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Product Selectivity in Photoelectrochemical Reduction of Benzyl Halides on Semiconductor Photocathodes

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Electrochemical reduction of benzyl halides on various cathodes was examined under illumination and in the dark. Product selectivity control in the reduction by illumination was accomplished only when *p*-type semiconductor photocathodes were used. By estimating the electrophilicity of benzyl halides from their rate constants for methanolysis under illumination and in the dark, it was proposed that the mechanism for the selectivity control by illumination involves a photo-assisted process for the nucleophilic attack of carbanion intermediate species formed by the two-electron reduction of the benzyl halides to the unreacted ones as electrophiles.

INTRODUCTION

In electroorganic chemistry, important studies have been made toward the product selectivity control. Electrochemical factors controlling the selectivity are a variety of electrolytic conditions such as electrode potential, current density, solvent, supporting electrolyte, pH, electrode material, etc. Recently, auxiliary energy application has been regarded as a promising method for the selectivity control.¹⁻⁵ For instance, illumination to an electrolytic system should produce photochemically active species to affect the corresponding electrode process and to result in the selectivity control in the electrochemical reaction. However, the species formed by illumination are deactivated by metal electrodes, since they absorb the excitation energy of the species.^{6,7} The selectivity control by illumination, therefore, had been considered to be limited on the ordinary metal electrodes. On the other hand, the selectivity control by illumination may be able to be accomplished on semiconductor electrodes, since they absorb photoenergy directly from illumination while do not absorb the energy of the excited species.

Our first approach to this subject was made by application of illumination to electrochemical reduction of ketones on semiconductor cathodes and it was found that current efficiencies for the corresponding hydrodimeric and hydromonomeric products were affected by illumination only when both the ketone molecules and p-type semiconductor cathodes were excited.⁸ This fact indicates that the double excitation of the both substrate molecules and semiconductor electrodes is required for the product selectivity control. However, any clear information on photobehavior of the excited molecules and electrodes was not sufficiently obtained. In this situation, it should be important to demonstrate additional examples of the selectivity control and verify the mechanism of the control.

In the present work, electrochemical reduction of benzyl halides is examined, because the reduction affords the hydrodimeric and hydromonomeric products, in analogy with that of ketones. We describe here the illumination effect on the product selectivity in the reduction on various semiconductor cathodes (Scheme I).

Scheme I Electrochemical reduction of benzyl halides in protic media

R-()	Сн _г х	e /2e+H*	<u>1</u> R-₹	_>-Сн₂Сн₂ -√_>- н	/ п-{_}-Снз	
			ŀ	lydrodimeric product	Hydromonomeric product	
la-c				2а-с	3a-c	
	a :	R = H	X⊭Br	Benzyl bromide (1a	•)	
	b:	R = <i>p</i> -Me	X ⊭ Br	p-Methylbenzyl bro	p-Methylbenzyl bromide (1b)	
	c :	R = H	X ⊭ Ci	Benzyl chloride (1c)	

RESULTS AND DISCUSSION

Voltammetry

As a preliminary study, voltammetric measurements for the electrochemical reduction of benzyl bromide (1a) on various cathodes were carried out in an acetonitrile solution containing Bu_4NClO_4 and Bu_4HSO_4 under illumination and in the dark. Fig. 1 shows voltammetric curves on p-type

Dedicated to Professor Hsien-Ju Tien on the occasion of his 65th birthday.

semiconductor cathodes. Cathodic dark currents flowed due to high doping density of p-type semiconductor materials such as p-Si, p-InP and p-GaAs used. Curves under illumination were shifted to potentials more positive than those in the dark,⁹⁻¹³ and the positive shift was observed with either an ultrahigh pressure mercury lamp or a xenon lamp. This means that bandgap excitation of the semiconductor photocathodes takes place under illumination. Furthermore, photocurrents observed under illumination with the xenon lamp were larger than those with the ultrahigh pressure mercury lamp on the p-type semiconductor cathodes. This fact reveals that the illumination with the xenon lamp was more efficient than the mercury one for the bandgap excitation. In contrast, no photocurrents were observed on ntype semiconductor and Sn metal cathodes because they are not excited under the illumination (Fig. 2). Similar voltammetric results were obtained in our previous work in which product selectivities in electrochemical reduction of aro-



Fig. 1. Voltammetric curves for electrochemical reduction of benzyl bromide (1a) on (a) p-Si, (b) p-InP and (c) p-GaAs cathodes under illumination (by an ultrahigh pressure mercury lamp, —---; by a xenon lamp, — - —) and in the dark (----).



Fig. 2. Voltammetric curves for electrochemical reduction of benzyl bromide (1a) on (a) n-Si, (b) n-InP and (c) Sn cathodes under illumination by an ultrahigh pressure mercury lamp (-----) and in the dark (-----).

matic ketones were controlled on illuminated p-type semiconductor cathodes.⁸ Considering such results, selectivity in electrochemical reduction of benzyl bromides is expected to be controlled by illumination.

Photoelectrochemical Reduction of Benzyl Bromide

Results for the electrochemical reduction of benzyl halides on various cathodes under illumination and in the dark are summarized in Table 1. The reduction in an acetonitrile solution containing Bu₄HSO₄ as a proton source gave the corresponding hydrodimeric and hydromonomeric products in total current efficiencies ranging from 47 to 87%. Illumination for 1.5 h without passing electricity resulted in a complete recovery of the starting compound unreacted. This fact suggests that no photochemical reduction takes place under the electrolytic conditions used. In electrochemical reduction of benzyl bromide (1a), it is noteworthy that p-Si, p-InP and p-GaAs cathodes give the dimeric product along with the monomeric one under illumination, while no dimeric product is formed in the dark (Runs 1, 2 and 3, respectively). It is also noted that the selectivity on the p-InP and p-GaAs cathodes with larger bandgaps (ca. 1.4 eV corresponding to ca. 880 nm of wavelength for excitation) is higher than that on the p-Si one with a smaller bandgap (ca. 1.1 eV corresponding to ca. 1100 nm). On the other hand, no formation of the dimeric product was also observed on the corresponding n-type semiconductors such as n-Si and n-InP (Runs 4 and 5, respectively), which can not be excited when cathodically polarized, as well as on an Sn cathode (Run 6). This fact indicates that the product selectivity for the dimeric product is affected only on the *p*-type semiconductor photocathodes excited by illumination as well as that for pinacols formed in the photoelectrochemical reduction of aromatic ketones in our previous report.⁸

A light source employed in this work is an ultrahigh pressure mercury lamp (350 W) which irradiates spectral lines in the range of ca. 220 to 450 nm. A benzyl bromide molecule possesses an absorption maximum at 230 nm tailing to ca. 290 nm. As depicted in Fig. 3, this energy band overlapps the irradiation spectrum of the lamp so that the double excitation of both the cathode and benzyl bromide molecule takes place under illumination with the lamp. Hence, it is preliminarily stated that the double excitation causes the product selectivity preferential for the dimeric product.



Fig. 3. Absorption spectrum of benzyl bromide (1a) measured in acetonitrile (solid line) and irradiation spectrum of an ultrahigh pressure mercury lamp (dotted line).

 Table 1. Influence of Illumination on Selectivity for Dimeric Product Obtained in Electrochemical Reduction of Benzyl Halides on Various Cathodes

Run	Benzyl halide	Cathode	Selectivity ⁸ for dimeric product and total current efficiency ^b for the reduction/%		
			Under illumination ^c	Under illumination ^d	In the dark
1	Benzyl bromide (1a)	p-Si	4 (76)	0 (79)	0 (73)
2	Benzyl bromide (1a)	p-InP	15 (86)	2 (74)	0 (79)
3	Benzyl bromide (1a)	p-GaAs	30 (76)	3 (68)	0 (47)
4	Benzyl bromide (1a)	n-Si	0 (67)	e	0 (67)
5	Benzyl bromide (1a)	n-InP	0 (74)	e	0 (87)
6	Benzyl bromide (1a)	Sn	0 (67)	e	0 (67)
7	p-Methylbenzyl bromide (1b)	p-GaAs	59 (68)	9 (56)	4 (48)
8 ′	Benzyl chloride (1c)	p-GaAs	8 (80)	3 (60)	0 (63)

^a Proportion of current efficiency for dimeric product to total current efficiency.

^b In parentheses.

^c By a 350 W ultrahigh pressure mercury lamp (> 220 nm).

^d By a 300 W xenon lamp (> 280 nm).

^e Not determined.

In contrast to the mercury lamp, a xenon lamp used in our experiments exhibites the continuous spectral output covering over 280 nm. The illumination with the xenon lamp, therefore, should favor the bandgap excitation of the p-type semiconductor cathodes. This is consistent with the voltammetric results in which the xenon lamp affords larger photocurrents than the mercury one (Fig. 1). However, the light irradiated from the xenon lamp do not have energy high enough to excite benzyl bromide molecules, in spite of higher light intensity than that of the mercury one. As shown in Table 1 (Runs 1, 2 and 3), little amount of the dimeric product is formed and the monomeric product is actually a sole product on the p-type semiconductor cathodes illuminated with the xenon lamp. Such a slight photo-effect on the selectivity for the dimeric product is due to a very small overlap of the xenon lamp output with only the tailing absorption of benzyl bromide. These facts suggest that the excitation of benzyl bromide molecules also plays indispensable roles to the product selectivity control. Namely, the double excitation of both the electrode (p-type semiconductor) and the substrate (benzyl bromide) is inevitably required for the product selectivity control preferential for the dimeric product.

Photoelectrochemical Reduction of *p*-Methylbenzyl Bromide and Benzyl Chloride

As shown in Table 1, selectivities for the dimeric products in electrochemical reduction of p-methylbenzyl bromide (1b) and benzyl chloride (1c) were also affected by illumination (Runs 7 and 8, respectively). Compared with promotion of the dimer formation by illumination in the reduction of unsubstituted benzyl bromide (increased from 0 to 30% selectivity at Run 3), a more significant increase from 4 to 59% of selectivity was observed in the reduction of p-methylbenzyl bromide, whereas a smaller increase from 0 to 8% was indicated in the case of benzyl chloride. In order to explain such a difference in magnitude of the illumination effect, absorption characteristics of the benzyl halides are presented in Table 2. p-Methylbenzyl bromide is excited more effectively due to its larger absorption maximum and coefficient than unsubstituted benzyl bromide. Benzyl chloride, on the other hand, is not sufficiently excited because its absorption maximum is observed at so short wavelength that not only the xenon lamp but also the mercury one cannot cover. Taking into account these absorption characteristics of benzyl halides, it is clearly stated that the more effectively the substrate halides are excited, the higher selectivity for the dimeric products is obtained.

Mechanism for Photoelectrochemical Reduction of Benzyl Halides

There have been a number of studies on mechanisms of electrochemical reduction of benzyl halides.¹⁴⁻¹⁶ In the first step, one-electron transfer from the cathode to the substrate halide takes place to afford the corresponding radical species. In general, coupling reaction of the radical is relatively slow [Path (a) in Scheme II], since the fast second electron transfer converts the radical into a carbanion. The carbanion formed thus is predominantly protonated in protic media to produce the monomeric product, though only part of the carbanion may react with the substrate benzyl halide as a relatively weak electrophile to give the dimeric product in the dark [Path (c)]. This is a reason for the predominant formation of the monomeric product in the dark. Therefore, the carbanion is actually regarded as a reactive intermediate species controlling the product selectivity. In this point of view, if the electrophilicity of benzyl halides might be increased by illumination, the experimental results in Table 1 should be reasonably rationalized by Path (b). Concerning photochemical behavior of benzyl halides, it is known that a radical pair (I) is formed by an initial homolytic cleavage of the carbon-halogen bond under illumination and then subsequent intramolecular electron transfer takes place to afford an ion pair (II) (Scheme III).¹⁷⁻¹⁹ This excited ion pair should possess a higher electrophilicity than original halides in the dark. Therefore, it can be postulated that the process in photoelectrochemical reduction of benzyl halides involves a reaction of electrogenerated carbanion with more electrophilic benzyl halides excited by illumination.

In order to evaluate the electrophilicity enhanced by il-

Table 2. Absorption Characteristics of Benzyl Halides in Acetonitrile

Benzyl halide	Absorption maximum λ _{max} /nm	Absorption coefficient $\varepsilon \times 10^2$ /dm ³ mol ⁻¹ cm ⁻¹
Benzyl bromide (1a)	230	75.6
<i>p</i> -Methylbenzyl bromide (1b)	235	98.6
Benzyl chloride (1c) ^a	217	73.6

^a With a weak absorption at $\lambda_{max} = 266 \text{ nm}$ with $\varepsilon \times 10^2 = 3.87 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$.





Hydromonomeric product

Scheme III Possible mechanism for formation of dimeric product under illumination

$$R - (X - CH_2 X - hv) = \left[R - (CH_2 \cdot \cdot X) \right]^* \xrightarrow{\text{Electron transfer}} \left[R - (CH_2^{\oplus} X^{\odot}) \right]^*$$

$$(X : \text{Halogen}) \qquad I \qquad II$$

lumination, rate constants for methanolysis of benzyl halides were estimated and listed in Table 3. The rate constants (k) were calculated on the basis of pseudo first-order equation

$$kt = \ln \frac{[RX]_{\sigma}}{[RX]_{\sigma} - [ROCH_3]_{t}}$$
(RX: Benzyl halides) (1)

where t is the reaction time, $[RX]_o$ and $[ROCH_3]_t$ represent the initial concentration of benzyl halides and the concentration of benzyl methyl ethers formed at the time (t), respectively. In the dark, the methanolysis was very slow. The order of k's of the benzyl halides is 1b > 1a > 1c as shown in Table 3. Under illumination, a drastic increase in k's was observed in all the benzyl halides, but the order of k's does not change. The increasing selectivity was also given by the same order of 1b > 1a > 1c in good agreement with the absorption characteristics of the benzyl halides (See Table 2), regardless under illumination and in the dark.

The above results indicate that the promotion of dimer

formation by illumination is closely correlated with the increase of electrophilicity of benzyl halides, revealing a photo-assisted electrophilic reaction in the reduction process. Hence, it seems resonable to describe a mechanism for the product selectivity control in the reduction of benzyl halides as follows: In the dark, a benzyl anion is formed by

Table 3. Rate Constants for Methanolysis of Benzyl Halides in Methanol at 25 °C

Benzyl halide	Mode	Rate constant/ $\times 10^{-5} \text{ min}^{-1}$
Benzyl bromide (1a)	 Dark	8.8
Benzyl bromide (1a)	Illumination ^a	517
p-Methylbenzyl bromide (1b)	Dark	40
p-Methylbenzyl bromide (1b)	Illumination ^a	620
Benzyl chloride (1c)	Dark	0
Benzyl chloride (1c)	Illumination ^a	96

^a By a 350 W ultrahigh pressure mercury lamp.

two-electron reduction and then is quickly protonated to afford the corresponding monomeric product. The dimeric product was little formed under this condition. Under illumination, part of the benzyl anion can react with excited benzyl halide having higher electrophilicity, giving the corresponding dimeric product. This *photo-assisted* reaction leads to an increase in the selectivity for the dimeric product.

On an illuminated semiconductor photoelectrode, the selectivity control may be caused by local heating on the electrode surface⁵ or positive shift of electrode potential²⁰ (See Fig. 1). The local heating is due to non-radiative relaxation of photoexcited electrons and the bandgap excitation results in a change in electrode potential. If these factors could influence on the selectivity, it should not depend on wavelength. However, from the above experimental results and considerations, influence of the local heating and the electrode potential shift are excluded.

It is noted that the ion pair (II) of excited benzyl halides is quenched on conducting metal and *n*-type semiconducting cathodes unexcited, and consequently the product selectivity control could not occur even under illumination. Stating again as a main conclusion in this study, the double excitation of both the cathodes (*p*-type semiconductors) and the substrates (benzyl halides) is inevitably required for the product selectivity control.

EXPERIMENTAL SECTION

Preparation of Working Cathodes

p-Si, *p*-GaAs, *n*-Si and Sn cathodes were prepared as previously reported.⁸ *p*-InP (Sumitomo Electric Ind. Co.; Zn-doped low resistivity type of (100)-single crystal; thickness, 0.45 mm; carrier density, $4-6 \times 10^{18}$ cc) and *n*-InP (Sumitomo Electric Ind. Co.; Sn-doped low resistivity type of (100)-single crystal; thickness, 0.35 mm; carrier density, 1- 4×10^{18} cc) electrodes were ohmically contacted with Zn-Ga and In-Ga alloys, respectively. The back side of the electrodes was covered with a silicone resin insulating film. The working surface (1.0 cm²) was etched by immersing in concentrated H₂SO₄ - 30% H₂O₂ - H₂O (3:1:1) for 30 s at 0 °C, and then rinsed with distilled water before each experiment.²¹

Electrolysis

A divided quartz cell equipped with a working electrode (p-type, n-type semiconductor or Sn cathode) and a Pt wire counter electrode (anode) was used for the electrochemical reduction of benzyl halides (1.0 mmol) in 0.05 mol dm⁻³ Bu₄NClO₄ and 0.05 mol dm⁻³ Bu₄HSO₄/CH₃CN at 25 \pm 1 °C. The cathodic solution (20 cm³) was degassed for 20 min with nitrogen before each experiment. Preparative electrolyses were galvanostatically carried out at 10 mA cm⁻² of current density by passing 0.3 × 96500 C mol⁻¹ of electricity using a potentio/galvanostat (Hokuto Denko Co., HABF501).

Light Source

A 350 W ultrahigh pressure mercury lamp (San-ei Electric Co., Supercure-352S) and a 300 W xenon lamp (ILC Technology Co., LX-300F) with an UV reflector were used as light sources. The working cathode surface in a quartz cell was irradiated through an optical window (quartz, 2 mm thickness) by the lamp. The light was focused on the irradiated area of ca. 1 cm² by using a quartz lens.

Measurement of Rate Constants for Methanolysis of Benzyl Halides

Benzyl halides (1.0 mmol) were reacted in 20 cm³ of methanol (HPLC grade) for 200 min, using a quartz cell. The solution was purged with nitrogen and was kept at 25 ± 1 °C. The reaction was followed by estimating the formation of benzyl methyl ethers every 50 min. The plot of ln ([RX]/[RX]_o – [ROCH₃]_t) against t gave the rate constant k [See Eq. (1)].

Analysis of Products

All reagents as the starting compounds and standard samples except for 1,2-di(*p*-tolyl)ethane (2b) (supplied by Lancaster) were commercially supplied by Tokyo Kasei Co. Benzyl bromide (1a) unreacted and toluenes (3a and 3c) formed were analyzed by HPLC (15 cm Inertsil C8 column; CH₃CN-H₂O, 35:65 vol. ratio) with an UV detector. Benzyl chloride (1c), *p*-methylbenzyl bromide (1b) unreacted and *p*-xylene (3b) formed were also analyzed by HPLC (30 cm Inertsil ODS-2 column; CH₃CN-H₂O, 60:40 vol. ratio) with an UV detector. Bibenzyls (2a and 2c) and 1,2-di(*p*tolyl)ethane (2b) formed were analyzed by GC (2 m PEG 20M column at 160 °C) with an FID. Analyses for the methanolysis products of benzyl halides were performed by GC (2 m OV-17 column at 90 °C).

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Key Words

Product selectivity; Semiconductor photoelectrode; Benzyl halide reduction.

REFERENCES

- 1. Matsuda, K.; Atobe, M.; Nonaka, T. Chem. Lett. 1994, 1619.
- 2. Atobe, M.; Matsuda, K.; Nonaka, T. Denki Kagaku 1994, 62, 1298.
- 3. Atobe, M.; Nonaka, T. Chem. Lett. 1995, 669.
- 4. Atobe, M.; Matsuda, K.; Nonaka, T. *Electroanalysis* 1996, 8, 784.
- 5. Tsunashima, K.; Nonaka, T. Chem. Lett. 1995, 862.
- 6. Gerischer, H.; Willig, F. Top. Curr. Chem. 1976, 61, 31.
- 7. Gerischer, H. J. Electrochem. Soc. 1978, 125, 218C.
- 8. Tsunashima, K.; Nonaka, T. Electrochim. Acta 1997, 42, 2081.

- 9. Laser, D.; Bard, A. J. J. Phys. Chem. 1976, 80, 459.
- 10. Koval, C. A.; Torres, R. J. Am. Chem. Soc. 1993, 115, 8368.
- 11. Quinlan, K. P. J. Electroanal. Chem. 1994, 369, 121.
- Beley, M.; Collin, J.-P.; Sauvage, J.-P.; Petit, J.-P.; Chatier, P. J. Electroanal. Chem. 1986, 206, 333.
- 13. Meulenkamp, E. A.; de Wit, A. R. *Electrochim. Acta* 1996, 41, 109.
- 14. Fry, A. J. Synthetic Organic Electrochemistry, 2nd ed.; Wiley: New York, 1989; Chapter 5.
- 15. Grimshaw, J.; Ramsey, J. S. J. Chem. Soc. (B) 1968, 60.
- 16. Fry, A. J.; Porter, J. M.; Fry, P. F. J. Org. Chem. 1996, 61, 3191.
- 17. McNeely, S. A.; Kropp, P. J. J. Am. Chem. Soc. 1976, 98, 4319.
- Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. J. Am. Chem. Soc. 1976, 98, 8135.
- 19. Cristol, S. J.; Greenwald, B. E. Tetrahedron Lett. 1976, 2105.
- Cheng, P.-C.; Nonaka, T. J. Electroanal. Chem. 1989, 269, 223.
- 21. Quinlan, K. P.; Rai, A. K.; Wittberg, T. N. J. Electrochem. Soc. 1994, 141, 1161.