Rates of Proton Transfer for *meso*-Tetraphenylporphyrin in 90% Dimethyl Sulphoxide–Water (v/v)

By FRANK HIBBERT* and KENNETH P. P. HUNTE

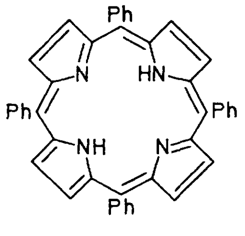
(*Department of Chemistry, Birkbeck College, Malet Street, London* WC1E 7HX)

Summary The rate of ionisation of the diprotonated form of *meso*-tetraphenylporphyrin (BH_2^{2+}) to the monoprotonated form (BH^+) has been measured by a temperature-jump study of the equilibration between B and BH_2^{2+} and is unusually slow.

RECENT n.m.r. measurements[1] with *meso*-tetraphenylporphyrin (B) and the conjugate acid (BH_2^{2+}) in $CDCl_3$ have been interpreted in terms of a slow overall proton exchange between B and BH_2^{2+}. In addition, BH^+ was not detectable in the solutions. Although this is not uncommon for porphyrins,[2] indicating that $K_1 < ca.\ K_2$, it is in contrast to what is observed for most dibasic acids. These features are of particular interest and we have therefore studied the equilibration between B and BH_2^{2+} directly using the temperature-jump technique in order to measure the individual rate coefficients and account for the slow overall exchange. The choice of solvent (90% Me_2SO–H_2O v/v) was determined by the technique and by the solubility of B.

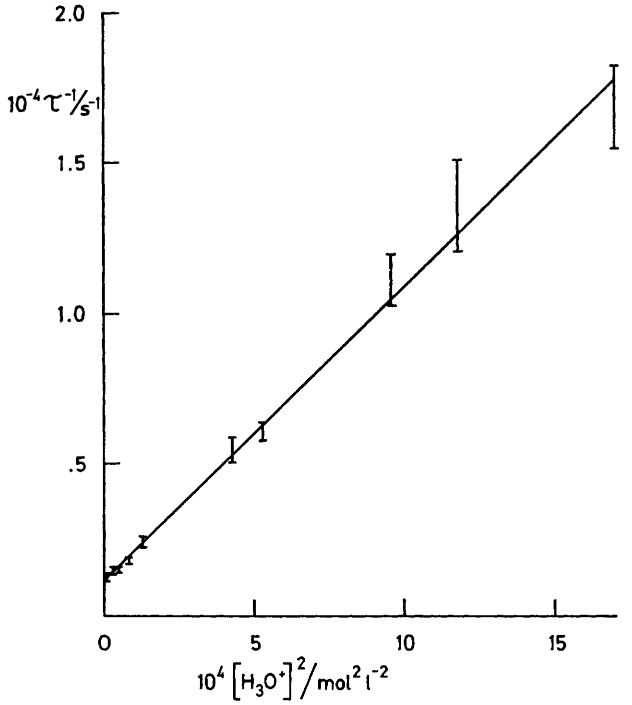
$$BH_2^{2+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} BH^+ + H_3O^+ \qquad K_1 = [BH^+][H_3O^+]/[BH_2^{2+}]$$

$$BH^+ + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B + H_3O^+ \quad K_2 = [B][H_3O^+]/[BH^+]$$


(B)

Solutions of B in 90% Me_2SO–H_2O containing HCl (0—0·08 M) and KCl to maintain constant ionic strength (0·08 M) gave spectra (390—750 nm) with five isosbestic points. Measurements at 417 and 448 nm (λ_{max} for B and BH_2^{2+} respectively) gave $K = [B][H_3O^+]^2/[BH_2^{2+}] = 1{\cdot}3 \pm 0{\cdot}2 \times 10^{-4}\ mol^2\ l^{-2}$ at 286·0 K. The results rule out[2c] the presence of significant concentrations of BH^+ and show that

$K_1 <$ *ca.* K_2. Chemical relaxation times for the equilibration between B and BH_2^{2+} were determined under similar conditions. Identical relaxation times were obtained by observing the increase in [B] at 425 nm or decrease in $[BH_2^{2+}]$ at 460 nm following the temperature-jump and τ was independent of the total concentration of porphyrin (2—4×10^{-6} M).



Assuming BH^+ is a low-concentration intermediate, the reciprocal relaxation time is given by equation (1) which reduces to equation (2) if $k_2[H_2O] >> k_{-1}\ [H_3O^+]$. The

$$1/\tau = (k_1k_2[H_2O]^2 + k_{-1}k_{-2}[H_3O^+]^2)/(k_{-1}[H_3O^+] + k_2[H_2O]) \qquad (1)$$

$$1/\tau = ca.\ k_1[H_2O] + (k_1[H_2O]/K)[H_3O^+]^2 \qquad (2)$$

values $k_1[H_2O] = 1{\cdot}2 \times 10^3\ s^{-1}$ and $K = 1{\cdot}2 \pm 0{\cdot}2 \times 10^{-4}\ mol^2\ l^{-2}$ are calculated from the Figure and the value of K is in good agreement with the equilibrium measurement.

The magnitude of the rate coefficient ($k_1[H_2O]$) for ionisation of BH_2^{2+} to BH^+ is that expected for the thermodynamically unfavourable ionisation of a protonated amine of pK *ca.* 7, assuming diffusion-controlled recombination of the amine with hydronium ion[3] (k_{-1} *ca.* $10^{10}\ l\ mol^{-1}\ s^{-1}$) The slow proton exchange of *meso*-tetraphenylporphyrin could therefore be explained by assuming $K_1 =$ *ca.* 10^{-7} M However this value is unlikely as it leads to $K_2 = K/K_1 = 10^3$ M and such a large difference between K_1 and K_2 is unreasonable, especially since K_1 and K_2 have similar values in nitrobenzene.[2a] A larger value for K_1 ($>10^{-7}$) close to that for K_2 means that the value of $k_1[H_2O]$ is anomalously low for an amine with p$K < 7$ and corresponds to a value for k_{-1} which is considerably below the diffusion limit Therefore BH_2^{2+} and BH^+ are showing different kinetic behaviour from that observed for most amines.[3] The result $K_1 <$ *ca.* K_2 is usually attributed[2b] to strong resonance stabilisation of BH_2^{2+} compared with BH^+. This explanation may also account for the low rates of proton transfer since it is well known that resonance stabilisation can introduce a barrier to proton transfer.[3,4] The presence[5] of intramolecular hydrogen bonds $>NH \cdots\cdots N<$ in B and BH^+ which are broken on proton transfer may be an additional factor which should lower the values of k_2 and k_{-2} as well as k_1 and k_{-1}. Since the results are well fitted by equation (2) it follows that $k_2[H_2O] >$ *ca.* $k_{-1}/10$ and using the values of $k_1[H_2O]$ and K it may be estimated that $k_{-2} >$ *ca.* $1 \times 10^6\ l\ mol^{-1}\ s^{-1}$, but no firm conclusion can be drawn from this value. In a favourable case, a study of this type will permit measurement of $k_1[H_2O]$ and k_{-2} and further systems are therefore being examined.

We thank the Royal Society for an equipment grant.

(*Received, 4th July* 1975; *Com.* 763.)

---

[1] R. J. Abraham, G. E. Hawkes, M. F. Hudson, and K. M. Smith, *J.C.S. Perkin II*, 1975, 204.

[2] (a) S. Aronoff, *J. Phys. Chem.*, 1958, **62**, 428; (b) J. E. Falk, 'Porphyrins and Metalloporphyrins,' Elsevier, Amsterdam, 1964, 29; (c) A. Stone and E. B. Fleischer, *J. Amer. Chem. Soc.*, 1968, **90**, 2735.

[3] M. Eigen, *Angew. Chem. Internat. Edn.*, 1964, **3**, 1.

[4] J. Hine, *J. Org. Chem.*, 1966, **31**, 1236.

[5] S. F. Mason, *J. Chem. Soc.*, 1958, 976.