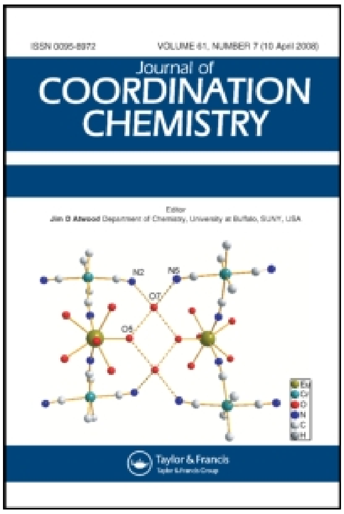

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^{1}H NMR STUDY OF WATER EXCHANGE IN BIS(NITRATO)DIAQUODIOXOURANIUM(VI)

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Kinetics of water exchange of bis(nitrato)diaquodioxouranium(VI) in 96.7% acetone–water have been studied by ^{1}H NMR spectroscopy, and the activation parameters $\Delta H^* = 21.0\,\mathrm{kJ\,mol^{-1}}$, $\Delta S^* = -86.5\,\mathrm{J\,K^{-1}\,mol^{-1}}$ determined.

Keywords: Dioxouranium(VI), solvent exchange kinetics

INTRODUCTION

The stereochemistry of the uranyl ion is dominated by the linear, or near linear, O–U–O grouping, which is normally surrounded equatorially by 4–6 other ligand atoms.[1] These equatorial ligands are coordinated more weakly than the uranyl oxygens,[2] and the observed coordination number depends upon factors such as ion size, chelating ability, *etc.* In contrast to other oxycations such as VO_2^{2+},[3] the uranyl oxygen atoms are inert to substitution.[4] However, the equatorial ligands are relatively labile, and considerable interest has been shown in ligand exchange processes in systems such as $UO_2^{2+}(aq)$,[5,6] dioxopentakis(ligand)uranium(VI) species,[7] various uranyl–chelate complexes[8-11] and mixed-ligand halide aquouranyl complexes.[5] We have been interested in water exchange in uranyl species in relation to its possible role in the decay of excited uranyl ion.[12] Direct proton magnetic resonance is one of the preferred methods for measuring both cation solvation number and the kinetics of ligand exchange in such systems.[5,13,14] By measuring spectra at low temperatures, using aqueous–organic solvent mixtures, it is possible to observe signals for both bulk and coordinated water, whilst measurements of the transverse relaxation time (T_2) for the ^{1}H NMR signal of the bulk water in the absence and presence of metal ions give water exchange rates.[5,14] We have recently studied the coordination behaviour of uranyl nitrate in acetone–water mixtures, and have found that the complex species at high acetone concentration is $[UO_2(NO_3)_2(H_2O)_2]$,[15] the structure of which has been well characterized in the solid state by both X-ray[16] and neutron[17] diffraction studies. Because of both the general interest in ligand exchange in uranyl complexes, and the lack of data on water exchange on any neutral uranyl species in solution we have used ^{1}H NMR spectroscopy to study this system.

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EXPERIMENTAL

^{1}H NMR species were run on a Varian XL-200 spectrometer equipped with a variable temperature probe (−150 to +220°C) at a frequency of 200 MHz, using the deuterium resonance of the solvent as a heteronuclear lock and acetone as internal reference. Solutions of uranyl nitrate (pro-analysis) were prepared using triply distilled water and 99.5% hexadeuteroacetone (B.D.H.) in the mole ratio $[UO_2(NO_3)_2 6H_2O]:[H_2O]:[(CD_3)_2CO] = 1:13.3:93.6$. Water exchange rate constants (k_{ex}) were determined from the transverse relaxation time of the bulk water in the presence (T_2) and the absence (T_{2F}) of uranyl nitrate using the expressions[5] $\frac{1}{T_2} - \frac{1}{T_2F} = \frac{1}{\tau_f}$ and $P_c K_{ex} = \frac{P_F}{\tau_f}$ where P_c and P_F are the mole fractions of co-ordinated and bulk water. The activation parameters ΔH^+ and ΔS^+ were calculated using the transition state expression $k_{ex} = \frac{n k_B T}{h} \exp(-\Delta H^+/RT) \exp(\Delta S^+/R)$, taking the hydration number (n) of two observed under these conditions.[15]

RESULTS AND DISCUSSION

As noted previously,[5,18,19] the ^{1}H NMR spectra of solutions of uranyl nitrate (0.14 M) in acetone–water (96.7% v/v) at low temperatures showed the presence of peaks associated with coordinated and bulk water. The kinetics of water exchange were studied over the temperature range 197–212 K, and a linear relationship was observed between the logarithm of the exchange rate constant and the reciprocal temperature (Figure 1). Activation parameters were determined for the exchange,

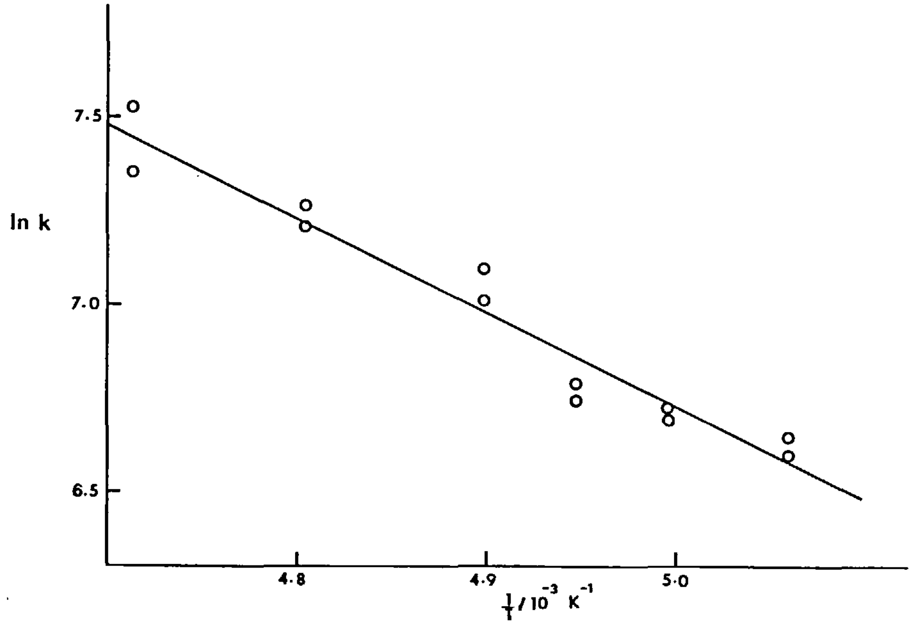

FIGURE 1 Arrhenius plot for water exchange in $[UO_2(NO_3)_2(H_2O)_2]$(0.14 M) in acetone–water (96.7% v/v).

and both these and calculated rate constants at 25°C are compared in Table I with those of various related systems. For the aquo complexes, the parameters given by Ikeda *et al.*[10] for $[UO_2(H_2O)_5]^{2+}$ are used. It can be seen that in going from $[UO_2(H_2O)_5]^{2+}$ to $[UO_2(NO_3)_2(H_2O)_2]$ there is a big decrease in ΔH^{+}. The water exchange in uranyl complexes is suggested to involve either a dissociative (D) or interchange (probably I_d) mechanism.[5-11] A mechanism with a dominant dissociative character would be expected, purely on steric grounds, to have a lower energy barrier in the bis(nitrato) complex, which has six ligand atoms coordinated in its equatorial plane. However, comparison with data for the halo and DMSO complexes suggests that electronic factors must also be involved. It is worthy of note that the thermodynamic data for water exchange in $[UO_2(NO_3)_2(H_2O)_2]$ do fit the enthalpy–entropy correlation suggested by Bennetto and Caldin[20] for solvent exchange on bivalent metal ions. Although solvent exchange reactions which show large negative ΔS^{+} values are normally thought to follow associative mechansims,[21] we think this unlikely in the present case. Instead, this entropy value probably reflects a combination of solvent effects[10,20] and the role of the transition state bond order in the water exchange.[22]

TABLE I

Kinetic parameters for ligand exchange in some uranyl complexes

Complex[a]	ΔH^{*}/kJ mol^{-1}	ΔS^{*}/J K^{-1} mol^{-1}	^{k}ex(298.2K)/s^{-1}	ref.
$[UO_2(NO_3)_2\underline{(H_2O)_2}]$	21.0 (±1.5)	−86.5 (±0.6)	7.89×10^4	this work
$[UO_2(H_2O)_5]^{2+}$	41.4 (±2.1)[b]	6.8(±10.6)[b]	7.8×10^{5}[b]	5
$[UO_2\underline{(H_2O)_3}DMSO]^{2+}$	23.4	−67.8	8.42×10^4	5
$[UO_2\underline{(H_2O)_3}Cl]^{+}$	25.5	−73.6	2.97×10^4	5
$[UO_2\underline{(H_2O)_3}Br]^{+}$	28.0	−56.5	8.49×10^4	5
$[UO_2(trmu)_5]^{2+}$[c]	56.6	2.2	983	7
$[UO_2(tmu)_5]^{2+}$[d]	81	88	1580	7

[a] The ligand involved in exchange is underlined where more than one ligand is present;
[b] Average of values for n = 5;
[c] trmu = trimethylurea;
[d] tmu = tetramethylurea.

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