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Replacement of Dimethyl Sulfoxide by Imidazole at the Axial Sites of Ferrous Phthalocyanine. II.

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Received December 15, 1969

Investigations on the replacement of d.m.s.o by Imidazole at a Ferrous phthalocyanine centre have been extended over a six-thousand fold range of Imidazole concentration by using the stopped-flow method. The observed rate constant is still directly proportional to Imidazole concentration even at the highest (1.45 M) *Imidazole concentrations, so that no experimental support for a limiting SN1 mechanism has been obtained. Reasons are presented to show that such a mechanism is not ruled out, but experimental support must now be sought in other solvent/nucleophile combinations with ferrous phthalocyanine.*

Introduction

Ferrous phthalocyanine (FePc) forms a complex with Imidazole of formula FePc(Imidazole)$_2$,[1] which is diamagnetic[2] and therefore contains low-spin Fe^{II}, a result confirmed by Mössbauer spectroscopy.[2,3] It also dissolves in dimethylsulfoxide (d.m.s.o.) to form a blue solution which we have shown to be diamagnetic,[4,5] and which therefore presumably contains low spin Fe^{II} in an octahedral field, leading to the formula FePc(d.m.s.o.)$_2$ for the species in solution, with d.m.s.o. molecules acting as axial ligands, the phthalocyanine ring acting as a tetradentate equatorial ligand. This blue solution gives the spectrum of FePc(Imidazole)$_2$ when a solution of imidazole in d.m.s.o. is added to it, and the change occurs at an easily measurable rate,[4,5] which is hardly surprising since the transformation is from one low-spin d^6 system to another. Dale[6] made a spectrophotometric study of equilibria involved in the replacement of d.m.s.o. by imidazole, and found the results best explained by a two-step equilibrium.

$$\text{FcPc(d.m.s.o.)}_2+\text{Imidazole} \overset{K_1}{\rightleftharpoons} \\ \text{FcPc(Imidazolc)(d.m.s.o)}+\text{d.m.s.o.}$$

$$\text{FePs(d.m.s.o.)(Imidazolc)}+\text{Imidazole} \overset{K_2}{\rightleftharpoons} \\ \text{FcPc(Imidazole)}_2+\text{d.m.s.o.}$$

We ourselves studied[4,5] the rate of formation of the complex FePc(Imidazole)$_2$ and found that, using $\sim 10^{-5}$ FePc(d.m.s.o)$_2$ solution and Imidazole concentrations of from 10^{-4} -10^{-2} *M*, the formation rate obeyed the law:

$$\frac{\text{d}}{\text{dt}}[\text{FePc(Imidazole)}_2] = k[\text{FePc(d.m.s.o.)}_2][\text{Imidazole}]$$

Dale's equilibria and this rate-law were reconciled[4,5] by assigning the role of stationary-state-intermediate to the complex FePc(Imidazole)(d.m.s.o.) and making the formation of this complex the rate-determining step. This step, the replacement of one neutral molecule by another, could occur via an associative mechanism involving a seven-coordinate transition state (S$_N$2 process). Under the conditions of our experiments, with d.m.s.o. present as the solvent and imidazole always present in excess relative to ferrous phthalocyanine, this mechanism would result in a linear plot of k_{obs} against [Imidazole], unless some medium effect due to imidazole were to intervene at higher imidazole concentrations. However, a dissociative mechanism in which departure of a coordinated d.m.s.o. molecule preceds co-ordination of imidazole can also account for the observed second-order kinetics, provided certain conditions are met.

$$\text{FePc(d.m.s.o.)}_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{FePc(d.m.s.o.)}+\text{d.m.s.o.}$$

$$\text{Imidazole}+\text{FcPc(d.m.s.o.)} \xrightarrow{k_2} \text{FePc(d.m.s.o.)(Imidazole)}$$

If the five co-ordinate intermediate, FePc(d.m.s.o.), is present in a very small concentration the steady state treatment can be applied, giving the rate-law;

$$\text{d[FePc(d.m.s.o.)(Imidazole]/dt} = \\ \frac{k_1k_2[\text{FePc(d.m.s.o.)}_2][\text{Imidazole}]}{k_{-1}[\text{d.m.s.o.}]+k_2[\text{Imidazole}]}$$

If $k_{-1}[\text{d.m.s.o.}] \gg k_2[\text{Imidazole}]$ then this reduces to:

$$\text{d[FePc(d.m.s.o.)(Imidazole)]/dt} = \\ \frac{k_1k_2[\text{FePc(d.m.s.o.)}_2][\text{Imidazole}]}{k_{-1}[\text{d.m.s.o.}]}$$

which is a second-order rate law, as d.m.s.o. is the solvent. The observed rate-constant will be k_1k_2/k_{-1}-

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(1) Von H. Giesemann, *J. Prakt. Chem.*, *4*, 169 (1956).
(2) A. Hudson and H. S. Whitfield, *Inorg. Chem.*, 6, 1120 (1967).
(3) B. W. Dale, R. J. P. Williams, P. R. Edwards, and C. E. Johnson, *Trans. Far. Soc.*, *64*, 620 (1968).
(4) J. G. Jones and M. V. Twigg, *Inorg. Nucl. Chem. Letters*, *5*, 333 (1969).
(5) J. G. Jones and M. V. Twigg, *Inorg. Chem.*, *8*, 2021 (1969).
(6) B. W. Dale, D. Phil. Thesis, Oxford (1966).

[d.m.s.o.]. In contrast to the associative mechanism, when [Imidazole] is increased a condition may be reached where k_{-1}[d.m.s.o.] is no longer greater than k_2[Imidazole], and when this occurs a plot of k_{obs} against [Imidazole] will exhibit curvature toward the imidazole concentration axis. As an extreme case the condition k_2[Imidazole]$\gg k_{-1}$[d.m.s.o.] may be reached, and then the rate will no longer depend on [Imidazole], but only on the value of k_1. This is known as a « limiting S_N1 process ». One relevant example of this behaviour occurs in the substitution of water by thiocyanate at a Co^{III} haematoporphyrin centre.[7]

We have tried to detect such rate plot curvature in our system by using stopped-flow techniques at 30°C which enable us to use much higher imidazole concentrations (1.45 *M*) than those used ($10^{-4}-10^{-2}M$) in previous[4,5] investigations.

In ionic systems there is another mechanism which can produce a plot of k_{obs} versus [entering group] which is curved towards the concentration axis. This involves the formation of an ion-pair encounter complex and a subsequent rate-determining ion/ion or ion/solvent[8] interchange. Our reactant and solvent are neutral, so we will discuss this possibility no further; one could speculate on prior formation of a charge-transfer-complex between imidazole and FePc(d.m.s.o.)$_2$, but we have no evidence of this.

Experimental Section

A detailed description of material preparation and solvent purification has already been given.[5] The stopped-flow apparatus used was an all-glass one evolved by Professor Caldin and his collaborators at this University. In this instrument the two driving syringes and the stopping syringe were at room temperature, but the solutions were held in glass coils before and after entering the quartz two-jet mixer. Mixer and storage coils were all immersed in a thermostat-bath controlled to better than 0.03°C. The driving syringes were driven pneumatically, and to obtain any one kinetic trace less than 1 ml of each reactant solution was used. A Bausch and Lomb 53-86-01 monochrometer was used, and the photomultiplier was linked via a cathode-follower and amplifier to a Consolidated Electrodynamics 5-127 recording oscillograph to follow changes in solution transmittance. The wavelength chosen to follow the reaction was 425 nm an absorption peak characteristic of the FePc(Imidazole)$_2$ species and not of the FePc(d.m.s.o.)$_2$ species. The concentration of FePc(d.m.s.o.)$_2$ solution was adjusted empirically so that the change in optical density was small (0.03 absorbance units), thus making measured changes in transmittance directly proportional to optical density changes. In all the kinetic experiments [FePc(d.m.s.o.)$_2$] $\sim 10^{-5}$ *M*, and the Imidazole is present in a thousand to a hundred-thousand-fold excess. Under such conditions transformation to FePc(Imidazole)$_2$ during the course of the reaction can be considered complete.

Results and Discussion

At all imidazole concentrations the rate of formation of FePc(Imidazole)$_2$ was accurately first order; a sample plot is shown in Figure 1. A plot of observed first-order rate constants against Imidazole concentration (Figure 2) exhibits no curvature towards the concentration axis even at the highest Imidazole concentrations employed. So we have obtained no positive evidence for a « limiting S_N1 process in the displacement of d.m.s.o. by imidazole at the low-spin Fe^{II} centre of ferrous phthalocyanine. Our earlier results[5] and the present ones are conveniently combined in Figure 3, where a plot of log k_{obs} against log[Imidazole] is of unit slope, confirming the unit order of formation of FePc(Imidazole)$_2$ with respect to Imidazole.

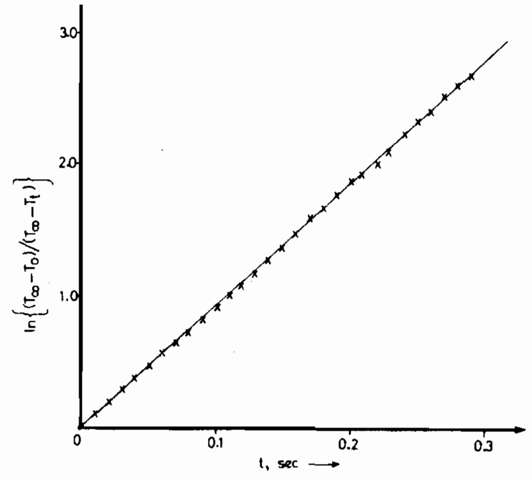

Figure 1. Stopped-flow first order plot. Wavelength = 425 nm, temperature = 30±0.03°C, [imidazole] = 1.435 *M*.

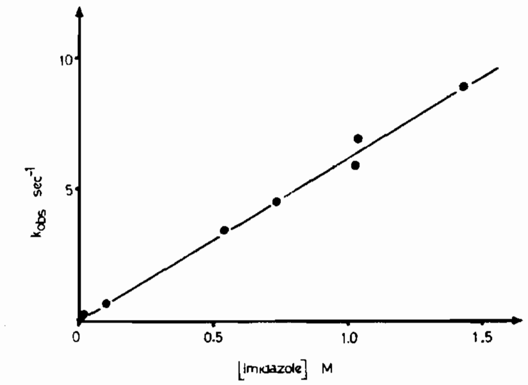

Figure 2. Variation of observed first order rate constants with imidazole concentration.

It is tempting to interpret these results as being in favour of an associative mechanism especially as

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(8) C. L. Langford, *J. Chem. Ed.*, *46*, 557 (1969).

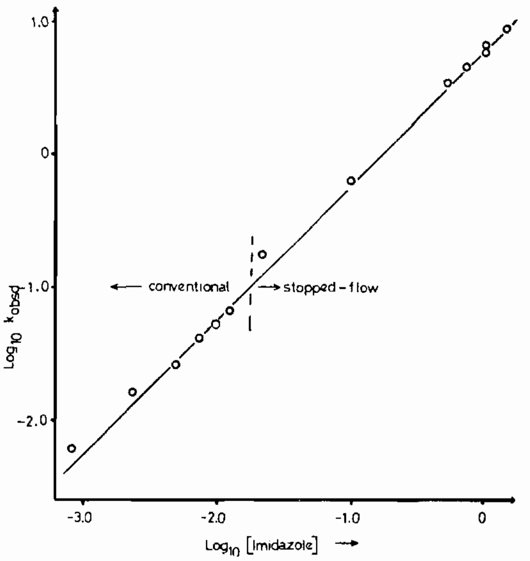

Figure 3. Extended range plot of $\log_{10} k_{obsd}$ against $\log_{10}$-[imidazole].

there is already some evidence in favour of associative mechanisms applying at other low-spin iron(II) centres.[8,9,10] However, closer examination of our results indicates that they do not rule-out a dissociative pathway. At the highest imidazole concentration, [d.m.s.o.]$\sim$10[Imidazole]; if $k_{-1} = 10k_2$, then k_{-1}[d.m.s.o.]$\simeq 100k_2$[Imidazole], which is quite sufficient for a second order rate law to be observed. In systems where a limiting S_N1 mechanism with a 5-co-ordinate intermediate has been observed for a d^6 system a ten-fold discrimination between nucleophiles is quite common. Thus in the system investigated by Wilmarth and his co-workers,[11] the intermediate $Co(CN)_5^{2-}$ is six times as reactive toward pyridine as toward hydrazine, and six times as reactive towards hydrazine as towards water.* In the $Co(SO_3)(NH_3)_4X$ system reported by Halpern and co-workers,[12] the intermediate $[Co^{III})(NH_3)_4 . SO_3]^+$ discriminates more selectively; with ammonia as entering group and different anions as leaving groups, the intermediate prefers the anions ten to a hundred times as much as ammonia.

Since ferrous phthalocyanine is not soluble enough for $k_{\text{solvent exchange}}(= k_{-1}$[d.m.s.o.]) to be determined directly by the n.m.r. method, we are currently attacking the problem by using more reactive nucleophiles, to make k_2[Nucleophile] larger and closer to k_{-1}[d.m.s.o.]. Another approach which promises well is to replace one axial ligand by another in a weakly co-ordinating solvent such as acetone, which has the strength of Halpern's system in that entering and leaving group concentrations can be independently varied. Extrapolation of results obtained in these systems to the ferrous phthalocyanine-imidazole-d.m.s.o. system is likely to be mistaken, for changes in solvents have effects on substitution reactions which can go beyond altering exchange rates at metal centres.[13]

Acknowledgments. We gratefully acknowledge support from the Science Research Council, England, and the use of Professor E. F. Caldin's facilities.

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(*) If 55.5 is taken as the molarity of water; it may not be kinetically correct (8) to take this bulk figure with water as solvent, but rather some number between 5 and 10, the number of water molecules in the second co-ordination sphere. Thus actually the intermediate may be about as reactive toard water as it is toward hydrazine.

(13) H. P. Bennetto and E. F. Caldin, *J. Chem. Soc.*, (D), 599 (1969).