PHOTOREDUCTION OF CO$_2$ USING METAL COMPLEXES

Etsuko Fujita
Chemistry Department, Brookhaven National Laboratory,
Upton, NY 11973-5000

Abstract

Photochemical reduction of CO$_2$ to fuels and chemicals is a challenging task. Work in the area of photochemical CO$_2$ reduction from the early 1980s to the present is summarized to provide a perspective on the achievements and problems involved in the process.

Introduction

Carbon dioxide fixation is an important area to study for the solution of problems related to the global environment and the depletion of fossil fuels. The chemical fixation involves conversion of recovered or separated CO$_2$ into useful chemicals and fuels. Economical fixation of CO$_2$ is only feasible if solar or hydraulic energy can be converted to chemical energy. There are several ways to use solar energy for CO$_2$ fixation: (1) solar-photochemical reduction of CO$_2$ typically to CO, HCOO$^-$, CH$_3$OH, and CH$_4$; (2) electroreduction of CO$_2$ [and water] using power generated by solar batteries typically to CO and HCOO$^-$ [and H$_2$]; (3) photoelectroreduction of CO$_2$ using semiconductors and surface-modified electrodes; (4) homogeneous and heterogeneous catalytic hydrogenation of CO$_2$ to methanol, formic acid, formamide, polymers, hydrocarbons, and others with solar generated H$_2$; and (5) genetically improved photosynthetic bacteria and algae-based CO$_2$ fixation [and H$_2$ production]. In this paper, we focus on photochemical reduction of CO$_2$ by homogeneous and microheterogeneous photocatalysts. Although many photo-induced stoichiometric reactions such as an insertion or addition of CO$_2$, reductive disproportionation to CO, metathesis of CN by CO$_2$, the formation of M-CO and M-OCHO complexes and in rare cases, the formation of M=O together with CO are known, we limit our discussion to
photocatalytic reactions using metal complexes as catalysts. Photoinduced CO₂ fixation systems containing enzymes are omitted.

**Photocatalytic systems for CO₂ reduction**

The potential for the reduction of CO₂ to CO₂⁻ is -1.9 V vs NHE, making the one-electron reduction mechanism highly unfavorable. In addition there is a large kinetic “overvoltage” for the one-electron reduction because of structural differences between linear CO₂ and bent CO₂⁻. In contrast, proton assisted multi-electron steps are much more favorable:

\[
\begin{align*}
\text{CO}_2 + 2\text{H}^+ + 2e^- &\rightarrow \text{HCO}_2\text{H} & E^0 &= -0.61 \text{ V} \\
\text{CO}_2 + 2\text{H}^+ + 2e^- &\rightarrow \text{CO} + \text{H}_2\text{O} & E^0 &= -0.53 \text{ V} \\
\text{CO}_2 + 4\text{H}^+ + 4e^- &\rightarrow \text{C} + 2\text{H}_2\text{O} & E^0 &= -0.20 \text{ V} \\
\text{CO}_2 + 4\text{H}^+ + 4e^- &\rightarrow \text{HCHO} + \text{H}_2\text{O} & E^0 &= -0.48 \text{ V} \\
\text{CO}_2 + 6\text{H}^+ + 6e^- &\rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} & E^0 &= -0.38 \text{ V} \\
\text{CO}_2 + 8\text{H}^+ + 8e^- &\rightarrow \text{CH}_4 + 2\text{H}_2\text{O} & E^0 &= -0.24 \text{ V}
\end{align*}
\]

Since the two-electron reduction to formic acid or CO requires a considerably lower potential than the one-electron reduction, electrolysis in the presence of catalysts can be carried out at considerably lower voltages. In the photochemical reduction of CO₂, the same considerations apply: the one-electron reduction to CO₂⁻ requires extremely strong reducing agents that are generally difficult to produce by photochemical methods.

Transition metal complexes have been used as photosensitizers and/or catalysts because: (1) they generally absorb visible light; (2) their excited states generally live long and promote rapid electron transfer; (3) their oxidation states accommodate multi-equivalent charge transfer to produce highly reduced and oxidized species; (4) they can provide vacant coordination site(s) for activation of small molecules. The systems used for photochemical CO₂ reduction can be categorized into several groups as shown below. The results from the various photocatalytic systems are summarized in Table 1.

**DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>Catalyst or Relay</th>
<th>Donor</th>
<th>Product(s)</th>
<th>(\Phi)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(bpy)_3^{2+}</td>
<td>TEOA</td>
<td>HCOO^-</td>
<td>0.01</td>
<td>4, 5</td>
<td></td>
</tr>
<tr>
<td>Ru(bpy)_3^{2+}</td>
<td>MV^{2+}</td>
<td>TEOA</td>
<td>HCOO^-</td>
<td>0.01</td>
<td>6</td>
</tr>
<tr>
<td>ReCl(bpy)(CO)_3</td>
<td>TEOA</td>
<td>CO</td>
<td>0.14</td>
<td>7, 8</td>
<td></td>
</tr>
<tr>
<td>ReBr(bpy)(CO)_3</td>
<td>TEOA</td>
<td>CO</td>
<td>0.15</td>
<td>10, 11</td>
<td></td>
</tr>
<tr>
<td>ReP(OEt)_3(bpy)(CO)_3</td>
<td>TEOA</td>
<td>CO</td>
<td>0.38</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Ru(bpy)_3^{2+}</td>
<td>Co^{2+}/bpy</td>
<td>TEA</td>
<td>CO, H_2</td>
<td>0.08</td>
<td>14</td>
</tr>
<tr>
<td>Ru(bpy)_3^{2+}</td>
<td>Co^{2+}/Me_2phen</td>
<td>TEA</td>
<td>CO, H_2</td>
<td>0.14</td>
<td>15</td>
</tr>
<tr>
<td>Ru(bpy)_3^{2+}</td>
<td>Ru(bpy)_2(CO)_2^{2+}</td>
<td>TEOA</td>
<td>HCOO^-</td>
<td>0.03 (HCOO^-)</td>
<td>18 - 20</td>
</tr>
<tr>
<td>Ru(bpy)_3^{2+}</td>
<td>Ru(bpy)_2(CO)_2^{2+}</td>
<td>BNAH</td>
<td>HCOO^-</td>
<td>0.15 (CO)</td>
<td>18 - 20</td>
</tr>
<tr>
<td>Ru(bpy)_3^{2+}</td>
<td>CoHMD^{2+}</td>
<td>H_2A</td>
<td>CO, H_2</td>
<td>0.001 (CO)</td>
<td>27</td>
</tr>
<tr>
<td>Ru(bpy)_3^{2+}</td>
<td>Nicyclam^{2+}</td>
<td>H_2A</td>
<td>CO, H_2</td>
<td>0.005 (CO)</td>
<td>28, 29</td>
</tr>
<tr>
<td>Ru(bpy)_3^{2+}</td>
<td>NiPr-cyclam^{2+}</td>
<td>H_2A</td>
<td>CO, H_2</td>
<td>0.15 (CO)</td>
<td>28, 29</td>
</tr>
<tr>
<td>Ru(bpy)_3^{2+}</td>
<td>bipyridinium^+</td>
<td>TEOA</td>
<td>CH_4, HCOO^-</td>
<td>0.25</td>
<td>47, 48</td>
</tr>
<tr>
<td>Ru(bpy)_3^{2+}</td>
<td>bipyridinium^+</td>
<td>TEOA</td>
<td>CH_4, HCOO^-</td>
<td>0.25</td>
<td>47, 48</td>
</tr>
<tr>
<td>Ru(bpy)_3^{2+}</td>
<td>Ru or Os colloid</td>
<td>H_2</td>
<td>10^-3 (H_2)</td>
<td>37, 39</td>
<td></td>
</tr>
<tr>
<td>p-Terphenyl</td>
<td>Cocyclam^{3+}</td>
<td>TEOA</td>
<td>CO, HCOO^-</td>
<td>0.25</td>
<td>47, 48</td>
</tr>
<tr>
<td>p-Terphenyl</td>
<td>CoHMD^{2+}</td>
<td>TEOA</td>
<td>CO, HCOO^-</td>
<td>0.07</td>
<td>52</td>
</tr>
</tbody>
</table>

\(\Phi\) denotes the quantum efficiency.  

Abbreviations used: TEOA = triethanolamine, MV^{2+} = methylviologen, TEA = triethylamine, bpy = 2,2'-bipyridine, Me_2phen = 2,9-Dimethyl-1,10-phenanthroline, BNAH = 1-benzyl-1,4-dihydronicotinamide, H_2A = ascorbic acid, cyclam = 1,4,8,11-tetraazacyclotetradecane and Pr-cyclam = 6-((N-R)pyridin-4-yl)methyl-1,4,8,11-tetraazacyclotetradecane where R = p-methoxybenzyl and benzyl.

(I) Ru(bpy)_3^{2+} both as a photosensitizer and a catalyst

It was reported in 1985\(^4,5\) that visible light irradiation of Ru(bpy)_3Cl_2 (bpy = 2,2'-bipyridine) in dimethylformamide (DMF) - triethanolamine (TEOA) media containing CO_2 leads to efficient and preferential reduction of CO_2 to formate. The Ru(bpy)_3^{2+} complex acts both as photosensitizer and as
precursor of the catalytic species. Reductive quenching of the excited state of the Ru(bpy)₃²⁺ by TEOA occurs, yielding the reduced Ru complex as shown in scheme I.

Scheme I. Reductive quenching

\[
\text{Ru(bpy)}₃²⁺ + \text{hv} \rightarrow *\text{Ru(bpy)}₃²⁺ \quad (7)
\]

\[
*\text{Ru(bpy)}₃²⁺ + \text{TEOA} \rightarrow \text{Ru(bpy)}₃³⁺ + \text{TEOA}⁺ \quad (8)
\]

\[
\text{TEOA}⁺ + \text{TEOA} \rightarrow \text{TEOA}⁻ + \text{TEOAH}⁺ \quad (9)
\]

\[
\text{TEOA}⁻ + \text{Ru(bpy)}₃²⁺ \rightarrow \text{TEOA}₀\text{x} + \text{Ru(bpy)}₃³⁺ \quad (10)
\]

However the reduced Ru complex cannot reduce CO₂ directly in the one-electron transfer process which requires -1.9 V since the Ru(bpy)₃²⁺/³⁺ potential is -1.26 V. Since the presence of water enhanced the reaction with an optimum concentration around 0.015 M (~15%), water may play a role in a photolabilization of bpy to form the active catalytic intermediate. The authors speculate that reduction of CO₂ to formic acid may involve the following sequential steps: (1) photogeneration of Ru(bpy)₃⁺; (2) ligand photolabilization; (3) hydride formation by protonation; (4) insertion of CO₂; and (5) release of the formate produced. However, possible intermediates such as Ru(bpy)₂(H₂O)(H)²⁺ and Ru(bpy)₂(H₂O)(OCOH)²⁺ have not been characterized. Quantum yields were not reported.

An aqueous system containing Ru(bpy)₃²⁺, methylviologen (MV²⁺) and TEOA photoreduces CO₂ to formate with a quantum yield of 0.01. In contrast to the previous system, the excited state of Ru(bpy)₃²⁺ is oxidatively quenched by MV²⁺ to form Ru(bpy)₃³⁺ and MV⁺ as shown in scheme II. However, direct electron transfer from MV⁺ to CO₂ is energetically impossible, since the reduction potential of MV²⁺/³⁺ is only -0.44 V. Although no mechanistic study was done, the authors suggest a mechanism which must involve proton participation as shown in eq. 1, since the pH of the CO₂ saturated solution is lower than pH 7. We believe the reactions 9 and 10 also produce Ru(bpy)₃⁺ which can effect CO₂ reduction. The actual mechanism may be quite complicated.

Scheme II. Oxidative quenching

\[
\text{Ru(bpy)}₃²⁺ + \text{hv} \rightarrow *\text{Ru(bpy)}₃²⁺ \quad (7)
\]

\[
*\text{Ru(bpy)}₃²⁺ + \text{MV}²⁺ \rightarrow \text{Ru(bpy)}₃³⁺ + \text{MV}⁺ \quad (11)
\]

\[
\text{Ru(bpy)}₃³⁺ + \text{TEOA} \rightarrow \text{Ru(bpy)}₃²⁺ + \text{TEOA}⁺ \quad (12)
\]

\[
\text{TEOA}⁺ + \text{TEOA} \rightarrow \text{TEOA}⁻ + \text{TEOAH}⁺ \quad (9)
\]

\[
\text{TEOA}⁻ + \text{Ru(bpy)}₃³⁺ \rightarrow \text{TEOA}₀\text{x} + \text{Ru(bpy)}₃²⁺ \quad (13)
\]

\[
\text{TEOA}⁻ + \text{Ru(bpy)}₃²⁺ \rightarrow \text{TEOA}₀\text{x} + \text{Ru(bpy)}₃³⁺ \quad (10)
\]

(II) ReX(CO)₃(bpy) or a similar complex as a photosensitizer
ReX(CO)3(bpy) (X = Cl, Br) has been used successfully as a photocatalyst for CO2 reduction to CO with TEOA in DMF. When X = Cl, a quantum yield of 0.14 was measured in the presence of excess Cl−. A formato-rehenium complex was isolated in the absence of excess Cl−. It is known that Re(bpy)(CO)3H undergoes a slow thermal reaction with CO2 to give the formato complex and the reaction is greatly enhanced by visible light. Detailed mechanistic studies using ReBr(CO)3(bpy) with TEOA or TEA indicate that TEOA, TEA (triethylamine) and Br− reductively quench the emission from the MLCT excited state of ReBr(CO)3(bpy) leading to prompt formation of ReBr(CO)3(bpy)−, which likely reacts with CO2. Re(CO)2(bpy){P(OEt)3}2+ is also a CO2 reduction catalyst which produces CO with a quantum yield up to 0.38. Both the quantum yield and turnover number of the photocatalytic reaction are strongly dependent on the irradiation light intensity and wavelength. The photophysical behavior was studied by means of time-resolved UV-vis and IR spectroscopies. The photo-generated reduced catalyst, Re(CO)2(bpy){P(OEt)3}2−, is also important for the activation of CO2. However, in both ReX(CO)3(bpy) and Re(CO)2(bpy){P(OEt)3}2+ systems it is still not known whether the CO2 activation involves reactions such as: (1) formation of an unstable intermediate with vacant coordination site(s) from loss of CO, X−, P(OEt)3, or the bpy ligand from ReX(CO)3(bpy)− or Re(CO)2(bpy){P(OEt)3}2−; (2) formation of the CO2 adduct from the unstable intermediate; (3) formation of the hydride species from the unstable intermediate followed by the insertion of CO2.

(III) Ru(bpy)32+ as a photosensitizer and another metal complex as a catalyst

It was reported in 1982 that a system containing Ru(bpy)32+/Co2+/tertiary amine as photosensitizer/catalyst/donor, respectively, is capable of catalytically generating CO (instead of formic acid) and H2 by reduction of CO2 and water under irradiation with visible light. When TEA is used as donor, the system produces CO and H2 in the ratio 0.68. The amount of gas (CO + H2) produced and the CO/H2 ratio depend markedly on the composition of the system and the amine used as donor. Addition of free bpy strongly decreases CO generation, but increases H2 production. Higher selectivity for CO2 reduction to CO was observed when TEOA was used instead of TEA.

The system was further studied by adding 4,4′,6,6′-tetramethyl-2,2′-bipyridine or 2,9-dimethyl-1,10-phenanthroline instead of bpy. 2,9-Dimethyl-1,10-phenanthroline is particularly effective in promoting CO and H2 formation, giving a quantum yield of 0.012 for CO and 0.065 for H2.

Since the systems described above contain free bipyridine-type ligands, the formation of the Co(I) species from the excited state of Ru(bpy)32+ in the Ru(bpy)32+/Co(bpy)32+/tertiary amine system has been examined in some detail. Stoichiometric studies with Co(bpy)32+ and CO2 were also carried out in order to elucidate the mechanism of the CO2 reduction. It was shown that Co(bpy)32+ can be generated from *Ru(bpy)32+ by various routes including reduction of *Ru(bpy)32+ to Ru(bpy)32+, followed by reaction with Co(bpy)32+, oxidation of the *Ru(bpy)32+ by Co(bpy)32+ to Ru(bpy)32+ and, in principle, energy transfer to form Ru(bpy)32+. The high-spin Co(bpy)32+ complex, which is substitution labile, is effective in reducing bpy to bpyH2, H2O to H2 and CO2 to CO (as the insoluble [Co(bpy)(CO)2]2), likely with Co(bpy)2(H2O)H2+ and/or Co(bpy)2(H2O)2+ as intermediate. Unfortunately neither the CO2 adduct nor the formato complex has been isolated.

Photochemical reduction of CO2 has been achieved by using TEOA in DMF or the NADH model compound, 1-benzyl-1,4-dihydronicotinamide (BNAH) in H2O/DMF, as a quencher in the presence of Ru(bpy)32+ and Ru(bpy)2(CO)22+. The system containing TEOA produces formate with a quantum yield of 0.14, whereas the system containing BNAH gave formate and CO with quantum yields of 0.03 and 0.15, respectively. The reduction potential of Ru(bpy)32+ (-1.33 V vs SCE in DMF) is more
negative than that of Ru(bpy)$_2$(CO)$_2^{2+}$ (-0.98 V) and nearly the same as Ru(bpy)$_2$(CO)(COO$^-$)$^+ (-1.30 V). Therefore, Ru(bpy)$_3^+$ formed photochemically functions as the reductant of Ru(bpy)$_2$(CO)$_2^{2+}$.

\[
\text{Ru(bpy)$_2$(CO)$_2^{2+}$} + 2e^- \rightarrow \text{Ru(bpy)$_2$(CO)} + \text{CO} \quad (14)
\]

\[
\text{Ru(bpy)$_2$(CO)} + \text{CO}_2 \rightarrow \text{Ru(bpy)$_2$(CO)}(\text{COO}^-$)$^+ \quad (15)
\]

\[
\text{Ru(bpy)$_2$(CO)$_2^{2+}$} + \text{OH}^- \rightarrow \text{Ru(bpy)$_2$(CO)}(\text{COOH})^+ \quad (16)
\]

\[
\text{Ru(bpy)$_2$(CO)(COOH)}^+ + \text{OH}^- \rightarrow \text{Ru(bpy)$_2$(CO)}(\text{COO}^-$)$^+ + \text{H}_2\text{O} \quad (17)
\]

\[
\text{Ru(bpy)$_2$(CO)(COO$^-$)$^+ + H^+ + 2e^-} \rightarrow \text{Ru(bpy)$_2$(CO)} + \text{HCOO}^- \quad (18)
\]

Suggested mechanisms$^{19}$ are shown in eqs. 14 and 15: the reduction of Ru(bpy)$_2$(CO)$_2^{2+}$ by two molecules of photogenerated Ru(bpy)$_3^+$ to yield CO with generation of Ru(bpy)$_2$(CO)(COO$^-$)$^+$ via Ru(bpy)$_2$(CO) as shown in eqs. 14 and 15 in CO$_2$-saturated DMF. Based on their electrochemical studies,$^{20}$ the authors propose$^{19}$ that the HCOO$^-$ is generated from Ru(bpy)$_2$(CO)(COO$^-$)$^+$ by a two-electron reduction involving participation of one proton as shown eq 18. They further explain,$^{19}$ that the change in the main product from HCOO$^-$ to CO is due to acid-base equilibria among Ru(bpy)$_2$(CO)$_2^{2+}$, Ru(bpy)$_2$(CO)(COOH)$^+$, and Ru(bpy)$_2$(CO)(COO$^-$)$^+$ as shown in eqs. 16 and 17. It is widely believed that HCOO$^-$ forms by CO$_2$ insertion into the M-H bond in other cases. Re(bpy)(CO)$_3$H reacts with CO$_2$ to afford Re(bpy)(CO)$_3$OC(O)H quantitatively.$^{21}$ [Ru(bpy)$_2$(CO)H]$^+$ reacts with CO$_2$ to form a formato complex, [Ru(bpy)$_2$(CO)O(O)CH], which produces HCOO$^-$ upon another one-electron reduction.$^{22}$ The doubly reduced species Ru(bpy)$_2$(CO) in eq. 14 may react with H$^+$ to form [Ru(bpy)$_2$(CO)H]$^+$, into which CO$_2$ may insert to form the formato complex. However, it is reported that the catalytic systems composed of Ru(bpy)$_3^{2+}$/Ru(bpy)$_2$(CO)$_2$/BNAH and Ru(bpy)$_3^{2+}$/[Ru(bpy)$_2$(CO)H]$^+$/BNAH shows essentially the same reactivity (i.e., production rates and selectivity) in CO$_2$ reduction.$^{19}$ Both systems produce more CO than HCOO$^-$ (CO/HCOO$^-$ = 5). As possible intermediates in the CO$_2$ reduction system, the molecular structures of [Ru(bpy)$_2$(CO)$_2$][PF$_6$]$_2$, [Ru(bpy)$_2$(CO)(CO)(O)CH$_3$]$_2$[B(C$_6$H$_5$)$_4$CH$_3$CN (as a model of [Ru(bpy)$_2$(CO)COOH$^-$])$^+$, [Ru(bpy)$_2$(CO)(η-CO$_2$)$_2$]$,^+$ and [Ru(bpy)$_2$(CO)(CH$_2$OH)]$^{2+}$ have been determined.$^{23-26}$ However isolation of the formate complex formed by CO$_2$ insertion into [Ru(bpy)$_2$(CO)H]$^+$ has not been reported. It would be highly desirable to elucidate the detailed mechanism of formate and CO formation in this photocatalytic system$^{19}$ using time-resolved spectroscopies.

Photochemical CO$_2$ reduction to CO (and formate in some cases) has been reported in a catalytic system using Ru(bpy)$_3^{2+}$ as the sensitizer, nickel or cobalt macrocycles (shown in Figure 1) as the electron relay catalyst, and ascorbate as a sacrificial reductive quencher. These systems also produce H$_2$ via reduction of water. When CoHMD$^{2+}$ is used as a catalyst at pH 4, the system produces a mixture of CO and H$_2$ with low selectivity (CO/H$_2$ = 0.06 - 0.3, depending on the conditions).$^{27}$ Nicyclam$^{2+}$ is reported to be an extremely efficient and selective catalyst for the electrochemical reduction of CO$_2$ to CO, even in H$_2$O.$^{32,33}$ When Nicyclam$^{2+}$ is used as a catalyst in the photochemical system,$^{28,29}$ however, the quantum yield of CO production is $5 \times 10^{-4}$ at pH 5 and the selectivity, CO/H$_2$, is ~0.8. (The yield of both CO and H$_2$ are pH dependent and typically more H$_2$ is produced than CO.) Nicyclam$^{2+}$ which is high-spin, six-coordinate with two cis water molecules, produces both CO and formate, while Nicyclam$^{2+}$, which is mainly low-spin, square-planar in H$_2$O, yields only CO from CO$_2$ reduction. [Co$^{III}$(L-H$^-$)]$^{2+}$ or [Ni$^{III}$(L-H$^-$)]$^{2+}$ (where L is a macrocyclic ligand) is suggested to be a common
intermediate for CO and H₂ production in these photocatalytic systems, however, new studies \(^{34-36}\) indicate that this may be incorrect (see section V).

\[
\text{cyclam} \quad \text{cyclam'} \quad \text{Pr-cyclam} \quad \text{HMD} \quad \text{DMD}
\]

Nicyclam complexes containing a pendant pyridinium group, which had been shown to function as effective mediators in the photochemical reduction of H₂O with a Pt colloid, \(^{37,38}\) were prepared and their catalytic behavior toward photochemical CO₂ reduction with Ru(bpy)₃²⁺ was examined. \(^{31}\) The system containing NiPr-cyclam²⁺ (R = p-methoxybenzyl and benzyl) at pH 5 evolved CO about 5 times more than that with underivatized Nicyclam²⁺. The selectivity (CO/H₂ = 0.1 - 0.65) depends on the conditions used, and typically more CO is produced with higher NiPr-cyclam²⁺ concentration.

(III) Ru(bpy)₃²⁺ and Ru(bpy)₃²⁺-type complexes as photosensitizers in microheterogeneous systems

The photoreduction of CO₂ to methane and hydrocarbons is achieved in aqueous solution containing Ru(bpy)₃²⁺, an electron donor, a bipyridinium charge relay, and Ru or Os colloids. \(^{37} \) The quantum yields for H₂ evolution (\( \sim 10^{-3} \)) and hydrocarbon formation (\( \sim 10^{-4} \) for CH₄, \( \sim 10^{-5} \) for C₂H₄) depend on the relay used. However, a similar system containing Ru(bpz)₃²⁺ (bpz = bipyrazine) as sensitizer without a bipyridinium charge relay leads to the formation of methane, ethylene and ethane without the evolution of H₂. \(^{37,39}\) The reduction of CO₂ is proposed to proceed via electron transfer followed by protonation of Ru- or Os metal-activated CO₂ rather than through a hydrogenation route, since no H₂ evolution occurs either in the presence of CO₂ or under argon with Ru(bpz)₃²⁺.

(IV) Other metal complexes as photosensitizers

Photoreduction of CO₂ to formaldehyde and HCOO⁻ has been carried out using an electron relay composed of trichlorobis(2,2':6',2''-terpyridyl)vanadium(III) as photosensitizer, MV²⁺ as electron acceptor, and ethylenediaminotetracetic acid (EDTA) or TEOA as sacrificial electron donor. \(^{40}\) The quantum yields of photoproduction of formaldehyde are 0.036 and 0.051 with EDTA and TEOA, respectively, at 690 nm. The system is potentially photocatalytic, however the amount of formaldehyde and HCOO⁻ produced are less than 10 % of the amount of photosensitizer used.

Since the one-electron reduction of CO₂ to CO₂⁻ requires -1.9 V vs NHE, it is difficult to produce CO₂⁻ by photochemical methods. The trinuclear cluster \([\text{Ni}_3(\mu_3-I)_2(\text{dppm})_3]\) \{dppm = bis(diphenylphosphino)methane\} is reported to reduce CO₂ to CO₂⁻ in THF when irradiated at \( \lambda > 300 \) nm. \(^{41}\) Photolysis of \([\text{Ni}_3(\mu_3-I)_2(\text{dppm})_3]\) in a 4:1 v/v THF/cyclohexene solution under 1 atm CO₂ led to
oxidation of [Ni₃(μ₃-I)₂(dppe)₃] and to the formation of cis- and trans-1,2-cyclohexanedicarboxylates. Although the system is not photocatalytic, it is a rare case of purported involvement of CO₂⁻. The authors assumed that the excited state of [Ni₃(μ₃-I)₂(dppe)₃] is quenched by CO₂ to form CO₂⁻, however no photophysical study of [Ni₃(μ₃-I)₂(dppe)₃] is reported. Mechanistic and kinetic studies using time-resolved spectroscopies and measurements of the excited state potential are required to verify the claim.

(V) Organic photosensitizers and ML²⁺ as catalysts

Irradiation of aromatic hydrocarbons such as phenanthrene, anthracene or pyrene in the presence of amine and carbon dioxide in aprotic solvents results in reductive carboxylation of the hydrocarbons.⁴²⁻⁴⁴ The reactions are considered to proceed via the anion radical of the hydrocarbon reacting with CO₂ and then abstracting hydrogen to yield the corresponding product. Unlike these hydrocarbons, oligo(p-phenylene) ranging from p-terphenyl to p-sexiphenyl catalyze the photoreduction of CO₂ to HCOO⁻ with TEA in a dried aprotic solvents such as DMF and CH₃CN.⁴⁵⁻⁴⁶ Although the apparent quantum yield is 0.072 with p-terphenyl, p-terphenyl concurrently undergoes photo-Birch reduction to form dihydrotetraphenyl derivatives and the system practically dies within 30 minutes. The turnover number for the formation of HCOO⁻ is 4. However the addition of cobalt macrocyclic complexes suppresses the degradative photo-Birch reduction, and leads to efficient formation of both carbon monoxide and formate.⁴⁷⁻⁴⁸ When the Co₃cyclam³⁺ complex is used, the total quantum yield for formation of carbon monoxide and formate is 0.25 at 313 nm in the presence of TEOA.

The kinetics and mechanism of CO formation in this system have been studied by continuous and flash photolysis techniques.⁴⁴ Transient spectra provide clear evidence for the sequential formation of the p-terphenyl radical anion, the CoIHMD⁺ complex, the [CoIHMD-CO₂]⁺ complex and the [S-CoIIIHMD-(CO₂²⁻)]⁺ complex (S = solvent) in the catalytic system. These species together with the [CoIHMD-CO]⁺ complex, had previously been identified by various spectroscopic techniques including UV-vis, IR, NMR, XANES and EXAFS.⁴⁵⁻⁴⁶ The XANES study indicates that six-coordinate [S-CoHMD-(CO₂²⁻)]⁺, in which a significant charge is transferred from metal to the bound CO₂, can be interpreted as a Co(III) carboxylate.⁵¹ The Co(I) complex transfers two electrons to the bound CO₂ moiety in this photocatalytic system.³⁴ The electron-transfer rate constant for the reaction of p-terphenyl radical anion with the CoIIHMD²⁺ is 1.1 × 10¹⁰ M⁻¹ s⁻¹ and is probably diffusion controlled because of the large driving force ( ~ 1.1 V). Flash photolysis studies yield a rate constant of 1.7 × 10⁸ M⁻¹ s⁻¹ and an equilibrium constant of 1.1 × 10⁴ M⁻¹ for the binding of CO₂ to CoIHMD⁺ in the catalytic system. These are consistent with those previously obtained by conventional methods in acetonitrile.³⁵,⁴⁹ The authors suggest that reactions 19-21 are responsible for the production of CO from [S-CoIIIHMD-(CO₂²⁻)]⁺ in the photolysis.

\[
[S-Co^{III}HMD-(CO_2^{2-})]^+ + HA \underset{HA = TEA, MeOH, TEOA}{\overset{=}{{\rightleftharpoons}}} [S-Co^{III}HMD-(COOH)^-]^{2+} + A^- \quad (19)
\]

\[
[S-Co^{III}HMD-(COOH)^+]^{2+} + \text{"e"}^{-} \quad \text{\text{\Longleftrightarrow} Co^{II}HMD^{2+} + CO + OH^{-}} \quad (20)
\]

\[
\text{OH}^{-} + \text{CO}_2 \underset{\text{Et}_2\text{NCCH}_3}{\rightleftharpoons} \text{HCO}_3^{-} \quad (21)
\]
The slow step is likely to be the C-O bond breakage in the bound carboxylic acid with either E2NC HCH3, or CoIIHMD+ acting as electron donor. Unfortunately the transient spectrum of [S-CoIIIHMD(CO22-)]+ is too weak to permit study of the proton dependence of its disappearance. Studies of catalytic systems with other cobalt macrocycles highlight some of the factors controlling the kinetics of the photoreduction of CO2. Steric hindrance and reduction potentials are important factors in the catalytic activity for photochemical CO2 reduction.

Recently photoreduction of CO2 to HCOO− (together with a small amount of CO and H2) was achieved by UV-irradiation of the system involving phenazine (Phen) as a photosensitizer, Cocyclam3+ as an electron mediator and TEA as an electron donor. The quantum yield for the formation of HCOO− is 0.07. Electron transfer from the photo-formed radical anion (Phen−) to Cocyclam3+ (k = 4.3 x 109 M−1 s−1) results in the formation of Cocyclam2+. Since the reduction potential of Cocyclam2+/+ is −1.9 V vs SCE in CH3CN, Phen− is hardly capable reducing Co(II) to Co(I). Therefore the authors suggest that: (1) PhenH+, produced by the protonation to Phen−, may transfer a hydrogen atom to Cocyclam*+ to form Cocyclam(H)2+; and (2) the insertion of CO2 into the hydride produces CO via the Corn-formate complex. Although preliminary results appear to support the proposed mechanism, the hydrogen atom transfer step needs to be investigated in detail.

Comparison between thermal hydrogenation and photochemical reduction of CO2.

In the early 1970's, several groups found that formic acid, esters, and amides can be prepared from carbon dioxide, hydrogen, and a third component (in many cases) in the presence of homogeneous transition metal (Ti, Ru, Rh, Pd, etc.) catalysts including Wilkinson's catalyst [Rh(PPh3)3Cl]. These reactions were carried out under a range of total gas pressure of 20 - 200 atm in the temperature range of 24 to 160 °C. For example, when [RhH(COD)]4 (COD = cyclooctadiene) is used as the catalyst precursor with TEA and dppb (dppb = Ph2P(CH2)4PPh2) as additives in DMSO under a total (H2 + CO2) pressure of 40 atm at room temperature, the system produces HCOO− with the turnover number of 2200 in 18 hrs. The TOF (turnover frequency), which is defined as the maximum initial rate of reaction per mole of catalyst, reaches 390 h−1. Various solvents were used for homogeneous hydrogenation of CO2 to formate including supercritical CO2. In supercritical CO2 with RuH2[P(CH3)3]4, TEA, and water, the remarkable TOF of 1400 h−1 was obtained. Mechanisms of formate (or formic acid) formation via CO, or carbonate, or hydride transfer to CO2 were considered in some cases. However, the mechanism involving CO2 insertion into a M-H bond is widely proposed. The reactive intermediate with vacant coordination site(s), derived from the metal catalyst, reacts with hydrogen to generate the metal hydride, followed by CO2 insertion to form the formato complex. More detailed mechanistic and kinetic studies are needed.

Photochemical CO2 reduction is normally carried out under 1 atm CO2 at room temperature. Therefore the concentration of dissolved CO2 in the solution is quite low (e.g. 0.28 M in CH3CN and 0.03 M in water). Under photochemical conditions, TON (which is defined as the maximum number of moles of product per mole of catalyst) and TOF are dependent on irradiation wavelength, light intensity, irradiation time, and catalyst concentration. In fact, the TON and TOF are sometimes derived from different experiments. They are not optimized in most photochemical experiments. Since the concentration of the actual catalyst is not known in some cases, it only gives some guidance in estimating the catalytic activity. The typical range of the apparent TOF for CO or HCOO− formation can be calculated to be 0.1 to 10 h−1, except for the Ru(bpy)32+/Ru(bpy)2(CO)22+ system, in which the apparent
TOF reaches 180 h⁻¹ based on [Ru(bpy)_2(CO)_2]^{2+}. Typically the photochemical reactions are monitored up to one day. Both apparent TOF and TON in photochemical CO₂ reduction systems seem smaller than those in hydrogenation reactions. The rates of the catalytic reaction and the catalyst stability are important issues for photochemical CO₂ reduction. The rate-determining step or steps for photochemical CO₂ reduction are not known. It is believed that dark reactions including bond formation and bond cleavage are much slower than photoexcitation or subsequent electron transfer reaction.

Can the catalysts in the photochemical system be replaced by catalysts used for hydrogenation in order to speed up the dark reaction? In photochemical methods, an oxidative addition of a proton to the reduced metal center (that typically forms by photo-induced electron-transfer) gives a metal hydride species, however, in hydrogenation methods the metal center with vacant coordination site(s) seems to react with H₂. Some dihydrogen adducts of the metal complexes have been shown to be in equilibrium with the hydride species. It would be desirable to study the properties and reactivities of such complexes in order to find better catalysts for CO₂ reduction and hydrogen production.

The area of hydrogenation of CO₂ to HCOOH, esters, amides, alcohols, and hydrocarbons with homogeneous and heterogeneous metal catalysts is currently under active study and is promising to some degree. However, can we find a cheap and clean source of H₂? At present, hydrogen is manufactured by thermal cracking of oil resources, consuming fossil fuels as well as generating carbon dioxide. Therefore we need to develop technologies to produce H₂ using solar energy.

**Challenge for photochemical CO₂ reduction and water splitting**

Solar energy conversion is a formidable problem. The system must satisfy the following conditions: (1) strong absorption in the visible region; (2) long-lived excited state; (3) efficient quenching of the excited state to produce highly reduced and oxidized intermediates; (4) no harmful side reaction to deactivate the photosensitizer or catalyst/mediator; (5) ability to undergo multi-electron transfer; (6) long-lived intermediates (or catalyst) to promote bond formation and cleavage reactions to desired products (These dark reactions are much slower than photo-process.); and (7) combining oxidizing and reducing cycles (to avoid the use of a sacrificial reagent). Although conditions 1 to 6 have been fulfilled to some degree, to our knowledge all previous attempts with homogeneous catalysts have failed to achieve condition 7 (except one report about water splitting). Do we need to design organized systems modeled upon natural photosynthesis? Should we accept a small TOF as nature does? What kind of catalyst can accommodate the four-equivalent charge for O₂ or HCHO production? How can we effectively couple the reduction or oxidation reactions with proton-, hydrogen-atom- or hydride-transfer reactions to lower the reaction barrier? Many questions still need to be answered in order to achieve efficient photochemical CO₂ reduction and water splitting.

**Acknowledgments**

Helpful comments from Drs. Norman Sutin and Carol Creutz are greatly acknowledged. The research at Brookhaven National Laboratory was carried out under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.
References


(11) Kutal, C.; Corbin, A. J.; Ferraudi, G. 1987, 6, 553-557.


(20) Ishida, H.; Tanaka, K.; Tanaka, T. Organometallics 1987, 6, 181-186.


(49) Fujita, E.; Szalda, D. J.; Creutz, C.; Sutin, N. J. Am. Chem. Soc. 1988, 110, 4870.
(51) Fujita, E.; Creutz, C.; Szalda, D. J.; Furenlid, L. R.; Renner, M. W.; van Eldik, R. To be published.