Photochemical CO$_2$ Reduction: Current Status and Challenges

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Utilization of CO$_2$

- Use as a solvent
- Intermediates or fine chemicals for the chemical industry
  - \(-\text{C(O)O}^-\) : acids, esters, lactones
  - \(-\text{O–C(O)O}^-\) : carbonates
  - \(-\text{NC(O)OR}^-\) : carbamic esters
  - \(-\text{NCO}\) : isocyanates
  - \(-\text{N–C(O)–N}\) : ureas
- Energy rich products
  - CO, CH$_3$OH, and hydrocarbons

The amount of CO$_2$ (115 Mt) used by the chemical industry is less than 0.5 % of the total annual CO$_2$ emissions----

*TOO MUCH CO$_2$ TO CONVERT TO CHEMICALS!*
CO₂ Hydrogenation

\[ \text{CO}_2 + \text{H}_2 \rightarrow \text{HCOO}^-, \text{MeOH}, \text{hydrocarbons} \]

- CO₂ to formate, etc.
  - In scCO₂ with (Me₃P)₄RuCl₂, TON: 4 X 10⁵, TOF: 8 X 10³ h⁻¹
  - Ir(PNP)H₃, TON: 3.5 X 10⁶, TOF: 7.3 X 10⁴ h⁻¹

- CO₂ to methanol
  - Cu/ZrO₂, Cu/ZnO, and Cu/ZrO₂/ZnO-based catalysts at 200-250 ºC
  - Poor selectivity

- H₂ supply: The big problem
  - \[ \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow 3 \text{H}_2(g) + \text{CO}(g) \rightarrow 4 \text{H}_2(g) + \text{CO}_2(g) \]
  - High-temperature steam reforming over a nickel catalyst

*Renewable H₂ is needed for CO₂ hydrogenation to be practical*
Strategy for CO₂ Reduction

- Reduction of CO₂ requires energy
  - ⇒ Solar electricity as energy source (Electrochem)
  - ⇒ Photon as energy source (Photochem)
- One electron process is unfavorable
  - ⇒ Multi-electron transfer catalysts

\[
\begin{align*}
\text{CO}_2 + e^- & \rightarrow \text{CO}_2^- & E^\circ = -1.9 \text{ V} \quad (\text{vs NHE at pH 7}) \\
\text{CO}_2 + H^+ + 2e^- & \rightarrow \text{HCO}_2^- & E^\circ = -0.49 \text{ V} \\
\text{CO}_2 + 2H^+ + 2e^- & \rightarrow \text{CO} + \text{H}_2\text{O} & E^\circ = -0.53 \text{ V} \\
\text{CO}_2 + 6H^+ + 6e^- & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} & E^\circ = -0.38 \text{ V}
\end{align*}
\]

Artificial photosynthesis for CO₂ reduction typically requires a photosensitizer, a catalyst and an electron donor.

Due to the complex nature, a reduction half reaction is normally investigated.

Products are CO, formate, and H₂.

Energy Storage:

\[ \text{CO}_2 + e^- \rightarrow \text{CO, HCOO}^-, \text{CH}_3\text{OH} \]
## Homogeneous Photochemical CO$_2$ Reduction

<table>
<thead>
<tr>
<th>System</th>
<th>Products</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(bpy)$_3^{2+}$/Co(Me$_2$Phen)$_3^{2+}$/TEOA</td>
<td>CO, H$_2$</td>
<td>0.012(CO), 0.065(H$_2$)</td>
</tr>
<tr>
<td>Ru(bpy)$_3^{2+}$/Ru(bpy)(CO)$_2^{2+}$/TEOA</td>
<td>HCOO$^-$</td>
<td>0.14</td>
</tr>
<tr>
<td>Ru(bpy)$_3^{2+}$/Ni(cyclam)$_2^{2+}$/H$_2$A</td>
<td>CO, H$_2$</td>
<td>0.001(CO)</td>
</tr>
<tr>
<td>Ru(bpy)$_3^{2+}$/Co(cyclam)$_2^{2+}$/H$_2$A</td>
<td>CO, H$_2$</td>
<td></td>
</tr>
<tr>
<td>Terphenyl/Co(HMD)$_2^{2+}$/TEA</td>
<td>CO, (H$_2$, HCOO$^-$)</td>
<td></td>
</tr>
<tr>
<td>Terphenyl/Co(cyclam)$_3^{3+}$/TEA</td>
<td>CO, H$_2$, HCOO$^-$</td>
<td>0.13(CO)</td>
</tr>
<tr>
<td>Metal porphyrins (or phthalocyanines)/TEA</td>
<td>CO, H$_2$, HCOO$^-$</td>
<td></td>
</tr>
<tr>
<td>Re(bpy)(CO)$_3^X$/TEOA</td>
<td>CO</td>
<td>0.14</td>
</tr>
<tr>
<td>Re(P(OEt)$_3$(bpy)(CO)$_3^{+}$/TEOA</td>
<td>CO</td>
<td>0.38</td>
</tr>
<tr>
<td>Re(bpy)(CO)$_3$(CH$_3$CN)$_2^+$, Re(((MeO)$_2$</td>
<td>CO</td>
<td>0.59</td>
</tr>
<tr>
<td>bpy)(CO)$_3$(P(OEt)$_3$)$_2^+$/TEOA</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Structures:**
- Me$_2$Phen
- bpy
- HMD
- cyclam
- Metal porphyrins
- Phthalocyanines
- Re(bpy)(CO)$_3$(CH$_3$CN)$_2^+$
- Re(((MeO)$_2$bpy)(CO)$_3$(P(OEt)$_3$)$_2^+$
Success and Challenges in CO$_2$ Reduction

- Light absorption and charge separation were coupled with dark reaction
- CO$_2$ was photochemically reduced to CO or formate, in a few cases, to methanol
- Quantum yield of CO formation is up to 0.60

- Slow reaction rate (~10 h$^{-1}$)
- Low stability of catalyst/photosensitizer (TN ~200 or less)
- Mechanism of CO$_2$ reduction?
- Controlling the selectivity (CO, formate, H$_2$, etc)
- Beyond CO or formate?
- Coupling reductive and oxidative half reactions: i.e., to remove a sacrificial electron donor
- Use of inexpensive catalyst/photosensitizer


Our CO$_2$ utilization research was featured in C&EN News (Apr. 30, 2007): David Grills holding a scCO$_2$ cell for use in spectroscopic investigation
Outline

- Terphenyl/Co macrocycle/TEA
  CO$_2$ binding, Mechanistic investigation of CO formation

- Re(bpy)(CO)$_3$X/TEA
  Understanding reaction mechanisms
  Improving reaction rates

- Photogeneration of renewable hydride donors
  Beyond CO or formate
Terphenyl/Co Macrocycle/TEA

- $\pi$-Terphenyl as a photosensitizer, triethylamine as an electron donor, and Co macrocycles as catalysts
- Co macrocycles suppress the hydrogenation of terphenyl: Stable photocatalytic system
- Efficient formation of CO with Co macrocycles: $\Phi_{313\ \text{nm}} = 0.13$ (CO per photon)

![Diagram of the photocatalytic system](image)

Properties of CoL⁺ and [CoL–CO₂]⁺

\[ \text{Co}^I\text{L}^+ + \text{CO}_2 \rightleftharpoons \text{CoL(CO}_2)^+ \]
\[ K = 1.2 \times 10^4 \text{ M}^{-1} \]

\[ \text{CoL(CO}_2)^+ + \text{S} \rightleftharpoons \text{SCoL(CO}_2)^+ \]
\[ \text{S} = \text{CH}_3\text{CN} \]

Reduced catalyst, CoIL⁺ (d⁸, low spin, sq. pl.)

Stretching frequencies in CD₃CN:

<table>
<thead>
<tr>
<th></th>
<th>(\nu_{\text{NH}})</th>
<th>(\nu_{\text{CN}})</th>
<th>(\nu_{\text{CO}_2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoL²⁺</td>
<td>3215</td>
<td>1661</td>
<td></td>
</tr>
<tr>
<td>CoL⁺</td>
<td>3201</td>
<td>1571</td>
<td></td>
</tr>
<tr>
<td>CoL(CO₂)⁺</td>
<td>3208</td>
<td>1648</td>
<td>1710</td>
</tr>
<tr>
<td>SCoL(CO₂)⁺</td>
<td>3145</td>
<td>1648</td>
<td>1544</td>
</tr>
</tbody>
</table>

Inorg. Chem., 1993, 32, 2657

Temp. dependent spectra of CoL(CO₂)⁺ in acetonitrile
The [S-CoL(CO$_2$)]$^+$ edge shifts by 1.2 eV relative to that of [Co$^{II}$L]$^{2+}$

This shift reveals significant metal-to-CO$_2$ charge transfer and suggests formation of a Co(III) carboxylate, [S-Co$^{III}$L(CO$_2$$^{2-}$)]$^+$

[Co$^{I}$L]$^+$ can transfer two electrons to a bound CO$_2$
Laser Flash Photolysis

- Sequential formation of the \( p \)-terphenyl radical anion (TP\(^{-}\)), Co\(^{I}L^{+}\), CoL(CO\(_{2}\))\(^{+}\) and [SCo\(^{III}\)L(CO\(_{2}\))\(^{2-}\)]\(^{+}\) are observed, indicating that Co\(^{I}L^{+}\) can transfer two electrons to a bound CO\(_{2}\).
- ET from TP\(^{-}\) to CoL\(^{2+}\): fast, \( 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \)
- CO\(_{2}\) binding: \( k = 1.8 \times 10^{8} \text{ M}^{-1} \text{ s}^{-1} \) and \( K_{\text{CO}_{2}} = 1 \times 10^{4} \text{ M}^{-1} \)
- Slow thermal reactions including C-OH bond cleavage

\[ \text{Time-resolved Spectrum of Co}^{I}L^{+} \]

\[ \text{Temperature-dependent transient spectra of CoL-CO}_{2}^{+} \]

\[ \text{J. Am. Chem. Soc., 1995, 117, 6708} \]
Photochemical $\text{CO}_2$ Reduction Using $\text{ReL(CO)}_3X$

$L = \text{bpy}$ or $\text{dmb}$
$\text{CO}_2$ Reduction by ReL(CO)$_3$X

- One- and two-electron pathways have been proposed
- CO$_2$ adducts have not been observed

\[
\text{ReL(CO)$_3$Cl} + e^- \rightarrow [\text{ReL(CO)$_3$Cl}]^- \\
\hspace{1cm} - e^- + \text{Cl}^- \\
\hspace{1cm} + \text{CO} + [\text{AO}]^- \\
\hspace{1cm} \text{e}^- + A
\]

\[
\text{[ReL(CO)$_3$Cl]}^- + \text{CO}_2 \rightarrow \text{[ReL(CO)$_3$(CO$_2$)]}^- \\
\hspace{1cm} + \text{CO} + [\text{AO}]^- \\
\hspace{1cm} \text{e}^- + A
\]

B.P. Sullivan et al. JCS, Chem. Commun. 1985
F.P.A. Johnson et al. Organometallics 1996
O. Ishitani et al. JACS, 2008
Reactivity of ReL(CO)₃ toward CO₂

[Re(dmb)(CO)₃]₂ ←[hv]→ 2Re(dmb)(CO)₃ + CO₂ adduct?

- Re(dmb)(CO)₃ reacts with CO₂ very slowly! $k_{CO₂} < 0.1$ M⁻¹ s⁻¹
- $Co^I L^+: k_{CO₂} = 1.8 \times 10^8$ M⁻¹ s⁻¹
- [Re(dmb)(CO)₃]₂(¹³CO₂) is the initial product
- The disappearance of [Re(dmb)(CO)₃]₂(CO₂) is first order in [CO₂]: $k = 9.7 \times 10^{-4}$ M⁻¹ s⁻¹
- Irradiation accelerates the reaction
- Final products: [Re(dmb)(CO)₃]₂(¹³CO₃) and Re(dmb)(CO)₃(O₂¹³COH)
- Yield of ¹³CO: 30 - 50% based on [Re]

*J. Am. Chem. Soc.*, 2003, 125, 11976
Observed Photocatalytic Reactions

\[ 2^*\text{[Re(dmb)(CO)\textsubscript{3}S]}^+ \rightarrow 2\text{[Re(dmb)(CO)\textsubscript{3}S]} \]

\[ \text{hv} \]

\[ 2\text{[Re(dmb)(CO)\textsubscript{3}S]} \rightarrow 2\text{[Re(dmb)(CO)\textsubscript{3}S]}^+ \]

\[ 2\text{[Re(dmb)(CO)\textsubscript{3}S]}^+ \rightarrow 2\text{[Re(dmb)(CO)\textsubscript{3}S]} + 2\text{TEA}^+ \]

\[ 2\text{[Re(dmb)(CO)\textsubscript{3}S]}^+ \rightarrow 2\text{[Re(dmb)(CO)\textsubscript{3}S]} + \text{CO}_2 \]

\[ 2\text{[Re(dmb)(CO)\textsubscript{3}S]} + \text{CO}_2 \rightarrow 2\text{[Re(dmb)(CO)\textsubscript{3}S]} + 2\text{S} \]

\[ \text{CO} + \text{CO}_3^{2-} \text{ (or HCO}_3^-) \rightarrow \text{CO}_2 + 2\text{S} + \text{hv} \]

Rate-determining step, first order in [CO\textsubscript{2}]

Turnover frequency \( \sim 10 \text{ h}^{-1} \)

\[ J. \text{Am. Chem. Soc., 2003, 125, 11976} \]
**CO₂ Reduction in scCO₂**

- [CO₂] up to 20 M (cf. ~100 mM/atm in conventional solvents)
- Physical properties of scCO₂ (incl. density, viscosity, dielectric constant) are easily tuned with pressure & temp. → selectivity, separation
- Add fluorinated groups to ligand framework and anions

\[
x = 6; \text{ReCl(dnb-F}_{26}\text{)(CO)}_3
\]

\[
x = 8; \text{ReCl(dub-F}_{34}\text{)(CO)}_3
\]

---

Grills

Doherty
Excited-State Investigations in scCO$_2$

- Reductive quenching rate constants in scCO$_2$ are only six times smaller than in CH$_3$CN.
- Given the much lower polarity of scCO$_2$ relative to CH$_3$CN, this relatively small difference in $k_q$ is quite remarkable.
- Further experiments on the photochemical properties and their activity in photocatalytic CO$_2$ reduction in scCO$_2$ or scCO$_2$/ionic liquid are currently in progress.

Inorg. Chem. 2009, 48, 1796
Biphasic Ionic Liquid/scCO$_2$ Systems

Grills

Retains all of the advantages of scCO$_2$, with none of the disadvantages
Renewable Hydride Donors toward CO$_2$ Reduction beyond CO
Hypothesis

Renewable hydride sources can be developed for producing solar fuels by reduction of stable abundant molecules such as CO$_2$ and H$_2$O

- The stoichiometric conversion of M-CO$_2$ complexes to M-CO, M-CHO, M-CH$_2$OH and M-CH$_3$ has been previously accomplished by NaBH$_4$ reduction (M = Ru(bpy)$_2$(CO)$_2^+$, Re(Cp)(NO)(CO))

- Can we replace NaBH$_4$ by a renewable (visible-light-generated) hydride donor?

\[
\begin{align*}
&M-CO_2^{n+} \rightarrow M-CO^{n+} \rightarrow M-CH(O)^{(n-1)+} \rightarrow M-CH_2(OH)^{(n-1)+}
\end{align*}
\]
NADPH (reduced nicotinamide adenine dinucleotide phosphate) acts as the source of two electrons and a proton.

Ru(bpy)$_2$(pbn)$_2^{2+}$, a complex with an NADP$^+$ model ligand, catalyzes the reduction of acetone to isopropanol: Current efficiency 90% at -1.14 V vs. Fc/Fc$^+$

The first example of *electrochemical catalytic reduction* of organic molecules by NADP$^+$/NADPH model complexes.


Tanaka
Hydrogenation of the pbn ligand takes place upon visible light irradiation (300-600 nm); detected by LCMS; $\Phi_{355} = 0.21$

Ru(bpy)$_2$(pbnHH)$_2^{2+}$, prepared by Na$_2$S$_2$O$_4$ reduction of Ru(bpy)$_2$(pbn)$_2^{2+}$, shows an identical spectrum

The results open a new door to photoinduced catalytic hydride-transfer reactions!
The disproportionation reaction pools the energy of two photons in \([\text{Ru}^{II}(\text{bpy})_2(\text{pbnHH})]^2^+\)
Hydride Transfer from Ru$^{II}$\((\text{bpy})_2(\text{pbnHH})\)]^{2+}$

- Ru(bpy)$_2$(pbnHH)$^{2+}$ transfer the hydride transfer to Ph$_3$C$^+$
- Ru(bpy)$_2$(pbnHH)$^{2+}$ cannot transfer the hydride to CO$_2$ or M–CO
- Can we prepare stronger hydride donors?
  - Theory indicates “Yes!”
Photochemical Formation of Strong H\textsuperscript{−} Donor

- The excited state of [Ru(bpy)\textsubscript{2}(pbnHH)]\textsuperscript{2+} is reductively quenched by DABCO or TEA (an electron donor)

- Photoinduced H\textsuperscript{−} transfer reactions to M-C\textsubscript{1} species are possible

Transverse absorption spectrum after 355 nm excitation of [Ru(bpy)\textsubscript{2}(pbnHH)]\textsuperscript{2+} in the presence of DABCO
Summary

- Photochemical reduction of CO₂ was achieved with high yields of CO and formate.
- CO₂ is activated by two-electron pathways:
  - Formation of a mononuclear carboxylate species (One M donates 2e⁻ to CO₂)
  - Formation of a binuclear species containing the M-C(O)O-M moiety (Each M center donates 1 e⁻ to CO₂)
- Slow reactions (bond formation/cleavage) may be accelerated using scCO₂.
- Renewable hydride donors can be generated by solar irradiation.
- Ru(bpy)₂(pbnnHH)²⁺ cannot reduce CO₂ or M–CO, however, theory indicates it is possible to produce stronger hydrides.
- By tuning the electron density of hydride donors, M–CO may be photochemically converted to M–CHO or M–CH₂OH.
- Photochemical CO₂ reduction is challenging:
  - Use of inexpensive catalyst/photosensitizer: Co, Ni, Fe/semiconductors?
  - Coupling reductive and oxidative half reactions: i.e., to remove a sacrificial electron donor.
Artificial Photosynthesis Studies at BNL

Sunlight absorption by BGNSCs and metal complexes

CO₂ and proton reduction by photogenerated hydrides and reduced complexes

Water oxidation by Ru complexes and metal hydrous oxide

Photogeneration of M–H and C–H hydride donors

Centi, J. Catal, 2009

Photoelectrolysis cells
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Mark Doherty  scCO$_2$
Patrick Achord  Theory

Koji Tanaka (IMS, Japan)  Hydrides
Takeshi Fukushima  Hydrides

Department of Energy, BES, Core program
DOE BES Hydrogen Fuel Initiative (from 2005)
DOE BES Solar Energy Utilization initiative (from 2007)