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Reaction of Carbon Monoxide with Ferrous Porphyrins. Kinetics and Equilibria for the Binding of Carbon Monoxide to Octamethyltetrabenzoporphyriniron(II) Derivatives

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Abstract: The six-coordinate complexes $L_2Fe(OMBP)$, where OMBP = the dianion of octamethyltetrabenzoporphyrin and L = 1-methylimidazole (1-MeIm), pyridine (py), or piperidine (pip), reversibly bind carbon monoxide in toluene solution. The equilibria and kinetics of these reactions are compared to analogous data obtained previously for carbonylation of other ferrous porphyrins and phthalocyanines. The intermediary structure of OMBP with respect to phthalocyanine (Pc) and porphyrins such as protoporphyrin IX (PpIX) and tetraphenylporphyrin (TPP) presents an opportunity to compare reactivity within a series of closely related tetradentate nitrogen macrocycles. Equilibrium constants, K, for the reaction $L_2Fe(OMBP) + CO \rightleftharpoons LFe(OMBP)(CO) + L$ are intermediate between those found for corresponding PpIX and TPP systems on one hand and Pc on the other. Large rate constants for dissociation of L indicate a substantial cis effect for the OMBP ligand, and a possible mechanism is presented for the porphyrin-induced lability of axial ligands. The carbonyl compounds, LFe(OMBP)(CO) and LFePc(CO), have been isolated.

A well-known[1,2] and important, but poorly understood, property of metalloporphyrins is the enhanced lability of axial ligands, and this undoubtedly accounts for the incorporation of such compounds into biological systems. For example, iron(II) complexes are generally substitution inert, and yet the lability of heme centers such as Fe(PpIX) is clearly critical for biological activity in many protein systems, especially those involving binding and activation of dioxygen.

Considerable inorganic chemistry can be interpreted in terms of kinetic and thermodynamic trans effects,[3,4] while in contrast cis effects are poorly characterized.[4,5] Biological chemistry appears to require subtle balances in the contributions from both of these properties[6] and it is essential to clarify the consequences of porphyrin substitution on the axial coordination properties of metalloporphyrins.

Studies of amine binding to four-coordinate ferrous porphyrins[7] and substitution reactions of bisamine ferrous porphyrins with RNC,[8] CO,[9] and O_2[2,10] have not explained unequivocally how porphyrins mediate the properties of a metal center. Our objective has been to gain further insight into this problem by examining the binding properties of a series of ferrous porphyrins. Octamethyltetrabenzoporphyriniron(II), Fe(OMBP), completes a series in which it is a structurally intermediate complex between more typical porphyrins, such as Fe(PpIX) and Fe(TPP), and a tetraazaporphyrin, FePc (Figure 1). The equilibria and kinetics defining the reaction of CO with derivatives of all of these systems are discussed in this paper.

Experimental Section

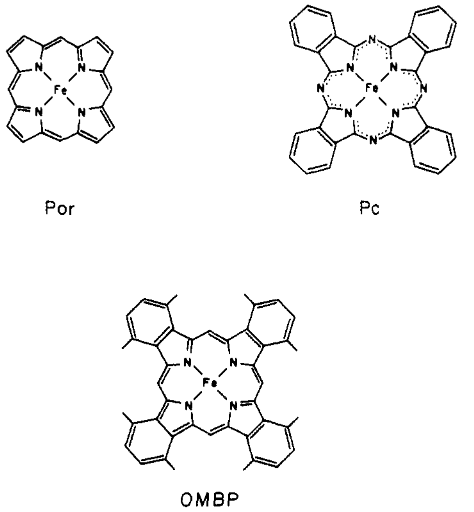
Inert atmosphere techniques were employed for all of the work described herein. The $(py)_2Fe(OMBP)$ complex was provided by J. R. Sams and T. B. Tsin of this department. Toluene was distilled from CaH_2 and stored under nitrogen. Pyridine (Fisher), piperidine (Fisher), and 1-methylimidazole (Aldrich) were distilled under anaerobic conditions from KOH and stored under nitrogen. Carbon monoxide was Matheson C.P. grade. Visible spectra were recorded on Perkin-Elmer 202 or Cary 14 spectrophotometers equipped with circulating constant-temperature baths. Infrared spectra were obtained in the solid state as Nujol mulls using a Perkin-Elmer 457. Carbonyl stretching frequencies were calibrated against the 1602-cm^{-1} peak of polystyrene and $\nu(CO)$ of CO gas and are considered accurate to $\pm 2\ cm^{-1}$.

Equilibrium Constant Measurements. Samples of $(py)_2Fe(OMBP)$ were weighed into a 1-mm path length spectrophotometric cuvette which was attached by a side arm to a reservoir bulb, fitted with a Teflon stopcock (Kontes Glass Co.) and an O-ring joint for attachment to a vacuum/gas-handling line. Toluene and appropriate quantities of amine required to give a reasonable variation in $[LFe(OMBP)(CO)]/[L_2Fe(OMBP)]$ with variation in CO pressure (0–1 atm) were placed in the reservoir bulb and degassed by four freeze-pump-thaw cycles. Solutions ($\sim 5\text{-}8 \times 10^{-5}$ M) were prepared by dissolving the compound in the solvent in vacuo. All solutions used for spectrophotometric measurements were prepared in a similar manner. For K_{CO}

Table I. Visible Spectra[a] of Fe(OMBP) Complexes and CO Stretching Frequencies (cm^{-1}) for LFe(P)(CO) Derivatives (P = OMBP, Pc)

	λ_{max}, nm ($\epsilon \times 10^{-4}$ M^{-1} cm^{-1})		
L	L_2Fe(OMBP)	LFe(OMBP)(CO)	ν(CO)[d]
py[b]	387 (8.6), 408 sh, 434 (19), 460 sh, 560 (1.7), 583 sh, 605 (10)	425 (15), 545 (1.8), 625 (9.0)	1966
1-MeIm[c]	403 (11), 428 sh, 444 (11), 558 (1.6), 582 sh, 606 (14)	428 (16), 560 (1.5), 623 (11)	1964
pip[c]	401 (12), 442 (6.0), 559 (1.5), 583 sh, 607 (11)	426 (18), 556 (1.8), 624 (11)	1972

[a] Spectra recorded using toluene solutions at room temperature. [b] Measured in the presence of excess py. [c] Complexes formed in situ. [d] ν(CO) for LFe(Pc)(CO) complexes: L = py, 1996; pip, 1995; 1-MeIm, 1994.



Por

Pc

OMBP

Figure 1. Structures of four-coordinate ferrous porphyrins (Por), phthalocyanine (Pc), and octamethyltetrabenzoporphyrin (OMBP).

determinations, the visible spectrum was recorded after addition of various CO pressures.[11] Analysis was carried out as described in the text. Plots of equilibrium and kinetic data were fitted with a linear regression program.

Kinetic Measurements. All reactions were studied by means of a Durrum 110 stopped-flow apparatus equipped with a 2-cm light path cuvette. Kinetics of the forward reaction were determined as a function of [L]/[CO]. During a typical experiment, a solution (~2 × 10^{-5} M) of L_2Fe(OMBP) in toluene, under nitrogen, containing a known concentration of excess amine L, was mixed with a toluene solution of known [CO]. For the reverse reaction a solution of LFe(OMBP)(CO) under CO was mixed with a toluene solution of L (~1 M).

Each value of k_{obsd} was calculated as an average of at least six determinations, i.e. at three wavelengths during each experiment using a minimum of two experiments. The precision obtained was always better than 10%.

Preparation of LFeP(CO) Complexes, P = OMBP and Pc. Two methods were used for the synthesis of the carbonyl complexes, the choice being dictated by the necessity of preventing CO dissociation from the more labile Pc systems. Schlenk-tube techniques employing a CO atmosphere were used in all cases.

(1) LFe(OMBP)(CO). A solution was prepared by adding, to 0.2 g of the solid $(py)_2$Fe(OMBP) complex, 10 mL of CO-saturated toluene containing an aliquot of L (1.5 mL of pip or 2.0 mL of 1-MeIm; or no py); this was stirred under CO for 24 h. Addition of 20 mL of CO-saturated methanol induced essentially quantitative precipitation of the product which was filtered, washed several times with methanol (in a Schlenk filter, under CO), and dried in vacuo (yields ≥80%).

(2) LFePc(CO). The bisamine complexes, L_2FePc, are readily obtained[12] and were used as starting materials for the general procedure described above. However, after precipitation the solvent was decanted and the product washed several times with CO-saturated methanol. The carbonyl complex was then dried in a CO stream and stored under CO (yields ≥80%).

Excellent analytical data, carried out by Mr. P. Borda of this department, were obtained for all the carbonylamine complexes, which display limited solubility in common organic solvents. Visible spectral and ν(CO) data for the complexes in toluene are given in Table I.

Results

Properties of L_2Fe(OMBP) Complexes. The $(py)_2$Fe(OMBP) complex (I) was prepared by Sams and Tsin[13] using a modification of the procedure reported[14] for the synthesis of $(py)_2$Mg(OMBP); $(1\text{-MeIm})_2$Fe(OMBP) was obtained by the displacement of py from I, but we have been unable to isolate the bis(piperidine) analogue. Complexes were readily prepared in situ by the addition of the appropriate amine ([amine]:[Fe complex] $\simeq$ 100:1) to toluene solutions of $(py)_2$Fe(OMBP). This complex (I) is air stable in the solid state but solutions react immediately with air or O_2 in the absence of excess pyridine. Addition of pyridine or other amines reduces this air sensitivity by inhibiting dissociation to a five-coordinate intermediate involved[2] in the oxidation process. In contrast to its air stability, I absorbs CO in the solid state.

Visible spectra of the L_2Fe(OMBP) complexes in toluene at 20 °C are given in Table I. The spectral parameters for I are independent of [py] from 5 × 10^{-4} to 12 M (neat py), and Beer's law is obeyed in the presence of added pyridine. However, solutions containing no added pyridine give identical peak positions, but the spectra show deviations from Beer's law at 20 °C and the 460-nm shoulder is greatly increased in intensity. Such features are absent on lowering the temperature (<−45 °C) when "normal" behavior is apparent. Aggregation phenomena[15] are unlikely at the low concentrations used (10^{-4} to 10^{-6} M), and the spectral behavior is suggestive of a dissociative process, eq 1 or 2:

$$(py)_2Fe(OMBP) \rightleftharpoons (py)Fe(OMBP) + py \qquad (1)$$

$$(py)_2Fe(OMBP) \rightleftharpoons Fe(OMBP) + 2\ py \qquad (2)$$

Equilibria analogous to eq 1 have been reported[16] for other ferrous porphyrins, but are usually found when steric interactions destabilize the six-coordinate species.[17] The 460-nm shoulder may be due to (py)Fe(OMBP).[18] The formation of four-coordinate porphyrins from bisamine complexes can be accomplished by heating solid samples in vacuo;[19] for 1, temperatures in excess of 180 °C are required.[13] Solution data for equilibria such as eq 2 with TPP and deuteroporphyrin[7c] give log $\beta_2 \geqslant 7$, and our observations with OMBP are consistent with such an overall equilibrium constant.

Addition of small quantities of 1-MeIm or piperidine to solutions of I gives pronounced and rapid spectral changes due to eventual formation of the L_2Fe(OMBP) complexes. Their visible spectra (Table I) are independent of amine concentrations from 100-fold excess (i.e., ~5 × 10^{-3} M) to neat amine. Attempts to determine K_1 and K_2 (eq 3 and 4) were made by adding neat amine (pip or 1-MeIm) to a 6 × 10^{-5} M solution of I containing 1.5 × 10^{-3} M py. Good isosbestic points were observed for an added [amine] up to about 10^{-2} M, and further amine addition then resulted in formation of a new set of isosbestic points, but quantitative evaluation of these data was precluded by the small absorbance changes within a given isosbestic system; the data are consistent with

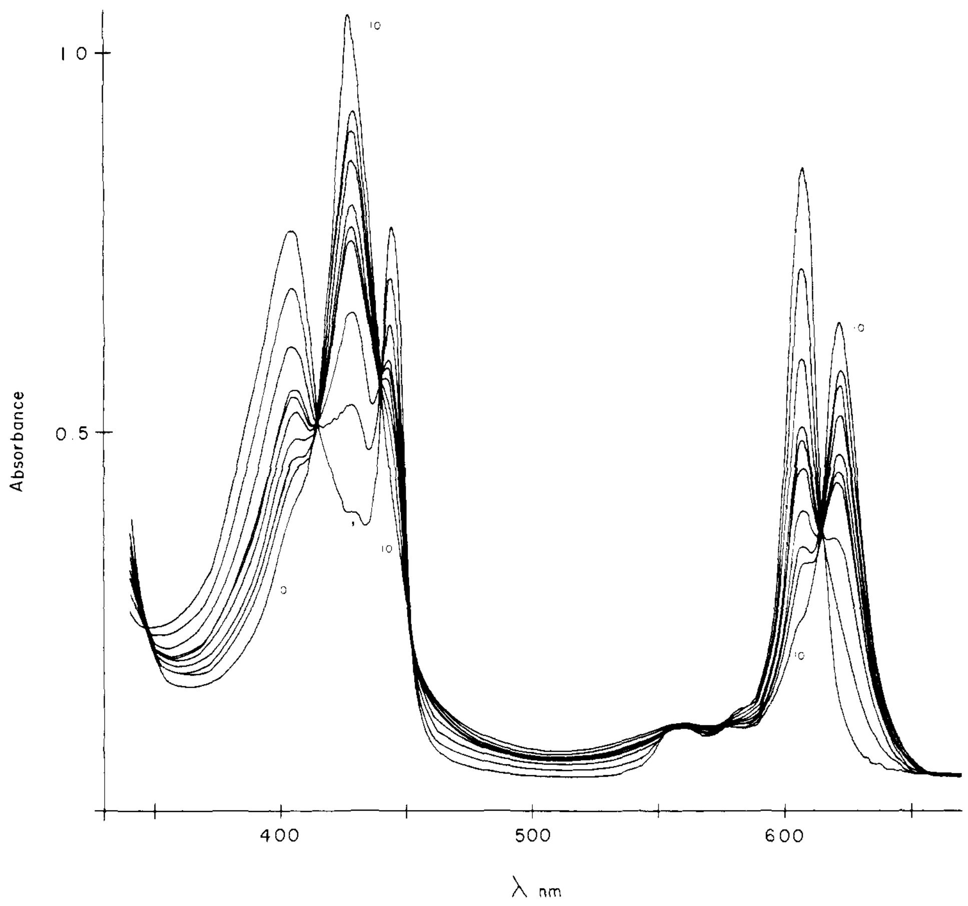


Figure 2. Spectral data for the determination of K for $(1\text{-MeIm})_2Fe(OMBP)$ + CO. Pressures of CO added to a toluene solution of $(1\text{-MeIm})_2Fe(OMBP)$ ($\sim 10^{-5}$ M) containing 1-MeIm (0.252 M) at 23 °C are, for spectra 1-10; 0, 21.7, 57.7, 101, 111, 133, 194, 269, 330, and 738 Torr.

eq 3 and 4, K_1 being somewhat less than 1 and $K_1 - K_2$ being less than 100.

$$(py)_2Fe(OMBP) + L \overset{K_1}{\rightleftharpoons} (py)(L)Fe(OMBP) + py \quad (3)$$

$$(py)(L)Fe(OMBP) + L \overset{K_2}{\rightleftharpoons} L_2Fe(OMBP) + py \quad (4)$$

Carbonylation Reactions (Equilibria). Addition of CO to solutions of the in situ fully formed $L_2Fe(OMBP)$ complexes resulted in a darkening of the characteristic green solutions and the appearance of a reflected red coloration. The reaction could be reversed by prolonged degassing of the solutions or by the addition of excess L. Typical spectral changes are shown in Figure 2. The dependence of the spectra on CO pressure (P_{CO}) and [L] is consistent only with the equilibrium:

$$L_2Fe(OMBP) + CO \overset{K}{\rightleftharpoons} LFe(OMBP)(CO) + L \quad (5)$$

and this is further confirmed by the isolation of the 1:1 CO adducts (see above).

The equilibrium expression may be written:

$$\log\left[\frac{A_0 - A}{A - A_\infty}\right] = \log K + \log(P_{CO}) - \log[L] \quad (6)$$

where A_0 and A_∞ are the absorbances of $L_2Fe(OMBP)$ and LFe(OMBP)(CO), respectively. A_∞ values determined by forcing equilibria 5 completely to the right were identical with those calculated from the extinction coefficients of the isolated carbonyls. Plots of $\log[(A_0 - A)/(A - A_\infty)]$ against $\log(P_{CO})$ were linear with slopes of 1 ± 0.05 (Figure 3). The K values were calculated in units of M $Torr^{-1}$ and converted to the unitless data given in Table II using the solubility[20] of CO in toluene (6.5×10^{-3} M atm^{-1}). There is no interference in the L = 1-MeIm or pip systems due to the presence of the very small amounts of displaced pyridine in solution.

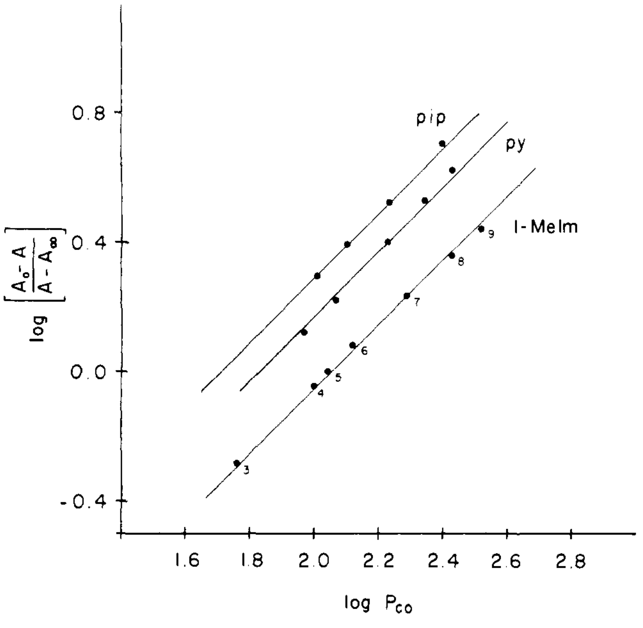


Figure 3. Plot of absorbance data for the $L_2Fe(OMBP)$ + CO equilibrium with varying CO pressure at constant: [pip] = 1.05 M, [py] = 0.123 M, [1-MeIm] = 0.252 M. For the 1-MeIm system, the data points are an average of those calculated at three wavelengths, 428, 606, and 623 nm, using the absorbance values from Figure 2.

Kinetics of Carbonylation. The fast forward reactions were

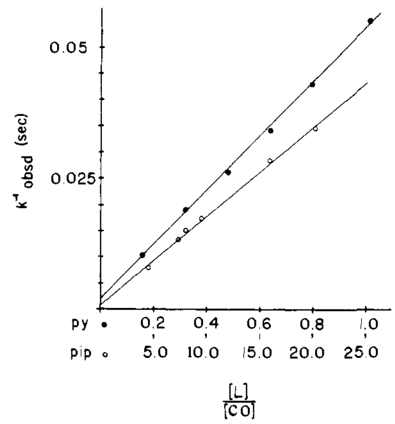


Figure 4. Plot of k_{obsd}^{-1} against [L]/[CO] for the reaction of $L_2Fe(OMBP)$ with CO (L = py, pip). Similar data were obtained for L = 1-MeIm.

studied as a function of added amine concentration at a constant or varied CO pressure, the excess amine also advantageously protecting the otherwise air-reactive solutions. The range of [L]/[CO] was chosen such that all reactions went to completion, and good first-order plots of log $[L_2Fe(OMBP)]$ vs. time were obtained.

For the mechanism:

$$L_2Fe(OMBP) \underset{+L,\,k_{-1}}{\overset{-L,\,k_1}{\rightleftharpoons}} LFe(OMBP) \underset{-CO,\,k_{-2}}{\overset{+CO,\,k_2}{\rightleftharpoons}} LFe(OMBP)(CO) \quad (7)$$

the rate law, assuming a steady-state concentration for the five-coordinate intermediate and neglecting k_{-2}, is:

$$\text{rate} = \frac{k_1k_2[L_2Fe(OMBP)][CO]}{k_{-1}[L] + k_2[CO]} = k_{obsd}[L_2Fe(OMBP)] \quad (8)$$

where k_{obsd} is a pseudo-first-order constant, since [L] and [CO] are effectively constant within each experiment. Thus:

$$k_{obsd}^{-1} = (k_1)^{-1} + k_{-1}[L]/k_1k_2[CO] \quad (9)$$

and plots of k_{obsd}^{-1} against [L]/[CO] gave excellent straight lines for all the amine systems (Figure 4). The parameters k_1 and k_{-1}/k_2 were determined from the intercepts and slopes, respectively, and values of k_{-2} were calculated from k_1, k_{-1}/k_2, and K (Table II). The k_{-2} values for L = py and 1-MeIm were in reasonable agreement with those obtained directly from a stopped-flow investigation of the reverse reaction using solutions prepared from in situ or solid samples of LFe(OMBP)(CO). The dissociative mechanism is confirmed by the invariance of the reverse reaction rates on the nature of the added amine.

Activation parameters for the carbonylation of $(py)_2Fe(OMBP)$ were estimated from the temperature dependence of k_1 over the range 8–23 °C to be $\Delta H^{\ddagger} \simeq 22$ kcal mol^{-1} and $\Delta S^{\ddagger} \simeq +28$ eu, although there are difficulties in thermostating a conventional Durrum 110 stopped-flow instrument at temperatures below ambient. The positive $\Delta S^{\ddagger}$ seems consistent with a dissociative mechanism.

Discussion

Kinetic and Equilibria Data. The data for the reactions of CO with iron octamethyltetrabenzoporphyrin complexes are summarized in Table II. The high error (±50%) in k_1 results from very small intercept values (Figure 4) and limits comparison within the OMBP series; nevertheless, for all three systems $k_1 > 300$ s^{-1}, and the complexes all display a pronounced amine lability. Piperidine likely has the greatest lability and this was found also in corresponding $(pip)_2FePc$[9b] and $(pip)_2Fe(TPP)$[9c] systems and was attributed to a long Fe-N bond resulting from steric interactions.[21]

The k_{-1}/k_1k_2 values, calculated from the slopes of Figure 4, are obtained within ±5% as are the equilibrium constants ($K = k_1k_2/k_{-1}k_{-2}$), and there is good agreement between the calculated and experimental k_{-2} values. Photochemically induced CO dissociation[22] is not important under our experimental conditions.

The calculated k_{-1}/k_2 ratios are dependent on the magnitude of k_1, and their interpretation should be considered cautiously; however, they are all $\geqslant 1$. The lower limits placed on k_1 do suggest that (pip)Fe(OMBP) has a kinetic preference for CO over amine by a factor of about 10 relative to LFe(OMBP), L = 1-MeIm or py, and this appears to be the major contribution to the enhanced binding of CO to $(pip)_2Fe(OMBP)$ (see below). Equilibrium and kinetic data for the reaction of L_2FeP complexes (L = py, pip; P = OMBP, PpIX, and Pc) with CO are given in Tables II and III. Notably, for the structurally intermediate OMBP complex, the equilibrium constant is also intermediate, but the relative contributions of the various rate constants are somewhat complex (Table III). Nevertheless, the high K values for the PpIX and TPP systems compared to the Pc system are due to both greater k_1 and much lower k_{-1}/k_2 values for the porphyrins. The data emphasize the enhanced lability of piperidine (and probably other amines) for the OMBP system relative to the other porphyrin and Pc systems, which are themselves labile compared with other iron(II) systems including macrocycles such as diphenyl glyoxime (for example, k_1 and k_{-2} for the (py) $_2Fe(DPGH)_2$ system[23] are, respectively, about 100 and 1000 times smaller than for the $(py)_2FePc$ system). Porphyrin substituent effects with PpIX and TPP seem small compared with those observed on changing to the OMBP and Pc systems (Table III).

The rates of CO dissociation (k_{-2}), unlike those of amine dissociation (k_1), are relatively insensitive to the nature of the in-plane ligand, although the CO stretching frequencies for

Table II. Kinetic and Equilibrium Data[a] for the Reaction of $L_2Fe(OMBP)$ Complexes with CO in Toluene at 23 °C

L	k_1,[b] s^{-1}	k_{-2},[c] s^{-1}	K[e]	k_{-1}/k_2
pip	1020	0.25	2340	1.7
1-MeIm	780	0.05 0.13[d]	260	57
py	490	0.09 0.17[d]	209	26

[a] See eq 5 and 7 for a definition of various constants. [b] Estimated error ±50%. [c] Unless indicated otherwise, values calculated from K and k_{-1}/k_1k_2; estimated error ±20%. [d] Determined directly, ±10%. [e] Estimated error ±0.05 in log K.

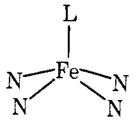
Table III. Kinetic and Equilibrium Data[a] for the Reaction of $(pip)_2FeP$ Complexes with CO in Toluene at 23 °C

P	k_1, s^{-1}	k_{-2}, s^{-1}	K	k_{-1}/k_2
OMBP	1020	0.25	2 340	1.7
PpIX[b]	20	0.06	230 000	0.002
TPP[b]	11	0.52	15 000	0.002
Pc[c]	0.50	0.13	0.85[d]	3.3

[a] See eq 5 and 7 for definition of various constants. [b] Reference 9c. [c] Reference 9b. [d] Value for the corresponding pyridine system is 0.37 (ref 9b).

the LFeP(CO) complexes exhibit significant differences (Table I). There is no obvious correlation between ν(CO) and the CO lability or the equilibrium constants, although an increase in amine lability (OMBP > PpIX > Pc) appears to parallel the decrease in ν(CO). For carbonyl derivatives of Fe(PpIX, dimethyl ester), ν(CO) typically[24] lies between the values reported here for the Pc and OMBP complexes; for (pip)Fe(TPP)(CO), ν(CO) is 1976 cm^{-1}.

Previously, arguments were advanced[9b] regarding the structure of the porphyrin and phthalocyanine five-coordinate intermediates as deduced from kinetic data. Steric considerations suggest that the relative rates of amine to CO addition (k_{-1}/k_2) for the intermediate should decrease with the extent that the iron lies out of the plane of the equatorial ligand system, as in **1**. The 1000-fold decrease in k_{-1}/k_2 for PpIX and TPP systems relative to Pc (and DPGH) systems (Table III) was rationalized in terms of the porphyrin intermediates resembling high-spin **1**, while the phthalocyanine and glyoxime intermediates were thought closer to structure **2**, of low or intermediate spin, and such conclusions seemed consistent with known structural and magnetic data. The OMBP data (Tables II and III) suggest an intermediate where the iron is more "in" than "out" of the porphyrin plane. The smaller k_{-1}/k_2 ratio for (pip)Fe(OMBP), very similar to the ratio for the Pc and DPGH systems, might reflect a slightly more out-of-plane structure relative to the other LFe(OMBP) intermediates, L = 1-MeIm or py, and such a movement could decrease unfavorable steric interactions[21] with the bulky piperidine. If the kinetic arguments are correct, the iron is more in the plane in the LFe(OMBP) intermediates than in the corresponding intermediates of the PpIX and TPP systems.



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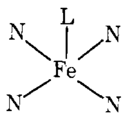

2

Metal Porphyrin Bonding. The equilibrium and kinetic data indicate considerable effects for the benzopyrrole and meso aza groups, while the carbonylation parameters for the PpIX and TPP derivatives are remarkably similar. Of interest is how the substituents change reactivity at the axial positions.

Porphyrin substituent effects are commonly correlated with porphyrin basicity, expressed by the first protonation of the free base (pK_3). Such pK_3 values should denote only differences in the σ-bonding abilities of various porphyrins and these can only alter the available *axial* electron density by changing the energy of the metal d orbitals. However, pK_3 data appear to be inversely related to the Soret peak maxima in porphyrin and metalloporphyrin electronic spectra; the larger pK_3 is, the more $\lambda_{\max}$ is shifted to higher energy.[25] Since such spectra are mainly due to $\pi \rightarrow \pi^*$ transitions, substituents must alter the relative energies of π orbitals, and it is these which in terms of symmetry are likely to influence axial ligand reactivity.

π interactions between transition metals (d_π; d_{xz}, d_{yz}) and porphyrins (π or π^*) are well established,[26] and for a strong metal-porphyrin bond the molecular orbitals of the system possess large contributions from both the metal and porphyrin, and possibly axial ligand, orbitals.[27] The concept of extensive d-orbital delocalization and concurrent loss of metal d character appears a likely general basis of porphyrin-induced labilization.[16] An interpretation of porphyrin substituent effects requires a detailed knowledge of changes in molecular orbital energies and population, and thus we are restricted to qualitative arguments involving atomic orbital interactions and possible electron transfer.

Replacement of the porphyrin methine carbons by aza groups is expected to inflict severe changes in the porphyrin and metal-porphyrin bonding. The radius of the central hole of phthalocyanines is smaller than that of porphyrins,[28] and the former are stronger ligand field molecules.[9b,28] There appears to be less available electron density on the central metal in FePc derivatives relative to the iron porphyrins, as indicated by the diminished back bonding to CO which is reflected in the high ν(CO) values. The DPGH systems show the same high ν(CO) values as the Pc complexes. These strong field ligands could cause a decrease in the metal d_{xz} and d_{yz} energies, and so result in poorer overlap with the COπ^* levels, or the ligands may be considered good π acceptors as suggested by FePc redox potential data.[29] It is tempting to attribute the lower kinetic lability of the Pc, and especially DPGH, complexes to a more electropositive metal, but the dramatic differences in k_{-2} for the DPGH and Pc carbonyl compounds despite identical infrared data underscore the inadequacy of such a rationale.

Different π systems, but similar central hole sizes, are anticipated[13b,c] for the ferrous porphyrins. Large ring current effects[30] demonstrate the increased π-electron density due to the benzene rings of OMBP[13b,c] and Pc, but the inability[31] of the TPP meso phenyl groups to orient themselves in the porphyrin plane will attenuate the π contribution from these substituents. Thus, it has been suggested[13b,c] that π-electron density will decrease in the order OMBP > Pc > TPP > PpIX, and Mössbauer data[13] for the four-coordinate ferrous porphyrins are quite consistent with this; π-$d\pi$ mixing (porphyrin $\rightarrow$ metal) decreases in the order Fe(OMBP) > Fe(TPP) > Fe(PpIX). For FePc, σ effects dominate, consistent with the enhanced ligand field. Similar data[13] for the bis(pyridine) adducts indicate that the π-donor strength of OMBP is maintained upon axial ligand coordination, although differences between the PpIX and TPP compounds are reduced.

The extensive π delocalization within the OMBP molecule would be expected to resist doming or other potential perturbations[32] of the porphyrin skeleton, and thus favor a more planar geometry for five-coordinate complexes of this porphyrin, consistent with our interpretation of the kinetic data.

For a planar geometry, only the d_{xz} and d_{yz} orbitals are of the proper symmetry to overlap with the porphyrin π system. Although an out-of-plane movement of the iron may reduce such overlap, nonplanarity allows considerably mixing of the d_{z^2} and filled porphyrin π orbitals (a_{2u} in D_{4h} symmetry).[33] Porphyrin-induced labilization is likely a consequence of subtle balances in: (1) the facile movement of the iron along the reaction coordinate, (2) lower to higher spin conversion which results in unpaired spin density in the d_{z^2} and $d_{x^2-y^2}$ levels, and (3) porphyrin $\rightarrow$ metal augmentation of electron density in both σ and π axial orbitals (ligand binding), which destabilizes six-coordinate and/or stabilizes five-coordinate species. Compared to other porphyrin systems, the large π donation, OMBP $\rightarrow$ Fe, may provide sufficient activation/stabilization without as large an out-of-plane iron movement. Poor σ donation[34] could sufficiently lower the d_{z^2} energy such that this orbital is occupied (intermediate spin) instead of empty (low spin) in OMBP "in-plane" five-coordinate species. Both the planarity of the FePc complexes and the poor matching of Fe($d\pi$) and Pc(π) orbitals will result in a decreased kinetic lability, as observed.

The smaller variation in dissociative rate constants for CO relative to L could be rationalized in terms of the synergic bonding character of the carbonyl group modulating the available electron density more effectively than amines.

In conclusion, the enhanced lability of axial amine ligands in iron(II) OMBP systems, relative to other porphyrin and phthalocyanines, has been discussed as a function of the structural and especially π-bonding properties. There is clearly a subtle and complex[38] interplay of π and σ effects, and the degree to which these effects will be realized will depend on the particular metalloporphyrin and property under consideration.

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