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Ultrasonic Effects on Electroorganic Processes. Part 22. Cathodic Crossed Hydrocoupling of Acetone with Acrylonitrile

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The ultrasonic effects on the cathodic-crossed hydrocoupling of acetone with acrylonitrile were examined. The total current efficiency of all products in the cathodic reduction of a mixture of acetone and acrylonitrile was little influenced by ultrasonic irradiation, while the product selectivity for crossed hydrocoupling products formed in the cathodic reduction was significantly increased by irradiation. This ultrasonic effect could be rationalized as being due to mass-transport promotion of acrylonitrile molecules as an electrophile to the cathode surface from the bulk of the electrolytic solution by the ultrasonic irradiation. Thus, the ultrasonic effect can be purposively applied to control the product selectivity in the crossed coupling reaction.

The application of ultrasound to chemical processes has received much attention from both fundamental and practical aspects.[1–10] A high-speed micro-jet stream generated by ultrasonic cavitation in a liquid is known to accelerate heterogeneous reactions on a solid surface by promoting mass transport in the solid-liquid interface.[1–3,5,8] An electrochemical reaction is one of the typical heterogeneous processes; therefore, ultrasonic effects on it seem to be very attractive to be investigated. In fact, recent sonoelectrochemical studies have been extensively reported in variety of areas, such as electrochemical measurement, kinetics, deposition (including electroplating), synthesis, and gas evolution.[7,8]

On the other hand, a number of electrochemical bimolecular reactions have been developed, some of which were used for syntheses in laboratories and industries, since the processes are effective means for not only constructing carbon-carbon bonds, but also for introducing functional groups into a carbon skeleton.[11,12] From this point of view, we have been interested in the application of ultrasounds to electrochemical bimolecular reactions, such as the cathodic hydrocoupling of carbonyl compounds[13–18] and olefins.[13,19] We have so far found significant ultrasonic effects upon an increase in the current efficiency and product selectivity. In this paper we report that the product selectivity for crossed hydrocoupling products, formed in a cathodic reduction of a mixture of acetone and acrylonitrile, is clearly increased under ultrasonic irradiation. Thus, this paper represents the first report of ultrasonic effects on a crossed-coupling reaction between two different kinds of compounds.

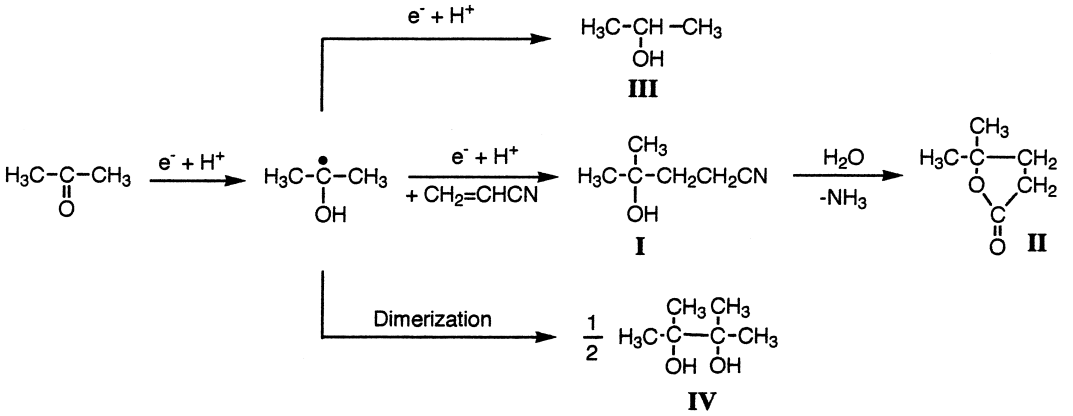
Experimental

An H-shaped divided cell equipped with a lead (99.9% pure) disc cathode (Diameter, 3.3 cm) and a platinum plate anode was used for the reduction of acetone in the presence of acrylonitrile. Unless otherwise stated, the electrolysis was carried out according to the following procedure. A catholyte (100 $\mathrm{cm^3}$ of 0.5 M H_2SO_4 aqueous solution; 1 M = 1 mol $\mathrm{dm^{-3}}$) containing acetone (10 M) and acrylonitrile (10 mM) was kept constant at 25 °C by using a cooling bath. Electrolysis was galvanostatically conducted by passing 3.0×10^{-3} F $\mathrm{mol^{-1}}$ based on acetone at a current density of 20 mA $\mathrm{cm^{-2}}$. A stepped horn (titanium rod with 1.9 cm diameter) connected with a PZT oscillator (20 kHz) was inserted into the catholyte. The output power of ultrasound was determined by an adiabatic measurement of the temperature raise of sonicated water.[20] The working electrode surface was positioned perpendicularly to the propagating direction of ultrasonic waves, 2.0 cm apart from the top of the horn. The reduction products were analyzed by GC with a PEG 1540 column at 60–160 °C.

Results and Discussion

It is known that the cathodic reduction of acetone with acrylonitrile gives a mixture of the corresponding crossed hydrocoupling products (I and II), as shown in Scheme 1.[21–23] In addition, non-crossed hydrocoupling products (III and IV) are also formed by the one- and two-electron reduction of acetone, respectively. In the present work, this reaction was used to examine the ultrasonic effects on the crossed-coupling reaction.

Table 1 shows the total current efficiency of all products (I, II, III, and V) and the product selectivity for the crossed hydrocoupling products (I and II) based on the total yield of products I, II, III, and V. The current efficiency and product selectivity were examined under three different conditions, such as still standing, mechanical stirring, and ultrasonic irradiation. The high, medium, and low selectivities were obtained under the following reaction modes: ultrasonic irradiation, mechanical stirring, and still standing, respectively, although the efficiency was little influenced by the reaction mode. In addition, the selectivity was greatly increased with an increase in the ultrasonic power. This result implies that the selectivity apparently depends on the agitation intensity of the solution; i.e. mass transport in a solid–liquid interface is particularly and remarkably



Scheme 1. Mechanism for the cathodic reduction of a mixture of acetone and acrylonitrile.

Table 1. Total Current Efficiency and Product Selectivity for the Crossed Hydrocoupling Products in the Cathodic Reduction of a Mixture of Acetone and Acrylonitrile

Reaction mode	Current efficiency /%	Product selectivity /%
Still	33	21
Mechanical[a)]	41	26
Ultrasonic (15 W)	33	39
Ultrasonic (25 W)	37	54
Ultrasonic (38 W)	41	59

a) Stirred by a propeller (1000 rpm).

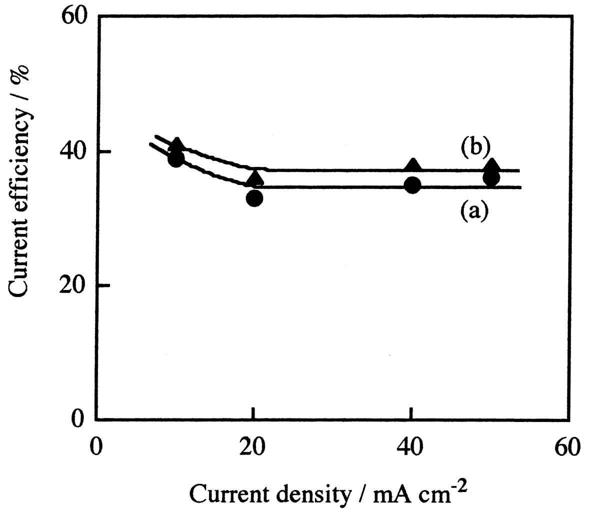


Fig. 1. Relationship between the total current efficiency of all products in the cathodic reduction of a mixture of acetone and acrylonitrile and the current density on the cathode under (a) still standing and (b) ultrasonic irradiation (25 W).

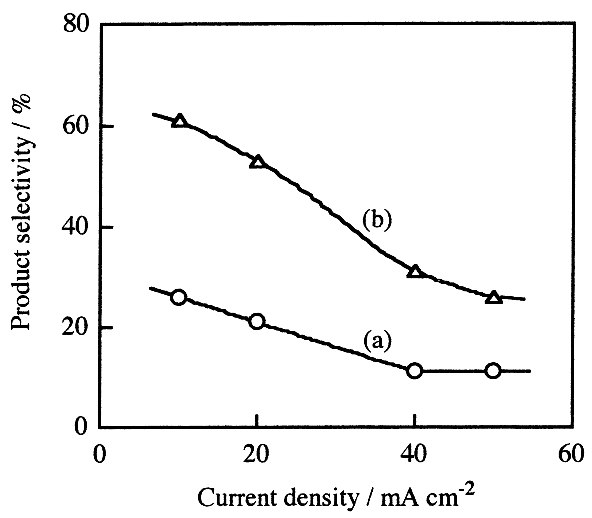


Fig. 2. Relationship between the product selectivity for the crossed hydrocoupling products and the current density on the cathode under (a) still standing and (b) ultrasonic irradiation (25 W).

increased under ultrasonic irradiation, where the mass transport is greatly promoted by a high-speed micro-jet stream generated by ultrasonic cavitation.[17,19,21–23]

Figures 1 and 2 show the total current efficiency and the product selectivity for the crossed hydrocoupling products, respectively, at various current densities. The current efficiency is not influenced by the current density on the cathode regardless of the presence or absence of ultrasonic irradiation, as shown in Fig. 1. Moreover, a slight increase in the current efficiency under ultrasonic irradiation was observed. On the other hand, Fig. 2 indicates that the product selectivity decreased with an increase in the current density either under irradiation or still standing. However, the selectivity under irradiation is apparently higher than that under still standing over wide ranges of the current density.

As mechanistically discussed below, the ultrasonic effect observed in the product selcectivity for the crossed coupling products is attributed to the promotion of the mass transfer of acetone and/or acrylonitrile molecules to the cathode surface from a cathodic bulk solution. Mass transport is also promoted by an increase in the concentration of the starting materials in electrolytic solutions. However, the product selectivity for the crossed hydrocoupling products was not affected by the acetone concentration over the wide range of 2–10 M under both still standing and ultrasonic irradiation. This fact indicates that the selectivity is not controlled by the mass transport of acetone molecules under the present electrolytic conditions.

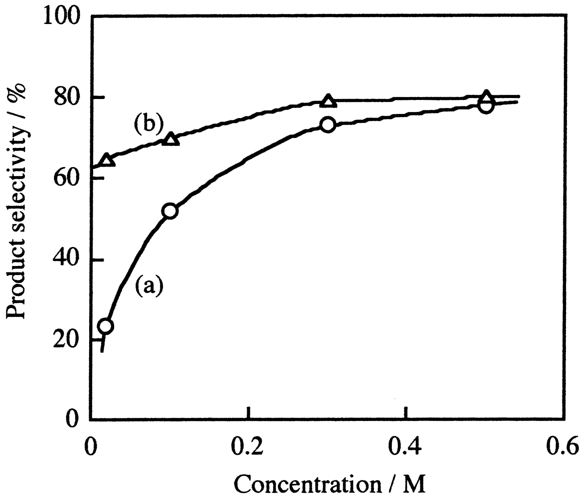


Fig. 3. Relationship between the product selectivity for the crossed hydrocoupling products and the concentration of acrylonitrile under (a) still standing and (b) ultrasonic irradiation (25 W).

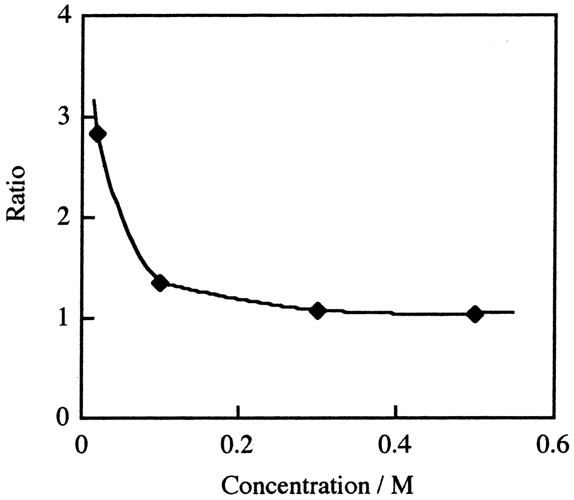


Fig. 4. Relationship between ratio of the product selectivity for the crossed hydrocoupling products under ultrasonic irradiation (25 W) to that under still standing and the concentration of acrylonitrile.

On the other hand, Fig. 3 shows the relationship between the product selectivity for the crossed hydrocoupling products and the concentration of acrylonitrile. The selectivity is increased along with an increase in the concentration of acrylonitrile regardless of the presence or absence of ultrasonic irradiation. However, it is noted that the difference between the selectivity under ultrasonic irradiation and that under still standing seems to be small at a high concentration. This fact suggests that the increase in the selectivity under ultrasonic irradiation is more significant at a lower concentration of acrylonitrile. Hence, the real magnitude of such a significance of the increase should be evaluated using the ratio of the selectivity under irradiation to that under still standing. As shown in Fig. 4, the selectivity ratio for the crossed hydrocoupling products is extreamely high at low concentration. Therefore, the ultrasonic effect on the product selectivity is due to the promotion of the mass transport of acrylonitrile molecules as an electrophile to the electrode surface from the bulk solution by the irradiation.

Thus, the ultrasonic effect can be purposively applied to control the selectivity in the crossed coupling reaction.

Conclusion

A significant ultrasonic effect on the increase in the product selectivity for the crossed hydrocoupling products was found in the cathodic reduction of a mixture of acetone and acrylonitrile. The ultrasonic effect can be rationalized based on the promotion of the mass transport of acrylonitrile molecules as an electrophile to the electrode surface from the bulk solution by ultrasonic irradiation.

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