J. Phys. Chem. A **2000,** *104,* 4475−4479

Ferrous Ions as Catalysts for Photochemical Reduction of CO_2 in Homogeneous Solutions

J. Grodkowski[†] and P. Neta*

Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8381

Received: September 27, 1999; In Final Form: March 7, 2000

Ferrous ions are found to catalyze the photochemical reduction of CO_2 to CO in acetonitrile (ACN) solutions containing triethylamine (TEA) or triethanolamine (TEOA) as reductive quenchers and *p*-terphenyl (TP) as a photosensitizer. TP is photoreduced to form the radical anion, $TP^{\bullet-}$, which reduces Fe(II) ions. The rate constant for the reduction of Fe(II) by $TP^{\bullet-}$ was determined by pulse radiolysis in ACN/TEOA solutions and found to be $(1.2 \pm 0.4) \times 10^8$ L mol^{-1} s^{-1}. The Fe(I) ions produced are expected to react with CO_2 to form an adduct that is equivalent to the adduct known to be formed upon reaction of $CO_2^{\bullet-}$ with Fe(II) complexes. Subsequent reduction of the Fe−CO_2 adduct leads to formation of CO. Fe(I) can also undergo protonation and form H_2. After extensive irradiation, photochemical production of CO stops, probably due to competition between CO and CO_2 for the Fe(I) binding sites. Addition of CO to the solution enhances the photochemical production of H_2.

Introduction

A number of studies have explored the use of transition-metal complexes as homogeneous catalysts for electrochemical[1] or photochemical[2,3] reduction of CO_2 as a means of energy storage.[4] Recent studies have shown that iron and cobalt porphyrins (MP) also are effective catalysts for the electrochemical[5] and photochemical[6] reduction of CO_2 to CO and formic acid. The mechanism was suggested to involve binding of the CO_2 to the highly reduced metalloporphyrin M^0P^{2-},

$$M^0P^{2-} + CO_2 \rightarrow (CO_2\text{-}MP)^{2-} \qquad (1)$$

followed by reaction with a proton

$$(CO_2\text{-}MP)^{2-} + H^+ \rightarrow M^{II}P + CO + OH^- \qquad (2)$$

or with another CO_2 molecule.

$$(CO_2\text{-}MP)^{2-} + CO_2 \rightarrow M^{II}P + CO + CO_3^{\,2-} \qquad (3)$$

In the photochemical studies,[6] the quantum yields for the reduction of the metalloporphyrin and, consequently, for the reduction of CO_2, were relatively low. In a recent study it has been shown that the yield can be dramatically increased by the use of *p*-terphenyl (TP) as a photosensitizer.[7] TP is photoreduced by triethylamine (TEA) very rapidly[8] to form the radical anion, $TP^{\bullet-}$,

$$TP \xrightarrow{h\nu} TP^* \qquad (4)$$

$$TP^* + Et_3N \rightarrow TP^{\bullet-} + Et_3N^{\bullet+} \qquad (5)$$

which can reduce Co and Fe porphyrins to their M^0P state.

$$TP^{\bullet-} + M^{II}P \rightarrow TP + M^IP^- \qquad (6)$$

$$TP^{\bullet-} + M^IP^- \rightarrow TP + M^0P^{2-} \qquad (7)$$

The rate constants for these reactions were determined by pulse radiolysis and found to be nearly diffusion-controlled.[7] The metalloporphyrins, however, were destroyed during the photochemical process and yet production of CO continued for extended periods of photolysis beyond that. These findings suggest that catalytic reduction of CO_2 to CO may be effected by the ferrous ions formed after decomposition of the porphyrin ligand. In the present study we find that ferrous ions indeed catalyze the photochemical reduction of CO_2 under similar conditions. Earlier studies have demonstrated photoreduction of CO_2 by ferrous ions in aqueous solutions,[9] but with very low yields that cannot explain the recent findings.[6,7] The present results show that the yields of such processes can be increased by several orders of magnitude by the addition of reductive quenchers and photosensitizers.

Experimental Section[10]

Comparative experiments were carried out with iron tetra-*m*-tolylporphyrin ($Fe^{III}TTP$) and with inorganic iron salts. Acetonitrile (ACN, Mallinckrodt analytical grade) was used as solvent without further purification. The solutions contained 5% (v/v) of either triethylamine (TEA, Aldrich, distilled over Na) or triethanolamine (TEOA, Aldrich) as reductive quenchers. In most experiments 3 mmol L^{-1} *p*-terphenyl (TP, Aldrich, recrystallized from alcohol) was used as a photosensitizer. Since earlier experiments[6,7] with metalloporphyrins were carried out in the presence of TEA, the same quencher was used for experiments with the iron salts. However, because TEA is a relatively strong base (pK_a in water 10.7), Fe^{3+} ions were found to form aggregated hydroxides and at concentrations >0.05 mmol L^{-1} these precipitated. When $Fe(ClO_4)_2$ (Aldrich) was

---

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

10.1021/jp993456f CCC: $19.00

used as the iron source, small amounts of Fe^{3+} were present in this material but larger amounts were produced when the solution was exposed to both TEA and air. Therefore, the solutions were deoxygenated before mixing the iron salt and the TEA. Despite these precautions, experiments could be carried out only at relatively low iron concentrations (≤ 0.1 mmol L^{-1}). To minimize aggregation and precipitation of Fe(III), TEOA was used as the reductive quencher, because this amine is a weaker base (pK_a in water is 7.8). This permitted us to prepare homogeneous solutions of $Fe(ClO_4)_2$ at concentrations ≤ 1.5 mmol L^{-1}. It should be noted, however, that TEOA is known[11] to coordinate Fe^{3+} and Fe^{2+} ions in aqueous solutions better than TEA, so that the results described below apply to TEOA complexes rather than to the $Fe(H_2O)_6{}^{2+}$ ion present in the starting material.

Experiments were performed with fresh solutions that were deoxygenated by bubbling with ultrahigh purity Ar or He or were saturated (~ 0.3 mol L^{-1}) with CO_2 (Matheson, 99.99%). Comparative experiments were also carried out with solutions saturated (~ 0.01 mol L^{-1}) with CO (Air Products, C. P. Grade). Photolysis was performed with an ILC Technology 300 W xenon lamp, using a water filter to absorb the IR and a Pyrex filter to absorb $\lambda < 300$ nm. The solution was placed either in a bulb surrounded by a water jacket or in a cell placed inside the water filter so that the solution was kept at room temperature. Earlier experiments have shown that absorption of light at $\lambda > 400$ nm leads to negligible photoreduction, even in the presence of the iron porphyrin,[6] which has strong absorptions in the visible range. The photoreduction process occurs predominantly via light absorption by TP. This compound has two peaks at 205 nm ($\epsilon = 5.9 \times 10^4$ L mol^{-1} cm^{-1}) and 279 nm ($\epsilon = 3.5 \times 10^4$ L mol^{-1} cm^{-1}), which are masked by the Pyrex filter, and a tail with $\epsilon_{300} = 1.6 \times 10^4$ L mol^{-1} cm^{-1}, $\epsilon_{310} = 5.1 \times 10^3$ L mol^{-1} cm^{-1}, and $\epsilon_{320} = 6 \times 10^2$ L mol^{-1} cm^{-1}. This absorption leads to the observed photochemistry, while other components in solution exhibit little absorbance in this range. Absorption spectra were recorded before and after irradiation with a Cary 3 spectrophotometer. The CO and H_2 evolved were determined by gas chromatography (Carboxen-1000 column, thermal conductivity detector).[6] Fast kinetic measurements were carried out by pulse radiolysis using 6 MeV electron pulses from a Varian linear accelerator. The kinetic spectrophotometric detection system utilized a Hamamatsu 75 W xenon lamp, a shutter and optical cutoff filters to minimize photolysis of the solution, a 2 cm optical path length irradiation cell, a Jobin-Yvon monochromator, a Hamamatsu R955 photomultiplier, and a Tektronix 420A digitizing oscilloscope. Reaction rate constants are reported with their estimated standard uncertainties. All experiments were performed at room temperature, 20 ± 2 °C.

Results and Discussion

Photochemical Production of CO and H_2. A comparison of the photochemical production of CO and H_2 in CO_2-saturated acetonitrile solutions containing 5% TEA, 3 mmol L^{-1} TP, and either Fe^{III}TTP or $Fe(ClO_4)_2$ is shown in Figure 1. It is found that formation of CO is considerably more efficient with the porphyrin. Production of H_2, however, begins with similar rates but diverges later.

The concentration of $Fe(ClO_4)_2$ could not be increased in this solvent mixture (see Experimental Section). Therefore, further experiments were carried out using TEOA instead of TEA. With Fe^{III}TTP, the photochemical production of CO was a factor of 2 less efficient with TEOA (Figure 2a) than with TEA (Figure 1), and production of H_2 was even less efficient. This is ascribed to the fact that TEOA is a weaker reductant than TEA, thus reacting more slowly with TP* (reaction 5). Furthermore, the alcohol groups in TEOA can donate a proton to $TP^{\bullet -}$,[12] in competition with reactions 6 and 7, and thus the yield of reduced metal complex is diminished. The total photochemical yield of CO and H_2 obtained with $Fe(ClO_4)_2$ also was lower with TEOA than with TEA. The yield of CO in this case was slightly higher than that obtained with the porphyrin (Figure 2a), probably due to the higher concentration of the iron compound used in the former case (the effect of concentration is discussed below). A noticeable difference between the two experiments is in the initial delay in CO formation, which is due to the difference in the photolysis time required to reduce Fe^{III}TTP vs $Fe(ClO_4)_2$ to the reactive intermediates.

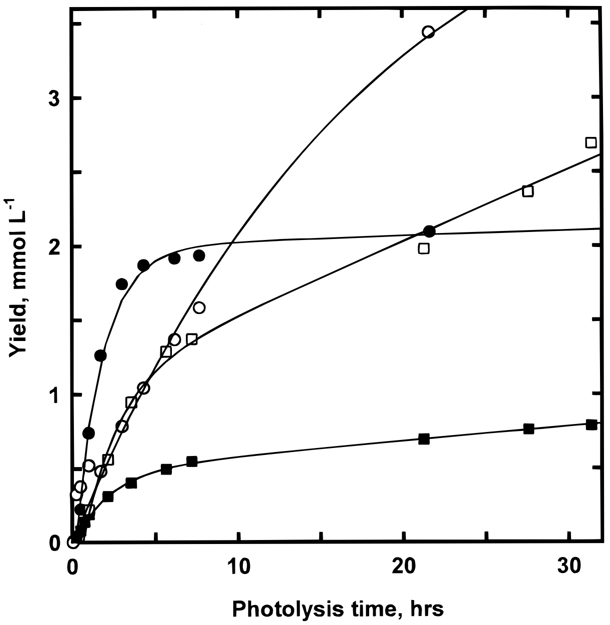

Figure 1. Photochemical production of CO (solid symbols) and H_2 (open symbols) in CO_2-saturated acetonitrile solutions containing 5% TEA, 3×10^{-3} mol L^{-1} TP, and either 3.4×10^{-5} mol L^{-1} FeTTP (circles) or 3.8×10^{-5} mol L^{-1} $Fe(ClO_4)_2$ (squares). The solutions were continuously stirred and photolyzed in a Pyrex bulb cooled by a water jacket, placed 10 cm away from an ILC Technology LX-300 UV Xe lamp. The solution volume was 35 mL, and the headspace above the solution was 8 mL.

When the concentration of $Fe(ClO_4)_2$ was increased by a factor of 6.6, the initial rate of photochemical production of CO increased by a factor of 1.3 (Figure 2b vs 2a). Moreover, the process continued for longer periods and the total amount of CO formed was 4 times greater. At the higher iron concentration, photochemical production of H_2 also was much higher.[13] Under these conditions, when CO_2 was replaced with He, no CO was formed but the yield of H_2 also dropped (to <50%). However, when CO_2 was replaced with CO, the rate of photochemical production of H_2 increased by a factor of 3 and the total yield by a factor of 2 (Figure 2b). This finding may be explained by the bonding of CO to an iron complex (see below).[14]

In blank experiments with the ACN/TEOA/TP/CO_2 solution, in the absence of the iron compound, the photochemical yield of CO was very small (<0.5% of that observed in the presence of the iron). When the iron compound was present, but the amine was absent, the yield of CO also was negligible (<0.5%). In the absence of TP, the yield of CO was very low, $\leq 0.7\%$, because TP is the main photoactive material under these conditions.

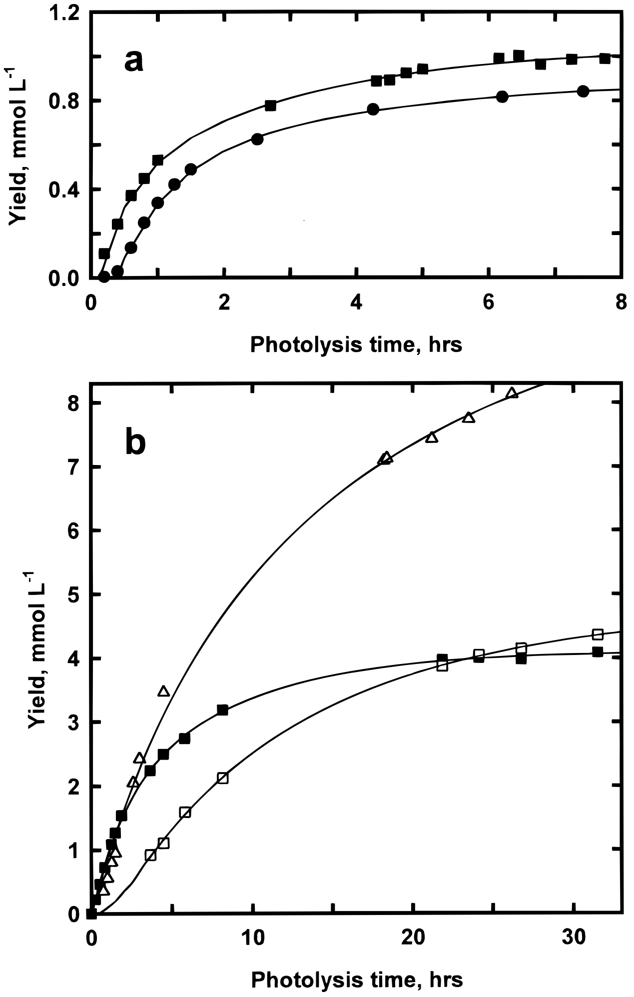

Figure 2. (a) Photochemical production of CO in CO_2-saturated acetonitrile solutions containing 5% TEOA, 3×10^{-3} mol L^{-1} TP, and either 3.6×10^{-5} mol L^{-1} FeTTP (●) or 5.0×10^{-5} mol L^{-1} $Fe(ClO_4)_2$ (■). The yield of H_2 was very low under these conditions. (b) Photochemical production of CO (■) and H_2 (□) in CO_2-saturated acetonitrile solutions containing 5% TEOA, 3×10^{-3} mol L^{-1} TP, and 3.3×10^{-4} mol L^{-1} $Fe(ClO_4)_2$ and photochemical production of H_2 (△) from a similar solution saturated with CO.

TABLE 1: Photochemical Decay of *p*-Terphenyl

	initial rate of TP decay[a]		
solution[a]	TEA	TEOA	TEOA, TEA[c]
Ar	65	11	32[d]
CO_2	28	14	39
CO	64	11	
H^+ (0.03), Ar		21	35
Fe (0.1), Ar	34	24	32
Fe (0.1), CO_2		10	33
Fe (0.1), CO		1.4	15
Fe (0.3), Ar		18	
Fe (0.3), CO_2		8	
Fe (0.5), Ar		12	24
Fe (0.5), CO_2		5	
Fe (1.0), Ar			17
Fe (1.5), Ar			9.5

[a] All solutions (4 mL) contained 1.5 mmol L^{-1} *p*-terphenyl and either TEA or TEOA (5% v/v) in acetonitrile, were saturated with the specified gas in 1 cm × 1 cm × 4 cm quartz cell, and were photolyzed by a 300 W Xe lamp at a distance of 10 cm through Pyrex and water filters. The iron was added as $Fe(ClO_4)_2$ and the H^+ as $HClO_4$; their concentrations in mmol L^{-1} are given in parentheses. [b] The initial rate of decay of TP, given in units of μmol L^{-1} min^{-1}, was calculated from changes in absorbance, measured at 314−320 nm, following photolysis for various times, generally up to 20 or 30 min. The standard uncertainties are estimated to be ±10%. [c] The solutions contained 5% TEOA and 10 mmol L^{-1} TEA. [d] The rate was 25 with 5 mmol L^{-1} TEA and 37 with 20 mmol L^{-1} TEA.

When the complete system of ACN/TEOA/TP/CO_2 containing 0.5 mmol L^{-1} Fe(II) was photolyzed in the 1 cm cell for 30 min with the full spectrum of the Xe lamp, i.e., without the 300 nm cutoff filter, the yield of CO was 6.7 times higher than that found with the filter. Under these conditions, when TP was not present in the solution, the yield of CO dropped to ∼30%, indicating that considerable photolysis takes place in the UV region via direct photoreduction of the iron by the amine. In fact, when either Fe(II) or TEOA was absent from this system, the yield dropped to $\leq 0.3\%$.

Photobleaching of TP. The above results show that the photochemical yields of CO and H_2 increase with iron concentration. This effect may be related to an increase in the extent of reaction of $TP^{\bullet -}$ with the iron complex, which can be expressed in the efficiency of the iron complex in protecting TP against photobleaching, as demonstrated below.

TP is photoreduced to $TP^{\bullet -}$ by the amine (reactions 4 and 5). In the absence of the iron compound, $TP^{\bullet -}$ undergoes protonation by a protic molecule[12] or by the proton formed from the oxidized amine following reaction 5. Subsequent decay of the radicals leads to the photobleaching of TP, i.e., to formation of hydrogenated products and addition products,[15] which have lower molar absorption coefficients than TP.

$$TP^{\bullet -} + ROH \rightarrow TPH^{\bullet} + RO^{-} \tag{8}$$

$$2TPH^{\bullet} \rightarrow \text{products} \tag{9}$$

Reactants that can accept an electron from $TP^{\bullet -}$ can protect TP against bleaching. For example:

$$TP^{\bullet -} + Fe(II) \rightarrow TP + Fe(I) \tag{10}$$

To determine such protection, we monitored the photochemical decomposition of TP by following its bleaching at 314 nm to 320 nm and the effect of various additives. The initial rate of photochemical bleaching of TP in deoxygenated ACN/TEA/TP solutions was decreased upon addition of CO_2 or Fe^{2+} (Table 1), due to the contributions of reactions 10 and 11.

$$TP^{\bullet -} + CO_2 \rightarrow TP + CO_2^{\bullet -} \tag{11}$$

Reaction 11 has been shown to have a very low rate constant, $k < 1 \times 10^6$ L mol^{-1} s^{-1}, but it has a significant contribution in the absence of competitors and is known to lead to formation of formic acid.[3,7] Saturating the solution with CO, however, did not protect TP from photochemical bleaching. The lack of effect of CO may be due in part to its solubility, which is ∼30 times lower than that of CO_2 in this solvent.

The rate of photobleaching was lower in the presence of TEOA as compared with TEA (Table 1). This is due to a lower photochemical yield of $TP^{\bullet -}$, as discussed above. Addition of $Fe(ClO_4)_2$ to an Ar-saturated ACN/TEOA/TP solution resulted in an *increased* rate of TP photobleaching. This is ascribed to the increase in acidity upon addition of this ferrous salt. In fact, addition of a low concentration of $HClO_4$ (equivalent to that introduced by the addition of the iron salt) also resulted in an increased rate of bleaching (Table 1). This effect may be rationalized if we assume that the decay of the radicals derived from TP takes place via two possible routes. $TP^{\bullet -}$ may react with $TP^{\bullet -}$ or with $TPH^{\bullet}$ via disproportionation, to recover half

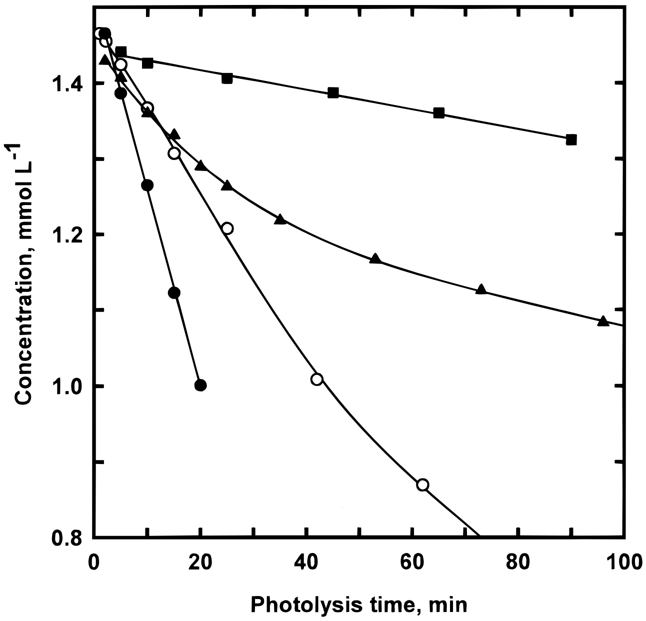

Figure 3. Photochemical bleaching of TP (1.5×10^{-3} mol L^{-1}) in acetonitrile solutions containing 5% TEOA and 1×10^{-4} mol L^{-1} Fe(ClO$_4$)$_2$, saturated with Ar (●), CO$_2$ (▲), or CO (■). The results under Ar but in the absence of the iron salt are shown for comparison (○).

of the TP that was initially reduced, e.g.,

$$TP^{\bullet-} + TPH^{\bullet} \rightarrow TP + TPH^{-} \quad (12)$$

whereas TPH$^{\bullet}$ reacts with TPH$^{\bullet}$ via dimerization, with no recovery of TP.[16]

$$2TPH^{\bullet} \rightarrow (TPH)_2 \quad (13)$$

TPH$^{\bullet}$ also reacts with other radicals, such as those derived from the amine, to form adducts.[15] The added acid reacts with TP$^{\bullet-}$ to form TPH$^{\bullet}$ and thus reduces the contribution of reaction 12 relative to that of reaction 13. To counteract this effect, we added small concentrations of TEA.

Addition of 5−20 mmol L^{-1} TEA to the ACN/TEOA/TP solution increased the rate of photochemical bleaching of TP (Table 1) due to enhanced quenching of TP* by the amine. Addition of Fe(ClO$_4$)$_2$ or HClO$_4$ in this case did not lead to increased photobleaching of TP because the added acid is neutralized by the TEA. Moreover, addition of increasing amounts of the iron salt resulted in increasing protection of the TP. This effect provides the rationale for the results in Figure 2b vs 2a discussed above. The low total yields obtained at low iron concentrations (Figure 2a) are clearly due to depletion of TP, while higher iron concentrations offer increased protection of TP and extended photochemical production of CO and H$_2$ (Figure 2b).

A comparison of the effects of CO and CO$_2$ on the photobleaching of TP in the presence of Fe(II) is demonstrated in Figure 3. In the presence of CO, the rate of photobleaching of TP was much lower than that observed under Ar. In the presence of CO$_2$, however, the rate was intermediate between those observed with Ar and with CO in the beginning of the photoreduction process but became considerably lower as the reaction progressed. This effect may be ascribed to the accumulation of CO in the solution.

Pulse Radiolysis Experiments. The rate constant for reaction 10 was determined in pulse radiolysis experiments similar to those described before for the metalloporphyrins.[7] In the radiolysis of a deoxygenated ACN solution containing TP, the solvated electrons react with TP to form TP$^{\bullet-}$, which exhibits intense absorption peaks at 480 nm and elsewhere.[17,18] The yield and lifetime of TP$^{\bullet-}$ were increased by the addition of TEA[19] or TEOA, which scavenge the positive ions and thus minimize the loss of electrons and radical anions. The rate of decay of TP$^{\bullet-}$ in ACN solutions containing 5% TEOA was 9×10^4 s^{-1} and this increased to 2.9×10^5 s^{-1} upon addition of 3.1×10^{-5} mol L^{-1} HClO$_4$. In the presence of 5% TEOA and 10 mmol L^{-1} TEA, however, the rate of decay was 6.5×10^4 s^{-1} and was not affected by the addition of the HClO$_4$. When Fe(ClO$_4$)$_2$ was introduced into the solution, because its concentration was relatively high, the small fraction of the iron ions that was present as Fe(III) reacted with TP$^{\bullet-}$. The rate constant for this reaction was determined by separate experiments with FeCl$_3$ and found to be $\sim 5 \times 10^9$ L mol^{-1} s^{-1}. To eliminate this fast reaction, all solutions were photolyzed by the analyzing light inside the irradiation cell until all Fe(III) was reduced to Fe(II) and then irradiated with the electron pulse to monitor the rate of decay of TP$^{\bullet-}$. The rate was found to increase linearly with the concentration of Fe(II), which was varied from 0.5 to 1.2 mmol L^{-1}, and from the linear dependence a rate constant $k_{10} = (1.2 \pm 0.4) \times 10^8$ L mol^{-1} s^{-1} was calculated. Similar experiments with solutions saturated with CO instead of Ar gave a rate constant of $(1.8 \pm 0.5) \times 10^8$ L mol^{-1} s^{-1}. CO by itself had no effect on the rate of decay of TP$^{\bullet-}$. Thus, the rate constant for reaction of TP$^{\bullet-}$ with the Fe^{II}TEOA complex is found to be much lower than the rate constants measured for Fe(II) porphyrins and phthalocyanines, suggesting that the reduction potential of Fe^{II}TEOA is more negative than the potentials of the other complexes and much closer to the reduction potential of TP.

Mechanism. From the above results we conclude that the mechanism of photochemical reduction of CO$_2$ to CO in the present system involves reaction of TP$^{\bullet-}$ with the Fe^{II}TEOA complex, reaction 10, to form the reactive Fe(I) species. We assume that this species reacts with CO$_2$ to form an adduct.

$$Fe^{+} + CO_2 \rightarrow (Fe{-}CO_2)^{+} \quad (14)$$

The adduct is then reduced by another Fe(I) or by a different reducing species (such as TP$^{\bullet-}$) to yield CO and Fe(II).

$$(Fe{-}CO_2)^{+} + Fe^{+} \rightarrow (Fe{-}CO_2) + Fe^{2+} \quad (15)$$

$$(Fe{-}CO_2) + H^{+} \rightarrow Fe^{2+} + CO + OH^{-} \quad (16)$$

A similar mechanism has been shown to operate in the catalyzed photoreduction of CO$_2$ by Ni(cyclam)[3b,20] and it may be expected to operate in the present system as well.

The complex formed by reaction 14 is similar to that formed by reaction of Fe^{2+} with CO$_2^{\bullet-}$.

$$Fe^{2+} + CO_2^{\bullet-} \rightarrow (Fe{-}CO_2)^{+} \quad (17)$$

Such complexes have been observed by following the reaction of CO$_2^{\bullet-}$ with Fe^{II}−NTA (nitrilotriacetate) and Fe^{II}−HEDTA [(*N*-hydroxyethyl)ethylenediaminetriacetate] in aqueous solutions.[21] Those complexes were found to react with another CO$_2^{\bullet-}$ radical to lead to an overall disproportionation of CO$_2^{\bullet-}$ into CO and CO$_2$.[21]

$$(Fe{-}CO_2)^{+} + CO_2^{\bullet-} + H^{+} \rightarrow Fe^{2+} + CO + CO_2 + OH^{-} \quad (18)$$

Both reaction 18 and reaction 15 involve reduction of the $(Fe-CO_2)^+$ complex and subsequent formation of CO.

Which of the above two mechanisms predominates in the present system depends on whether $TP^{\bullet -}$ reacts with Fe(II) (reaction 10) or with CO_2 (reaction 11). Although $k_{10}/k_{11} > 100$, the concentration of CO_2 generally was >100 times higher than the concentration of Fe(II). Therefore, we cannot rule out a contribution by reaction 11. Either one of the above mechanisms involves formation of the $(Fe-CO_2)^+$ complex. Such short-lived complexes with NTA and HEDTA as ligands have been shown to exhibit absorption spectra with maxima near 400 nm.[21] However, the formation of such complexes under the present conditions cannot be verified since pulse radiolysis of the present system produces organic radicals from ACN and TEOA and these radicals react rapidly with Fe(II) to form similar alkyl-iron complexes, with similar absorption spectra to that of $(Fe-CO_2)^+$.

Photochemical production of H_2 took place along with production of CO. The mechanism of H_2 formation probably involves protonation of the Fe(I) complex to form a hydride,

$$Fe^+ + H^+ \rightarrow HFe^{2+} \qquad (19)$$

which then accepts another proton to form H_2 and Fe(III), as suggested before.[22]

$$HFe^{2+} + H^+ \rightarrow H_2 + Fe^{3+} \qquad (20)$$

In some of the present experiments on photochemical reduction of CO_2, the amount of CO produced reached a plateau after extended photolysis, but production of H_2 continued for longer irradiation times, indicating that TP was not depleted. Therefore, it is likely that the limit on the yield of CO is due to competition between CO and CO_2 for the binding site on the iron. CO is known to bind to Fe(II) and Fe(I) porphyrins,[7] but binding to the Fe-TEOA complexes is expected[23] to be weaker. Since the rate constant for reaction of $TP^{\bullet -}$ with Fe(II) in the absence and presence of CO was practically the same, it may be concluded that no binding of CO to Fe^{II}TEOA is evident. On the other hand, since CO protects TP against photobleaching in the presence of Fe^{II}TEOA much more than does CO_2 (Figure 3), it may be suggested that CO binds to the Fe^{I}TEOA complex. Such binding may explain the enhanced production of H_2 through reactions 19 and 20 and the decrease in the extent of TP photobleaching if we assume that reaction 10 is reversible and that CO pulls the equilibrium to the right by binding to the product. This assumption is reasonable in view of the finding that the rate constant for reaction 10 is only 1.2×10^8 L mol^{-1} s^{-1}, while the parallel rate constants for the iron porphyrins are 2 orders of magnitude higher.[7]

Acknowledgment. This research was supported in part by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy. We thank Dr. Peter Hambright for helpful discussions.

References and Notes

(1) Fisher, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7361. Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1414. 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.

(2) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1985**, 56. Grant, J. L.; Goswami, K.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2105. Craig, C. A.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Phys. Chem.* **1990**, *94*, 7957. Kelly, C. A.; Mulazzani, Q. G.; Venturi, M.; Blinn, E. L.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1995**, *117*, 4911.

(3) (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.

(4) *Catalytic Activation of Carbon Dioxide*, Ayers, W. M., Ed.; ACS Symposium Series, Vol. 363; American Chemical Society: Washington, DC, 1988. 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. Sutin, N.; Creutz, C.; Fujita, E. *Comments Inorg. Chem.* **1997**, *19*, 67.

(5) 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.

(6) Grodkowski, J.; Behar, D.; Neta, P.; Hambright, P. *J. Phys. Chem. A* **1997**, *101*, 248. Behar, D.; Dhanasekaran, T.; Neta, P.; Hosten, C. M.; Ejeh, D.; Hambright, P.; Fujita, E. *J. Phys. Chem.* **1998**, *102*, 2870.

(7) Dhanasekaran, T.; Grodkowski, J.; Neta, P.; Hambright, P.; Fujita, E. *J. Phys. Chem. A* **1999**, *103*, 7742.

(8) Fujiwara, H.; Kitamura, T.; Wada, Y.; Yanagida, S.; Kamat, P. V. *J. Phys. Chem. A* **1999**, *103*, 4874.

(9) Getoff, N. *Z. Naturforsch. B* **1962**, *17*, 87. Åkermark, B.; Eklund-Westlin, U.; Baeckström, P.; Löf, R. *Acta Chem. Scand. B* **1980**, *34*, 27. Borowska, Z.; Mauzerall, D. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 6577.

(10) 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.

(11) Bechtold, T.; Burtscher, E.; Turcanu, A.; Bobleter, O. *J. Appl. Electrochem.* **1997**, *27*, 1021. Bechtold, T.; Burtscher, E.; Amann, A.; Bobleter, O. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2451. Bechtold, Th.; Burtscher, E.; Gmeiner, D.; Bobleter, O. *J. Electroanal. Chem.* **1991**, *306*, 169.

(12) Arai, S.; Dorfman, L. M. *J. Chem. Phys.* **1964**, *41*, 2190. Arai, S.; Tremba, E. L.; Brandon, J. R.; Dorfman, L. M. *Can. J. Chem.* **1967**, *45*, 1119.

(13) Additional experiments indicated that at higher iron concentrations, and particularly in the presence of TEA, the yield of H_2 increased while that of CO remained the same. This is ascribed to the formation of aggregated iron oxides, which can catalyze photochemical production of H_2 but not CO.

(14) Since it has been shown that radiolytic reduction of Fe^{2+} in 2-propanol solutions saturated with CO leads to formation of $Fe(CO)_5$ (Remita, H.; Derai, R.; Delcourt, M. O. *J. Chim. Phys.* **1991**, *88*, 845; *Radiat. Phys. Chem.* **1991**, *37*, 221), we examined our ACN/TEOA/TP/Fe/CO_2 solutions after extensive photolysis but detected no IR peaks corresponding to the iron carbonyls. When we prepared $Fe(CO)_5$ in 2-propanol by radiolysis and mixed it with our photolysis system, we readily detected the IR peaks of the iron carbonyl, but these rapidly disappeared upon photolysis. These results rule out the possibility that iron carbonyls are formed in our system.

(15) Barltrop, J. A. *Pure Appl. Chem.* **1973**, *33*, 179.

(16) This reaction is known for other cyclohexadienyl type radicals, e.g.: Bhatia, K. *Radiat. Res.* **1974**, *59*, 537; Klein, G. W.; Schuler, R. H. *Radiat. Phys. Chem.* **1978**, *11*, 167.

(17) Matsuoka, S.; Kohzuki, T.; Pac, C.; Ishida, A.; Takamuku, S.; Kusaba, M.; Nakashima, N.; Yanagida, S. *J. Phys. Chem.* **1992**, *96*, 4437.

(18) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: New York, 1988; p 141.

(19) Arai, S.; Kira, A.; Imamura, M. *J. Chem. Phys.* **1971**, *54*, 5073.

(20) Kelly, C. A.; Blinn, E. L.; Camaioni, N.; D'Angelantonio, M.; Mullazani, Q. G. *Inorg. Chem.* **1999**, *38*, 1579.

(21) Goldstein, S.; Czapski, G.; Cohen, H.; Meyerstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 3903.

(22) Jayson, G. G.; Keene, J. P.; Stirling, D. A.; Swallow, A. J. *Trans. Faraday Soc.* **1969**, *65*, 2453. Nenadović, M. T.; Mićić, O. I.; Muk, A. A. *J. Chem. Soc., Dalton Trans.* **1980**, 586.

(23) Judging from a comparison of iron porphyrins to the simpler Fe-(saen) complexes: Floriani, C.; Calderazzo, F. *J. Chem. Soc. A* **1971**, 3665.