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Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77204-5641

Electrochemistry of Five- and Six-Coordinate σ-Bonded Cobalt Porphyrins. Reactions of $(TPP)Co(C_2H_5)(py)$ and (TPP)Co(R) Where TPP Is the Dianion of Tetraphenylporphyrin and R = CH_3, C_2H_5, or CH_2Cl

K. M. Kadish,* B. C. Han, and A. Endo

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The electrochemistry of five- and six-coordinate cobalt(III) σ-bonded porphyrins is reported in pyridine, tetrahydrofuran, and methylene chloride containing 0.1 M tetrabutylammonium perchlorate or 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The investigated compounds are represented as $(TPP)Co(C_2H_5)(py)$ and (TPP)Co(R) where TPP is the dianion of tetraphenylporphyrin and R = CH_3, C_2H_5, or CH_2Cl. Each complex undergoes up to two reductions and two oxidations, all of which occur at the porphyrin π ring system. The electrochemical data for $(TPP)Co(CH_3)$ are compared to data for $(TPP)M(CH_3)$ where M = Rh, Al, Ga, In, or Tl and clearly indicate the absence of a metal-centered reduction for the Co(III) complex in nonaqueous media. The formation constant for conversion of $(TPP)Co(C_2H_5)$ to $(TPP)Co(C_2H_5)(py)$ was calculated as $K = 8.9$ in CH_2Cl_2, and the electrochemistry of $(TPP)Co(C_2H_5)(py)$ was also investigated in pyridine. The oxidation of this six-coordinate species involves an overall two-electron transfer at the same potential and leads to $[(TPP)Co(py)_2]^+$ and $[C_5H_5N(C_2H_5)]^+$, the latter of which was electrochemically identified by comparison to a sample of $C_5H_5N(C_2H_5)Br$ which was investigated under the same solution conditions.

Introduction

Numerous reports of σ-bonded cobalt porphyrins have appeared in the literature,[1-15] but only limited data are available on the electrochemistry of these types of complexes. It is known that a chemical[6] or electrochemical[10,12] oxidation of (P)Co(R) (where P is the dianion of a given porphyrin ring and R is a σ-bonded alkyl or aryl group) will lead to migration of the R group from the cobalt central metal to one of the four nitrogen atoms of the porphyrin ring to give the N-substituted $[N\text{-}RPCo^{II}]^+$ species. It is also known that a reduction of (P)Co(R) leads to formation of $[(P)Co]^-$ or $[(P)Co(R)]^-$, depending upon the solvent, the time scale of the measurement, and/or the specific σ-bonded axial ligand.[11-14] However, neither the initial site of electron transfer nor the overall mechanism for reduction or oxidation of (P)Co(R) has been investigated in any detail. This is done in the present paper, which characterizes the electrode reactions of $(TPP)Co(C_2H_5)(py)$ and (TPP)Co(R) where R = CH_3, C_2H_5, or CH_2Cl.

Experimental Section

Chemicals. (TPP)Co(R) (R = CH_3, C_2H_5, CH_2Cl) were synthesized according to literature methods.[1,10,11] The resulting compounds are light sensitive, and all experiments were carried out in the dark. Spectroscopic grade THF was purchased from Aldrich Chemical Co. and purified by distillation, first from CaH_2 and then from sodium/benzophenone just prior to use. Spectroscopic grade methylene chloride (CH_2Cl_2) and pyridine (py) were distilled over CaH_2 under a N_2 atmosphere prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) and tetra-*n*-butylammonium hexafluorophosphate ($(TBA)PF_6$, Fluka Chemical Co.) were twice recrystallized from absolute ethanol and dried in the oven at 40 °C. 1-Ethylpyridinium bromide, $[C_5H_5NC_2H_5]Br$, was purchased from Eastman Kodak Co. and used directly without further purification.

Instrumentation. An IBM EC 225 voltmmetric analyzer was used for cyclic voltammetric measurements. The electrochemical cell consisted of a platinum-button working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode (SCE). The bulk electrolysis cell was modified for Schlenk techniques and consisted of platinum-gauze working and counter electrodes. A platinum-tipped glass frit was used to separate the two compartments for vacuum operation. ESR spectra were taken with an IBM Model 100D ESR spectrometer equipped with an ER 040-X microwave bridge and an ER 080 power supply. For low-temperature measurements, the cavity was cooled by a steam of liquid nitrogen that was constantly passed through a variable-temperature insert. The *g* values were measured relative to diphenylpicrylhydrazyl (DPPH; $g = 2.0037 \pm 0.0002$). UV–visible spectra were measured with an IBM 9430 spectrophotometer using matched 1.0-cm quartz cells.

Table I. Half-Wave Potentials (V, vs SCE) for the Room-Temperature Oxidation and Reduction of (TPP)Co(R) in CH_2Cl_2 or THF Containing 0.2 M TBAP

		oxidn		redn	
R	solvent	1st	2nd	1st	2nd
CH_3	CH_2Cl_2	0.96	1.19	−1.38	
	THF	1.04		−1.39	−1.86
C_2H_5	CH_2Cl_2	0.98[a]	1.23[a]	−1.40[a]	−1.88[a]
CH_2Cl	CH_2Cl_2	0.96	1.17	−1.37[b]	
	THF	1.05		−1.42[b]	

[a] Measured at a microelectrode with a scan rate of 10 V/s. [b] Peak potential measured at a scan rate of 0.1 V/s.

Results

Electrochemistry of (TPP)Co(R) Where R = CH_3, CH_2Cl, or C_2H_5. Cyclic voltammograms illustrating the oxidation and reduction of $(TPP)Co(CH_3)$ and $(TPP)Co(CH_2Cl)$ in CH_2Cl_2, 0.1 M TBAP are shown in Figure 1. Each compound undergoes two reversible one-electron oxidations and a single one-electron or multielectron reduction within the potential range of the solvent. The reduction of $(TPP)Co(CH_3)$ is reversible at all temperatures; this contrasts with $(TPP)Co(CH_2Cl)$ or $(TPP)Co(C_2H_5)$, both of which are irreversibly reduced in CH_2Cl_2 at room temperature but reversibly reduced either at low temperature (see Figure 1b) or at room temperature under conditions of rapid potential sweep rate. The potentials for each electrode reaction of these three compounds are listed in Table I.

The singly reduced $(TPP)Co(CH_2Cl)$ and $(TPP)Co(C_2H_5)$ complexes are unstable in THF, but this is not the case for $(TPP)Co(CH_3)$, which undergoes two well-defined one-electron-transfer reactions in this solvent. The half-wave potentials of −1.39 and −1.86 V are slightly positive of those for reduction of $(TPP)Rh(CH_3)$ under the same experimental conditions ($E_{1/2}$ = −1.45 and −1.90 V),[16] and the cyclic voltammograms of these

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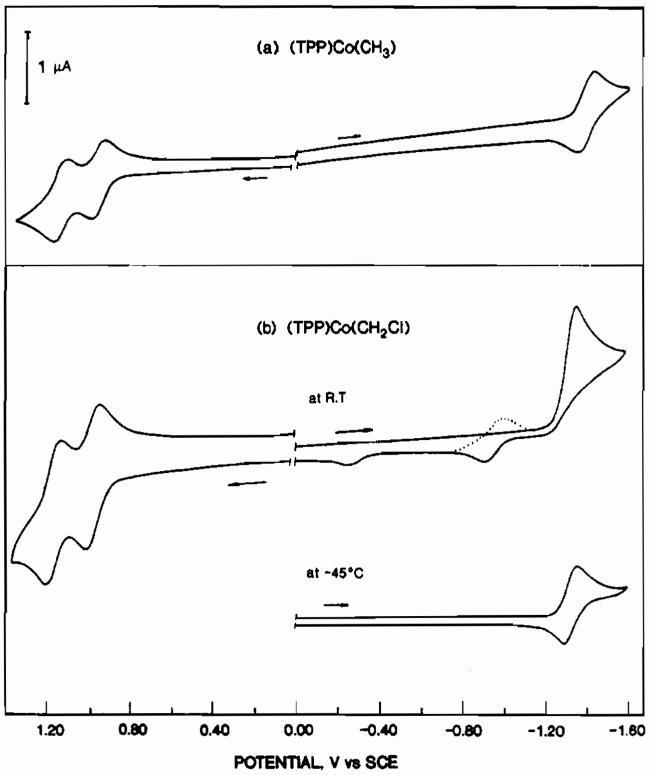

Figure 1. Cyclic voltammograms of (a) (TPP)Co(CH$_3$) and (b) (TPP)Co(CH$_2$Cl) in CH$_2$Cl$_2$ containing 0.1 M TBAP. Scan rate = 0.1 V/s.

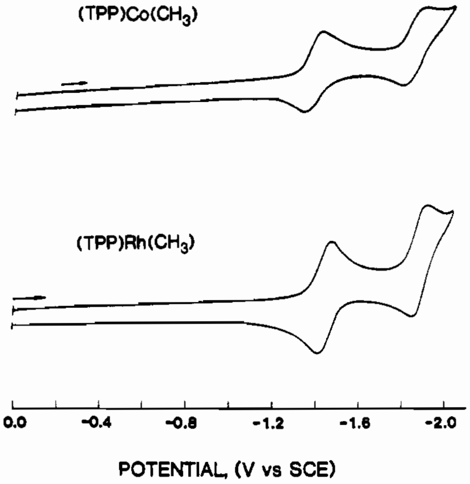

Figure 2. Cyclic voltammograms illustrating the reduction of (TPP)Co(CH$_3$) and (TPP)Rh(CH$_3$) in THF, 0.1 M TBAP. Scan rate = 0.1 V/s.

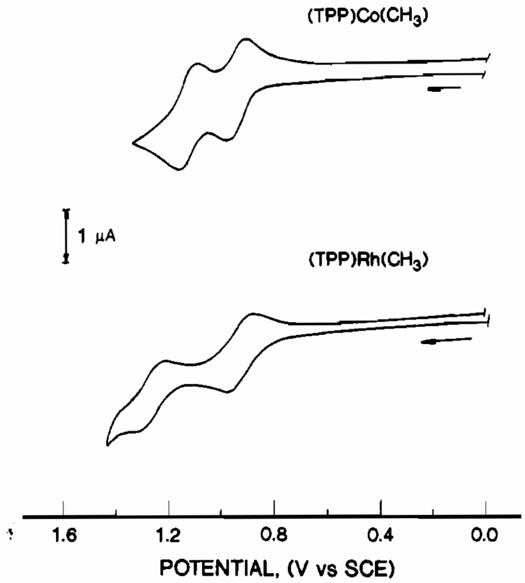

Figure 3. Cyclic voltammograms illustrating the oxidation of (TPP)Co(CH$_3$) and (TPP)Rh(CH$_3$) in CH$_2$Cl$_2$, 0.1 M TBAP. Scan rate = 0.1 V/s.

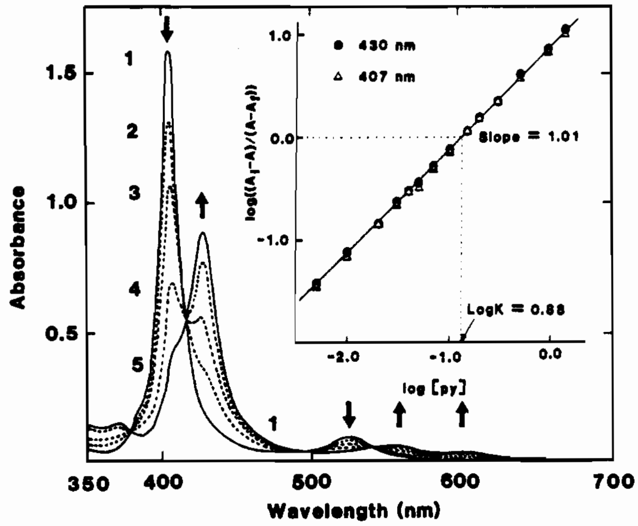

Figure 4. UV-visible spectra taken during a titration of 5 × 10^{-6} M (TPP)Co(C$_2$H$_5$) in CH$_2$Cl$_2$, 0.1 M (TBA)PF$_6$ by pyridine and analysis of the spectral data at 407 and 430 nm. The [py]/[porphyrin] ratios in the figure are as follows: (1) 0; (2) 4 × 10^3; (3) 2 × 10^4; (4) 4 × 10^4; (5) 1.8 × 10^5.

compounds are almost superimposable, as shown in Figure 2.

The conversion of [(TPP)Co(C$_2$H$_5$)]$^+$ to [(N-C$_2$H$_5$TPP)Co^{II}]$^+$ has been well characterized in CH$_2$Cl$_2$,[10] but this reaction is not observed by cyclic voltammetry when (TPP)Co(C$_2$H$_5$) is oxidized at a microelectrode using rapid potential scan rates. Under these conditions, reversible one-electron transfers are obtained at $E_{1/2}$ = 0.98 and 1.23 V. Electrooxidized (TPP)Co(CH$_3$) and (TPP)Co(CH$_2$Cl) are relatively stable in CH$_2$Cl$_2$ on the conventional cyclic voltammetry time scale, and both neutral derivatives are characterized by two well-defined one-electron oxidations at almost identical potentials of $E_{1/2}$ = 0.96 and 1.19 V. The first is within experimental error of $E_{1/2}$ for oxidation of (TPP)Rh(CH$_3$). However, the second oxidation of (TPP)Co(CH$_3$) is shifted negatively by 80 mV with respect to the same reaction of (TPP)Rh(CH$_3$) ($E_{1/2}$ = 1.27 V); this is shown in Figure 3 for the two σ-bonded CH$_3$ complexes in CH$_2$Cl$_2$.

Spectral Characterization of (TPP)Co(C$_2$H$_5$)(py) in CH$_2$Cl$_2$/py Mixtures. The five-coordinate (TPP)Co(C$_2$H$_5$) complex in CH$_2$Cl$_2$ has major bands located at 407 and 524 nm. Both bands decrease in intensity upon addition of pyridine to solution, and at the same time, new peaks appear at 430, 551, and 616 nm. The diagnostic plot of log [(A_i − A)/(A − A_f)] vs log [py] is linear (see Figure 4) and has a slope of 1.01, indicating a binding of one pyridine molecule as shown in eq 1. The formation constant for this reaction is 8.9.

$$\text{(TPP)Co(C}_2\text{H}_5\text{)} + \text{py} \rightleftarrows \text{(TPP)Co(C}_2\text{H}_5\text{)(py)} \qquad (1)$$

Electrochemistry of (TPP)Co(C$_2$H$_5$)(py) in Pyridine. Single-sweep cyclic voltammograms for the oxidation and reduction of (TPP)Co(C$_2$H$_5$)(py) in pyridine containing 0.1 M (TBA)PF$_6$ are illustrated in Figure 5. The compound at room temperature undergoes one irreversible oxidation at E_p = 0.81 V (reaction III) and one irreversible reduction at E_p = −1.49 V (reaction I) for a scan rate of 0.1 V/s. The first reduction is reversible at −40 °C, and under these conditions, a second reversible one-electron reduction is observed at $E_{1/2}$ = −1.86 V (reaction II). The single

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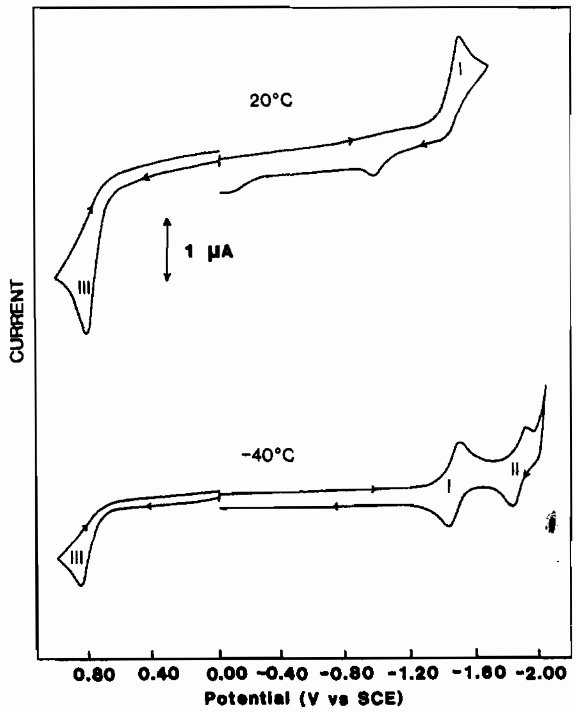


Figure 5. Cyclic voltammograms illustrating the oxidation and reduction of (TPP)Co(C_2H_5)(py) in pyridine containing 0.1 M (TBA)PF_6. Scan rate = 0.1 V/s.

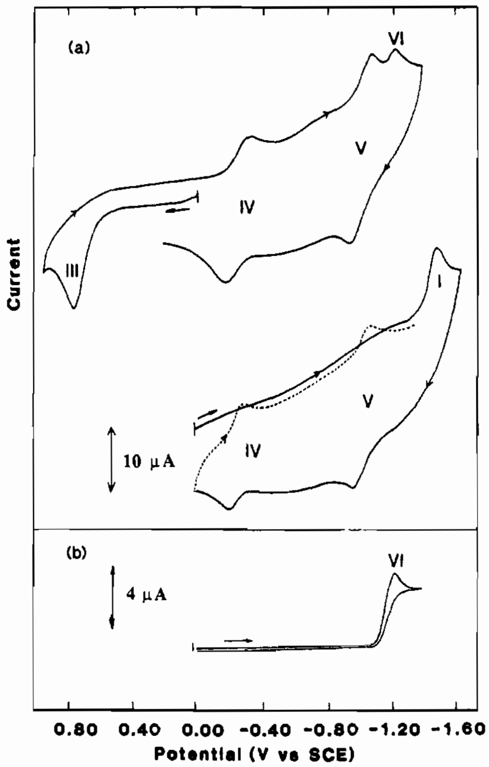


Figure 6. Thin-layer cyclic voltammograms of (a) (TPP)Co(C_2H_5)(py) and (b) [$C_5H_5N(C_2H_5)$]Br in pyridine containing 0.1 M (TBA)PF_6. Scan rate = 2 mV/s.

oxidation of (TPP)Co(C_2H_5)(py) remains irreversible in pyridine at -40 °C.

Thin-layer cyclic voltammograms of (TPP)Co(C_2H_5)(py) in pyridine containing 0.1 M (TBA)PF_6 are shown in Figure 6a. An oxidation of the initial Co(III) complex (reaction III) leads to new reduction peaks at $E_{1/2} = -0.25$ V (reaction IV), $E_{1/2} = -1.01$ V (reaction V), and $E_p = -1.21$ V (reaction VI) for a scan rate of 2 mV/s. The first two reductions are also observed on repetitive sweeps following an initial reduction of (TPP)Co(C_2H_5)(py), but the third process (reaction VI) does not appear under these conditions and is only observed after oxidation of (TPP)Co(C_2H_5)(py). This latter peak has an E_p which is identical with one obtained for the irreversible reduction of [$C_5H_5N(C_2H_5)$]Br in pyridine (see Figure 6b).

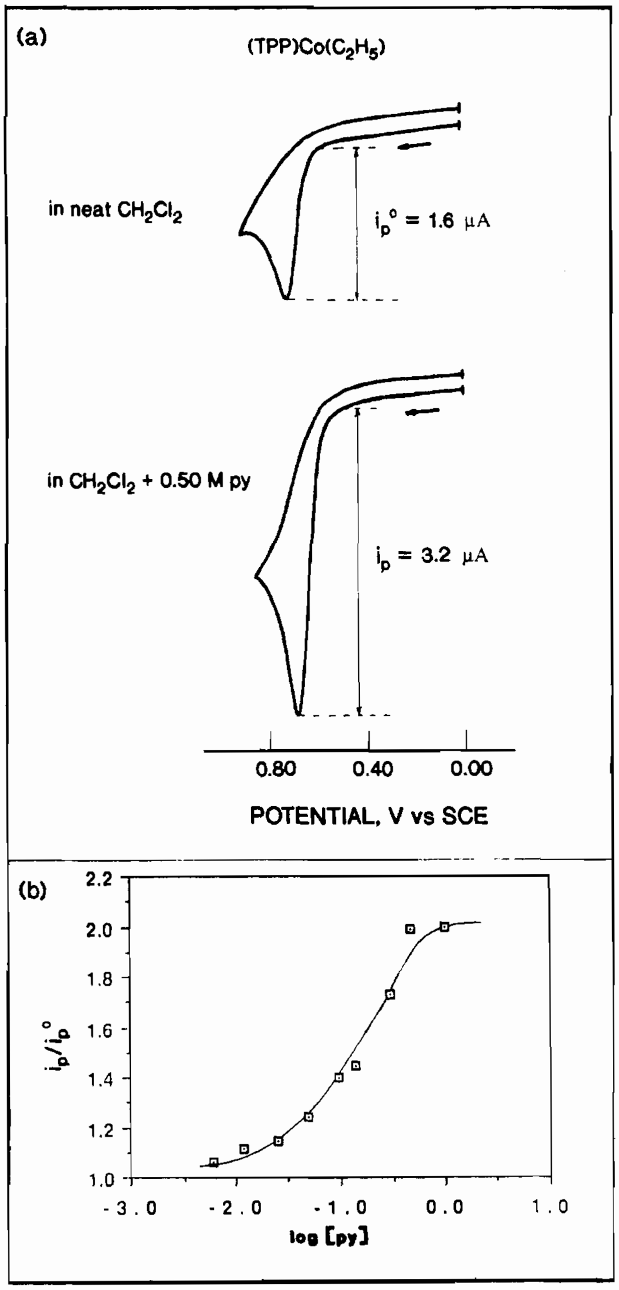


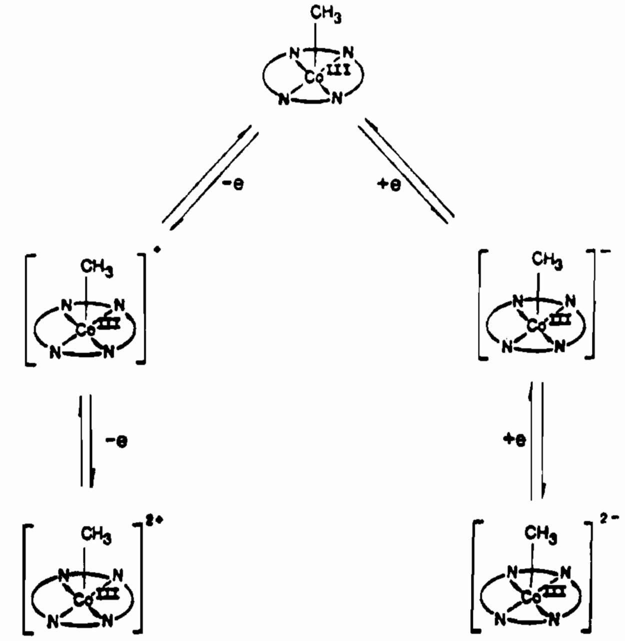
Figure 7. (a) Cyclic voltammograms for the oxidation of (TPP)Co(C_2H_5) in CH_2Cl_2 and CH_2Cl_2 containing 0.5 M py and 0.1 M (TBA)PF_6. (b) Ratio of i_p/i_p^0 vs log [py] where i_p^0 is the oxidation peak current in CH_2Cl_2 containing 0.1 M (TBA)PF_6 and i_p is the value in the mixed CH_2Cl_2/py solvent.

The maximum peak current for the irreversible oxidation of (TPP)Co(C_2H_5) doubles upon going from neat CH_2Cl_2 to neat pyridine as a solvent, and the ratio of these two currents varies between a value of 1.0 and 2.0 as a function of pyridine concentration in mixed CH_2Cl_2/py solutions. This is shown in Figure 7, which also correlates the ratio of i_p/i_p^0 (where i_p^0 is the peak current in CH_2Cl_2) with the py concentration in a CH_2Cl_2/py mixture.

Discussion

Reversible Electrode Reactions of (TPP)Co(R). The room-temperature reduction of (TPP)Co(R) complexes with σ-bonded aryl groups is irreversible in DMSO containing 0.1 M TBAP and

Scheme I



has been associated with an overall conversion of (TPP)Co(R) to $[(TPP)Co^I]^-$ as shown in eq 2.[13]

$$(TPP)Co(R) + 2e^- \rightarrow [(TPP)Co^I]^- + \text{products} \qquad (2)$$

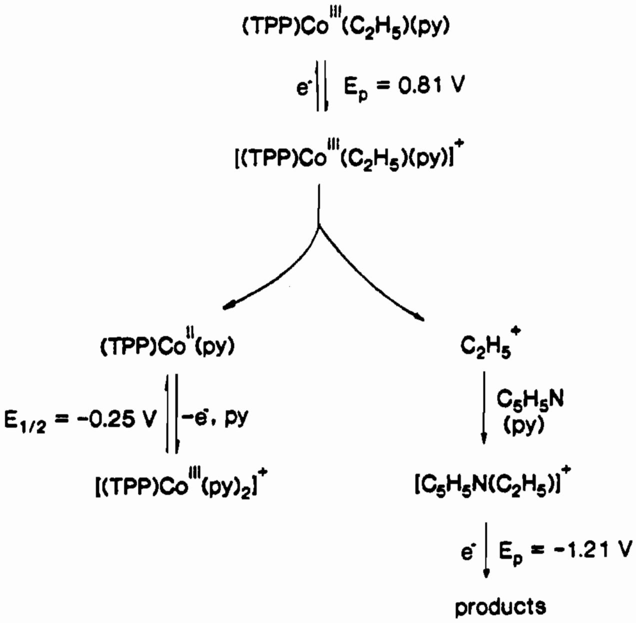
The above reaction occurs at potentials of −1.30 to −1.33 V vs SCE and a similar $E_p = -1.37$ V was obtained in this study for the irreversible reduction of $(TPP)Co(CH_2Cl)$ in CH_2Cl_2 (see Figure 1). The peak current for reduction of $(TPP)Co(CH_2Cl)$ in CH_2Cl_2 is about double that for oxidation of the same compound, and a new reversible process appears at $E_{1/2} = -0.93$ V after the initial electroreduction (see Figure 1b). This process is not present on the first negative potential scan and is associated with the Co(II)/Co(I) couple of neutral and reduced (TPP)Co, which is formed after loss of the σ-bonded axial ligand.

The first reduction of $(TPP)Co(C_2H_5)$ is also irreversible in CH_2Cl_2; this agrees with data in the literature for the first reduction of several alkylcobalt porphyrins in DMSO.[13] In contrast, $(TPP)Co(CH_3)$ is reversibly reduced in CH_2Cl_2, and the voltammogram under these conditions is shown in Figure 1a.

It has been suggested[13,14] that (TPP)Co(R) is initially reduced at the Co(III) center, but the data in Figures 1 and 2 suggest formation of only porphyrin π anion radicals and dianions. The absolute difference in $E_{1/2}$ between the two reductions of $(TPP)Co(CH_3)$ in THF is 470 mV (see Table I and Figure 1), which compares with a 440-mV separation between the two ring-centered reductions of $(TPP)Rh(CH_3)$ under the same solution conditions.[3] Both values are comparable with separations of 380–450 mV between the two ring-centered reductions of main-group methyl σ-bonded tetraphenylporphyrin complexes such as $(TPP)M(CH_3)$[19] where M = Al, In, Ga, or Tl. This fact, along with the virtually identical current–voltage curves for reduction of (TPP)Co(R) and (TPP)Rh(R) where R = CH_3, C_2H_5, or CH_2Cl, gives further proof that only ring-centered reductions are observed for σ-bonded Co(III) porphyrins in nonaqueous media.

The absolute potential difference between $E_{1/2}$ for the first oxidation and the first reduction of (TPP)Co(R) also indicates formation of porphyrin π anion and π cation radicals. The separation between the HOMO and LUMO of $(TPP)Co(CH_3)$ is 2.34 V in CH_2Cl_2 (see Table I) and compares with a separation of 2.38 V for $(TPP)Co(C_2H_5)$ under the same conditions. Both values of $\Delta E_{1/2}$ are within the $\Delta E_{1/2} = 2.25 \pm 0.15$ V, which is generally observed for electrochemical generation of porphyrin π cation and π anion radicals of TPP complexes.[15] In addition, $\Delta E_{1/2}$ between the two successive one-electron oxidations of (TPP)Co(R) is 0.21 V for R = CH_2Cl, 0.23 V for R = CH_3, and 0.25 V for R = C_2H_5, all of which suggest the stepwise formation of π cation radicals and dications. Thus, the voltammetric data are all self-consistent and indicate that the (TPP)Co(R) electrode reactions involve only the porphyrin π ring system, as shown in Scheme I for the case of $(TPP)Co(CH_3)$.

Scheme II



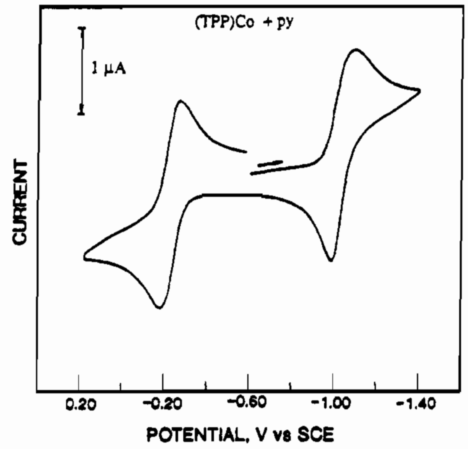


Figure 8. Cyclic voltammogram of (TPP)Co in pyridine containing 0.1 M $(TBA)PF_6$ at a scan rate of 0.10 V/s.

Irreversible Oxidation of $(TPP)Co(C_2H_5)(py)$. The data in Figure 7 are consistent with an overall two-electron oxidation of $(TPP)Co^{III}(C_2H_5)(py)$ to give $[(TPP)Co^{III}(py)_2]^+$ and $[C_5H_5N(C_2H_5)]^+$ as final products in pyridine. The proposed mechanism for this reaction is shown in Scheme II and was ascertained by the following observations: (i) the ratio of the first oxidation peak current to the first reduction peak current, $i_p(ox)/i_p(red)$, in pyridine is equal to 1.70 at a scan rate of 50 mV/s; (ii) when a CH_2Cl_2 solution of $(TPP)Co(C_2H_5)$ is titrated with pyridine, the ratio of oxidation peak current in pyridine/CH_2Cl_2 mixtures to that in neat CH_2Cl_2, i_p/i_p^0, approaches 2.0 as shown in Figure 7. These data clearly indicate the occurrence of a one-electron oxidation in CH_2Cl_2 and an overall two-electron oxidation in pyridine or CH_2Cl_2/pyridine mixtures.

The cyclic voltammograms in Figures 6 and 7 are consistent with an electrochemical ECE type mechanism and with a rapid loss of C_2H_5 following the first or second one-electron oxidation of $(TPP)Co(C_2H_5)(py)$ in pyridine. The formation of $[C_5H_5N(C_2H_5)]^+$ as one of the final electrooxidation products is suggested

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by data for the reduction of $[C_5H_5N(C_2H_5)]Br$ in pyridine containing 0.1 M $(TBA)PF_6$ (Figure 6b). This compound has a single irreversible reduction process at $E_p = -1.20$ V and may be compared to a similar irreversible peak which is located at $E_p = -1.21$ V after the overall two-electron oxidation of $(TPP)Co(C_2H_5)(py)$.

The formation of $[(TPP)Co(py)_2]^+$ as a porphyrin product after oxidation of $(TPP)Co(C_2H_5)(py)$ in pyridine follows from analysis of current-voltage curves for the reduction and oxidation of $[(TPP)Co(py)_2]^+$ under similar experimental conditions. A cyclic voltammogram of (TPP)Co in pyridine is shown in Figure 8 and has reversible peaks located at $E_{1/2} = -0.25$ and -1.01 V. These potentials are similar to the $E_{1/2}$ values of peaks IV and V in Figure 6 and are thus also consistent with the proposed oxidation/reduction mechanism shown in Scheme II.

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Registry No. TBAP, 1923-70-2; $(TBA)PF_6$, 3109-63-5; THF, 109-99-9; CH_2Cl_2, 75-09-2; $[C_5H_5N(C_2H_5)]^+$, 15302-96-2; $[(TPP)(CH_3)Co^{III}]$, 29130-60-7; $[(TPP)(C_2H_5)Co^{III}]$, 61730-43-6; $[(TPP)(CH_2Cl)Co^{III}]$, 65856-25-9; $[(TPP)(CH_3)Co]^+$, 136599-76-3; $[(TPP)(C_2H_5)Co]^+$, 136599-77-4; $[(TPP)(CH_2Cl)Co]^+$, 136599-78-5; $[(TPP)(CH_3)Co]^{2+}$, 136599-79-6; $[(TPP)(C_2H_5)Co]^{2+}$, 136599-80-9; $[(TPP)(CH_2Cl)Co]^{2+}$, 136599-81-0; $[(TPP)(CH_3)Co]^-$, 109123-06-0; $[(TPP)(C_2H_5)Co]^-$, 119679-61-7; $[(TPP)(CH_2Cl)Co]^-$, 119679-60-6; $[(TPP)(CH_3)Co]^{2-}$, 136599-82-1; $[(TPP)(C_2H_5)Co]^{2-}$, 136599-83-2; $[(TPP)(C_2H_5)(py)Co^{III}]$, 111112-56-2; $[(TPP)(py)_2Co]^+$, 47902-90-9; $[(TPP)Rh(CH_3)]$, 103562-25-0; pyridine, 110-86-1.

Contribution from the Department of Chemistry,
University of Florida, Gainesville, Florida 32611-2046

Oxidation of Alkanes by Cobalt(II) Salts of Weakly Coordinating Anions

Alan S. Goldstein and Russell S. Drago*

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Catalysts which effect the selective oxidation of alkanes under mild reaction conditions are highly desired. Commercial processes exist which involve the oxidation of alkanes by O_2 with cobalt carboxylate catalysts. Elevated temperatures and pressures are required, and the metal ion function is to decompose hydroperoxides formed in a radical-chain process. We have demonstrated that a weakly solvated cobalt-acetonitrile complex, $[Co(NCCH_3)_4](PF_6)_2$, with a weakly coordinating anion catalyzes the air oxidation of alkanes under mild conditions (75 °C and 3 atm). Cyclohexane and adamantane are converted to the corresponding alcohol and ketone products. The commercial catalyst for cyclohexane oxidation does not function under these milder conditions. Experiments indicate a mechanism in which the metal ion functions both as an initiator and as a hydroperoxide decomposition catalyst.

Introduction

Autoxidation reactions tend to oxidize organic substrates via radical-chain processes leading to a nonselective product distribution.[1] However, selective, economically feasible autoxidation processes can be carried out with metal ion catalysts. Currently, cyclohexane is oxidized industrially using air under conditions of 165 °C and 10 atm.[2,3] The major products of this oxidation, cyclohexanol and cyclohexanone, referred to as KA oil, are precursors for the production of adipic acid (a precursor for Nylon 6,6). In view of the current interest in the activation of alkanes, the selective catalytic oxidation of cyclohexane under mild conditions is of fundamental and commercial significance.[4]

In this article we report that the cobalt-acetonitrile complex $[Co(NCCH_3)_4](PF_6)_2$ (in acetonitrile) is capable of catalyzing the oxidation of alkanes under mild conditions using O_2 as the primary oxidant. Under our reaction conditions (75 °C, 3 atm of air) cyclohexane is oxidized to a $\sim$3:2 ratio of cyclohexanol and cyclohexanone. The catalyst used in the commercial process[5] for the oxidation of cyclohexane, $Co(oct)_2$ (oct = 2-ethylhexyl octanoate), is unreactive under our reaction conditions. We report experiments to determine if this novel reactivity involves a catalyst that is more effective at peroxide decomposition than the commercial catalyst (initiating the chain reaction at lower hydroperoxide thresholds) or if a high oxidation state form of the metal complex reacts with the substrate to initiate the reaction.

Experimental Section

Materials. Adamantane (Aldrich), silver hexafluorophosphate (Aldrich), anhydrous cobalt(II) chloride (Alfa), cyclopentanone (Aldrich), benzene (Fisher), and ceric ammonium nitrate (Fisher) were used as received. Acetonitrile was stored over 4-Å molecular sieves prior to use. Cyclohexane was stored over P_2O_5 prior to use.

Cobalt-Acetonitrile Complex, $[Co(NCCH_3)_4](PF_6)_2$. The catalyst used for the oxidations described herein was prepared "in situ" in acetonitrile. Stoichiometric amounts of anhydrous $CoCl_2$ and $AgPF_6$ were combined in acetonitrile. The precipitated AgCl was filtered off. The resulting solution was tested for Ag^+ and Cl^-, since trace amounts of these ions decrease the activity of the catalyst. Blanks were performed using both AgCl and $AgPF_6$ in the absence of any cobalt. These resulted in no oxidation.

Physical Measurements. The NMR spectra were recorded on a multinuclear Varian VXR 300MHz spectrometer. The UV/vis spectra were obtained using a Perkin-Elmer Lambda 6 spectrometer. The products of the oxidation reactions were analyzed and quantified using a Varian 3300 gas chromatograph equipped with a FID detector and a chromosorb 15% DEGS column (6 ft). Further analysis of the reaction products were performed by GCMS using a Varian 3400 gas chromatograph interfaced with a Finnigan MAT ITDS 700 mass spectrometer. The column employed for this technique was a 15-m dbl column. Electrochemical studies were performed in acetonitrile with a PAR Model 175 universal programmer attached to a Model 173 potentiostat/galvanostat. Solutions of 0.05 M Co^{2+} and 0.1 M in tetrabutylammonium hexafluorophosphate were employed.

Oxidations. Oxidations were carried out in a batch reactor using a 250-mL Parr pressure apparatus as previously described.[6] A standard reaction consisted of the following: catalyst (10^{-5} mol), acetonitrile (10

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(4) Tolman, C.; Druliner, J. D.; Nappa, M. J.; Herron, N. Alkane Oxidation Studies in Du Pont's Central Research Department. In *Activation and Functionalization of Alkanes*; Hill, C., Ed.; John Wiley and Sons: New York, 1989.

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