# Substituent Effects on the Acidities and Rates of Ionisation of Protonated *meso*-Tetra-arylporphyrins

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Equilibrium constants and rates of equilibration between the basic (B) and diprotonated ($BH_2^{2+}$) forms of *meso*-tetra-arylporphyrins with various *para*-substituents in the phenyl rings have been determined in 90% $Me_2SO-H_2O$ (v/v) for comparison with previous results for *meso*-tetraphenylporphyrin. Spectrophotometric measurements were unable to detect the presence of significant concentrations of the monoprotonated porphyrins and an overall equilibrium constant $K = [B][H_3O^+]^2/[BH_2^{2+}]$ was measured. Values of the rate coefficients for ionisation of the di- to the mono-protonated porphyrins were obtained from the kinetic results. These rate coefficients and the acidities of the diprotonated porphyrins, as measured by the values of $K$, increase as the substituent is made more strongly electron withdrawing.

We have shown that in 90% $Me_2SO-H_2O$ (v/v) equilibration between *meso*-tetraphenylporphyrin (B) and its diprotonated form ($BH_2^{2+}$) occurs slowly.[1] Spectrophotometric titration of *meso*-tetraphenylporphyrin with acid gave spectra consistent with the conversion of B to $BH_2^{2+}$ and the monoprotonated porphyrin ($BH^+$) was not detected. The monoprotonated forms of *meso*-tetraphenylporphyrin [2] and other porphyrins [3] have been detected under other conditions.

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

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

For *meso*-tetraphenylporphyrin a value of the rate coefficient $k_1$ in equation (1) was obtained from the kinetic results. The measurements have now been extended to other *meso*-tetra-arylporphyrins in order to study the effect of substituents on the rate and equilibrium. It is anticipated that for a porphyrin differing in basicity from *meso*-tetraphenylporphyrin, the equilibrium constants for steps (1) and (2) may be changed such that the monoprotonated species is formed in measurable concentrations under our conditions. In addition for a porphyrin which behaves slightly differently from *meso*-tetraphenylporphyrin it may be possible to obtain values for the other rate coefficients in equations (1) and (2).

## RESULTS AND DISCUSSION

*Equilibrium Measurements.*—For each porphyrin (1; X = MeO, Me, H, Cl, or CN), solutions in 90% $Me_2SO-H_2O$ (v/v) gave visible spectra (400—800 nm) which varied in the presence of increasing concentrations of hydrochloric acid from the spectrum of the free base to the spectrum of the doubly protonated porphyrin. The ionic strength of the solutions was kept constant at 0.08M by the addition of potassium chloride and the porphyrin concentrations were *ca.* $1 \times 10^{-5}$M. Isosbestic points were observed at *ca.* 430, 480, 555, 570, and 590 nm for each porphyrin except for the methoxy-derivative for which isosbestic points were found at 433, 486, and 602 nm. For all the porphyrins the isosbestic point at

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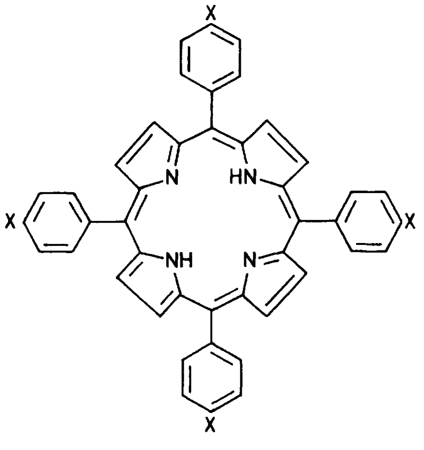
[1] F. Hibbert and K. P. P. Hunte, *J.C.S. Chem. Comm.*, 1975, 728; *J.C.S. Perkin II*, 1977, 1624.

[2] S. Aronoff, *J. Phys. Chem.*, 1958, **62**, 428.

[3] W. S. Caughey, W. J. Fujimoto, and B. P. Johnson, *Biochemistry*, 1966, **5**, 3830; A. H. Convin, A. B. Chivvis, R. W. Poor, D. G. Whitten, and E. W. Baker, *J. Amer. Chem. Soc.*, 1968, **90**, 6577; H. Baker, P. Hambright, and L. Wagner, *ibid.*, 1973, **95**, 5942; R. F. Pasternack, N. Sutin, and D. H. Turner, *ibid.*, 1976, **98**, 1908.

*ca.* 480 nm was less clearly defined than the other points. This may indicate that at 480 nm, the monoprotonated porphyrins absorb strongly and the slight variation in exact position of the isosbestic point may mean that $BH^+$ is being detected. However the excellent isosbestic points observed at the other wavelengths show that only low concentrations of $BH^+$ are present compared with B and $BH_2^{2+}$.



(1)

The equilibria between the porphyrin bases and diprotonated forms were studied quantitatively in 90% $Me_2SO-H_2O$ (v/v) at 12.8 °C and at an ionic strength 0.08M. Spectrophotometric measurements were made at *ca.* 420 nm where the absorbance is due mainly to the base porphyrins or at *ca.* 440 or 660 nm where the diprotonated forms absorb most strongly. The absorbances of solutions of the base or acid forms were linearly dependent upon porphyrin concentration ($5.0 \times 10^{-7}$–$2.5 \times 10^{-5}$M), showing that dimerisation does not occur in these solutions. Overall equilibrium constants $K = [B][H_3O^+]^2/[BH_2^{2+}]$ were determined as previously described [1] and the results are given in Table 1. Similar values of the equilibrium constant for *meso*-tetrakis-(*p*-methoxyphenyl)porphyrin were obtained with lithium chloride or potassium chloride as the added electrolyte to maintain constant ionic strength.

TABLE 1

Ionisation of substituted porphyrins in 90% $Me_2SO-H_2O$ (v/v). $K = [B][H_3O^+]^2/[BH_2^{2+}]$; ionic strength 0.08M; temperature 12.8 °C

| Porphyrin | λ/nm | | $10^6$[Porphyrin]/M | $10^4K$/mol² l⁻² |
|---|---|---|---|---|
| (1; X = OMe) | 690 | | 1.6—6.4 | 0.0066 ± 0.0008 |
| (1; X = Me) | 442 | 662 | 2.0—3.6 | 0.15 ± 0.02 |
| (1; X = H) | 417 | 448 | 0.4—1.6 | 1.3 ± 0.2 [a] |
| (1; X = Cl) | 660 | | 2.7—11.1 | 3.0 ± 0.4 |
| (1; X = CN) | 439 | 650 | 2.8—13.9 | 70 ± 10 |

[a] Results taken from ref. 1.

As seen from the results in Table 1, electron-withdrawing groups increase the overall equilibrium constant between B and $BH_2^{2+}$ and the values of the equilibrium constants (CN > Cl > H > Me > MeO) are in the same order as the Hammett σ values [4] for the substituents. The acidities of these porphyrins have been studied previously in dimethylformamide and very similar substituent effects were observed.[5] The acid concentrations at which the porphyrins are half-protonated ($[B] = [BH_2^{2+}]$) in 90% $Me_2SO-H_2O$ (v/v) are roughly three-fold lower than in dimethylformamide.

*Kinetic Measurements.*—Rates of equilibration between B and $BH_2^{2+}$ were studied in 90% $Me_2SO-H_2O$ (v/v) containing hydrochloric acid ($5 \times 10^{-4}$—0.08M) at 12.8 °C and an ionic strength 0.08M using the temperature-jump method. Porphyrin concentrations were in the range $2 \times 10^{-6}$—$1 \times 10^{-5}$M. After the rapid temperature rise the chemical relaxation to the new equilibrium position was followed spectrophotometrically by observing the increase in absorbance at *ca.* 440 nm due to an increase in concentration of B or by observing the decrease in absorbance due to a decrease in concentration of $BH_2^{2+}$ at *ca.* 460 or 660 nm. The optimum wavelengths were slightly different for each porphyrin. For equations (1) and (2) in which $BH^+$ is a low concentration intermediate, the reciprocal relaxation time for the equilibration between B and $BH_2^{2+}$ is given by equation (3) which reduces to equation (4) if $k_2[H_2O] > k_{-1}[H_3O^+]$.

$$1/\tau = (k_1k_2[H_2O]^2 + k_{-1}k_{-2}[H_3O^+]^2)/(k_{-1}[H_3O^+] + k_2[H_2O]) \quad (3)$$

$$1/\tau = k_1[H_2O] + (k_1[H_2O]/K)[H_3O^+]^2 \quad (4)$$

Reciprocal relaxation times were measured, for each porphyrin, at different acid concentrations. The reciprocal relaxation times were independent of the total concentration of porphyrin. Plots of reciprocal relaxation time against $[H_3O^+]$ curved upwards, although for *meso*-tetrakis-(*p*-cyanophenyl)porphyrin the effect was not large because the porphyrin was only half-protonated at the highest acid concentrations used. Plots of reciprocal relaxation time against $[H_3O^+]^2$ were accurately linear for all the porphyrins showing that equation (4) is obeyed and the values of $k_1[H_2O]$ and K derived from these plots are given in Table 2. The values of

TABLE 2

Kinetic results for ionisation of substituted porphyrins in 90% $Me_2SO-H_2O$ (v/v)

| Porphyrin | $10^{-3}k_1[H_2O]$/s⁻¹ | $10^4K$/mol² l⁻² |
|---|---|---|
| (1; X = OMe) | 0.13 ± 0.03 | 0.008 ± 0.002 |
| (1; X = Me) | 0.5 ± 0.1 | 0.16 ± 0.03 |
| (1; X = H) | 1.2 ± 0.1 [a] | 1.3 ± 0.2 [a] |
| (1; X = Cl) | 1.8 ± 0.2 | 3.3 ± 0.4 |
| (1; X = CN) | 6.5 ± 0.5 | 90 ± 10 |

[a] Results taken from ref. 1.

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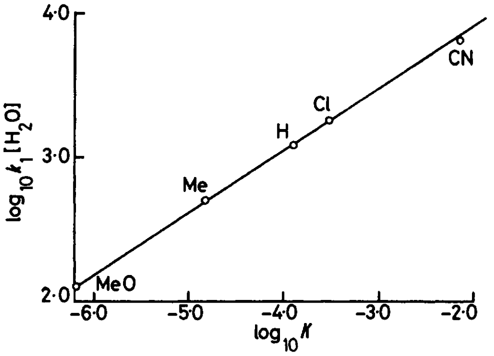
[4] K. B. Wiberg, 'Physical Organic Chemistry,' Wiley, New York, 1964, p. 281.

[5] M. Meot-Ner and A. D. Adler, *J. Amer. Chem. Soc.*, 1975, **97**, 5107.

$K$ agree well with the results obtained from the equilibrium measurements. One of the reasons for studying porphyrins of varying basicity was to find a porphyrin for which equation (3) is required to fit the acid dependence of the reciprocal relaxation time. In this case values for $k_1[H_2O]$ and $k_{-2}$ would be obtained from the kinetic results. For the porphyrins which we have studied up to now, equation (4) is a sufficiently good approximation.

Proton transfer from the diprotonated form of *meso*-tetrakis-(*p*-methoxyphenyl)porphyrin to water occurs with a rate coefficient $k_1[H_2O] = 1.3 \times 10^2$ s$^{-1}$ and is the slowest reaction studied in this work. It is unusual for proton transfer from nitrogen to occur slowly and possible explanations were given to account for the low rate observed for *meso*-tetraphenylporphyrin.[1] The rate coefficient for proton transfer from $BH_2^{2+}$ to give $BH^+$ increases along the series of porphyrins as the substituent is made more electron withdrawing. The equilibrium constant for the overall equilibrium between $BH_2^{2+}$ and B which is taken as a measure of the acidity of $BH_2^{2+}$ varies in the same direction. These results are shown as a Brönsted plot in the Figure. The overall equilibrium constant is a product of equilibrium constants $K = K_1K_2$, where $K_1$ and $K_2$ are the equilibrium constants for reactions (1) and (2) respectively. The rate coefficient $k_1[H_2O]$ refers to the first proton transfer. If it is assumed that substituent effects on the values of $K_1$ and $K_2$ are similar, a change of $\Delta\log K$ in the overall equilibrium constant on introducing a substituent will be accompanied by a change $0.5\Delta\log K_1$ in the equilibrium constant of reaction (1). Hence the slope of the Brönsted plot $\alpha$ of 0.44 means that for the first step, the rate of proton transfer is almost directly proportional to the equilibrium constant. It follows that the transition state for proton transfer in reaction (1) resembles the products of reaction. This is expected if reaction (1) is thermodynamically unfavourable. Previously[1] it was concluded from the failure to observe monoprotonated *meso*-tetraphenylporphyrin that reaction (1) was thermodynamically unfavourable and this was thought to be one of the factors contributing to the low rate of proton transfer.



Variation of rate coefficient for proton transfer from diprotonated *meso*-tetra-arylporphyrins with dissociation constant

EXPERIMENTAL

*Materials.*—*meso*-Tetrakis-(*p*-methoxyphenyl)-, *meso*-tetra-*p*-tolyl-, and *meso*-tetrakis-(*p*-chlorophenyl)-porphyrin were prepared by reaction of the corresponding substituted benzaldehyde with pyrrole in boiling propionic acid under nitrogen.[6] The products were recrystallised from methylene chloride–methanol. After conversion of any chlorin impurity to the porphyrin by oxidation,[7] the samples were dried at 80—90 °C in a vacuum oven. The identity of the porphyrins was confirmed by their visible spectra in benzene[8] and by the n.m.r. spectra of solutions in $CF_3COOD$–$CDCl_3$. *meso*-Tetrakis-(*p*-cyanophenyl)porphyrin was prepared by refluxing *p*-cyanobenzaldehyde with pyrrole in acetic acid[9] and purified by recrystallisation from chloroform–methanol and from pyridine. The visible spectrum in pyridine was similar to the reported spectrum[9] and a solution in $CF_3CO_2D$ gave a satisfactory n.m.r. spectrum.

*Equilibrium and Kinetic Measurements.*—The procedures used to measure equilibrium constants and relaxation times were the same as previously described for *meso*-tetraphenylporphyrin.[1]

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[6] A. D. Adler, F. R. Longo, and J. D. Finarelli, *J. Org. Chem.*, 1967, **32**, 476.

[7] G. H. Barnett, M. F. Hudson, and K. M. Smith, *J.C.S. Perkin I*, 1975, 1401.

[8] G. M. Badger, R. A. Jones, and R. L. Laslett, *Austral. J. Chem.*, 1964, **17**, 1028; D. W. Thomas and A. E. Martell, *J. Amer. Chem. Soc.*, 1956, **78**, 1338.

[9] N. Dattagupta and T. J. Bardos, *J. Heterocyclic Chem.*, 1966, **3**, 495.