

A Photoelectrochemical Fixation of Carbon Dioxide.
Spontaneous Up Quality Conversion of Organic Compound

Jo-ji UEDA, Seiichiro NAKABAYASHI, Jun-ichi USHIZAKI, and Kohei UOSAKI*

Physical Chemistry Laboratory, Department of Chemistry, Faculty of Science,
Hokkaido University, Sapporo, 060

A photosynthetic semiconductor electrochemical cell with Mg electrode as a sacrificial anode was assembled. This photoelectrochemical cell spontaneously fixes carbon dioxide into organic molecule such as benzyl chloride to form phenyl acetic acid which costs 7.5 times more than the sources. Among the semiconductor electrodes investigated, p-GaP showed highest current efficiency, 47%.

An artificial carbon dioxide fixation attracts the great interests in ecological background. Electrochemical and photochemical fixations of CO₂ have been extensively studied.^{1-7,9,10)} However, most of the studies concentrate on direct reduction of carbon dioxide on the electrode. The practical system requires the breakeven between the cost for the input energy to drive the cell and the value of the products. The products of direct electrolysis of CO₂ are CO¹⁾, formic acid^{1,2)}, methanol,^{1,3)} and so on, which are not so valuable. Thus, it is more attractive to synthesize valuable organic compounds electrochemically by fixing carbon dioxide into organic substances. Electrochemical CO₂ reduction requires fairly negative potential and therefore, there have been many attempts to reduce the overpotential by using suitable catalysts. For example, Komeda et al. electrochemically fixed CO₂ into CH₃C(O)SEt and C₆H₅C(O)SEt and obtained CH₃C(O)COO⁻ and C₆H₅C(O)COO⁻ respectively, using (Et₄N)₃[Mo₂Fe₆S₈(SEt)₉] as a catalyst.⁴⁾ Colloidal semiconductor microcrystallites are often used as a photocatalyst. Kanemoto et al. demonstrated that CO₂ and benzophenone photochemically yield benzilic acid in the presence of colloidal CdS microcrystallites as photocatalyst and triethylamine as a sacrificial electron donor.⁵⁾ Inoue et al. photochemically fixed CO₂ into oxoglutaric acid using CdS as a photocatalysts, isocitrate dehydrogenase as a catalysts, methyl viologen as an electron mediator and triethanolamine as an electron donor.⁶⁾

Electrochemical reduction of benzyl chloride in the presence of CO₂ led directly to benzyl phenylacetate by using a Pt as the anode.⁸⁾ On the other hand, if one uses Mg as an anode, the reductive intermediate of the benzyl chloride captures CO₂ to form phenyl acetic acid. In this case, anodic process is the dissolution of Mg²⁺. It is well recognized that the rate of CO₂ insertion process is dramatically enhanced in the presence of freshly prepared Mg²⁺ ion, which is commonly prepared by anodic dissolution of Mg counter electrode.^{9,10)} It has been well known that electrical energy required to drive various electrochemical reactions are reduced quite significantly by using illuminated semiconductor electrodes.^{7,11,12)}

In this article, we demonstrate that the combination of p-type semiconductor electrodes and magnesium counter electrode spontaneously photoconverts benzyl chloride to phenyl acetic acid without the external electric power.

A conventional three electrode system was used for the electrochemical measurements with Pt and Ag/Ag⁺

as the counter and the reference electrodes, respectively. The electrode potential is represented with respect to SCE in this article. The photo-excitation of semiconductor electrodes was conducted by 500 W xenon arc lamp through proper combination of optical filters.

The aprotic solvents used for electrolyte preparation were acetonitrile and dimethyl formamide dried over P_4O_{10} under continuous stirring for at least 24 h. The solvents were transferred to the freshly prepared descant by trap to trap distillation under vacuum. This process was repeated for three times. The oxygen dissolved was removed by freeze-pump-thaw cycles. Supporting electrolyte used was a tetra-n-butylammonium tetrafluoroborate which was dried under vacuum.

In the photosynthetic experiments, a two electrode cell consists of p-type semiconductor electrode and Mg counter electrode was used. Two electrodes were connected through zero-shunt ammeter so that current flow during photo-electrolysis could be measured. The product was analyzed by JASCO HPLC system with combination of 870-UV optical detector.

The typical electrochemical behaviors of the direct reduction of CO_2 on Pt and p-GaP electrode in acetonitrile solution are depicted in Fig. 1. The cathodic current for CO_2 reduction started to flow around -2.0 V and -1.0 V at Pt and photoexcited p-GaP, respectively. With the presence of benzyl chloride, the cathodic current started around -0.5 V as presented in Fig. 2. The electrochemical behavior of Mg electrode is also shown in Fig. 2.

The anodic dissolution of Mg started at -1.8 V. As the anodic dissolution of Mg proceeds at more cathodic potential than the photo-electrochemical reduction of benzyl chloride, the combination of p-type semiconductor and Mg counter electrode forms a photoelectrochemical cell. Because the anodic dissolution current of Mg is larger than the cathodic photocurrent of p-type semiconductor electrodes, the potential of the semiconductor electrodes under the photoelectrochemical cell operation are close to the onset potential of the Mg dissolution reaction, i.e., -1.8V.

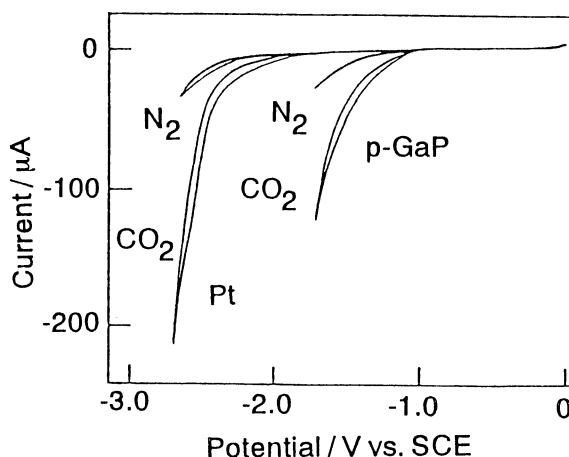


Fig.1. Direct electrochemical reduction of CO_2 at Pt and illuminated p-type GaP electrodes in acetonitrile solution.

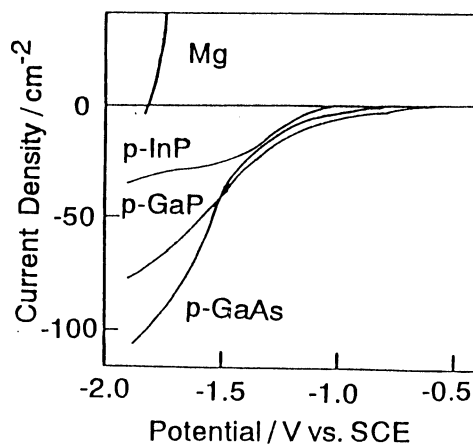


Fig.2. Electrochemical behaviors of p-type photoexcited semiconductors and Mg electrodes in CO_2 saturated acetonitrile solution with 50 mM of benzyl chloride.

The short circuit current of the cell was measured as a function of both the concentration of benzyl chloride and irradiation intensities as shown in Fig.3. The photocurrent increases linearly with the light power up to certain point and then the deviation from the linear relation was observed. The higher concentration of benzyl chloride shifts the point to higher light intensity where the deviation starts. This result suggests that the electron transfer occurring on the electrode is not direct reduction of CO_2 but reduction of benzyl chloride.

After the continuous photo-electrolysis under CO_2 bubbling, the product analysis was carried out. The major product is phenyl acetic acid. The amount of the phenyl acetic acid and the current efficiency of the reaction are

shown in Table 1 for three p-type semi-conductor photocathodes. Although the data scatters to some

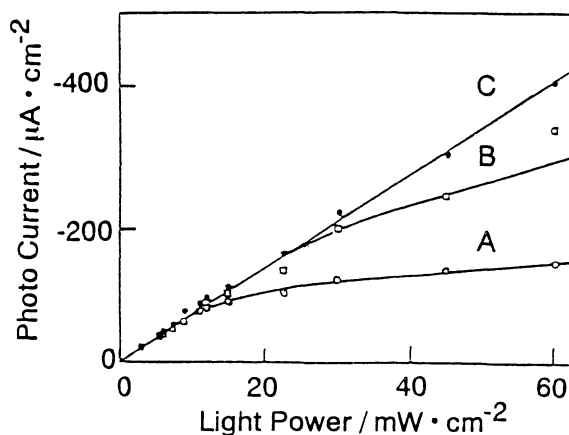


Fig.3. Short circuit photocurrent of p-GaP synthetic photocell as a function of benzyl chloride concentration and irradiation intensity under CO_2 saturated condition. The concentration of benzyl chloride are 50, 100, and 500 mM for curve A, B, and C, respectively.

Table 1. Current yield of phenyl acetic acid in various p-type semiconductor synthetic photocell in acetonitrile solution at 25 °C

Electrode	Current μA	Time h	Amount of Product nmol	Current Efficiency %
p-GaP				
(50 mM) ^{a)}	3	20	530	44
(2 M) ^{a)}	2	24	360	47
p-GaAs				
(50 mM) ^{a)}	4	20	630	42
(2 M) ^{a)}	7	16	1000	42
p-InP				
(50 mM) ^{a)}	0.2	20	—	—

a) Concentration of benzyl chloride.

extent, the yield increases in the order of p-type InP, GaAs and GaP, successively. Only the trace amount of phenyl acetic acid was produced at InP electrode. From the flatband potentials measured in the dark and the band gap energy of the semiconductors, the energy of the photocreated electrons on the conduction band is determined as 1.10, -1.01 and -2.09 V vs. SCE for p-type InP, GaAs and GaP, respectively. The reactivity of the electrodes has no relation with the energy of electrons in the conduction band.

The current efficiency was improved by 40% by carrying the reaction at 275K. The temperature effect must be mainly due to the increase of the saturation concentration of CO₂ in the aprotic electrolytes.

As a comparison, the potentiostatically controlled photoelectrolysis was conducted also with a platinum counter electrode at -1.8V vs. SCE. After the continuous electrolysis, the analysis of the solution revealed that only trace amount of phenyl acetic acid was produced. Even by adding magnesium sulfate in the solution, the phenyl acetic acid was not detected.

These results shows that the photoelectrochemical carbon dioxide insertion to benzyl chloride is initiated by the reduction of benzyl chloride on p-type semiconductor electrode and carbon dioxide is captured by the reductive intermediate of benzyl chloride, which is drastically accelerated by the presence of freshly prepared magnesium ion in the solution. The detailed study of the mechanism is under way in this laboratory.

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