

Ultrasonic Effects on Electroorganic Processes. Part 9. Current Efficiency and Product Selectivity in the Electroreduction of Alkyl Halides to Alkyl Stannanes at a Reactive Tin Cathode

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The ultrasonic effects on the electroreduction of methyl and allyl halides (RX) to the corresponding stannanes (R_3SnSnR_3 and R_4Sn) at a reactive (consumable) tin cathode were examined. The current efficiency and product selectivity for the reduction were found to be greatly affected by ultrasonic irradiation. For instance, the selectivity for $(CH_3)_3SnSn-(CH_3)_3$ to $(CH_3)_4Sn$ from CH_3I was significantly increased under irradiation. This fact is rationalized as being due to because the intermediate species $[(CH_3)_3Sn\cdot]$ formed by the primary one-electron reduction of CH_3I are activated for their coupling by mobilization on/from the cathode surface under irradiation. On the other hand, the ultrasonic effects on the reduction of CH_3Br and C_3H_5Br seemed to be slightly different from those in the reduction of CH_3I .

In recent years, the ultrasonic effects on electrochemical processes have received much attention,^{1–3)} since the processes are typical heterogeneous reactions at solid (electrode)–liquid (electrolytic solution) interfaces, and should be greatly affected by the mass transport of the substrate and by intermediate species to and from the interfaces. The mass transport should be promoted by ultrasonic cavitation and/or agitation. However, ultrasonic waves have not been applied to practical electrochemical processes, except for electroplating.^{1,4–14)} More recently, some interesting studies on ultrasonic effects in a variety of electrochemical fields have been reported as follows: measurements,^{2,15–40)} mass-transport phenomena,^{15,22–35,41,42)} electron-transfer kinetics,^{39,41)} luminescence,^{43–45)} metal-powder deposition,^{30,46,47)} gas electrodes,^{16–18,48)} organic synthesis,^{1,3,34–36,41,42,49–59)} polymerization,^{1,20,60–66)} sacrificial anodes,^{60,67,68)} and metal oxide-film formation.⁶⁹⁾

Controls of the current efficiency and product selectivity are important in synthetic electrochemistry. Walton et al.^{1,53)} and Fry et al.⁵⁵⁾ reported some influences of ultrasound on the product selectivity in the electrooxidation (Kolbe electrolysis) of carboxylates and the electroreductive silylation of dihalogenoalkanes, respectively. In our previous work, significant ultrasonic effects on the current efficiency and/or product selectivity were also found in the reduction of aldehydes, ketones, olefins, and carboxylic acids; these effects could be rationalized experimentally and theoretically as being due to the promotion of the mass transport of these substrate molecules to the electrode surface from the bulk solution by ultrasonic waves.^{33–35,41,42,58,59)} For all the above-mentioned electroreactions, ordinary (unconsumed) electrodes were used.

On the other hand, in a previous paper⁴¹⁾ we reported a unique ultrasonic effect on a copper anode dissolving in car-

boxylic acid solutions as Cu^{2+} to give the corresponding cupric carboxylates. In the present work a consumable tin cathode, which reacts stoichiometrically with alkyl halides to form the corresponding hexaalkyldistannanes and tetraalkylstannanes, as shown in Scheme 1, was used under ultrasonic irradiation. This was an extensive study dealing with ultrasonic effects involving a consumable cathode, following our preliminary short communication.⁵⁷⁾ In this reduction, the ultrasonic effect seems to be mechanistically quite different from that in the anodic dissolution of copper.

Experimental

An H-type divided cell was equipped with a glass frit diaphragm, a tin-plate cathode (2×2 cm), a platinum anode, an ultrasonic stepped horn (Titanium alloy rod; diameter, 6 mm), a stirring magnet bar, a balloon, and a thermistor, as shown in Fig. 1. The cell was cooled by circulating cold water in a thermostated bath. Unless otherwise stated, the electrolysis was carried out according to the following procedure. A catholyte (DMF, 30 cm³) containing tetrabutylammonium perchlorate (0.25 M, 1 M = 1 mol dm⁻³) and alkyl halide (RX, 0.5 M) was kept at $25 \pm 2^\circ C$ during electrolysis, and was not mechanically stirred. The electrolysis was carried out galvanostatically at 10 mA cm⁻² by passing 0.1 F mol⁻¹ (1 F = 96480 C) based on RX.

An ultrasonic generator (Power Sonic Model 50, YAMATO) with a PZT oscillator (20 kHz) and a stepped horn was used for ultrasonic irradiation during a electrolysis. The ultrasound intensity (power level) is indicated by the input power to the oscillator in this paper. The output power from the horn was estimated to be more than 95% of the input power, according to a calibration performed by the manufacturer. Usually, in this work, 17 W of the input power, which corresponds to ca. 60 W cm⁻² of the output power, was used, unless stated otherwise.

The reduction products, such as methyl tin and allyl tin compounds, were analyzed by GC (PEG 6000 column at 60–100 °C) and HPLC (Ultron S-C18 column, H₂O : CH₃CN = 1 : 3 v/v), re-

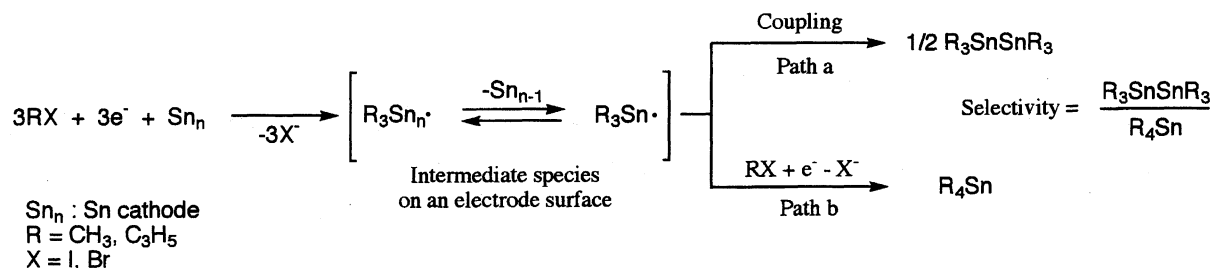
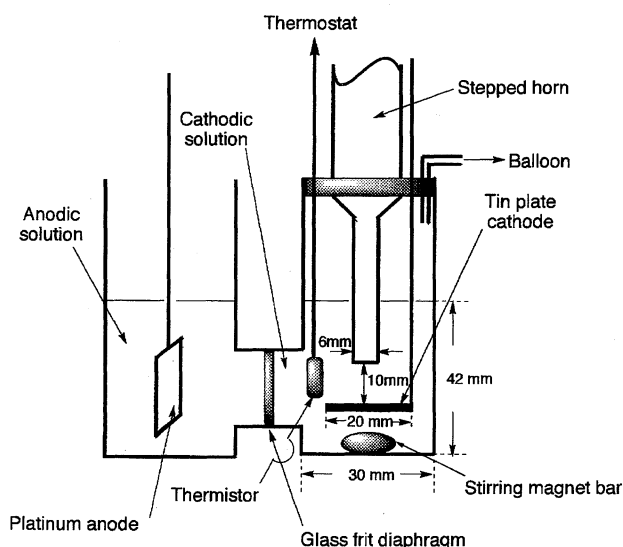
Scheme 1. Electroreduction of alkyl halides to the corresponding alkyl stannanes at a reactive tin cathode.⁷⁰⁻⁷⁴⁾

Fig. 1. Electrolytic cell for the electroreduction of alkyl halides at a reactive tin cathode under ultrasonic irradiation.

spectively. The current efficiency refers to the organotin products. Hydrocarbons as minor products were qualitatively analyzed.

Results and Discussion

It is known that the electroreduction of methyl and allyl halides (RX) on a reactive (consumable) tin cathode gives the corresponding stannanes (R₄Sn) and/or distannanes (R₃SnSnR₃) via absorbed intermediate species (trialkylstannyl radicals: R₃Sn· and R₃Sn_n·),⁷⁰⁻⁷⁴⁾ as shown in Scheme 1. In the present work, this reaction was used as a model for examining ultrasonic effects in the formation of organotin products from a consumable tin cathode.

Scheme 1 demonstrates a simplified reaction mechanism for the reduction of RX to R₃SnSnR₃ and R₄Sn on the tin cathode. However it is likely that the mechanism is actually more complicated.⁷⁰⁻⁷⁴⁾ For instance, a plausible explanation for Path a (Scheme 1) is that free R₃Sn· radicals undergo coupling whilst diffusing toward the bulk of the electrolytic solution. Ulery⁷¹⁾ and Brown et al.⁷³⁾ describe that the radicals can diffuse on the cathode surface. On the other hand, a detailed explanation for Path b (Scheme 1) has not been given so far. In any case, though the entire mechanism has not been completely verified, it can be stated that radicals mobilized from/on the cathode prefer Path a leading to R₃SnSnR₃, while those fixed on the cathode undergo a second electron-transfer, leading to the formation of R₄Sn in

Path b (Scheme 1). Ultrasonic irradiation to the cathode may help to mobilize them.

Fleishmann et al.⁷⁰⁾ and Ulery⁷²⁾ reported that only methyl and allyl halides among a variety of halides gave the corresponding organotin products along with small amounts of the hydrocarbons, while the other halides (ethyl, butyl, and benzyl) gave only hydrocarbons. In fact, these phenomena could be reproduced in our preliminary investigation. Therefore, ultrasonic effects on the reduction of methyl and allyl halides to the organotin products were purposively examined in this study. Although the above-mentioned difference between methyl and allyl halides and the others might be explained on the basis of C-Sn bond formation on the tin cathode surface,⁷¹⁻⁷³⁾ the mechanism has not been clarified.

In the reduction of methyl iodide, the current efficiency was calculated based on the total amount of the organotin products [(CH₃)₃SnSn(CH₃)₃ + (CH₃)₄Sn] formed. Any weight loss of the tin cathode during the electrolysis was almost equal to the amount of tin contained in the products, as shown in Table 1. This suggests that ultrasonic erosion of the tin cathode was insignificant.

When no current was passed under irradiation, no reduction products were formed, and only a negligibly small amount of weight loss of the tin cathode was observed. This fact suggests that the reduction of methyl iodide to the corresponding organotin compounds requires passage of a current, and that ultrasonic erosion does not practically take place.

Figure 2 shows the efficiency and selectivity for the formation of hexamethyldistannane [(CH₃)₃SnSn(CH₃)₃] in the electroreduction of methyl iodide in DMF under ultrasonic irradiation at different powers (0-17 W). The efficiency decreased along with an increase in the power. This ultrasonic effect is contrary to that observed previously in the electroreductive dimerization of a variety of organic compounds at ordinary (unconsumable) cathodes.^{33-35,58,59)} The increase in the efficiency at ordinary cathodes under irradiation

Table 1. Amount of Tin in Organotin Products and Weight Loss of Tin Cathode in the Reduction of Methyl Iodide (1.0 M)

Ultrasonic power/W	Amount of tin in organotin products/mg	Weight loss of tin cathode/mg
0	55	58
6	55	58
17	51	53

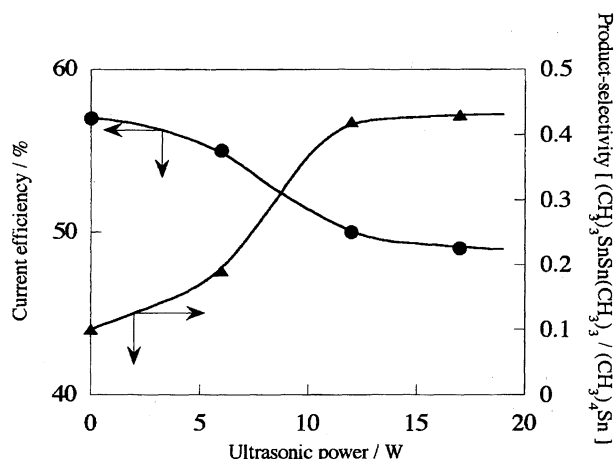


Fig. 2. Current efficiency and product selectivity [(CH₃)₃SnSn(CH₃)₃ / (CH₃)₄Sn] in the electroreduction of methyl iodide (1.0 M) under ultrasonic irradiation with various powers (0–17 W).

tion was rationalized as being due to a significant promotion of the mass transport of the reactant molecules to the electrode surface from the bulk solution by ultrasonic agitation. Hydrocarbons (CH₄ and C₂H₆) derived from the reduction of CH₃I were detected in the DMF catholyte by GC-MS. On the other hand, the reductive decomposition of the supporting salt (Bu₄NClO₄) to Bu₃N was suppressed under irradiation. Yeager et al.¹⁸⁾ reported that the formation of gaseous products is promoted by ultrasounds. Hence, the formation of hydrocarbons might be more preferably promoted than that of the organotin products under irradiation. This is plausible explanation for the decrease in the efficiency for the organotin products with an increase in the ultrasonic power.

On the other hand, the selectivity was increased along with an increase in the ultrasonic power, as shown in Fig. 2. This ultrasonic effect is analogous to that observed in the reduction of carbonyl compounds at an unconsumed lead cathode.^{35,75,76)} The reduction gives the corresponding hydrodimeric (HD) and hydromonomeric (HM) products, which correspond to (CH₃)₃SnSn(CH₃)₃ and (CH₃)₄Sn, respectively, in the reduction of methyl iodide at the consumable tin cathode. The selectivity (HD/HM) is increased under ultrasonic irradiation, and the increase is rationalized as being due to the promotion of a coupling reaction (Path a' in Scheme 2) of surface radical intermediate species (RR'COH), leading to the formation of HD. The radical species undergo coupling after diffusing into the bulk solution from the elec-

trode surface. The mass transfer is promoted by ultrasound, and, consequently, the selectivity for HD is increased along with an increase in the ultrasonic power.^{34,35)} Along the same line of thinking, the promotion of the formation (Path a in Scheme 1) of (CH₃)₃SnSn(CH₃)₃ at the tin cathode under irradiation may be rationalized. In addition to the diffusion of R₃Sn· radicals from the cathode toward the bulk solution, as described above, it is considered that the radicals diffused on the cathode surface (Scheme 1) quite differently from RR'COH radicals on the unconsumed lead cathode (Scheme 2).⁷¹⁾ Consequently, the R₃Sn· radicals were activated for coupling in Path a by mobilization from/on the tin cathode surface under irradiation.

The current efficiency and selectivity obtained with mechanical stirring by a small magnet bar without irradiation were between those at 0 W and 17 W of ultrasonic power without stirring.

As shown in Fig. 3, over a wide range of concentrations (0–1.0 M) of methyl iodide the efficiency and selectivity under irradiation were lower and higher, respectively, than those without irradiation. These facts can be simply explained as the promotion of mass-transport effects by ultrasound. The increases in efficiency and selectivity along with an increase in the concentration were also observed without irradiation. Hence, the increase is not uniquely associated with the irradiation.

The efficiency and selectivity in a current-density range of 5 to 50 mA cm⁻² under irradiation were lower and higher,

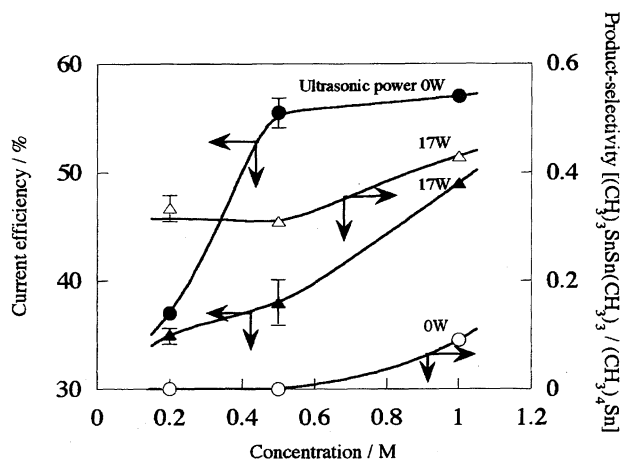
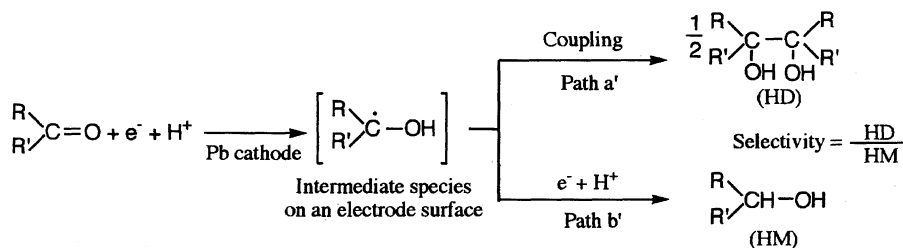


Fig. 3. Current efficiency and product selectivity [(CH₃)₃SnSn(CH₃)₃ / (CH₃)₄Sn] in the electroreduction of methyl iodide in various concentrations (0.2–1.0 M).



Scheme 2. Electroreduction of carbonyl compounds to the corresponding alcoholic compounds at a non-reactive lead cathode.^{35,74,75)}

respectively, than those without the irradiation, as shown in Fig. 4. Furthermore, the dependence of efficiency upon the irradiation depended upon the current density. It is noted that these ultrasonic effects at the consumable tin cathode were considerably different from those observed in the reduction of carbonyl compounds at unconsumed cathodes,^{75,76} as indicated related to Fig. 2 and Scheme 2.

The efficiency and selectivity under irradiation were lower and higher, respectively, than those without irradiation over the temperature range of -10 to $+25$ °C, as shown in Fig. 5. Thus, it is clear that both the efficiency and selectivity increase with temperature. We have reported that the efficiency and selectivity for HD (See Scheme 2) in the reduction of carbonyl compounds at an unconsumed cathode without ultrasonic irradiation increase with increasing temperature.⁷⁷ Hence, the increase in the efficiency and selectivity at the tin cathode either with or without irradiation may be rationalized as being due to an increase in the diffusion coefficients along with temperature elevation.

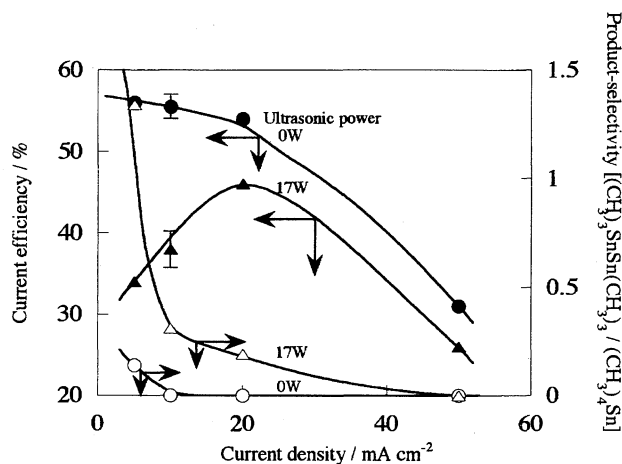


Fig. 4. Current efficiency and product selectivity $[(\text{CH}_3)_3\text{SnSn}(\text{CH}_3)_3 / (\text{CH}_3)_4\text{Sn}]$ in the electroreduction of methyl iodide at various current densities (5 – 50 mA cm^{-2}).

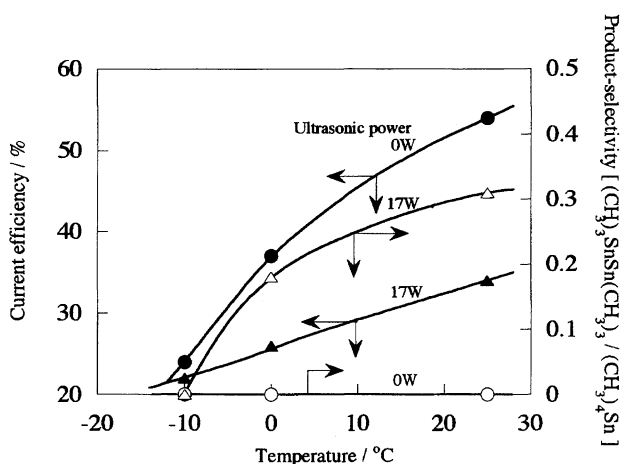


Fig. 5. Current efficiency and product selectivity $[(\text{CH}_3)_3\text{SnSn}(\text{CH}_3)_3 / (\text{CH}_3)_4\text{Sn}]$ in the electroreduction of methyl iodide at various temperatures (-10 – $+25$ °C).

The reduction of methyl bromide was carried out at 0 °C because of its low boiling point (4.5 °C). In a DMF solution, ultrasonic effects on the reduction of methyl bromide were similar to those in the reduction of the iodide. On the other hand, in a 0.25 M $(\text{C}_2\text{H}_5)_4\text{NBr} / \text{CH}_3\text{CN} + \text{H}_2\text{O}$ ($7:1$ vol ratio) solution, the reduction gave results quite different from those in a DMF solution. The selectivity $[(\text{CH}_3)_3\text{SnSn}(\text{CH}_3)_3 / (\text{CH}_3)_4\text{Sn}]$ was 0.76 without irradiation, while no distannane was formed under irradiation. Furthermore, a considerable amount of white precipitate was formed under irradiation. From an elemental analysis, a chemical formula of $\text{C}_{2.6}\text{H}_{7.1}\text{Sn}_{1.0}\text{O}_{3.2}$ for the precipitate was obtained. Although the molecular structure has not been determined, the precipitate seems to consist of mixtures of stannyl compound complexes having two and three methyl groups per tin atom.

A halogen exchange reaction of methyl iodide with bromine easily took place in a 0.25 M $(\text{C}_2\text{H}_5)_4\text{NBr} / \text{CH}_3\text{CN} + \text{H}_2\text{O}$ ($7:1$) solution. Therefore, the reduction of methyl iodide could not be examined in this solution.

The reduction of allyl bromide at a tin cathode in DMF and $\text{CH}_3\text{CN} + \text{H}_2\text{O}$ solutions gave only the corresponding tetraallylstannane $[(\text{C}_3\text{H}_5)_4\text{Sn}]$ without hexaallyldistannane $[(\text{C}_3\text{H}_5)_3\text{SnSn}(\text{C}_3\text{H}_5)_3]$.⁷² Figure 6 shows current efficiency for $(\text{C}_3\text{H}_5)_4\text{Sn}$ formed at different current densities. Although the electrolysis at a current density as high as 100 mA cm^{-2} in DMF could not be performed with and without ultrasonic irradiation because of the high cell voltage, due to high electric resistance, it was clearly shown regarding both solutions that along with an increase in the current density the efficiency under irradiation increased, while it decreased without irradiation. The former fact is important from a synthetic aspect for $(\text{C}_3\text{H}_5)_3\text{Sn}_4$, since it is indicated that a high efficiency can be obtained at a high reaction rate (current density) by irradiation. White precipitates were also formed in a $\text{CH}_3\text{CN} + \text{H}_2\text{O}$ solution under irradiation, as in the reduction of methyl bromide. Elemental analysis of the precipitates indicated a chemical formula of $\text{C}_{3.6}\text{H}_{12.7}\text{Sn}_{1.0}\text{O}_{0.5}$. Based on this data, the precipitates seem to consist of mixtures of stannyl compound complexes with one or two allyl groups

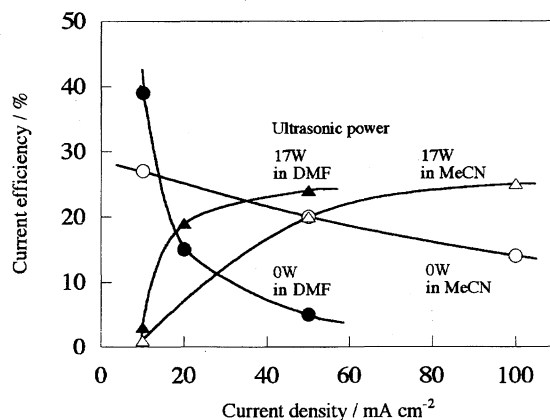


Fig. 6. Current efficiency for $(\text{C}_3\text{H}_5)_4\text{Sn}$ in the electroreduction of allyl bromide at various current densities (5 – 100 mA cm^{-2}) in 0.25 M $\text{Bu}_4\text{NClO}_4 / \text{DMF}$ and 1.5 M $(\text{C}_2\text{H}_5)_4\text{NBr} / \text{CH}_3\text{CN} + \text{H}_2\text{O}$ ($7:1$ vol ratio).

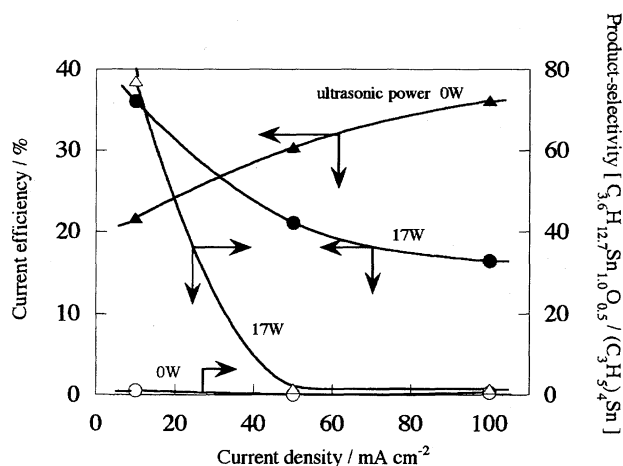


Fig. 7. Current efficiency and product selectivity $[C_{3.6}H_{12.7}Sn_{1.0}O_{0.5}/(C_3H_5)_4Sn]$ in the electroreduction of allyl bromide at various current densities (10–100 $mA\ cm^{-2}$) in a 1.5 M $(C_2H_5)_4NBr/CH_3CN + H_2O$ (7 : 1 vol ratio).

per tin atom.

Figure 7 shows the total current efficiency $[C_{3.6}H_{12.7}Sn_{1.0}O_{0.5} + (C_3H_5)_4Sn]$ and selectivity $[C_{3.6}H_{12.7}Sn_{1.0}O_{0.5}/(C_3H_5)_4Sn]$ at various current densities with and without ultrasonic irradiation. The selectivity with irradiation is always higher than that without irradiation, and decreases with increasing current density, as does the selectivity of $(CH_3)_3SnSn(CH_3)_3/(CH_3)_4Sn$ in the reduction of methyl iodide (Fig. 4). However, it is noted that the efficiencies with and without irradiation depend on the current density in a manner quite different from that in the reduction of methyl iodide.

Conclusions

Significant ultrasonic effects on the current efficiency and product selectivity were found in the electroreduction of methyl and allyl halides to the corresponding organic distannanes and monostannanes at consumable tin cathodes. The effects seem to be quite different from those generally observed in reactions at unconsumed electrodes.

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References

- 1) T. J. Mason, J. P. Lorimer, and D. J. Walton, *Ultrasonics*, **28**, 333 (1990).
- 2) O. Nomoto, Y. Kikuchi, and J. Saneyoshi, "Cho-onpa Binran," Nikkan Kogyo Shinbunsha, Tokyo (1991), pp. 120, 231, and 1102.
- 3) H. Tsukiji, H. Goto, and M. Tashiro, *Cho-onpa Techno*, **4**, 41 (1992).
- 4) R. Walker, *Chem. Br.*, **26**, 251 (1990).
- 5) B. A. Shenoi, K. S. Indira, and R. Subramanian, *Met. Finish.*, **68**, 57 (1970).
- 6) R. Walker and T. Walker, *Ultrasonics*, **13**, 79 (1975).
- 7) M. C. Hsiao and C. C. Wan, *Plat. Surf. Finish.*, **76**, 46 (1989).
- 8) W. R. Wolfe, H. Chessin, E. Yeager, and F. Hovorka, *J. Electrochem. Soc.*, **12**, 590 (1954).
- 9) E. Namgoong and J. S. Chun, *Thin Solid Films*, **120**, 153 (1984).
- 10) C. A. Marrese, *Anal. Chem.*, **59**, 217 (1987).
- 11) V. A. Roll, *Z. Metallkd.*, **41**, 339 (1950).
- 12) V. A. Roll, *Z. Metallkd.*, **41**, 413 (1950).
- 13) V. A. Roll and G. Schrag, *Z. Metallkd.*, **42**, 197 (1950).
- 14) G. O. Mallory, *Trans. Inst. Met. Finish.*, **56**, 81 (1978).
- 15) N. Moriguchi, *J. Chem. Soc. Jpn.*, **55**, 749 (1934).
- 16) N. Moriguchi, *J. Chem. Soc. Jpn.*, **55**, 751 (1934).
- 17) H. G. Schmid and L. Ehret, *Z. Electrochem.*, **43**, 597 (1937).
- 18) E. Yeager, T. S. Oey, and F. Hovorka, *J. Phys. Chem.*, **57**, 268 (1953).
- 19) R. G. Compton, J. C. Eklund, S. D. Page, G. H. W. Sanders, and J. Booth, *J. Phys. Chem.*, **98**, 12410 (1994).
- 20) A. Benahcene, C. Petrier, and G. Reverdy, *New J. Chem.*, **19**, 989 (1995).
- 21) H. G. Schmid and L. Ehret, *Z. Electrochem.*, **43**, 408 (1937).
- 22) S. A. Perusich and R. C. Alkire, *J. Electrochem. Soc.*, **138**, 700 (1991).
- 23) S. A. Perusich and R. C. Alkire, *J. Electrochem. Soc.*, **138**, 708 (1991).
- 24) V. Yegnaraman and S. Bharathi, *Bull. Electrochem.*, **8**, 84 (1992).
- 25) C. R. S. Hagan and L. A. Coury, Jr., *Anal. Chem.*, **66**, 399 (1994).
- 26) J. Klima, C. Bernard, and C. Degrand, *J. Electroanal. Chem.*, **367**, 297 (1994).
- 27) J. Klima, C. Bernard, and C. Degrand, *J. Electroanal. Chem.*, **399**, 147 (1995).
- 28) R. G. Compton, J. C. Eklund, and S. D. Page, *J. Phys. Chem.*, **99**, 4211 (1995).
- 29) D. J. Walton, S. S. Phull, A. Chyla, J. P. Lorimer, T. J. Mason, L. D. Barke, M. Murphy, R. G. Compton, J. C. Eklund, and S. D. Page, *J. Appl. Electrochem.*, **25**, 1083 (1995).
- 30) J. Reisse, H. Francois, J. Vandercammen, O. Fabre, A. K. Mesmaeker, C. Maerschalk, and J.-L. Delplancke, *Electrochim. Acta*, **39**, 37 (1994).
- 31) P. R. Birkin and S. S. Martinez, *J. Chem. Soc., Chem. Commun.*, **1995**, 1807.
- 32) H. D. Dewald and B. A. Peterson, *Anal. Chem.*, **62**, 779 (1990).
- 33) M. Atobe and T. Nonaka, "189th Electrochem. Soc. Meet.," Los Angeles, May 6–10, 1996, Extended Abstr., No. 1007.
- 34) K. Matsuda, M. Atobe, and T. Nonaka, *Chem. Lett.*, **1994**, 1619.
- 35) M. Atobe, K. Matsuda, and T. Nonaka, *Electroanalysis*, **8**, 784 (1996).
- 36) J. C. Eklund, D. N. Waller, T. O. Rebbitt, F. Marken, and R. G. Compton, *J. Chem. Soc., Perkin Trans. 2*, **1995**, 1981.
- 37) R. G. Compton, J. C. Eklund, S. D. Page, and T. O. Rebbitt, *J. Chem. Soc., Dalton Trans.*, **1995**, 389.
- 38) R. G. Compton, J. C. Eklund, F. Marken, and D. N. Waller, *Electrochim. Acta*, **41**, 315 (1996).
- 39) F. Marken, J. C. Eklund, and R. G. Compton, *J. Electroanal. Chem.*, **395**, 335 (1995).

- 40) H. Zhang and L. A. Coury, Jr., *Anal. Chem.*, **65**, 1552 (1993).
41) M. Atobe and T. Nonaka, *Ultrason. Sonochem.*, **4**, 17 (1997).
42) M. Atobe and T. Nonaka, *J. Electroanal. Chem.*, **425**, 161 (1997).
43) D. J. Walton, S. S. Phull, D. M. Bates, J. P. Lolimer, and T. J. Mason, *Electrochim. Acta*, **38**, 307 (1993).
44) D. J. Walton, S. S. Phull, D. M. Bates, J. P. Lolimer, and T. J. Mason, *Ultrasonics*, **30**, 186 (1992).
45) D. J. Walton, S. S. Phull, D. Colton, P. Richards, A. Chyla, T. Javed, L. Clarke, J. P. Lorimer, and T. J. Mason, *Ultrason. Sonochem.*, **1**, S23 (1994).
46) B. Go, I. Ichikawa, and J. Chiba, *Denki Kagaku*, **60**, 327, (1992).
47) A. Durant, J.-L. Delplancke, R. Winard, and J. Reisse, *Tetrahedron Lett.*, **36**, 4257 (1995).
48) F. Cataldo, *J. Electroanal. Chem.*, **332**, 325 (1992).
49) T. F. Connors and J. F. Rusling, *Chemosphere*, **13**, 415 (1984).
50) B. Gautheron, G. Tainturier, and C. Degrand, *J. Am. Chem. Soc.*, **107**, 5579 (1985).
51) T. Tsonkov, M. Parlapanski, and S. Djendova, *Oxid. Commun.*, **17**, 321 (1994).
52) A. Durant, H. Francois, J. Reisse, and A. K.-D. Mesmaeker, *Electrochim. Acta*, **41**, 277 (1996).
53) A. Chyla, J. P. Lorimer, T. J. Mason, G. Smith, and D. J. Walton, *J. Chem. Soc., Chem. Commun.*, **1989**, 603.
54) K. Uneyama, S. Watanabe, and Y. Tokunaga, "12th Electroorg. Chem. Symp.," Hiroshima, Japan, July 1990, Abstr., No. 5.
55) A. J. Fry, J. Touster, U. N. Sirisoma, and B. Raimundo, "Electroorganic Synthesis," ed by D. R. Little and N. Weinberg, Marcel Dekker, Inc., New York (1991), p. 99.
56) M. Tashiro, H. Tsuzuki, H. Goto, and S. Mataka, *Chem. Express*, **6**, 403 (1991).
57) M. Atobe, K. Matsuda, and T. Nonaka, *Denki Kagaku*, **62**, 1298 (1994).
58) M. Atobe and T. Nonaka, *Chem. Lett.*, **1995**, 669.
59) M. Atobe and T. Nonaka, *Chem. Lett.*, **1997**, 323.
60) T. Shono and R. Nishida, *Kagaku to Kogyo*, **45**, 1107 (1992).
61) U. Akbulut, L. Toppare, and B. Yurttas, *Polymer*, **27**, 803 (1986).
62) S. P. Aybar, B. Hacıoglu, and U. Akbulut, *J. Polym. Sci.*, **29**, 1971 (1991).
63) S. Osawa, M. Ito, K. Tanaka, and J. Kuwano, *Synth. Met.*, **18**, 145 (1987).
64) S. Osawa, M. Ito, K. Tanaka, and J. Kuwano, *Polym. Phys.*, **30**, 19 (1992).
65) M. Atobe, S. Fuwa, N. Sato, and T. Nonaka, *Denki Kagaku*, **65**, 495 (1997).
66) N. Sato and T. Nonaka, *Chem. Lett.*, **1995**, 805.
67) E. d'Incan, S. Sibille, J. Perichon, M.-O. Moigeon, and J. Chaussard, *Tetrahedron Lett.*, **27**, 4175 (1986).
68) T. Ishiwata, T. Nonaka, and M. Umezawa, *Chem. Lett.*, **1994**, 1631.
69) C. Yoshimura and M. Mimura, *Hyomen Gijutsu*, **45**, 731 (1994).
70) M. Fleishmann, G. Mengoli, and D. Pletcher, *Electrochim. Acta*, **18**, 231 (1973).
71) H. E. Ulery, *J. Electrochem. Soc.*, **120**, 1493 (1973).
72) H. E. Ulery, *J. Electrochem. Soc.*, **119**, 1474 (1972).
73) O. R. Brown, E. R. Gonzalez, and A. R. Wright, *Electrochim. Acta*, **18**, 369 (1973).
74) H. E. Ulery, *J. Electrochem. Soc.*, **116**, 1201 (1969).
75) P.-C. Cheng, T. Nonaka, and T.-C. Chou, *Bull. Chem. Soc. Jpn.*, **64**, 1911 (1991).
76) P.-C. Cheng and T. Nonaka, *Bull. Chem. Soc. Jpn.*, **64**, 3500 (1991).
77) K. Tsunashima and T. Nonaka, *Chem. Lett.*, **1995**, 862.
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