

COMMUNICATIONS TO THE EDITOR

Nuclear Magnetic Resonance Study of Hindered Internal Rotation in Urea in Solution

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Sir: Recent studies on rotational barriers around the C-N bonds in alkyl-substituted ureas¹ and thioureas^{2,3} indicate that they are considerably lower than in comparable simple amides.⁴ No investigation of the C-N barrier in urea in solution has been published, but solid urea has been studied by broad line nmr⁵ and by nqr techniques,⁶ and both methods have given results interpretable in terms of dynamic reorientation around bonds.

We wish to report a variable temperature pmr study of urea-¹⁴N in solution. Initially our aim was to study the di-¹⁵N-enriched compound, but no solvent was found in which its spin-spin coupling pattern could be sufficiently well resolved at low temperatures. For this reason ordinary urea, in spite of the quadrupole broadening by the ¹⁴N nuclei, showed narrower pmr signals than the ¹⁵N-enriched compound. The choice of solvents for a variable temperature study of urea is very limited, and only one usable solvent, dimethylformamide (DMF), has been found. Since the effects of hydrogen bonding can be of great importance for urea, two solvent mixtures, DMF-dimethyl sulfoxide (DMSO) and acetone-tetramethylurea (TMU) were also used to obtain at least some variation in solvent polarity. All spectra were recorded on a Varian Associates A-60A spectrometer equipped with a V-6040 temperature controller. (For Results, see Table I).

The appearance of the proton nmr spectra of urea in the TMU-acetone mixture (see below) at various temperatures is shown in Figure 1. The resulting spectra were analyzed in terms of a two-site exchange process, according to the theory of Gutowsky, *et al.*,⁷ and rate constants were evaluated from digitized spectra at temperatures near coalescence by means of an iterative computer program.⁸ The variation in effective natural line width was accounted for by interpolation between slow and fast exchange values and the variation in non-exchanging chemical shift difference by extrapolation of slow exchange values. The free energy of activation, ΔG^\ddagger , was calculated from the Eyring equation, assuming the transmission coefficient to be unity. The uncertainties in the natural line widths and the extrapolated shift differences for the NH signal(s) are too great to make an evaluation of the activation parameters ΔH^\ddagger and ΔS^\ddagger seem meaningful (*cf.* ref 9).

The ΔG^\ddagger value for hindered rotation around the amide bonds in urea is significantly (≈ 1.6 kcal/mol)

Table I: Results

System (weight fractions) ^a	T, °K ^b	τ , sec ^c	ΔG^\ddagger , kcal mol ⁻¹ ^c
Urea:DMF 0.030:0.970	218	0.057	11.4
	220	0.037	11.3
	224	0.016	11.1
	226	0.009	11.0
		Mean value	11.2
Urea:DMSO:DMF 0.028:0.273:0.699	220	0.063	11.5
	222	0.047	11.5
	224	0.027	11.4
	229	0.016	11.4
		Mean value	11.5
Urea:acetone:TMU 0.021:0.355:0.624	220	0.048	11.3
	224	0.032	11.5
	226	0.023	11.4
	230	0.012	11.3
		Mean value	11.4
			Total mean value 11.33

^a All systems were more or less supercooled at low temperatures. ^b The estimated accuracy is $\pm 2^\circ$. The reproducibility was better than $\pm 1^\circ$. ^c The error limits are of the order of 10-30% for τ and ± 0.1 kcal mol⁻¹ for ΔG^\ddagger . This was found by calculating τ and ΔG^\ddagger values using combinations of line-shape parameters and temperatures, taking into account maximum reasonable error limits.

higher than for the dimethylamino group in a trialkyl-substituted urea.¹ Possible rationalizations for this increased barrier height are as follows: (i) stabilization of the ground state by intermolecular hydrogen bonding; (ii) increased electron delocalization across the C-N bond; and/or (iii) removal of steric interaction between N-methyl groups and NH protons that are both trans to the carbonyl oxygen. Probably all three factors are of importance. Unfortunately, no large variations in solvent composition or urea concentration

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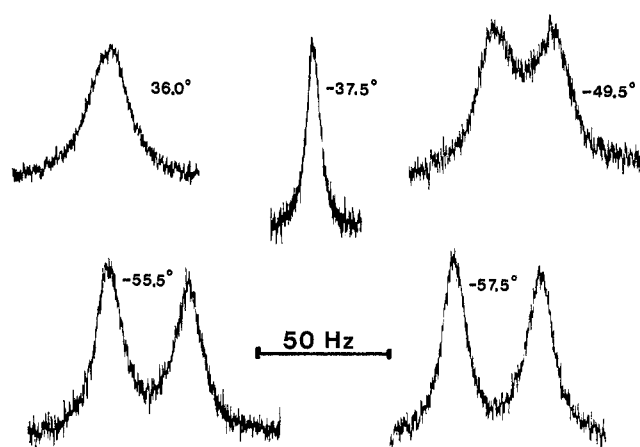


Figure 1. The 60-MHz spectrum of urea in TMU-acetone at various temperatures.

were possible, but it should be noted that the differences in ΔG^\ddagger are very close to being zero within the experimental error for the systems studied.

Extrapolated nqr data⁶ indicate that the rate of rotation around the amide bond in solid urea is only a factor of 100 lower than in solution at -50° .

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