— Communication —

Development of a Novel Electrolytic System Using KBr as a Mediator and Solid-Supported Acids as a Supporting Electrolyte

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Received January 30, 2006 ; Accepted April 30, 2006

We have successfully developed a novel electrolytic system using KBr as a mediator and solid-supported acids as a supporting electrolyte. In this system, solid-supported acids such as Amberlyst 15Dry (-SO₃H) serve as not only a promoter of the dissociation of KBr but also a supporting electrolyte. Anodic oxidation of some benzyl alcohols using KBr and Amberlyst 15Dry (-SO₃H) in the presence of 2,6-lutidine was successfully carried out to provide the corresponding benzaldehydes in good to excellent yields.

Key Words : Mediator, Potassium Bromide, Solid-Supported Acid, Supporting Electrolyte

1 Introduction

In electroorganic synthesis, supporting electrolytes are required in order to provide sufficient electrical conductivity to the organic solvents for electrolyses. Inorganic salts such as potassium and sodium salts are typical supporting electrolytes in water because many of them are naturally-occurring and cheap. However, inorganic salts can not be used as supporting electrolytes in many aprotic organic solvents since they have poor solubility. Therefore, tetraalkylammonium salts are generally used for electroorganic synthesis.¹⁾ On the other hand, it is well known that the protons of solid-supported acids (-SO₃H, strong cation-exchange resins) are exchanged for metal ions.²⁾ Therefore, solid-supported acids would promote the dissociation of potassium bromide (KBr) even in aprotic organic solvents to provide both bromide anions (Br⁻) and protons to some extent simultaneously [Eq. (1)]. This system would be suitable for electroorganic synthesis using a Br⁻/Br⁺ mediator. Herein, we report a novel electrolytic system using KBr as a mediator and solid-supported acids as a supporting electrolyte.

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 HABF-501.

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 anodic oxidation of benzyl alcohols

Anodic oxidation of benzyl alcohols was carried out with platinum plate electrodes (2 × 2 cm²) in 0.05 M KBr/0.2 M (based on the concentration of -SO₃H) Amberlyst 15Dry (-SO₃H)/0.2 M 2,6-lutidine/MeCN/CH₂Cl₂ (10 cm³, MeCN/CH₂Cl₂ = 50/50 v/v %) using an undivided cell. Controlled potential electrolysis was applied. The conversion of starting materials was monitored by TLC. After the electrolysis, the electrolytic solution was filtered through a glass filter to remove the Amberlyst 15Dry (-SO₃K and -SO₃H). The filtrate was passed through a short column of silica gel eluting with CHCl₃. Then, the eluent was evaporated under vacuum. The products were isolated by Shimadzu LC-6AD liquid chromatography eluting with MeCN and identified by authentic samples using ¹H NMR and mass spectroscopy. The recovered Amberlyst 15Dry (-SO₃K) was washed with methanol (200 cm³) and 1 M aq. HCl (120 cm³). The regenerated Amberlyst 15Dry (-SO₃H) was dried at 80 °C under vacuum. Then, it was reused.

3 Results and Discussion

At first, the cyclic voltammogram of KBr (0.05 M based on the used KBr) in MeCN/CH₂Cl₂ (50/50 v/v %) was measured. As shown in Fig. 1(a), two pairs of typical redox peaks (*E*_p^{ox} = 0.80 and 1.20 V vs SCE) were slightly observed. Next, the cyclic voltammogram of Amberlyst 15Dry (-SO₃H) (0.2 M based on the concentration of -SO₃H) in MeCN/CH₂Cl₂ (50/50 v/v %) was also measured. As shown in Fig. 1(b), ionic conductivity was hardly observed. This indicates that the ion pairs of -SO₃⁻ and H⁺ held together by Coulomb force,³⁾ therefore, it was difficult to provide the sufficient electrical conductivity. Then, the cyclic voltammogram of 0.05 M KBr + 0.2 M Amberlyst 15Dry (-SO₃H) in MeCN/CH₂Cl₂

Fig. 1 Cyclic voltammograms of (a) 0.05 M KBr in MeCN/CH₂Cl₂ (50/50 v/v %), (b) 0.2 M Amberlyst 15Dry (-SO₃H) in MeCN/CH₂Cl₂ (50/50 v/v %), (c) 0.05 M KBr + 0.2 M Amberlyst 15Dry (-SO₃H) in MeCN/CH₂Cl₂ (50/50 v/v %), recorded at a Pt disk electrode ($\phi = 0.8$ mm). The scan rate was 100 mV s⁻¹.

(50/50 v/v %) was measured. As shown in Fig. 1(c), the oxidation current for Br⁻ (over 0.5 V vs. SCE) and the reduction current for H⁺ (under 0 V vs. SCE) were markedly observed. From these results, it is clear that the cation exchange reaction between KBr and Amberlyst 15Dry (-SO₃H) takes place, and the resulting protons derived from Amberlyst 15Dry (-SO₃H) seem to act as the main carrier of an electronic charge [Eq. (1)].

It is well known that benzyl alcohols can be efficiently oxidized to benzaldehydes by using a Br⁻/Br⁺ mediator.⁴⁾ Then, anodic oxidation of *p*-methoxybenzyl alcohol (**1**) was investigated using KBr as a mediator and solid-supported acids as a supporting electrolyte. The typical experimental procedure is illustrated in Fig. 2. At first,

Fig. 2 Experimental procedure.

anodic oxidation of **1** in 0.05 M KBr/MeCN was attempted at 1.3 V vs SCE. However, it was difficult to get efficient current density because of the low solubility of KBr in MeCN (entry 1).⁵⁾ Next, controlled potential electrolysis of **1** was carried out at 1.3 V vs SCE in 0.05 M KBr/0.2 M Amberlyst 15Dry (-SO₃H)/MeCN in the presence of 2,6-lutidine which suppresses acid-catalyzed ionization of **1** to the corresponding benzyl cation,⁶⁾ however, only a trace amount of *p*-methoxybenzaldehyde (**2**) was formed (entry 2). In this case, a large amount of **1** was recovered after the electrolysis. On the other hand, **2** was obtained in moderate yield when the concentration of KBr was reduced to 0.01 M (entry 3). These indicate that the yield of **2** was greatly affected by the concentration of Br⁻, and the desired reaction seems to proceed more efficiently at a lower concentration of Br⁻. Actually, it has been reported that a lower concentration of Br⁻ is suitable for the indirect anodic oxidation of organic compounds using a Br⁻/Br⁺ mediator, because a higher concentration of Br⁻ preferentially generates

Table 1 Anodic Oxidation of *p*-Methoxybenzyl Alcohol (**1**) Using KBr and Solid-Supported Acids.

entry	MeCN/CH ₂ Cl ₂ (v/v %)	KBr (M)	solid-supported acid (0.2 M) ^a	base (0.2 M)	yield ^b (%)
1	100/0	0.05	—	—	—
2	100/0	0.05	Amberlyst 15Dry (-SO ₃ H)	2,6-lutidine	trace ^c
3	100/0	0.01	Amberlyst 15Dry (-SO ₃ H)	2,6-lutidine	49
4	50/50	0.05	Amberlyst 15Dry (-SO ₃ H)	2,6-lutidine	98
5	50/50	0.05	Amberlyst 15Dry (-SO ₃ H)	Et ₃ N	trace ^c
6	50/50	0.05	Amberlyst 15Dry (-SO ₃ H)	—	trace ^d
7	50/50	0.05	Nafion NR-50 (-SO ₃ H)	2,6-lutidine	80

^a Based on the concentration of -SO₃H. ^b Isolated yield. ^c A large amount of **1** was recovered.

^d Complex mixture.

Table 2 Recyclability of Amberlyst 15Dry (-SO₃H).

cycle	yield ^a (%)
1 st	98
2 nd	92
3 rd	90
4 th	97
5 th	90

^aIsolated yield

Br₃⁻ which has lower oxidation ability.⁷⁾ Moreover, when CH₂Cl₂ was used as a co-solvent (50%), the desired reaction proceeded smoothly to provide **2** in excellent yield (entry 4). The marked increased yield is probably due to the suppression of the dissociation of KBr in a mixed solvent of MeCN/CH₂Cl₂ leading to the low concentration of Br⁻, and a solvent effect of CH₂Cl₂. CH₂Cl₂ is more commonly used in a Br⁻/Br⁺ redox mediatory system compared with MeCN. In the presence of Et₃N instead of 2,6-lutidine, only a trace amount of **2** was formed and **1** was mostly recovered after the electrolysis (entry 5). In this case, Et₃N was mainly oxidized at the anode. Furthermore, only a trace amount of **2** was formed in the absence of a base (entry 6). Finally, **2** was obtained in high yield using Nafion NR-50 (-SO₃H) as a solid-supported acid (entry 7). From these results, bromide ions derived from the cation exchange reaction between KBr and solid-supported acids (-SO₃H) seem to act as a mediator.

The recyclability of solid-supported acids was also examined. Anodic oxidation of **1** was successfully carried out 5 times under the conditions of entry 4 in Table 1 by the recycling of Amberlyst 15Dry (-SO₃H) (Fig. 2). As shown in Table 2, the yield of **2** was always more than 90% and did not decrease at all upon the reuse of Amberlyst 15Dry (-SO₃H). This clearly suggests that Amberlyst 15Dry (-SO₃H) are recyclable for many times.

Next, anodic oxidation of other benzyl alcohols was also carried out as shown in Table 3. Although the current efficiency depended on the oxidation potentials of benzyl alcohols, the corresponding benzaldehydes were obtained in good to excellent yields. From these results, it was demonstrated that the electrolytic system using KBr as a mediator and Amberlyst 15Dry (-SO₃H) as a supporting electrolyte is effective for the anodic oxidation of benzyl alcohols.

4 Conclusion

We have successfully developed a novel electrolytic system using KBr as a mediator and solid-supported acids as a supporting electrolyte. This system enables us to use KBr as a mediator in MeCN/CH₂Cl₂. Furthermore, solid-supported acids serve as not only a promoter of the dissociation of KBr but also a supporting electrolyte. Limitation of this new methodology and the further application for electroorganic synthesis are now under investigation.

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Table 3 Anodic Oxidation of Benzyl Alcohols Using KBr and Amberlyst 15Dry (-SO₃H).

<div style="text-align: center;"> </div>				
entry	R	E_p^{ox} (V vs SCE) ^a	electricity (F/mol)	yield ^b (%)
1	OMe	1.63	3	98 (65) ^c
2	H	2.32	9	70 (16)
3	NO ₂	2.75	9.5	69 (15)

^a Oxidation potentials (E_p^{ox}) of benzyl alcohols (0.01 M) were measured in 0.1 M *n*-Bu₄NBF₄/MeCN, recorded at a Pt disk electrode (ϕ = 8 mm). The scan rate was 100 mV s⁻¹. ^b Isolated yield. ^c Current efficiency.