lower than the value k_Q obtained for monomer fluorescence quenching and may represent an inherently lower efficiency[2,17] at the encounter pair stage for quenching of

Table II. Photophysical Parameters for the Pyrene–DTBN System in Benzene Solution at 25°

Parameter	Process	This study	Other studies
k_Q	DTBN quenching of pyrene monomer	$8.4 \times 10^9\ M^{-1}$ sec^{-1}	
k_Q'	DTBN quenching of pyrene excimer	$4.1 \times 10^9\ M^{-1}$ sec^{-1}	
k_E	Excimer formation	11.3×10^9 M^{-1} sec$^{-1\ a}$	$7.5 \times 10^9\ M^{-1}$ sec$^{-1\ b}$
k_{-E}	Excimer dissociation	1.5×10^7 sec^{-1}	1.0×10^7 sec$^{-1\ b}$
τ_M	Monomer lifetime at high dilution $(10^{-6}\ M)$	335 nsec	435 nsec^b
τ_E	Excimer lifetime	~46 nsec	64 nsec^b

^{a} Calculated from value in cyclohexane, ref 3. ^{b} Reference 3, in cyclohexane.

excited state molecular aggregates by DTBN and/or a lower diffusion coefficient for the excimer relative to the

monomer.[2,20] The present data cannot differentiate between these alternatives.

The direct lifetime measurements precluded the need for *assuming values* for bimolecular rate constants for quenching by DTBN. For example, if we had assumed in the present study that $k_Q' = k_Q = 8.4 \times 10^9\ M^{-1}$ sec^{-1},[2] the value of τ_E^0 from the Stern–Volmer slope (eq III) would have been 23 nsec (rather than ~46 nsec), implying $k_{-E} = 2.9 \times 10^7$ sec^{-1} (rather than 1.5×10^7 sec^{-1}) (eq I). These potential errors demonstrate that, even with a rather efficient quencher such as DTBN, great care must be exercised in assuming the magnitude of the quenching rate constants in a purely steady state experiment. Further, because of the apparently indiscriminant quenching of both singlet and triplet states[21] by DTBN, we caution photochemists using it as a mechanistic probe to be careful in reaching conclusions about the multiplicity of reactive excited states from such data.

Kinetics and Equilibria for Carbon Monoxide Binding to Ferrous Phthalocyanine Complexes

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Contribution from the Departments of Chemistry, York University, Downsview, Ontario, Canada, and University of British Columbia, Vancouver, British Columbia, Canada. Received May 26, 1973

Abstract: Six-coordinate low-spin ferrous phthalocyanine complexes (L_2FePc, where L = imidazole (Im), pyridine (py), piperidine (pip), and 2-methylimidazole (2-MeIm)) reversibly bind carbon monoxide in toluene solution *via* a dissociative mechanism. Equilibrium constants (K) for the reaction L_2FePc + CO $\rightleftarrows$ LFePc(CO) + L decrease in the order 2-MeIm > pip > py $\gg$ Im. Limiting first-order rate constants for the dissociation of L parallel K. A substantial trans effect of imidazole is observed in the dissociation of CO from LFePc(CO). Equilibrium and kinetic data for the phthalocyanine complexes are compared with those of some corresponding iron(II) porphyrins and glyoxime complexes, and a possible correlation between reactivity and stereochemistry of the five-coordinate intermediates is tentatively proposed.

The most important inorganic complexes in biological systems undoubtedly involve the heme group (an iron protoporphyrin IX complex). Vaska and Yamaji[3] have recently reported the kinetics of the reaction of carbon monoxide with bisdiphenylglyoxime complexes of iron(II), L_2Fe(DPGH)$_2$, where L = various pyridines. While the reaction of these complexes with CO is qualitatively similar to the corresponding reactions of iron(II) porphyrin complexes (L_2FeP), kinetic and equilibrium data for the iron porphyrins show them to be far more labile and to bind CO better than the glyoxime systems;[4] both systems involve a

dissociative mechanism and five-coordinate intermediates. The enhanced lability of ligands coordinated to axial positions of metal porphyrins has been reported for a number of normally substitution-inert metal ions.[5-7]

In order to assess those features of the porphyrin ligand which give rise to these properties, we have undertaken an investigation of the reaction of CO with another potential model for the heme group, ferrous phthalocyanine (FePc).

While FePc has long been recognized as a potential

(1) York University.
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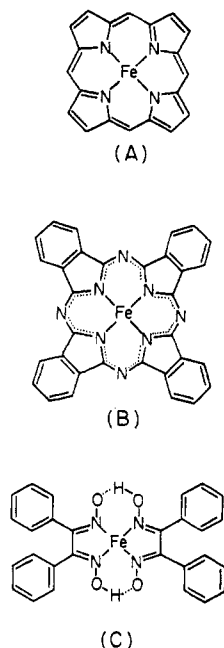(7) S. S. Eaton, G. R. Eaton, and R. H. Holm, *J. Organometal. Chem.*, **39**, 179 (1972).

Figure 1. Structures of four-coordinate ferrous porphyrin (A), phthalocyanine (B), and bis(diphenylglyoxime) (C).
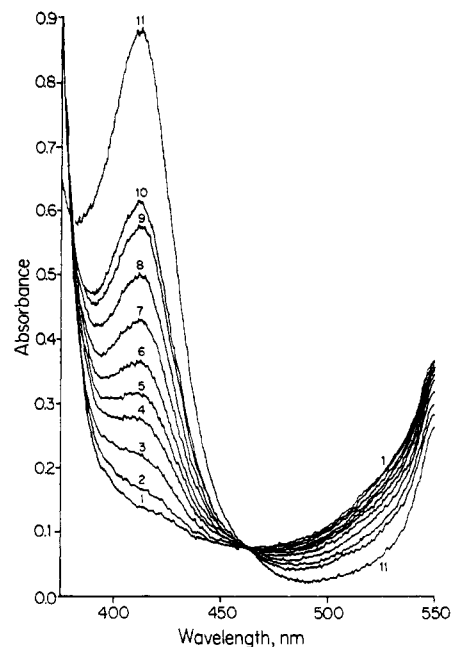

Figure 2. Spectral data for the determination of K for $(py)_2FePc$ (eq 1). Aliquots of 0.026 M pyridine in toluene added to 30.3 ml of a toluene solution of $(py)_2FePc(CO)$ ($\sim 5 \times 10^{-5}$ M), under 737 Torr of CO, at 23°; for spectra 1–10, the aliquots (ml) are 0.0, 0.1, 0.3, 0.5, 0.7, 1.0, 1.5, 2.5, 4.0, and 6.0. Spectrum 11 for $(py)_2FePc$ involves a further addition of 0.1 ml of neat pyridine and evacuation of CO.

model for the heme group,[8] no report of O_2, CO, or NO binding to this moiety has appeared, although Fallab, et al.,[9] have described the formation of a binuclear oxygen species $(2Fe:O_2)$ from an iron(II) phthalocyaninetetrasulfonate complex. A kinetic study[10,11] of the reaction of $FePc(DMSO)_2$ with imidazole showed that the reaction was first order in both complex and imidazole, and so failed to indicate a limiting dissociative mechanism, presumably due to the high concentration of competing ligand (DMSO) used as solvent (see eq 4).

Ferrous phthalocyanine is structurally more closely related to iron porphyrins than the glyoxime system (Figure 1). In addition, the phthalocyanine complexes[12] are more easily handled than the rather air-sensitive iron(II) porphyrins.[13]

Experimental Section

Materials. Ferrous phthalocyanine (FePc) was purchased from Eastman and used without further purification. Imidazole and 2-methylimidazole (Aldrich Chemical Co.) were recrystallized from benzene prior to use and dried *in vacuo*. 1-Methylimidazole (Aldrich), pyridine (Fisher), and piperidine (Fisher) were distilled from KOH prior to use and stored under nitrogen. Carbon monoxide was Matheson C.P. Grade. Toluene was freshly distilled from CaH_2 and degassed before use. The six-coordinate diamagnetic L_2FePc complexes (L = amines)[12] were prepared by dissolving FePc in the liquid amine or a chloroform solution of the solid amines. The complexes, precipitated upon addition of methanol, were filtered and dried *in vacuo*. All compounds analyzed satisfactorily for C, H, and N.

Equilibrium Constant Measurements. Method A. A solution of L_2FePc ($\sim 5 \times 10^{-5}$ M) in toluene, containing a convenient con-

centration of ligand L (10^{-3} M for L = pip, for example) to allow a reasonable variation in the concentration ratio [LFePc(CO)]: [L_2FePc] for a variation of CO pressure from 0–1 atm was thoroughly degassed *in vacuo* in a 1-cm path length spectrophotometric cell fitted with a stop-cock for attachment to a gas-handling line and a second side arm with stopper or serum cap. Various CO pressures were then added by connecting the cell to the vacuum line, the pressures being read with a cathetometer from a U-tube mercury manometer. Pressures were corrected for the vapor pressure of toluene. The visible spectrum was recorded at each pressure; excellent isosbestic points were observed (Figure 2). The various L_2FePc complexes exhibited an absorption maximum between 413 and 422 nm. The LFePc(CO) complexes have not been isolated and characterized at this stage because of the facile loss of CO in the absence of a CO atmosphere, but the equilibria data analyze only for reaction 1 and this is undoubtedly the reaction occurring.

Method B. Alternatively, a solution of L_2FePc in toluene was shaken with 1 atm of CO to give the carbonyl complex LFePc(CO). Aliquots of ligand solution in toluene ($\sim 10^{-2}$ M) were then added by means of a syringe through a serum cap in the spectrophotometric cell. The spectrum was then recorded after each addition. Absorbance corrections for dilution were kept small, resulting in good isosbestic points. Neat ligand was added and the cell evacuated to obtain the limiting spectrum of L_2FePc. Experiments for L = Im were more conveniently carried out at [L_2FePc] $\sim 5 \times 10^{-6}$ M in a 10-cm cell owing to the much smaller equilibrium constant for CO binding.

Kinetic Measurements. Stopped Flow. Reactions with half-lives of less than 1 min were studied by means of a Durrum 110 stopped-flow apparatus with a 2-cm light path cuvette. For the forward reaction, solutions of L_2FePc and toluene saturated with 1 atm of CO were used. For the reverse reaction, a solution of LFePc(CO), prepared by saturating a solution of L_2FePc in toluene with CO, was mixed with a toluene solution of the ligand (typically 1 M). Attempts to study the reactions as a function of temperature using the conventional thermostating capability of the Durrum instrument were not possible owing to an anomaly in the oscilloscope trace which occurred for reactions of half-life between 0.1 and 0.5 sec, apparently due to small temperature gradients between the mixing chamber and cuvette. The problem disappeared when operating near room temperature. Some preliminary activation parameters were obtained on the slower reactions of the imidazole

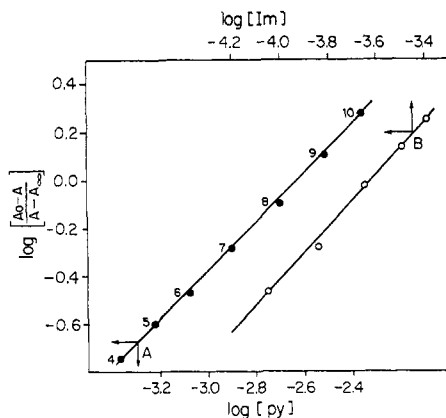(8) B. W. Dale, *Trans. Faraday Soc.*, **65**, 331 (1969).

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Fgure 3. (A) Plot of absorbance data of Figure 2 according to eq 2 at constant CO pressure (numbers refer to spectra of Figure 2). (B) Similar plot for absorbance data of the $(Im_2FePc + CO)$ equilibrium at 737 Torr of CO.

complex on a Cary 14 spectrophotometer as described below. Results obtained at ambient temperatures on the stopped-flow apparatus were in agreement with those obtained on the Cary-14.

Cary-14. Dissociation of Imidazole. A solution of Im_2FePc ($\sim$5 $\times$ 10^{-5} M) was thermostated in a 5-ml gas-tight syringe. The Cary-14 spectrophotometer was set at 420 nm and the chart speed adjusted to suit the rate of the reaction. The visible cell (containing 1 atm of CO) was placed in a thermostated cell compartment and equilibrated at the same temperature as the reaction solution. The cell was quickly filled via the syringe through a serum cap, shaken, and the spectrophotometer activated. (In this procedure, the first few seconds of the reaction are lost.)

Dissociation of CO from ImFePc(CO). Sometimes the more soluble 1-methylimidazole was used to displace CO from ImFePc-(CO); 3 ml of a thermostated solution of ImFePc(CO), stored under CO, was syringed into a visible cell containing 0.1 ml of 1-methylimidazole, and the kinetics were followed by monitoring the absorbance at 420 nm as described above. Rates of CO displacement using excess 1-methylimidazole, piperidine, pyridine, and imidazole were identical.

Results

Equilibrium Measurements. Upon exposure of toluene solutions of the six-coordinate, diamagnetic L_2FePc complexes to CO, a change in color from green to blue is observed. The color change and corresponding spectral change are readily reversible upon evacuation or addition of excess ligand (e.g., Figure 2). The dependence of the equilibrium on CO pressure and [L] is consistent only with the equilibrium

$$L_2FePc + CO \rightleftharpoons LFePc(CO) + L \qquad (1)$$
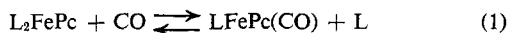
for which

$$K = \frac{[LFePc(CO)][L]}{[L_2FePc][CO]}$$

Absorbance changes (A) as a function of [L] and CO pressure (P_{CO}) were analyzed using the expression

$$\log\left[\frac{A_0 - A}{A - A_\infty}\right] = \log K + \log (P_{CO}) - \log [L] \qquad (2)$$

where A_0 is the absorbance of L_2FePc and A_∞ is the absorbance of $LFePc(CO)$. Plots of log $[(A_0 - A)/(A - A_\infty)]$ vs. log [L] or log (P_{CO}) were linear with slope 1.0 $\pm$ 0.05, consistent with the assumed equilibrium. Typical data are shown in Figures 3 and 4 which yield the equilibrium constants given in Table I; the K values were calculated in units of M/Torr and converted to unitless values using the solubility of CO
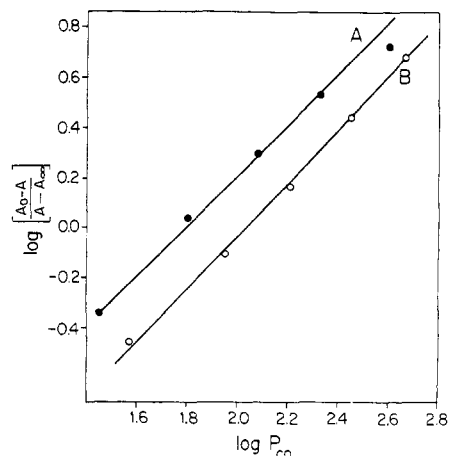
Figure 4. (A) Plot of absorbance data for the $[(2\text{-MeIm})_2FePc + CO]$ equilibrium according to eq 2 with varying CO pressure at constant $[2\text{-MeIm}] = 4 \times 10^{-3}$ M. (B) Similar plot for absorbance data of the $[(pip)_2FePc + CO]$ equilibrium at $[pip] = 8 \times 10^{-4}$ M.

Table I. Kinetic and Equilibrium Data[a] for the Reaction of Iron Phthalocyanine and Related Complexes with CO in Toluene at 23°

	k_1,[b] sec^{-1}	k_{-2},[b] sec^{-1}	K^c	k_{-1}/k_2
Im_2FePc	0.0026	0.02	0.03	4.2[d]
$(pip)_2FePc$	0.50	0.13	0.85	3.3[d]
$(py)_2FePc$	0.12	0.09	0.37	3.4[d]
$(2\text{-MeIm})_2FePc$	33[e]	0.7[f]	7.8	5.8[e]
		0.4[g]		
$(pip)_2Fe(PpIX)^h$	$\sim$20	0.06	2.3 $\times$ 10^5	0.002
$(pip)_2Fe(TPP)^h$	$\sim$11	0.52	1.5 $\times$ 10^4	0.002
$(py)_2Fe(DPGH)_2^i$	0.004	2.5 $\times$ 10^{-5}	43	3.9

[a] See eq 1 and 3 for a definition of various constants. [b] Estimated error $\pm$10%. [c] Estimated error $\pm$0.05 in log K. [d] Calculated from $K = k_1k_2/k_{-1}k_{-2}$. [e] Calculated from dependence of k_{obsd} on L (see text). [f] Calculated from k_1, k_{-1}/k_2, and K. [g] Measured limiting rate constant in chloroform solution. [h] Reference 4, PpIX = protoporphyrin IX, TPP = tetraphenylporphyrin. [i] Reference 3; chlorobenzene at 25°; DPGH$_2$ = diphenylglyoxime; K is calculated from the reported kinetic data; $\Delta H_1^\ddagger = 23.6$, $\Delta S_1^\ddagger = 19$ eu; $\Delta H_{-2}^\ddagger = 26.0$, $\Delta S_{-2}^\ddagger = 17$ eu (note, from the data given we calculate $\Delta S_1^\ddagger = +9$ eu, and $\Delta S_{-2}^\ddagger = +7$ eu).

in toluene $(6.5 \times 10^{-3}$ M/atm). The ligand dependence of the equilibrium constants according to eq 2 rules out the presence of significant amounts of four- or five-coordinate complexes (FePc or LFePc) under the conditions of the experiments.

Kinetics. First-order plots of log [L_2FePc] vs. time were obtained for the forward reaction of eq 1 measured under conditions when LFePc(CO) is finally fully formed (Figure 5). The observed first-order rate constants were shown to be for a dissociative reaction $(k_1$, Table I) by the invariance of the k_{obsd} upon dilution or halving the CO pressure (except for the L = 2-MeIm system). Some preliminary temperature dependence data for the forward reaction with L = imidazole give $\Delta H_1^\ddagger = \sim$27 kcal mol^{-1} and $\Delta S_1^\ddagger = \sim$+15 eu.

Good first-order plots of log [LFePc(CO)] vs. time were obtained also for the reverse reaction of eq 1 (Figure 6). The reaction rate was the same whether the ligand L added to the carbonyl complex was 10^{-2} M imidazole, 1 M pyridine, or 1 M piperidine. These results show that a dissociative mechanism is involved, and the rate constants (k_{-2}) are given in Table I; the re-
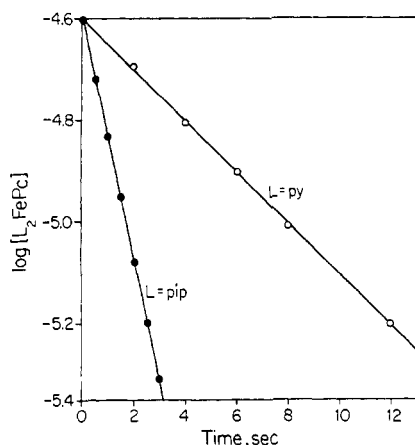
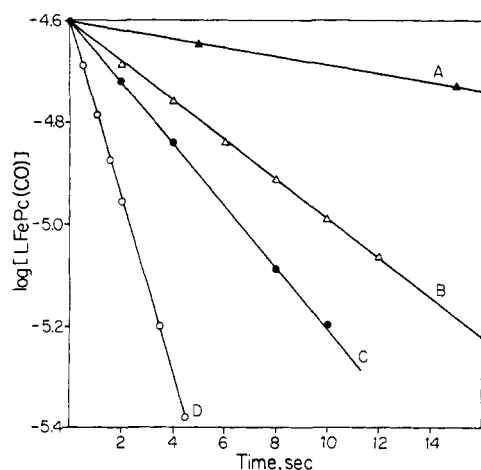Figure 5. First-order kinetic plots of log [L₂FePc] vs. time for the reaction of L₂FePc (L = pip, py) with CO in toluene at 23°.

Figure 6. First-order kinetic plot of log [LFePc(CO)] vs. time for the reaction of LFePc(CO) with L at 23°: A, B, and C in toluene, L = Im, py, and pip, respectively; D in chloroform for L = 2-MeIm.

sults also show that displacement of the ligand trans to CO is slow compared to dissociation of CO, at least for the LFePc(CO) systems with L = imidazole, piperidine, and pyridine. Again, there were some differences with the 2-methylimidazole system (see below). Preliminary temperature dependence data for CO dissociation from the imidazole complex yield the parameters $\Delta H_{-2}^{\ddagger} = \sim 24$ kcal mol⁻¹ and $\Delta S_{-2}^{\ddagger} = \sim +10$ eu.

For the 2-methylimidazole system, it was not possible to determine directly the forward and reverse limiting rates. A problem in studying the forward reaction was that the (2-MeIm)₂FePc complex was appreciably soluble only in the presence of excess 2-methylimidazole. The forward reaction was therefore studied at varying added ligand concentrations at a constant CO pressure (370 Torr); in each case the carbonyl is fully formed, and the observed first-order rate constants are given in Table II. For the mechanism

$$L_2FePc \xrightleftharpoons[+L,k_{-1}]{-L,k_1} LFePc \xrightleftharpoons[-CO,k_{-2}]{+CO,k_2} LFePc(CO) \qquad (3)$$
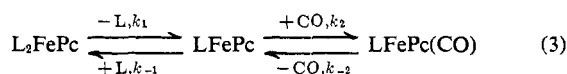
and assuming a steady-state concentration of the five-coordinate intermediate (and neglecting k_{-2}), the rate law is given by

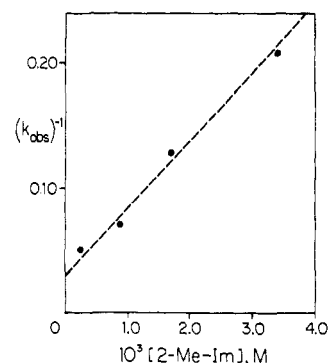$$\frac{d[LFePc(CO)]}{dt} = \frac{k_1k_2[L_2FePc][CO]}{k_{-1}[L] + k_2[CO]} \qquad (4)$$

Figure 7. Plot of $(k_{obsd})^{-1}$ vs. [2-MeIm] for the reaction (2-MeIm)₂-FePc + CO according to eq 4 at constant CO (370 Torr).

Table II. Dependence of k_{obsd} on [2-MeIm] for the Reaction of CO with (2-MeIm)₂FePc in Toluene at Constant CO Pressure (370 Torr) and 23°

10³[2-MeIm], M	3.4	1.7	0.85	0.42
k_{obsd}, sec⁻¹	4.8	7.8	14	20

The observed rate constant is thus $k_1k_2[CO]/(k_{-1}[L] + k_2[CO])$, and, since [L] and [CO] remain effectively constant for each experiment, k_{obsd} is a pseudo-first-order constant. A plot of $(k_{obsd})^{-1}$ vs. [L] gives a linear plot (Figure 7) from which k_1 and k_{-1}/k_2 have been determined (Table I). Using these values and the measured K value yield a calculated k_{-2} value of 0.7 sec⁻¹ for CO dissociation. However, 2-methylimidazole was insufficiently soluble in toluene to study directly the CO dissociation from (2-MeIm)FePc(CO) by a procedure similar to that used for the other ligand systems. Attempts to dissociate CO using 1-methylimidazole produced a non-first-order oscilloscope trace; the initial fast reaction slowed down markedly. The rate for CO dissociation was measured, however, by carrying out the reaction of excess 2-MeIm with the (2-MeIm)FePc-(CO) complex in chloroform solution (Figure 6D), and the k_{-2} value of 0.4 sec⁻¹ is considered in reasonable agreement with the value calculated for the toluene system.

The k_{-1}/k_2 values for the imidazole, piperidine, and pyridine systems (Table I) were estimated using the measured k_1, k_{-2}, and K values.

Discussion

The mechanism of the reaction of the ferrous phthalocyanines is identical with that reported for the similar iron porphyrin and iron diphenylglyoxime systems;[3,4] the dissociative mechanism is summarized in eq 3. The kinetic and equilibrium data are given in Table I.

As expected, the rates of ligand dissociation (k_1) show a greater variation than do the rates of CO dissociation (k_{-2}) with changes in L. The variation is considerably greater than that reported for substituted pyridine ligands in the L₂Fe(DPGH)₂ systems[3] and is most likely due to the more diverse set of axial ligands studied in the present work rather than to a difference in the two in-plane ligands.

Among the phthalocyanine systems, a most striking difference in the kinetic and equilibrium data occurs for the imidazole ligand systems. The considerably diminished lability of the amine ligand and the CO

ligand for the L = imidazole system is of particular interest since imidazole ligands are trans to the reactive ligand in heme proteins and vitamin B_{12}. Previous workers have indicated an increased lability for oxygen donor ligands trans to imidazole in a FePc system[11] and in a cobalamin(III) system.[5]

The data show a substantially diminished lability for imidazole and CO ligands trans to imidazole. This trans effect of imidazole may be understood in terms of its π-donor properties which result in enhanced π back-bonding from Fe to CO. Enhanced oxygen binding to cobalt porphyrins at an axial position trans to an imidazole ligand has been attributed to a similar effect.[14] The considerably smaller k_1 value for imidazole as compared to piperidine is consistent with structural data on the axial Fe–N bond lengths in $(pip)_2Fe^{II}(TPP)$[15a] and in the $Im_2Fe^{III}(TPP)^+$ cation[15b] (TPP = tetraphenylporphyrin). A shorter bond in the imidazole complex (by $\sim$0.15 Å in these two complexes) would almost certainly be maintained in an iron(II) imidazole complex.[16] The longer Fe–N bond length in the $(pip)_2Fe(TPP)$ complex has been attributed in part to steric effects. We believe such steric interactions are also present in the phthalocyanine system and account for the greater lability of the piperidine complex compared with the pyridine complex, despite the greater basicity of piperidine. Mossbauer data for the L_2FePc complexes[17] show the same trend for binding strength of the axial ligand: Im > py > pip.

The values of k_{-1}/k_2 reflect the relative rates of addition of amine vs. CO to the five-coordinate intermediate. As in the diphenylglyoxime study,[3] the values of k_{-1}/k_2 are relatively constant and are of the same order of magnitude as those reported for the diphenylglyoxime complexes (Table I). The overall equilibrium constants (K) for the various phthalocyanine systems are seen to generally parallel the k_1 values.

The marked difference in kinetic data for the L = Im and 2-MeIm systems is undoubtedly due to a steric effect. The use of 2-MeIm was prompted by a report of a five-coordinate high-spin complex of iron tetraphenylporphyrin,[18] and it is of interest that we see no spectral evidence for a five-coordinate complex in the phthalocyanine system down to 2-MeIm concentrations of $\sim$10^{-4} M. Similar steric effects would be expected in the porphyrin and phthalocyanine systems, although it should be pointed out that the (2-MeIm)Fe(TPP) complex is not well characterized in solution. In this regard, the kinetic CO dependence for the binding of CO can provide a useful means of detecting five-coordinate complexes, particularly in cases where there might be little difference in visible spectra between LFePc and L_2FePc.

While no evidence for five coordination was obtained in the 2-MeIm system, the kinetic data indicate a substantial labilization of the sterically hindered ligand; a difference of 10^4 in the rate of dissociation of L between

Im and 2-MeIm is observed. In addition, a substantial decrease in the strength of the Fe–CO bonding is also indicated. This could result from the bulky ligand forcing the iron atom slightly out of the plane of the phthalocyanine ligand,[19] and such a distortion could weaken the bonding with the CO.

The observed oscilloscope traces for displacement of CO from (2-MeIm)FePc(CO) using 1-MeIm indicate that the 2-MeIm ligand trans to the carbonyl is labile. The rapid initial rate became slow after about 0.1 sec and eventually approached a rate which was probably that for CO dissociation from (1-MeIm)FePc(CO). No evidence for dissociation of L trans to CO was observed for the other ligand systems studied.

Table I also summarizes data reported previously for reaction of CO with some porphyrin and glyoxime systems. The $(pip)_2FePc$ system is seen to be reasonably similar to the $(pip)_2Fe(porphyrin)$ systems in terms of lability (k_1, k_2), and both phthalocyanine and porphyrin systems are much more labile than the glyoxime systems. Rose, $et\ al.$,[20] have also reported on reversible ligation studies of some low-spin iron(II) complexes containing a planar tetraimine macrocyclic ligand; a reversible carbonylation reaction appears to be relatively slow and is more akin to the glyoxime systems.

Enhanced lability of axial ligands in porphyrin systems is currently of much interest.[4,21] Hodgkinson and Jordan[21] have attributed the labilizing effect in some iron(III) porphyrin systems (compared to hexasolvated iron(III) systems) to a more positive $\Delta S^{\ddagger}$, although the comparison of activation parameters refers here to differently charged complexes. It is unfortunate that we were unable to obtain kinetic parameters for the FePc pyridine system in order to compare with the $Fe(DPGH)_2$ pyridine system. In the latter system (Table I), CO dissociation is slower than pyridine dissociation due to a higher activation energy, and we anticipate the same for the L_2FePc systems (L = py, pip). The Im_2FePc system is quite different, in that CO dissociation is faster than imidazole dissociation and is due probably to a lower $\Delta H^{\ddagger}$. The enhanced lability of CO in the phthalocyanine–imidazole system compared to the glyoxime–pyridine system appears to be due to a lower $\Delta H^{\ddagger}$, but no such general conclusion can be drawn for phthalocyanine vs. glyoxime systems, since the imidazole system appears exceptional within the phthalocyanine series as discussed above. The $\Delta S^{\ddagger}$ values for the imidazole system are positive as expected for dissociative reactions. Data for dissociation of axial ligands from the iron(II) diphenylglyoxime complexes give $\Delta S^{\ddagger}$ values of 17–21 eu, although these appear to have been calculated incorrectly and seem to be $\sim$10 eu too high (see Table I, footnote i). $\Delta S^{\ddagger}$ values between $+2$ and $+7$ eu have been reported for some low-spin ruthenium(II) and iron(III) porphyrin systems.[7,22]

More detailed discussion on these interesting systems

(14) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, $J.$ $Amer.$ $Chem.$ $Soc.,$ **95,** 1796 (1973).

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(16) See, $e.g.,$ H. C. Stynes and J. A. Ibers, $Inorg.$ $Chem.,$ **10,** 2304 (1971).

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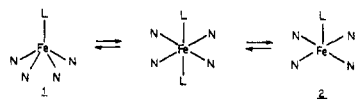
Figure 8. Possible structures of five-coordinate intermediates in dissociative reactions of heme models.

must await activation parameter data for the L_2FePc (L = py, pip), L_2Fe(porphyrin) (L = py, pip, Im), and $L_2Fe(DMGH)_2$ (L = Im) systems, studies that are currently in progress.

The Nature of the Intermediate. The intermediate in these dissociative reactions of six-coordinate Fe(II) complexes is a five-coordinate species, and it is of particular interest to speculate upon the spin state and geometry of the intermediate. The active site of hemoglobin and myoglobin is known to be a five-coordinate high-spin iron(II) porphyrin complex with an imidazole of a histidine residue occupying the fifth coordinate site; oxygenation leads to a six-coordinate low-spin system. Structural studies of iron porphyrins[15,23,24] have led to the generally accepted proposal that the iron atom will lie at least 0.5 Å out of the plane of the porphyrin ligand in the high-spin complex and will move essentially into the plane in low-spin complexes[25] and the motion of the iron atom with respect to the porphyrin plane upon oxygenation of hemoglobin has been demonstrated by difference Fourier techniques.[26] Such motion has been proposed to trigger conformational changes which result in the cooperativity of hemoglobin.[27] It is of interest to consider whether spin change and movement of the iron with respect to the plane also play a role in the intermediates present in the dissociative reactions of iron porphyrins, and related complexes.

Considering the two possible extreme structures for the five-coordinate intermediate given in Figure 8, some statement can be made about the relative rate of addition of ligands. On the basis of steric considerations, the addition of a bulky amine ligand to a high-spin intermediate, **1**, will be less favorable than the corresponding rate of addition to a low-spin species, **2**, at least relative to the rate of addition of a nonbulky ligand such as CO.[28]

Strictly speaking, definitive statements about the kinetic intermediate cannot be made since only the relative rates of addition of L/CO are known. In terms of the free energy profile for the reaction, only the difference in free energy ($\Delta G_{-1}^{\ddagger} - \Delta G_2^{\ddagger}$) is known, and there is no information about the depth of the well in which the intermediate lies. If the assumption is made that the intermediate lies close to the transition states both in free energy and geometry,[29] then some statement about the structure of the intermediate can be made based on the kinetic data. In particular, a comparison of the kinetic data for the diphenylglyoxime,

phthalocyanine, and porphyrin systems reveals a striking difference in the relative rates of addition of L vs. CO to the five-coordinate intermediates (k_{-1}/k_2, Table I); the value for the porphyrin systems is about 10^3 times smaller than those for the other tetradentate ligand systems and this difference may arise from a difference in the structure and spin state of the intermediates. We propose that the intermediate in the porphyrin systems is close to structure **1** and resembles the active site of hemoglobin and myoglobin with the iron atom out of the plane and high spin; the larger values of k_{-1}/k_2 for the phthalocyanine and glyoxime systems suggest that the intermediates here are of low or intermediate spin with structures closer to **2**. The small k_{-1}/k_2 value in the porphyrin systems also accounts for their much larger K values.

While the above interpretation of relative rates of CO and L addition to the undetected five-coordinate intermediate is admittedly speculative, the structural and magnetic data which are available on these systems would appear to support our proposals regarding the geometry of the intermediates. The in-plane metal–nitrogen distances in the phthalocyanines[30] and glyoximes (1.9 Å)[31] are about 0.1 Å shorter than those in corresponding porphyrins (~2.0 Å). Considering the estimated sizes of low- and high-spin iron(II), Hoard[30] has suggested that high-spin iron would have to move so far out of the plane in the $Fe^{II}Pc$ as to drastically weaken the bonding. From another point of view, the shorter metal–nitrogen distances in the iron glyoxime and phthalocyanine complexes (as compared with the iron porphyrins) result in a stronger ligand field and thus maintain a low or intermediate spin in the five-coordinate complexes. Mossbauer data[12,13,17,32] for L_2FePc and L_2Fe(porphyrin) systems are consistent with a weaker ligand field for the porphyrin ligand compared with phthalocyanine and add support to our in- and out-of-plane hypothesis. The resistance of the porphyrin skeleton to undue radial contraction has been proposed to account for the long Fe–N distances in iron porphyrins.[25,30] This inflexibility may also account for a greater tendency of the five-coordinate porphyrin systems to go high spin and thus for the iron to move out of the plane. It is noteworthy that at 25° the square-planar FePc has a lower magnetic moment (3.71 BM)[33] than Fe(TPP) (4.4 BM),[18] and (THF)$_2$Fe(TPP) is reported[18] to have a magnetic moment of 5.1 BM, while (DMSO)$_2$FePc is diamagnetic.[11]

The above hypothesis with respect to the geometry and spin state of the five-coordinate intermediate in the reactions of heme models is by no means proved but is presented as a working hypothesis to explain the large differences between the porphyrin and the other model systems. Such a hypothesis is currently being tested by further structural and kinetic studies.

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