Effects of *N*-Methylation on the Rates and Equilibrium Constants for Protonation of *meso*-Tetraphenylporphyrin in 98% (v/v) Dimethyl Sulphoxide–Water

By **Keith A. Freeman** and **Frank Hibbert**,* Department of Chemistry, Birkbeck College, Malet Street, London WC1E 7HX

Equilibrium constants for the first and second protonations of *N*-methyl-*meso*-tetraphenylporphyrin have been measured in 90% and 98% (v/v) Me_2SO-H_2O. The interconversion of the mono- and di-protonated forms of *N*-methyl-*meso*-tetrakis-(*p*-methoxyphenyl)porphyrin occurs slowly and the rate coefficient for thermodynamically favourable protonation of the monoprotonated form by hydronium ion has a value of 4.3×10^5 l mol^{-1} s^{-1} in 98% (v/v) Me_2SO-H_2O. The results are compared with kinetic and equilibrium results for *meso*-tetraphenyl- and *meso*-tetrakis-(*p*-methoxyphenyl)-porphyrins for which only the overall equilibrium between the porphyrin and diprotonated species could be studied since the monoprotonated species were undetectable in 90% and 98% (v/v) Me_2SO-H_2O. Possible reasons for the differences in behaviour are discussed.

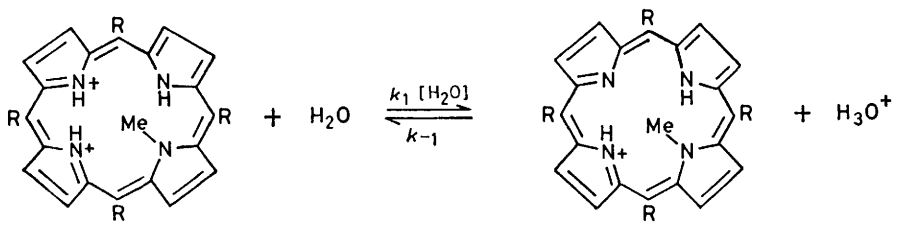
PORPHYRINS exhibit wide variations in their acid-base behaviour. In contrast to the behaviour of other dibasic acids, ionisation of the first proton from several diprotonated porphyrins occurs with a lower dissociation constant than ionisation of the second proton and as a consequence the monoprotonated porphyrins are formed in undetectably low concentrations[1] (Class I). For several other porphyrins, although the first dissociation constant (K_1) of the diprotonated porphyrin is smaller than the second dissociation constant (K_2), the difference between K_1 and K_2 is not as great as for porphyrins giving Class I type behaviour and in this case the monoprotonated species can be detected in low concentration[1a,2] (Class II). There are also examples (Class III) where the relative magnitude of the dissociation constants is in the expected order for a dibasic acid ($K_1 > K_2$) and both ionisations can then be studied separately at different acid concentrations.[3] For porphyrins giving Class II and Class III ionisation behaviour, values for both dissociation constants can be obtained but for Class I type behaviour only the product K_1K_2 of equilibrium constants can be determined for the overall equilibrium between the porphyrin and the diprotonated species.

We have made kinetic measurements of the ionisation of several porphyrins using the temperature-jump technique. For the kinetic experiments it was necessary to use Me_2SO-H_2O mixtures around 90% (v/v) and equilibrium measurements were made under the same conditions. For porphyrins showing Class I ionisation behaviour it was found that the reciprocal relaxation time for equilibration between the free base and diprotonated species was proportional to the square of the acid concentration and from this dependence the rate coefficient for ionisation of the diprotonated porphyrin to give the monoprotonated species was calculated.[4] The rate coefficients were extremely low compared with the rates of ionisation of other protonated amines. From the complex dependence of reciprocal relaxation time on acid concentration for Class II porphyrins, forward and reverse rate coefficients for interconversion of the diprotonated and monoprotonated porphyrins were obtained.[5] The rate coefficients were again very low compared with the values normally found for proton transfer to and from nitrogen. We now present kinetic and equilibrium results for *N*-methyl-*meso*-tetraphenylporphyrin and *N*-methyl-*meso*-tetrakis-(*p*-methoxyphenyl)porphyrin. We find that both porphyrins give Class III type ionisation behaviour in 85—98% (v/v) Me_2SO-H_2O mixtures. This was expected in view of similar findings for *N*-methyl-*meso*-tetraphenylporphyrin in nitrobenzene[6] and in chloroform.[7] We chose to study a Class III porphyrin because in theory the kinetics of both ionisation steps could be studied and this had not been possible for Class I and II porphyrins. It is conceivable for Class I and II porphyrins that there is a connection between the slow ionisation behaviour and the unusual relative magnitude of the first and second dissociation constants of the diprotonated porphyrins. For a Class III porphyrin showing the usual order of first and second dissociation constants it is therefore of interest to find out whether proton transfer is also slow.

RESULTS

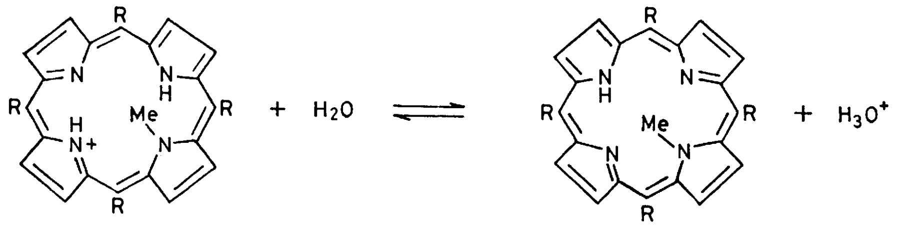
N-*Methyl*-meso-*tetraphenylporphyrin*.— Equilibrium measurements of the protonation of *N*-methyl-*meso*-tetraphenylporphyrin were made in 90 and 98% (v/v) Me_2SO-H_2O with porphyrin concentrations *ca.* 1×10^{-5} mol l^{-1} in the presence of varying concentrations of hydrochloric acid. Protonation occurs in two separate steps as found previously in nitrobenzene[6] and in chloroform,[7] and these are shown in equations (1) and (2) in which R = Ph. In 98% (v/v) Me_2SO-H_2O the first protonation, equation (2), occurred at acid concentrations in the range 0—0.000 3 mol l^{-1} and good isosbestic points at 487 and 591 nm were observed in the visible spectrum for solutions of *N*-methyl-*meso*-tetraphenylporphyrin in the presence of increasing concentrations of acid as the free base was converted into the monocation. The equilibrium between the monocation and dication, equation (1), was studied in the presence of 0.003—0.05 mol l^{-1} hydrochloric acid and again a good isosbestic point was observed (at 641 nm). The changes in absorbance at fixed wavelength for solutions of the porphyrin at various acid concentrations in these ranges were used to obtain values for the equilibrium constants for equations (1) and (2). For equilibrium (1) absorbance readings were taken at 680 nm where the absorbance is due to the dication and for equilibrium (2) readings were taken at

574 nm (base peak) and 615 nm (monocation peak). In 98% (v/v) $Me_2SO–H_2O$ at 20.0 °C the values $K_1 = 2.1 \pm 0.1 \times 10^{-2}$ mol l^{-1} and $K_2 =$ *ca.* 1×10^{-5} mol l^{-1} were obtained. These results refer to an ionic strength of 0.1 mol l^{-1}, maintained constant by addition of lithium chloride. In 90% (v/v) $Me_2SO–H_2O$ at 20.0 °C the results were $K_1 = 4.1 \pm 0.2 \times 10^{-2}$ mol l^{-1} and $K_2 =$ *ca.* 3×10^{-5} mol l^{-1}. In this case the ionic strength was kept at 0.08 mol l^{-1} by addition of potassium chloride. The previous work[4] with *meso*-tetraphenylporphyrin was carried out under these latter conditions but because of the limited solubility of potassium chloride in 98% (v/v) $Me_2SO–H_2O$ it was necessary to use lithium chloride to maintain constant ionic strength in this solvent. Isosbestic points for equilibria (1) and (2) were also observed in 85 and 95% (v/v) $Me_2SO–H_2O$.



(1)

$K_1 = [\text{monocation}][H_3O^+]/[\text{dication}]$



(2)

$K_2 = [\text{base}][H_3O^+]/[\text{monocation}]$

In some cases spectra were run at different porphyrin concentrations (1×10^{-5} mol l^{-1} with 4-cm path length cells or 4×10^{-5} mol l^{-1} using 1-cm cells). At all concentrations in the different solvent mixtures the spectral changes were identical to those reported for chloroform solutions.[6,7]

Similar experiments were previously carried out for *meso*-tetraphenylporphyrin in 80—98% (v/v) $Me_2SO–H_2O$ but the spectral changes which again occurred with good isosbestic points corresponded to an equilibrium between the free base and dication and the monocation was not detected.[4a] From the value of the overall equilibrium constant and the conclusion that only low concentrations of the monocation are present it is possible to estimate limiting values for the individual equilibrium constants for protonation of *meso*-tetraphenylporphyrin and these are given in the Table together with the results obtained for *N*-methyl-*meso*-tetraphenylporphyrin. In 90% (v/v) $Me_2SO–H_2O$ for *meso*-tetraphenylporphyrin it is found that $pK_2 - pK_1 \leqslant 0$ whereas for *N*-methyl-*meso*-tetraphenylporphyrin $pK_2 - pK_1 = 3$. In nitrobenzene previous studies have shown that $pK_2 - pK_1 = 0.5$ for *meso*-tetraphenylporphyrin[1a] and $pK_2 - pK_1 = 1.8$ for the *N*-methyl derivative.[6]

In principle it should be possible to make separate kinetic measurements for equilibrium (1) and (2) using the temperature-jump method. However, under the present conditions, equilibrium (2) between the free base and monocation could not be studied kinetically because at the low acid concentrations necessary to observe this equilibrium the solution was not buffered and the electrical discharge used to bring about the rapid temperature jump changed the hydrogen ion concentration. For equilibrium (1) between the dication and monocation at acid concentrations *ca.* 0.03 mol l^{-1} a chemical relaxation was observable for solutions of *N*-methyl-*meso*-tetraphenylporphyrin in 90 and 98% (v/v) $Me_2SO–H_2O$. The relaxations were rapid and it was difficult to obtain accurate results but it was concluded that the relaxations occurred outside the time required for the temperature jump. In order to achieve the most favourable conditions for studying the kinetics of equilibrium (1) it was decided to investigate in detail the protonation of *meso*-tetrakis-(*p*-methoxyphenyl)porphyrin [R = $MeOC_6H_4$ in equations (1) and (2)] in 98% (v/v) $Me_2SO–H_2O$. It was shown in earlier studies that the introduction

Rate coefficients and equilibrium constants for ionisation of protonated porphyrins[a]

	$10^{-3}k_1[H_2O]$ / s^{-1}	$10^{-5}k_{-1}$ / mol l^{-1} s^{-1}	10^2K_1[d] / mol l^{-1}	10^2K_2[d] / mol l^{-1}	$10^4K_1K_2$ / mol² l^{-2}	$Me_2SO–H_2O$ % (v/v)
TPP[b]	1.2		<1.0	>1.0	1.3	90
TPP[b]	0.19		<0.8	>0.8	0.63	95
NMeTPP[c]			4.1 ± 0.2	*ca.* 0.003	*ca.* 0.012	90
NMeTPP[c]			2.1 ± 0.2	*ca.* 0.001	*ca.* 0.002	98
MeOTPP[b]	0.13		<0.09	>0.09	0.008	90
MeOTPP[c]	0.0020 ± 0.0005		<0.05	>0.05	0.0030 ± 0.0006	98
NMeMeOTPP	1.4 ± 0.2	4.3 ± 0.6	0.25 ± 0.02	<0.001	<0.000 25	98

[a] TPP = tetraphenylporphyrin, NMeTPP = *N*-methyl-*meso*-tetraphenylporphyrin, MeOTPP = *meso*-tetrakis-(*p*-methoxyphenyl)porphyrin, and NMeMeOTPP = *N*-methyl-*meso*-tetrakis-(*p*-methoxyphenyl)porphyrin. Rate coefficients and equilibrium constants refer to equations (1) and (2) which are written for the *N*-methylated porphyrins. [b] Results taken from ref. 4. [c] Present work. [d] Equilibrium constants refer to finite ionic strength (see text).

of a *p*-methoxy-group into each of the phenyl rings in *meso*-tetraphenylporphyrin [4b] increases the relaxation times by a factor of *ca.* 10 and also that the relaxations are slower in Me_2SO-H_2O solvents with higher fractions of Me_2SO.[4a]

N-*Methyl*-meso-*tetrakis*-(p-*methoxyphenyl*)*porphyrin*.— In Me_2SO-H_2O mixtures *N*-methyl-*meso*-tetrakis-(*p*-methoxyphenyl)porphyrin is present as the monocation even in the absence of added acid. The second protonation, shown in equation (1) with $R = MeOC_6H_4$, was studied spectrophotometrically in 98% (v/v) Me_2SO-H_2O containing 4×10^{-5} mol l^{-1} *N*-methyl-*meso*-tetrakis-(*p*-methoxyphenyl)porphyrin at 20.0 °C and an ionic strength maintained at 0.1 mol l^{-1} by addition of lithium chloride with acid concentrations in the range 0.001—0.02 mol l^{-1}. A good isosbestic point at 672 nm in the visible spectrum was observed as the monocation was converted into the dication in the presence of increasing concentrations of hydrochloric acid. An equilibrium constant $K_1 = 2.5 \pm 0.2 \times 10^{-3}$ mol l^{-1} was calculated from measurements of the absorbance at 730 nm due to the dication. Substitution of methoxy-groups into *N*-methyl-*meso*-tetraphenylporphyrin brings about an increase in the basicity of the free base and monocation. Similarly *meso*-tetrakis-(*p*-methoxyphenyl)porphyrin was found to be more strongly basic than *meso*-tetraphenylporphyrin.[4b]

In 98% Me_2SO-H_2O *meso*-tetrakis-(*p*-methoxyphenyl)-porphyrin gives similar results to those observed for *meso*-tetraphenylporphyrin and only the overall equilibrium between the free base and dication could be observed. The value of the equilibrium constant at ionic strength 0.1 mol l^{-1} and 20.0 °C was determined from absorbance measurements of the dication peak at 466 nm. The value is shown in the Table together with the estimated values of the individual equilibrium constants for the first and second protonations.

The kinetics of equilibrium (1) with $R = MeOC_6H_4$ involving *N*-methyl-*meso*-tetrakis-(*p*-methoxyphenyl)-porphyrin were studied using the temperature-jump method. Measurements were made at 20.0 °C in 98% (v/v) Me_2SO-H_2O containing lithium chloride to maintain a constant ionic strength of 0.10 mol l^{-1} with 5×10^{-5} mol l^{-1} porphyrin and at hydrochloric acid concentrations in the range 0.001—0.02 mol l^{-1}. Chemical relaxation of equilibrium (1) after a rapid temperature jump of 2.1 °C was observed at *ca.* 470 nm where the dication absorbs strongly. The variation in chemical relaxation time with acid concentration is shown in the Figure and from these results forward and reverse rate coefficients for interconversion of the dication and monocation of *N*-methyl-*meso*-tetrakis-(*p*-methoxyphenyl)porphyrin were calculated using equation (3). The values are given in the Table and the ratio

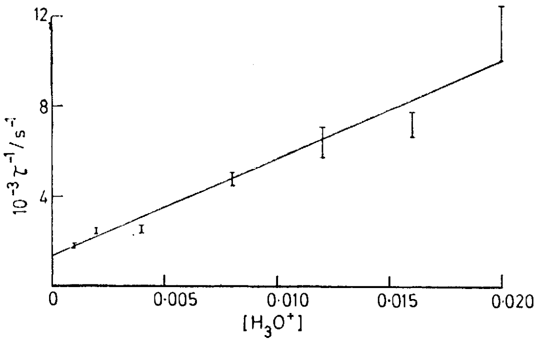
$$\tau^{-1} = k_1[H_2O + k_{-1}[H_3O^+] \qquad (3)$$

$k_1[H_2O]/k_{-1} = 3.3 \pm 0.9 \times 10^{-3}$ mol l^{-1} is in agreement with the separately measured equilibrium constant $K_1 = 2.5 \pm 0.2 \times 10^{-3}$ mol l^{-1}.

For comparison the kinetics of the protonation-deprotonation of *meso*-tetrakis-(*p*-methoxyphenyl)porphyrin were studied under the same conditions. Previous measurements [4b] had been made in 90% (v/v) Me_2SO-H_2O. Chemical relaxations for solutions of the free base and dication were observed at 460 nm where the absorbance is due to the dication. We have previously shown [4] that for equilibria (1) and (2) in which the monocation is present in low concentrations the reciprocal relaxation time for equilibration between the free base and dication varies linearly with the square of the acid concentration. This was again observed for *meso*-tetrakis-(*p*-methoxyphenyl)porphyrin in 98% (v/v) Me_2SO-H_2O and the value of $k_1[H_2O]$ derived from this dependence is shown in the Table. A value for K_1K_2 was also obtained from the kinetics and this result ($K_1K_2 = 3 \pm 1 \times 10^{-7}$ mol² l^{-2}) is in agreement with the value $K_1K_2 = 3.0 \pm 0.6 \times 10^{-7}$ mol² l^{-2} determined from equilibrium measurements.

DISCUSSION

The equilibrium results show that introduction of an *N*-methyl substituent into *meso*-tetraphenylporphyrin and *meso*-tetrakis-(*p*-methoxyphenyl)porphyrin modifies the properties sufficiently to change the ionisation behaviour from Class I observed for the non-methylated porphyrins to Class III observed for the *N*-methyl derivatives. The values of the equilibrium constants for reactions (1) and (2) involving these compounds are given in the Table. In 90% (v/v) Me_2SO-H_2O the first dissociation constant of the diprotonated species is at least 5-fold larger for *N*-methyl-*meso*-tetraphenylporphyrin than for *meso*-tetraphenylporphyrin and the second dissociation constant is at least 200-fold lower for the *N*-methyl derivative than for *meso*-tetraphenylporphyrin. This latter effect is similar to the result observed for octaethylporphyrin, for which the value of K_2 in toluene–acetic acid mixtures was lowered *ca.* 10^4-fold by methylation.[8] The changes in K_1 and K_2 brought about by *N*-methylation are sufficiently large that the monocation of *N*-methyl-*meso*-tetraphenylporphyrin is observable and the relative values of the first and second dissociation constants of the diprotonated form of *N*-methyl-*meso*-tetraphenylporphyrin are as expected for a dibasic acid. The large effect of *N*-methylation on the individual values of K_1 and K_2 is quite remarkable, especially as protonation is occurring at nitrogen atoms other than the *N*-methylated site. Evidence is available to support the view that many porphyrins, particularly in the monocationic [9] and dicationic [10] forms, exist in a non-planar conformation. This is thought [11] to arise because of steric interactions between the inner hydrogen atoms and has been put



Variation of chemical relaxation time with acid concentration for equilibration between the dication and monocation of *meso*-tetrakis-(*p*-methoxyphenyl)porphyrin in 98% (v/v) Me_2SO-H_2O

forward as a possible explanation for the failure to detect the monocations of Class I porphyrins, for example *meso*-tetraphenylporphyrin.[11] Thus formation of the buckled monocation involves attack on the planar free base in which the basic nitrogen atoms may be inaccessible whereas protonation of the monocation involves attack at an already buckled ring with an exposed nitrogen site so that formation of the dication occurs more readily than formation of the monocation. It is conceivable that the effect of the *N*-methyl substituent on the properties of *meso*-tetraphenylporphyrin can also be explained in this way. In *N*-methyl-*meso*-tetraphenylporphyrin the free base may be buckled because of the steric interaction between the hydrogen atoms and the *N*-methyl substituent, and the basic nitrogen atoms may therefore be exposed. Hence protonation of the free base is no less favourable than protonation of the monocation. This means that the monocation will be observable and the dication will behave as expected for a dibasic acid. However our kinetic results show that the ionisation behaviour of *N*-methyl-*meso*-tetraphenylporphyrin is not fully normal.

The rate coefficients given in the Table show that the interconversion of the dication and monocation of *N*-methyl-*meso*-tetrakis-(*p*-methoxyphenyl)porphyrin occurs more slowly than expected for a reaction involving protonation at nitrogen. In addition, n.m.r. spectra of solutions of *N*-methyl-*meso*-tetraphenylporphyrin in $CDCl_3$ containing CF_3CO_2D have been interpreted in terms of a slow proton transfer equilibrium between the free base porphyrin and the monocation.[7] Hence it appears that both steps in the ionisation of the diprotonated form of *N*-methyl-*meso*-tetraphenylporphyrin occur slowly.

Thermodynamically favourable protonation of the monocation of *N*-methyl-*meso*-tetrakis-(*p*-methoxyphenyl)porphyrin in 98% (v/v) Me_2SO–H_2O occurs with a rate coefficient which is four or five orders of magnitude below the diffusion-limited value expected for protonation of nitrogen.[12] A similar value was found in 95% (v/v) Me_2SO–H_2O for mesoporphyrin-IX dimethyl ester which gives Class II ionisation behaviour.[5] We have shown previously[5] that protonation of a substituted phenolate ion by hydronium ion in 98% (v/v) Me_2SO–H_2O is rapid with a rate coefficient $> ca.\ 10^8$ l mol^{-1} s^{-1}. Hence it seems likely that normal[12] proton transfers will occur at the diffusion limited rate in 98% (v/v) Me_2SO–H_2O in the thermodynamically favourable direction. However in view of recent results in moist[13] and pure Me_2SO[14] we cannot entirely rule out the possibility that proton transfers to nitrogen do not reach the diffusion limit in 98% (v/v) Me_2SO–H_2O even when in water the same reactions are diffusion controlled.

The difference between the rate coefficients for ionisation of the diprotonated forms of *meso*-tetrakis-(*p*-methoxyphenyl)porphyrin and the *N*-methyl derivative means that *N*-methylation increases the rate coefficient by a factor of 700. This is a very large effect in view of the fact that deprotonation is not occurring from the nitrogen where a methyl group has been introduced. It is possible that the deprotonation–protonation site is more accessible in the *N*-methyl monocation. However the difference between the values of the first ionisation constants of the diprotonated forms of *meso*-tetrakis-(*p*-methoxyphenyl)porphyrin and *N*-methyl-*meso*-tetrakis-(*p*-methoxyphenyl)porphyrin which is at least a factor of five will be partly responsible for the difference in rate. Answers to some of the remaining questions about the ionisation behaviour of porphyrins may be provided by results for water soluble Class I porphyrins and their *N*-methylated derivatives which currently are being studied in aqueous solution.

EXPERIMENTAL

Materials.— *N*-Methyl-*meso*-tetraphenylporphyrin and *N*-methyl-*meso*-tetrakis-(*p*-methoxyphenyl)porphyrin were prepared from *meso*-tetraphenylporphyrin and *meso*-tetrakis-(*p*-methoxyphenyl)porphyrin by methylation with methyl fluorosulphonate using the method of Lavallee.[6] The products were purified by chromatography on alumina and characterised by their n.m.r. spectra:[7] *N*-methyl-*meso*-tetraphenylporphyrin, $\delta(CDCl_3)$ *ca.* 7—9 (m, 28 H, aromatic), −3.95 (s, 3 H, NMe); *N*-methyl-*meso*-tetrakis-(*p*-methoxyphenyl)porphyrin, $\delta(CF_3CO_2D)$ *ca.* 8 and 9 (m, 24 H, aromatic), 4.41 (s, 12 H, OMe), −3.80 (s, 3 H, NMe). The visible spectra of the free bases, monocations, and dications were also compatible with published spectra;[7] *N*-methyl-*meso*-tetraphenylporphyrin (98% Me_2SO–H_2O): free base $\lambda_{max.}$ 533 nm (log ε *ca.* 4.0), 573 (4.2), 610 (3.6), and 672 (3.7), monocation 617 (4.2) and 673 (4.2), dication 680 (4.7); *N*-methyl-*meso*-tetrakis-(*p*-methoxyphenyl)porphyrin (98% Me_2SO–H_2O): monocation 645 (3.9) and 700 (3.9), dication 715 (4.7).

Techniques.—The experimental procedures for obtaining equilibrium results and relaxation times were similar to those used previously.[5] In the temperature-jump measurements a discharge of 20 kV from a 0.01 μF capacitor was used to raise the temperature of the reaction solution by 2.1 °C and this occurred in *ca.* 10—15 μs. Two independent methods were used to establish that the optical density change after the temperature jump corresponded to a perturbation of the equilibrium between the dication and monocation of *N*-methyl-*meso*-tetrakis-(*p*-methoxyphenyl)porphyrin. Firstly, the value of the equilibrium constant between the dication and monocation determined from spectrophotometric equilibrium measurements was in good agreement with the value calculated from the dependence of reciprocal relaxation time on acid concentration. Secondly, for an equilibrium such as that shown in equation (1) it can be shown that the total change in optical density which occurs after a temperature jump (relaxation amplitude) will go through a maximum value as the hydronium ion concentration is varied and the maximum will occur at $[H_3O^+] = K_1$. In confirmation of this the maximum of the measured relaxation amplitude occurred at $[H_3O^+] = 0.002$ in good agreement with the value of $K_1 = 2.5 \times 10^{-3}$ mol l^{-1} determined spectrophotometrically.

The solvent mixtures used for the kinetic and equilibrium measurements were made up by volume from Me_2SO (AnalaR) and H_2O (double distilled). For some experiments the dimethyl sulphoxide was prepared by distillation under vacuum from Me_2SO (AnalaR) containing sodium hydroxide.

The Royal Society is thanked for equipment grants and support from the S.R.C. for a postdoctoral research assistant is gratefully acknowledged.

[8/2122 *Received*, 11*th December*, 1978]

REFERENCES

[1] (*a*) S. Aronoff, *J. Phys. Chem.*, 1958, **62**, 428; (*b*) W. S. Caughey, W. J. Fujimoto, and B. P. Johnson, *Biochemistry*, 1966, **5**, 3830.

[2] R. F. Pasternack, P. R. Huber, P. Boyd, G. Engasser, L. Francesconi, E. Gibbs, P. Fasella, G. Cerio Venturo, and L. de Hinds, *J. Amer. Chem. Soc.*, 1972, **94**, 4511; H. Baker, P. Hambright, and L. Wagner, *J. Amer. Chem. Soc.*, 1973, **95**, 5942.

[3] A. Neuberger and J. J. Scott, *Proc. Roy. Soc.*, 1952, **A213**, 307; A. H. Corwin, A. B. Chivvis, R. W. Poor, D. G. Whitten, and E. W. Baker, *J. Amer. Chem. Soc.*, 1968, **90**, 6577.

[4] (*a*) F. Hibbert and K. P. P. Hunte, *J.C.S. Perkin II*, 1977, 1624; (*b*) B. A. Conroy, K. A. Freeman, F. Hibbert, K. P. P. Hunte, H. J. Robbins, and K. D. Somasundram, *J.C.S. Perkin II*, 1977, 2076.

[5] K. A. Freeman, F. Hibbert, and K. P. P. Hunte, *J.C.S. Perkin II*, 1979, 1237.

[6] D. K. Lavallee and A. E. Gebala, *Inorg. Chem.*, 1974, **13**, 2004.

[7] H. M. G. Al-Hazimi, A. H. Jackson, A. W. Johnson, and M. Winter, *J.C.S Perkin I*, 1977, 98.

[8] R. Grigg, R. J. Hamilton, M. L. Jozefowicz, C. H. Rochester, R. J. Terrell, and H. Wickwar, *J.C.S. Perkin II*, 1973, 407.

[9] C. P. Hrung, M. Tsutsui, D. L. Cullen, E. F. Meyer, jun., and C. N. Morimoto, *J. Amer. Chem. Soc.*, 1978, **100**, 6068.

[10] E. B. Fleischer, *Accounts Chem. Res.*, 1970, 105.

[11] E. B. Fleischer and A. L. Stone, *Chem. Comm.*, 1967, 332.

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

[13] M. M. Kreevoy and Y. Wang, *J. Phys. Chem.*, 1977, **81**, 1924.

[14] J.-J. Delpuech and B. Bianchin, *J. Amer. Chem. Soc.*, 1979, **101**, 383.