**REDOX REACTIONS OF METALLOPORPHYRINS AND THEIR ROLE IN
CATALYZED REDUCTION OF CARBON DIOXIDE**

Final Report

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The aim of this project was to investigate the role of highly reduced metalloporphyrins and related metal complexes as catalysts for reduction of carbon dioxide. First we studied iron porphyrins¹ as potential catalysts for photochemical reduction of CO₂ because such complexes were effective catalysts for electrochemical reduction of CO₂.² The reduction of several iron porphyrins was studied by photochemical and radiation chemical methods. Experiments in aqueous solutions were carried out with the water soluble complexes of TSPP (meso-tetrakis(4-sulfonatophenyl)porphyrin) and the three isomeric TMPyP (meso-tetrakis(N-methyl-X-pyridinium)porphyrin), and studies in organic solvents were done with TPP (tetraphenylporphyrin) and some of its phenyl-substituted derivatives. All starting materials were in the form of ClFe^{III}P and were reduced to Fe^{II}P and then to [Fe^IP]⁻ (the peripheral charges of the water soluble porphyrins are neglected in this notation). Radiolytic reduction was carried out in aqueous solutions containing an alcohol or formate ions as scavengers for H[•] and [•]OH radicals. Photochemical reduction was carried out mainly in DMF (N,N-dimethylformamide) or MeCN (acetonitrile) solutions containing TEA (triethylamine) as a reductive quencher.

The [Fe^IP]⁻ state was observed as a stable product in organic solvents but was stable in water only with TM2PyP at high pH. In organic solvents, it was unreactive toward CO₂ and only further photoreduction in the presence of CO₂ resulted in the formation of (CO)Fe^{II}P and subsequently of free CO. Turnover numbers ≈ 70 molecules of CO per porphyrin molecule were reached, while the porphyrin ligand was also reduced via protonation of the reduced macrocycle. Catalysis of CO₂ reduction took place when the porphyrin ligand and the medium were such that the [Fe^IP]⁻ state was relatively long-lived so that it could undergo further reduction to the [Fe⁰P]²⁻ state. More stable [Fe^IP]⁻ species were obtained when the medium was less acidic and less protic and when the ligand P inhibited protonation (e.g. by steric hindrance to the bending required for protonation). The medium, however, also plays an additional role in promoting CO formation by providing protons to extract the oxide ion. Thus, these two opposing effects of the medium proton donating ability have to be balanced to achieve optimal catalysis.

Subsequent experiments were carried out with cobalt porphyrins,³ which form a more stable [Co^IP]⁻ state. This product also was unreactive toward CO₂ and further reduction led to formation of species which were suggested to be [Co⁰P]²⁻ and which reacted with CO₂. Catalyzed photochemical reduction of CO₂ to CO and formate was confirmed with CoTPP in acetonitrile solutions containing TEA. Catalytic reduction of CO₂ was also confirmed by cyclic voltammetry and was shown to occur at the potential at which [Co^IP]⁻ is reduced to [Co⁰P]²⁻ and to involve a homogeneous solution catalysis rather than catalysis by porphyrin adsorbed on the electrode.

Thus iron and cobalt porphyrins (MP) can act as photosensitizers and catalysts for

photochemical reduction of CO₂ to CO in homogeneous solutions. In these experiments, the metalloporphyrins were photoreduced to their [M⁰P]²⁻ states and these electron-rich species reduced CO₂ to CO. The photoreduction was efficient for the ClM^{III}P to M^{II}P stage and probably took place by an intramolecular electron transfer from an axially bound TEA.

However, TEA did not complex significantly to the more reduced M^{II}P or [M^IP]⁻ centers and the quantum efficiency was much lower for the subsequent M^{II}P to [M⁰P]²⁻ reduction steps and for CO production.

Moreover, the Et₂N-HCH₃ radical reduces M^{II}P more slowly than it reduces ClM^{III}P, but it is not likely to reduce [M^IP]⁻, since the reduction potentials for M^IP/M⁰P are more negative than that for the Et₂N-HCH₃ radical.⁴

In an attempt to follow the formation and reactions of the transient intermediates involved in this catalytic process, we carried out pulse radiolysis experiments. To avoid reactions of organic radicals with Co^{II}P and Fe^{II}P that lead to organometallic products, RM^{III}P, we carried out the experiments in aqueous solutions containing formate ions as scavengers for H[•] and [•]OH radicals. The reactions of these radicals with formate produce [•]CO₂⁻ radicals, which reduced Fe^{II}P and Co^{II}P relatively rapidly (*k* of the order of 10⁸ L mol⁻¹ s⁻¹) to yield the corresponding M(I) porphyrins.

Further reaction of [•]CO₂⁻ radicals with M(I) porphyrins did not form the M(0) species but rather a complex with a different spectrum. It has been suggested that the initial product of the reaction is the complex (CO₂-MP)²⁻.

This is the same complex that is expected to be produced by reaction of [M⁰P]²⁻ with CO₂.

This complex may decompose by reaction with protons or with another CO₂ to yield CO.

Alternatively, it may release CO₂ and form a transient hydride, HM^{III}P, which will form either H₂ or a hydrogenated porphyrin ligand (see below).

The photochemical yield for reduction of M^{II}P to [M⁰P]²⁻ and for formation of CO was

relatively small under the above conditions. We obtained considerably higher quantum yields by adding p-terphenyl (TP) as a sensitizer.⁵ This compound forms an excited state that is rapidly quenched by TEA to produce the radical anion, $\text{TP}^{\bullet-}$.⁶ The reduction potential of the $\text{TP}/\text{TP}^{\bullet-}$ couple is highly negative (-2.45 V vs SCE in DMA)⁷ and since the reduction potentials for $\text{Fe}^{\text{I}}/\text{Fe}^0\text{TPP}$ (-1.64 V vs SCE)² and $\text{Co}^{\text{I}}/\text{Co}^0\text{TPP}$ (-2.02 V vs SCE)³ are less negative, $\text{TP}^{\bullet-}$ can reduce the metalloporphyrins down to their $[\text{M}^0\text{P}]^{2-}$ state.

The rate constants for these reactions, determined by pulse radiolysis in deoxygenated solutions of TP in DMF by monitoring the rate of decay of $\text{TP}^{\bullet-}$ as a function of porphyrin concentration, were essentially diffusion-controlled, close to $1 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ for both $\text{M}^{\text{II}}\text{P}$ and $[\text{M}^{\text{I}}\text{P}]^-$. The direct reaction of $\text{TP}^{\bullet-}$ with CO_2 was quite slow.

Catalytic photoreduction of CO_2 to CO by the metalloporphyrins was found to slow down and eventually stop after extended photolysis. The cause for this limit was found to be due both to depletion of starting materials and to accumulation of products. A side reaction that took place along with the reduction of CO_2 led to hydrogenation of the porphyrin macrocycle. The early hydrogenation products, such as chlorins and bacteriochlorins, also catalyzed the photochemical reduction of CO_2 to CO. However, further hydrogenation led to formation of colorless products and to degradation of the metal complex. Moreover, the photochemical production of CO was found to be limited by the CO accumulated in solution, which binds to the metal center and prevents the binding of CO_2 . This competitive binding was found to be unimportant with the porphyrins and thus should not prevent the formation of the catalytically active $[\text{M}^0\text{P}]^{2-}$ state. However, when the porphyrin macrocycle is gradually hydrogenated, the mechanism of catalyzed reduction of CO_2 may shift from the M^0 to the M^{I} oxidation state and then CO binding to the M^{I} complex may compete with CO_2 binding and inhibit its reduction.

Because photoreduction of CO_2 with metalloporphyrins involved hydrogenation and degradation of the macrocycle as a side reaction that limits the catalytic process, we investigated (a) whether any catalytic process takes place with the metal ions released from the porphyrin when the macrocycle is decomposed, (b) whether incorporation of the metalloporphyrin in the cavity of zeolites may protect it from degradation, and (c) whether related macrocycles may exhibit a higher catalytic activity or higher longevity in the catalytic process.

To address question (a), we carried out experiments in the same medium (organic solvent, amine, p-terphenyl, CO_2) but replaced the metalloporphyrins with inorganic salts.⁸ We found that ferrous ions in this medium form complexes with the amines, are reduced by the $\text{TP}^{\bullet-}$ radical anions, although 100 times more slowly than the metalloporphyrins, and catalyze reduction of

CO₂ until competitive binding of CO sets in. On the other hand, cobalt ions did not catalyze the reduction of CO₂ in this medium.

To address question (b) we first examined a metalloporphyrin that was incorporated into a MCM-41 zeolite type structure. We found that this matrix did not protect the porphyrin from degradation because the cavity was relatively large and the porphyrin was released into the solution after it was reduced. We then used CoPc that was synthesized inside the small cavity of sodium Y zeolite so that it cannot be released into the homogeneous phase. With such a zeolite suspended in solution, reduction of CO₂ to CO was almost as efficient as in homogeneous solutions with similar concentrations of the metal complex. However, the phthalocyanine macrocycle was not protected by the zeolite against degradation and the production of CO eventually stopped. This system did not show any advantage over the homogeneous system for photochemical reduction of CO₂.

To address question (c) we examined corrins, phthalocyanines, and corroles. Corrins contain fewer double bonds than porphyrins (6 instead of 11), phthalocyanines have a more highly aromatic structure and are known to be more resistant to degradation, and corroles have a smaller macrocycle cavity (missing one meso bridge, as in corrins, but with 10 double bonds).

Cobalt and iron phthalocyanines⁹ (Co^{II}Pc and Fe^{II}Pc) were readily reduced to [Co^IPc]⁻ and [Fe^IPc]⁻, which did not react with CO₂. Reduction of [Co^IPc]⁻ formed a product which was characterized as the radical anion, [Co^IPc^{•-}]²⁻, on the basis of its absorption spectra in the visible and IR regions. This species was stable under dry anaerobic conditions and reacted rapidly with CO₂. Catalytic formation of CO and formate was confirmed by photochemical experiments in DMF and MeCN solutions containing TEA. The photochemical yields were greatly enhanced by the addition of TP. The TP^{•-} radical anion reduced the phthalocyanines very rapidly. The rate constants for reduction of Co^{II}Pc, [Co^IPc]⁻, and [Fe^IPc]⁻ by TP^{•-}, determined by pulse radiolysis in DMF solutions, were nearly diffusion-controlled. The mono-reduced species formed from [Co^IPc]⁻ was unstable under the pulse radiolysis conditions but was longer-lived under the flash photolysis conditions. Therefore, we utilized the latter technique to examine the reaction of this species with CO₂.

For the laser flash photolysis experiments, [Co^IPc]⁻ was produced by CW photolysis of Co^{II}Pc in MeCN/TEA/TP. During this preparation significant amounts of protons were also produced, which accumulated as Et₃NH⁺. Flash photolysis of [Co^IPc]⁻ solutions in the presence of NaOCH₃, added to scavenge the protons, showed production of the TP^{•-} radical within the laser pulse. The TP^{•-} decayed with $\tau \approx 5 \mu\text{s}$. The transient spectrum produced evolved ($\tau \approx 100 \mu\text{s}$) to a spectrum stable for $> 20 \text{ ms}$. At 8 ms after the flash the observed spectrum was identical to that of [Co^IPc^{•-}]²⁻ obtained by sodium reduction. In the absence of NaOCH₃, flash photolysis

produced $\text{TP}^{\bullet-}$ which disappeared to produce a spectrum that again evolved ($\tau \approx 60 \mu\text{s}$) to a final spectrum that was stable for $> 20 \text{ ms}$, but was not the same as that obtained with NaOCH_3 . This suggests that, in the absence of NaOCH_3 , the reduced Co complex is protonated.

In CO_2 saturated solution, the initial and final spectra were the same as in the solutions with no added CO_2 and the final spectrum was stable for $> 20 \text{ ms}$. The only evidence of CO_2 binding was in the decay of the initially formed species that decayed slightly faster with added CO_2 than without. From these results we conclude that the reaction with CO_2

was either slower than we can observe with flash photolysis or the amount of the CO_2 adduct formed was small. This conclusion of weak CO_2 binding to the doubly reduced $[\text{Co}^{\text{I}}\text{Pc}^{\bullet-}]^{2-}$ complex is in contrast with earlier observations of strong CO_2 binding to singly reduced cobalt complexes of flexible (saturated) macrocycles like cyclam.¹⁰ While part of the stability of the CO_2 binding to cyclam-like complexes was ascribed to hydrogen bonding interactions between the bound CO_2 and the macrocycle, additional effects are also important. The extended π -system of the phthalocyanine can better accommodate negative charge donated from the reduced metal center, which reduces the charge on the metal that can be back donated to the CO_2 . Furthermore, the relatively rigid planar structure of the phthalocyanine and the consequently 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.

Studies with cobalt corrins¹¹ showed that these complexes are far more efficient than cobalt porphyrins or phthalocyanines in catalyzing the photoreduction of CO_2 under identical conditions and that the corrins persisted in solutions to provide much higher total yields of CO and formate. These finding may be explained by the more flexible structure of the corrin macrocycle, due to the lower number of double bonds, which may permit better binding of CO_2 . Nevertheless, the corrins were eventually degraded and production of CO stopped.

Studies with iron and cobalt corroles were undertaken because this macrocycle was known to stabilize the higher metal oxidation states and it was speculated that reduction of CO_2 might be effected by the M(I) complexes rather than M(0) . This speculation was based on the behavior of the oxidation products,¹² while the reduction products have not been studied before. Therefore, we examined the reduction products of iron and cobalt corroles by various methods.¹³ Chemical, electrochemical, and photochemical reductions of the stable metal corroles

$\text{Ph}_3\text{PCo}^{\text{III}}(\text{tpfc})$ ($\text{tpfc} = 5,10,15\text{-tris(pentafluorophenyl)corrole}$), $\text{ClFe}^{\text{IV}}(\text{tpfc})$, and $\text{ClFe}^{\text{IV}}(\text{tdcc})$ ($\text{tdcc} = 5,10,15\text{-tris(2,6-dichlorophenyl)corrole}$) were carried out in MeCN solutions. Stepwise reduction to the M(II) and M(I) states was observed in all cases. Gradual reduction with sodium amalgam permitted recording of the optical absorption spectra of the various oxidation states and showed that the M(I) state reacted with CO_2 . Cyclic voltammetry in MeCN solutions permitted determination of the half-wave potentials and also indicated that in CO_2 -saturated solutions the M(I) complexes reacted with CO_2 . Photochemical reduction in CO_2 -saturated MeCN solutions containing TEA and TP led to production of CO and H_2 . The finding that the M(I) oxidation states of the cobalt and iron corroles can react with CO_2 is in contrast with the case of the respective porphyrins and phthalocyanines, which do not react with CO_2 until they are reduced beyond the M(I) state. Despite this difference in mechanism the total concentrations of CO and H_2 produced using corroles were similar to those obtained with porphyrins. This finding indicates that despite the fact that the corroles react with CO_2 in their M(I) oxidation state while the porphyrins have to be reduced beyond the M(I) state to react with CO_2 , in both cases the reduced species are hydrogenated at the macrocycle and are deactivated to similar extents.

In the experiments described above, the termination of CO production was not found to be associated with further reduction of CO to formaldehyde, methanol, or methane but rather with side reactions leading to different products. Previous electrochemical studies indicated that reduction of CO_2 at a copper electrode led to formation of not only CO but also of further reduction products, including methane.¹⁴ It may be speculated, therefore, that if CO_2 can be reduced at the surface of copper colloids, reduction might produce methane as well. Preliminary photochemical experiments indicated that it was not possible to reduce Cu(II) ions to small metallic particles dispersed in MeCN solutions and we resorted to radiolytic experiments in aqueous solutions to study the mechanism.¹⁵ Radiolysis of aqueous solutions containing CO_2 and Cu(II) ions under reducing conditions led first to reduction of the Cu(II) and then to formation of CO. Experiments under various conditions showed that although Cu(II) was often reduced to colloidal Cu(0) particles, formation of CO required the presence of Cu(I) . It also required that CO_2 be first reduced to the $\cdot\text{CO}_2^-$ radical. The $\cdot\text{CO}_2^-$ radical was produced radiolytically by reaction of CO_2 with e_{aq}^- or by reaction of formate ions with $\text{H}\cdot$ and $\cdot\text{OH}$ radicals and photochemically by reaction of formate with the acetone triplet. The $\cdot\text{CO}_2^-$ radicals were reduced to CO via addition to Cu(I) and subsequent reaction of the product with another Cu(I) . The first reaction produces CuCO_2 , which undergoes protonation at $\text{pH} < 4$. The reaction of the neutral CuCO_2 with Cu(I) leads to reduction of the copper to form Cu_2^+ and subsequently Cu(0) particles.^{16,17} However, the reaction of the protonated form, CuCO_2H^+ , with Cu(I) leads to oxidation of the copper and formation of CO in the form of the CuCO^+ complex. After most of

the copper was converted into CuCO^+ , subsequent reactions involved this species instead of Cu^+ and led to further production of CO. From pulse radiolysis measurements, the rate constants for the reactions of the $\cdot\text{CO}_2^-$ radicals with Cu^+ and CuCO^+ were found to be $\approx 1 \times 10^9$ and 1.5×10^8 $\text{L mol}^{-1} \text{s}^{-1}$, respectively. The protonated adduct formed by the latter reaction at pH 3.4, $\text{Cu}(\text{CO})\text{CO}_2\text{H}^+$, reacted with CuCO^+ with a rate constant $\approx 5 \times 10^5$ $\text{L mol}^{-1} \text{s}^{-1}$ to produce more CO. Thus, the addition of $\cdot\text{CO}_2^-$ radicals to Cu^+ is the first step toward the production of CO in acidic solutions. A similar addition reaction may take place with Cu(I) sites in the small copper aggregates, Cu_n^+ . The adduct formed by this reaction may react with another Cu(I) in solution to form CO. It may be speculated, however, that a Cu(0) site within the same aggregate, if the particle is sufficiently small, may rapidly reduce the adduct before it leaves the particle. Such a reaction is unlikely when the copper particle is large because its reduction potential is much less negative.¹⁷ This was evident from the finding that production of CO stopped when all the copper was in the form of metallic particles.

Experiments were also carried out with CO-saturated solutions to test whether CO can be reduced by a similar mechanism as CO_2 . Photolysis of CO-saturated solutions containing acetone, 2-PrOH, PVA, and CuSO_4 , led to production of Cu(0) particles, which were stable after extended photolysis, with no consumption of CO. However, radiolysis of CO-saturated solutions of Cu(II) and 2-PrOH led to production of Cu(0) particles and subsequently to a decrease in CO concentration ($G \approx 0.5 \times 10^{-7} \text{ mol J}^{-1}$). This preferential reduction of the copper ions is in contrast with the radiolytic results in CO_2 -saturated solutions and is due to the fact that both the solubility of CO in water and its reactivity towards e_{aq}^- are much lower (factors of 45 and 4.5, respectively) than those of CO_2 . Thus, most solvated electrons and all other reducing radicals produced by the radiolysis react with copper ions leading to production of Cu(0) particles and only when this process is nearly complete can CO react with e_{aq}^- . Therefore, the reaction between $\cdot\text{CO}^-$ radicals and Cu(I) could not be evaluated under these conditions.

In contrast with the difficulties encountered in the photochemical reduction of Cu(II) ions to a reactive catalyst in MeCN solutions, we found that Fe ions can be photoreduced in MeCN/TEA/TP solutions to a species that can reduce CO_2 to CO, as discussed above, and can also reduce CO. Preliminary experiments with CO-saturated solutions showed that the amount of CO in the photolysis cell (the total in the liquid and gas phase) decreased dramatically upon photolysis. However, formaldehyde was not detected in solution, possibly because it could have been further reduced to methanol. CH_4 also was not detected among the gases. Careful GC/MS search for methanol did not confirm any significant amounts but detected other products that were probably formed by dimerization of formyl radicals. This suggests that CO is reduced within the iron complex to CHO and these species are not reduced further but rather undergo

dimerization, either from within the complex or after being released into the solution.

Other avenues for photochemical reduction of CO_2 beyond the CO stage were explored. Insertion of CO into hydridorhodium porphyrins has been reported. Under photochemical conditions, CO-saturated Rh^{III} -porphyrin solutions containing TEA, TP, and acetic acid formed the hydride ($\text{HRh}^{\text{III}}\text{P}$) but further photolysis led mainly to degradation of the porphyrin. Direct photochemical reduction of CO_2 to CH_4 with colloidal metal catalysts was reported by two groups, one indicating much lower yields than the other. Our attempts to reproduce the reported results gave very low yields of CH_4 which appeared to be produced from sources other than CO_2 . Because of the very low yields this system was not studied further.

In summary, porphyrins, phthalocyanines, corrins, and corroles, which contain Fe or Co as the metal center, are capable of catalyzing the photochemical reduction of CO_2 to CO in homogeneous solutions. Complexes containing Ni, Rh, Ru, or Mn are not active in such processes. Complexes of Fe and Co with the various macrocyclic ligands show slightly different activities and may act via slightly different mechanisms, but in all cases the catalytic system does not persist. Photochemical reduction of CO_2 is accompanied by a side reaction leading to reduction of the macrocyclic ligand and degradation of the complex. This appears to be a disadvantage suffered by many homogeneous catalysts for photochemical reduction of CO_2 . Heterogeneous catalysis appears to offer more persistent catalysts and will hopefully lead to a working system.

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