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Influence of Substituted Pyridines on the Redox Reactions of Iron Porphyrins

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The electroreduction mechanisms of (perchlorato)- and (chlorato)(*meso*-tetraphenylporphinato)iron and (perchlorato)- and (chlorato)(octaethylporphinato)iron were investigated as a function of complexation by substituted pyridines in dichloromethane. Formation constants for bis adducts were measured for 11 substituted pyridines with pK_a values ranging from 0.67 to 9.71. $\Delta \log K/\Delta pK_a$ quotients are listed and compared to quotients in the literature for other metalloporphyrins.

Introduction

A knowledge of ligand binding properties of synthetic Fe porphyrins and electrooxidation–reduction mechanisms involving Fe(III) and Fe(II) porphyrins is essential for interpretation of structure–function relationships of hemoproteins.[1,2] Formation constants for both the mono- and bis-ligand adducts of Fe(III) and Fe(II) are dependent on the electronic and steric factors of the added ligand, the nature of the counterion on Fe(III), and the solvent composition.[3]

In an earlier study[4,5] we reported stability constants for addition of nitrogeneous bases to Fe(III) porphyrins according to reactions 1 and 2 and Fe(II) porphyrins according to re-

$$\text{(P)Fe(S)X} + 2\text{L} \rightleftarrows \text{(P)Fe(L)}_2{}^+\text{X}^- + \text{S} \qquad (1)$$

$$\text{(P)Fe(S)}_2{}^+\text{X}^- + 2\text{L} \rightleftarrows \text{(P)Fe(L)}_2{}^+\text{X}^- + 2\text{S} \qquad (2)$$

actions 3 and 4. In the above reactions P represents the

$$\text{(P)Fe(S)} + 2\text{L} \rightleftarrows \text{(P)Fe(L)}_2 + \text{S} \qquad (3)$$

$$\text{(P)Fe(S)}_2 + 2\text{L} \rightleftarrows \text{(P)Fe(L)}_2 + 2\text{S} \qquad (4)$$

porphyrin structure, L an axial ligand (usually a substituted pyridine or imidazole), X an anion (usually a halide), and S a solvent molecule.

In this paper we wish to report how the electroreduction mechanisms are changed by complexation of substituted pyridines to intermediate-spin porphyrin complexes[6,7] of (OEP)FeClO_4,[8] (TPP)FeClO_4, (OEP)Fe, and (TPP)Fe. For comparative purposes, we have also investigated the electrode reactions of (OEP)FeCl and (TPP)FeCl with the same ligands.

Experimental Section

Chemicals. (TPP)FeCl and $\text{((TPP)Fe)}_2\text{O}$ were used as received from Strem Chemical Co. The porphyrins (OEP)FeCl, (OEP)FeClO_4, and (TPP)FeClO_4 were prepared by acid hydrolysis of the respective μ-oxo dimer as per the method of Dolphin et al.[7] All substituted pyridines were used as received from Aldrich. The solvent CH_2Cl_2 was purchased from Fisher Scientific and was distilled over P_2O_5. Tetrabutylammonium chloride ((TBA)Cl) and the supporting electrolyte tetrabutylammonium perchlorate (TBAP), Eastman Chemicals, were dried in vacuo. All solutions were made 0.1 M in TBAP and were deoxygenated by bubbling solvent-saturated N_2 through the solution for 10 min.

Instrumentation. Cyclic voltammetric measurements were made with an EG&G Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat driven by a PAR Model 175 universal programmer. Scans were recorded either with a Houston Omnigraphic 2000 X-Y recorder or with a Tektronix Model 5111 storage oscilloscope. A conventional three-electrode system was utilizied. A Pt button served as the working electrode, and a Pt wire was used as the counterelectrode. A commercial saturated calomel electrode (SCE) was utilized as the reference electrode. Current–voltage curves were measured at 0.02–10 V/s, while all titrations were recorded either at 0.05 or 0.10 V/s. At faster scan rates IR loss was held to a minimum by the use of a positive-feedback device built into the Model 176 current follower.

Differential pulse polarographic measurements were made with a PAR Model 174 polarographic analyzer utilizing a conventional three-electrode system. A scan rate of 10 mV/s, a pulse interval of 0.5 s, and a pulse amplitude of 25 mV were the instrumental parameters imposed on the dropping-mercury electrode. For all electrochemical measurements the SCE was separated from the bulk of the solution with a fritted-glass bridge filled with solvent and supporting electrolyte. Stability constants were determined from the shifts of half-wave potentials as a function of ligand concentration. The method of calculation has been described in previous publications.[5,9] All potentials are reported in volts vs. the SCE.

Results and Discussion

Electrode Reactions in CH_2Cl_2. Figure 1a illustrates a typical cyclic voltammogram of (OEP)FeClO_4 in CH_2Cl_2–0.1 M TBAP. The oxidation at 1.02 V is within experimental error of that reported by Felton et al.[10] and is identical with that observed for (OEP)FeCl (see Figure 1b). The reduction at −1.29 V can also be compared to the half-wave potential of −1.33 V obtained in Me_2SO for reduction of (OEP)FeOH.[11] This reaction has been attributed in an earlier paper to formation of the anion radical[11] while in later papers similar electroreductions of other iron(II) porphyrins were shown to yield Fe(I) complexes.[12,13] Felton and co-workers[10] have characterized the oxidation at 1.02 V as the production of an Fe(IV) species (which may be further oxidized to yield a cation radical).

As seen in Figure 1, changes in the counterion of $[\text{(OEP)Fe}]^+$ (i.e., Cl^- or ClO_4^-) have no effect on the oxidation potentials to produce Fe(IV) or the reduction potentials to produce Fe(I). In contrast, however, a dramatic effect is

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(1) "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier Scientific Publishing Co., New York, 1975.

(2) D. Dolphin, Ed., "The Porphyrins", Academic Press, New York, 1978.

(3) F. A. Walker, M. W. Lo, and M. T. Ree, *J. Am. Chem. Soc.*, **98**, 5552 (1976).

(4) K. M. Kadish and L. A. Bottomley, *J. Am. Chem. Soc.*, **99**, 2380 (1977).

(5) K. M. Kadish, L. A. Bottomley, and D. Beroiz, *Inorg. Chem.*, **17**, 1124 (1978).

(6) C. A. Reed, T. Mashiko, S. P. Bentley, M. E. Kastner, W. R. Scheidt, K. Spartalion, and G. Lang, *J. Am. Chem. Soc.*, **101**, 2948 (1979).

(7) D. H. Dolphin, J. R. Sams, and T. B. Tsin, *Inorg. Chem.*, **16**, 711 (1977).

(8) Abbreviations used in this paper are octaethylporphyrin = OEP^{2-}, tetraphenylporphyrin = TPP^{2-}, dichloromethane = CH_2Cl_2, and pyridine = py.

(9) K. M. Kadish, L. A. Bottomley, and J. S. Cheng, *J. Am. Chem. Soc.*, **100**, 273 (1978).

(10) R. H. Felton, G. S. Owen, D. Dolphin, A. Forman, D. C. Borg, and J. Fajer, *Ann. N.Y. Acad. Sci.*, **206**, 504 (1973).

(11) J. H. Fuhrhop, K. M. Kadish, and D. G. Davis, *J. Am. Chem. Soc.*, **95**, 5104 (1973).

(12) D. Lexa, M. Momenteau, and J. Mispelter, *Biochim. Biophys. Acta*, **338**, 151 (1974).

(13) K. M. Kadish, G. Larson, D. Lexa, and M. Momenteau, *J. Am. Chem. Soc.*, **97**, 282 (1975).

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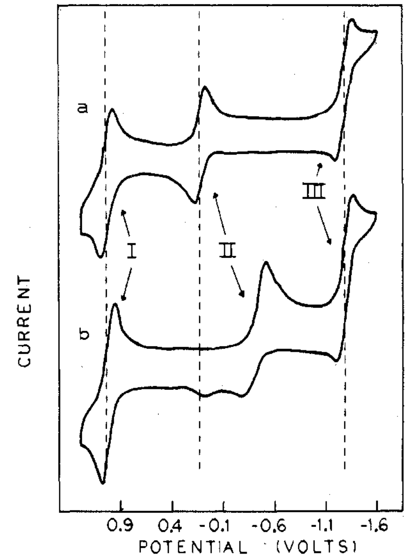

Figure 1. Cyclic voltammograms of (a) (OEP)$FeClO_4$ and (b) (OEP)FeCl in CH_2Cl_2–0.1 M TBAP. The designations I, II, and III correspond to the reactions Fe(IV)/Fe(III), Fe(III)/Fe(II), and Fe(II)/Fe(I), respectively. Porphyrin concentrations were 1.5×10^{-3} M.

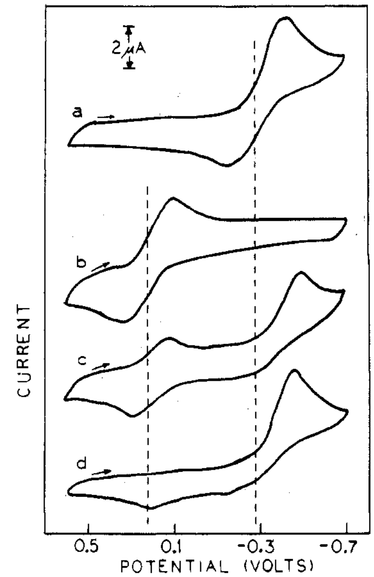

Figure 2. Cyclic voltammograms showing the Fe(III)/Fe(II) reaction for (a) (OEP)FeCl + 3.3 equiv of (TBA)Cl, (b) (OEP)$FeClO_4$, (c) (OEP)$FeClO_4$ + 0.5 equiv of (TBA)Cl and (d) (OEP)ClO_4 + 1 equiv of (TBA)Cl.

observed for the reaction Fe(III)/Fe(II). (OEP)$FeClO_4$ (Figure 1a) exhibits Nernstian separated cathodic and anodic peaks ($E_{pc} - E_{pa}$ = 70 mV) while (OEP)FeCl (Figure 1b) has a single reduction peak −0.53 V and two oxidation peaks at −0.35 and 0.02 V. The peak at −0.35 V is 180 mV anodic of the reduction peak while the second oxidation peak at 0.02 V is 550 mV removed from the reduction process.

In order to investigate the effect of Cl^- on the reduction mechanism, we added (TBA)Cl to solutions of (OEP)FeCl and (OEP)$FeClO_4$ while keeping the ionic strength constant. The results of this are shown in Figure 2. After addition of 0.5 equiv of (TBA)Cl, the cyclic voltammograms indicated a mixture of (OEP)FeCl and (OEP)$FeClO_4$ in solution (Figure 2c). Upon addition of 1 equiv it appeared that only (OEP)-FeCl was present, as indicated by the similarity of the cyclic voltammogram on Figure 2d to the cyclic voltammogram of (OEP)FeCl (Figure 1b).

Table I. Reduction Potentials of (TPP)$FeClO_4$ in CH_2Cl_2 Containing 1.0 M Substituted Pyridine

			$E_{1/2}$, V	
no.	L	pK_a[a]	Fe(III)/ Fe(II)[c]	Fe(II)/ Fe(I)[d]
1	3,5-dichloropyridine	0.67	0.31	−1.38
2	3-cyanopyridine	1.40	0.29	−1.43
3	4-cyanopyridine	1.86	0.30	−1.32
4	3-chloropyridine	2.81	0.21	−1.46
5	3-bromopyridine	2.84	0.21	−1.45
6	4-acetylpyridine	3.51	0.18	NO[b]
7	pyridine	5.28	0.06	−1.52
8	3-picoline	5.79	0.05	−1.52
9	4-picoline	5.98	0.02	−1.55
10	3,4-lutidine	6.46	0.01	NO[b]
11	4-(dimethylamino)pyridine	9.71	−0.17	NO[b]

[a] K. Schoefield, "Hetero-Aromatic Nitrogen Compounds", Plenum Press, New York, 1967, p 146. [b] NO = not observable within solvent system range. [c] Computed from cyclic voltammetric data where $E_{1/2} = {}^1/_2(E_{pc} + E_{pa})$. [d] See ref 14.

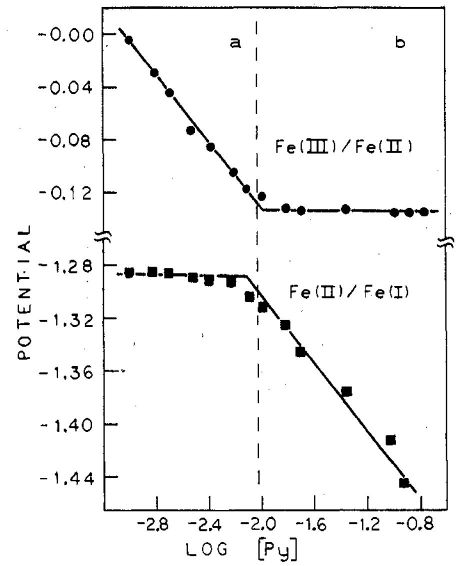

Figure 3. Potential vs. log [py] in bulk solution for the electroreduction of (OEP)$FeClO_4$ in pyridine. Squares correspond to peak potentials obtained by differential-pulse polarography while circles are half-wave potentials as obtained by cyclic voltammetry.

Mechanism of (TPP)$FeClO_4$ and (OEP)$FeClO_4$ Reduction in the Presence of Substituted Pyridines. The electrode reactions of (OEP)$FeClO_4$ were investigated in CH_2Cl_2 containing 11 nonsterically hindered substituted pyridines. These ligands and their pK_a's are listed in Table I. Cyclic voltammograms and differential pulse polarograms were obtained in CH_2Cl_2 solutions containing between 10^{-3} and 1.0 M ligand.

For the determination of number of ligands involved in the redox process, half-wave potentials were measured and plotted as a function of log [ligand]. This is illustrated in Figure 3 for the electrode reactions of (OEP)$FeClO_4$ in CH_2Cl_2–pyridine mixtures. This figure has been divided into two regions of pyridine concentration on the basis of the prevailing electron-transfer reactions.

In region A, addition of pyridine to (OEP)$FeClO_4$ produced no changes from $E_{1/2} = -1.29$ V as obtained by differential-pulse polarography[14] for the (OEP)Fe $\rightleftarrows$ $[(OEP)Fe]^-$

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(14) Process is overlapped with solvent background at Pt electrode. Reversibility of the process was verified by classical polarography. The half-wave potential was calculated from differential-pulse polarographic data for which $E_{1/2} = E_p + {}^1/_2$(pulse amplitude). See ref 15.

(15) G. A. Heath and G. Hefter, *J. Electroanal. Chem. Interfacial Electrochem.*, **84**, 295 (1977).

Scheme I

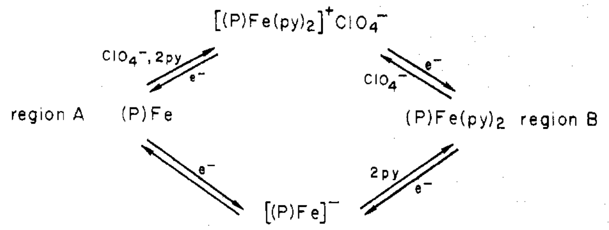

Table II. Formation Constants for Addition of Substituted Pyridines to (TPP)Fe and (TPP)FeClO$_4$ in CH$_2$Cl$_2$

L	pK_a^{a}	log β_2^{II}	log β_2^{III}
3,5-dichloropyridine	0.67	5.5	3.4
3-cyanopyridine	1.40	6.2	4.7
4-cyanopyridine	1.86	4.2	2.6
3-chloropyridine	2.81	6.7	6.7
3-bromopyridine	2.84	6.8	6.8
4-acetylpyridine	3.51	7.0^b	7.6^c
pyridine	5.28	7.8, 7.45^c	10.2
3-picoline	5.79	7.8	10.5
4-picoline	5.98	8.3	11.4
3,4-lutidine	6.46	8.3^b	11.7^b
4-(dimethylamino)pyridine	9.71	9.7^b	16.3^b

[a] K. Schoefield, "Hetero-Aromatic Nitrogen Compounds", Plenum Press, New York, 1967, p 146. [b] Extrapolated from the least-squares best fit to the data presented in Figure 4. [c] Taken from ref 27 where log β_2^{II} was measured in benzene.

reduction (identified as process III, Figure 1). In contrast, potentials for Fe(III) reduction (identified as process II) shifted by 126 mV per 10-fold change of pyridine concentration in this region.

This dependence of potential on pyridine concentration was reversed in region B. Here half-wave potentials for the Fe(III) $\rightleftarrows$ Fe(II) reaction were invariant, but $E_{1/2}$ for reduction of Fe(II) shifted cathodically by 111 mV/log [py]. In both regions the shift of potential with pyridine closely approximates the theoretical value[16] of 118 mV ($\Delta E_{1/2}/\Delta$ log [L] = $0.059p/n$ where n = 1 and p = 2) and leads to the reduction mechanism in Scheme I involving Fe(III) and Fe(II).

In both regions A and B, Fe(III) is complexed by two pyridine molecules. This is reduced by one of two pathways depending on pyridine concentration. In region A (low pyridine concentration) Fe(II) is not complexed, and the left-hand pathway is followed. In region B (high pyridine concentration) Fe(II) is complexed by two molecules, and electrode reaction proceeds by the right-hand pathway. Both (P)Fe and (P)-Fe(py)$_2$ are reduced to identical uncomplexed [(P)Fe]$^-$. For each ligand in Table I, the electroreduction mechanism in 1.0 M ligand was identical with that shown in Scheme I. Values of β_2^{III} and β_2^{II} are listed in Table II for (TPP)Fe(L)$_2^+$ClO$_4^-$ and (TPP)Fe(L)$_2$.

The half-wave potential for (TPP)Fe(py)$_2^+$/(TPP)Fe(py)$_2$ occurred at +0.06 V. In contrast, $E_{1/2}$ for each of the other complexes was either positive or negative of this value and linearly related to the pK_a of the substituted pyridine. This is shown in Figure 4 and Table I. Since $E_{1/2}$ is also a direct measure of the ratio log ($\beta_2^{III}/\beta_2^{II}$) (where β_2^{III} is for reaction 5 and β_2^{II} for reaction 6), we have plotted this term on the

$$\text{(P)FeClO}_4 + 2\text{L} \rightleftharpoons \text{(P)Fe(L)}_2^+ + \text{ClO}_4^- \qquad (5)$$

$$\text{(P)Fe} + 2\text{L} \rightleftarrows \text{(P)Fe(L)}_2 \qquad (6)$$

right-hand axis of Figure 4. Also shown in Figure 4 are the half-wave potentials[14] for the reduction of Fe(II) and the corresponding log β_2^{II} for each substituted pyridine.

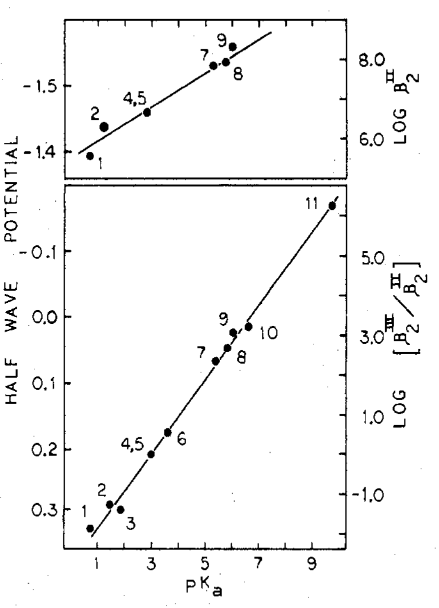

Figure 4. Plot of half-wave potentials, log β_2^{II}, and log [$\beta_2^{III}/\beta_2^{II}$] as a function of p$K_a$ of the substituted pyridine. The electrode reactions correspond to Fe(III)/Fe(II) and Fe(II)/Fe(I). Each solution contains 1.0 M substituted pyridine in CH$_2$Cl$_2$–0.1 TBAP. Numbers correspond to the substituted pyridines listed in Table I.

Table III. Literature Values of Δ log K/ΔpK_a for Substituted Pyridine Complexes of Various Metalloporphyrins

complex	solvent	Δ log K/ΔpK_a^{b}	ref
(TPP)Mn^{II}(L)	CH$_2$Cl$_2$^{a}	0.33	18
(TPP)Fe^{II}(L)$_2$	CH$_2$Cl$_2$^{a}	0.44	this work
((*p*-OCH$_3$)TPP)Co^{II}(L)	toluene	0.148	19
(TPP)Zn^{II}(L)	benzene	0.24	20, 21
(TPP)Cd^{II}(L)	benzene	0.34	22
(TPP)Hg^{II}(L)	benzene	0.44	22
(TPP)Cr^{III}Cl(L)	toluene	0.32	17
(TPP)Mn^{III}Cl(L)	CH$_2$Cl$_2$^{a}	0.35	18
(TPP)Fe^{III}(L)$_2^+$Cl$^-$	CHCl$_3$	0.81	3
(TPP)Fe^{III}(L)$_2^+$ClO$_4^-$	CH$_2$Cl$_2$^{a}	1.40	this work

[a] Solvent contains 0.1 M TBAP. [b] log K calculated for the generalized reaction (P)M + nL $\rightleftarrows$ (P)M(L)$_n$. See individual references for details.

The most positive reduction potentials occurred for [(TPP)Fe(L)$_2$]$^+$ClO$_4^-$ where L = 3,5-dichloropyridine ($E_{1/2}$ = +0.31 and −1.38 V) while the most negative occurred where L = 4-(dimethylamino)pyridine ($E_{1/2}$ = −0.17 V and $E_{1/2} >$ −1.6 V). This 480 mV difference for the Fe(III)/Fe(II) reaction is associated with a 10^8 increase in higher oxidation-state stability between the most difficult to reduce complex containing 4-(dimethylamino)pyridine and that containing 3,5-dichloropyridine.

It is interesting to note that the slope of the line in Figure 4 gives a Δ log ($\beta_2^{III}/\beta_2^{II}$)/$\Delta$p$K_a$ = 0.96 while Δ log (β_2^{II})/ΔpK_a = 0.44. Combination of these slopes will yield a Δ log (β_2^{III})/ΔpK_a = 1.40. This may be compared to the slope of 0.81 obtained for (TPP)FeCl reactions with substituted pyridines in chloroform.[3] Other values of Δ log K/ΔpK_a with substituted pyridines have been measured and are listed in Table III.

Previous investigations of metalloporphyrin–ligand binding have contained plots of Δ log K/ΔpK_a.[17-22] These were

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(16) D. R. Crow, "Polarography of Metal Complexes", Academic Press, London, 1969.

(17) Extrapolated from Figure 5 of D. A. Summerville, R. D. Jones, B. R. Hoffman, and F. Basolo, *J. Am. Chem. Soc.*, **99**, 8195 (1977).

(18) K. M. Kadish and S. Kelly, *Inorg. Chem.*, **18**, 2968 (1979).

(19) F. A. Walker, *J. Am. Chem. Soc.*, **95**, 1150 (1973).

(20) C. H. Kirksey, P. Hambright, and C. B. Storm, *Inorg. Chem.*, **8**, 2141 (1969).

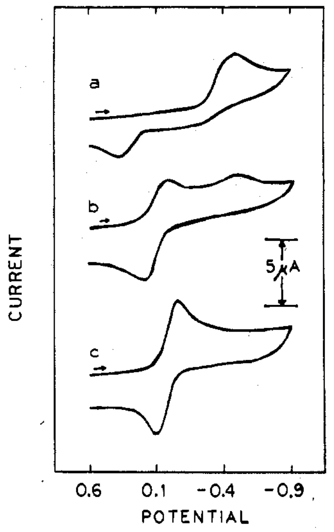

Figure 5. Cyclic voltammograms of 1.4 mM (TPP)FeCl in CH_2Cl_2–0.1 M TBAP containing 1.0 M (a) 3,5-dichloropyridine, (b) 4-acetylpyridine, and (c) 3,4-lutidine.

constructed in order to test the extent of σ and π interactions between the added ligand and the metal center. The ligand series most widely used in these investigations is the substituted pyridines since a wide range of pK_a values is available. With this series, an experimental $\Delta \log K/\Delta pK_a$ quotient greater than zero would indicate that σ bonding dominates the ligand to metal interaction. For all $(TPP)M^{II}$ complexes reported in nonaqueous media (see Table II) the average quotient is 0.32 ± 0.11. This is contrary to the reported trend with water-soluble Fe(II) porphyrins in which an inverse relationship had been observed.[23]

Quotients for two of the three $[(TPP)M^{III}]^+$ systems lie within the average range reported for $(TPP)M^{II}$ systems. The quotient for the Fe(III) system is 2.5–4 times higher. This would appear to rule out the higher metal oxidation state as the reason for the increase in the magnitude of the Fe(III) quotient. Also, Fe(III) is the only M(III) complex studied which forms bis adducts with the ligand series. However, preliminary studies of $[(TPP)Cr(L)_2]^+$ indicate an increased value of $\Delta \log \beta_2^{III}/\Delta pK_a$ so that charge stabilization of the ion pair may contribute to the larger value.[24]

Mechanism of (TPP)FeCl Reduction in the Presence of Substituted Pyridines. The mechanism for reduction of (TPP)FeCl in DMF–pyridine mixtures has been extensively investigated.[4,5] Both mono- and bis(pyridine) adducts are observed for iron(III) while iron(II) yields only six-coordinate complexes.[14] Formation constants for $(TPP)Fe(py)_2$ have been measured as 4×10^5 in DMF while β_2 for $(TPP)Fe(py)_2{}^+Cl^-$ is 0.4 in DMF and 0.5 in $CHCl_3$.[3] No data have been published regarding the stability constants for complexation of substituted pyridines by (TPP)FeCl in CH_2Cl_2, although, presumably, they would be similar to those obtained in $CHCl_3$.

In this study the redox behavior and ligand-binding characteristics of (TPP)FeCl were elucidated with the substituted pyridines listed in Table I. Similar to the studies with $(TPP)FeClO_4$, each solution was made 1.0 M in ligand, and the cyclic voltammograms were recorded.

Overall, three different electrode mechanisms could be elucidated for electroreduction. Pyridines with $pK_a < 3.0$ (e.g., Figure 5a) were characterized by an Fe(III) ⇌ Fe(II) reaction which had cathodic and anodic peaks separated by ca. 600 mV. Pyridines in the range of $3.0 < pK_a < 5.4$ (e.g., Figure 5b) yielded cyclic voltammograms characterized by two reduction processes but only one oxidation process. The more cathodic reduction process potential corresponded to that obtained in the absence of ligand whereas the more anodic process was identical with that obtained when the starting product was $(TPP)FeClO_4$. Pyridines with $pK_a > 5.4$ (e.g., Figure 5c) gave Nernstian couples whose anodic and cathodic peak potentials were identical with those obtained when $(TPP)FeClO_4$ was the starting material.

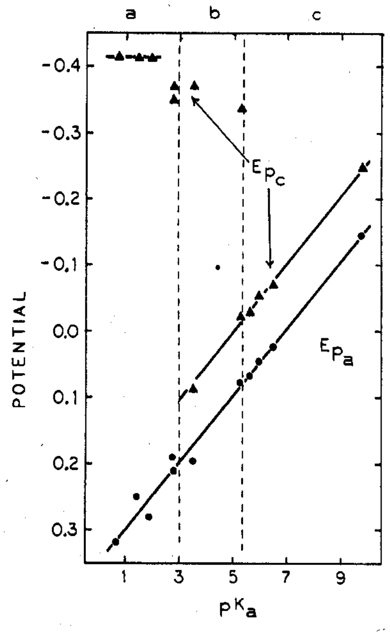

Figure 6. Plot of peak potential vs. ligand pK_a for (TPP)FeCl in CH_2Cl_2–1.0 M ligand mixtures: ●, E_{pa}; ▲, E_{pc}. Cyclic voltammograms typical of each pK_a region are shown in Figure 5. Ligands are listed in Table I.

Scheme II

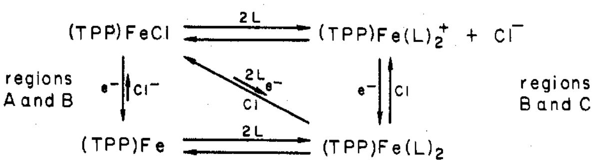

Figure 6 illustrates the individual cathodic peaks, E_{pc}, and anodic peaks, E_{pa}, obtained for each ligand as a function of pK_a. This figure is divided into three regions according to the prevailing redox behavior. On the basis of Figures 5 and 6, Scheme II is formulated for electroreduction of $(TPP)Fe(L)_2{}^+Cl^-$ in 1.0 M ligand where L is one of the substituted pyridines in Table I. This mechanism is almost identical with the one published earlier for the reduction of (TPP)FeCl in DMF–pyridine mixtures.[3,4]

In region A, the reactant is always (TPP)FeCl which is reduced to (TPP)Fe. This converts to be $(TPP)Fe(L)_2$ which is reoxidized (by the diagonal path) at a potential which is shifted anodically due to complex formation. In this case a 500–600 mV separation of the cathodic and anodic peaks is observed. The cathodic peak, E_{pc}, is invariant with change in pK_a of the base because the cathodic process does not involve a pyridine ligand. In contrast, E_{pa} involves oxidation of $(TPP)Fe(L)_2$ to (TPP)FeCl (or $[(TPP)Fe]^+$) and hence shifts as a function of the ligand pK_a as described in the previous section.

Increasing the pK_a of the substituted pyridine yields increased formation constants for the bis-ligand adducts and hence shifts the equilibria of iron(III) toward (TPP)Fe-

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[21] S. J. Cole, G. C. Curthoys, E. A. Magnusson, and J. N. Phillips, *Inorg. Chem.*, **11**, 1024 (1972).
[22] C. H. Kirksey and P. Hambright, *Inorg. Chem.*, **9**, 958 (1970).
[23] J. E. Falk, J. N. Phillips, and E. A. Magnusson, *Nature (London)*, **212**, 1531 (1966).
[24] K. M. Kadish and L. A. Bottomley, unpublished results.

$(L)_2{}^+Cl^-$. Thus, in region B both $(TPP)Fe(L)_2{}^+Cl^-$ and (TPP)FeCl are present in solution at 1.0 M ligand. In this case, both reactants may be reduced to form the ultimate product, $(TPP)Fe(L)_2$, which is reoxidized to form $(TPP)Fe(L)_2{}^+Cl^-$ and some (TPP)FeCl. Again, this oxidation potential is dependent on the pK_a of the added ligand. Finally, with ligand of $pK_a > 5.4$, $\beta_2{}^{III}$ is significantly increased such that the solutions contain only $(TPP)Fe(L)_2{}^+Cl^-$. In this region a reversible couple is obtained corresponding to the reaction $(TPP)Fe(L)_2{}^+Cl^-/(TPP)Fe(L)_2$.

It is interesting to note that above $pK_a = 5.3$, superimposable cyclic voltammograms are obtained for the reduction of $(TPP)FeClO_4$ or (TPP)FeCl in CH_2Cl_2 solutions containing 1.0 M substituted pyridines. This would imply the same reactant and product in solution, which, under the experimental conditions, would be $(TPP)Fe(L)_2{}^+ClO_4{}^-$. Since $ClO_4{}^-$ is present in 100-fold excess when compared to Cl^-, this seems reasonable.

Reversible cyclic voltammograms were obtained throughout the series of $(TPP)Fe(L)_2{}^+ClO_4{}^-$ because the ligands were strongly complexed with Fe(III). When Cl^- was present (introduced as (TPP)FeCl) competition existed for one of the axial positions. Pyridines with pK_a values below 3.0 are not sufficiently basic to compete with Cl^-. Pyridines with pK_a values greater than 5.3 so effectively σ donate to the Fe center that (TPP)FeCl is no longer present in solution.

Effect of Counterion. Walker and co-workers[3] have reported log $\beta_2{}^{III}$ values of −0.30 and 1.40 for addition of pyridine and 3,4-lutidine, respectively, to (TPP)FeCl. The values listed in Table II for addition of the same ligands to $(TPP)FeClO_4$ are 10.2 and 11.7, respectively. The reaction which was studied by Walker can be represented as

$$(TPP)FeCl + 2L \rightleftharpoons (TPP)Fe(L)_2{}^+ + Cl^- \qquad (7)$$

When this reaction is combined with reaction 5 the following reaction is obtained:

$$(TPP)FeClO_4 + Cl^- \rightleftharpoons (TPP)FeCl + ClO_4{}^- \qquad (8)$$

Reaction 8 describes the exchange of Cl^- for $ClO_4{}^-$. The exchange constant K_{ex} is defined in eq 9 where $\beta_2{}^{III}(Cl^-)$

$$K_{ex} = \frac{[(TPP)FeCl][ClO_4{}^-]}{[(TPP)FeClO_4][Cl^-]} = \frac{\beta_2{}^{III}(Cl^-)}{\beta_2{}^{III}(ClO_4{}^-)} \qquad (9)$$

represents the quotient describing reaction 7 and $\beta_2{}^{III}(ClO_4{}^-)$ represents the quotient describing reaction 5. Using $\beta_2{}^{III}(Cl^-)$[3] and $\beta_2{}^{III}(ClO_4{}^-)$ obtained for addition of pyridine, we calculated $K_{ex} = 10.5$. With the formation constants obtained for addition of 3,4-lutidine, $K_{ex} = 10.3$.

As part of this study we have clearly demonstrated that a large formation constant is obtained for pyridine addition to $(TPP)FeClO_4$ and that the value of $\beta_2{}^{III}$ is increased by approximately 10 orders of magnitude when compared to (TPP)FeCl. However, we are still left with answering the question of spin-state influence on $\beta_2{}^{II}$.

It has been firmly established[25] that all six-coordinate Fe porphyrin complexes with nitrogenous bases are low spin. (TPP)FeCl has been shown to be high spin[25] while $(TPP)FeClO_4$ has been assigned as an intermediate-spin complex in nonbonding media.[6,26] Thus, complexation of (TPP)FeCl by substituted pyridine involves a concomitant change in spin state from high to low spin whereas complexation of $(TPP)FeClO_4$ involves a spin change from intermediate to low spin. In all cases $K_2 \gg K_1$ for stepwise addition of nitrogenous bases to (TPP)FeCl.[1,2] The greater magnitude of K_2 has been attributed to the change in Fe spin state upon addition of the second ligand. When no spin-state change occurs, $K_1 \geq K_2$. At this time, however, we are unable to determine the influence of spin state on $\beta_2{}^{III}$ for complexation of $(TPP)FeClO_4$. Since the intermediate-spin complexes already have partial spin pairing, it might be predicted that the ratio K_2/K_1 would be smaller for these complexes when compared to K_2/K_1 for high-spin complexes of (TPP)FeCl. This hypothesis is presently under investigation.

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Registry No. $(TPP)FeClO_4$, 59370-87-5; (TPP)FeCl, 14187-12-3; $(OEP)FeClO_4$, 57034-06-7; (OEP)FeCl, 25442-51-7; $(TPP)Fe(3,5\text{-dichloropyridine})_2$, 72318-23-1; $(TPP)Fe(3\text{-cyanopyridine})_2$, 72318-24-2; $(TPP)Fe(4\text{-cyanopyridine})_2$, 71667-46-4; $(TPP)Fe(3\text{-chloropyridine})_2$, 72318-25-3; $(TPP)Fe(3\text{-bromopyridine})_2$, 72318-26-4; $(TPP)Fe(4\text{-acetylpyridine})_2$, 71667-47-5; $(TPP)Fe(\text{pyridine})_2$, 16999-25-0; $(TPP)Fe(3\text{-picoline})_2$, 72318-27-5; $(TPP)Fe(4\text{-picoline})_2$, 68136-93-6; $(TPP)Fe(3,4\text{-lutidine})_2$, 72318-28-6; $(TPP)Fe(4\text{-(dimethylamino)pyridine})_2$, 71667-49-7; $[(TPP)Fe(3,5\text{-dichloropyridine})_2]ClO_4$, 72332-29-7; $[(TPP)Fe(3\text{-cyanopyridine})_2]ClO_4$, 72318-30-0; $[(TPP)Fe(4\text{-cyanopyridine})_2]ClO_4$, 70936-33-3; $[(TPP)Fe(3\text{-chloropyridine})_2]ClO_4$, 72318-32-2; $[(TPP)Fe(3\text{-bromopyridine})_2]ClO_4$, 72332-31-1; $[(TPP)Fe(\text{pyridine})_2]ClO_4$, 70936-34-4; $[(TPP)Fe(3\text{-picoline})_2]ClO_4$, 72318-34-4; $[(TPP)Fe(4\text{-picoline})_2]ClO_4$, 72318-36-6; $[(TPP)Fe(3,4\text{-lutidine})_2]ClO_4$, 72318-37-7; $[(TPP)Fe(4\text{-(dimethylamino)pyridine})_2]ClO_4$, 72318-38-8.

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