Kinetic and Equilibrium Studies of the Protonation of *meso*-Tetraphenylporphyrin in Dimethyl Sulphoxide–Water [1]

By **Frank Hibbert** * and **Kenneth P. P. Hunte**, Department of Chemistry, Birkbeck College, Malet Street, London WC1E 7HX

The equilibrium between *meso*-tetraphenylporphyrin (B) and its diprotonated form (BH_2^{2+}) has been studied spectrophotometrically in 98, 90, and 80% $Me_2SO–H_2O$ (v/v). Visible spectra of solutions of the porphyrin containing varying concentrations of hydrochloric acid show good isosbestic points. The equilibrium involves the free base and the diprotonated species; the monoprotonated porphyrin (BH^+) is not present in sufficiently high concentrations to be detected. The position of equilibrium and the rates of equilibration between B and BH_2^{2+} have been measured in 95, 90, and 85% $Me_2SO–H_2O$ (v/v). The reaction is slow, with relaxation times (measured by the temperature-jump method) in the range 40—5 000 μs. Values of the rate coefficient for proton removal by water from BH_2^{2+} to give BH^+ were obtained for each solvent mixture from the acid dependence of the reciprocal relaxation time. In comparison with other proton transfers from nitrogen acids, proton transfer from the diprotonated form of *meso*-tetraphenylporphyrin is exceptionally slow. This may arise because the reaction is strongly disfavoured thermodynamically; other possible factors are discussed.

THERE is considerable interest in the behaviour of porphyrins towards acids and bases. The equilibria involving the free base (B) and the mono- and diprotonated species have been studied most widely, and these are shown in equations (1)—(3) for *meso*-tetraphenylporphyrin.

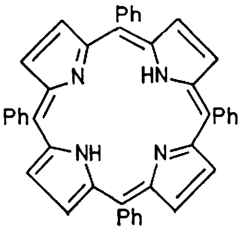
$$BH_2^{2+} + 2H_2O \rightleftharpoons B + 2H_3O^+ \qquad K = [B][H_3O^+]^2/[BH_2^{2+}] \quad (1)$$

$$BH_2^{2+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} BH^+ + H_3O^+$$

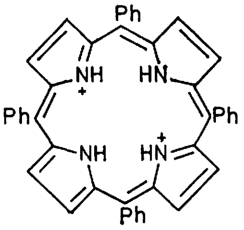
$$K_1 = k_1[H_2O]/k_{-1} = [BH^+][H_3O^+]/[BH_2^{2+}] \quad (2)$$

$$BH^+ + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B + H_3O^+$$

$$K_2 = k_2[H_2O]/k_{-2} = [B][H_3O^+]/[BH^+] \quad (3)$$



B



BH_2^{2+}

The free base can also lose one or two protons in basic solution [2] and in strong acid the diprotonated species can undergo further protonation.[3] This paper is concerned with equilibria (1)—(3).

The monoprotonated forms of several porphyrins have been difficult to detect. For example it has often been observed that the addition of increasing concentrations of acid to solutions of these porphyrins results in a gradual change in visible spectrum from that of the base to that of the diprotonated species. Isosbestic points have been observed and the spectra are consistent with the presence of negligible concentrations of the monoprotonated porphyrin.[4,5] This behaviour corresponds to a dissociation constant (K_1) for the diprotonated porphyrin which is smaller than that (K_2) of the monoprotonated species, and this is in contrast with what is observed for most dibasic acids. In some cases, spectral changes on titration with acid have shown that for other porphyrins the protons are added in two discrete steps, and two sets of isosbestic points are then observed.[2,5] Intermediate behaviour has also been reported where the spectral changes are consistent with the formation of the monoprotonated species only over limited ranges of acidity.[4,6,7] The spectra at different acid concentrations then do not pass through isosbestic points. The results can be analysed to give equilibrium constants for the two proton additions and the two dissociation constants have very similar values. It is clear that a variety of modes of behaviour of porphyrins towards acids and bases is observed. The ionisation behaviour also appears to depend upon the choice of solvent.

Before the preliminary publication of this work,[1] no detailed kinetic studies of proton transfer to porphyrins had been reported. However n.m.r. spectral measurements with solutions of *meso*-tetraphenylporphyrin in chloroform containing trifluoroacetic acid had been interpreted in terms of a slow proton exchange between the free base and the diprotonated porphyrin.[8] The monoprotonated species was not detected in these solutions. Previous measurements of the visible spectra of solutions of *meso*-tetraphenylporphyrin in nitrobenzene containing perchloric acid showed the intermediate behaviour described above and it was claimed

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that the monoprotonated species was present over a very limited range of acidity.[4] In contrast, for acidified solutions of *N*-methyltetraphenylporphyrin in nitrobenzene and in dimethylformamide two discrete proton additions have been observed.[5c] We now report, in full, kinetic and equilibrium measurements on the acid–base equilibria (1)—(3) involving *meso*-tetraphenylporphyrin in $Me_2SO–H_2O$. The low solubility of the porphyrin precludes the use of fully aqueous solutions.

RESULTS

Visible Spectra.—Spectra for solutions of *meso*-tetraphenylporphyrin in the presence of varying concentrations of hydrochloric acid were measured in the range 400—750 nm. Solutions in 98, 90, and 80% $Me_2SO–H_2O$ (v/v) were studied at 25 °C. In 98% $Me_2SO–H_2O$ the ionic strength was maintained constant at 0.02M by addition of potassium chloride, and in 90 and 80% $Me_2SO–H_2O$ the ionic strength was adjusted to 0.08M. In 80 and 90% $Me_2SO–H_2O$ the acid concentration was varied in the range 0.001—0.08M, and in 98% $Me_2SO–H_2O$ the acid concentrations were 0.001—0.02M. Experiments were carried out at several porphyrin concentrations between 1×10^{-6} and 2×10^{-5}M by using, where necessary, optical cells with 4 cm path lengths and a five-fold absorbance scale expander on the spectrophotometer. In all cases the spectra at a fixed porphyrin concentration in the presence of various concentrations of acid showed clean isosbestic points, and at low and high acid concentrations the spectra corresponded with the known spectra of the free base and diprotonated forms of *meso*-tetraphenylporphyrin, respectively. Isosbestic points were observed at 426, 477, 560, 576, and 590 nm. Typical spectra are shown in Figure 1, which refers to measurements in 98% $Me_2SO–H_2O$. The isosbestic point at 426 nm can only be seen at lower porphyrin concentrations. For *meso*-tetraphenylporphyrin in these solvent mixtures no evidence was obtained for the presence of the monoprotonated porphyrin. We note that if either B and BH^+ or BH^+ and BH_2^{2+} had very similar spectra, one set of isosbestic points would be observed on converting B to BH_2^{2+} even if high concentrations of BH^+ were present. We assume that this is not the explanation of the present results. To confirm that the spectral changes corresponded to the addition of two protons, accurate equilibrium constants were also determined.

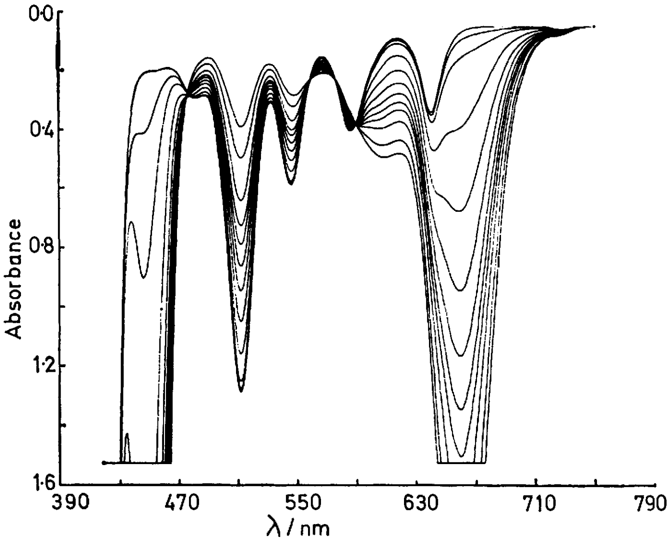

FIGURE 1 Spectra of solutions of *meso*-tetraphenylporphyrin in 98% $Me_2SO–H_2O$ (v/v) containing 0.001—0.02M-HCl and at ionic strength 0.02M; the absorbance at 660 nm increases as the acid concentration is increased

Equilibrium Constants.—The equilibrium between the base (B) and acid (BH_2^{2+}) forms in 90% $Me_2SO–H_2O$ (v/v) at 12.8 °C and at ionic strength 0.08M was studied spectrophotometrically at 417 and 448 nm. At 417 nm the extinction coefficient (ε) of the base is much larger than that of the acid [$\varepsilon_{417}(B) = 4.3 \times 10^5$; $\varepsilon_{417}(BH_2^{2+}) = 3.0 \times 10^4$ l mol^{-1} cm^{-1}], whereas at 448 nm the acid absorbs most strongly [$\varepsilon_{448}(B)$ *ca.* 0, $\varepsilon_{448}(BH_2^{2+}) = 3.7 \times 10^5$]. The absorbances due to B at 417 nm and to BH_2^{2+} at 448 nm varied linearly with concentration over the range $(0.1—3) \times 10^{-6}$M. The apparent extinction coefficients (ε_{app} = measured absorbance/stoicheiometric porphyrin concentration) of solutions of *meso*-tetraphenylporphyrin containing hydrochloric acid concentrations in the range 0.002—0.06M were measured at four different porphyrin concentrations [$(0.39—1.6) \times 10^{-6}$M] using optical cells with 1 or 4 cm path length. The degree of protonation of the porphyrin in each solution was calculated from the results at both wavelengths using equation (4). Values for the equilibrium constants of reaction (1) were calculated using equation (5), and the results were constant within experimental error and gave an average value $K = 1.3 \pm 0.2 \times 10^{-4}$ mol^2 l^{-2}. These results confirm that for acidified solutions of *meso*-tetraphenylporphyrin in 90% $Me_2SO–H_2O$ the acid–base equilibrium involves the free base and the diprotonated species, and negligible concentrations of BH^+ are present. Hence for equilibria (2) and (3) it follows that $K_1 \leqslant K_2$. The overall equilibrium constant is given by $K = K_1K_2$.

$$[B]/[BH_2^{2+}] = [\varepsilon_{app} - \varepsilon(BH_2^{2+})]/[\varepsilon(B) - \varepsilon_{app}] \quad (4)$$

$$K = [H_3O^+]^2[\varepsilon_{app} - \varepsilon(BH_2^{2+})]/[\varepsilon(B) - \varepsilon_{app}] \quad (5)$$

Kinetic Measurements.—Chemical relaxation times for equilibrium (1) were measured by the temperature-jump method. An equilibrium mixture of *meso*-tetraphenylporphyrin and its diprotonated form was subjected to a rapid temperature increase and the chemical reaction to the new equilibrium position was observed spectrophotometrically. The equilibrium is disturbed in favour of products by an increase in temperature and the decrease in absorbance at 460 nm which accompanied the decrease in concentration of BH_2^{2+} was followed. Some measurements were also made at 425 nm of the increase in absorbance due to the increase in concentration of B. Observations were also taken at 670 nm where the absorbance is mostly due to the diprotonated form. Identical values of the reciprocal relaxation time were obtained at the various wavelengths.

Relaxation times were determined in 95, 90, and 85% $Me_2SO–H_2O$ at 12.8 °C and ionic strength 0.06M. In 90% $Me_2SO–H_2O$ measurements were also made at ionic strength 0.08M. The reaction could not be studied in solvent mixtures containing larger fractions of water because of the very low solubility of the porphyrin and the increased rate of reaction. For each solvent mixture relaxation times were measured at several hydrochloric acid concentrations in the range 0.0004—0.05M. The relaxation times were found to be independent of the total concentration of porphyrin in the range (2—6) × 10^{-6}M. The variation of reciprocal relaxation time with hydrochloric acid concentration in 90% Me_2SO–H_2O at ionic strength 0.08M is shown in Figure 2. For equilibria (2) and (3) with H_3O^+ in excess as compared with B and BH_2^{2+}, and BH^+ present in negligible concentrations, the acid dependence of the reciprocal relaxation time for equilibration between B and BH_2^{2+} is given by equation (6), in which all the rate coefficients are expressed in second-order units.

$$1/\tau = (k_1k_2[H_2O]^2 + k_{-1}k_{-2}[H_3O^+]^2)/(k_{-1}[H_3O^+] + k_2[H_2O]) \quad (6)$$

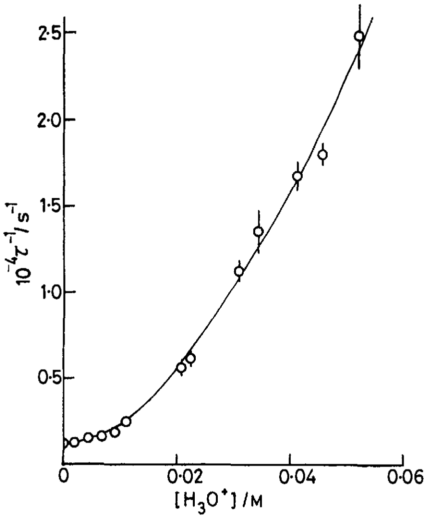

FIGURE 2 Variation of reciprocal relaxation time with hydrochloric acid concentration for solutions of *meso*-tetraphenylporphyrin in 90% Me_2SO–H_2O (v/v) at 12.8 °C and ionic strength 0.08M; the line is drawn from equation (7) with $k_1[H_2O] = 1.2 \times 10^3$ and $K = 1.3 \times 10^{-4}$

Equation (6) predicts that at low acid concentrations where $k_2[H_2O] > k_{-1}[H_3O^+]$, the reciprocal relaxation time will vary with $[H_3O^+]^2$. At higher acid concentrations where $k_2[H_2O] < k_{-1}[H_3O^+]$, the reciprocal relaxation time will depend upon $[H_3O^+]$. Figure 3 shows that, over the acid concentrations we have studied, the reciprocal relaxation time in 90% Me_2SO–H_2O depends upon $[H_3O^+]^2$. The results are well fitted by equations (7) and (8), which are

$$1/\tau = k_1[H_2O] + (k_1[H_2O]/K)[H_3O^+]^2 \quad (7)$$

$$1/\tau = 1.2 \times 10^3 + 0.9 \times 10^7[H_3O^+]^2 \quad (8)$$

obtained from equation (6) by making the assumption $k_2[H_2O] > k_{-1}[H_3O^+]$. The lines in Figures 2 and 3 are plots of equation (8).

Therefore our results in 90% Me_2SO–H_2O at an ionic strength 0.08M lead to values of $k_1[H_2O] = 1.2 \pm 0.1 \times 10^3$ s^{-1} and $K = 1.3 \pm 0.2 \times 10^{-4}$ mol^2 l^{-2}; the latter result is in good agreement with the value obtained from equilibrium measurements. The values of $k_1[H_2O]$ and K in 95, 90, and 85% Me_2SO–H_2O at ionic strength 0.06M are shown in the Table. Values for the other rate coefficients in equations (2) and (3) cannot be obtained but a lower limit may be estimated for k_{-2}, the rate coefficient for protonation of the free base. Since the kinetic results are fitted by equation (7) it follows that $k_2[H_2O] > k_{-1}[H_3O^+]$ under our experimental conditions, and therefore $k_2[H_2O] \geqslant k_{-1}/10$. From the value of the overall equilibrium constant $K = K_1K_2 = k_1k_2[H_2O]^2/k_{-1}k_{-2}$ and the measured value of $k_1[H_2O]$, it can be shown that $k_{-2} \geqslant 1 \times 10^6$ l mol^{-1} s^{-1}. In a case where expression (6) is needed to fit the acid dependence of the reciprocal relaxation time, a precise value for k_{-2} would be obtained and other porphyrins are being investigated with this in mind.

Kinetic results for *meso*-tetraphenylporphyrin in Me_2SO–H_2O at 12.8 °C

Solvent Me_2SO–H_2O (% v/v)	Ionic strength (M)	$10^{-3}k_1[H_2O]/s^{-1}$	$10^4K/mol^2\,l^{-2}$
90	0.08	1.2 ± 0.1	1.3 ± 0.2
95	0.06	0.19 ± 0.01	0.63 ± 0.07
90	0.06	1.5 ± 0.2	1.1 ± 0.3
85	0.06	6.5 ± 0.5	1.7 ± 0.4

The slow step in the ionisation of *meso*-tetraphenylporphyrin can be identified by the following argument. Since we were unable to detect BH^+ spectrophotometrically it is assumed that $K_1 \leqslant K_2$ and since $K = K_1K_2 = 1.3 \times 10^{-4}$, the result $K_1 <$ *ca.* 10^{-2} is obtained. Hence equilibrium (2) is thermodynamically unfavourable in the forward direction and $k_1[H_2O] < k_{-1}/100$. Our kinetic results show that $k_2[H_2O] > k_{-1}[H_3O^+]$; hence by using the foregoing inequality it follows that $k_1[H_2O] < k_2[H_2O]$. Since $k_{-2} > 1 \times 10^6$ and $k_1[H_2O] = 1.2 \times 10^3$, the result $k_1[H_2O] < k_{-2}[H_3O^+]$ is also obtained. Hence the slow step in the interconversion of B and BH_2^{2+} is the removal of a proton by water from the diprotonated species to give the monoprotonated porphyrin.

Amplitude of Relaxation.—The total change in optical density which occurs after the temperature perturbation depends upon a number of factors. For a solution with fixed hydrochloric acid and porphyrin concentrations, the total change in optical density (relaxation amplitude) depends upon the wavelength of observation. Since an increase in temperature disturbs equilibrium (1) in favour of products an increase in absorbance was observed when

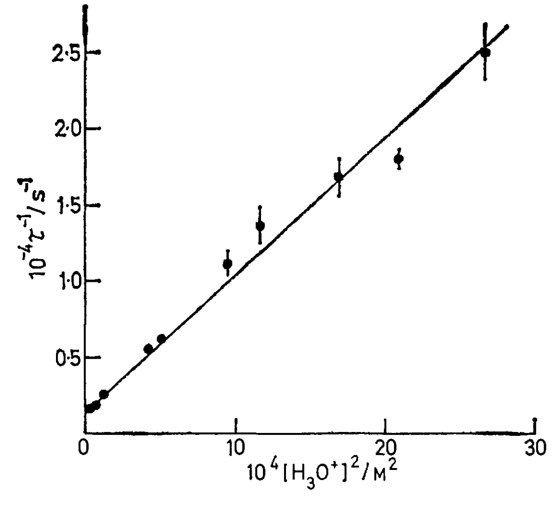

FIGURE 3 Variation of reciprocal relaxation time with $[H_3O^+]^2$ for solutions of *meso*-tetraphenylporphyrin in 90% Me_2SO–H_2O (v/v) at 12.8 °C and ionic strength 0.08M; the line is drawn from equation (7) with $k_1[H_2O] = 1.2 \times 10^3$ and $K = 1.3 \times 10^{-4}$

measurements were made at wavelengths at which the absorbance is due mainly to the free base. At wavelengths where the diprotonated species absorbs most strongly, a decrease in absorbance was observed after the temperature jump. The relaxation amplitude at different wavelengths was well correlated with the difference in extinction coefficients of the base and diprotonated forms of *meso*-tetraphenylporphyrin. Slight differences of wavelength for the two sets of data were observed, but this is due to the difference in slit widths between the temperature-jump instrument and the spectrophotometer used to measure the extinction coefficients. It was also observed that the relaxation amplitude varied directly with the total concentration of porphyrin. In addition, for our experimental conditions, the amplitude is predicted to have a maximum value when equal concentrations of B and BH_2^{2+} are present in solution. The amplitude was measured at fixed wavelength for solutions containing a constant total concentration of porphyrin but with varying hydrochloric acid concentrations. The acid concentration at which the largest amplitude was observed agreed well with the concentration predicted from the measured equilibrium constant. These results confirm that the observed chemical relaxation refers to a proton-transfer equilibrium between B and BH_2^{2+} as in equation (1).

DISCUSSION

The results of the spectrophotometric equilibrium measurements show that in 98, 90, and 80% Me_2SO-H_2O the acid–base equilibrium of *meso*-tetraphenylporphyrin involves the free base and diprotonated forms and that undetectably low concentrations of the monoprotonated porphyrin are present. It is not possible to estimate the maximum concentration of BH^+ which may be present. For solutions of the porphyrin in chloroform containing trifluoroacetic acid the monoprotonated porphyrin could not be detected by n.m.r. measurements.[8] However acid-base titration of *meso*-tetraphenylporphyrin with perchloric acid in nitrobenzene resulted in a series of visible spectra which did not show clean isosbestic points.[4] It was therefore deduced that the monoprotonated porphyrin was present and dissociation constants $K_1 =$ *ca.* 14×10^{-5} and $K_2 =$ *ca.* 4.2×10^{-5} were calculated for the first and second ionisations. The change in solvent from nitrobenzene to 90% Me_2SO-H_2O (v/v) alters the ionisation behaviour of *meso*-tetraphenylporphyrin. The monocation becomes undetectable in 90% Me_2SO-H_2O and also much higher acid concentrations (*ca.* 100-fold) are required to bring about the conversion of B into BH_2^{2+}.

The relaxation times observed for *meso*-tetraphenylporphyrin (40—5 000 μs) are unusual for a proton transfer involving a nitrogen acid. Most proton transfers involving nitrogen acids in aqueous solution occur at the diffusion-limited rate[9] in the thermodynamically favourable direction (normal proton transfer) and therefore give much shorter relaxation times which could not be measured with our equipment. In Me_2SO-H_2O, normal proton transfers also occur at the diffusion-limited rate.[10] Our observations therefore confirm the conclusions based on n.m.r. measurements in chloroform that for *meso*-tetraphenylporphyrin proton transfer is slow.

In 90% Me_2SO-H_2O at ionic strength 0.08M the rate coefficient for proton transfer to water from the diprotonated form of *meso*-tetraphenylporphyrin to give the monoprotonated species has the value $k_1[H_2O] = 1.2 \times 10^3$ s^{-1}. If we assume that reaction in the reverse direction of equilibrium (2) is diffusion-limited ($k_{-1} = 1 \times 10^{10}$ l mol^{-1} s^{-1}), the result $k_1[H_2O] = 1.2 \times 10^3$ s^{-1} is the value expected for a strongly thermodynamically unfavourable proton transfer with an equilibrium constant $K_1 = 1.2 \times 10^{-7}$ mol l^{-1}. The overall equilibrium constant between B and BH_2^{2+} is given by $K = K_1K_2$. Hence if $K_1 = 1.2 \times 10^{-7}$ mol l^{-1} a value $K_2 = 1.1 \times 10^3$ mol l^{-1} is calculated from the measured value of the overall equilibrium constant. Hence the slowness of proton transfer from BH_2^{2+} to give BH^+ could arise because the reaction is strongly thermodynamically unfavourable. This explanation is also compatible with the failure to observe BH^+ spectrophotometrically. However the values of K_1 and K_2 required by this analysis are unlikely since it would be most unexpected for dissociation of the second proton from a dibasic acid to be ten orders of magnitude *more* favourable than dissociation of the first proton. Also the values of K_1 and K_2 in nitrobenzene differ only by a factor of three.[4] It therefore appears that although the foregoing explanation partly accounts for the slow proton transfer there are probably additional factors.

One factor which may be important in lowering the rate coefficients for equilibrium (2) below the values expected for a normal proton transfer to and from nitrogen is intramolecular hydrogen bonding. It has been concluded from the i.r. spectra of several porphyrins that in the free base the two protons are held in intramolecular hydrogen bonds.[11] One hydrogen bond may also be present in BH^+ and this is ruptured on conversion into BH_2^{2+}. The effect of a hydrogen bond in lowering the rate of a thermodynamically favourable proton transfer is well known and can be quite large.[12] This factor may bring about a lowering in the value of k_{-1} and since the forward and reverse rate coefficients are related through the equilibrium, the value of $k_1[H_2O]$ will be lower than the result which would be predicted from the value of the equilibrium constant by assuming that the reverse protonation is diffusion-controlled. One of the reasons usually given for the instability of some monoprotonated porphyrins and the very similar values observed for the first and second dissociation constants of these porphyrins is that the diprotonated form is strongly resonance-stabilised as

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

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[12] F. Hibbert, *J.C.S. Perkin II*, 1974, 1862.

compared with the monoprotonated porphyrin.[13] If the conversion of BH_2^{2+} into BH^+ involves changes in resonance stabilisation, an energy barrier to proton transfer could be introduced. However this effect is usually thought to be more important in proton transfer from carbon acids than from oxygen or nitrogen acids.[14] It has also been suggested [8a] that the buckling of the porphyrin ring on protonation [15] may be responsible for the high energy barrier to proton transfer.

The results in the Table show that the overall equilibrium constant for dissociation of BH_2^{2+} to give B increases by a factor of three in going from 95 to 85% Me_2SO-H_2O. However the rate coefficient for proton removal from BH_2^{2+} by water increases by more than thirty-fold. One of the reasons for the difference in effects on rate and equilibrium is that the overall equilibrium constant is a product of equilibrium constants for both proton transfers whereas the rate coefficient refers to the first step. In order to explain the effects of solvents in changing the ionisation behaviour of several porphyrins it has been proposed [16] that the monoprotonated forms are less stable in solvents of low dielectric constant. The solvent dependence of the rate of proton transfer which we have observed for *meso*-tetraphenylporphyrin may also be explained in this way. If the result of going to solvents with higher fractions of water is to stabilise the monocation relative to the free base and diprotonated species, the value of K_1 will be increased and the value of K_2 will be decreased. The overall equilibrium constant will change slightly because of the opposing effects on K_1 and K_2. However if the value of K_1 increases, the forward reaction in equation (2) will become less thermodynamically unfavourable and the increase in rate coefficient can therefore be understood. Further studies will be made with substituted *meso*-tetraphenylporphyrins which are soluble in solvent mixtures containing larger mole fractions of water.

Kinetic experiments with *meso*-tetra-(*N*-methyl-4-pyridyl)porphyrin in aqueous solution were reported [7] after the preliminary publication of this work.[1] The results are different from the results observed for *meso*-tetraphenylporphyrin. Relaxation times were in the range 0.04—0.2 μs; *cf.* 40—5 000 μs observed for *meso*-tetraphenylporphyrin. In addition for *meso*-tetra-(*N*-methyl-4-pyridyl)porphyrin, the monoprotonated porphyrin was detected in aqueous solution and individual equilibrium constants were obtained for each proton loss from the diprotonated species. The dependence of reciprocal relaxation time on hydrogen ion concentration was different from that observed for *meso*-tetraphenylporphyrin and a mechanism was proposed involving a slow equilibration between the free base and monoprotonated porphyrin. The slowness was attributed to the slow conversion of an unreactive planar form of the porphyrin base into a reactive buckled form. For *meso*-tetraphenylporphyrin the rate-determining step is the removal of the first proton from the diprotonated species. This process occurs rapidly for *meso*-tetra-(*N*-methyl-4-pyridyl)porphyrin. The difference between the two porphyrins may arise because for the reaction of *meso*-tetraphenylporphyrin in 90% Me_2SO-H_2O step (2) may be strongly thermodynamically unfavourable in the forward direction whereas for *meso*-tetra-(*N*-methyl-4-pyridyl)porphyrin this step is not strongly unfavourable and the monoprotonated species can be observed.

EXPERIMENTAL

Materials.—A commercial (Aldrich) sample of *meso*-tetraphenylporphyrin which was shown to have a purity greater than 98%, on the basis of its visible spectrum in benzene,[17] was used without purification. The solvent mixtures were made up by volume; for example 90% Me_2SO-H_2O (v/v) was prepared by adding 90 parts by volume of Me_2SO (AnalaR) to 10 parts by volume of doubly distilled water. Some of the experiments were carried out in solvent mixtures made up from AnalaR Me_2SO which had been distilled from calcium hydride under reduced pressure in a stream of nitrogen, and identical results were obtained.

Equilibrium Measurements.—Visible spectra of solutions of B and BH_2^{2+} leading to the identification of isosbestic points were run at room temperature on a Perkin-Elmer 402 spectrophotometer. Accurate measurements on the equilibrium between B and BH_2^{2+} were made at 12.8 °C using a Unicam SP 500 spectrophotometer. The solutions were thermostatted in the optical cells by circulation of water from an external bath and the temperature of the solution in the cell was measured.

Kinetic Measurements.—Kinetic results were obtained using the temperature-jump instrument manufactured by Messanlagen Studiengesellschaft (Göttingen). The reaction solutions were thermostatted and the temperature (11.6 °C) was measured with a thermocouple in the reaction cell. A 15 kV discharge from a 0.01 μF capacitor was used to raise the temperature to 12.8 °C and this occurred in *ca.* 30 μs. The chemical relaxation at this temperature was observed spectrophotometrically and relaxation times were calculated as previously described.[12] At least five measurements of the relaxation time were made for each solution and the average was taken. The heating time (30 μs) was measured for a solution containing 2-nitrodiphenylamine (2.6×10^{-4}M), sodium hydroxide (0.004M), and potassium chloride (0.076M) in 90% Me_2SO-H_2O. In this solution the proton transfer equilibrium is established very rapidly and the optical density of the solution (460 nm) immediately changes in response to a change in temperature.

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