Interaction of Cyanide with Iron(II) Phthalocyanine: Kinetics and Equilibria

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The kinetics and equilibria for the reaction between cyanide and iron(II) phthalocyanine [Fe(pc)] (H_2pc = phthalocyanine) in dimethyl sulfoxide (dmso) were studied at 25 °C. The complex $[Fe(pc)(CN)_2]^{2-}$ is formed in two consecutive pseudo-first-order processes with $k_{2f} = 17.5 \pm 0.8$ dm^3 mol^{-1} s^{-1} and $k_{3f} = 0.20 \pm 0.05$ dm^3 mol^{-1} s^{-1}, where k_{2f} and k_{3f} are the rate constants for the binding of the first and second cyanide ligands, respectively. The equilibrium constants were found to be $K_2 = 3.0 \times 10^3$ dm^3 mol^{-1} and $K_3 = 5.7 \times 10^2$ dm^3 mol^{-1}, for the formation of $[Fe(pc)(CN)(dmso)]^-$ and $[Fe(pc)(CN)_2]^2$ respectively.

Metal phthalocyanines [M(pc)] (H_2pc = phthalocyanine) and their derivatives are of great technological importance for the manufacture of blue-green dyes.[1] Research on the use of the phthalocyanine complexes as catalysts, photoconductors and photosensitizers is currently in progress.[2–11] Iron(II) phthalocyanine [Fe(pc)] is a widely investigated porphyrin-like molecule with a strong tendency to axial ligation.[12,13] Many ligands bind reversibly to [Fe(pc)],[14–20] making it possible for the rate and equilibrium constants to be determined. The study of the co-ordination of cyanide to [M(pc)] complexes is an important step in the exploration of complexes that may act as antidotes for cyanide intoxication. Iron(III) methaemoglobin is known to play an important role in cyanide detoxification,[21] and an understanding of cyanide co-ordination to [Fe(pc)] would be particularly useful due to the similarity between [Fe(pc)] and iron porphyrin complexes. The cyano complexes of [Fe(pc)] are known,[22–25] but there has been no report on the kinetics of cyanide binding to this complex.

When $[Fe^{II}(pc)]$ is dissolved in dimethyl sulfoxide (dmso) the axially co-ordinated $[Fe^{II}(pc)(dmso)_2]$ species is known to be formed.[20,24] Axially ligated $[Fe^{II}(pc)L_2]$ complexes are always low spin in strongly co-ordinating solvents such as dmso.[26] This is in contrast to the chemistry of the iron(II) porphyrins where both intermediate- and high-spin complexes have been observed. The species $[Fe^{II}(pc)]$ only exhibits intermediate spin configurations when solvents of low co-ordinating ability such as dichlorobenzene are employed.[24,26]

It has been proposed that axial ligand substitutions in porphyrin and phthalocyanine complexes are dissociative, resulting in the formation of a highly reactive five-coordinate intermediate.[19,20] The overall ligand substitution may be represented by reactions (1)–(3), where L and E represent the

$$[Fe(pc)L_2] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(pc)L] + L \qquad (1)$$

$$[Fe(pc)L] + E \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Fe(pc)L(E)] \qquad (2)$$

$$[Fe(pc)L(E)] + E \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Fe(pc)E_2] + L \qquad (3)$$

leaving and entering ligand, respectively. Kinetic studies on the replacement of dmso in $[Fe(pc)(dmso)_2]$ by imidazole or pyridine, have shown that the exchange of the first dmso ligand occurs faster than that of the second ligand.[14] The co-ordination of the first ligand to ruthenium phthalocyanine also occurs very rapidly.[27] Kinetic and equilibrium data for cyanide binding to [Fe(pc)] are reported in this work.

Experimental

Iron(II) phthalocyanine was obtained from Kodak and purified by sublimation. The complex $K_2[Fe^{II}(pc)(CN)_2]$[22] was prepared by treating [Fe(pc)] with an excess of potassium cyanide in refluxing dimethylformamide (dmf) for 3 h. The solid obtained after evaporation of the dmf was washed in water and acetone, and characterized by elemental analysis, IR and electronic absorption spectroscopies. IR (KBr disc): 3420m, 2120m [ν(C≡N)], 1609w, 1502m, 1460m, 1421m, 1324s, 1290m, 1164m, 1120s, 1075m, 910m, 780m, 759m and 731s cm^{-1}.

Dimethyl sulfoxide was distilled before use. Cyanide concentrations were determined by titration with silver nitrate.

Kinetic and equilibrium studies were run at 25 °C and monitored with the Beckman UV 5240 spectrophotometer. Cyanide binding was followed by monitoring the increase in the intensity of the Q band of the monocyano $\{[Fe(pc)(CN)(dmso)]^-\}$ or dicyano $\{[Fe(pc)(CN)_2]^{2-}\}$, complexes. Accurate concentrations were determined from Q-band absorptions using $\varepsilon = 7.49 \times 10^4$ and 1.33×10^5 dm^3 mol^{-1} cm^{-1} for dmso solutions of [Fe(pc)] and $[Fe(pc)(CN)_2]^{2-}$ respectively.[25] Typically a known volume of the dmso solution of [Fe(pc)] $\{$giving $[Fe(pc)(dmso)_2]\}$ was added to a spectrophotometric cell of 1 cm path length, then a known volume of the dmso solution of potassium cyanide was added to the cell and the absorption spectra monitored.

Infrared spectra (KBr discs) were collected with a Perkin-Elmer 180 IR spectrophotometer.

Results and Discussion

Fig. 1(*a*) shows absorption spectral changes observed when dmso solutions of potassium cyanide (1.04×10^{-4} mol dm^{-3}) were added to $[Fe(pc)(dmso)_2]$ (3.7×10^{-6} mol dm^{-3}) in dmso. The Q band of the $[Fe(pc)(dmso)_2]$ complex is centred at 653 nm,[25] Fig. 1(*a*)(i). On addition of cyanide, the Q band shifts first to 660 nm [Fig. 1(*a*)(ii)] and finally to 667 nm [Fig. 1(*a*)(iii)]. The spectra shown in Fig. 1(*a*(ii) and 1(*a*)(iii) are formed isosbestically, see for example, Fig. 1(*b*). The presence of isosbestic points is a clear indication that only two species exist in solution at each stage. The final spectrum, Fig. 1(*a*)(iii), is identical to that observed for $[Fe^{II}(pc)(CN)_2]^{2-}$ in dmso. The spectrum shows a split in the Soret band that is typical of dicyano complexes.[24,25] Further addition of cyanide had no effect on the spectrum. Thus, the final product of the reaction of cyanide with $[Fe^{II}(pc)(dmso)_2]$ is the dicyano complex $[Fe^{II}(pc)(CN)_2]^{2-}$

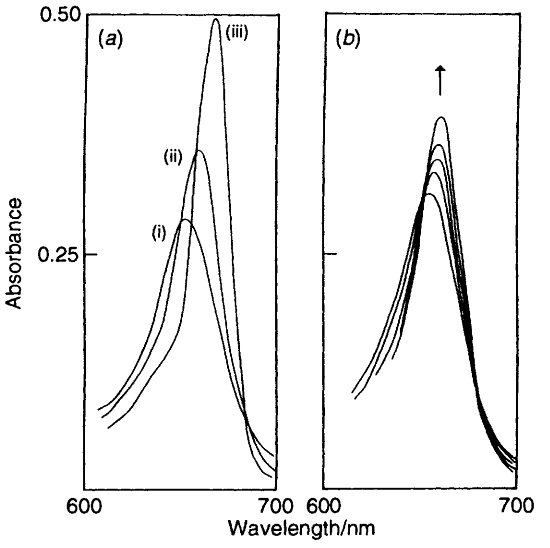

Fig. 1 (*a*) Absorption spectral changes observed on addition of CN^- (1.04×10^{-4} mol dm^{-3}) to $[Fe(pc)(dmso)_2]$ (3.7×10^{-6} mol dm^{-3}) in dmso; (i) $[Fe(pc)(dmso)_2]$, (ii) $[Fe(pc)(CN)(dmso)]^-$, (iii) $[Fe(pc)(CN)_2]^{2-}$. (*b*) Absorption spectral changes observed when cyanide (3.2×10^{-5} mol dm^{-3}), corresponding to a CN^- : $[Fe(pc)(dmso)_2]$ ratio of < 10:1, was added to $[Fe(pc)(dmso)_2]$ (4.4×10^{-6} mol dm^{-3}) in dmso. The final product is $[Fe(pc)(CN)(dmso)]^-$

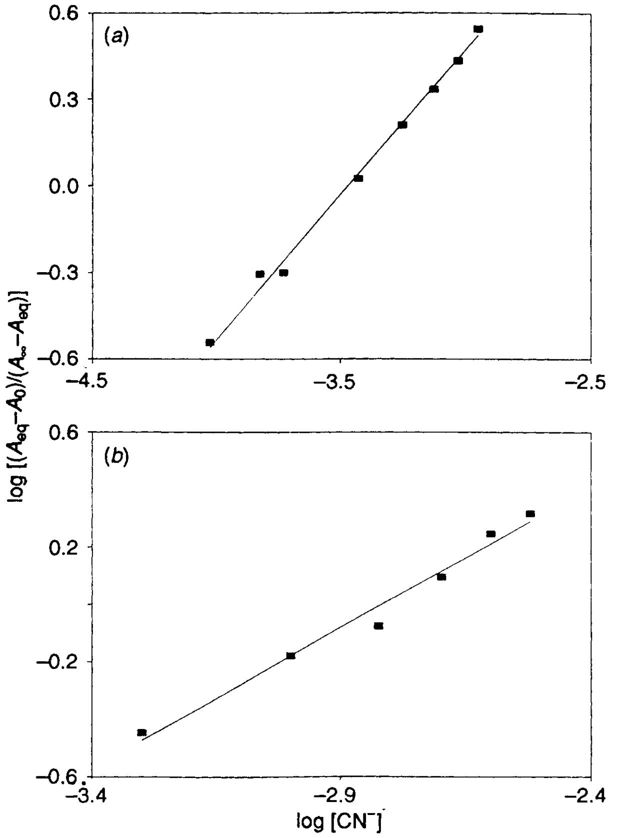

Fig. 2 Plot of $\log[(A_{eq} - A_0)/(A_\infty - A_{eq})]$ *vs.* $\log[CN^-]$ for the formation of (*a*) $[Fe(pc)(CN)(dmso)]^-$ and (*b*) $[Fe(pc)(CN)_2]^{2-}$

Dimeric (or polymeric) [M(pc)] complexes can be formed as a result of bridging between two or more phthalocyanine rings. Cyanide is known to act as a bridging ligand in some metal–phthalocyanine complexes.[28,29] Aggregation results in considerable broadening of the Q band of the [M(pc)] complexes.[30,31] The absorption spectra of $[Fe^{II}(pc)(CN)_2]^{2-}$, Fig. 1(*a*)(iii), is typical of monomeric [M(pc)] complexes, suggesting that this complex is non-aggregated in solution. There has been no report on the formation of cyanide bridges between the phthalocyanine rings in the previously reported spectra of $[Fe^{II}(pc)(CN)_2]^{2-}$.[22,24,25]

The initial species formed, after the addition of cyanide, with the Q band centred at 660 nm is most likely the monocyano complex, $[Fe(pc)(CN)(dmso)]^-$, where only one dmso ligand has been exchanged for the cyanide. Exchange of axial ligands in $[Fe(pc)L_2]$ complexes occurs in a stepwise manner[14–16] as shown by reactions (2) and (3). The co-ordination of the first ligand normally occurs very rapidly and causes only minor spectral changes, the spectrum of [Fe(pc)(py)(dmso)] (py = pyridine) is only red-shifted by 2 nm from the spectrum of $[Fe(pc)(dmso)_2]$.[16] A much larger shift (*ca.* 7 nm) is observed however, on co-ordination of the first cyanide to $[Fe(pc)(dmso)_2]$.

It was possible to follow the kinetics and equilibria for the formation of the monocyano species when low cyanide concentrations $\{[CN^-]:[Fe(pc)] < 10:1\}$ were used. Fig. 1(*b*) shows spectral changes observed when CN^- (3.2×10^{-5} mol dm^{-3}) was added to $[Fe(pc)(dmso)_2]$ (4.4×10^{-6} mol dm^{-3}) in dmso solution. These changes are associated with the formation of the monosubstituted complex. Equilibrium data for the formation of $[Fe(pc)(CN)(dmso)]^-$ were analysed by standard spectrophotometric techniques using equation (4), where A_{eq} is

$$\log[(A_{eq} - A_0)/(A_\infty - A_{eq})] = \log K + n\log[CN^-] \quad (4)$$

the equilibrium absorbance at 660 nm, corresponding to the absorbance wavelength of $[Fe(pc)(CN)(dmso)]^-$ and A_0 is the absorbance at 660 nm corresponding to 0% formation of this complex. The absorbance for the complete formation of the complex, A_∞, was estimated from the final absorption spectra. Plots of $\log[(A_{eq} - A_0)/(A_\infty - A_{eq})]$ *vs.* $\log[CN^-]$, Fig. 2(*a*), gave straight lines with unit slope ($n = 1.00 \pm 0.05$) and an equilibrium constant for the co-ordination of the first CN^-, $K_2 = 3.0 \times 10^3$ dm^3 mol^{-1}. The value of *n* shows that only one mole of cyanide is co-ordinated at this stage, and confirms a stepwise axial ligand substitution mechanism. It is interesting to observe that this equilibrium constant is in the same range as that reported for the co-ordination of isocyanide to $[Fe(pc)(py)_2]$ and $[Fe(pc)(pip)_2]$ (pip = piperidine) complexes,[17] and is lower than the equilibrium constant for the replacement of dmso by pyridine or imidazole, Table 1.

The rate constants for the formation $[Fe(pc)(CN)(dmso)]^-$ were estimated from absorption changes obtained at low cyanide concentrations $\{[CN^-]:[Fe(pc)] = 5\text{–}10:1\}$; a larger excess of cyanide resulted in fast formation of this complex and hence measuring absorption changes accurately were difficult. Since an excess of cyanide was employed, pseudo-first-order conditions were assumed in estimating the rate constants for the first cyanide co-ordination to [Fe(pc)].

Equation (5) gives the rate law for the dissociative mechanism shown by reactions (6) and (7).[14]

$$k_{obs} = \frac{k_1k_2[CN^-]}{k_{-1}[dmso]} + k_{2r} \quad (5)$$

$$[Fe(pc)(dmso)_2] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(pc)(dmso)] + dmso \quad (6)$$

$$[Fe(pc)(dmso)] + CN^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Fe(pc)(CN)(dmso)]^- \quad (7)$$

The rate constant for the forward reaction, k_{2f}, is given by k_1k_2/k_{-1}[dmso] and k_{2r}, the rate constant for the reverse reaction is equal to k_{-2}. Plots of k_{obs} *vs.* cyanide concentration were linear, Fig. 3(*a*), showing that the reaction was first order in cyanide. Least-squares analysis gave $k_{2f} = 17.5 \pm 0.8$ dm^3

Table 1 Equilibrium data for axial ligand exchange in iron(II) phthalocyanine complexes

Complex	X[a]	$K_2{}^b$/dm^3 mol^{-1}	$K_3{}^b$/dm^3 mol^{-1}	Ref.
[Fe(pc)(dmso)$_2$][c]	py	4.0×10^5	3.0×10^2	15
[Fe(pc)(dmso)$_2$][c]	Him	6.4×10^5	7.4×10^3	14
[Fe(pc)(dmso)$_2$][c]	CN	3.0×10^3	5.7×10^2	This work
[Fe(pc)(py)$_2$][d]	PhCH$_2$NC	3.2×10^3	2.0	17
[Fe(pc)(pip)$_2$][d,e]	PhCH$_2$NC	3.2×10^3	3.2	17
[Fe(pc)(mim)$_2$][d,f]	PhCH$_2$NC	4.0×10^2	0.2	17

[a] X = nucleophile; py = pyridine, Him = imidazole. [b] Equilibrium constants K_2 and K_3 are as defined in the text. [c] Solvent dmso. [d] Solvent toluene. [e] pip = Piperidine. [f] mim = *N*-Methylimidazole.

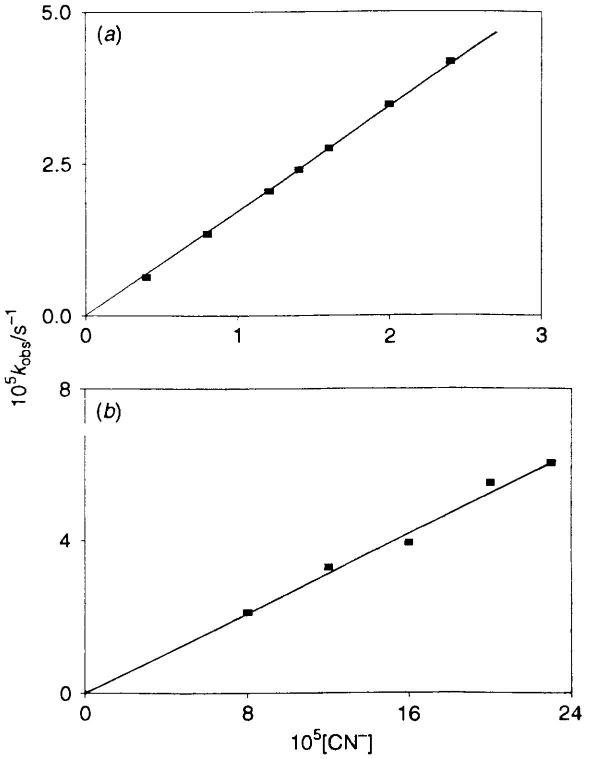

Fig. 3 Observed rate constants, k_{obs}/s^{-1}, for (*a*) the first cyanide uptake [reactions (6) and (7)] and (*b*) the second cyanide uptake [reactions (8) and (9)]

mol^{-1} s^{-1}. The equilibrium constant for the first cyanide co-ordination, K_2, is given by k_{2f}/k_{2r}. From this relationship, k_{2r} was estimated to be 4×10^{-5} s^{-1}, showing a smaller rate for the reverse reaction than has been reported before[14,16] for axial ligand exchange in iron phthalocyanine complexes, see Table 2.

When [Fe(pc)(dmso)] was treated with large concentrations of cyanide (greater than 25-fold excess), the formation of the monocyano complex was very fast and was immediately followed by the formation of the dicyano complex [Fe(pc)(CN)$_2$]$^{2-}$ with a Q-band absorption centred at 667 nm. Monitoring absorbances at 667 nm resulted in linear plots, Fig. 2(*b*), of $\log[(A_{eq} - A_0)/(A_\infty - A_{eq})]$ *vs.* $\log[CN^-]$. Least-squares analysis gave the equilibrium constant for the co-ordination of the second cyanide, $K_3 = 5.7 \times 10^2$, and $n = 0.98 \pm 0.05$.

Pseudo-first-order rate conditions were adopted for the determination of kinetic data for the formation of the dicyano complex. Plots of k_{obs} *vs.* [CN$^-$] were linear, Fig. 3(*b*), showing that the reaction is first order in cyanide. The specific rate constants for the forward and reverse reactions, k_{3f} and k_{3r} respectively, can be obtained from reactions (8) and (9).

$$[Fe(pc)(CN)(dmso)]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(pc)(CN)]^- + dmso \quad (8)$$

$$[Fe(pc)(CN)]^- + CN^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Fe(pc)(CN)_2]^{2-} \quad (9)$$

The forward rate constant k_{3f} is given by k_1k_3/k_{-1}[dmso] and $k_{3r} = k_{-3}$. Least-squares analysis gave a value of 0.20 ± 0.05 dm^3 mol^{-1} s^{-1} for k_{3f}. Combining K_3 and k_{3f} gave $k_{3r} = 3.5 \times 10^{-4}$ s^{-1}. The fact that the formation of the dicyano complex is first order in cyanide does show that [Fe(pc)(CN)$_2$]$^{2-}$ only forms after complete formation of [Fe(pc)(CN)(dmso)]$^-$. The values of k_{2r} and k_{3r} are too low to allow a direct determination from kinetic experiments.

Conclusion

The results reported in this work demonstrate that the substitution of the dmso ligands by cyanide in [Fe(pc)(dmso)$_2$] is a stepwise process described by reactions (6)–(9), with the co-ordination of the first CN$^-$ ligand occurring faster than that of the second ligand. Comparison with other substitution reactions, Table 1, shows that the equilibrium constants for the substitution of dmso by CN$^-$ are much smaller than for substitution of dmso by pyridine and imidazole. Also, for the latter substitution, K_2, the equilibrium constant for the replacement of the first dmso ligand is larger than K_3, the equilibrium constant for the replacement of the second dmso ligand, by a factor of $\geqslant 100$. For CN$^-$ substitution reactions, however, K_2 is less than ten times larger than K_3. The smaller value of K_3 as compared to K_2, reflects the extra stability gained by dmso through π-back bonding in [Fe(pc)(py)(dmso)] with respect to [Fe(pc)(dmso)$_2$] on substitution of dmso by pyridine.[16] The fact the values of K_3 and K_2 for the replacement of dmso by cyanide, are not too different suggests that the dmso ligand in [Fe(pc)(CN)(dmso)]$^-$ is destabilized by the π-accepting abilities of CN$^-$. π-Acceptor ligands destabilize each other when located in *trans* positions. The presence of CN$^-$ *trans* to dmso makes it easier for the dmso ligand to be detached. The extra stability of dmso caused by π-back bonding present in [Fe(pc)(py)(dmso)], is absent in [Fe(pc)(CN)(dmso)]$^-$.

The rate constants reported for the formation of [Fe(pc)(CN)$_2$]$^{2-}$ are a measure of the ease of dissociation of the bond between Fe and the leaving ligand. The data presented in this work confirm that dmso is much more labile than CN$^-$. The rate constant corresponding to the dissociation of the first dmso, k_{2f}, is 10^5 times larger than k_{2r}, the rate for the dissociation of CN$^-$ in [Fe(pc)(CN)(dmso)]$^-$. Similarly, for the dissociation of dmso from [Fe(pc)(CN)(dmso)]$^-$ and CN$^-$ from [Fe(pc)(CN)$_2$]$^{2-}$, k_{3f} is 10^3 larger than k_{3r}. It is also observed that k_{3r} is larger than k_{2r}, showing that the dissociation of CN$^-$ *trans* to another CN$^-$ is easier than the dissociation of CN$^-$ *trans* to dmso. This is not surprising since CN$^-$ is expected to be a strong π acceptor, and when CN$^-$ ligands are *trans* to each other, they have a large destabilizing effect on each other.

A direct comparison between the rates of cyanide co-ordination by iron phthalocyanine and the structurally similar iron porphyrin complexes is not reliable since most of the work done on the latter has been in aqueous solutions. It is however

Table 2 Kinetic data for axial ligand exchange in metal phthalocyanine complexes in dmso

Complex	X[a]	$K_f{}^b$/dm^3 mol^{-1} s^{-1}	$K_r{}^b$/s^{-1}	Ref.
First ligand exchange				
[Fe(pc)(dmso)$_2$]	py	1.5×10^4	4×10^{-2}	15
[Fe(pc)(dmso)$_2$]	Him	9.8×10^3	1.5×10^{-2}	14
[Fe(pc)(dmso)$_2$]	CN	17.5	4×10^{-5}	This work
Second ligand exchange				
[Fe(pc)(py)(dmso)]	py	36	0.15	15
[Fe(pc)(Him)(dmso)]	Him	5.4	7.3×10^{-4}	14
[Ru(pc)(CN)(dmso)]$^-$	CN	7.2×10^{-2}		27
[Fe(pc)(CN)(dmso)]$^-$ [c]	CN	0.2	3.5×10^{-4}	This work

[a] X as in Table 1. [b] K_f corresponds to k_{2f} for first CN$^-$ co-ordination and to k_{3f} for second CN co-ordination and are as defined in the text. [c] Solvent dmf.

interesting that the rate constant for cyanide co-ordination to iron(II) myoglobin is given as 0.1 dm^3 mol^{-1} s^{-1},[32] a value very close to that reported here for the second cyanide co-ordination.

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