Electronic Effects in Transition Metal Porphyrins. 2. The Sensitivity of Redox and Ligand Addition Reactions in Para-Substituted Tetraphenylporphyrin Complexes of Cobalt(II)

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Abstract: Electrochemical oxidation, by cyclic voltammetry, of a series of Co^{II}(p-X)TPP complexes yields first [Co^{III}(p-X)TPP]$^+$, followed by the π cation radical [Co^{III}(p-X)TPP]$^{2+}$ and then the dication [Co^{III}(p-X)TPP]$^{3+}$, in discrete reversible one-electron transfer steps. Reduction of the same series of compounds yields first [Co^{I}(p-X)TPP]$^-$, followed by the π anion radical [Co^{I}(p-X)TPP]$^{2-}$, again in discrete one-electron steps. In each case, a Hammett relationship is observed between the reversible $E_{1/2}$ values and the σ constants for the four substituents, X, on the four phenyl rings of [Co(p-X)TPP]$^{n\pm}$. Ring oxidations or reductions are considerably more sensitive to substituents than are metal oxidation or reduction. In addition, results of an investigation in five solvent systems indicate that the Hammett reaction constant for Co^{II}(p-X)TPP metal reduction is less sensitive to solvent effects than is that for Co^{II}(p-X)TPP metal oxidation, indicating that axial ligation is more important in the Co(II)/Co(III) system than in the Co(II)/Co(I) system. $E_{1/2}$ values for the Co^{II}(p-X)TPP reduction are less negative than those for Schiffs' base B$_{12}$ model compounds and for vitamin B$_{12}$ itself, but more negative than those for a series of cobalt(II) tetradehydrocorrins. The equilibrium constants for addition of one molecule of Lewis base (electron pair donor) to [Co^{II}(p-X)TPP]^0 in toluene solution also follow a Hammett relationship, with $\rho = 0.168$ (pyridine) and $\rho = 0.145$ (piperidine) at 25 °C. Equilibrium constants for addition of molecular oxygen to Co^{II}(p-X)TPP·py have been measured in toluene solution as a function of temperature. Again, a Hammett relationship was observed, and ρ was temperature dependent. The extrapolated value of ρ at 20 °C is -0.056 for addition of O$_2$ to Co^{II}(p-X)TPP to form a dioxygen complex. In comparison, ρ for oxidation of Co^{II}(p-X)TPP (calculated from ΔG_{ox}) to yield [Co^{III}(p-X)TPP]$^+$ is -0.31 (Me$_2$SO) to -0.79 (benzonitrile). The derived value of the dissociation constant for the reaction $\mathrm{CoTPP{\cdot}b{\cdot}O_2 \rightleftarrows CoTPP{\cdot}B + O_2^-}$ is estimated to be in the range of $10^{-11.9}$ to $10^{-16.7}$ M^{-1}.

The degree and mode of transmission of electron density from various points on the porphyrin ring through the σ and π orbitals of the four porphyrin nitrogens to the central metal ion have long been an interest of those who have investigated the physical properties and chemical reactions of metalloporphyrins.[3-7] Because of the conjugated nature of the porphyrin ring system, electron donating or withdrawing substituents on the periphery of the molecule have been shown to affect the basicity of the porphyrin nitrogens.[3,4] This, in turn, often affects the visible absorption spectra, redox potentials, and axial ligation reactions of the free bases and/or their respective metalloporphyrin complexes.[3,5-7]

One of the best means of quantifying the effects of electron-donating or -withdrawing groups on the reactions and physical properties of metalloporphyrins is the Hammett relationship.[8]

$$\Delta \log K = \log (K^{\mathrm{X}}/K^{\mathrm{H}}) = \sigma\rho \qquad (1\mathrm{a})$$

Here, σ is the characteristic of the electron donating/withdrawing properties of substituent X, and ρ measures the sensitivity of the reaction under study to substituents. The values of σ are defined from the ionization constants of substituted benzoic acids, for which ρ is defined as 1.0 for equation 1a.[8] This relationship is valid for both equilibrium and rate constants, and, suitably modified, can be applied to electrochemical redox potentials.[9]

$$\Delta E_{1/2} = E_{1/2}{}^{\mathrm{X}} - E_{1/2}{}^{\mathrm{H}} = \sigma\rho_{\mathrm{EMF}} \qquad (1\mathrm{b})$$

In the case of reversible electrochemical reactions, $E_{1/2}$ values are related to log K_{eq} through the Nernst equation, so that eq 1a and 1b differ by the factor $2.303RT/nF$, and $\rho_{\mathrm{EMF}} = 0.058\rho$ at 20 °C for one-electron redox reactions.

Symmetrically substituted tetraphenylporphyrin complexes such as those of structure I provide a reasonably large series of compounds of very similar structure, and thus relatively constant solvation energies. Furthermore, aggregation of tetraphenylporphyrins is minor compared to symmetrical alkyl and natural porphyrins.[10] Thus equilibrium constants, redox potentials, and other properties may be compared quantitatively within this series without the necessity of estimating contributions due to differences in aggregation, common in the natural porphyrins. In a recent investigation of the reaction of piperidine with a series of Ni(m-X)TPP, Ni(p-X)TPP, and VO(p-X)TPP complexes,[7] Hammett $\sigma\rho$ relationships were observed, and ρ was shown to be about equally sensitive to inductive and resonance contributions of X in para substituted complexes. This suggests that the π orbitals of the phenyl rings are able to overlap significantly with porphyrin π orbitals, even though the phenyl rings are prevented from being coplanar with the porphyrin ring by unfavorable steric interactions between ortho-H of the phenyl groups and pyrrole-H of the porphine ring. The relevant Hammett equations in these systems are actually

$$\log (K^{\mathrm{X}}/K^{\mathrm{H}}) = 4\sigma\rho \qquad (1\mathrm{c})$$

$$\Delta E_{1/2} = 4\sigma\rho_{\mathrm{EMF}} \qquad (1\mathrm{d})$$

because of the presence of four substituents, X.

The reactions of Co(II) porphyrins with amines[11,12]

$$\mathrm{CoP + B \overset{K_B}{\rightleftarrows} CoP{\cdot}B} \text{ (five-coordinate amine complex)} \qquad (2)$$

and molecular oxygen[12,13]

$$\mathrm{CoP{\cdot}B + O_2 \overset{K_{O2}}{\rightleftarrows} CoP{\cdot}B{\cdot}O_2} \text{ (oxygen adduct)} \qquad (3)$$

have been investigated in detail for P = (p-OCH$_3$)TPP[11,13] and protoporphyrin IX dimethyl ester,[12] and the oxidation potentials of Co^{II}(p-OCH$_3$)TPP reported in several solvents:[14]

$$[\mathrm{Co^{II}P}] \rightleftarrows [\mathrm{Co^{III}P}]^+ + \mathrm{e}^- \qquad (4)$$

However, the effect of substituents upon reactions 2-4 or other redox reactions to yield cobalt(I) and cobalt(I) π anion radicals or cobalt(III) π cation radicals and dication radicals have not been reported, although the Co(II) $\rightleftarrows$ Co(I) reactions of the related vitamin B_{12} and model B_{12} systems have been extensively investigated.[15-17]

In a previous publication,[18] we reported that the effect of substituents on the redox properties of para-substituted tetraphenylporphyrins $H_2(p\text{-X})TPP$ varies with solvent polarity and that the reaction constant, ρ_{EMF}, for anion radical formation increased in magnitude on going from dimethyl sulfoxide to methylene chloride. This study has now been extended to include an investigation of cobalt metalloporphyrin redox reactions in several solvents as well as an elucidation of substituent effects on electron pair addition (from axial ligands), single electron addition (from an electrode), and O_2 addition to cobalt(II) porphyrins containing electron-donating or -withdrawing groups at the para positions of the four phenyl groups.

The reactions investigated in this study are the following:

$$[Co^{II}(p\text{-X})TPP]^0 + B \rightleftarrows [Co^{II}(p\text{-X})TPP{\cdot}B]^0 \qquad (5)$$

$$[Co^{II}(p\text{-X})TPP{\cdot}B]^0 + O_2 \rightleftarrows [Co(p\text{-X})TPP{\cdot}B{\cdot}O_2]^0 \quad (6)$$

where B = pyridine and piperdine

$$[Co^{III}(p\text{-X})TPP]^{3+} + e \rightleftarrows [Co^{III}(p\text{-X})TPP]^{2+} \qquad (7)$$

$$[Co^{III}(p\text{-X})TPP]^{2+} + e \rightleftarrows [Co^{III}(p\text{-X})TPP]^{+} \qquad (8)$$

$$[Co^{III}(p\text{-X})TPP]^{+} + e \rightleftarrows [Co^{II}(p\text{-X})TPP]^{0} \qquad (9)$$

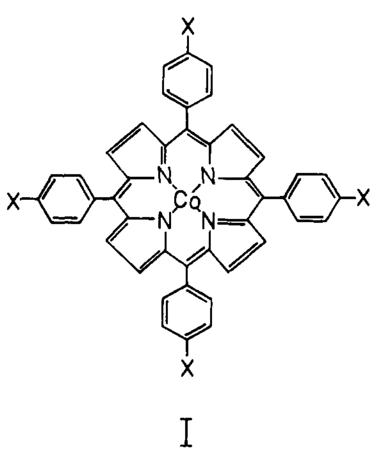
$$[Co^{II}(p\text{-X})TPP]^{0} + e \rightleftarrows [Co^{I}(p\text{-X})TPP]^{-} \qquad (10)$$

$$[Co^{I}(p\text{-X})TPP]^{-} + e \rightleftarrows [Co^{I}(p\text{-X})TPP]^{2-} \qquad (11)$$

The Roman numeral indicates the charge on the cobalt and the Arabic numeral gives the total charge on the complex. The cobalt(II) complex has zero charge so that $[Co^{III}(p\text{-X})TPP]^{2+}$ thus represents a cation radical containing cobalt(III) and $[Co^{I}(p\text{-X})TPP]^{2-}$ represents an anion radical containing cobalt(I).

Experimental Section

Chemicals. The para-substituted tetraphenylporphyrin free bases, $H_2(p\text{-X})TPP$, where X = OCH_3, CH_3, H, F, Cl, CN, and NO_2, were prepared by the method of Adler et al.[19] and chromatographed on silica gel (Baker chromatographic grade) with dichloromethane at least once before use. Formation of the Co(II) complexes, Co(p-X)TPP, structure I, was accomplished by the method of Adler et al.[20]



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The products were chromatographed at least three times as described above for $H_2(p\text{-X})TPP$, and one final time using benzene as the solvent. Each time the center cut only was retained. Visible spectra (λ_{max}, ϵ) of the Co(p-X)TPP complexes were very similar to those reported previously for Co(p-OCH_3)TPP.[21]

Toluene was distilled from calcium hydride shortly before use. Pyridine and piperdine were distilled from zinc dust and then barium oxide. Methylene chloride (Burdick and Jackson, "distilled-in-glass"), benzonitrile (Beckman Chemicals, Inc. "aniline-free"), n-butyronitrile (MCB, reagent), dimethyl sulfoxide (Me_2SO) (MCB, Spectroquality), and pyridine (MCB, Spectroquality) were used as received for electrochemical studies. Dried N,N-dimethylformamide (DMF) (MCB, reagent) was distilled at reduced pressure from activated alumina immediately before use. Tetrabutylammonium perchlorate (TBAP) and tetraethylammonium perchlorate (TEAP) (Southwestern Analytical, Inc., Polarographic Quality) were recrystallized from methanol and dried under reduced pressure.

Optical and Electron Spin Resonance Spectroscopic Measurements. Equilibrium constants for reaction 5 were measured on a Cary 14 spectrophotometer equipped with a circulating constant temperature bath by methods described previously;[11] those for reaction 6 were estimated by comparing the relative ESR signal intensities of the five-coordinate pyridine complex and its oxygen adduct obtained under 1 atm of air to those obtained previously[13] for reaction 3. The ratios of observed signal intensities of five-coordinate amine complex to O_2 adduct remained constant at a given temperature through several heating and cooling cycles. The ESR spectra were recorded on a Varian E-12 ESR spectrometer.

Cyclic Voltammetry. Cyclic voltammograms were obtained either on a P.A.R. 174 polarographic analyzer, in conjunction with a Houston Instruments 2000 X-Y recorder, with a 1-s pen response, or on a P.A.R. 173 potentiostat. A three-electrode system was used, consisting of platinum working and counter electrodes, and a commercial saturated calomel electrode (SCE), separated from the bulk of the solution by a bridge filled with solvent and supporting electrolyte. Solutions in the bridge were changed periodically to avoid aqueous contamination from entering the cell via the SCE. All solutions were purged of oxygen by passing purified nitrogen through them for 10 min just before running cyclic voltammograms. For methylene chloride solutions, the nitrogen was saturated with methylene chloride prior to entering the cell, to avoid evaporation. After degassing, a blanket of nitrogen was kept over the solution. The auxilary instrumentation and cell design have been described in a previous publication.[22]

The $E_{1/2}$ values were measured as that potential lying midway between the oxidation and reduction peak for a given couple. For reversible reactions, the reduction peak potential is 0.029 mV more anodic than $E_{1/2}$. This is the potential at which the current is equal to 85.17% of the diffusion peak current and is virtually interchangeable with the thermodynamically significant formal potential, $E°$.[23]

All experiments were carried out in a controlled temperature room of 20 ± 1° and potentials are reported with respect to the saturated calomel electrode (SCE).

Results and Discussion

Redox Reactions of Cobalt(III) and Cobalt(II). A typical cyclic voltammogram of $Co^{II}(p\text{-X})TPP$ is shown in Figure 1, in which the electrochemical processes are identified by equation number. (See introductory section.) The reduction of Co^I to form the anion radical (eq 11) is outside the range of the solvent, butyronitrile, and is only observed in DMF and Me_2SO.[24,26] This latter species has been identified as having broad visible bands and a split Soret band of low intensity (λ 608 (2.2×10^3), 511 (1.5×10^4), 427 (6.6×10^4), and 362 nm (5.4×10^4)).[24] This spectrum is similar to a cation radical spectrum but differs significantly from the usual broad banded anion radical spectrum obtained with other free base and metalloporphyrins. The redox potential of $Co^{II}TPP$ reduction (reaction 10) is only slightly dependent on the solvent conditions and has been reported in the literature as occurring at −0.82 V in Me_2SO,[26,27] −0.76 V in DMF,[15] and −0.77 V vs. SCE in DMF containing 10^{-2} M KCN.[15] In the presence of coordinating ligands such as CN^- or pyridine, cobalt(II) is known to be monocoordinated[11,12] but on reduction to cobalt(I) the axial ligand may or may not be bound to the metal, depending on the specific solution conditions.[15,16]

In contrast to the invariance with solvent of the cobalt(II) reduction potential, oxidation of cobalt(II) to cobalt(III)

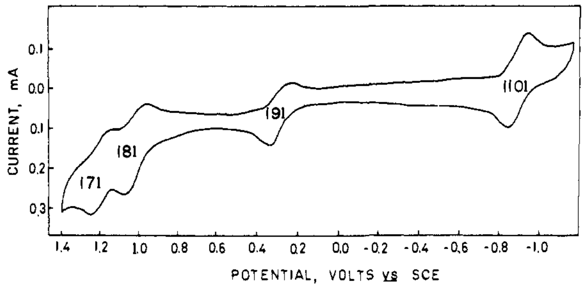

Figure 1. Typical cyclic voltammogram of 2.78 mM Co(p-OCH_3)TPP in butyronitrile, 0.1 M TBAP. Scan rate = 0.100 V/s. Numbers in parentheses refer to the redox process involved, and correspond to eq 7-10.

Table I. Reversible Half-Wave Potentials for Co(p-X)TPP in Various Solvents[e]

Solvent	$E_{1/2}$ (V vs. SCE)[a] Reaction 7	8	9	10	11
Pyridine[b]	—	—	−0.214	−1.030	—
Me_2SO[b]	—	—	0.130	−0.814	−1.870
DMF[c]	—	—	0.300[d]	−0.770	−1.880
Butyronitrile[b]	1.35	1.16	0.395	−0.812	—
Benzonitrile[c]	1.31	1.10	0.486	−0.858	—
Methylene chloride[b]	1.20	1.00	—	−0.855	—

[a] Not corrected for liquid junction potentials. [b] 0.1 M TBAP. [c] 0.1 M TEAP. [d] Reference 15. [e] See text for explanation of reaction numbers.

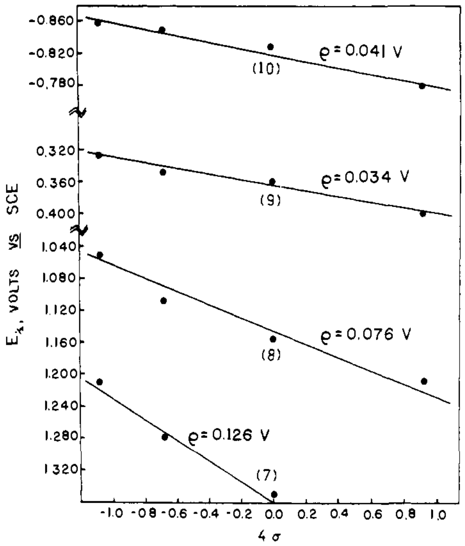

Figure 2. Plot of $E_{1/2}$ vs. 4σ for the electrode reactions 7-10 of 2.78 mM Co(p-X)TPP in butyronitrile, 0.1 M TBAP.

(reaction 9) is markedly dependent on the coordinating ability of the solvent. This is dramatically shown in Table I where the half-wave potentials of reactions 7 to 11 are listed for several solvents.

In strongly coordinating solvents such as Me_2SO and pyridine a facile oxidation of cobalt(II) is observed while in solvents such as benzonitrile the oxidation is shifted anodically by 344-700 mV and becomes somewhat irreversible, as determined by the separation of the anodic and cathodic peak potentials. Under the same solution conditions, little change in reversibility was observed for the reduction of Co^{II}(p-X)TPP and the potentials shifted only slightly between Me_2SO and benzonitrile. Basolo et al.[14] have reported that the ease of oxidation of cobalt(II) complexes is directly proportional to the base strength of the bound axial ligand and that a plot of $E_{1/2}$ vs. pK_a yields a linear relationship. In this study, we have observed a similar relationship between the half-wave potential for the oxidation of Co(II) to Co(III) and the coordinating ability of aprotic solvents. The coordinating ability of aprotic solvents for cations decreases in the following order:[28] pyridine > dimethyl sulfoxide > dimethylformamide > butyronitrile > benzonitrile. This follows the order of ease of Co(II) oxidation in each solvent. In the nonbonding solvent CH_2Cl_2, oxidation of Co(II) was irreversible. These results are also in accord with Corwin et al. who reported that the oxidation of Co(II) was solvent dependent.[25,29] The $E_{1/2}$ value for the III ⇄ II couple of CoTPP in pyridine (Table I) is in good agreement with the value obtained for Co(p-OCH_3)TPP by Basolo and co-workers,[14] shifted as expected for the change in para substituent. However, preliminary investigations in this solvent system suggest to us that more than one coordination number is present for Co(II), and the system is under further investigation.

Costa and co-workers[16] have found that Co(II) ⇄ Co(I) redox potentials are considerably more sensitive to equatorial ligand substituents than are Co(III) ⇄ Co(II) redox potentials, among a series of vitamin B_{12} model complexes, including B_{12} itself. In contrast, the latter redox potentials are much more sensitive to axial ligand properties than the former. They interpret these results as indication that the Co(III) ⇄ Co(II) reaction is dominated by strong axial ligand interaction whereas, in the Co(II) ⇄ Co(I) reaction, axial ligand interaction is weak and equatorial ligand electronic properties are thus more important. The data of Table II bear this out in the porphyrin system as well, with ρ for the Co(II) ⇄ Co(I) reaction being generally larger than ρ for the Co(III) ⇄ Co(II) reaction. The ρ values for both reactions are positive, indicating that electron-withdrawing substituents X, structure I, favor both reductions. The $E_{1/2}$ values for the III ⇄ II reduction of CoTPP (Table I) are less negative than the Schiff base B_{12} model compounds and vitamin B_{12} itself,[16] but more negative than a series of tetradehydrocorrin B_{12} model compounds.[17]

Porphyrin Ring Oxidations and Reductions. In nonaqueous media, porphyrins and metalloprophyrins may be oxidized in two single-electron transfer steps to yield π cation radicals and dications,[30] or reduced in two single-electron transfer steps to yield π anion radicals or dianions.[31] Differentiation of metal from ring oxidation is often accomplished by spectroscopic[22,30-33] or electrochemical techniques.[34,35]

In this study Co(p-X)TPP was observed to undergo a reversible reduction of the porphyrin ring to yield an anion radical (reaction 11) as well as two oxidations of the porphyrin ring (reactions 7 and 8). These latter two reactions are observed in Figure 1 at $E_{1/2}$ = +1.05 and +1.21 V vs. SCE. Plots of $E_{1/2}$ vs. 4σ are shown in Figure 2 for all electrode reactions of Figure 1 and reaction constants for reactions 7-11 are summarized in Table II for several solvents.

As seen from Table II, the reaction constant for the porphyrin ring reactions vary from 0.130 V for the oxidation of Co^{III}(p-X)TPP (reaction 7) in benzonitrile to 0.063 V for the reduction of Co^{I}(p-X)TPP in DMF (reaction 11). All of the ρ values for the reduction of the porphyrin ring are significantly larger in magnitude than the reaction constants for the metal redox reaction of either cobalt(III) or cobalt(II) in the same solvent system (reactions 9 and 10). From this table, it appears that porphyrin ring oxidation to yield π cations is more sensitive to substituents than porphyrin ring reduction to yield π anions. This is in agreement with spectroscopic studies[6] which indicate an added positive charge in the ring increases substituent effects and that the largest effect is observed with acid dications.

However, in contrast to the electrode reactions of cobalt

Table II. Reaction Constants for Electrooxidation–Reduction of Co(p-X)TPP in Five Solvents

		ρ(V)[a]				
Eq	Reaction	Me_2SO[b]	DMF[c]	Butyronitrile[b]	Benzonitrile[c]	CH_2Cl_2[b]
7	$[Co^{III}(p\text{-}X)TPP]^{3+} + e\ [Co^{III}(p\text{-}X)TPP]^{2+}$	*d*	*d*	0.126	0.130	0.085
8	$[Co^{III}(p\text{-}X)TPP]^{2+} + e\ [Co^{III}(p\text{-}X)TPP]^{+}$	*d*	*d*	0.076	0.100	0.085
9	$[Co^{III}(p\text{-}X)TPP]^{+} + e\ [Co^{II}(p\text{-}X)TPP]^{0}$	0.018	*e*	0.034	0.044	*e*
10	$[Co^{II}(p\text{-}X)TPP]^{0} + e\ [Co^{I}(p\text{-}X)TPP]^{-}$	0.038	0.034	0.041	0.044	0.046
11	$[Co^{I}(p\text{-}X)TPP]^{-} + e\ [Co^{I}(p\text{-}X)TPP]^{2-}$	0.087	0.063	*d*	*d*	*d*

[a] Calculated from eq 1d. [b] 0.1 M TBAP. [c] 0.1 M TEAP. [d] Outside of solvent potential range. [e] Ill-defined or irreversible peaks.

Table III. Equilibrium Constants for the Reaction

$$Co(p\text{-}X)TPP + B \xrightleftharpoons{K_B} Co(p\text{-}X)TPP{\cdot}B^{a}$$

		Log K_B	
X	σ_x[b]	Piperidine	Pyridine
OCH_3	−0.268	3.386 ± 0.043[c]	2.685 ± 0.026[c]
CH_3	−0.170	3.517 ± 0.017	2.742 ± 0.018
H	0.000	3.616 ± 0.090	2.880 ± 0.030
F	0.062		2.972 ± 0.044
Cl	0.227	3.698 ± 0.028	3.004 ± 0.061
CN	0.660	3.937 ± 0.062	3.268 ± 0.036
NO_2	0.778	4.036 ± 0.170	3.386 ± 0.015
ρ[d]		0.145 ± 0.017	0.168 ± 0.013
SD[e]		0.029	0.030

[a] In toluene solution, 25 °C. [b] From ref 8. [c] Taken from ref 11. [d] Calculated from eq 1c, using σ values from ref 8. Error limits in ρ are determined from linear least-squares analysis. [e] Standard deviation for agreement between experimental and calculated (e.g., 1c) values of log K_B.

porphyrin complexes we have observed that, in an identical solvent, VO, Fe, and Mn para substituted tetraphenyl porphyrins exhibit greatest sensitivity to ring reduction[36] while the free base porphyrins have an equal sensitivity to substituents for the formation of cation and anion radicals.[18]

Callot et al.[37] have reported that reduction of ring substituted tetraphenylporphyrins to form anion radicals in DMF gives an identical reaction constant of 0.38 V for porphyrins containing the central metals, Cu(II), Ni(II), and Pd(II), as well as the free base porphyrin. However, they did not observe the corresponding oxidations and so no conclusions may be reached regarding relative sensitivities.

Lewis Base (Lone Pair) Addition to Co(II). In Table III are listed the values of log K_B for reaction 5, where B = piperidine and pyridine. Hammett plots of the log $K_B{}^X$ for values vs. σ_X are shown in Figure 3. The positive ρ indicates that electron-withdrawing substituents favor the reaction by making Co(II) a better Lewis acid. The data of Table III and Figure 3 indicate that the sensitivity of reaction 5 to substituents is similar for amine donors of different electronic properties and basicities. Piperidine, pK_a(BH^+) = 11.12,[38] is capable of σ-donation only, while pyridine, pK_a(BH^+) = 5.17,[38] is capable of both σ-donation to cobalt and π-acceptance of d_π electrons from cobalt. Only a slight increase in ρ is observed on going from piperidine to pyridine, suggesting that the effect of decreased σ-donating capability is approximately balanced by π-accepting ability.

The effect of solvent polarity on K_B appears to be small. The data of Table III were obtained in toluene solution, a solvent of very low polarity. In butyronitrile, of intermediate polarity, the spectral change is considerably smaller, which significantly reduces the precision of the measurement of K_B. However, the values of log K_B obtained for B = pyridine (X = OCH_3, log K_B = 2.87 ± 0.14; X = CN, log K_B = 3.04 ± 0.17) are within experimental error of those obtained in toluene solution. It is reasonable to expect that solvent polarity (in the absence of solvent coordination) should have very little effect upon K_B, since reaction 5 involves only ligand addition to an available coordination site, and no creation of charge. That butyronitrile does not coordinate to Co(II) porphyrins was confirmed by addition of increasingly larger aliquots of butyronitrile to toluene solutions of CoTPP. Only a slight change occurred in the 520-nm band, and that at solvent compositions >50% butyronitrile. The progressive change was a broadening of the band, typical of nonspecific dielectric effects, and not the same as the change observed on addition of axial bases such as pyridine. If, however, the observed spectral changes are interpreted as being due to coordination of butyronitrile, then the K_B indicative of this coordination is less than 0.2 M^{-1}.

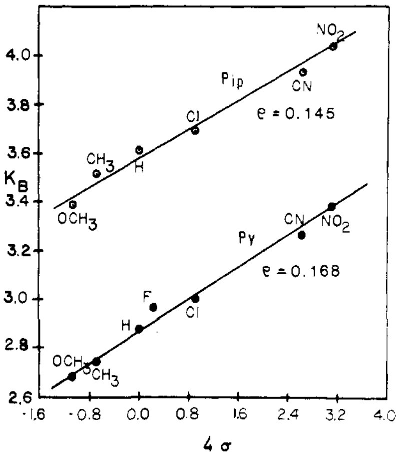

Figure 3. Plot of log K_B vs. 4σ for the addition of pyridine and piperidine to Co(p-X)TPP according to reaction 5.

Comparison of ρ for reactions of piperidine with (p-X)TPP complexes of V(IV),[7] Co(II), and Ni(II)[7] in toluene solution (Table V) reveals that the stoichiometry of the reaction (two molecules piperidine per Ni, one each for V and Co) has the most dramatic effect upon the sensitivity of the reaction to the electronic properties of substituents. If these effects are due only to stoichiometry, then division of ρ for Ni(II) by 2 ($\rho/2$ = 0.166) will allow comparison to the Co(II) and V(IV) systems. The resultant trend in decreasing ρ(0.166, 0.145, 0.112) as the number of d electrons decreases (d^8, d^7, d^1) suggests that the greater the number of d electrons on the metal, the greater the sensitivity of ligand addition to the effects of substituents on the phenyl rings. However, the effects are small, and may also be interpreted in terms of differences in M–N bond length or out-of-plane distance of M in reactant vs. products. Moreover, charge effects in metalloprophyrin–axial ligand complex formation, exemplified by the reaction of Fe(p-X)TPPCl with two molecules of N-methylimidazole to produce an ion paired product in which the metal center carries a positive charge, are so great as to reverse the sign of ρ(= −0.39 for this reaction).[39]

Comparison of Lone Pair and Single Electron Addition to Co(II). The d^7 Co(II) ion may be considered to be a free radical, because the single unpaired electron is in the d_{z^2} orbital, easily accessible to reaction with other free radicals.[40] The free radical nature of Co(II) corrins has recently been recognized to have important implications to the mechanism of reaction of several coenzyme B_{12} containing enzymes.[41] The presence of an axial base, to form the five-coordinate amine adduct, greatly enhances the free radical reactivity of cobalt(II) porphyrins,[40] and conversely, the loss of the axial 5,6-dimethylimidazole from coenzyme B_{12} is believed to weaken the carbon-cobalt bond and lead to homolytic fission, which is believed to initiate the reaction of enzyme with substrate.[41] Thus, it is interesting to compare the sensitivity of Lewis base (electron pair) and single electron addition to substituents of Co(p-X)TPP. In order to make this comparison, the electrochemical ρ_{EMF} for reaction 10 must be converted to the thermodynamic scale by multiplication of ρ_{EMF} by $nF/2.303RT$. This is equivalent to conversion of $E_{1/2}$ for reaction 10 to log K_{red} for the series of Co(p-X)TPP complexes and then calculation of ρ for this series of equilibrium reactions. The thermodynamic ρ values are summarized in Table V, along with the ρ values for Lewis base addition and other reactions. In noncoordinating solvents (butyronitrile, benzonitrile, methylene chloride), ρ for single-electron addition is 0.71–0.79, while ρ for electron pair (Lewis base) addition to the same series of Co(II) complexes is only 0.145–0.168. Since the d_{z^2} orbital is weakly involved in σ and σ^* bonding interactions in the porphyrin plane, in addition to its more significant axial σ and σ^* interactions, the effect of substituents on addition of an electron to the d_{z^2} orbital should be transmitted through the σ molecular framework. The fact that ρ for single-electron addition is much larger than that for electron pair addition is probably due to the fact that the electron pair must compete with the unpaired electron for occupation of the d_{z^2} σ orbital, thus producing an antibonding interaction, whereas addition of a single electron to the d_{z^2} orbital does not involve antibonding (σ^*) d_{z^2} interactions.

In solvents capable of coordination to Co(II) porphyrins (DMF, Me_2SO), ρ for single-electron addition is slightly smaller (0.59, 0.65), possibly indicative of the coordination number change from four to five or six.

Molecular Oxygen Addition to Five-Coordinate Cobalt(II) Porphyrins. The data of Table IV reveal the fact that the reaction constant ρ_{O_2} for addition of molecular oxygen to Co(p-X)TPP·py is dependent upon temperature. A plot of ρ_{O_2} vs. T^{-1} is linear and yields the extrapolated value −0.056 at 20 °C. It is this value which is most appropriate to compare to $E_{1/2}$ values for removal of an electron from Co(p-X)TPP. Thus the dependence of reaction 6 on "equatorial ligand" electronic effects is much smaller at ambient temperatures than assumed,[14] and at very high temperatures the dependence would actually be expected to reverse directions, although stability of the O_2 adduct would be vanishingly small under such conditions.

The negative sign of ρ_{O_2} at 20 °C and below indicates that electron-withdrawing substituents such as NO_2 cause addition of molecular oxygen to Co(p-X)TPP·py to be less favorable. Thus the *most* stable O_2 adduct is Co(p-OCH_3)TPP·py·O_2. In contrast, Co(p-OCH_3)TPP·py is the *least* stable five-coordinate pyridine adduct of the series. The opposite sign of the reaction constant of ρ_{O_2} points up the fact that addition of O_2 to Co(II) must be viewed either as an oxidation (to Co(III)-O_2^-, or partial oxidation), or as an electrophilic addition reaction (to Co(II)-O_2). The accepted formation is the former.[42,44]

The effect of solvent polarity on the equilibrium constant for reaction 3 has been reported; K_{O_2} increases as solvent polarity increases.[43] We find that K_{O_2} for reaction of CoTPP·Py with O_2 at −38 °C is a factor of ten larger in butyronitrile than in toluene. Data for a limited number of substituents also indicate that ρ_{O_2} is more temperature dependent in butyronitrile and larger in magnitude over the temperature range of measurement in butyronitrile (at − 48 °C, ρ_{O_2} = −0.15; at −39°, ρ_{O_2} = −0.13; at −28°, ρ_{O_2} = −1.10, leading to an extrapolated ρ_{O_2} = +0.04 in butyronitrile at 20 °C).

Table IV. Equilibrium Constants for the Reaction

$$\text{Co}(p\text{-X})\text{TPP(Py)} + O_2 \overset{K_{O_2}}{\rightleftarrows} \text{Co}(p\text{-X})\text{TPP(Py)}(O_2)^a$$

	Log K_{O_2}		
X	T = −72 °C	T = −56.5 °C	T = −38 °C
OCH_3	3.10^b	2.38^b	1.65^b
CH_3	3.07	2.78	1.61
H	2.98	2.22	1.48
F	3.00	2.23	1.53
Cl	2.90	2.21	1.45
CN	2.76	2.06	1.44
NO_2	2.66	—	—
ρO_2	-0.105 ± 0.015^c	-0.093 ± 0.012^c	-0.082 ± 0.020^c
	ρO_2 extrap to 20°:	−0.056	

[a] In toluene solution. [b] Calculated from data taken from ref 13. [c] Calculated by linear least-squares analysis of the log K_{O_2} vs. σ_X data.

Comparison of Molecular Oxygen Addition to and Electrooxidation of Cobalt(II) Porphyrins. From the reduction potentials of the series of $[Co^{III}(p\text{-X})TPP]^+$ complexes, eq 9, ΔG_{red} may be calculated. Since the electrochemical process is reversible, $\Delta G_{ox} = -\Delta G_{red}$, where ΔG_{ox} is the free energy of removal of an electron from Co^{II}(p-X)TPP, the reverse of eq 9. Thus $\rho_{ox} = -\rho_{red} = -0.41$ V in butyronitrile for example (Table II). Conversion of the electrochemical reaction constant to the thermodynamic scale yields ρ_{ox} = −0.71 as listed in Table V. This value is approximately a factor of 12 larger in magnitude than the extrapolated thermodynamic reaction constant for addition of O_2 to Co(p-X)TPP·B in toluene solution, indicating that electrochemical removal of an electron from Co(II) (reverse of eq 9) is much more sensitive to electronic effects of substituents than is partial removal by dioxygen to form the oxygen adduct, eq 6, usually formulated as Co(III)-O_2^-.[42,44]

Pratt and co-workers[45] have reported the observation of an ESR signal identical with that obtained by treating cobalamin(II) with molecular oxygen, upon mixing aquocobalamin(III) and electrochemically generated O_2^- in DMF. This observation prompts us to utilize the electrochemical and thermodynamic data of the present work to estimate the dissociation constant for the reaction:

$$\text{CoTPP}\cdot\text{B}\cdot O_2 \rightleftarrows \text{Co}^{III}\text{TPP}\cdot\text{B}^+ + O_2^- \tag{12}$$

The reactions which make up the Hess' law cycle and their ΔG values are as follows:

$$\text{CoTPP}\cdot\text{B}\cdot O_2 \rightleftarrows \text{Co}^{II}\text{TPP}\cdot\text{B} + O_2 \qquad \Delta G = +0.8 \text{ kcal/mol} \tag{13}$$

$$\text{Co}^{II}\text{TPP}\cdot\text{B} + \text{B} \rightleftarrows \text{Co}^{II}\text{TPP}\cdot\text{B}_2 \qquad \Delta G \simeq +1.3 \text{ kcal/mol} \tag{14}$$

$$\text{Co}^{II}\text{TPP}\cdot\text{B}_2 \rightleftarrows \text{Co}^{III}\text{TPP}\cdot\text{B}_2^+ + e \qquad \Delta G = -7.7 \text{ kcal/mol} \tag{15}$$

$$\text{Co}^{III}\text{TPP}\cdot\text{B}_2^+ \rightleftarrows \text{Co}^{III}\text{TPP}\cdot\text{B}^+ + \text{B} \qquad \Delta G \simeq +2.7 \text{ to } 4.0 \text{ kcal/mol} \tag{16}$$

$$O_2 + e^- \rightleftarrows O_2^- \quad \Delta G = +18.9\text{–}24.0 \text{ kcal/mol} \tag{17}$$

Table V. Hammett Reaction Constants (ρ) for Addition of an Electron or Axial Ligand and Removal of an Electron from the Central Metal of Several Series of M(p-X)TPP Complexes

Reaction	Temp, °C	ρ, calcd from log K	ρ_{EMF} (V)
$\mathrm{Co^{II}}(p\text{-X})\mathrm{TPP} + \mathrm{py} \rightleftarrows \mathrm{Co^{II}}(p\text{-X})\mathrm{TPP{\cdot}py}$	25	0.168[a]	—
$\mathrm{Co^{II}}(p\text{-X})\mathrm{TPP} + \mathrm{pip} \rightleftarrows \mathrm{Co^{II}}(p\text{-X})\mathrm{TPP{\cdot}pip}$	25	0.145[a]	—
$\mathrm{VO^{IV}}(p\text{-X})\mathrm{TPP} + \mathrm{pip} \rightleftarrows \mathrm{VO^{IV}}(p\text{-X})\mathrm{TPP{\cdot}pip}$	25	0.112[b]	—
$\mathrm{Ni^{II}}(p\text{-X})\mathrm{TPP} + 2\mathrm{pip} \rightleftarrows \mathrm{Ni^{II}}(p\text{-X})\mathrm{TPP{\cdot}2pip}$	22	0.331[b]	—
$\mathrm{Co^{II}}(p\text{-X})\mathrm{TPP{\cdot}py} + \mathrm{O_2} \rightleftarrows \mathrm{Co}(p\text{-X})\mathrm{TPP{\cdot}py{\cdot}O_2}$	−72	−0.105[a]	—
	−56	−0.093[a]	—
	−38	−0.082[a]	—
	20[d]	−0.056[a]	—
$[\mathrm{Co^{II}}(p\text{-X})\mathrm{TPP}]^0 + \mathrm{e^-} \rightleftarrows [\mathrm{Co^{I}}(p\text{-X})\mathrm{TPP}]^-$	20	0.71[c,e]	0.041[e]
$[\mathrm{Co^{II}}(p\text{-X})\mathrm{TPP}]^0 \rightleftarrows [\mathrm{Co^{III}}(p\text{-X})\mathrm{TPP}]^+ + \mathrm{e^-}$	20	−0.59[c,e]	−0.034[e]

[a] This work. [b] Reference 7. [c] Calculated from $\rho_{\mathrm{EMF}}/0.058$. [d] Extrapolated. [e] Solvent = butyronitrile.

The ΔG estimated for reaction 13 is based on the value of $-\log K_{\mathrm{O_2}} = -0.6$ extrapolated from the low temperature data obtained in butyronitrile to 20 °C. ΔG for reaction 14 is calculated from $K_{\mathrm{eq}} \simeq 0.1\ \mathrm{M^{-1}}$, estimated from the data of ref 13 (the extrapolated value of K_{eq} for B = 3,4-lutidine = $0.14\ \mathrm{M^{-1}}$ at 20°). ΔG for reaction 15 is calculated from the $E_{1/2}$ in pyridine (Table I) corrected for liquid junction potential using the ferrocene/ferrocenium couple. The corrected potential is −0.334 V. ΔG for reaction 16 is based on the estimated range of K_{eq} ($\simeq$100–1000 $\mathrm{M^{-1}}$), by analogy to the $\mathrm{Fe^{III}TPP}$ system,[39] and ΔG for reaction 17 is calculated from the range of $E_{1/2}$ values for the one-electron reduction of molecular oxygen in several nonaqueous solvents (−0.82 to −1.04 V).[47] The sum of these free energy values gives $\Delta G = +16.0\text{–}22.4$ kcal/mol for reaction 12 in nitrile solvents, or $K_{\mathrm{dissoc}} = 10^{-11.9}$ to $10^{-16.7}$.

This is a very small number; in comparison K_{dissoc} for the reaction

$$\mathrm{FeTPPCl} \rightleftarrows \mathrm{FeTPP^+} + \mathrm{Cl^-} \tag{18}$$

in chloroform at 25 °C is estimated to be 10^{-6} M.[39] Thus, the tendency toward dissociation of the oxygen adduct into Co(III) and $\mathrm{O_2^-}$ is much less than that for more typical $\mathrm{M^{III}X^-}$ porphyrin complexes in which the location of the electrons is more clear cut. This emphasizes the unique nature of the electronic configuration and bonding in the oxygen adduct, and suggests that charge transfer from Co to $\mathrm{O_2}$ is far from complete.

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