Inorg. Chem. **1989**, *28*, 3743–3747 **3743**

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Oxidative Electrochemistry of Cobalt Tetraphenylporphyrin under a CO Atmosphere. Interaction between Carbon Monoxide and Electrogenerated $[(\mathrm{TPP})\mathrm{Co}]^+$ in Nonbonding Media

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Received December 12, 1988

The electrooxidation of (TPP)Co (where TPP is the dianion of tetraphenylporphyrin) was carried out in $\mathrm{CH_2Cl_2}$ and benzene under a CO atmosphere and provides the first evidence for the binding of CO with electrooxidized $[(\mathrm{TPP})\mathrm{Co}]^+$. (TPP)Co undergoes two reversible oxidations in $\mathrm{CH_2Cl_2}$, 0.1 M tetra-*n*-butylammonium perchlorate under 1 atm of CO. The first reaction occurs at $E_{1/2} = 0.72$ V and involves the abstraction of one electron to give a π cation radical $[(\mathrm{TPP})\mathrm{Co^{II}(CO)}]^+$ or $[(\mathrm{TPP})\mathrm{Co^{III}(CO)}]^+$ in which the central cobalt metal has been oxidized. A further oxidation of $[(\mathrm{TPP})\mathrm{Co(CO)}]^+$ occurs at $E_{1/2} = 1.10$ V and involves the reversible abstraction of two electrons to give $[(\mathrm{TPP})\mathrm{Co^{III}}]^{3+}$ as a final product. The singly oxidized species has a UV–visible spectrum similar to that of other $[(\mathrm{TPP})\mathrm{Co^{III}(L)}]^+$ or $[(\mathrm{TPP})\mathrm{Co^{III}(L)_2}]^+$ complexes, and the formation constant for CO binding to $[(\mathrm{TPP})\mathrm{Co}]^+$ in $\mathrm{CH_2Cl_2}$ was calculated as $\log K_1 = 4.3$. In contrast to results in $\mathrm{CH_2Cl_2}$, (TPP)Co undergoes three oxidations in benzene, 0.1 M tetrahexylammonium perchlorate under 1 atm of CO. These oxidations occur at $E_{1/2} = 0.90$, 1.05, and 1.24 V vs SCE and generate $[(\mathrm{TPP})\mathrm{Co(CO)}]^+$, $[(\mathrm{TPP})\mathrm{Co^{III}}]^{2+}$, and $[(\mathrm{TPP})\mathrm{Co^{III}}]^{3+}$ as electrooxidation products. The binding of $\mathrm{CH_3CN}$ to electrooxidized (TPP)Co was also investigated in $\mathrm{CH_2Cl_2}$. Both $[(\mathrm{TPP})\mathrm{Co^{III}(CH_3CN)}]^+$ and $[(\mathrm{TPP})\mathrm{Co^{III}(CH_3CN)_2}]^+$ could be electrogenerated, and formation constants for the stepwise binding of $\mathrm{CH_3CN}$ to $[(\mathrm{TPP})\mathrm{Co}]^+$ were calculated as $\log K_1 = 4.4$ and $\log \beta_2 = 6.6$. One $\mathrm{CH_3CN}$ ligand could also bind to doubly oxidized $[(\mathrm{TPP})\mathrm{Co^{III}}]^{2+}$, and the calculated formation constant of $\log K_1 = 2.1$ provides the first binding constant for a neutral ligand to a Co(III) porphyrin π cation radical. Finally, an overall oxidation/reduction mechanism is presented for the electrooxidation of (TPP)Co in $\mathrm{CH_2Cl_2}$ or benzene solutions under an $\mathrm{N_2}$ or a CO atmosphere.

Introduction

The electrochemistry[1-11] of cobalt(II) and cobalt(III) porphyrins complexed with, or in the presence of, diatomic molecules has been limited to NO and $\mathrm{O_2}$. Studies with respect to NO have mainly involved a characterization of (P)Co(NO) redox reactions in nonaqueous media. $[(\mathrm{P})\mathrm{Co(NO)}]^+$ and $[(\mathrm{P})\mathrm{Co(NO)(L)}]^+$ (where P is the dianion of a given porphyrin macrocycle and L is a neutral ligand) can be chemically or electrochemically generated, and the oxidative conversion of (P)Co(NO) to its singly oxidized cation radical has been well characterized in solution.[2,4,5]

Early electrochemical studies involving cobalt porphyrins and dioxygen were concerned primarily with measurements of $\mathrm{O_2}$ binding ability,[6,11] but more recent studies have focused on the catalytic four-electron reduction of dioxygen to water using various monometallic[7,8] or bimetallic[9,10] cobalt porphyrins as catalysts. No $(\mathrm{P})\mathrm{Co(O_2)_2}$ complex has ever been reported, but the mixed-ligand species $(\mathrm{P})\mathrm{Co(CO)(O_2)}$ and (P)Co(CO)(NO) can be formed at low temperature.[12]

The spectroscopic data on cobalt(II) and cobalt(III) porphyrin NO[13-15] and $\mathrm{O_2}$[13,15-17] adducts are extensive, but less information is available on cobalt porphyrin complexes containing bound CO ligands.[12,13,15,18] Carbon monoxide interacts with cobalt(II) porphyrins very weakly, and the mono- or bis(carbonyl) adducts of (P)Co are only formed at low temperature under a CO atmosphere.[12,15,18] There has also been an interest in the reaction between carbon monoxide and synthetic cobalt(III) complexes as models for vitamin $\mathrm{B_{12}}$,[19] but the interaction of CO with a synthetic cobalt(III) porphyrin has never been reported.

This work presents the first electrochemical study of (TPP)Co under a CO atmosphere. Electrooxidations were carried out in the noncoordinating solvents $\mathrm{CH_2Cl_2}$ and benzene and provide the first clear evidence for the binding of CO with electrogenerated $[(\mathrm{TPP})\mathrm{Co}]^+$ in solution. The electrochemistry of (TPP)Co in $\mathrm{CH_2Cl_2}$ containing $\mathrm{CH_3CN}$ is also reported, and an overall mechanism for the binding of either CO or $\mathrm{CH_3CN}$ to the singly oxidized cobalt porphyrin is presented.

Experimental Section

Chemicals. (TPP)Co was synthesized by using literature methods.[6] CP grade carbon monoxide was obtained from Union Carbide Corp., Linde Division. Spectroanalyzed grade methylene chloride was obtained from Fisher Scientific Co. and used as supplied. HPLC grade acetonitrile ($\mathrm{CH_3CN}$) (Mallinckrodt Co.), pyridine (py) (Fisher Scientific Co.), and dimethyl sulfoxide ($\mathrm{Me_2SO}$) (Aldrich Chemical Co.) were freshly distilled from $\mathrm{CaH_2}$ under argon before use. Tetra-*n*-butylammonium perchlorate (TBAP) was utilized as supporting electrolyte. This salt was obtained from Fluka Chemical Co., twice recrystallized from absolute ethanol, and stored at 40 °C under vacuum before use. AR grade benzene was vigorously stirred with concentrated sulfuric acid. After separation of the sulfuric acid, the solvent was washed with 0.1 M sodium hydroxide and water, predried with sodium sulfate and then distilled from sodium before use. Tetrahexylammonium perchlorate (THAP) was used as supporting electrolyte for the voltammetric study in benzene. It was obtained from Alfa Co., twice recrystallized from methanol, and vacuum-dried before use. The concentration of supporting electrolyte was 0.1 M, and all potentials are reported vs SCE.

Instrumentation. Cyclic voltammetric and steady-state measurements were obtained by using an IBM Model 225A voltammetric analyzer and an Omnigraphic 2000 X-Y recorder. IR loss was minimized by the use of positive-feedback devices built into the IBM Model 225A. A three-electrode geometry was used and consisted of a 0.8-mm² platinum working electrode, a large-surface platinum counter electrode, and a saturated calomel reference electrode (SCE) for conventional cyclic voltammetric measurements. For steady-state experiments, a micro-

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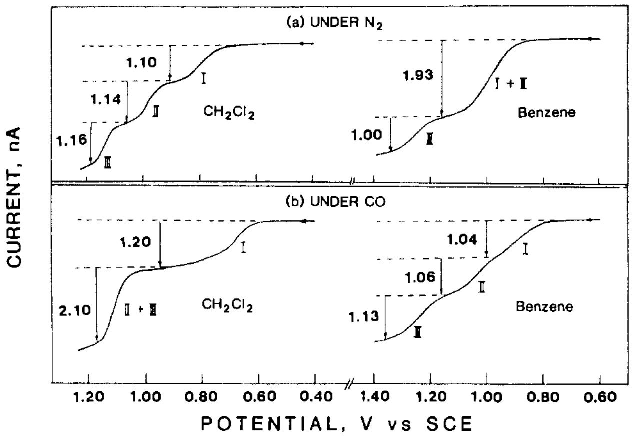

Figure 1. Steady-state voltammograms for the oxidation of (TPP)Co in CH_2Cl_2 and benzene at a 25-μm Pt microelectrode (a) under 1 atm of N_2 and (b) under 1 atm of CO.

working electrode was used. This electrode was constructed by sealing a 25-μm-diameter platinum wire (Johnson-Mathey, Inc.) into a Pyrex tube.

A Matheson Model 8250 modular Dyna-Blender with flowmeter was used to deliver set nitrogen/carbon monoxide mixtures which varied between 0.01 and 1 atm. The vapor pressure of methylene chloride (382 mmHg at 23 °C) was subtracted from the total pressure in calculating the partial pressure of CO. Solubility coefficients were not found for CO dissolved in methylene chloride, but the solubility coefficients of CO in benzene and in chloroform are about the same.[20] The solubility coefficient of CO in benzene is 6.7×10^{-3}/atm,[21] and this value was used to calculate the binding constant of CO with $[(TPP)Co]^+$ in CH_2Cl_2.

UV-visible spectroelectrochemical measurements were obtained with an IBM Model 225A voltammetric analyzer coupled with a Tracor Northern 1710 multichannel analyzer. The cell for obtaining thin-layer spectra has been described elsewhere.[22]

Results and Discussion

Voltammetric Characterization of (TPP)Co Oxidation in CH_2Cl_2 under a CO Atmosphere. Figure 1a shows microelectrode steady-state voltammograms for the oxidation of (TPP)Co in CH_2Cl_2 and benzene under an N_2 atmosphere. Three electrooxidations (labeled I, II, and III) are observed in CH_2Cl_2. Each oxidation involves a one-electron transfer, which occurs respectively at $E_{1/2}$ = 0.82, 0.99, and 1.17 V vs SCE. These three processes have been well characterized in the literature, and the UV-visible and ESR spectra of the singly, doubly, and triply electrooxidized species have been presented under a variety of experimental conditions.[22-24]

In contrast to the above, (TPP)Co undergoes only two electrooxidations in benzene under an N_2 atmosphere. The first process involves an overall two-electron conversion of (TPP)Co to $[(TPP)Co^{III}]^{2+}$, while the second involves a one-electron conversion of $[(TPP)Co^{III}]^{2+}$ to $[(TPP)Co^{III}]^{3+}$. An initial two-electron porphyrin oxidation has previously been noted for (TPP)Co[25] in benzene and toluene and as well as for $(TPP)H_2$ and (TPP)M (M = Cu(II), Zn(II), or Ni(II)) in toluene.[26,27] The two oxidations of (TPP)Co in benzene occur at $E_{1/2}$ = 1.00 and 1.27 V, and the products of each electron transfer have been characterized by UV-visible spectroscopy.[25]

Table I. Half-Wave Potentials (V vs SCE) and Number of Electrons Transferred for the Oxidation of (TPP)Co in Methylene Chloride (0.1 M TBAP) and Benzene (0.1 M THAP) under CO or N_2

		$E_{1/2}$ (no. of electrons)[b]		
solvent	axial ligand[a]	1st	2nd	3rd
CH_2Cl_2	none	0.82 (1)	0.99 (1)	1.17 (1)
	CO (1 atm)	0.72 (1)	1.10 (2)	
benzene	none	1.00 (2)	1.27 (1)	
	CO (1 atm)	0.90 (1)	1.05 (1)	1.24 (1)

[a] ClO_4^- may be associated with each oxidized complex. [b] Value determined by analysis of current-voltage curves from steady-state voltammograms.

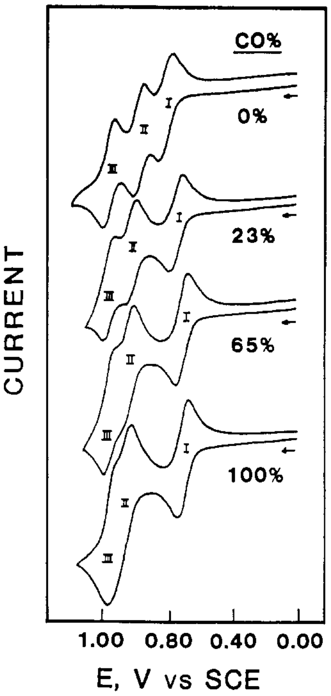

Figure 2. Cyclic voltammograms for the oxidation of (TPP)Co in CH_2Cl_2, 0.1 M TBAP under different CO partial pressures. Scan rate = 0.1 V/s.

Steady-state voltammograms for the electrooxidation of (TPP)Co in CH_2Cl_2 and benzene under 1 atm of CO are illustrated in Figure 1b, and the half-wave potentials for each process are listed in Table I. In both solvents, the first oxidation (process I) is shifted to more negative potentials while the second (process II) is shifted to more positive potentials with respect to the same reactions under an N_2 atmosphere. This leads to an increased potential separation in $E_{1/2}$ between processes I and II and results in a significant changeover in voltammetric behavior from what is observed under an N_2 atmosphere. The changeover in electrooxidative behavior as a function of the gas above the solution is remarkable and, in light of the 100-mV negative shift in process I, is clearly consistent with an interaction between CO and the singly oxidized cobalt porphyrin species.

The positive shift in $E_{1/2}$ for process II is also consistent with a decreased interaction between CO and the doubly oxidized species, and this was confirmed by cyclic voltammograms of (TPP)Co in CH_2Cl_2 under various gas mixtures of N_2 and CO (Figure 2). Under an N_2 atmosphere (0% CO), reversible oxidation processes are observed at $E_{1/2}$ = 0.82, 0.99, and 1.17 V. This is similar to what is observed in the steady-state voltammogram. However, $E_{1/2}$ for process I shifts negatively from 0.82 V with increase of CO pressure above the solution and is located at 0.72 V under 1 atm of CO. The ratio of cathodic to anodic peak current for this oxidation/reduction is approximately 1.0, and the anodic to cathodic peak potential separation is 62 ± 2 mV at a scan rate of 0.1 V/s, thus indicating a reversible one-electron transfer. The second oxidation of (TPP)Co (process II) also remains reversible but shifts positively in potential with increase in the CO partial pressure. The third oxidation (process

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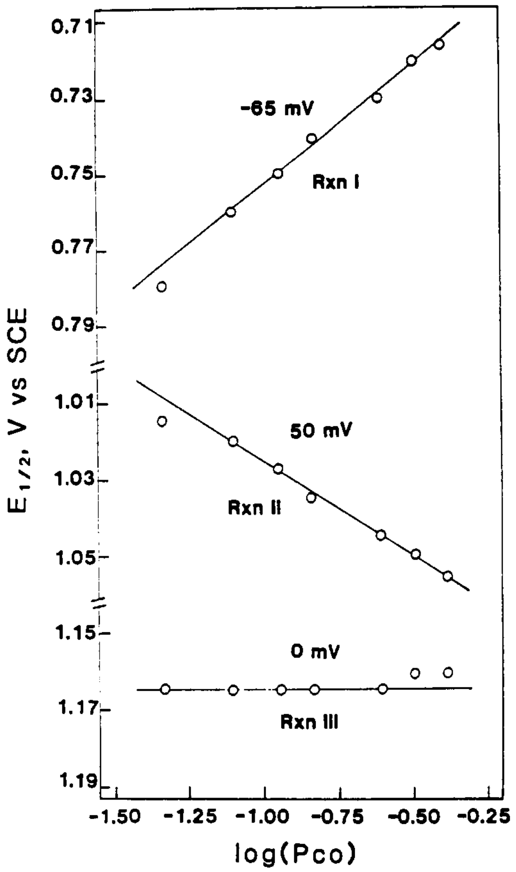

Figure 3. Dependence of $E_{1/2}$ on the corrected CO partial pressure for the three oxidations of (TPP)Co in CH_2Cl_2, 0.1 M TBAP. Reactions I, II, and III are indicated in Figure 2.

III) does not shift with increase of CO partial pressure and becomes almost totally overlapped with the second oxidation (process II) under 1 atm of CO.

Plots of $E_{1/2}$ vs log P_{CO} for the three (TPP)Co oxidations are shown in Figure 3. The −65 mV shift of $E_{1/2}$ per 10-fold increase of P_{CO} for reaction I can be compared to a theoretical slope of −59 mV for the case where one CO molecule binds to the product of the first electrooxidation[28] as shown by eq 1.

$$(TPP)Co + CO \rightleftarrows [(TPP)Co(CO)]^+ + e^- \qquad (1)$$

A CO molecule does not remain complexed to the cobalt center after the second oxidation and dissociates as shown in eq 2. This

$$[(TPP)Co(CO)]^+ \rightleftarrows [(TPP)CO^{III}]^{2+} + CO + e^- \qquad (2)$$

results in a 50-mV positive shift in $E_{1/2}$ for each 10-fold change in the CO pressure, and this slope can be compared to a theoretical slope of 59 mV for the reaction given in eq 2.

There is no apparent interaction of CO with $[(TPP)Co^{III}]^{2+}$, and $E_{1/2}$ for the third oxidation is independent of the CO partial pressure. Thus, under both an N_2 and a CO atmosphere, the third oxidation process is given by eq 3.

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

The cyclic voltammetric data in Figures 2 and 3 are consistent with the steady-state voltammetric data in Figure 1 and unambiguously provide evidence for the binding of CO to the singly oxidized $[(TPP)Co]^+$ as shown in eq 4. A formation constant

$$[(TPP)Co]^+ + CO \overset{K_1}{\rightleftarrows} [(TPP)Co(CO)]^+ \qquad (4)$$

for the above CO-binding reaction with $[(TPP)Co]^+$ was calculated as log K_1 = 4.3 by using the data in Figure 3 and standard electrochemical equations that relate changes in $E_{1/2}$ to partial pressures of the gas above the solution.[28]

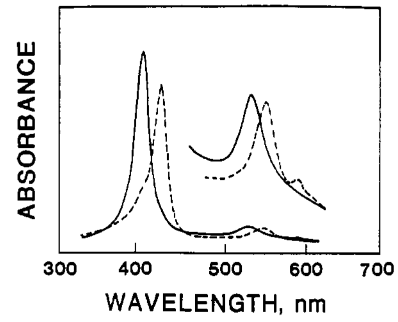

Figure 4. Thin-layer spectra before (—) and after (- - -) controlled-potential electrolysis of (TPP)Co in CH_2Cl_2, 0.1 M TBAP under 1 atm of CO at 0.90 V.

Table II. Spectral Characteristics of Electrooxidized $[(TPP)Co]^+$ and $[(TPP)Co(L)_n]^+$ in CH_2Cl_2 Containing 0.1 M TBAP

compd[a]	ligand, L	λ_{max}, nm ($\epsilon \times 10^{-4}$, cm^{-1} M^{-1})		
$[(TPP)Co]^+$	none	427 (21)	541 (1.5)	580 (sh)
$[(TPP)Co(L)]^+$	CO	431 (23)	545 (1.6)	582 (0.3)
	CH_3CN	432 (25)	545 (1.8)	582 (0.3)
$[(TPP)Co(L)_2]^+$	CH_3CN	435 (28)	549 (2.0)	585 (0.4)
	Me_2SO[b]	434 (23)	546 (1.5)	583 (0.4)
	py[c]	437 (26)	551 (1.3)	588 (0.5)

[a] ClO_4^- may be associated with each oxidized species. [b] Spectra obtained in neat Me_2SO containing 0.1 M TBAP. [c] Spectra obtained in neat py containing 0.1 M TBAP.

Spectroelectrochemical Characterization of $[(TPP)Co(CO)]^+$ Formation. The oxidation of (TPP)Co in CH_2Cl_2 under a CO atmosphere was monitored by thin-layer UV–visible spectroelectrochemistry and gave spectral changes such as those shown in Figure 4. (TPP)Co has bands at 410 and 527 nm under 1 atm of CO, and the spectrum of the neutral complex under CO is identical with the one obtained under an N_2 atmosphere.

The UV–visible spectrum obtained after a one-electron oxidation of (TPP)Co under 1 atm of CO (dashed line, Figure 4) is characterized by Soret and visible bands that are red-shifted by about 4 nm compared with the spectrum of $[(TPP)Co]^+$ in CH_2Cl_2, 0.1 M TBAP under N_2. Also, both bands of the oxidized complex have slightly larger molar absorptivities under CO than under N_2. These spectral data are summarized in Table II, which also lists spectral data for other $[(TPP)Co^{III}(L)]^+$ and $[(TPP)Co^{III}(L)_2]^+$ complexes where L = CH_3CN, Me_2SO, or py.

The electrooxidation site in cobalt(II) porphyrins is dependent upon the solvent and supporting electrolyte as well as upon the presence of any coordinating ligands in solution.[29–31] The chemical or electrochemical oxidation of $(P)Co^{II}$ in bonding solvents generally leads to $[(P)Co^{III}]^+$ but in dry CH_2Cl_2 can lead to a cobalt(II) π cation radical that has been characterized by UV–visible spectra for the case of $(TPP^{\bullet+})Co^{II}SbCl_6^-$,[30] $(OEP^{\bullet+})Co^{II}ClO_4^-$,[29] and $(TPP^{\bullet+})Co^{II}ClO_4^-$.[31] The latter species has a UV–visible spectrum with a much decreased Soret band molar absorptivity and a broad visible band in the range of 500–700 nm.[31] This spectrum is similar to that of other tetraphenylporphyrin π cation radicals[32] but differs substantially from the spectrum of $[(TPP)Co^{III}(L)_2]^+ClO_4^-$ where L = Me_2SO or py. These latter Co(III) complexes have spectral features similar to neutral (TPP)Co, but the Soret and visible bands are slightly decreased in intensity and are red-shifted by ~20 nm with respect to the original Co(II) complex.

Spectral changes associated with the Co(II)/Co(III) reaction of (TPP)Co have been monitored under numerous solution con-

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Table III. Reactions of (TPP)Co under Different Solution Conditions

Case I. In CH_2Cl_2 under N_2
$(TPP)Co \rightleftarrows [(TPP)Co]^+ + e^-$
$[(TPP)Co]^+ \rightleftarrows [(TPP)Co]^{2+} + e^-$
$[(TPP)Co]^{2+} \rightleftarrows [(TPP)Co]^{3+} + e^-$

Case II. In Benzene under N_2
$(TPP)Co \rightleftarrows [(TPP)Co]^{2+} + 2e^-$
$[(TPP)Co]^{2+} \rightleftarrows [(TPP)Co]^{3+} + e^-$

Case III. In CH_2Cl_2 under CO
$(TPP)Co + CO \rightleftarrows [(TPP)Co(CO)]^+ + e^-$
$[(TPP)Co(CO)]^+ \rightleftarrows [(TPP)Co]^{3+} + CO + 2e^-$

Case IV. In Benzene under CO
$(TPP)Co + CO \rightleftarrows [(TPP)Co(CO)]^+ + e^-$
$[(TPP)Co(CO)]^+ \rightleftarrows [(TPP)Co]^{2+} + CO + e^-$
$[(TPP)Co]^{2+} \rightleftarrows [(TPP)Co]^{3+} + e^-$

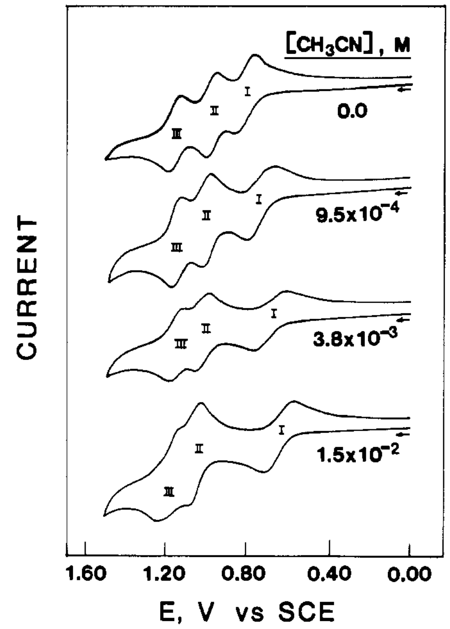

Figure 5. Cyclic voltammograms for the oxidation of (TPP)Co in CH_2Cl_2 containing 0.1 M TBAP and different CH_3CN concentrations. Scan rate = 0.1 V/s.

ditions[1] and are almost identical with the spectra shown in Figure 4 for the conversion of (TPP)Co to $[(TPP)Co(CO)]^+$ in CH_2Cl_2 under a CO atmosphere. The similarity of the final spectrum to those of $[(TPP)Co^{III}(Me_2SO)_2]^+$ or $[(TPP)Co^{III}(py)_2]^+$ (see Table II) might suggest that $[(TPP)Co(CO)]^+$ exists as a genuine Co(III) species under our experimental conditions.

Oxidation Mechanism. The electrochemical and spectra data are self-consistent with the overall sequence of oxidation steps given in Table III. Four different reaction sequences are observed under different solution conditions, but in each case, (TPP)Co is oxidized by an overall three-electron transfer to give $[(TPP)Co^{III}]^{3+}$ as a final product. Thus, the same initial Co(II) and final Co(III) products are observed, but the overall sequence of steps varies significantly. In cases I and IV, the oxidations involve three one-electron-transfer steps that are well-separated in potential while in cases II and III the reactions involve a global two-electron oxidation for the first and the last process, respectively.

Electrooxidation of (TPP)Co in Methylene Chloride Containing CH_3CN. The reactions between CH_3CN and cobalt porphyrins have been compared to similar reactions between CO and cobalt porphyrins,[15,18,19] and the electrochemistry of (TPP)Co in CH_2Cl_2 containing CH_3CN was therefore carried out in the present study. A good comparison between CO and CH_3CN as an axial ligand should be obtained at low concentrations of CH_3CN in CH_2Cl_2 and not at higher concentrations of CH_3CN where properties of the mixed-solvent system are substantially different from those of the nonbonding, low dielectric constant solvent, CH_2Cl_2.

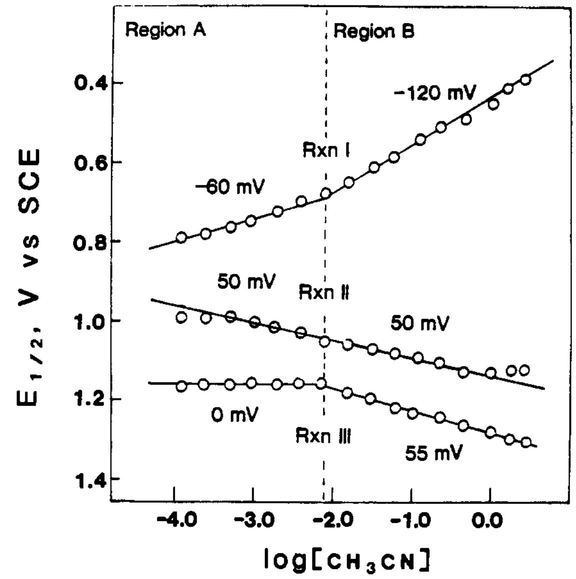

Figure 6. Dependence of $E_{1/2}$ on CH_3CN concentration for the three oxidations of (TPP)Co in CH_2Cl_2, 0.1 M TBAP. Reactions I, II, and III are indicated in Figure 5.

Table IV. Formation Constants for the Binding of $[(TPP)Co]^+$ with Neutral Ligands in CH_2Cl_2, 0.1 M TBAP

	ligand				
	CO	CH_3CN	DMF	Me_2SO	py
log K_1	4.3[a]	4.4[a]			
log β_2		6.6[a]	5.7[b]	9.2[b]	15.6[b]

[a] This work. [b] Reference 33.

Figure 5 shows voltammograms of (TPP)Co in CH_2Cl_2 containing different concentrations of CH_3CN, while Figure 6 gives a plot of $E_{1/2}$ for each (TPP)Co electrooxidation as a function of the CH_3CN concentration. The dependence of $E_{1/2}$ on CH_3CN concentration (Figure 6) can be divided into two distinct regions. Region A encompasses the range of concentrations where $[CH_3CN]$ is less than 10^{-2} M and gives data that is both quantitatively and qualitatively similar to that observed for the oxidation of (TPP)Co in CH_2Cl_2 under a CO atmosphere. In this region, the $E_{1/2}$ for oxidation process I shifts by −60 mV per 10-fold increase of $[CH_3CN]$ while process II shifts by 50 mV and process III remains invarient. All of these data are consistent with the binding of one CH_3CN molecule to the singly oxidized cobalt complex and the overall sequence of steps given in Scheme I.

Scheme I

$$(TPP)Co + CH_3CN \rightleftarrows [(TPP)Co^{III}(CH_3CN)]^+ + e^-$$

$$[(TPP)Co^{III}(CH_3CN)]^+ \rightleftarrows [(TPP)Co^{III}]^{2+} + CH_3CN + e^-$$

$$[(TPP)Co^{III}]^{2+} \rightleftarrows [(TPP)Co^{III}]^{3+} + e^-$$

The formation constant for the binding of CH_3CN to $[(TPP)Co]^+$ was calculated as log K_1 = 4.4 by using the data in Figure 6. This formation constant is given in Table IV and is comparable with the binding constant of log K_1 = 4.3 for CO with $[(TPP)Co]^+$ in CH_2Cl_2.

The data in region A of Figure 6 are qualitatively and quantitatively similar to the data in Figure 3 and indicate that an overlapping of reactions II and III would result at ~1.0 M CH_3CN if no changes in oxidation mechanism were to result. However, this is not the case, and a mechanism change does occur as the bulk solution properties change from those of pure CH_2Cl_2 to those of a CH_2Cl_2/CH_3CN mixture. Shifts in $E_{1/2}$ as a function of log $[CH_3CN]$ under these latter solution conditions are illustrated in region B of Figure 6.

$[(TPP)Co^{III}(CH_3CN)_2]^+$ is formed as a final electrooxidation product in CH_2Cl_2 solutions containing greater than 10^{-2} M CH_3CN. This leads to a change in the $E_{1/2}$ vs log $[CH_3CN]$ slope

(Figure 6, region B) and data that are consistent with the sequence of electron-transfer steps shown in Scheme II.

Scheme II

$$(TPP)Co + 2CH_3CN \rightleftarrows [(TPP)Co^{III}(CH_3CN)_2]^+ + e^-$$

$$[(TPP)Co^{III}(CH_3CN)_2]^+ \rightleftarrows [(TPP)Co^{III}(CH_3CN)]^{2+} + CH_3CN + e^-$$

$$[(TPP)Co^{III}(CH_3CN)]^{2+} \rightleftarrows [(TPP)Co^{III}]^{3+} + CH_3CN + e^-$$

The experimental slopes of $E_{1/2}$ vs log [CH_3CN] for reactions 1-3 are −120, 50, and 55 mV, and these values compare favorably with theoretical slopes of −118, 59, and 59 mV for the sequence of steps shown in Scheme II.

Formation constants of log β_2 = 6.6 and log K_1 = 2.1 were calculated for the binding of two CH_3CN ligands to [(TPP)Co]$^+$ and one CH_3CN ligand to [(TPP)Co^{III}]$^{2+}$. This latter reaction is given by eq 5 and is the first formation constant ever measured

$$[(TPP)Co^{III}]^{2+} + CH_3CN \overset{K_1}{\rightleftarrows} [(TPP)Co^{III}(CH_3CN)]^{2+} \quad (5)$$

for axial ligand binding to the doubly oxidized [(TPP)Co^{III}]$^{2+}$. The log β_2 value of 6.6 for CH_3CN binding to [(TPP)Co]$^+$ compares to values of log β_2 between 5.7 and 15.6 for the binding of other neutral ligands to the singly oxidized complex.[33]

The oxidative chemistry of (TPP)Co in the presence of high and low concentrations of CH_3CN was also monitored by thin-layer UV-visible spectroscopy. In CH_2Cl_2 containing less than 10^{-2} M CH_3CN, the oxidized compound is characterized by a Soret band at 432 nm, a major visible band at 545 nm, and a shoulder at 582 nm. This spectrum is similar to the spectrum of [(TPP)Co(CO)]$^+$ under 1 atm of CO, which has a Soret band at 431 nm, a major visible band at 545 nm, and a shoulder at 582 nm (see Table II). The spectrum of the singly oxidized species under these solution conditions is attributed to five-coordinate [(TPP)Co^{III}(CH_3CN)]$^+$.

Different spectra are obtained for electrooxidized (TPP)Co in CH_2Cl_2 containing [CH_3CN] greater than 10^{-2} M. Under these conditions, the UV-visible bands are located at 435, 549, and 585 nm. This 3-4-nm red shift gives a spectral pattern similar to that of [(TPP)Co^{III}(L)$_2$]$^+$ where L = Me_2SO or py, and the spectrum in CH_2Cl_2/CH_3CN mixtures is assigned to the six-coordinate [(TPP)Co^{III}(CH_3CN)$_2$]$^+$.

Conclusion

The combination of cyclic voltammetry with thin-layer UV-visible spectral data of (TPP)Co in methylene chloride and benzene clearly indicates a binding of one CO molecule to the singly oxidized [(TPP)Co]$^+$. This is the first evidence of CO binding to an oxidized cobalt porphyrin under any solution conditions. This bound CO is lost upon further electrooxidation to generate the porphyrin π cation radical. A similar set of rections occur between CH_3CN and electrooxidized [(TPP)Co]$^+$ at low acetonitrile concentrations, and this contrasts with results at high CH_3CN concentrations where the formation of [(TPP)Co^{III}(CH_3CN)$_2$]$^+$ is observed.

Acknowledgment. The support of the National Science Foundation (Grant CHE-8515411) and the National Institutes of Health (Grant GM25172) is gratefully acknowledged.

Registry No. [(TPP)Co], 14172-90-8; [(TPP)Co]$^{2+}$, 28132-69-6; [(TPP)Co]$^{3+}$, 60430-19-5; [(TPP)Co(CO)]$^+$, 122189-71-3; [(TPP)Co(CH_3CN)$_2$]$^+$, 122189-73-5; [(TPP)Co(CH_3CN)]$^+$, 122189-72-4; CO, 630-08-0; CH_3CN, 75-05-8; CH_2Cl_2, 75-09-2; benzene, 71-43-2.

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Fluoride-Assisted Stabilization of Manganese(III) in Aqueous Medium. A General Approach to the Synthesis of Mixed-Ligand Fluoro Complexes of Manganese(III)

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Received October 7, 1988

The importance of fluoride as a stabilizing ligand for manganese(III), both in aqueous solution as well as in solid complexes, has been emphasized, and a host of new mixed-ligand fluoro complexes have been synthesized from aqueous solutions. While $K_3[MnF_2(C_2O_4)_2]\cdot 3H_2O$ has been synthesized from a redox reaction of $KMnO_4$ with $H_2C_2O_4\cdot 2H_2O$ in the presence of KF at ca. 0 °C, the other mixed-ligand fluoromanganates(III), with EDTA, HPO_4^{2-}, and glycine (glyH) being the coligands, have been synthesized from the reactions of MnO(OH) in 48% HF with the corresponding ligands in water in the presence of alkali-metal fluoride (for EDTA and HPO_4^{2-}) and alkali-metal carbonate (for glyH). Three molecular complexes, $[MnF_3(H_2O)(phen)]\cdot 2H_2O$, $[MnF_3(H_2O)(bpy)]\cdot 2H_2O$, and $[MnF_3(urea)_2]\cdot 3H_2O$ have been prepared also from the reactions of MnO(OH) in 40% HF with the respective ligand solutions. All the compounds, except $K_3[MnF_2(C_2O_4)_2]\cdot 3H_2O$, are stable in the absence of moisture. Their characterization and structural assessment are based on the results of elemental analyzes, chemical determination of oxidation state, IR and electronic spectroscopic studies, magnetic susceptibility measurements, and in a few cases pyrolysis studies. Whereas the room-temperature magnetic moment of $[MnF_3(urea)_2]\cdot 3H_2O$ is 4.3 μ_B, those of the others lie in the range 4.78-5.0 μ_B. A magnetostructural correlationship has been explored by comparing the present empirical magnetic moments with those of the binary fluoromanganates(III). Pyrolysis of $[MnF_3(urea)_2]\cdot 3H_2O$ at ca. 500 °C affords MnF_3, a compound of acknowledged importance.

Introduction

Manganese can adopt a wide spectrum of oxidation states, and this ability is reflected in its redox functions in biological systems.[1] The tripositive state of the metal is important in this context and requires a special attention not only because it is difficult to stabilize in aqueous medium[2] and many of its complexes demonstrate unusual magnetic and structural features[3-7] but also because it has biochemical relevance in diverse redox functions, including water splitting by photosynthetic enzymes,[8] dispro-

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