Proton Magnetic Resonance Study of Inter- and Intra-molecular Site Exchange on the Dioxopentakis(tetramethylurea)uranium(VI) Ion

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The species $[UO_2(tmu)_5]^{2+}$ is shown from ^1H n.m.r. studies to be the predominant dioxuranium(VI) species existing in tetramethylurea (tmu) solutions in CD_2Cl_2 and CD_3CN solvents. The kinetic parameters characterizing rotation about the carbonyl carbon–nitrogen bond in the tmu ligand are k(195 K) = 126 ± 7 s^{-1}, $\Delta H^‡$ = 29.0 ± 0.5 kJ mol^{-1}, and $\Delta S^‡$ = −52 ± 3 J K^{-1} mol^{-1}. The rate law for tmu exchange is rate = $5k_{ex.}[UO_2(tmu)_5{}^{2+}]$ over a 59.3- and 23.7-fold variation of [tmu] in CD_2Cl_2 and CD_3CN solvents respectively, consistent with a dissociative exchange mechanism. The kinetic parameters in the two solvents show no significant differences, a typical data set being $k_{ex.}$(273 K) = 73 ± 7 s^{-1}, $\Delta H^‡$ = 80 ± 2 kJ mol^{-1}, and $\Delta S^‡$ = 85 ± 7 J K^{-1} mol^{-1} in a solution in which $[UO_2(tmu)_5{}^{2+}]$, [tmu], and $[CD_2Cl_2]$ = 0.130, 0.404, and 12.91 mol dm^{-3} respectively. In general, the kinetic parameters for tmu exchange are consistent with the surface charge density of the uranium(VI) centre seen by the equatorial ligands being between that on aluminium(III) and the bivalent first-row transition-metal ions.

DIOXOPENTAKIS(TETRAMETHYLUREA)URANIUM(VI) ion, $[UO_2(tmu)_5]^{2+}$, is a particularly interesting species since it facilitates the determination of the barrier to rotation about the carbonyl carbon–nitrogen bond in the tmu ligand, one of the first such studies in a urea,[1] and also permits the extension of ligand-exchange studies of $[UO_2L_5]^{2+}$ ions. As a consequence of earlier studies, it has been shown that the $\Delta H^‡$–$\Delta S^‡$ linear free-energy relation for dissociative ligand exchange on $[UO_2L_5]^{2+}$ [L = trimethyl phosphate (tmp),[2] triethyl phosphate (tep),[2] dimethyl methylphosphonate (dmmp),[3] and dimethylacetamide (dma) [4]] is consistent with the surface charge density of the uranium(VI) centre seen by the equatorial ligands (L) being intermediate between that of the aluminium(III) centre in $[AlL_6]^{3+}$ and the bivalent first-row transition-metal-ion centre in $[ML_6]^{2+}$. The present study of tmu exchange on $[UO_2(tmu)_5]^{2+}$, in CD_2Cl_2 and CD_3CN solvents, tests the generality of this observation.

EXPERIMENTAL

The salt $[UO_2(tmu)_4][ClO_4]_2$ was prepared under dry nitrogen by heating hydrated dioxouranium(VI) perchlorate (G. F. Smith) (2.5 g) under reflux with triethyl orthoformate [5,6] (10 g) at 320—330 K for 1 h. Dry tetramethylurea (2.7 g) was then added at room temperature and the resulting pale yellow crystals were filtered off, washed with dry diethyl ether, and pumped 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 [7] {Found: C, 26.05; H, 5.20; N, 11.85; U, 25.15. Calc. for $[UO_2(tmu)_4][ClO_4]_2$: C, 25.75; H, 5.20; N, 12.0; U, 25.5%}. The yield was 95%. Analyses for U as $[UO_2]^{2+}$ were made with an ion-exchange technique [8] and C, H, and N analyses were carried out by the Australian Microanalytical Service, Melbourne. **CAUTION:** No explosion hazard was encountered with $[UO_2(tmu)_4][ClO_4]_2$ but it should be noted that *such perchlorate salts are potentially explosive*.

Solutions of $[UO_2(tmu)_4][ClO_4]_2$ and tmu in CD_2Cl_2 diluent (CEA, 99.4%) and CD_3CN (CEA, 99.6%) were prepared under dry nitrogen in volumetric flasks (5 cm^3). Each solution was transferred to a 5-mm o.d. n.m.r. tube and was degassed on a vacuum line prior to sealing *in vacuo* not more than 1 h before commencement of the n.m.r. experiment. The redistilled tmu, CD_2Cl_2, and CD_3CN were thoroughly dried over Linde 4A molecular sieves prior to use.

Proton n.m.r. spectra were run at 90 MHz on a Bruker HX90E spectrometer in the PFP mode using a deuterium lock. Depending on the concentration of the sample, up to 12 spectra were computer (Nicolet BNC 12) averaged and these spectra were then digitized on to paper tape (averaging from 500 to 800 data points per spectrum respectively, ranging from fast- to slow-exchange conditions) prior to lineshape analysis through a CDC 6400 computer. The spectrometer temperature control was better than ±0.3 K. Infrared measurements were made in Nujol mulls between NaCl plates or in CH_2Cl_2 in a NaCl cell using a Perkin-Elmer 457 spectrophotometer.

RESULTS AND DISCUSSION

The tetrakis(tetramethylurea) species exhibits a single intense perchlorate i.r. absorption (ν_3) at 1 100 cm^{-1} in Nujol mulls and CH_2Cl_2 solution consistent with all the perchlorate Cl–O bonds being equivalent [9] as indicated in the formula $[UO_2(tmu)_4][ClO_4]_2$ assigned to the crystalline solid isolated from solution (see Experimental section). A similar six-co-ordinate environment for the uranium(VI) centre has been observed in solution [10] and the solid state [11] for the $[UO_2\{OP(NMe_2)_3\}_4]^{2+}$ ion. Addition of tmu to solutions of $[UO_2(tmu)_4][ClO_4]_2$ in CD_2Cl_2 and CD_3CN (Table) produces seven-co-ordinate $[UO_2(tmu)_5]^{2+}$, which also exhibits a single intense perchlorate i.r. absorption at 1 100 cm^{-1}, as the predominant species in solution as shown from the ^1H n.m.r. studies discussed below. This is the second system reported to undergo a change in co-ordination number on transfer from the solid to the solution phase, the first being the aqueous system in which $[UO_2(OH_2)_5]^{2+}$ and $[UO_2(OH_2)_4]^{2+}$ are the dominant species in the solid [12] and solution phases [13,14] respectively. This variation of co-ordination number with phase is a reflection of the ability of U^{VI} to vary its co-ordination number from six to eight [15] in the ground state, and further appears to indicate that a fine balance exists between the factors (which have been discussed elsewhere [14-16]) determining co-ordination number.

In the CD_2Cl_2 and CD_3CN solutions 1—11 (Table), in which the number of moles of tmu ligand added exceeded

Solution composition and kinetic parameters for the dioxouranium(VI)–tetramethylurea system

Solution	$[UO_2(tmu)_4(ClO_4)_2]$ [a]	[tmu] [b]	$[CD_2Cl_2]$	$[CD_3CN]$	CN [c]	$k_{ex.}$(273 K) [d]	$\Delta H^\ddagger$ [e]	$\Delta S^\ddagger$ [e]
		mol dm^{-3}				s^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}
1	0.130 00	0.534 00	12.91		4.8 ± 0.1	73 ± 7	80 ± 2	85 ± 7
2	0.077 54	0.487 80	13.06		5.2 ± 0.1	62 ± 6	86 ± 2	105 ± 7
3	0.039 10	0.261 40	14.26		5.2 ± 0.1	64 ± 8	83 ± 2	94 ± 7
4	0.011 89	0.074 81	14.92		5.1 ± 0.1	70 ± 7	72 ± 2	55 ± 7
5	0.008 26	0.055 19	15.33		4.8 ± 0.1	69 ± 8	79 ± 3	80 ± 10
6	0.001 20	0.008 01	15.46		4.9 ± 0.1	72 ± 15	79 ± 11	81 ± 42
7	0.192 80	1.153 00		14.13	5.1 ± 0.1	63 ± 4	80 ± 1	83 ± 5
8	0.084 59	0.488 40		16.95	5.0 ± 0.1	89 ± 4	81 ± 1	90 ± 3
9	0.044 73	0.267 50		17.71	5.0 ± 0.1	74 ± 2	72 ± 1	55 ± 2
10	0.012 65	0.073 06		18.93	4.9 ± 0.1	86 ± 4	77 ± 1	75 ± 3
11	0.008 130	0.048 62		19.29	4.9 ± 0.1	74 ± 4	81 ± 1	88 ± 3
						k(195 K)		
12	0.070 56		15.25		4 [f]	151 ± 10	15.2 ± 0.6	−122 ± 3
13	0.084 91	0.083 46	15.02		5 [f]	126 ± 7	29.0 ± 0.5	−52 ± 3

[a] With the exception of solution 12, the predominant species in solution is $[UO_2(tmu)_5]^{2+}$. [b] This is the formal concentration of tmu added; however, on formation of $[UO_2(tmu)_5]^{2+}$ the actual concentration of free tmu ranges from 0.404 00 to 0.006 81 mol dm^{-3} in solutions 1—6 respectively, *etc.* [c] CN = Number of tmu molecules co-ordinated per $[UO_2]^{2+}$ ion as determined from integration of the signals due to free and co-ordinated tmu in the range 190—250 K. [d] Taken from the linear regression line, the error quoted being one standard deviation. [e] The errors quoted are single standard errors. [f] No free tmu resonance was observed and hence it was assumed that four and five tmu ligands were co-ordinated in solutions 12 and 13 respectively.

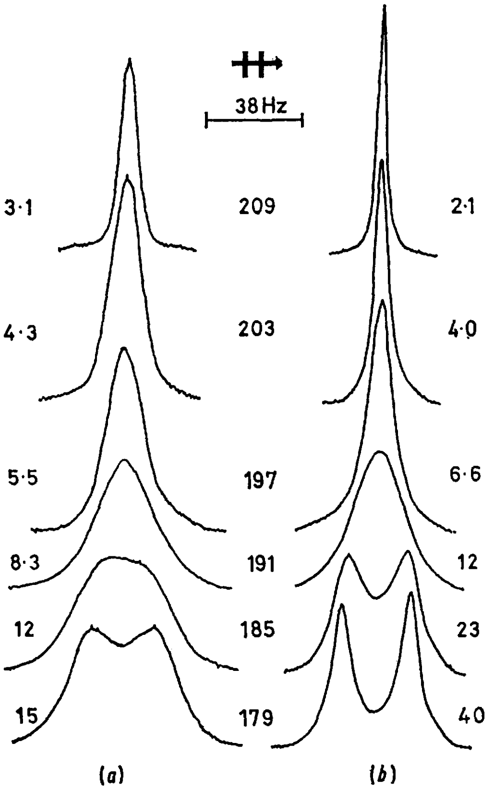

FIGURE 1 Experimental ^1H n.m.r. coalescence phenomena accompanying rotation about the carbonyl C–N bond in tetramethylurea ligands in (*a*) $[UO_2(tmu)_4]^{2+}$ and (*b*) $[UO_2(tmu)_5]^{2+}$. The best-fit τ values (in ms) appear to the left and right of the Figure respectively, and the experimental temperatures (T/K) appear in the centre

the number of moles of the dioxouranium(VI) species added as $[UO_2(tmu)_4][ClO_4]_2$, a ^1H resonance arising from co-ordinated tmu was observed downfield from that arising from free tmu in the range 170—250 K. A comparison of the integrated areas of these resonances indicated that five tmu ligands are co-ordinated by each dioxouranium(VI) ion within experimental error such that $[UO_2(tmu)_5]^{2+}$ is the predominant species in these solutions. Solution 13 (Table), which was almost equimolar in added tmu ligand and $[UO_2(tmu)_4][ClO_4]_2$, exhibited a ^1H resonance due to co-ordinated tmu only in the range 170—250 K, consistent with $[UO_2(tmu)_5]^{2+}$ being the predominant species in solution. In solutions in which tmu ligand was added in less than equimolar amounts, only one ^1H resonance arising from co-ordinated tmu was observed indicating that the ^1H chemical shift between the co-existing $[UO_2(tmu)_4]^{2+}$ and $[UO_2(tmu)_5]^{2+}$ species was <0.05 p.p.m.

At 170 K, the lowest temperature examined in this study, the ^1H n.m.r. spectrum of tmu in CD_2Cl_2 was a singlet consistent with rotation about the carbonyl C–N bond being in the fast-exchange limit. In contrast, $[UO_2(tmu)_4]^{2+}$ in CD_2Cl_2 (solution 12) exhibited a doublet (the components of which were separated by 26.8 Hz at 170 K, with full widths at half-height for the downfield and upfield components of 16.8 and 17.7 Hz, respectively), which coalesced to a singlet over the range 179—209 K as seen in Figure 1. Similarly $[UO_2(tmu)_5]^{2+}$ in CD_2Cl_2 (solution 13) also exhibited a doublet at 170 K (component separation, downfield and upfield widths 28.3, 6.6, and 6.2 Hz respectively) which also coalesced to a singlet in the range 179—209 K (Figure 1). These two coalescence phenomena are consistent with rotation about the carbonyl C–N bond in the tmu ligand in $[UO_2(tmu)_4]^{2+}$ and $[UO_2(tmu)_5]^{2+}$ respectively passing from the dynamic n.m.r. slow- to the fast-exchange limit, and appear to be some of the first observations of this process in a urea.[1] The experimental spectra were subjected to a complete lineshape analysis for two-site exchange.[17] As a consequence of 170 K being just above the freezing point for the two solutions, only the small temperature range 170—177 K was available for the extrapolation of doublet component separations and linewidths into the dynamic n.m.r. temperature range for $[UO_2(tmu)_5]^{2+}$. Hence, after the best-fit site lifetimes (τ) had been obtained by minimizing the mean of the squares of the residuals between the experimental and simulated lineshapes through a previously described program [17] using the extrapolated component separations and linewidths, these input parameters were varied systematically to optimize the above minimization to give the final τ values (Figure 1). In fact, the differences between the final input component separation which varied with T [30.1 (179), 31.1 Hz (203 K)] and the downfield and upfield full widths at half-height which also varied with T [1.1, 0.5 (179); 1.0, 0.4 Hz (203 K)] and the extrapolated values were small. (Nevertheless the extrapolation of the initial component separations and linewidths from the small 170—177 K temperature range may still have introduced some systematic error into the derived τ values.) The kinetic parameters derived from a linear regression analysis of a plot of τT against $1/T$ are k (195 K) $= 126 \pm 7$ s^{-1}, $\Delta H^{\ddagger} = 29.0 \pm 0.5$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -52 \pm 3$ J K^{-1} mol^{-1} where the errors quoted are, respectively, one standard deviation, one standard error, and one standard error. In the case of $[UO_2(tmu)_4]^{2+}$ the slow-exchange limit did not appear to have been reached at 170 K and hence as a reasonable approximation the initial input values of the doublet component separation and linewidth were the final values for the $[UO_2(tmu)_5]^{2+}$ system. As in the previous case these input values were then allowed to vary systematically to optimize the minimization between the experimental and simulated lineshapes [final input component separation and linewidth varied with T: 38.3, 0.9, 1.2 (179); 39.3, 0.7, 1.2 Hz (203 K)] and obtain the τ values in Figure 1. The derived kinetic parameters are: k (195 K) $= 151 \pm 10$ s^{-1}, $\Delta H^{\ddagger} = 15.2 \pm 0.6$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -122 \pm 3$ J K^{-1} mol^{-1} where the errors are the same quantities as in the previous case.

It is apparent from the above discussion that the kinetic parameters derived for rotation about the carbonyl C–N bond of the tmu ligand in $[UO_2(tmu)_4]^{2+}$ are less reliable than those in $[UO_2(tmu)_5]^{2+}$, but it is clear that the barrier to rotation about the carbonyl C–N bond in tmu is increased on co-ordination to U^{VI}. In CD_2Cl_2 solution the i.r. C=O stretch and N–C–N asymmetric stretch frequencies of free tmu occurred at 1 635 and 1 505 cm^{-1} respectively, whereas in both $[UO_2(tmu)_4]^{2+}$ and $[UO_2(tmu)_5]^{2+}$ these frequencies were respectively decreased and increased (as is also observed [18] on co-ordination of tmu to Co^{2+}, Zn^{2+}, and Pb^{2+}) to give an overlapping band at 1 550 cm^{-1}. Thus co-ordination of tmu decreases and increases the bond orders of C=O and N–C–N respectively which might be expected to increase the barrier to rotation about the carbonyl C–N bond. (A similar correlation between an increase in rotation barrier height and an i.r. frequency change has been observed [19] in the Li$^+$–HCONMe$_2$ system.) In addition the sterically restricted first co-ordination sphere of $[UO_2(tmu)_n]^{2+}$ (n = 4 or 5) may further inhibit rotation.

In both CD_2Cl_2 and CD_3CN diluents, coalescence of the ^{1}H n.m.r. singlets characterizing the free and co-ordinated sites occurs as tmu exchanges between them (Figure 2). In contrast to the rotation study, good extrapolated singlet separations and linewidths were obtained over the range 210—250 K (where tmu is in the fast-rotation site-exchange limit in both free and co-ordinated sites) and a typical set of experimental and best lineshapes is shown in Figure 2. In this particular case the chemical-shift difference and the co-ordinated and free tmu linewidths varied with T from 30.2, 1.64, 1.28 (260) to 30.8, 1.62, 1.28 Hz (290 K). The mean lifetime τ_B of tmu in the first co-ordination sphere of $[UO_2]^{2+}$ is given by equation (1) where τ_F is the lifetime of free tmu and

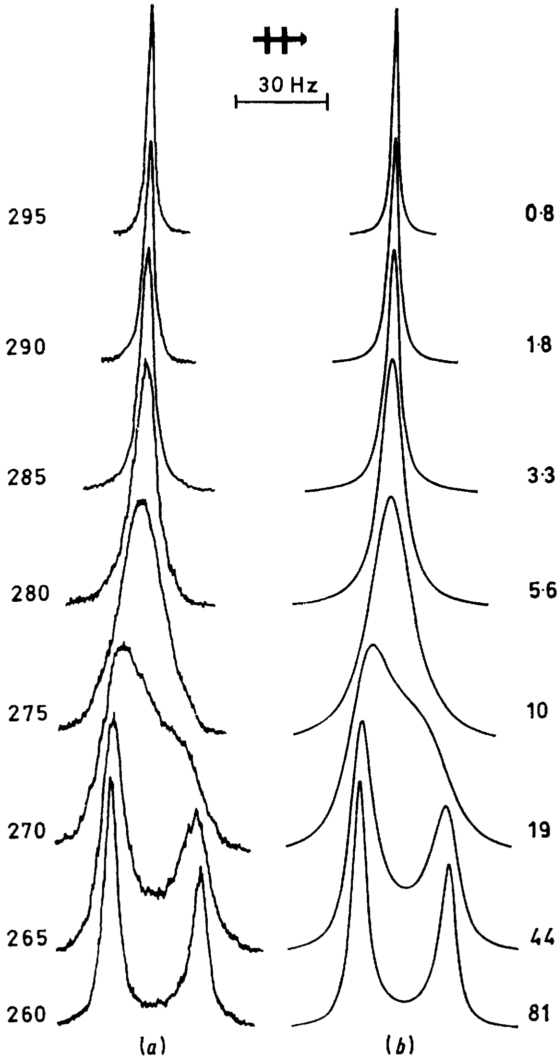

FIGURE 2 Experimental (a) and best-fit calculated ^{1}H n.m.r. lineshapes (b) of a $[UO_2(tmu)_5]^{2+}$ (0.1300 mol dm^{-3})–tmu (0.404 0 mol dm^{-3})–CD_2Cl_2 (12.91 mol dm^{-3}) solution. Experimental temperatures (T/K) and best fit τ_B values (in ms) appear on the left- and right-hand sides of the Figure respectively. The concentrations of the exchanging species are calculated from those of solution 1 on the basis that $[UO_2(tmu)_5]^{2+}$ is the predominant dioxouranium(VI) species in solution

x_B and x_F are the mol fractions of co-ordinated and free tmu, and the observed first-order exchange rate constant is given by equation (2).

$$1/\tau_B = x_F/\tau_F x_B = k_{ex.} \\ = \boldsymbol{kT/h}\exp(-\Delta H^{\ddagger}/RT)\exp(\Delta S^{\ddagger}/R) \quad (1)$$

$$5k_{ex.} = \mathrm{rate}/[\mathrm{UO_2(tmu)_5}^{2+}] \quad (2)$$

In Figure 3 the product $\tau_B T$ is plotted against $1/T$ for all the solutions studied from which it may be seen that over the 59.3-fold variation in [tmu] in CD_2Cl_2 solutions 1—6 the maximum variation of $k_{ex.}$(273 K) is from 62 to 73 s^{-1} and similarly over the 23.7-fold [tmu] range in CD_3CN solutions 7—11 {[tmu] range calculated on the basis that $[\mathrm{UO_2(tmu)_5}]^{2+}$ is the predominant dioxouranium(VI) species in solution} the maximum variation of $k_{ex.}$(273 K) is from 63 to 89 s^{-1} (Table). There may be some chemical contribution to the variations in $k_{ex.}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ within each of the CD_2Cl_2 and CD_3CN data sets (Table), but the random nature of the variations suggests that their major sources probably arise in experimentation and data handling. It is clear, however, that the small variation of $k_{ex.}$ within each data set is consistent with the exchange of tmu on $[\mathrm{UO_2(tmu)_5}]^{2+}$ being independent of [tmu], and further that no meaningful distinction can be drawn between the kinetic parameters characterizing the process in CD_2Cl_2 and CD_3CN. The [tmu] independence of $k_{ex.}$ is consistent with either a dissociative (*D*) exchange mechanism in which a reactive intermediate $[\mathrm{UO_2(tmu)_4}]^{2+}$ is formed as in equation (3) or a dissociative interchange (I_D) mechanism[20] in which, although the rate-determining step is still primarily bond breaking, the exchange occurs through an associated species in which a tmu molecule resides in the second co-ordination sphere [equation (4)].

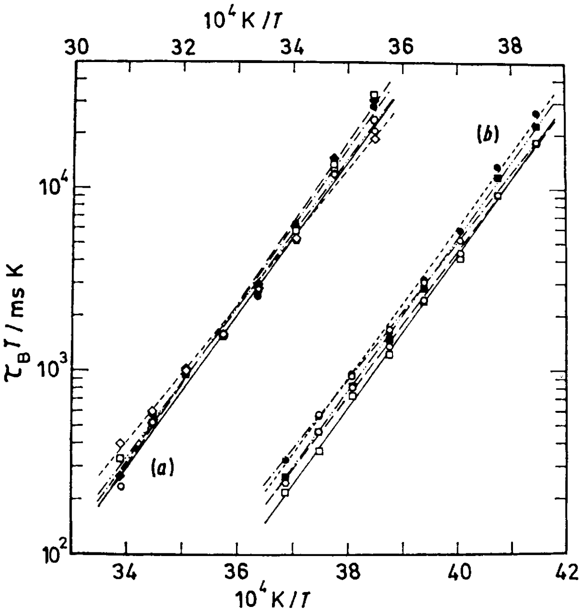

FIGURE 3 Semilogarithmic plots of $\tau_B T$ data for the $[\mathrm{UO_2(tmu)_5}]^{2+}$ system. The data for the CD_2Cl_2 solutions (*a*) refer to the lower temperature scale. Data points for solutions 1—6 are respectively represented by ○, ♦, □, open hexagons and ●, and the linear regression lines in the same order are represented by ——, — — —, — · — · —, – – – –, — ·· — ·· —, and —— (the lines for solutions 1 and 6 are almost indistinguishable). The data for the CD_3CN solutions (*b*) refer to the upper temperature scale. Data points for solutions 7—11 are respectively represented by ●, □, ○, open hexagons, and ■, and the linear regression lines in the same order are represented by – – – –, ——, — · — · —, — — —, and — ·· — ·· —

$$\left.\begin{array}{l}[\mathrm{UO_2(tmu)_5}]^{2+} + \mathrm{tmu}^* \xrightarrow[\text{slow}]{k} [\mathrm{UO_2(tmu)_4}]^{2+} + \mathrm{tmu} + \mathrm{tmu}^* \\ \qquad\qquad\qquad\xrightarrow[\text{fast}]{} [\mathrm{UO_2(tmu)_4(tmu^*)}]^{2+} + \mathrm{tmu}\end{array}\right\}(k_{ex.} = k) \quad (3)$$

$$[\mathrm{UO_2(tmu)_5}]^{2+} + \mathrm{tmu}^* \\ \underset{\text{fast}}{\overset{K_{as.}}{\rightleftharpoons}} [\mathrm{UO_2(tmu)_5}^{2+}\cdots\mathrm{tmu}^*] \\ \xrightarrow[\text{slow}]{k'} [\mathrm{UO_2(tmu)_4(tmu^*)}^{2+}\cdots\mathrm{tmu}] \quad (4) \\ \{k_{ex.} = k'K_{as.}[\mathrm{tmu}]/(1 + K_{as.}[\mathrm{tmu}])\}$$

(*a*) when $K_{as.}[\mathrm{tmu}] \gg 1$, $k_{ex.} = k'$

(*b*) when $K_{as.}[\mathrm{tmu}] \ll 1$, $k_{ex.} = k'K_{as}[\mathrm{tmu}]$

For the I_D mechanism to be operative the limiting condition (*a*) of equation (4) must apply over the concentration ranges studied in which case $K_{as.} > 1\,000$ dm^3 mol^{-1} {calculated on the assumption that 90% of $[\mathrm{UO_2(tmu)_5}]^{2+}$ exists as the associated species in solution 6}. This value seems very high by comparison to $K_{as.} = 0.35$ dm^3 mol^{-1} calculated from the Fuoss equation[21] for an interaction distance of 700 pm. In view of these factors and the i.r. evidence for the probable existence of $[\mathrm{UO_2(tmu)_4}]^{2+}$ as a discrete entity in the solution and solid states it seems likely that exchange occurs through the *D* mechanism [equation (3)].

The average of the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for tmu exchange on $[\mathrm{UO_2(tmu)_5}]^{2+}$ lie on the $\Delta H^{\ddagger}$–$\Delta S^{\ddagger}$ linear free-energy relation observed for related $[\mathrm{UO_2L_5}]^{2+}$ systems which exchange L by a dissociative type of mechanism.[2] The lack of a significant difference between the kinetic parameters for exchange in CD_2Cl_2 and CD_3CN diluents suggests that either interactions outside the first co-ordination sphere have little effect on dissociative types of exchange processes,[22] or that whilst such interactions can make significant contributions to transition-state energetics these contributions are very similar for the two diluents used in this study.[23]

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