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Electrochemistry of Nitrite Reductase Model Compounds. 1. Electrochemistry of Iron Tetraphenylchlorin

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The electrochemistry of iron tetraphenylchlorin was studied in several solvents and in the presence of substituted pyridines and amines. Iron tetraphenylchlorin was found to be both quantitatively and qualitatively similar to iron tetraphenylporphyrin. The variations in the cumulative formation constants of substituted pyridines with ferrous and ferric chlorin were measured with differential pulse polarography and cyclic voltammetry. The formation constants for pyridines with ferric chlorin, β_2^{III}, were found to vary linearly with the pK_a of the pyridine with a slope of 1.22 ± 0.14. By contrast, the β_2^{II} values for the ferrous chlorin–pyridine complex were not linearly related to the pK_a of the pyridine. These results appeared to indicate that significant π-interactions (back-bonding) are involved in the ferrous complexes, which are not significant for the ferric species. When amines are used that cannot participate in π-bonding, a much greater sensitivity of the β_2^{II} values to the pK_a of the amine was observed than was previously assumed. In addition to the electrochemical results, the UV–visible spectra of chloro(tetraphenylchlorinato)iron(III), Fe(TPC)Cl, and its μ-oxo complex, $(FeTPC)_2O$, were reported. Fe(TPC)Cl had bands at 385, 415, 600, 646, and 740 nm, while $(FeTPC)_2O$ had bands at 406, 537, 605, and 646 nm.

Introduction

The mechanism of multielectron reduction of substrates by enzymes is one of the most important areas of bioenergetics. Most of the enzymes that catalyze these reactions are large complex membrane-bound enzymes such as cytochrome *c* oxidase or nitrogenase. One class of enzymes that is quite tractable to study and model is the assimilatory and dissimilatory nitrite reductases. The assimilatory nitrite reductases reduce nitrite to ammonia by six electrons.[1] In almost all cases, the enzyme contains a siroheme[2] (an iron isobacteriochlorin) and an Fe_4S_4 cluster.[3] The dissimilatory nitrite reductases reduce nitrite to nitrous oxide or dinitrogen.[4–6] This denitrification process is an important pathway for the loss of fixed nitrogen in the soil. The usual prosthetic groups are heme *c* and heme d_1 (an iron chlorin).[7–11] The crucial question that needs to be addressed is as follows: Is there any fundamental chemical reason for the presence of more saturated hemes in these nitrite reductases instead of the more common heme *c*? In order to answer this question, a detailed study of iron chlorins and iron isobacteriochlorins has begun in this laboratory, with the work on iron chlorins being reported here.

Iron tetraphenylchlorin is a model of the heme d_1 prosthetic group that is present in nitrite reductases in such species as *Pseudomonas aeruginosa*[12] and *Thiobacillus denitrificans*.[13,14] A chlorin structure has also been observed in *Neurospora crassa* catalase.[15] The electrochemistry of porphyrins is relatively extensive while the electrochemistry of the more saturated porphyrins and their iron complexes is quite meager. Iron(III) complexes of octaethylporphyrin (FeOEP), octaethylchlorin (FeOEC), and octaethylisobacteriochlorin (FeOEiBC) all reduce at about the same potential.[16–18] The potential of the second wave for the complexes (except FeOEP) is not known. Similar results have been observed for zinc tetraphenylporphyrin, chlorin, isobacteriochlorin, and bacteriochlorin.[19] The electrochemistry of nickel tetraphenylchlorin has recently been reported.[20]

In this work, the electrochemistry and spectroscopy of chloro(tetraphenylchlorinato)iron(III), Fe(TPC)Cl, its μ-oxo complex, $(FeTPC)_2O$, and its complexes with pyridine ligands will be examined. The purpose of this work will be to compare the results of Fe(TPC)Cl electrochemistry with the abundant literature for Fe(TPP)Cl in order to detect any fundamental chemical differences between the two. In addition, this work enabled us to examine more closely the importance of π-interactions between the iron and coordinated pyridines, and the unusually large slope for the variation of the iron–pyridine cumulative formation constants as a function of the pK_a of the pyridine.

Experimental Section

Equipment. Cyclic voltammetric data were obtained with either an ECO 553 potentiostat with an EG&G Princeton Applied Research (PARC) 175 waveform generator or an EG&G PARC 174A polarographic analyzer. For scan rates below 200 mV/s, a Hewlett-Packard 7045 (for ECO 553) or 7035B (for PARC 174A) X-Y recorder was used. For scan rates greater than 200 mV/s, the data were acquired with a California Computer System 2210 computer, using the ECO 553 potentiostat system. A three-electrode IBM cell was used for all experiments, which consisted of a platinum working electrode, a platinum auxiliary electrode, and an aqueous Ag/AgCl (saturated KCl) or a Ag/0.1 M $AgNO_3$ reference electrode, as noted in the work. The differential pulse polarograms (DPP) were obtained with the PARC 174A system. The UV–visible spectra were obtained on a Perkin-Elmer 320 UV–visible spectrophotometer with a Perkin-Elmer 3600 data station.

Chemicals. Tetraphenylchlorin (TPC) was obtained from the diimide reduction of TPP.[21] The insertion of iron was performed by adding anhydrous ferrous chloride to TPC and then refluxing in DMF for 90 min.[22] Any exposure of the refluxing solution to air will significantly reduce the yield. The final product was purified by column chroma-

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Table I. $E_{1/2}$ Values for Fe(TPP)Cl and Fe(TPC)Cl in Various Solvents[a]

	$E_{1/2,1}$		$E_{1/2,2}$	
solvent	Fe(TPP)Cl	Fe(TPC)Cl	Fe(TPP)Cl	Fe(TPC)Cl
CH_2Cl_2	−0.68	−0.67	−1.44	−1.43
DMF	−0.64	−0.62	−1.50	−1.51
Me_2SO	−0.51	−0.57	−1.56	−1.55

[a] V vs. $Ag/AgNO_3$ in acetonitrile.

tography on alumina. Crystals were obtained from the evaporation of chloroform, with the addition of heptane. All the substituted pyridines were obtained from Aldrich Chemical Co. and were used as obtained, except as noted. The solvents were obtained from Aldrich Chemical Co. in the highest available purity. Tetraethylammonium (TEAP) and tetrabutylammonium (TBAP) perchlorates were obtained from G. F. Smith Chemical Co. The TPP was purchased from Strem Chemical Co. or Aldrich Chemical Co. Tetraphenylphosphonium chloride (Ph_4PCl) was obtained from Aldrich Chemical Co.

Procedures. All solutions were degassed with prepurified dinitrogen that had been saturated with the solvent prior to obtaining the voltammograms. The formation constant for the bis(pyridine)iron(II) complex, β_2^{II}, was obtained from the shift in the potential of the second wave, as measured by differential pulse polarography, with use of the equation[23]

$$\beta_2^{II} = 10^{\Delta E_p/0.059}/M_{py}^2 \tag{1}$$

where $\Delta E_p = E_{pu} - E_{pc}$, M_{py} is the bulk concentration of pyridine, and E_{pu} and E_{pc} are the differential pulse polarographic peak potentials of the second wave in the absence and presence of the substituted pyridine, respectively. Pyridine concentrations from 1 mM to 1 M were used for all ligands, and the log β_2^{II} values were obtained from the average value calculated from each concentration. The ratio of the formation constant for $Fe(TPC)(py)_2^+$, β_2^{III}, to β_2^{II} can be obtained from the $E_{1/2}$ value of the couple as measured by cyclic voltammetry. The equation used is

$$\beta_2^{III}/\beta_2^{II} = 10^{\Delta E_{1/2}/0.059} \tag{2}$$

where $\Delta E_{1/2} = E_{1/2,u} - E_{1/2,c}$ and $E_{1/2,u}$ and $E_{1/2,c}$ are the half-wave potentials of the iron(III) reduction without pyridine and with pyridine, respectively.

All the UV-visible spectra in methylene chloride were obtained on solutions that contained 0.1 M TBAP and 1 mM Ph_4PCl (except where noted). The formation constants for the Fe(TPC)Cl-substituted pyridines were calculated on a VAX 11/780 computer with the program SPECDEC,[24] using the IMSL library for matrix operations.

Results

Electrochemistry without Pyridine. The cyclic voltammetric reduction of Fe(TPC)Cl in organic solvents occurs in two waves as has been observed for Fe(TPP)Cl

$$Fe^{III}(TPC)Cl + e^- \rightleftharpoons Fe^{II}(TPC) + Cl^- \tag{3}$$

$$Fe^{II}(TPC) + e^- \rightleftharpoons Fe^{I}(TPC)^- \tag{4}$$

where E_1 and E_2 refer to the $E_{1/2}$ values of the first and second waves, respectively. While the first wave was chemically reversible, the ΔE_p values were somewhat greater than the theoretical value of 57 mV for a reversible electron transfer.[25] Reversibility improved if chloride as tetraphenylphosphonium chloride were added. Exhaustive coulometry in methylene chloride and Me_2SO verified that the first wave was one electron, and the peak current functions (compared to those of Fe(TPP)Cl) for the first and second waves were consistent with each wave being one electron. Recent work[26] has shown that Fe(TPP) will associate with chloride ion, so one would expect similar results here, though no extensive study was made of this possibility. The $E_{1/2}$ values in three different solvents are shown in Table I, along with a comparison with Fe(TPP)Cl. As can be seen, there is little difference in the redox potentials between Fe(TPP)Cl and Fe(TPC)Cl. While the data are limited, the similarity of the $E_{1/2}$ potential shifts with changes in solvent indicates that the solvation of the chlorin species is similar to that of the porphyrin in these solvents. In analogy with Fe(TPP), the product of the second wave is probably a Fe(I) species.[27,28]

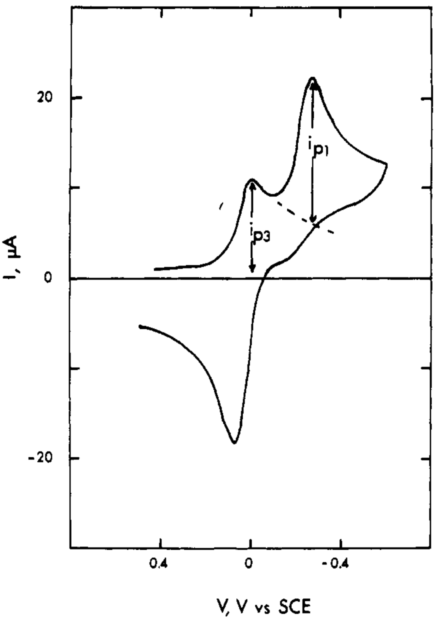

Figure 1. Cyclic voltammogram of 0.4 mM Fe(TPC)Cl in 20 mM pyridine with 0.1 M TBAP in methylene chloride (scan rate 0.20 V/s).

Table II. Effect of Pyridine on the Cyclic Voltammetry of Fe(TPC)Cl[a]

M_{py}, mM	$E_{pc,1}$[b]	$i_{pc,1}$[c,d]	$E_{pc,3}$[b]	$i_{pc,3}$[d]	$E_{pa,3}$[b]
0.0	−0.31	39.5			
1.0	−0.30	40.7		2.5	0.04
1.8	−0.30	27.7	−0.01	3.0	0.06
3.2	−0.28	22.0	−0.01	4.2	0.04
5.6	−0.28	23.7	−0.01	4.2	0.05
10	−0.28	21.8	−0.02	5.1	0.05
18	−0.25	20.7	−0.02	12.4	0.07
32	−0.27	13.8	−0.02	12.9	0.07
56	−0.25	8.7	−0.01	17.8	0.09
100	−0.22	7.9	−0.01	23.8	0.08
180		4.3	−0.01	24.0	0.09
328		3.7	−0.01	26.5	0.09

[a] Conditions: solvent = methylene chloride, ν = 200 mV/s, 0.4 mM Fe(TPC)Cl, 0.1 M TBAP. [b] V vs. aqueous Ag/AgCl. [c] i_{pc} value corrected for first wave; all i_p values in µA. [d] 1 refers to Fe(TPC)(py)Cl reduction, 3 refers to $Fe(TPC)(py)_2$ couple.

Electrochemistry with Pyridine. The electrochemical behavior of Fe(TPC)Cl in the presence of pyridine is shown in Figure 1. The results, which are similar to what has been seen by Kadish and Bottomley,[29] are summarized in Table II and are consistent with the mechanism

$$\begin{tikzcd}
Fe^{III}(TPC)Cl + e^- \arrow[r] \arrow[d, shift right, "py"'] & Fe^{II}(TPC) + Cl^- \arrow[d, shift right, "py"'] & (5) \\
Fe^{III}(TPC)(py)Cl + e^- \arrow[r] \arrow[u, shift right, "K_1^{III}"'] \arrow[d, shift right, "py"'] & Fe^{II}(TPC)(py) + Cl^- \arrow[u, shift right, "K_1^{II}"'] \arrow[d, shift right, "py"'] & (6) \\
Fe^{III}(TPC)(py)_2^+ + e^- \arrow[r, shift left] \arrow[u, shift right, "K_2^{III}"'] & Fe^{II}(TPC)(py)_2 \arrow[l, shift left] \arrow[u, shift right, "K_2^{II}"'] & (7)
\end{tikzcd}$$

where E_3 refers to the $E_{1/2}$ of the bis(pyridine) complex and $\beta_2 = K_1K_2$. The second cathodic wave appears to be irreversible due

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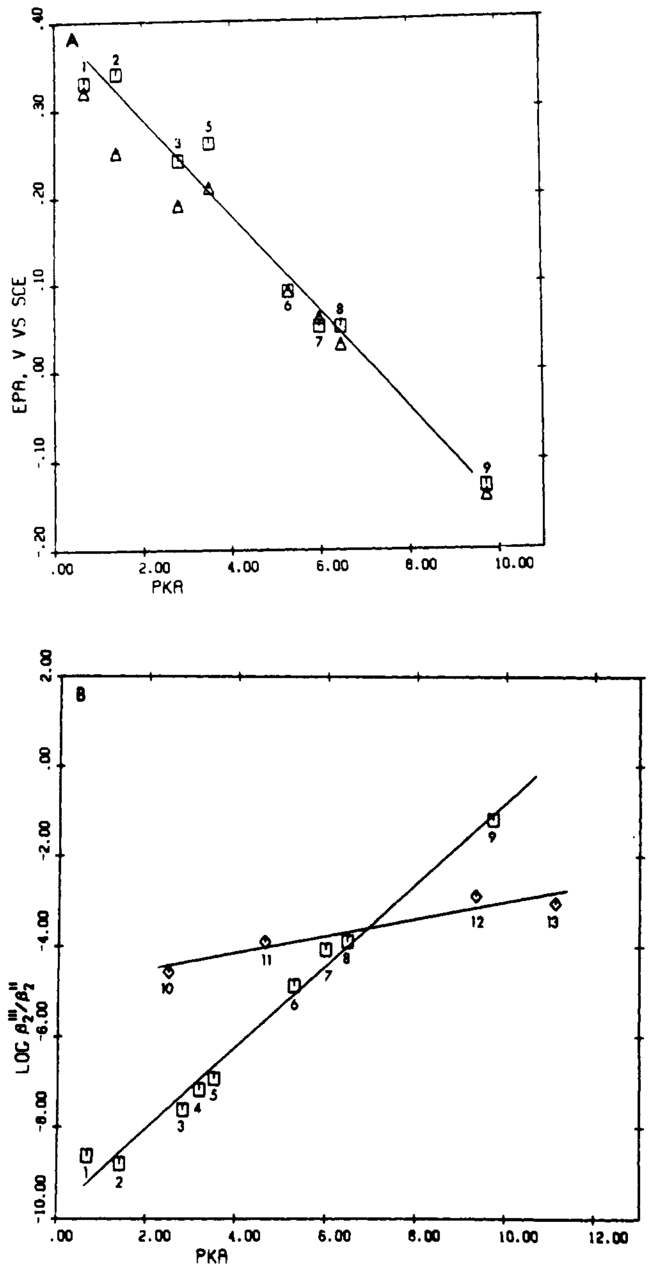

Figure 2. (A) Variation of $E_{p,a}$ for the $FeL(py)_2^+/FeL(py)_2$ couple as a function of the pK_a of the ligand (1.0 M ligand). L = Δ for TPP, □ for TPC. The straight line is the least-squares fit for the Fe(TPC) data. The TPP data are from ref 30. (B) Variation of the log $\beta_2^{III}/\beta_2^{II}$ values as a function of the pK_a of the ligand. Line A refers to the pyridine ligands (ligands 1–9), while line B refers to the amine ligands (ligands 10–13). L = Δ for TPP, □ for TPC with pyridines, and ◊ for TPC with amines.

to the rapid reaction of pyridine with Fe(TPC)(py) to form the bis complex. Even at 20 V/s, no reverse wave was observed at the E_1 potential. It is not clear from the voltammetric data whether Fe(TPC)Cl or Fe(TPC)(py)Cl is present under the conditions used. Later in this work, though, spectrophotometric data will show that a stepwise addition of pyridine to the ferric chlorin is most probable, meaning that there is a significant region of stability for Fe(TPC)(py)Cl. The first cathodic wave is due to the reduction of the $Fe(TPC)(py)_2^+$ species that is present in solution at equilibrium or may be formed by the K_2^{III} reaction during electrolysis. The variation of the peak current function $i_{pc}/v^{1/2}C$ with scan rates from 20 mV/s to 20 V/s shows that the interconversion between Fe(TPC)(py)Cl and $Fe(TPC)(py)_2^+$ is quite slow. At scan rates above 200 mV/s, there is no evidence of any kinetic enhancement of the first reduction wave. Using the theory of Nicholson and Shain for the chemical equilibrium preceding an electron transfer,[25] one can estimate that the rate of formation of the ferric bis(pyridine) complex is on the order of 10–50 M^{-1} s^{-1}. As the concentration of pyridine is increased, the new wave at E_3 (reaction 7) is enhanced while the peak at E_1 disappears. The data for pyridine are shown in Table II. The rise in current at E_3 occurs simultaneously with the appearance of $Fe(TPC)(py)_2^+$ in the UV–visible spectra. This is further confirmation that the E_3 wave is due to the direct reduction of the bis(pyridine) complex present at equilibrium.

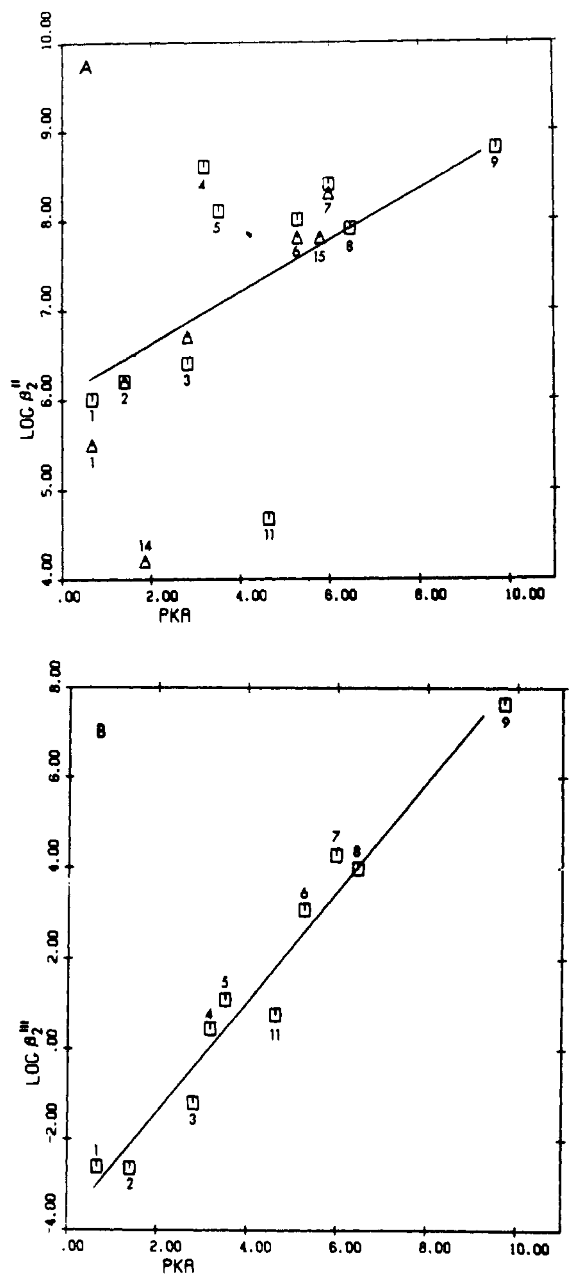

Figure 3. Variation of log β_2^{II} (A) or log β_2^{III} (B) as a function of the pK_a of the pyridine and amine ligands: (□) Fe(TPC); (Δ) Fe(TPP).[30] Straight lines are the least-squares fits for the Fe(TPC)–pyridine data. Ligand 14 = 4-cyanopyridine; ligand 15 = 3-picoline.

The variation in the E_{pa} value of the bis(pyridine) ferric/ferrous couple as a function of the pK_a of the pyridine used is shown in Figure 2A and the log $(\beta_2^{III}/\beta_2^{II})$ values, which are calculated from the $E_{1/2}$ values by using eq 2, are shown in Table III and Figure 2B. In Figure 2B, the ligands were divided into two classes: substituted pyridines and amines where the nitrogen contains only σ bonds. As can be seen in this figure, there is a significant difference in the effect of Brønsted acidity of the ligand on the ratio of the cumulative formation constants, and these two classes of ligands yielded two different linear relationships. This will be

Table III. Variation of the Formation Constants for the Fe(TPC)-Pyridine Complexes as a Function of the pK_a of the Ligand

no.	ligand	pK_a	$\log \beta_2^{III}/\beta_2^{II}$	$\log \beta_2^{II}$ [b]	$\log \beta_2^{III}$	$\log K_2^{III}$
1.	3,5-dichloropyridine	0.67	−8.6	6.0 (5.5)	−2.6	<−4.0
2.	3-cyanopyridine	1.40	−8.8	6.2 (6.2)	−2.6	<−4.0
3.	3-chloropyridine	2.81	−7.6	6.4 (6.7)	−1.2	<−4.0
4.	3-acetylpyridine	3.18	−7.2	8.6	0.4	−4.0
5.	4-acetylpyridine	3.51	−7.0	8.1	1.1	−3.6[d]
6.	pyridine	5.28	−4.9	8.0 (7.8)	3.1	−2.8
7.	4-picoline	5.98	−4.1	8.4 (8.3)	4.3	−1.9
8.	3,4-lutidine	6.46	−3.9	7.9	4.0	−1.9
9.	4-(dimethylamino)pyridine	9.71	−1.2	8.8	7.6	0.1
10.	*m*-nitroaniline	2.47	−4.6	3.8[c]	−0.8[c]	<−4.0
11.	aniline	4.63	−3.9	4.8	0.8	−3.3
12.	benzylamine	9.33	−2.9			−3.0
13.	piperidine	11.12	−3.0	12.7[c]	9.7[c]	>0.5

[a] Schoefield, K. "Hetero-Aromatic Nitrogen Compounds"; Plenum Press: New York, 1967; p 146. [b] Values in parentheses from ref 30 for Fe(TPP). [c] β_2^{III} was calculated from Figure 3 on the basis of the linearity of the $\log K_2^{III}$ vs. pK_a data. From this value and the $\log \beta_2^{III}/\beta_2^{II}$ data, $\log \beta_2^{II}$ was calculated. [d] No added chloride ion.

Table IV. UV-Visible Spectra of Fe(TPC)Cl and $(FeTPC)_2O$[a]

compound	λ_{max}, nm	$10^{-3}\epsilon_{max}$, M^{-1} cm^{-1}
Fe(TPC)Cl	385	74 ± 2
	415	89 ± 3
	600	16.4 ± 0.5
	646	4.5 ± 0.2
	740	4.9 ± 0.2
$(FeTPC)_2O$	406	194 ± 4
	537	13.2 ± 0.3
	605	16.5 ± 0.7
	646	32.0 ± 0.6

[a] Solvent = methylene chloride.

discussed in detail later in this paper. In Figure 3, the values of $\log \beta_2^{III}$ and $\log \beta_2^{II}$ as a function of the pK_a of the substituted pyridine are plotted. The $\log \beta_2^{II}$ values for all the reported complexes were measured for ligand concentrations between 1 mM and 1 M pyridine by using eq 1. The shift in potential of the differential pulse polarographic wave was consistent with a reversible one-electron transfer with the loss of two pyridine molecules upon reduction (see eq 1). This conclusion was also confirmed for $Fe^{I}TPP$, where a recent X-ray structure of this species, which was obtained from a solution that contained large amounts of pyridine, did not have any pyridine coordinated to it.[28] The variation of $\log \beta_2^{III}$ as a function of pK_a is linear with the slope of 1.22 ± 0.14. But, the same linearity does not occur for the iron(II)-pyridine complexes. In addition to pyridines, a series of amines that were incapable of π-interactions with the iron were also examined. Unfortunately, it was impossible to measure the β_2^{II} values for many of the amines. For example, *m*-nitroaniline reduces before $Fe(TPC)(L)_2$, and benzylamine and piperidine did not yield reversible second waves that varied with ligand concentration, even when piperidine was further purified. The K_2^{III} values for these ligands were calculated and, except for benzylamine, were consistent with the K_2^{III} values for the pyridines. In this way, it is possible to estimate the β_2^{III} values from the linear plots in Figure 3B and, from this, estimate β_2^{II} values. The nonlinearity of the iron(II)-pyridine plots will be discussed in more detail in the Discussion.

Spectroscopic Studies. In addition to the electrochemical studies, the visible spectra of these complexes were also obtained, and the results are summarized in Table IV. In the presence of substituted pyridines, the bands at 385, 600, and 740 nm disappear, the Soret band is enhanced, and a new band at 640 nm appears. These spectral shifts are due to the formation of the bis(pyridine) complex, and the equilibrium constants are defined as

$$K_1^{III} = [Fe(TPC)(py)Cl]/[Fe(TPC)Cl][py]$$

$$K_2^{III} = [Fe(TPC)(py)_2^+][Cl^-]/[Fe(TPC)(py)Cl][py]$$

The values of K_2^{III} were obtained from the least-squares fit of the absorbance changes of these bands as a function of ligand concentration. In order to simplify the data analysis, 1 mM chloride (as Ph_4PCl) was added to the solutions to buffer the chloride ion concentration. In addition, 0.1 M TBAP was used to maintain the ionic strength and to make comparisons between the electrochemical and spectroscopic data easier. The least-squares analysis of the data consistently showed that the spectral changes corresponded to the addition of one pyridine molecule and the loss of one Cl^- from the complex. In other words, $Fe(TPC)(py)Cl$ was completely formed before $Fe(TPC)(py)_2^+$ became the dominant species. The spectral changes for the formation of the mono(pyridine) complex are slight, indicating a weak interaction between the pyridine and the iron. This interaction may be more akin to a solvation effect, rather than a strong covalent bond. $\log K_2^{III}$ vs. the pK_a of the pyridine used is plotted in Figure 4. The slope of the line is 0.63 ± 0.08. The only significant deviation from this line (not included in the slope calculation) is benzylamine. Further purification of benzylamine did not affect the results.

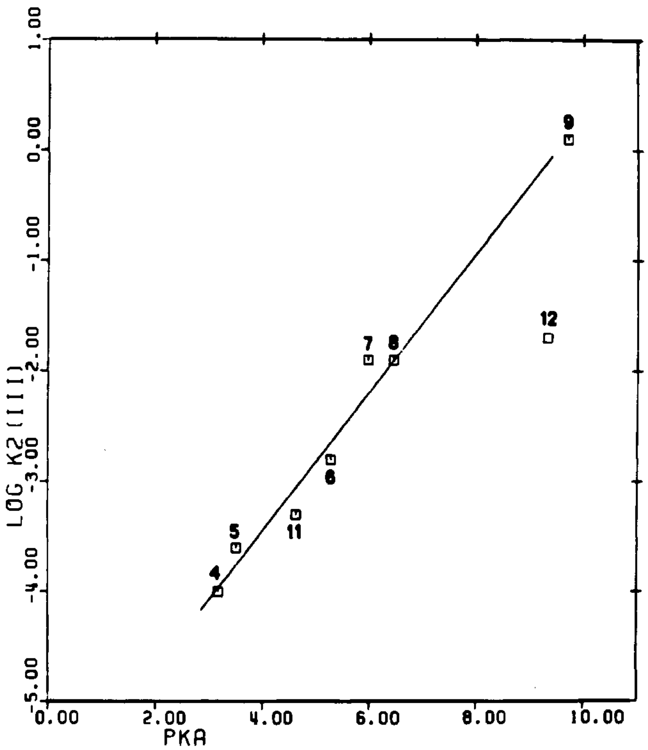

Figure 4. Variation of $\log K_2^{III}$ for $Fe(TPC)^+$ as a function of the pK_a of the pyridine or amine used. The straight line is the least-squares fit of the data.

Discussion

A comparison between Fe(TPP)Cl and Fe(TPC)Cl can be seen by examining Tables I and III and Figures 2 and 3. The potentials

Table V. Linear Free Energy Relationships for Substituted Pyridine Complexes of Various Metal Tetraphenylporphyrins and Chlorins

complex	solvent	$\Delta \log \beta_2/\Delta pK_a$	ref
$Fe(TPP)(L)_2$	CH_2Cl_2	0.44	30
$Fe(TPP)(L)_2^+$	CH_2Cl_2	1.40	30
$Fe(TPC)(L)_2$	CH_2Cl_2	0.29 ± 0.29	this work
$Fe(TPC)(L)_2^+Cl^-$	CH_2Cl_2	1.21 ± 0.16	this work
$Fe(TPP)(L)_2^+Cl^-$	$CHCl_3$	0.81	33
$[(Fe(TPP)L)_2N]^+$	$EtCl_2$	0.81	34
$Cr(TPP)(L)_2$	DMF	0.55	35
$Cr(TPP)(L)_2$	DMF	−0.16	35

of the first and second waves in various solvents were almost identical for these two porphyrin complexes. In addition, the formation constants for the bis(pyridine) adducts with iron(II) and iron(III), which are shown in Table III, and Figure 3, were almost identical, showing that the saturation of one of the double bonds on the porphyrin has little effect on the Lewis acidity of the iron complex. In particular, the variation of the log of the iron(III)–pyridine formation constant as a function of the pK_a of the pyridine used had slopes of 1.4 ± 0.1 and 1.22 ± 0.14 for Fe(TPP)[30] and Fe(TPC), respectively. This is in accordance with the recent theoretical work on the energy of the molecular orbitals of FeL(py)(CO) complexes, where L = porphyrin, chlorin, bacteriochlorin, and isobacteriochlorin.[31,32] In this case, the energy of the t_{2g} orbitals varied little as the degree of saturation of the porphine changed. Thus, there appears to be little chemical difference between these models of heme *c* and heme d_1, which are present in dissimilatory nitrite reductases. We must be cautious still in extrapolating this conclusion too far because little work has been done on the further reduction of these complexes with the nitrosyl ligand present (which is the first step in the enzymatic reduction of nitrite). Differences may appear in the reduction of these ligands. In addition, the dissimilatory nitrite reductases do not reduce nitrite to ammonia but only to dinitrogen. The assimilatory nitrite reductases, which contain isobacteriochlorin, reduce nitrite by six electrons to ammonia.

A closer comparison of the Fe(TPP) and Fe(TPC) results for the effect of the pyridine pK_a on the log β_2^{II} values yields the most significant conclusions of this work. While the log of the iron(III) formation constants varies in a linear manner as a function of pK_a, the iron(II) values yield a very poor linear relationship. In fact, the standard deviation of the slope of the log β_2^{II} vs. pK_a plot is equal to the value of the slope. This leads to the inescapable conclusion that the Brønsted basicity (σ-bond strength) is not the controlling factor in the strength of the iron–pyridine (amine) bond. For example, the formation constants for 3- and 4-acetylpyridine with Fe(TPP) and Fe(TPC) are about 2 orders of magnitude larger than those expected for similar ligands. In fact, 3-acetylpyridine, with a pK_a of 3.18, had a formation constant about equal to that of 4-(dimethylamino)pyridine, with a pK_a of 9.71. Significant deviations in the other direction have been seen for 4-cyanopyridine (Fe(TPP)[30]) and 3,4-lutidine and aniline (Fe(TPC), this work). These results are in distinct contrast to those of previous workers (examples are shown in Table V), who obtained quite linear free energy relationships for these same ligands with other metal–porphyrin complexes. The source of these deviations may be significant back-bonding between Fe(II) and the pyridine π-system. Because σ- and π-interactions between the substituted pyridine and the iron porphine are affected in opposite ways as the substituent is changed, it appears that the bonding between the ferrous porphine and the pyridine ligand has significant contributions from both σ- and π-effects. One or the other may dominate, depending upon the exact steric and electronic factors that may control the bonding between the iron and a specific pyridine.

This hypothesis can be tested further if we examine ligands that have no possibilities of π-interactions, such as piperidine, aniline, nitroaniline, and benzylamine. The effect of these amines on the log $\beta_2^{III}/\beta_2^{II}$ vs. pK_a plots can be seen most graphically in Figure 2B. There are two linear relationships for this curve. If the ligand is a pyridine, the slope of this curve is large (0.90), while if the ligand is an amine, the slope is significantly smaller (0.19). This difference in slope must be due to the changes in the log β_2^{II} values, not the log β_2^{III} values. There are two ways that can ascertain this, even though it was difficult to measure the individual formation constants. The log K_2^{III} values for all these ligands (except benzylamine) were consistent with the pyridine values; hence, we may expect the β_2^{III} values to be similarly consistent. Second, the log β_2^{III} value for aniline is consistent with those of other pyridines, while the log β_2^{II} value deviated significantly. In addition to this work, a recent infrared study[36] of iron(II)–protoporphyrin–nitrosyl complexes also showed that π-bonding between iron(II) and pyridine was quite significant, yielding two linear relationships in the ν_{NO} vs. pK_a curves: one for pyridines and a second for amines. In summary, it is clear that amine and pyridine complexes of ferrous porphyrins show quite nonlinear free energy relationships, which argue quite strongly for significant π-interactions between an aromatic π-system and the ferrous atom.

There is one final note that can be made on the linear free energy slopes that have been determined in this work. Because the log $\beta_2^{III}/\beta_2^{II}$ vs. pK_a slope for the amines is so small, this means that the log β_2^{II} vs. pK_a slope should be almost as large as the ferric slope. It is possible to estimate a value of 1.0 for the ferrous slope. In terms of strictly σ-interactions, this would make both the ferric and ferrous porphyrins equally unusual in having such a large slope. In previous work,[30] the large ferrous slope was masked out by the effect of π-interactions. In addition, examination of Table V shows that ferrous and ferric porphyrins consistently have unusually large slopes of their linear free energy relationships, if we remember that the Fe(TPP) and Fe(TPC) values for pyridines are not linear and should be excluded from consideration. Finally, it is interesting to note that the slope of the log K_2^{III} vs. pK_a plot is almost exactly half of the log β_2^{III} vs. pK_a plot. This indicates that there is no unusual substituent effect upon the addition of the second pyridine and that both K_1^{III} and K_2^{III} are equally affected by changes in the σ-bond strength of the ligand.

While the slopes of pK_a vs. log β_2^{III} are smaller for Fe(TPC) than for Fe(TPP), the differences are not statistically significant. But, it is still interesting that they are both numerically smaller. In light of these differences, work has begun in this laboratory to see if this trend continues as the porphyrin is saturated even further to form bacteriochlorins and isobacteriochlorins.

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Registry No. Fe(TPC)Cl, 94483-24-6; $(FeTPC)_2O$, 94483-25-7; $Fe(TPC)(py)_2^+$, 94483-26-8; $Fe(TPC)(py)_2$, 94483-27-9; $Fe(TPC)(L)_2^+$ (L = 3,5-dichloropyridine), 94483-28-0; $Fe(TPC)(L)_2$ (L = 3,5-dichloropyridine), 94483-40-6; $Fe(TPC)(L)_2^+$ (L = 3-cyanopyridine), 94483-29-1; $Fe(TPC)(L)_2$ (L = 3-cyanopyridine), 94483-41-7; $Fe(TPC)(L)_2^+$ (L = 3-chloropyridine), 94483-30-4; $Fe(TPC)(L)_2$ (L = 3-chloropyridine), 94483-42-8; $Fe(TPC)(L)_2^+$ (L = 3-acetylpyridine), 94483-31-5; $Fe(TPC)(L)_2$ (L = 3-acetylpyridine), 94483-43-9; $Fe(TPC)(L)_2^+$ (L = 4-acetylpyridine), 94483-32-6; $Fe(TPC)(L)_2$ (L = 4-acetylpyridine), 94483-44-0; $Fe(TPC)(L)_2^+$ (L = 4-picoline), 94483-33-7; $Fe(TPC)(L)_2$ (L = 4-picoline), 94483-45-1; $Fe(TPC)(L)_2^+$ (L = 3,4-

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lutidine), 94483-34-8; Fe(TPC)(L)$_2$ (L = 3,4-lutidine), 94483-46-2; Fe(TPC)(L)$_2^+$ (L = 4-(dimethylamino)pyridine), 94483-35-9; Fe(TPC)(L)$_2$ (L = 4-(dimethylamino)pyridine), 94483-47-3; Fe(TPC)(L)$_2^+$ (L = *m*-nitroaniline), 94483-36-0; Fe(TPC)(L)$_2$ (L = *m*-nitroaniline), 94483-48-4; Fe(TPC)(L)$_2^+$ (L = aniline), 94483-37-1; Fe(TPC)(L)$_2$ (L = aniline), 94483-49-5; Fe(TPC)(L)$_2^+$ (L = benzylamine), 94483-38-2; Fe(TPC)(L)$_2$ (L = benzylamine), 94483-50-8; Fe(TPC)(L)$_2^+$ (L = piperidine), 94483-39-3; Fe(TPC)(L)$_2$ (L = piperidine), 94483-51-9.

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Chromium(V) Oxidations of Organic Compounds[1]

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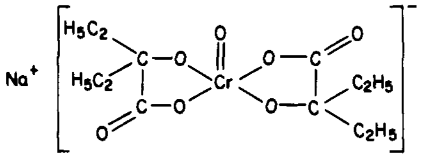
Sodium bis[2-ethyl-2-hydroxybutanoato(2−)]oxochromate(V) is sufficiently stable in aqueous solutions in the pH range 3–4 to allow the study of the oxidation of a series of organic substrates. Oxalic acid, primary and secondary 2-hydroxy acids, and 2-oxo acids react rapidly at 25 °C while for tertiary 2-hydroxy acids, alcohols, aldehydes, and diols a higher temperature (60 °C) was required. The rates of chromium(V) relative to chromium(VI) oxidations range from 0.08 to over 400.

Introduction

Our recent success in preparing a class of relatively stable water-soluble chromium(V) compounds[2] has opened the way to direct and more systematic investigation of the oxidative properties of chromium(V) in aqueous systems. In this study we are examining the reactions of sodium bis[2-ethyl-2-hydroxybutanoato(2−)]oxochromate(V) (I) with a number of organic compounds and comparing them to the well-known oxidations by chromium(VI).



I

Experimental Section

Materials. Oxalic acid (Fisher), lactic acid (Fisher), 2-oxoglutaric acid (Eastman), 3-oxoglutaric acid (Eastman), 3-phenyllactic acid (Aldrich), glycolic acid (Aldrich), glyoxylic acid (Aldrich), mandelic acid (Aldrich), pyruvic acid (Aldrich), tartaric acid (Aldrich), formaldehyde (Baker, 37% solution), acetaldehyde (Eastman), 1-propanol (Fisher), 2-propanol (Fisher), cyclopentanol (Aldrich), cyclohexanol (Aldrich), ethylene glycol (Fisher), 1,2-propanediol (Aldrich), 2,3-butanediol (Aldrich), pinacol (Aldrich), citric acid (Aldrich), 2-hydroxy-2-methylpropanoic acid (Eastman), 2-hydroxy-2-methylbutanoic acid (Aldrich), and 2-ethyl-2-hydroxybutanoic acid (Aldrich) were used as received. 2-Hydroxy-2-phenylpropanoic acid hemihydrate (Aldrich, 95%) was recrystallized from acetone–hexane and dried in vacuo (30 min at 100 °C) to remove crystalline water. Propanal (Aldrich) and butanal (Aldrich) were freshly distilled. Cyclobutanol (98.5% by GLC) was prepared from cyclopropylcarbinol.[3] Sodium bis[2-ethyl-2-hydroxybutanoato(2−)]oxochromate(V) monohydrate was prepared from sodium dichromate and 2-ethyl-2-hydroxybutanoic acid in acetone.[2] Freshly prepared solutions of chromium(V) were kept in a freezer for no longer than 3–4 days. Solutions of carboxylic acids (0.1 M, 0.5 M) were partially neutralized with sodium hydroxide to achieve the pH 3.0. The pH was verified on a Beckman Expand-Mate pH meter equipped with a Fisher combination electrode. For pH >3 Fisher Cerified buffer solutions were used. Stock solutions of chromium(VI) were prepared from sodium dichromate (Baker Analyzed).

Rate Measurements. At 25 °C chromium(V) and chromium(VI) oxidation rates were measured from decreases in absorbance at 350 nm (ϵ(Cr(V)) = 1209) on a Cary Model 15 recording spectrophotometer equipped with a thermostated cell holder. In a typical run 6–7 μL of a 0.2 M aqueous solution of chromium(V) or 6–7 μL of a 0.1 M solution of sodium dichromate were injected into 2 mL of a 0.1 M solution of the substrate, resulting in a chromium(V) or chromium(VI) concentration of (6–7) × 10^{-4} M. Pseudo-first-order rate constants were determined from plots of log *A* vs. time.

At 60 °C chromium(V) rates were monitored at 750 nm (ϵ = 38, maximum). In a typical experiment 2 mL of a 0.5 M solution of a substrate and 0.01 M of 2-ethyl-2-hydroxybutanoic acid (pH 3.0) were equilibrated for 30 min, and the reaction was initiated by injection of 100 μL of a 0.2 M solution of chromium(V), resulting in a 0.01 M chromium(V) concentration. Chromium(VI) rates were measured at 350 nm (2 mL of 0.5 M substrate, 6 μL of 0.1 M $Na_2Cr_2O_7$; 6 × 10^{-4} M Cr(VI)). Solutions of alcohols, diols, and aldehydes were prepared in hydrochloric acid–potassium phthalate buffer (22.3 mL of 0.1 M HCl + 50 mL of 0.1 M phthalate, pH 3.0).

Product Analysis. The yields of carbon dioxide were determined manometrically at 25 °C in a Warburg apparatus.[4] An aqueous solution of a substrate (3 mL; 0.5 M) was placed into the flask and purged with carbon dioxide for 15 min, and the reaction was initiated by the injection of chromium(V) (50 μL; 0.5 M aqueous solution) by a Hamilton syringe through a side arm fitted with a serum cap. The apparatus was calibrated by the carbon dioxide that was generated by the oxidation of excess oxalic acid under the same conditions.

The yields of formic, acetic, propanoic, and butanoic acids were determined by GLC and those of all other products by HPLC chromatography. Oxidations (0.5 M substrate, 0.05 M Cr(V)) were carried out at 25 or 60 °C with use of sealed reaction ampules (Wheaton Scientific, size 1–2 mL). HPLC analyses were carried out with a Waters Associates Model 6000 A liquid chromatograph equipped with a Model 440 absorbance detector (254 nm) and a C_{18} reverse-phase column. A solvent system was composed of water–methanol–acetic acid (400:100:25, v/v). In GLC analyses 1-mL samples of the reaction mixture were extracted with 1 mL of diethyl ether, chilled in ice, and analyzed on a Fisher-Victoreen Series 4400 gas chromatograph using a 6-ft UC-W98 10% silicon rubber column. The analysis of formic acid was carried out with a TCD detector. Calibration graphs were constructed for each product.

Stability of Chromium(V) Solutions. Solutions of sodium bis[2-ethyl-2-hydroxybutanoato(2−)]oxochromate(V) were prepared in an appropriate amount of perchloric acid or a buffer (Fisher Certified). At 25 °C the disappearance of chromium(V) was monitored at 550 nm (1-cm cell, 2-mL sample; Figure 1). At this wavelength chromium(V) is a dominant absorbing species (ϵ = 105). Absorbances of chromium(VI) (ϵ = 1.5) and chromium(III) (ϵ = 8) are sufficiently low to be negligible in a qualitative study.[5] A 1-h time perid was arbitrarily chosen to allow comparison under different conditions. At the end of the period samples were analyzed by iodometric titration to determine the total content of oxidizing chromium species (chromium(V) and chromium(VI); Table I).

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