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Photofixation of carbon dioxide in semiconductor particulate and microbial systems

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Abstract. Photocatalytic reduction of CO_2 to HCOOH and HCHO was carried out in a $Pt/CdS/RuO_2$ semiconductor particulate system using $[Ru^{III}(EDTA\text{-}H)H_2O]$ complex as catalyst. Upon illumination at 505 nm (band gap energy of CdS), the system produced HCOOH and HCHO at rates equal to $3{\cdot}05 \times 10^{-2}\,M\,h^{-1}$ and $2{\cdot}0 \times 10^{-2}\,M\,h^{-1}$, respectively. Trace amounts of CH_2OH, CH_4 and CO were also detected in the reaction vessel. Photobiological conversion of CO_2 to formic acid was achieved by using *Halobacterium halobium* MMT_{22} in aqueous solution at a rate equal to $0{\cdot}45\,M\,h^{-1}$. A one-and-half-fold increase in the rate of formation of formic acid was observed when the photobiological reduction of CO_2 was performed in the presence of L-ascorbic acid as electron-donating agent and $[Ru^{III}(bipy)_3]^{2+}$ as photosensitizer.

Keywords. Photofixation; semiconductor particulate system; *Halobacterium halobium*; photobiological conversion; artificial photosynthesis.

1. Introduction

Photochemical activation and reduction of carbon dioxide is the major goal of artificial photosynthesis (Hawecker *et al* 1985a). Reduction of CO_2 to formate (Hawecker *et al* 1985b), formaldehyde (Inoue *et al* 1979), carbon monoxide (Grant *et al* 1987) and methane (Willner *et al* 1987) were reported using homogeneous catalysis (Lehn and Ziessel 1982), a semiconductor particulate system (Hallman 1978) or an enzyme-coupled system (Willner and Mandler 1987). Eggins *et al* (1988) have recently reported the formation of C_2 acids from CO_2 by its photoreduction with CdS particulate system.

Biological CO_2 fixation is carried out by microbial autotrophic and heterotrophic systems in the presence of light (Dijlhuizen and Hander 1985). In the photosynthesis of ATP (Arlette and Stoeckenius 1974) by *H. halobium*, carbon dioxide uptake is largely increased. In this case, carbon dioxide is fixed through reductive pathways with the production of NADH during illumination (Danon and Kaplan 1977) by the reversal of electron transport. This reduced nicotinamideadeninedinucleotide (NADH) functions as an electron donor in photobiological CO_2 fixation (Arnon 1978). Photochemical conversion of CO_2 (at 400 nm) to CO and $HCOO^-$ was achieved by using the NADH model compound (Ishida *et al* 1988) and 1-benzyl-1,4-dihydronicotinamide (BNAH) as the electron donor in H_2O/DMF solution of $[Ru(bipy)_3]Cl_2$.

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As a part of our continued interest in the development of a low energy photocatalytic method for activation of small molecules (Taqui Khan *et al* 1988), we report in this paper the photochemical and photobiological reduction of carbon dioxide to formic acid and formaldehyde. The photocatalytic reduction of CO_2 was carried out in a $Pt/CdS/RuO_2$ semiconductor (photocatalyst) particulate system in the presence of $[Ru^{III}(EDTA\text{-}H)H_2O]$ as catalyst. Photobiological conversion of CO_2 to formic acid was achieved by using *Halobacterium halobium* MMT_{22}.

2. Experimental

2.1 *Materials*

The complex $K[Ru^{III}(EDTA\text{-}H)Cl]$ was prepared by following the published method (Diamentis and Dubrawski 1981). The complex rapidly gets aquated when dissolved in water to give a neutral species $[Ru^{III}(EDTA\text{-}H)(H_2O)]$ 1 at low pH (< 3) (Matsubara and Creutz 1979). The complex $[Ru^{III}(bipy)_3]Cl_2$ was prepared as per a published procedure (Liu and Bailar 1964). L-ascorbic acid and all other chemicals used were of AR grade.

For preparation of Pt (4% w/w)/CdS/RuO_2 (0·5% w/w) electronic grade cadmium sulphide (Ventron, FRG) was freshly coated with Pt and RuO_2. Platinisation (Kraeutler and Bard 1978) of CdS was performed by illumination, at 400 nm, of an aqueous solution of 0·5 g CdS dispersed in 100 ml of 0·1 mM H_2PtCl_6 for 2 h. RuO_2 loading in CdS was done by following the reported procedure (Erbs *et al* 1984) via photodecomposition of RuO_4 present in appropriate concentration in an aqueous solution. The resulting $Pt/CdS/RuO_2$ powder (particle size 1 mμ) has a surface area of about 13·01 $m^2 g^{-1}$.

The extreme halophile *H. halobium* MMT_{22} was isolated from brine solution and incubation carried out at 40°C under illumination as described earlier (Taqui Khan and Bhatt 1990).

2.2 *Photocatalytic reduction of CO_2 in a semiconductor particulate system*

In a typical experiment, the system containing CO_2 (saturated aqueous solution, pH = 3·0), $K[Ru^{III}(EDTA\text{-}H)Cl]$ (1×10^{-3} M) and 50 mg of $Pt/CdS/RuO_2$ was irradiated at 505 nm by a 250-watt Xe lamp (Applied Photophysics) in a water-jacketted cell. The gaseous products were collected in an attached manometer. The aqueous phase was analysed for the reduction products of CO_2 i.e. HCOOH and HCHO by Nash's (1953) method at chosen intervals of photolysis time. Acetylacetone, acetic acid and ammonium chloride were required to prepare the Nash reagent. The products were estimated by monitoring the absorption peak at 412 nm ($\varepsilon = 8{\cdot}00 \times 10^3$ M^{-1} cm^{-1}) due to formation of diacetyldihydrolutidine (DDL) by using a Shimadzu UV-Vis 160 spectrophotometer. Formation of HCOOH and HCHO were further confirmed by HPLC analysis.

2.3 *Photobiological conversion of CO_2*

Photobiological reduction of CO_2 by *H. halobium* MMT_{22} was carried out at 40°C by following the same technique as adapted in photochemical oxidation of CO_2 in

a semiconductor particulate system. For this purpose 1 mg (wet weight) of *H. halobium* MMT_{22} was taken in 35 ml of NaCl (25%) solution. The pH of the solution was kept at 7·0. The reaction mixture was illuminated at 460 nm and 5 ml of sample was taken out at two-hour intervals and centrifuged to make cell-free solution prior to analysis for formic acid. In a second set of experiments, solutions of HCO_3^- (1·0 M) (in place of CO_2), photosensitizer $Ru(bipy)_3^{2+}$ (10^{-4} M) *H. halobium* MMT_{22} and electron donor L-ascorbic acid ($1 \times 10^{-3} - 10^{-1}$ M) were irradiated at 460 nm. Samples were withdrawn at chosen intervals of time and subjected to product analysis.

2.4 *Product analysis*

The liquid samples HCOOH and HCHO were analysed spectrophotometrically by using the Nash reagent. The product HCOOH and HCHO were also analysed by HPLC. CH_3OH was analysed by gas chromatography (Shimadzu GC 9A) using a Carbowex column (20 M 10%, Anakrom 90%) at FID. All gaseous samples (CH_4, H_2, O_2 and CO) were analysed by gas chromatography using molecular sieve columns at FID and TCD.

3. Results and discussion

3.1 *Photochemical reduction of CO_2 in a Pt/CdS/RuO_2 semiconductor particulate system*

The photocatalytic reduction of CO_2 in a Pt/CdS/RuO_2 particulate system was carried out by illuminating the reaction mixture containing Pt/CdS/RuO_2 semiconductor powder, [Ru(EDTA-H)(H_2O)] (1) catalyst and CO_2 at 505 nm. The concentration of $HCOO^-$ and HCHO built up gradually with photolysis time as shown in figure 1. The rates of formation of HCOOH and HCHO were found to be $3{\cdot}05 \times 10^{-2}$ and $2{\cdot}00 \times 10^{-2}$ M h^{-1}, respectively. The corresponding turnover-rates are 30·5 mol of HCOOH per mole of catalyst (complex 1) per hour and 20·0 mol of HCHO per mole of catalyst (complex 1) per hour, respectively. In this study, a total of 0·22 M of HCOOH and 0·1 M of HCHO are produced in a 6-hour irradiation period under the specified conditions.

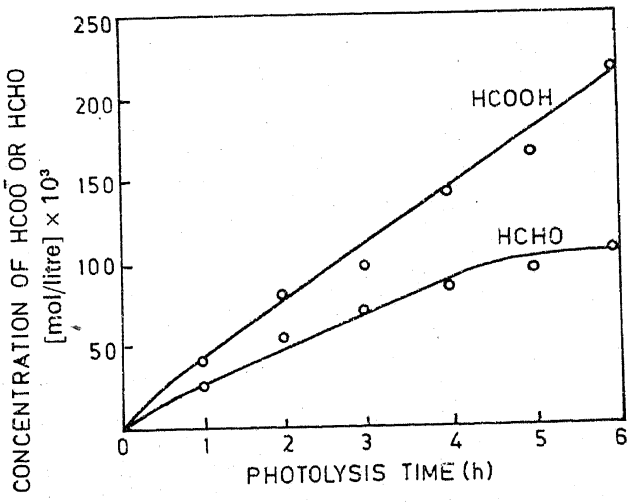
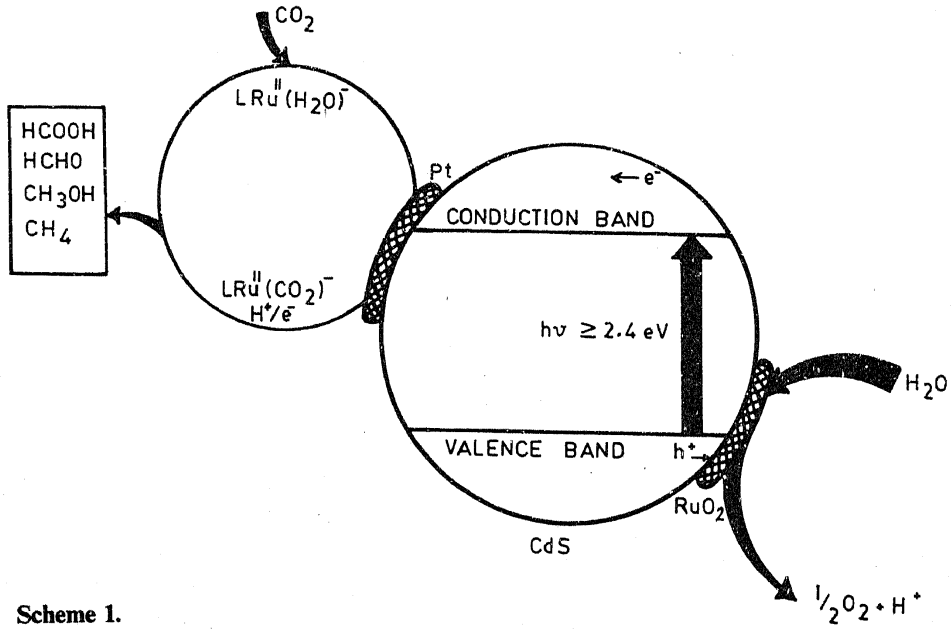


Figure 1. The concentration buildup of HCOOH and HCHO with photolysis time.

No formic acid or formaldehyde was formed when the experiments were conducted in the absence of any of the following: carbon dioxide, complex 1, $Pt/CdS/RuO_2$ or light. In the absence of complex 1 only traces of HCOOH and HCHO are formed that represent the background concentrations. In the absence of CO_2, the amount of O_2 evolved at any instant is approximately one-half that of H_2 evolved. In the presence of CO_2, however, the H_2 evolution was markedly inhibited because of competitive reduction of CO_2 to formate.

The rate of reduction was found to be first order in both complex 1 and dissolved CO_2 concentrations. At constant concentrations of complex 1 and CO_2, the rate of reaction increased with the increase in hydrogen ion concentration ($10^{-4} - 10^{-2}$ M) in solution. On the basis of the above experimental data the mechanism in scheme 1 is proposed for the photoreduction of CO_2 by the present system.



Scheme 1.

In the proposed mechanism (scheme 1) electrons and holes are generated in the conduction and valence bands, respectively, when the system $Pt/CdS/RuO_2$ is irradiated at band gap energy ($g = 2{\cdot}4$, ev = 505 nm). In the absence of complex 1 and CO_2, photolysis of water takes place to generate H_2 and O_2 in the conduction and valence bands, respectively. Because of the favourable potential of the Ru^{III}/Ru^{II} couple in complex 1, it is reduced to $LRu^{II}(H_2O)^-$ 1a by the electron of the conduction band. Complex 1a thereafter reacts with CO_2 to give an intermediate complex $LRu^{III}(CO_2)^-$ 2. The formation of complex 2 was shown spectrophotometrically. The coordinated CO_2 in complex 2 is then reduced by conduction-band electrons by successive $2e^-/2H^+$ and $4e^-/4H^+$ transfer to CO_2 in parallel steps to give HCOOH and HCHO, respectively, with the generation of complex 1a which is recycled.

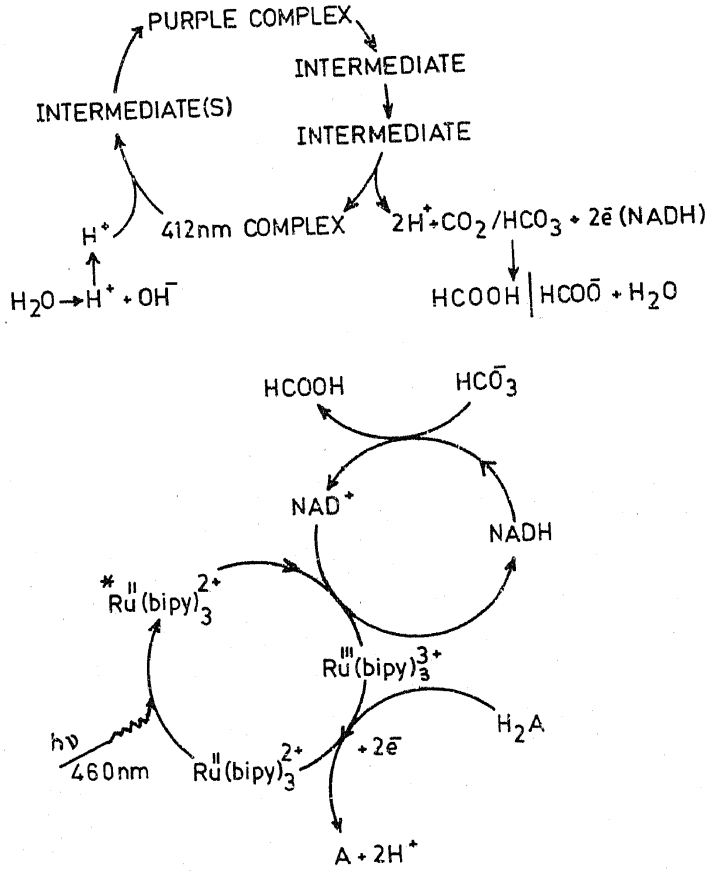
The potentials for the multielectron reduction of CO_2 at pH 7 (NHE) are as follows (Goren *et al* 1990):

$$CO_2(aq) + 2H^+ + 2e^- \rightarrow HCOOH, \qquad E^\circ = 0{\cdot}61\ V,$$
$$CO_2(aq) + 4H^+ + 4e^- \rightarrow HCHO + H_2O, \qquad E^\circ = 0{\cdot}48\ V,$$
$$CO_2(aq) + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O, \qquad E^\circ = 0{\cdot}38\ V,$$
$$CO_2(aq) + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O, \qquad E^\circ = 0{\cdot}24\ V.$$

On the basis of the above potentials, it is believed that the activation of coordinated CO_2 in complex 2 (scheme 1) is potentially favourable to the extent that the requirements of $2e^-/2H^+$ and $4e^-/4H^+$ for the formation of HCOOH and HCHO are readily fulfilled at the conduction band. We have earlier found that the $LRu^{II}N_2^-$ system is an efficient catalyst for the photoreduction of N_2 in the $Pt/CdS/RuO_2$ particulate system (Taqui Khan *et al* 1988).

3.2 *Photobiological reduction of CO_2 to formic acid*

In the presence of light, each bacteriorhodopsin cycle in the purple membrane of *H. halobium* MMT_{22} releases 2–3 protons under anaerobic conditions. The protons are released at the exterior of the cell. As CO_2 is fixed through the reductive pathways and NADH is produced during illumination by reversal of electron transport; the carbon uptake is markedly increased with the reduction of CO_2 to HCOOH. No other products of CO_2 reduction such as formaldehyde, methanol or methane were detected in the reaction mixture. The key role of the $NADH/NAD^+$ couple in the photobiological conversion of CO_2 was confirmed by studying the effect of the electron donating agent (L-ascorbic acid). The rate of formic acid production increases 2.2 times when 1 mg of L-ascorbic acid is added to the reacting medium. L-ascorbic acid reduces the oxidised NAD^+ by donating electrons to form dehydro ascorbic acid.



Scheme 2.

The use of $Ru^{II}(bipy)_3^{2+}$ as photosensitizer was reported by Kiwi *et al* (1982) for photolysis of water. Here, using $Ru^{II}(bipy)_3^{2+}$ as photosensitizer and L-ascorbic acid as electron-donating agent, the photobiological reduction of HCO_3^- by *H. halobium* MMT_{22} was performed. The reaction mixture was illuminated at 460 nm which is the optimum wavelength in this reaction.

Addition of $Ru^{II}(bipy)_3^{2+}$ photosensitizer substantially increased the formation of formic acid ($0{\cdot}66\,M\,h^{-1}$). The mechanism of reduction of HCO_3^- by *H. halobium* MMT_{22} in presence of L-ascorbic acid and $Ru^{II}(bipy)_3^{2+}$ is shown in scheme 2. $Ru^{II}(bipy)_3^{2+}$ gets excited by absorbing light (460 nm) to $^*Ru^{II}(bipy)_3^{2+}$, which readily transfers electrons to NAD^+ and is converted to $Ru^{III}(bipy)_3^{3+}$. The oxidised $Ru^{III}(bipy)_3^{3+}$ is reduced to $Ru^{II}(bipy)_3^{2+}$ again by taking an electron from the electron-donating ascorbic acid (scheme 2) and thus repeats the NADH/NAD^+ cycle for HCO_3^- reduction as shown in scheme 2.

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