Iron Porphyrin-Catalyzed Reduction of CO_2. Photochemical and Radiation Chemical Studies

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Several iron porphyrins have been reduced by photochemical and radiation chemical methods, in organic solvents and in aqueous solutions, from $Fe^{III}P$ to $Fe^{II}P$ to $Fe^{I}P$ and beyond. In aqueous solutions, the $Fe^{I}P$ state is relatively stable for the tetrakis(*N*-methyl-2-pyridyl)porphyrin at high pH but is shorter lived in neutral and acidic solutions. The $Fe^{I}P$ state of tetrakis(*N*-methyl-3-pyridyl)porphyrin and tetrakis(*N*-methyl-4-pyridyl)porphyrin are short-lived at any pH. Decay of $Fe^{I}P$ is accelerated by H^+ and by CO_2, probably via reaction with the $Fe^{0}P$ state formed upon disproportionation of $Fe^{I}P$. These reactions may lead to formation of H_2 and CO, respectively, and to formation of the chlorin, $Fe^{II}PH_2$, as a side product. The $Fe^{I}P$ state is also observed as a stable product in several organic solvents. This is observed by photolysis of iron tetraphenylporphyrin and several of its derivatives (e.g., trimethyl-, dichloro- and pentafluorophenyl), mainly in dimethylformamide and acetonitrile solutions, using triethylamine as a reductive quencher. Further photoreduction in the presence of CO_2 results in catalyzed reduction of CO_2 to CO and formation of (CO)$Fe^{II}P$. The yield of free CO increases with time of photolysis and reaches turnover numbers of ~70 molecules of CO per porphyrin molecule.

Introduction

Catalyzed reduction of CO_2 has been studied extensively as a means of energy storage.[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 these are nickel and cobalt cyclam (and related tetraaza macrocycles),[3−5] ruthenium and rhenium bipyridine complexes,[2,6] and several metalloporphyrins. Of the last group, iron porphyrins have been demonstrated to be the most efficient catalysts in the electrochemical reduction of CO_2 to CO.[7] The mechanism of transition-metal-catalyzed reduction of CO_2 has been shown to involve an intermediate complex between the metal and CO_2. Certain such complexes have been observed as stable products or short-lived intermediates, e.g., with Ni(cyclam)$^+$ and with CoL$^+$ (L = various tetraaza macrocycles).[5,8] The rate of formation of CO_2 complexes and their stability constants were strongly dependent on the ligand structure and were particularly sensitive to steric effects. By comparison with the flexible structures of cyclam and related macrocycles, porphyrins have larger and more rigid planar structures which are more likely to hinder the binding of CO_2 to the metal center or to destabilize the complex formed. Furthermore, because of their conjugated π-system, porphyrin ligands readily accept electrons in a process that may compete with the reduction of the metal center and thus hinder reduction of CO_2. Nevertheless, several iron porphyrins have been shown to catalyze electrochemical reduction of CO_2,[7] and the mechanism was suggested to involve formation of an intermediate Fe−CO_2 complex after the initial $Fe^{III}P$ is reduced in three distinct steps to reach the $Fe^{0}P$ oxidation state.

In the present study we utilize photochemical and radiation chemical techniques to examine several iron porphyrins in terms of their one-electron reduction steps and their possible role as catalysts for photoreduction of CO_2. Iron(III) porphyrins are known to undergo photoreduction to $Fe^{II}P$ upon excitation at their ligand-to-metal charge transfer band (at wavelengths below the Soret band), the axial ligand oxidized being either an alkoxide[9] or a halide.[10]

$$XFe^{III}P \xrightarrow{h\nu} X^{\bullet} + Fe^{II}P \tag{1}$$

The $Fe^{II}P$ produced in alcohol solutions was not affected by further illumination,[9] but we find that it can be photoreduced in several solvents in the presence of strong reductive quenchers such as triethylamine. Continued photolysis under certain conditions is found to lead to reduction of CO_2 to CO. Reduction of $Fe^{II}P$ was studied also by radiolysis. The stability of the $Fe^{I}P$ produced depends on the porphyrin structure and the medium.

Experimental Section[11]

Most photochemical experiments were carried out with iron tetraphenylporphyrin, and most radiolysis experiments were carried out with water-soluble porphyrins. The porphyrins used and their abbreviations are as follows: tetraphenylporphyrin (TPP), tetramesitylporphyrin (TMP, mesityl = 2,4,6-trimethylphenyl), tetrakis(2,6-dichlorophenyl)porphyrin (TCPP), tetrakis(pentafluorophenyl)porphyrin (TFPP), 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetramesitylporphyrin (OBTMP), the picket fence porphyrin α,α,α,α-tetrakis[2-(2,2-dimethylpropionamidyl)-phenyl]porphyrin (PFP), octaethylporphyrin (OEP), tetrakis(4-sulfonatophenyl)porphyrin (TSPP), tetrakis(*N*-methyl-4-pyridyl)-

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porphyrin (TM4PyP), tetrakis(*N*-methyl-3-pyridyl)porphyrin (TM3PyP), tetrakis(*N*-methyl-2-pyridyl)porphyrin (TM2PyP), and tetraphenylchlorin (TPC). They were obtained from Mid-Century Chemicals (Posen, IL) in the form of chloroiron(III) porphyrins, $ClFe^{III}P$. Triethylamine (TEA) and triethanolamine (TEOA) were from Aldrich; *N*,*N*-dimethylformamide (DMF), 2-propanol (2-PrOH), ethanol (EtOH), tetrahydrofuran (THF), acetonitrile, sodium formate, and the inorganic compounds were analytical grade reagents from Mallinckrodt. Water was purified with a Millipore Super-Q system. Fresh solutions were prepared before each experiment and were irradiated after purging with Ar or He to remove oxygen or with CO_2.

Photolysis was performed with either a 300 or 900 W xenon lamp, using water filters to absorb the IR and UV cutoff filters as specified. Radiolysis was performed in a Gammacell 220 ^{60}Co source with a dose rate of either 0.8 or 2.7 Gy s^{-1}. Changes in porphyrin structure were derived from spectrophotometric measurements, and the CO evolved was determined by gas chromatography (Carboxen-1000 column, thermal conductivity detector). To observe short-lived intermediates, pulse radiolysis was carried out with the apparatus described before,[12] which utilizes 50 ns pulses of 2 MeV electrons from a Febetron Model 705 accelerator. All experiments were performed at room temperature, 20 ± 2 °C.

Results and Discussion

Iron porphyrins were reduced by photochemical and by radiation chemical methods in various solvents. Reduction of $Fe^{III}P$ to the stable $Fe^{II}P$ was readily achieved under anaerobic conditions in various solvents, but reduction to $Fe^{I}P$ was discernible only at short times (by pulse radiolysis) or under conditions that this species is stable for many minutes. The photochemical experiments also provided evidence for catalyzed reduction of CO_2 to CO by some of the reduced porphyrins. We describe first the stepwise photochemical reduction in organic solvents, then the catalyzed CO_2 reduction, and finally the photochemical and radiolytic results in aqueous solutions.

Photochemical Reduction of $Fe^{III}P$ in Organic Solvents. Fe(III) porphyrins undergo photoreduction to the $Fe^{II}P$ state by excitation at the ligand-to-metal charge transfer band.[9,10] We carried out photoreduction of $ClFe^{III}TPP$ in DMF (and in acetonitrile, dimethyl sulfoxide, tetrahydrofuran, benzonitrile, and ethanol) and found that the process is greatly accelerated by the addition of triethylamine. (The time of photolysis was reduced by at least an order of magnitude.) In most experiments, $ClFe^{III}TPP$ was dissolved in DMF containing 5% TEA, where it forms several possible complexes with the solvent and the amine: $Et_3N(Cl)Fe^{III}TPP$, $DMF(Cl)Fe^{III}TPP$, $(Et_3N)_2Fe^{III}TPP$, $(Et_3N)(DMF)Fe^{III}TPP$. In dilute solutions the spectrum had two main peaks at 409 and 569 nm. Upon photolysis, these peaks decreased in intensity and were replaced with peaks at 432 and 560 nm ascribed to $Fe^{II}TPP$.[13] Photoreduction was very rapid with a 325 nm cutoff filter, but the rate decreased by a factor of ~30 with a 385 nm cutoff filter and by a factor of ~150 with a 420 nm cutoff filter. These results suggest that excitation at the Soret band does not lead to reduction and that the observed process is most likely an intramolecular electron transfer from the axially bound TEA to the iron center.

$$Et_3N(Cl)Fe^{III}P \xrightarrow{h\nu} Et_3N^{\bullet+} + Cl^- + Fe^{II}P \tag{2}$$

The $Et_3N^{\bullet+}$ radical cation is capable of oxidizing the $Fe^{II}P$. This back electron transfer, however, may be suppressed by a competing reaction[14] that converts the radical cation into a reducing species, which may reduce another $Fe^{III}P$.

$$Et_3N^{\bullet+} + Et_3N \rightarrow Et_3NH^+ + Et_2N\dot{C}HCH_3 \tag{3}$$

$$Et_2N\dot{C}HCH_3 + ClFe^{III}P \rightarrow Et_2N^+{=}CHCH_3 + Fe^{II}P + Cl^- \tag{4}$$

The efficiency of photoreduction was the same with 5 and 10% TEA and was reduced by only 40% when the TEA volume fraction was lowered to 1%. We chose 5% TEA (0.36 mol L^{-1}) as the standard concentration for most subsequent experiments. Saturating the above solutions with CO_2 (~0.24 mol L^{-1}) had little effect on the rate of photoreduction.

The quantum yield for photoreduction under the present conditions was estimated by comparison with the reported value for photoreduction of $Fe^{III}TPP$ in alkaline ethanol solutions, which is 0.016 for photolysis at 355 nm.[15] By running parallel experiments with $Fe^{III}TPP$ in alkaline ethanol and in DMF solutions containing 5% TEA, at 360 ± 20 nm (using a combination of filters), we found the latter system to be about 3 times more efficient. This leads to a quantum yield for photoreduction of $Fe^{III}TPP$ in DMF/TEA of approximately 0.05.

Photochemical Reduction of $Fe^{II}P$ in Organic Solvents. Further illumination of the solutions of $Fe^{II}TPP$, obtained in the above experiments, resulted in reduction of this species to $Fe^{I}TPP$, but the process was much less efficient. With the 325 or 385 nm cutoff filters, the efficiency of photoreduction of $Fe^{II}TPP$ was about 20% that of photoreduction of $Fe^{III}TPP$ under the same conditions. With the 420 nm cutoff filter, however, reduction of $Fe^{II}TPP$ was about 10 times slower than reduction of $Fe^{III}TPP$. The mechanism must be similar to that outlined above, i.e., excitation of the ligand-to-metal charge transfer band.

$$Et_3NFe^{II}P \xrightarrow{h\nu} Et_3N^{\bullet+} + (Fe^{I}P)^- \tag{5}$$

The concentration of TEA had a stronger effect here than in the photoreduction of $Fe^{III}TPP$; decreasing TEA from 5 to 1% decreased the rate of photoreduction of $Fe^{II}TPP$ by a factor of 3.5 (as compared with a factor of only 1.7 for the first reduction step). This effect may be due to weaker binding of TEA to $Fe^{II}TPP$, as compared with $Fe^{III}TPP$, thus requiring higher TEA concentrations to bind more of the $Fe^{II}TPP$ in order to increase the effectiveness of reaction 5.

It should be noted that photoreduction in alkaline ethanol solutions not containing TEA was considerably less efficient. The quantum efficiency for the Fe^{III} to Fe^{II} reduction step was about 3 times lower, as mentioned above, but for the Fe^{II} to Fe^{I} reduction step it was extremely low. In fact, even after photolysis for periods 100 times longer than those required for reduction of $Fe^{II}TPP$ in DMF/TEA, no reduction was observable in alkaline ethanol.

Photoreduction of $Fe^{II}TPP$ in most cases did not lead to quantitative conversion into $Fe^{I}TPP$ (Figure 1a). As the peaks of $Fe^{II}TPP$ (431 and 562 nm) gradually decayed, new peaks ascribed to $Fe^{I}TPP$ (~520 nm peak and weak bands at 670 and 710 nm) were formed, but upon continued photolysis additional peaks became apparent, mainly those of $(CO)Fe^{II}TPP$ (sharper peaks at 420 and 540 nm), the chlorin (where one β-pyrrole double bond is saturated), $Fe^{II}PH_2$ (424 and 613 nm), and then the isobacteriochlorin (where the β-pyrrole double bonds of two adjacent pyrrole rings are saturated), $Fe^{II}{-}PH_4$ (420 and 600 nm).

Under CO_2, however, a steady-state concentration of $Fe^{I}TPP$ was achieved within a short time, and most of the porphyrin was converted to $(CO)Fe^{II}TPP$ (Figure 1b). Only much longer irradiations resulted in reduction and eventual destruction of

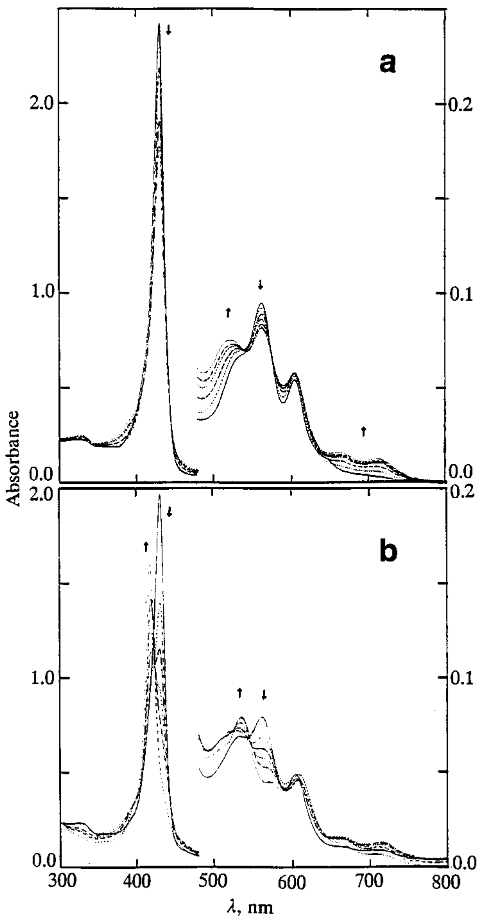

Figure 1. Photochemical reduction of $Fe^{II}TPP$ (5×10^{-5} mol L^{-1}) solutions in DMF containing 5% TEA: (a) under Ar and (b) under CO_2. The arrows show bleaching of the $Fe^{II}TPP$ absorptions and formation of the $Fe^{I}TPP$ absorptions. Under CO_2 the absorptions of both $Fe^{I}TPP$ and $(CO)Fe^{II}TPP$ are seen (see text).

the macrocycle. The relatively rapid formation of $(CO)Fe^{II}TPP$ under CO_2 suggests that CO is formed from CO_2. The observation of some $(CO)Fe^{II}TPP$ even in solutions bubbled with Ar indicates that some CO is formed from another source as well. This will be discussed below.

The various porphyrin products formed were distinguished also by their sensitivity to O_2. $Fe^{I}TPP$ is oxidized very rapidly, $Fe^{II}TPP$ is oxidized within minutes, $(CO)Fe^{II}TPP$ is oxidized much more slowly, within hours, and all yield $Fe^{III}TPP$, but the $Fe^{II}-PH_4$ is oxidized to products with only weak absorptions, indicating that the macrocycle is probably broken.[16] $(CO)Fe^{II}TPP$ also could be converted to $Fe^{II}TPP$ by bubbling the solution with Ar.

Catalyzed Photoreduction of CO_2. Photolysis of the iron porphyrins in DMF solutions containing 5% TEA and saturated with CO_2 led to stepwise reduction as described above and formation of $(CO)Fe^{II}P$ as the most stable product. This already indicates some reduction of CO_2 to CO under these conditions. Photolysis of $(CO)Fe^{II}TPP$ is known to decompose this complex to CO and $Fe^{II}TPP$ with a high quantum yield.[17] $Fe^{II}TPP$ can then recombine with CO or bind a different axial ligand such as TEA. In the latter case, photolysis will lead to further reduction of the iron and thus enable subsequent reduction of CO_2. Binding of CO to $Fe^{II}TPP$, therefore, inhibits the catalyzed photoreduction of CO_2, but only to a limited extent.

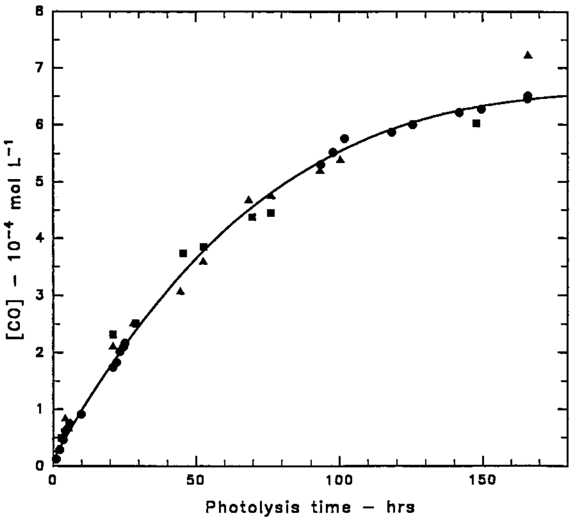

Figure 2. Photochemical production of CO in DMF solutions containing $ClFe^{III}TPP$, 5% TEA, and saturated with CO_2. Corrected for the small yield of CO observed under He (see text). The concentrations of $ClFe^{III}TPP$ were 1×10^{-5} (■), 2×10^{-5} (●), and (▲) 5×10^{-5} mol L^{-1}. The solutions were irradiated in a Pyrex bulb cooled by a water jacket, placed 10 cm away from an ILC Technology LX-300 UV lamp.

Continued photolysis builds up concentrations of CO much greater than the concentration of the porphyrin, and these could be analyzed by gas chromatography. For example, with a concentration of 2×10^{-5} mol L^{-1} $Fe^{III}TPP$, photoreduction to $Fe^{II}TPP$ and then partially to $Fe^{I}TPP$ was achieved within ~5 min, and subsequently CO production could be detected within 15 min of photolysis (under the conditions of Figure 2). The yield of CO increased with photolysis time and reached a turnover number of 40 CO molecules per porphyrin molecule. During photolysis, the porphyrin solution gradually turned green, as a result of chlorin formation, and eventually turned yellow, indicating destruction of the macrocycle, and production of CO eventually stopped. Reduction of CO_2 to CO also takes place by the chlorin, as confirmed by an experiment in which authentic $ClFe^{III}TPC$ was used as the starting material. The results indicate that the efficiency of the chlorin in reducing CO_2 is similar to that of the original porphyrin.

To estimate the amount of CO that may be produced from other sources, similar photolysis experiments were carried out in solutions saturated with He instead of CO_2. (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.) The amount of CO formed was about 4 times lower than that formed under CO_2. These results were obtained with a porphyrin concentration of 1×10^{-5} mol L^{-1}, but at higher porphyrin concentrations the amount of CO formed under He was relatively smaller; with 1×10^{-4} mol L^{-1} porphyrin it was negligibly small compared to that formed in the presence of CO_2. The possibility that this CO is formed following fragmentation of the porphyrin macrocycle is ruled out, since CO began to be produced at the early stages of the photolysis, before substantial amounts of the porphyrin were decomposed. Furthermore, CO was also formed to a similar extent in the photolysis of iron phthalocyanine under the same conditions. The possibility that CO is a product of TEA oxidation is also ruled out, since photochemical experiments with 1% TEA and 10 mM $S_2O_8^{2-}$ in water, where UV photolysis leads to formation of $SO_4^{\bullet -}$ which oxidizes TEA, showed that the persulfate was decomposed but not CO was formed. Most likely, CO is formed from the DMF solvent, not by direct photolysis, but only in the presence of the porphyrin, i.e., through partial complexation of FeP with DMF (instead of TEA) and direct photolysis of the complex $HCON(CH_3)_2-FeTPP$ to result in oxidation of the solvent-ligand to $^{\bullet}CON$-

$(CH_3)_2$. This radical may decompose to CO and $^{\bullet}N(CH_3)_2$, as indicated by the radiolysis of neat DMF, which yields considerable amounts of CO ($G = 0.27\ \mu mol\ J^{-1}$) probably via the same intermediate. This is further confirmed by replacing DMF with acetonitrile as solvent for the photoreduction of FeP with TEA. The yield of CO in solutions saturated with CO_2 was similar in the two solvents, but the yield of CO in the absence of CO_2 was 30 times lower in acetonitrile than in DMF.

The yield of CO from CO_2 was determined by subtracting the amount of CO formed under He from that measured under CO_2. The corrected yield as a function of photolysis time (Figure 2) is found to be similar for 1×10^{-5}, 2×10^{-5}, and 5×10^{-5} mol L^{-1} FeTPP. Under the conditions used in these experiments, all the light is absorbed by the solution even at the lowest porphyrin concentration used, and therefore, the yield does not increase with concentration. The plateau level also remains the same, indicating faster decomposition of the porphyrin at higher concentrations. This may be due to competition between reaction of $Fe^{0}TPP$ with CO_2 and reaction of $Fe^{0}TPP$ with other reduced porphyrin species leading to the reduction or destruction of the macrocycle. The former reaction is pseudo-first-order and thus independent of initial $Fe^{III}TPP$ concentration, but the latter process is second-order and thus will increase in importance at high absorbances (high local concentrations of reduced porphyrin). As a result, decomposition of the macrocycle is more effective at higher concentrations. With 1×10^{-5} mol L^{-1} $Fe^{III}TPP$, the yield of CO at the plateau level corresponds to a turnover number of 70.

Various iron porphyrins have been studied under the same conditions for comparison with the FeTPP. Both the rate of CO production and its total yield varied slightly. The rate was similar with TPP and TMP, was slightly lower (~20%) with TCPP and TFPP, and slightly higher (10%) with OBTMP. OEP was less effective (by 30%), PFP even less (50%), the tetrapropylporphycene gave only one-third of the yield, and the phthalocyanine was much less effective.

In electrochemical reduction of CO_2 with iron porphyrins,[7] it has been shown that the process is catalyzed by water and by Brönsted acids in general. Therefore, no effort was made in the present study to dry the organic solvents from traces of water. In fact, addition of 0.1−5% water was found to increase the rate of production of CO from CO_2. However, the rate of CO production from the DMF solvent also was increased by addition of water, and it was difficult to determine the effect of water on the catalytic reduction of CO_2. This effect could be quantitated in acetonitrile solutions, where the yield of CO from other sources was very low. Addition of 1% water increased the yield of CO from CO_2 by 30% while the yield in the absence of CO_2 remained very low. Experiments using water as solvent are discussed below.

Photochemical Reduction of Iron Porphyrins in Aqueous Solutions. These experiments were carried out mainly with $Fe^{III}TM2PyP$, which yields the most stable $Fe^{I}P$ state. Photolysis of this porphyrin in aqueous solutions containing 5% TEA and 0.05 mol L^{-1} $NaHCO_3$ at pH 11.4, deoxygenated by bubbling with Ar, resulted in rapid reduction of $Fe^{III}TM2PyP$ (~430 and ~580 nm) to $Fe^{II}TM2PyP$ (442 and 564 nm). Subsequent photoreduction was ~40 times less efficient and produced $Fe^{I}TM2PyP$. This product exhibits a weak maximum at ~430 nm and broad absorptions around 520 nm and around 600−800 nm, similar to those reported previously[18] and to those described above for $Fe^{I}TPP$. Along with $Fe^{I}TM2PyP$, two other reduction products were formed in small yields, the phlorin anion, $Fe^{II}PH^{-}$ (the product of two-electron reduction and single protonation at a meso position), exhibiting a very broad band centered at 800 nm, and the chlorin, $Fe^{II}PH_2$, with a sharp peak at 620 nm. Upon standing for several hours, the phlorin anion changed to the chlorin,[19] while the $Fe^{I}P$ reverted to $Fe^{II}P$. Exposure to O_2 converted these products to the chlorin, $Fe^{III}PH_2$ (655 nm), and the original $Fe^{III}P$.

Photolysis of $Fe^{III}TM2PyP$ in the presence of TEA and $NaHCO_3$ was also carried out in solutions that were bubbled with CO_2. Bubbling CO_2 decreased the pH to 8.8, and since at this pH the TEA is protonated to about 99%, the photolysis was less efficient, by a factor of 20 for the initial stage and by a factor of about 100 for the second reduction step. The product at this pH was predominantly the chlorin, $Fe^{II}PH_2$ (peaks at 418 and 616 nm). In an attempt to increase the efficiency of photoreduction, we replaced TEA ($pK_a = 10.7$) with TEOA ($pK_a = 7.8$). The quantum yield for photoreduction of $Fe^{III}TM2PyP$ was practically identical with these two amines and very similar to that found with $Fe^{III}TPP$ in DMF. Photoreduction of $Fe^{II}TM2PyP$, however, was much less efficient with TEOA, by a factor of ~500 in 5% TEOA solutions at pH 11 and by a factor of ~4000 in neutral solutions. This may result from weaker binding of TEOA to the Fe^{II} center and/or lower reduction potential, as compared with TEA, owing to the lower electron density on the amine nitrogen.

Continued photolysis of $Fe^{II}TM2PyP$ in aqueous solutions containing 5% TEA, 0.1 mol L^{-1} $NaHCO_3$, and CO_2 led to production of CO at concentrations similar to those of the porphyrin. Without $NaHCO_3$ the pH was lower, and the amount of CO formed was at least 10 times lower.

In contrast with the above results for $Fe^{III}TM2PyP$, the other water-soluble porphyrins examined, $Fe^{III}TM3PyP$ and $Fe^{III}TSPP$, when photoreduced under similar conditions, formed mainly the $Fe^{II}P$ products, with only small yields of the chlorin and decomposition products. No stable $Fe^{I}P$ state was observed, and no CO was detected under the same conditions that $Fe^{III}TM2PyP$ gave considerable CO yield. It should be noted, however, that when $Fe^{III}TSPP$ was photolyzed in DMF solutions, substantial amounts of CO were detected.

Radiolytic Reduction of Iron Porphyrins in Aqueous Solutions. Radiolytic reduction of Fe(III) porphyrins in aqueous[20] and in alcohol[21] solutions has been shown to lead to efficient production of Fe(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 as a scavenger for $H^{\bullet}$ and $^{\bullet}OH$, i.e., reduction of the porphyrin by all e_{aq}^{-} and $\dot{C}O_2^{-}$ radicals.

$$H_2O \rightsquigarrow e_{aq}^{-},\ H^{\bullet},\ {}^{\bullet}OH,\ H^{+},\ H_2,\ H_2O_2 \tag{6}$$

$$H^{\bullet}/{}^{\bullet}OH + HCO_2^{-} \rightarrow H_2/H_2O + \dot{C}O_2^{-} \tag{7}$$

$$ClFe^{III}P + e_{aq}^{-} \rightarrow Cl^{-} + Fe^{II}P \tag{8}$$

$$ClFe^{III}P + \dot{C}O_2^{-} \rightarrow Cl^{-} + Fe^{II}P + CO_2 \tag{9}$$

Further reduction by γ-radiolysis led to formation of various products from the various porphyrins studied under different conditions. Radiolytic reduction of $Fe^{II}TM2PyP$ in alkaline solutions led to the spectral changes shown in Figure 3, i.e., decrease of the two main peaks of $Fe^{II}TM2PyP$, shift of the Soret peak to 430 nm, and buildup of broad absorptions at 650−800 nm, indicating formation of $Fe^{I}TM2PyP$. As in the photolysis experiments, this product was formed along with small yields of the phlorin anion (broad 800 nm absorption) and the chlorin (sharp ~620 nm peak). The $Fe^{I}TM2PyP$ is

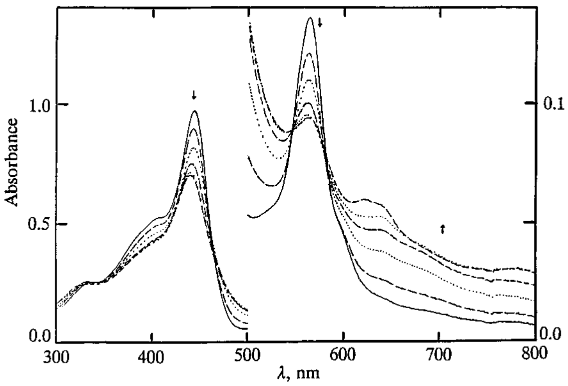

Figure 3. Radiolytic reduction of FeIITM2PyP (5×10^{-5} mol L^{-1}) in deoxygenated aqueous solutions containing 0.1 mol L^{-1} $HCOO^-$ and 1 mol L^{-1} KOH. The arrows show the stepwise increase or decrease in absorbance after each irradiation with a dose of 29 Gy.

stable under these conditions for many hours while the phlorin anion changes to the chlorin.[19] At lower pH, $Fe^{I}TM2PyP$ decayed more rapidly. For example, at pH 10 it decayed over 20 h and at pH 7 within 2 h. In neutral solutions, the radiolytic yield of $Fe^{I}TM2PyP$ was about half that observed in alkaline solutions and was produced along with considerable yields of the chlorin (peaks at 424 and 620 nm).

Several experiments were also carried out by using 2-PrOH as an OH scavenger instead of formate, and surprisingly, the results were different. Instead of reduction of $Fe^{II}TM2PyP$ to $Fe^{I}TM2PyP$ in alkaline solutions, the predominant product was the phlorin anion. The difference between these two systems may be due to a different mechanism of reaction of the two reducing species. Whereas $\dot{C}O_2^-$ reduces $Fe^{II}TM2PyP$ to $Fe^{I}TM2PyP$, the $(CH_3)_2\dot{C}O^-$ and $(CH_3)_2\dot{C}OH$ radicals formed from 2-PrOH add to the metal center of $Fe^{II}TM2PyP$ to form a transient $HO(CH_3)_2C{-}Fe^{III}TM2PyP$, which does not decompose to $Fe^{I}TM2PyP$ rapidly. Instead, this species survives in solution until it receives another electron. The electron is then added preferentially to the ligand to form the radical anion $HO(CH_3)_2C{-}Fe^{III}TM2PyP^{\bullet-}$. Release of $(CH_3)_2CO$ and H^+ from this species and protonation at the meso position of the porphyrin will form the phlorin anion observed.

Radiolytic reduction of $Fe^{II}TM3PyP$ did not yield a stable $Fe^{I}TM3PyP$ under any conditions. Reduction in neutral solutions resulted in the formation of the chlorin (peaks at 428 and 620 nm) whereas reduction in alkaline solutions formed the phlorin anion.[22]

Pulse Radiolysis Studies of Iron Porphyrins in Aqueous Solutions. To observe the short-lived species that lead to the above products, we utilized pulse radiolysis, where the solutions were irradiated with a short electron pulse and the differential absorption spectra were monitored within microseconds to milliseconds after the pulse. For these experiments, the starting materials, $Fe^{III}P$, were first reduced to $Fe^{II}P$ by H_2 on Pd and then pulse irradiated. The differential spectrum in Figure 4a shows bleaching of the $Fe^{II}TM2PyP$ absorption at 550 nm and formation of strong absorption below 520 nm and broad absorption at 600−840 nm. These changes are in agreement with those found by γ-radiolysis for the reduction of $Fe^{II}TM2PyP$ to $Fe^{I}TM2PyP$. The results indicate that even in slightly acidic solutions $Fe^{I}TM2PyP$ is the first product of reduction of $Fe^{II}TM2PyP$. The transient spectra obtained with $Fe^{II}TM3PyP$, $Fe^{II}TM4PyP$, and $Fe^{II}TSPP$ are generally quite similar to those obtained with $Fe^{II}TM2PyP$ and indicate formation of the $Fe^{I}P$ state by one-electron reduction. The alternative possibility, i.e., formation of the π-radical anions $Fe^{II}P^{\bullet-}$, is ruled out, since no strong broad peaks around 700 nm, characteristic for π-radical anions, have been observed in any of the above experiments. Thus, all the Fe^{II} porphyrins studied in aqueous solutions are reduced first at the metal to yield $Fe^{I}P$.[23]

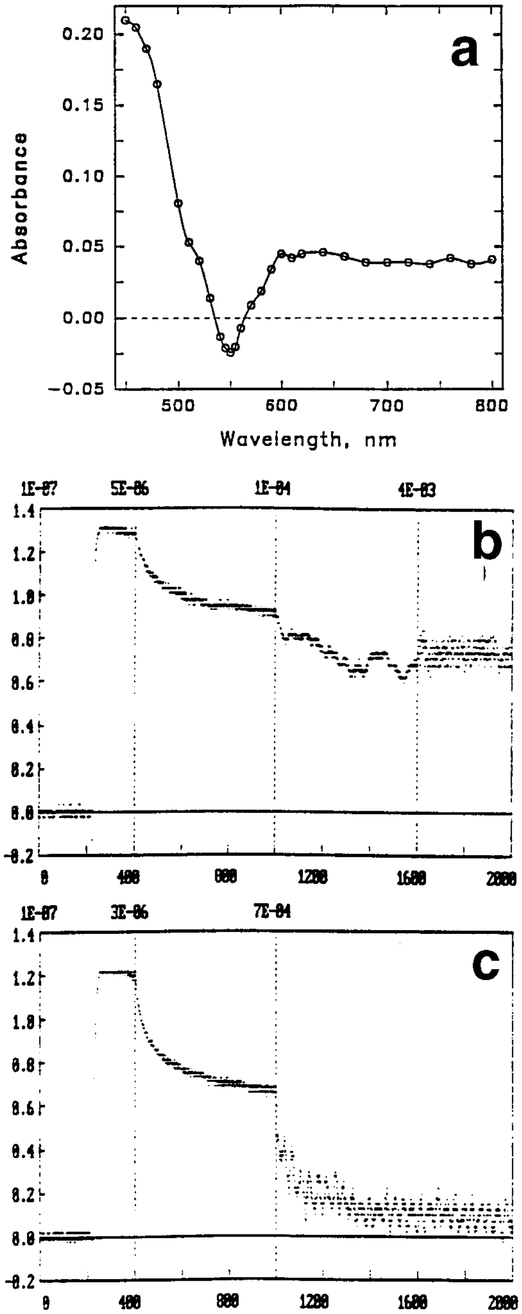

Figure 4. (a) Differential absorption spectrum recorded by pulse radiolysis of aqueous solutions containing 5×10^{-5} mol L^{-1} $Fe^{II}TM2PyP$ and 0.01 mol L^{-1} $HCOO^-$ at pH 3.7, 20 μs after the pulse. (b) Absorbance (×10) vs time over four time scales: 0.1 μs, 5 μs, 100 μs, and 4 ms per point, covering 2000 points, monitored at pH 8.6. (c) Absorbance (×10) vs time over three time scales: 0.1, 3, and 700 μs per point, covering 2000 points, monitored in solutions containing bicarbonate and CO_2 at pH 6.7.

The stability of the $Fe^{I}P$ species was dependent on the porphyrin and the medium. $Fe^{I}TM4PyP$ and $Fe^{I}TM3PyP$ decayed over several milliseconds, both in neutral and in alkaline solutions, via second-order processes. A rate constants of $2k = (1.4 \pm 0.4) \times 10^8$ L mol^{-1} s^{-1} was derived for $Fe^{I}TM4PyP$ at pH 6.7, and a rate constant of $2k = (1.0 \pm 0.3) \times 10^8$ L mol^{-1} s^{-1} was calculated for $Fe^{I}TM3PyP$ at pH 6.9 and 3.6. $Fe^{I}TM2PyP$ exhibited a different decay behavior. Despite the above findings from the γ-radiolysis experiments that this species is stable under certain conditions, at least partial decay was observed in the millisecond range. This observation is rationalized by the existence of four atropisomers of the TM2PyP ligand (due to inhibition of free rotation of the four *N*-methylpyridinium groups at the meso positions).[24] For porphyrins with more highly inhibited rotation, such as the tetrakis(2-(*N*-methylisonicotinamido)phenyl)porphyrin, where the four isomers could be separated, it has been shown that the pK_a for protonation of the free bases varied between 2.2 and 2.9, and the rates of metal incorporation varied by an order of magnitude for the different isomers.[25] Since decay of the Fe^I-TM2PyP is probably affected by protonation, it is likely that the different isomers will exhibit different decay behavior.

The decay of Fe^ITM2PyP was monitored at 700 nm by pulse radiolysis of solutions containing 0.01 mol L^{-1} formate ions under various conditions (two representative traces are shown in Figure 4b,c). At pH 8.6 (buffered with borate), 30% of the initial absorbance decayed within ~3 ms, 15% decayed within ~30 ms, and the remaining absorbance was stable beyond the limit of the pulse radiolysis detection, i.e., >10 s. This remaining absorbance was also observed several minutes after irradiation in the γ source and decayed within hours. At pH 6.7 (in solutions containing formate but no added buffer), the decay was similar, and the remaining absorbance was slightly lower, 50% of the initial value. At pH 6.7 with added phosphate buffer (2×10^{-3} mol L^{-1}), larger fractions of the absorbance decayed in each step, within ~3 and ~100 ms, leaving only 30% for the long-lived fraction. When the pH was decreased to 2.9 and 2.3, or when the solution was at pH 6.9 but was bubbled with CO_2, the fraction of remaining absorbance at 700 nm was only 10%; most of the absorbance decayed in two distinct steps, within ~2 and ~300 ms. The decay of Fe^I-TM2PyP was also monitored throughout the wavelength range studied (from 450 to 840 nm). At most wavelengths, the differential absorbance returned to zero, indicating that most of the original Fe^{II}TM2PyP is recovered; some absorbance remained around 610 nm, which indicates formation of the chlorin.

The first and second decay steps were sufficiently separated in time to permit kinetic fitting of each step independently of the other. The first step obeys second-order rate law quite closely, at different dose per pulse, and the calculated rate constants were $(1.5 \pm 0.5) \times 10^8$ L mol^{-1} s^{-1} in neutral solution and about 50% higher in the presence of CO_2 or in acidic solutions. The slower step was also fitted to second-order kinetics, although in this case, because of the smaller signals and increased noise (analyzing light instability), the second-order fit and the derived rate constants (10^6-10^7 L mol^{-1} s^{-1}) were considerably less certain. The second-order decay may involve reaction of an unstable isomer of Fe^ITM2PyP with any of the isomers, until the unstable ones are depleted. If the four isomers of Fe^ITM2PyP have different reactivities, up to four decay steps may be observed. In neutral solutions, two decay steps are observed, presumably for two or three isomers, and the remaining one or two isomers are stable. In acidic solutions, or in the presence of CO_2, the first decay step is larger and appears to encompass both isomers that were seen to decay in two steps in neutral solutions; i.e., the decay for the second step is accelerated by the acid or CO_2 and merges with the first step. The first step is also expected to be accelerated, but its rate does not appear to increase since it already approaches the diffusion-controlled limit.[26] The isomer that was stable in neutral solution decays in acidic solutions (but more slowly than the second step in neutral).

The second-order behavior of the decay processes, along with the findings that most of the original Fe^{II}TM2PyP is recovered and small amounts of the chlorin are formed, suggests that the decay takes place via disproportionation.

$$2(Fe^IP)^- \rightleftarrows Fe^{II}P + (Fe^0P)^{2-} \tag{10}$$

Possibly, very little Fe^0P is present in this equilibrium, but the reaction is shifted to the right due to reaction of Fe^0P with water, H^+, or CO_2. These reactions lead to formation of short-lived hydride or carboxylate complexes.

$$(Fe^0P)^{2-} + H_2O \rightarrow (HFe^{II}P)^- + OH^- \tag{11}$$

$$(Fe^0P)^{2-} + CO_2 \rightarrow (CO_2{-}Fe^{II}P)^{2-} \tag{12}$$

Subsequent protonation of these species will lead to formation of H_2 or CO.

$$(HFe^{II}P)^- + H_2O \rightarrow H_2 + Fe^{II}P + OH^- \tag{13}$$

$$(CO_2{-}Fe^{II}P)^{2-} + H_2O \rightarrow CO + Fe^{II}P + 2OH^- \tag{14}$$

Protonation of the macrocycle to form the chlorin also takes place concurrently.

Earlier studies on iron protoporphyrin[27] suggested that the Fe^IP state, even at pH 10, undergoes protonation to form the hydride, which reacts with water to yield H_2 and $Fe^{III}P$. The present results indicate, however, that Fe^ITM2PyP does not undergo protonation in neutral solutions. The difference is clearly due to the difference in reduction potentials of these two porphyrins. Electrochemical results[18] indicated that the reduction waves for Fe^{II}/Fe^ITM2PyP and for H^+/H_2 overlapped at pH < 4.2 but became more separated as the pH increased. Thus, protonation of Fe^ITM2PyP should be unimportant in neutral solutions.[28] Even at pH 2.9, our results indicate second-order decay behavior and no formation of $HFe^{III}P$ or $Fe^{III}P$, suggesting that direct protonation of Fe^ITM2PyP does not compete effectively with the proton-enhanced second-order decay. Electrochemical results with FeTPP[29] also indicated that reduction of H^+ to H_2 is catalyzed by the Fe^0 and not by the Fe^I state.

Summary and Conclusions

Fe(III) porphyrins are readily reduced by photochemical and radiation chemical methods to the stable $Fe^{II}P$ products and then to Fe^IP. Photochemical reduction in DMF solutions takes place by excitation of the ligand-to-metal charge transfer band, where the ligand is an axially bound triethylamine. The quantum yield for the first reduction step is ~0.05 but for the second reduction only ~0.01. Continued photolysis in the presence of CO_2 results in the formation of CO. However, the porphyrin ligand is also partially reduced, first to the chlorin, which also catalyzes photochemical reduction of CO_2, but eventually the porphyrin macrocycle is destroyed and CO production stops before a turnover number of 100 is achieved. This value is considerably lower than the turnover number achieved in the electrochemical reduction of CO_2 by iron porphyrins,[7] probably because photoinduced side reactions in the homogeneous system lead to attack on the porphyrin macrocycle. Several substituted porphyrins are examined, but no great enhancement of catalytic activity or long-term porphyrin stability is found. Encapsulation or binding of the porphyrin may offer some advantage in this respect. It is noted, however, that despite the susceptibility of the porphyrin macrocycle to stepwise reduction and eventual cleavage, the turnover numbers for CO production found in the present study compare favorably with those reported in photochemical studies with different complexes of iron or nickel.[4a,5a]

Radiolytic reduction was studied only in aqueous solutions to avoid the possibility of attachment of radiolytically produced organic radicals to the $Fe^{II}P$ species (to form $R-Fe^{III}P$). The $Fe^{I}P$ state is less stable in water than in organic solvents. Only some of the atropisomers of $Fe^{I}TM2PyP$ exhibit long-term stability in water, mainly in alkaline solutions. Time-resolved studies suggest that the $Fe^{I}P$ species does not reduce H^+ or CO_2 directly, but rather disproportionates to $Fe^{II}P$ and $Fe^{0}P$, and the latter serves as the reductant (in line with the conclusions of the electrochemical studies)[7]. Catalyzed reduction of CO_2 to CO was less efficient in water than in organic solvents, although the reaction in organic solvents is enhanced by small amounts of water.

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References and Notes

(1) *Catalytic Activation of Carbon Dioxide*; Ayers, W. M., Ed. *ACS Symp. Ser.* **1988**, *No. 363*. Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, 1988. *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide*; Sullivan, B. P., Ed.; Elsevier: Amsterdam, 1993.

(2) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1414.

(3) Fisher, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7361. Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1986**, *108*, 7461. Fujita, E.; Haff, J.; Sanzenbacher, R.; Elias, H. *Inorg. Chem.* **1994**, *33*, 4627.

(4) (a) Grant, J. L.; Goswami, K.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2105. (b) Craig, C. A.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Phys. Chem.* **1990**, *94*, 7957. (c) Kelly, C. A.; Mulazzani, Q. G.; Venturi, M.; Blinn, E. L.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1995**, *117*, 4911.

(5) (a) Fujita, E.; Brunschwig, B. S.; Ogata, T.; Yanagida, S. *Coord. Chem. Rev.* **1994**, *132*, 195. (b) Ogata, T.; Yanagida, S.; Brunschwig, B. S.; Fujita, E. *J. Am. Chem. Soc.* **1995**, *117*, 6708. (c) Matsuoka, S.; Yamamoto, K.; Ogata, T.; Kusaba, M.; Nakashima, N.; Fujita, E.; Yanagida, S. *J. Am. Chem. Soc.* **1993**, *115*, 601. (d) Ogata, T.; Yamamoto, Y.; Wada, Y.; Murakoshi, K.; Kusaba, M.; Nakashima, N.; Ishida, A.; Takamuku, S.; Yanagida, S. *J. Phys. Chem.* **1995**, *99*, 11916.

(6) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1985**, 56.

(7) Hammouche, M.; Lexa, D.; Savéant, J.-M.; Momenteau, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *249*, 347. Hammouche, M.; Lexa, D.; Momenteau, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1991**, *113*, 8455. Bhugun, I.; Lexa, D.; Savéant, J.-M. *J. Am. Chem. Soc.* **1994**, *116*, 5015. Bhugun, I.; Lexa, D.; Savéant, J.-M. *J. Am. Chem. Soc.* **1996**, *118*, 1769.

(8) Fujita, E.; Szalda, D. J.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 4870. Creutz, C.; Schwarz, H. A.; Wishart, J. F.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 1153; **1991**, *113*, 3361. Fujita, E.; Creutz, C.; Sutin, N.; Szalda, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 343. Fujita, E.; Creutz, C.; Sutin, N.; Brunschwig, B. S. *Inorg. Chem.* **1993**, *32*, 2657.

(9) Bizet, C.; Morliere, P.; Brault, D.; Delgado, O.; Bazin, M.; Santus, R. *Photochem. Photobiol.* **1981**, *34*, 315. Hoshino, M.; Ueda, K.; Takahashi, M.; Yamaji, M.; Hama, Y. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 405.

(10) Hendrickson, D. N.; Kinnaird, M. G.; Suslick, K. S. *J. Am. Chem. Soc.* **1987**, *109*, 1243. Suslick, K. S.; Watson, R. A. *New J. Chem.* **1992**, *16*, 633.

(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.

(12) Neta, P.; Huie, R. E. *J. Phys. Chem.* **1985**, *89*, 1783.

(13) Brault, D.; Rougee, M. *Biochemistry* **1974**, *13*, 4598.

(14) DeLaive, P. J.; Foreman, T. K.; Giannotti, C.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 5627.

(15) Hoshino, M.; Ueda, K.; Takahashi, M.; Yamaji, M.; Hama, Y. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 405.

(16) The identity of the reduced products was confirmed by experiments with an authentic sample of $ClFe^{III}TPC$ (tetraphenylchlorin). Solution of this compound in DMF with 5% TEA exhibited main peaks at 405 and 624 nm. Upon photolysis this was reduced to the $Fe^{II}TPC$ (424 and 614 nm), and further photoreduction produced $Fe^{II}TPiBC$ (420 and 600 nm). Exposure to O_2 resulted in the oxidation of $Fe^{II}TPC$ to $Fe^{III}TPC$, but Fe^{II}-TPiBC gave products with only weak broad absorptions, probably due to cleavage of the macrocycle.

(17) Hoshino, M.; Ueda, K.; Takahashi, M.; Yamaji, M.; Hama, Y.; Miyazaki, Y. *J. Phys. Chem.* **1992**, *96*, 8863.

(18) Chen, S.-M.; Sun, P.-J.; Su, Y. S. *J. Electroanal. Chem.* **1990**, *294*, 151.

(19) Transformation of phlorin anion to chlorin has been observed previously with TM2PyP (Mosseri, S.; Nahor, G. S.; Neta, P.; Hambright, P. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2567) and other porphyrin derivatives (Fuhrhop, J.-H. *Struct. Bonding (Berlin)* **1974**, *18*, 1).

(20) Brault, D.; Bizet, C.; Morliere, P.; Rougee, M.; Land, E. J.; Santus, R.; Swallow, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 1015. Brault, D.; Neta, P. *J. Am. Chem. Soc.* **1981**, *103*, 2705.

(21) Baral, S.; Neta, P.; Hambright, P. *Radiat. Phys. Chem.* **1984**, *24*, 245.

(22) Radiolytic reduction of $Fe^{II}TM3PyP$ at pH 12 in aqueous solutions containing 0.013 mol L^{-1} 2-PrOH resulted in the formation of the phlorin anion with a strong peak at 816 nm. This product was readily oxidized by O_2 to yield $Fe^{III}TM3PyP$. In the absence of O_2 it was stable and did not change to the chlorin (in contrast with the findings for the ortho isomer, FeTM2PyP). Radiolytic reduction of $Fe^{II}TM3PyP$ at pH 12 in the presence of 0.01 mol L^{-1} $HCOO^-$ resulted in the formation of a product with a different absorption, a strong broad peak at 666 nm. This product also was stable in the absence of O_2 and also was oxidized by O_2 to the porphyrin $Fe^{III}TM3PyP$. Thus, it behaves like the phlorin anion, and it is not clear why the spectrum is different than that found in the presence of 2-PrOH.

(23) One-electron reduction of $Fe^{II}P$, in principle, may lead to production of either $Fe^{I}P$ or $Fe^{II}P^-$. Both species are unstable in neutral aqueous solutions and may decay by disproportionation and protonation. Decay of metalloporphyrin π-radical anions ($MP^{\bullet-}$) is known to lead to formation of either a phlorin anion, MPH^-, in alkaline solutions or a chlorin, MPH_2, in neutral solutions. Both of these products have been observed with the iron porphyrins under different conditions. This result, however, is not sufficient evidence for formation of the radical anion since $Fe^{I}P$ also may decay to give similar products. The decay may be via disproportionation, involving electron transfer from the metal to the ligand, in a process that is enhanced by protonation (similar to that suggested before for nickel porphyrins: Nahor, G. S.; Neta, P.; Hambright, P.; Robinson, L. R.; Harriman, A. *J. Phys. Chem.* **1990**, *94*, 6659).

(24) Rodgers, K. R.; Reed, R. A.; Su, O.; Spiro, T. G. *Inorg. Chem.* **1992**, *31*, 2688.

(25) Hambright, P.; Turner, A.; Cohen, J. S.; Lyon, R. C.; Katz, A.; Neta, P.; Adeyemo, A. *Inorg. Chim. Acta* **1987**, *128*, L11. Valiotti, A.; Adeyemo, A.; Williams, R. F. X.; Ricks, L.; North, J.; Hambright, P. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2653.

(26) The diffusion-controlled limit for average neutral species in water is 6×10^9 L mol^{-1} s^{-1}. This value will be decreased by the Coulombic interaction between charged species. For doubly charged ions the decrease is by a factor of 50 and for triply charged ions by a factor of 10^4 (Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265). The triply charged $Fe^{I}TM2PyP$ does not exhibit the full effect of the three charges since these are not localized at the same point but rather at distinct points at the edges of the molecule (Nwaeme, J.; Hambright, P. *Inorg. Chem.* **1984**, *23*, 1990).

(27) Sorek, Y.; Cohen, H.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 233.

(28) Protonation may be important for the protoporphyrin because its reduction potential is much more negative. Iron protoporphyrin is expected to have an Fe^{II}/Fe^{I} reduction potential about 0.2 V more negative than that for $Fe^{II}TPP$ (by comparison with the value for $Fe^{II}OEP$: Lexa, D.; Savéant, J.-M.; Wang, D. L. *Organometallics* **1986**, *5*, 1428) whereas pyridyl porphyrins have reduction potentials more positive than that of TPP. Therefore, the likelihood of protonation and water reduction by the $Fe^{I}P$ state is diminished and becomes unimportant in our experiments.

(29) Bhugun, I.; Lexa, D.; Savéant, J.-M. *J. Am. Chem. Soc.* **1996**, *118*, 3982.