Cobalt Porphyrin Catalyzed Reduction of CO_2. Radiation Chemical, Photochemical, and Electrochemical Studies

D. Behar,[†] T. Dhanasekaran, and P. Neta*

Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

C. M. Hosten, D. Ejeh, and P. Hambright

Department of Chemistry, Howard University, Washington, D.C. 20059

Etsuko Fujita

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973

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Several cobalt porphyrins (CoP) have been reduced by radiation chemical, photochemical, and electrochemical methods, in aqueous and organic solvents. In aqueous solutions, the $Co^{I}P$ state is stable at high pH but is shorter lived in neutral and acidic solutions. Stable $Co^{I}P$ is also observed in organic solvents and is unreactive toward CO_2. One-electron reduction of $Co^{I}P$ leads to formation of a species that is observed as a transient intermediate by pulse radiolysis in aqueous solutions and as a stable product following reduction by Na in tetrahydrofuran solutions. The spectrum of this species is not the characteristic spectrum of a metalloporphyrin π-radical anion and is ascribed to $Co^{0}P$. This species binds and reduces CO_2. Catalytic formation of CO and HCO_2^- is confirmed by photochemical experiments in acetonitrile solutions containing triethylamine as a reductive quencher. Catalytic reduction of CO_2 is also confirmed by cyclic voltammetry in acetonitrile and butyronitrile solutions and is shown to occur at the potential at which $Co^{I}P$ is reduced to $Co^{0}P$. As compared with CoTPP, fluorinated derivatives are reduced, and catalyze CO_2 reduction, at less negative potentials.

Introduction

Catalyzed reduction of CO_2 has been studied extensively.[1] A number of transition-metal complexes have been utilized as electron-transfer mediators to achieve electrochemical[2,3] or photochemical[4−6] reduction of CO_2. Among the porphyrin complexes studied, iron porphyrins have been demonstrated to be the most efficient homogeneous catalysts in the electrochemical reduction of CO_2 to CO.[7] The mechanism was suggested to involve formation of an intermediate Fe−CO_2 complex after the initial $Fe^{III}P$ is reduced to the $Fe^{0}P$ oxidation state. Recent photochemical studies also demonstrated reduction of CO_2 catalyzed by reduced iron porphyrins,[8] although the turnover numbers for the porphyrins were not very high due to reductive decomposition of the macrocycle. In the present study we extend this work to cobalt porphyrins. We utilize radiation chemical, photochemical, and electrochemical techniques to examine several cobalt porphyrins for their one-electron reduction steps and their possible role as catalysts for photoreduction of CO_2.

Electrocatalytic reduction of CO_2 by cobalt porphyrins[9] and phthalocyanines[10] in aqueous solutions has been reported to yield CO and formic acid. More efficient electrocatalysis has been found with cobalt phthalocyanines deposited on the surface of carbon electrodes.[11] Reduction of the Co center in these complexes to the Co^{I} state did not lead to catalytic reduction of CO_2. Catalytic reduction was apparent only at potentials corresponding to those for reduction of the Co^{I} state. The present study is aimed at characterizing the species produced by this reduction, which has been assumed to be reduced at the ligand,[12] and to examining its role in electrochemical and photochemical reduction of CO_2.

Experimental Section[13]

Most photochemical and electrochemical experiments in organic solvents were carried out with cobalt tetraphenylporphyrin (TPP), which was supplied in the form of Co^{II}TPP. Several experiments were carried out with derivatives of Co^{II}-TPP, where each phenyl ring contained either a 3-F (T3FPP) or a 3-CF_3 group (T3CF_3PP) or was perfluorinated (TF_5PP). Experiments in aqueous solutions were carried out with the water-soluble cobalt porphyrins, which were supplied in the form of $ClCo^{III}P$. These included tetrakis(4-sulfonatophenyl)porphyrin (TSPP), tetrakis(*N*-methyl-4-pyridyl)porphyrin (TM4PyP), tetrakis(*N*-methyl-3-pyridyl)porphyrin (TM3PyP), tetrakis(*N*-methyl-2-pyridyl)porphyrin (TM2PyP), and tetrakis(*N*,*N*,*N*-trimethyl-4-aminophenyl)porphyrin (TAP). These water-soluble porphyrins bear four negative or positive charges at the meso substituents. Because the effect of these charges on the redox reactions is secondary, and to have similar notations for all the porphyrins in terms of the ligand or metal oxidation state, we do not include these peripheral charges in our abbreviated notations. The porphyrins were obtained from Mid-Century Chemicals (Posen, IL). Triethylamine (TEA) was from Aldrich; acetonitrile, *N*,*N*-dimethylformamide (DMF), 2-propanol (2-

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[†] On leave from the Soreq Nuclear Research Center, Yavne, Israel.

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PrOH), sodium formate, and the inorganic compounds were analytical grade reagents from Mallinckrodt. Butyronitrile (BuN), TEA, and tetrahydrofuran (THF) were purified by published methods[14] and stored in a vacuum over activated molecular sieves, NaK, and NaK, respectively. Tetrapropylammonium perchlorate (TPAP) was recrystallized twice from a mixture of water and ethanol and was dried under vacuum. (*Warning*: the perchlorate salts may be explosive and potentially hazardous.) Water was purified with a Millipore Super-Q system.

Fresh solutions were prepared before each experiment. Irradiations were performed with solutions that were bubbled with Ar or He to remove oxygen or were saturated with CO_2. Radiolysis was performed in a Gammacell 220 ^{60}Co source with a dose rate of either 0.8 Gy s^{-1} or 2.7 Gy s^{-1}. Photolysis was performed with a 300 W xenon lamp, using water filters to absorb the IR and cutoff filters to absorb at $\lambda < 320$ nm. Changes in porphyrin structure were derived from spectrophotometric measurements, and the CO evolved was determined by gas chromatography (Carboxen-1000 column, thermal conductivity detector). Formate ions were analyzed by a Dionex DX-500 ion chromatograph using an AS-11 column and NaOH solutions as eluent. To observe short-lived intermediates, pulse radiolysis was carried out with the apparatus described before,[15] which utilizes 50 ns pulses of 2 MeV electrons from a Febetron model 705 accelerator. Reaction rate constants are reported with their estimated standard uncertainties. All experiments were performed at room temperature, (20 ± 2) °C. Some of the porphyrins were also reduced by using a sodium mirror in THF by standard vacuum line procedures using home-built glassware at 25 °C.[16] An excess of Na was generally used, and the end point of each reduction was carefully monitored by the loss of isosbestic points. The Na chamber was removed from the cell before the addition of research grade CO_2.

Cyclic voltammograms were recorded with a BAS100B electrochemical analyzer with scan rates ranging from 20 mV s^{-1} to 1 V s^{-1}. A conventional three-electrode system consisting of a Au, Pt, or glassy carbon working electrode, a Pt counter electrode, and a standard calomel reference electrode was used. Ferrocene was added as an internal standard at the end of all experiments. All potentials are given with reference to the standard calomel electrode. Thin-layer spectroelectrochemistry was performed using an in-house designed cell. The electrochemical system was similar to that used in the cyclic voltammetric studies except that the working electrode was a gold mesh with 60% transmission obtained from Buckbee-Mears. For the electrochemical studies the porphyrin, $(0.1-1) \times 10^{-3}$ mol L^{-1}, was dissolved in anhydrous acetonitrile or butyronitrile, and the supporting electrolyte was tetrabutylammonium perchlorate or tetrapropylammonium perchlorate. The solutions were purged with Ar or CO_2.

Results and Discussion

Radiolytic Reduction of Cobalt Porphyrins. Radiolytic reduction of Co(III) porphyrins in aqueous[17] and in alcohol[18] solutions has been shown to lead to efficient production of Co(II) porphyrins, i.e., with a radiolytic yield corresponding to quantitative reaction of all reducing radicals with the porphyrin. We obtained the same results with the water-soluble porphyrins upon γ-irradiation in aqueous solutions containing formate ions as scavengers for $H^\bullet$ and $^\bullet OH$. The radiolytic yields for reduction of $Co^{III}P$ to $Co^{II}P$ in deaerated solutions containing 5×10^{-5} mol L^{-1} porphyrin, 1×10^{-2} mol L^{-1} HCO_2^-, and 0.2 mol L^{-1} KOH were ~0.66 μmol J^{-1} for the various porphyrins, equivalent to the total yield of radicals under these conditions, indicating reduction of the porphyrin by all e_{aq}^- and $^\bullet CO_2^-$ radicals.

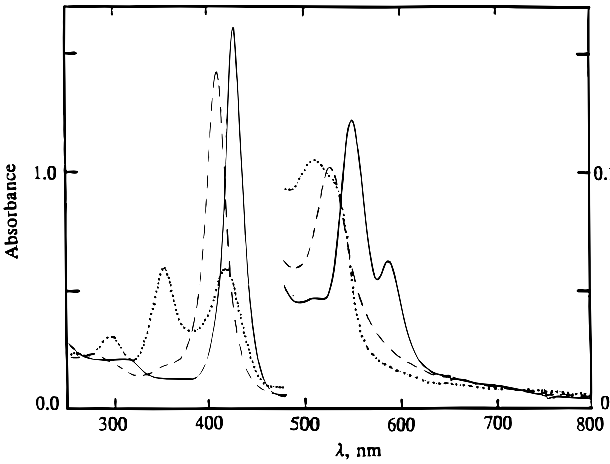

Figure 1. Radiolytic reduction of Co^{III}TSPP in deoxygenated aqueous solutions containing 0.01 mol L^{-1} HCO_2^- and 0.2 mol L^{-1} KOH, showing the spectra of Co^{III}TSPP (solid line), Co^{II}TSPP (dashed line), and Co^{I}TSPP (dotted line).

$$H_2O \rightsquigarrow e_{aq}^-, H^\bullet, {}^\bullet OH, H^+, H_2, H_2O_2 \qquad (1)$$

$$H^\bullet/{}^\bullet OH + HCO_2^- \rightarrow H_2/H_2O + {}^\bullet CO_2^- \qquad (2)$$

$$ClCo^{III}P + e_{aq}^- \rightarrow Cl^- + Co^{II}P \qquad (3)$$

$$ClCo^{III}P + {}^\bullet CO_2^- \rightarrow Cl^- + Co^{II}P + CO_2 \qquad (4)$$

After complete reduction of $Co^{III}P$ to $Co^{II}P$, further irradiation of the solution led to formation of $Co^{I}P$. The radiolytic reduction yield for this step under alkaline conditions, where $Co^{I}P$ is stable, was 0.68 μmol J^{-1}, indicating that reactions 5 and 6 are also quantitative.

$$Co^{II}P + e_{aq}^- \rightarrow Co^{I}P \qquad (5)$$

$$Co^{II}P + {}^\bullet CO_2^- \rightarrow Co^{I}P + CO_2 \qquad (6)$$

The optical absorption spectra of Co^{III}TSPP and its Co^{II} and Co^{I} states, produced by radiolytic reduction at high pH, are shown in Figure 1. Similar results were obtained with Co^{III}TAP, Co^{III}TM2PyP, and Co^{III}TM3PyP. Co^{III}TM4PyP, however, was reduced to a mixture of Co^{I}TM4PyP and the phlorin anion Co^{II}TM4PyPH$^-$ (with broad 820 nm absorption). The $Co^{I}P$ products were stable for hours (in the absence of O_2) at pH > 12 but disappeared more rapidly as the pH was decreased; they disappeared within minutes at neutral pH and were not observed in acidic solutions. The products of these decays were not examined in detail; CoTSPP in neutral solutions gave the chlorin (sharp peak at −620 nm), and CoTM4PyP gave some phlorin anion and related products but little chlorin. These results show that clean and stable $Co^{I}P$ species in aqueous solutions can be prepared from four of the above five porphyrins but only at high pH. We can utilize these preparations to carry out pulse radiolysis experiments with these solutions to observe the transient species produced by the next one-electron reduction step.

To observe the short-lived species produced from $Co^{I}P$, we prepared solutions of $Co^{I}P$ by γ-radiolysis of $Co^{III}P$ in alkaline media, as described above, and then irradiated samples of these

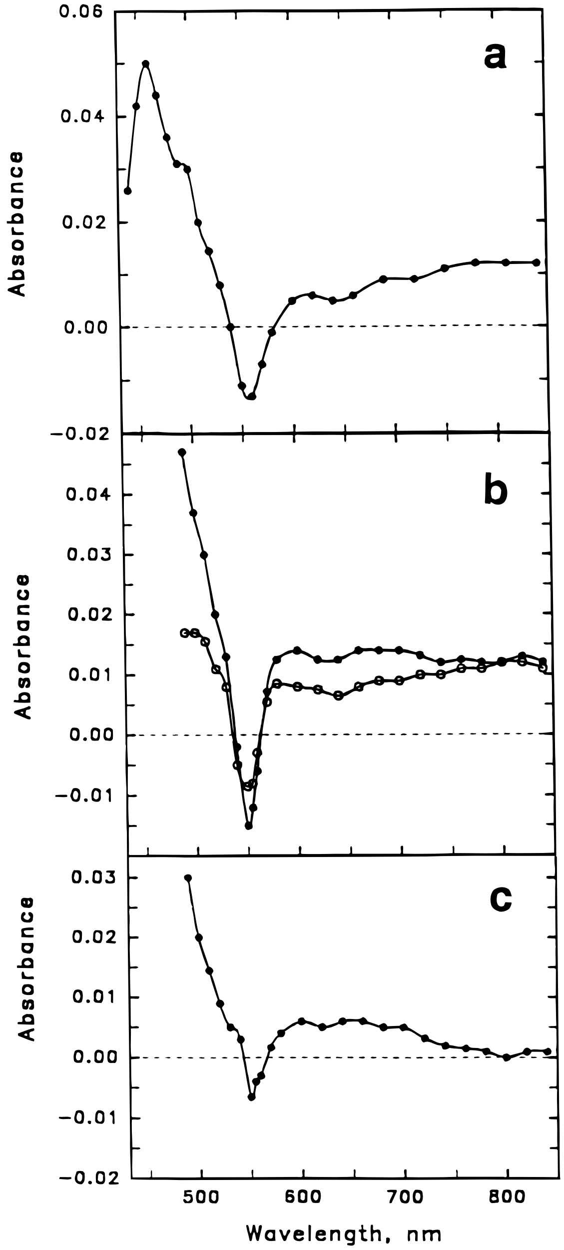

Figure 2. Differential absorption spectra recorded by pulse radiolysis of deoxygenated aqueous solutions containing 3×10^{-5} mol L^{-1} Co^{I}P, 0.01 mol L^{-1} HCO_2^-, and 0.2 mol L^{-1} KOH: (a) Co^{I}TM2PyP, 3 μs after the pulse; (b) Co^{I}TM3PyP, 3 μs (○) and 15 μs (●) after the pulse; (c) the difference between the two spectra shown in (b). The solutions of Co^{I}P were prepared by γ-radiolysis of Co^{III}P solutions in the above medium.

solutions with a short electron pulse and monitored the differential absorption after the pulse. In all cases we observed the rapid decay of the e_{aq}^- absorption at 700 nm, indicating that the porphyrins were reduced by e_{aq}^-. The rate constant for this reaction was determined by following the decay of the e_{aq}^- absorption as a function of porphyrin concentration and found to be $(2.1 \pm 0.4) \times 10^{10}$ L mol^{-1} s^{-1} for the negatively charged Co^{I}TSPP and $(4 \pm 1) \times 10^{10}$ L mol^{-1} s^{-1} for the positively charged Co^{I}TM3PyP, in line with previous values for different porphyrins.[19]

The absorbance remaining after the decay of e_{aq}^- can be ascribed to the porphyrin reduction product. The differential absorption spectra monitored with Co^{I}TM2PyP (Figure 2a) and Co^{I}TM3PyP (Figure 2b) show bleaching of the Co^{I}P absorption at 550 nm and formation of very broad absorptions at 600−840 nm, with molar absorptivities of about 1.7×10^3 L mol^{-1} cm^{-1} and with no clear peak. These absorptions are different than the typical spectra of π-radical anions produced from the corresponding complexes of Zn, Al, or Sn,[17,18,20] where an intense peak is found near 700 nm with molar absorptivity near 1×10^4 L mol^{-1} cm^{-1}. From this difference we suggest that the species formed from Co^{I}P may be Co^{0}P. The differential spectra monitored upon one-electron reduction of Co^{I}TSPP and Co^{I}TAP also exhibit broad absorptions in the 600−800 nm region, with no intense peaks, and are also ascribed to the Co^{0}P species. These species are expected to be the reactive intermediates which bind and reduce CO_2.

$$\mathrm{Co^{I}P} + e_{aq}^- \rightarrow \mathrm{Co^{0}P} \tag{7}$$

$$\mathrm{Co^{0}P} + \mathrm{CO_2} \rightarrow (\mathrm{CO_2{-}CoP}) \tag{8}$$

$$(\mathrm{CO_2{-}CoP}) + \mathrm{H_2O} \rightarrow \mathrm{CO} + \mathrm{Co^{II}P} + 2\mathrm{OH^-} \tag{9}$$

These reactions, however, could not be observed by pulse radiolysis because it was not possible to prepare stable Co^{I}P for these experiments in the presence of CO_2. Although Co^{I}P does not react with CO_2 (see below), the presence of CO_2 in water requires a pH near neutral where the Co^{I}P is relatively short-lived (decays within minutes).[21]

The product of reaction 8 may be produced also by reaction of Co^{I}P with $^{\bullet}CO_2^-$ radicals. This reaction is expected to be slower than reaction 7 and may take place by two routes: either to produce the same adduct as in reaction 8

$$\mathrm{Co^{I}P} + {}^{\bullet}\mathrm{CO_2^-} \rightarrow (\mathrm{CO_2{-}CoP}) \tag{10}$$

or via electron transfer, reaction 11.

$$\mathrm{Co^{I}P} + {}^{\bullet}\mathrm{CO_2^-} \rightarrow \mathrm{Co^{0}P} + \mathrm{CO_2} \tag{11}$$

For Co^{I}TM3PyP and Co^{I}TM2PyP the rapid decay of the e_{aq}^- absorption was followed by a slower increase of absorbance over the next 10−20 μs, due to reaction with $^{\bullet}CO_2^-$. From this slower formation, a rate constant of $\sim 5 \times 10^9$ L mol^{-1} s^{-1} is estimated for reaction of $^{\bullet}CO_2^-$ with Co^{I}TM3PyP. This value is in the same range as the rate constants reported for several other TMPyP metal complexes.[22] For Co^{I}TSPP and Co^{I}TAP, however, no slower formation step was observed, indicating that the $^{\bullet}CO_2^-$ radicals decay by self-reaction rather than react with these porphyrins. From the concentration of the porphyrins, the concentration of $^{\bullet}CO_2^-$ formed in the pulse, and the known rate constant for the self-decay of $^{\bullet}CO_2^-$, we estimate an upper limit of $\leqslant 1 \times 10^8$ L mol^{-1} s^{-1} for the reaction of $^{\bullet}CO_2^-$ with these two porphyrins. This upper limit is lower than the rate constant reported for reduction of Co^{II}TSPP by $^{\bullet}CO_2^-$ radicals,[17b] but it does not rule out an efficient reaction under low-dose rate conditions, as in the γ-radiolysis experiments discussed below.

The reaction of $^{\bullet}CO_2^-$ with Co^{I}TM2PyP, observed following the reaction of e_{aq}^-, results in increased absorbance (or bleaching) at all wavelengths examined, with nearly the same ratio, suggesting that the reaction leads to reduction of the porphyrin (reaction 11). The yield is quite low, indicating that only about 20% of the $^{\bullet}CO_2^-$ radicals lead to reduction. The rest probably decay by other modes. On the other hand, the reaction of $^{\bullet}CO_2^-$ with Co^{I}TM3PyP results in increased absorbance in the 580−720 nm range but little increase in the 740−840 nm range, and the ratios of absorbances at the other wavelengths also vary (Figure 2b). This suggests that the

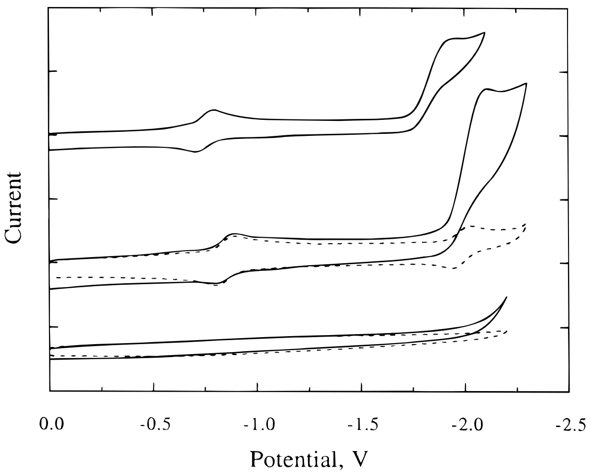

Figure 3. Cyclic voltammograms of $Co^{II}TPP$ (center) and $Co^{II}T3CF_3PP$ (top) in butyronitrile solutions saturated with Ar (dotted line) and with CO_2 (solid line). The solutions contained 5×10^{-4} mol L^{-1} porphyrin and 0.1 mol L^{-1} tetrapropylammonium perchlorate, and the scan rate was 100 mV s^{-1}. The bottom voltammogram is with the same solution in the absence of porphyrin. The current scale is 100 μA/division.

product of this reaction is not the same as the product of reaction 7, and the difference spectrum (Figure 2c) may be ascribed to the adduct formed by reaction 10, which is observed at high pH before it decays to final products. This adduct may decompose to yield $Co^{II}P$, as in reaction 9. Alternatively, at high pH, it may decompose to CO_2 and the reduced porphyrin, leading to the same product as reaction 7. The relative contributions of these two routes may be estimated from the yields of products in γ-radiolysis experiments.

Comparative γ-radiolysis experiments were carried out with $Co^{I}TSPP$ and $Co^{I}TM3PyP$ in aqueous solutions containing 0.01 mol L^{-1} HCO_2^- and 0.2 mol L^{-1} KOH. We found that $Co^{I}TM3PyP$ is removed by the radiolysis with a yield of ~0.18 μmol J^{-1} to produce a mixture of products (chlorin, phlorin anion, and further reduced products), which upon exposure to O_2 recovers ~70% of the $Co^{III}TM3PyP$ present in the original solution. (This result indicates that ~70% of the products were reduced and protonated at meso positions, since these products are known to be readily oxidized to the original porphyrins, whereas chlorins are not oxidized by O_2.) By considering that the radiolytic conversion of $Co^{I}TM3PyP$ into stable products probably involves more than one-electron reduction, the observed radiolytic yield indicates at least partial reduction of $Co^{I}TM3PyP$ by $^{\bullet}CO_2^-$ with possibly some oxidation via reaction 9, though the contribution of the latter route is uncertain. On the other hand, removal of $Co^{I}TSPP$ by the radiolysis took place with a yield of only 0.04 μmol J^{-1}, i.e., at least 4 times lower than that for reduction of $Co^{I}TM3PyP$, suggesting that reaction 9 plays a more important role in this case, though it does not occur quantitatively. The products formed upon reduction of $Co^{I}TSPP$ after long irradiations did not yield any $Co^{III}TSPP$ upon exposure to O_2, indicating that the reduction products were protonated at pyrrole rings rather than at meso positions.[23]

Electrochemistry of Cobalt Porphyrins. Cyclic voltammograms of Ar-saturated solutions of $Co^{II}TPP$ in freshly distilled and dry butyronitrile, using a glassy carbon working electrode, show two successive reversible reduction steps, to $Co^{I}TPP$ and then to $Co^{0}TPP$, separated by 1.15 V (Figure 3). The reduction potentials for these processes are −0.86 and −2.02 V vs SCE, in agreement with previous results in several solvents.[24] The oxidation of $Co^{II}TPP$ to $Co^{III}TPP$ was also observed at a potential of +0.60 V using a Pt working electrode. The transformation of $Co^{II}TPP$ (412 nm peak) to $Co^{I}TPP$ (peaks at 361 and 421 nm) at a potential of −1.0 V was also confirmed by spectroelectrochemical experiments in CH_3CN.

When the $Co^{II}TPP$ (5×10^{-4} mol L^{-1}) solution was saturated with CO_2, the electrochemical wave for the $Co^{II}P/Co^{I}P$ step was unaffected but the wave for the $Co^{I}P/Co^{0}P$ step was increased by a factor of 8 (at a scan rate of 100 mV s^{-1}). A catalytic current of 240 μA was observed, compared with only 30 μA for the $Co^{II}P/Co^{I}P$ wave. This catalytic reduction of CO_2 took place at a potential ~300 mV less negative than that required for direct reduction of CO_2 in a similar solution without porphyrin (Figure 3). These findings are in line with recent electrochemical results[25] and with the photochemical experiments described below.

To confirm that CO_2 reduction is indeed effected by the $Co^{0}P$ species, and to enhance the electrochemical catalysis by shifting the wave to less negative potentials, we examined several derivatives of $Co^{II}TPP$ that are expected to be more readily reduced. First, we attempted to use the perfluoro derivative, $Co^{II}TF_5PP$. This compound was reduced in two reversible waves at potentials of −0.61 V and −1.61 V vs SCE, i.e., 0.25 and 0.41 V less negative than $Co^{II}TPP$. However, in the presence of CO_2, the reduction waves were similar to those under Ar, indicating no catalysis of CO_2 reduction. The reason for this lack of catalysis may be the reduction of the perfluorinated rings (see below). To prevent this route, we studied two other porphyrins with a lower degree of fluorination, and thus with reduction potentials less negative than those of $Co^{II}TPP$ but more negative than those of $Co^{II}TF_5PP$. These were $Co^{II}T3CF_3PP$, with reduction potentials of −0.75 V and −1.81 V vs SCE, and $Co^{II}T3FPP$, with potentials of −0.79 V and −1.89 V (Table 1). The catalyzed reduction of CO_2 took place at the $Co^{I}P/Co^{0}P$ potential for both of these porphyrins and occurred at −1.81 V (Figure 3) and −1.89 V, respectively. These potentials are less negative than that required for direct reduction of CO_2 in the absence of porphyrin, and the currents were increased 4 and 6 times, respectively, using 5×10^{-4} mol L^{-1} porphyrin solutions and 100 mV s^{-1} scan rate. Thus, $Co^{II}T3CF_3PP$ and $Co^{II}T3FPP$ catalyze CO_2 reduction at less negative potentials than does $Co^{II}TPP$, but the catalytic current is smaller.

The catalytic current, i_p, is given by eq 12 if a reversible electron-transfer reaction is followed by a fast catalytic reaction[26] (assuming that the reaction is first order in catalyst and that $[CO_2] \gg$ [cat.]).

$$i_p = nFA[\text{cat.}](Dk[CO_2])^{1/2} \qquad (12)$$

In this equation, n is the number of electrons per molecule reduced, F is the Faraday constant, A is the area of the electrode, D is the diffusion coefficient of the catalyst, and k is the rate constant for the homogeneous reaction. Plots of the observed catalytic current vs [CoT3FPP] (Figure 4a) and vs $[CO_2]^{1/2}$ (Figure 4b) fit straight lines. These indicate that the reaction is homogeneous, not an electrode−surface reaction, and the reaction is first-order in CO_2. These results suggest a mechanism for the electrochemical reduction of CO_2 involving reactions 7 and 8.

Chemical Reduction of Cobalt Porphyrins. The short lifetimes of the reduced cobalt porphyrins studied by radiolytic and photochemical methods may be due to the presence of water or traces of oxygen or impurities. To overcome this limitation, we reduced several cobalt porphyrins in highly purified THF solutions under vacuum by successive exposures to distilled sodium metal. The spectra of the solutions were monitored after

TABLE 1: Electrochemical and Spectral Properties of Cobalt Porphyrins

porphyrin	$E_{1/2}$, V vs SCE[a]	λ_{max}, nm ($10^{-3}\epsilon$, L mol^{-1} cm^{-1})[b]
$Co^{II}TPP$	−0.86	282 (28.6), 413 (271), 529 (16.6), 606 (3.2)
$[Co^{I}TPP]^-$	−2.02	260 (27.4), 300 (33.9), 364 (53.1), 426 (59.7), 510 (12.1), 544 sh (8.4), 620 (3.7), 778 (2.5)
$[Co^{0}TPP]^{2-}$		314 (30.9), 420 (33.2), 498 (14.6), 528 sh (12.2), 650 (5.2)
$Co^{II}T3FPP$	−0.79	240 (27.7), 282 (27.6), 414 (284), 528 (16.6), 600 sh (2.0)
$[Co^{I}T3FPP]^-$	−1.89	260 (27.8), 302 (39.0), 366 (69.4), 424 (75.4), 514 (14.9), 536 (14.2), 622 (3.5), 682 (1.6), 776 (1.1)
$[Co^{0}T3FPP]^{2-}$		318 (37.3), 390 sh (39.3), 422 (44.7), 442 sh (41.6), 500 (19.8), 522 sh (18.4), 638 sh (4.6)
$Co^{II}T3CF_3PP$	−0.75	284 (26.0), 416 (296), 512 sh (10.7), 528 (16.1), 600 sh (2.5)
$[Co^{I}T3CF_3PP]^-$	−1.81	260 (29.5), 302 (42.7), 366 (67.3), 422 (86.5), 510 (17.2), 536 sh (16.0), 628 (4.3), 778 (1.8)
$[Co^{0}T3CF_3PP]^{2-}$		320 (33.8), 424 (40.5), 442 sh (36.6), 494 (19.9), 638 sh (7.4)
$Co^{II}TF_5PP$	−0.61	288 (21.5), 408 (274), 524 (13.5), 544 sh (9.5)
$[Co^{I}TF_5PP]^-$	−1.61	300 (25.3), 366 (44.4), 422 (48.0), 500 sh (7.7), 544 (11.0), 630 (2.3)

[a] In butyronitrile. [b] Molar absorptivities were calculated by assuming 100% conversion from the $Co^{II}P$ species in THF.

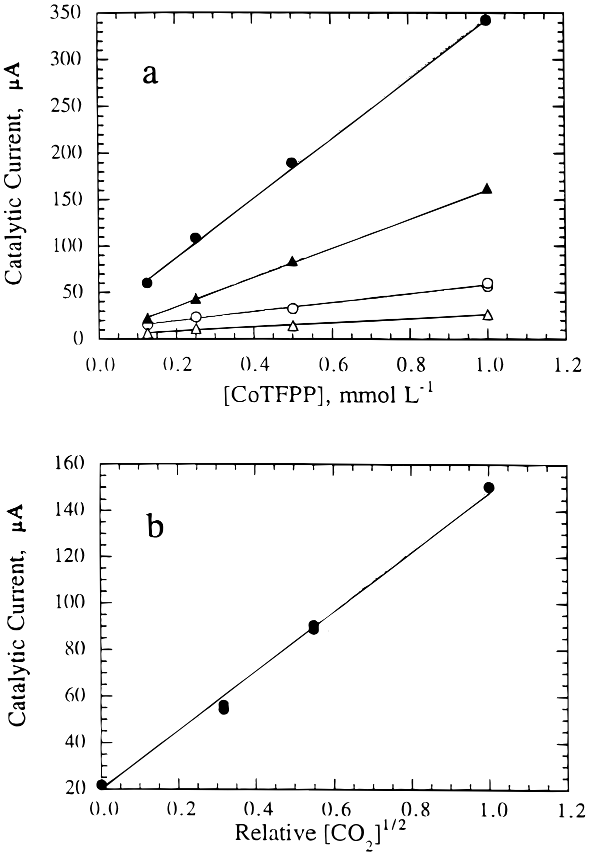

Figure 4. (a) Observed catalytic and noncatalytic currents vs the concentration of $Co^{II}T3FPP$ in butyronitrile solutions saturated with CO_2: (●) catalytic current with 100 mV s^{-1} scan rate at the $Co^{I}P/Co^{0}P$ potential, (▲) catalytic current with 20 mV s^{-1} scan rate at the $Co^{I}P/Co^{0}P$ potential, (○) noncatalytic current with 100 mV s^{-1} scan rate at the $Co^{II}P/Co^{I}P$ potential, (△) noncatalytic current with 20 mV s^{-1} scan rate at the $Co^{II}P/Co^{I}P$ potential. (b) Observed catalytic current vs relative $[CO_2]^{1/2}$ for a 5×10^{-4} mol L^{-1} solution of $Co^{II}TPP$; 100 mV s^{-1} scan rate; 10%, 30%, and 100% CO_2 were used.

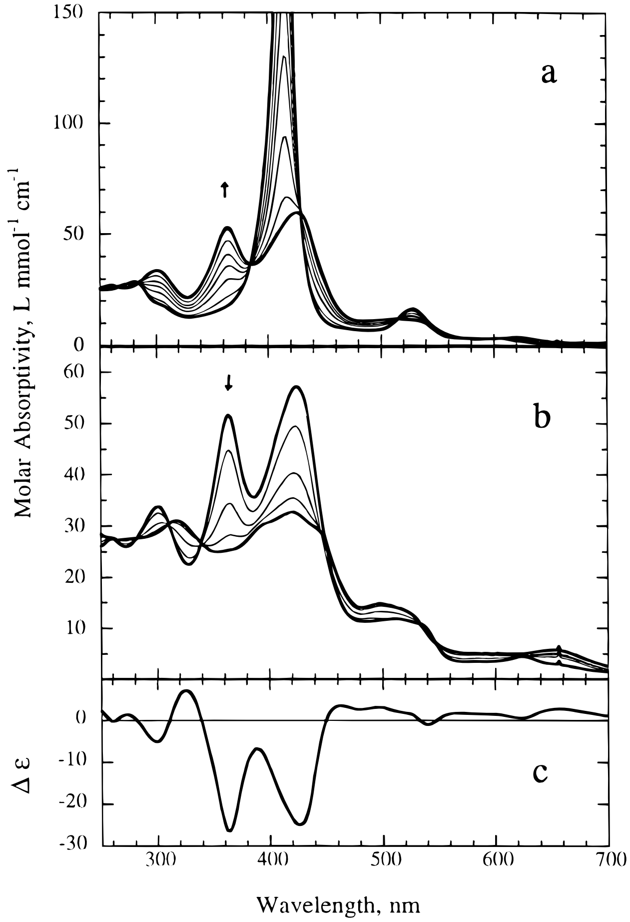

Figure 5. (a) Spectral changes upon sodium reduction of $Co^{II}TPP$ in THF. (b) Spectral changes upon sodium reduction of $Co^{I}TPP$ in THF. (c) The $Co^{I}TPP/Co^{0}TPP$ difference spectrum in THF.

each reduction step. In all cases, gradual reduction of the $Co^{II}P$ to the $Co^{I}P$ state was readily achieved, as demonstrated by the spectral changes (Figure 5a and Table 1), which are similar to those reported before.[27] The spectrum is consistent with formation of $Co^{I}TPP$ with some back-donation from the metal into the porphyrin system (see small absorptions at 620 and 778 nm with molar absorptivities of 3700 and 2500 L mol^{-1} cm^{-1}, respectively). Subsequent reduction of $Co^{I}P$ led to formation of a product that does not exhibit the typical spectrum of a π-radical anion, as seen from Figure 5b. The molar absorptivity of the peak at 650 nm is only 5200 L mol^{-1} cm^{-1}, consistent with some back-donation from the metal into the porphyrin systems. This reduced species, with a large splitting of the Soret band (314 and 420 nm), may be ascribed to $Co^{0}P$. Such a large splitting (360 and 452 nm) was observed in the spectrum of $Fe^{0}TPP$ in DMSO[28a] and THF[28b] together with peaks in the visible region. The molar absorptivities (in 10^3 L mol^{-1} cm^{-1}) of the peaks for $Fe^{0}TPP$ are as follows: in DMSO,[28b] 362 nm (44.8), 459 nm (55.7), 526 nm (21.6), 556 nm (12.6), 760 nm (4.1), and 840 nm (5.7); and in THF,[28b] 358 nm (66.8), 450 nm (68.6), 514 nm (25.2), 710 nm (5.4), and 778 nm (7.8). The molar absorptivities of the peaks at 500−800 nm for $Fe^{0}TPP$ are similar to those for $Co^{0}TPP$, indicating a similar amount of mixing with the porphyrin π-radical anion. Further reduction of $Co^{0}TPP$ and $Fe^{0}TPP$ or reduction in a wet solvent seems to produce a species absorbing at ∼840 nm, indicating formation of a phlorin anion. Both $Co^{I}TPP$ and Co^{0}-

TPP are very sensitive to oxygen and moisture, and opening the solution to air leads to their immediate oxidation to Co$^{\mathrm{II}}$TPP.

The differential absorption spectrum shown in Figure 5c is obtained by subtracting the spectrum of Co$^{\mathrm{I}}$TPP from that of Co^{0}TPP. This is in general agreement with those obtained by pulse radiolysis of water-soluble porphyrins (Figure 2).

Since TEA is used as reductive quencher in the photochemical experiments described below, we determined whether TEA binds to Co$^{\mathrm{II}}$TPP, Co$^{\mathrm{I}}$TPP, and Co^{0}TPP by repeating the above experiments with solutions containing 5% TEA in THF. The spectra of all the species were found to be identical to those observed without TEA. This is consistent with the results that the cyclic voltammograms of Co$^{\mathrm{II}}$TPP in Ar-saturated butyronitrile solutions with and without TEA are identical. It seems that, if TEA binds to any these species, the binding constant is quite small.

Addition of $\mathrm{CO_2}$ to a THF solution containing Co$^{\mathrm{I}}$TPP did not cause any spectral change. However, addition of $\mathrm{CO_2}$ to a solution containing Co^{0}TPP produced the spectrum of Co$^{\mathrm{I}}$TPP instantly, and this gradually changed to Co$^{\mathrm{II}}$TPP within several hours. The presence of TEA in the solution accelerated the reaction to complete the change to Co$^{\mathrm{II}}$TPP within 1 h. We did not detect any formation of Co$^{\mathrm{III}}$TPP or (CO)Co$^{\mathrm{III}}$TPP in the solution.[29] The reaction of $\mathrm{CO_2}$ with Co^{0}TPP is expected to form the complex ($\mathrm{CO_2}$−CoTPP) (reaction 8), which will decompose to CO and Co$^{\mathrm{II}}$TPP (reaction 9). This $\mathrm{CO_2}$ complex was not observed under the present experimental conditions. Its decomposition may be facilitated by any acid that can accept the oxide ion (e.g., reaction 9); in this case excess $\mathrm{CO_2}$ may serve as the oxide acceptor.

$$(\mathrm{CO_2{-}CoTPP}) + \mathrm{CO_2} \rightarrow \mathrm{CO} + \mathrm{Co^{II}TPP} + \mathrm{CO_3}^{2-} \qquad (13)$$

It appears that the Co$^{\mathrm{II}}$TPP formed by this reaction is rapidly reduced by the remaining Co^{0}TPP in a comproportionation reaction to form Co$^{\mathrm{I}}$TPP.

$$\mathrm{Co^{0}TPP} + \mathrm{Co^{II}TPP} \rightleftarrows 2\mathrm{Co^{I}TPP} \qquad (14)$$

Subsequent decay of Co$^{\mathrm{I}}$TPP may be via a slow reverse reaction 14 followed by the rapid reaction 8.

Since Co^{0}TPP is formed at a very negative potential (−2.02 V vs SCE), it seemed worthwhile to investigate the interaction of $\mathrm{CO_2}$ with other Co porphyrins which have less negative Co$^{\mathrm{I}}$P/Co^{0}P potentials. Replacing the phenyl with pyridyl groups lowers the reduction potential of the porphyrin, but the solubility of Co$^{\mathrm{II}}$TPyP was very low. Then we lowered the reduction potential by using fluorinated derivatives. First we studied Co$^{\mathrm{II}}$TF$_5$PP. The UV−vis spectra of the species formed by Na reduction of Co$^{\mathrm{II}}$TF$_5$PP in THF indicated formation of Co$^{\mathrm{I}}$TF$_5$PP with good isosbestic points, but further reduction showed a decrease of all the peaks in the 300−800 nm region, with no apparent formation of Co^{0}TF$_5$PP. This decay may be due to reduction of the macrocycle or of the perfluorinated phenyl groups. It is known that perfluorobenzene, unlike mono- or difluorobenzenes, reacts rapidly with e_{aq}^{-} and eliminates F^{-}.[30] Therefore, it is likely that the electron added to Co$^{\mathrm{I}}$TF$_5$PP may be partially delocalized on the perfluorophenyl rings and lead to defluorination. This was confirmed by reducing Co$^{\mathrm{II}}$TF$_5$PP in γ-irradiated alkaline methanol solution until the absorption of the Co$^{\mathrm{I}}$ species disappeared and finding F^{-} ions as products. The yield corresponds approximately to only one F^{-} ion per molecule of porphyrin, indicating that other routes, such as protonation of the reduced macrocycle, also play a role under these conditions. To prevent these side reactions, we studied the spectral changes associated with reduction of Co$^{\mathrm{II}}$T3FPP and Co$^{\mathrm{II}}$T3CF$_3$PP and found them (Table 1) to be quite similar to those observed with Co$^{\mathrm{II}}$TPP. In both of these porphyrins, the Co$^{\mathrm{I}}$P species do not react with $\mathrm{CO_2}$ but the Co^{0}P species do.

Photochemical Reduction of Cobalt Porphyrins. Photochemical reduction of Co$^{\mathrm{III}}$P and Co$^{\mathrm{II}}$P was studied mainly in acetonitrile solutions containing 5% TEA (0.36 mol L^{-1}) as a reductive quencher. The reduction mechanism is similar to that discussed for iron porphyrins.[8]

$$\mathrm{Et_3N(Cl)Co^{III}P} \xrightarrow{h\nu} \mathrm{Et_3N^{\bullet +}} + \mathrm{Cl^-} + \mathrm{Co^{II}P} \qquad (15)$$

$$\mathrm{Et_3N^{\bullet +}} + \mathrm{Et_3N} \rightarrow \mathrm{Et_3NH^+} + \mathrm{Et_2N\dot{C}HCH_3} \qquad (16)$$

$$\mathrm{Et_2N\dot{C}HCH_3} + \mathrm{ClCo^{III}P} \rightarrow \mathrm{Et_2N^+{=}CHCH_3} + \mathrm{Co^{II}P} + \mathrm{Cl^-} \qquad (17)$$

Photolysis of various Co$^{\mathrm{III}}$ porphyrins under these conditions produced clean Co$^{\mathrm{II}}$P solutions in all cases. Reduction of Co$^{\mathrm{II}}$P to Co$^{\mathrm{I}}$P took place with lower quantum yields, due to the fact that TEA does not bind to the cobalt in these reduced states, as indicated by the electrochemical and spectroscopic results discussed above. Clean Co$^{\mathrm{I}}$P was formed from all the Co(II) porphyrins examined, except for Co$^{\mathrm{II}}$TM4PyP, which formed directly a mixture of Co$^{\mathrm{I}}$P and the phlorin anion Co$^{\mathrm{II}}$PH^{-} (with a broad peak at 820 nm).[31] The water-soluble porphyrins were also photolyzed in aqueous TEA solutions and gave essentially the same results. Co$^{\mathrm{II}}$TPP was also photolyzed in DMF/TEA solutions and formed the same product. Photolysis was then carried out in $\mathrm{CO_2}$-saturated solutions. The Co$^{\mathrm{I}}$P state was readily obtained and was stable in organic solvents in the presence of $\mathrm{CO_2}$ but was not observed in aqueous solutions due to the lower pH under $\mathrm{CO_2}$.

Photolysis of Co$^{\mathrm{II}}$P in organic solvents saturated with $\mathrm{CO_2}$ was found to lead first to formation of Co$^{\mathrm{I}}$P, then to production of CO and $\mathrm{HCO_2}^{-}$, and finally to reduction and destruction of the porphyrin macrocycle. The concentrations of CO and $\mathrm{HCO_2}^{-}$ measured after photolysis were much greater than the initial concentrations of the porphyrins, indicating catalytic photoreduction. To estimate the amount of CO and $\mathrm{HCO_2}^{-}$ that may be produced from other sources, similar photolysis experiments were carried out in solutions saturated with He instead of $\mathrm{CO_2}$.[32] The concentrations of CO and $\mathrm{HCO_2}^{-}$ formed under He were much lower than those formed under $\mathrm{CO_2}$ in all solvents, but the difference was largest in acetonitrile, where the background levels were generally <1%. As discussed before,[8] photolysis of FeP in DMF solutions formed CO from DMF via excitation of a DMF−FeP complex, and a similar mechanism may operate with CoP. This mechanism is practically unimportant in acetonitrile solutions. Therefore, subsequent measurements were done with acetonitrile solutions. The yield of CO as a function of photolysis time (Figure 6) indicates that 1×10^{-5} mol L^{-1} Co$^{\mathrm{II}}$TPP leads to production of about 80 times that concentration of CO. But the porphyrin gradually degrades to colorless products and CO production stops. The same photolysis also produced formate at concentrations about 4−5 times greater than the concentrations of CO. Thus, the total turnover number for $\mathrm{CO_2}$ reduction by CoTPP is >300. The other porphyrins were compared to CoTPP after photolysis under similar conditions, and the yields of CO and formate were generally lower than those found with CoTPP. The yield of CO was lower by about a factor of 2 for CoT3FPP, CoT3CF$_3$-

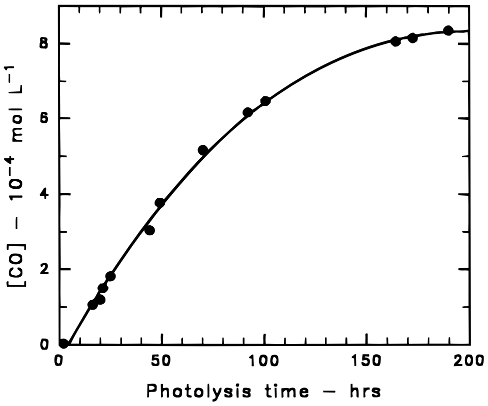

Figure 6. Photochemical production of CO in acetonitrile solution containing 1×10^{-5} mol L^{-1} $Co^{II}TPP$, 5% TEA, saturated with CO_2. The solution was photolyzed in a Pyrex bulb cooled by a water jacket, placed 10 cm away from an ILC Technology LX-300 UV lamp.

PP, and CoTM2PyP, but much lower for CoTM3PyP and CoTM4PyP. Clearly, ring reduction in the latter cases decreases the efficiency of CO_2 reduction. The yield of formate also was lower (by a factor of about 1.5−2) with CoT3FPP and $CoT3CF_3$-PP than with CoTPP. It was noticed, however, that the ratio between the yields of CO and HCO_2^- obtained with the porphyrins varied by about a factor of 2. The possible mechanisms contributing to these variations are under study.

Summary and Conclusions

Reduction of cobalt(II) porphyrins ($Co^{II}P$) to $Co^{I}P$ and $Co^{0}P$ can be carried out by radiolytic, photochemical, and electrochemical methods and by sodium reduction in THF. $Co^{0}P$ is stable in aprotic solvents but short-lived in aqueous solutions. Its optical absorption spectrum is different from that expected for a π-radical anion, but some back-donation from the cobalt to the ligand is indicated. Whereas $Co^{I}P$ is unreactive toward CO_2, $Co^{0}P$ reacts rapidly with CO_2 to form $Co^{II}P$, CO, and formate. The expected complex of CO_2 with the cobalt porphyrin was not observed in the current experiments at room temperature. Since the reduction potential of $Co^{I}P/Co^{0}P$ is highly negative, −2.02 V vs SCE for the CoTPP pair, the complex with CO_2 probably undergoes very rapid electron transfer and subsequent reactions to yield the products. The formate is produced by protonation, and CO is produced by loss of oxide ion. Both of these reactions may be effected by traces of protons in the photochemical system, but in the highly purified and dry THF excess CO_2 may act as an oxide acceptor. Catalyzed reduction of CO_2 is observed in cyclic voltammetry experiments in acetonitrile or butyronitrile solutions and in photochemical experiments in acetonitrile solutions containing TEA as a reductive quencher. TEA does not appear to bind to the cobalt center in $Co^{II}P$ and $Co^{I}P$, and thus the quantum yield for the reduction is very low. It may be possible to increase the quantum yield by use of a sensitizer such as *p*-terphenyl.[5c] These experiments are underway in an attempt to produce and characterize the CO_2−CoTPP by laser flash photolysis.

By substituting the phenyl rings of the CoTPP with electron-withdrawing groups, such as F and CF_3, the reduction potentials become less negative, and the electrochemical catalyzed reduction of CO_2 occurs at less negative potentials, corresponding to those for the respective $Co^{I}P/Co^{0}P$ pairs. On the other hand, the catalytic currents were smaller. In agreement with the latter observation, the yields of CO and HCO_2^- in the photochemical experiments were somewhat lower with CoT3FPP and $CoT3CF_3$-PP than with CoTPP. In all cases the porphyrin macrocycle is eventually reduced and decomposed, and production of CO and formate stops. Studies with other porphyrin-type complexes are underway in an attempt to extend the catalytic efficiency and longevity of this system.

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(31) It was further noticed that as the mixture of $Co^ITM4PyP$ and $Co^{II}TM4PyPH^-$ underwent slow oxidation in the dark, the phlorin anion gradually disappeared and more Co^IP was formed. This is in agreement with the previous suggestion that one-electron reduction of $Co^ITM4PyP$ yields first the π-radical anion $Co^ITM4PyP^{\bullet-}$, and this undergoes an intramolecular electron transfer from the cobalt to the porphyrin ligand.[12a] Under the present conditions, this $Co^{II}TM4PyP^{2-}$ product undergoes reversible protonation at the meso position to form the phlorin anion, $Co^{II}TM4PyPH^-$, and when this is oxidized back to the radical anion, $Co^{II}TM4PyP^{\bullet-}$, the reverse intramolecular electron transfer leads to production of $Co^ITM4PyP$.

(32) He was chosen to deoxygenate the solution, rather than Ar or N_2, because He was the carrier gas in the GC and because Ar and N_2 have GC peaks just ahead of the CO peak, which prevents accurate measurement of low CO concentrations.