# The Barrier to Internal Rotation in Monosubstituted Amides

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*Summary* The barrier to internal rotation in *N*-methylformamide and *N*-methylacetamide has been shown to be comparable to those in *NN*-dimethylamides, by n.m r. lineshape analysis of the *N*-methyl signals.

THE barrier to internal rotation in formamide and several disubstituted amides[1] has been studied by $^1H$ n.m.r. spectroscopy, but no reliable data are available for higher unsubstituted or monosubstituted amides. The accurate evaluation of the rate constants for internal rotation in monosubstituted amides is rendered difficult by the far from favourable population ratio, the *cis*:*trans* ratio being 1:12 [2] and 1:32 [3] in neat *N*-methylformamide (NMF) and *N*-methylacetamide (NMA) in $H_2O$, respectively. Furthermore, quadrupole broadening of the NH proton signal necessitates the use of either $^{15}N$ enriched samples or $^{14}N$ spin decoupling. Both methods have been used for formamide.[4,5]

We now report the results of an n.m.r. total lineshape analysis of the *N*-methyl signals in the spectra of NMF and NMA to obtain the barriers to internal rotation. For NMF a 10 mol % solution in 1,2-dichloroethane was used, and for NMA a 35 mol % solution in this solvent and a water solution containing 20 mol % NMA were used. Evaluation of the rate constants (accurate to ±20%) was carried out by fitting computer-plotted theoretical spectra to the experimental ones.

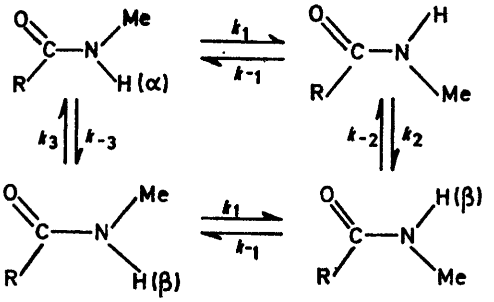
*Activation parameters for internal rotation in* NMF *and* NMA

| | $\Delta G_1^\ddagger$ | $\Delta G_2^\ddagger$ | $\Delta H_1^\ddagger$ | $\Delta H_2^\ddagger$ | $\Delta S_1^\ddagger$ | $\Delta S_2^\ddagger$ |
|---|---|---|---|---|---|---|
| NMF in $C_2H_4Cl_2$ | 19·0 | 20·6 | 17·5 | 22·4 | −4 | +5 |
| NMA in $C_2H_4Cl_2$ | 18·0 | 20·8 | 19·8 | 22·6 | +5 | +5 |
| NMA in $H_2O$ | 18·8 | 21·3 | 19·8 | 23·2 | +3 | +5 |

Energy values are in kcal $mol^{-1}$ for $\Delta G^\ddagger$ and $\Delta H^\ddagger$ and in cal $mol^{-1}$ $K^{-1}$ for $\Delta S^\ddagger$, at 60 ± 0·4 °C. Estimated errors are ±0·3 kcal $mol^{-1}$, ±1·8 kcal $mol^{-1}$ and ±5 cal $mol^{-1}$ $K^{-1}$, for $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$, respectively.

In the amides studied two rate processes may take place, internal rotation around the N–C(O) bond and intermolecular proton exchange (Scheme). The symbols $\alpha$ and $\beta$ on the *N*-proton indicate two possible spin states. This Scheme is not an exact reflection of chemical reality. It simply depicts two processes that will affect the lineshape of the N-methyl signals.

When both intra- and intermolecular exchange processes are slow, two *N*-methyl resonances are observed, one due to the *cis*- and one to the *trans*-conformer These are further split into doublets owing to the spin coupling to the *N*-proton ($J_{HNMe}$ *ca.* 5 Hz). When proton exchange is slow, and internal rotation becomes more rapid, the lines begin to broaden, but the larger (*trans*) signal does not change considerably. On the other hand, when proton exchange becomes faster all the lines broaden.



SCHEME

There is no simple way of obtaining the relative proton exchange rates of the *cis*- and *trans*-conformers and we have assumed these rates to be equal. The rate of the intermolecular exchange processes have been evaluated from the line shape of the dominant *N*-methyl signals, since the change in their lineshape is almost exclusively governed by this process. Proton exchange was slow ($k_1, k_2 < 1$) up to at least 80 °C in the dichloroethane solutions and for the water solution up to 60 °C.

For formamide it has been shown that proton exchange, in several solvents, is slow enough to allow for the evaluation of the barrier to internal rotation,[4,5] without taking proton exchange into account.

The free energy, enthalpy and entropy of activation for the internal rotation are given in the Table. These activation parameters are in much better agreement with those of other amides[1] than are the potential barriers for NMF given by Miyazawa[6] (14 kcal $mol^{-1}$) and Suzuki[7] (28 kcal $mol^{-1}$) on the basis of i.r. data. Both $\Delta G_2^\ddagger$ (NMF) and $\Delta G_2^\ddagger$ (NMA) are approximately equal to $\Delta G^\ddagger$ (DMF) (20·7 kcal $mol^{-1}$) in tetrachloroethane.[8] It is, however, difficult to draw any conclusions from these data, since the concentrations are so high that NMF and NMA, to a large extent, form dimers or polymers.[9] This association is probably due to hydrogen bonds between N–H and C=O and will presumably increase the barrier to internal rotation.

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