Mixed-Kolbe Electrolysis Using Solid-Supported Bases

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We have successfully developed a novel mixed-Kolbe electrolysis system using solid-supported bases. Mixed-Kolbe electrolysis of carboxylic acids using solid-supported bases was carried out to provide the corresponding mixed-Kolbe products in moderate to good yields. In this system, solid-supported bases were recyclable even under high current density.

Key Words : Carboxylic Acid, Mixed-Kolbe Electrolysis, Solid-Supported Base, Supporting Electrolyte

1 Introduction

In electroorganic synthesis, large amounts of supporting electrolytes are required in order to provide sufficient electrical conductivity to the solvents for electrolyses.¹⁾ However, the use of supporting electrolytes causes their separation and industrial waste problems after the electrolysis. On the other hand, we have recently developed a novel electrolytic system using solid-supported bases for anodic methoxylation and acetoxylation.^{2, 3)} In this system, no supporting electrolytes are required, and protic organic solvents such as methanol serve as both a solvent and a supporting electrolyte generated *in situ* in the presence of solid-supported bases [Eqs. (1) and (3)]. However, the cell voltage in solid-supported bases/MeOH was higher than that of a conventional method using supporting electrolytes such as Et₄NOTs/MeOH. This is due to the relatively low acidity of MeOH (pK_a = 15.5). Therefore, the concentrations of methoxide ions and protons derived from MeOH are not enough to provide sufficient electrical conductivity. On the other hand, carboxylic acids have higher acidity, therefore, they would be dissociated into carboxylate ions and protons efficiently in the presence of solid-supported bases [Eq. (2)]. This system would be more suitable for electroorganic synthesis under high current density. In this paper, we report a novel mixed-Kolbe electrolysis system using solid-supported bases for *in situ* generation of a supporting electrolyte from carboxylic acids as a substrate.

2 Experimental

2.1 General

¹H NMR spectra were recorded on JEOL JNM EX-270

(270 MHz) spectrometer in CDCl₃. The chemical shift for ¹H NMR spectra was given in δ (ppm) from internal TMS. EI mass spectra were recorded on Shimadzu GCMS-QP5050A mass spectrometer. Cyclic voltammetry was performed by using a computer-controlled electrochemical system (ALS/CHI 600), and preparative electrolysis experiments were carried out with a Hokuto Denko Potentiostat/Galvanostat HA-105.

2.2 Cyclic voltammetry

Cyclic voltammetry was carried out with a three-electrode system using a platinum disk (φ = 0.8 mm) working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) as a reference electrode.

2.3 General procedure for mixed-Kolbe electrolysis

Mixed-Kolbe electrolysis of carboxylic acids (1–9 mmol) was carried out with platinum plate electrodes (2 × 2 cm²) in MeOH/MeCN (50/50 v/v %, 10 cm³) containing various solid-supported bases (0.1 M based on the concentration of a base, silica gel size: 40–63 μm) using an undivided cell. Constant current electrolysis (100 mA cm⁻²) was applied with stirring. After the electrolysis, the electrolytic solution was passed through a glass filter (pore size: 40–60 μm) to remove the solid-supported bases. The eluent was evaporated, and the residue was purified by Shimadzu LC-6AD liquid chromatography eluting with MeCN to give a pure coupling product, which was identified by authentic samples using ¹H NMR and mass spectroscopy.

3 Results and Discussion

At first, the cyclic voltammogram of silica gel-supported piperidine/MeOH (0.1 M based on the concentration of piperidine) was measured. As shown in Fig. 1(a), the oxidation current for MeOH (over 1.5 V vs. SCE) and the reduction current for protons were observed. Next, the cyclic voltammogram of sebacic acid monomethyl ester (**1**, 0.1 M) + acetic acid (**2**, 0.6 M) in 0.1 M silica gel-supported piperidine/MeOH was also measured. As shown in Fig. 1(b), the reduction current for protons was remarkably increased. From these result, it is clear that silica gel-supported piperidine preferentially dissociates

Fig. 1 Cyclic voltammograms of (a) 0.1 M silica gel-supported piperidine/MeOH and (b) **1** (0.1 M) + **2** (0.6 M) in 0.1 M silica gel-supported piperidine/MeOH, recorded at Pt disk electrode ($\phi = 0.8$ mm). The scan rate was 100 mV s^{-1} .

carboxylic acids into carboxylate ions and protons, and the resulting ions seem to act as the carriers of an electronic charge [Eqs. (2) and (3)].

Next, mixed-Kolbe electrolysis of **1** and **2** was investigated under various electrolytic conditions as shown in Table 1.⁴⁾ The typical experimental procedure is illus-

Fig. 2 Experimental procedure.

trated in Fig. 2. Mixed-Kolbe electrolysis of **1** and **2** in 0.1 M silica gel-supported piperidine/MeOH was carried out to provide the corresponding coupling product **3** in 30% yield (entry 1). In this case, **1** was considerably recovered. The cell voltage in entry 1 was 45–50 V, while it was higher than 100 V in the absence of **1** and **2**. This great decrease of the cell voltage indicates that **1** and **2** serve as not only substrates but also supporting electrolytes generated *in situ* [Eqs. (2) and (3)]. In entries 2–8, acetonitrile (MeCN) was used as a co-solvent in order to suppress the oxidation of MeOH. Although the yield of **3**

Table 1 Mixed-Kolbe Electrolysis of **1** and **2** Using Solid-Supported Bases.

$\text{MeO}_2\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H} \quad \mathbf{1} + \text{CH}_3\text{CO}_2\text{H} \quad \mathbf{2} \xrightarrow[\text{Pt-Pt}]{\begin{array}{c} 0.1 \text{ M } \text{Si} \text{ Base} \\ \text{MeOH/MeCN} \\ 100 \text{ mA/cm}^2, 0^\circ\text{C} \end{array}} \text{MeO}_2\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H} \quad \mathbf{3}$					
entry	2 (equiv.)	MeOH/MeCN (v/v%)	base	electricity ^a (F/mol)	yield ^b (%)
1	6	100/0	$\text{p}K_a=11.1^c$	10	30
2	1	50/50		4.5	29
3	4	50/50		9	45
4	6	50/50		10	45
5	9	50/50		10	30
6	6	50/50	$\text{p}K_a=5.2$	10	52
7	6	50/50	$\text{p}K_a=7.0$	9	48
8	6	50/50	$\text{p}K_a=26.2^d$	10	27

^aElectricity based on **1**. ^bIsolated yield based on **1**. ^cAcidity of the conjugated acid devoid of the solid. ^d $\text{p}K_a$ in MeCN.

Table 2 Mixed-Kolbe Electrolysis of Carboxylic Acids Using Silica Gel-Supported Pyridine.

0.1 M

$\text{MeOH/MeCN}=50/50 \text{ v/v\%}$
 $10 \text{ F/mol, } 100 \text{ mA/cm}^2$
 Pt -Pt, 0 °C

carboxylic acid 1 + carboxylic acid 2 (6 equiv.) $\xrightarrow{\hspace{10em}}$ product

entry	carboxylic acid 1	carboxylic acid 2	product	yield ^a (%)
1	MeO ₂ C(CH ₂) ₄ CO ₂ H	CH ₃ CO ₂ H	MeO ₂ C(CH ₂) ₄ CH ₃	66
2	MeO ₂ C(CH ₂) ₄ CO ₂ H	CH ₃ (CH ₂) ₄ CO ₂ H	MeO ₂ C(CH ₂) ₈ CH ₃	54 ^b
3	MeO ₂ C(CH ₂) ₈ CO ₂ H	CH ₃ (CH ₂) ₄ CO ₂ H	MeO ₂ C(CH ₂) ₁₂ CH ₃	65 ^c

^aIsolated yield based on carboxylic acid 1. ^b*n*-Decane was also formed in 28% yield based on CH₃(CH₂)₄CO₂H (carboxylic acid 2). ^cA considerable amount of *n*-decane was also formed.

was 30% and **1** was considerably recovered in MeOH (entry 1), the yield of **3** was increased to 45% and **1** was completely consumed in MeOH/MeCN (entry 4). Then, the effect of the concentration of **2** was investigated as shown in entries 2-5. The yield of **3** and the cell voltage at the later stage of electrolysis depended on the concentration of **2**. The cell voltage in entries 2-4 was increased with the electricity. Therefore, in entries 2 and 3, it was difficult to carry on with the constant current electrolysis until the complete consumption of **1**. Although the cell voltage was increased with the electricity, constant current electrolysis of **1** was carried out until the complete consumption of **1** to provide **3** in 45% yield in entry 4. On the other hand, the cell voltage in entry 5 was not increased with the electricity. However, the yield of **3** in entry 5 was lower than that in entry 4. Therefore, 6 equiv. of **2** was suitable for this mixed-Kolbe electrolysis. Next, mixed-Kolbe electrolysis of **1** and **2** was carried out using various silica gel-supported bases. As shown in entries 6-8, **3** was obtained in better yields using relatively weak bases. From these results, silica gel-supported pyridine is suitable as a solid-supported base for this mixed-Kolbe electrolysis. Furthermore, mixed-Kolbe electrolysis of **1** and **2** was successfully carried out 3 times under the conditions of entry 6 in Table 1 by the recycling of silica gel-supported piperidine without neutralization (Fig. 2). The yield of **3** was always *ca.* 50% [52% (1st), 47% (2nd), 52% (3rd)] and did not decrease at all upon the reuse of silica gel-supported pyridine. This clearly suggests that solid-supported bases are recyclable because they are not subject to oxidative decomposition at the electrode surface even under high current density (100 mA cm⁻²).

Next, mixed-Kolbe electrolysis of some carboxylic acids was also carried out using silica gel-supported pyridine. As shown in Table 2, the corresponding coupling products were obtained in moderate to good yields. From these results, it was demonstrated that the electrolytic system using solid-supported bases is effective

for the mixed-Kolbe electrolysis.

4 Conclusion

We have developed a novel mixed-Kolbe electrolysis system using solid-supported bases. In this system, no supporting electrolytes are required, and carboxylic acids serve as both a substrate and a supporting electrolyte generated *in situ* in the presence of solid-supported bases. In addition, the cell voltage in the presence of carboxylic acids was much lower compared with that in their absence. Furthermore, in spite of high current density, solid-supported bases are stable enough and recyclable in the mixed-Kolbe electrolysis. We hope that this new electrolytic system will make significant contributions to green sustainable chemistry and open a new aspect of electroorganic synthesis.

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