Pergamon

0277-5387(95)00090-9

Polyhedron Vol. 14, No. 17–18, pp. 2325–2329, 1995
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0277-5387/95 $9.50+0.00

EQUILIBRIUM AND KINETIC STUDIES OF THE REACTION BETWEEN PYRIDINE AND COBALT(II) PHTHALOCYANINE IN DMSO

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(*Received* 25 *November* 1994; *accepted* 10 *February* 1995)

Abstract—Kinetics and equilibria for the reaction between pyridine and cobalt(II) phthalocyanine [CoPc] (H_2Pc = phthalocyanine) in dimethyl sulphoxide (DMSO) were studied at 25°C. The complex, $CoPc(py)_2$, is formed in two consecutive steps. The formation of the mono-substituted CoPc(py)(DMSO) occurs first with a pseudo-first-order rate constant of $k_{1f} = 7.7 \pm 0.3 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}. The final disubstituted $CoPc(py)_2$ complex is formed with $k_{2f} = 1.1 \pm 0.1 \times 10^{-4}$ dm^3 mol^{-1} s^{-1}. The equilibrium constants were found to be $K_1 = 160 \pm 20$ dm^3 mol^{-1} and $K_2 = 15 \pm 3$ dm^3 mol^{-1} for the formation of CoPc(py)(DMSO) and $CoPc(py)_2$, respectively.

Transition metal phthalocyanine (MPc, Pc(−2) = phthalocyanine dianion) complexes are well known for their catalytic activity in a wide range of redox processes.[1] Cobalt(II) phthalocyanine (Co(II)Pc) complexes have in particular, been intensively studied with respect to their own electrochemical properties,[2–7] their ability to catalyse the reduction of oxygen[1] and their use as chemical electrocatalysts in the detection of small organic molecules such as thiols.[8,9] MPc complexes are known to bind reversibly a variety of molecules such as cyanide,[10] carbon monoxide,[11] pyridine (py)[12] and imidazole,[13] hence it is possible to measure both the equilibrium and kinetic constants in these complexes. CoPc complexes containing pyridine in axial positions have been reported.[1,14] Solid $CoPc(py)_2$ dissolves in weakly coordinating solvents, but the coordinated pyridine molecules are known to be readily lost in solution.[14] The loss of axial ligands results in a change in the site of oxidation in CoPc complexes. Oxidation in $CoPc(py)_2$ occurs at the central cobalt metal, the loss of the axial pyridine ligands results in oxidation occurring at the phthalocyanine ring.[2] It is thus of interest to study the kinetics and equilibria of pyridine binding to CoPc.

The kinetics and equilibria for the interaction between MPc complexes and pyridine have concentrated on the reactions of Fe^{II} Pc.[11,12] There have been no kinetic or equilibria data reported on the axial ligand exchange reactions of CoPc. Axial ligand substitution reactions in phthalocyanine complexes are dissociative and occur in a stepwise manner.[11–13,15–18] The replacement of the first axial ligand occurs much faster than that of the second.[10–12,18] The results of the stepwise substitution of axial dimethylsulphoxide (DMSO) ligands by pyridine in $CoPc(DMSO)_2$ (reactions 1 and 2) are reported.

$$\text{py} + [\text{CoPc(DMSO)}_2] \overset{K_1}{\rightleftharpoons} [\text{CoPc(DMSO)(py)}] + \text{DMSO} \quad (1)$$

$$\text{py} + [\text{CoPc(py)(DMSO)}] \overset{K_2}{\rightleftharpoons} [\text{CoPc(py)}_2] + \text{DMSO} \quad (2)$$

The data are compared with the kinetic and equilibria data for axial ligand exchange reactions in FePc complexes.

EXPERIMENTAL

Cobalt (II) phthalocyanine was obtained from Kodak and purified by a succession of organic solvents until it gave a satisfactory spectral analysis. $CoPc(py)_2$ was synthesized by Soxhlet extracting CoPc with pyridine, following the method of Cariati *et al.*[14] After evaporation of pyridine, the purple powder was washed with hexanes giving pure $CoPc(py)_2$. The complex was characterized by IR and UV/vis spectroscopy.

The axial binding of pyridine to CoPc was monitored spectrophotometrically at 657 and 672 nm where relatively large absorbance changes are observed on adding pyridine to DMSO solutions of CoPc. Accurate concentrations were determined from the Q band absorptions using $\varepsilon = 125\,000$ dm^3 mol^{-1} cm^{-1} for CoPc in DMSO.[19]

Equilibria and kinetic data were carried out at 25°C and monitored with the Beckman UV 5240 spectrophotometer. Typically a known volume of the DMSO solution of CoPc in the concentration range 5×10^{-6} to 1×10^{-5} mol dm^{-3} was added to a 1 cm path length cell. A known concentration of the pyridine solution in DMSO was then added to the cell and the absorption spectral changes were monitored. DMSO was dried in alumina and distilled before use.

RESULTS

Equilibrium studies

The solution of CoPc in DMSO is known to result in a six-coordinate complex,[19–21] hence the starting complex is expected to be the $CoPc(DMSO)_2$ species. When pyridine was added to solutions of CoPc in DMSO, the Q band centred at 657 nm first increased in intensity until a maximum was reached after which the Q band decreased in intensity and a new band centred at 672 nm was formed (Fig. 1). This new band was formed with an isosbestic point at 663 nm (Fig. 1b). Further addition of pyridine resulted only in the increase of the intensity of the 672 nm band, no further shifting in the wavelength of this band occurred. This observation suggests that the final spectra corresponds to the fully substituted, $CoPc(py)_2$. The final spectra in Fig. 1(b) is similar to the spectra obtained for the solution of $CoPc(py)_2$ in DMSO.

The increase in the intensity of the original Q band, centred at 657 nm on addition of pyridine to solutions of $CoPc(DMSO)_2$ is attributed to the formation of the monosubstituted, CoPc(DMSO)(py) species. It is not surprising that there was no noticeable wavelength change on substitution of the first DMSO ligand in $CoPc(DMSO)_2$. Substitutions of first ligands in MPc complexes are normally accompanied by a very small wavelength change, for example, the substitution of the first DMSO ligand for pyridine in $FePc(DMSO)_2$ caused only a 2 nm wavelength shift.[12] The spectral changes observed on addition of pyridine to DMSO solutions of CoPc are thus expected to be the result of the exchange of the DMSO ligands for pyridine first by reactions (1) and finally by reaction (2).

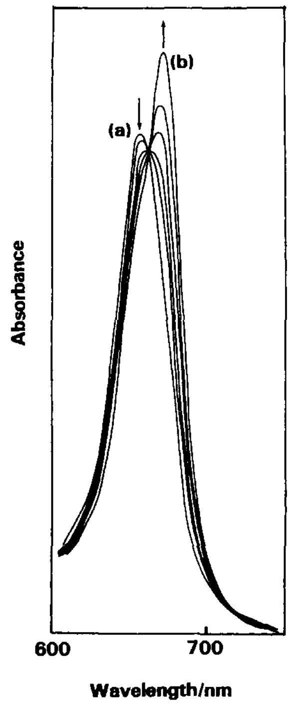

Fig. 1. Absorption spectral changes observed on addition of pyridine (0.05 mol dm^{-3}) to $[CoPc(DMSO)_2]$ (5.0×10^{-6} mol dm^{-3}) in DMSO. (a) Changes associated with the disappearance of the CoPc(DMSO)(py) complex. (b) Changes associated with the formation of the $CoPc(py)_2$ complex.

Figure 2(a) shows a plot of $\log[(A_{eq} - A_0)/(A_\infty - A_{eq})]$ vs log[py], eq. (3), for spectral changes occurring at 657 nm and corresponding to reaction (1).

$$\log[(A_{eq} - A_0)/(A_\infty - A_{eq})] = \log K + n \operatorname{Log}[py] \qquad (3)$$

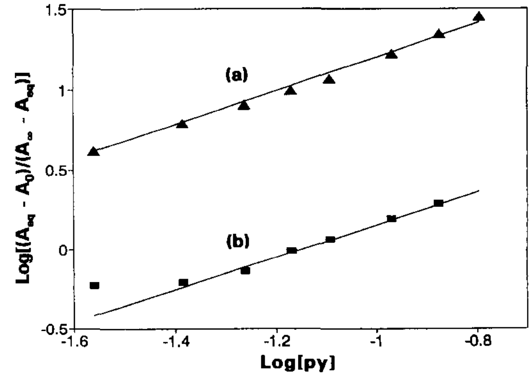

Fig. 2. Plots of $\log[(A_{eq} - A_0)/(A_\infty - A_{eq})]$ vs log[py], for the formation of (a) CoPc(DMSO)(py) and (b) $CoPc(py)_2$.

where A_{eq} is the equilibrium absorbance at 657 nm and A_0 is the absorbance before addition of pyridine. A_∞, the absorbance after complete replacement of the first axial DMSO, was estimated from the final absorbance at 657 nm. Figure 2(a) shows a linear plot with a slope of unity ($n = 1.04 \pm 0.05$). The linearity of the plot confirms the involvement of 1 mol of pyridine at this stage hence the stepwise coordination of pyridine to CoPc. Least square analysis gave an equilibrium constant for reaction 1, $K_1 = 160 \pm 20$ dm^3 mol^{-1}.

The coordination of the second pyridine ligand is associated with the spectral changes shown in Fig. 1(b) with a new Q band maxima at 672 nm. The equilibrium data for the formation of bis-coordinated $CoPc(py)_2$ by reaction (2) were analysed by eq. (3). In this case, A_{eq} is the equilibrium absorbance at 672 nm, A_0 is the absorbance at 672 nm corresponding to 0% formation of the $CoPc(py)_2$ and A_∞, the absorbance for the complete formation of the complex. Plots of $\log[(A_{eq}-A_0)/(A_\infty-A_{eq})]$ vs $\log[py]$ were again linear at high pyridine concentrations (Fig. 2b). Deviations from linearity that were evident at low pyridine concentrations suggest that there is a considerable presence of the monosubstituted CoPc(DMSO)(py) complex at these concentrations. Figure 2(b) shows a linear plot with a unit slope at high pyridine concentrations, again confirming the stepwise nature of the coordination of pyridine to CoPc. An equilibrium constant, $K_2 = 15 \pm 3$ dm^3 mol^{-1} for the formation of $CoPc(py)_2$ by reaction (2), was obtained from least square analysis of the data shown in Fig. 2(b).

Kinetic studies

In agreement with the equilibrium data observations discussed above, the time dependence of the absorbance of DMSO solutions of CoPc in the presence of an excess pyridine confirms a stepwise nature of the coordination of pyridine to $CoPc(DMSO)_2$. The time scales for the coordination of the first and second pyridine are quite different, interference could thus be minimized by an appropriate choice of time. The large excess of pyridine (typically 0.02–0.2 mol dm^{-3}) compared to $CoPc(DMSO)_2$ (5×10^{-6} to 1×10^{-5} mol dm^{-3}) ensured that both the first and the second coordination of the pyridine ligand conformed to pseudo-first-order rate law.

Axial ligand substitution reactions in metallophthalocyanines are dissociative with the formation of a highly reactive five-coordinate intermediate.[11,12] The overall axial ligand substitution in CoPc may thus be represented by reactions (4) and (5) for the first pyridine substitution and (6) and (7) for the second pyridine substitution.

$$[CoPc(DMSO)_2] \underset{k_{+DMSO}}{\overset{k_{-DMSO}}{\rightleftharpoons}} [CoPc(DMSO)] + DMSO \tag{4}$$

$$py + [CoPc(DMSO)] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [CoPc(DMSO)(py)] \tag{5}$$

$$[CoPc(DMSO)(py)] \underset{k_{+DMSO}}{\overset{k_{-DMSO}}{\rightleftharpoons}} [CoPc(py)] + DMSO \tag{6}$$

$$py + [CoPc(py)] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [CoPc(py)_2] \tag{7}$$

It may readily be shown that the observed rate constant, k_{obs}, takes the general form $k_{obs} = k_f[py] + k_r$.[11,12] For the first (reactions 4 and 5) and second (reactions 6 and 7) pyridine substitutions in CoPc, k_{obs} is given by eqs (8) and (9), respectively.

$$k_{obs}^1 = k_{1f}[py] + k_{1r} \tag{8}$$

$$k_{obs}^2 = k_{2f}[py] + k_{2r} \tag{9}$$

where k_{1f} and k_{2f} are the rate constants of the forward reactions and k_{1r} and k_{2r} are the rate constants for the reverse reactions. The forward rate constant, k_{1f}, is given by $k_{-DMSO}k_1/k_{+DMSO}[DMSO]$ and k_{2f} by $k_{-DMSO}k_2/k_{+DMSO}[DMSO]$. Figure 3 shows that k_{obs}^1 and k_{obs}^2 are linearly dependent on the pyridine concentration with small but definite intercepts. Least square analysis gave $k_{1f} = 7.7 \pm 0.3 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} and $k_{2f} = 1.1 \pm 0.1 \times 10^{-4}$ dm^3 mol^{-1} s^{-1}. The rate constants for the reverse reactions were estimated from the intercepts to be $k_{1r} = 5.0 \times 10^{-5}$ s^{-1} and $k_{2r} = 7.3 \times 10^{-6}$ s^{-1}. Using these values of rate constants, the value of the equilibrium constant for the first pyridine coordination, reaction (1), is estimated to be $K_1 = 154$ dm^3 mol^{-1} from the relationship $K_1 = k_{1f}/k_{1r}$. Similarly for the coordination of the second pyridine ligand by reaction (2), K_2 is estimated to be 15 dm^3 mol^{-1} ($K_2 = k_{2f}/k_{2r}$). Both values of the calculated equilibrium constants are in excellent agreement with the experimental values, within experimental errors.

DISCUSSION

The equilibrium constants reported here for the coordination of pyridine to $CoPc(DMSO)_2$ are lower than the corresponding equilibrium constants

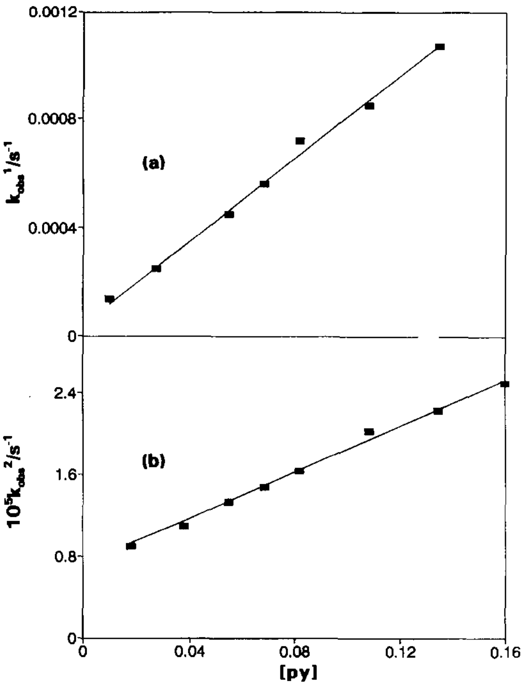

Fig. 3. Observed rate constants for (a) the first pyridine uptake, $k_{obs}^1(s^{-1})$ and (b) the second pyridine uptake, $k_{obs}^2(s^{-1})$.

for the reaction of pyridine with $FePc(DMSO)_2$ (Table 1). For example the equilibrium constant for the formation of FePc(DMSO)(py) is 2500 times higher than that for the formation of CoPc (DMSO)(py). As expected for axial ligand exchange reactions in metallophthalocyanines, the equilibrium constant K_2 for the coordination of the second pyridine molecule to CoPc(DMSO)(py) is much smaller than the equilibrium constant for the coordination of the first pyridine molecule to $CoPc(DMSO)_2$, K_1. It is expected that DMSO is bonded to cobalt via the sulphur in both CoPc(DMSO)(py) and $CoPc(DMSO)_2$, hence DMSO behaves as a π acceptor. The relative magnitudes of K_1 and K_2 can be explained in terms of the extra stability gained by DMSO through π-back bonding in CoPc(DMSO)(py). This extra stability is lost in $CoPc(DMSO)_2$ since π acceptor ligands destabilize each other when located in *trans* positions. The fact that the formation FePc (DMSO)(py) from $FePc(DMSO)_2$ is more favoured than the formation of CoPc(DMSO)(py) from $CoPc(DMSO)_2$ may be due to either a smaller Fe—DMSO bond energy in $FePc(DMSO)_2$ as compared to Co—DMSO bond energy in CoPc $(DMSO)_2$, or to a larger Fe—py bond energy in FePc(DMSO)(py) as compared to Co—py bond energy in CoPc(DMSO)(py). Similarly for $CoPc(py)_2$ and $FePc(py)_2$, the lower equilibrium constant for the formation of the former could be due to a larger metal—DMSO bond energy or a smaller metal—py bond energy. The observation that the pyridine ligands in $CoPc(py)_2$ are readily lost in some solutions[10] suggests that the Co—py bond is relatively weak.

The rate constants for the formation of CoPc (DMSO)(py), k_{1f} and $CoPc(py)_2$, k_{2f} are much smaller than the corresponding rate constants for the formation of FePc(DMSO)(py) and $FePc(py)_2$. It is currently accepted that the mechanism for axial ligand substitutions in porphyrins and phthalocyanines is dissociative with the formation of a five-coordinate intermediate.[12,18] This intermediate is expected to be highly reactive. Five-coordinate CoPc(L) complexes containing a base molecule on the axial position are stable,[14] and solid CoPc(py) has been synthesized. The coordination of pyridine to CoPc(py) by eq. (7) will thus be expected to be less favoured, hence give a smaller k_{2f} than the coordination of pyridine to the more reactive FePc(py).

If we assume that the rate constants are also a measure of the ease of dissociation of the bond between Co and the leaving ligand, then the fact that k_{2f} is approximately 16 times larger than k_{2r}

Table 1. Equilibrium and kinetic data for the formation MPc(DMSO)(py) and $MPc(py)_2$ by the reaction of pyridine with $MPc(DMSO)_2$ complexes[a]

Complex formed	K ($dm^3\ mol^{-1}$)	k_f ($dm^3\ mol^{-1}\ s^{-1}$)	$k_r(s^{-1})$	Ref.[b]
FePc(DMSO)(py)	4.0×10^5	1.5×10^4	4.0×10^{-2}	11
CoPc(DMSO)(py)	1.6×10^2	7.7×10^{-3}	5.0×10^{-5}	tw
$FePc(py)_2$	3.0×10^2	36	0.15	11
$CoPc(py)_2$	15	1.1×10^{-4}	7.3×10^{-6}	tw

[a] Equilibrium constant $K = K_1$ or K_2 for the first and second ligand substitutions, respectively. $k_f = k_{1f}$ or k_{2f} and $k_r = k_{1r}$ or k_{2r} as defined in the text.
[b] tw = this work.

could be attributed to the slightly easier dissociation of the DMSO ligand *trans* to pyridine as compared to the dissociation of pyridine *trans* to another pyridine molecule. For the coordination of pyridine to $FePc(DMSO)_2$, k_{2f} is approximately 250 times larger than k_{2r} (Table 1). As discussed above, DMSO gains stability through π-back bonding and since there is more electron density on the Co^{II} ion than on the Fe^{II} ion, the dissociation of DMSO from FePc(DMSO)(py) is expected to be easier than from CoPc(DMSO)(py). Similarly for the coordination of the first ligand, k_{1f} for the formation FePc(DMSO)(py) is approximately 10^5 times larger than k_{1r}. For the formation of CoPc(DMSO)(py), k_{1f} is only 150 times larger than k_{1r}.

Acknowledgements—This work was supported by Rhodes University and by the Foundation for Research Development in South Africa.

REFERENCES

1. J. H. Zagal, *Coord. Chem. Rev.* 1992, **119**, 93.
2. T. Nyokong, Z. Gasyna and M. J. Stillman, *ACS Symp. Ser.* 1986, **321**, 309.
3. P. A. Bernstein and A. B. P. Lever, *Inorg. Chem.* 1990, **29**, 608.
4. M. N. Golovin, P. Seymour, K. Jayaraj, Y. S. Fu and A. B. P. Lever, *Inorg. Chem.* 1990, **29**, 1719.
5. G. C. S. Collins and D. J. Schffrin, *J. Electroanal. Chem.* 1982, **139**, 335.
6. A. B. P. Lever and J. P. Wilshire, *Can. J. Chem.* 1976, **54**, 2514.
7. L. D. Rollman and R. T. Iwamoto, *J. Am. Chem. Soc.* 1968, **90**, 1455.
8. X. Huang and W. Th. Kok, *Anal. Chim. Acta* 1993, **273**, 245.
9. T. J. O'Shea and S. M. Lunte, *Anal. Chem.* 1994, **66**, 307.
10. T. Nyokong and J. Guthrie-Stratcham, *Inorg. Chim. Acta* 1993, **208**, 239.
11. G. Pennesi, C. Ercolani, G. Rossi, P. Ascenzi, M. Brunori and F. Monacelli, *J. Chem. Soc. Dalton Trans.* 1985, 1113.
12. G. Pennesi, C. Ercolani, P. Ascenzi, M. Brunori and F. Monacelli, *J. Chem. Soc. Dalton Trans.* 1985, 1107.
13. J. G. Jones and M. V. Twigg, *Inorg. Chem.* 1969, **8**, 2120.
14. F. Cariati, D. Galizziori, F. Marazzorni and C. Busetto, *J. Chem. Soc. Dalton Trans.* 1975, 556.
15. D. A. Sweigart, *J. Chem. Soc. Dalton Trans.* 1976, 1476.
16. D. V. Stynes, *Inorg. Chem.* 1977, 1170.
17. J. Martinsen, M. Miller, D. Trojan and D. A. Sweigart, *Inorg. Chem.* 1980, **19**, 2162.
18. T. Nyokong, *J. Chem. Soc. Dalton Trans.* 1993, 3601.
19. M. J. Stillman and T. Nyokong, in *Phthalocyanines: Properties and Applications* (Edited by C. C. Leznoff and A. B. P. Lever). VCH, New York (1989).
20. M. J. Stillman and A. J. Thomson, *J. Chem. Soc. Faraday Trans.* 2 1974, **70**, 790.
21. M. J. Stillman and A. J. Thomson, *J. Chem. Soc. Faraday Trans.* 2 1974, **70**, 805.