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Anodic oxidation of organic compounds based on the cation exchange reaction between KBF_4 and solid-supported acids

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ABSTRACT

We have developed a novel electrolytic system for anodic oxidation of organic compounds based on the cation exchange reaction between potassium tetrafluoroborate (KBF_4) and solid-supported acids. It was clarified by cyclic voltammetry as well as preparative electrolyses that hydrogen tetrafluoroborate (HBF_4) derived from the cation exchange reaction acts as a supporting electrolyte in MeCN. On the basis of the electrolytic system, anodic oxidation of 1,2,4-trimethoxybenzene was carried out to provide the corresponding homocoupling product in quantitative yield. Furthermore, anodic oxidation of benzyl alcohols having not only electron-donating but also electron-withdrawing groups at the para position was successfully achieved by optimizing the reaction conditions.

1. Introduction

Organic electrosynthesis has recently attracted much attention as one of the most promising green sustainable processes in organic synthesis, because it is based on "mass-free" electron transfer between electrodes and substrates [1,2]. Therefore, it can avoid not only the use of conventional redox reagents but also their separation and waste after the reaction. However, it requires large amounts of supporting electrolytes to provide sufficient ionic conductivity to the solvents for electrolysis. The use of supporting electrolytes causes their separation and waste after the electrolysis. While several electrolytic systems have been developed to minimize or eliminate the addition of supporting electrolytes [3–9], they require special equipment and/or conditions.

Quaternary ammonium salts are generally used in organic electrosynthesis as supporting electrolytes owing to their good solubility in organic solvents. On the other hand, naturally occurring inorganic metal salts and their derivatives are more ideal supporting electrolytes compared to synthetic quaternary ammonium salts from the viewpoints of economical and environmental impacts. However, their poor solubility in many organic solvents restricts their use in organic electrosynthesis. In order to achieve an environmentally friendly electrolytic system, we have recently developed a novel electrolytic system using solid-supported acids [10,11]. It is based on the cation exchange reaction between inorganic metal halides and solid-supported acids [Eq. (1)], and the resulting hydrogen halides act as a supporting electrolyte. The cation exchange reaction promotes the dissociation of inorganic metal halides in organic solvents by shifting the equilibrium to the right. On the basis of the electrolytic system, we have successfully carried out anodic fluorination and indirect anodic oxidation of organic compounds. In these reactions, hydrogen halides derived from the cation exchange reaction play roles of a key reagent as well as a supporting electrolyte. Although the electrolytic system using solid-supported acids is useful for anodic fluorination and indirect anodic oxidation of organic compounds, its application has been limited to such special reactions.

(1)

In order to extend the generality of the electrolytic system, we focused on potassium tetrafluoroborate (KBF_4) as an inorganic metal salt, because tetrafluoroborate (BF_4^-) has a high anodic discharge potential. Therefore, the cation exchange reaction between KBF_4 and solid-supported acids [Eq. (2)] would generate hydrogen tetrafluoroborate (HBF_4) as a supporting electrolyte and thus offer an ideal electrolytic system for anodic oxidation of organic compounds. It should be applied to anodic oxidation of various organic compounds, which even have high oxidation potentials. Furthermore, while HBF_4 is toxic and corrosive, it would be possible to generate HBF_4 in situ without its careful handling. We herein report anodic oxidation of organic compounds based

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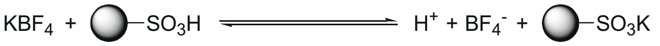
on the cation exchange reaction between KBF_4 and solid-supported acids.



(2)

2. Experimental

2.1. General

^1H NMR spectra were recorded on a JEOL JNM EX-270 (^1H: 270 MHz) spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. EI mass spectra were recorded on a Shimadzu PARVUM2 gas chromatograph–mass spectrometer.

2.2. Materials

Amberlyst 15Dry, Nafion NR-50, and Si-SCX-2 were purchased from Organo Corp., Aldrich, and Silicycle, respectively. Aciplex was prepared by hydrolysis of Aciplex F (terminal group: SO_2F), which was obtained from Asahi Kasei Chemicals. They were used after decantation. All other reagents were purchased from commercial suppliers and used without further purification.

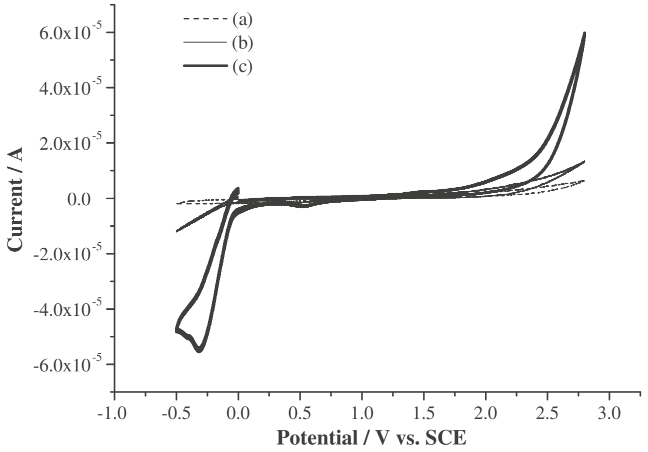


Fig. 1. Cyclic voltammograms of (a) 0.1 M KBF_4, (b) 0.5 M Amberlyst 15Dry, and (c) 0.1 M KBF_4 and 0.5 M Amberlyst 15Dry in MeCN, recorded at a Pt disk electrode (φ = 0.8 mm). The scan rate was 100 mV s^{-1}.

2.3. Cyclic voltammetry

Cyclic voltammetry was performed by using a computer-controlled electrochemical analyzer (ALS/CH Instruments 610B). Cyclic voltammetry was carried out with a three-electrode system using a platinum disk working electrode (φ = 0.8 mm), a platinum wire counter electrode, and a saturated calomel electrode (SCE) as a reference electrode.

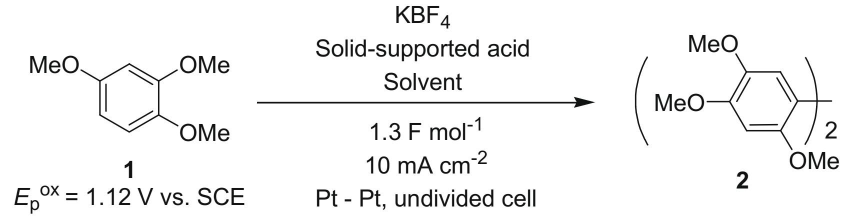
2.4. General procedure for anodic oxidation of organic compounds based on the cation exchange reaction between KBF_4 and Amberlyst 15Dry

Preparative electrolysis experiments were carried out with a DC power supply (Matsusada Precision PK-80M). Anodic oxidation of a substrate (1 mmol) was carried out with platinum plate electrodes (2×2 cm^2) in MeCN (10 ml) containing 0.1 M KBF_4 and 0.5 M Amberlyst 15Dry (based on the concentration of SO_3H) using an undivided cell. Constant current electrolysis was conducted with magnetic stirring at room temperature. The conversion of the substrate was monitored by TLC. After the electricity was passed until the complete consumption of the substrate, the electrolytic solution was passed through a glass filter (pore size: 5–10 μm) to remove Amberlyst 15Dry. The filtrate was passed through a short column of silica gel eluting with $CHCl_3$. The eluent was evaporated under vacuum and the residue was purified by using a Shimadzu LC-6AD HPLC system eluting with MeCN to give a pure product, which was identified by comparison with the literature values (**2**) [12] and authentic samples (**4**, **6**, **8**, **10**, **12**, and **14**) using ^1H NMR and mass spectroscopy.

2.5. Regeneration of the spent Amberlyst 15Dry

The spent Amberlyst 15Dry was washed with MeOH (200 ml) and regenerated by treating with 1 M aq. HCl (120 ml). After the regenerated Amberlyst 15Dry was washed with MeOH (20 ml) and then MeCN (20 ml), it was dried at 80 °C for 2 h under vacuum.

Table 1
Anodic coupling reaction of **1** using KBF_4 and solid-supported acids.



Entry	KBF_4 (M)	Solid-supported acid	Solvent	Yield (%)[a]
1	0.1	–	MeCN	–[b]
2	–	0.1 M Amberlyst 15Dry (SO_3H)	MeCN	–[b]
3	0.1	0.1 M Amberlyst 15Dry (SO_3H)	MeCN	98
4	0.1	0.5 M Amberlyst 15Dry (SO_3H)	MeCN	Quant.
5	0.1	0.5 M Amberlyst 15Dry (SO_3H)	CH_2Cl_2	–[b]
6	0.1	0.5 M Amberlite (CO_2H)	MeCN	Quant.
7	0.1	0.5 M Nafion NR-50 (SO_3H)	MeCN	88
8	0.1	0.5 M Aciplex (SO_3H)	MeCN	Quant.
9	0.1	0.2 M Si-SCX-2 (SO_3H)	MeCN	76

[a] Isolated yield.

[b] The cell voltage was too high to perform the electrolysis.