ALKYLIMIDAZOLIUM FLUOROHYDROGENATES ROOM TEMPERATURE MOLTEN SALTS

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ABSTRACT

Reaction of some N-alkylimidazolium chloride with anhydrous hydrogen fluoride (HF) gives involatile room temperature molten salt, RR'ImF-2.3HF where RR'Im = 1,3-dimethylimidazolium (DMIm), 1-ethyl-3-methylimidazolium (EMIm), 1-methyl-3-propylimidazolium (PrMIm), 1-butyl-3-methylimidazolium (BMIm), 1-methyl-3-pentylimidazolium (PeMIm), 1-hexyl-3-methylimidazolium (HMIm). Vacuum stable salts at room temperature exhibit the same composition regardless of the type of the cation. High specific conductivities, 110 and 100 mScm-1, are observed at 298 K for DMImF-2.3HF and EMImF-2.3HF, respectively. Substitution of the proton or the longer alkyl side chains for the ethyl group of the imidazolium cation decreases the conductivity. These salts are stable in air and do not etch a Pyrex glass container at ambient conditions. Electrochemical windows of these salts range around 3V. Elongation of the alkyl side chain on the cation tends to extend the cathode limit. These salts act as good Lewis bases against binary fluorides of some main group elements and transition metals to give ionic salts without involatile byproducts.

INTRODUCTION

Since the invention of a moisture stable room temperature molten salt (RTMS), 1-ethyl-3-methylimidazolium tetrafluoroborate in 1992 (1), several tens of RTMS have been reported by the combinations of alkylimidazolium cations and inorganic and organic fluorooanions (2,3). Especially, studies on the 1-ethyl-3-methylimidazolium tetrafluoroborate have been most extensively reported to date. Number of reports of the alkylimidazolium RTMS containing remarkably stable bis((trifluoromethyl)sulfonyl) amide anion have been increasing in the last five years. These salts are single salt containing only one kind of cation and anion. The order of conductivity ranges 10^1-10^4 mScm^{-1} (2,3).

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The authors have recently reported a new RTMS, EMImF-2.3HF, synthesized by a reaction of 1-ethyl-3-methylimidazolium chloride (EMICl) and anhydrous hydrogen fluoride (4-6). It has been found that this salt possesses a high electrical conductivity of $10^{2}$ mScm$^{-1}$. In the present study, physical properties of some alkylimidazolium fluoro hydrogenate molten salts including EMImF-2.3HF are reported as well as the electrochemical behavior. In addition, syntheses of alkylimidazolium salts including some new RTMS using RR’ImF-2.3HF as starting reagents are described.

**EXPERIMENTAL**

Some 1-alkyl-3-methylimidazolium chlorides were supplied by Sanko Chemical Industry, Co. Ltd.. The others were prepared by the reaction of 1-methylimidazole and alkyl chlorides. For purification of the chloride, the salt was dissolved in acetonitrile dried over molecular sieves and then precipitated from the solution by adding ethyl acetate. The chlorides were weighed and charged in a plastic reaction tube and interacted with a large excess anhydrous HF at 273–298 K. Volatile gases were eliminated by nitrogen gas purge and successive pumping with a rotary pump. The composition of the vacuum stable salt, RR’ImF-2.3HF, was doubly checked by elemental analysis and gravimetry.

A series of 1-ethyl-3-methylimidazolium fluorometallates were synthesized by the reaction of some binary fluorides and EMImF-2.3HF. Large excess volatile fluorides such as BF$_3$, PF$_5$, AsF$_5$ and SbF$_5$ were reacted with EMImF-2.3HF. After the reaction, excess fluoride and HF evolved were eliminated by pumping through a chemical trap at around 343 K. Stoichiometric reactions were performed for involatile fluorides such as NbF$_5$ and TaF$_5$ and evolved HF was eliminated in the same manner (6). Reactions are highly exothermic and must be controlled carefully by cooling.

Viscosities of the molten salts were determined with the aid of Ubbelohde-type glass viscometers or a Brookfield Engineering Laboratories DV-III cone and plate rheometer. Ostwald-type viscometers made of FEP polymer were occasionally used for air-sensitive salts. Densities of the salts were measured with a pycnometer method. Conductivities of the salts were measured by an impedance technique using a calibrated cell with platinum disk electrodes. Electrochemical windows of the salts were measured by cyclic voltammetry using a glassy carbon working electrode. The potential was measured against Pt QRE. Redox potentials of ferrocene were separately measured against Pt QRE in the salts to be used as a reference for comparison of the electrochemical windows.

**RESULTS AND DISCUSSION**

Vacuum stable salts obtained at ambient condition exhibit similar composition, RR’ImF-2.3HF. Vibrational spectroscopy suggests the absence of free HF and the existence of oligomeric fluoro hydrogenate anions such as H$_2$F$_3^-$ and H$_3$F$_4^-$. Neither the changes in weight nor IR spectrum of the salts are observed after exposure to air for one day. These melts do not etch borosilicate glasses such as Pyrex, no difference being
observed in IR spectrum before and after interaction. Most of the measurements were performed using Pyrex glass apparatus in this study.

Table 1 summarizes some physical properties of alkylimidazolium fluorohydrogenates. The conductivities of DMImF-2.3HF and EMImF-2.3HF are comparable to that of 1M KCl aqueous solutions. The conductivity of these salts decreases as the viscosity of the salt increases. The viscosity increases with the molecular weight, namely, the elongation of the alkyl side chain of the cation. The Arrhenius plots of viscosity (Figure 1) and conductivity (Figure 2) slightly show upward and downward curvature at lower temperatures, respectively. The activation energies calculated from the slope of the linear Arrhenius region around 298 K are listed in Table 2. A similar tendency and a relatively small discrepancies between the activation energies of viscosity and conductivity suggests that the high conductivity of the salts can be explained by the low viscosity of them without introducing some special conduction mechanism such as ion hopping.

Figure 3 shows the electrochemical windows of the RTMS. The widths of the windows are distributed around 3 V. The anode limits are about 1 V vs Fc/Fc⁺, not changing very much by the difference of the cations. The reaction is considered to be some oxidation of the cations presumably accompanied by fluorination of them. Cathode limit is roughly −2 V vs Fc/Fc⁺, however, somewhat lower for HMImF-2.3HF. Hydrogen evolution from the glassy carbon electrode is observed at the cathode limits of the salts. However, it has not been clarified yet if the accompanying reactions such as the reduction of the cations exist.

These RTMS act as Lewis bases against metal fluorides to give some fluorometallates including molten salts. Involatile byproducts are not formed in this process, giving the salts with high purity. Reactions are highly exothermic and must be controlled carefully. Table 3 shows some results of the reaction of EMImF-2.3HF and some gaseous, liquid and solid binary fluorides. Large excess of the gaseous and liquid fluorides were reacted with EMImF-2.3HF whereas stoichiometric amount was used for solid fluorides. Raman spectra shown in Figure 4 indicate the formation of hexafluorometallate salts except the case of SbF₅. It has been revealed that the room temperature vacuum stable salt obtained by the reaction of EMImF-2.3HF and excess SbF₅ is not a simple SbF₅⁺ salt but that containing oligomeric anions such as Sb₂F¹⁴⁺ and Sb₃F₁₆⁺. The stoichiometric reaction of EMImF-2.3HF and solid fluorides, NbF₅ and TaF₅, gives new RTMS, EMImNbF₆ and EMImTaF₆, respectively (7). The similarities of the physical properties other than densities in Table 4 are due to the similar sizes of niobium and tantalum atoms to give similar sizes of their hexafluorometallate anions.

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**Table 1.** Some physical constants of alkylimidazolium fluorohydrogenates RR'ImF·2.3HF at 298 K.

| Salts        | M.W. | Density / g/cm³ | Viscosity / cP | Specific conductivity / mS cm⁻¹ |
|--------------|------|-----------------|----------------|-------------------------------|
| DMImF·2.3HF  | 162  | 1.17            | 5.1            | 110                           |
| EMImF·2.3HF  | 176  | 1.13            | 4.9            | 100                           |
| PrMImF·2.3HF | 190  | 1.11            | 7.0            | 61                            |
| BMImF·2.3HF  | 204  | 1.08            | 19.6           | 33                            |
| PeMImF·2.3HF | 218  | 1.05            | 26.7           | 27                            |
| HMImF·2.3HF  | 232  | 1.00            | 25.8           | 16                            |

**Table 2.** Comparison of activation energies calculated from the Arrhenius plots of the viscosities and conductivities of the RR’ImF·2.3HF.

| Salts        | Activation energy of viscosity / kJ mol⁻¹ | Activation Energy of conductivity / kJ mol⁻¹ |
|--------------|------------------------------------------|---------------------------------------------|
| DMImF·2.3HF  | 15.4                                     | 9.7                                         |
| EMImF·2.3HF  | 12.7                                     | 10.1                                        |
| PrMImF·2.3HF | 17.0                                     | 11.5                                        |
| BMImF·2.3HF  | 24.9                                     | 14.2                                        |
| PeMImF·2.3HF | 26.5                                     | 15.8                                        |
| HMImF·2.3HF  | 26.5                                     | 17.9                                        |
Table 3. Reaction products of EMImF-2.3HF and some binary fluorides

| MF₂   | EMImF-2.3HF (mmol) | MF₃ (mmol) | EMImMF₃⁺⁺ (mmol) | EMImMF₅⁺⁺ (mmol) | State at 298K |
|-------|-------------------|------------|------------------|------------------|----------------|
| BF₃   | 9.88              | Large excess | EMImBF₄ 9.88     | 9.84             | Liquid         |
| PF₅   | 6.51              | Large excess | EMImPF₆ 6.51     | 6.69             | Solid          |
| AsF₅  | 3.97              | Large excess | EMImAsF₆ 3.97    | 4.12             | Solid          |
| SbF₅  | 3.18              | Large excess | EMImSbF₆ 3.18    | 7.09*            | Liquid         |
| NbF₅  | 5.22              |             | EMImNbF₆ 5.22    | 5.10             | Liquid         |
| TaF₅  | 4.48              |             | EMImTaF₆ 4.48    | 4.38             | Liquid         |

*Due to the formation of Sb₂F₁₁ and Sb₃F₁₆ salts.

Figure 1. Arrhenius plots of viscosities of RR’ImF-2.3HF.
Figure 2. Arrhenius plots of conductivities of RR’ImF-2.3HF.

Figure 3. Comparison of electrochemical windows of RR’ImF-2.3HF. WE: GC disk, CE: Pt. Scan rate: 10 mV s\(^{-1}\).
Figure 4. Raman spectra of (a) EMImBF$_4$, (b) EMImPF$_6$, (c) EMImAsF$_6$, (d) EMImSb$_5$F$_{11}$, (e) EMImNbF$_6$, (f) EMImTaF$_6$ and (g) solid EMImCl. The solid circles in the figure indicate peaks ascribed to the fundamental modes of the MF$_{n+1}^-$ anions.