$(1.82 \pm 0.07) \times 10^{-1}$	
	1.95	$(2.73 \pm 0.02) \times 10^{-1}$	
	2.75	(2.34 ± 0.05)	
0.0636	1.90	$(1.02 \pm 0.04) \times 10^{-2}$	298
	2.36	$(6.44 \pm 0.07) \times 10^{-1}$	
	2.55	$(9.14 \pm 0.07) \times 10^{-1}$	
0.0434	2.06	$(4.86 \pm 0.07) \times 10^{-1}$	298
		$(6.98 \pm 0.04) \times 10^{-2}$	288
		$(3.10 \pm 0.03) \times 10^{-2}$	282

[a] The constants k_{obs} have been calculated from eq (4).

A possible reaction mechanism may involve protonation of the “yl”-oxygen and a major electron rearrangement in the “yl” bonds as indicated by Schreckenbach et al.[16] In a following communication, we will discuss the intimate mechanism of the exchange reaction and the relationship between the lability of the trans-oxygen atoms in uranyl(VI) complexes and the chemical bonding in the coordination sphere of uranium using quantum chemical ab initio calculations.

Experimental Methods

Chemicals and Test Solutions. A 1.998 M stock solution of ^{17}O-enriched uranyl(VI) perchlorate was prepared by the dilution of 2.724 g of a 2.997 M stock solution of uranyl(VI) perchlorate with 0.657 g of ^{17}O-enriched water (29 atom % enrichment from ISOTEC), followed by UV irradiation over night. The isotope enrichment of $UO_2{}^{2+}$ was approximately 10%, and that of the water was 0.2% in the test solutions used. The 2.997 M stock solution had an excess of H^+ equal to 0.197 M, as determined by cation exchange analysis. All of the test solutions were prepared from the 1.998 M stock solution using double-distilled water, analytical-grade perchloric acid, sodium perchlorate, and tetra-methyl ammonium hydroxide (TMA-OH) from Aldrich. The composition of the various test solutions used to investigate the “yl”-exchange in the binary U(VI)−water system at $1.48 \leq -\log[H^+] \leq 2.75$ is given in Table 1. The proton concentration of the samples was adjusted by the addition of perchloric acid or sodium hydroxide solutions. The actual value was calculated from the measured $-\log[H^+]$ corrected for the “Irving factor” in the working media.[17] The $-\log[H^+]$ values of the test solutions measured before and after each NMR experiment agreed within ±0.02 logarithmic units.

“Yl”-Exchange in 3.5 M TMA-OH. In a previous experiment,[18] we noted that there was no measurable exchange at 25 °C. The experiment was therefore repeated and followed at three different temperatures, −5, 25, and 50 °C. The peaks for the 25 °C measurements over a period of 2600 h are shown in Supporting Information part a of Figure S1. The test solution of 50.0 mM U(VI) in 3.5 M TMA-OH was prepared by adding 0.20 mL of the $U^{17}O_2{}^{2+}$ perchlorate stock solution to 8 mL of a 3.5 M TMA-OH solution and then removing the precipitate of TMA-perchlorate by filtration. To investigate if there is a photochemical exchange pathway, another test solution was irradiated by UV light, and the result is shown in Supporting Information part b of Figure S1.

“Yl”-Exchange in $(UO_2)_2(\mu\text{-}OH)_2F_2(Oxalate)_2{}^{4-}$. A test solution containing about 4% of the total amount of uranium as the complex $(UO_2)_2(\mu\text{-}OH)_2F_2(\text{oxalate})_2{}^{4-}$ was prepared in order to study if “yl”-exchange can take place in a complex with two bridging hydroxides but no coordinated water in the first coordination sphere. The composition was: 20.0 mM U(VI), 120.0 mM NaF, and 40.0 mM Na_2Oxalate, prepared by using reagents of analytical grade; the pH of the solution was 7.76. The test solution of $(UO_2)_2(\mu\text{-}OH)_2F_2(\text{oxalate})_2{}^{4-}$ was kept for a period of 1 week in darkness before measuring the ^{17}O and ^{19}F NMR spectra.

Photochemical “yl”-Exchange in $UO_2(CO_3)_3{}^{4-}$. To test if the “yl”-oxygen can be photochemically exchanged with the water solvent in $UO_2(CO_3)_3{}^{4-}$ that does not contain water in the first coordination sphere, we prepared a test solution in which more than 99.9% of the U(VI) was present as $UO_2(CO_3)_3{}^{4-}$. The composition of the solution was: $[U(VI)] = 20.0$ mM, $Na_2CO_3 = 109$ mM, pH $= 10.15$, prepared from the stock solution of ^{17}O-enriched $UO_2{}^{2+}$ and solid water free sodium carbonate. Carbonate was used as a ligand because it cannot be photochemically oxidized. The test solution was illuminated with UV light for a period of 20 h, after which the ^{17}O NMR spectrum was recorded; there was no measurable exchange of the “yl”-oxygen with the solvent.

NMR Measurements and Sample Preparation. The ^{17}O NMR spectra (67.8 MHz) were recorded on a Bruker DMX500 spectrometer (11.7 T) in H_2O using a $NaClO_4$ ionic medium at a constant sodium concentration, $[Na^+] = 1.00$ M. The test solutions were measured at 25 °C, using a 5 or 10 mm normal broadband NMR probe head without lock and tap water as the reference. The probe temperature was measured by a calibrated Pt-100 resistance thermometer and adjusted using a Bruker Eurotherm variable-temperature control unit. The kinetic experiments were made using a home-written pulse program in 2D fashion. A series of spectra at different total concentrations of uranium(VI) were recorded at different pH in the range 1.48−2.75 by collecting 128 FIDs for each spectrum. Within one series, the number of collected spectra and the delay between them were selected in accordance with the rate of reaction at the given pH. Usually, 16, 32, or 64 spectra were measured with a variable time interval of 300−900 s between them, resulting in a total experimental time of 2−16 h. All of the test solutions were kept in darkness to avoid the possible influence of photochemically mediated “yl”-exchange. We tried to study the rate of exchange under the conditions used by Gordon and Taube ($[U(VI)]_{tot} = 0.40$ and 0.95 M and $[H^+] = 0.0939$ and 0.939 M, respectively), but it was not possible to obtain reliable rate constants using the NMR method at these slow exchange rates. This was also the case in the experiments at high pH, as will be described later. The error in the NMR peak integrals are typically ±5% in our experiments. The change in the peak integrals in the long-time experiments at high pH was within this range, and these data can therefore not be used to determine rate constants, cf. part a of Figure S1 in the Supporting Information.

As the rate of mixing is slower than the half-life for the “yl”-exchange in $(UO_2)_2(OH)_2{}^{2+}$, 0.13 s, the method of mixing of the test solutions at different pH may affect the isotope enrichment at the starting point of the experiments (but not the rate of exchange). The effect is small but noticeable in the acid region, but probably much larger when preparing the test solutions in 3.5 M TMA-OH using solid TMA-OH, cf. Discussion.

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Results

The rate of reaction for the "yl"-exchange does not involve any chemical changes in the system, and the rate of isotope exchange was obtained by plotting $\ln(I_o/I)$ versus time for test solutions with different total concentrations of [U(VI)] and different hydrogen ion concentrations [H^+]. I_o and I are the peak integrals of the ^{17}O signal at time zero and t. The rate constant for each test solution, k_{obs} was calculated from the variation of the peak integral as a function of time, and a typical example is shown in Figure 1.

Experimental Data in the −log[H$^+$] Range 1.48−2.64. The speciation diagram calculated from the known equilibrium constants[9] in 1 M perchlorate, cf. Figure S 2 of the Supporting Information, shows that less than 3% of the uranium is present as $(UO_2)_2(OH)_2^{2+}$ and even less as $(UO_2)_3(OH)_5^+$, in the $-\log[H^+]$ range studied. The experimental data of $k_{obs}/[UO_2^{2+}]_{tot}^2$ as a function of $1/[H^+]^2$ are shown in Figure 2.

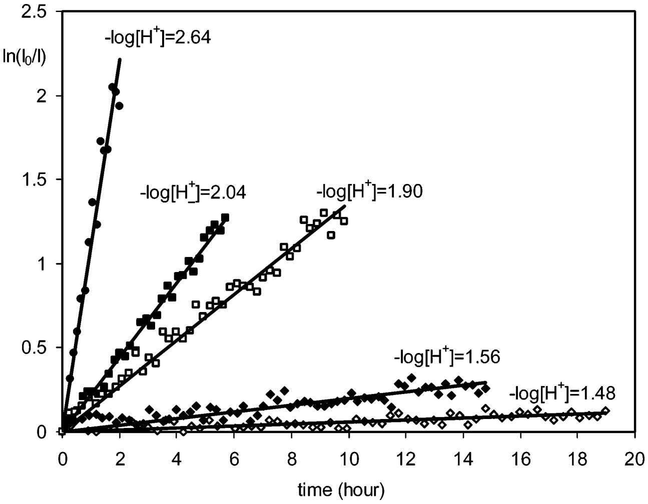

Figure 1. Determination of the rate constants, k_{obs}, in series 1 from experimental ^{17}O peak integrals; the various rate constants are given in Table 1. The total concentration of uranium is 0.0297 M.

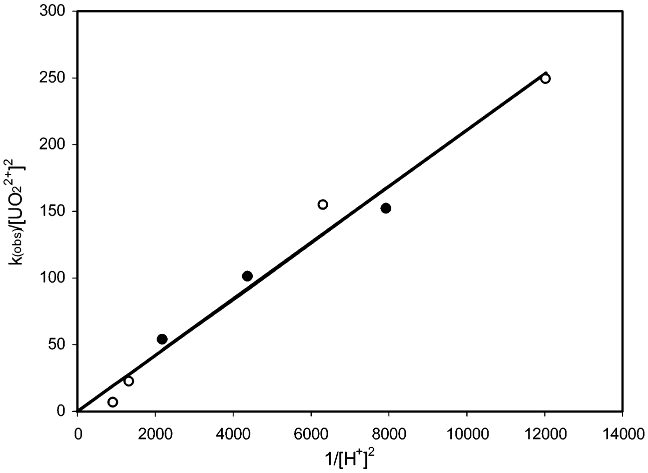

Figure 2. Plot of $k_{obs}/[UO_2^{2+}]_{tot}^2$ versus $1/[H^+]^2$, demonstrating that the main pathway for the exchange "$U^{17}O_2$" + $H_2O \rightleftharpoons$ "UO_2" + $H_2{}^{17}O$ involves the complex $(UO_2)_2(OH)_2^{2+}$, in the concentration range investigated. The intercept is zero within the experimental error, and from the slope we obtain $k = (2.11 \pm 0.08) \times 10^{-2}$ h^{-1}. Empty circles, $[UO_2^{2+}]_{tot} = 0.0297$ M; filled circles, $[UO_2^{2+}]_{tot} = 0.0424$ M.

$$\frac{k_{obs}}{[UO_2^{\;2+}]_{tot}^{\;2}} = \frac{k}{[H^+]^2} \qquad (4)$$

The linear plot shows that the predominant exchange pathway takes place via $(UO_2)_2(OH)_2^{2+}$, with the rate constant $k = (2.11 \pm 0.08) \times 10^{-2}$ h^{-1}. This rate equation is consistent with the following two-step mechanism:

$$2U^{17}O_2^{\;2+} + 2H_2O \rightleftharpoons (U^{17}O_2)_2(OH)_2^{\;2+} + 2H^+ \quad (5)$$

$$(U^{17}O_2)_2(OH)_2^{\;2+} + H_2O \rightleftharpoons (UO_2)_2(OH)_2^{\;2+} + H_2{}^{17}O \quad (6)$$

The first reaction is a rapid equilibrium[19−21] that is followed by the rate-determining step (6), where the back-reaction can be neglected in our experiments. The rate equation deduced from this mechanism is:

$$\vec{v} = \frac{d[(UO_2)_2(OH)_2^{\;2+}]}{dt} = k_{2,2}[(UO_2)_2(OH)_2^{\;2+}] = \frac{k_{2,2}{}^{*}\beta_{2,2}[UO_2^{\;2+}]^2}{[H^+]^2} \quad (7)$$

$^*\beta_{2,2}$ is the equilibrium constant for reaction (5) and $k_{2,2}$ is the rate constant for reaction (6). In the concentration range studied, the concentration of [UO_2^{2+}] is very close to the total concentration of uranyl(VI). We have $k = k_{2,2} \times {}^*\beta_{2,2}$, where $\log{}^*\beta_{2,2} = -5.95 \pm 0.08$ and ${}^*\beta_{22} = (1.12 \pm 0.21) \times 10^{-6}$ M in the ionic medium used, resulting in the rate constant $k_{2,2} = (1.88 \pm 0.22) \times 10^4$ h^{-1}.

In a separate experiment, we determined the activation parameters for the exchange reaction by measuring the rate constants at three different temperatures 282, 288, and 298 K. The resulting Eyring plot is shown in Figure 3, from which the following activation parameters were obtained: $\Delta H^\ddagger = 119.3 \pm 12.7$ kJ mol^{-1} and $\Delta S^\ddagger = 81 \pm 44$ J mol^{-1} K^{-1}. The accuracy of the activation enthalpy is reasonably good, whereas the activation entropy is very uncertain because of the small temperature range used. The activation enthalpy is in excellent agreement with the one obtained by Mashirov et al.,[8] $\Delta H^\ddagger = 119.5 \pm 5$ kJ/mol, calculated from their experimental Arrhenius activation energy, $\Delta E^\ddagger = 122 \pm 5$ kJ/mol. The measured activation enthalpy is a composite quantity, $\Delta H^\ddagger = \Delta H_{2.2} + \Delta H^\ddagger_{2,2}$, where $\Delta H_{2,2} = 38.8 \pm 6.1$ kJ/mol is the enthalpy of reaction[9] for reaction (4), hence $\Delta H^\ddagger_{2,2} = 80 \pm 14$ kJ/mol.

The rate of exchange increases rapidly at higher pH, where one also has the additional complication of precipitation of $UO_2(OH)_2$(s). We have therefore no quantitative data here, only the qualitative observation that the rate of exchange between the next complex, presumably $(UO_2)_3(OH)_5^+$, is even faster than for $(UO_2)_2(OH)_2^{2+}$.

The Rate of Exchange for the Reaction $U^{17}O_2(OH)_4^{2-}$ + $H_2O \rightleftharpoons UO_2(OH)_4^{2-}$ + $H_2{}^{17}O$. This experiment was done

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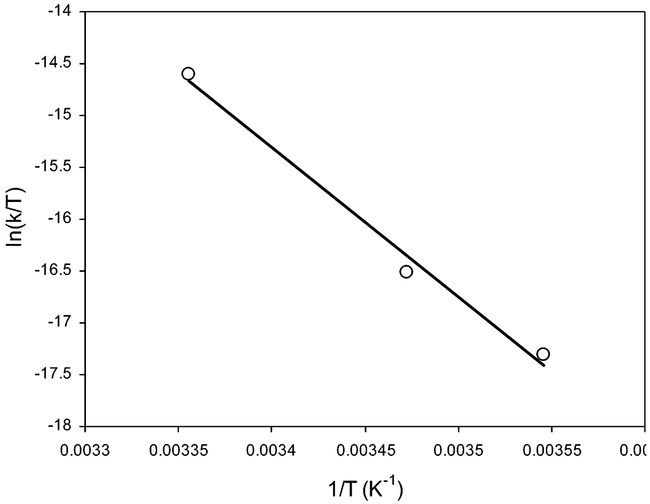

Figure 3. Eyring plot for the yl-exchange, measured at $[UO_2^{2+}]_{tot} = 0.0434$ M and $-\log[H^+] = 2.06$. The activation parameters are $\Delta H^{\ddagger} = 119 \pm 13$ kJ mol^{-1}, $\Delta S^{\ddagger} = 81 \pm 44$ J mol^{-1} K^{-1}.

in a test solution with a uranyl(VI) concentration of 50.0 mM in 3.5 M TMA-OH, and the exchange was followed at different temperatures without a noticeable change in the peak integrals (within the experimental uncertainty ± 5 %) demonstrating no, or very slow exchange, cf. part a of Figure S1 in the Supporting Information.

The Rate of Exchange for the Reaction $(U^{17}O_2)_2(\mu\text{-}OH)_2(F)_2(Oxalate)_2^{4-} + H_2O \rightleftharpoons (UO_2)_2(\mu\text{-}OH)_2(F)_2(Oxalate)_2^{4-} + H_2{}^{17}O$. The ^{17}O and ^{19}F NMR spectra of $(UO_2)_2(\mu\text{-}OH)_2(F)_2(oxalate)_2^{4-}$ are shown in Supporting Information, Figure S3, and demonstrate that no significant “yl”-exchange has taken place during a period of 1 week. The concentration of this complex in the test solution used is about 0.8 mM at the used pH (7.76); a concentration of $(UO_2)_2(\mu\text{-}OH)_2^{2+}$ of this magnitude would result in a complete “yl”-exchange within minutes.

Photochemical “yl”-Exchange in $UO_2(CO_3)_3^{4-}$. There was no measurable exchange between $U^{17}O_2(CO_3)_3^{4-}$ and the solvent after a 20 h illumination of the test solution with a UV lamp.

Discussion

A combination of the available experimental data for the “yl”-exchange from the previous[2−4,8] and the present study results in the following rate equation that describes a stoichiometric mechanism involving a set of parallel exchange reactions, each involving a separate hydroxide complex and water, under the conditions used $[UO_2^{2+}]$ is $[UO_2^{2+}]_{tot}$.

$$\vec{v} = \frac{k_1[UO_2^{2+}]}{[H^+]} + \frac{k_2[UO_2^{2+}]^2}{[H^+]^2} + \sum_n \frac{k_n[UO_2^{2+}]^n}{[H^+]^m} \qquad (8)$$

The experimental data from Mashirov et al.[8] (cf. their Tables 1 and 2) indicate that the main pathway for “yl”-exchange involves the complex $(UO_2)_2(OH)_2^{2+}$ in the pH range 1−2.5 for total concentrations of U(VI) between 0.003 and 0.03 M. At higher uranium concentrations and at higher pH, the reaction order with respect to uranium increases and is larger than 2, but the experimental uncertainty is large. This was interpreted by Mashirov et al.[8] as a result of a parallel exchange pathway involving $(UO_2)_2(OH)_3^+$, $(UO_2)_2(OH)_4(aq)$, and a cyclic trimer $(UO_2)_3(OH)_3^{3+}$; however, the very large amount of accurate data for the hydrolysis of uranyl(VI) gives no indication of the formation of species with these compositions,[9] and, accordingly, we do not accept the interpretation given. A more likely exchange pathway might involve the well-established complex $(UO_2)_3(OH)_5^+ \equiv (UO_2)_3(O)(OH)_3^+$. Mashirov et al.[8] have not reported any rate constant, only plots of the half-lives for the exchange reactions as a function of pH and the total concentration of uranium. These graphs allow only a crude estimate of the rate constants that are given in Table 2; their scatter indicates that the experimental data are not very accurate, and, in addition, there seems to be a systematic error between the different experiments. However, the calculated rate constants, $k \approx (0.6 - 6) \times 10^{-2}$ h^{-1}, are not too different from the ones we have found. One possible reason for the large variation in the rate constants is that Mashirov et al.[8] did not use a constant ionic strength/ionic medium in their experiment; the ionic strength varied between approximately 1 and 300 mM. In addition, they have used the measured pH rather than the hydrogen ion concentration in the interpretation of the rate data, and this error is substantially larger than the claimed 0.02 pH units.

Table 2. Experimental Half-Lives in Hours from the Experimental Data Presented in Figures 1 and 2 in Mashirov et al.[8] [a]

	$U_{tot} = 30$ mM	$U_{tot} = 10$ mM	$U_{tot} = 3.0$ mM
pH	log $t_{1/2}$ (h); k (h^{-1})	log $t_{1/2}$ (h); k (h^{-1})	log $t_{1/2}$ (h); k (h^{-1})
1.50	2.05; 0.62×10^{-2}	2.55; 1.86×10^{-2}	3.00; 7.4×10^{-2}
2.0	1.05; 0.68×10^{-2}	1.60; 1.73×10^{-2}	2.10; 6.1×10^{-2}
2.50		0.55; 1.86×10^{-2}	1.10; 5.8×10^{-2}

[a] The Rate Constant k in h^{-1}, Has Been Calculated by Us.

Gordon and Taube[2,3] report a rate equation that is different from the one reported by us and Mashirov et al.[8] Assuming that there is an exchange path involving $UO_2(OH)^+$ with the rate constant determined by Gordon and Taube, this should give a contribution that is less than 0.03% to the exchange under the conditions used in our experiments. As indicated in the experimental section, it is not possible to determine the very low exchange rates reported by Gordon and Taube using the NMR method applied in the present study. The rate constant for the $(UO_2)_2(OH)_2^{2+}$ determined by us and Mashirov et al. applied under the conditions used by Gordon and Taube would result in more than 99.9% of the exchange through the binuclear pathway. This is not concordant with their observations. We have no explanation for this discrepancy but note that their experimental method is complicated, involving the precipitation of solid uranyl ferrocyanide that is then heated with $HgCl_2$ to release the uranyl oxygen as CO_2 that is subsequently analyzed using mass spectrometry to give the rate of exchange; the NMR method is certainly much more direct. The concentrations of $UO_2(OH)^+$ and $(UO_2)_2(OH)_2^{2+}$ used in our experiments have comparable magnitude, cf. Figure S2 in the Supporting Information, demonstrating that the exchange involving $UO_2(OH)^+$ is significantly slower than that of $(UO_2)_2(OH)_2^{2+}$. All of the studies made so far indicate that there is no, or a very slow, "yl"-exchange between $UO_2(OH_2)_5^{2+}$and water solvent.

The Rate-Determining Step in the Proposed Stoichiometric Mechanism. The experimental rate equation is consistent with a mechanism where reaction (6) is rate determining. The dynamics in the uranyl hydroxide system has been studied experimentally using temperature relaxation,[19] stopped-flow technique,[20] and ^{17}O NMR spectroscopy;[21] the latter study is directly relevant for the experimental conditions used in the present study. It demonstrates that the rate equation for the formation/dissociation of $(UO_2)_2(OH)_2^{2+}$ is different from the one observed in the present study and also that the rate is faster than the rate of "yl"-exchange, confirming that reaction (5) is not rate determining in the "yl"-exchange. Reaction (6) is not an elementary reaction; it is shorthand for several consecutive elementary reactions. We have no information on the molecular details of these, only indications from mechanistic discussions based on quantum chemical modeling that will be presented in part two of this study.[22]

"Yl"-Exchange in $UO_2(OH)_4^{2-}$/$UO_2(OH)_5^{3-}$. Our observations in the present and a previous study[18] show that there is no measurable "yl"-exchange at high pH, where the mononuclear complexes $UO_2(OH)_4^{-}$ and $UO_2(OH)_5^{2-}$ are predominant. Clark et al.[4] have measured what they claim is the rate of exchange between the "yl"-oxygen and water in 3.5 M TMA-OH, using the line-broadening of the average ^{17}O NMR signal from these complexes at different temperatures. The rate constant and activation parameters are k (283 K) (18 ± 6) s^{-1} and $\Delta H^{\ddagger} = 41.0 \pm 1.3$ kJ/mol. A rate constant of this magnitude will result in a rapid loss of the $^{17}O_{yl}$ signal, as also noted by Clark et al.[4] They therefore made the exchange experiments in a test solution that contained a high concentration of $H_2{}^{17}O$, assuming the two-site (UO_2^{2+} and H_2O) exchange

$$U^{17}O_2(^{17}OH)_{4/5}{}^{2-/3-} + H_2{}^{17}O \rightleftharpoons U^{17}O_2(^{17}OH)_{4/5}{}^{2-/3-} + H_2{}^{17}O \quad (9)$$

They also confirmed the rapid loss of the spin label by Raman spectra, using test solutions obtained by mixing a UO_2^{2+} stock solution prepared from solid uranyl nitrate or chloride, with a 3.5 M TMA-OH and a 98% $H_2{}^{18}O$ enrichment. If the "yl"-exchange is rapid, as proposed by Clark et al., they should observe complete isotope mixing in this test solution, resulting in an approximately 97% ^{18}O enrichment in the uranyl(VI) group. Clark et al. report a Raman difference spectrum of two test solutions in 3.5 M TMA-OH, one 0.14 M solution prepared from nonenriched uranyl ions and the other a 0.18 M solution prepared from a uranyl solution enriched to approximately 97% in ^{18}O (ref 4, p 1464). If the isotope exchange is fast, the area under the negative and positive peaks in the inset in Figure 3 of ref 4 should scale as the corresponding uranyl concentrations; a visual estimate indicates that the negative peak corresponding to the ^{18}O-enriched test solution is significantly smaller than the one for the ^{16}O test solution; hence, one cannot have isotope equilibrium in the test solution prepared by mixing solid $UO_2Cl_2 \cdot H_2O$ with 98% $H_2{}^{18}O$ and solid TMA-OH. We suggest that the inconsistency between the ^{17}O NMR observations of Clark et al. and in the present study might be due to the way the test solutions were prepared. We prepared our test solutions by rapid mixing of two solutions (1.998 M UO_2^{2+} in 0.14_4 M $HClO_4$) and then rapidly filtering the precipitate of TMA-ClO_4, while Clark et al. mixed a 1.22 M stock solution of UO_2^{2+}(aq) in 1.0 M $HClO_4$ with solid TMA-OH. Both procedures will result in the precipitation of TMA-ClO_4, but in the latter case, a larger amount is formed and primarily on the surface of the solid TMA-OH. We suggest that this results in a slower pH equilibration and a more extensive "yl"-exchange during the equilibration phase; the half-life of the "yl"-exchange in $(UO_2)_2(OH)_2^{2+}$ is only 0.13 s. As indicated in the Experimental Section, we have noticed that even the mixing of an acid stock solution of ^{17}O-enriched UO_2^{2+}(aq) with a solution of higher pH will result in partial "yl"-exchange before equilibrium is attained (this is of no consequence for the determination of the rate of exchange).

To test if the "yl"-exchange is influenced by light (the experiments by Clark et al. have been made in daylight), we have repeated our experiments under UV irradiation and note that, also in this case, the "yl"-exchange is very slow (part b of Figure S1 in the Supporting Information). To conclude, we suggest that the NMR experiments of Clark et al. do not refer to "yl"-exchange, but to two-site exchange between $UO_2(OH)_4^{2-}$ and $UO_2(OH)_5^{3-}$ that are present in their (and our) test solutions, as previously discussed by Moll et al. .[18]

"Yl"-Exchange Involving $(UO_2)_2(\mu\text{-}OH)_2(F)_2(Oxalate)_2^{4-}$. The observation that there was no noticeable exchange between $(U^{17}O_2)_2(\mu\text{-}OH)_2(F)_2(oxalate)_2^{4-}$ and the water solvent indicates that coordinated water must be present in the binuclear complex in order for exchange to take place. This seems to be the case also in complexes of higher nuclearity, as observed by Moll et al. in the ternary uranyl(VI)−hydroxide−sulfate system.[18]

Comment on the Photochemical "yl"-Oxygen−Water Exchange. The quenching of luminescence from the first photoexcited state of the uranyl(VI) aquo ion, $^*UO_2^{2+}$(aq), has been extensively discussed,[15] and one of the mechanisms proposed involves hydrogen transfer from the solvent water, forming $^*U(O)(OH)^{2+}$; this might explain the rapid exchange between "yl"-oxygen and water. However, the experiment with the photoexcited $UO_2(CO_3)_3^{4-}$ ion shows that no significant exchange takes place, indicating that hydrogen abstraction is only important if it originates from coordinated water, rather than the solvent; we will discuss proton abstraction in the photoexcited states of the uranyl aquo ion in a following communication. The photochemical exchange

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between $UO_2(OH)_4^{2-}$ and $UO_2(OH)_5^{3-}$ and water is slow, cf. part b of Figure S1 in the Supporting Information, and might also be due to photo reduction and precipitation of UO_2.

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Supporting Information Available: Part a of Figure S1 shows ^{17}O NMR spectra of test solutions of $UO_2(OH)_4^{2-}/UO_2(OH)_5^{3-}$ at different times; part b of Figure S1 shows the NMR spectra of a test solution after UV irradiation over different times. Figure S2 shows the species distribution between the different uranyl(VI) species under the experimental conditions used in the present study. Figure S3 shows the ^{17}O and ^{19}F NMR spectra of $(UO_2)_2(\mu\text{-}OH)_2F_2(\text{oxalate})_2^{4-}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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