Ligand Intra- and Inter-molecular Exchange Processes in Dioxopentakis(trimethylurea)uranium(VI). A Proton Nuclear Magnetic Resonance Study

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The complex $[UO_2(trmu)_5]^{2+}$ is shown to be the predominant dioxouranium(VI) species in the presence of trimethylurea (trmu) in CD_3CN solution. The kinetic parameters characterizing rotation about the C–NMe$_2$ bond in co-ordinated trmu are $k_r(298.2\ K) = 925 \pm 37\ s^{-1}$, $\Delta H^\ddagger = 44.7 \pm 0.6$ kJ mol^{-1}, and $\Delta S^\ddagger = -38.3 \pm 2.4$ J K^{-1} mol^{-1}. Rotation about the C–NHMe bond is in the fast-exchange limit on the ^{1}H n.m.r. time-scale. The rate law for intermolecular trmu exchange is rate = $5k_{ex}[UO_2(trmu)_5{}^{2+}]$ over a twelve-fold variation of free trmu concentration, consistent with the operation of a *D* mechanism or, less probably, an *I* mechanism with a stability constant $\geqslant 200$ dm^3 mol^{-1} for the encounter complex. The exchange parameters are $k_{ex}(298.2\ K) = 983 \pm 8\ s^{-1}$, $\Delta H^\ddagger = 56.6 \pm 0.6$ kJ mol^{-1}, and $\Delta S^\ddagger = 2.2 \pm 1.9$ J K^{-1} mol^{-1}. The data are compared with those from other dioxouranium(VI) systems.

Dioxopentakis(trimethylurea)uranium(VI) ion, $[UO_2(trmu)_5]^{2+}$, provides the opportunity to study labile ligand (trmu) exchange in the equatorial plane of a metal complex in which both apical sites are occupied by oxo ligands inert to substitution,[1–17] and also to establish a profile of the dynamics of rotation about the carbon–nitrogen bonds in co-ordinated methyl-substituted ureas, which is not well established for their free state because of the greater rates of rotation about carbon-nitrogen bonds therein.[18–20] We have studied both of these processes by ^{1}H n.m.r. spectroscopy, and the mechanistic implications of the derived kinetic data are discussed.

Experimental

The complex $[UO_2(trmu)_5][ClO_4]_2$ was prepared under dry nitrogen by heating hydrated dioxouranium(VI) perchlorate (G. F. Smith) (2.0 g) under reflux with triethyl orthoformate (27 g) at 330 K for 90 min. After cooling to room temperature, trimethylurea (2.1 g) dissolved in a 10% ethanol–90% triethyl orthoformate solution (10 cm^3) was added to the reaction mixture. The resultant yellow crystals of $[UO_2(trmu)_5][ClO_4]_2$ were filtered off, washed with a 10% ethanol–90% triethyl orthoformate solution (20 cm^3), and pumped on a vacuum line for 12 h. All preparative and handling procedures were carried out under dry nitrogen, unless otherwise stated, and exposure of $[UO_2(trmu)_5][ClO_4]_2$ to light was kept to a minimum to avoid the possibility of photochemically induced redox processes. The product yield was 85% {Found: C, 24.65; H, 5.30; N, 14.6; $UO_2{}^{2+}$, 27.55. Calc. for $[UO_2(trmu)_5][ClO_4]_2$: C, 24.5; H, 5.15; N, 14.3; $UO_2{}^{2+}$, 27.6%}. Analyses for $UO_2{}^{2+}$ as a bipositive ion were carried out using an ion-exchange method,[21] and C, H, and N analyses were performed by the Australian Microanalytical Service, Melbourne. **CAUTION**: No explosion hazard was encountered with $[UO_2(trmu)_5][ClO_4]_2$, but it should be noted that perchlorate salts of metal complexes are sometimes explosive. Solutions of $[UO_2(trmu)_5][ClO_4]_2$ in CD_3CN (Aldrich 99%, dried over Linde 3A molecular sieves) were prepared by weight under dry nitrogen, and were then degassed and sealed in 5-mm n.m.r. tubes under vacuum.

Proton n.m.r. spectra were run on a Bruker CXP300 n.m.r. spectrometer at 300.13 MHz, with the deuterium frequency of CD_3CN as lock. Sample temperature control was better than ±0.3 K, and was monitored with a platinum resistance thermometer. Depending on the sample, up to 5 000 transients were collected and stored as 8 192 datum-point blocks prior to Fourier transformation. Lineshape analyses[22] of the Fourier-transformed spectra were carried out on a Nicolet BNC 12 minicomputer after transferring the data from the CXP300 system to a Diablo disk system. Other computing was carried out on a VAX 11-780 computer. Chemical shifts were measured directly from the proton impurity resonance of CD_3CN, and were then recalculated on the basis of the 1.95 p.p.m. downfield shift of this resonance from SiMe$_4$. Infrared spectra were run as Nujol mulls between sodium chloride plates using a Perkin-Elmer 683 spectrophotometer.

Results

Perchlorate i.r. absorptions were observed at 1 073 and 625 cm^{-1} for $[UO_2(trmu)_5][ClO_4]_2$ in Nujol mulls, consistent with perchlorate retaining its T_d symmetry and the equatorial plane of dioxouranium(VI) being occupied solely by five trmu ligands in the solid state. Carbonyl absorptions were observed at 1 585 cm^{-1} for $[UO_2(trmu)_5][ClO_4]_2$ and 1 633 cm^{-1} for trmu. A shift of the carbonyl frequencies to lower values on co-ordination of trmu is consistent with a decrease in the carbonyl bond order, and is usually accompanied by an increase in the carbon–nitrogen bond order. This should be confirmed by an increase in the carbon–nitrogen absorbance frequency, but the overlapping of absorbances in the range 1 400—1 530 cm^{-1} precluded unequivocal frequency assignments.

The spectra of a CD_3CN solution of $[UO_2(trmu)_5][ClO_4]_2$ and trmu recorded over a range of temperatures are shown in Figure 1. Integration of the resonances arising from free and co-ordinated trmu over the range 240—275 K produced area ratios consistent with 5.0 ± 0.1 co-ordinated trmu ligands per $UO_2{}^{2+}$, and $[UO_2(trmu)_5]^{2+}$ being the dominant dioxouranium(VI) species in solution. No resonances arising from free trmu were observed in the spectra of CD_3CN solutions of $[UO_2(trmu)_5][ClO_4]_2$ alone. {A range of populations of the two possible trmu isomers is expected to be co-ordinated in solutions of $[UO_2(trmu)_5]^{2+}$, but as separate resonances corresponding to differently populated $[UO_2(trmu)_5]^{2+}$ are not observed it is concluded that the influence of the population differences on the chemical shift is negligible.} It is seen from Figure 1 that coalescence of the NMe$_2$ resonances of co-ordinated trmu occurs as the temperature is increased, as a consequence of an increase in the rate of rotation of these

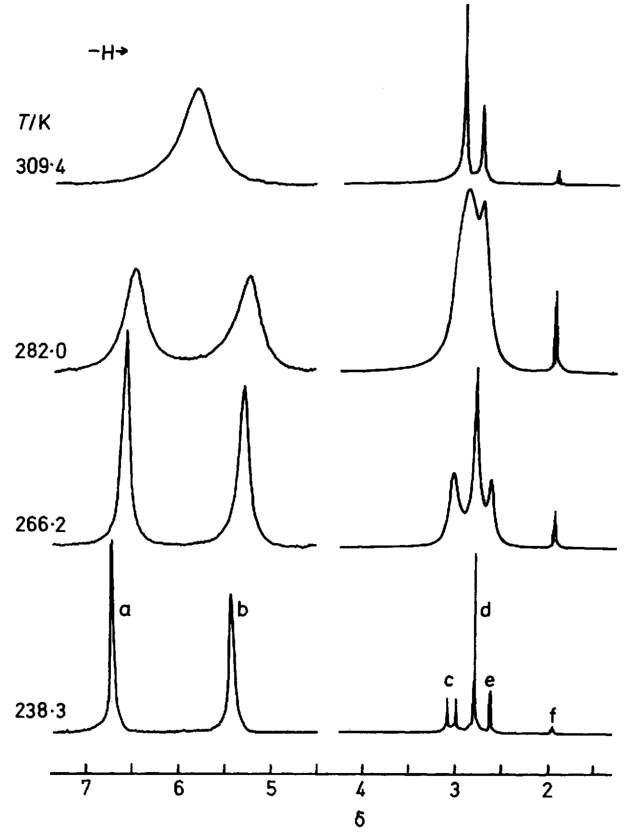


Figure 1. Temperature variation of the 300.13-MHz spectrum of a solution of $[UO_2(trmu)_5][ClO_4]_2$ (0.0864 mol dm^{-3}) and trmu (0.4532 mol dm^{-3}) in CD_3CN. The resonances (with their chemical shifts in p.p.m. from $SiMe_4$ shown in brackets) arise from: $[UO_2(trmu)_5]^{2+}$, a [6.71, q, J(H–H) = 4.9, N*H*Me], c (3.09 and 3.00 NMe_2), d (2.81, NH*Me*); free trmu, b (5.41, N*H*Me), d (2.81, NMe_2), e [2.63, d, J(H–H) = 4.4 Hz, NH*Me*]; and the proton impurity in CD_3CN, f (1.95). The left-hand side of the spectrum is plotted on a greater vertical scale than is the right-hand side

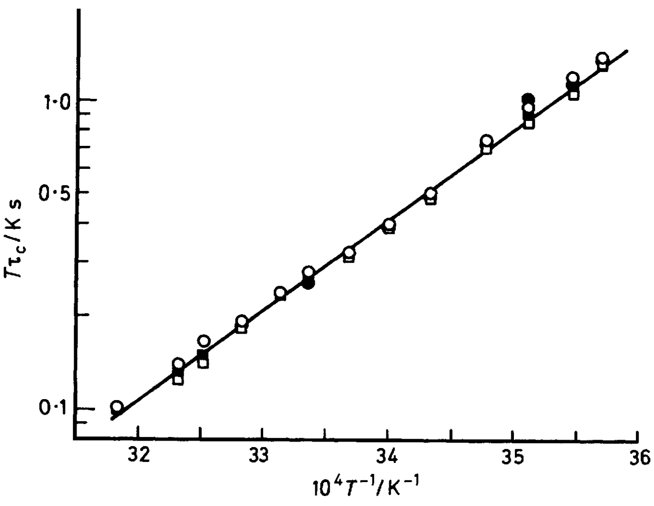


Figure 2. Variation of $T\tau_c$ with $1/T$ for intermolecular exchange of trmu in $[UO_2(trmu)_5]^{2+}$. The data for solutions i—iv in Table 1 are shown as ○, ●, □, and ■ respectively

groups about the carbon–nitrogen bond. The singlet NMe_2 resonance of free trmu indicates that rotation about the carbon–nitrogen bond is at the fast-exchange limit of the n.m.r. time-scale at the lowest temperature studied. The singlet H and doublet Me resonances of NHMe of both co-ordinated and free trmu also indicate that rotation about the carbon–nitrogen bond is in both cases at the fast-exchange limit of the n.m.r. time-scale. {The spin–spin splittings observed for the NHMe methyl doublets of free and co-ordinated trmu correspond to J(H–H) = 4.4 and 4.9 Hz respectively; as a consequence of intermolecular trmu exchange and overlap of resonances, the latter coupling is resolved only in solutions of $[UO_2(trmu)_5][ClO_4]_2$ alone. Similarly the quartet proton resonance of NHMe is resolved only at low temperature as a consequence of chemical exchange processes.} At higher temperatures coalescence of NHMe proton and methyl and NMe_2 methyl resonances arising from co-ordinated and free trmu occurs as intermolecular trmu exchange becomes increasingly rapid (Figure 1).

The occurrence of the various coalescences in different temperature ranges facilitates determination of the kinetic parameters characterizing the C–NMe_2 bond rotation in co-ordinated trmu from the NMe_2 doublet coalescence, and the trmu ligand exchange in $[UO_2(trmu)_5]^{2+}$ from coalescence of the H resonances of the NHMe groups of co-ordinated and free trmu using complete lineshape analysis methods which have been described in detail elsewhere.[22] For a solution in which $[UO_2(trmu)_5{}^{2+}]$ and $[CD_3CN]$ = 0.0585 and 18.56 mol dm^{-3} respectively, the observed rate constants for rotation about the C–NMe_2 bond, k_r/s^{-1}, and the corresponding experimental temperatures (K) shown in parentheses are: 12.5 (242.9), 15.5 (244.8), 19.5 (247.6), 24.5 (250.4), 35.0 (254.1), 42.5 (256.9), 55.0 (259.7), 72.5 (263.4), 95.0 (266.2), and 143 (270.8), where the error in k_r does not exceed $\pm 5\%$. The kinetic parameters characterizing C–NMe_2 bond rotation in co-ordinated trmu, determined from a linear regression fit of these data to equation (1), are: $k_r = 86.2 \pm 1.2$ s^{-1} (265.0 K), $\Delta H^‡ = 44.7 \pm 0.6$ kJ mol^{-1}, and $\Delta S^‡ = -38.3 \pm 2.4$ J K^{-1} mol^{-1}.

$$k_r = (k_BT/h)\exp[(-\Delta H^‡/RT) + (\Delta S^‡/R)] \qquad (1)$$

The mean lifetime of a single co-ordinated trmu ligand, τ_c ($= \tau_f X_c/X_f = 1/k_{ex}$), where τ_f is the mean lifetime of free trmu, X_c and X_f are the mole fractions of co-ordinated and free trmu, and k_{ex} is an observed first-order rate constant, characterizing intermolecular ligand exchange in $[UO_2(trmu)_5]^{2+}$, was determined from complete lineshape analyses[22] of the coalescing H resonances of the NHMe groups of co-ordinated and free trmu observed at *ca.* 3-K intervals over the range 280.1—314.2 K. The variation of τ_c with temperature for the four solutions studied is shown in Figure 2. The kinetic parameters for trmu exchange in $[UO_2(trmu)_5]^{2+}$ were derived through an equation analogous to (1); data for the four solutions studied (and their compositions) appear in Table 1. The rate of ligand exchange for a given solution is as in equation (2).

$$\text{Rate} = 5k_{ex}[UO_2(trmu)_5{}^{2+}] \qquad (2)$$

Discussion

It is seen from Table 1 that the kinetic parameters for the intermolecular exchange of trmu in $[UO_2(trmu)_5]^{2+}$ show little dependence on concentration, consistent with equation (2) being the overall exchange rate law in the concentration range studied. This is consistent with a D mechanism. The postulation of the six-co-ordinated reactive intermediate, $[UO_2(trmu)_4]^{2+}$, required by this mechanism is afforded plausibility by the observation of six-co-ordinated ground-state species, $[UO_2(ligand)_4]^{2+}$, both in the solid state and in solution.[4,6,11,23]

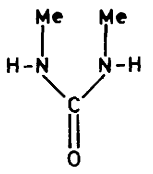
Table 1. Solution compositions and kinetic parameters for intermolecular exchange of trimethylurea in dioxopentakis(trimethylurea)uranium(VI)

Solution	$[UO_2(trmu)_5{}^{2+}]$	$[trmu]_{free}$	$[CD_3CN]$	k_{ex}(298.2 K)/s^{-1}	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}
		mol dm^{-3}				
i	0.1345	0.6955	15.88	939 ± 13	56.1 ± 1.0	0.3 ± 3.3
ii	0.0864	0.4532	16.82	981 ± 15	57.6 ± 1.2	5.5 ± 3.9
iii	0.0301	0.1697	17.54	1 020 ± 12	56.1 ± 0.9	0.8 ± 3.0
iv	0.0106	0.0582	18.13	993 ± 10	56.7 ± 0.8	2.6 ± 2.7
i—iv combined				983 ± 8	56.6 ± 0.6	2.2 ± 1.9

Table 2. Kinetic parameters for rotation about carbon–nitrogen bonds in co-ordinated ureas (L) in $[UO_2L_5]^{2+}$ and in ureas in the free state

Compound	Solvent	Bond	k_r(265 K)/s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
$[UO_2(1,1\text{-dmu})_5]^{2+}$ [a]	CD_3CN	C–NMe$_2$	39.1	49.1 ± 0.7	−28.3 ± 2.7
$[UO_2(1,1\text{-dmu})_5]^{2+}$ [a]	CD_3CN	C–NH$_2$	2 960	61.1 ± 0.5	53.1 ± 2.2
$[UO_2(1,3\text{-dmu})_5]^{2+}$ [a]	CD_3CN	C–NHMe (isomer **I**)	77.8	53.2 ± 0.7	−1.7 ± 3.0
$[UO_2(1,3\text{-dmu})_5]^{2+}$ [a]	CD_3CN	C–NHMe (isomer **II**)	317	47.6 ± 0.7	−16.3 ± 2.6
$[UO_2(1,3\text{-dmu})_5]^{2+}$ [a]	CD_3CN	C–NHMe (isomer **III**)	96.0	58.8 ± 0.7	3.8 ± 2.4
$[UO_2(trmu)_5]^{2+}$ [b]	CD_3CN	C–NHMe	Large?		
$[UO_2(trmu)_5]^{2+}$ [b]	CD_3CN	C–NMe$_2$	86.2	44.7 ± 0.6	−38.3 ± 2.4
$[UO_2(tmu)_5]^{2+}$ [c]	CD_2Cl_2	C–NMe$_2$	20 400	29.0 ± 0.5	−52 ± 3
1,1-dmu [d]	$(CD_3)_2CO$	C–NMe$_2$	4 465	36.8 ± 0.4	−35.2 ± 1.6
1,1-dmu [e]	$(CD_3)_2CO$	C–NH$_2$	330 (211 K)		
1,3-dmu [a]	CD_3CN	C–NHMe	Large		
trmu [b]	CD_3CN	C–NHMe	Large		
trmu [b]	CD_3CN	C–NMe$_2$	Large		
tmu [c]	$CHFCl_2$–$(CD_3)_2CO$	C–NMe$_2$	187 (135 K)		

[a] Ref. 18. 1,1-dmu = 1,1-Dimethylurea, 1,3-dmu = 1,3-dimethylurea. Three isomers of 1,3-dmu exist:



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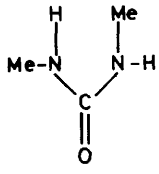

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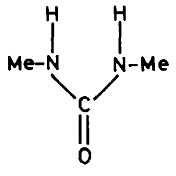

III

[b] This work. [c] Ref. 6. [d] A. M. Hounslow, personal communication. [e] Ref. 19.

The rate law (2) is also consistent with the operation of an *I* mechanism under conditions where all the $[UO_2(trmu)_5]^{2+}$ exists in an encounter complex in which the entering trmu resides in the second co-ordination sphere, and trmu exchange proceeds through interchange of trmu between the first and second co-ordination spheres of the encounter complex. For this condition to apply for the most dilute solution studied (solution iv in Table 1) the formation constant for the encounter complex would be ⩾200 dm^3 mol^{-1}. This seems unlikely as the encounter complex formed between $[UO_2(dmf)_5]^{2+}$ and dimethylformamide (dmf) in CD_2Cl_2 is reported to be characterized by a low stability constant, K(223.2 K) = 1.59 ± 0.11 kg mol^{-1}.[14] (At the high concentrations studied the statistical probability of dmf residing in the first co-ordination sphere is substantial and the reported K may reflect this factor to a significant extent.) The more highly charged $[Tb(dmf)_8]^{3+}$ forms an analogous encounter complex with dmf in dmf–$MeNO_2$ with a formation constant K(239.2 K) = 0.42 ± 0.01 kg mol^{-1}.[24] For the encounter complex formed between uncharged $[UO_2(acac)_2(dmso)]$ (acac = acetylacetonate) and dimethyl sulphoxide (dmso) in CD_2Cl_2 (dielectric constant = 8.93), K(283.2 K) = 4.6 ± 2.1 dm^3 mol^{-1} has been reported, but in $(CD_3)_2CO$, which has a higher dielectric constant of 20.7, no encounter complex was detected.[13] A value of K(274.3 K) = 16.2 dm^3 mol^{-1} characterizes the encounter complex formed between $[UO_2\{(NMe_2)_2P(O)NMeP(O)(NMe_2)_2\}_2(EtOH)]$ and ethanol in CD_2Cl_2–CD_3NO_2 solution, but in this case a specific hydrogen-bonding interaction between ethanol in the first and second co-ordination spheres may account for the high K value.[12] These observations suggest that it is unlikely that an encounter complex exists in significant amounts in the $[UO_2(trmu)_5]^{2+}$ solutions of Table 1, and that the predominant trmu exchange mechanism is of the *D* type.

The species most closely related to $[UO_2(trmu)_5]^{2+}$, for which ligand exchange has been reported, $[UO_2(tmu)_5]^{2+}$ (tmu = tetramethylurea), is also characterized by a k_{ex} independent of the free ligand concentration in CD_3CN solution.[6] The kinetic parameters characterizing these two dioxouranium(VI) species are: k_{ex}(298.2 K) = 983 and 1 580 s^{-1}; $\Delta H^‡$ = 56.6 and 81 kJ mol^{-1}; and $\Delta S^‡$ = 2.2 and 88 J K^{-1} mol^{-1} respectively. The similar k_{ex}(298.2 K) values are a consequence of very different $\Delta H^‡$ and $\Delta S^‡$ values, which suggests that the substantially similar ligands are not the only determinants of the magnitude of these parameters. It appears that these differences are a consequence of the compensating changes in the bonding distances of four of the equatorial ligands as the fifth exchanges, which are linked to changes occurring in the axial dioxouranium(VI) distances and *vice versa.* As the order of each of the axial bonds is $\geqslant 2$, small changes in their distances in the transition state probably substantially influence the bond-distance changes in the equatorial plane and thereby the activation thermodynamics. Nevertheless both $[UO_2(trmu)_5]^{2+}$ and $[UO_2(tmu)_5]^{2+}$ conform well to the isokinetic relationship (3) established when

$$\Delta H^\ddagger = \Delta G^\ddagger + T\Delta S^\ddagger \qquad (3)$$

their activation data are combined with those characterizing the exchange processes of the uncharged unidentate oxygen-donor ligands dimethylformamide, methylacetamide, dimethylacetamide, diethylacetamide, dimethyl sulphoxide, trimethyl phosphate, triethyl phosphate, dimethyl methylphosphonate, and dimethylphenylphosphine oxide in $[UO_2(ligand)_5]^{2+}$, which also exhibit k_{ex} independent of the free ligand concentration.[1–11] A linear regression analysis of this wide range of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ through equation (3) yields an isokinetic temperature (T_{iso}) of 293.8 ± 13.7 K and $\Delta G^\ddagger_{iso} = 54.5 \pm 0.6$ kJ mol^{-1} at that temperature. Similar isokinetic relationships for $[Al(ligand)_6]^{3+}$ and $[Mg(ligand)_6]^{2+}$, which undergo ligand exchange through a *D* mechanism, yield $T_{iso} = 317$ and 251.5 K and $\Delta G^\ddagger_{iso} = 75.3$ and 41.8 kJ mol^{-1} respectively.[3,25] As the values for $[UO_2(ligand)_5]^{2+}$ are intermediate between those for the aluminium(III) and magnesium(II) systems, it is concluded that the surface charge density (which is a major determinant of lability for ligand exchange occurring through a *D* mechanism) experienced by ligands in the equatorial plane of dioxouranium(VI) lies between those of aluminium(III) and magnesium(II).

The co-ordination of ureas to UO_2^{2+} markedly decreases the rate of rotation about their carbon–nitrogen bonds by comparison to the rates observed for ureas in the free state (Table 2). This is probably mainly a consequence of the increase in carbon–nitrogen bond order which occurs with co-ordination of the urea through oxygen. The new data for $[UO_2(trmu)_5]^{2+}$ reveal a trend in which k_r increases, $\Delta H^\ddagger$ decreases, and $\Delta S^\ddagger$ becomes more negative for rotation about the C–NMe_2 bond in the sequence of co-ordinated ureas: $H_2NCONMe_2$, $MeHNCONMe_2$, $Me_2NCONMe_2$. The transition state for rotation about a urea C–NR_2 bond is envisaged to have the NR_2 entity perpendicular to the carbonyl plane. As the two urea carbon–nitrogen bonds are cross-conjugated, steric interactions causing NR_2 to twist out of the carbonyl plane will destabilize the ground state and stabilize the transition state if the second NR_2 simultaneously becomes more closely coplanar with the carbonyl group, with a consequent increase in the order of the carbon–nitrogen bond between them.[18,20] Thus the observed trends in k_r and $\Delta H^\ddagger$ for rotation about the C–NMe_2 bonds in co-ordinated 1,1-dimethylurea (dmu), trmu, and tmu may be explained as a consequence of the kinetic effects of the steric crowding with the ureas, which increases from 1,1-dmu to tmu, superimposed on the effects of co-ordination. (The origins of the magnitudes and variations of $\Delta S^\ddagger$ are not readily apparent.)

Acknowledgements

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References

1 R. P. Bowen, S. F. Lincoln, and E. H. Williams, *Inorg. Chem.*, 1976, **15**, 2126.
2 J. Crea, S. F. Lincoln, and E. H. Williams, *Aust. J. Chem.*, 1976, **29**, 2183.
3 J. Crea, R. Diguisto, S. F. Lincoln, and E. H. Williams, *Inorg. Chem.*, 1977, **16**, 2825.
4 G. J. Honan, S. F. Lincoln, and E. H. Williams, *Inorg. Chem.*, 1978, **17**, 1855.
5 G. J. Honan, S. F. Lincoln, and E. H. Williams, *J. Solution Chem.*, 1978, **7**, 443.
6 G. J. Honan, S. F. Lincoln, and E. H. Williams, *J. Chem. Soc., Dalton Trans.*, 1979, 320.
7 G. J. Honan, S. F. Lincoln, T. M. Spotswood, and E. H. Williams, *Inorg. Chim. Acta*, 1979, **33**, 235.
8 G. J. Honan, S. F. Lincoln, T. M. Spotswood, and E. H. Williams, *J. Chem. Soc., Dalton Trans.*, 1979, 1220.
9 G. J. Honan, S. F. Lincoln, and E. H. Williams, *Aust. J. Chem.*, 1979, **32**, 1851.
10 A. M. Hounslow, S. F. Lincoln, P. A. Marshall, and E. H. Williams, *Aust. J. Chem.*, 1981, **34**, 2543.
11 A. E. Bakas, A. M. Hounslow, S. F. Lincoln, and N. J. Maeji, *Aust. J. Chem.*, 1982, **35**, 1489.
12 L. Rodehuser, P. R. Rubini, K. Bokolo, and J-J. Delpuech, *Inorg. Chem.*, 1982, **21**, 1061.
13 Y. Ikeda, H. Tomiyashu, and H. Fukutomi, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1060.
14 H. Doine, Y. Ikeda, H. Tomiyashu, and H. Fukutomi, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1989.
15 Y. Ikeda, H. Tomiyashu, and H. Fukutomi, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2925.
16 Y. Ikeda, H. Tomiyashu, and H. Fukutomi, *Inorg. Chem.*, 1984, **23**, 3197.
17 H. Fukutomi and Y. Ikeda, *Inorg. Chim. Acta*, 1986, **115**, 227.
18 S. F. Lincoln and A. White, *Inorg. Chim. Acta*, 1985, **110**, 107.
19 M. L. Martin, M. L. Filleux-Blanchard, and G. J. Martin, *Org. Magn. Reson.*, 1980, **13**, 396.
20 L. M. Jackman, in 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, p. 203.
21 A. I. Vogel, 'Quantitative Inorganic Analysis,' 3rd edn., Longmans, Green and Co., London, 1961, p. 702.
22 S. F. Lincoln, *Prog. React. Kinet.*, 1977, **9**, 1.
23 L. R. Nasimbeni and A. L. Rodgers, *Cryst. Struct. Commun.*, 1976, **5**, 301.
24 D. L. Pisaniello, L. Helm, P. Meier, and A. E. Merbach, *J. Am. Chem. Soc.*, 1983, **105**, 4528.
25 D. L. Pisaniello and S. F. Lincoln, *Aust. J. Chem.*, 1979, **32**, 715.

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