Hydrogen Bonding and Ultrasonic Relaxation in *N*-Methylacetamide

JØRGEN RASSING and OLE ØSTERBERG

Chemistry Laboratory III, University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

The structural character and the nature of molecular association of amides are of particular interest because of the importance of amides in biological systems. As a result a variety of investigations of these systems have been carried out, for instance infrared and Raman spectra,[1] NMR-spectra,[2] dipole moments,[3–6] dielectric constants,[7] dielectric loss,[8] diffusion constants,[9] vapor pressure lowering,[10] viscosity,[11] and surface tension [11] have been reported for several amides including *N*-methylacetamide (NMA) and dimethylacetamide (DMA).

From these investigations one can conclude, that the amide group is planar and that NMA exists predominantly in one configuration, namely in *trans*-form. Because of this configuration and a strong tendency to form hydrogen bonds a stepwise association of NMA molecules occurs with the result that chain polymers are formed. This effect does not occur in DMA because of the absence of aminohydrogens for bonding to oxygens of neighboring molecules.

The rate constants involved in the molecular association are primary factors in the hydrogen-bond interaction which is so important in the various configurations of peptide and protein chains. Although the ultrasonic absorption technique has been very successfully applied in investigating hydrogen-bond kinetics [12–14] it has never to our knowledge been used on the NMA/DMA system.

The present work shows that in the frequency range investigated (1 to 70 Mc) a relaxation occurs in NMA, but not in DMA. Relaxation curves for pure NMA and mixtures of NMA and DMA are given in Fig. 1. The parameters computed for a single relaxation process from these results are given in Table 1. The amides used were the purest grade obtainable. NMA was fractionally recrystallized at room temperature.

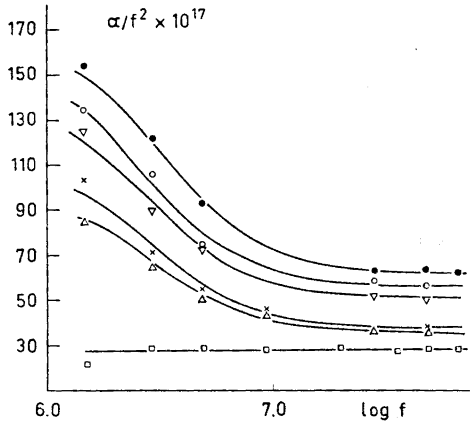

Fig. 1. Ultrasonic relaxation curves for NMA and NMA/DMA-mixtures at 45.0°C. x_{NMA} is the mole fraction of NMA.
●: pure NMA; ○: $x_{NMA}=0.897$; ▽: $x_{NMA}=0.805$; ×: $x_{NMA}=0.575$; △: $x_{NMA}=0.508$; □: pure DMA.

Table 1. Ultrasonic relaxation parameters for NMA/DMA mixtures at 45°C.

Mole fraction NMA	$A\times10^{17}$ sec² cm⁻¹	$B\times10^{17}$ sec² cm⁻¹	f_c Mc
1.000	103	62	3.4
0.897	100	56	2.6
0.805	85	51	2.9
0.575	74	37	2.9
0.508	58	36	3.6

Relaxation data fitted to equation for single relaxation frequency, f_c:

$$\alpha/f^2=A/[1+(f/f_c)^2]+B$$

where α is the amplitude absorption coefficient and f is the frequency.

The observed relaxation can be attributed either to an internal rotation of the same form as that found for methyl formate,[15] or to the equilibrium between hydrogen-bonded chains. If the relaxation is caused by a rotation, *i.e.* by a perturba-

tion of an equilibrium which is maintained by two monomolecular reactions, the A-parameter, used in Table 1 would depend linearly on the concentration. Since this does not seem to be the case (see Table 1) the hydrogen-bond mechanism is the more probable.

The equilibrium between monomers and hydrogen-bonded polymers of NMA molecules is represented by a large number of reaction steps. If only chains are formed the simplest reaction scheme would be:

$$N_1+N_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} N_2$$

$$N_2+N_1 \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} N_3$$

$$\vdots \quad \vdots \qquad \vdots \quad \vdots$$

$$N_i+N_1 \underset{k_{i+1,i}}{\overset{k_{i,i+1}}{\rightleftharpoons}} N_{i+1}$$

where $k_{i,i+1}$ and $k_{i+1,i}$ are the forward and backward rate constants, respectively, and N_x denotes a polymer with x molecules of NMA.

This type of a mechanism would in general cause a distribution of relaxation times rather than a single relaxation time, τ. If this distribution is sufficiently narrow, *i.e.* if $\tau_{max}/\tau_{min}<4$ the sound absorption data will show one relaxation time only within experimental error.[16] A kinetic interpretation of this relaxation time is complicated and can be done explicitly only if further assumptions are introduced. If $k_{12}=k_{23}=\cdots=k_f$ and $k_{21}=k_{32}\cdots=k_b$ the following expression is obtained:[17]

$$1/\tau = k_b[K[N_1]+1]$$

where $[N_1]$ is the equilibrium concentration of monomeric NMA and K is the equilibrium constant. The same expression is obtained even if the rate constants for the first reaction step are different from the rate constants for the remaining steps. It is seen that in this approximation the order of magnitude of the equilibrium constant determines whether or not the relaxation time is concentration dependent. Since the observed relaxation time appears to be independent of the concentration this means that $K[N_1]\ll 1$ and consequently $k_b=1/\tau=3.1\times 10^7 \pm 16$ % sec^{-1}.

We want to express our appreciation to professor Thor A. Bak for helpful discussions.

1. Mizushima, S. *Structure of Molecules and Internal Rotation*, Academic, New York 1954, pp. 117–152.
2. Gutowsky, H. S. and Holm, C. H. *J. Chem. Phys.* **25** (1956) 1228.
3. Bates, W. W. and Hobbs, M. E. *J. Am. Chem. Soc.* **73** (1951) 2151.
4. Kumler, W. D. and Porter, C. W. *J. Am. Chem. Soc.* **56** (1934) 2549.
5. Meighan, R. M. and Cole, R. H. *J. Phys. Chem.* **68** (1964) 503.
6. Lee, C. M. and Kumler, W. D. *J. Am. Chem. Soc.* **84** (1962) 571.
7. Leader, G. R. and Gormly, J. F. *J. Am. Chem. Soc.* **73** (1951) 5731.
8. Bass, S. J., Nathan, W. I., Meighan, R. M. and Cole, R. H. *J. Phys. Chem.* **68** (1964) 509.
9. Longsworth, L. G. *J. Coll. and Interface Science* **22** (1966) 3.
10. Davies, M. and Thomas, D. K. *J. Phys. Chem.* **60** (1956) 763.
11. Gopal, R. and Rizui, S. A. *J. Indian. Chem. Soc.* **43** (1966) 179.
12. Maier, W., Borucki, L., Dischler, R., Manogg, R. and Rieseberg H. *Z. physik. Chem. (Frankfurt)* **26** (1960) 27.
13. Rassing, J., Østerberg, O. and Bak, T. A. *Acta Chem. Scand.* **21** (1967) 1443.
14. Hammes, G. G. and Spivey, H. O. *J. Am. Chem. Soc.* **88** (1966) 1621.
15. Karpovich, J. *J. Chem. Phys.* **22** (1954) 1767.
16. Rassing, J. and Lassen, H. *Acta Chem. Scand. In press.*
17. Rassing, J. and Heilmann, O. J. *To be published.* Discussed briefly (in Danish) in the report from 13. Nordiske Kemikermøde 1968, p. 122.

Received January 2, 1969.