7203026 and MPS 74-23000. We are also grateful to Professor D. N. Hendrickson and members of his group for assistance in collecting low-temperature magnetic susceptibility data.

Registry No. $[(\eta^5\text{-}C_5H_5)_2TiCl]_2MnCl_2\cdot 2(OC_4H_8)$, 55799-99-0; $(\eta^5\text{-}C_5H_5)_2TiCl_2$, 1271-19-8; $(\eta^5\text{-}C_5H_5)_2VCl_2$, 12083-48-6; $[(\eta^5\text{-}C_5H_5)_2TiCl]_2ZnCl_2\cdot 2C_6H_6$, 54040-41-4; $[(\eta^5\text{-}C_5H_5)_2TiBr]_2ZnBr_2$, 54004-69-2; $[(\eta^5\text{-}C_5H_5)_2TiCl]_2BeCl_2$, 54004-68-1; $[(CH_3C_5H_4)_2Ti]_2ZnCl_4$, 54064-96-9; $[(CH_3)_2Si(C_5H_4)_2Ti]_2ZnCl_4$, 55800-01-6.

Supplementary Material Available: Figure 9, showing temperature dependence of magnetic susceptibility and effective moment per Ti for $[(\eta^5\text{-}CH_3C_5H_4)_2TiCl]_2ZnCl_2$, Table VII, listing observed and calculated structure factors for $[(\eta^5\text{-}C_5H_5)TiCl]_2MnCl_2\cdot 2OC_4H_8$, and Tables VIII–XII, giving magnetic data for $[(\eta^5\text{-}C_5H_5)_2TiCl]_2ZnCl_2\cdot 2C_6H_6$, $[(\eta^5\text{-}C_5H_5)TiBr]_2ZnBr_2\cdot 2C_6H_6$, $[(\eta^5\text{-}C_5H_5)_2TiCl]_2BeCl_2\cdot 2C_6H_6$, $[(\eta^5\text{-}CH_3C_5H_4)_2TiCl]_2ZnCl_2$, and $[(CH_3)_2Si(\eta^1,\eta^5\text{-}C_5H_4)_2TiCl]_2ZnCl_2$ (24 pages). Ordering information is given on any current masthead page.

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Proton Magnetic Resonance Study of Ligand Exchange on Tetrakis(hexamethylphosphoramide)dioxouranium(VI)

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^{1}H NMR studies show the rate law for hexamethylphosphoramide (HMPA) exchange on $UO_2(HMPA)_4{}^{2+}$ to be rate = $4(k_1 + k_2[HMPA])[UO_2(HMPA)_4{}^{2+}]$ in CD_2Cl_2 diluent, where $k_1(273\ K) = 12.5 \pm 1.1\ s^{-1}$, $\Delta H^{\ddagger} = 14.0 \pm 3.0$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -172 \pm 11$ J K^{-1} mol^{-1} and $k_2(273\ K) = 173 \pm 15$ mol^{-1} dm^3 s^{-1}, $\Delta H^{\ddagger} = 22.2 \pm 3.0$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -120 \pm 9$ J K^{-1} mol^{-1}. This two-term rate law contrasts with the first-order rate law observed for the exchange of oxygen donor ligands L in some $UO_2L_5{}^{2+}$ species, and the origins of the two different rate laws are discussed in terms of dissociative and associative exchange mechanisms.

Introduction

In the solid state the presence of four, five, and six oxygen donor ligand atoms in the equatorial plane of dioxouranium(VI) species is well established.[1-3] These ground-state occupancies might indicate the possibilities of similar variations in transition-state equatorial occupancies but the monodentate oxygen donor ligand (L) species $UO_2L_5{}^{2+}$ so far investigated in several noncoordinating solvents (L = dimethylacetamide (DMA),[4] dimethyl methylphosphonate (DMMP),[5] trimethyl phosphate (TMP),[6] triethyl phosphate (TEP),[6] tetramethylurea (TMU),[7] and dimethyl sulfoxide (Me_2SO)[8]) have all exhibited a first-order ligand exchange rate law consistent with a dissociative (D) or dissociative interchange (I_D) mechanism and a six-coordinate (including the axial oxo ligands) transition state or reactive intermediate. Consequently, ligand exchange studies on $UO_2(HMPA)_4{}^{2+}$ (where HMPA is hexamethylphosphoramide) have been carried out in order to determine the effect of the reduced equatorial plane occupancy of the ground state of this species on the ligand exchange mechanism.

Experimental Section

Dioxotetrakis(hexamethylphosphoramide)uranium(VI) perchlorate was prepared under dry nitrogen by refluxing hydrated dioxouranium(VI) perchlorate (G. Frederick Smith) (2.5 g) with triethyl orthoformate (10 g) at 320–330 K for 1 h.[9,10] Dry HMPA (Koch-Light) (3.75 g) was then added at room temperature, and the resultant pale yellow crystals were filtered off, washed with dry ether, and pumped down on a vacuum line for several hours. At all times exposure of the product to light was kept to a minimum to minimize the possibility of photochemically induced redox processes.[11] Anal. Calcd for $[UO_2(HMPA)_4](ClO_4)_2$: C, 24.31; H, 6.12; N, 14.18; P, 10.45; U, 20.07. Found: C, 24.16; H, 6.13; N, 14.54; P, 10.5; U, 19.87. The yield was 96%. Analyses for U as $UO_2{}^{2+}$ were made with an ion-exchange technique,[12] and C, H, and N analyses were carried out by the Australian Microanalytical Service, Melbourne. No explosion hazard was encountered with $[UO_2(HMPA)_4](ClO_4)_2$, but it should be noted that *such perchlorate salts are potentially explosive.*

Solutions of $[UO_2(HMPA)_4](ClO_4)_2$ and HMPA in CD_2Cl_2 diluent (CEA 99.4%) were prepared under dry nitrogen in 5-cm^3 volumetric flasks. Each solution was transferred to a 5 mm o.d. NMR tube and was degassed on a vacuum line prior to sealing under vacuum not more than 1 h before commencement of the NMR experiment. The redistilled HMPA and CD_2Cl_2 were thoroughly dried over Linde 4A molecular sieves prior to use.

Proton NMR spectra were run at 90 MHz on a Bruker HX90E spectrometer in PFP mode using a deuterium lock. Depending upon the concentration of the sample, up to ten spectra were computer (Nicolet BNC-12) averaged, and these spectra were then digitized

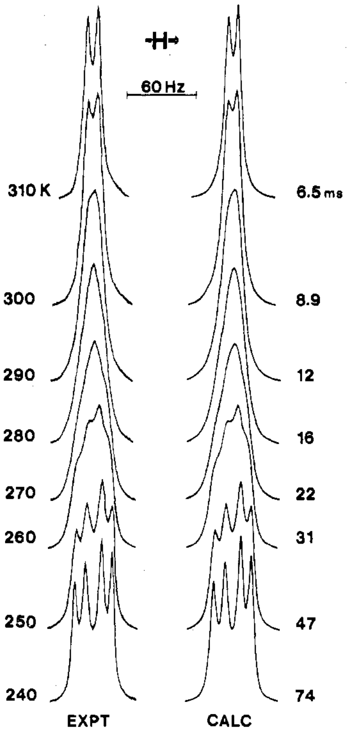

Figure 1. Experimental and best-fit calculated ^1H NMR line shapes of a $UO_2(HMPA)_4^{2+}$ (0.04452 mol dm^{-3})–HMPA (0.1896 mol dm^{-3})–CD_2Cl_2 (13.89 mol dm^{-3}) solution. Experimental temperatures (K) and best-fit τ values appear to the left and right of the figure, respectively. The doublet of coordinated HMPA is downfield.

Table I. Solution Compositions and Coordination Numbers of UO_2^{2+} in HMPA

Soln	$[UO_2(HMPA)_4^{2+}]$,[a] mol dm^{-3}	[HMPA],[b] mol dm^{-3}	$[CD_2Cl_2]$, mol dm^{-3}	CN[c]
i	0.1561	0.6647	11.58	4.00 ± 0.05
ii	0.1314	0.4870	13.17	4.10 ± 0.05
iii	0.04452	0.1896	13.89	3.95 ± 0.05
iv	0.01306	0.06094	14.65	3.95 ± 0.05
v	0.00511	0.01907	15.70	3.95 ± 0.05

[a] Added as $[UO_2(HMPA)_4](ClO_4)_2$. [b] Added as HMPA. [c] CN = number of HMPA molecules coordinated per UO_2^{2+} ion as determined from integration of the doublets of coordinated and free HMPA within the temperature range 180–230 K.

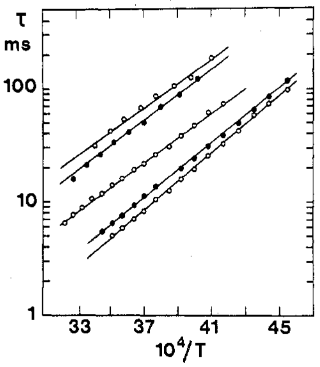

Figure 2. Semilogarithmic plots of τ data for the $UO_2(HMPA)_4^{2+}$ system against $1/T$. The data for solutions i–v appear in the order of increasing τ magnitude and the solid lines are the linear regression best-fit lines.

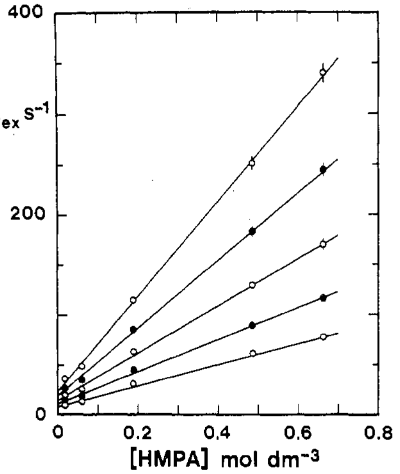

Figure 3. Plots of k_{ex} data sets against [HMPA] where k_{ex} decreases in the sequence 300, 290, 280, 270, and 260 K for a given [HMPA] value. The solid lines are the linear regression best-fit lines to eq 2.

onto paper tape (averaging from 400 to 900 data points per spectrum respectively ranging from fast to slow exchange conditions) prior to line-shape analysis through a CDC 6400 computer. The spectrometer temperature control was better than ±0.3 K.

Results and Discussion

The doublet arising from coordinated HMPA ($J_{^1H-^{31}P}$ = 10.1 Hz) appears downfield from free HMPA ($J_{^1H-^{31}P}$ = 9.0 Hz) under slow-exchange ^1H NMR conditions as may be seen in Figure 1. Over the temperature range 180–230 K, in which chemical exchange induced line shape modification was negligible, the ratios of the free and coordinated doublet area integrations were consistent with $UO_2(HMPA)_4^{2+}$ being the greatly predominant species over the 34.8-fold concentration range investigated (Table I), in agreement with other studies.[13] It is assumed that the structure of $UO_2(HMPA)_4^{2+}$ in solution is similar to that reported in the solid state[1] where the four HMPA ligands occupy the equatorial plane about the dioxouranium(VI) axis. At higher temperatures, coalescence phenomena (Figure 1) consistent with ligand exchange were observed and the mean site lifetimes (τ) characterizing HMPA in $UO_2(HMPA)_4^{2+}$ were derived through a complete line-shape analysis using a computer program which minimizes the mean of the squares of the residuals between the experimental and calculated line shapes to give the best-fit τ values.[14] Typical best-fit calculated line shapes and τ values for solutions (Table I) are shown in Figure 1. (In this particular case the half-widths at half-height of the doublet components of free and coordinated HMPA and the chemical shift between the doublet centers in the absence of chemical exchange, which are required input in the fitting procedure, varied respectively from 2.18, 2.50, and 23.95 Hz at 240 K to 1.20, 1.80, and 23.20 Hz at 310 K.) Similar line-shape variations were observed for the other four solutions (Table I) but whereas the temperature ranges over which exchange induced line shape modification occurred were similar, such line-shape modification commenced at a lower temperature as [HMPA] increased from solution v to i. The observed first-order exchange rate law for any one of these solutions is given by eq 1.

$$4/\tau = 4k_{ex} = (\text{exchange rate})/[UO_2(HMPA)_4^{2+}] \qquad (1)$$

The derived τ values for the five solutions are plotted semilogarithmically against $1/T$ in Figure 2 from which it is seen that there is a systematic dependence of τ upon [HMPA]. The logarithm of τ varied linearly with $1/T$ and each data set was subjected to a linear regression analysis to produce the best-fit lines shown in Figure 2, from which best-fit τ values were then interpolated. Some of these interpolated k_{ex} ($=1/\tau$) values are plotted against [HMPA] in Figure 3 in which it is seen that the overall exchange rate law is given by eq 2.

A semilogarithmic plot of k_1/T and k_2/T against $1/T$ yields the kinetic parameters k_1(273 K) = 12.5 ± 1.1 (0.1) s^{-1}, $\Delta H^{\ddagger}$

$$4k_{ex}[UO_2(HMPA)_4^{2+}] = 4(k_1 + k_2[HMPA])[UO_2(HMPA)_4^{2+}] \qquad (2)$$

= 14.0 ± 3 (0.1) kJ mol^{-1}, and $\Delta S^{\ddagger} = -172 \pm 11$ (1) J K^{-1} mol^{-1} and k_2(273 K) = 173 ± 15 (1) mol^{-1} dm^3 s^{-1}, $\Delta H^{\ddagger}$ = 22.2 ± 3.0 (0.01) kJ mol^{-1}, and $\Delta S^{\ddagger} = -120 \pm 9$ (0.03) J K^{-1} mol^{-1}, where the error in parentheses represents one standard deviation for the rate constants and one standard error in the activation parameters as derived from linear regression analyses through eq 3.

$$k = (KT/h) \exp(-\Delta H^{\ddagger}/RT) \exp(\Delta S^{\ddagger}/R) \qquad (3)$$

As a consequence of the interpolations involved in the derivation of k_1 and k_2, these errors are unrealistically small, and estimated overall errors appear as the large quoted errors. (The latter errors were calculated by assuming a 10% higher value for each of the best-fit lines in Figure 2 at the highest experimental temperatures and a 10% lower value at each of the lowest experimental temperatures and by drawing new lines through each pair of points from which new k_{ex} values were then interpolated. New k_1, k_2, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ values were derived from these data. The procedure was then repeated with the 10% higher and lower values reversed at the experimental temperature extremes to yield a second new set of k_1, k_2, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ values. These two sets of kinetic parameters are considered to represent the upper limits of systematic error.)

The k_1 term is consistent with a dissociative (D)[15] ligand exchange process proceeding through a reactive intermediate, $UO_2(HMPA)_3^{2+}$. Other authors have shown that a linear free energy relationship exists between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for predominantly dissociative ligand exchange processes such that small $\Delta H^{\ddagger}$ values and negative $\Delta S^{\ddagger}$ values may arise as observed here.[6,16] The k_2 term is consistent with either a dissociative interchange (I_D)[15] ligand exchange mechanism in which the rate-determining step is still primarily bond breaking, but with a synchronous exchange of HMPA between first and second coordination spheres also occurring, or an associative (A)[15] ligand exchange mechanism proceeding through a transition state of stoichiometry $UO_2(HMPA)_5^{2+}$. The usual strategem of testing for an A mechanism by noting the variation in k_2 as the nature of the incoming ligand is varied is inapplicable in this system as the nature of the coordinated and incoming ligand cannot be independently varied. Nevertheless the observation of ground-state $UO_2L_5^{2+}$ species in solution[4-8] lends plausibility to the postulated $UO_2(HMPA)_5^{2+}$ transition required by the A mechanism.

Hexamethylphosphoramide is the strongest oxygen donor (donor number DN = 38.8) characterized by Gutmann[17] but only occupies four equatorial ligand sites in ground-state $UO_2(HMPA)_4^{2+}$ whereas structurally similar TMP (DN = 23.0) and TEP (probable DN ≈ 23 as DN = 23.7 for tributyl phosphate), which are of similar bulk to HMPA, produce $UO_2L_5^{2+}$ ground-state species which undergo exchange through D or I_D mechanisms. Overall it is probable that compensatory extension or contraction of both axial and equatorial bonds serve to maintain a virtually constant total bond order in these ground-state species and the $UO_2(HMPA)_3^{2+}$ or $UO_2(HMPA)_5^{2+}$ and $UO_2L_4^{2+}$ excited species. While a fine balance between steric interactions and donor power probably determines the ground-state stoichiometry of $UO_2(HMPA)_4^{2+}$, it is likely that the latter factor provides the major stabilization in $UO_2(HMPA)_3^{2+}$. Conversely, in the case of TEP (which is sterically very similar to HMPA while being a weaker donor) it is probably the steric interactions which tip the balance to the higher coordination number $UO_2(TEP)_5^{2+}$ ground state and dissociative transition state. Some support for these hypotheses may be adduced from solid-state studies which show the mean U=O and U—OP(N(Me)$_2$)$_3$ distances[1] to be 1.74 and 2.27 Å, respectively, in $UO_2(HMPA)_4^{2+}$ whereas in $UO_2(H_2O)_5^{2+}$ (DN = 18 for H_2O) the U=O and U—OH$_2$ mean distances[2] are 1.71 and 2.45 Å, respectively, which is consistent with an increase in the uranium(VI) to equatorial ligand bond order as the number of such ligands decreases. Unfortunately, there are no other published structures in which the equatorial plane is occupied only by monodentate oxygen donors, but for a given equatorial occupancy by mono- and bidentate oxygen donors an inverse relationship between the U=O distance and the equatorial ligand distance has been observed.[3] Additionally, it appears that for similar U=O distances the equatorial ligand distance is greater when the equatorial occupancy is six than when it is five.[3]

The ability of HMPA to stabilize species of reduced coordination number is observed[18] in $Al(HMPA)_4^{3+}$ which undergoes ligand exchange through an A mechanism (in contrast to the AlL_6^{3+} species[18,19] (L = DMF, Me$_2$SO, TMP, DMMP, dimethyl hydrogen phosphite) which undergo ligand exchange through a D mechanism) and $CoBr_2(HMPA)_2$ and $CoCl_2(HMPA)_2$ which exhibit the HMPA exchange rate eq 4 whereas the exchange of L in CoL_2X_2 (where X = Cl or Br and I; and L = 2-picoline or triphenylphosphine) occurs through an A mechanism alone.[20]

$$\text{rate} = 2(k_1 + k_2[HMPA])[CoX_2(HMPA)_2] \qquad (4)$$

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Registry No. $[UO_2(HMPA)_4](ClO_4)_2$, 59954-64-2; $UO_2(HMPA)_4^{2+}$, 59954-63-1; HMPA, 680-31-9.

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