

Note

Equilibrium and kinetic study of piperidine binding to phthalocyaninatoiron(II) in dimethyl sulfoxide

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Abstract

The reaction between piperidine (Pip) and phthalocyaninatoiron(II) ([Fe(pc)]) in dimethyl sulfoxide (dmsO) has been studied at 20.0 °C, from both equilibrium and kinetic viewpoints. In excess of Pip, the adduct [Fe(pc)(Pip)₂] is formed via two consecutive pseudo-first-order processes. The observed rate constants have the general form: $k_{\text{obs}} = k_{1f}[\text{Pip}] + k_{1r}$, with $k_{1f}' = (8.7 \pm 0.2) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{1f}'' = (8.3 \pm 0.2) \times 10^1 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, for the binding of the first and second Pip molecule, respectively. Equilibrium experiments yield $K_1' = (1.0 \pm 0.1) \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ and $K_1'' = (1.3 \pm 0.1) \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ for the stepwise formation of the [Fe(pc)(dmsO)(Pip)] and [Fe(pc)(Pip)₂] adducts, respectively. From the values of the second-order rate constants (k_{1f}' and k_{1f}'') and of the equilibrium constants (K_1' and K_1''), the dissociation rate constants have been estimated to be $k_{1r}' = (8.7 \pm 1) \times 10^{-2} \text{ s}^{-1}$ and $k_{1r}'' = (6.4 \pm 0.7) \times 10^{-2} \text{ s}^{-1}$. Present results are discussed in the light of related previous studies.

Key words: Kinetics and mechanism; Iron complexes; Phthalocyanine complexes; Amine complexes; Piperidine binding; Thermodynamics

Introduction**

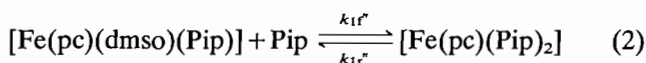
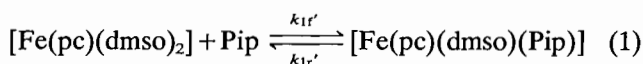
The relevance of the study of the axial reactivity of the phthalocyaninatoiron(II) molecule ([Fe(pc)]) is related to its porphyrin-like structure and to its potential catalytic activity [1a, b].

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**Phthalocyaninatoiron(II), [Fe(pc)]; piperidine, Pip; pyridine, Pyr; imidazole, Him; dimethyl sulfoxide, dmsO.

Solution studies have shown that [Fe(pc)] binds axially a variety of molecules such as O₂, CO, NO, Pyr and Him [2–12]. Except with dioxygen, which leads irreversibly to the formation of a μ -oxo-bis[phthalocyaninatoiron(III)] derivative [2, 3], all other ligands (including dmsO) bind reversibly [2–12] so that both equilibrium and kinetic constants can be measured.

Following our interest in this field, the results of a kinetic and equilibrium investigation on the stepwise substitution of axial dmsO by Pip in [Fe(pc)(dmsO)₂] (reactions (1) and (2), free solvent omitted) are reported here[†].



These data have been analysed in parallel with those concerning other ligands (i.e. O₂, CO, NO, Pyr and Him) under comparable conditions [2–12].

Experimental

Materials

Phthalocyaninatoiron(II) was an Eastman Kodak product and was purified as previously described [4]. Dimethyl sulfoxide (Merck) and piperidine (Fluka) were distilled under reduced pressure over CaH₂ and KOH, respectively, before use. All dmsO solutions used in this work were oxygen-free^{††}.

Equilibrium measurements

The axial binding of Pip was monitored spectrophotometrically at 435, 658 and 664 nm where relatively large absorbance changes are observed upon addition of the base to a dmsO solution of [Fe(pc)] (see Fig. 1). As shown in Fig. 1, 658 and 664 nm are the isobestic points for the second and the first reaction step, respectively. A Varian Cary 219 and a Jasco J-510 double-beam spectrophotometer, equipped with a water-circulating thermostating system, were used. The general

[†]Throughout this paper equilibrium and kinetic constants will have the same symbols as those used for the corresponding quantities in refs. 5, 6 and 12.

^{††}Although the reaction between dioxygen and [Fe(Pc)] at the concentration levels used for the latter is very slow [2, 3] and would not interfere with present experiments, all the measurements here described have been carried out under nitrogen.

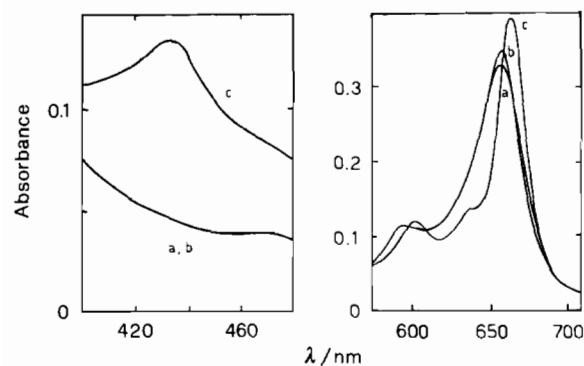


Fig. 1. Spectra of a 4.3×10^{-6} mol dm^{-3} dmsO solution of $[\text{Fe}(\text{pc})]$ in the absence (a) as well as in the presence of 1.0×10^{-4} mol dm^{-3} (b) and 1.0×10^{-1} mol dm^{-3} (c) Pip in the ranges 400–480 and 575–700 nm. Temperature 20.0 °C.

procedure was as described in refs. 5 and 12. A spectrophotometric cell of suitable pathlength (1 or 5 cm) was filled with a known volume (3 or 25 ml, respectively) of a dmsO solution of $[\text{Fe}(\text{pc})]$ in the concentration range 2×10^{-7} – 1×10^{-5} mol dm^{-3} {the accurate value of the $[\text{Fe}(\text{pc})]$ concentration was obtained from the absorption at 653 nm ($\epsilon = 7.49 \times 10^4$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) [13]. Since there is no evidence of $[\{\text{Fe}(\text{pc})\}_n]$ polymerisation in dmsO [2], all the experiments here reported are assumed to refer to the monomeric species $[\text{Fe}(\text{pc})]$. A dmsO solution of Pip of known concentration was then added by means of a microsyringe. Added volumes were always negligible with respect to the starting volume. Also the fraction of Pip bound to the iron was always negligible compared to the total ligand concentration. After thermal equilibration (5 min) at 20.0 °C, the spectrum from 350 to 700 nm was recorded and the absorbance changes at 435, 658 and 664 nm analysed as described below.

Kinetic measurements

The kinetic processes which follow the addition of Pip to $[\text{Fe}(\text{pc})(\text{dmsO})_2]$ were studied spectrophotometrically at 435, 658 and 664 nm, and at 20.0 °C. Fast kinetics were run on a Durrum-Gibson rapid-mixing stopped-flow apparatus, whilst slow runs were carried out on a Varian Cary 219 and a Jasco J-510 double-beam spectrophotometer, equipped with the Hi-Tech Scientific SFA-11 Rapid Kinetics Accessory. The concentration of Pip was always in large excess ($\geq 8 \times$) over the concentration of the iron complex and in all cases excellent pseudo-first-order plots were obtained. Further experimental details are reported in refs. 5 and 12.

Results

Equilibrium measurements

The optical changes measured upon addition of Pip to $[\text{Fe}(\text{pc})(\text{dmsO})_2]$ solutions are reported in Fig. 2 as $\log[(D - D_1)/(D_2 - D)]$ versus $\log[\text{Pip}]$ (D_1 is the absorbance at the start, D that at a given concentration of free Pip, and D_2 that after complete replacement of axial dmsO) [5, 12]. Over the whole Pip concentration range explored (i.e. 1.0×10^{-6} mol $\text{dm}^{-3} \leq [\text{Pip}] \leq 2.0 \times 10^{-2}$ mol dm^{-3}), the observations at 658 nm lay on a straight line of unitary slope ($n = 1.00 \pm 0.02$). Moreover, the observations at 435 and 664 nm lay on a common straight line, again of unitary slope ($n = 1.00 \pm 0.02$), nearly two powers of ten shifted towards higher Pip concentrations. For a two-step equilibrium such as that shown in reactions (1) and (2), the general eqn. (3) holds, where K_1' and K_1'' are the apparent equilibrium constants of reactions (1) and

$$\frac{D - D_1}{D_2 - D} = \frac{K_1' [\text{Pip}] (\varphi + K_1'' [\text{Pip}])}{1 + K_1' [\text{Pip}] (1 - \varphi)} \quad (3)$$

(2), respectively, and $\varphi = (\epsilon_i - \epsilon_1)/(\epsilon_2 - \epsilon_1)$ (ϵ_1 , ϵ_i and ϵ_2 are the molar absorbances of $[\text{Fe}(\text{pc})(\text{dmsO})_2]$, $[\text{Fe}(\text{pc})(\text{dmsO})(\text{Pip})]$ and $[\text{Fe}(\text{pc})(\text{Pip})_2]$, respectively). Under the experimental conditions chosen here, φ is equal to zero at 664 nm and to 1 at 658 nm. At these wavelengths eqn. (3) reduces to eqns. (4) and (5),

$$\frac{D - D_1}{D_2 - D} = \frac{K_1' K_1'' [\text{Pip}]^2}{1 + K_1' [\text{Pip}]} \quad (4)$$

$$\frac{D - D_1}{D_2 - D} = K_1' [\text{Pip}] (1 + K_1'' [\text{Pip}]) \quad (5)$$

respectively (see refs. 5 and 12).

It can be readily shown that, under anticooperative conditions (i.e. $K_1'' \ll K_1'$), the logarithmic plot of eqns. (4) and (5) must be linear with unitary slope within the ligand concentration ranges where optical changes are observed (i.e., $0.01 \leq (D - D_1)/(D_2 - D) \leq 100$). The

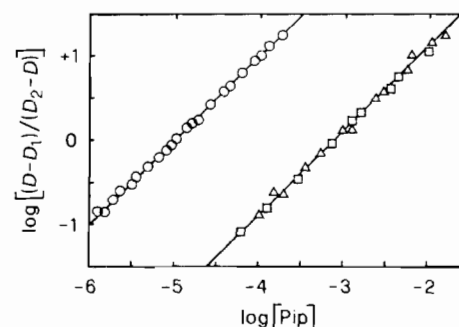


Fig. 2. Plot of $\log((D - D_1)/(D_2 - D))$ vs. $\log[\text{Pip}]$ at 658 (O), 435 (□) and 664 (Δ) nm. Temperature 20.0 °C.

plots shown in Fig. 2 indicate that this is indeed the case and a non-linear least-squares procedure gives $K_1' = (1.0 \pm 0.1) \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$ and $K_1'' = (1.3 \pm 0.1) \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$, at 20.0 °C (uncertainties are standard deviations).

The data at 435 nm (squares in Fig. 2) overlap with those measured at 664 nm (triangles in Fig. 2). This indicates that eqn. (5) holds at both wavelengths and, hence, $\varphi = 0$ also at 435 nm, where the increase in absorbance is only due to reaction (2). This behaviour is not surprising since it is also found in the substitution of axial dmsO in $[\text{Fe}(\text{pc})(\text{dmsO})_2]$ by Pyr and Him [5, 12].

Kinetic measurements

In agreement with the equilibrium observations discussed above, the time dependences of the absorbance of dmsO solutions of $[\text{Fe}(\text{pc})]$ in the presence of excess Pip at 435 and 664 nm, on one hand, and at 658 nm, on the other hand, each show a simple one-exponential decay. The time scales of the processes are so different that any interference is negligible. In the presence of excess Pip (typically, $[\text{Fe}(\text{pc})] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$; $8.0 \times 10^{-5} \text{ mol dm}^{-3} \leq [\text{Pip}] \leq 5.0 \times 10^{-2} \text{ mol dm}^{-3}$), both processes conform to a pseudo-first-order rate law.

Both the observed rate constants k_{obs}' and k_{obs}'' show a linear dependence on Pip concentration (see Fig. 3), according to eqns. (6) and (7)

$$k_{\text{obs}}' = k_{1f}'[\text{Pip}] + k_{1r}' \quad (6)$$

$$k_{\text{obs}}'' = k_{1f}''[\text{Pip}] + k_{1r}'' \quad (7)$$

The least-squares analysis of the data yields $k_{1f}' = (8.7 \pm 0.2) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{1r}' = (8.3 \pm 0.2) \times 10^1 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Both intercepts k_{1r}' and

k_{1r}'' are too low to be determined being zero within the experimental error.

As shown in Fig. 3, the observed rate constants measured at 435 nm (squares in Fig. 3) nicely overlap with those measured at 664 nm (triangles in Fig. 3) for the slowest step, thus confirming the above given assignment of the process responsible for the spectral changes observed in the 400–480 nm region (see Fig. 1).

As both reactions (1) and (2) are reversible, k_{1f}' and k_{1r}' may be identified with the forward and k_{1r}' and k_{1r}'' with the reverse rate constants of the related processes. If the equilibrium constants K_1' and K_1'' are used together with k_{1f}' and k_{1f}'' , the values $k_{1r}' = (8.7 \pm 1) \times 10^{-2} \text{ s}^{-1}$ and $k_{1r}'' = (6.4 \pm 0.7) \times 10^{-2} \text{ s}^{-1}$ are obtained; these values are indeed too low to allow their determination from kinetic experiments, and are consistent with the apparent zero least-squares intercepts calculated as above (see Fig. 3).

Discussion

The results presented in this paper and shown in Table 1 demonstrate that the substitution of the axial dmsO molecules of $[\text{Fe}(\text{pc})(\text{dmsO})_2]$ is a stepwise process, correctly described by the overall reactions (1) and (2), with the binding of the first Pip occurring more rapidly and being thermodynamically favoured with respect to the binding of the second Pip.

This anticooperative behaviour represents a common feature for various stepwise substitution processes and, in particular, is closely similar to the behaviour of the $[\text{Fe}(\text{pc})(\text{dmsO})_2]/\text{Pyr}$ and $[\text{Fe}(\text{pc})(\text{dmsO})_2]/\text{Him}$ systems which have been previously investigated in our laboratories [5, 12]. As with Pyr and Him [5, 12], the incoming of the first Pip into the coordination sphere of iron(II) causes spectral changes limited to the high-intensity charge transfer band centred at 656 nm (see Fig. 1). The absence of any detectable effect of the first Pip–dmsO substitution in the blue region seems thus to be a general rule, at least when N-donor atoms are involved [5, 12].

Table 1 reports the equilibrium and kinetic data for the substitution of an axial dmsO in $[(\text{T})\text{Fe}(\text{pc})(\text{dmsO})]$ by Y (T = inert, *trans* dmsO or N-base; Y = Pyr, Him or Pip).

It is generally accepted that axial substitutions of porphyrinato and phthalocyaninato derivatives are essentially dissociative with the formation of a highly reactive, hence scarcely selective, pentacoordinated intermediate [2–7, 12, 14–17]. Thus, the overall ligand substitution may be separated into the steps (8) and (9), and it is readily demonstrated that the observed

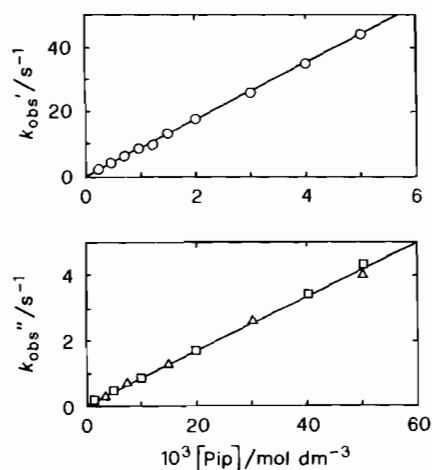
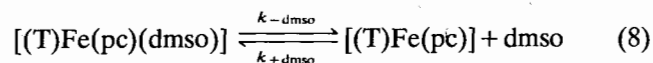
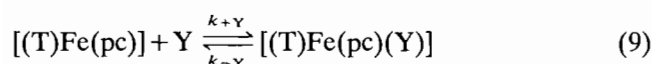


Fig. 3. Observed rate constants for reactions (1) and (2). The top panel shows the fast process observable at 658 nm (○). The bottom panel shows the slow process observable at 435 (□) and 664 (△) nm. Temperature 20.0 °C.

TABLE 1. Equilibrium and kinetic data (at 20.0 °C) for the reaction: $[(T)Fe(pc)(dmsO)] + Y \xrightleftharpoons[k_{1r}]{k_{1f}} [(T)Fe(pc)(Y)] + dmsO$

T	Y	K_1^a ($dm^3 mol^{-1}$)	k_{1f}^b ($dm^3 mol^{-1} s^{-1}$)	k_{1r}^c (s^{-1})	Reference
dmsO	Pyr	3.9×10^5	1.5×10^4	4.0×10^{-2}	5
dmsO	Him	6.4×10^5	9.8×10^3	1.5×10^{-2}	12
dmsO	Pip	1.0×10^5	8.7×10^3	8.7×10^{-2}	this work
dmsO	CO	1.4×10^4	1.3×10^3	1.2×10^{-1}	4
dmsO	NO	1.1×10^6	2.2×10^4	2.0×10^{-2}	7
Pyr	Pyr	3.0×10^2	3.6×10^1	1.5×10^{-1}	5
Pyr	CO	6.5×10^3	8.8×10^2	1.6×10^{-1}	6
Him	Him	7.4×10^3	5.4	7.3×10^{-4}	12
Pip	Pip	1.3×10^3	8.3×10^1	6.4×10^{-2}	this work

^a $K_1 = K_1'$ or K_1'' . ^b $k_{1f} = k_{1f}'$ or k_{1f}'' . ^c $k_{1r} = k_{1r}'$ or k_{1r}'' .



pseudo-first order rate constant has the form $k_{obs} = k_{1f}[Y] + k_{1r}$ (such as in Fig. 3), with $k_{1f} = k_{-dmsO}k_{+Y}/k_{+dmsO}[dmsO]$ and $k_{1r} = k_{-Y}$. Furthermore, since the pentacoordinate intermediate is poorly selective, $k_{+dmsO} \approx k_{+Y}$ and hence, $k_{-dmsO} \approx k_{1f}[dmsO]$. Thus, the rate of dmsO substitution is expected to be independent of the nature of the incoming ligand Y. Present results are consistent with these expectations; although Pip is much more basic ($pK_b = 2.88$) than Pyr ($pK_b = 8.75$) and Him ($pK_b = 7.05$), the rate constants for the first substitution step in $[Fe(pc)(dmsO)_2]$ by these bases are within a factor of only 1.8. This situation remains essentially unchanged if substitution by NO is also included [12], whilst some discrimination seems to operate towards the slow-reacting carbon monoxide [4].

The rate constants of the reverse processes, k_{1r} , should, instead, depend on the nature of the leaving ligand, Y. Thus, it is somewhat surprising to find that proton basicity of the N-donor ligands Pyr, Him and Pip has only a limited effect, and that the most basic is also the most labile group.

The *trans* effect on the release of dmsO from $[(T)Fe(pc)(dmsO)]$ in the series T = Pyr (incoming ligand Pyr)*, Him or Pip is also small, while it becomes very large when T = dmsO is included in the series.

The base strength in aqueous solution as measured by the pK_b values may not be a satisfactory measure of the nucleophilic, σ N-Fe interaction in dmsO, never-

theless a definitely stronger metal-nitrogen bond and, hence, a definitely slower rate of bond cleavage should be expected for the aliphatic-type amine Pip with respect to Pyr and Him.

The absence of such an effect suggests that other compensating factors, such as π -bonding [6], may be operating.

Finally, it has to be noted that for the $[(T)Fe(pc)(X)]$ complexes with T = X = Him, Pyr or Pip, Him is considerably more inert than both Pyr and Pip which show comparable reactivities. This trend parallels the one observed in acetone [18] and has, at the moment, no obvious explanations.

Acknowledgements

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*For T = Pyr, only the value of k_{1f} for the replacement of dmsO by Pyr itself is considered here. The substitution by CO is considerably faster and may be a consequence of a change in the reaction mechanism. It is perhaps worth remembering that the substitution of CO by Pyr in $[Fe(pc)(Pyr)(CO)]$ leads to a transient species containing 2 Pyr and 1 CO molecules [6], hardly in agreement with a simple dissociative scheme.

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