

Slow Proton Transfer Involving Amino-groups

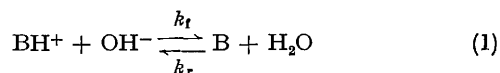
By FRANK HIBBERT

(Department of Chemistry, Birkbeck College, Malet Street, London WC1E 7HX)

Summary Proton transfer occurs 10^5 times more slowly for 1,8-bis(dimethylamino)naphthalene than for other amines, largely because of a strong intramolecular hydrogen bond in the protonated amine.

THE unexpectedly high thermodynamic basicity of 1,8-bis(dimethylamino)naphthalene (B) results from the relief of steric strain which occurs on protonation.¹ It is of interest to study the consequences of this effect on the rate of proton transfer. Such a study also permits an assessment of B as a strongly basic but weakly nucleophilic catalyst.

Using the temperature-jump method, relaxation times were determined for the equilibrium (1) in aqueous solution at 298K. Observations were made at 335 nm of the



increase in [B] and at 285 nm of the decrease in [BH⁺]. In CF₃CH₂OH/CF₃CH₂O⁻ buffers (pH = 11.3 to 12.4; ionic strength $I = 0.1\text{M}$) containing low concentrations of B and BH⁺, the relaxation time (τ) followed equation (2). The relaxation times were independent of the concentration of

$$1/\tau = 3.8 \times 10^3 + 1.9 \times 10^5[\text{OH}^-] \quad (2)$$

amine and at a fixed pH were independent of the buffer concentration. Equation (2) is of the expected form and gives values for k_f and k_r of $1.9 \pm 0.4 \times 10^6$ and $70 \pm 10 \text{ l mol}^{-1} \text{ s}^{-1}$ respectively. The ratio $k_f/k_r = 2.7 \pm 0.8 \times 10^3$ (at $I = 0.1\text{M}$) is compatible with the measured equilibrium constant¹ (2.6×10^3 , $I = 0.0\text{M}$). Over the pH range 10.9 to 11.7 in phosphate buffers, the relaxation time is approxi-

mately independent of pH ($1/\tau = 4.0 \pm 0.5 \times 10^3 \text{ s}^{-1}$). In this range the predominant contribution is from the reverse reaction (k_r) corresponding to the first term in equation (2). A value for k_r of $72 \pm 9 \text{ l mol}^{-1} \text{ s}^{-1}$ is obtained, in good agreement with the result from trifluoroethanol buffers. A similar experiment in D₂O gave $k_r(\text{D}_2\text{O}) = 27 \pm 2 \text{ l mol}^{-1} \text{ s}^{-1}$.

Reaction of BH⁺ with hydroxide ion is thermodynamically favourable yet occurs at a rate which is 10^5 times slower than the expected, diffusion-limited rate. This is the slowest observed proton transfer from a nitrogen (or oxygen) acid to hydroxide ion² and contrasts with the behaviour of other amines. One factor is largely responsible. Attack of hydroxide ion will be hindered² by a strong intramolecular hydrogen bond^{1,3} which is present in a six-membered ring in BH⁺. A possible further but less important factor which reduces the rate of proton transfer is associated with the considerable strain in B. The structure of B¹ will be such as to reduce steric and lone pair interactions. It is conceivable that these interactions make the transition state for proton transfer even more strained than B itself.

These factors result in an unusual slow proton transfer from nitrogen. In the reverse direction proton abstraction from water occurs at a rate similar to that expected for a base which is five pK units weaker than B. This means that 1,8-bis(dimethylamino)naphthalene will behave as a relatively weak base catalyst.

An equipment grant from the Royal Society is acknowledged.

(Received, 26th April 1973; Com. 599.)

¹ R. W. Alder, P. S. Bowman, W. R. S. Steele, and D. R. Winterman, *Chem. Comm.*, 1968, 723.

² M. Eigen, W. Kruse, G. Maass, and L. de Maeyer, *Progr. Reaction Kinetics*, 1964, 2, 285; E. M. Eyring and D. L. Cole, Nobel Symposium 5, Interscience, 1967, 255.

³ M. R. Truter and B. L. Vickery, *J.C.S. Dalton*, 1972, 395; E. Haselbach, A. Henriksson, F. Jachimowicz, and J. Wirz, *Helv. Chim. Acta*, 1972, 55, 1757.