CHEMISTRY LETTERS, pp. 1109-1112, 1983.

PHOTOREDUCTION OF CARBON DIOXIDE TO FORMIC ACID MEDIATED BY A METHYLVIOLOGEN ELECTRON RELAY

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Carbon dioxide was photochemically reduced to formic acid in the aqueous system of tris(2,2'-bipyridine)ruthenium(II) - methylviologen - triethanolamine under carbon dioxide atmosphere. Photoirradiation of the system for 4 h gave 4.5×10^{-3} M of formic acid(quantum yield $(\psi) \approx 0.01$) as determined by isotachophoresis.

Photochemical reduction of CO_2 coupled with the oxidation of water is an ultimate goal of simulating the photosynthetic system. Most of the works on solar energy conversion have been directed to splitting of water to hydrogen and oxygen,1) but scarcely to photochemical reduction of CO_2. Since CO_2 is an abundant carbon source, the conversion of CO_2 to organic compounds is of primary importance as a solar energy conversion process as well as a branch of C_1 chemistry.

Previously, we reported that CO_2 was photochemically reduced to oxalic acid and formic acid in the combined system, an aromatic hydrocarbon - an electron donor - an electron acceptor, in aqueous acetonitrile.2) However, the reduction quantum yields of CO_2 to the carboxylic aicds were quite poor ($\lesssim 10^{-4}$). In the present letter, we report a new CO_2 photoreduction system consisting of tris(2,2'-bipyridine) ruthenium(II) ($Ru(bpy)_3$, 6×10^{-5} M), methylviologen (MV^{2+}, 0.02 M), and triethanolamine (TEOA, 0.6 M) under CO_2 atmosphere in aqueous solution. Photoirradiation of the present system resulted in the formation of formic acid in a better yield than that by the previous system.2) (M : mol dm^{-3})

The preparation and purification of $Ru(bpy)_3$ have been reported.3) TEOA (Kanto Chem. Ind.) and MV^{2+} (Nakarai Chem.) were used as supplied. Deionized water was doubly distilled prior to use. Photoreaction was carried out in a pyrex tube (10 ϕ, 3 ml) with purging CO_2 gas (50 ml/min). A light source was a 300 W high pressure Hg lamp with a $CuSO_4$ chemical filter ($\lambda > 320$ nm). The yield of formic acid was determined by a Shimadzu isotachophoretic analyzer IP - 1B. The terminating electrolyte was a 0.01 M caproic acid in aqueous solution and the leading electrolyte was a mixture of β-alanine (0.02 M) and Triton X-100 (0.2 %) in a 0.01 M aqueous HCl solution. The applied electrophoretic current and the potential gradient values were set at 75 mA and 256 mV/cm^2, respectively. Figure 1a shows an isotachopherogram of authentic formic acid. The solid line represents the potential gradient value and qualitative analysis can be made by the potential unit (PU) value defined as Eq. 1, where P_{si}, P_L, and P_T are the potential gradient values of formic acid, the leading electrolyte, and the terminating electrolyte, respectively (Figure 1a). The dotted line is the differential of the potential gradient value. The peak to peak distance denoted by W in Figure 1a corresponds to formic acid concentration rendering quantitative analysis of the acid.

$$\text{PU value} = \frac{P_{si} - P_L}{P_T - P_L} \quad (1)$$

The well-known photochemical formation and accumulation of MV^+ when the $Ru(bpy)_3 - MV^{2+}$ - TEOA system is irradiated under anaerobic conditions[4] is suppressed under CO_2 atmosphere. This quenching action is expected to involve reduction of CO_2. From the PU values of authentic carboxylic acids and an isotachopherogram of the reaction mixture (Figure 1b), we confirmed that formic acid and

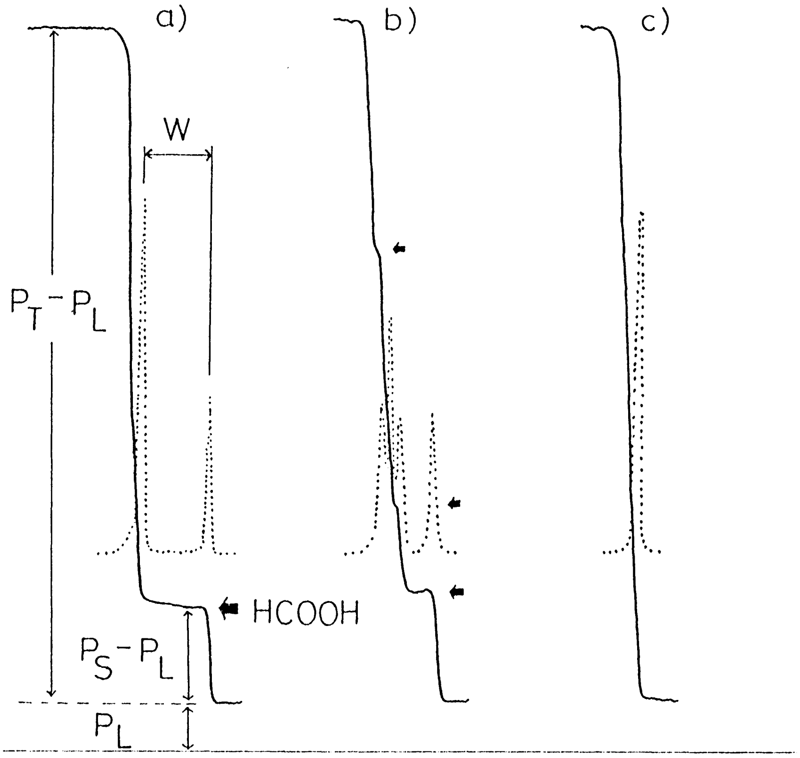
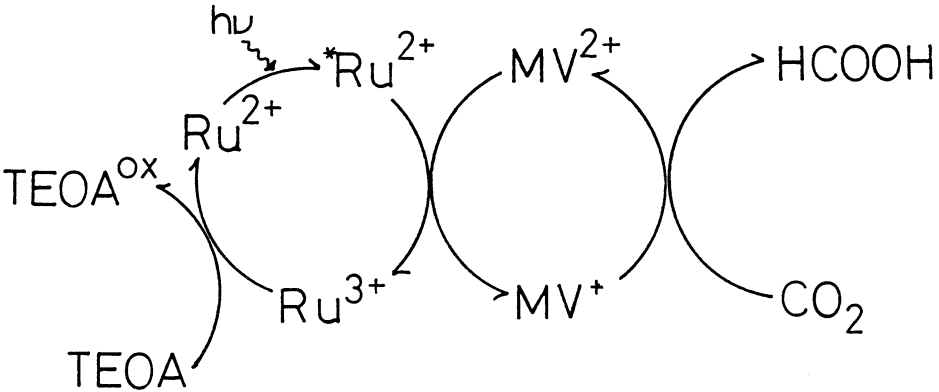


Fig. 1.
Isotachopherograms of
a) authentic formic acid,
b) the reaction mixture, $Ru(bpy)_3 - MV^{2+}$ - TEOA - CO_2, irradiation for 4 h.
c) the reaction mixture, $Ru(bpy)_3 - MV^{2+} - CO_2$, irradiation for 4 h.

two unknown carboxylic acids were produced. The yield of formic acid was $4.5\mathrm{x}10^{-3}$ M after 4 h irradiation and the quantum yield of CO_2 reduction to formic acid was calculated to be ≈ 0.01. We confirmed by the following observations that CO_2 was photochemically reduced to formic acid. i) Dark reaction of the system under CO_2 atmosphere gave no carboxylic acid. ii) Photoreaction of the $Ru(bpy)_3$ - MV^{2+} - CO_2 system did not bring about the formation of any carboxylic aicds (Figure 1c), indicating that formic acid was not the decomposition product of MV^{2+} and that a sacrificial electron donor such as TEOA was necessary for the photoreduction of CO_2 to formic acid. iii) After photoirradiation of the system under CO_2 atmosphere for 4 h, MV^{2+} was recovered in 92 % yield, corresponding to the decomposition of $1.6\mathrm{x}10^{-3}$ M of MV^{2+}, which is about one third of formic acid produced. Consequently, MV^{2+} was proved to act as a restorable electron relay for the CO_2 reduction. iv) Although TEOA is known to be oxidatively decomposed by electron transfer to $Ru(bpy)_3^{3+}$, our controlled experiments showed that formic acid was not a decomposition product of TEOA.5) v) TEOA is not an essential component. The sacrificial reducing agent may be substituted by EDTA, giving a comparable amount of formic acid ($\approx 4\mathrm{x}10^{-3}$ M).

From these results, we conclude that formic acid is produced by reduction of CO_2 by MV^{+}. However, direct electron transfer from MV^{+} to CO_2 is energetically totally impossible. The redox potential of CO_2 is about or more negative than 2.0 V (vs. SCE)6) whereas that of MV^{2+} is -0.44 V (vs. NHE).7) Providing that the mechanism involving $CO_2^{\cdot -}$ prevails similar to the previous pyrene(or perylene) - N,N-dimethylaniline - 1,4-dicyanobenzene(or 9-cyanoanthracene) system,2) it seems to be a contradiction that the present highly endoergonic reaction proceeds with



Scheme

an efficiency more than 100 times better than the previous nearly thermoneutral system. We must seek for another possible reaction pathway.

Reduction of CO_2 occurs at a lower potential when protons participate as shown below. Coupling with oxidation of MV^+ to MV^{2+}, the reaction is still slightly

$$CO_2 + 2H^+ + 2e \longrightarrow HCOOH \qquad E^{0'} = -0.61 \text{ V (vs. NHE at pH 7)}^{8)}$$

endoergonic. However, bubbling of CO_2 will shift the pH towards acidic side so that the $E^{0'}$ value may become more positive. If the participation of proton is considered, the reducing power of MV^+ is nearly sufficient and the magnitude of $_{HCOOH}$ will be controlled kinetically. Simultaneous two-electron reduction reacting with two MV^+ species in a homogeneous system would not be efficient. This is probably a partial reason for rather poor quantum yield of CO_2 reduction to formic acid ($\Psi_{HCOOH} \approx 0.01$) while the formation of MV^+ is an efficient process ($\Psi_{MV^+} = 0.22$).4) Further mechanistic details will be published elsewhere.

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5) Photoreactions of the $Ru(bpy)_3$ - TEOA - CO_2, $Ru(bpy)_3$ - TEOA - $K_2S_2O_8$ - N_2, tris(2,2'-bipyrazine)ruthenium(II) - TEOA - CO_2, and $Ru(bpy)_3$ - TEOA - MV^{2+} - N_2 or Ar systems did not lead to the formation of formic acid. In the last system, intensive coloration occured due to accumulation of MV^+ and the photoirradiation conditions could not be identical with other systems.

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(Received May 16, 1983)