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Reduction of Cobalt and Iron Phthalocyanines and the Role of the Reduced Species in Catalyzed Photoreduction of CO_2

J. Grodkowski,[†] **T. Dhanasekaran,**[‡] **and P. Neta***
Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

P. Hambright
Department of Chemistry, Howard University, Washington, DC 20059

B. S. Brunschwig, K. Shinozaki, and E. Fujita
Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973

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The role of cobalt and iron phthalocyanines in catalytic CO_2 reduction has been studied. Chemical, photochemical, and radiolytic reductions of the metal phthalocyanines (Pc) have been carried out in organic solvents, and reduction of their tetrasulfonated derivatives (TSPc) in aqueous solutions. $Co^{II}Pc$ and $Fe^{II}Pc$ are readily reduced to $[Co^{I}Pc]^{-}$ and $[Fe^{I}Pc]^{-}$, which do not react with CO_2. Reduction of $[Co^{I}Pc]^{-}$ yields a product which is characterized as the radical anion, $[Co^{I}Pc^{\bullet -}]^{2-}$, on the basis of its absorption spectra in the visible and IR regions. This species is stable under dry anaerobic conditions and reacts rapidly with CO_2. Catalytic formation of CO and formate is confirmed by photochemical experiments in DMF and acetonitrile solutions containing triethylamine (TEA) as a reductive quencher. The photochemical yields are greatly enhanced by the addition of *p*-terphenyl (TP). The radical anion, $TP^{\bullet -}$, formed from the reductive quenching of the singlet excited state with TEA, reduces the phthalocyanines very rapidly. The rate constants for reduction of $Co^{II}Pc$, $[Co^{I}Pc]^{-}$, and $[Fe^{I}Pc]^{-}$ by $TP^{\bullet -}$, determined by pulse radiolysis in DMF solutions, are nearly diffusion-controlled. The mono-reduced species formed from $[Co^{I}Pc]^{-}$ is unstable under the pulse radiolysis conditions but is longer-lived under the flash photolysis conditions. The interaction of this species with CO_2 is either too weak or too slow to detect in the current experiments, where a competing reaction with protons predominates.

Introduction

The increase in atmospheric CO_2 levels has stimulated research into photocatalytic CO_2 reduction.[1] A number of transition metal complexes are known to act as electron-transfer mediators for photochemical[2,3] or electrochemical[4] reduction of CO_2. Recent studies have shown that iron and cobalt porphyrins (MP) are effective homogeneous catalysts for the electrochemical[5] and photochemical[6,7] reduction of CO_2 to CO and formic acid. The mechanism is believed to involve binding of the CO_2 to the reduced porphyrin, $[M^{0}P]^{2-}$. In the photochemical studies, the turnover numbers for the porphyrins were low due to reductive decomposition of the macrocycle. In the present study we extend this work to examine whether cobalt and iron phthalocyanines also catalyze photoreduction of CO_2 in homogeneous solutions and whether they exhibit higher efficiency or longer durability than the porphyrins. Electrocatalytic reduction of CO_2 by cobalt tetrasulfonatophthalocyanines[8] 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.[9] The present study is aimed at characterizing the species produced by reduction of the cobalt and iron phthalocyanines (Pc), including the tetrasulfonatophthalocyanines (TSPc)[10] and the tetra(*tert*-butyl)phthalocyanines (TBPc), and at examining their role in photochemical reduction of CO_2. The TSPc and TBPc complexes are more soluble in water or organic solvents, respectively. Chemical, photochemical, and radiation chemical methods were used.

Experimental Section[11]

Experiments in organic solvents were carried out with cobalt and iron phthalocyanines, which were supplied in the form of $Co^{II}Pc$ and $ClFe^{III}Pc$. Most experiments, however, were carried out with 2,9,16,23-tetra(*tert*-butyl)phthalocyanine, $Co^{II}TBPc$, which is more soluble than $Co^{II}Pc$. Experiments in aqueous solutions were carried out with the water-soluble tetrasulfonated phthalocyanines, $Co^{II}TSPc$ and $ClFe^{III}TSPc$.[10] The phthalocyanines were obtained from Mid-Century Chemicals (Posen, IL). Water was purified with a Millipore Super-Q system. Triethylamine (TEA) was obtained from Aldrich and was refluxed over sodium and distilled under nitrogen. Acetonitrile (MeCN), *N*,*N*-dimethylformamide (DMF), methanol (MeOH), 2-propanol (2-PrOH), sodium formate, *p*-terphenyl, and the inorganic compounds were "Baker Analyzed" reagents. Tetrahydrofuran (THF) and MeCN, used as solvents for sodium reduction, were purified by published methods[12] and stored in a vacuum over NaK and activated molecular sieves, respectively. All experiments were performed at room temperature, (22 ± 2) °C.

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* Author to whom correspondence should be addressed.

[†] On leave from the Institute of Nuclear Chemistry and Technology, Warsaw, Poland.

[‡] Current address: Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556.

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For the radiolysis and photolysis experiments, fresh solutions were deoxygenated by bubbling with Ar, He, or CO_2. Radiolysis was performed in a Gammacell 220 ^{60}Co source with a dose rate of 0.5 Gy s^{-1}. Photolysis was performed with a 300 W xenon lamp, using water filters to absorb the IR and Pyrex filters to absorb the UV ($\lambda < 310$ nm). Absorption spectra of the phthalocyanines were recorded before and after irradiation, the CO evolved was determined by gas chromatography (Carboxen-1000 column, thermal conductivity detector), and the formate ions formed were analyzed (after dilution with water) by a Dionex DX-500 ion chromatograph using an AS-11 column and NaOH solutions as eluent. Two types of photochemical experiments were carried out. In one type, 35 mL solutions in a 43 mL Pyrex bulb were saturated with CO_2 and then photolyzed with the Xe lamp. After various intervals, the headspace was analyzed for CO by gas chromatography. In the other type of experiments, 4 mL samples of the CO_2-saturated solutions in 1 × 1 × 4 cm optical cells were photolyzed for various intervals and then analyzed for CO in the headspace and for formic acid in the solution. In both types of photolysis experiments, the irradiation cell was cooled by water to maintain the solution at room temperature. Actinometry was carried out with ferric oxalate solutions at (316 ± 4) nm using a combination of a glass interference filter and a $NiSO_4$ solution filter.

Pulse radiolysis experiments were carried out with the apparatus described before,[13] which utilizes 50 ns pulses of 2 MeV electrons from a Febetron model 705 pulser. Reaction rate constants are reported with their estimated standard uncertainties.

The UV−vis−IR spectra of reduced CoTBPc species were recorded in THF solutions following stepwise reduction of Co^{II}TBPc by a sodium mirror using standard vacuum line procedures. 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.

Laser flash photolysis experiments were carried out with $[Co^{I}TBPc]^-$, which was produced from Co^{II}TBPc either by sodium reduction in THF solutions or by photolysis in MeCN or THF solutions containing TEA and TP. Since the lifetime of the TP radical anion ($TP^{\bullet -}$), formed from the reductive quenching of the excited state with TEA, is longer in MeCN than in THF, subsequent flash photolysis experiments were carried out in MeCN. The details of the laser flash photolysis system are as described before.[14]

Cyclic voltammograms in THF 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 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.

Results and Discussion

Radiolytic Reduction of the Phthalocyanines in Aqueous Solutions. Radiolytic reduction of the cobalt and iron phthalocyanines was performed in deoxygenated aqueous solutions containing formate ions as scavengers for $H^\bullet$ and $^\bullet OH$ radicals, where the complex is reduced via reactions 3 and 4 (as has been reported for porphyrins[6,7,15]):

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

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

$$Co^{II}TSPc + e_{aq}^- \rightarrow [Co^{I}TSPc]^- \qquad (3)$$

$$Co^{II}TSPc + {}^\bullet CO_2^- \rightarrow [Co^{I}TSPc]^- + CO_2 \qquad (4)$$

When formate is replaced with 2-propanol, similar reductions take place by e_{aq}^- and by the $(CH_3)_2\dot{C}OH$ or $(CH_3)_2\dot{C}O^-$ radicals derived from 2-PrOH. In aqueous 50% 2-PrOH (6.7 mol L^{-1}) Co^{II}TSPc[10] is fully monomeric (λ_{max} 326, 600, 664 nm) and is radiolytically reduced to $[Co^{I}TSPc]^-$ (λ_{max} 315, 430, 475, 710 nm) (Figure 1a). Co^{II}TSPc in aqueous solutions with no added alcohol is a mixture of monomers and dimers,[16] and at the concentrations used in the present study only 15%−30% is monomeric. The dimeric $[Co^{II}TSPc]_2$ ($\lambda_{max} \sim 310$, 622 nm) is reduced to stable $[Co^{I}TSPc]_2^{2-}$ (λ_{max} 312, 448, 688 nm) (Figure 2a). In all cases, the reduction was quantitative, i.e., the radiolytic yields were ≈ 0.7 μmol J^{-1}, close to the known radiolytic yield (0.65 μmol J^{-1}) of reducing radicals in this medium, indicating that all reducing radicals formed react efficiently with phthalocyanine. The λ_{max} values found in this study are in agreement with those reported before.[16] The Co(I) complex is stable in the absence of O_2 but is quantitatively reoxidized by O_2 to the Co(II) complex.

The λ_{max} values given above were very similar in neutral and alkaline solutions, but in acidic solutions the spectrum was blue shifted by several nanometers, possibly due to protonation of the sulfonate groups. The monomer/dimer mixture $[Co^{I}TSPc]^-$/$[Co^{I}TSPc]_2^{2-}$ produced by radiolysis in deoxygenated formic acid solutions at pH 2 underwent partial reoxidation to Co^{II}TSPc/$[Co^{II}TSPc]_2$ within several hours, whereas no such recovery was found at pH 5. Slow partial protonation of $[Co^{I}TSPc]^-$/$[Co^{I}TSPc]_2^{2-}$ in strong acid may lead to formation of an unstable hydride. However, no long-lived hydride was found.

Irradiation of the $[Co^{I}TSPc]^-$/$[Co^{I}TSPc]_2^{2-}$ mixture at all pH values led to a gradual bleaching of all the peaks (Figures 1a and 2a show representative results in alkaline solutions). The final products are probably formed by disproportionation of the reduced $[Co^{I}TSPc]^-$/$[Co^{I}TSPc]_2^{2-}$ leading to hydrogenation of the macrocycle. Addition of O_2 after the bleaching did not recover all of the original complex. The radiolytic yield for reduction of $[Co^{I}TSPc]^-$/$[Co^{I}TSPc]_2^{2-}$ in aqueous formate solutions, to form the colorless products, was ∼10 times lower than that for reduction of Co^{II}TSPc/$[Co^{II}TSPc]_2$ to $[Co^{I}TSPc]^-$/$[Co^{I}TSPc]_2^{2-}$. The lower yield implies that the second step consumes more than one electron per phthalocyanine molecule, as well as a complicated reaction of $^\bullet CO_2^-$ with $[Co^{I}TSPc]^-$/$[Co^{I}TSPc]_2^{2-}$ (see below).

Similar experiments with $ClFe^{III}$TSPc (mostly dimeric[17] in aqueous formate solutions, pH 7.6) showed stepwise reduction of this complex (λ_{max} 327, 628 nm) to $[Fe^{II}TSPc]_2$ (λ_{max} 322, 428, 606, 667 nm) and then to $[Fe^{I}TSPc]_2^{2-}$ (λ_{max} 320, 490, 600(sh), 700, 830 nm). Further reduction led to bleaching of all peaks. Air oxidation led to full recovery of $[Fe^{II}TSPc]_2$ from the Fe(I) complex but not from the further reduced species. Both $[Co^{I}TSPc]^-$ and $[Fe^{I}TSPc]^-$ (monomer−dimer mixtures), prepared by radiolytic reduction in the presence of formate and CO_2 at pH 5.8, were stable for hours in the absence of O_2.

Pulse radiolysis of $[Co^{I}TSPc]^-$ (or its monomer/dimer mixture) was carried out to observe the short-lived species produced by one-electron reduction. The $[Co^{I}TSPc]^-$ was prepared by reduction of Co^{II}TSPc with H_2 on Pd (5% in alumina) or by γ-radiolytic reduction. Pulse radiolysis experiments with Co^{II}TSPc were carried out for comparison. Co^{II}TSPc (monomeric, deoxygenated aqueous solutions, 50% 2-PrOH, pH 12.4) was reduced in two steps, by a rapid reaction

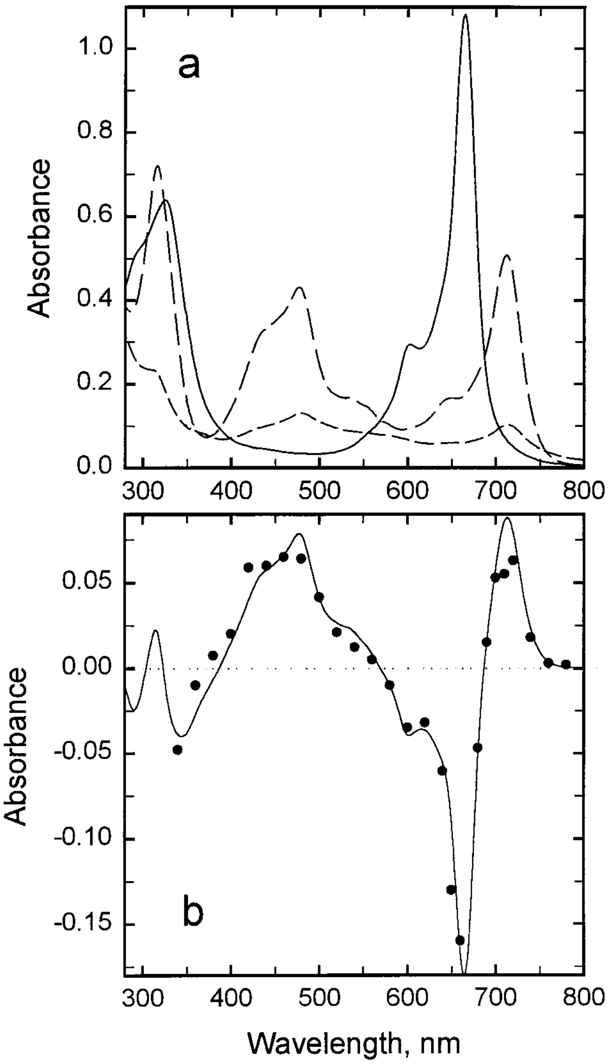

Figure 1. (a) Absorption spectra recorded upon γ-radiolytic reduction of $Co^{II}TSPc$ (solid line) to $[Co^{I}TSPc]^-$ (long-dashed line) and subsequent products (short-dashed line) in deoxygenated aqueous solutions containing 50% 2-PrOH at pH 12.8. (b) Differential absorption spectrum recorded by pulse radiolysis of deoxygenated aqueous solutions containing 50% 2-PrOH and 1.7×10^{-5} mol L^{-1} $Co^{II}TSPc$ at pH 12.4, recorded 500 μs after the pulse, dose per pulse 5 Gy.

with e_{aq}^- ($k \sim 2 \times 10^{10}$ L mol^{-1} s^{-1}) and a slower reaction with $(CH_3)_2\dot{C}O^-$ ($k \sim 7 \times 10^8$ L mol^{-1} s^{-1}). The spectra monitored after either step were identical, indicating that both reactions yield the same product. The difference spectrum (Figure 1b, circles) is in good agreement with the calculated difference (solid line) between the spectra of $Co^{II}TSPc$ and $[Co^{I}TSPc]^-$ from Figure 1a.

Pulse radiolytic reduction of $[Co^{I}TSPc]_2^{2-}$ (mostly dimeric, 0.1 mol L^{-1} formate solutions, pH 13) also took place in two steps. The rate constants for reactions with e_{aq}^- and with $^{\bullet}CO_2^-$ radicals were determined by following the kinetics of e_{aq}^- decay at 760 nm and the kinetics of product formation at 550 nm as a function of phthalocyanine concentration. The rate constants were found to be $(6.5 \pm 1.0) \times 10^9$ L mol^{-1} s^{-1} for e_{aq}^- and $(5.5 \pm 0.8) \times 10^7$ L mol^{-1} s^{-1} for $^{\bullet}CO_2^-$. The difference spectrum monitored after reduction (Figure 2b) shows bleaching of $[Co^{I}TSPc]_2^{2-}$ and formation of absorption mainly at 480−580 nm, which may be ascribed to the reduced complex. The spectral changes observed at different times after the pulse were similar, indicating that reduction took place by both e_{aq}^- and $^{\bullet}CO_2^-$ to form the same species. Experiments in neutral solutions, however, showed that the difference spectrum monitored 10 μs after the pulse has somewhat similar absorption at 480−580 nm as that observed at high pH, but the spectrum monitored 500 μs later, after the reaction with $^{\bullet}CO_2^-$ is complete (Figure 2c), is different. At 680 nm there is further bleaching of the reactant, at 580 nm the absorbance increases, and at 480 nm does not change. Under N_2O, where the reaction with e_{aq}^- is eliminated and replaced by reaction with $^{\bullet}CO_2^-$, the spectrum observed after 500 μs was similar to that found at 500 μs in the absence of N_2O. Experiments at pH 5.8 under CO_2, where again the reaction with e_{aq}^- is replaced by reaction with $^{\bullet}CO_2^-$, showed a spectrum (Figure 2d) with a peak at 580 nm but no peak at 480 nm. As suggested for other Co(I) complexes,[18] the reaction of $[Co^{I}TSPc]^-$ with $^{\bullet}CO_2^-$ may proceed via addition:

$$[Co^{I}TSPc]^- + {}^{\bullet}CO_2^- \rightarrow [CO_2CoTSPc]^{2-} \qquad (5)$$

The adduct can react via two routes: (a) at high pH with OH^- to form $[Co^{I}TSPc^{\bullet-}]^{2-}$ and HCO_3^-, and (b) at low pH with water or protons to form a hydride $[HCo^{II}TSPc]^-$. As the pH is changed the rate of formation of the hydride or $[Co^{I}TSPc^{\bullet-}]^{2-}$ predominates. This suggests that the 480 and 580 nm peaks are due mainly to $[Co^{I}TSPc^{\bullet-}]^{2-}$ and $[HCo^{II}TSPc]^-$, respectively. We cannot rule out, however, that the monomer−dimer equilibrium is also changing with protonation. The 580 nm absorption at pH 5.8 was found to decay over 10 s. The kinetics followed a first-order rate law with $k = (0.24 \pm 0.03)$ s^{-1}. To further characterize these intermediates, reduction was carried out in organic solvents.

Reduction of Cobalt Phthalocyanine by Sodium. Stepwise reduction of $Co^{II}TBPc$ was carried out by sodium mirror in THF solutions. The colors and the optical absorption spectra of the various reduction products (Figure 3 and Table 1) are similar to those observed by Clack and Yandle.[19] In THF solutions UV−vis spectra show no indication of dimer formation. $Co^{II}TBPc$ and the one-electron-reduced species exhibit absorptions in the UV and visible regions but no absorptions in the near-IR region (800−1600 nm), indicating that the electron is primarily located at the cobalt center to produce $[Co^{I}TBPc]^-$. The species formed by subsequent reductions, however, exhibit intense IR absorptions. The second reduction product has peaks at 918 and 1152 nm and, therefore, may be characterized as a π-radical anion[19] $[Co^{I}TBPc^{\bullet-}]^{2-}$ rather than $[Co^{0}TBPc]^{2-}$. All subsequent reduction products also exhibit IR absorptions. Addition of a large excess of 18-crown-6 to the THF solution to inhibit formation of ion pairs such as $Na_2[Co^{I}TBPc^{\bullet-}]$ did not change the spectral features significantly.

Addition of CO_2 to the THF solution of $[Co^{I}TBPc^{\bullet-}]^{2-}$ resulted in an immediate color change from dark red to olive-green. The spectrum of the product was that of $[Co^{I}TBPc]^-$, which remained stable for many hours in the presence of CO_2. We interpret these findings by the following reactions:

$$[Co^{I}TBPc^{\bullet-}]^{2-} + CO_2 \rightarrow [CO_2CoTBPc]^{2-} \qquad (6)$$

$$[CO_2CoTBPc]^{2-} + CO_2 \rightarrow Co^{II}TBPc + CO + CO_3^{2-} \qquad (7)$$

$$Co^{II}TBPc + [Co^{I}TBPc^{\bullet-}]^{2-} \rightarrow 2\,[Co^{I}TBPc]^- \qquad (8)$$

$$Co^{II}TBPc + [CO_2CoTBPc]^{2-} \rightarrow 2\,[Co^{I}TBPc]^- + CO_2 \qquad (9)$$

$[Co^{I}TBPc^{\bullet-}]^{2-}$ reacts with CO_2 to form a complex, which decomposes to CO and $Co^{II}TBPc$. This decomposition may be enhanced by CO_2, since no protons are available to accept the

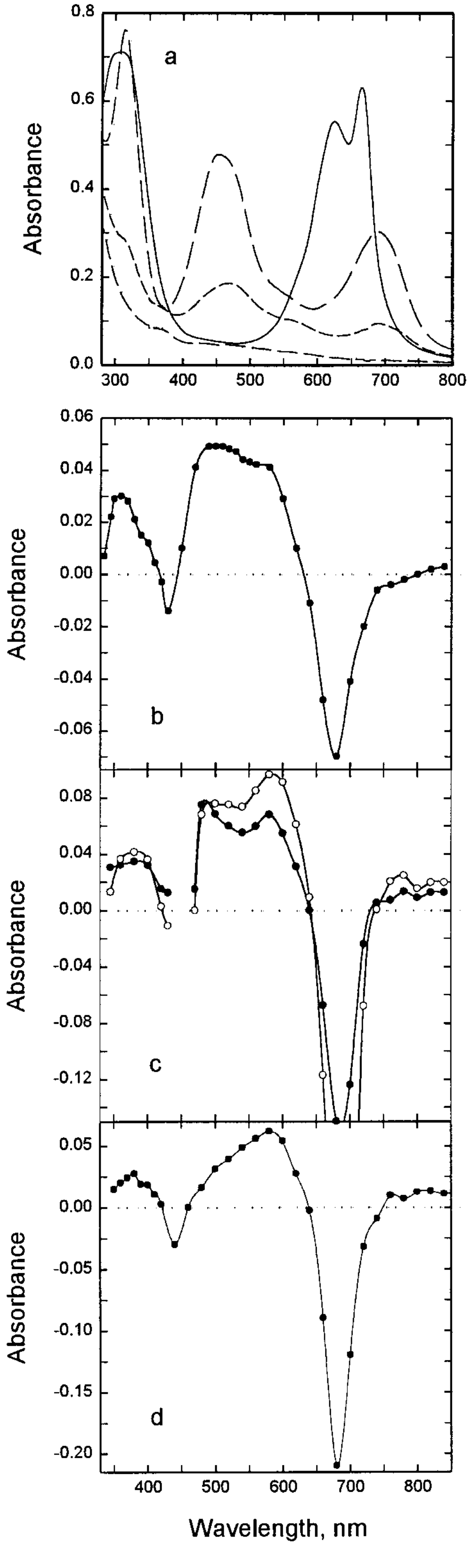

Figure 2. (a) Absorption spectra recorded upon γ-radiolytic reduction of a mixture of $[Co^{II}TSPc]_2$ (>70%) and $Co^{II}TSPc$ (<30%) (solid line) to a mixture of $[Co^{I}TSPc]_2^{2-}$ and $[Co^{I}TSPc]^-$ (long-dashed line) and subsequent products (short-dashed lines) in deoxygenated aqueous solutions containing 0.1 mol L^{-1} HCO_2^- at pH 13.[29] (b,c,d) Differential absorption spectra recorded by pulse radiolysis of aqueous solutions containing 0.1 mol L^{-1} HCO_2^- and $[Co^{I}TSPc]^-/[Co^{I}TSPc]_2^{2-}$, prepared by reduction of $Co^{II}TSPc/[Co^{II}TSPc]_2$ with H_2 on Pd; (b) 6×10^{-5} mol L^{-1} complex, pH 13, Ar-saturated, spectrum monitored 15 μs after the pulse, dose per pulse 5 Gy; (c) 7×10^{-5} mol L^{-1} complex, pH 7.6, Ar, 10 μs (●) and 500 μs (○), dose per pulse 13 Gy; (d) 1×10^{-4} mol L^{-1} complex, 0.01 mol L^{-1} HCO_3^-, pH 5.8, bubbled CO_2, 500 μs after the pulse, dose per pulse 13 Gy.

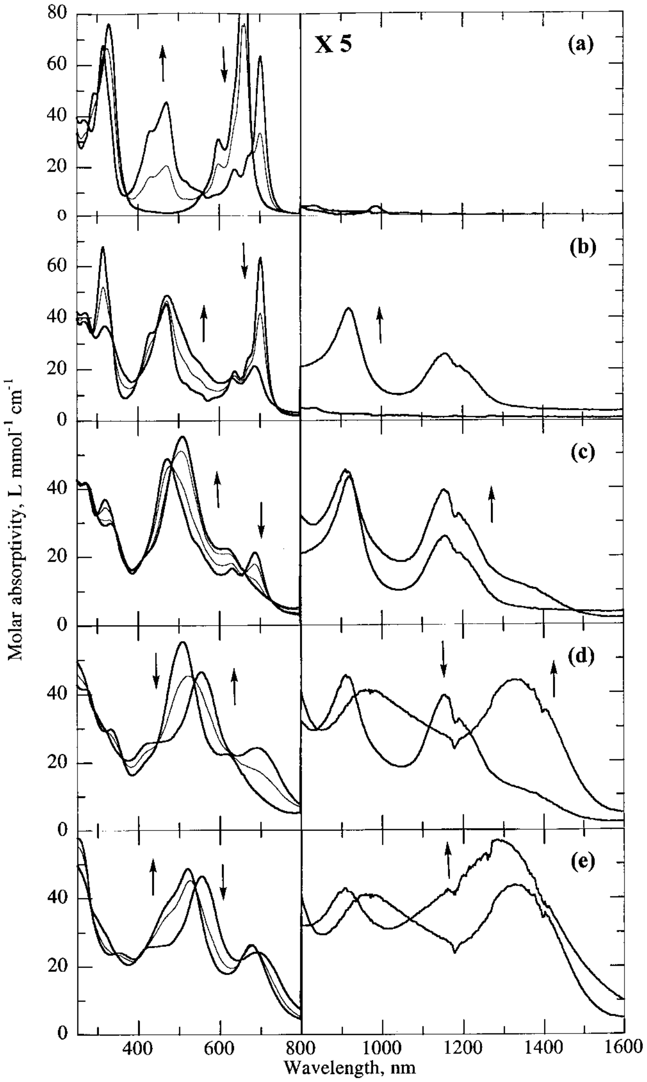

Figure 3. Absorption spectra recorded upon reduction of $Co^{II}TBPc$ by sodium mirror in THF solutions: (a) blue $Co^{II}TBPc \rightarrow [Co^{I}TBPc]^-$, olive-green, (b) $[Co^{I}TBPc]^- \rightarrow [Co^{I}TBPc^{\bullet -}]^{2-}$, red, (c) $[Co^{I}TBPc^{\bullet -}]^{2-} \rightarrow [CoTBPc]^{3-}$, purple, (d) $[CoTBPc]^{3-} \rightarrow [CoTBPc],^{4-}$ violet, (e) $[CoTBPc]^{4-} \rightarrow [CoTBPc],^{5-}$ violet.

TABLE 1: Spectroscopic Properties of CoTBPc in THF[a]

CoTBPc	color	λ_{max}, nm (10^{-3} ϵ, L mol^{-1} cm^{-1})
$Co^{II}TBPc$	blue	240 (47), 294 (50), 330 (78), 598 (31), 662 (130)
$[Co^{I}TBPc]^-$	olive-green	268 (40), 313 (70), 430 (35), 468 (47), 636 (19), 674sh (25), 701 (65)
$[Co^{I}TBPc^{\bullet -}]^{2-}$	red	272 (43), 318 (36), 470 (47), 628 (16), 688 (19), 918 (6.1), 1152 (3.7)
$[CoTBPc]^{3-}$	purple	278sh (42), 338 (29), 426sh (22), 508 (55), 610sh (22), 914 (6.4), 1150 (5.6)
$[CoTBPc]^{4-}$	violet	420sh (26), 556 (47), 696 (24), 965 (5.8), 1330 (6.2)
$[CoTBPc]^{5-}$	violet	356 (25), 466sh (40), 519 (52), 675 (28), 908 (6.0), 1282 (8.1)

[a] Molar absorption coefficients were calculated by assuming 100% conversion from $Co^{II}TBPc$. Their estimated standard uncertainties are ±10%.

oxide. The subsequent reactions, eqs 8 and 9, must be fast to effect practically complete conversion of the phthalocyanine into $[Co^{I}TBPc]^-$. $[Co^{I}TBPc]^-$ does not react with CO_2. These results are in agreement with previous spectroelectrochemical results,[9a] where $[Co^{I}Pc]^-$ was reduced to $[Co^{I}Pc^{\bullet -}]^{2-}$ in DMF solutions,

TABLE 2: Absorption Peaks of Various M^{II} and M^{I} Phthalocyanines in Different Solvents

CoPc	solvent	λ_{max}, nm				
Co^{II}TBPc	THF	240	294	330	598	662
Co^{II}TBPc	MeCN	240sh	290	324	601	663
Co^{II}TBPc	DMF		295sh	329	601	664
Co^{II}Pc	DMF		288	328	594	656
Co^{II}TSPc	H_2O/PrOH			326	600	664
[Co^{II}TSPc]$_2$	H_2O			~310		622
[Co^{I}TBPc]$^-$	THF	313	430	468	636	701
[Co^{I}TBPc]$^-$	MeCN	311	427	467	638	702
[Co^{I}Pc]$^-$	DMF	310	422	464	632	698
[Co^{I}TSPc]$^-$	H_2O/PrOH	315	430	475		710
[Co^{I}TSPc]$_2$$^{2-}$	H_2O	312	448			688
Fe^{II}Pc	DMF	320	422	596	630	656
[Fe^{I}Pc]$^-$	DMF	322	518	597	660	830
[Fe^{II}TSPc]$_2$	H_2O	322	428	606		667
[Fe^{I}TSPc]$_2$$^{2-}$	H_2O	320	490	600sh	700	830

with similar spectra to those in Figure 3. In the presence of CO_2, electrochemical reduction resulted[9a] in no net change in the spectrum of [Co^{I}Pc]$^-$, indicating that the reduction product is oxidized by CO_2.

Electrochemical Reduction of Cobalt Phthalocyanine. Cyclic voltammetry measurements were carried out with Co^{II}TBPc in THF, using tetrabutylammonium hexafluorophosphate as an electrolyte and a glassy carbon working electrode. In Ar-saturated solutions two reversible reduction steps were observed, $E_{1/2}$(Co^{II}TBPc/Co^{I}TBPc$^-$) = −0.48 V and $E_{1/2}$(Co^{I}TBPc$^-$/Co^{I}TBPc^{2-}) = −1.54 V vs SCE, in the same range as reported before.[20] In the presence of CO_2, the first wave remained practically unchanged while the second showed increased current, indicating catalyzed reduction of CO_2 by [Co^{I}TBPc$^{\bullet-}$]$^{2-}$. This result is in agreement with an earlier report[8] and consistent with the reactions discussed in the previous section.

Photochemical Reduction of the Phthalocyanines. Cobalt and iron phthalocyanines have been shown to undergo photoreduction.[17,21] In analogy with the previous studies on metalloporphyrins,[6,7] we utilized TEA (5%, 0.36 mol L^{-1}) to photoreduce the phthalocyanines in organic solvents. In DMF solutions, Fe^{II}Pc was reduced to [Fe^{I}Pc]$^-$ and Co^{II}Pc was reduced to [Co^{I}Pc]$^-$; the positions of the observed absorptions are shown in Table 2 and are in agreement with literature values[19] and with those found in THF solutions for CoTBPc (Table 1). Photoreduction of Co^{II}TBPc to [Co^{I}TBPc]$^-$ in acetonitrile/TEA shows that the change in solvent and the substitution with the four *tert*-butyl groups have only small effects on the peak positions (Table 2). Furthermore, the spectra in the absence and presence of 5% TEA had identical peaks and very similar absorption coefficients, suggesting that the interaction of the metal center with TEA is weak. Further reduction of the Co(I) and Fe(I) complexes led to bleaching of all the peaks, indicating that the expected one-electron reduction products are unstable under these conditions.

The photochemical yields are increased by using *p*-terphenyl (TP) as a sensitizer, as demonstrated for Fe and Co porphyrins.[22] Photoreduction of Co^{II}TBPc to [Co^{I}TBPc]$^-$ in MeCN/TEA solutions became 70 times faster upon addition of 3 mmol L^{-1} TP. The quantum yield for this photoreduction process (316 nm, 5.4 × 10^{-5} mol L^{-1} Co^{II}TBPc, CO_2-saturated MeCN, 5% TEA, 3 mmol L^{-1} TP) was found to be 0.42 (molecules reduced per photon absorbed). The quantum yield decreased with decreasing concentration of Co^{II}TBPc and when the MeCN was not completely dry. These effects are due to the competition for the TP$^{\bullet-}$ between Co^{II}TBPc and water. Protonation of TP$^{\bullet-}$ forms TPH$^{\bullet}$, which does not reduce Co^{II}TBPc. The photo-Birch reduction of TP to produce dihydroterphenyl derivatives in DMF and MeCN was previously reported.[23]

Further photolysis of the above solutions led to complete bleaching. The quantum yield for this second step (with 5.4 × 10^{-5} mol L^{-1} Co^{II}TBPc) was 0.10 and CO was detected (~4 × 10^{-5} mol L^{-1}). When the resulting colorless solution was saturated with O_2, half of the original Co^{II}TBPc was recovered, indicating that part of the colorless products are intact macrocyclic complexes that can be reoxidized to yield the starting material. Whether the products can be reoxidized to the starting material depends on the extent and site of hydrogenation (as is known for the analogous porphyrin complexes). Further photolysis decreased the extent of oxidative recovery and produced much more CO (further details are given below).

Photoreduction of [Co^{I}TBPc]$^-$ in the presence of TEA and TP did not produce the expected [Co^{I}TBPc$^{\bullet-}$]$^{2-}$ because this product undergoes rapid protonation. To stabilize the product we made the solution alkaline by adding 1 mmol L^{-1} of sodium methoxide (as 1% of a 0.1 mol L^{-1} methanolic solution). Under these conditions, upon deoxygenation of the Co^{II}TBPc solution the color turned from blue to olive-green and the spectrum was that of the [Co^{I}TBPc]$^-$. A similar thermal reduction in the presence of base has been noted before with a Rh-porphyrin.[24] Photolysis of this [Co^{I}TBPc]$^-$ solution led to spectral changes which were identical to those observed upon sodium reduction of [Co^{I}TBPc]$^-$ to [Co^{I}TBPc$^{\bullet-}$]$^{2-}$ and indicate that the same product is formed. This photoreduction was quantitative in DMF solutions but not so in MeCN solutions due to the limited solubility of sodium methoxide. In DMF, further photolysis of the [Co^{I}TBPc$^{\bullet-}$]$^{2-}$ led to several additional steps of spectral changes, but none of these spectra matched those observed upon sodium reduction. Presumably, these photoreduction products of [Co^{I}TBPc$^{\bullet-}$]$^{2-}$ undergo protonation, leading to gradual saturation of the phthalocyanine double bonds. After extensive reduction, reoxidation by O_2 recovered only 6% of the original Co^{II}TBPc.[25]

Photochemical Reduction of CO_2. Preliminary photochemical experiments were carried out to compare CO yields of the FePc with FeTPP (CO_2-saturated DMF, 5% TEA).[6] The results show that FePc is less effective than FeTPP; the rate of production and the maximum yield of CO for FePc were 30% and 45% as compared with the FeTPP.[6] Photochemical production of CO increased upon TP addition. The total yield of CO (3 mmol L^{-1} TP, 0.15 mmol L^{-1} Fe^{II}Pc) reached 3.5 mmol L^{-1}, i.e., 10 times higher, and 20 times faster than in the absence of TP.

Further experiments on the photoreduction of CO_2 were performed using Co^{II}TBPc in MeCN (containing TEA and TP). The yield of formate lags behind the yield of CO (Figure 4a) in the early stages of photolysis but continues to rise after the yield of CO levels off. This indicates that the two products are formed via different routes. We determined the amount of Co^{II}TBPc recovered upon oxidation of the products by O_2. After 4, 15, and 30 min photolysis, the concentration of CO was 0.13, 0.48, and 0.99 mmol L^{-1}, respectively, and the fraction of recovered Co^{II}TBPc was 42%, 14%, and 3.4%, respectively. After longer photolysis times, only 1% was recovered. As discussed above, only a small fraction of the CO produced is formed by the [Co^{I}TBPc$^{\bullet-}$]$^{2-}$, while a parallel reaction leads to partial hydrogenation of the macrocycle. The partially hydrogenated products act as catalysts for CO_2 reduction, and upon oxidation they can reform the original Co^{II}TBPc. However, further hydrogenation leads to products that are not readily oxidized to the starting material, and the highly hydrogenated

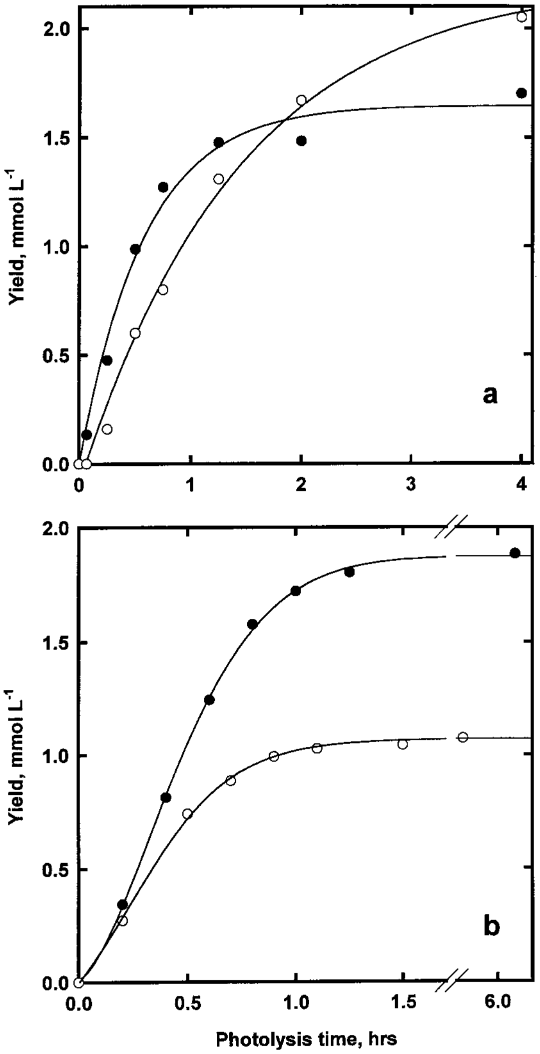

Figure 4. Photochemical production of CO and formate in CO_2-saturated MeCN solutions containing 5% TEA, 3×10^{-3} mol L^{-1} TP, and $\mathrm{Co^{II}TBPc}$. (a) The yields of CO (●) and formate (○) in solutions containing 4×10^{-5} mol L^{-1} $\mathrm{Co^{II}TBPc}$, photolyzed in individual spectrophotometer cells. (b) The yield of CO in solutions photolyzed in a Pyrex bulb, containing 4×10^{-5} (●) and 2×10^{-5} (○) mol L^{-1} $\mathrm{Co^{II}TBPc}$. The standard uncertainties are ± 10%.

products are not effective as reduction catalysts, possibly because of competition between CO and CO_2 for the metal binding site, as discussed before,[21] or because the complex decomposes. This explains why the rate of production and the total yield of CO parallels the concentration of $\mathrm{Co^{II}TBPc}$ (Figure 4b). The continued production of formate is ascribed to direct reaction of $\mathrm{TP}^{\bullet-}$ with CO_2, which was found to produce formate even in the absence of the metal complex.[23] From Figure 4 we calculate a turnover number of ~50 for CO production (moles of CO produced per mole of $\mathrm{Co^{II}TBPc}$).

Kinetics and Mechanisms. As has been found with the analogous porphyrins,[6,7] Fe(I) and Co(I) phthalocyanines are unreactive toward CO_2. Only the further reduced complexes react with CO_2. Direct photochemical reduction of these complexes by TEA is not efficient since there is no significant binding of TEA to the metal center. The use of *p*-terphenyl as a sensitizer is based on the highly efficient formation of the *p*-terphenyl radical anion by reaction of the singlet excited state of TP with TEA:[23]

$$\mathrm{TP} \xrightarrow{h\nu} \mathrm{TP}^* \tag{10}$$

$$\mathrm{TP}^* + \mathrm{Et_3N} \rightarrow \mathrm{TP}^{\bullet-} + \mathrm{Et_3N}^{\bullet+} \tag{11}$$

and the rapid reduction of the phthalocyanine by $\mathrm{TP}^{\bullet-}$, which has a highly negative reduction potential (−2.45 V vs SCE in dimethylamine):[23]

$$\mathrm{TP}^{\bullet-} + \mathrm{M^{II}Pc} \rightarrow \mathrm{TP} + [\mathrm{M^IPc}]^- \tag{12}$$

$$\mathrm{TP}^{\bullet-} + [\mathrm{M^IPc}]^- \rightarrow \mathrm{TP} + [\mathrm{M^IPc}^{\bullet-}]^{2-} \tag{13}$$

The TEA radical cation reacts with another TEA molecule to form a carbon-centered radical ($E_{1/2} = -1.12$ V vs SCE in MeCN)[26] that can reduce $\mathrm{Co^{II}Pc}$ but not $[\mathrm{Co^IPc}]^-$:

$$\mathrm{Et_3N}^{\bullet+} + \mathrm{Et_3N} \rightarrow \mathrm{Et_3NH}^+ + \mathrm{Et_2N\dot{C}HCH_3} \tag{14}$$

$$\mathrm{Et_2N\dot{C}HCH_3} + \mathrm{Co^{II}Pc} \rightarrow \mathrm{Et_2N^+{=}CHCH_3} + [\mathrm{Co^IPc}]^- \tag{15}$$

Pulse irradiation of a deoxygenated solution of TP (0.05 mol L^{-1}) in DMF leads to formation of $\mathrm{TP}^{\bullet-}$, which has several intense peaks between 400 and 500 nm and between 800 and 920 nm.[23,27] By monitoring the rate of decay at 840 nm as a function of phthalocyanine concentration, we determined the rate constants $k_{12} \cong 2 \times 10^{10}$ L mol^{-1} s^{-1} for $\mathrm{Co^{II}Pc}$, and $k_{13} = (7.8 \pm 1.2) \times 10^9$ L mol^{-1} s^{-1} for $[\mathrm{Co^IPc}]^-$ and $\cong 1 \times 10^{10}$ L mol^{-1} s^{-1} for $[\mathrm{Fe^IPc}]^-$, i.e., both reactions 12 and 13 are essentially diffusion controlled.

Although the reaction of $\mathrm{TP}^{\bullet-}$ with CO_2 is very slow ($k_{16} \sim 10^6$ L mol^{-1} s^{-1}),[3b,22]

$$\mathrm{TP}^{\bullet-} + \mathrm{CO_2} \rightarrow \mathrm{TP} + {}^\bullet\mathrm{CO_2}^- \tag{16}$$

it will compete with reaction 12 in our experiments, where the concentration of CO_2 is 4 orders of magnitude higher than that of the phthalocyanine. It is likely that most of the ${}^\bullet CO_2^-$ formed by reaction 16 will react with the MPc. When the phthalocyanine is hydrogenated, their reaction with ${}^\bullet CO_2^-$ radicals become slower and then these radicals may undergo disproportionation to form CO_2 and formate. This explains the lower yield of formate in the early stages of photolysis but higher yields later (Figure 4a).

To elucidate the mechanism of CO_2 reduction we carried out laser flash photolysis experiments with $[\mathrm{Co^ITBPc}]^-$. The $[\mathrm{Co^ITBPc}]^-$ was produced by CW photolysis of $\mathrm{Co^{II}TBPc}$ in MeCN with TP and TEA. During the preparation of the Co(I) complex significant amounts of protons are produced by reaction 14 ($[\mathrm{H}^+] = [\mathrm{Co(I)}]/2 = 2 \times 10^{-5}$ mol L^{-1}).

Flash photolysis of $[\mathrm{Co^ITBPc}]^-$ solutions in the presence of $NaOCH_3$ (4 mmol L^{-1}), added to scavenge protons, showed production of the $\mathrm{TP}^{\bullet-}$ radical within the laser pulse. The $\mathrm{TP}^{\bullet-}$ decays with $\tau \approx 5$ μs ($k \approx 10^9$ L mol^{-1} s^{-1}). The transient spectrum produced evolves ($\tau \approx 100$ μs) to a spectrum stable for > 20 ms (Figure 5a). At 8 ms after the flash the observed spectrum is identical to that of $[\mathrm{Co^ITBPc}^{\bullet-}]^{2-}$ obtained by sodium reduction. The initially produced spectrum shows a bleach at 700 nm due to loss of the Co(I) complex. In the region between ≈530 and ≈650 nm the initially formed spectrum has increased absorbance compared to the final spectrum. This spectral change is not likely to be due to formation of ion-pairs since reductions of $\mathrm{Co^{II}TBPc}$ by Na mirror with excess crown ether, to coordinate any free Na^+, gave practically the same spectra as in the absence of the crown ether. The spectral changes could result from an initially formed complex $[\mathrm{Co^ITBPc}^{\bullet-}]^{2-}|\mathrm{TP}$ or alternatively from structural changes in

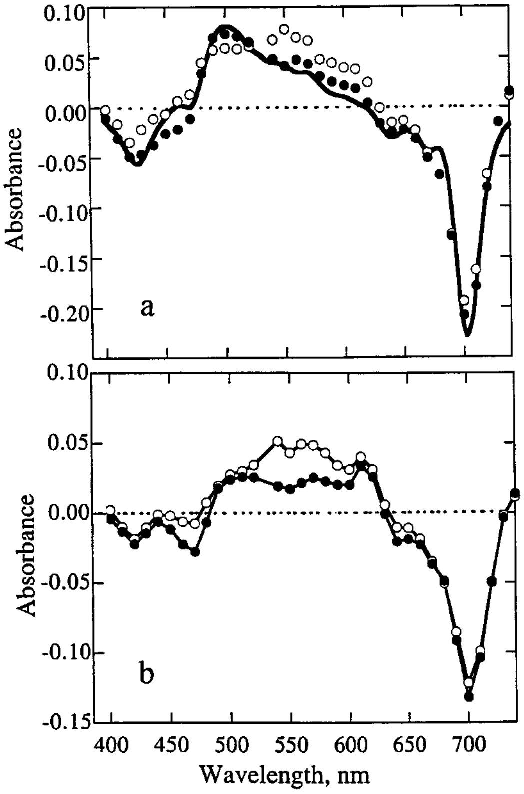

Figure 5. Differential absorption spectra recorded by flash photolysis of MeCN solutions containing 4 × 10^{-5} mol L^{-1} $[Co^ITBPc]^-$, 0.36 mol L^{-1} TEA, and 1 × 10^{-4} mol L^{-1} TP under vacuum. The spectra were monitored 10 μs (○) and 8 ms (●) after each laser pulse; (a) with 4 × 10^{-3} mol L^{-1} $NaOCH_3$, the solid line is the calculated difference spectrum obtained by Na mirror reduction of $[Co^ITBPc]^-$ in THF, (b) without $NaOCH_3$.

the $[Co^ITBPc^{\bullet -}]^{2-}$ (e.g., planarity of the macrocycle or metal movement relative to the plane of the macrocycle).

In the absence of $NaOCH_3$, flash photolysis produced the $TP^{\bullet -}$ radical which disappeared to produce a spectrum that again evolves ($\tau \approx 60$ μs) to a final spectrum that is stable for >20 ms. The initial species observed 10 μs after the flash exhibits a spectrum with peaks at 550 and 610 nm, somewhat similar to the initially observed spectrum with $NaOCH_3$. The final spectrum (Figure 5b) is not the same as that obtained with $NaOCH_3$. This suggests that, in the absence of $NaOCH_3$, the reduced Co complex is protonated:

$$[M^IPc^{\bullet -}]^{2-} + Et_3NH^+ \rightarrow [HMPc^{\bullet}]^- + Et_3N \qquad (17)$$

In CO_2-saturated solution, the initial and final spectra are the same as in the solutions with no added CO_2 and the final spectrum is stable for >20 ms. The only evidence of CO_2 binding is in the decay of the initially formed species that decays slightly faster with added CO_2 than without. From the above results we conclude that the reaction with CO_2

$$[M^IPc^{\bullet -}]^{2-} + CO_2 \rightarrow [CO_2MPc]^{2-} \qquad (18)$$

is either slower than we can observe with flash photolysis or the amount of the CO_2 adduct formed is small.

This conclusion of weak CO_2 binding to the doubly reduced $[Co^ITBPc^{\bullet -}]^{2-}$ complex is in contrast with earlier observations of strong CO_2 binding to singly reduced cobalt complexes of flexible (saturated) macrocycles such as cyclam.[3b,18,28] While part of the stability of the CO_2 binding to cyclam-like complexes is due to the hydrogen bonding interactions between the bound CO_2 and the macrocycle, we believe that additional effects are important. The extended π system of the phthalocyanine can better accommodate negative charge donated from the reduced metal center. This reduces the charge on the metal that can be back-donated to the CO_2. It may also be suggested that the relatively rigid planar structure of the phthalocyanine and the consequentially weaker axial ligation leads to the weak binding of CO_2. The photochemical formation of CO suggests that such binding does take place, but this binding does not compete favorably with the protonation reaction leading to hydrogenation of the macrocycle. When the phthalocyanine macrocycle is partially hydrogenated, it becomes more flexible and can probably bind CO_2 more strongly and catalyze its reduction, as observed in this work.

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(10) The $M^{II}Pc$ and $M^{II}TBPc$ complexes are neutral while the water-soluble $M^{II}TSPc$ complexes have an overall charge of 4− due to the four sulfonate groups on the periphery of the phthalocyanine. Because the effect of these charges on the redox reactions is secondary, and to have similar notations for all the phthalocyanines, we do *not* include these peripheral charges in our abbreviated notations. We will designate all of the metal(II) complexes as $M^{II}XPc$ while the singly and doubly reduced species are designated as $[M^IXPc]^-$ and $[M^IXPc^{\bullet -}]^{2-}$, respectively, where XPc = Pc, TBPc, or TSPc.

(11) The mention of commercial equipment or material does not imply recognition or endorsement by the National Institute of Standards and

Technology, nor does it imply that the material or equipment identified are necessarily the best available for the purpose.

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