Determination of the activation volume of the rotation of the dimethylamino group in *N,N*-dimethylamides

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A recently developed high-pressure cell for use in a standard high-resolution nmr spectrometer is described here; the cell (figure 1) is a modification of a design first published by Yamada (1974). It fits into the standard 12 mm probe configuration of a Varian XL-100-15 spectrometer. The nmr cell proper consists of a carefully annealed glass capillary with $1 \cdot 5$ mm inner diameter and 7 mm outer diameter. The neck of this capillary is glued with epoxy resin into the bore of a copper–beryllium nipple. The upper end of the capillary is connected to a Teflon shrink hose containing the solution under investigation and serving as the pressure-transmitting medium. The field homogeneity of the Varian 15 in magnet is sufficient for a resolution of 1 Hz or slightly better in this design without spinning the probe. The cell has been operated successfully from $+150$ to -100 °C. Careful selection of the capillaries allows working pressures of up to $2 \cdot 5$ kbar.

High resolution nmr at variable temperatures has become the most prominent method for the determination of the energies of activation of simple conformational rearrangements in the liquid phase. From the coalescence temperature of the two resonance signals, t_c, and from the frequency difference at low temperatures, $\delta \nu$, energies and entropies of activation can be obtained in an almost routine fashion (Günther 1973).
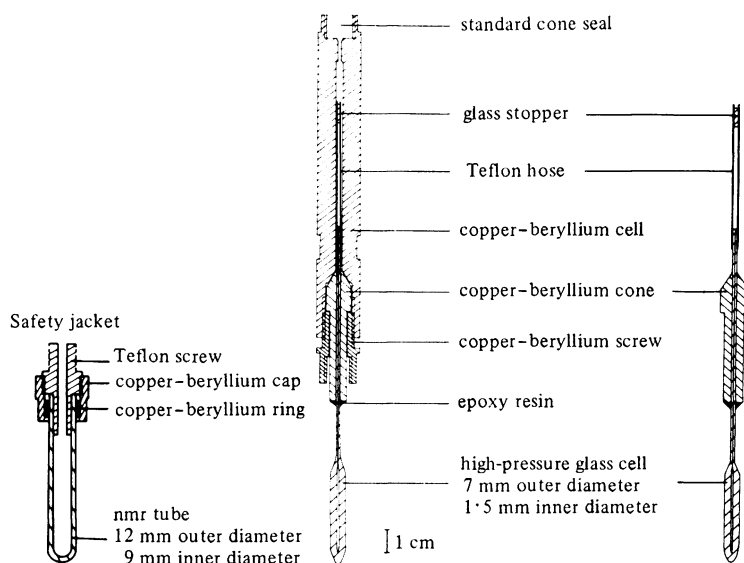

Figure 1. High-pressure cell for use in standard high-resolution nmr spectrometers.

As an example, we studied the rotation of the dimethylamino group in N,N-dimethyl-acetamide, in N,N-dimethylformamide, and in N,N-dimethylbenzamide, around the C–N bond. The spectral parameters found for these compounds are given in table 1. Inserting $\Delta G^{\ddagger}$, Gibbs' free energy, and k_c, the inversion rate at t_c, obtained at the various pressures into Arrhenius' equation yields a formula for the temperature dependence of the inversion rate, k.

Table 1. Parameters of the proton signals used in the evaluation of the activation parameters. The compounds were dissolved in 40% d_6-acetone–20% tetramethylsilane.

Compound	t_c (°C)		$\delta\nu$ (s^{-1})		$\Delta G^{\neq}$ (kcal mol^{-1})	
	0·05 kbar	2·0 kbar	0·05 kbar	2·0 kbar	0·05 kbar	2·0 kbar
N,N-dimethylformamide	125	134	16·3	17·3	20·7	21·2
N,N-dimethylacetamide	74	83	17·1	17·7	17·9	18·4
N,N-dimethylbenzamide	13	19·5	11·3	10·3	15·0	15·4
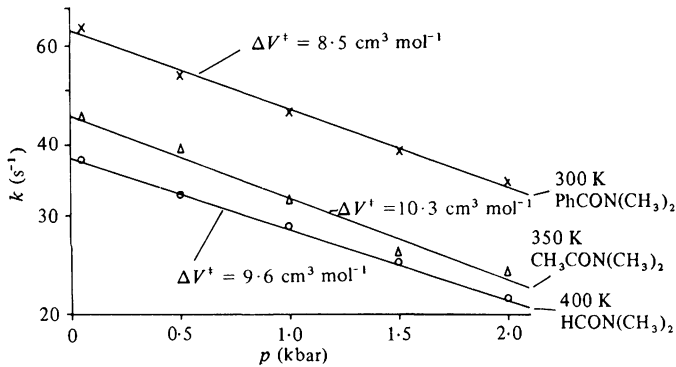
Figure 2. Semilogarithmic plot of the inversion rate k of the dimethylamino group for three N,N-dimethylamides as a function of pressure.

The results, plotted in figure 2, were calculated for integral temperatures in the vicinity of the respective coalescence temperatures. Raising the pressure to 2 kbar reduces the inversion rate in all three amides by ~50%. With the knowledge of the slope of the curves, the activation volumes $\Delta V^{\ddagger}$ can be derived from

$$\frac{\mathrm{d}(\ln k)}{\mathrm{d}p} = \frac{\Delta V^{\ddagger}}{RT} .$$

Though ΔG^{*} varies by ~30%, the variation of $\Delta V^{\ddagger}$ is considerably smaller. The change from 8·5 cm^3 mol^{-1} for dimethylbenzamide to 10·3 cm^3 mol^{-1} for dimethyl-acetamide is almost within the range of experimental reproducibility. The variation of $\Delta G^{\ddagger}$ with the change of the third substituent at the carbonyl carbon is explained by the influence of this substituent on the double bond character of the C–N bond (Emsley et al 1966). The relative independence of the activation volume from this substituent allows, in our opinion, a more geometric or steric explanation of $\Delta V^{\ddagger}$.

References
Emsley J W, Feeney J, Sutcliffe L H, 1966 *High Resolution Nuclear Magnetic Resonance-Spectroscopy* Vol 1 (Oxford: Pergamon Press) p 556
Günther H, 1973 *NMR-Spektroskopie* (Stuttgart: Georg Thieme Verlag) p 239
Yamada H, 1974 *Rev. Sci. Instrum.* **45** 690

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