Decomposition of Fluorinated Ionic Liquids to Fluoride Ions Using Superheated Water: An Efficient Approach for Recovering Fluorine from the Waste of Fluorinated Ionic Liquids

Hisao HORI*

Department of Chemistry, Faculty of Science, Kanagawa University, 2946 Tsuchiya, Hiratsuka, Kanagawa 259-1293, Japan

* Corresponding author: h-hori@kanagawa-u.ac.jp

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Hisao HORI*

Department of Chemistry, Faculty of Science, Kanagawa University, 2946 Tsuchiya, Hiratsuka 259-1293, Japan

*Corresponding author: h-hori@kanagawa-u.ac.jp
ABSTRACT

Fluorinated ionic liquids are cutting-edge materials investigated for electrolytic media for energy-related applications. Although their industrial usages are being spread, waste treatment techniques for these materials are not well established, because they are thermally and chemically stable, owing to the presence of strong carbon-fluorine bonds, and incineration produces hydrogen fluoride gas, which seriously damages incinerators. We describe herein our recent efforts to decompose fluorinated ionic liquids to F⁻ ions (i.e., mineralization) by use of superheated water, with the aim for closing the loops on fluorine element. A methodology that enables complete mineralization of the ionic liquids bearing [(CF₃SO₂)₂N]⁻ anion moiety is demonstrated.

Keywords: Ionic Liquid, Superheated Water, Fluorine, Mineralization
1. Introduction

Ionic liquids (ILs) have been of great interest in recent decades because they have unique characteristics such as non-volatility, non-flammability, high solvation ability, etc.\textsuperscript{1,2} Especially, fluorinated ILs (F-ILs), which consist of an organic cation and a perfluorinated organic anion, are employed for components of many energy devices because they show not only general characteristics of ILs, but also satisfy the requisites for electrochemical applications, that is, large electrochemical window, high ion-conductivity, and high heat capacity.\textsuperscript{3-5} While applications of F-ILs were increased, their life cycle assessment\textsuperscript{6} and toxicity\textsuperscript{7,8} were reported. Some F-ILs are biodegradable.\textsuperscript{9} However, the degradation is mostly limited in the organic cation, and does not lead complete decomposition of the ILs. For example, bis(trifluoromethanesulfonyl)imide, [(CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}N], which is frequently used as an anion moiety in F-ILs, does not biodegrade.\textsuperscript{10}

Hence, waste treatment methodologies that achieve complete mineralization of F-ILs are desired. For the waste treatment allowing complete mineralization, incineration is an option. However, it needs high temperatures to destruct the strong carbon-fluorine bonds.\textsuperscript{11} Furthermore, during the treatment, gaseous hydrogen fluoride (HF) generates, which seriously degrades the firebricks of incinerators. If F-ILs could be destructed to F\textsuperscript{-} ions by means of an environmentally benign methodology, then conventional technology can be used to treat F\textsuperscript{-}, by adding some calcium-ion source (typically Ca(OH)\textsubscript{2}) to aqueous F\textsuperscript{-} to form harmless CaF\textsubscript{2}. CaF\textsubscript{2} is a raw material for hydrofluoric acid, which is a raw material for all organofluorine chemicals. Thus, the development of a methodology for the mineralization of F-ILs could contribute to closing the loops of fluorine element. There were several reports on the thermal degradation of F-ILs.\textsuperscript{12-15} However, the majority of these works have described the aging of the F-ILs in view of battery performance. We would like to stress that the extent of degradation that lowers battery performance is considerably smaller than that required for efficient waste treatment.
Reaction using superheated- or supercritical water is environmentally benign in waste treatment engineering because the reaction can form useful products or transform undesirable compounds into harmless species.\textsuperscript{16–19}

Figure 1 shows a schematic of phase diagram of water. Supercritical water is a water state at temperature and pressure that are higher than the critical point (374 °C, 22.1 MPa). On the other hand, superheated water (it is also called as ‘subcritical water’ or ‘pressurized hot water’) is a liquid state water under high pressure, where the temperature is below the critical temperature (374 °C). Some articles note that the lowest temperature of superheated water is 100 °C. However, because the unique properties of superheated water (high dissolving power towards nonpolar organic compounds, high hydrolyzing power, etc.) begin to appear at 200–250 °C, we could image that superheated water is liquid water at around 200 °C or higher. In the recycling of non-metallic fractions from electronic waste (E-waste), treatment using superheated- or supercritical water is indicated to have a smaller environmental impact than pyrolysis.\textsuperscript{20} Furthermore, in contrast to the pyrolysis of organofluorine chemicals, even though toxic carbonyl fluoride (COF\textsubscript{2}) generates during the treatment, it can easily undergo hydrolysis to CO\textsubscript{2} and HF;\textsuperscript{21} and HF is present as F\textsuperscript{−} in the resulting reaction solution. In this comprehensive paper, we describe our recent efforts on the mineralization of two F-ILs, that is, [Me\textsubscript{3}PrN][(CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}N] and 1-methyl-1-propylpiperidinium bis(trifluoromethanesulfonyl)imide, i.e., [C\textsubscript{3}mpip][(CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}N], and a Li salt Li[(CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}N], using superheated water combined with reducing or oxidizing agents.\textsuperscript{22–24} The structure of these compounds are illustrated in Fig. 2.

2. Experimental
2.1 Materials
[Me3PrN][CF3SO2]2N] and [C3mpip][(CF3SO2)2N] were purchased from Kanto Chemical (Tokyo, Japan). Li[(CF3SO2)2N] was obtained from SynQuest Labs (Alachua, FL, USA). Argon (99.99 %), CO2 (1.00 %)/N2, CHF3 (0.971 %)/N2, and CH3SH (96.6 ppmv)/N2 gases were supplied from Nissan Tanaka (Saitama, Japan). N2O (99.5 %) was obtained from GL Sciences (Tokyo, Japan). Solvents and reagents not mentioned above were obtained from FUJIFILM Wako Pure Chemical (Osaka, Japan).

2.2 Procedures for superheated water reactions

An autoclave (35 mL volume) attached with a screw cap, both of which were made of stainless-steel, was employed for all reactions. The screw cap was jointed to two needle valves through stainless steel tubes. One valve was jointed to a gas supply line, and another was jointed to a pressure gauge and a gas sampling port. A gold vessel (25 mL volume, 2.8 cm i.d.) was fitted into the autoclave to exclude the possibility of contamination from the autoclave material. The substrate ([Me3PrN][(CF3SO2)2N], [C3mpip][(CF3SO2)2N], or Li[(CF3SO2)2N]), a reducing agent (zerovalent Fe or FeO) or an oxidizing agent (KMnO4), and pure (Milli-Q) water (10 mL), were placed into the gold vessel in the autoclave. The autoclave was pressurized with argon to 0.6 MPa, and sealed. Then, the autoclave was heated to the planned reaction temperature at ca. 10 °C min⁻¹. After holding at the reaction temperature for a specified time, the autoclave was quickly cooled to 25 °C by an air blower. The gas in the autoclave headspace was collected with a sampling bag through the sampling port, and subjected to analysis. After collecting the gas, the screw cap of the autoclave was opened, and the liquid-solid mixture in the gold vessel was collected and separated by centrifugation. The separated component was subjected to analysis.
2.3 Procedures for Analysis

Major gaseous products were analyzed by using a gas chromatograph (GC 323; GL Sciences, Tokyo) equipped with a thermal conductivity detector and an activated carbon column. Argon was used as the carrier gas. A gas chromatography-mass spectrometry (GC/MS) system (QP2010 SE, Shimadzu, Kyoto) with a fused-silica capillary column (Rt-Q-BOND; Restek, Bellefonte, PA, USA) was used for the detection of minor gaseous products. The carrier gas was helium, and the injector temperature was held at 120 °C. The analyte was injected into the apparatus in split mode (20/1 ratio), and analyses were conducted in full-scan mode ($m/z$ 2.0–200). The oven temperature program was as follows: holding at 30 °C for 5 min, raising to 200 °C at 20 °C min$^{-1}$, and then holding at that temperature for 20 min.

An ion-chromatograph (IC-2001; Tosoh, Tokyo) with an analytical column (Tosoh TSKgel Super IC-Anion) was used for the quantification of inorganic anions. The mobile phase was an aqueous solution consisted of Na$_2$B$_4$O$_7$ (6 mmol L$^{-1}$), H$_3$BO$_3$ (15 mmol L$^{-1}$), and NaHCO$ _3$ (0.2 mmol L$^{-1}$). The flow rate was 0.8 mL min$^{-1}$. The [(CF$_3$SO$_2$)$_2$N]$^-$ anion was quantified by using an HPLC system (IC-2010, Tosoh) with conductometric detection. The analytical column was Tosoh TSKgel Super ODS-100Z. The mobile phase was a mixture (50:50, v/v) of methanol and aqueous 20 mmol L$^{-1}$ NaH$_2$PO$_4$ (pH 3.0 adjusted by H$_3$PO$_4$) with the flow rate of 0.8 mL min$^{-1}$.

An HPLC-mass spectrometry (LC/MS) instrument (2010 EV; Shimadzu) with a Tosoh TSKgel ODS-80TSGA column was employed to detect reaction intermediates. The mobile phase was a mixture (50:50, v/v) of methanol and aqueous 1 mmol L$^{-1}$ CH$_3$COONH$_4$ (pH 4.0 adjusted by acetic acid). The total organic carbon (TOC) concentrations were measured with a TOC analyzer (N/C 3100 BU; Analytik Jena, Jena, Germany). X-ray diffraction (XRD)
patterns of the resulting solid were measured by using an XRD instrument (MultiFlex; Rigaku, Tokyo) with Cu Kα radiation.

3. Results and discussions

3.1 Reactivity of F-ILs and a Li salt in pure superheated water

In the beginning we investigated the reactivity of F-ILs and Li[(CF₃SO₂)₂N] in pure superheated water, by performing reactions under argon atmosphere without any reducing- or oxidizing agent. Li[(CF₃SO₂)₂N] is not an IL, but it is also used as an electrolyte,²⁵,²⁶ and suitable to evaluate the stability of anion moiety in the F-ILs. Table 1 summarize the data, where each reaction was performed with a constant reaction solution volume (10 mL) and reaction time (6 h). When Li[(CF₃SO₂)₂N] was reacted at 344 °C, virtually no reaction did occur (entry 1): 99 % of the [(CF₃SO₂)₂N]⁻ anion involved in the initial Li salt remained, and the F⁻ extent was negligible (the F⁻ yield on the basis of the fluorine atom content in the initial Li salt was ~0 %). This result reflects the anion’s high stability. Likewise, when [Me₃PrN][(CF₃SO₂)₂N] was heated at 300 °C or 342 °C, virtually no decomposition of the anion moiety was observed (entries 2 and 3). [C₃mpip][(CF₃SO₂)₂N] also showed almost no decomposition of the anion at 300 °C (entry 4). These data indicate that [(CF₃SO₂)₂N]⁻ was quite stable in pure superheated water at least up to ca. 340 °C, regardless the difference in the cation moiety.

3.2 Reductive approach

As described above, [(CF₃SO₂)₂N]⁻, the anion of both F-ILs and the Li salt, showed little decomposition in pure superheated water. Therefore, we performed reactions with iron-based reducing agents, because we previously reported that perfluoroalkanesulfonates (CₙF₂₃₋SO₃⁻,


where \( n = 2–8 \) allowed efficient decomposition to \( F^- \) ions in superheated water in the presence of zerovalent Fe.\(^{27}\)

When Li[\((CF_3SO_2)_2N] was reacted in superheated water with powdered zerovalent Fe (9.60 mmol) at 344 °C for 6 h, the remaining proportion of \([\((CF_3SO_2)_2N]^-\) markedly decreased to 1 %, accompanied by \( F^- \) release with 69 % yield (Table 1, entry 5). FeO also induced the decomposition of \( [\((CF_3SO_2)_2N]^-\), producing \( F^- \) ions with 48 % yield (entry 6) at almost the same temperature (345 °C), although the reactivity was lower than that induced by zerovalent Fe.

Because zerovalent Fe and FeO accelerated the \([\((CF_3SO_2)_2N]^-\) decomposition to \( F^- \) ions, we investigated the reactivity with these reducing agents in more detail. Figure 3A displays reaction-time dependences of \([\((CF_3SO_2)_2N]^-\) and \( F^- \) amounts in the reaction solution and the gaseous product amounts generated from the reactions of Li[\((CF_3SO_2)_2N] with zerovalent Fe. CO\(_2\) and trace of CF\(_3\)H were found as gaseous products. The \([\((CF_3SO_2)_2N]^-\) amount decreased with increasing reaction time, and the decrease was followed by \( F^- \) formation. After 6 h, the \([\((CF_3SO_2)_2N]^-\) content decreased to 0.22 \( \mu \)mol, reflecting 99 % disappearance of the charged amount. Simultaneously, the \( F^- \) amount reached 67.1 \( \mu \)mol, or 69 % yield. Extending reaction time to 18 h led to 70.0 \( \mu \)mol \( F^- \) ions, or 72 % yield. As for gaseous products, the CF\(_3\)H amount increased at the first 1 h and then reduced. After 18 h, CF\(_3\)H was almost undetectable. That is, CF\(_3\)H decomposed under the reaction conditions. This fact is advantageous because CF\(_3\)H has a global warming potential of 12400 for one hundred years.\(^{28}\)

When the reaction was performed with zerovalent Fe at 344 °C for 6 h, 3.38 mmol of H\(_2\) was detected. This observation indicates that zerovalent Fe reacted not only with the substrate but also with superheated water (Eq. 1).

\[
3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2
\] (1)
Consistently, the XRD pattern of the recovered Fe powder showed peaks assignable to Fe$_3$O$_4$. Eq. 1 and the formed H$_2$ amount indicate that 2.54 mmol of the zerovalent Fe was consumed by the reaction with H$_2$O. This value was considerably higher than the charged amount of Li[(CF$_3$SO$_2$)$_2$N] (16.2 µmol). In other words, the majority of zerovalent Fe reacted with water, rather than with the substrate. We also investigated temperature dependence of the reaction for a constant reaction time (6 h). At 193 °C, [(CF$_3$SO$_2$)$_2$N]$^-$ did not decompose. The [(CF$_3$SO$_2$)$_2$N]$^-$ amount began to decrease at above 243 °C, and the F$^-$ amount increased with rising temperature. When the reaction was performed at 375 °C, at which temperature the water exceeded the critical temperature, [(CF$_3$SO$_2$)$_2$N]$^-$ was not detected, and F$^-$ yield reached 71 %. Extended reaction time at 375 °C somewhat increased the F$^-$ amount. After 18 h, the F$^-$ yield reached 77 %. This is the highest value among reactions of Li[(CF$_3$SO$_2$)$_2$N] with zerovalent Fe.

To monitor reaction intermediates, the reaction solutions were analyzed by LC/MS. The total-ion current (TIC) mass chromatograms of several reaction solutions showed a peak that yielded signals at m/z 148, which assignable to [CF$_3$SO$_2$NH]$^-$. This observation indicates that the degradation of [(CF$_3$SO$_2$)$_2$N]$^-$ proceeded via cleavage of the nitrogen-sulfur bond. When the reaction solutions obtained from reactions at 344 °C were subjected to the LC/MS measurement, the peak intensity of [CF$_3$SO$_2$NH]$^-$ increased at the initial stage of the reaction (below 1 h) and then decreased, confirming that [CF$_3$SO$_2$NH]$^-$ was a reaction intermediate.

As described above, zerovalent Fe led to the [(CF$_3$SO$_2$)$_2$N]$^-$ decomposition. However, most of Fe was used by the reaction with H$_2$O. Iron(II) oxide (FeO) causes disproportionation to zerovalent Fe and Fe$_3$O$_4$ at above 257 °C (Eq. 2).$^{29,30}$

$$4\text{FeO} \rightarrow \text{Fe} + \text{Fe}_3\text{O}_4 \tag{2}$$

If the disproportionation occurred in superheated or supercritical water, zerovalent Fe would form, and the in situ formed Fe might preferentially react with the substrate than with...
water. To examine this assumption, several reactions of Li[(CF$_3$SO$_2$)$_2$N] with FeO were performed, although its reactivity at 345 °C for 6 h was lower than that of zerovalent Fe (compare entries 5 with 6 in Table 1).

Figure 3B displays reaction-time dependences of the [(CF$_3$SO$_2$)$_2$N]$^-$ anion and the product amounts obtained from reactions at 345 °C in the presence of FeO. During the reaction period until ~6 h, [(CF$_3$SO$_2$)$_2$N]$^-$ degraded more slowly in the presence of FeO than in the presence of zerovalent Fe (Fig. 3A). However, the F$^-$ amount still increased and reached 69.3 µmol (71 % yield) at 18 h, at which time the yield was almost the same as the yield obtained when zerovalent Fe was employed (72 %).

We examined the effect of temperature on the reactivity of Li[(CF$_3$SO$_2$)$_2$N] with FeO. The [(CF$_3$SO$_2$)$_2$N]$^-$ amount decreased at above ~300 °C. At 378 °C, F$^-$ amount increased to 75.8 µmol (78 % yield), which was higher than the yield (71 %) obtained from the reaction using zerovalent Fe. Extended reaction time further increased the F$^-$ formation. When the reaction was performed with FeO at 378 °C for 18 h, the F$^-$ yield reached 86 %. This is the highest yield among all the reductive reactions of Li[(CF$_3$SO$_2$)$_2$N]. We monitored the fate of the FeO particles. When the reactions were performed at 345 °C for 6 h, the XRD pattern of the recovered solid showed only peaks assignable to zerovalent Fe and Fe$_3$O$_4$, indicating that disproportionation of FeO to zerovalent Fe and Fe$_3$O$_4$ (Eq. 2) occurred. We also performed a reaction of Li[(CF$_3$SO$_2$)$_2$N] with Fe$_3$O$_4$ at 345 °C for 6 h. The result showed that 97 % of the initial anion remained and the F$^-$ yield was only 4 %. Hence, the efficient [(CF$_3$SO$_2$)$_2$N]$^-$ decomposition with FeO is induced by in situ formed zerovalent Fe. In other words, when FeO was used, the in situ formed zerovalent Fe acted as the real reducing agent and it reacted preferentially with [(CF$_3$SO$_2$)$_2$N]$^-$, as opposed to water.

Because treatment of Li[(CF$_3$SO$_2$)$_2$N] in superheated or supercritical water with zerovalent Fe or FeO clearly enhanced the decomposition of its anion moiety, we applied this
methodology to [Me3PrN][CF3SO2]2N. (Note: Li[(CF3SO2)2N] is soluble whereas [Me3PrN][CF3SO2]2N is insoluble in water at room temperature). Enhancement of the F\(^{-}\) formation induced by these reducing agents was also observed. For example, [Me3PrN][CF3SO2]2N produced F\(^{-}\) ions with 52 % yield after the reaction with zerovalent Fe at 345 °C for 6 h (entry 7 in Table 1). Figure 4A displays temperature dependences of [(CF3SO2)2N]\(^{-}\) and F\(^{-}\) amounts in the reaction solution and CO2 and CF3H amounts in the gas phase after the reactions of [Me3PrN][CF3SO2]2N using FeO for 6 h.

At 246 °C, no decomposition of [(CF3SO2)2N]\(^{-}\) was observed. Decomposition of the anion began at 296 °C, and the remaining amount was decreased at higher temperatures, while the F\(^{-}\) amount increased. At 376 °C, [(CF3SO2)2N] \(^{-}\) was not detected and the F\(^{-}\) amount reached 90.3 µmol, or 84 % yield. Besides F\(^{-}\), trace of SO4\(^{2-}\) was detected (0.50 µmol). In the gas phase, CO2 was detected at 296 °C, and the extent gradually increased at higher temperatures. CF3H was present at 296 °C, and the amount became a maximum at 344 °C and then decreased at a higher temperature (376 °C). This result indicates that the formed CF3H could be decomposed at 376 °C. In the gas phase, CH3SH, CH3S2CH3, and C2H6 were present as minor products (Fig. 4B). CH3SH and CH3S2CH3 were detected at 296 °C, and the amounts increased with temperature to 344 °C and then decreased at 376 °C. These results demonstrate that the minor gaseous products decomposed at 376 °C. On the other hand, C2H6 was detected above 296 °C, and the extent increased with rising temperature.

The reaction-time dependences of the [(CF3SO2)2N] \(^{-}\) and F\(^{-}\) amounts in the reaction solution and the CO2 and CF3H amounts in the gas phase produced from the reactions using FeO at 376 °C are shown in Fig. 5A. The amount of [(CF3SO2)2N] decreased with time, and disappeared after 6 h. Instead, the F\(^{-}\) amount increased and reached 96.6 µmol at 18 h, or 90 % yield. This yield was the highest yield obtained under all reaction conditions using FeO, and somewhat exceeded the F\(^{-}\) yield achieved from Li[(CF3SO2)2N] under the same
conditions (86 %). In contrast, the CF$_3$H amount increased until 2 h and then turned to decrease. At 18 h, CF$_3$H was almost disappeared, indicating that the formed CF$_3$H degraded under the reaction conditions. As for the minor gaseous products (Fig. 5B), the CH$_3$S$_2$CH$_3$ and CH$_3$SH amounts became highest at ca. 2 and 6 h, respectively, and then reduced as the time increased. CH$_3$S$_2$CH$_3$ disappeared after 18 h. In contrast, the C$_2$H$_6$ amount increased with increasing time. This result indicates that C$_2$H$_6$ was a final product of this reaction system. When the reactions were carried out in the presence of the reducing agent (either zerovalent Fe or FeO) at above 350 °C, the resulting reaction solutions were weakly acidic. For example, the pH values of the resulting solutions after the reactions of [Me$_3$PrN][(CF$_3$SO$_2$)$_2$N] at 376 °C for 2 h to 18 h were almost constant, 5.8–6.0.

According to these reductive approaches, the highest F$^-$ yields from Li[(CF$_3$SO$_2$)$_2$N] and [Me$_3$PrN][(CF$_3$SO$_2$)$_2$N] were 86 % and 90 %, obtained from the reactions with FeO at 378 °C and 376 °C, respectively, under which conditions the water was at supercritical state.

As described above, the reactions in supercritical water gave higher F$^-$ yields than those in superheated water. A plausible explanation for the higher reactivity in supercritical water than in superheated water is as follows. The dielectric constants of water at supercritical- and superheated states are ~5 (at 377 °C, 23 MPa)$^{31}$ and ~13 (at 350 °C, 16.5 MPa),$^{32}$ respectively. That is, the value is lower for supercritical water. The density of supercritical water (0.25 g mL$^{-1}$ at 376 °C, 22.5 MPa) is also lower than that of superheated water (0.57 g mL$^{-1}$ at 350 °C, 16.5 MPa).$^{33}$ Therefore, when the reaction is performed in supercritical water with the reducing agent (zerovalent Fe or FeO), the solubility of the ionic substrate in supercritical water becomes lower than in superheated water. This phenomenon is likely to accelerate the adsorption of the substrate on the surface of the reducing agent, which enhances the mineralization of the substrate. The disproportionation rate of FeO to zerovalent Fe and Fe$_3$O$_4$ can also increase at higher temperature,$^{29,30}$ i.e., in supercritical water than in superheated water.
Although the majority of fluorine atoms in \( \text{Li}[(\text{CF}_3\text{SO}_2)_{2}\text{N}] \) and \([\text{Me}_3\text{PrN}][(\text{CF}_3\text{SO}_2)_{2}\text{N}]\) were transformed into \( \text{F}^- \) ions by use of supercritical water, an economic assessment for the recycling of non-metallic fractions from E-waste indicated that supercritical water technology has a higher energy consumption than pyrolysis.\(^2^0\) To achieve complete mineralization at lower temperature, we examined reactions by oxidative approaches, as described below.\(^2^4\)

### 3.3 Oxidative approach

First, we examined reactions for \([\text{Me}_3\text{PrN}][(\text{CF}_3\text{SO}_2)_{2}\text{N}]\) with \(\text{KMnO}_4\) at 300°C for 6 h. When \(\text{KMnO}_4\) was present in the reaction system, the \([\text{CF}_3\text{SO}_2]^-\) amount dramatically decreased (Fig. 6A). In accordance with decreasing \([\text{CF}_3\text{SO}_2]^-\) amount, \(\text{F}^-\) formed markedly. When 1.58 mmol \(\text{KMnO}_4\) was used (i.e., 158 mmol L\(^{-1}\) as the concentration), the \(\text{F}^-\) amount increased to 71.8 µmol, or 73 % yield (Table 2, entry 2). Furthermore, in contrast to the reductive approaches, \(\text{SO}_4^{2-}\) clearly generated in the reaction solution. At 1.58 mmol \(\text{KMnO}_4\), the \(\text{SO}_4^{2-}\) amount was 17.6 µmol, or 53 % yield calculated from the equation: (moles of \(\text{SO}_4^{2-}\))/(moles of sulfur atoms in the initial \([\text{Me}_3\text{PrN}][(\text{CF}_3\text{SO}_2)_{2}\text{N}]\)). \(\text{CO}_2\) were detected in the gas phase. When the \(\text{KMnO}_4\) amount was 1.58 mmol, the \(\text{CO}_2\) amount was 2.65 µmol, or 2 % yield, based on the carbon atom moles in the initial \([\text{Me}_3\text{PrN}][(\text{CF}_3\text{SO}_2)_{2}\text{N}]\). When 1.58 mmol \(\text{KMnO}_4\) was used, the pH of the resulting reaction solution was 12.6. This basicity was ascribed to the hydroxide ions generated from the reaction between \(\text{KMnO}_4\) and superheated water (Eq. 3).

\[
4\text{KMnO}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{MnO}_2 + 3\text{O}_2 + 4\text{KOH}
\]  

(3)

The high basicity of the reaction solution led to the transformation of the formed \(\text{CO}_2\) molecules into \(\text{CO}_3^{2-}\) in the reaction solution rather than as \(\text{CO}_2\) in the gas phase. Under these conditions, mineralization of the carbon content should be evaluated by TOC, as described
later. Traces of N₂O (~0.1 µmol) and CF₃H (~0.01 µmol) were also detected in the gas phase when the reactions were performed with KMnO₄ (Fig. 6B).

[C₃mpip][(CF₃SO₂)₂N] was also decomposed under the same conditions. The remaining anion extent was reduced with increasing KMnO₄ concentration, accompanied by increasing F⁻ formation. When 1.58 mmol KMnO₄ was used, the F⁻ and SO₄²⁻ yields were 83 % and 74 %, respectively (Table 2, entry 5), which were somewhat higher than those for [Me₃PrN][(CF₃SO₂)₂N] (73 % and 53 %, respectively; Table 2, entry 2).

Because both F-ILs formed large F⁻ and SO₄²⁻ amounts from the reactions with KMnO₄, temperature dependences of the reactions were examined. When [Me₃PrN][(CF₃SO₂)₂N] was reacted for 6 h with 1.58 mmol KMnO₄ at 250 °C, 83 % of the initial [(CF₃SO₂)₂N]⁻ remained. At 300 °C, the anion completely disappeared, and the F⁻ and SO₄²⁻ formations increased with rising temperature. The F⁻ and SO₄²⁻ yields reached 92 % and 95 % at 350 °C (Table 2, entry 3), indicating that the majority of the anion was mineralized. [C₃mpip][(CF₃SO₂)₂N] also effectively decomposed. At 350 °C, the F⁻ and SO₄²⁻ yields reached 95 % and 96 %, respectively (Table 2, entry 6).

Figure 7A displays reaction-time dependences of the remaining [(CF₃SO₂)₂N]⁻ and formed F⁻ and SO₄²⁻ amounts in the reaction solution, wherein [Me₃PrN][(CF₃SO₂)₂N] was reacted at 300 °C with 1.58 mmol KMnO₄. The [(CF₃SO₂)₂N]⁻ concentration became almost below the detection limit after 3 h, and F⁻ and SO₄²⁻ formations increased with time. After 18 h, the F⁻ extent reached 97.3 µmol, corresponding to 98 % yield, and the SO₄²⁻ amount was 32.3 µmol, or 98 % yield. These results indicate that quasi-complete mineralization of fluorine and sulfur atoms in the initial [Me₃PrN][(CF₃SO₂)₂N] were achieved. In the gas phase, a few CO₂ amount (2–5 µmol) and traces of CF₃H (0.01–0.4 µmol) and N₂O (0.1–0.2 µmol) were observed (Fig. 7B).
Regarding to the fate of nitrogen content in the ILs, N_2O was detected in the gas phase as mentioned above. However, the amount was very few. Alternatively, NO_3^- and NO_2^- were found in the reaction solutions. Figure 7C shows the reaction-time dependences of NO_3^- and NO_2^- amounts derived from [Me_3PrN][CF_3SO_2]_2N. The NO_3^- amount increased with time. After 18 h, the amount reached 29.9 µmol, or 91% yield calculated from the equation: (moles of NO_3^-)/(moles of nitrogen atoms in the initial [Me_3PrN][CF_3SO_2]_2N). The NO_2^- extent increased until 6 h, and then turned to decrease. This result indicates that NO_2^- was an intermediate. After 18 h, the NO_2^- amount was 2.22 µmol, or 7% yield calculated from the equation: (moles of NO_2^-)/(moles of nitrogen atoms in the initial [Me_3PrN][CF_3SO_2]_2N). At this time, the sum of the NO_3^- and NO_2^- yields was 98%. Therefore, almost all nitrogen atoms in the initial [Me_3PrN][CF_3SO_2]_2N were converted into NO_3^- and NO_2^-.

To estimate the mineralization of carbon content in the F-IL, the TOC concentration in the reaction solution was quantified. TOC represents the carbon atom extent that composes organic compounds in the reaction solution. The TOC concentration after the reaction of [Me_3PrN][CF_3SO_2]_2N with 1.58 mmol KMnO_4 at 300 °C for 18 h was below the detection limit, 0.4 mmol L^{-1} (4 µmol in the reaction solution volume, 10 mL). The amount of carbon atoms in the initial [Me_3PrN][CF_3SO_2]_2N was 132 µmol (= 16.5 × 8). Hence, based on the detection limit, the result shows that at least 97% of the carbon atoms in the initial [Me_3PrN][CF_3SO_2]_2N was mineralized.

Similar to the results observed for [Me_3PrN][CF_3SO_2]_2N, [C_3mpip][CF_3SO_2]_2N markedly mineralized at 300 °C by use of 1.58 mmol KMnO_4. After 18 h, the F^- and SO_4^{2-} yields were 94% and 97%, respectively. TOC in the reaction solution at 18 h was below the detection limit, indicating that at least 98% of the carbon atoms in the initial [C_3mpip][CF_3SO_2]_2N (185 µmol [= 16.8 × 11]) was mineralized. The NO_3^- and NO_2^- yields
were 96 % and 5 % at 18 h, and the sum of the yields (101 %) indicates that all nitrogen atoms in the initial F-IL were mineralized.

To elucidate the fate of KMnO₄, we carried out ICP analysis and the result revealed that no manganese-containing component remained in the reaction solutions. That is, the manganese species that acted as the real oxidizing agent was not present in the reaction solution. After each reaction using KMnO₄, a precipitate formed. XRD patterns of the precipitates obtained after the reaction showed peaks only assignable to MnO₂. These observations suggest that in situ formed MnO₂ plays as the real oxidizing agent for the mineralization of the F-ILs.

The reaction solutions were analyzed by LC/MS. The TIC mass chromatogram of the reaction solution of [Me₃PrN][(CF₃SO₂)₂N] showed a peak at m/z 228, which corresponded to [CF₃SO₂NSO₃H]⁻, in addition to a peak that yielded a signal at m/z 280, which corresponded to the initial anion, [(CF₃SO₂)₂N]⁻. When [Me₃PrN][(CF₃SO₂)₂N] or [C₃mpip][(CF₃SO₂)₂N] was reacted at 300 °C with 1.58 mmol KMnO₄, the peak intensity of [(CF₃SO₂)₂N]⁻ decreased with the reaction time. In contrast, the peak intensity of [CF₃SO₂NSO₃H]⁻ was initially increased (~ 6 h) and then decreased. These results indicate that [CF₃SO₂NSO₃H]⁻ was an intermediate, and the [(CF₃SO₂)₂N]⁻ decomposition proceeded through cleavage of the carbon-sulfur bond.

Based on these observations and reported researches, we can propose a mineralization process of the anion (Scheme 1). After the cleavage of the carbon-sulfur bond, CF₃ radical can form. The radical in water reacts with dioxygen that derived from the reaction of MnO₄⁻ and water (Eq. 3) to form CF₃OH. The unstable alcohol is converted into HF and COF₂ (Eq. 4).34 The carbonyl fluoride is easily hydrolyzed to CO₂ and HF (Eq. 5).21 The formed HF results in F⁻ in the reaction solution.

\[
\text{CF}_3\text{OH} \rightarrow \text{COF}_2 + \text{HF} \quad (4)
\]
\[
\text{COF}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{HF} \quad (5)
\]
As a minor path, the CF₃ radical reacts with water to form CF₃H. However, in the presence of KMnO₄, owing to the excess O₂ formation, CF₃H formation can be effectively suppressed.

After two CF₃ groups were removed from the anion, the resulting N(SO₃H)₂⁻ moiety is unstable so oxidizes to SO₄²⁻, NO₃⁻, and NO₂⁻. NO₂⁻ is further oxidized to NO₃⁻.

As for the decomposition of the cation [C₃mpip]⁺, no intermediate was detected by the GC/MS and LC/MS. However, [C₃mpip]⁺ may produce a piperidium peroxide to undergo ring cleavage, in a similar way that is proposed in the oxygen-induced electrochemical degradation of [C₃mpip]⁺. The ring-opened intermediate is further oxidized to CO₂ and NO₃⁻ as the final products.

We also examined the reactivity of [C₃mpip][(CF₃SO₂)₂N] by use of other oxidizing agents, that is, H₂O₂ and O₂. When the F-IL was reacted in the presence of 20 mmol H₂O₂ (in 10 mL; 2.0 mol L⁻¹ as the concentration) at 350 °C for 6 h, 94 % of the initial [(CF₃SO₂)₂N]⁻ anion content remained, and the F⁻ ions were released with only 1 % yield (entry 7 in Table 2). A reaction with dioxygen was also performed. When the F-IL was reacted at 387 °C for 6 h with 4.9 mmol O₂, under which conditions the water was at supercritical state, the remaining proportion of the anion was 12 %. However, this decrease did not lead high F⁻ formation (the F⁻ yield was 30 %, entry 8 in Table 2). This result indicates that while O₂ seems to play an important role in the mineralization of F-ILs using KMnO₄, its sole use is not effective.

4. Conclusions

We investigated the decomposition of [Me₃PrN][(CF₃SO₂)₂N], [C₃mpip][(CF₃SO₂)₂N], and Li[(CF₃SO₂)₂N] in superheated or supercritical water by reductive or oxidative approaches. Although these compounds little decomposed in pure superheated water, they were efficiently decomposed to F⁻ ions by use of zerovalent Fe or FeO as a reducing agent. When Li[(CF₃SO₂)₂N] was reacted at 344 °C for 6 h with zerovalent Fe, the F⁻ yield was 69 %. [Me₃PrN][(CF₃SO₂)₂N] also produced F⁻ ions with 52 % yield under almost the same
conditions (345 °C, 6 h). Although the decomposition of Li[(CF3SO2)2N] induced by FeO was initially slower than that induced by zerovalent Fe, the former reactivity increased at prolonged reaction time and also at higher temperature, owing to the disproportionation of FeO to generate zerovalent Fe. When Li[(CF3SO2)2N] was reacted at 378 °C with FeO, the F⁻ yield reached 86 % after 18 h. Likewise, when the reaction of [Me3PrN][(CF3SO2)2N] was carried out with FeO at 376 °C, the F⁻ yield reached 90 % after 18 h. That is, the majority of fluorine atoms in these compounds were converted into F⁻.

Oxidative approach using KMnO₄ was more efficient to mineralize these F-ILs, allowing almost complete mineralization (not only fluorine, but also sulfur, carbon, and nitrogen content in the substrates) at a lower temperature of 300 °C. When [Me₃PrN][(CF3SO2)2N] was reacted for 18 h with KMnO₄, the F⁻ and SO₄²⁻ yields were both 98 %, and at least 97 % of the carbon content in the initial [Me₃PrN][(CF3SO2)2N] was mineralized. Simultaneously, the nitrogen content in the initial IL was converted into NO₃⁻ and NO₂⁻ with the yield of 91 % and 7 %, respectively. The sum of the yields (98 %) showed that the nitrogen atoms in the initial IL were almost completely mineralized. [C₃mpip][(CF3SO2)2N] was also efficiently mineralized under the same conditions, leading to 94 % F⁻ and 97 % SO₄²⁻ yields and at least 98 % of the carbon content in the initial [C₃mpip][(CF3SO2)2N] was mineralized. The NO₃⁻ and NO₂⁻ yields were 96 % and 5%, respectively, and the sum of the yields (101 %) showed that all nitrogen content in the initial F-IL was mineralized. Compared to the reductive approach using FeO, the oxidative approach using KMnO₄ lowered the reaction temperature required for quasi-complete mineralization by approximately 80 °C. Extension of this methodology to other organofluorine compounds are being investigated in our laboratory.

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Table 1. Reactivity of Li[(CF$_3$SO$_2$)$_2$N] and F-ILs in superheated water in the absence or presence of a reducing agent.

| Entry$^{a}$ | Substrate          | Charged amount (µmol) | Reducing agent [amount (mmol)] | $T$ (°C) | $P$ (MPa) | Remaining [(CF$_3$SO$_2$)$_2$N]$^-$ (%) | F yield (%) |
|------------|--------------------|----------------------|--------------------------------|---------|---------|---------------------------------------|----------|
| 1$^{ab}$   | Li[(CF$_3$SO$_2$)$_2$N] | 16.2                 | none                           | 344     | 15.9    | 99                                    | 0        |
| 2$^{c}$    | [Me$_3$PrN][(CF$_3$SO$_2$)$_2$N] | 16.5                 | none                           | 300     | 7.6     | 100                                   | 0        |
| 3$^{c}$    | [Me$_3$PrN][(CF$_3$SO$_2$)$_2$N] | 17.9                 | none                           | 342     | 15.0    | 99                                    | 1        |
| 4          | [C$_3$mpip][(CF$_3$SO$_2$)$_2$N] | 16.9                 | none                           | 300     | 7.6     | 99                                    | 1        |
| 5$^{b}$    | Li[(CF$_3$SO$_2$)$_2$N] | 16.2                 | Fe (9.60)                      | 344     | 15.5    | 1                                     | 69       |
| 6$^{b}$    | Li[(CF$_3$SO$_2$)$_2$N] | 16.2                 | FeO (9.60)                     | 345     | 15.7    | 37                                    | 48       |
| 7$^{c}$    | [Me$_3$PrN][(CF$_3$SO$_2$)$_2$N] | 17.9                 | Fe (9.60)                      | 345     | 16.0    | 0                                     | 52       |
| 8$^{c}$    | [Me$_3$PrN][(CF$_3$SO$_2$)$_2$N] | 17.9                 | FeO (9.60)                     | 344     | 15.4    | 6                                     | 44       |

$^{a)}$ Initial reaction solution volume, 10 mL; reaction time, 6 h. $^{b)}$ Taken from reference 22. $^{c)}$ Taken from reference 23.
Table 2. Reactivity of F-ILs in superheated water in the presence of a reducing agent.

| Entry | Substrate | Charged amount (µmol) | Oxidizing agent [amount (mmol)] | T (°C) | P (MPa) | Remaining [(CF₃SO₂)₂N] (%) | F⁻ yield (%) | SO₄²⁻ yield (%) |
|-------|-----------|-----------------------|---------------------------------|--------|---------|--------------------------|--------------|----------------|
| 1     | [Me₃PrN][(CF₃SO₂)₂N] | 16.5 | KMnO₄ (1.58) | 250 | 3.8 | 83 | 10 | 4 |
| 2     | [Me₃PrN][(CF₃SO₂)₂N] | 16.5 | KMnO₄ (1.58) | 300 | 7.9 | 0 | 73 | 53 |
| 3     | [Me₃PrN][(CF₃SO₂)₂N] | 16.5 | KMnO₄ (1.58) | 350 | 15.1 | 0 | 92 | 95 |
| 4     | [C₃mpip][(CF₃SO₂)₂N] | 16.8 | KMnO₄ (1.58) | 250 | 3.8 | 83 | 11 | 7 |
| 5     | [C₃mpip][(CF₃SO₂)₂N] | 16.8 | KMnO₄ (1.58) | 300 | 7.8 | 0 | 83 | 74 |
| 6     | [C₃mpip][(CF₃SO₂)₂N] | 16.8 | KMnO₄ (1.58) | 350 | 15.5 | 0 | 95 | 96 |
| 7     | [C₃mpip][(CF₃SO₂)₂N] | 20.4 | H₂O₂ (20) | 350 | 16.2 | 94 | 1 | 4 |
| 8     | [C₃mpip][(CF₃SO₂)₂N] | 15.9 | O₂ (4.9) | 387 | 23.0 | 12 | 30 | 72 |

*a) Initial reaction solution volume, 10 mL; reaction time, 6 h.
Figure 1. Schematic of phase diagram of water. The green line represents saturated vapor pressure curve, and our reactions were mainly performed under the conditions at which temperatures and pressures on this curve.
Figure 2. Structures of F-ILs and a Li salt employed in this study.
Figure 3. Reaction-time dependences of the amounts of [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N]<sup>−</sup> and F<sup>−</sup> in the reaction solution and the amounts of gaseous products generated from reactions of Li[(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N] (16.2 μmol) in superheated water with (A) zerovalent Fe at 344 °C and (B) FeO at 345 °C. Charged Fe or FeO amount was 9.60 mmol and the reaction solution volume was 10 mL. Reproduced from reference 22 with permission from American Chemical Society.
**Figure 4.** Temperature dependences of (A) the amounts of [(CF$_3$SO$_2$)$_2$N]$^-$ and F$^-$ in the reaction solution and the amounts of CO$_2$ and CF$_3$H in the gas phase and (B) the amounts of minor gaseous products. [Me$_3$PrN][(CF$_3$SO$_2$)$_2$N] (17.9 µmol), pure water (10 mL) and FeO (9.60 mmol) were charged into the autoclave, which was pressurized with argon (0.60 MPa) and heated at the planned temperature for 6 h. Reproduced from reference 23 with permission from Elsevier.
Figure 5. Reaction-time dependences of (A) the amounts of [(CF$_3$SO$_2$)$_2$N]$^-$ and F$^-$ in the reaction solution and the amounts of CO$_2$ and CF$_3$H in the gas phase and (B) the amounts of minor gaseous products generated from reactions at 376 °C. The charged amounts of [Me$_3$PrN][(CF$_3$SO$_2$)$_2$N], FeO, and pure water were the same as those described in the caption of Fig. 4. Reproduced from reference 23 with permission from Elsevier.
Figure 6. Effect of initial KMnO₄ amount on (A) the amounts of [(CF₃SO₂)₂N]⁻, F⁻, and SO₄²⁻ in the reaction solution and (B) the amounts of gaseous products. [Me₃PrN][(CF₃SO₂)₂N] (16.5 µmol), KMnO₄, and pure water (10 mL) were charged into the autoclave, which was pressurized with argon (0.60 MPa) and heated at 300 °C for 6 h. Error bars at 1.58 mmol KMnO₄ were obtained from three reactions under the same conditions. The figure was prepared from reference 24 with permission from American Chemical Society and additional data.
Figure 7. Reaction-time dependences of (A) the amounts of \([\text{CF}_3\text{SO}_2\text{N}]^-, \text{F}^-\) and \(\text{SO}_4^{2-}\) in the reaction solution and (B) the amounts of gaseous products, and (C) the amounts of \(\text{NO}_2^-\) and \(\text{NO}_3^-\) in the reaction solution. \([\text{Me}_3\text{PrN}]\text{[CF}_3\text{SO}_2\text{N}]\) (16.5 µmol), KMnO₄ (1.58 mmol) and pure water (10 mL) were charged into the autoclave, which was pressurized with argon (0.60 MPa) and heated at 300 °C. Error bars at 6 h and 18 h were obtained from three and two reactions under the same conditions, respectively. The figure was prepared from reference 24 with permission from American Chemical Society and additional data.
Scheme 1. Plausible mineralization processes for the \([\text{CF}_3\text{SO}_2\text{N}]^-\) anion in superheated water with KMnO₄.