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Ultrasonic Effects on Electroorganic Processes.[1)] Product-selectivity in Electroreduction of Benzaldehydes

Kazuya MATSUDA, Mahito ATOBE, and Tsutomu NONAKA*
Department of Electronic Chemistry, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

Ultrasonic irradiation to electroorganic systems resulted in significant effects on product-selectivity in the reduction of benzaldehydes and others. By the irradiation, the selectivity of reduction products formed by consuming fewer electrons was drastically enhanced. The effects were rationalized as due to not cavitation but agitation of electrolytic solutions by ultrasonic waves.

Significant effects of ultrasonic irradiation on chemical reactions are well known in a variety of systems. In general, the effects are rationalized as due to cavitation and agitation in homogeneous and heterogeneous reaction systems, respectively. Although electrochemical reactions are typical heterogeneous ones between solid electrodes and liquid electrolytes, the application of ultrasonic irradiation to them has been limited so far except for electroplating[2)] and sacrificial anodes.[3, 4)]

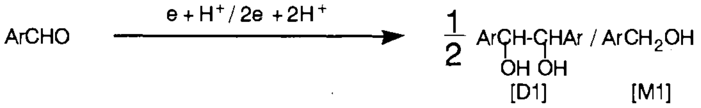
Ultrasonic irradiation effects on electrochemical systems were reported in copper powder preparation from a Cu (II) / EDTA bath,[5)] chlorine formation from NaCl and HCl baths,[6)] generation of chalcogen anions from S, Se and Te anodes,[7)] electrochemiluminescence enhancement,[8)] and anodic preparation of polythiophene films.[9, 10)] The effect has been very rarely reported in electroorganic synthesis. Mason *et al*. reported that product-distribution in the Kolbe electrolysis of cyclohexanecarboxylic and phenylethanoic acids was considerably affected by ultrasonic irradiation.[2)]

From the above point of view, we aimed to explore a much clearer effect of ultrasonic irradiation controlling product-selectivity in the electroreduction of benzaldehydes in the present work.

An H-shaped divided cell equipped with a lead disc cathode (diameter, 3.3 cm) and a platinum anode was used for electroreduction of benzaldehydes (3 mmol) in a 0.25 M H_2SO_4/ 50% CH_3OH catholyte (70 cm^3). The cell was placed in an ordinary ultrasonic cleaning bath (100 W, 36 kHz) filled with water, or an ultrasonic horn (a titanium lod with 0.6 cm diameter) connected with a PZT oscillator (0 - 20 W, 20 kHz) was inserted into the cathode chamber. In either case, the cathode surface was positioned perpendicularly to propagating direction of ultrasonic wave. The electrolysis was carried out galvanostatically at a current density of 20 mA cm^{-2} by passing 0.5 mol electron mol^{-1} of charge at 20 - 25 °C.

Starting benzaldehydes, hydrodimeric and hydromonomeric products were analyzed by gas chromatography. Dimethyl maleate, benzyl bromide and benzoic acid (3 mmol) were also electroreduced in a manner similar to that for benzaldehyde, except for composition of cathodic solutions (See foot notes of Table 3).

It is well known that electroreduction of aromatic aldehydes gives the corresponding dihydrobenzoins (hydrodimeric products, D1) and benzyl alcohols (hydromonomeric products, M1) as shown in the following equation:



$$\mathrm{ArCHO} \xrightarrow{e + H^+ / 2e + 2H^+} \frac{1}{2}\ \underset{[\mathrm{D1}]}{\underset{\mathrm{OH}}{\mathrm{ArCH}}\text{-}\underset{\mathrm{OH}}{\mathrm{CHAr}}} \ / \ \underset{[\mathrm{M1}]}{\mathrm{ArCH_2OH}}$$

In previous work,[10] we found that product-selectivity ([D1] / [M1]) depends on the magnitude of stirring of catholyte. In order to examine an ultrasonic irradiation effect on the selectivity, in this work, the electroreduction of benzaldehydes was carried out using three different stirring modes such as still standing, mechanical stirring by a rotating magnet bar, and ultrasonic irradiation.

As shown in Table 1, benzyl alcohol (M1) was a main product in still standing of the catholyte (Run 1), while dihydrobenzoin (D1) became a main product and the product-selectivity was reversed when the catholyte was mechanically stirred (Run 2). More interestingly, when the electrolysis was carried out by placing the cell in an ultrasonic cleaning bath (100 W, 36 kHz), the value of [D1] / [M1] increased so remarkably that D1 could be considered as a sole product except for unknown by-products (Run 3). The selectivity somewhat decreased at a position of the cell more apart from the bottom of the bath (Run 4). Regardless of ultrasonic irradiation, the stereochemistry (*dl* / *meso* ratio) of D1 was not influenced and large amount (ca. 30%) of the unknown by-products, which seem to be complex mixtures of hydroquinoid-type dimeric products,[11, 12] were formed.

Table 1. Electroreduction of benzaldehyde

Run	Stirring mode	Current efficiency for [D1] + [M1] /%	Selectivity [D1] / [M1]	Yield of unknown products /%
1	Still	36	0.6	26
2	Mechanical[a)]	63	2.5	29
3	Ultrasonic[b)]	65	34	30
4	Ultrasonic[c)]	65	24	32

a)Stirred by a rotating magnet bar. b)Cathode was positioned 6 cm apart from the bottom of an ultrasonic cleaning bath (100 W, 36 kHz). c)Cathode was positioned 8 cm apart from the bottom of the bath.

As shown in Table 2, a significant ultrasonic irradiation effect on the product-selectivity was observed in the reduction of p-methylbenzaldehyde (Runs 5 - 7) similarly to benzaldehyde. In addition, p-methylbenzaldehyde did not give any unknown by-products because its p-position is blocked by a methyl group.[13] Influence of ultrasonic power on the selectivity was also examined using an ultrasonic horn inserted into the catholyte. The selectivity ([D1] / [M1]) was increased with an increase in the power (Runs 8 - 10). An increase in distance between the cathode and the horn caused a decrease in the selectivity (Runs 9 and 11).

In the previous work,[13] we established a theoretical method for estimating a mass transport coefficient (k_m) of p-methylbenzaldehyde in acidic solutions from an [D1] / [M1] value obtained in the electroreduction. Values of k_m's obtained by simulation using this method are given in Table 2 (Runs 6 - 10). On the other hand, k_m can be easily obtained directly from a limiting current density in a case where it appears on a potential-current curve in voltammetry. Fortunately, the limiting current could be observed as shown in Fig. 1. Thus, k_m's at different ultrasonic powers (4 - 12 W) could be obtained (See Runs 6 and 8 - 10) and agreed with the corresponding values estimated by the theoretical simulation within usual limit of variation.

The above fact suggests that the ultrasonic irradiation effect on the selectivity is resulted in not by the

Table 2. Electroreduction of p-metylbenzaldehyde

Run	Stirring mode	Current efficiency for [D1] + [M1] /%	Selectivity [D1] / [M1]	Mass transport coefficient (k_m) $/10^{-3}$ cm s^{-1} Simulated a)	Found b)
5	Still	35	0.0	2.8	-
6	Mechanical c)	74	1.0	3.9	3.7
7	Ultrasonic d)	77	>100	9.0	-
8	Ultrasonic e, f)	72	6.3	6.2	5.5
9	Ultrasonic e, g)	80	12	7.0	7.0
10	Ultrasonic e, h)	89	24	8.4	8.0
11	Ultrasonic e, i)	70	7.5	6.5	-

a)From [D1] / [M1] values. b)From limiting current densities on potential-current curves. c)Stirred by a rotaing magnet bar. d)Cathode was positioned 6 cm apart from the bottom of an ultrasonic cleaning bath (100 W, 36 kHz). e)The cathode was positioned 1.7 cm apart from the top of an ultrasonic horn (20 kHz). f)Ultrasonic power, 4 W. g)Ultrasonic power, 8 W. h)Ultrasonic power, 12 W. i)The cathode was positioned 3.4 cm apart from the top of the horn (20 kHz).

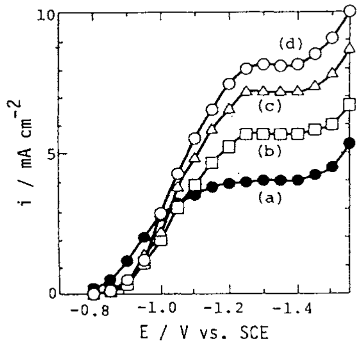


Fig. 1 Potential-current curves of p-methylbenzaldehyde (10 mM) at a lead cathode (2 cm^2) in 0.25 M H_2SO_4 / 50% CH_3OH.
Stirring mode: (a) Mechanical, (b) Ultrasonic (4 W), (c) Ultrasonic (8 W), and (d) Ultrasonic (12 W).

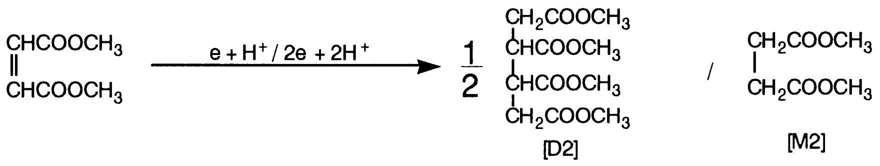
Table 3. Electroreduction of dimethyl maleate, benzyl bromide and benzoic acid

Run	Starting compound	Stirring mode	Current efficiency for [D2] + [M2], [D3] + [M3] or [M4] + [M5] /%	Selectivity [D2] / [M2], [D3] / [M3] or [M4] / [M5]
12	Dimethyl maleate a)	Still	66	0.0
13	Dimethyl maleate a)	Mechanical b)	93	0.3
14	Dimethyl maleate a)	Ultrasonic c)	96	0.4
15	Benzyl bromide d)	Still	40	0.0
16	Benzyl bromide d)	Mechanical b)	40	0.3
17	Benzyl bromide d)	Ultrasonic c)	40	0.9
18	Benzoic acid e)	Still	1	0.0
19	Benzoic acid e)	Mechanical b)	17	0.2
20	Benzoic acid e)	Ultrasonic c)	54	1.5

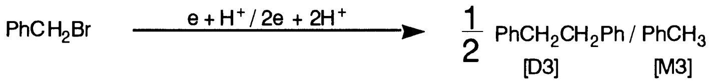
a) Electrolyzed at a lead cathode in an aqueous 0.025 M KH_2PO_4 / 0.025 M Na_2HPO_4 / 0.5 M NaCl solution. b)Stirred by a rotating magnet bar. c)The cathode was positioned 1.7 cm apart from the top of an ultrosonic horn (12 W, 20 kHz). d)Electrolyzed at a lead cathode in a methanolic 0.5 M $(C_2H_5)_4NBr$ solution. e)Electrolyzed at a lead cathode in an aqueous 0.05 M H_2SO_4 / 0.2 M citric acid solution.

cavitation but by the agitation.

The effect of ultrasonic irradiation on product-selectivity was also examined in the electroreduction of organic compounds other than benzaldehydes under similar conditions except for composition of electrolytic solutions. As shown in Table 3 (Runs 12 - 17), the formation of hydrodimeric products, D2 and D3 was accelerated in the reduction of dimethyl maleate and benzyl bromide under ultrasonic irradiation similarly to the case of benzaldehydes.



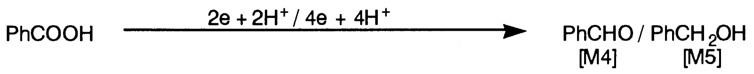
$$\begin{array}{c}CHCOOCH_3\\ \|\\ CHCOOCH_3\end{array} \xrightarrow{e + H^+ / 2e + 2H^+} \frac{1}{2}\underset{[D2]}{\begin{array}{l}CH_2COOCH_3\\ |\\ CHCOOCH_3\\ |\\ CHCOOCH_3\\ |\\ CH_2COOCH_3\end{array}} \Bigg/ \underset{[M2]}{\begin{array}{l}CH_2COOCH_3\\ |\\ CH_2COOCH_3\end{array}}$$



$$PhCH_2Br \xrightarrow{e + H^+ / 2e + 2H^+} \frac{1}{2}\underset{[D3]}{PhCH_2CH_2Ph} / \underset{[M3]}{PhCH_3}$$

Considering the above results, it is concluded that ultrasonic irradiation promotes the formation of the hydrodimeric products, in other words, the reduction products formed by consuming fewer electrons.

The reduction of benzoic acid proceeds in a quite different manner from the above, since it gives not the corresponding hydrodimeric product but hydromonomeric 2- and 4-electronreduction products such as benzaldehyde (M4) and benzyl alcohol (M5) (Runs 18 - 20).



$$PhCOOH \xrightarrow{2e + 2H^+ / 4e + 4H^+} \underset{[M4]}{PhCHO} / \underset{[M5]}{PhCH_2OH}$$

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