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PHOTOREDUCTION OF CO_2 USING METAL COMPLEXES

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Abstract

Photochemical reduction of CO_2 to fuels and chemicals is a challenging task. Work in the area of photochemical CO_2 reduction from the early 1980s to the present is summarized to provide a perspective on the achievements and problems involved in the process.

Introduction

Carbon dioxide fixation is an important area to study for the solution of problems related to the global environment and the depletion of fossil fuels. The chemical fixation involves conversion of recovered or separated CO_2 into useful chemicals and fuels. Economical fixation of CO_2 is only feasible if solar or hydraulic energy can be converted to chemical energy. There are several ways to use solar energy for CO_2 fixation: (1) solar-photochemical reduction of CO_2 typically to CO, $HCOO^-$, CH_3OH, and CH_4; (2) electroreduction of CO_2 [and water] using power generated by solar batteries typically to CO and $HCOO^-$ [and H_2]; (3) photoelectroreduction of CO_2 using semiconductors and surface-modified electrodes; (4) homogeneous and heterogeneous catalytic hydrogenation of CO_2 to methanol, formic acid, formamide, polymers, hydrocarbons, and others with solar generated H_2; and (5) genetically improved photosynthetic bacteria and algae-based CO_2 fixation [and H_2 production]. In this paper, we focus on photochemical reduction of CO_2 by homogeneous and microheterogeneous photocatalysts. Although many photo-induced stoichiometric reactions such as an insertion or addition of CO_2, reductive disproportionation to CO, metathesis of CN by CO_2, the formation of M-CO and M-OCHO complexes and in rare cases, the formation of M=O together with CO are known,[1] we limit our discussion to photocatalytic reactions using metal complexes as catalysts. Photoinduced CO_2 fixation systems containing enzymes[2,3] are omitted.

Photocatalytic systems for CO_2 reduction

The potential for the reduction of CO_2 to $CO2^{\cdot -}$ is -1.9 V vs NHE, making the one-electron reduction mechanism highly unfavorable. In addition there is a large kinetic "overvoltage" for the one-electron reduction because of structural differences between linear CO_2 and bent $CO_2^{\cdot -}$. In contrast, proton assisted multi-electron steps are much more favorable:

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

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

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

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

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

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

Since the two-electron reduction to formic acid or CO requires a considerably lower potential than the one-electron reduction, electrolysis in the presence of catalysts can be carried out at considerably lower voltages. In the photochemical reduction of CO_2, the same considerations apply: the one-electron reduction to $CO_2^{\cdot -}$ requires extremely strong reducing agents that are generally difficult to produce by photochemical methods.

Transition metal complexes have been used as photosensitizers and/or catalysts because: (1) they generally absorb visible light; (2) their excited states generally live long and promote rapid electron transfer; (3) their oxidation states accommodate multi-equivalent charge transfer to produce highly reduced and oxidized species; (4) they can provide vacant coordination site(s) for activation of small molecules. The systems used for photochemical CO_2 reduction can be categorized into several groups as shown below. The results from the various photocatalytic systems are summarized in Table 1.

Table 1. Photocatalytic Reduction of CO_2 [a]

Sensitizer	Catalyst or Relay	Donor	Product(s)	Φ	Ref.
$Ru(bpy)_3^{2+}$		TEOA	$HCOO^-$		4, 5
$Ru(bpy)_3^{2+}$	MV^{2+}	TEOA	$HCOO^-$	0.01	6
$ReCl(bpy)(CO)_3$		TEOA	CO	0.14	7, 8,
$ReBr(bpy)(CO)_3$		TEOA	CO	0.15	10,11
$ReP(OEt)_3(bpy)(CO)_3$		TEOA	CO	0.38	13
$Ru(bpy)_3^{2+}$	Co^{2+}/bpy	TEA	CO, H_2		14
$Ru(bpy)_3^{2+}$	Co^{2+}/Me_2phen	TEA	CO, H_2	0.08	15
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)_2^{2+}$	TEOA	$HCOO^-$	0.14	18 - 20
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)_2^{2+}$	BNAH	$HCOO^-$, CO	0.03 ($HCOO^-$) 0.15 (CO)	18 - 20
$Ru(bpy)_3^{2+}$	$CoHMD^{2+}$	H_2A	CO, H_2		27
$Ru(bpy)_3^{2+}$	$Nicyclam^{2+}$	H_2A	CO, H_2	0.001 (CO)	28, 29
$Ru(bpy)_3^{2+}$	$NiPr\text{-}cyclam^{2+}$	H_2A	CO, H_2	~0.005 (CO)	31
$Ru(bpz)_3^{2+}$	$bipyridinium^+$, Ru colloid	TEOA	CH_4	10^{-4} (CH_4)	37, 39
$Ru(bpy)_3^{2+}$	$bipyridinium^+$, Ru or Os olloid	TEOA	CH_4 H_2	10^{-4} (CH_4) 10^{-3} (H_2)	37
p-Terphenyl	$Cocyclam^{3+}$	TEOA	CO, $HCOO^-$, H_2	0.25 (CO + $HCOO^-$)	47, 48
p-Terphenyl	$CoHMD^{2+}$	TEOA	CO, $HCOO^-$, H_2		34, 48
Phenazine	$Cocyclam^{3+}$	TEOA	$HCOO^-$	0.07	52

[a] Abbreviations used: TEOA = triethanolamine, MV^{2+} = methylviologen, TEA = triethylamine, bpy = 2,2'-bipyridine, Me2phen = 2,9-Dimethyl-1,10-phenanthroline, BNAH = 1-benzyl-1,4-dihydronicotinamide, H_2A = ascorbic acid, cyclam = 1,4,8,11-tetraazacyclotetradecane and Pr-cyclam = 6-((N-R)pyridin-4-yl)methyl-1,4,8,11-tetraazacyclotetradecane where R = p-methoxybenzyl and benzyl.

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

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

Scheme I. Reductive quenching

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

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

$$TEOA^{\cdot +} + TEOA \longrightarrow TEOA^{\cdot} + TEOAH^{+} \qquad (9)$$

$$TEOA^{\cdot} + Ru(bpy)_3^{2+} \longrightarrow TEOA_{ox} + Ru(bpy)_3^{+} \qquad (10)$$

However the reduced Ru complex cannot reduce CO_2 directly in the one-electron transfer process which requires -1.9 V since the $Ru(bpy)_3^{2+/+}$ potential is -1.26 V. Since the presence of water enhanced the reaction with an optimum concentration around 0.015 M (~15 %), water may play a role in a photolabilization of bpy to form the active catalytic intermediate. The authors speculate that reduction of CO_2 to formic acid may involve the following sequential steps: (1) photogeneration of $Ru(bpy)_3^{+}$; (2) ligand photolabilization; (3) hydride formation by protonation: (4) insertion of CO_2; and (5) release of the formate produced. However, possible intermediates such as $Ru(bpy)_2(H_2O)(H)^{2+}$ and $Ru(bpy)_2(H_2O)(OCOH)^{2+}$ have not been characterized. Quantum yields were not reported.

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.[6] 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^{+} as shown in scheme II. 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 mechanistic study was done, the authors suggest a mechanism which must involve proton participation as shown in eq.1, since the pH of the CO_2 saturated solution is lower than pH 7. We believe the reactions 9 and 10 also produce $Ru(bpy)_3^{+}$ which can effect CO_2 reduction. The actual mechanism may be quite complicated.

Scheme II. Oxidative quenching

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

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

$$Ru(bpy)_3^{3+} + TEOA \longrightarrow Ru(bpy)_3^{2+} + TEOA^{\cdot +} \qquad (12)$$

$$TEOA^{\cdot +} + TEOA \longrightarrow TEOA^{\cdot} + TEOAH^{+} \qquad (9)$$

$$TEOA^{\cdot} + Ru(bpy)_3^{3+} \longrightarrow TEOA_{ox} + Ru(bpy)_3^{2+} \qquad (13)$$

$$TEOA^{\cdot} + Ru(bpy)_3^{2+} \longrightarrow TEOA_{ox} + Ru(bpy)_3^{+} \qquad (10)$$

(II) $ReX(CO)_3(bpy)$ or a similar complex as a photosensitizer

$ReX(CO)_3(bpy)$ (X = Cl, Br) has been used successfully as a photocataystst for CO_2 reduction to CO with TEOA in DMF.[7,8] 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^-. It is known that $Re(bpy)(CO)_3H$ undergoes a slow thermal reaction with CO_2 to give the formato complex and the reaction is greatly enhanced by visible light.[9] Detailed mechanistic studies[10,11] using $ReBr(CO)_3(bpy)$ with TEOA or TEA indicate that TEOA, TEA (triethylamine) and Br^- reductively quench the emission from the MLCT excited state of $ReBr(CO)_3(bpy)$ leading to prompt formation of $ReBr(CO)_3(bpy)^-$, which likely reacts with CO_2. $Re(CO)_2(bpy)\{P(OEt)_3\}_2^+$ is also a CO_2 reduction catalyst which produces CO with a quantum yield up to 0.38. Both the quantum yield and turnover number of the photocatalytic reaction are strongly dependent on the irradiation light intensity and wavelength.[12] The photophysical behavior was studied by means of time-resolved UV-vis and IR spectroscopies.[13] The photo-generated reduced catalyst, $Re(CO)_2(bpy)\{P(OEt)_3\}_2$, is also important for the activation of CO_2. However, in both $ReX(CO)_3(bpy)$ and $Re(CO)_2(bpy)\{P(OEt)_3\}_2^+$ systems it is still not known whether the CO_2 activation involves reactions such as: (1) formation of an unstable intermediate with vacant coordination site(s) from loss of CO, X^-, $P(OEt)_3$, or the bpy ligand from $ReX(CO)_3(bpy)^-$ or $Re(CO)_2(bpy)\{P(OEt)_3\}_2$; (2) formation of the CO_2 adduct from the unstable intermediate; (3) formation of the hydride species from the unstable intermediate followed by the insertion of CO_2.

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

It was reported in 1982 that 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.[14] 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.

The system was further studied by adding 4,4',6,6'-tetramethyl-2,2'-bipyridine or 2,9-dimethyl-1,10-phenanthroline instead of bpy.[15] 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.

Since the systems described above contain free bipyridine-type ligands, the formation of the Co(I) 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.[16] Stoichiomeric studies with $Co(bpy)_3^+$ and CO_2 were also carried out in order to elucidate the mechanism of the CO_2 reduction.[16,17] 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, is effective in reducing bpy to $bpyH_2$, H_2O to H_2 and CO_2 to CO (as the insoluble $[Co(bpy)(CO)_2]_2$), likely with $Co(bpy)_2(H_2O)H^{2+}$ and/or $Co(bpy)_2(H_2O)_2^+$ as intermediate. Unfortunately neither the CO_2 adduct nor the formato complex has been isolated.

Photochemical reduction of CO_2 has been achieved by using TEOA in DMF or the NADH model compound, 1-benzyl-1,4-dihydronicotinamide (BNAH) in H_2O/DMF, as a quencher in the presence of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_2(CO)_2^{2+}$.[18,19] The system containing TEOA produces formate with a quantum yield of 0.14, whereas the system containing BNAH gave formate and CO with quantum yields of 0.03 and 0.15, respectively. The reduction potential of $Ru(bpy)_3^{2+}$ (-1.33 V vs SCE in DMF) is more negative than that of $Ru(bpy)_2(CO)_2^{2+}$ (-0.98 V) and nearly the same as $Ru(bpy)_2(CO)(COO^-)^+$ (-1.30 V). Therefore, $Ru(bpy)_3^+$ formed photochemically functions as the reductant of $Ru(bpy)_2(CO)_2^{2+}$.

$$Ru(bpy)_2(CO)_2^{2+} + 2e^- \longrightarrow Ru(bpy)_2(CO) + CO \tag{14}$$

$$Ru(bpy)_2(CO) + CO_2 \longrightarrow Ru(bpy)_2(CO)(COO^-)^+ \tag{15}$$

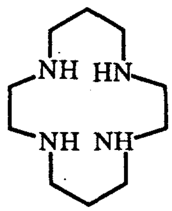
$$Ru(bpy)_2(CO)_2^{2+} + OH^- \longrightarrow Ru(bpy)_2(CO)(COOH)^+ \tag{16}$$

$$Ru(bpy)_2(CO)(COOH)^+ + OH^- \longrightarrow Ru(bpy)_2(CO)(COO^-)^+ + H_2O \tag{17}$$

$$Ru(bpy)_2(CO)(COO^-)^+ + H^+ + 2e^- \longrightarrow Ru(bpy)_2(CO) + HCOO^- \tag{18}$$

Suggested mechanisms[19] are shown in eqs. 14 and 15: the reduction of $Ru(bpy)_2(CO)_2^{2+}$ by two molecules of photogenerated $Ru(bpy)_3^+$ to yield CO with generation of $Ru(bpy)_2(CO)(COO^-)^+$ via $Ru(bpy)_2(CO)$ as shown in eqs. 14 and 15 in CO_2-saturated DMF. Based on their electrochemical studies,[20] the authors propose[19] that the $HCOO^-$ is generated from $Ru(bpy)_2(CO)(COO^-)^+$ by a two-electron reduction involving participation of one proton as shown eq 18. They further explain,[19] that the change in the main product from $HCOO^-$ to CO is due to acid-base equilibria among $Ru(bpy)_2(CO)_2^{2+}$, $Ru(bpy)_2(CO)(COOH)^+$, and $Ru(bpy)_2(CO)(COO^-)^+$ as shown in eqs. 16 and 17. It is widely believed that $HCOO^-$ forms by CO_2 insertion into the M-H bond in other cases. $Re(bpy)(CO)_3H$ reacts with CO_2 to afford $Re(bpy)(CO)_3OC(O)H$ quantitatively.[21] $[Ru(bpy)_2(CO)H]^+$ reacts with CO_2 to form a formato complex, $[Ru(bpy)_2(CO)O(O)CH]$, which produces $HCOO^-$ upon another one-electron reduction.[22] The doubly reduced species $Ru(bpy)_2(CO)$ in eq. 14 may react with H^+ to form $[Ru(bpy)_2(CO)H]^+$, into which CO_2 may insert to form the formato complex. However, it is reported that the catalytic systems composed of $Ru(bpy)_3^{2+}/Ru(bpy)_2(CO)_2$/BNAH and $Ru(bpy)_3^{2+}/[Ru(bpy)_2(CO)H]^+$/BNAH shows essentially the same reactivity (i.e., production rates and selectivity) in CO_2 reduction.[19] Both systems produce more CO than $HCOO^-$ ($CO/HCOO^- \approx 5$). As possible intermediates in the CO_2 reduction system, the molecular structures of $[Ru(bpy)_2(CO)_2](PF_6)_2$, $[Ru(bpy)_2(CO)(CO(O)OCH_3)](B(C_6H_5)_4 \cdot CH_3CN$ (as a model of $[Ru(bpy)_2(CO)(COOH)]^+$), $[Ru(bpy)_2(CO)(\eta\text{-}CO_2)]$, and $[Ru(bpy)_2(CO)(CH_2OH)]^+$ have been determined.[23-26] However isolation of the formate complex formed by CO_2 insertion into $[Ru(bpy)_2(CO)H]^+$ has not been reported. It would be highly desirable to elucidate the detailed mechanism of formate and CO formation in this photocatalytic system[19] using time-resolved spectroscopies.

Photochemical CO_2 reduction to CO (and formate in some cases) has been reported[27-31] in a catalytic system using $Ru(bpy)_3^{2+}$ as the sensitizer, nickel or cobalt macrocycles (shown in Figure 1) as the electron relay catalyst, and ascorbate as a sacrificial reductive quencher. These systems also produce H_2 via reduction of water. When $CoHMD^{2+}$ is used as a catalyst at pH 4, the system produces a mixture of CO and H_2 with low selectivity (CO/H_2 = 0.06 - 0.3, depending on the conditions).[27] $Nicyclam^{2+}$ is reported to be an extremely efficient and selective catalyst for the electrochemical reduction of CO_2 to CO, even in H_2O.[32,33] When $Nicyclam^{2+}$ is used as a catalyst in the photochemical system,[28,29] however, the quantum yield of CO production is 5×10^{-4} at pH 5 and the selectivity, CO/H_2, is ~0.8. (The yield of both CO and H_2 are pH dependent and typically more H_2 is produced than CO.) $Nicyclam'^{2+}$ which is high-spin, six-coordinate with two cis water molecules, produces both CO and formate, while $Nicyclam^{2+}$, which is mainly low-spin, square-planar in H_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 suggested to be a common intermediate for CO and H_2 production in these photocatalytic systems, however, new studies[34-36] indicate that this may be incorrect (see section V).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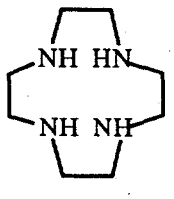
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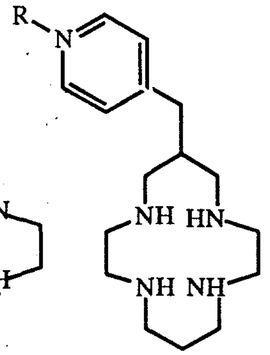
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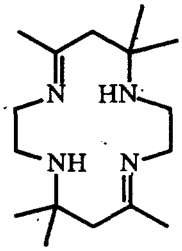
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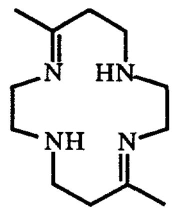
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Nicyclam complexes containing a pendant pyridinium group, which had been shown to function as effective mediators in the photochemical reduction of H_2O with a Pt colloid,[37,38] were prepared and their catalytic behavior toward photochemical CO_2 reduction with $Ru(bpy)_3^{2+}$ was examined.[31] The system containing $NiPr\text{-}cyclam^{2+}$ (R = p-methoxybenzyl and benzyl) at pH 5 evolved CO about 5 times more than that with underivatized $Nicyclam^{2+}$. The selectivity (CO/H_2= 0.1 - 0.65) depends on the conditions used, and typically more CO is produced with higher $NiPr\text{-}cyclam^{2+}$ concentration.

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

The photoreduction of CO_2 to methane and hydrocarbons is achieved in aqueous solution containing $Ru(bpy)_3^{2+}$, an electron donor, a bipyridinium charge relay, and Ru or Os colloids.[37] The quantum yields for H_2 evolution ($\sim10^{-3}$) and hydrocarbon formation ($\sim10^{-4}$ for CH_4, $\sim10^{-5}$ for C_2H_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.[37,39] 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 $Ru(bpz)_3^{2+}$.

(IV) Other metal complexes as photosensitizers

Photoreduction of CO_2 to formaldehyde and $HCOO^-$ has been carried out using an electron relay composed of 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.[40] The quantum yields of photoproduction of formaldehyde are 0.036 and 0.051 with EDTA and TEOA, respectively, at 690 nm. The system is potentially photocatalytic, however the amount of formaldehyde and $HCOO^-$ produced are less than 10 % of the amount of photosensitizer used.

Since the one-electron reduction of CO_2 to $CO_2^{\cdot-}$ requires -1.9 V vs NHE, it is difficult to produce $CO_2^{\cdot-}$ 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 $CO_2^{\cdot-}$ in THF when irradiated at $\lambda > 300$ nm.[41] 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 is not photocatalytic, it is a rare case of purported involvement of $CO_2^{\cdot -}$. The authors assumed that the excited state of $[Ni_3(\mu_3\text{-}I)_2(dppm)_3]$ is quenched by CO_2 to form $CO_2^{\cdot -}$, however no photophysical study of $[Ni_3(\mu_3\text{-}I)_2(dppm)_3]$ is reported. Mechanistic and kinetic studies using time-resolved spectroscopies and measurements of the excited state potential are required to verify the claim.

(V) Organic photosensitizers and ML^{2+} as catalysts

Irradiation of aromatic hydrocarbons such as phenanthrene, anthracene or pyrene in the presence of amine and carbon dioxide in aprotic solvents results in reductive carboxylation of the hydrocarbons.[42-44] The reactions are considered to proceed via the anion radical of the hydrocarbon reacting with CO_2 and then abstracting hydrogen to yield the corresponding product. Unlike these hydrocarbons, oligo(p-phenylene) ranging from *p*-terphenyl to *p*-sexiphenyl catalyze the photoreduction of CO_2 to $HCOO^-$ with TEA in a dried aprotic solvents such as DMF and CH_3CN.[45,46] Although the apparent quantum yield is 0.072 with *p*-terphenyl, *p*-terphenyl concurrently undergoes photo-Birch reduction to form dihydroterphenyl derivatives and the system practically dies within 30 minutes. The turnover number for the formation of $HCOO^-$ is 4. However the addition of cobalt macrocyclic complexes suppresses the degradative photo-Birch reduction, and leads to efficient formation of both carbon monoxide and formate.[47,48] When the $Cocyclam^{3+}$ complex is used, the total quantum yield for formation of carbon monoxide and formate is 0.25 at 313 nm in the presence of TEOA.

The kinetics and mechanism of CO formation in this system have been studied by continuous and flash photolysis techniques.[34] Transient spectra provide clear evidence for the sequential formation of the *p*-terphenyl radical anion, the $Co^{I}HMD^+$ complex, the $[Co^{I}HMD\text{-}CO_2]^+$ complex and the $[S\text{-}Co^{III}HMD\text{-}(CO_2^{2-})]^+$ complex (S = solvent) in the catalytic system. These species together with the $[Co^{I}HMD\text{-}CO]^+$ complex, had previously been identified by various spectroscopic techniques including UV-vis, IR, NMR, XANES and EXAFS.[35,36,49-51] The XANES study indicates that six-coordinate $[S\text{-}CoHMD\text{-}(CO_2^{2-})]^+$, in which a significant charge is transferred from metal to the bound CO_2, can be interpreted as a Co(III) carboxylate.[51] The Co(I) complex transfers two electrons to the bound CO_2 moiety in this photocatalytic system.[34] The electron-transfer rate constant for the reaction of *p*-terphenyl radical anion with the $Co^{II}HMD^{2+}$ is $1.1 \times 10^{10}\ M^{-1}\ s^{-1}$ and is probably diffusion controlled because of the large driving force (~ 1.1 V). Flash photolysis studies yield a rate constant of $1.7 \times 10^{8}\ M^{-1}\ s^{-1}$ and an equilibrium constant of $1.1 \times 10^{4}\ M^{-1}$ for the binding of CO_2 to $Co^{I}HMD^+$ in the catalytic system. These are consistent with those previously obtained by conventional methods in acetonitrile.[35,49] The authors suggest that reactions 19-21 are responsible for the production of CO from $[S\text{-}Co^{III}HMD\text{-}(CO_2^{2-})]^+$ in the photolysis.

$$[S\text{-}Co^{III}HMD\text{-}(CO_2^{2-})]^+ + HA \rightleftharpoons [S\text{-}Co^{III}HMD\text{-}(COOH)^-]^{2+} + A^- \qquad (19)$$

$$HA = TEA,\ MeOH,\ TEA^+$$

$$[S\text{-}Co^{III}HMD\text{-}(COOH)^-]^{2+} + \text{“}e^-\text{”} \longrightarrow Co^{II}HMD^{2+} + CO + OH^- \qquad (20)$$

$$\text{“}e^-\text{”} = Co^{I}HMD^+,\ Et_2NC^{\cdot}HCH_3,$$

$$OH^- + CO_2 \rightleftharpoons HCO_3^- \qquad (21)$$

The slow step is likely to be the C–O bond breakage in the bound carboxylic acid with either $Et_2NC^{\cdot}HCH_3$, or $Co^{I}HMD^{+}$ acting as electron donor. Unfortunately the transient spectrum of $[S\text{-}Co^{III}HMD(CO_2^{2-})]^{+}$ is too weak topermit study of the proton dependence of its disappearance. Studies of catalytic systems with other cobalt macrocycles[34] highlight some of the factors controlling the kinetics of the photoreduction of CO_2. Steric hindrance and reduction potentials are important factors in the catalytic activity for photochemical CO_2 reduction.

Recently photoreduction of CO_2 to $HCOO^-$ (together with a small amount of CO and H_2) was achieved by UV-irradiation of the system involving phenazine (Phen) as a photosensitizer, $Cocyclam^{3+}$ as an electron mediator and TEA as an electron donor.[52] The quantum yield for the formation of $HCOO^-$ is 0.07. Electron transfer from the photo-formed radical anion ($Phen^{\cdot -}$) to $Cocyclam^{3+}$ ($k = 4.3 \times 10^9\ M^{-1}\ s^{-1}$) results in the formation of $Cocyclam^{2+}$. Since the reduction potential of $Cocyclam^{2+/+}$ is ~-1.9 V vs SCE in CH_3CN, $Phen^{\cdot -}$ is hardly capable reducing Co(II) to Co(I). Therefore the authors suggest that: (1) $PhenH^{\cdot}$, produced by the protonation to $Phen^{\cdot -}$, may transfer a hydrogen atom to $Cocyclam^{2+}$ to form $Cocyclam(H)^{2+}$; 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.

Comparison between thermal hydrogenation and photochemical reduction of CO_2.

In the early 1970's, several groups found that formic acid, esters, and amides can be prepared from carbon dioxide, hydrogen, and a third component (in many cases) in the presence of homogeneous transition metal (Ti, Ru, Rh, Pd, etc.) catalysts including Wilkinson's catalyst $[Rh(PPh_3)_3Cl]$.[53,54] 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 = cycloocatadiene) 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. The TOF (turnover frequency), which is defined as the maximum initial rate of reaction per mole of catalyst, reaches 390 h^{-1}.[55] 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 1400 h^{-1} was obtained.[56] Mechanisms of formate (or formic acid) formation via CO, or carbonate, or hydride transfer to CO_2 were considered in some cases. However, the mechanism involving CO_2 insertion into a M-H bond is widely proposed. The reactive intermediate with vacant coordination site(s), derived from the metal catalyst, reacts with hydrogen to generate the metal hydride, followed by CO_2 insertion to form the formato complex. More detailed mechanistic and kinetic studies are needed.

Photochemical CO_2 reduction is normally carried out under 1 atm CO_2 at room temperature. Therefore the concentration of dissolved CO_2 in the solution is quite low (e.g. 0.28 M in CH_3CN and 0.03 M in water). Under photochemical conditions, TON (which is defined as the maximum number of moles of product per mole of catalyst) and TOF are dependent on irradiation wavelength, light intensity, irradiation time, and catalyst concentration. In fact, the TON and TOF are sometimes derived from different experiments. They are not optimized in most photochemical experiments. Since the concentration of the actual catalyst is not known in some cases, it only gives some guidance in estimating the catalytic activity. The typical range of the apparent TOF for CO or $HCOO^-$ formation can be calculated to be 0.1 to 10 h^{-1}, except for the $Ru(bpy)_3^{2+}/Ru(bpy)_2(CO)_2^{2+}$ system, in which the apparent

TOF reaches 180 h^{-1} based on [$Ru(bpy)_2(CO)_2^{2+}$]. Typically the photochemical reactions are monitored up to one day. Both apparent TOF and TON in photochemical CO_2 reduction systems seem smaller than those in hydrogenation reactions. The rates of the catalytic reaction and the catalyst stability are important issues for photochemical CO_2 reduction. The rate-determining step or steps for photochemical CO_2 reduction are not known. It is believed that dark reactions including bond formation and bond cleavage are much slower than photoexcitation or subsequent electron transfer reaction.

Can the catalysts in the photochemical system be replaced by catalysts used for hydrogenation in order to speed up the dark reaction? In photochemical methods, an oxidative addition of a proton to the reduced metal center (that typically forms by photo-induced electron-transfer) gives a metal hydride species, however, in hydrogenation methods the metal center with vacant coordination site(s) seems to react with H_2. Some dihydrogen adducts of the metal complexes have been shown to be in equilibrium with the hydride species. It would be desirable to study the properties and reactivities of such complexes in order to find better catalysts for CO_2 reduction and hydrogen production..

The area of hydrogenation of CO_2 to HCOOH, esters, amides, alcohols, and hydrocarbons with homogeneous and heterogeneous metal catalysts is currently under active study. and is promising to some degree. However, can we find a cheap and clean source of H_2? At present, hydrogen is manufactured by thermal cracking of oil resources, consuming fossil fuels as well as generating carbon dioxide. Therefore we need to develop technologies to produce H_2 using solar energy.

Challenge for photochemical CO_2 reduction and water splitting

Solar energy conversion is a formidable problem. The system must satisfy the following conditions: (1) strong absorption in the visible region; (2) long-lived excited state; (3) efficient quenching of the excited state to produce highly reduced and oxidized intermediates; (4) no harmful side reaction to deactivate the photosensitizer or catalyst/mediator; (5) ability to undergo multi-electron transfer; (6) long-lived intermediates [or catalyst] to promote bond formation and cleavage reactions to desired products [These dark reactions are much slower than photo-process.]; and (7) combining oxidizing and reducing cycles [to avoid the use of a sacrificial reagent]. Although conditions 1 to 6 have been fulfilled to some degree, to our knowledge all previous attempts with homogeneous catalysts have failed to achieve condition 7 (except one report[57] about water splitting). Do we need to design organized systems modeled upon natural photosynthesis? Should we accept a small TOF as nature does? What kind of catalyst can accommodate the four-equivalent charge for O_2 or HCHO production? How can we effectively couple the reduction or oxidation reactions with proton-, hydrogen-atom- or hydride-transfer reactions to lower the reaction barrier? Many questions still need to be answered in order to achieve efficient photochemical CO_2 reduction and water splitting.

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