Product-Selectivity Control in an Electroorganic Process by Temperature. Electroreduction of Acetophenone

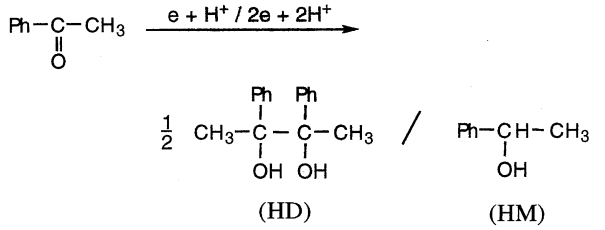
Katsuhiko Tsunashima and Tsutomu Nonaka*
Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226

(Received June 5, 1995)

Product–selectivity for the electroreduction of acetophenone to the corresponding hydrodimeric and hydromonomeric products was greatly affected by temperature.

Product–selectivity control is very important in chemical synthesis, and is generally achieved by purposive selection of reagents, catalysts, reaction media, reaction conditions *etc.* In electrochemical reaction, factors controlling the selectivity are a variety of electrolytic conditions such as electrode potential, current density, solvent, supporting electrolyte, pH, electrode material, and so on.

In our previous work,[1-3] it was found that the product–selectivity for the electroreduction of carbonyl compounds was be significantly controlled by their concentration, flow rate of the electrolytic solution and rotating speed of the cathode, and could be theoretically predicted in good agreement with the experimental values on the basis of a mathematical reaction model involving mass transport coefficients. For instance, in the reduction of acetophenone, the formation ratio of the corresponding hydrodimeric product (HD) to hydromonomeric product (HM) as an index for the product–selectivity increased from 0.7 to 4.4, 0.4 to 2.9 and 1.0 to 3.0 with increases in the concentration (from 0.08 to 0.24 mol dm^{-3}), the flow rate (1.0 to 5.8 m min^{-1}) and the rotating speed (250 to 1000 min^{-1}), respectively, under certain electrolytic conditions given.



We wish here to report that the product–selectivity (R) for the reduction of acetophenone can be more drastically increased with an increase in temperature, as the first demonstration of distinct temperature dependence of the selectivity, though it has not been generalized yet.

A divided H–shaped cell equipped with an Sn cathode (1.5 cm^2) and a Pt anode was used for the reduction of acetophenone (2.5 mmol) in 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ / $CH_3CN–H_2O$ (5 vol %) (50 cm^3). The electrolysis was carried out galvanostatically by passing 0.5 × 96500 C mol^{-1} of electricity at 60 mA cm^{-2} of current density. Acetophenone and the reduction products (HD and HM) were analyzed by HPLC and GC.

As shown in Table 1, R was increased from 3.8 to 19.4 when temperature was elevated from 0 to 60 °C, while the *dl* / *meso* ratio of HD was kept constant at ca. 1 similarly to that obtained under mass transport–controlled conditions.[1] Current efficiency for the reduction also increased with temperature elevation. Hydrogen evolution was observed at 0 °C. This fact may suggest that the efficiency is controlled by the mass transport, but it is not clear whether the selectivity also is similarly controlled. The mass transport conditions to give a large value of R as 19.4 seems to be difficult to be practically realized, because they require, for instance, an extremely high speed rotation of the cathode such as several thousands per minute according to a theoretical consideration.[2] Although the product–selectivity control by temperature has not been mechanistically clarified, it should practically afford a new useful method for electroorganic synthesis.

Table 1. Electroreduction of acetophenone on an Sn cathode at various temperatures

Temperature / °C	R [a]	Current efficiency / %
0	3.8	67
20	3.6	88
40	10.4	93
60	19.4	104

a Formation ratio of HD / HM.

Table 2. Electroreduction of acetophenone on a p–Si cathode at various temperatures

Temperature / °C	R [a]	Current efficiency / %
0	0.3	64
20	2.8	86
40	4.0	102
60	5.6	82

a Formation ratio of HD / HM.

When a B–doped low resistivity type of p–Si [(100) –single crystal ; resistance, 0.06 – 0.12 Ω cm^{-1} ; carrier density, 2 – 4 × 10^{17} cc] was used as a cathode for the reduction of acetophenone in the dark, R increased from 0.3 to 5.6 with temperature elevation from 0 to 60 °C (See Table 2). This fact suggests that the temperature dependence of the product–selectivity is not an unusual phenomenon observed only at an Sn cathode.

This study was financially supported by a Grant–in–Aid for Scientific Research on Priority Area (New Development of Organic Electrochemistry) from The Ministry of Education, Science and Culture.

References

1 P. -C. Cheng and T. Nonaka, *J. Electroanal. Chem.*, **269**, 223 (1989).
2 P. -C. Cheng, T. Nonaka, and T. -C. Chou, *Bull. Chem. Soc. Jpn.*, **64**, 1911 (1991).
3 P. -C. Cheng and T. Nonaka, *Bull. Chem. Soc. Jpn.*, **64**, 3500 (1991).