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Carbon Dioxide (Reduction)

The twin problems of global warming, caused by an increase in atmospheric carbon dioxide (CO_2) concentrations, and limited fossil fuel resources have stimulated research in the utilization of CO_2. These problems would be partially alleviated by the development of artificial photochemical systems that could economically fix CO_2 into fuels or useful chemicals. During the past one and a half decades, intensive efforts have been directed toward the photochemical production of carbon monoxide (CO) and formic acid (HCOOH) from CO_2. These systems have several common elements: they all contain photosensitizers (such as metalloporphyrins, ruthenium or rhenium complexes with bipyridine), electron mediators or catalysts, and sacrificial electron donors (such as tertiary amines or ascorbic acid). Recent progress along these lines has resulted in advances in our understanding of the interaction of CO_2 molecules with metal complexes, and the factors controlling the efficient storage of solar energy in the form of reduced carbon compounds.

Strategy of CO_2 Reduction. Natural photosynthesis by chlorophyll molecules involves the generation of carbohydrates and oxygen from the abundant raw materials CO_2 and H_2O using sunlight as the driving force. Photosynthesis is balanced by the oxidation of the reduced carbon compounds back to CO_2 and H_2O through combustion, decay and respiration. Life on earth is sustained by maintaining this balance between the production and removal of atmospheric CO_2. However, widespread use of fossil fuels has upset this balance and led to the emission of 6 gigatons (6×10^9 tons) of carbon per year as carbon dioxide. This has raised levels of carbon dioxide in the atmosphere from ~280 ppm in pre-industrial times to the present 360 ppm.

Because of the high infrared absorbance and long atmospheric lifetime of CO_2, global warming through the greenhouse effect is taking place.

The stability of CO_2 makes economical utilization of carbon dioxide as a feedstock for fuels or chemicals a formidable challenge. The potentials, E° (*vs.* a normal hydrogen electrode, NHE, at pH = 7), for the reduction of CO_2 to HCOOH, CO and methanol (CH_3OH) are shown below. The fact that the proton-assisted, multi-electron routes to these products require much less energy than the one-electron process to $CO_2^{\cdot -}$ ($E° = -1.9$ V) suggests that is might be a considerable advantage to employ multi-electron transfer routes using transition-metal complexes.

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \qquad E° = -0.61\ \mathrm{V} \qquad (1)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E° = -0.53\ \mathrm{V} \qquad (2)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \qquad E° = -0.38\ \mathrm{V} \qquad (3)$$

Transition-metal complexes consist of a central atom or ion surrounded by a set (typically 2 to 6) of other atoms, ions or small molecules, the latter being called ligands. Transition-metal complexes have often been used as photochemical and thermal catalysts because they can absorb a significant portion of the solar spectrum, have long-lived excited states, can promote multi-electron transfer, and can activate small molecules through binding. In transition-metal complexes, a central metal has octahedral, tetrahedral, square planar, square-pyramidal, or trigonal-pyramidal symmetry depending on the surrounding ligands. Reduced metal centers such as M^IL, in which the oxidation number of the central metal (M) is plus one and the ligand (L) has four-coordinating atoms, typically have one or more vacant coordinate sites. These sites can be used to bind and activate CO_2 (or other small molecules). The oxidative addition of CO_2 to $M^{I}L$ to form a metallocarboxylate, $M^{III}L(CO_2^{2-})$, stabilizes the CO_2 moiety through two-electron transfer. The $M^{III}L(CO_2^{2-})$ can then react with H^+ to form $M^{III}L$, CO and OH^-. An example of this behavior will be presented in the next section.

Because the CO_2 reduction process is thermodynamically uphill, economical CO_2 fixation is possible only if renewable energy, such as solar energy, is used as the energy source. Solar energy can be harnessed to drive CO_2 conversion by: (1) artificial photosynthesis using homogeneous and heterogeneous systems, (2) electrochemical reduction using solar electric power, and (3) hydrogenation of CO_2 using solar-produced hydrogen. Here we will focus on recent progress in artificial photosynthesis that is driven by a photon absorption, charge separation through electron transfer reactions, and energy storage in dark reaction, similar to the processes occurring in natural photosynthetic systems.

Photocatalytic CO_2 Reduction. The systems that have been used for photochemical CO_2 reduction studies can be divided into the following groups:

1. $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) as both the photosensitizer and the catalyst;
2. $Ru(bpy)_3^{2+}$ as the photosensitizer and another metal complex as the catalyst:
3. $ReX(CO)_3(bpy)$ (X = halide or phosphine-type ligand) or a similar complex as both the photosensitizer and the catalyst;
4. $Ru(bpy)_3^{2+}$ or $Ru(bpy)_3^{2+}$-type complex as the photosensitizer in microheterogeneous systems;

5. a metalloporphyrin as both the photosensitizer and the catalyst; and
6. organic photosensitizers with transition-metal complexes as catalysts.

Photochemical CO_2 reduction is normally carried out in aqueous solutions or organic solvents 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 acetonitrile and 0.03 M in water). These systems produce formate and CO as products, however the formate-to-CO ratio varies from system to system. The total quantum yield reaches up to 40 % assuming that one photon produces one molecule of product. With a ruthenium bipyridine-type complex and Ru or Os colloids, methane is produced with a low quantum yield. Mechanisms, as shown in Figures 1 and 2, are generally believed to involve: (1) light absorption by a photosensitizer to produce the excited state; (2) a quenching reaction between the excited state and an electron donor to produce a reduced complex; (3) electron transfer from the reduced complex to a catalyst; and (4) activation of CO_2 by the reduced catalyst. Metallocarboxylates (and metallocarboxylic acids) are postulated intermediates in photochemical and electrochemical CO_2 reduction and the water-gas-shift reaction.

____(Figures 1 and 2)_____

However, in many cases the actual species invoked to interact with CO_2 are not detected in catalytic systems. Metallocarboxylates are typically prepared by: (1) insertion of CO into the M-OH bond; (2) reaction of OH- with M-CO; or (3) direct carboxylation of reduced metal complexes. Several binding modes including η^1-C-coordination and η^2-side-on coordination modes have been characterized by x-ray diffraction studies, but the M-O-C-O (η^1-end-on) arrangement has never been observed (See Figure 3).

___ (Figures 3 and 4) _____

Cobalt and nickel tetraazamacrocyclic complexes ($CoHMD^{2+}$ and $Ni(cyclam)^{2+}$, in which HMD and cyclam are more saturated ligands than a porphyrin, P, as shown in Figure 4) have been used as catalysts to produce CO in photochemical and electrochemical CO_2 reduction. The square-planar $Co^{I}HMD^{+}$ complex has been found to add nucleophilically to CO_2 to yield the square-pyramidal, five-coordinate η^1 adduct, $[CoHMD(\eta^1\text{-}CO_2)]^+$, containing a bent OCO moiety bonded to cobalt through carbon. The CO_2 adduct is thermochromic, being purple at room temperature and yellow at low temperature. Temperature-dependent visible and infrared spectra of the CO_2 adduct indicate a solvent molecule (S) binds from the opposite side of CO_2 to form the six-coordinate $[S\text{-}CoHMD(CO_2)]^+$ (octahedral) species at the expense of the five-coordinate $[CoHMD(\eta^1\text{-}CO_2)]^+$ as shown in eq. (5).

$$Co^{I}HMD^{+} + CO_2 \leftrightarrow [CoHMD(CO_2)]^{+} \qquad (4)$$

$$[CoHMD(CO_2)]^{+} + S \leftrightarrow [S\text{-}CoHMD(CO_2)]^{+}\ (S = \text{solvent}) \qquad (5)$$

X-ray absorption edge spectroscopy and FTIR studies confirm that significant charge-transfer occurs from Co(I) to the bound CO_2 in both the five- and the six-coordinate species. The electron density of the five-coordinate $[CoHMD(\eta^1\text{-}CO_2)]^+$ is the same as that of $[Co^{II}HMD]^{2+}$ consistent with theoretical predictions. The six-coordinate species exhibits significant charge-transfer and can be interpreted as a Co(III) carboxylate, $[S\text{-}Co^{III}HMD(CO_2^{2-})]^{+}$. This is the first unambiguous evidence that active metal complexes, such as $Co^{I}HMD^{+}$, can promote two-electron transfer to the bound CO_2 and thereby facilitate its reduction.

The cobalt macrocycle mediates electron transfer in the photoreduction of CO_2 with *p*-terphenyl (TP) as a photosensitizer and a tertiary amine as a sacrificial electron donor in a 5:1 acetonitrile/methanol mixture. The kinetics and mechanism of this system have been studied by continuous- and flash-photolysis techniques. Transient spectra provide evidence for the sequential formation of the TP radical anion, the $CoHMD^{+}$ complex, the $[CoHMD(CO_2)]^{+}$ complex and the $[S\text{-}Co^{III}HMD(CO_2^{2-})]^{+}$ complex in the catalytic system. This study provides clear evidence that (1) a photon captured by TP promotes the one-electron reduction of $Co^{II}HMD^{2+}$ to $Co^{I}HMD^{+}$; (2) $Co^{I}HMD^{+}$ reacts with CO_2 to form $[CoHMD(CO_2)]^{+}$; and (3) the cobalt center provides two electrons to the CO_2 moiety to produce a $[S\text{-}Co^{III}HMD(CO_2^{2-})]^{+}$ species, which can react with a proton to produce $[S\text{-}Co^{III}HMD(COOH)]^{2+}$. The reversible intramolecular two-electron-transfer process, sensitive to temperature, solvent, and pressure changes, could be of fundamental importance in processes involving the reduction of CO_2. The rate-determining step in the photocatalytic system appears to be a C-O bond breaking step of $[S\text{-}Co^{III}HMD(COOH)]^{2+}$.

Catalytic photoreduction of CO_2 to CO and formate has also been carried out by visible-light irradiation of acetonitrile solutions containing cobalt and iron porphyrins as catalysts and as photosensitizers, and triethylamine as a reductive quencher. In contrast to the $Co^{I}HMD^{+}$ complex mentioned above, both $[Co^{0}P]^{2-}$ and $[Fe^{0}P]^{2-}$ react rapidly with CO_2 and reduce it to CO and formate ($HCOO^{-}$). The two-electron interconversion of $[M^{0}P]^{2-}$ and $M^{II}P$ is important here.

Further, $[M^0P]^{2-}$ does not react with the CO produced, thus avoiding poisoning of the catalyst. In the case of $[Fe^0P]^{2-}$, the formation of an equilibrium mixture of $Fe^{II}P(CO)$ and $Fe^{II}P$ was observed after the addition of CO_2 to a solution containing $[Fe^0P]^{2-}$. $Fe^{II}P(CO)$ loses CO upon two-electron reduction of the metal center and reform the catalyst, $[Fe^0P]^{2-}$.

None of the approaches described above can be used for the commercialization of CO_2 reduction. All the systems require a sacrificial reagent. The stability of the systems is limited, the catalytic activities are too low, and the overall costs are too high for commercialization. Hopefully, the insight obtained from a fundamental understanding of the reactions occurring in the above systems will provide the knowledge for the future design of practical systems. One fundamental and formidable challenge is the replacement of the "sacrificial" electron donors by species that will lead to useful (or benign) chemicals in their own right.

Bibliography. E. Fujita, *Photochemical Carbon Dioxide Reduction with Metal Complexes*, Coordination Chemistry Review, vol. 185-186, 373-384, 1999; N. Sutin, C. Creutz, and E. Fujita, *Photo-Induced Generation of Dihydrogen and Reduction of Carbon Dioxide Using Transition Metal Complexes*, Comments Inorg, Chem. vol. 19, 67-92, 1997; T. Inui, M. Anpo, K. Izui, S. Yanagida, and T. Yamaguchi (Eds.) Advances in Chemical Conversions for Mitigating Carbon Dioxide, Studies in Surface Science and Catalysis, Vol. 114, Amsterdam, Elsevier, 1998; E. Fujita, L. R. Furenlid, and M. W. Renner, *Direct XANES Evidence for Charge Transfer in Co-CO_2 Complexes*, J. Am. Chem. Soc., vol 119, 4549-4550, 1997.

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Keywords:

Carbon dioxide, Reduction, Fixation, Artificial photosynthesis, Photocatalysis

Figure Caption

Figure 1 Photochemical CO_2 reduction with an electron donor (D), a photosensitizer (P) and a catalyst (ML)

Figure 2 Artificial photosynthesis: D = electron donor, P = photosensitizer, and ML = catalyst

Figure 3 Coordination geometry of M-CO_2 adducts

Figure 4 Structure of ligands, R = C_6H_5, 3-F-C_6H_5, 3-CF_3-C_6H_4, and C_6F_5

Figure 1

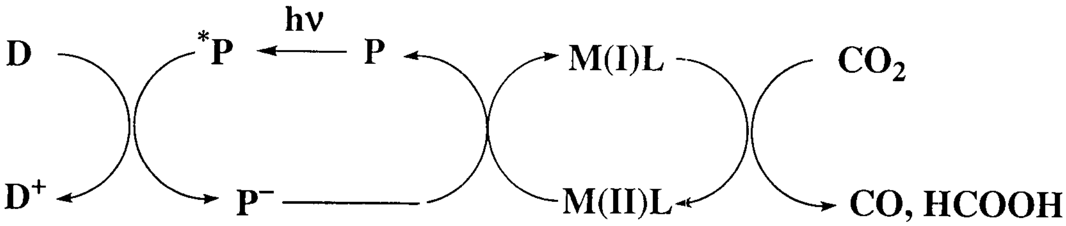


Figure 2

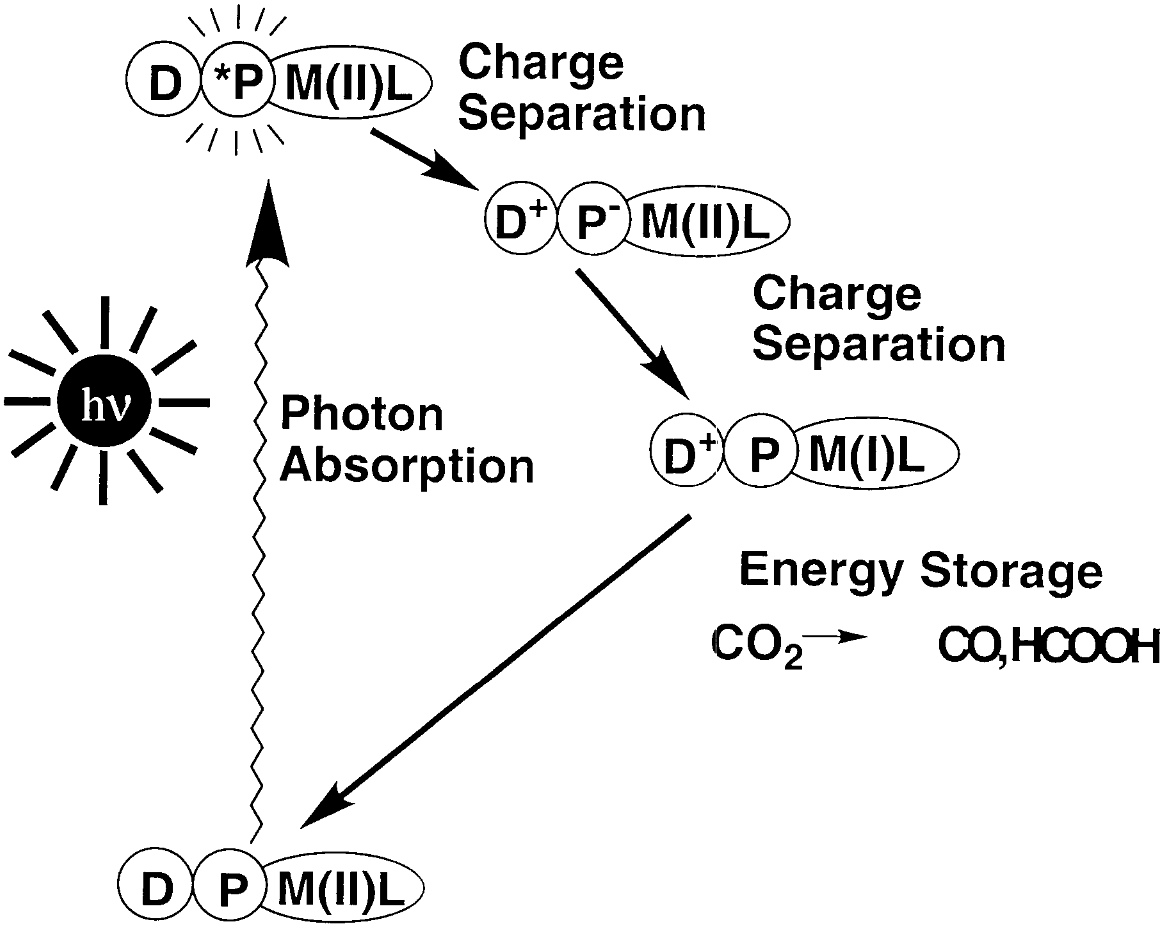
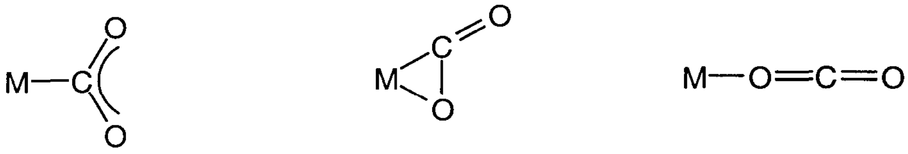
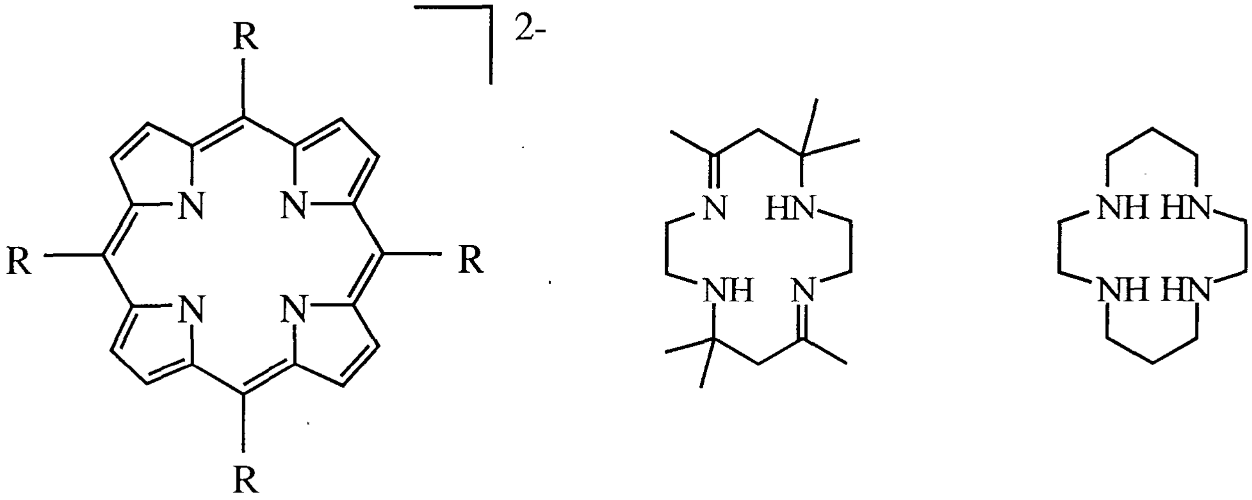


Figure 3



η^1-C coordination η^2-side-on coordination η^1-end-on coordination

Figure 4



P HMD cyclam