

Cobalt Porphyrin Catalyzed Reduction of CO₂. Radiation Chemical, Photochemical, and Electrochemical Studies

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Received: January 7, 1998; In Final Form: February 25, 1998

Several cobalt porphyrins (CoP) have been reduced by radiation chemical, photochemical, and electrochemical methods, in aqueous and organic solvents. In aqueous solutions, the Co^IP state is stable at high pH but is shorter lived in neutral and acidic solutions. Stable Co^IP is also observed in organic solvents and is unreactive toward CO₂. One-electron reduction of Co^IP 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 Co⁰P. This species binds and reduces CO₂. Catalytic formation of CO and HCO₂[−] is confirmed by photochemical experiments in acetonitrile solutions containing triethylamine as a reductive quencher. Catalytic reduction of CO₂ is also confirmed by cyclic voltammetry in acetonitrile and butyronitrile solutions and is shown to occur at the potential at which Co^IP is reduced to Co⁰P. As compared with CoTPP, fluorinated derivatives are reduced, and catalyze CO₂ reduction, at less negative potentials.

Introduction

Catalyzed reduction of CO₂ 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 CO₂. Among the porphyrin complexes studied, iron porphyrins have been demonstrated to be the most efficient homogeneous catalysts in the electrochemical reduction of CO₂ to CO.⁷ The mechanism was suggested to involve formation of an intermediate Fe–CO₂ complex after the initial Fe^{III}P is reduced to the Fe⁰P oxidation state. Recent photochemical studies also demonstrated reduction of CO₂ 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 CO₂.

Electrocatalytic reduction of CO₂ by cobalt porphyrins⁹ and phthalocyanines¹⁰ 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 CO₂. 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 CO₂.

Experimental Section¹³

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-CF₃ group (T3CF₃PP) or was perfluorinated (TF₅PP). 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*-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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ProH), sodium formate, and the inorganic compounds were analytical grade reagents from Mallinckrodt. Butyronitrile (BuN), TEA, and tetrahydrofuran (THF) were purified by published methods¹⁴ 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 CO₂. Radiolysis was performed in a Gammacell 220 ⁶⁰Co 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 CO₂.

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) × 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 CO₂.

Results and Discussion

Radiolytic Reduction of Cobalt Porphyrins. Radiolytic reduction of Co(III) porphyrins in aqueous¹⁷ and in alcohol¹⁸ 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[•] and •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 HCO₂⁻, and 0.2 mol L⁻¹ KOH were ~0.66 μ mol J⁻¹ for the various porphyrins,

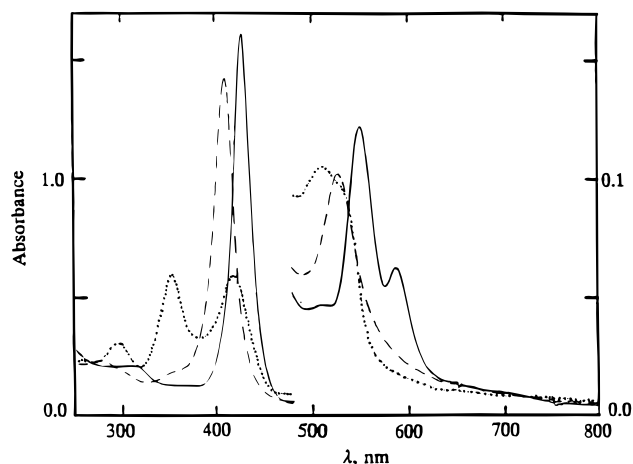
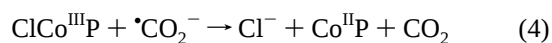
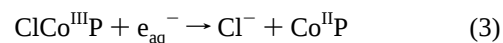
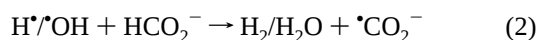
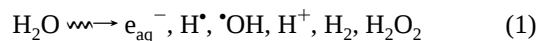
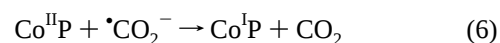
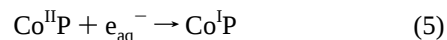


Figure 1. Radiolytic reduction of Co^{III}TSPP in deoxygenated aqueous solutions containing 0.01 mol L⁻¹ HCO₂⁻ and 0.2 mol L⁻¹ KOH, showing the spectra of Co^{III}TSPP (solid line), Co^{II}TSPP (dashed line), and Co^ITSPP (dotted line).

equivalent to the total yield of radicals under these conditions, indicating reduction of the porphyrin by all e_{aq}⁻ and •CO₂⁻ radicals.



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



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^ITM4PyP and the phlorin anion Co^{II}TM4PyP⁻ (with broad 820 nm absorption). The Co^IP products were stable for hours (in the absence of O₂) 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^IP 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^IP, we prepared solutions of Co^IP by γ -radiolysis of Co^{III}P in alkaline media, as described above, and then irradiated samples of these

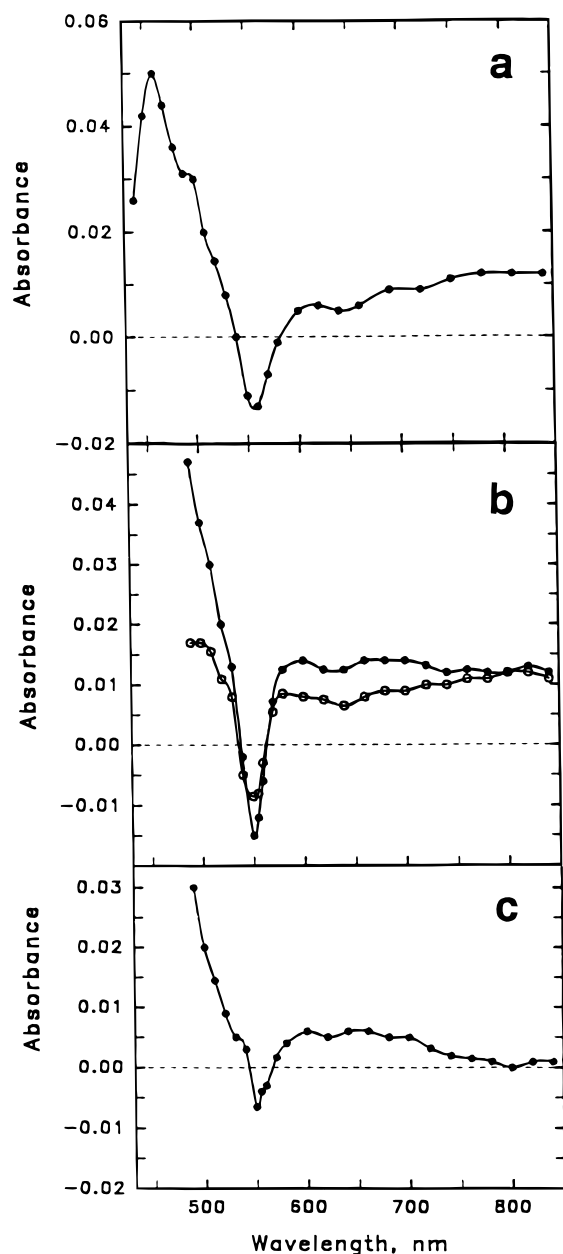
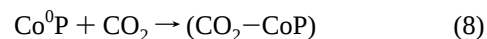
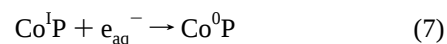


Figure 2. Differential absorption spectra recorded by pulse radiolysis of deoxygenated aqueous solutions containing $3 \times 10^{-5} \text{ mol L}^{-1} \text{ Co}^{\text{I}}\text{P}$, $0.01 \text{ mol L}^{-1} \text{ HCO}_2^-$, and $0.2 \text{ mol L}^{-1} \text{ KOH}$: (a) $\text{Co}^{\text{I}}\text{TM2PyP}$, $3 \mu\text{s}$ after the pulse; (b) $\text{Co}^{\text{I}}\text{TM3PyP}$, $3 \mu\text{s}$ (○) and $15 \mu\text{s}$ (●) after the pulse; (c) the difference between the two spectra shown in (b). The solutions of $\text{Co}^{\text{I}}\text{P}$ were prepared by γ -radiolysis of $\text{Co}^{\text{III}}\text{P}$ 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 $(2.1 \pm 0.4) \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ for the negatively charged $\text{Co}^{\text{I}}\text{TSPP}$ and $(4 \pm 1) \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ for the positively charged $\text{Co}^{\text{I}}\text{TM3PyP}$, in line with previous values for different porphyrins.¹⁹

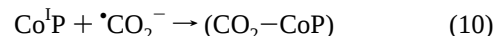
The absorbance remaining after the decay of e_{aq}^- can be ascribed to the porphyrin reduction product. The differential absorption spectra monitored with $\text{Co}^{\text{I}}\text{TM2PyP}$ (Figure 2a) and $\text{Co}^{\text{I}}\text{TM3PyP}$ (Figure 2b) show bleaching of the $\text{Co}^{\text{I}}\text{P}$ absorption at 550 nm and formation of very broad absorptions at 600 –

840 nm , with molar absorptivities of about $1.7 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ 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 $1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. From this difference we suggest that the species formed from $\text{Co}^{\text{I}}\text{P}$ may be Co^0P . The differential spectra monitored upon one-electron reduction of $\text{Co}^{\text{I}}\text{TSPP}$ and $\text{Co}^{\text{I}}\text{TAP}$ also exhibit broad absorptions in the 600 – 800 nm region, with no intense peaks, and are also ascribed to the Co^0P species. These species are expected to be the reactive intermediates which bind and reduce CO_2 .

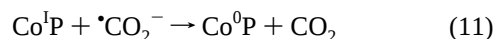


These reactions, however, could not be observed by pulse radiolysis because it was not possible to prepare stable $\text{Co}^{\text{I}}\text{P}$ for these experiments in the presence of CO_2 . Although $\text{Co}^{\text{I}}\text{P}$ does not react with CO_2 (see below), the presence of CO_2 in water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

The product of reaction 8 may be produced also by reaction of $\text{Co}^{\text{I}}\text{P}$ with $\cdot\text{CO}_2^-$ 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



or via electron transfer, reaction 11.



For $\text{Co}^{\text{I}}\text{TM3PyP}$ and $\text{Co}^{\text{I}}\text{TM2PyP}$ the rapid decay of the e_{aq}^- absorption was followed by a slower increase of absorbance over the next 10 – $20 \mu\text{s}$, due to reaction with $\cdot\text{CO}_2^-$. From this slower formation, a rate constant of $\sim 5 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ is estimated for reaction of $\cdot\text{CO}_2^-$ with $\text{Co}^{\text{I}}\text{TM3PyP}$. This value is in the same range as the rate constants reported for several other TMPyP metal complexes.²² For $\text{Co}^{\text{I}}\text{TSPP}$ and $\text{Co}^{\text{I}}\text{TAP}$, however, no slower formation step was observed, indicating that the $\cdot\text{CO}_2^-$ radicals decay by self-reaction rather than react with these porphyrins. From the concentration of the porphyrins, the concentration of $\cdot\text{CO}_2^-$ formed in the pulse, and the known rate constant for the self-decay of $\cdot\text{CO}_2^-$, we estimate an upper limit of $\leq 1 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ for the reaction of $\cdot\text{CO}_2^-$ with these two porphyrins. This upper limit is lower than the rate constant reported for reduction of $\text{Co}^{\text{I}}\text{TSPP}$ by $\cdot\text{CO}_2^-$ 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 $\cdot\text{CO}_2^-$ with $\text{Co}^{\text{I}}\text{TM2PyP}$, 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 $\cdot\text{CO}_2^-$ radicals lead to reduction. The rest probably decay by other modes. On the other hand, the reaction of $\cdot\text{CO}_2^-$ with $\text{Co}^{\text{I}}\text{TM3PyP}$ 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

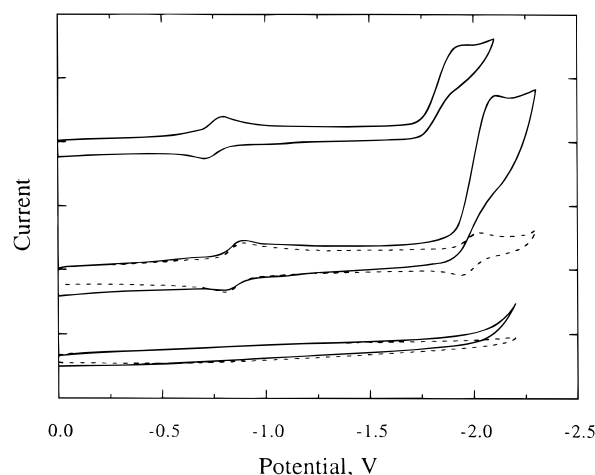


Figure 3. Cyclic voltammograms of Co^{II}TPP (center) and Co^{II}T3CF₃-PP (top) in butyronitrile solutions saturated with Ar (dotted line) and with CO₂ (solid line). The solutions contained 5×10^{-4} mol L⁻¹ porphyrin and 0.1 mol L⁻¹ tetrapropylammonium perchlorate, and the scan rate was 100 mV s⁻¹. The bottom voltammogram is with the same solution in the absence of porphyrin. The current scale is 100 μ A/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 CO₂ 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^ITSP and Co^ITM3PyP in aqueous solutions containing 0.01 mol L⁻¹ HCO₂⁻ and 0.2 mol L⁻¹ KOH. We found that Co^ITM3PyP is removed by the radiolysis with a yield of ~ 0.18 μ mol J⁻¹ to produce a mixture of products (chlorin, phlorin anion, and further reduced products), which upon exposure to O₂ recovers $\sim 70\%$ of the Co^{II}TM3PyP present in the original solution. (This result indicates that $\sim 70\%$ 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 O₂.) By considering that the radiolytic conversion of Co^ITM3PyP into stable products probably involves more than one-electron reduction, the observed radiolytic yield indicates at least partial reduction of Co^ITM3PyP by $\cdot\text{CO}_2^-$ with possibly some oxidation via reaction 9, though the contribution of the latter route is uncertain. On the other hand, removal of Co^ITSP by the radiolysis took place with a yield of only 0.04 μ mol J⁻¹, i.e., at least 4 times lower than that for reduction of Co^ITM3PyP, 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^ITSP after long irradiations did not yield any Co^{III}TSP upon exposure to O₂, 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^ITPP and then to Co⁰TPP, 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^ITPP (peaks at 361 and 421 nm) at a potential of -1.0 V was also confirmed by spectroelectrochemical experiments in CH₃CN.

When the Co^{II}TPP (5×10^{-4} mol L⁻¹) solution was saturated with CO₂, the electrochemical wave for the Co^{II}P/Co^IP step was unaffected but the wave for the Co^IP/Co⁰P step was increased by a factor of 8 (at a scan rate of 100 mV s⁻¹). A catalytic current of 240 μ A was observed, compared with only 30 μ A for the Co^{II}P/Co^IP wave. This catalytic reduction of CO₂ took place at a potential ~ 300 mV less negative than that required for direct reduction of CO₂ in a similar solution without porphyrin (Figure 3). These findings are in line with recent electrochemical results²⁵ and with the photochemical experiments described below.

To confirm that CO₂ reduction is indeed effected by the Co⁰P 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}TF₅PP. 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 CO₂, the reduction waves were similar to those under Ar, indicating no catalysis of CO₂ 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}TF₅PP. These were Co^{II}-T3CF₃PP, 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 CO₂ took place at the Co^IP/Co⁰P 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 CO₂ 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}-T3CF₃PP and Co^{II}T3FPP catalyze CO₂ 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 reaction²⁶ (assuming that the reaction is first order in catalyst and that $[\text{CO}_2] \gg [\text{cat.}]$).

$$i_p = nFA[\text{cat.}](Dk[\text{CO}_2])^{1/2} \quad (12)$$

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 $[\text{CoT3FPP}]$ (Figure 4a) and vs $[\text{CO}_2]^{1/2}$ (Figure 4b) fit straight lines. These indicate that the reaction is homogeneous, not an electrode-surface reaction, and the reaction is first-order in CO₂. These results suggest a mechanism for the electrochemical reduction of CO₂ 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	$\lambda_{\max}$, nm ($10^{-3}\epsilon$, L mol ⁻¹ cm ⁻¹) ^b
Co ^{II} TPP	-0.86	282 (28.6), 413 (27.1), 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 (28.4), 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 ₃ PP	-0.75	284 (26.0), 416 (296), 512 sh (10.7), 528 (16.1), 600 sh (2.5)
[Co ^I T3CF ₃ PP] ⁻	-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 ₃ PP] ²⁻		320 (33.8), 424 (40.5), 442 sh (36.6), 494 (19.9), 638 sh (7.4)
Co ^{II} TF ₃ PP	-0.61	288 (21.5), 408 (274), 524 (13.5), 544 sh (9.5)
[Co ^I TF ₃ PP] ⁻	-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.

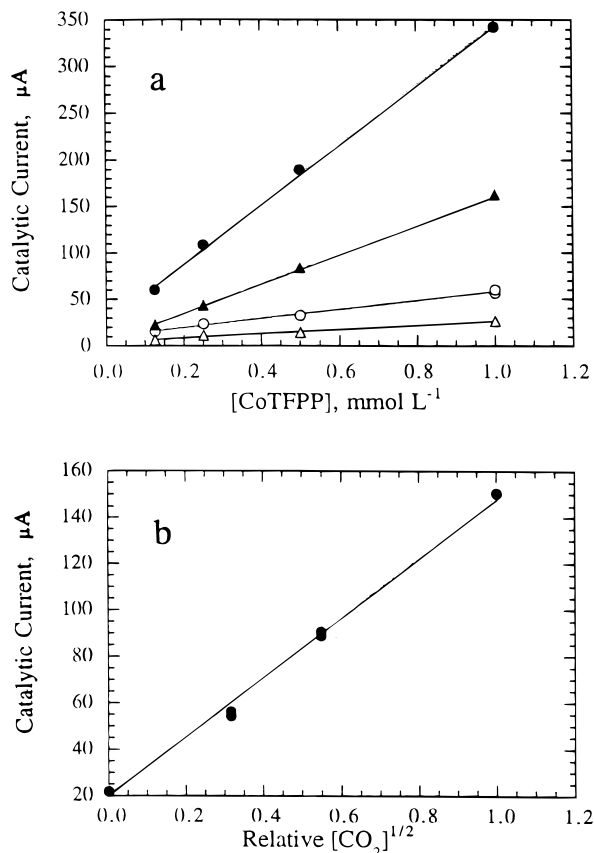


Figure 4. (a) Observed catalytic and noncatalytic currents vs the concentration of Co^{II}T3FPP in butyronitrile solutions saturated with CO₂: (●) catalytic current with 100 mV s⁻¹ scan rate at the Co^{II}P/Co⁰P potential, (▲) catalytic current with 20 mV s⁻¹ scan rate at the Co^{II}P/Co⁰P potential, (○) noncatalytic current with 100 mV s⁻¹ scan rate at the Co^{II}P/Co⁰P potential, (△) noncatalytic current with 20 mV s⁻¹ scan rate at the Co^{II}P/Co⁰P potential. (b) Observed catalytic current vs relative [CO₂]^{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% CO₂ were used.

each reduction step. In all cases, gradual reduction of the Co^{II}P to the Co^IP 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^ITPP 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^IP 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

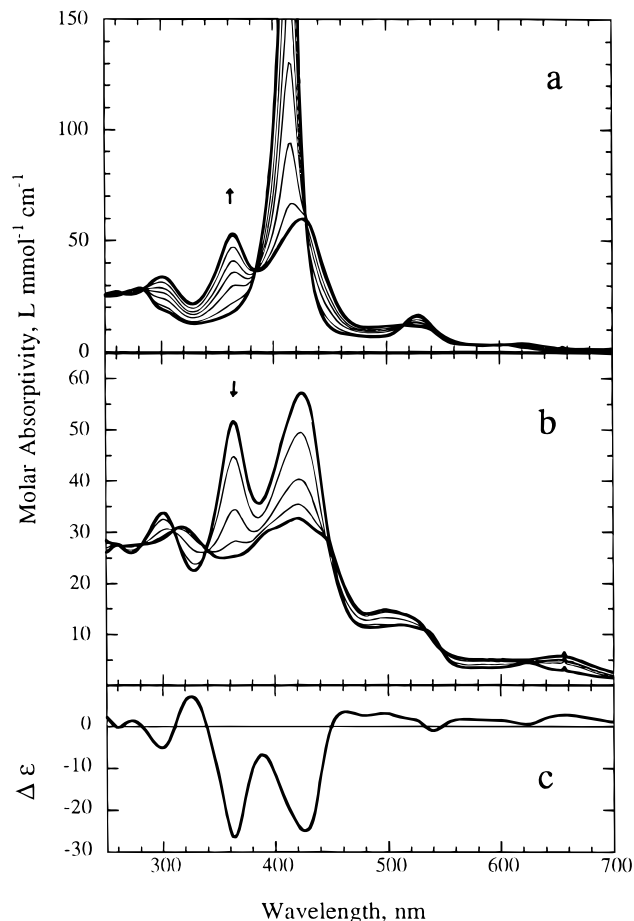


Figure 5. (a) Spectral changes upon sodium reduction of Co^{II}TPP in THF. (b) Spectral changes upon sodium reduction of Co^ITPP in THF. (c) The Co^ITPP/Co⁰TPP difference spectrum in THF.

porphyrin systems. This reduced species, with a large splitting of the Soret band (314 and 420 nm), may be ascribed to Co⁰P. Such a large splitting (360 and 452 nm) was observed in the spectrum of Fe⁰TPP in DMSO^{28a} and THF^{28b} together with peaks in the visible region. The molar absorptivities (in 10³ L mol⁻¹ cm⁻¹) of the peaks for Fe⁰TPP 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 Fe⁰TPP are similar to those for Co⁰TPP, indicating a similar amount of mixing with the porphyrin π -radical anion. Further reduction of Co⁰TPP and Fe⁰TPP or reduction in a wet solvent seems to produce a species absorbing at ~840 nm, indicating formation of a phlorin anion. Both Co^ITPP and Co⁰-

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

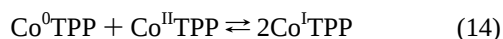
The differential absorption spectrum shown in Figure 5c is obtained by subtracting the spectrum of Co^ITPP from that of Co⁰TPP. This is in general agreement with those obtained by pulse radiolysis of water-soluble porphyrins (Figure 2).

Since TEA is used as reductive quencher in the photochemical experiments described below, we determined whether TEA binds to Co^{II}TPP, Co^ITPP, and Co⁰TPP 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^{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 CO₂ to a THF solution containing Co^ITPP did not cause any spectral change. However, addition of CO₂ to a solution containing Co⁰TPP produced the spectrum of Co^ITPP instantly, and this gradually changed to Co^{II}TPP within several hours. The presence of TEA in the solution accelerated the reaction to complete the change to Co^{II}TPP within 1 h. We did not detect any formation of Co^{III}TPP or (CO)Co^{III}TPP in the solution.²⁹ The reaction of CO₂ with Co⁰TPP is expected to form the complex (CO₂-CoTPP) (reaction 8), which will decompose to CO and Co^{II}TPP (reaction 9). This CO₂ 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 CO₂ may serve as the oxide acceptor.



It appears that the Co^{II}TPP formed by this reaction is rapidly reduced by the remaining Co⁰TPP in a comproportionation reaction to form Co^ITPP.

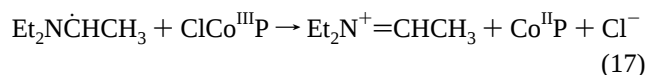
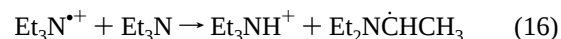
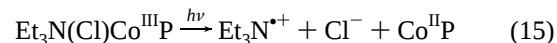


Subsequent decay of Co^ITPP may be via a slow reverse reaction 14 followed by the rapid reaction 8.

Since Co⁰TPP is formed at a very negative potential (−2.02 V vs SCE), it seemed worthwhile to investigate the interaction of CO₂ with other Co porphyrins which have less negative Co^IP/Co⁰P potentials. Replacing the phenyl with pyridyl groups lowers the reduction potential of the porphyrin, but the solubility of Co^{II}TPyP was very low. Then we lowered the reduction potential by using fluorinated derivatives. First we studied Co^{II}-TF₅PP. The UV-vis spectra of the species formed by Na reduction of Co^{II}TF₅PP in THF indicated formation of Co^ITF₅-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 Co⁰TF₅PP. 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^ITF₅PP may be partially delocalized on the perfluorophenyl rings and lead to defluorination. This was confirmed by reducing Co^{II}TF₅PP in γ-irradiated alkaline methanol solution until the absorption of the Co^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^{II}T3FPP and Co^{II}T3CF₃PP and found them (Table 1) to be quite similar to those observed with Co^{II}TPP. In both of these porphyrins, the Co^IP species do not react with CO₂ but the Co⁰P species do.

Photochemical Reduction of Cobalt Porphyrins. Photochemical reduction of Co^{III}P and Co^{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



Photolysis of various Co^{III} porphyrins under these conditions produced clean Co^{II}P solutions in all cases. Reduction of Co^{II}P to Co^IP 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^IP was formed from all the Co(II) porphyrins examined, except for Co^{II}TM4PyP, which formed directly a mixture of Co^IP and the phlorin anion Co^IPH[−] (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^{II}TPP was also photolyzed in DMF/TEA solutions and formed the same product. Photolysis was then carried out in CO₂-saturated solutions. The Co^IP state was readily obtained and was stable in organic solvents in the presence of CO₂ but was not observed in aqueous solutions due to the lower pH under CO₂.

Photolysis of Co^{II}P in organic solvents saturated with CO₂ was found to lead first to formation of Co^IP, then to production of CO and HCO₂[−], and finally to reduction and destruction of the porphyrin macrocycle. The concentrations of CO and HCO₂[−] measured after photolysis were much greater than the initial concentrations of the porphyrins, indicating catalytic photoreduction. To estimate the amount of CO and HCO₂[−] that may be produced from other sources, similar photolysis experiments were carried out in solutions saturated with He instead of CO₂.³² The concentrations of CO and HCO₂[−] formed under He were much lower than those formed under CO₂ 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^{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 CO₂ 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, CoT3CF₃-

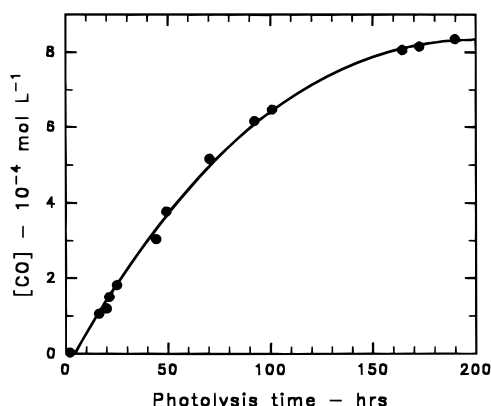


Figure 6. Photochemical production of CO in acetonitrile solution containing 1×10^{-5} mol L⁻¹ Co^{II}TPP, 5% TEA, saturated with CO₂. The solution was photolyzed in a Pyrex bulb cooled by a water jacket, placed 10 cm away from an ILC Technology LX-300 UV lamp.

PP, and CoTM2PyP, but much lower for CoTM3PyP and CoTM4PyP. Clearly, ring reduction in the latter cases decreases the efficiency of CO₂ reduction. The yield of formate also was lower (by a factor of about 1.5–2) with CoT3FPP and CoT3CF₃-PP than with CoTPP. It was noticed, however, that the ratio between the yields of CO and HCO₂⁻ 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^IP and Co⁰P can be carried out by radiolytic, photochemical, and electrochemical methods and by sodium reduction in THF. Co⁰P 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^IP is unreactive toward CO₂, Co⁰P reacts rapidly with CO₂ to form Co^{II}P, CO, and formate. The expected complex of CO₂ with the cobalt porphyrin was not observed in the current experiments at room temperature. Since the reduction potential of Co^IP/Co⁰P is highly negative, -2.02 V vs SCE for the CoTPP pair, the complex with CO₂ 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 CO₂ may act as an oxide acceptor. Catalyzed reduction of CO₂ 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 Co⁰P, 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 CO₂-CoTPP by laser flash photolysis.

By substituting the phenyl rings of the CoTPP with electron-withdrawing groups, such as F and CF₃, the reduction potentials become less negative, and the electrochemical catalyzed reduction of CO₂ occurs at less negative potentials, corresponding to those for the respective Co^IP/Co⁰P pairs. On the other hand, the catalytic currents were smaller. In agreement with the latter observation, the yields of CO and HCO₂⁻ in the photochemical experiments were somewhat lower with CoT3FPP and CoT3CF₃-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.

Acknowledgment. This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contracts DE-AI02-95ER14565 (NIST) and DE-AC02-76CH00016 (BNL). C.M.H. is indebted to NIH for support of the preliminary electrochemical experiments at Howard University under MBRS Grant No. S06GM-08016. P.H. is indebted to NASA for support of his work under Grant No. NCC-5-184.

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(21) Because of the instability of Co^IP in water in the presence of CO₂, we attempted to prepare Co^IP by γ -radiolysis of Co^{II}P in deaerated 2-propanol and acetonitrile solutions. This attempt did not succeed. Radiolysis of organic solvents always produces organic radicals in addition to the solvated electrons, and these radicals (R) are known to react with Co^{II}P via combination with the metal center to yield R-Co^{III}P. Potentially these products may be reduced by solvated electrons to R-Co^{II}P, which may decompose to Co^IP. But, in fact, the reduction did not proceed effectively in this manner, and we were unable to produce clean and stable Co^IP by radiolysis in organic solvents. This may be the result of the lower yield of solvated electrons as compared with the yield of organic radicals, but may be also due to reaction of the organic radicals with the Co^IP that is partially formed and possibly due to reduction of R-Co^{III}P or R-Co^{II}P at the ligand instead of at the metal (as observed for Rh porphyrins by Grodkowski et al.: Grodkowski, J.; Neta, P.; Abdallah, Y.; Hambright, P. *J. Phys. Chem.* **1996**, *100*, 7066).

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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^{•-}, and this undergoes an intramolecular electron transfer from the cobalt to the porphyrin ligand.^{12a} Under the present conditions, this Co^{II}TM4PyP²⁻ 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^{•-}, the reverse intramolecular electron transfer leads to production of Co^ITM4PyP.

(32) He was chosen to deoxygenate the solution, rather than Ar or N₂, because He was the carrier gas in the GC and because Ar and N₂ have GC peaks just ahead of the CO peak, which prevents accurate measurement of low CO concentrations.