Axial Ligand Dissociation of Phthalocyaninatoiron(II) Adducts; Further Evidence for a Dissociative Mechanism of Substitution

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The kinetics of reaction of [Fe(pc)L_2] (pc = phthalocyaninate, L = imidazole or 4-aminopyridine) with dimethyl sulphoxide have been studied over the range 20—45 °C. The rate-determining step is loss of the first ligand. Dilution with acetone or benzene enhances the observed first-order rate constant such that it is proportional to the reciprocal of the concentration of dmso over the range 1—14 mol dm^{-3}. This is shown to be consistent with a *D* mechanism and some rate constants for the individual steps are derived. A comparison of *trans* effects at the phthalocyaninatoiron(II) centre is made.

We have studied the reactions of phthalocyaninatoiron(II) [Fe(pc)] in dimethyl sulphoxide (dmso) with a variety of bases (L = imidazoles,[1] pyridines,[1,2] and phosphines[2]) to form [Fe(pc)L_2] species which are six-co-ordinate with ligands L occupying the axial sites.[3] The observed kinetics are first order in complex and entering-ligand concentrations; with pyridines and phosphines there is an additional term which can be identified with the reverse reaction, replacement of base by dmso. In all cases, starting with [Fe(pc)(dmso)$_2$], the rate-determining step studied is the first; the reaction [Fe(pc)L(dmso)] $\longrightarrow$ [Fe(pc)L_2] is faster and, under the reaction conditions, effectively irreversible. Because the leaving ligand is present in such large concentration, being the solvent, one cannot decide between an associative mechanism, or an I_d mechanism, or a *D* mechanism with k_{-1}[dmso] $>$ k_2[L], k_{-1} and k_2 being the rate constants for attack of dmso and base respectively on the five-co-ordinate stationary-state intermediate. Mixtures of inert solvents so far chosen to mix with dmso either change the chemistry of the system or cause [Fe(pc)] to precipitate from dmso solution.

In this paper simple concentration-jump techniques[4] are used to study the formation of [Fe(pc)(dmso)$_2$] from [Fe(pc)L_2]. Some of the solubility difficulties already described do not exist in this system and more information can be obtained.

EXPERIMENTAL

Preparation of Solid Adducts.—Finely ground imidazole (12.0 g) and [Fe(pc)] (2.0 g) were heated under nitrogen for 2 h. After cooling the green solid was broken up, ground, stirred with ethanol (50 cm^3), filtered off, and washed twice with ethanol (30 cm^3). The dark purple solid was then dried *in vacuo* at room temperature, yield 2.2 g (89%) (Found: C, 64.3; H, 3.3; Fe, 8.2; N, 24.3. Calc. for

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[1] J. G. Jones and M. V. Twigg, *Inorg. Chem.*, 1969, **8**, 2120; *Inorg. Chim. Acta*, 1975, **12**, L15; H. P. Bennetto, J. G. Jones, and M. V. Twigg, *ibid.*, 1970, **4**, 80.

[2] B. W. Adams, D. J. Farrington, J. G. Jones, and M. V. Twigg, International Co-ordination Chemistry Conference, Dublin, 1974, p. 345; D. J. Farrington, Ph.D. Thesis, New University of Ulster, 1972.

[3] T. Kobayashi, F. Kurokawa, T. Ashida, N. Uyeda, and E. Suito, *Chem. Comm.*, 1971, 1631.

[4] D. Y. Chao and Z. A. Schelly, *J. Phys. Chem.*, 1975, **79**, 2734.

$C_{38}H_{24}FeN_{12}$: C, 64.8; H, 3.4; Fe, 7.9; N, 23.9%). The analogous bis(4-aminopyridine), bis(4-methylpyridine), and bis(pyridine) complexes were similarly prepared and satisfactory analyses obtained. All the adducts were found to be diamagnetic by the Gouy method.

Kinetic Procedures.—A small measured volume (0.05 or 0.1 cm^3) of a relatively concentrated (*ca.* 1×10^{-3} mol dm^{-3}) solution of $[Fe(pc)L_2]$ in dmso was added to a measured volume (2.5 or 3.0 cm^3) of solvent contained in a 10-mm quartz cell. The cell had previously been equilibrated in the thermostatted (±0.1 °C) cell holder of either a Beckman DB or a Perkin-Elmer–Hitachi 124 spectrophotometer. The contents of the cell were then thoroughly mixed by rapid shaking and the absorbance at a wavelength characteristic of the bis(base) complex was then followed with respect to time on a chart recorder. Observed absorbance changes were *ca.* 0.25 units. Excellent exponential decays in optical density were observed and plots of $\ln(A_t - A_\infty)$ against time were linear up to 85% completion of reaction. The rate constants reported were obtained graphically from such plots.

Solvents.—Dimethyl sulphoxide (B.D.H.) was distilled at *ca.* 1 mmHg * pressure from calcium hydride, under an atmosphere of dry nitrogen. Benzene and acetone were AnalaR, and used as received.

RESULTS AND DISCUSSION

The solid complexes $[Fe(pc)L_2]$ dissolve readily in dmso, acetone, or benzene {in contrast to [Fe(pc)] itself}, forming green solutions with visible spectra characteristic of bis(base) adducts (Table 1). When *ca.* 0.001 mol dm^{-3} solution of adduct was diluted 50—100-fold

$$[Fe(pc)L_2] + 2dmso \longrightarrow [Fe(pc)(dmso)_2] + 2L$$

with dmso a blue solution was obtained which had the spectrum of [Fe(pc)(dmso)]. These observations, and the product, agree with previously determined [5] stability constants for the reactions (1) and (2) where $K_1 =$ [Fe(pc)L(dmso)]/$[Fe(pc)(dmso)_2]$[L] and $K_2 =$ $[Fe(pc)L_2]$/[Fe(pc)L(dmso)][L]. Solvent is omitted from K_1 and K_2, as in ref. 5.

TABLE 1

Visible absorption spectra of $[Fe(pc)L_2]$ complexes in dmso

L	$\lambda_{max.}$/nm ($\log_{10}\epsilon$)					
dmso	653	(4.86)	594	(4.38)		
imH	662	(5.08)	598	(4.49)	426	(4.30)
$4NH_2$-py	655	(5.09)	593	(4.50)	425	(4.30)
py	655	(5.07)	593	(4.49)	413	(4.32)
2Me-imH	662	(50.1)	598	(4.44)	426	(4.22)

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

$$[Fe(pc)L(dmso)] + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Fe(pc)L_2] + dmso \quad (2)$$

Reactions of all but the most stable complexes were too fast to follow by conventional means. Those of imidazole (imH) and 4-aminopyridine (K_1 and K_2 each greater than 5×10^3 dm^3 mol^{-1} at 25 °C) reacted at convenient rates and spectra scanned repetitively over the range 400—700 nm revealed no evidence of any intermediate product or long-lived intermediate. Clean isosbestic points at 595, 607, and 678 nm were observed for the transformation of $[Fe(pc)(imH)_2]$ to $[Fe(pc)(dmso)_2]$. Table 2 shows the first-order rate constants determined over the range 20—45 °C.

TABLE 2

First-order rate constants for reactions of $[Fe(pc)L_2]$ in dmso at various temperatures

L	θ_c/°C	$k_{obs.}/s^{-1}$	$k_{calc.}$*
imH	20.0	3.66×10^{-4}	4.01×10^{-4}
$4NH_2$-py	20.0	1.49×10^{-3}	1.49×10^{-3}
imH	25.0	9.03×10^{-4}	8.54×10^{-4}
imH	25.0	8.30×10^{-4}	8.54×10^{-4}
$4NH_2$-py	25.0	3.15×10^{-3}	3.31×10^{-3}
$4NH_2$-py	24.0	0.15×10^{-3}	3.31×10^{-3}
imH	30.0	1.83×10^{-3}	1.78×10^{-3}
imH	30.0	1.83×10^{-3}	1.78×10^{-3}
$4NH_2$-py	30.0	7.18×10^{-3}	7.15×10^{-3}
imH	35.0	3.66×10^{-3}	3.60×10^{-3}
imH	35.0	3.80×10^{-3}	3.60×10^{-3}
$4NH_2$-py	35.0	1.59×10^{-2}	1.51×10^{-3}
$4NH_2$-py	35.0	1.51×10^{-2}	1.51×10^{-3}
$4NH_2$-py	35.0	1.54×10^{-2}	1.51×10^{-3}
$4NH_2$-py	35.0	1.56×10^{-2}	1.51×10^{-3}
imH	40.0	7.35×10^{-3}	7.15×10^{-3}
imH	40.0	7.00×10^{-3}	7.15×10^{-3}
imH	40.0	7.40×10^{-3}	7.15×10^{-3}
$4NH_2$-py	40.0	3.03×10^{-2}	3.10×10^{-2}
$4NH_2$-py	40.0	2.94×10^{-3}	3.10×10^{-2}
imH	45.0	1.33×10^{-2}	1.39×10^{-2}
imH	45.0	1.36×10^{-2}	1.39×10^{-2}
imH	45.0	1.33×10^{-2}	1.39×10^{-2}

* Calculated from derived activation parameters: L = imH, $\Delta H^‡ = 25.8 \pm 0.4$ kcal mol^{-1}, $\Delta S^‡ = 14.0 \pm 1.5$ cal K^{-1} mol^{-1}; L = $4NH_2$-py, $\Delta H^‡ = 27.1 \pm 0.4$ kcal mol^{-1}, $\Delta S^‡ = 20.9 \pm 1.3$ cal K^{-1} mol^{-1}. Quoted errors are standard deviations corrected for the appropriate number of degrees of freedom such that doubling them produces 95% confidence limits.

The reactivity of the 4-aminopyridine complex is some three times that of the imidazole complex, due to a more favourable entropy of activation [$T\Delta(\Delta S^‡)$ 2.1 kcal mol^{-1} at 27 °C] which more than counteracts the greater activation enthalpy of the 4-aminopyridine complex [$\Delta(\Delta H^‡)$ 1.3 kcal mol^{-1}]. The large positive values of $\Delta S^‡$ (14 cal K^{-1} mol^{-1} for imidazole and 21 cal K^{-1} mol^{-1} for 4-aminopyridine) provide support for the *D* mechanism suggested by the experiments of Stynes and James [6] and Sweigart.[7]

One question which arises is to which rate process do our observed constants apply, to the reverse of equation (2) or the reverse of equation (1)? It is most likely that the reverse of equation (2) describes the rate-determining step. First, let us consider that the reverse of equation (1) describes the rate-determining step. Using the terminology of our earlier paper [5] for imidazole, $k_1/k_{-1} = K_1' = K_1[\text{dmso}] = [Fe(pc)L(dmso)][dmso]/[Fe(pc)(dmso)_2][L] = 14.1 \times (10 \pm 4) \times 10^4$ (at 25 °C) $= (1.4 \pm 0.5) \times 10^6$. We have already measured [1] k_1, and since $k_1 = 3.08 \pm 0.14$ dm^3 mol^{-1} s^{-1} we deduce $k_{-1} =$

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 cal = 4.184 J.

[5] J. G. Jones and M. V. Twigg, *Inorg. Chim. Acta*, 1974, **10**, 103.

[6] D. V. Stynes and B. R. James, *J. Amer. Chem. Soc.*, 1974, **96**, 2733.

[7] D. A. Sweigart, *J.C.S. Dalton*, 1976, 1476.

$(2.3 \pm 0.7) \times 10^{-6}$ s^{-1}. This is not in agreement with the measured value at 25 °C of 8.5×10^{-4} s^{-1}. Turning now to the reverse of equation (2), $k_2/k_{-2} = K_2' = K_2[\text{dmso}] = [\text{Fe(pc)L}_2][\text{dmso}]/[\text{Fe(pc)L(dmso)}][\text{L}] = 14.1 \times (6.3 \pm 2) \times 10^3 = (8.9 \pm 2.8) \times 10^4$. We do not know k_2 for this system, but if we put $k_{\text{obs.}} = k_{-2} = 8.5 \times 10^{-4}$ we can calculate $k_2 = 76$ dm^3 mol^{-1} s^{-1}. This is in agreement with what is known about this system,[1] namely that k_2 must be more than ten times greater than k_1 (ref. 8).* For the present experiments $k_{\text{obs.}}$ is identified with k_{-2}.

Stynes and James [6] found that reaction (3) in toluene

$$[\text{Fe(pc)(imH)}_2] + \text{CO} \rightleftharpoons [\text{Fe(pc)(imH)(CO)}] + \text{imH} \quad (3)$$

had a rate independent of [CO], and the rate-determining step is therefore represented by k_a in equation (4).

$$[\text{Fe(pc)(imH)}_2] \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} [\text{Fe(pc)(imH)}] + \text{imH} \quad (4)$$

$$[\text{Fe(pc)(imH)}] + \text{CO} \xrightarrow{k_b} [\text{Fe(pc)(imH)(CO)}] \quad (5)$$

The activation parameters ($\Delta H^\ddagger$ *ca.* 27 kcal mol^{-1}, $\Delta S^\ddagger$ *ca.* 15 cal K^{-1} mol^{-1}) are very similar to those we obtain which lends support to the suggestion that our rate-determining step is loss of imidazole from [Fe(pc)(imH)$_2$].

We wished to test this further, and accordingly studied the reaction in a series of acetone–dmso and benzene–dmso mixtures. Solutions of the bis complexes in acetone and benzene are stable when diluted with acetone or benzene, which are therefore inert solvents towards these complexes. Dilution with dmso-rich solutions gave as final product [Fe(pc)(dmso)$_2$]. In solutions rich in co-solvent (*i.e.* [dmso] < 5 mol dm^{-3}) the final spectrum was more like that of [Fe(pc)L$_2$], but with diminished optical density at wavelengths characteristic of bis(base) species (425 and 655 nm). The product could therefore be a mixture of [Fe(pc)L$_2$] and [Fe(pc)(dmso)$_2$], or be the intermediate product [Fe(pc)(dmso)], or an equilibrium mixture of all three species. Procedure towards equilibrium was first order throughout, but when solvent mixtures containing less dmso were used the observed first-order rate constant increased (Table 3). For the reactions involving both the bis(imidazole) and the bis(4-aminopyridine) complexes the observed rate constant varied inversely with dmso concentration from 14 down to 1 mol dm^{-3} (Figure 1). This behaviour rules out an associative mechanism, but it is in agreement with a reversible reaction and a *D* mechanism. Assuming this, we can write equations (6) and (7). Here, k_1, k_{-1}, *etc.* are not the same as those in equations (1) and (2). In fact they represent a further dissection of the constants in equation (2). If [Fe(pc)L]

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

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

$$k_{\text{obs.}} = \frac{k_1k_2[\text{dmso}] + k_{-1}k_{-2}[\text{L}]}{k_{-1}[\text{L}] + k_2[\text{dmso}]} \quad (8)$$

is a stationary-state intermediate then it can be shown † that equation (8) is applicable. Then, if $k_2[\text{dmso}] > k_{-1}[\text{L}]$ this approximates to equation (9). Comparison with Figure 1 shows that (9) provides a good description

TABLE 3

Variation of observed rate constant for base loss from [Fe(pc)L$_2$] with solvent composition at 35.0 °C

	[dmso]/mol dm^{-3}	$10^2k_{\text{obs.}}$/s^{-1}
(*a*) Leaving base is imH	14.1	0.37
	8.4	0.57
	7.0	0.55
	6.1	0.70
	3.8	0.83
	2.4	1.15
	2.0	1.28
	1.6	1.74
	0.57	2.27
	0.29	4.37
(*b*) Leaving base is 4NH$_2$-py	14.1	1.57
	8.4	2.19
	6.1	2.57
	3.8	2.69
	2.4	3.64
	1.6	6.10
	1.0	11.8

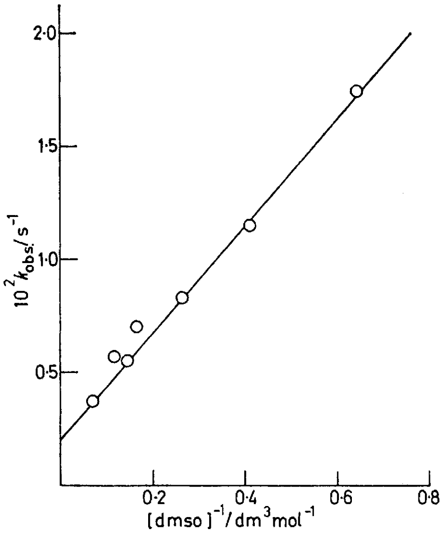

FIGURE 1 Variation of the observed rate constant for loss of imidazole from [Fe(pc)(imH)$_2$] with 1/[dmso] in dmso–acetone mixtures at 35.0 °C

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* In this reference a computer was employed to show that k_2 had to be at least ten times greater than k_1 for the observed plots of $\ln[(A_\infty - A_0)/(A_\infty - A_t)]$ against t to be straight lines through the origin for the two-step transformation [Fe(pc)(dmso)] $\xrightarrow{\text{L}}$ [Fe(pc)L$_2$]. Such plots are indeed straight lines through the origin.[1] The effect of changing the absorption coefficients of [Fe(pc)(dmso)$_2$], [Fe(pc)L(dmso)], and [Fe(pc)L$_2$] was calculated, but those of [Fe(pc)(dmso)$_2$] and [Fe(pc)L$_2$] can be determined directly and that of [Fe(pc)L(dmso)] can be deduced from equilibrium studies; all are listed in ref. 9.

† The stationary state treatment is covered in, for example, K. J. Laidler, 'Chemical Kinetics,' 2nd edn., McGraw-Hill, London, 1965, pp. 327—329, 441—443, and the relation between d(product)/d*t* and $k_{\text{obs.}}$ for a reversible reaction is deduced in the same text, pp. 19—20.

[8] M. V. Twigg, Ph.D. Thesis, University of Kent at Canterbury, 1970.

[9] D. V. Stynes, *Inorg. Chem.*, 1977, **16**, 1170.

of the observed behaviour, with the positive intercept on the k axis giving k_1 and the gradient giving $[L]k_{-2}k_1/k_2$. At very low [dmso], the behaviour deviates from equation (9) because $k_2[\text{dmso}] \sim k_{-1}[L]$.

$$k_{\text{obs.}} = k_1 + \frac{k_{-2}k_{-1}[L]}{k_2[\text{dmso}]} \tag{9}$$

Further refinements can be based on a treatment of a kinetically similar system given by Jensen and Kiskis.[10] If Jensen's treatment were applied directly to our system, then k_{-2} would first be estimated from a plot of $k_{\text{obs.}}$ against [dmso] at small values of the latter, where the plot tends to be linear and k_{-2} is the intercept on the k axis. Then the function $(k_{\text{obs.}} - k_{-2})^{-1}$ would have been plotted against $[\text{dmso}]^{-1}$. This treatment does work, but has serious drawbacks in that k_{-2} is difficult to estimate since $k_{\text{obs.}}$ is increasing very steeply at small values of [dmso]. A variant which suits our system better is to subtract k_1, which is the intercept of our first plot, from both sides of (8) to give (10). Plots of

$$(k_{\text{obs.}} - k_1)^{-1} = (k_{-2} - k_1)^{-1} + \{k_2[\text{dmso}]/k_1[L](k_{-2} - k_1)\} \tag{10}$$

$(k_{\text{obs.}} - k_1)^{-1}$ against [dmso] are linear as suggested by (10) (Figure 2).*

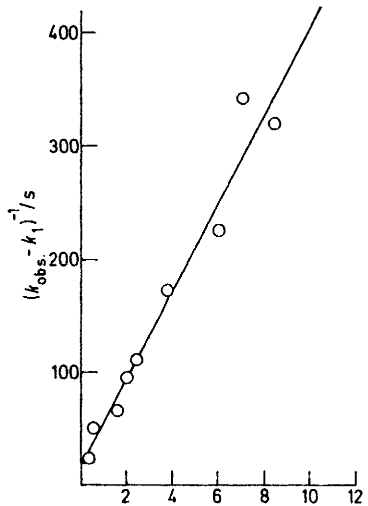

FIGURE 2 Plot of $1/(k_{\text{obs.}}—k_1)$ against [dmso] for loss of imidazole from $[\text{Fe(pc)(imH)}_2]$ in dmso–acetone mixtures at 35.0 °C

TABLE 4

Graphical derivation of kinetic parameters [as in equations (6) and (7)]

	L	
	imH	4NH$_2$-py
(*a*) Plot of $k_{\text{obs.}}$ against 1/[dmso] at 35.0 °C		
(*i*) Intercept = k_1	2×10^{-3}	1×10^{-2} s^{-1}
(*ii*) Gradient = $k_{-2}k_{-1}[L]/k_2$	2.4×10^{-2}	8.0×10^{-2} mol dm^{-3} s^{-1}
(*iii*) Gradient/14.1$[L]k_1 = K_2$	8.5×10^{-3}	5.7×10^{3} dm^3 mol^{-1}([L] = 1×10^{-4} mol dm^{-3})
(*iv*) Gradient/k_1[dmso] = $[\text{Fe(pc)L}_2]/[\text{Fe(pc)L(dmso)}]$	0.84	0.57 ([dmso] = 14 mol dm^{-3}]
	12	8 ([dmso] = 1 mol dm^{-3})
(*v*) Gradient/$k_{-2}[L] = k_1/k_{-2}$	1.6×10^{3}	1.9×10^{3} ([L] = 1×10^{-4} mol dm^{-3})
(*b*) Plot of $1/(k_{\text{obs.}}—k_1)$ against [dmso] at 35.0 °C		
(*i*) Intercept = $1/(k_{-2}$-$k_1)$ which gives k_{-2}	15×10^{-2}	59×10^{-2} s^{-1}
(*ii*) Gradient/intercept = $k_2/k_{-1}[L]$ combined with (*a*) (*ii*) gives k_{-2}	14×10^{-2}	54×10^{-2} s^{-1}
(*iii*) Intercept/gradient[L] = k_{-1}/k_2	1.7×10^{3}	1.5×10^{3} ([L] = 1×10^{-4} mol dm^{-3})
(*iv*) Intercept·k_{-2}/gradient [dmso]$[L]k_1 = K_2$	9.4×10^{3}	6.2×10^{3} dm^3 mol^{-1} ([L] = 1×10^{-4} mol dm^{-3})
(*v*) Intercept·k_{-2}/gradient [dmso]k_1 = $[\text{Fe(pc)L}_2]/[\text{Fe(pc)L(dmso)}]$	0.92	0.62 ([dmso] = 14 mol dm^{-3})
	14	9 ([dmso] = 1 mol dm^{-3})

A considerable amount of information can be extracted from plots of $k_{\text{obs.}}$ against 1/[dmso] and $(k_{\text{obs.}} - k_1)^{-1}$ against [dmso], as detailed in Table 4. In calculating the results the following procedure was adopted. First, a single least-squares line was drawn through the points in Figure 1, where [dmso] > 1. Then the point for pure solvent was given undue weight, since it is the best defined point, and the best line drawn through this point, close to the least-squares line, to give k_1. Other parameters were then calculated using the procedures outlined in Table 4. The following points emerge. Slightly different ways of calculating the rate constants give very similar values, and where [dmso] > 1 mol dm^{-3} it is indeed true that $k_2[\text{dmso}] > k_{-1}[L]$, which accounts for our empirical plot of $k_{\text{obs.}}$ against $[\text{dmso}]^{-1}$. Values of the constants obtained from the plot of $(k_{\text{obs.}} - k_1)^{-1}$ against [dmso] successfully account for the variation of observed rate constant with dmso concentration (Figure 3). Useful chemical information is also obtained. Thus, 4-aminopyridine leaves $[\text{Fe(pc)L}_2]$ some five times faster than imidazole from the corresponding bis(imidazole) complex, and dmso leaves $[\text{Fe(pc)(4NH}_2\text{-py)(dmso)}]$ about four times faster than from [Fe(pc)(imH)(dmso)]. These two observations are in agreement with 4-aminopyridine having a 4—5 times greater *trans* effect than imidazole in these systems at 35 °C. Comparing k_1 and k_{-2} it is seen that imidazole leaves $[\text{Fe(pc)(imH)}_2]$ *ca.* 75 times more slowly than from [Fe(pc)(imH)(dmso)]; *i.e.* with imidazole as *trans* group, dmso is a much better

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* In our experiments there is not a constant amount of L present throughout the reaction, so it is surprising that equations (9) and (10) work well. It can be shown that equation (9) holds under our conditions if the same initial concentration of complex is used for different values of [dmso], and if the reaction involves a small displacement of equilibrium, both conditions holding in our experiments. No account has been taken of specific solvent–solute interactions, so the rate constants we derive should be taken as indicative and not absolute.

[10] F. R. Jensen and R. C. Kiskis, *J. Amer. Chem. Soc.*, 1974, **96**, 5820.

leaving group than imidazole (the same appears to be true of 4-aminopyridine, but to a lesser extent). The five-co-ordinate intermediates [Fe(pc)L] (L = imH or $4NH_2$-py) prefer the heterocyclic bases to dmso (by a factor of 10^3—10^4), with the aminopyridine intermediate being slightly less selective. Both intermediates are surprisingly discriminating, but this finding is similar to a recent one[11] for the intermediate [Fe(p)(pip)] discriminating between piperidine (pip) and carbon monoxide [(p) is *meso*-tetraphenylporphyrin or protoporphyrin IX]. So far, intermediates of the [Fe(pc)L] type have been found to be much less discriminating ($k_{-1}/k_2 \sim 4$), but it is noticeable that where this is so the overall formation constant of [Fe(pc)L(L′)] from [Fe(pc)L_2] and L′ is small; in our case the formation constants of [Fe(pc)L_2] from [Fe(pc)L(dmso)] and L are large, as is the case in the formation of [Fe(pc)L(CO)] from [Fe(pc)L_2] and CO. An intermediate case is the discrimination of [Fe(pc)(mim)] between RNC and *N*-methylimidazole (mim) ($k_{-1}/k_2 \sim 11$, $K \sim 300$ calculated from data in ref. 9). At the extreme opposite end of the scale is [Fe(pc)(CNR)][12] which prefers 2-methylimidazole (2Me-imH) to RNC by about two orders of magnitude; the formation of [Fe(pc)$(CNR)_2$] from [Fe(pc)(CNR)(2Me-imH)] has a very small formation constant ($K \sim 0.1$). There is, however, no simple numerical relation between K and the discrimination ratio because K includes both the discrimination ratio and terms involving the relative rates of bond fission in [Fe(pc)L_2] and [Fe(pc)L(L′)].

TABLE 5

Rates of dissociation of phthalocyaninatoiron(II) adducts

Leaving group	Rate constant[a] (s^{-1}) for given *trans* group									
	dmso	2Me-imH	P(OR)$_3$	NBu$^n_3$	pip	py	$4NH_2$-py	imH	mim	$PhCH_2NC$
dmso	84[b]						0.6[c]	0.01[d]		
2Me-imH	7.6[e]	33[f,g]								
P(OR)$_3$			19[g,h]							
$MeC_6H_4NO_2$-*p*				13[g,i]						
pip	2.6[j]				0.5[f]					
2Me-py	0.5[e]									
py	0.2[e]					0.12[f]				
CO		0.5			0.13[f]	0.09[f]			0.02[g,k]	
mim										p.1[g,l]
$4NH_2$-py	1×10^{-4}[c]						3×10^{-3}[d]			
imH	2×10^{-6}[c]							6×10^{-4}[c] 2.5×10^{-3}[f,g]		
$PhCH_2NC$					2×10^{-4}[g,l]	8×10^{-5}[g,l]			5.8×10^{-4}[g,l]	0.2[g,l]

[a] At 25.0 °C and in dmso unless otherwise stated. [b] Lower limit from reaction of [Fe(pc)$(dmso)_2$] with P(OEt)$_3$.[2] [c] This work at 35 °C. [d] Estimated from results at 30, 35, and 40 °C. [e] Ref. 2. [f] Ref. 6 in toluene at 23 °C. [g] In toluene. [h] R = Bu.[7] [i] Ref 12. [j] T. C. Webb and K. J. Baird, Undergraduate Thesis, New University of Ulster, 1973. [k] Ref. 6. [l] Ref. 9.

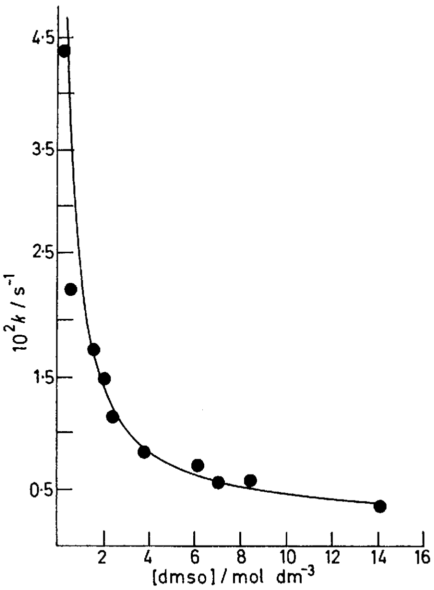
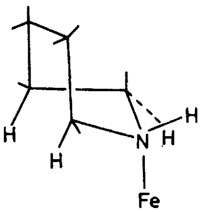
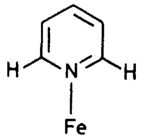


FIGURE 3 Comparison of observed (●) and calculated rate constants (——) for loss of imidazole from [Fe(pc)$(imH)_2$] in dmso–acetone mixtures at 35.0 °C

There now exists a small body of information on *trans* effects in base dissociation from [Fe(pc)L(L′)] adducts (L and L′ being the same or different) and this is conveniently summarised in Table 5. This is arranged so that the rate of a particular reaction decreases down and from left to right across the Table. These rate constants relate to simple dissociation processes characterised by a single rate constant. Although the data are limited the following *trans*-effect order is indicated: dmso > $PhCH_2NC$ > pip > py > imH, with the effect of 2Me-imH perhaps greater than that of dmso. This is open to some doubt since results for imidazole leaving *trans* to imidazole indicate that there is a medium effect (the reaction is five times faster in toluene than in dmso), and this when applied to 2Me-imH leaving *trans* to dmso (in dmso) and *trans* to itself (in toluene) indicates that 2Me-imH could have a lower intrinsic *trans* effect than





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[11] D. V. Stynes and B. R. James, *J.C.S. Chem. Comm.*, 1973, 325.

[12] J. J. Watkins and A. L. Balch, *Inorg. Chem.*, 1975, **14**, 2720.

dmso. Table 5 also enables an ordering of the relative lability of the dissociating ligands: dmso $>$ 2Me-imH $>$ pip $>$ 2Me-py $>$ py $>$ 4NH$_2$-py $>$ imH. The more basic a ligand is towards a proton the less labile it is, and the greater is the formation constant of [Fe(pc)L$_2$].[4] This generalisation is invalid if there is steric hindrance between the ligand and the macrocycle, *e.g.* piperidine *versus* pyridine, 2-methylimidazole *versus* imidazole. Solubility difficulties restrict the amount of data obtainable, and we are hopeful that further information concerning labilities and *trans* effects will result from our planned work on more soluble substituted derivatives of [Fe(pc)].

[8/180 *Received, 3rd February,* 1978]