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CHAPTER 11

CARBON DIOXIDE FIXATION

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11. 1 Introduction

Natural photosynthesis involves the photogeneration of reduced carbon compounds and oxygen from the abundant raw materials carbon dioxide and water. Photosynthesis is balanced by the oxidation of the reduced carbon compounds back to carbon dioxide and water through respiration, decay and combustion. This dynamic cycle maintains a level of carbon dioxide in the atmosphere that sustains life on earth. However, widespread use of fossil fuels upsets this balance and has led to rising levels of carbon dioxide in the atmosphere that may result in global warming through the greenhouse effect.

As fossil fuels are depleted and global warming becomes more significant, solar, hydroelectric, geothermal, wind, biomass, and nuclear energy sources will become dominant. While biomass is produced directly using sunlight and CO_2, it is unlikely that natural photosynthesis will be able to meet all of our needs for fuels and chemicals in the future. Our current worldwide energy consumption on an annual basis is approximately 10% of the energy stored in photosynthetic processes (Hall and Rao, 1994). Put another way, if all of our current energy needs were to be met by natural photosynthesis, 10% of all biomass grown each year would have to be harvested and converted into useful energy with 100% efficiency. Although natural photosynthesis will play an important role in the production of fuels and chemicals in the future, it would be unwise to rely exclusively on natural photosynthesis for future renewable supplies of fuels and chemicals. As the world's population increases, there will be increased demand for use of biological resources for food and shelter.

Nonbiological artificial photosynthetic systems offer the possibility of producing fuels and chemicals from CO_2 and sunlight in fewer steps and with higher efficiencies than is possible in natural systems. It may also be possible to design such systems to operate under conditions and in environments where plant growth is not optimal or practical. By directly producing a single fuel or chemical with high

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selectivity the number of purification and processing steps could be significantly reduced compared to processing biomass to fuels and chemicals.

The objective of this chapter is to provide a general overview of various pathways for artificial carbon dioxide fixation using solar energy. The pathways to be considered for solar carbon dioxide fixation are: (1) homogeneous photochemical reduction of CO_2, (2) heterogeneous photochemical reduction of CO_2, (3) photoelectrochemical CO_2 fixation, (4) electrochemical reduction of CO_2 using solar electric power, and (5) solar production of hydrogen followed by hydrogenation of CO_2. Although all of these pathways will be discussed, the direct photochemical reduction of CO_2 will be treated in more detail. This particular topic was chosen for a more detailed treatment for two reasons. First these systems contain all of the major components required for solar CO_2 fixation: excited state formation through light absorbance by sensitizers, energy transduction by electron transfer, and energy storage through chemical transformation by catalysts. Second, these systems illustrate many of the difficulties involved in solar CO_2 fixation. Finally we will conclude with a brief discussion of the relationships between CO_2 sequestration and CO_2 utilization.

Before turning to these topics the thermodynamic requirements for various CO_2-reduction reactions should be considered. Because of the stability and chemical inertness of CO_2, energy and catalysts will be needed to transform CO_2 into fuels and chemicals. The potential for the reduction of CO_2 to $CO_2^{\bullet -}$ is -1.9 V vs. NHE, and typical reduction potentials required at either Pt and Hg working electrodes are -2.0 V to -2.5 V, depending on the solvents and electrolytes used. The bent radical anion, $CO_2^{\bullet -}$, is the initial product under these conditions, and is extremely reactive. It absorbs in the UV region ($\lambda_{max} = 235$ nm, $\varepsilon = 3000\ M^{-1}$) and is protonated only in strong acidic solutions (Neta et al 1969, Buxton and Sellers 1973). The pK_a of the protonated species, $\cdot CO_2H$, is 1.4. In aprotic organic solvents such as CH_3CN and DMF, the main reduction products are oxalic acid and CO (Amotore and Saveant 1981).

Proton-assisted multielectron steps are much more favorable than the one-electron process as shown below (at pH 7 in aqueous solution versus NHE, 25 °C, 1 atmosphere for the gases, and 1 M for the other solutes).

$$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H \qquad E^\circ = -0.61\ V \qquad (1)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E^\circ = -0.53\ V \qquad (2)$$

$$CO_2 + 4H^+ + 4e^- \rightarrow C + 2H_2O \qquad E^\circ = -0.20\ V \qquad (3)$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \qquad E^\circ = -0.48\ V \qquad (4)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \qquad E^\circ = -0.38\ V \qquad (5)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E^\circ = -0.24\ V \qquad (6)$$

Since the two-electron reduction to formic acid or CO requires a lower potential than the one-electron reduction, electrolysis in the presence of catalysts can be carried out at considerably lower voltages. Similarly, the four-, six-, and eight-electron reductions of CO_2 can be carried out at much more positive potentials than are required for the one-electron reduction.

11. 2 Homogeneous photochemical reduction of CO_2

In the photochemical reduction of CO_2, the one-electron reduction to $CO_2^{\cdot -}$ requires extremely strong reducing agents that are generally difficult to produce by photochemical methods. As a result catalysts are used that can accept multiple electrons during the catalytic cycle of CO_2 reduction. Transition-metal complexes are used as both sensitizers and catalysts since they can absorb a significant part of the solar spectrum, have long-lived excited states, and can promote the activation of small molecules. Organic dyes are also used as photosensitizers in many systems.

The artificial systems used for photochemical CO_2 reduction studies can be divided into several groups: (1) $Ru(bpy)_3^{2+}$ both as a photosensitizer and a catalyst; (2) $Ru(bpy)_3^{2+}$ as a photosensitizer and another metal complex as a catalyst; (3) $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$-type complexes as photosensitizers in microheterogeneous systems; (4) $ReX(CO)_3(bpy)$ or a similar complex both as a photosensitizer and a catalyst; (5) porphyrins both as a photosensitizer and a catalyst; (6) other metal complexes as a catalyst; and (7) organic photosensitizers and a metal complex as a catalyst. Figure 1 illustrates a typical artificial photosystem where P is a photosensitizer, MX is a metal complex catalyst and D is an electron donor.

Although many photoinduced stoichiometric reactions such as 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 the formation of M=O together with CO are known, we focus our discussion on photocatalytic reactions using metal complexes as catalysts. Photoinduced CO_2 fixation systems containing enzymes are omitted.

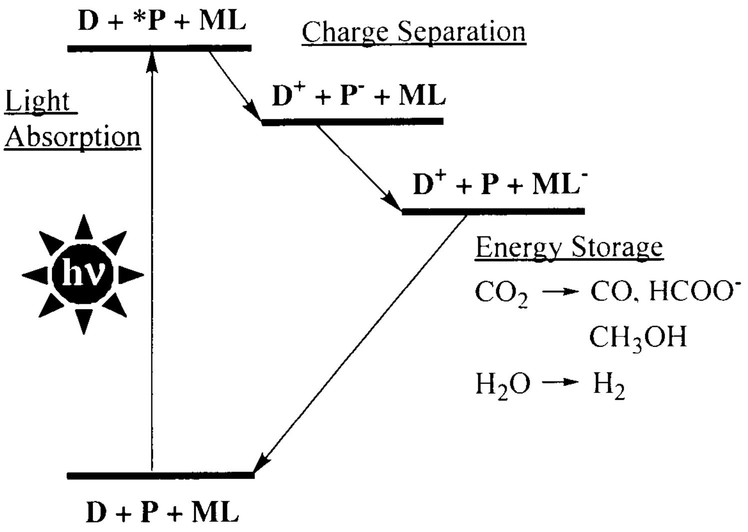

Figure 11.2 Artificial Photosynthesis with a metal complex catalyst (ML), electron donor (D) and photosensitizer (P)

11.2.1 Reduction of CO_2 to CO and $HCOO^-$ with $Ru(bpy)_3^{2+}$ both as a photosensitizer and a catalyst

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 (Hawacker, Lehn et al. 1985; Lehn and Ziessel 1990). The $Ru(bpy)_3^{2+}$ complex acts both as photosensitizer and as precursor of the catalytic species. In this system, the reductive quenching of the excited state of the $Ru(bpy)_3^{2+}$ by TEOA is believed to produce the reduced Ru complex as shown in scheme I.

Scheme I. Reductive quenching

$$Ru(bpy)_3^{2+} + h\nu \rightarrow {}^*Ru(bpy)_3^{2+} \qquad (7)$$

$$^*Ru(bpy)_3^{2+} + TEOA \rightarrow Ru(bpy)_3^{+} + TEOA^{\bullet +} \qquad (8)$$

$TEOA^{\bullet+} + TEOA \rightarrow TEOA^{\bullet} + TEOAH^{+}$ (9)

$TEOA^{\bullet} + Ru(bpy)_3^{2+} \rightarrow TEOA_{ox} + Ru(bpy)_3^{+}$ (10)

However, the reduced Ru complex cannot reduce CO_2 directly in a one-electron transfer process because the $Ru(bpy)_3^{2+/+}$ potential is -1.26 V (vs NHE in water) and the $CO_2/CO_2^{\bullet-}$ couple requires -1.9 V. The observation that water enhanced the reaction, with an optimum concentration around 0.015 M (~15 %), suggests water may play a role in a photolabilization of bpy to form the active catalytic intermediate. The authors speculate that reduction of CO_2 to formic acid may involve the following sequential steps: (1) photogeneration of $Ru(bpy)_3^{+}$, (2) ligand photolabilization; (3) bis(bipyridine)ruthenium hydride formation by protonation: (4) insertion of CO_2 into Ru-H and (5) release of the formate produced, perhaps facilitated by excess of bipyridine or by transfer of a second electron.

An aqueous system containing $Ru(bpy)_3^{2+}$, methylviologen (MV^{2+}) and TEOA photoreduces CO_2 to formate with a quantum yield of 0.01 (Kitamura and Tazuke 1983). (The quantum yield in this chapter is defined as mol of the product/einsteins absorbed by the photosensitizer, unless otherwise noted.) In contrast to the previous system, the excited state of $Ru(bpy)_3^{2+}$ is oxidatively quenched by MV^{2+} to form $Ru(bpy)_3^{3+}$ and MV^{+} (reaction 11). However, direct electron transfer from MV^{+} to CO_2 is energetically impossible, since the reduction potential of $MV^{2+/+}$ is only -0.44 V. Although no detailed mechanistic study was done, the authors suggest a mechanism which involves proton participation as shown in eq.1, since the pH of the CO_2 saturated solution is lower than pH 7. Reactions 9 and 10 also produce $Ru(bpy)_3^{+}$ which can effect CO_2 reduction as discussed above. Moreover, the difficulty of ruling out formation of formic acid in degradative reactions has been noted (Legros and Soumillion 1985).

Scheme II. Oxidative quenching

$Ru(bpy)_3^{2+} + h\nu \rightarrow {}^{*}Ru(bpy)_3^{2+}$ (7)

${}^{*}Ru(bpy)_3^{2+} + MV^{2+} \rightarrow Ru(bpy)_3^{3+} + MV^{+}$ (11)

$Ru(bpy)_3^{3+} + TEOA \rightarrow Ru(bpy)_3^{2+} + TEOA^{\bullet+}$ (12)

$TEOA^{\bullet} + Ru(bpy)_3^{3+} \rightarrow TEOA_{OX} + Ru(bpy)_3^{2+}$ (13)

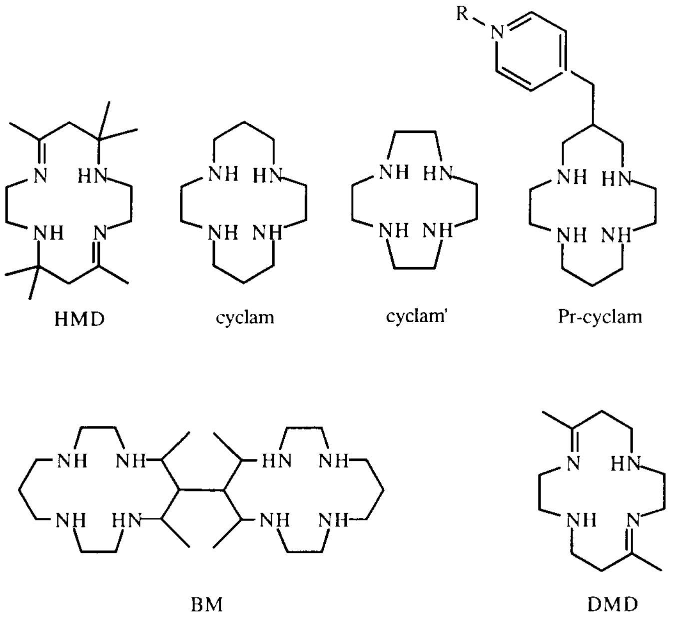

Figure 11.3 Structures of ligands.

Table 11. 1 Photocatalytic Reduction of CO_2 [a]

Sensitizer	Catalyst or Relay	Donor	Product(s)	Φ^b, mol einstein^{-1}	Ref.
$Ru(bpy)_3^{2+}$		TEOA	$HCOO^-$	0.049^c	(Hawacker et al. 1985) (Lehn and Ziessel 1990)
$Ru(bpy)_3^{2+}$		TEOA	$HCOO^-$	0.096^d	(Lehn and Ziessel 1990)
$Ru(bpy)_3^{2+}$	MV^{2+}	TEOA	$HCOO^-$	0.01	(Kitamura and Tazuke 1983)
$Ru(bpy)_3^{2+}$	Co^{2+}/bpy	TEA	CO, H_2		(Lehn and Ziessel 1982)
$Ru(bpy)_3^{2+}$	Co^{2+}/Me_2phen	TEA	CO, H_2	0.012 (CO) 0.065 (H_2)	(Ziessel et al. 1986)
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)_2^{2+}$	TEOA	$HCOO^-$	0.14	(Ishida et al. 1987) (Ishida et al. 1988) (Ishida et al. 1990)
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)_2^{2+}$	BNAH	$HCOO^-$, CO	0.03 ($HCOO^-$) 0.15 (CO)	(Ishida et al. 1987) (Ishida et al. 1988) (Ishida et al. 1990)
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)(H)^+$	TEOA	$HCOO^-$	0.15	(Lehn and Ziessel 1990)
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)(X)^{n+}$ X−Cl and CO	TEOA	$HCOO^-$		(Lehn and Ziessel 1990)
$Ru(bpy)_3^{2+}$	$CoHMD^{2+}$	H_2A	CO, H_2		(Tinnemans et al. 1984)
$Ru(bpy)_3^{2+}$	$Ni(cyclam)^{2+}$	H_2A	CO, H_2	0.001 (CO)	(Grant et al. 1987) (Craig et al. 1990)
$Ru(bpy)_3^{2+}$	$Ni(Pr\text{-}cyclam)^{2+}$	H_2A	CO, H_2	~0.005 (CO)	(Kimura et al. 1994)
$Ru(bpy)_3^{2+}$	$(Ni_2BM)^{4+}$	H_2A	CO, H_2	~0.008 (CO)	(Mochizuki et al. 1996)
$Ru(bpz)_3^{2+}$	Ru colloid	TEOA	CH_4	10^{-4} $(CH_4)^c$	(Maidan and Willner 1986) (Willner et al. 1987)

$Ru(bpy)_3^{2+}$	bipyridinium$^+$, Ru or Os colloid	TEOA	CH_4 H_2	10^{-4} (CH_4)[c] 10^{-3} (H_2)[c]	(Willner et al. 1987)
$ReCl(bpy)(CO)_3$		TEOA	CO	0.14	(Hawecker et al. 1983) (Hawecker et al. 1986)
$ReBr(bpy)(CO)_3$		TEOA	CO	0.15	(Kutal et al. 1985) (Kutal et al. 1987)
$ReP(OEt)_3(bpy)(CO)_3^+$		TEOA	CO	0.38	(Hori et al. 1996)
$RePPh_3(bpy)(CO)_3^+$		TEOA	CO	0.05	(Hori et al. 1997)
$ReP(OEt)_3(dmb)(CO)_3^+$		TEOA	CO	0.18	(Koike et al. 1997)
$ReP(O\text{-}i\text{-}Pr)_3(bpy)(CO)_3^+$		TEOA	CO	0.20	(Koike et al. 1997)
$Re(CNpy)(bpy)(CO)_3^+$		TEOA	CO	0.13	(Hori et al. 1999)
p-Terphenyl	$Co(cyclam)^{3+}$	TEOA	CO, $HCOO^-$, H_2	0.075 ($HCOO^-$) 0.05 (CO)	(Matsuoka et al. 1991) (Matsuoka et al. 1993)
p-Terphenyl	$CoHMD^{2+}$	TEOA	CO, $HCOO^-$, H_2		(Matsuoka et al. 1993) (Ogata et al. 1995)
p-Terphenyl	Fe and Co porpyrins	TEA	CO, $HCOO^-$, H_2		(Dhanasekaran et al. 1999)
Phenazine	$Co(cyclam)^{3+}$	TEOA	$HCOO^-$	0.035	(Ogata et al. 1995)
Fe porphyrins		TEA	CO		(Grodkowski et al. 1997)
Co porphyrins		TEA	$HCOO^-$, CO		(Behar et al. 1998)

[a] Abbreviations used: TEOA = triethanolamine, MV^{2+} = methylviologen, TEA = triethylamine, bpy = 2,2'-bipyridine, dmb = 4,4'-dimethyl-2,2'-bipyridine, Me_2phen = 2,9-Dimethyl-1,10-phenanthroline, Cnpy = 4-CN-pyridine, BNAH = 1-benzyl-1,4-dihydronicotinamide, H_2A = ascorbic acid, cyclam = 1,4,8,11-tetraazacyclotetradecane, BM = 6,6'-bi(5,7-dimethyl-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, TPP = 5,10,15,20-tetraphenyl-21H,23H-porphine. [b] Unless otherwise noted, the quantum yield of product formation is defined as the formation rate divided by the light intensity. [c] with 15 % water in DMF. [d] with 15 % water and excess bpy in DMF. [c] Assuming two or eight photons produce one molecule of the product.

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II.2.2 Ru(bpy)$_3^{2+}$ as a photosensitizer and another metal complex as a catalyst

A system containing Ru(bpy)$_3^{2+}$/Co^{2+}/tertiary amine as photosensitizer/catalyst/donor, respectively, is capable of catalytically generating CO (instead of formic acid) and H_2 by reduction of CO_2 and water under irradiation with visible light (Lehn and Ziessel 1982). When TEA is used as donor, the system produces CO and H_2 in the ratio 0.68. The amount of gas (CO + H_2) produced and the CO/H_2 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 H_2 production. Higher selectivity for CO_2 reduction to CO was observed when TEOA was used instead of TEA. This system was further studied by adding 4,4',6,6'-tetramethyl-2,2'-bipyridine or 2,9-dimethyl-1,10-phenanthroline instead of bpy (Ziessel, Hawecker et al. 1986). 2,9-Dimethyl-1,10-phenanthroline is particularly effective in promoting CO and H_2 formation, giving a quantum yield of 0.012 for CO and 0.065 for H_2 in a DMF medium.

Because the systems described above contain free bipyridine-type ligands, the formation of the Co(I) bipyridyl species from the excited state of Ru(bpy)$_3^{2+}$ in the Ru(bpy)$_3^{2+}$/Co(bpy)$_3^{2+}$/tertiary amine system has been examined in some detail (Keene et al., 1985). Stoichiomeric studies with Co(bpy)$_3^+$ and CO_2 were also carried out in order to elucidate the mechanism of the CO_2 reduction. It was shown that Co(bpy)$_3^+$ can be generated from *Ru(bpy)$_3^{2+}$ by various routes including reduction of *Ru(bpy)$_3^{2+}$ to Ru(bpy)$_3^+$ followed by reaction with Co(bpy)$_3^{2+}$, oxidation of the *Ru(bpy)$_3^{2+}$ by Co(bpy)$_3^{2+}$ to Ru(bpy)$_3^{3+}$ and, in principle, energy transfer to form Ru(bpy)$_3^{2+}$. The high-spin Co(bpy)$_3^+$ complex, which is substitution labile, reduces bpy to bpyH_2, H_2O to H_2, and CO_2 to CO (as the insoluble [Co(bpy)(CO)$_2$]$_2$). The latter likely involves Co(bpy)$_2$(H_2O)H^{2+} and/or Co(bpy)$_2$(H_2O)$_2^+$ as intermediates. Since formate is not an important reaction product it is unlikely that CO_2 insertion into the Co-H bond occurs to an appreciable extent.

Photochemical reduction of CO_2 has been achieved by using TEOA in DMF or 1-benzyl-1,4-dihydronicotinamide (BNAH) in H_2O/DMF as a quencher in the presence of Ru(bpy)$_3^{2+}$ and Ru(bpy)$_2$(CO)$_2^{2+}$ under illumination at $\lambda > 400$ nm (Ishida et al., 1987; Ishida et al., 1988; Ishida, Terada et al. 1990). 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. Similar experiments with Ru(bpy)$_2$(CO)(X)$^+$ (X = Cl, and H) in TEOA/DMF were also reported to form formate from CO_2 (Lehn and Ziessel 1990). [Ru(bpy)$_2$(CO)(COO)] and [Ru(bpy)$_2$(CO)(COOH)]$^+$ are prepared by the addition of two and one OH^-, respectively, to $[Ru(bpy)_2(CO)_2]^+$ (eqs. 14 and 15). Air stable species, $[Ru(bpy)_2(CO)_2](PF_6)_2$ (Tanaka et al. 1993), $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$ (Tanaka et al., 1992), and $[Ru(bpy)_2(CO)(COOH)](CF_3SO_3)(H_2O)$ (Toyohara et al.,1996) have been characterized by x-ray diffraction and various types of spectroscopy. In the photochemical system, it is proposed that the reactions 16-19 are taking place.

$$Ru(bpy)_2(CO)_2^{2+} + OH^- \rightarrow Ru(bpy)_2(CO)(COOH)^+ \quad (14)$$

$$Ru(bpy)_2(CO)(COOH)^+ + OH^- \rightarrow Ru(bpy)_2(CO)(COO) + H_2O \quad (15)$$

$$Ru(bpy)_2(CO)_2^{2+} + 2e^- \rightarrow Ru(bpy)_2(CO) + CO \quad (16)$$

$$Ru(bpy)_2(CO)X^+ + 2e^- \rightarrow Ru(bpy)_2(CO) + X^- \quad (17)$$

$$Ru(bpy)_2(CO) + CO_2 \rightarrow Ru(bpy)_2(CO)(COO) \quad (18)$$

$$Ru(bpy)_2(CO)(COO) + H^+ + 2e^- \rightarrow Ru(bpy)_2(CO) + HCOO^- \quad (19)$$

However, electrochemical reduction of $[Ru(bpy)_2(CO)_2]^{2+}$ in CH_3CN leads to the formation of a polymeric film, $[Ru(bpy)(CO)_2]_n$, on the electrode surface (Chardon-Noblat et al., 1994) Similarly, Na-Hg reduction of $[Ru(bpy)_2(CO)_2]^{2+}$ in CH_3CN immediately produces a blue solution; and black precipitates, $[Ru(bpy)(CO)_2]_n$, form in 30 minutes (Fujita 1999). Interestingly, both Tanaka's and Ziessel's groups reported a decrease of catalytic activity with formation of a black precipitate during photoreduction of CO_2. Therefore the proposed mechanism of CO production from $[Ru(bpy)_2(CO)_2]^{2+}$ with two molecules of $Ru(bpy)_3^+$ serving as the electron source (eq. 16) is not involved in photochemical CO_2 reduction. Recent results indicate that reduction of $[Ru(bpy)_2(CO)Cl]^+$ by two electrons produces $[Ru^I(bpy)(bpy^{\bullet-})(CO)]$, which reacts with CO_2 to form $Ru(bpy)_2(CO)(COO)$ (Fujita 1999).

The production of formate in $Ru(bpy)_3^{2+}/Ru(bpy)_2(CO)_2^{2+}$/TEOA/DMF is assumed to involve the isomerization of the carboxylate complex associated with protonation, or reduction of the carboxylic acid adduct associated with protonation as shown in eq 19 (Ishida et al., 1990; Lehn and Ziessel 1990). This is contrary to what was found in electrochemical CO_2 reduction using similar complexes (Pugh et al., 1991). It is widely believed that $HCOO^-$ forms by CO_2 insertion into the M-H bond in other cases. For example, $Re(bpy)(CO)_3H$ reacts with CO_2 to afford

$Re(bpy)(CO)_3OC(O)H$ quantitatively (Sullivan and Meyer 1986). The doubly reduced intermediate, $[Ru(bpy)_2(CO)]$, in reactions 16 and 17 may react with protons to form $[Ru(bpy)_2(CO)H]^+$. However $[Ru(bpy)_2(CO)H]^+$ does not react with CO_2, but the mono-reduced species, $[Ru(bpy)_2(CO)H]$, reacts with CO_2. The reduction of $[Ru(bpy)_2(CO)H]^+$ (-1.45 V vs SCE in CH_3CN) by $Ru(bpy)_3^+$ (-1.33 V) is uphill. It would be highly desirable to elucidate the detailed mechanism of formate and CO formation in this photocatalytic system using time-resolved spectroscopies. It is also of interest to understand why the major product (formate vs CO) changes when different electron donors are used.

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 (Grant et al., 1987; Craig et al., 1990) or cobalt macrocycles 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) (Tinnemans et al., 1984). $Ni(cyclam)^{2+}$ is reported to be an extremely efficient and selective catalyst for the electrochemical reduction of CO_2 to CO, even in H_2O, and involves a Ni(I) species adsorbed on a Hg surface. When $Ni(cyclam)^{2+}$ is used as a catalyst in the photochemical system, however, the quantum yield of CO production is 5×10^{-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. $Ni(cyclam')^{2+}$, which is high-spin, six-coordinate with two cis water molecules, produces both CO and formate, while $Ni(cyclam)^{2+}$, which is mainly low-spin, square-planar in H_2O, yields only CO from CO_2 reduction. $[Co^{III}L\text{-}H^-]^{2+}$ or $[Ni^{III}L\text{-}H^-]^{2+}$ (where L is a macrocyclic ligand) is originally suggested to be a common intermediate for CO and H_2 production in these photocatalytic systems. However, new studies indicate that this may be incorrect (See 11.2.6) (Ogata et al. 1995).

$Ni(cyclam)^{2+}$ complexes containing a pendant pyridinium group, which had been shown to function as effective mediators in the photochemical reduction of H_2O with a Pt colloid, were prepared and their catalytic behavior toward photochemical CO_2 reduction with $Ru(bpy)_3^{2+}$ and ascorbate was examined (Kimura et al., 1994). The system containing $Ni(Pr\text{-}cyclam)^{2+}$ (See Fig. 11.3.) at pH 5 evolved CO about 5 times more rapidly than when underivatized $Ni(cyclam)^{2+}$ was used. The selectivity (CO/H_2 = 0.1 - 0.65) depends on the experimental conditions, and typically more CO is produced at higher $Ni(Pr\text{-}cyclam)^{2+}$ concentrations.

A bismacrocyylcic Ni(II) complex, Ni_2BM^{4+}, in which the two dimethylcyclam units are linked by C-C bonds as shown in Fig. 11.3, has been used as a catalyst with with $Ru(bpy)_3^{2+}$ and ascorbate (pH = 4) under illumination with a high-pressure Hg lamp (Mochizuki et al., 1996). The rate of CO production using the bismacrocyclic complex was about eight times as large as that obtained with $Ni(cyclam)^{2+}$ under the same conditions. The CO/H_2 ratio was 15 with the bismacrocyclic complex, while the value was 0.11 with $Ni(cyclam)^{2+}$.

11.2.3 $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$-type complexes as photosensitizers in microheterogeneous systems

The photoreduction of CO_2 to methane and hydrocarbons has been achieved in aqueous solution containing $Ru(bpy)_3^{2+}$, an electron donor, a bipyridinium charge relay, and Ru or Os colloids (Maidan and Willner 1986; Willner et al., 1987). The quantum yields for H_2 evolution ($\sim10^{-3}$ assuming two photons produce one H_2) and hydrocarbon formation ($\sim10^{-4}$ assuming eight photons produce one CH_4) depend on the relay used. However, a similar system containing $Ru(bpz)_3^{2+}$ (bpz = bipyrazine) as sensitizer without a bipyridinium charge relay leads to the formation of methane, ethylene and ethane without the evolution of H_2. The reduction of CO_2 is proposed to proceed via electron transfer followed by protonation of Ru- or Os metal-activated CO_2 rather than through a hydrogenation route, since no H_2 evolution occurs either in the presence of CO_2 or under argon with $Ru(bpz)_3^{2+}$.

11.2.4 $Re(bpy)(CO)_3X$, $Re(bpy)(CO)_2X_2$ or similar complexes both as photosensitizers and catalysts

$Re(bpy)(CO)_3X$ (X = Cl, Br) has been used successfully as a photocatayst for CO_2 reduction to CO with TEOA in DMF (Hawecker et al., 1983; Kutal et al., 1985; Hawecker et al., 1986; Kutal et al., 1987). When X = Cl, a quantum yield of 0.14 was measured in the presence of excess Cl^-. A formato-rhenium complex was isolated in the absence of excess Cl^-. $Re(bpy)(CO)_3\{P(OEt)_3\}^+$ is also a CO_2 reduction catalyst which produces CO with a quantum yield up to 0.38 (Hori et al. 1996). Both the quantum yield and turnover number of the photocatalytic reaction are strongly dependent on the irradiation light intensity and wavelength. $Re(bpy)(CO)_3H$ is known to undergo a slow thermal reaction with CO_2 in THF to give the formato complex and the reaction is greatly enhanced by visible light (Sullivan and Meyer 1984). However, such intermediates are generally considered to produce formate, not CO. Transient absorption and FTIR studies of $Re(bpy)(CO)_3X^{n+}$ (when X = Cl, n = 0, when X = acetonitrile, n = 1) (Shu and Wrighton 1988; Kalyanasundaram 1986;

George, Johnson et al. 1993) or $Re(bpy)(CO)_2\{P(OEt)_3\}_2^+$ (Ishitani et al. 1994) indicate that the emission from the MLCT excited state of $Re(bpy)(CO)_3X^{n+}$ or $Re(bpy)(CO)_2\{P(OEt)_3\}_2^+$ are reductively quenched leading to prompt formation of $Re(bpy)(CO)_3X^{(n-1)+}$ or $Re(bpy)(CO)_2\{P(OEt)_3\}_2$. Extensive electrochemical studies indicate that $Re(bpy)(CO)_3Cl$ gives the corresponding radical anion, $Re(bpy)(CO)_3Cl^{\bullet -}$, which may only react with CO_2 after dissociation of the chloride ligand. The CO_2 activation seems to have two independent routes, the 1e pathway via $Re(bpy)(CO)_3^{\bullet}$ and a 2e pathway via $Re(bpy)(CO)_3^-$ (van Outersterp et al. 1995; Johnson et al. 1996). Rhenium carboxylate ($Re\text{-}CO_2$) and rhenium carboxylic acid (Re-COOH) are proposed as intermediates in photochemical and electrochemical reduction of CO_2, but no direct evidence has been obtained. $Re(dmbpy)(CO)_3(COOH)$ and $(CO)_3(dmbpy)Re\text{-}C(O)\text{-}O\text{-}Re(dmbpy)(CO)_3$ (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) have been prepared by different routes and characterized (Gibson and Yin 1998).

11.2.5 Porphyrins both as a photosensitizer and a catalyst

Photocatalytic formation of CO and formate has been confirmed using CO_2–saturated DMF or acetonitrile solutions containing an iron or cobalt porphyrin, as a catalyst and TEA as a reductive quencher (Grodkowski et al. 1997; Behar et al. 1998). The cobalt and iron porphyrins involved were tetraphenylporphyrin (TPP) and its derivatives in which each phenyl ring contained either a 3-F or a $3\text{-}CF_3$ group or was perfluorinated. Neither Co(I) nor Fe(I) porphyrins react with CO_2, but the further reduced species, which are described as M(0) porphyrins from the spectral features, react with and reduce CO_2. Catalytic reduction of CO_2 is also confirmed by cyclic voltammetry and is shown to occur at the potential at which the M(I) porphyrin is reduced to the M(0) porphyrin. With $Fe^{III}TPPCl$ the yield of CO reaches turnover numbers of 70 molecules of CO per porphyrin molecule. Turnover numbers of at least 50 and 200 have been observed for CO and formate, respectively, with $Co^{II}TPP$. The porphyrin gradually degrades to colorless products and the reduction stops. The yield of CO was lower when fluorinated metalloporphyrins were used. An attempt to observe and characterize the $CO_2\text{–}Co^0TPP$ failed due to the low quantum yield for the formation of Co^0TPP.

11.2.6 Other metal complexes as a photosensitizer and a catalyst

Photoreduction of CO_2 to formaldehyde and $HCOO^-$ has been reported using trichlorobis(2,2':6',2"-terpyridyl)vanadium(III) as photosensitizer, MV^{2+} as electron acceptor, and ethylenediaminetetraacetic acid (EDTA) or TEOA as sacrificial electron donor (Aliwi 1992). 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 CO_2 to $CO_2^{\bullet -}$ requires -1.9 V vs NHE, it is difficult to produce $CO_2^{\bullet -}$ by photochemical methods. The trinuclear cluster $[Ni_3(\mu_3\text{-}I)_2(dppm)_3]$ {dppm = bis(diphenylphosphino)methane} is reported to reduce CO_2 to $CO_2^{\bullet -}$ in THF when irradiated at $\lambda > 300$ nm (Morgenstern et al. 1993). Photolysis of $[Ni_3(\mu_3\text{-}I)_2(dppm)_3]$ in a 4:1 v/v THF/cyclohexene solution under 1 atm CO_2 led to oxidation of $[Ni_3(\mu_3\text{-}I)_2(dppm)_3]$ and to the formation of *cis*- and *trans*-1,2-cyclohexanedicarboxylates. Although the system does not seem photocatalytic, it is a rare case of purported involvement of $CO_2^{\bullet -}$. $[Ni_3(\mu_3\text{-}I)_2(dppm)_3]$ does not emit, but the authors assumed that the excited state of $[Ni_3(\mu_3\text{-}I)_2(dppm)_3]$ is quenched by CO_2 to form $CO_2^{\bullet -}$. Mechanistic and kinetic studies using time-resolved spectroscopies and measurements of the excited state potential are required to verify the claim.

11.2.7 Organic photosensitizers and metal complexes 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 (Tazuke and Ozawa 1975; Tazuke and Kitamura 1978; Tazuke et al. 1986). These stoichiometric reactions are considered to proceed via the anion radicals of the hydrocarbons (which are formed by the reductive quenching of the excited state of hydrocarbons by amine) reacting with CO_2 and then abstracting hydrogen to yield the corresponding product. Unlike these hydrocarbons, oligo(*p*-phenylene) ranging from *p*-terphenyl to *p*-sexiphenyl acts as a photocatalyst in the photoreduction of CO_2 to $HCOO^-$ with TEA in a dried aprotic solvents such as DMF and CH_3CN (Matsuoka et al. 1992). The quantum yield of HCOOH is 0.018 at 313 nm with *p*-terphenyl, *p*-terphenyl concurrently undergoes photo-Birch reduction to form dihydroterphenyl derivatives and the generation of $HCOO^-$ stops 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 without significant H_2 in a 5:1 acetonitrile/methanol mixture (Matsuoka et al. 1993).

When the Co(cyclam)$^{3+}$ complex is used, the quantum yields for formation of carbon monoxide and formate are 0.05 and 0.075, respectively, at 313 nm in the presence of TEOA.

The kinetics and mechanism of CO formation in p-terphenyl/Co^{II}HMD/TEA have been studied by continuous and flash photolysis techniques (Ogata et al. 1995). Transient spectra provide clear evidence for the sequential formation of the *p*-terphenyl radical anion, Co^{I}HMD^{+}, [Co^{I}HMD-CO$_2$]$^{+}$ and [S-Co^{III}HMD-(CO$_2^{2-}$)]$^{+}$ (S = solvent) in the catalytic system. The Co^{I}HMD^{+} complex, [Co^{I}HMD-CO$_2$]$^{+}$ and [(CH$_3$CN)-Co^{III}HMD-(CO$_2^{2-}$)]$^{+}$ together with [Co^{I}HMD-CO]$^{+}$, have been identified by various spectroscopic techniques including UV-vis, IR, NMR, XANES and EXAFS (Fujita et al. 1988; Fujita et al. 1991; Fujita et al. 1993; Fujita et al. 1997; Fujita and van Eldik 1998). The CO$_2$ binding constants for Co^{I}HMD^{+} in CH$_3$CN and in H$_2$O (Creutz et al. 1991) are 1.2 x 10^{4} and 4.5 x 10^{8} M^{-1}, respectively. The complex is thermochromic, being purple at room temperature and yellow at low temperature (–100 °C) with $\Delta H° = -7.0$ kcal mol^{-1} and $\Delta S° = -27$ cal K^{-1} mol^{-1} for eq. 21 in CH$_3$CN. The pressure dependence of the equilibrium constant shows that increasing pressure shifts the equilibrium toward the six-coordinate species with an overall reaction volume $\Delta V° = -17.7 \pm 1.0$ mL mol^{-1} at 15 °C in CH$_3$CN.

$$\mathrm{CoHMD^{+} + CO_2 \leftrightarrow [CoHMD(CO_2)]^{+}} \qquad (20)$$

$$\mathrm{[CoHMD(CO_2)]^{+} + S \leftrightarrow [CoHMD(CO_2)(S)]^{+}} \qquad (21)$$

The XANES study indicates that six-coordinate [(CH$_3$CN)-CoHMD-(CO$_2^{2-}$)]$^{+}$, in which a significant charge is transferred from metal to the bound CO$_2$, can be interpreted as a Co(III) carboxylate. This assignment is consistent with the shift of the asymmetric $\nu_{\mathrm{CO_2}}$ from 1706 cm^{-1} for [CoHMD(CO$_2$)]$^{+}$ to 1544 cm^{-1} for [CoHMD(CO$_2$)(CH$_3$CN)]$^{+}$. Although the Co(III) carboxylates have been postulated as intermediates in CO$_2$ reduction and water-gas shift reactions, the XANES results provided the first unambiguous evidence that active metal catalysts, such as Co^{I}HMD^{+}, can promote two-electron transfer to the bound CO$_2$. This reversible intramolecular two-electron-transfer reaction, responsive to temperature and pressure changes, could be of fundamental importance to processes dealing with the reduction of CO$_2$ in photocatalytic systems. The electron-transfer rate constant for the reaction of *p*-terphenyl radical anion with Co^{II}HMD^{2+} is 1.1 × 10^{10} 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 × 10^{8} M^{-1} s^{-1} and an equilibrium constant of 1.1 ×

10^4 M^{-1} for the binding of CO_2 to $Co^{I}HMD^{+}$ in the catalytic system. These rate constants are consistent with those previously obtained by conventional methods in acetonitrile.

$$TP + TEA + h\nu \rightarrow TP^{\bullet -} + TEA^{\bullet +} \qquad (22)$$

$$TP^{\bullet -} + Co^{II}HMD^{2+} \rightarrow TP + Co^{I}HMD^{+} \qquad (23)$$

$$Co^{I}HMD^{+} + CO_2 \leftrightarrow CoHMD(CO_2)^{+} \qquad (24)$$

$$CoHMD(CO_2)^{+} + S \leftrightarrow [S\text{-}Co^{III}HMD\text{-}(CO_2^{2-})]^{+} \qquad (25)$$

$S = MeOH$ or CH_3CN

$$[S\text{-}Co^{III}HMD\text{-}(CO_2^{2-})]^{+} + HA \rightarrow [S\text{-}Co^{III}HMD\text{-}(COOH)^{-}]^{2+} + A^{-} \qquad (26)$$

$HA = HTEA^{+}, MeOH, H_2O$

$$[S\text{-}Co^{III}HMD\text{-}(COOH)^{-}]^{2+} + e^{-} \rightarrow Co^{II}HMD^{2+} + CO + OH^{-} \qquad (27)$$

$e^{-} = TP^{\bullet}, Co^{I}HMD^{+}, Et_2NC^{\bullet}HCH_3$

The $Co^{I}HMD^{+}$ produced reacts efficiently to form the CO_2 adduct while hydride formation is suppressed by limiting the amount of possible proton sources. This study clearly shows evidence that the cobalt macrocycle provides two electrons to the CO_2 moiety to produce a stable $SCo^{III}HMD(CO_2^{2-})^{+}$ species. The rate-determining step in the continuous photolysis system seems to be the second electron transfer to $SCo^{III}HMD(CO_2^{2-})^{+}$, followed by a bond-breaking step. Either $Et_2NC^{\bullet}HCH_3$, $Co^{I}HMD^{+}$, or the continuously formed $TP^{\cdot -}$ may be the source of the second electron. The C–O bond breakage in the bound carboxylic acid is likely to be the slow step. Unfortunately the transient UV-vis spectrum of $[S\text{-}Co^{III}HMD(CO_2^{2-})]^{+}$ is too weak to permit studies of the proton dependence of its disappearance.

Recently photoreduction of CO_2 to $HCOO^{-}$ (together with a small amount of CO and H_2) was achieved by UV-irradiation of a system involving phenazine (phena) as a photosensitizer, $Co(cyclam)^{3+}$ as an electron mediator and TEA as an electron donor (Ogata et al. 1995). The quantum yield for the formation of $HCOO^{-}$ is 0.035. Electron transfer from the photo-formed radical anion ($Phena^{\bullet -}$) to $Co(cyclam)^{3+}$ ($k = 4.3 \times 10^9$ M^{-1} s^{-1}) results in the formation of $Co(cyclam)^{2+}$. Since the reduction potential of Co(cyclam)$^{2+/+}$ is ~-1.9 V vs SCE in CH_3CN. Phena$^{\bullet -}$ is not capable of reducing Co(II) to Co(I). Therefore the authors suggest that: (1) PhenaH$^{\bullet}$, produced by the protonation to Phena$^{\bullet -}$, may transfer a hydrogen atom to Co(cyclam)$^{2+}$ to form Co(cyclam)(H)$^{2+}$; and (2) the insertion of CO_2 into the hydride produces CO via the Co^{III}-formate complex. Although preliminary results appear to support the proposed mechanism, the hydrogen atom transfer step needs to be investigated in detail.

11.2.8 Challenges on photochemical reduction of CO_2 using molecular sensitizers

Solar energy conversion using molecular sensitizers is a formidable problem. The system must satisfy the following conditions:

(1) strong absorption in the visible region;
(2) long-lived excited state(s);
(3) efficient quenching of the excited state to produce highly reduced and oxidized intermediates;
(4) no side reactions that 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 slower than photo-process.]; and
(7) no use of sacrificial reagents.

Although conditions 1 to 6 have been fulfilled to some degree, to our knowledge all previous attempts of CO_2 reduction with homogeneous catalysts have failed to achieve condition 7. Do we need to design organized systems modeled upon natural photosynthesis? Should we accept a small turnover frequency as nature does? What kind of catalyst can accommodate the six-electron transfer for CH_3OH 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 CO_2 reduction.

11.3 Heterogeneous photochemical reduction of CO_2

Photocatalytic reduction of CO_2 in aqueous slurries containing 200 – 400 mesh semiconductor powders such as SiC, GaP, CdS, ZnO, TiO_2, or WO_3 was first reported in 1979 (Inoue et al. 1979). The products were formic acid, formaldehyde, methyl alcohol, and a trace amount of methane. The quantum yields for the production of HCHO and methanol were estimated to be less than 10^{-3} using a TiO_2 catalyst. Photogenerated carriers (electrons in the conduction band and positive holes in the valence band) were considered to promote multi-electron reduction of CO_2 and multi-hole oxidation of water. Semiconductors such as $SiTiO_3$, $CaFe_2O_4$, Nd_2O_3, Sm_2O_3 and EuO_2 have also been used. In efforts to enhance the yield of CO_2 reduction, surface treatment with a metal oxide, loading metal on semiconductors, and the addition of a hole scavenger such as Na_2S_2 were tried.

After quantum size effects in light absorption and chemical reactivity were discovered (Rossetti et al. 1983), a remarkable improvement in photocatalytic reduction of CO_2 was achieved using quantized or colloidal semiconductors. Quantized TiO_2 particles in SiO_2 metrices (Q-TiO_2/SiO_2), prepared by a sol-gel technique, showed that the efficiencies for formate and methane obtained with Q-TiO_2/SiO_2 irradiation at 280 nm increased with decreasing Ti/Si ratios (Inoue et al. 1994). Quantized TiO_2 particles anchored within micropores of the Y – zeolite cavities (Anpo, Yamashita et al. 1997), or anchored on Vycor (Anpo and Chiba 1992), or immobilized poly(vinylpyrrolidine) film were also used for photochemical CO_2 reduction. When poly(vinylpyrrolidine) film with TiO_2 was placed in a CO_2-saturated propylene carbonate containing propan-2-ol as a hole scavenger and was illuminated ($\lambda > 300$ nm), methanol was selectively produced from CO_2. Labeling experiments confirmed the methanol production from CO_2 (Kuwabata et al. 1995). Freshly prepared colloidal ZnS crystals catalyzed photoreduction of CO_2 in water (pH 7) with NaH_2PO_2 and Na_2S under UV irradiation, resulting in the formation of formic acid, CO, H_2 and HPO_3^{2-} (from $H_2PO_2^-$). The quantum yield for formic acid was 0.12 at 313 nm. The activity of quantized ZnS suspensions depended on preparation methods, particle size, the pH of the system, and synergistic effects of electron donors. In order to avoid competitive H_2 evolution from water, transparent colloidal solutions of ZnS nanocrystallites were prepared using organic solvents as well as CaS nanocrystallites (Kanemoto et al. 1996). With colloidal ZnS (hexagonal microcrystals, average size ~ 2 nm) in DMF, photochemical CO_2 reduction in the presence of TEA as a sacrificial electron donor produced formate, CO, and H_2 (77:1:6) under UV light ($\lambda > 290$ nm) irradiation. The quantum yield for formation of formate, the main product, was 0.07 at $\lambda = 302$ nm. However the addition of zinc ions to the system changes the product distribution (1:2.5:1.5) without adversely affecting the efficiency. A remarkable product switching between formate and CO may result from the surface modification. The formation of surface sulfur vacancies and the adsorptive activation of CO_2 on ZnS may be an important factor in successive electron transfer in CO_2 reduction.

11.4 Photoelectrochemical Reduction of CO_2

In photoelectrochemical processes, the molecular sensitizer is replaced with a p-type semiconductor electrode such as Si, In, GaP, GaAs, CdTe, WSe, or InP. By irradiating with light with more energy than the bandgap of the semiconductor electrode, electrochemical CO_2 reduction can be achieved at much lower bias potentials than attainable without irradiation. The electric field gradient, which exists at the interface between the semiconductor and solution, produces a charge separation with the electrons moving to the electrode surface for CO_2 reduction. The holes generated in the bulk of the semiconductor are typically transferred to a metal anode where an oxidation reaction occurs. In contrast to molecular sensitizers, no quenching reagent is required, but typically an onset potential ranging from -0.1 to -1.3 V (vs. NHE) is required. In a typical photoelectrochemical cell the anode and cathode compartments are separated, and separation of the oxidized and reduced products occurs naturally. Bare semiconductors are used for photoelectrochemical CO_2 reduction with and without metal catalysts in H_2O or organic solvents. The major reduction products are HCOOH and CO, but methanol formation is also reported in some cases. Using nickel and cobalt macrocyclic complexes in aqueous media or water containing organic solvents, CO_2 reduction to produce CO was achieved on bare semiconductors such as Si and GaP with onset potentials as low as -0.2 V vs. NHE (Bradley et al. 1983; Beley et al. 1986). Polymer coated semiconductors have also been used to overcome corrosion problems. With p-Si and p-WSe electrodes modified by electropolymerization of $[Re(CO)_3(v\text{-}bpy)Cl]$, where v-bpy is 4-vinyl-4′-methyl-2,2-bipyridine, CO_2 reduction to CO at essentially unit efficiency was observed with onset potentials of -0.65 V (vs SSCE) (Cabrera and Abruña 1986).

11.5 Electrochemical reduction of carbon dioxide using solar electric power

In this process, solar cells generate electricity that is used to reduce CO_2 to fuels or chemicals in typical electrolytic cells. The electrochemical reactions in these cells are usually catalyzed to increase the efficiency with which the electrical energy is converted into chemical energy. A potential advantage of this approach is that it allows the properties of the light harvesting reaction and the catalytic reaction for CO_2 reduction to be optimized separately. Both homogeneous and heterogeneous catalysts will be discussed briefly.

A number of metal electrodes have been surveyed for their ability to catalyze the electrochemical reduction of CO_2 (Eggins and McNeill 1983). In general the products of these reactions are CO or formate. A noteworthy exception is copper. Copper electrodes have been shown to catalyze the electrochemical reduction of CO_2 to methane with relatively high selectivity (Hori, et al. 1989). This reaction is sensitive to conditions, and the current efficiencies for various products are dependent on the temperature, supporting electrolyte, and the pH at the electrode surface. For example, current efficiencies of 65-70% for ethylene production have been reported for a gas diffusion electrode using KOH as the electrolyte (Hori et. al. 1988, Sammells and Cook 1993). The overpotentials for these reactions are high, exceeding 1 volt in most cases, and these overpotentials appear to be required for the formation and conversion of certain intermediates to hydrocarbons. The reduction to methane occurs by formation of CO on the copper surface as supported by the observation of an IR band at 2087 cm^{-1} assigned to a linear η^1-CO (Hori, et. al. 1994). It has also been observed that CO reduction gives a product distribution on copper electrodes that is similar to that observed for CO_2 under the same conditions. Prolonged electrolysis at copper electrodes was found to result in electrode deactivation, however, this problem can be overcome by periodic anodic excursions which reactivate the electrode surface (Shiratsuchi, et. al. 1993, Jermann and Augustynski 1994).

In addition to metal electrodes and the semiconductor electrodes, electrodes of metal alloys and metal oxides have also been studied. The reduction products and reduction potentials of metal alloy electrodes have clearly been shown to be more than a simple additive function of the two metals involved. For example, Cu-Ni alloys produce methanol at nearly thermodynamic potentials, however the current efficiency was only 7% (Watanabe et. al. 1991). The products observed at a pure Cu electrode do not include methanol, and the overpotentials for methane and ethylene formation exceed 1 V. Perovskites of the general formula $Ln_{0.9}Sr_{0.1}CuO_3$ (Ln = La, Gd, Pr) have been incorporated into gas diffusion electrodes for studying CO_2 reduction (Sammells and Cook 1993). In this case the main products were ethanol and *n*-propanol which were produced with a total current efficiency exceeding 40%. Although the overpotentials in this case exceeded 2 V, the current efficiencies for rather complex products is impressive. These results clearly demonstrate the importance of considering other electrode materials in addition to pure metals or semiconductors.

Modification of electrode surfaces with molecular catalysts can also enhance electrode performance. One of the first examples of this approach was the modification of carbon electrodes with transition metal phthalocyanine (Meshitsuka et al. 1974; Lieber and Lewis 1984). There are several advantages that result from such a process including easy separation and recovery of the catalyst from the electrolyte solution, the use of very small amounts of catalyst because it is localized at the electrode interface, and stabilization of the catalyst. A number of different approaches have been used for electrode modification for CO_2 reduction and these are described in a review (Collin and Sauvage 1989). Generally these procedures transfer a homogeneous catalyst (which will be discussed below) to an electrode surface without any unique differences between the homogeneous catalyst and that anchored to the surface. This has the attractive feature that the catalyst can first be optimized in solution. Once the desired properties are obtained, the catalysts can be attached to the electrode surface to take advantage of some of the features discussed above.

In some cases the catalyst that exists at the electrode surface is uniquely different from both the homogeneous precursor and the bulk electrode itself. One example of this phenomenon is the adsorption of the Ni(cyclam)$^{2+}$ catalyst onto a mercury electrode during the reduction CO_2 to CO in aqueous solutions (Beley et al. 1986). This adsorbed species is much more active and selective than the parent species in homogeneous solutions using carbon electrodes. Although the importance of adsorption has been established in this system, the precise nature of the interaction of the complex with mercury or CO_2 is not known. The catalytic activities of geometric isomers of Ni(2,3,9,10-tetramethyl-cyclam)$^{2+}$ for CO_2 reduction are quite different and structural differences may be very important factor for adsorption onto mercury electrode and CO_2 binding (Fujita et al. 1994). A knowledge of the structure of the catalytically active species would be very useful in designing more active homogeneous catalysts.

A second example of a surface modified species that is different from its homogeneous precursor is the $Ru(bpy)(CO)_2$ polymer that forms on electrode surfaces as a result of the reduction of $[Ru(bpy)(CO)_2Cl_2]$ or $[Ru(bpy)_2(CO)_2]^{2+}$ (Chardon-Noblat et al. 1994; Collomb-Dunand-Sauthier et al. 1994). These polymer modified electrodes catalyze the reduction of CO_2 to CO when the bipyridine ring is unsubstituted, but the selectivity can be switched to formate by incorporating an isopropyl substituent on the bipyridine ligand. The origin of this difference in selectivity is not known. These results are important because they point to the possibility of unique electrode-catalyst interactions that can stabilize or enhance the catalytic activity not only of metal electrodes but also of semiconductor electrodes.

At high current densities the rate-limiting step is the transfer of CO_2 to the electrode surface. This has led to a number of studies of CO_2 reduction at high pressures, or the use of organic solvents such as methanol in which CO_2 solubility is much higher than in water to studies in supercritical CO_2, and to the use of gas diffusion electrodes and microporous electrodes (Fujishima et. al. 1998, Yamamoto 1998). All these methods represent reasonable approaches to overcoming the low concentrations of CO_2 typically found in solutions. However, as the CO_2 concentration becomes very high in solution, the solution resistance also increases significantly which leads to large energy losses.

Over the past 20 years a number of homogeneous electrocatalysts for CO_2 reduction have also been reported. These catalysts may be conveniently grouped into three major classes: (1) metal complexes with macrocyclic ligands, (2) metal complexes with bipyridine ligands, and (3) metal complexes with phosphorus ligands. The first report of macrocylic complexes catalyzing the reduction of CO_2 was by Meshitsuka and coworkers using cobalt and nickel phthalocyanines adsorbed on graphite electrodes (Meshitsuka et al. 1974). Although this is not a homogeneous system, it was followed by the work of Eisenberg who demonstrated that discrete metal complexes of cobalt and nickel could catalyze the reduction of CO_2 to CO (Fisher and Eisenberg 1980). Further studies of these complexes have shown that the binding of CO_2 to the reduced forms of these complexes can be significantly affected by the presence of alkali metal ions or even hydrogen bonding to the macrocycle (Gambarotta et al. 1982; Fujita et al. 1991; Fujita et al. 1993). High rates of reduction of CO_2 to CO have been observed for an iron porphyrin complex at relatively negative potentials (-1.6 V vs SCE) using trifluoroethanol as the proton source (Bhugun et. al. 1994).

Catalysts based on bipyridine ligands were first reported by Lehn and coworkers (Hawecker et al. 1983) in which a rhenium complex originally intended to serve as a photosensitizer was also found to function as a CO_2 reduction catalyst. In this case the product was CO. A number of bipyridine-complexes containing Re, Ru, Rh, Os and various first row transition metal complexes have since been reported. One of the most intriguing results from this class of compounds is the observation that under certain conditions four- and six-electron reductions can be observed (Nagao et. al. 1994). However, the catalytic rates and/or the selectivity for these more highly reduced products are not high.

Only a few transition metal phosphine complexes have been reported to catalyze the reduction of CO_2, although a large number of CO_2 complexes of this class are known. Wagenknecht and coworkers reported the first example of a catalyst belonging to this class, a rhodium diphosphine complex, but these complexes had large overpotentials, low catalytic rates, and low turnover numbers (Slater and

Wagenknecht 1984). The most extensively studied metal phosphine complexes for CO_2 reduction are the $[Pd(triphosphine)(solvent)]^{2+}$ complexes (DuBois 1997). Catalysts with high selectivity, high rates, and low overpotentials have been prepared and characterized. One of the unique features of these catalysts is the presence of two potential coordination sites if the solvent dissociates during the catalytic cycle. These two sites are needed for the coordination of water and CO following cleavage of the C-O bond of CO_2. It is thought that this feature contributes to the high rates observed for these catalysts. However, as with most other homogeneous catalysts, the major product is a two-electron reduction product, CO, and turnover numbers are low. Bimetallic catalysts based on linking two $[Pd(triphosphine)(solvent)]^{2+}$ units suggest the possibility of very high catalytic rates for these complexes, but again turnover numbers are low.

Before leaving the topic of electrocatalysis, the scope of the reactions that have been catalyzed should be examined, because it provides some indication of the range of catalytic reactions that may become feasible as the performance of the catalysts improve. The two-electron reduction of CO_2 to CO (a potential feedstock) or formate can be catalyzed by a number of homogeneous and heterogeneous systems, but not with the low overpotentials, high rates, and high stability that would be needed for a commercial process. The production of hydrocarbons such as methane and ethylene demonstrate that complex multi-electron reduction processes can be carried out, but without the selectivity or energy efficiency that is desired. The production of ethylene is a particularly intriguing reaction, because it is a direct precursor to polyethylene and a two-carbon feedstock. The production of alcohols ranging from methanol to *n*-propanol has also been reported as discussed above. Another class of reactions is the reductive carboxylation of alkynes and alkenes (Dérien et. al. 1991, Filardo et. al. 1984). These reactions suggest the possibility of forming carboxylic acids such as adipic acid and other useful acids directly from CO_2 and olefins.

11.6 Solar production of hydrogen followed by hydrogenation of CO_2

This approach has the advantage that it is the most technologically advanced because commercial processes are currently available for converting CO and hydrogen into methanol. Modifications of these catalysts have resulted in catalysts capable of converting CO_2 to methanol. For example, bench scale tests for producing 50 kg of methanol per day have been carried out at RITE in Japan (Ushikoshi et. al. 1997). The same approach of adapting known CO reduction catalysts to reactions using CO_2 may be applicable to other reactions besides methanol production. It would also be possible to shift CO_2 to CO using hydrogen and carry out reactions that are already known for CO.

However, there are disadvantages as well. The production of hydrogen utolizing solar electricity will require a large electrolysis unit comparable to that needed for direct reduction of CO_2. Additional capital investments will need to be made for carrying out the CO_2 reduction with hydrogen, and more if the CO_2 needs to be shifted to CO first. There is also a loss in efficiency that is inherent with each additional step. If both the electrolysis step and the hydrogenation step were carried out with a 70% efficiency the overall efficiency would be only 50%. A second problem is the lower conversions obtained using CO_2 compared to CO because the equilibria are not as favorable as with CO at the same temperature. To obtain comparable conversions of CO_2, catalysts need to be developed that operate at lower temperatures than the analogous catalysts for CO reduction.

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 such as $Rh(PPh_3)_3Cl$. 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 = $Ph_2P(CH_2)_4PPh_2$) as additives in DMSO under a total (H_2 + CO_2) pressure of 40 atm at room temperature, the system produces $HCOO^-$ with the turnover number of 2200 in 18 hrs (Leitner. et al. 1994). 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 CO_2 to formate including supercritical CO_2. In supercritical CO_2 with $RuH_2[P(CH_3)_3]_4$, TEA, and water, the remarkable TOF of 4000 h^{-1} was obtained for formate production (Jessop, et al. 1996). DMF was produced with $RuCl_2(dppe)_2$, where dppe = $Ph_2P(CH_2)_2PPh_2$, with the very large turnover frequency of 360,000 h^{-1} in supercritical CO_2 (Kröcher, et al. 1997).

11.7 Comparison of different pathways

Homogeneous systems based on molecular sensitizers. These systems tend to be the most complicated, but they are probably the most similar to natural photosynthesis. The multiple components present in these fully integrated systems make optimization difficult. Sacrificial electron donors (or acceptors) that are used in these systems need to be eliminated and replaced with coupled oxidation (and reduction) reactions. This will mean that both oxidized and reduced products will be formed together. One advantage of studying such homogeneous systems is the capability they afford of detecting short-lived intermediates using flash techniques. Therefore studies of these systems can provide mechanistic information that may be difficult or impossible to obtain using other techniques

Photoelectrochemistry. These systems still maintain the integrated nature in which both sensitizer and catalyst are part of the system. It offers the advantage that quenchers are not necessarily required because rapid charge separation occurs in the semiconductor. However, there are frequently problems with electrode stability and high overpotentials are needed in the absence of catalysts. There are two ways in which such systems could offer advantages over systems in which solar cells are coupled with electrochemical cells. First, the performance of the semiconductor could be enhanced by its interaction with the solution. Second, specific interactions between semiconductor and the catalyst could result in the formation of extremely active catalysts.

Electrochemical reduction of carbon dioxide using solar electric power. This route allows independent optimization of catalyst and solar cell performance. This approach can use a variety of electrochemical techniques to determine thermodynamics and mechanisms, but it does not provide spectroscopic data on transient intermediates. There are a variety of promising reactions that suggest the ultimate potential utility of this approach, but many obstacles need to be overcome. Among these are facile four-, six-, and eight-electron reductions for homogeneous catalysts, lower overpotentials and higher selectivity for heterogeneous catalysts, and improved stability for all classes of catalysts. However, the potential to generate renewable chemicals and fuels using this approach has clearly been demonstrated.

Hydrogenation of CO_2 using solar generated hydrogen. This is currently the most advanced approach to CO_2 reduction, but it will require more steps than direct electrochemical reduction of CO_2. These features suggest that this route may be the first one used, but it will probably not be the favored route in the long term. Its role as a transitional technology may be very important however.

We believe that all of the pathways have common mechanistic features and that insights gained in studying one type of system will have relevance to the others. For example, in homogeneous systems (both photochemical and electrochemical) it appears that the formation of formate is preceded by hydride formation. For heterogeneous catalysts, this pathway is thought to lead to methanol production, but not to methane or higher hydrocarbons. If $M\text{-}CO_2$ bonds are formed, reduction generally results in CO formation. Reduction of CO is then thought to lead to formyl, hydroxymethyl, or methylene intermediates with the ultimate formation of methane and ethylene etc., but not to methanol. It will be important to identify what structural features promote and retard different steps involved in the different catalytic processes.

11.8 Relationship of CO_2 Utilization and CO_2 Sequestration

Both CO_2 utilization and CO_2 sequestration can play important roles in carbon management and both may be needed. CO_2 sequestration assumes the continued use of fossil fuels with control arising from capture and storage or disposal of CO_2. One of the attractive features of sequestration is that it would allow the continued use of fossil fuels and much of the energy infrastructure in use now. CO_2 utilization attempts to use CO_2 as a feedstock for producing fuels and chemicals. This will require a renewable energy input such as solar to drive these endothermic reactions, but avoids the need for CO_2 storage or disposal. CO_2 sequestration and utilization may be viewed as competitive (fossil vs. renewable energy sources), but in other ways they are complementary (both reduce the amount of CO_2 being added to the atmosphere) and advances in some of the same technologies (separations) will be required for the success of either.

11.9 Summary

Solar carbon dioxide fixation offers the possibility of a renewable source of chemicals and fuels in the future. Its realization rests on future advances in the efficiency of solar energy collection and development of suitable catalysts for CO_2 conversion. Recent achievements in the efficiency of solar energy conversion and in catalysis suggest that this approach holds a great deal of promise for contributing to future needs for fuels and chemicals.

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