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On the Reduction Products of Carbon Dioxide at a p-Type Gallium Phosphide Photocathode in Aqueous Electrolytes

Kaname Ito,* Shoichiro Ikeda, Makoto Yoshida, Soji Ohta, and Takaya Iida
Department of Synthetic Chemistry, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466

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Synopsis. Formic acid, formaldehyde, and methanol, previously reported as photoelectrochemical reduction products of CO_2, were observed to be obtained also by photolysis of cell materials such as electrolytes and epoxy resin. The reduction product of CO_2 at a p-GaP photocathode in aqueous electrolytes was experimentally confirmed to be mainly formic acid.

Halmann[1)] observed formic acid, formaldehyde, and methanol as reduction products of CO_2 at a p-type gallium phosphide (p-GaP) photocathode in aqueous lithium carbonate electrolyte. Tamura *et al.*[2)] reported that their yield increased with addition of crown ether to the electrolyte. In our similar experiments[3)] oxalic acid, glycolic acid, ethanol, and acetaldehyde were also observed.

Here, similar organic compounds will be shown to be produced also by photolysis of cell materials such as electrolytes and epoxy resin. When experimental conditions were improved so as to produce no organic compound as a photolytic product, the products obtained by photoelectrochemical reduction of CO_2 in aqueous electrolytes were mainly formic acid.

Experimental

The photoelectrochemical cell with a quartz window was made of Teflon. The structure was designed to separate the cathode chamber from the anode chamber by an ion-exchange membrane, Nafion-315, and to allow operation with a small volume of catholyte of *ca.* 5 ml for easy determination of the products.

The photocathode was prepared by molding p-GaP wafer of *ca.* 1 cm^2 with epoxy resin; it was etched in aqua regia for 1 min before use. The photocathode set in the cell was illuminated through the quartz window and aqueous electrolytes by a 300 W Xenon lamp (Varian). The platinum plate served as an anode and the silver-silver chloride electrode as a reference electrode.

The electrolytes used were 0.1 mol dm^{-3} aqueous solutions of Li_2CO_3, $(C_2H_5)_4NClO_4$ (TEAP), $(C_2H_5)_4NBr$ (TEABr), $(n\text{-}C_4H_9)_4NBr$ (TBABr), and Li_2CO_3 plus 15-crown-5.

The products were detected and determined by high performance liquid chromatography on a column of Shodex HC-125S for carboxylic acids and by steam chromatography on a column of Chromosorb 101 for alcohols and aldehydes.

Results and Discussion

Photoelectolysis as a blank test of the present experiment was performed by bubbling N_2 gas instead of CO_2 to Li_2CO_3 or TEAP solution in the above mentioned cell and by illuminating the p-GaP photocathode with the Xenon lamp. The results are shown in Table 1, in which the results previously reported as photoelectrochemical reduction products of CO_2 are also listed for comparison. The products in N_2 and in CO_2 atmospheres are quite similar, so that they are assumed to be produced by photolysis of cell materials such as electrolytes and epoxy resin.

In order to determine the photolytic products from various electrolytes, they were individually illuminated in quartz test tubes by a 300 W Xenon lamp alone or with the UV-37 filter, Toshiba, to cut off light of wavelength shorter than 370 nm. The results, as summarized in Table 2, show that the photolysis of the electrolytes by illumination of the Xenon lamp alone produces acetaldehyde from TEABr and TEAP, acetaldehyde and ethanol from TBABr, and many kinds of products from 15-crown-5, and also that the photolysis of them by the Xenon lamp with the filter does not produce any organic compounds from TEABr, TEAP, and TBABr, but a large amount of formic acid and a small amount of oxalic acid from 15-crown-5.

The comparison of the results shown in Tables 1 and 2 suggests that formic, oxalic and glycolic acids are produced by photolysis of epoxy resin used for mount-

TABLE 1. PHOTOELECTROLYTIC PRODUCTS UNDER N_2 AND CO_2 ATMOSPHERES IN THE CELL WITH VARIOUS ELECTROLYTES AND A p-GaP PHOTOCATHODE MOLDED BY EPOXY RESIN

Photoelectrolysis was performed up to 10 C at −1.2 V *vs.* Ag/AgCl electrode by illuminationg with a 300 W Xenon lamp alone.

Atmosphere	Electrolyte	n/μmol					
		HCOOH	$CH_3OH+HCHO$[a)]	$(COOH)_2$	$HOCH_2COOH$	CH_3CHO	C_2H_5OH
N_2	Li_2CO_3	1.5	0.04	0.1	2.1	0.02	0.02
	TEAP	1.3	0.03	t	1.3	0.36	0.06
CO_2	TEABr	2.3	0.12	0.28	4.8	0.9	t
	TBABr	1.9	t[b)]	0.18	1.9	0.17	t
	15-Crown-5	6.5	t	0.25	1.5	0.29	t

a) Methanol and formaldehyde were represented as $CH_3OH+HCHO$ in the present paper because they were not able to be separated by the steam chromatographic technique; the amount of product was calculated as an amount of methanol. b) t; Trace amount of product.

Table 2. Photolytic products of various electrolytes in quartz test tube illuminated by a 300 W Xenon lamp alone or with the filter, Toshiba UV-37, under N_2 atmosphere

Filter of Xe lamp	Time / h	Electrolyte	n/μmol HCOOH	$CH_3OH+HCHO$	$(COOH)_2$	$HOCH_2COOH$	CH_3CHO	C_2H_5OH
Not used	25	Li_2CO_3	n[a]	n	n	n	n	n
	28	TEAP	n	n	n	n	0.24	n
	24	TEABr	n	n	n	n	0.28	n
	26	TBABr	n	n	n	n	0.21	0.14
	29	15-Crown-5	16.7	0.55	0.22	n	0.07	1.01
Used	24	TEAP	n	n	n	n	n	n
	26	TEABr	n	n	n	n	n	n
	24	15-Crown-5	13.1	n	0.22	n	n	n

a) n: No product.

Table 3. Photolytic products in the catholyte of the Teflon cell with various electrolytes, a p-GaP photocathode and an ion-exchange memberane, when the epoxy resin region of the photocathode was shielded by a Pt foil and the illumination was carried out by a 300 W Xenon lamp with UV-37 filter under N_2 atmosphere

Time / h	Electrolyte	n/μmol HCOOH	$CH_3OH+HCHO$	$(COOH)_2$	$HOCH_2COOH$	CH_3CHO	C_2H_5OH
24	TEAP	n[a]	n	n	n	n	n
48	TEAP	n	n	n	n	n	n
48	TEABr	n	n	n	n	n	n
48	TBABr	n	n	n	n	n	n
24	15-Crown-5 $+Li_2CO_3$	11.6	n	0.16	n	n	n

a) n: No product.

Table 4. Photoelectrochemical reduction products of CO_2 under the improved exprimental conditions

Photoelectrolysis was performed up to 100 C at -1.5 V *vs.* Ag/AgCl electrode.

Electrolyte	HCOOH n/μmol(cur. eff. %)	$CH_3OH+HCHO$ n/μmol
TEAP	25.0 (4.8)	t[a]
TEABr	18.0 (3.5)	t
TBABr	22.0 (4.3)	n[b]
Li_2CO_3	2.0 (0.4)	n

a) t: Trace amount of product. b) n: No product.

ing of a p-GaP electrode. This was experimentally confirmed, although the results are not shown in the present paper.

However, the photolysis of the electrolytes and epoxy resin as cell materials could be prevented, as shown in Tables 3, when the epoxy resin region of a p-GaP electrode was shielded by a platinum foil, the UV-37 filter was set in front of the Xenon lamp to cut off ultraviolet rays, and TEABr, TEAP, or TBABr (except 15-crown-5) was used as an electrolyte.

Under such improved experimental conditions, the photoeletrochemical reduction of CO_2 was carried out up to 100 C at -1.5 V *vs.* Ag/AgCl electrode. The products, as shown in Table 4, were mainly formic acid and sometimes a trace amount of formaldehyde plus methanol.

Accordingly, it may be concluded that the photoelectrochemical reduction products of CO_2 at a p-GaP electrode in aqueous electrolytes are mainly formic acid and the many kinds of products involving large part of formic acid in the previous papers[1–3] are due to photolysis of cell materials. This conclusion coincides with the previously reported fact that only formic acid is mainly produced by electrochemical reduction of CO_2 in aqueous electrolytes.[4,5]

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