Control of Product Distribution by Use of Surfactants in Cathodic Reduction of Acetophenone

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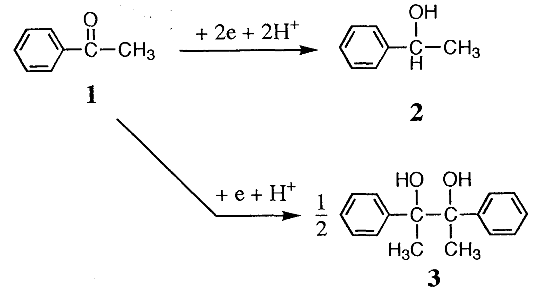
In cathodic reduction of acetophenone to 1-phenylethanol and 2,3-diphenyl-2,3-butandiol, 1-phenylethanol was selectively yielded using micelle formed cationic surfactants at control potential –2.1 V.

The control of product distribution is one of the important problem in organic syntheses. In electrochemical reactions, there are wide variety of electrolytic conditions such as electrode potential, current density, solvent, supporting electrolyte, pH and electrode material, which affect the selectivity of products.[1] Recently, Nonaka studied the effect of ultrasounds[2] and composite plated electrodes[3] on the product distribution in the electroreduction of benzaldehydes. There have been few studies, however, on the effect of ionic surfactants on the electrolysis, and the product distribution ratios were rather low in these studies ([main product]/[miner product] = 4.4 and 3.3).[4,5] In this study, we report the additive effect of ionic surfactants on the product distribution in the cathodic reduction of acetophenone (**1**) to monomeric product 1-phenylethanol (**2**) and dimeric product 2,3-diphenyl-2,3-butandiol (**3**). Using cationic surfactants, monomeric product **2** was selectively yielded.



Typical electrolytic conditions were as follows. The reaction was carried out in an H-type separated cell, equipped with and lead plate cathode (12 cm^2), platinum plate anode (4.0 cm^2), and saturated calomel electrode (SCE). Acetophenone (4.3 mmol) was electrolyzed in 100 mL of an aqueous sodium sulfate solution (0.5 M (1 M = 1 mol dm^{-3})) containing 2.7 mmol of additives such as cetyltrimethylammonium bromide (CTAB) at room temperature under the constant-potential conditions at –2.1 V vs SCE. The anolyte used was 100 mL of aqueous sodium sulfate solution (1.0 M). The catholyte was stirred in nitrogen atmosphere during the electrolysis. After passing 5 mF (1.2 F mol^{-1} (1 F = 96484.56 C)) of electric charge, the catholyte was subjected to HPLC analysis.

The additive effect of the surfactants on the product distribution in the electroreduction of **1** is summarized in Table 1.[6] In the presence of the cationic surfactant (CTAB), the product distribution ratio [**2**]/[**3**] increased upto 17, which was 16 times greater than the value of 1.1 obtained in the absence of the surfactant. The addition of anionic surfactant (sodium dodecyl sulfate, SDS) or nonionic surfactant (polyethylene-glycol monolauryl ether, PELE) to the catholyte, however, scarcely changed the ratio (about 3). The electrolysis in ethanol, which affords a relatively hydrophobic environment, gave the low [**2**]/[**3**] ratio. From the result in Table 1, it is understood that the cationic surfactant was effective for the selective production of **2** in the electroreduction of acetophenone We also found similar results on use of benzaldehyde as a substrate.

Table 1. Effect of additive on product distribution in constant potential electrolysis of acetophenone

additive	yield/%[a]			current efficiently/%		
	2	**3**	[**2**]/[**3**]	**2**	**3**	total
CTAB	40	2.3	17	67	4.0	71
SDS	23	7.4	3.1	40	13	53
PELE	23	6.7	3.4	40	12	52
none	19	18	1.1	33	30	63
Ethanol[b]	4.4	33	0.13	8	56	64

[a] [product]/[initial acetophenone], [b] Determined with 1.0 M of $NaClO_4$ in ethanol.

The effect of CTAB concentration on yield of **2** and **3** was shown in Figure 1. With increasing the concentration of CTAB (the critical micelle concentration (cmc) of CTAB was around 1 mM),[7] the yield of **2** increased remarkably, while the yield of **3** decreased. It is suggested, therefore, that this product distribution change was occurred by taking reactant **1** into the positive charged micelle of CTAB enough.

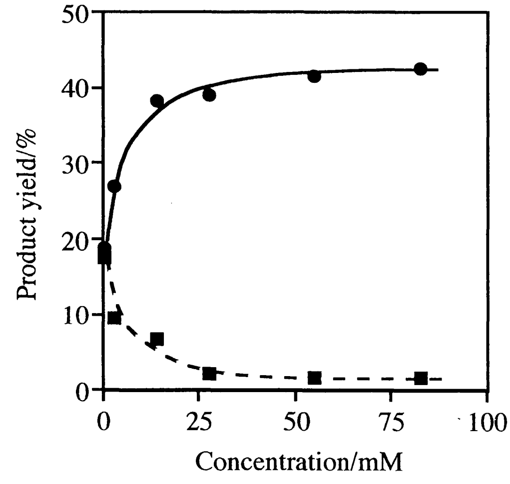


Figure 1. Effect of CTAB amount on yield of **2** (circle) and **3** (square).

Table 2. Effect of cationic additives on product distribution

additive	yield/%[a] 2	yield/%[a] 3	[2]/[3]
n-$C_{16}H_{33}(CH_3)_3N^+\cdot Br^-$ (CTAB)	40	2.3	17
n-$C_{12}H_{25}(CH_3)_3N^+\cdot Br^-$	40	3.5	11
n-$C_{10}H_{21}(CH_3)_3N^+\cdot Br^-$	35	4.7	7.6
n-$C_8H_{17}(CH_3)_3N^+\cdot Br^-$	28	6.7	4.2
n-$C_6H_{13}(CH_3)_3N^+\cdot Br^-$	23	9.5	2.4
$(CH_3)_4N^+\cdot Br^-$	23	15	1.6
$(n$-$C_4H_9)_4N^+\cdot Br^-$	11	11	2.4
phenyl$(CH_3)_3N^+\cdot Br^-$	26	4.4	7.8
n-$C_{16}H_{33}(CH_3)_3N^+\cdot Cl^-$	37	3.0	12
none	19	18	1.1

[a] [product]/[initial acetophenone].

The effect of the chain length in alkyltrimethylammoniums was summarized in Table 2. With increasing the chain length from C_1 to C_{16} the ratio [**2**]/[**3**] was significantly increased. In the presence of C_{16} and C_{12} surfactants that formed micelle in this experimental conditions (cmc < 27 mM),[7] the ratios were over 10, while the additive with C_1-, C_6- and C_8-alkyl groups (cmc > 27 mM) gave the low [**2**]/[**3**] ratio. Tetrabutylammonium chloride also did not significantly increase the [**2**]/[**3**] ratio. From the results in Tables 1 and 2, it is concluded that the micelle formed cationic surfactants with long alkyl-chain (over C_{10}) can favor the selective formation of **2**.

The yields of **2** and **3** were slightly affected by the reduction potential in the absence of surfactants, as seen in Figure 2. In the presence of CTAB, however, the yield of **2** increased remarkably with electrode potential being negative, while the yield of **3** decreased. From these results, the molar ratio [**2**]/[**3**] found in the presence of CTAB increased markedly with the electrode potential being negative, while the ratio did not change so much in the absence of CTAB. The maximum [**2**]/[**3**] ratio of 17 was obtained in the electrolysis at −2.1 V vs SCE.

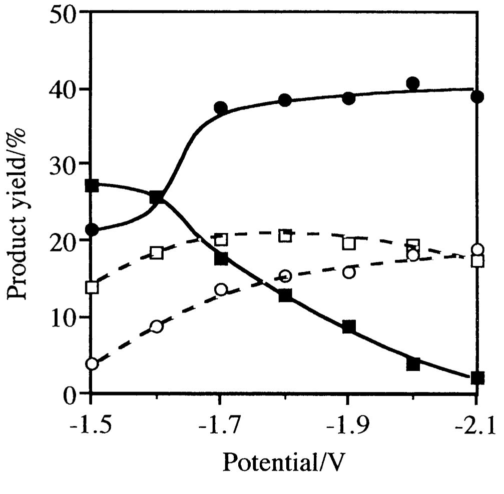
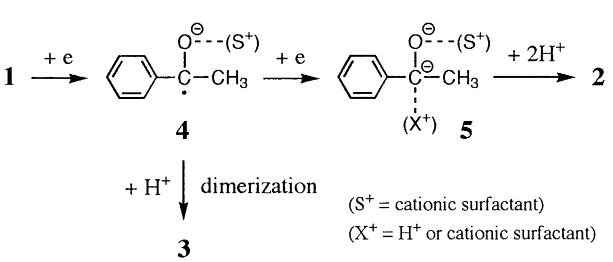


Figure 2. Effect of potential on yield of **2** (circle) and **3** (square). Solid line is the present of CTAB. Dashed line is the absent of CTAB.

From the results above, the monomeric product **2** was found to be selectively formed in the presence of the cationic surfactant with long alkyl-chain in the electroreduction of acetophenone **1** at −2.1 V vs SCE. It is well known that the electroreduction of carbonyl compounds proceeds in two-step one-electron transfer, as illustrated in Scheme 1.



Scheme 1.

The stability and/or reactivity of the reaction intermediates **4** and **5** should determine the product distribution. By the formation of the ion pair between the negative charge on the intermediate **4** and the positive charge on the micelle formed cationic surfactants with the long alkyl chain,[8] the dimerization of **4** to **3** should be suppressed, allowing the further one-electron reduction of **4** to give the monomeric product **2**. The ion pairing between CTAB and **5** will also favor the transformation of **4** to **5** by increasing the stability of **5**. The effect of electrode potential in Figure 2 can be explained as follows. At relatively negative potential (around −2.1 V vs SCE), the local concentration of CTAB in the vicinity of electrode should increase by electrostatic interaction between the negative charge on the electrode and the positive charge on the surfactant. Thus the anionic species **4** and **5** generated on the surface of the electrode should be stabilized more effectively by ion pairing to favor the formation of **2**.

In conclusion, the present study provides a novel method for controlling the product distribution in electrochemical reactions. The proposed method will be applied to the control of products distribution in other electrochemical reactions.

The mechanistic study for the interaction of surfactant and intermediate is now in progress.

References and Notes

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6 After passing 25 mF (5.8 F mol^{-1}) of electric charge in the present of CTAB, products **2** and **3** were yielded 77 and 4.5%, respectively, and the product distribution ratio [**2**]/[**3**] was 17.
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