

## Carbon Management: Implications for R&amp;D in the Chemical Sciences Workshop

**Carbon Dioxide as a Feedstock**

Carol Creutz and Etsuko Fujita  
 Chemistry Department  
 Brookhaven National Laboratory  
 Upton NY 11973-5000

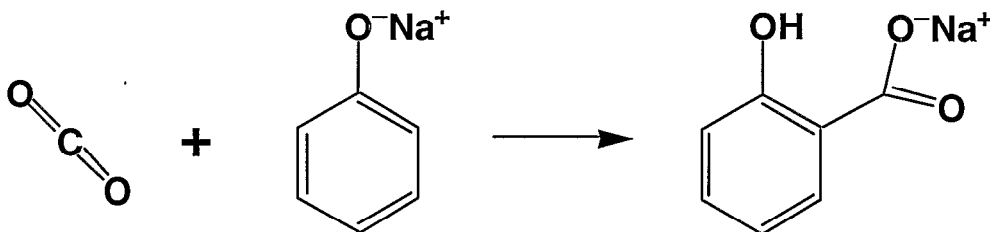
This report is an overview on the subject of carbon dioxide as a starting material for organic syntheses of potential commercial interest and the utilization of carbon dioxide as a substrate for fuel production. It draws extensively on literature sources,<sup>1-3</sup> particularly on the report<sup>1</sup> of a 1999 Workshop on the subject of catalysis in carbon dioxide utilization, but with emphasis on systems of most interest to us.

Atmospheric carbon dioxide is an abundant (750 billion tons in atmosphere), but dilute source of carbon (only 0.036 % by volume),<sup>3</sup> so technologies for utilization at the production source are crucial for both sequestration and utilization. Sequestration—such as pumping CO<sub>2</sub> into sea or the earth—is beyond the scope of this report, except where it overlaps utilization, for example in converting CO<sub>2</sub> to polymers. But sequestration dominates current thinking on short term solutions to global warming, as should be clear from reports from this and other workshops.<sup>4,5</sup>

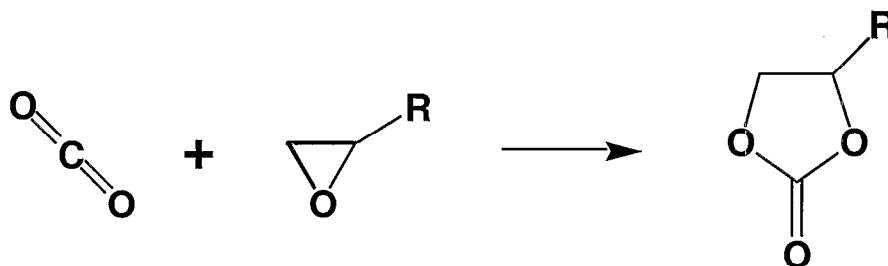
The 3500 million tons estimated to be added to the atmosphere annually at present can be compared to the 110 million tons used to produce chemicals, chiefly urea (75 million tons), salicylic acid, cyclic carbonates and polycarbonates.<sup>1</sup> Increased utilization of CO<sub>2</sub> as a starting material is, however, highly desirable, because it is an inexpensive, non-toxic starting material. There are ongoing efforts to replace phosgene as a starting material.<sup>6</sup> Creation of new materials and markets for them will increase this utilization, producing an increasingly positive, albeit small impact on global CO<sub>2</sub> levels. The other uses of interest are utilization as a solvent and for fuel production and these will be discussed in turn.

**Principal current uses of carbon dioxide.**

Urea. Urea synthesis is currently the largest use of carbon dioxide in organic synthesis. Urea, C(O)(NH<sub>2</sub>)<sub>2</sub>, is the most important nitrogen fertilizer in the world. It is also an intermediate in organic syntheses such as production of melamine and urea resins, used as adhesives and bonding agents. Salicylic acid is used in pharmaceuticals.



Cyclic organic carbonates, high melting, but extremely high boiling, serve as solvents for natural and synthetic polymers such as lignin, cellulose, nylon, polyvinyl chloride. They are extensively used in the production of polyacrylic fibers and paints.



Ethylene and propylene carbonates have many uses in chemical synthesis; also they react with ammonia and amines to form carbamates; from reaction with diamines they yield di(hydroxyethyl)carbamates which can further react with urea to form polyurethanes.

The figure below (an abbreviated version of that given by Aresta<sup>6</sup>) provides a broad summary of current and projected utilization of carbon dioxide.

## Utilization of CO<sub>2</sub> in Synthetic Chemistry

- **Intermediates or fine chemicals for the chemical industry**

-C(O)O- : Acids, esters, lactones

-O-C(O)O- : Carbonates

-NC(O)OR- : Carbamic esters

-NCO : Isocyanates

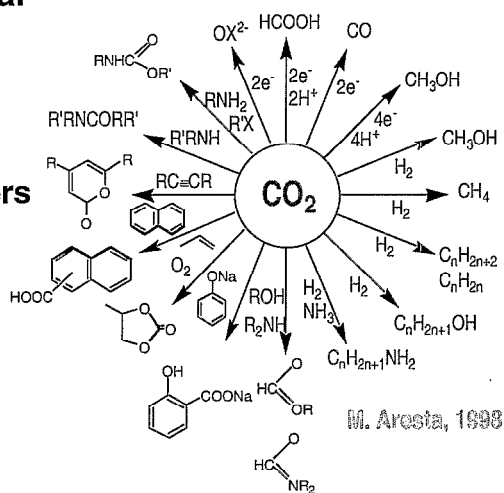
-N-C(O)-N : Ureas

- **Use as a solvent**

- **Energy rich products**

CO, CH<sub>3</sub>OH

Hydrocarbons and their derivatives



At 6 o'clock to 11:00 are summarized the reactions that utilize CO<sub>2</sub> to produce organic chemicals or intermediates for the chemical industry. The first examples, for example, salicylic acid, are utilizations that are in current practice. Also included are reactions that hold promise for extensive utilization in the future. Many of these involve insertion of carbon dioxide into Y-X bonds, often the C-H bond. The products of interest include esters, carbamic esters, salicylic acid, and cyclic carbonates. Reactions commonly involve formal insertion of carbon dioxide into an X-H bond—as the N-H in urea

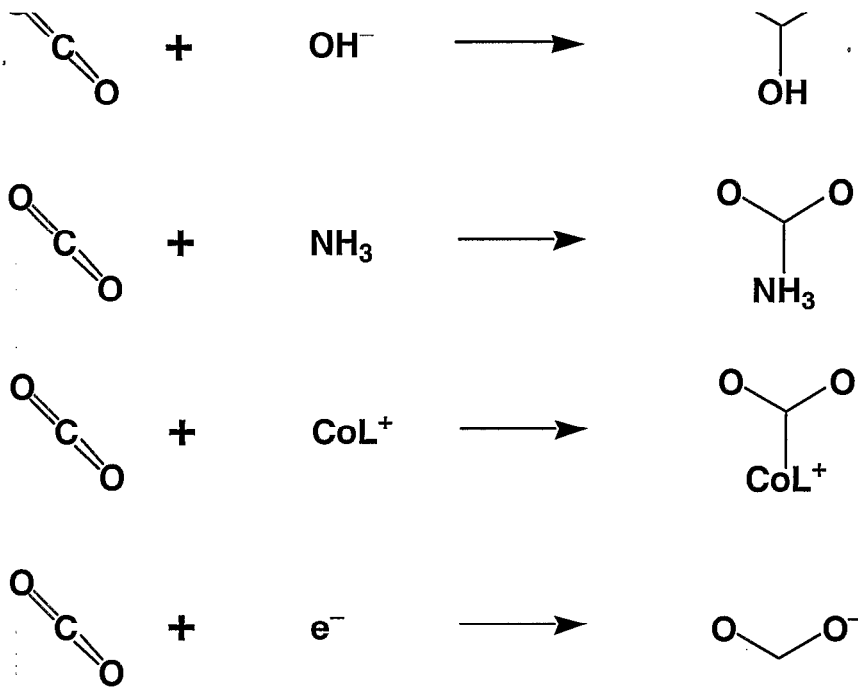
formation. Novel insertions are under active investigation: incorporation of CO<sub>2</sub> into polymers—polycarbonates, polypyrones, lactone intermediates, and polyurethanes. Of particular interest is the incorporation of carbon dioxide into polymers, an active area of research and very promising for future applications.<sup>1,7</sup> However, the impact of new materials and processes in this area will ultimately depend on market forces, a factor that can be frustrating to the researchers. From 2 to 6 o'clock are hydrogenation reactions and from 12 to 2 o'clock are hydrogenations accomplished by electrons and protons—both directed toward fuel formation.

### **Carbon Dioxide as Solvent**

Supercritical carbon dioxide is a hydrophobic solvent which can replace organic solvents in a number of applications. Its critical temperature is 31°C and it is of very low viscosity. When carbon dioxide is substituted for an organic solvent, solvent costs may be reduced and emission of toxic organics can be reduced. Furthermore, separation of the products and catalyst can be easily controlled by changing the carbon dioxide pressure. Currently supercritical carbon dioxide is used in caffeine extraction, dry cleaning, and parts degreasing. These processes can involve high-capacity plants over 50 x 10<sup>6</sup> lb (22.5 x 10<sup>6</sup> kg) per year in the case of decaffeination processes.<sup>8</sup> Potential future or developing applications include utilization in food and pharmaceutical processing to defray future liability costs, production of pharmaceutical nanoparticles for injection, polymerizations,<sup>9</sup> emulsion polymerization of water soluble monomers, enhanced oil recovery, and homogeneous<sup>10</sup> and phase-separable catalysis, including that based on ionic liquid solvents.<sup>11</sup>

### **Reactivity of Carbon Dioxide**

Carbon dioxide is a linear molecule in which the oxygen atoms are weak Lewis (and Bronsted) bases and the carbon is electrophilic. Reactions of carbon dioxide are dominated by nucleophilic attacks at the carbon, which result in bending of the O-C-O angle to ca 120°, as illustrated below. Depicted are four very different reactions, hydroxide attack on CO<sub>2</sub> to form bicarbonate, the initial addition of ammonia to CO<sub>2</sub> which ultimately produces urea, the binding of CO<sub>2</sub> to a macrocyclic cobalt(I) complex which catalyzes CO<sub>2</sub> reduction,<sup>12,13</sup> and the addition of an electron to CO<sub>2</sub> to yield the carbon dioxide radical ion. The first three also exemplify the reactivity of CO<sub>2</sub> with respect to nucleophilic attack on the carbon.



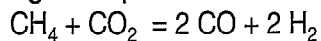
**Thermodynamic Barriers to CO<sub>2</sub> Utilization.** Carbon dioxide is a very stable molecule and accordingly energy must generally be supplied to drive the desired transformation. Thus high temperatures, extremely reactive reagents, electricity, or the energy from photons may be exploited to carry out carbon dioxide reactions:

## Overcoming the Thermodynamics

### Approach

### Energy Source

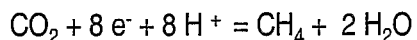
- High temperatures



- Solar furnace

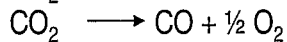
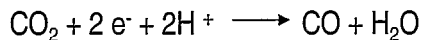
1200 °C

- Electrochemical reaction



- Solar cell; nuclear power

- Photochemical reaction



- Light from sun

- VUV light

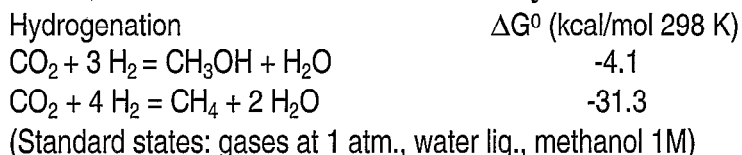
Above are given illustrations in which the energy source is renewable or nuclear. (“Renewable” refers to solar electric, wind hydroelectric, geothermal, solar thermal, and biomass based energy sources.) The reaction,  $\text{CH}_4 + \text{CO}_2 = 2 \text{CO} + 2 \text{H}_2$ , is called the carbon dioxide reforming of methane. If combined with metal production *in situ*, with solar furnaces to achieve the high temperatures needed (e.g. 1200 °C, could significantly mitigate CO<sub>2</sub> produced in cement, lime and metal (iron, aluminum) production, about

10% of total CO<sub>2</sub> released annually.<sup>3</sup> For electrochemical reduction of CO<sub>2</sub> to methane, energy may be derived from a solar cell or nuclear power. Reduction may also be accomplished photochemically by utilizing a dye to absorb visible light, since carbon dioxide itself does not absorb visible light. Interestingly, with vacuum ultraviolet irradiation of carbon dioxide yields oxygen and carbon monoxide.

### **Conversion of Carbon Dioxide to Fuels: Direct Hydrogenation**

With abundant renewable energy sources carbon dioxide can be converted to fuels by reduction to methanol or methane. The value of a fuel is based on its energy content and its ease of transport and storage. (Thus methane is less desirable than methanol because of its low fuel density and high cost of transport.) The high energy density of carbon-based fuels and their availability as either gases, liquids, or solids are important reasons for the dominant position of fossil fuels in the current market place. Today carbon dioxide is a by-product of fuel use, not a feedstock for fuel production. Utilization of CO<sub>2</sub> converted to fuels using renewable or nuclear power produces no net emission of CO<sub>2</sub> (when carbon dioxide produced by energy consumption in the reduction process is excluded) and it would complement the renewable production of fuels from biomass which is likely to be insufficient to meet future world demands. Catalysis can play an important role in this area. The objective is to develop strategies for reduction of CO<sub>2</sub> that can be adapted to utilization at different sources and to attain fuel products widely utilizable with current and future technologies.

Hydrogenation of carbon dioxide to methanol is slightly exergonic, and to methane to a greater extent, because of the favorable thermodynamics of water formation:



Catalysis of hydrogenations leading to N, N-dimethylformamide, formate, and hydrocarbons is being successfully addressed.<sup>10,14</sup> Reduction to carbon monoxide is also useful when the carbon monoxide-hydrogen mixtures can be used to augment feeds in industrial processes such as ethylene and methanol production. Methanol, lower hydrocarbons (methane, ethane, ethylene, etc), CO, and HCOOH have been prepared from CO<sub>2</sub>/H<sub>2</sub> using several different metal and metal oxide catalysts at elevated temperature and pressure.<sup>15</sup> Selectivity and catalytic activity depend on the catalyst used (i.e. metal/metal oxide, size, etc.), additives, support, temperature, CO<sub>2</sub>/H<sub>2</sub> ratio, and pressure. Copper on ZnO seems to be the most active catalyst for methanol production.<sup>15,16</sup> A small-scale test plant with a production capacity of 50 kg/day methanol was constructed at the Research Institute of Innovation Technology of the Earth to examine the performance of a Cu/ZnO -based multicomponent catalysts (Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/Ga<sub>2</sub>O<sub>3</sub>) under practical conditions.<sup>17</sup> Selectivity for methanol production was found to be very high and direct methanol production from CO<sub>2</sub> may be

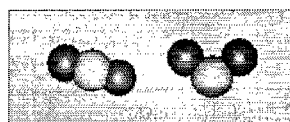
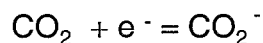
commercially feasible with an inexpensive source of H<sub>2</sub>.<sup>17</sup> Use of hydrogen for this reduction chemistry is not, however, economically attractive at present because of the cost of hydrogen, but inexpensive production of hydrogen by solar or nuclear power sources could radically alter this scenario.

### Conversion of Carbon Dioxide to Fuels: Indirect Hydrogenation

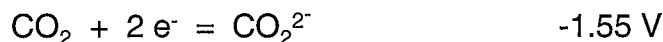
Hydrogen (H<sub>2</sub>) may be replaced by electrons and protons, available, for example, in electrochemical reduction in aqueous media. One-electron reduction of carbon dioxide to the radical anion CO<sub>2</sub><sup>-</sup> presents thermodynamic and kinetic barriers. In aqueous solution the reduction potential is -1.9 V vs. SHE<sup>18</sup>. The barrier to outer-sphere electron transfer for the couple is large because of the very different geometries of the linear, neutral carbon dioxide and the bent radical anion.<sup>19</sup> Thus direct (uncatalyzed) electroreduction requires a significant overvoltage. As shown below, the thermodynamic barriers are reduced by protonating the reduction product.<sup>13,20</sup> However, because of the close proximity of the hydrogen potential, reduction of H<sup>+</sup>/H<sub>2</sub>O to H<sub>2</sub> may also occur, depending on the system.

## CO<sub>2</sub> Reduction: Thermodynamic and kinetics issues

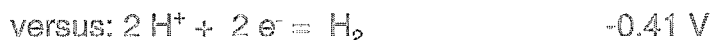
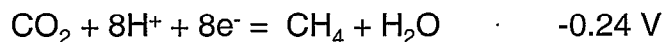
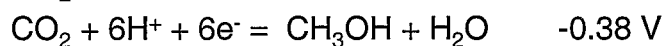
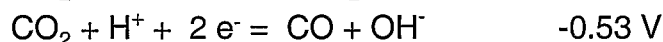
### One-electron reduction



### Two-electron reduction



### Proton-assisted pH 7 vs. SHE 25 °C



*Standard states: For aqueous solutions, gases 1 atm, others 1 M*

**Electrochemical reduction.** As noted earlier, direct electroreduction is achieved at high overvoltage. An unreactive metal or carbon electrode produces carbon dioxide radical anion, which may undergo dimerization to oxalate or disproportionation to carbon monoxide and carbonate.<sup>21</sup> By contrast, non-innocent metals, through active sites on their surfaces, can direct CO<sub>2</sub> reduction to hydrogenated products and at much smaller applied voltage, because of the high efficiency of the heterogeneous catalysis. Particularly noteworthy is the work of Hori which showed that copper produces high

yields of methane from aqueous bicarbonate at 0 °C—and high yields of ethylene at 45 °C.<sup>22</sup>

In these systems, the metal serves a dual role, both delivering electrons and stabilizing the reduced fragments. In the case of copper, the reduction is believed to involve the sequence:

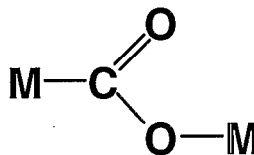
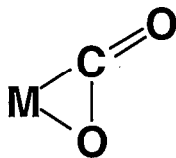
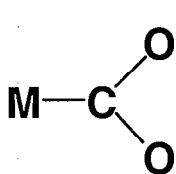


The metals Ru, Cd, Hg, In, Sn, Pb yield formate; Au, Ag, and Zn yield CO, while Al, Ga, Pt, Fe, Ni, Ti exhibit little activity.<sup>3</sup> Other important areas of electrochemical reduction are homogeneous catalysis; surface modified by a “molecular” catalyst, and photo-electrochemical systems

**Homogeneous catalysis of carbon dioxide reduction.** Homogeneous catalysts may fulfill the role of the surface metal catalytic sites in the above systems (for example, Cu). Homogeneous catalysis is important in electrochemical reductions systems, as well as photochemical systems. Indeed the two approaches share many features, as will be discussed later.

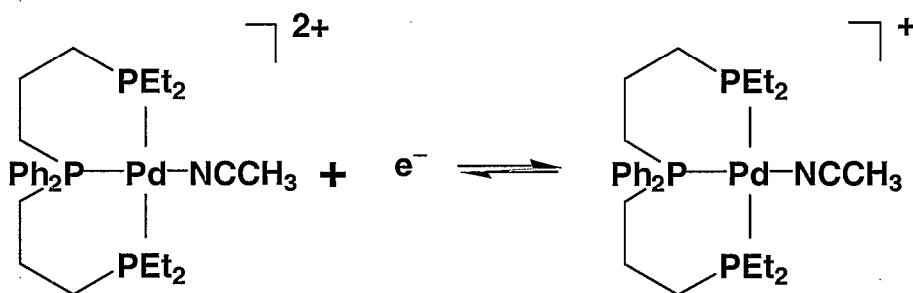
Catalysts lower the overpotential for CO<sub>2</sub> reduction by: undergoing reduction at a potential ( $E_{\text{cat}}$ ) less negative than that for direct CO<sub>2</sub> reduction; binding CO<sub>2</sub>; undergoing a second reduction at (or positive of)  $E_{\text{cat}}$ . For homogeneous catalysis,<sup>21</sup> two-electron reduction to give CO, HCO<sub>2</sub><sup>-</sup>, or C<sub>2</sub>O<sub>4</sub><sup>2-</sup> is most frequently observed and added proton sources may be required.

**Transition metal catalysis.** Binding of carbon dioxide to transition metal centers has been reviewed.<sup>23,24</sup> Among the several modes in which the metal may bind the CO<sub>2</sub> are the three shown below, end-on, C  $\eta^1$ ; C, O  $\eta^2$ ; and bimetallic motifs in which one metal



binds C  $\eta^1$  and another metal binds O  $\eta^1$ .

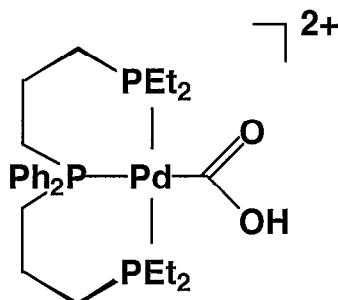
**Electrochemical Systems.** Electrocatalysis by transition metal complexes is elegantly illustrated by the work of DuBois and colleagues.<sup>25</sup> In the absence of CO<sub>2</sub>, the Pd(II) complex undergoes 2-electron reduction, but when CO<sub>2</sub> is present, the one-electron



reduction product binds

CO<sub>2</sub> (DMF as solvent). With added acid, carbon monoxide is produced catalytically from carbon dioxide. This chemistry likely involves the protonated carbon dioxide adduct (hydroxycarbonyl complex) below.<sup>26</sup>

Catalytic turnover numbers greater than 100 have been reported for this and related

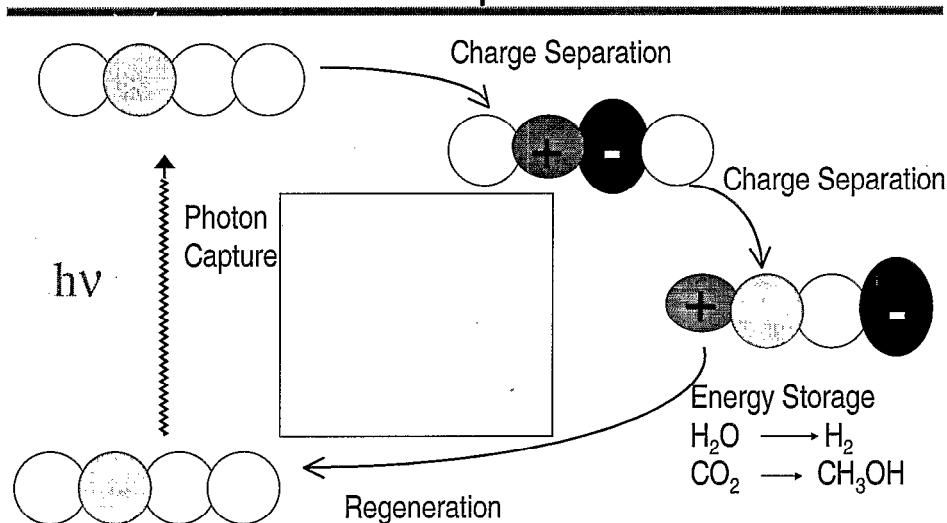


compounds. Some H<sub>2</sub> is produced in parallel, evidently via a hydride complex.

Other systems for electrochemical CO<sub>2</sub> reduction utilize transition metal complexes of nitrogen-containing (nickel and cobalt) macrocycles (including porphyrins and phthalocyanines) and (ruthenium, cobalt, and rhenium) complexes of 2,2'-bipyridine.<sup>27</sup>

**Photochemical systems.**<sup>28</sup> Photochemical reduction systems require efficient light harvesting, usually by a so-called dye or sensitizer, and efficient charge separation and energy utilization. Transition metal complexes, particularly tris(2,2'-bipyridine)ruthenium(II), serve as sensitizers.

### Photoinduced Charge Transfer with Transition Metal Complexes

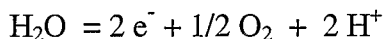




The overall reaction carried out must be a useful one. That is, in addition to carbon dioxide reduction, the complementary oxidation process (which provides the electrons) should be a desirable one. Both reduction and oxidation processes generally require catalysis. For carbon dioxide reduction, a number of the catalysts used in electrochemical systems are also effective in the photochemical systems, as outlined below.

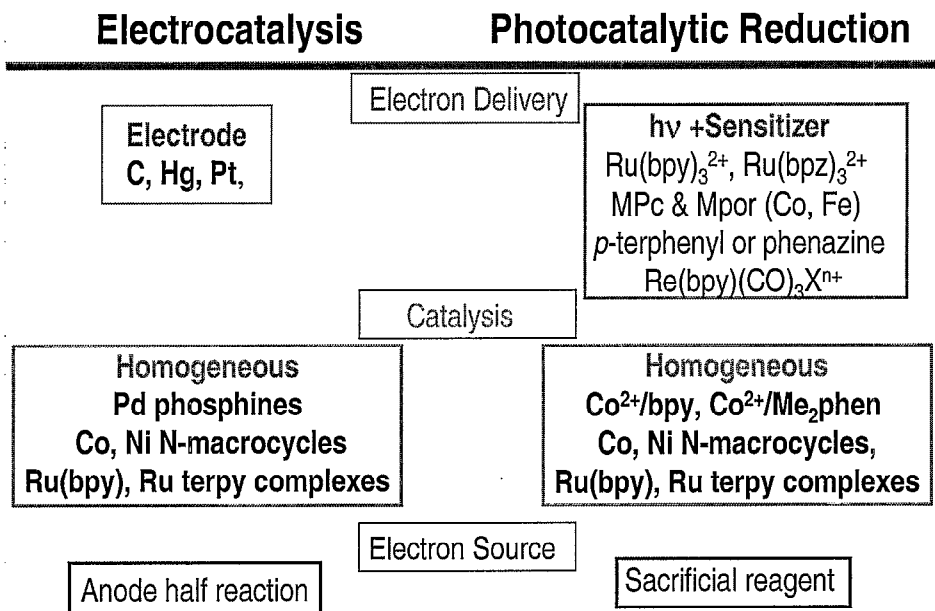
### Comparison of electrochemical and photochemical systems.

When the catalytic reduction of carbon dioxide is truly homogeneous (occurs in the solution), electrochemical and photochemical systems may have much in common. The means of electron delivery differs, of course, with photoinduced electron transfer processes serving the role of the electrode in the photochemical system. Many of the catalyst systems studied so far, cobalt and nickel macrocycle systems, for example, work in both kinds of experiments. In both approaches, the ultimate source of these electrons is an issue. Sacrificial reagents (generally organic compounds that become oxidized) are commonly used and one of the challenges is to replace these reactions with processes that are less costly and wasteful. For aqueous systems, it would be highly desirable to use the water oxidation half-reaction, *i.e.*



for this purpose so that the overall reaction would be

$\text{CO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + 3/2 \text{O}_2$  The challenge remains the effective development and deployment of water oxidation catalysts.



At present, electrochemical reduction of CO<sub>2</sub> yields carbon monoxide, formate, methane, etc. with good current efficiencies and, in photochemical systems, quantum yields for carbon monoxide (and/or formate) are up to 40%.

### Opportunities

There are many areas in which ongoing and future research can lead to new modes of carbon dioxide utilization. These include:

Utilization of CO<sub>2</sub> in new polymers—uses, markets.

Development and understanding of both homo- and heterogeneous catalysts for—  
Polymerization, hydrogenation, electrochemical and photochemical processes

Utilization of soluble and surface anchored nanoparticles of metal and semiconductor clusters  
Reactions/catalysis in supercritical CO<sub>2</sub>

Electrochemical and photochemical electron sources in the presence of proton sources can avoid use of expensive H<sub>2</sub>, but both need:

Faster catalytic processes, more stable catalytic systems  
Development of useful second half reaction, i.e. elimination of sacrificial reagent/useful anode reaction

**Acknowledgment.** We thank D. L. DuBois for helpful comments. This research was carried out at Brookhaven National Laboratory under contract DE-AC02-98CH10886 with the U.S. Department of Energy and was supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

### References

- 1)Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; Dubois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**.
- 2)Behr, A. *Carbon dioxide activation by metal complexes*; VCH: Cambridge, 1988.
- 3)Halmann, M. M.; Steinberg, M. *Greenhouse Gas Carbon Dioxide Mitigation*; CRC Press: Boca Raton, 1999.
- 4)Benson, S.; Chandler, W.; Edmonds, J.; Levine, M.; Bates, L.; Chum, H.; Dooley, J.; Grether, D.; Houghton, J.; Logan, J.; Wiltsee, G.; Wright, L. *Carbon Management: Assessment of Fundamental Research Needs*; U.S. D. O. E., 1997.
- 5)Reichle, D.; Houghton, J.; Kane, B.; Ekmann, J.; Benson, S.; Clarke, J.; Dahlman, R.; Hendrey, G.; Herzog, H.; Hunter-Cevera, J.; Jacobs, G.; Judkins, R.; Ogden, J.; Palmisano, A.; Socolow, R.; Stringer, J.; Surles, T.; Wolsky, A.; Woodward, N.; York, M. *Carbon Sequestration Research and Development*; U. S. D.O.E., 1999.
- 6)Aresta, M. *Advances in Chemical Conversions for Mitigating Carbon Dioxide; Studies in Surface Science and Catalysis* **1998**, 114, 65-76.
- 7)Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, 153, 155-174.
- 8)Ghenciu, E. G.; Beckman, E. J. *www.AccessScience.com* **1998**.
- 9)Kendall, J. L.; Canelas, D. A.; Young, J. L.; DeSimone, J. M. *Chem. Rev.* **1999**, 99, 543-563.

- 10) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1999**, *99*, 475–493.
- 11) Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. *Nature* **1999**, *399*, 28–29.
- 12) Fujita, E.; Creutz, C.; Sutin, N.; Szalda, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 343–353.
- 13) Fujita, E. *Coord. Chem. Rev.* **1999**, *185–186*, 373–384.
- 14) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *99*, 259–271.
- 15) Arakawa, H. *Advances in Chemical Conversions for Mitigating Carbon Dioxide; Studies in Surface Science and Catalysis* **1998**, *114*, 19–30.
- 16) Kieffer, R.; Udron, L. *Advances in Chemical Conversions for Mitigating Carbon Dioxide; Studies in Surface Science and Catalysis* **1998**, *114*, 87–96.
- 17) Inui, T.; Anpo, M.; Izui, K.; Yanagida, S.; Yamaguchi, Y. *Advances in Chemical Conversions for Mitigating Carbon Dioxide*; Delmon, B. and Yates, J. T., Ed.; Elsevier: Amsterdam, 1998; Vol. 114.
- 18) Schwarz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1989**, *93*, 409–414.
- 19) Schwarz, H. A.; Creutz, C.; Sutin, N. *Inorg. Chem.* **1985**, *24*, 433–439.
- 20) N. Sutin; Creutz, C.; Fujita, E. *Comments. Inorg. Chem.* **1997**, *19*, 67–92.
- 21) Keene, F. R.; Sullivan, B. P. *Mechanisms of the electrochemical reduction of carbon dioxide catalyzed by transition metal complexes*; Sullivan, B. P., Krist, K. and Guard, H. E., Ed.; Elsevier: New York, NY, 1993, pp 118–140.
- 22) Hori, Y.; Murata, A.; Takahashi, R. *J. Chem. Soc., Faraday Trans. I* **1989**, *85*, 2309–2326.
- 23) Creutz, C. *Carbon Dioxide Binding to Transition-Metal Centers*; Sullivan, B. P., Ed.; Elsevier, 1990, pp in press.
- 24) Gibson, D. H. *Chem. Rev.* **1996**, 2063–2095.
- 25) Wander, S. A.; Miedaner, A.; Noll, B. C.; Barkley, R. M.; DuBois, D. L. *Organometallics* **1996**, 3360–3373.
- 26) DuBois, D. L.; Miedaner, A.; Haltiwanger, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 8753.
- 27) Collin, J. P.; Sauvage, J. P. *Coord. Chem. Rev.* **1989**, *93*, 245–268.
- 28) Fujita, E.; Brunshwig, B. S. *Homogeneous Redox Catalysis of CO<sub>2</sub> Fixation*; Balzani, V., Rogers, M. A. J., Mattay, J., Astruc, D., Gray, H. B. and Winkler, J., Ed.; Wiley-VCH, 2000.