Gas Phase ¹H-N.M.R. Study of the Hindered Internal Rotation in Dimethylacetamide

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Summary.—The ^1H n.m.r. spectra of dimethylacetamide in the gas phase give an activation energy of $\Delta F^{\neq}_{298} = 15{\cdot}64 \pm 0{\cdot}1$ kcal mol^{-1} for the rotation about the amide C–N bond, significantly smaller than that found in solution.

The rate of rotation about the C–N partial double bond in amides depends on the nature of the solvent,[1-3] the amide concentration,[1,3] and the external pressure.[4] To date, the barrier has been determined in solution only, so that discussion of substituent effects[1–3,5] and comparison with MO-calculations[6] seems to be questionable. We have now measured the rotational barrier of dimethylacetamide (DMA) in the gas phase.

The low density of gaseous DMA at 298 K yields a low collision frequency corresponding to broad ^{1}H-n.m.r. lines (*ca.* 80 Hz halfwidth). At least 5×10^4 N m^{-2} $(CD_3)_2O$ was added to effect line narrowing and as a deuterium lock. Under these conditions the ^{1}H-n.m.r. spectra of the *N*-methyl groups showed two distinct signals at 280 K ($\Delta\delta$ = 17 Hz) which coalesced at *ca.* 305 K into a single sharpened line at higher temperatures.† The lineshape was simulated assuming an uncoupled AB type system (Program CLATUX)[7]. The unresolved ^5J(H,H) coupling between the C–CH_3 and the N–CH_3 protons[8] was taken into account applying different T_2 values for the two N–CH_3 signals. This procedure did not influence the rate constants derived in the coalescence region.[9] For samples containing *ca.* 40 N m^{-2} DMA and 0·5 or $2{\cdot}5 \times 10^5$ N m^{-2} $(CD_3)_2O$ a free energy of activation, $\Delta F^{\neq}_{298} = 15{\cdot}64 \pm 0{\cdot}1$ kcal mol^{-1} (65·5 ± 0·4 kJ mol^{-1}) was obtained. The poor signal-to-noise ratio of the gas phase spectra and the small chemical shift difference between the *N*-methyl signals did not allow an accurate differentiation between the energy and entropy contributions to $\Delta F^{\neq}_{298}$. Concerning the slight activation entropies associated with C–N rotations in *NN*-dimethylamides[2] a discussion of the barrier on the basis of free energy alone seemed to be sufficient.

All the activation data previously found for DMA in solution exceed the value measured in the gas phase. Even in the non-polar solvent iso-octane $\Delta F^{\neq}_{298}$ (17·3 kcal mol^{-1}) is significantly higher while more polar solvents increase the barrier further.[1,3] In addition, the positive activation volume of DMA in aprotic solvents[4] indicates that the internal pressure of the solvent would also hinder the rotation. At the present stage of development of dynamic n.m.r. spectroscopy in the gas phase (only one study on the hindered rotation in *N*-nitrosodimethylamine has been published)[10] the relative contributions of the solvent polarity and the internal pressure to the increased barrier in solution cannot be separated. Finally, it does not seem to be fortuitous that a rotational barrier for DMA of 14·93 kcal mol^{-1}, close to the value in the gas phase, has been recently calculated by *ab initio* methods.[6]

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† The spectra were measured at 360 MHz in 10 mm tubes.

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