

(BCHTN)]²⁺ is attributed to both the large steric strains among the three linked chelate rings and the low basicity of the ligand.

It is significant to note that there is a substantial difference in the relative rates of these reactions and that the order of labilities parallels the order of aqueous solution instabilities of these complexes. These data prompt further investigations to see whether

there is a simple quantitative relation between $\log k^{\text{NiL}}$ or $\log k_{\text{H}}^{\text{NiL}}$ and $\log K$. Figures 5 and 6 show such plots.

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Cobalt(I) Porphyrin Catalysis of Hydrogen Production from Water

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Cobalt complexes of three water-soluble porphyrins, *meso*-tetrakis(*N,N,N*-trimethylanilinium-4-yl)porphine chloride (CoTMAP), *meso*-tetrapyrro-4-ylporphine (CoTPyP), and *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphine chloride (CoTMPyP), have been examined as catalysts of H₂O reduction to H₂. They have been shown to catalyze H₂ production via controlled-potential electrolysis (-0.95 V vs. SCE at Hg-pool electrode; 0.1 M trifluoroacetic acid) at rates approximately 10-fold greater than background and with nearly 100% current efficiency. Reversible cyclic voltammograms were observed in dry Me₂SO, with Co(III)/Co(II) and Co(II)/Co(I) potentials near their expected values. Addition of water (0.5-2%) increased the cathodic peak and decreased the anodic peak at the Co(II)/Co(I) couple, consistent with electrocatalytic H₂O reduction. In aqueous buffers, catalytic currents were observed for CoTMPyP, which increased with decreasing pH, but at a rate less than expected, due to porphyrin adsorption. Adsorption was more pronounced for CoTMAP, which showed no catalytic current except at very low pH. The rate of CoTMAP reaction with H₂O, however, is extremely fast as shown by spectrophotometry in dry acetonitrile; a lower limit for the Co(I)-H₂O reaction rate constant was estimated to be approximately 10⁴ M⁻¹ s⁻¹. Co(I) reactivity and cobalt hydride stability are discussed in comparison with the reactivity and stability of related compounds.

Introduction

All schemes for storing energy by the electrochemical or photochemical reduction of water to hydrogen require catalysis of H₂ evolution, since the activation energy for splitting the OH bond and bringing nascent H atoms together is otherwise prohibitive. Platinum metal is an excellent catalyst for this purpose and is very widely used in studies of water splitting. Platinum is costly, however, and also can easily be poisoned by contaminants in the water, such as sulfur-containing molecules. Aside from these practical considerations, it is of interest to develop molecular catalysts for H₂ evolution in order to bring into clearer focus the chemical requirements for this aspect of water splitting. Cobalt(I) complexes are attractive candidates for such catalysts, since Co(I), being a powerful nucleophile, is readily protonated and the resulting cobalt hydride decomposes by proton attack or disproportionation to form H₂ (see Figure 1). This chemistry has been characterized for Co(I) complexes of cyanide,¹⁻⁴ vitamin B₁₂,⁵⁻¹⁰ dimethylglyoxime,¹¹ bipyridyl,^{12,13} and various macrocyclic ligands.¹⁴

In this study, we examined the formation and decomposition of Co(I) porphyrins with a view toward developing an efficient electrocatalyst for H₂ evolution. We have been drawn to metalloporphyrins as agents for electrode modification because of their ease of deposition¹⁵⁻¹⁹ via peripheral substituents and their favorable electron-transfer characteristics. In addition, porphyrins absorb light strongly in the visible region and offer attractive possibilities for photochemistry. In the case of Co(II) porphyrins, excitation into the allowed $\pi-\pi^*$ transitions may be followed by electron transfer to the d_{z²} orbital, leading to transient formation of a Co(I) porphyrin radical cation. Protonation of this species might provide a pathway for photochemical H₂ production. Indeed Tait et al.²⁰ have interpreted the prompt photoinduced difference spectrum of cobalt(II) octaethylporphyrin as belonging to a charge-transfer state, which subsequently relaxes with a lifetime of 10-20 ps. This state is clearly too short-lived to be of any use in photochemistry, but it is conceivable that the lifetime might be increased through modifications of the porphyrin.

Experimental Section

Free-base porphyrins *meso*-tetrakis(*N,N,N*-trimethylanilinium-4-yl)porphine chloride, *meso*-tetrapyrro-4-ylporphine, and *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphine chloride were obtained from Mid-Century Chemicals (Posen, IL). These were subsequently metalated to form the corresponding Co(II) derivatives, CoTMAP, CoTPyP, and CoTMPyP, respectively, according to published protocols²¹⁻²³ with several

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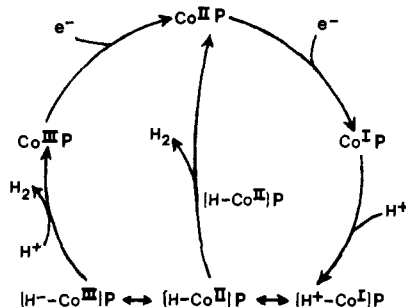


Figure 1. Scheme for cobalt porphyrin catalysis of H_2 production from water.

modifications, as follows. About 100 mg of the free base was dissolved in 25 mL of reagent grade dimethylformamide (DMF). A 20–30-fold molar excess of cobaltous acetate hexahydrate was dissolved with constant stirring in a 100-mL three-neck boiling flask in a minimal quantity of glacial acetic acid at the boiling point, maintained by a hot oil bath. The DMF solution was added dropwise to the heated acid solution with continuous stirring, and the mixture was refluxed under nitrogen atmosphere for 12–36 h. The metalation reactions were monitored by UV/vis spectroscopy of aliquots withdrawn at various intervals and diluted with 0.5 M HCl. The metalation reactions were considered complete when an absorption band near 600 nm, due to the free base, was no longer detectable.

Owing to the particular solubility characteristics of the cobalt porphyrin derivatives, two methods were employed for their purification. Crude CoTPyP was precipitated from the above reaction mixture following the addition of 100 mL of water and adjustment to pH 8–9 with 10 M NaOH. The precipitate was collected by suction filtration, redissolved in a minimal volume of dilute HCl, and reprecipitated with dilute NaOH. This precipitate was repeatedly suspended in water and centrifuged at low speed to remove excess cobalt. The spectrum of the final product was consistent with the observations of Choi et al.²² Crude CoTMAP and crude CoTMPyP were precipitated as the perchlorate salts by addition of concentrated perchloric acid to the cooled reaction mixtures. Portions of the precipitates, collected by suction filtration, were dissolved in reagent grade dimethyl sulfoxide (Me_2SO), and the solutions were applied to a silica gel column and eluted with 0.05 M HCl. Colored CoTMAP- and CoTMPyP-containing fractions were collected from the column and were evaporated by flowing nitrogen over the liquid while the fractions were protected from light. Spectra of CoTMPyP prepared in this manner were identical with those described by Pasternack and Cobb.²⁴

Acetonitrile was dried over calcium hydride for a minimum of 24 h and distilled at least once from fresh calcium hydride under oxygen-free nitrogen. Me_2SO was twice vacuum distilled from calcium hydride immediately prior to use. All water was deionized and distilled.

Tetrabutylammonium perchlorate (TBAP) was purchased from Fisher Scientific Co. (Springfield, NJ) as a powder containing a substantial quantity of water. Purification of TBAP was effected by recrystallizing it twice from reagent grade ethyl acetate followed by drying in a vacuum desiccator. This TBAP was stored in a glovebox under an oxygen-free argon atmosphere.

Trifluoroacetic acid (TFA), sodium trifluoroacetate (NaTFA), and buffer components including formic acid, acetic acid, sodium acetate, mono- and dibasic sodium phosphate, sodium tetraborate, and boric acid were reagent grade. Buffers were prepared according to standard procedures as described by Perrin and Dempsey.²⁵

Aqueous solutions were deoxygenated by bubbling with oxygen-free nitrogen immediately before use. Anaerobic techniques utilizing septa and cannulae were employed for transfer of nonaqueous solutions.

Glassy-carbon electrodes (geometric area 0.07 cm^2) were obtained from Bioanalytical Systems (West Lafayette, IN), polished with fine alumina powder to a mirrorlike finish, and rinsed with the respective electrochemical solvent before use. Reticulated glassy-carbon electrodes were a gift from ERG Corp. (Oakland, CA). Electrolytic grade mercury was used for the Hg-pool electrodes. Platinum-mesh electrodes were immersed in cold, concentrated nitric acid and washed thoroughly with water. For electrolyses in nonaqueous solvents, platinum electrodes were

Table I. Comparison of Water-Splitting Electrocatalysts

complex	$E(A^+/A)^a$	$E(\text{appl})^a$	medium	% H_2 yield ^b
CoTMAP	-0.66 ^c	-0.95	0.1 M TFA	>90
CoTMPyP	-0.75 ^c	-0.95	0.1 M TFA	>90
CoTPyP	^d	-0.95	0.1 M TFA	>90
$Co(C_5H_5CO_2H)_2^+e^-$	-0.87	-0.90	0.1 M KCl, pH 6.5	42/>95 ^f
$Co(\text{sepulchrate})^{3+}e^-$	-0.54	-0.7	0.1 M KCl, pH 4.0	55/>95 ^f
$Co(4,11\text{-diene-N}_4)^g$	-0.70 ^h	-1.6	0.1 M KNO_3	93 ⁱ

^a In V vs. SCE. ^b Based on 2 × mol of H produced/equiv of charge passed during electrolysis. ^c Measured in Me_2SO with 0.1 M TBAP. ^d Sparingly soluble in Me_2SO . ^e From ref 26. ^f Obtained with Pt colloid added. ^g From ref 27. ^h From ref 42. ⁱ Run under a carbon dioxide atmosphere; carbon monoxide was a coproduct.

oven-dried and stored in a glovebox under argon atmosphere.

Cyclic voltammetry and controlled-potential electrolyses were conducted with the use of conventional three-electrode potentiostats, either Model CV-27 manufactured by Bioanalytical Systems or Model 173 from Princeton Applied Research Corp. (Princeton, NJ) equipped with their Model 175 programmer and Model 179 coulometer. Measurements were performed in three-electrode cells with glass frits to separate working and auxiliary electrode compartments and with a Luggin capillary to provide contact with the reference electrode chamber. A saturated KCl calomel electrode (SCE) purchased from Fisher Scientific Co. was used as a reference for all electrochemical measurements.

Gas chromatographic analyses of gases evolved via electrolyses in aqueous media were performed with a Model 3700 gas chromatograph from Varian Associates (Palo Alto, CA). H_2 was quantitatively determined on a column (8 ft × 0.25 in.) packed with Carbosieve S supplied by Supelco (Bellefonte, PA). Temperatures were held at 40 °C for the column, 100 °C for the injection port, and 260 °C for the detector compartment. A thermal conductivity detector was employed with an operating filament current of 140–160 mA. The carrier gas was high-purity argon from Matheson (Secaucus, NJ), flowing at a rate of 35–40 mL/min. Samples of gas were 0.5-mL amounts drawn into gastight syringes provided by Alltech Associates (Deerfield, IL). The retention times for H_2 and N_2 were 1 and 6 min, respectively. Reference volumes of H_2 were produced by cathodic electrolysis at a platinum-mesh electrode.

Ultraviolet and visible spectra were determined with a Model 8450A spectrophotometer manufactured by Hewlett-Packard Co. (Palo Alto, CA).

Results

A. Electrolysis. H_2 Production Efficiency. We tested three water-soluble cobalt porphyrins, CoTMAP, CoTMPyP, and CoTPyP, for their ability to catalyze H_2 evolution at a mercury-pool electrode. The electrode, in contact with 0.1 M trifluoroacetic acid containing approximately 2 mM cobalt porphyrin, was potentiostated at -0.95 V vs. SCE. The H_2 produced during 20-min electrolyses, which correspond to about 65% of the porphyrin present, was determined by gas chromatography. The amount of H_2 corresponded to essentially 100% of the integrated current (5.0 C). For other cobalt complexes, lower current efficiencies have been reported^{12,26,27} (see Table I), unless heterogeneous catalysts are added. The observed current efficiency means that the reduction of the porphyrin rings, a possible side reaction, was negligible. This was confirmed by visible spectroscopy, which showed only the cobalt(II) porphyrin present following reductive electrolysis. Similar experiments with the potential held at either +0.6 V (with a reticulated glassy-carbon electrode) or -0.3 V, which yielded either the Co(III) or the Co(II) form, respectively, produced no H_2 . Furthermore, in control experiments run without cobalt porphyrins, the background current and H_2 production were about 10% of the values in the presence of cobalt porphyrins. Thus, the cobalt porphyrins are demonstrated

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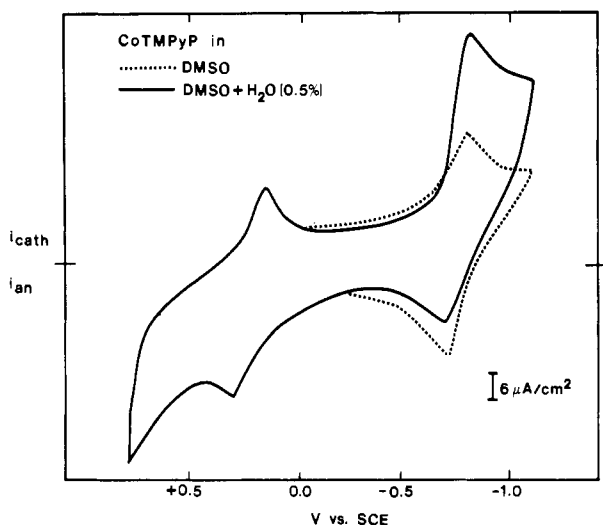


Figure 2. Cyclic voltammograms of CoTMPyP (0.5 mM) in Me₂SO/0.1 M TBAP, with and without water, at highly polished glassy carbon electrode (scan rate 100 mV/s).

to be effective catalysts for H₂ evolution and show no evidence of catalyst decomposition.

B. Cyclic Voltammetry in Me₂SO Solution. Figure 2 shows cyclic voltammograms with a carbon electrode for CoTMPyP in Me₂SO. Two redox processes are seen, at +0.15 and -0.75 V, obtained by averaging the potentials of oxidation and reduction maxima corresponding to Co(III)/Co(II) and Co(II)/Co(I) oxidation state changes. Ring reduction occurs at more negative potentials. The waves are quasi-reversible with peak separations of 180 and 110 mV, respectively. Similar results are obtained with CoTMAP, for which the redox potentials are +0.30 V for Co(III)/Co(II) and -0.66 V for Co(II)/Co(I). These potentials are in the ranges observed for other cobalt porphyrins³⁰⁻³² and are calculated with reasonable accuracy ($E_{1/2}(-N(CH_3)_3^+) = +0.19$ and -0.69 V vs. SCE for the two redox couples) from the Hammett relationship given by Walker et al.³⁰ for para-substituted cobalt tetraphenylporphyrins

$$E_{1/2}(X) = E_{1/2}(X = H) + 4(\sigma(X))\rho$$

where $\rho = 0.018$ and 0.038 V for the Co(III)/Co(II) and Co(II)/Co(I) couples, respectively, and $E_{1/2}(X = H) = -0.814$ V vs. SCE in Me₂SO. The Hammett parameter $\sigma(X = -N(CH_3)_3^+) = 0.82$ has been reported elsewhere.³³ Walker's relationship cannot be used for CoTMPyP, which has substituted pyridyl in place of substituted phenyl.

Figure 2 also shows that addition of a small quantity of water to the Me₂SO solution (0.5–2%) leaves the Co(III)/Co(II) wave essentially unaltered but increases the amplitude of the Co(II)/Co(I) reduction peak while diminishing the oxidation peak, consistent with the catalysis of H₂O reduction to H₂ via the electrogenerated Co(I).³⁴ An adsorption prewave^{35,36} was often observed following the addition of water, although appearance of the prewave depended on the extent of electrode polishing.

C. Cyclic Voltammetry in Aqueous Media. Catalysis and Adsorption. Figure 3 shows cyclic voltammograms in the region of the Co(II)/Co(I) couple for CoTMPyP in buffered aqueous media at a Hg-pool electrode. As the pH is lowered, an increase

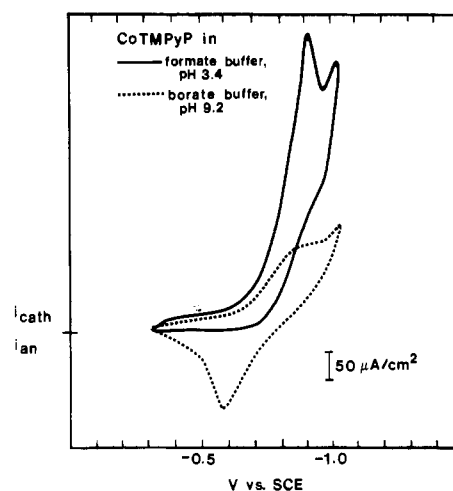


Figure 3. Cyclic voltammograms of CoTMPyP (0.5 mM) in buffered 0.1 M NaTFA at Hg-pool electrode (scan rate 100 mV/s).

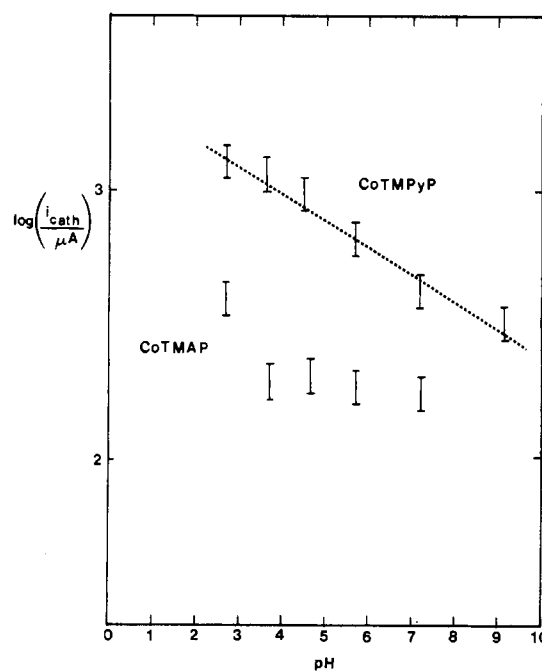


Figure 4. Plot of log (peak cathodic current) vs. pH for Co(II) porphyrin (1 mM) reduction at Hg-pool electrode (1 cm²) [scan rate 100 mV/s (background currents subtracted)].

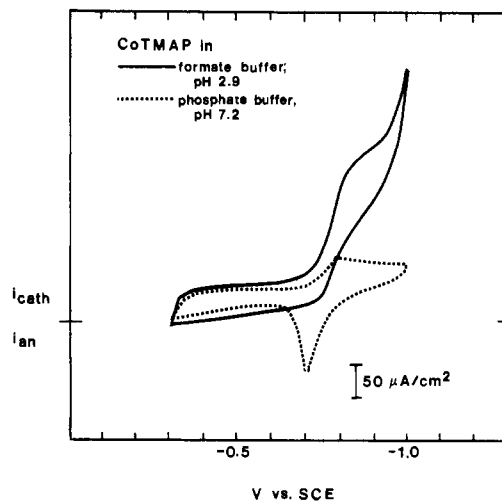


Figure 5. Cyclic voltammograms of CoTMAP (0.5 mM) in buffered 0.1 M NaTFA at Hg-pool electrode (scan rate 100 mV/s).

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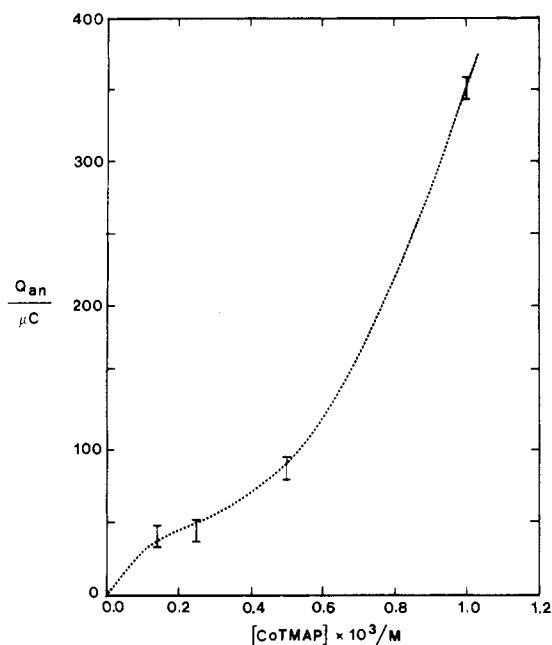


Figure 6. Plot of charge vs. concentration of CoTMAP for Co(I) oxidation wave at Hg-pool electrode (1 cm²) in acetate-buffered 0.1 M NaTFA, pH 7.2 (scan rate 100 mV/s).

in the reduction current is seen, whereas the oxidation current disappears, consistent with H₂ catalysis via Co(I). The magnitude of the catalytic current, indicative of the rate of H₂ production, increases with decreasing pH. However, the process is not simple. Figure 4 is a plot of the logarithm of the catalytic, cathodic current vs. pH; it has a slope of 0.1, instead of the expected value of unity for rate-limiting Co(I) protonation or proton attack on cobalt hydride. We attribute this shallow response to the adsorption of porphyrin at the electrode surface. Strong adsorption from aqueous media by many metalloporphyrins, notably cobalt (methylpyridyl)porphyrins, has been reported.^{23,28}

Adsorption is even stronger for CoTMAP in aqueous buffers as shown by the cyclic voltammograms in Figure 5. In this case, the Co(II) reduction wave is accompanied by a sharp spike for the return oxidation wave, characteristic of adsorption.³⁶ The magnitude of the cathodic current remains independent of pH to values as low as pH 3 (see Figure 4). Moreover, a plot of the charge associated with the anodic spike vs. CoTMAP concentration at pH 7.2 (shown in Figure 6) shows distinctly nonlinear behavior with an adsorption plateau in the 0.1–0.3 mM range.

We found evidence of adsorption with all electrode materials tested, including platinum, glassy carbon, tin oxide, and the Hg pool, in the presence of water. Unfortunately, the strong electrode adsorption precludes the proper evaluation of the kinetics and mechanism of H₂ evolution catalyzed by Co(I) porphyrins using electrochemical techniques.

D. Cobalt(I) Reactivity via Spectrophotometry. Figure 7 compares UV/vis absorption spectra for CoTMAP in the cobalt oxidation states III, II, and I. These species were prepared reversibly by controlled-potential electrolyses in carefully dried and deoxygenated acetonitrile at +0.6, -0.3, and -1.0 V vs. SCE, respectively. The spectra are in close accord with those reported for CoTPP^{37,38} (see Table II). If traces of oxygen or moisture were admitted to the solution containing Co^ITMAP, the spectrum changed immediately to that of the Co(II) moiety. Prolonged exposure to air resulted in a mixture of the Co(II) and Co(III) forms. To test further the Co^ITMAP reactivity, we conducted a mixing experiment in a dry, anaerobic spectrophotometer cell. Into the cell containing 2 mL of 10⁻⁶ M Co^ITMAP in dry acetonitrile was injected 0.5 mL of acetonitrile containing 5 μL of

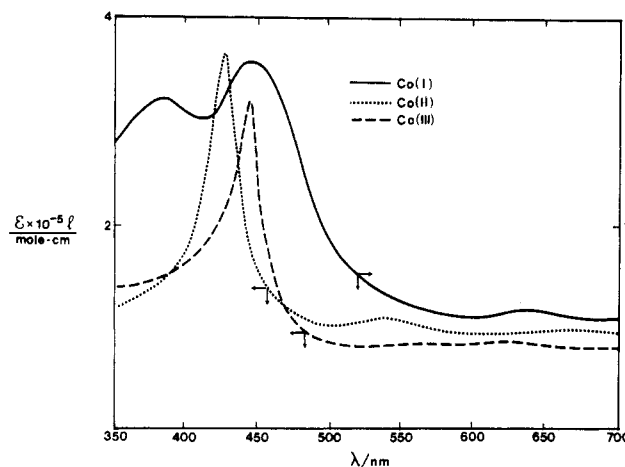


Figure 7. UV/vis spectra of redox states of CoTMAP prepared by electrolysis in acetonitrile/0.1 M TBAP.

Table II. UV/Vis Absorption Data for Redox States of CoTMAP and CoTPP^a

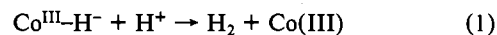
porphyrin	solvent	wavelength (log ε) ^b		
		Co(I)	Co(II)	Co(III)
CoTMAP	acetonitrile/ 0.1 M TBAP	392 (5.2)	429 (5.6)	448 (5.5)
		446 (5.3)	551 (5.0)	562 (4.8)
		644 (4.7)		626 (4.9)
CoTPP ^c	tetrahydrofuran	370 (4.3)	425 (5.1)	442 (5.1)
		431 (4.5)	540 (4.1)	556 (4.0)
		525 (3.8)		597 (3.7)
CoTPP ^d	pyridine	362 (4.7)		
		427 (4.8)		
		511 (4.2)		
		608 (3.3)		

^a Cobalt *meso*-tetraphenylporphyrine. ^b At absorbance maxima, in nm. ^c From ref 38. ^d From ref 37.

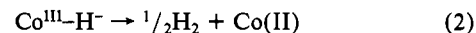
H₂O with a gastight syringe. The absorbance at 430 nm, the Soret absorption maximum for Co^ITMAP, was monitored and was found to stabilize within the mixing time of approximately 2 s. A control in which H₂O-free acetonitrile was injected showed a small absorbance change (approximately one-tenth of the water-added samples), indicating the introduction of small amounts of impurities, most likely air. Identical results were obtained when the experiment was repeated with fresh samples. We conclude that the water rapidly oxidizes Co^ITMAP, even at the low concentrations used in this experiment. From the final concentration of CoTMAP (0.8 μM) and water (50 μM), we estimate a lower limit for the second-order rate constant for the reaction between the two at 10⁴ M⁻¹ s⁻¹.

Discussion

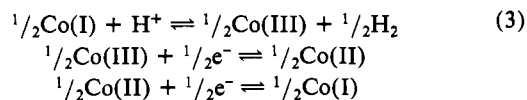
As indicated in the catalytic scheme drawn in Figure 1, there are two possible pathways for H₂ evolution from cobalt hydrides. The first involves proton attack



and subsequent Co(III) reduction at an electrode or by Co(I). The second involves disproportionation of the hydride



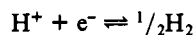
The thermodynamic requirements for these pathways differ due to the intermediacy of the Co(III)/Co(II) redox couple in the first one. If pathway 1 is followed, then the overall chemistry can be described as



with the net result

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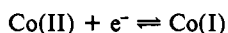
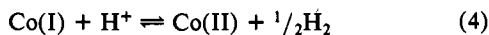
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The electromotive force for reaction 3 is then

$$E(3) = E(\text{H}^+/\text{H}_2) - \frac{1}{2}E(\text{Co(III)}/\text{Co(II)}) - \frac{1}{2}E(\text{Co(II)}/\text{Co(I)})$$

If pathway 2 is followed, the same net result is achieved by



and the electromotive force for reaction 4 is given by

$$E(4) = E(\text{H}^+/\text{H}_2) - E(\text{Co(II)}/\text{Co(I)})$$

Since $E(\text{Co(III)}/\text{Co(II)})$ is more positive than $E(\text{Co(II)}/\text{Co(I)})$, reaction 4 must have a greater driving force than reaction 3. At low pH, however, reaction 3 may be favored kinetically, provided it can proceed spontaneously at all. This condition, $E(3) > 0$, will be satisfied as long as

$$E(\text{Co(III)}/\text{Co(II)}) + E(\text{Co(II)}/\text{Co(I)}) < 2E(\text{H}^+/\text{H}_2)$$

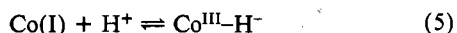
Since $E(\text{H}^+/\text{H}_2) = -0.24$ V on the SCE scale and the CoTMAP potentials give

$$E(\text{Co(III)}/\text{Co(II)}) + E(\text{Co(II)}/\text{Co(I)}) = +0.30 - 0.66 = -0.36 \text{ V}$$

$E(3) = -0.06$ V, which corresponds to an equilibrium constant of about 0.1. By comparison, $E(4) = +0.42$ V, corresponding to a much larger equilibrium constant ($K = 1 \times 10^7$) for reaction 4.

Chao and Espenson¹¹ studied the decomposition of the hydride of bis(dimethylglyoximate)(tri-*n*-butylphosphine)cobalt and found first- and second-order concentration dependencies, the contributions varying with pH. Rate constants for pathways 1 and 2 were estimated at 0.42 and $3.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Therefore, the disproportionation pathway is favored unless $[\text{H}^+]/[\text{Co}^{\text{III}}\text{-H}^-]$ exceeds 8×10^4 . For this cobaloxime in ethanolic solution, $E(\text{Co(III)}/\text{Co(II)})$ and $E(\text{Co(II)}/\text{Co(I)})$ have been reported³⁹ to be -0.52 and -0.75 V vs. SCE, respectively. From the equation above, $E(3)$ is estimated to be $+0.40$ V. This value for $E(3)$ is much higher than that for CoTMAP, for which the rate constant for pathway 1 is therefore expected to be much slower. We conclude that cobalt porphyrin catalysis of H_2 evolution proceeds via reaction 4, i.e. a bimolecular reaction between cobalt porphyrin hydrides formed transiently by protonation of the Co(I) species.

If the equilibrium constants for reactions 2 and 4 are known, predicting the $\text{p}K$ of the cobalt hydride becomes possible. Combining the protic equilibria of reactions 2 and 4 with



$$\log K(5) = \text{p}K_a$$

one finds $\log K(4) = \log K(2) + \text{p}K_a$. Chao and Espenson¹¹ estimated $\log K(2)$ to be 0.9 for the cobaloxime under discussion. From $E(4) = E(\text{H}^+/\text{H}_2) - E(\text{Co(II)}/\text{Co(I)}) = +0.51$ V and the corresponding $\log K(4) = 8.6$, we calculate a $\text{p}K_a$ value of 7.7. The value determined experimentally by Schrauzer and Holland⁴⁰

in aqueous methanol is about 10.5. The discrepancy probably reflects the differing conditions under which the experimental quantities were estimated.

The hydridopentacyanocobaltate(I) ion possesses a weakly basic Co(I) and a corresponding $\text{p}K_a$ of approximately 20. The equilibrium constant has been determined for the analogous reaction (2) to be 6.2×10^{-6} .¹ Accordingly, $\log K(4) = 14.8$ and $E(4) = +0.87$ V. This gives a predicted value for $E(\text{Co(II)}/\text{Co(I)})$ of -1.11 V vs. SCE, which is in reasonable agreement with the experimentally determined value of -1.3 V.⁴¹

Hydridocobalamin, the hydride form of vitamin B₁₂, is a much stronger acid than the hydridocobaloxime discussed above with a $\text{p}K_a$ approximated at 1,¹¹ even though $E(\text{Co(II)}/\text{Co(I)})$ for the "base-off" form is similar.¹⁰ This difference of nearly 10 $\text{p}K_a$ units must be due primarily to the phosphine ligand of the cobaloxime, which greatly increases the basicity of Co(I),⁴ without apparently changing the Co(II)/Co(I) energy differences. The lower $\text{p}K_a$ for hydridocobalamin implies a larger equilibrium constant for reaction 2 (calculated to be 10^{15}) and is consistent with the known instability of this species. Hydridocobaloxime is also unstable if the "soft" phosphine ligand is replaced by a "hard" ligand such as H_2O ,⁴⁰ which results in lower basicity for the Co(I) form. Aqueous cobalt porphyrins are no doubt similar to "base-off" cobalamin and aquocobaloxime in possessing low Co(I) basicity and low stability for the hydride.

The reaction of Co^ITMAP with water is surprisingly fast, the estimated rate constant ($>10^4 \text{ M}^{-1} \text{ s}^{-1}$) being larger than that measured for cobalt(I) pentacyanide¹ ($10^{3.3} \text{ M}^{-1} \text{ s}^{-1}$), which has a substantially more negative $E(\text{Co(II)}/\text{Co(I)})$.⁴¹ This rate is also faster than that of the macrocyclic complex $\text{Co}^{\text{I}}(4,11\text{-diene-N}_4)$,¹⁴ $10^{1.7} \text{ M}^{-1} \text{ s}^{-1}$ ($E(\text{Co(II)}/\text{Co(I)}) = -0.70$ V vs. SCE).⁴² This complex reacts 8 orders of magnitude faster with H_3O^+ than with H_2O .¹⁴ Such a rate augmentation for Co^ITMAP would make its reaction with H_3O^+ diffusion controlled. Bis(dimethylbipyridyl)- and bis(bipyridyl)cobalt(I) complexes have been shown^{12,13} to react rapidly with H_3O^+ , with bimolecular rate constants of $10^8 \text{ M}^{-1} \text{ s}^{-1}$ ($E(\text{Co(II)}/\text{Co(I)}) = -1.0$ V) and $10^7 \text{ M}^{-1} \text{ s}^{-1}$ ($E(\text{Co(II)}/\text{Co(I)}) = -0.89$ V), respectively. However, the mechanism appears to be complicated, involving ligand dissociation and electron and H atom transfer, and, hence, may not be relevant to other Co(I) systems.

These considerations establish that cobalt porphyrins should be excellent molecular catalysts for H_2 evolution, especially in neutral solution where the reversible hydrogen electrode potential ($E(\text{H}^+/\text{H}_2) = -0.66$ V vs. SCE at pH 7) approaches $E(\text{Co(II)}/\text{Co(I)})$, but the Co(I) reaction rate ($>10^4 \text{ M}^{-1} \text{ s}^{-1}$) remains rapid. If these molecules are to be used in electrochemical schemes, however, then the problem of electron transfer and reaction inhibition by adsorption will have to be overcome. Effective electrode catalysis will require appropriate tailoring of the porphyrin-electrode interface.

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Registry No. CoTMAP⁴⁺, 80137-20-8; CoTMPyP⁴⁺, 79346-65-9; CoTMAP³⁺, 96482-70-1; CoTMAP⁵⁺, 79619-73-1; CoTPyP, 14244-55-4; TFA, 76-05-1; C, 7440-44-0; Hg, 7439-97-6; H_2 , 1333-74-0; H_2O , 7732-18-5.

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