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The Pressure Dependence of Oxygen Isotope Exchange Rates Between Solution and Apical Oxygen Atoms on the $[UO_2(OH)_4]^{2-}$ Ion**

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A key concern in the use of nuclear energy is the disposal and long term storage of spent fuel. The aqueous chemistry of the uranyl(VI) ion under strongly alkaline conditions, such as those found in many above-ground waste storage tanks, remains poorly understood. To this effect, the oxygen atom exchange between the uranyl oxygen atoms and bulk solvent water has been studied by ^{17}O NMR spectroscopy under acidic[1] and alkaline conditions[2–4] using line-broadening by Clark et al. and, recently, saturation-transfer methods by Szabó, Grenthe et al., but no determination of activation volumes has been attempted. Such data are invaluable in verifying theoretical models for reaction pathways.[5] The activation volume probes the transition state and complements molecular dynamics simulations. Herein, the activation volume of the oxygen atom exchange of the uranyl oxygen atoms with bulk water has been determined by experiments at 60 °C between 0.1 and 350 MPa as a function of uranyl and hydroxide concentrations.

A common method for determining exchange that involves coordinated oxygen atom species and bulk water is by line-broadening studies according to the method by Swift and Connick,[6,7] in which the broadening of a signal because of rapidly occurring dynamic processes is followed. While this is experimentally straightforward, the separation of contributing factors to the observed line width is often difficult. Such is particularly the case when there are several exchangable oxygen atoms, such as apical "yl" and equatorial waters or hydroxo ligands. Saturation-transfer measurements provides an alternative approach which, assuming that certain conditions are met—such as well-separated NMR signals and slow longitudinal relaxation—offers a more direct and precise determination of exchange rates.[4] Here, one site, for example, ^{17}O in bulk water, is selectively excited with a 180° pulse and magnetization is transferred through chemical exchange to another site, e.g. ^{17}O in UO_2^{2+}:

$$\frac{dM_{z,a}}{dt} = -\frac{(M_{z,a}(t) - M_{z,a}^{\infty})}{T_{1,a}} + k_b M_{z,b}(t) - k_a M_{z,a}(t) \qquad (1)$$

$$\frac{dM_{z,b}}{dt} = -\frac{(M_{z,b}(t) - M_{z,b}^{\infty})}{T_{1,b}} - k_b M_{z,b}(t) + k_a M_{z,a}(t) \qquad (2)$$

With selective inversion, the x and y components of the magnetization may be omitted and the system may be completely described by the z component of the Bloch equations. We here adopt a McConnell formalism for exchange (see Supporting Information for derivation of model equation). M_i is the bulk magnetic moment, T_1 denotes the longitudinal relaxation for sites a and b, and k is the pseudo first-order rate constant.[7] For a selective 180° pulse at t_0 on site b, the initial conditions in the ideal case become $M_{z,b}(t_0) = -M_{z,b}^{\infty}$ and $M_{z,a}(t_0) = M_{z,a}^{\infty}$ which allows for the analytical solution of the set of differential equations. In practice, long, shaped pulses are required to provide for a truly selective 180° pulse during the life-time of which some relaxation of b will occur, so that $M_{z,b}(t_0) \geq -M_{z,b}^{\infty}$. The system was thus solved for $M_{z,b}(t_0) = -M_{z,b}^{0}$ and $M_{z,a}(t_0) = M_{z,a}^{0}$.

The activation volume ($\Delta V^{\ddagger}$) is defined by Equation (3) (R gas constant, T temperature, k rate coefficient, P pressure), and can be determined by measuring rates as a function of pressure.

$$\Delta V^{\ddagger} = -RT\left(\frac{\delta \ln(k)}{\delta P}\right)_T \qquad (3)$$

According to transition-state theory the activation volume can then be interpreted as the difference in molar volume between the transition state and the sum of the partial molar volumes of the reactants and thus offers a less ambiguous measure than activation entropy as to whether a reaction is associative or dissociative, in addition to giving an indication as to the species involved. The activation volume is one of a few properties of the transition state that can be accurately probed and therefore it is an invaluable indicator towards the mechanism of exchange reactions.[10]

The speciation of U^{VI} as a function of concentration and pH is complicated and partly unresolved. However, while a range of monomeric, dimeric, and trimeric species have been observed at acidic conditions, at highly alkaline pH (3.5 M $N(CH_3)_4OH_{(aq)}$) monomeric uranyl hydroxide species form. Clark et al. suggested the dominant species to be $[UO_2(OH)_5]^{3-}$ based on EXAFS (extended X-ray absorption

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fine structure) and UV/Vis spectroscopy,[1] whereas Szabó, Grenthe et al. have suggested that $[UO_2(OH)_4]^{2-}$ is the main species.[5,4] While there is some disagreement as to which one is the major species, it is, however, clear that a rapid equilibrium between $[UO_2(OH)_4]^{2-}$ and $[UO_2(OH)_5]^{3-}$ is present. We here assign the stoichiometry to $[UO_2(OH)_4]^{2-}$ to simplify the discussion; we have no information about the relative accuracy of the tetra- or pentahydroxy stoichioimetric assignment. There is certainly no evidence for polynuclear species under these conditions, such as would be evident in new peak appearances or peak broadenings with increases in concentration.

Clark et al.[2] determined ambient-pressure activation enthalpy and entropy of the exchange of the uranyl oxygen atoms in $[UO_2(OH)_4]^{2-}$ to be (41 ± 1.7) kJ mol^{-1} and (-75 ± 25) J K^{-1} mol^{-1}, respectively, in 3.5 M $N(CH_3)_4OH$ through ^{17}O NMR signal line-broadening. This is in good agreement with the values of (36.6 ± 0.4) kJ mol^{-1} and (-75 ± 17) J K^{-1} mol^{-1} observed by Szabó et al. under the same conditions using the saturation-transfer method that we employ here. In addition, the detailed rate law was investigated and found to be first-order with respect to hydroxide concentration and second-order with respect to uranyl concentration. After ruling out the presence of binuclear complexes in solution the authors concluded that the first-order dependence on hydroxide is due to the equilibrium between the tetrahydroxy and the pentahydroxy uranyl species, whereas the second-order dependence on uranium concentration is due to the formation of a binuclear $[UO_2(OH)_4]\cdot[UO_2(OH)_5]^{5-}$ transition state.

Herein we have investigated the pressure effects on the rates of oxygen atom exchange at the "yl" oxygen atoms at different total U^{VI} and hydroxide concentrations. We first confirmed agreement with the rate law proposed by Grenthe and Szabo[4] at low pressure, then extended the results to high pressure in order to probe the activated equilibria. Samples consisted of solutions of 16–73 mM uranyl nitrate in aqueous solutions of 2.0–3.5 M $N(CH_3)_4OH$ (Table 1). Using a custom-built high-pressure NMR probe, the samples were kept at 333 K and the pressure varied between 0.1 and 350 MPa. The peak corresponding to the "yl" oxygen atom was put on resonance and was given a selective 180° tip angle using a 500-µs Gaussian-shaped pulse. The perturbed water magnetization was then allowed to mix with the equilibrium "yl" magnetization through chemical exchange for some variable time (a mixing time). A 90° pulse was used to tip magnetization into the x–y plane for detection. Due to the large difference in chemical shift between the two sites, the spectrometer frequency was alternated between the "yl" frequency, or the bulk-water frequency, in order to digitize either with sufficient resolution. The time-domain signals were fitted to decaying exponential functions and the amplitude values were compiled as a function of mixing time.

Table 1: Activation volumes determined at (333.0 ± 0.1) K.

C_{UO_2} [10^{-3} mol dm^{-3}][a]	C_{OH} [mol dm^{-3}][b]	$C_{OH,free}$ [mol dm^{-3}][c]	$\Delta V^{\neq} \pm \sigma$ [cm^3 mol^{-1}]
22.4	1.99	1.9	-9.8 ± 0.8
45	2.07	1.89	-9.2 ± 0.5
56.6	2.12	1.89	-9.0 ± 0.7
24.3	1.48	1.38	-9.8 ± 1.3
21.5	1.98	1.89	-10.4 ± 1
16.1	2.96	2.9	-9.8 ± 1.1
73	1.9	1.61	-9.06 ± 0.63

[a] Total concentration of uranyl nitrate. [b] Total concentration of added $N(CH_3)_4OH$. [c] Free hydroxide concentration assuming complete reaction with uranyl nitrate to form tetrahydroxy species.

The model described above was then fitted to the resulting data array using a least-squares fitting routine that employed an interior-reflective Newton search method. A value for exchange rate and associated uncertainty are obtained for each pressure. The uncertainty in the fitting of the saturation-transfer model was always larger than the uncertainty in the linear curve fit of the pressure dependence, thus it became necessary to propagate this larger error through the calculations to the reported activation volume. To accomplish this, a random, normally distributed array of 1000 points having a mean value of the regressed rate and a standard deviation of regression was generated for each pressure. Then a single point from each array was randomly chosen and linearly regressed to obtain a value for slope. This process of picking points from the normally distributed array was repeated 1000 times and the average slope was obtained. The standard deviation of this process is the reported uncertainty. Thus the values and uncertainties are conservative and reasonable.

Activation volumes were obtained by Equation (4), where k^0 is the rate at P^0 (ca. 5 MPa).

$$\ln\left(\frac{k}{k^0}\right) = \frac{-\Delta V^{\neq}}{RT}P + \frac{\Delta V^{\neq}}{RT}P^0 \qquad (4)$$

An attractive feature of this equation is that the activation volume is independent of the absolute magnitude of the measured rates, and depends only on the relative change in rate with pressure. Thus, as long as the only variable being changed is pressure, any reaction can be treated as if exhibiting first-order kinetics. As a consequence, the activation volume should not change with either reactant concentrations or temperature, but remain constant for a given reaction as long as the reaction mechanism is unchanged. Any significant deviation can be interpreted as an indication of a change in reaction mechanism.

The activation volumes were measured at conditions given in Table 1; $\Sigma[U^{VI}] = 16$–73 mM and $\Sigma[OH^-]$ from 1.5–3.0 M and 333 K (Figure 1). All reaction rate coefficients are consistent with the ambient-pressure studies of Szabo and Grenthe.[4] The rate coefficients used to yield activation volumes in Table 1 by using Equation (4) were not corrected for the dependence on $\Sigma[U^{VI}]$ or on Σ[TMAOH], but these dependencies do not affect the derivatives with respect to pressure and thus the values of $\Delta V^{\neq}$.

We were motivated in this study to alleviate the absence of high-pressure studies on actinide elements that could yield information about reaction mechanisms.[10] Although we here report large negative activation volumes, it would be a mistake to interpret these values by careless application of the Langford–Gray formalism relating $\Delta V^{\neq}$ to involvement of second-shell hydration waters in the activated state.[11] We find, as did Szabó and Grenthe,[4] that the rates depend on the

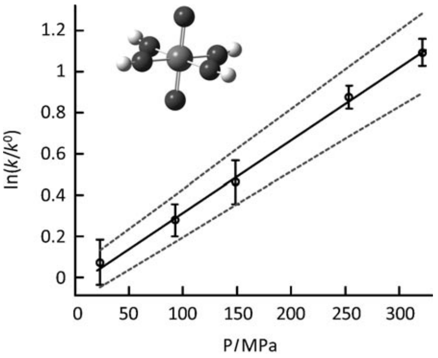

Figure 1. $\ln(k/k_0)$ as a function of pressure. $\Sigma[\mathrm{U^{VI}}] = 22.4$ mM, $T = 333$ K. The slope of these data indicates an activation volume, which in this case was $\Delta V^{\ddagger} = (-9.8 \pm 0.8)$ cm^3 mol^{-1}, and the dashed lines indicate the standard error of the slope. The error bars indicate the standard error of each rate datum.

square of the total dissolved uranium concentrations and thus the pathway probably involves a yet undetected dimeric intermediate or dimeric activated complex. We see no spectroscopic evidence that such an intermediate is stable, but we cannot rule out the possibility that the volume change to form this intermediate is folded into our $\Delta V^{\ddagger}$ measurements, since the putative intermediate may be at concentrations too low for us to detect. The interpretation may also be complicated by the possibility that the isotope-exchanging moiety is a hydroxide ion at these high pH conditions, although we consider this to be unlikely.

The large negative activation volume is consistent with molecular association in the transition state. We certainly find no trends that might suggest reaction pathways that change with pressure or variations in concentration. The large negative activation volume, however, argues strongly against a rate-controlling step where a rapidly exchanging equatorial hydroxy rotates upward internally to form the new axial "yl" oxygen atom. Such internal shuffling of oxygen atoms would not require such a large and negative activation volume, except for the caveat that our measurement may include the reaction volume for equilibrium between $[\mathrm{UO_2(OH)_4}]^{2-}$ and a yet undetected precursor to the activated complex.

Experimental Section

Samples were prepared by dissolving uranyl nitrate into 40% ^{17}O-enriched water that had been degassed by vacuum distillation. This resulting solution was acidic and was combined with a pre-weighed amount of TMAOH ($\mathrm{TMA = N(CH_3)_4^+}$) and then double-sealed in a high pressure NMR tube. The TMAOH was used as received from Acros. The high-pressure sample assembly was completely isolated from the atmosphere. The samples were submerged in a hexane fluid during the NMR measurements, thereby further preventing air leakage into the sample during the measurements. All NMR measurements were conducted on the day of sample preparation. There was no visual evidence of precipitation, which would have been uranyl carbonate, nor any NMR evidence of additional solutes.

^{17}O-NMR experiments were carried out on a wide-bore Bruker Avance (11.7 T) spectrometer using a high-pressure probe system similar to that described by Jonas et al.[12] The probe pressure was generated with a high-pressure syringe pump coupled to a valve system to maintain and regulate pressures throughout the experiment. Isohexane was used as the pressure conduit and pressures were continuously monitored and were never allowed to fluctuate more than 0.5% during data acquisition. Temperature was kept constant via a circulating water bath and was monitored with a type-T thermocouple situated in the probe body near the probe head and at pressure. Thermal equilibrium was established after each pressure jump before data was acquired.

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[1] I. Farkas, I. Banyai, Z. Szabo, U. Wahlgren, I. Grenthe, *Inorg. Chem.* **2000**, *39*, 799.
[2] D. L. Clark, S. D. Conradson, R. J. Donohoe, D. W. Keogh, D. E. Morris, P. D. Palmer, R. D. Rogers, C. D. Tait, *Inorg. Chem.* **1999**, *38*, 1456.
[3] Z. Szabó, I. Grenthe, *Inorg. Chem.* **2007**, *46*, 9372.
[4] Z. Szabó, I. Grenthe, *Inorg. Chem.* **2010**, *49*, 4928.
[5] a) M. A. Lee, N. W. Winter, W. H. Casey, *J. Phys. Chem.* **1994**, *98*, 8641; b) F. P. Rotzinger, *J. Am. Chem. Soc.* **1996**, *118*, 6760; c) T. Kowall, P. Caravan, H. Bourgeois, L. Helm, F. P. Rotzinger, A. E. Merbach, *J. Am. Chem. Soc.* **1998**, *120*, 6569.
[6] a) T. J. Swift, G. M. Anderson, R. E. Connick, M. Yoshimine, *J. Chem. Phys.* **1964**, *41*, 2553; b) T. J. Swift, R. E. Connick, *J. Chem. Phys.* **1962**, *37*, 307.
[7] H. M. McConnell, *J. Chem. Phys.* **1958**, *28*, 430.
[8] H. Moll, T. Reich, Z. Szabo, *Radiochim. Acta* **2000**, *88*, 411.
[9] U. Wahlgren, H. Moll, I. Grenthe, B. Schimmelpfennig, L. Maron, V. Vallet, O. Gropen, *J. Phys. Chem. A* **1999**, *103*, 8257.
[10] D. T. Richens, *The Chemistry of Aqua Ions*, Wiley, Chichester, **1997**, pp. 10–20; T. Asano, W. J. Le Noble, *Chem. Rev.* **1978**, *78*, 407.
[11] a) C. H. Langford, H. B. Gray, *Ligand Substitution Processes*, 2nd ed., Benjamin, New York, **1974**, p. 120; b) T. W. Swaddle, *Inorg. Chem.* **1983**, *22*, 2663–2665.
[12] J. W. Jonas, P. Koziol, X. Peng, C. Reiner, D. Campbell, *J. Magn. Reson. Ser. B* **1993**, *102*, 299–309.