Slow Proton Transfer Involving Amino-groups

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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 $CF_3CH_2OH/CF_3CH_2O^-$ buffers (pH = 11·3 to 12·4; ionic strength I = 0·1M) containing low concentrations of B and BH$^+$, the relaxation time (τ) followed equation (2). The relaxation times were independent of the concentration of 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 $1{\cdot}9 \pm 0{\cdot}4 \times 10^5$ and 70 ± 10 l mol^{-1} s^{-1} respectedly. The ratio $k_f/k_r = 2{\cdot}7 \pm 0{\cdot}8 \times 10^3$ (at I = 0·1M) is compatible with the measured equilibrium constant[1] ($2{\cdot}6 \times 10^3$, I = 0·0M). Over the pH range 10·9 to 11·7 in phosphate buffers, the relaxation time is approximately independent of pH ($1/\tau = 4{\cdot}0 \pm 0{\cdot}5 \times 10^3 s^{-1}$). 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 ± 9 l mol^{-1} s^{-1} is obtained, in good agreement with the result from trifluoroethanol buffers. A similar experiment in D_2O gave $k_r(D_2O) = 27 \pm 2$ l mol^{-1} s^{-1}.

$$BH^+ + OH^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B + H_2O \qquad (1)$$

$$1/\tau = 3{\cdot}8 \times 10^3 + 1{\cdot}9 \times 10^5[OH^-] \qquad (2)$$

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 ion[2] and contrasts with the behaviour of other amines. One factor is largely responsible. Attack of hydroxide ion will be hindered[2] 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 B[1] 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*, 26*th April* 1973; *Com.* 599.)

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