Equilibrium and Kinetic Study of the Reaction between Phthalocyaninatoiron(II) and Carbon Monoxide in Dimethyl Sulphoxide in the Presence of Pyridine. Evidence for the Formation of a Transient†

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The equilibrium and the rate constants for axial substitution of [Fe(pc)(dmso)X] [pc = phthalocyaninate, dmso = dimethyl sulphoxide, X = pyridine (py) or carbon monoxide] by CO and py, respectively, have been measured at 20 ± 0.5 °C in dmso as solvent. These data confirm the low stability and the high lability of the metal–dmso bond. Also metal-to-dmso π-back bonding seems to operate. Solvent effects are of minor importance. The rate data suggest that the five-co-ordinate intermediate of the dissociative substitution process discriminates to a limited degree between the incoming nucleophiles. Evidence for the formation of a long-lived transient containing two pyridine and one carbon monoxide molecule is given and discussed.

Dynamic and thermodynamic studies on a number of adducts of formula [Fe(pc)X(Y)] (pc = phthalocyaninate, X and Y = axial ligands such as heterocyclic N-bases, carbon monoxide, or isocyanides) have been mainly directed towards the effect of the porphyrin-like macrocycle (*cis* effect)[1,2] and of the axial ligands (*trans* effect)[1–5] with the aim of achieving a better understanding of the structural and electronic factors which influence the mechanism of action of haem-containing proteins. In the latter, both the porphyrin ring and an axial nitrogenous ligand (usually a histidine moiety) *trans* to the reactive site seem to be essential in determining their unique properties.

Some of the work on [Fe(pc)X(Y)] complexes has been carried out in non-co-ordinating solvents such as toluene[1,3–5] and acetone[2] and part in the weakly co-ordinating dimethyl sulphoxide (dmso).[6–9] Recently, we reported a study[10] on the exchange of dmso by CO on [Fe(pc)(dmso)$_2$] in dmso solution. This reaction is clean and reversible with a 1:1 [Fe(pc)]:CO stoicheiometry, and may be used conveniently to measure the *trans*-labilizing effect of a N-base B on the leaving dmso molecule as well as on the leaving CO in mixed complexes of formula [Fe(pc)(B)X] (X = dmso or CO). This study, besides extending to a co-ordinating medium the information on the solvent effect, provides a further insight into the mechanism of the *trans* effect. With this in mind, we planned to investigate the carbonylation reaction of [Fe(pc)] in the presence of several N-bases in dmso. In this paper we report the results obtained with B = pyridine. Preliminary knowledge was required of the equilibrium and kinetics of adduct formation between [Fe(pc)] and N-bases, and a re-examination of previously published material appeared to be necessary, see the preceding paper.[11]

Unexpectedly, during this research we found evidence for the formation of a long-lived transient containing two pyridine molecules and one carbon monoxide molecule per Fe(pc) unit (seven-co-ordinate Fe^{II}?). Some preliminary data concerning this species are given.

Experimental

The purification of [Fe(pc)], dmso, and pyridine is described elsewhere.[10,11] Carbon monoxide was a high-purity gas.[10]

Equilibrium Measurements.—The experiments for the measurement of equilibrium constants in dmso were carried out either by adding CO to solutions of [Fe(pc)] containing known amounts of pyridine, or by adding pyridine to solutions of [Fe(pc)] exposed to a constant CO pressure (1 atm). The concentration of [Fe(pc)] was generally in the range (0.1—3) × 10^{-5} mol dm^{-3}. At this level the reaction of [Fe(pc)] with dioxygen[12] is sufficiently slow to allow handling of the solutions without special precautions. The 1-cm cell used in the experiments was sealed to a glass vessel (*ca.* 250 cm^3) provided with a stopcock for connection to a vacuum line and an outlet closed with a serum cap, through which gaseous CO or a suitably concentrated dmso solution of pyridine could be added by means of precision syringes. After each reagent addition, the system was allowed to reach equilibrium, in a thermostat bath at 20 ± 0.5 °C, with shaking, for 5 min. Spectra were recorded at 20 ± 0.5 °C on either a Cary 219 or a Perkin-Elmer 330 instrument and analysed, as described later, in order to obtain equilibrium constants.

Kinetic Measurements.—Kinetic experiments were carried out by using both stopped-flow and flash-photolysis techniques. In the stopped-flow experiments one of the reservoirs was filled with a solution of [Fe(pc)] (*ca.* 1 × 10^{-5} mol dm^{-3}) containing a known amount of pyridine (variable). The other reservoir was filled with a dmso solution equilibrated with a known pressure of CO and a concentration of pyridine equal to that in the first reservoir. The concentration of CO was assumed to be proportional to the pressure ([CO] = 1.1 × 10^{-3} mol dm^{-3} under 1 atm of CO[10]). Care was taken to avoid loss of gas from the solution during handling. Measurements were carried out at 660 nm; the temperature was controlled at 20 ± 0.5 °C. Since CO bound to [Fe(pc)] is readily photolysed[10] with a very high quantum yield, some photodissociation was even determined by the monitoring light beam of the stopped-flow apparatus. Hence, the experiments were carried out at variable slit widths and the results extrapolated to zero width. Flash-photolysis experiments were carried out using an apparatus which has been previously described.[13] The kinetics of recombination after photolysis were followed at 660 nm. Photolysis caused by the monitoring light was taken into account and appropriate

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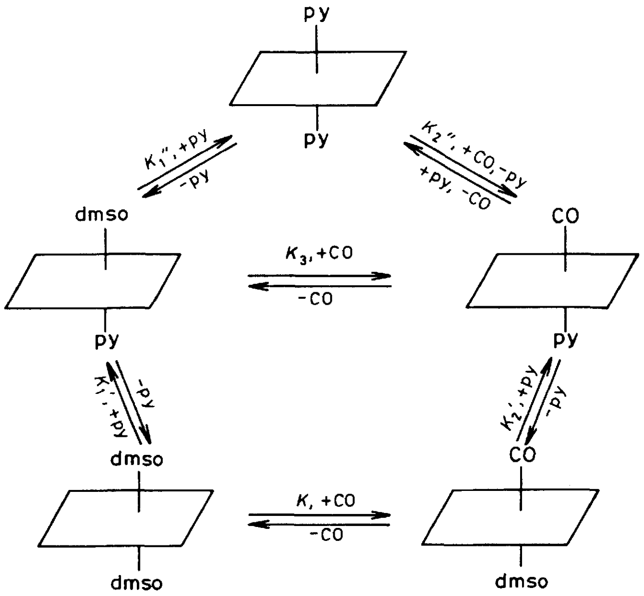
† *Non-S.I. unit employed:* atm = 101 325 Pa.

corrections applied.[10] (The magnitude of the correction used, to allow for photodissociation of the complex by the monitoring light of both fast kinetic apparatuses, was about 40%.)

In both stopped-flow and flash-photolysis experiments pseudo-first-order conditions were always applied and, consequently, only first-order reactions observed.

Results and Discussion

Equilibrium Measurements.—When both CO and pyridine are added to a solution of [Fe(pc)] in dmso, the equilibria in the Scheme are expected to be established. Expressions (1′)—(4) can then be written, where K, K_1', and K_1'' are known, being determined directly.[10,11]



Scheme. Only the axial ligands are shown for each metal complex

$$K_1' = [(\mathrm{dmso,py})]/[(\mathrm{dmso,dmso})][\mathrm{py}] \qquad (1')$$

$$K_1'' = [(\mathrm{py,py})]/[(\mathrm{dmso,py})][\mathrm{py}] \qquad (1'')$$

$$K_2' = [(\mathrm{py,CO})]/[(\mathrm{dmso,CO})][\mathrm{py}] \qquad (2')$$

$$K_2'' = [(\mathrm{py,py})][\mathrm{CO}]/[(\mathrm{py,CO})][\mathrm{py}] \qquad (2'')$$

$$K_3 = [(\mathrm{py,CO})]/[(\mathrm{dmso,py})][\mathrm{CO}] \qquad (3)$$

$$K = [(\mathrm{dmso,CO})]/[(\mathrm{dmso,dmso})][\mathrm{CO}] \qquad (4)$$

Constant K_3. Only four of the six equilibria shown in the Scheme are independent and sufficient to describe completely the [Fe(pc)]–CO–py system. Elementary mass law-based considerations indicate that if CO is added to a solution of [Fe(pc)] in dmso at *constant* pyridine concentration the set of compounds with axial ligands (dmso,dmso), (dmso,py), and (py,py) on one hand, and (dmso,CO) and (py,CO) on the other, behave with respect to the carbonylation reaction as if they were two pure species, related to each other as in equation (5). It

$$\frac{[(\mathrm{dmso,CO})] + [(\mathrm{py,CO})]}{[(\mathrm{dmso,dmso})] + [(\mathrm{dmso,py})] + [(\mathrm{py,py})]} = K_{3(\mathrm{app})}[\mathrm{CO}] \qquad (5)$$

can be shown that $K_{3(\mathrm{app})}$ can be expressed in terms of the already known equilibrium constants K, K_1', and K_1'' and K_3 as in equation (6). Moreover, the changes in absorbance, D, upon

$$K_{3(\mathrm{app})} = \frac{K + K_1'K_3[\mathrm{py}]}{1 + K_1'[\mathrm{py}] + K_1'K_1''[\mathrm{py}]^2} \qquad (6)$$

addition of CO also conform to the simple mass law-based equation (7) (D_1 and D_2 are the absorbances before addition of

$$\frac{1}{D - D_1} = \frac{1}{K_{3(\mathrm{app})}(D_2 - D_1)} \cdot \frac{1}{[\mathrm{CO}]} + \frac{1}{D_2 - D_1} \qquad (7)$$

CO and upon complete carbonylation, respectively). Thus $K_{3(\mathrm{app})}$ can be determined experimentally from optical data and insertion of $K_{3(\mathrm{app})}$ into equation (6) allows the equilibrium constant K_3 to be obtained.

Experiments were carried out by gradually adding CO to solutions of [Fe(pc)] containing a known concentration of pyridine in the range 1×10^{-4}—6×10^{-3} mol dm^{-3}. Relatively large spectral changes were observed essentially in correspondence with the most intense visible absorption centred at 655 nm, which shifts to 661 nm increasing in absorption coefficient by a factor of *ca.* 1.6. Minor changes are observed in the range explored (350—700 nm).

The optical data were treated according to equation (7). Excellent linear plots of $1/(D - D_1)$ *vs.* $1/[\mathrm{CO}]$ were obtained at any given pyridine concentration and the $K_{3(\mathrm{app})}$ values were calculated from the ratios of the intercept and slope of each plot. A best-fit procedure was used for the calculation of K_3 from equation (6). The result is shown in Figure 1: the best fit of calculated to experimental values of $K_{3(\mathrm{app})}$ is obtained for $K_3 = (6.5 \pm 0.5) \times 10^3$ dm^3 mol^{-1}.

The value of K_3, together with the known values of K, K_1', and K_1'', can be used to calculate both K_2'' and K_2' from the expressions $K_2'' = K_1''/K_3 = 4.6 \times 10^{-2}$ and $K_2' = K_1'K_3/K = 1.9 \times 10^5$ dm^3 mol^{-1}.

Constant K_2'. According to the value of K (1.4×10^4 dm^3 mol^{-1}),[10] under 1 atm of CO pressure ([CO] = 1.1×10^{-3} mol dm^{-3})[10] more than 90% of [Fe(pc)] is in the form of the monocarbonyl adduct (axial ligands dmso,CO). Stepwise addition of pyridine to such a solution {2.4×10^{-6} mol dm^{-3} [Fe(pc)]} results in a small, albeit definite and reproducible, change in intensity of the band at 661 nm (increase of *ca.* 3%). At concentrations of pyridine higher than 1×10^{-5} mol dm^{-3} (limit 6.2×10^{-5} mol dm^{-3}) the spectrum does not show any further changes, thus indicating the attainment of a plateau (Figure 2). The optical data from several independent experiments, when analysed according to equation (8)[11] (D_1 and D_2 are the

$$\log[(D - D_1)/(D_2 - D)] = \log K_a + n \log[\mathrm{py}] \qquad (8)$$

absorbances before addition of py and at the plateau, respectively), yield a linear plot. Least-squares analysis of the plot gives $n = 0.97 \pm 0.03$ and $K_a = (2.6 \pm 0.9) \times 10^5$ dm^3 mol^{-1} (see below). The value of $n = 1$ (within the error limits) indicates that the reaction leads essentially to the formation of complexes with axial ligands (py,CO) from (dmso,CO), which is conclusively supported by the following additional facts: (*a*) on pumping off of the gaseous phase, the spectrum changes to that of (dmso,py); (*b*) further addition of pyridine (highest limit 0.5 mol dm^{-3}) causes the spectrum to change remarkably (*ca.* 15% decrease at 661 nm with an associated shift to 656 nm and appearance of a band in the Soret region, centred at 414 nm, band B of ref. 14) the final spectrum, attained in almost 2 d at room temperature or after a few seconds of exposure to intense light (see below), being superimposable upon that of the (py,py) complex.

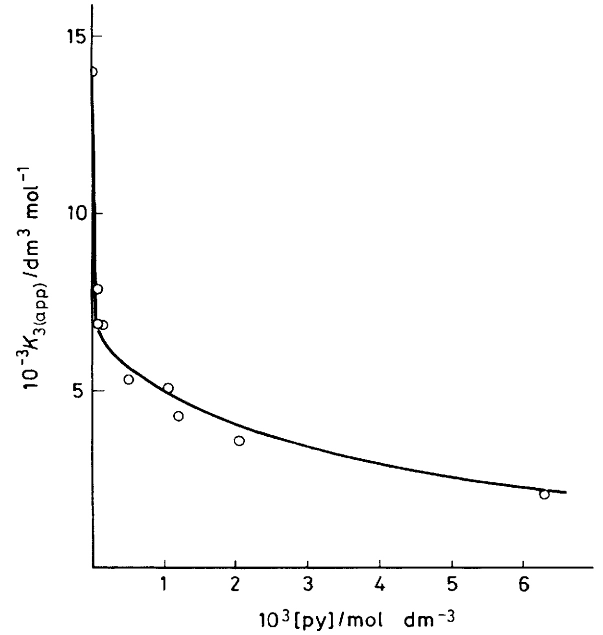


Figure 1. Calculated (line) and experimental values of $K_{3(\text{app})}$. The line was calculated according to equation (6) with $K_3 = 6.5 \times 10^3$ dm^3 mol^{-1}

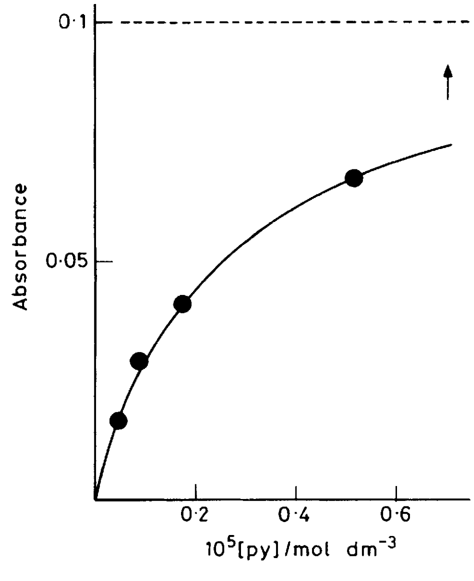


Figure 2. Plot of the difference in absorbance at 661 nm of a 2.4×10^{-6} mol dm^{-3} [Fe(pc)] solution containing 1.1×10^{-3} mol dm^{-3} CO upon addition of pyridine. The arrow points to the plateau (dashed line)

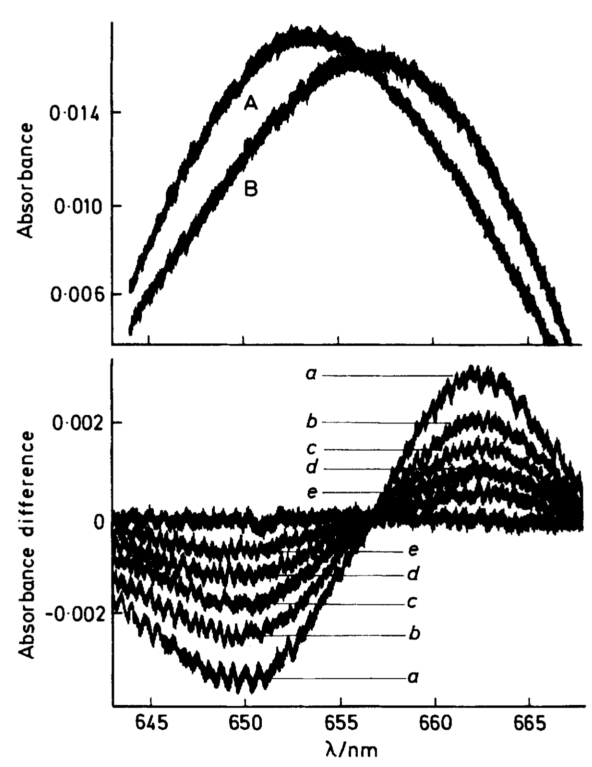


Figure 3. Upper: spectra of solutions A and B (see text) relative to a dmso reference, showing the small but significant change in $\lambda_{\text{max.}}$. Lower: difference spectra of solution B against A as a function of time, t = 0 (*a*), 2 (*b*), 4 (*c*), 6 (*d*), and 8 h (*e*)

Although mainly related to the conversion of the complex (dmso,CO) into (py,CO), the apparent equilibrium constant K_a may not coincide with K_2', since $p_{CO} = 1$ atm does not ensure complete carbonylation of both (dmso,py) and (dmso,dmso). Owing to the very low values of [py] the bis(pyridine) adduct (py,py) is practically absent and only equilibria (1′), (2′), (3), and (4) (Scheme) need to be considered. Again, it is easy to demonstrate that at a constant carbon monoxide concentration the mass-law relationship (9) holds with $K_a = K_2'K(1 +$

$$\{[(\text{dmso,py})] + [(\text{py,CO})]\}/\{[(\text{dmso,dmso})] + [(\text{dmso,CO})]\} = K_a[\text{py}] \quad (9)$$

$K_3[\text{CO}])/(1 + K[\text{CO}])K_3$. Substitution of the appropriate values gives $K_2' = (2.4 \pm 0.8) \times 10^5$ dm^3 mol^{-1}, which compares well with the value calculated above (1.9×10^5 dm^3 mol^{-1}) and is not significantly different from K_a.

Attempts to measure K_2'': *the formation of an unknown intermediate.* When further pyridine is added to a solution containing essentially the species (CO,py) {*i.e.* [Fe(pc)] $\approx 1 \times 10^{-5}$, [CO] $= 1.1 \times 10^{-3}$, and [py] $\approx 1 \times 10^{-4}$ mol dm^{-3}} the band at 661 nm decreases in intensity, also slightly shifting (to 656 nm) and the band at 414 nm increases. The increase in D at 414 nm is strictly proportional to the corresponding decrease in absorbance at any wavelength about 661 nm, with the final spectrum closely resembling that of the (py,py) complex. Again, it can be readily shown that for the simultaneous equilibria (1″), (2″), and (3) (Scheme) {both (dmso,dmso) and (dmso,CO) species may be ignored for [py] $\geqslant 10^{-4}$ mol dm^{-3}} at constant CO concentration the mass-law equation (10) holds with $K_a =$

$$[(\text{py,py})]/\{[(\text{py,CO})] + [(\text{dmso,py})]\} = K_a[\text{py}] \quad (10)$$

$K_2''K_1''/(K_2'' + K_1''[\text{CO}])$. Hence, the spectral changes, observed at either 661 or 414 nm, when analysed according to equation (8), were expected to yield a linear plot with unit slope and log K_a as the intercept. Indeed, linear plots with $n = 1.1 \pm 0.05$ were observed for several independent experiments. However, a K_a value of $(5.1 \pm 0.3) \times 10^2$ dm^3 mol^{-1} was obtained, totally inconsistent with K_1'' and K_2''; equation (10) would, in fact, predict a K_a value *ca.* 14 times lower (37 dm^3 mol^{-1}).

This striking inconsistency for a long time resisted any critical revision of the experimental procedure adopted. Finally, it was realized that, after addition of a large excess of pyridine to a CO-containing [Fe(pc)] solution, the measured spectrum, albeit

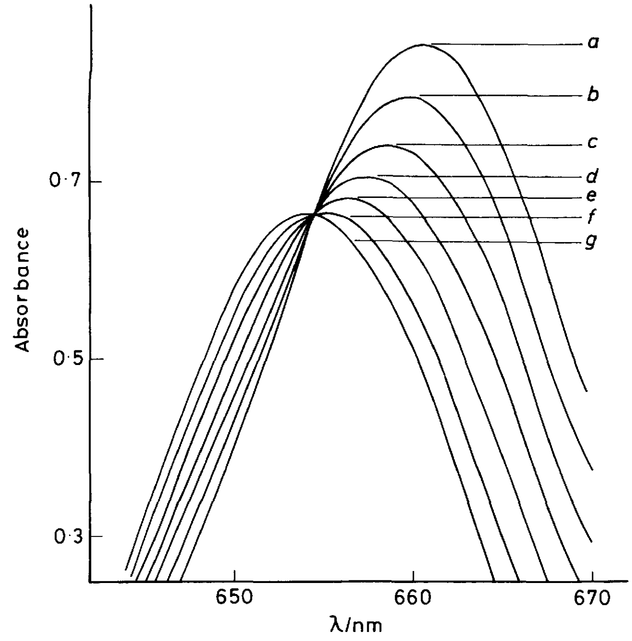


Figure 4. Spectral changes of a 1 × 10^{-5} mol dm^{-3} [Fe(pc)] solution containing 1.1 × 10^{-3} mol dm^{-3} carbon monoxide and 1.0 × 10^{-4} mol dm^{-3} pyridine, upon addition of more pyridine and irradiation (see text). 10^3[py] = 0.1 (*a*), 5.0 (*b*), 12.4 (*c*), 25.0 (*d*), 49.0 (*e*), 96.2 (*f*), and 404.0 mol dm^{-3} (*g*)

Table 1. Observed rate constant (flash photolysis) for the carbonylation of [Fe(pc)] in the presence of 1 × 10^{-4} mol dm^{-3} pyridine

10^4[CO]/mol dm^{-3}	0.53	1.6	3.2	5.3	8.5	11.0
$k_{obs.}$*/s^{-1}	0.26	0.24	0.40	0.56	0.83	1.25

* Corrected for photostationary dissociation induced by monitoring light.

Table 2. Observed rate constants (stopped flow) for the carbonylation of [Fe(pc)] in the presence of pyridine

10^4[CO]	10^4[py]	$k_{obs.}/s^{-1}$	
mol dm^{-3}		*a*	*b*
5.5	10	0.48 (3)	
	5.0	0.46 (8)	
	3.1	0.50 (2)	
	2.5	0.47 (5)	
	1.1	0.60 (9)	0.51
4.2	5.0	0.49 (1)	
	1.1	0.62 (3)	0.59
3.2	5.0	0.43 (2)	
	1.1	0.58 (4)	0.53
2.8	10	0.35 (3)	
	5.0	0.49 (3)	
	3.1	0.37 (1)	
	2.5	0.40 (2)	
	1.0	0.38 (6)	0.40
1.5	5.0	0.40 (3)	
	3.1	0.27 (1)	0.38
1.3	1.0	0.22 (3)	0.22
0.7	10	0.23 (2)	
	5.2	0.22 (1)	
	2.5	0.25 (3)	0.23

[a] Average values from independent experiments, the number of which is given in parentheses. [b] Average over all the runs at the same CO concentration.

very close to that of the bis(pyridine) derivative, was not *exactly* coincident with it. This observation was nicely confirmed by the following procedure. Two identical reaction vessels of the type described in the Experimental section were filled with equal volumes (3.00 cm^3) of the same [Fe(pc)] solution (*ca.* 8.0 × 10^{-6} mol dm^{-3}). An oil-pump vacuum was generated in both vessels. In one of them (solution A), normal pressure was restored by means of pure nitrogen and 80 μl of pure pyridine were added. In the other vessel (solution B) pure CO (up to 1 atm) and, afterwards, 80 μl of pure pyridine were introduced. The concentration of base (0.33 mol dm^{-3}) was sufficient to convert 99% of the iron complex of solution A into the bis(pyridine) derivative. The spectra of both solutions were recorded, against dmso, after equilibration for 5 min at 20 °C. Large wavelength scale expansion (1 nm cm^{-1}) was used in order to reveal minor differences in the spectra (range explored 645—665 nm). Other instrumental operating conditions are given in the caption to Figure 3, where the spectra are shown. There is no doubt that a definite, albeit small, difference in energy exists between the bands of solutions A and B [Figure 3]. When solution A is used as the reference the difference spectrum of Figure 3 [spectrum (*a*)] is obtained. This behaviour is independent of the [Fe(pc)] concentration within the range 7 × 10^{-5}—7 × 10^{-6} mol dm^{-3}. That the difference spectrum between solutions A and B is due to a new, thermodynamically unstable species is demonstrated by the fact that the observed difference tends to disappear over a period of *ca.* 2 d [Figure 3]. This is a kinetically well defined first-order process with an observed rate constant $k_{obs.}$ = (4.7 ± 0.3) × 10^{-5} s^{-1}. Consistently, if the sequence of addition of CO and py to solution B is reversed (*i.e.* 1 atm of CO is employed *after* addition of pyridine), no difference spectrum whatever develops, *i.e.* solutions A and B are spectrophotometrically indistinguishable. Furthermore, the difference spectrum may be caused to collapse immediately to a horizontal line in two ways: (*a*) by pumping off CO from solution B or, (*b*) by exposing the solution for a few seconds to an intense (300 W) source of light. We stress here that the described behaviour, although having no obvious explanation and concerning minor spectral details, was systematic and strictly reproducible in that no dependence was observed on variables such as the operator, the type of instrument, the source of the materials, *etc.*

On the basis of the above observations it can be concluded that addition of pyridine to a solution containing essentially the complex (CO,py) leads to the formation of an unstable intermediate, very likely containing two pyridine molecules and one CO molecule (seven-co-ordinate?). Obviously, the apparent equilibrium constant K_a measured under these conditions (5.1 × 10^2 dm^3 mol^{-1}) has nothing to do with K_2''. Nevertheless, taking advantage of the photosensitivity of the unstable intermediate, K_2'' could be determined as follows. Under experimental conditions in which mainly the complex (py,CO) is formed {*i.e.* [Fe(pc)] ≈ 1 × 10^{-5}, [CO] = 1.1 × 10^{-3}, and [py] ≈ 1 × 10^{-4} mol dm^{-3}}, at 20 ± 0.5 °C, further pyridine was added portion-wise so as to cover the concentration range 0.5 × 10^{-2}—0.40 mol dm^{-3} and the spectra (644—670 nm) taken after systematic exposure for 1 min to intense light followed by a 5-min equilibration at 20 °C. By using an appropriate scale expansion the series of spectra shown in Figure 4 was obtained with a well defined isosbestic point at 654.5 nm. The last spectrum with the maximum at 654 nm is coincident with that of the (py,py) complex.[11] When the optical data are analysed according to equation (8), the slope of the

Table 3. Equilibrium and kinetic constants for reaction (11) (20 °C, solvent dmso except when otherwise stated)

T	X	Y	K^a	k_f/dm^3 mol^{-1} s^{-1}	k_r/s^{-1}	Ref.
dmso	dmso	CO	2.0×10^5	1.3×10^3	0.12	10
dmso	dmso	py	5.6×10^6	$\approx 1.5 \times 10^4$	$\approx 4 \times 10^{-2}$	11
py	dmso	CO	9.1×10^4	8.8×10^2	0.16	This work
py	dmso	py	4.2×10^3	35	0.15	11
CO	dmso	py	2.7×10^6			This work
py	CO	py	4.6×10^{-2}			This work
py	CO	py	21^b		0.12^b	2
py	py	CO			0.09^b	2

[a] For the sake of comparison, when X = dmso the equilibrium constants reported in the text have been multiplied by [dmso] = 14 mol dm^{-3}. [b] Toluene as solvent; 23 °C.

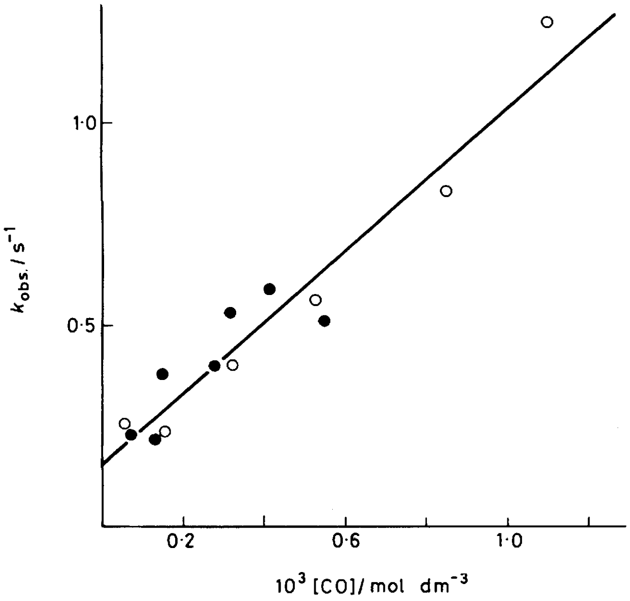


Figure 5. Pseudo-first-order observed rate constants, $k_{obs.}$, for CO uptake by a 1×10^{-5} mol dm^{-3} [Fe(pc)] solution in the presence of 1×10^{-4} mol dm^{-3} pyridine as a function of carbon monoxide concentration. (○) Flash-photolysis experiments; (●) stopped-flow experiments

linear plot is 1.00 ± 0.05 and the intercept yields K_a = 39.0 ± 2.0 dm^3 mol^{-1}, a value comfortably close to that calculated by means of equation (10) and consistent with the indirect estimate of K_2'' (see above).

Experimental work is being carried out to throw more light on the nature and structure of this unusual (seven-co-ordinate?) transient.

Kinetic Measurements.—The kinetics of CO uptake by the (dmso,py) complex have been studied by means of both flash-photolysis and stopped-flow techniques. In the former experiments a solution of [Fe(pc)] (*ca.* 1×10^{-5} mol dm^{-3}) containing pyridine (1×10^{-4} mol dm^{-3}) was equilibrated at 20 °C with a known concentration of carbon monoxide. The photoinduced dissociation of the carbonyl derivative (py,CO) yielded a non-equilibrium solution of the monopyridine derivative (dmso,py), which was reconverted into (py,CO) during the subsequent relaxation process. In all cases, pseudo-first-order reactions were observed and the rate constants for the attainment of equilibrium are reported in Table 1 and shown graphically in Figure 5. As expected for reaction (3) in the Scheme the rate constant is a linear function of [CO], *i.e.* $k_{obs.} = k_{3r} + k_{3f}[CO]$, where k_{3r} and k_{3f} are the rate constants for the reverse and forward steps respectively. The results of the stopped-flow experiments are given in Table 2. In these experiments [py] was varied by a factor of 10, being never lower than 1×10^{-4} mol dm^{-3}, to ensure total conversion of the (dmso,dmso) into the (dmso,py) complex. Due to the operating conditions, the maximum CO concentration in these experiments was 5.5×10^{-4} mol dm^{-3}. The rate constants were essentially independent of the base concentration and thus those obtained at the same CO concentration were averaged regardless of [py]. These data, also reported in Figure 5, are in substantial agreement with the flash-photolysis results. Least-squares analysis of all the data yields $k_{3f} = (8.8 \pm 0.5) \times 10^2$ dm^3 mol^{-1} s^{-1} and $k_{3f} = 0.16 \pm 0.03$ s^{-1}. The ratio k_{3f}/k_{3r} [= $(5.7 \pm 1.3) \times 10^3$ dm^3 mol^{-1}] is coincident, within the experimental error, with K_3.

Conclusions

Table 3 collects equilibrium and rate constants for the replacement of an axial ligand in phthalocyaninatoiron(II) derivatives, *i.e.* for reaction (11). Although the data concern a

$$[Fe(pc)T(X)] + Y \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [Fe(pc)T(Y)] + X;\ K = k_f/k_r \quad (11)$$

limited number of ligands, some conclusions may be drawn.

First, it may be noted that the equilibrium constants for reactions where dmso is substituted by either CO or py are from 10^4 to 10^8 greater than that for the replacement of CO *trans* to py by py. This suggests an intrinsically lower strength of the metal–dmso bond compared to metal–CO and metal–py bonds, as expected for the lower σ-donor ability of dmso. The data of Table 3 also indicate that both ligands T and Y affect the value of *K*. Thus, when T = dmso or CO, dmso is more readily substituted by py than when T = py itself. On the other hand, the *trans* ligand seems not to be so important when Y = CO.

The analysis of the kinetic data is more complicated. It is widely accepted that axial-substitution reactions of phthalocyaninatometal derivatives are dissociative, with formation of a reactive, hence scarcely selective, intermediate.[1–4] Furthermore, in the case of iron(II) systems, the transition state is believed to be one where the metal does not move appreciably out of the equatorial plane and is still low spin.[1,2] On the basis of these considerations one would expect the rate of rupture of the metal–ligand bond to be sensitive to the nature of the leaving ligand and to some sort of *trans* effect.

The values of k_r (Table 3), the rate constant for cleavage of the Fe–Y bond, are instead essentially independent of both Y and T. Some of them have been measured in toluene[2] and appear to be insensitive also to the solvent. Of course the data are too limited to warrant any generalization or definitive conclusion.

The rate constants for the forward reactions are composite as $k_f = k_{-X}k_{+Y}/k_{+X}[X]$ where k_{-X}, k_{+Y}, and k_{+X} are defined in equations (12) and (13). As mentioned above, an important aspect of the mechanism of axial substitution of phthalocyaninatoiron(II) adducts is that the discrimination factor k_{+Y}/k_{+X} should be close to unity and, indeed, this has been proven for this class of compounds in acetone[3] and in toluene.[2] The k_f values reported in Table 3 are consistent with discrimination factors significantly different from unity. Comparison of the appropriate values suggests that the ratio k_{+py}/k_{+CO} is about 10 for T = dmso and about 4×10^{-2} for T = py. Clearly, more information is needed to rationalize these observations in terms of solvent effects and/or specific interactions between the incoming nucleophile and the five-co-ordinate intermediate.

$$[\mathrm{Fe(pc)T(X)}] \underset{k_{+X}}{\overset{k_{-X}}{\rightleftharpoons}} [\mathrm{Fe(pc)T}] + \mathrm{X} \qquad (12)$$

$$[\mathrm{Fe(pc)T}] + \mathrm{Y} \underset{k_{-Y}}{\overset{k_{+Y}}{\rightleftharpoons}} [\mathrm{Fe(pc)T(Y)}] \qquad (13)$$

According to recent structural studies on phthalocyaninatometal derivatives,[15] an out-of-plane geometry for the five-co-ordinated metal under suitable circumstances does not seem inconceivable, although arguments have been put forward in favour of a substantial rigidity of the planar [Fe(pc)] moiety.[2,3] If further evidence can be obtained in support of the discrimination factors calculated here the problem of the structure of the five-co-ordinate intermediate in the axial-replacement reactions of [Fe(pc)T(X)] [*i.e.* (T,X)] complexes might be worth reconsideration, at least in some cases.

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