Equilibrium and Kinetic Study of Pyridine Binding to Phthalocyaninatoiron(II) in Dimethyl Sulphoxide

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The reaction between pyridine (py) and phthalocyaninatoiron(II), [Fe(pc)], in dimethyl sulphoxide (dmso) has been studied from the kinetic and the equilibrium viewpoints at 20 ± 0.5 °C. In the presence of a large excess of pyridine the adduct $[Fe(pc)(py)_2]$ is formed *via* pseudo-first-order kinetics. The observed rate constants have the general form $k_{obs.} = k_{1f}[py] + k_{1r}$, with $k_{1f}' \approx 1.5 \times 10^4$ dm^3 mol^{-1} s^{-1} and $k_{1f}'' = 35.5 \pm 0.7$ dm^3 mol^{-1} s^{-1} and $k_{1r}'' = 0.15 \pm 0.02$ s^{-1}, for the binding and dissociation of the first and second py molecules, respectively. From the values of the equilibrium constant [$K_1' = (3.9 \pm 0.1) \times 10^5$ dm^3 mol^{-1}] and of the second-order rate constant (k_{1f}') for the binding of the first py molecule, the dissociation rate constant has been estimated to be $k_{1r}' \approx 4 \times 10^{-2}$ s^{-1}. The value of the equilibrium constant for the binding of the second py ($K_1'' = 300 \pm 28$ dm^3 mol^{-1}), determined directly, is in good agreement with the corresponding value (240 ± 40 dm^3 mol^{-1}) obtained from the ratio k_{1f}''/k_{1r}''). The data obtained in the present study are discussed in the light of related previous studies.

Phthalocyaninatoiron(II), [Fe(pc)], is a widely investigated porphyrin-like molecule which exhibits a strong tendency towards axial ligation, as shown by the number of adducts which have been characterized in the solid state.[1,2] Solution studies on [Fe(pc)], as well as on other metal phthalocyanine derivatives, are severely limited by the insolubility of these complexes in water and in non-donor or weak-donor solvents. Dimethyl sulphoxide (dmso) is among the few solvents in which [Fe(pc)] dissolves appreciably. Recently, a kinetic study of the reaction of [Fe(pc)] with O_2 in dmso[3] showed that the mechanism is complex; in contrast, a simple and reversible binding of CO to [Fe(pc)] has been observed in the same solvent.[4] It seemed interesting to investigate further the carbonylation process in the presence of an N-base such as pyridine, piperidine, imidazole, or *N*-methylimidazole, in order to evaluate the *trans* effect on both the dynamic and thermodynamic aspects of the general reaction (1) (omitting free dmso), where B is an axially co-ordinated base (variable over a large range of structural parameters).

$$[Fe(pc)(B)(dmso)] + CO \rightleftharpoons [Fe(pc)(B)(CO)] \quad (1)$$

A complete understanding of the equilibrium and kinetic aspects of the binding of each N-base B to [Fe(pc)] in dmso was first required. Data were available on systems in dmso where B is imidazole,[5–9] pyridine,[7–9] and substituted pyridines.[8,9] However, some of the published results are conflicting[7,9] and hence a reinvestigation of reaction (2) was undertaken from

$$[Fe(pc)(dmso)_2] + 2B \rightleftharpoons [Fe(pc)(B)_2] \quad (2)$$

both the thermodynamic and kinetic viewpoints. This paper reports the results for B = pyridine (py).

Experimental

Materials.—Phthalocyaninatoiron(II) was an Eastman product and was purified as previously described.[4] Dimethyl sulphoxide (Merck, spectrograde) was distilled under reduced pressure over CaH_2 before use. Pyridine was freshly distilled over CaO.

Equilibrium Measurements.—The equilibria (3) and (4) were monitored spectrophotometrically in the region(s) of maximum change in absorbance (see later). A Cary 219 instrument,

$$[Fe(pc)(dmso)_2] + py \overset{K_1'}{\rightleftharpoons} [Fe(pc)(dmso)(py)] \quad (3)$$

$$[Fe(pc)(dmso)(py)] + py \overset{K_1''}{\rightleftharpoons} [Fe(pc)(py)_2] \quad (4)$$

equipped with a water-circulating thermostatting system, was used for the measurements. Typically, a spectrophotometric cell of suitable path length (1 or 5 cm) was filled with a known volume (*ca.* 3 or 25 cm^3, respectively) of a dmso solution of [Fe(pc)] in the concentration range 1×10^{-6}—1×10^{-5} mol cm^{-3}. An accurate value of the concentration was obtained from the absorption at 653 nm ($\varepsilon = 7.49 \times 10^4$ dm^3 mol^{-1} cm^{-1}).[10] Within the above range of concentration, solutions of [Fe(pc)] are sufficiently air stable[3] to allow their handling without the need to exclude contact with dioxygen. A dmso solution of pyridine of known concentration was then added to the above solution by means of a microsyringe; although the volumes added were generally in the range 5—100 μl and negligible with respect to the starting volume, the dilution effect was taken into account. After thermal equilibrium (temperature: 20 ± 0.5 °C) had been achieved the spectrum was recorded and the absorbance *D* measured at a convenient wavelength [655—657 nm for reaction (3) and 654 nm for reaction (4), see later].

Since the spectral changes corresponding to the entry of the first pyridine molecule are very small, 5-cm cells were used. In this case it was found more convenient to measure directly the difference spectrum by using as a reference the starting solution of [Fe(pc)].

The changes in absorbance, $D - D_1$ (D_1 = absorbance in the absence of base) were analysed according to equations (5) and (6), from which the equilibrium constant ($K = K_1'$ or K_1''),

$$\frac{1}{(D - D_1)} = \frac{1}{K(D_2 - D_1)} \cdot \frac{1}{[\mathrm{py}]} + \frac{1}{D_2 - D_1} \quad (5)$$

$$\log [(D - D_1)/(D_2 - D)] = \log K + n \log [\mathrm{py}] \quad (6)$$

the absorption change for complete conversion ($D_2 - D_1$), and the number, n, of pyridine molecules co-ordinated in each step may be obtained.

Kinetic Measurements.—The kinetics of the exchange of axial dmso with pyridine were studied by the stopped-flow method. A Durrum-Gibson rapid-mixing stopped-flow apparatus was used with a 2-cm light path. The experiments were carried out at 20 ± 0.5 °C. The wavelength chosen was 655 nm for both reactions (3) and (4). For reaction (3) the maximum scale expansion was used (full range = 0.006 absorbance units per cm). Pseudo-first-order conditions were adopted with respect to pyridine, the concentration of which was, in all experiments, at least ten times higher than the concentration of [Fe(pc)].

Results and Discussion

Equilibrium Measurements.—Constant K_1'. When a pyridine solution of suitable concentration ([py] $\geqslant 3 \times 10^{-4}$ mol dm^{-3}) is added to a 1×10^{-5} mol dm^{-3} solution of [Fe(pc)] the spectrum does not appear to change {base:[Fe(pc)] mol ratio $\leqslant$ 1:1}. However, when the complex concentration is lowered to *ca.* (0.7—1.0) $\times 10^{-6}$ mol dm^{-3}, a *very accurate* comparison of the absolute spectra *before* and *after* the addition of 1×10^{-5} mol dm^{-3} pyridine (and accounting for the dilution) reveals a small but systematic increase (*ca.* 2%) of the main charge-transfer absorption band (originally at 653 nm) which is also systematically red-shifted by *ca.* 2 nm. No other changes are observed in the whole range 300—800 nm.

The above small changes, assumed to be due to reaction (3), were better documented by difference spectroscopy (see Experimental section). Figure 1 shows a typical series of difference spectra obtained at increasing pyridine concentration. Although these measurements are at the limits of the instrumental sensitivity (full scale range = 0.020 absorption units), the spectral pattern shown is clean and reproducible with two well resolved isosbestic points at 647 and 665 and a maximum absorption change at 657 nm.

The overall absorbance increase, $D_2 - D_1$, which may be estimated directly from the difference spectra, was also obtained as the reciprocal of the intercept of the linear plot of $1/(D - D_1)$ *vs.* $1/[\mathrm{py}]$ ($n = 1$) [see equation (5)]. Dividing ($D_2 - D_1$) by the concentration of [Fe(pc)], an increase in molar absorbance $\varepsilon_2 - \varepsilon_1$ = 1 200 ± 200 dm^3 mol^{-1} cm^{-1} was calculated at λ = 657 nm. The equilibrium constant K_1' can also be obtained from equation (5): least-squares analysis of two separate experiments gives $K_1' = (3.9 \pm 0.1) \times 10^5$ dm^3 mol^{-1}.

Constant K_1''. Addition of pyridine up to *ca.* 0.1 mol dm^{-3} to a [Fe(pc)] solution causes a relatively large modification of the spectrum, particularly in the 600—700 nm range, where the band at 654 nm increases, and in the 390—450 nm range, where the (Soret) band at 414 nm develops, as shown in Figure 2. The absorbance at 414 is a strictly linear function of that at 654 nm, as shown in Figure 3. It is important to note that the best line (least-squares) drawn through the experimental points intercepts the abscissa at a small, yet, definitely non-zero value of $\Delta\varepsilon(654)$, 700 ± 200 dm^3 mol^{-1} cm^{-1}, this behaviour being systematic. Furthermore, the presence of four isosbestic points at 588, 597, 645, and 664 nm indicates that only two coloured species are involved in the reaction. Due to the relatively large spectral changes observed in this case, 1-cm cells could be used and, consequently, the [Fe(pc)] concentration could be raised to *ca.* 1×10^{-5} mol dm^{-3}.

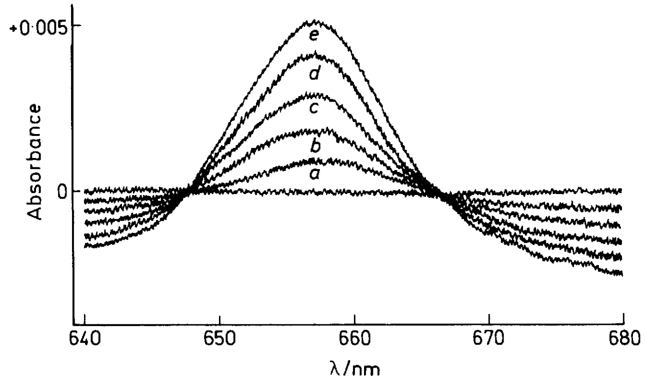

Figure 1. Difference spectrum of (7.6×10^{-7} mol dm^{-3}) [Fe(pc)] after addition of pyridine. 10^7[py]/mol dm^{-3} = 4.0 (*a*), 10 (*b*), 25 (*c*), 50 (*d*), and 100 (*e*). The last spectrum corresponds virtually to 100% [Fe(pc)(dmso)(py)]

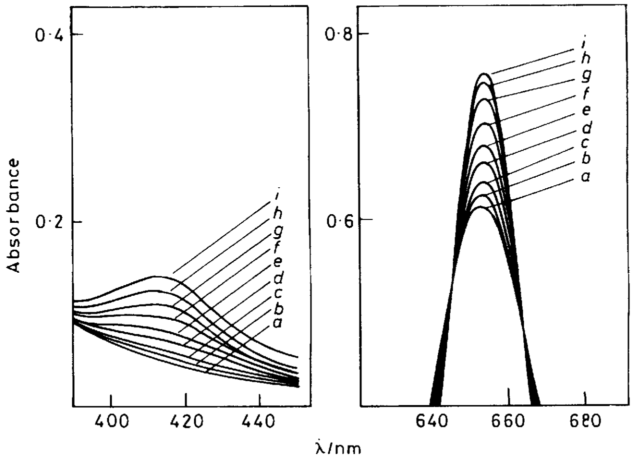

Figure 2. Spectral modifications after addition of pyridine to a 1×10^{-5} mol dm^{-3} [Fe(pc)] solution. 10^3[py]/mol dm^{-3} = 0 (*a*), 0.34 (*b*), 0.68 (*c*), 1.4 (*d*), 2.7 (*e*), 5.0 (*f*), 9.4 (*g*), 18 (*h*), and 74 (*i*). The last spectrum corresponds virtually to 100% [Fe(pc)(py)$_2$]

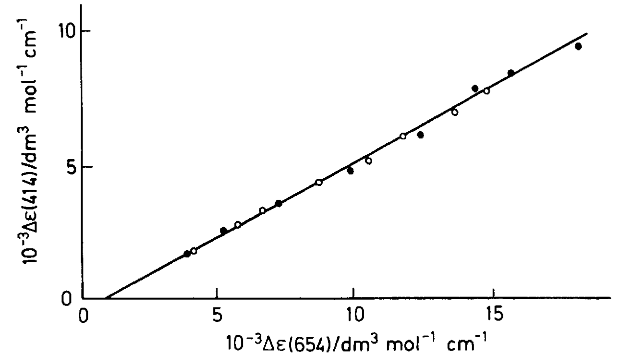

Figure 3. Linear dependence of the increase in molar absorbance at 414 nm on the increase in molar absorbance at 654 nm for [Fe(pc)] solutions [1.55×10^{-5} (○) and 1.07×10^{-5} (●) mol dm^{-3}] upon addition of pyridine up to *ca.* 0.1 mol dm^{-3}

It should be stressed that the last spectrum reported in Figure 2 [spectrum (*i*)] is that expected for a 100% conversion into [Fe(pc)(py)$_2$], as judged from the position of its maxima and the

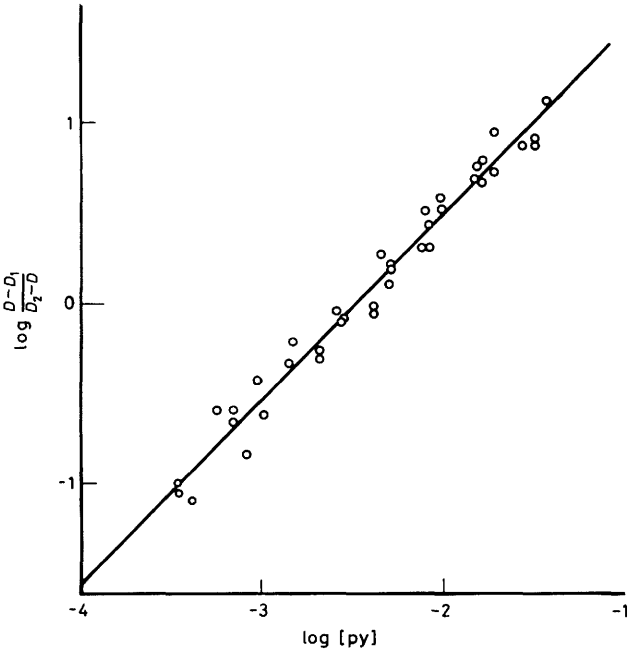

Figure 4. Plot of log $[(D - D_1)/(D_2 - D)]$ *vs.* log [py] for $1 \times 10^{-4} \leqslant$ [py] $\leqslant 0.1$ mol dm^{-3} [equilibrium (4)]

corresponding absorption coefficients[10] [$\varepsilon(654) = 1.30 \times 10^5$, $\varepsilon(414\ \text{nm}) = 2.05 \times 10^4$ dm^3 mol^{-1} cm^{-1}]. Accordingly, further addition of even pure pyridine had no effect on the spectrum, once the (small) dilution effect had been taken into account. Therefore, it can be safely concluded that the final product of the reaction monitored by the spectral changes in Figure 2 is indeed the bis(pyridine) adduct [Fe(pc)(py)$_2$]. Figure 4 shows a plot of equation (6) for a series of six independent experiments. Least-squares calculations give $n = 1.027 \pm 0.019$ and $K_1'' = 300 \pm 28$ dm^3 mol^{-1}.

Kinetic Measurements.—Attempts were made to measure the rate of binding of the first pyridine molecule in the co-ordination sphere of iron(II) [reaction (3)]. A fast process of very small amplitude * was observed at 655 nm, with half-lives of the order of 10—50 ms for $1 \times 10^{-5} \leqslant$ [py] $\leqslant 1 \times 10^{-4}$ mol dm^{-3}. Figure 5(*a*) shows a typical stopped-flow trace for this fast reaction. Due to the very small increase in absorbance, the corresponding rate constants were not reproducible to better than ±50%. Nevertheless they appear to be roughly proportional to the concentration of base. We identify this fast process with reaction (3) (forward). The available data only allow a rough estimate of the second-order rate constant ($k_{1f}' \approx 1.5 \times 10^4$ dm^3 mol^{-1} s^{-1}) and for the reverse reaction only the magnitude can be obtained from the equation $K_1' = k_{1f}'/k_{1r}'$ ($k_{1r}' \approx 4 \times 10^{-2}$ s^{-1}).

This fast reaction is followed by a second process [Figure 5(*b*)], which we assign (see below) to the axial ligation of the second pyridine [reaction (4)]. As the attainment of equilibrium (4) is much slower and takes place with a much larger change in absorbance, its rate could be measured with a higher degree of accuracy. The observed pseudo-first-order rate constants, $k_{1(\text{obs.})}''$, are plotted in Figure 6 against the pyridine concentration. The rate of the forward reaction is first order with respect to [py] with $k_{1f}'' = 35.3 \pm 0.7$ dm^3 mol^{-1} s^{-1}, whilst the rate constant for the reverse process is $k_{1r}'' = 0.15 \pm 0.02$ s^{-1}. These values yield an equilibrium constant $K_1'' = 240 \pm 40$ dm^3 mol^{-1}, in good agreement with the value measured directly (300 ± 28 dm^3 mol^{-1}, see above).

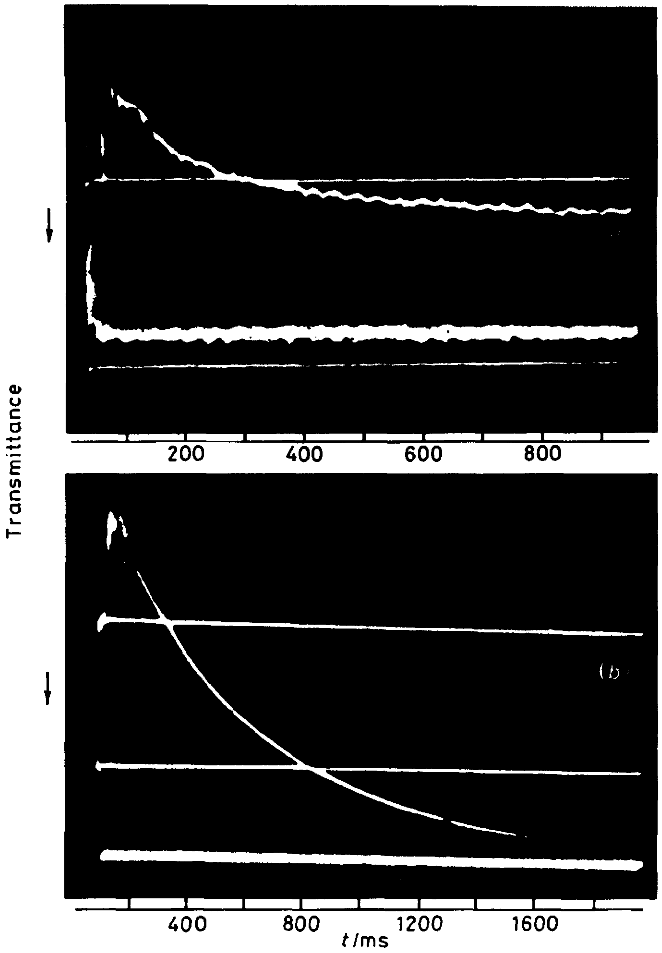

Figure 5. Stopped-flow oscillographic traces for reactions (3) and (4) mol dm^{-3} ($\lambda = 655$ nm). (*a*) Fast and slow processes {reactions (3) and (4), [py] = 4.4×10^{-4} mol dm^{-3}}; (*b*) slow process {reaction (4), [py] = 5×10^{-2} mol dm^{-3}}. At the pyridine concentration used in (*b*), process (*a*) is lost in the dead-time of the stopped-flow apparatus (3 ms). The distance between the two horizontal lines in (*a*) and (*b*) refers to the total transmittance change

Since our findings are in disagreement with data reported in the literature,[7,9] which themselves are conflicting, it seems of primary importance to discuss in detail the interpretation of the experimental facts described above. Also, we shall try to explain why quite different conclusions have been drawn from previous results on the same system.

There is no doubt that the spectrum of [Fe(pc)] in the presence of 0.1 mol dm^{-3} (or higher concentrations) of pyridine is that of [Fe(pc)(py)$_2$]. This is proven by the fact that this spectrum is superimposable upon that of a [Fe(pc)] solution of the same concentration in pure pyridine, where it would be hard to conclude that less than 100% of the bis(base) adduct is formed. It is appropriate to remember that [Fe(pc)(py)$_2$] is obtained by evaporation of a pyridine solution of [Fe(pc)],[2] or, merely, by contact of solid [Fe(pc)] with vapours of the base at room temperature.

Unless we admit that the mono- and bis-(base) adducts have exactly the same spectrum in the range 350—700 nm, the linear plot of Figure 4 refers to the gradual formation of [Fe(pc)(py)$_2$]

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* At 655 nm the amplitude of this fast process was about 10% of the total absorbance change for formation of the bis(pyridine) derivative and compared well with that obtained from static measurements (8%).

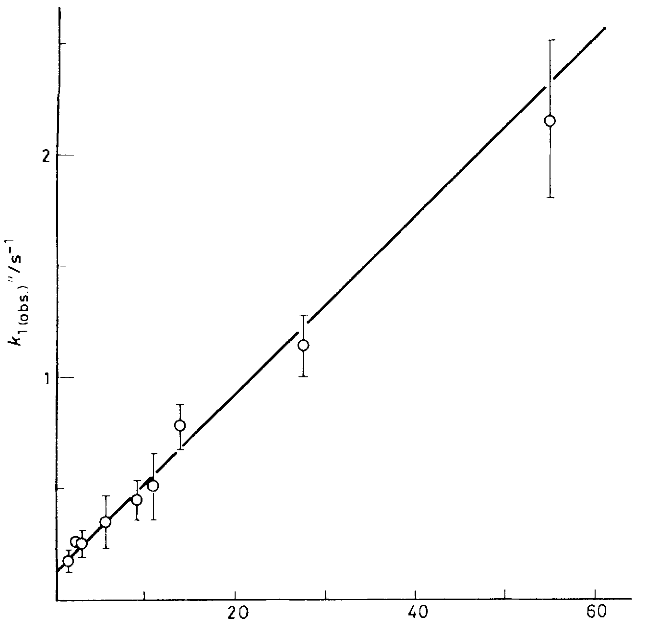

Figure 6. Observed rate constants, $k_{1(\mathrm{obs.})}''$, for the second pyridine uptake [reaction (4), forward] *versus* base concentration. Bars indicate dispersion of experimental data

and the unit value of n is consistent with the starting compound being the mono adduct [Fe(pc)(dmso)(py)]. Consequently, beyond any reasonable doubt the equilibrium constant obtained from this plot refers to reaction (4). This, in turn, implies that equilibrium (3) must be completely shifted to the right at very low pyridine concentration, and that the spectral changes due to this reaction must be looked for.

The difference spectra shown in Figure 1 and the linear plot of $1/(D - D_1)$ *vs.* 1/[py] indicate that definite (although small) spectral changes do occur in the range $0 \leqslant [\mathrm{py}] \leqslant 1 \times 10^{-5}$ mol dm^{-3} and they conform to a mass law-based equation, such as (5), with $n = 1$. Thus, the formation of [Fe(pc)(dmso)(py)] causes only a small increase of the band at 655 nm, while the Soret region is empty; further addition of base leads to the bis adduct with absorption changes at both 414 and 655 nm.

The plot of Figure 3 gives additional support to this hypothesis, since a positive intercept of the straight line with the abscissa, corresponding to the increase in ε on going from [Fe(pc)(dmso)$_2$] to [Fe(pc)(dmso)(py)] is expected and is indeed observed. This intercept should also coincide with the value of $\varepsilon_2 - \varepsilon_1$ obtained from equation (5) [equilibrium (3)]. The values (1 200 ± 200 and 700 ± 200 dm^3 mol^{-1} cm^{-1}, respectively; $\lambda = 657$ nm) are sufficiently close to allow us to conclude that they refer to the same entity.*

Of course, it is conceivable that the spectra of [Fe(pc)(dmso)(py)] and [Fe(pc)(py)$_2$] are coincident. In this case, provided that the equilibrium constant for reaction (4) were relatively small ($K_1'' < 10$ dm^3 mol^{-1}), the plot in Figure 4 would be still linear with $n = 1$ and would refer to reaction (3) rather than (4). However, aside from the difficulty of having two species with exactly the same spectrum over a relatively large wavelength range, the observations at low pyridine concentrations would remain unexplained.†

The interpretation of the kinetic results given above is consistent with the interpretation of the equilibrium results. At a suitably chosen pyridine concentration, the oscillographic profiles of the stopped-flow experiments show a fast process, followed by a second, relatively slow, reaction (Figure 5). Both stages result in an increase in absorbance, but the first reaction is associated with a much smaller change, as expected for equilibrium (3) on the basis of the static changes shown in Figure 1. Furthermore, excellent agreement is found between K_1'' and the ratio k_{1f}''/k_{1r}''.

The stepwise addition of pyridine to [Fe(pc)] in dmso has been studied by Jones and Twigg[7] whose conclusions differ from ours. These authors analysed the increase in absorbance by an iterative method where the absorption coefficient of the mono adduct, [Fe(pc)(dmso)(py)], was unknown. The procedure, based on a minimization of the differences between calculated and experimental absorbances, was believed to converge towards the 'true' ε value and yield, simultaneously, correct values for K_1' and K_1''. The values given in ref. 7 are: ε{[Fe(pc)(dmso)(py)]} = 2.8×10^4 dm^3 mol^{-1} cm^{-1}, $K_1' = 100$ and $K_1'' = 2.5$ dm^3 mol^{-1}, in total disagreement with our results. The computing procedure used by Jones and Twigg would be indeed applicable to systems such as the present one, provided that the difference between ε values of [Fe(pc)(dmso)(py)] and of both [Fe(pc)(dmso)$_2$] and [Fe(pc)(py)$_2$] were definitely outside the experimental error and/or the two equilibria significantly overlapped. If ε{[Fe(pc)(dmso)(py)]} ≈ ε{[Fe(pc)(py)$_2$]} (and $K_1' \gg K_1''$, as appears to be the case) the first step may well remain unrecognized. Of course, best-fit values for ε{[Fe(pc)(dmso)(py)]}, K_1' and K_1'' will be obtained; nevertheless, their significance is doubtful. In this respect it is appropriate to note that if the values of K_1', K_1'', ε{[Fe(pc)(dmso)$_2$]}, ε{[Fe(pc)(dmso)(py)]}, and ε{[Fe(pc)(py)$_2$]} quoted in ref. 7 are used to calculate the absorbance of a [Fe(pc)] solution in increasing concentrations of base, a curve with a maximum at [py] ≈ 0.1 mol dm^{-3} is obtained since the absorption coefficients reported in that reference are in the order [Fe(pc)(dmso)(py)] > [Fe(pc)(py)$_2$] > [Fe(pc)(dmso)$_2$]. The value of D at the maximum is *ca.* 15% higher than the limiting value for 100% [Fe(pc)(py)$_2$] as obtained in pure pyridine. Not only did we never observe this trend, but even in ref. 7 it is mentioned that the absorbance does not change significantly on going from 0.1 mol dm^{-3} to pure pyridine.

The system [Fe(pc)]–py–dmso has been also investigated by Kadish *et al.*[9] These authors reported the results of spectrophotometric titrations of [Fe(pc)] with py, given as a logarithmic plot of the type shown here in Figure 4. The experimental conditions were very similar to ours but, surprisingly, they find a linear plot with $n = 2$. It is not clear to us whether this result was obtained *only* in the presence of tetraethylammonium perchlorate, used as supporting electrolyte for electrochemical experiments, but it would be surprising if the presence of this salt were responsible for the $n = 2$ result; *i.e.* for $K_1'' \gg K_1'$. We have no explanation for this result which is also in contrast with those of Jones and Twigg.[7] We may only observe that the pyridine concentration range used by Kadish *et al.* is very narrow (less than a factor of 2.5, whilst the present study covers a total range of more than a factor of 100), this being very likely the reason for their incorrect estimate of the slope. The value of log [py] at zero ordinate is close to our

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* Small systematic errors, *e.g.* in the wavelength, and the use of an unweighted least-squares procedure may be responsible for the difference between these two values, obtained in different experiments and under somewhat different conditions.

† We may also anticipate that the results of the carbonylation study in the presence of pyridine[11] are in agreement with the mono adduct [Fe(pc)(dmso)(py)] being predominant over both [Fe(pc)(dmso)$_2$] and the bis adduct [Fe(pc)(py)$_2$] at [py] ≈ 1×10^{-4} mol dm^{-3}.

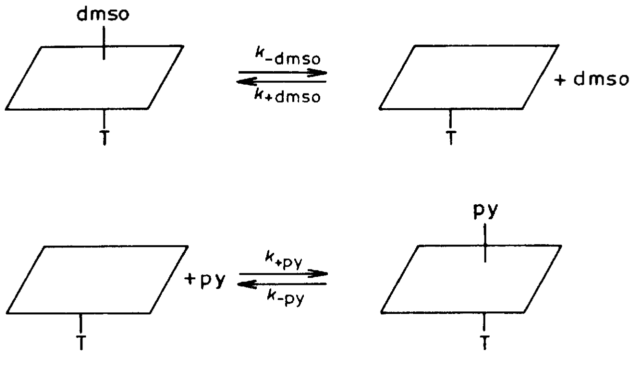
corresponding value (−2.25 against −2.48); this means [see equation (6)] that the discrepancy comes essentially from the slope of the binding curve (*i.e.* from the *n* value).

Conclusions

The axial substitution of dmso molecules by pyridine in $[Fe(pc)(dmso)_2]$ appears to follow a simple stepwise mechanism. Ligation of the first pyridine is both much faster and thermodynamically easier than the uptake of the second base to give $[Fe(pc)(py)_2]$. Since the equilibrium constants of reactions (3) and (4) differ by a factor of 10^3, the substitution of the second dmso is disfavoured by *ca.* 4 kcal mol^{-1} (*ca.* 16.7 kJ mol^{-1}). If solvation effects are ignored, this may be due to a greater Fe–dmso bond energy in [Fe(pc)(dmso)(py)] with respect to $[Fe(pc)(dmso)_2]$ and/or to a smaller Fe–py bond energy in $[Fe(pc)(py)_2]$ with respect to [Fe(pc)(dmso)(py)]. It is known that dmso is bonded *via* sulphur to iron in $[Fe(pc)(dmso)_2]$[12] and very likely in mixed complexes. Hence, it is expected to behave as a π-acceptor ligand thus gaining some extra stability *via* π-back bonding, as observed with other π acceptors such as phosphines and nitriles.[13–15] This extra stability should be largely lost when two dmso molecules are competing for the same electron cloud from opposite axial sites, as occurs in $[Fe(pc)(dmso)_2]$. We believe that the values of K_1' and K_1'' reflect essentially the extra stability gained by dmso through π-back bonding in [Fe(pc)(dmso)(py)] with respect to $[Fe(pc)(dmso)_2]$.

It is currently accepted that the mechanism of axial-substitution reactions of haem-like molecules, such as porphyrin and phthalocyanine derivatives, is dissociative with formation of a five-co-ordinate intermediate.[1,12–14,16] The latter is assumed to be so reactive to be unable to discriminate efficiently between different incoming nucleophiles.[1,14] Some of our results[11] seem to justify some caution on this point; nevertheless, it is still true that the discrimination is not very large. Thus, if a dissociative mechanism with a weakly-selective intermediate is assumed to operate in the system under study, axial binding may be thought to proceed according to the reversible path in the Scheme (T = *trans* dmso or py). Hence, $k_{1f}' = k_{-dmso}'k_{+py}'/k_{+dmso}'[dmso]$ and $k_{1f}'' = k_{-dmso}''k_{+py}''/k_{+dmso}''[dmso]$ whilst $k_{1r}' = k_{-py}'$ and $k_{1r}'' = k_{-py}''$. Moreover, if $k_{+py}' \approx k_{+dmso}'$ and $k_{+py}'' \approx k_{+dmso}''$, as required if the five-co-ordinate intermediate is scarcely selective, $k_{-dmso}' \approx 14\,k_{1f}'$ and $k_{-dmso}'' \approx 14\,k_{1f}''$ ([dmso] = 14 mol dm^{-3}). Consequently, each of the four rate constants obtained in this work is a more or less direct measure of the ease of dissociation of the pertinent bond between Fe and the leaving ligand. The lability sequence appears to be [(dmso)Fe(pc)(dmso)] > [(py)Fe(pc)(dmso)] ⩾ [(py)Fe(pc)(py)] ≈ [(dmso)Fe(pc)(py)] (the right-hand ligand is the leaving ligand), which seems to reflect essentially the σ-donor properties of the leaving ligand.

Despite the number of kinetic studies of axial substitution on [Fe(pc)], there are few data for comparison with ours. In fact the rate constant is reported in other solvents, only for the release of pyridine from $[Fe(pc)(py)_2]$, *i.e.* in acetone[14] (0.8 s^{-1}) and toluene[17] (0.12 s^{-1}). Both values are close to ours (0.15 s^{-1}), suggesting a minor rôle for the solvent in the dissociation step, at least when aprotic solvents are concerned.



Scheme.

References

1 L. J. Boucher, in 'Coordination Chemistry of Macrocyclic Compounds,' ed. G. A. Nelson, Plenum Press, New York, 1979, p. 481.
2 F. H. Moser and A. L. Thomas, 'The Phthalocyanines,' CRC Press, Boca Raton, 1983, vol. 1, pp. 8 and 36—38.
3 C. Ercolani, G. Rossi, F. Monacelli, and M. Verzino, *Inorg. Chim. Acta*, 1983, **73**, 95.
4 C. Ercolani, F. Monacelli, G. Pennesi, G. Rossi, E. Antonini, P. Ascenzi, and M. Brunori, *J. Chem. Soc., Dalton Trans.*, 1981, 1120.
5 J. G. Jones and M. V. Twigg, *Inorg. Chem.*, 1968, **8**, 2120.
6 H. P. Bennetto, J. G. Jones, and M. V. Twigg, *Inorg. Chim. Acta*, 1970, **4**, 180.
7 J. G. Jones and M. V. Twigg, *Inorg. Chim. Acta*, 1974, **10**, 103.
8 J. G. Jones and M. V. Twigg, *J. Chem. Soc., Dalton Trans.*, 1978, 1709.
9 K. M. Kadish, L. A. Bottomley, and J. S. Chang, *J. Am. Chem. Soc.*, 1978, **100**, 2731.
10 B. W. Dale, *Trans. Faraday Soc.*, 1969, **65**, 331.
11 G. Pennesi, C. Ercolani, G. Rossi, P. Ascenzi, M. Brunori, and F. Monacelli, following paper.
12 F. Calderazzo, G. Pampaloni, D. Vitali, I. Collamati, G. Dessy, and V. Fares, *J. Chem. Soc., Dalton Trans.*, 1980, 1965.
13 D. A. Sweigart, *J. Chem. Soc., Dalton Trans.*, 1976, 1476.
14 D. V. Stynes, *Inorg. Chem.*, 1977, **16**, 1170.
15 F. Pomposo, D. Carruthers, and D. V. Stynes, *Inorg. Chem.*, 1982, **21**, 4245.
16 J. Martinsen, M. Miller, D. Trojan, and D. A. Sweigart, *Inorg. Chem.*, 1980, **19**, 2162.
17 D. V. Stynes and B. R. James, *J. Am. Chem. Soc.*, 1974, **96**, 2733.

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