

Review

# Highly selective electrochemical fluorination of organic compounds in ionic liquids

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## Abstract

Recent studies on electrochemical partial fluorination in ionic liquid fluoride salts are reviewed. At first, historical background and some problems of electrochemical fluorination in organic solvents are briefly mentioned. Solvent-free electrochemical fluorinations in ionic liquids are explained as follows. Ultrasonication was found to improve both the yield and current efficiency for electrochemical fluorination of  $\alpha$ -phenylthioacetate, which is mainly attributable to marked mass transport promotion of the substrate and the suppression of anode passivation. Highly regioselective and efficient fluorination of cyclic ethers, lactones, and cyclic carbonate was achieved in  $\text{Et}_4\text{N}^+\cdot 4\text{HF}^-$  and  $\text{Et}_3\text{N}^+\cdot 5\text{HF}^-$ . Selective fluorination of hardly oxidizable phthalide was realized using a combination of imidazolium and fluoride ionic liquids. The unique effect of imidazolium ionic liquids on electrochemical fluorodesulfurization of 3-phenylthiophthalide was explained. Reuse of ionic liquids for electrochemical fluorination is also possible.

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**Keywords:** Anodic fluorination; Ionic liquid; Fluorodesulfurization; Ultrasonication

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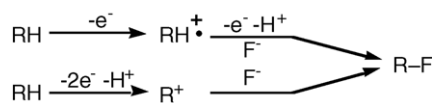
## 1. Introduction

In recent years, room temperature molten salts, ionic liquids have proved to be a new class of promising solvents because of their excellent properties such as good electroconductivity, non-flammability, thermal stability,

non-volatility, and reusability [1–3]. In addition, if a combination of cation and anion is appropriately made, aprotic media having a wide electrochemical window can be obtained. Therefore, when ionic liquids are used as electrolytic media, organic electrolytic reactions, particularly electroorganic synthesis would be possible without any organic solvents. Although ionic liquids have already been shown to be promising media for batteries, fuel cells, photovoltaic cells, and electroplating processes, there have

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Scheme 1.

still been a limited number of papers dealing with organic electrosynthesis [4].

Electrochemical partial fluorination of various compounds has been studied mainly in organic solvents containing supporting fluoride salts such as  $\text{Et}_3\text{N}\cdot n\text{HF}$  ( $n = 2\text{--}5$ ) and  $\text{Et}_4\text{NF}\cdot n\text{HF}$  ( $n = 3\text{--}5$ ) [5,6]. Since the discharge potential of fluoride ions is extremely high ( $>+2.9$  V versus SCE at Pt anode in MeCN), the fluorination proceeds via a (radical) cation intermediate as shown in Scheme 1.

The fluorinated product selectivity and fluorination efficiency are very often greatly affected by the kinds of solvents and supporting fluoride salts [7,8]. Therefore, a choice of combination of a solvent and supporting fluoride salt is of much importance. The use of organic solvents like acetonitrile sometimes causes anodic passivation which results in low efficiency for anodic fluorination. In order to avoid anode passivation and acetamidation, anodic fluorination in liquid fluoride salts without any solvents is an alternative method. Meurs and Eilenburg carried out anodic fluorination of benzene derivatives, naphthalene, olefins, furan, benzofuran, and phenanthroline in liquid  $\text{Et}_3\text{N}\cdot 3\text{HF}$  and they obtained the corresponding partially fluorinated products in less than 50% yields [9]. Noel and co-worker also reported that electrochemical fluorination of aromatics containing active methylene groups was promoted in  $\text{Et}_3\text{N}\cdot 3\text{HF}$  [10]. However, there are still limited examples of anodic fluorination in such ionic liquid fluoride salts.

In this review article, selective electrochemical fluorination of organic compounds in ionic liquids like  $\text{Et}_3\text{N}\cdot n\text{HF}$  ( $n = 3, 4$ ),  $\text{Et}_4\text{NF}\cdot n\text{HF}$  ( $n = 4, 5$ ), and imidazolium salts as reaction media is described.

## 2. Selective electrochemical fluorination

### 2.1. Electrochemical mono- and difluorination of ethyl $\alpha$ -phenylthioacetate in $\text{Et}_3\text{N}\cdot 3\text{HF}$ ionic liquid under ultrasonication

More than 10 years ago, Laurent's group and our group achieved independently anodic  $\alpha$ -fluorination of ethyl

$\alpha$ -phenylthioacetate (**1**) in  $\text{Et}_3\text{N}\cdot 3\text{HF}/\text{MeCN}$  [11,12]. Since anode passivation takes place during the anodic fluorination, pulse electrolysis is necessary. Anodic difluorination of **1** was unsuccessful in the same electrolytic solution, while anodic fluorination of  $\alpha$ -monofluorinated acetate (**2**) gave the  $\alpha,\alpha$ -difluorinated product **3** in moderate yield after passing a large excess amount of electricity (Scheme 2) [13].

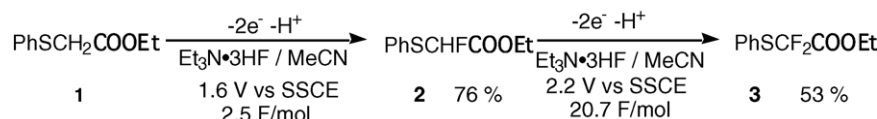
In order to overcome the above problems, anodic fluorination of **1** in neat  $\text{Et}_3\text{N}\cdot 3\text{HF}$  without a solvent was investigated under ultrasonication [14]. As shown in Fig. 1, a limiting diffusion oxidation current of **1** increased markedly under ultrasonication compared with that under mechanical stirring. The viscosity of the ionic fluoride salt is higher than that of ordinary organic solvents, therefore, the mass transport of substrate **1** to the anode surface from the bulk of the fluoride salt is slower than that in organic solvents. The enhanced oxidation current is attributed to the markedly promoted mass transport of **1**. Application of ultrasonication to the ionic liquid  $\text{Et}_3\text{N}\cdot 3\text{HF}$  generates cavitation, which generates a micro-jet stream, promoting mass transport of **1** to the anode surface from the bulk of the ionic liquid. The result indicates that the ionic liquid  $\text{Et}_3\text{N}\cdot 3\text{HF}$  behaves just like ordinary solvents under ultrasonication.

Anodic fluorination of  $\alpha$ -phenylthioacetate (**1**) in ionic liquid  $\text{Et}_3\text{N}\cdot 3\text{HF}$  proceeds smoothly without anode passivation under ultrasonication to provide the  $\alpha$ -monofluorinated product **2** in high yield and with high current efficiency. Notably, anodic difluorination of **1** can be also achieved in the same ionic liquid under ultrasonication as shown in Scheme 3 [14]. Thus, the current efficiency for the anodic difluorination of **1** was greatly improved as compared with that without ultrasonication. As described above,  $\text{Et}_3\text{N}\cdot 3\text{HF}$  ionic liquid is highly useful for selective anodic fluorination.

However,  $\text{Et}_3\text{N}\cdot 3\text{HF}$  is rather easily oxidized at ca. 2 V versus  $\text{Ag}/\text{Ag}^+$ , therefore, this ionic salt is not suitable for the fluorination of substrates having high oxidation potentials.

### 2.2. Electrochemical fluorination in $\text{R}_4\text{NF}\cdot n\text{HF}$ ( $n > 3,5$ ) ionic liquids

Momota et al. developed a new series of liquid fluoride salts,  $\text{R}_4\text{NF}\cdot n\text{HF}$  ( $\text{R} = \text{Me}, \text{Et}, \text{and } n\text{-Pr}, n > 3,5$ ) that are useful in partial fluorination [15,16]. These electrolytes are non-viscous liquids that have high electroconductivity and anodic stability. Thus, anodic partial fluorination of arenes such as benzene [16], mono-, di-, and trifluorobenzenes [17], chlorobenzene [18], bromobenzene [19], toluene [20,21], and quinolines [22] was successfully carried out at high current densities by employing these liquid fluoride salts in



Scheme 2.

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