



Efficient FeO-induced decomposition of the fluorinated room-temperature ionic liquid $[\text{Me}_3\text{PrN}][(\text{CF}_3\text{SO}_2)_2\text{N}]$ to fluoride ions in subcritical and supercritical water



Hisao Hori*, Akihiro Takahashi, Takaaki Ito

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

ARTICLE INFO

Article history:

Received 29 February 2016
Received in revised form 9 April 2016
Accepted 12 April 2016
Available online 20 April 2016

Keywords:

Ionic liquid
Iron oxide
Supercritical water
Mineralization
Recovery

ABSTRACT

Decomposition of $[\text{Me}_3\text{PrN}][(\text{CF}_3\text{SO}_2)_2\text{N}]$, a typical room-temperature ionic liquid used for electrochemical devices, in subcritical and supercritical water was investigated with the aim of developing a technique to recover the fluorine component from ionic liquid wastes. When the reaction was carried out in pure subcritical water at 342 °C for 6 h, 99% of the anionic moiety, $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$, remained, and the F^- yield was only 1%. In contrast, in the presence of zerovalent iron, the yield of F^- increased to 52%. Although the reactivity of FeO toward the anionic moiety in subcritical water was lower than that of zerovalent iron, the reactivity of FeO increased dramatically when the water was heated to the supercritical state, under which conditions FeO underwent *in situ* disproportionation to form zerovalent iron and Fe_3O_4 . Specifically, when the reaction was carried out at 376 °C for 18 h, the F^- yield reached 90%, which was the highest yield obtained under the tested conditions. In addition, under these conditions, the formation of environmentally undesirable CF_3H was suppressed.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Ionic liquids (ILs) have been widely investigated as reaction and extraction media for green chemistry applications [1,2], including as absorbents for post combustion CO_2 capture [3,4] and desulfurization of oils [5,6]. Furthermore, there has been increasing interest in the electrochemical applications of ILs, mainly as electrolytes that are safer than organic solvents [7–9]. In particular, ILs with perfluorinated anions are being introduced in many electrochemical devices, such as lithium-ion batteries, polymer electrolyte membrane fuel cells, and dye-sensitized solar cells, owing to the nonflammability, high thermal stability, wide electrochemical windows, high ion conductivity, and low viscosity of ILs [7–12]. Trimethylpropylammonium bis(trifluoromethanesulfonyl)imide, $[\text{Me}_3\text{PrN}][(\text{CF}_3\text{SO}_2)_2\text{N}]$, is a typical fluorinated room-temperature IL for these applications. Wider use of ILs will require that methods for treatment of IL wastes be established. Incineration is one possible method. However, high temperatures are necessary to break the strong C–F bonds, and incineration generates hydrogen fluoride gas, which can seriously damage the firebrick of an incinerator. In addition, because perfluorinated

anions such as $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ and $[(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}]^-$ do not biodegrade under either aerobic or anaerobic conditions [13], conventional microbial degradation processes are not applicable for treatment of IL wastes. If fluorinated ILs could be decomposed to F^- by means of an environmentally benign technique, the well-established protocol for treatment of F^- could be used, whereby Ca^{2+} is added to the system to form CaF_2 , which is a raw material for hydrofluoric acid. Thus, the development of such a method would allow the recycling of fluorine, the global demand for which is increasing [14].

Several studies have focused on the degradation of ILs in which $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ is the anion [15–18]. However, the previous studies either examined the thermal stability or aging characteristics of ILs related to battery performance [15–17] or examined ILs as promoters for the preparation of metal nanoparticles [18]; none of the studies focused on IL decomposition from the point of view of waste treatment. The extent of degradation that reduces battery performance is substantially lower than the extent required for effective treatment of waste. In view of waste treatment, we previously investigated the decomposition of $\text{Li}[(\text{CF}_3\text{SO}_2)_2\text{N}]$, which is also used as an electrolyte in electrochemical devices, in subcritical and supercritical water [19]. However, the lithium salt is not an IL.

* Corresponding author.

E-mail address: h-hori@kanagawa-u.ac.jp (H. Hori).

Reaction in subcritical or supercritical water is recognized as an innovative and environmentally benign waste-treatment technique, owing to the high diffusivity and low viscosity of these media, as well as their ability to hydrolyze many organic compounds [20]. Subcritical water is defined as hot water at sufficient pressure to maintain the liquid state, and supercritical water is defined as water at temperatures and pressures higher than the critical point, that is, 374 °C and 22.1 MPa. Recently, supercritical water was used for pilot- and practical-plant-scale decomposition of hazardous compounds such as trinitrotoluene [21] and polychlorinated biphenyls [22], and subcritical water is widely used for the hydrothermal treatment of biomass [23]. We previously demonstrated that environmentally persistent and bioaccumulative perfluoroalkylsulfonates such as perfluorooctanesulfonate ($C_8F_{17}SO_3^-$) are efficiently decomposed in subcritical water in the presence of zerovalent metals such as iron [24] and this methodology was expanded to decompose a perfluoroalkyl sulfonic acid membrane polymer for fuel cells [25].

$[Me_3PrN][(CF_3SO_2)_2N]$ and $Li[(CF_3SO_2)_2N]$ have the same anionic moiety, but because $[Me_3PrN][(CF_3SO_2)_2N]$ is insoluble whereas $Li[(CF_3SO_2)_2N]$ dissolves readily in water at room temperature, the reactivities of these two chemicals in subcritical and supercritical water may differ. Therefore, in this study, we investigated the decomposition of $[Me_3PrN][(CF_3SO_2)_2N]$ in subcritical and supercritical water in the presence of an iron-based reducing agent (zerovalent iron or FeO) or an oxidizing agent (O_2). This is the first report not only on the decomposition of fluorinated room-temperature ILs in subcritical and supercritical water but also on a technique aimed at waste treatment that achieves almost complete conversion of the fluorine component of the IL to F^- .

2. Experimental

2.1. Materials

N,N,N-Trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)imide $[Me_3PrN][(CF_3SO_2)_2N]$ was obtained from Kanto Chemicals (Tokyo, Japan). Zerovalent iron (>99.9%, particle size, <53 μm) and FeO (>99.9%, <53 μm) powders were purchased from Kojundo Chemical Laboratory (Saitama, Japan) and used as received. Argon (99.99%), O_2 (99.999%), $CO_2(0.995\%)/N_2$, $CF_3H(0.971\%)/N_2$, and $CH_3SH(96.6\text{ ppmv})/N_2$ gases were purchased from Taiyo Nippon Sanso (Tokyo, Japan). Other reagents were of high purity and were obtained from Wako Pure Chemical Industries (Osaka, Japan).

2.2. Reaction procedures

Reactions were carried out in a stainless steel high-pressure reactor (35.1-mL volume) equipped with a thermocouple and a stainless steel screw cap. The screw cap was connected to a pressure gauge for measuring the pressure in the reactor and to a sampling port for analyzing gaseous products. A gold vessel (24.6 mL, 2.8-cm i.d.) was fitted into the reactor to prevent contamination from the reactor material. In a typical run, argon-saturated pure water (Milli-Q, 10 mL), $[Me_3PrN][(CF_3SO_2)_2N]$ (17.9 μmol), and zerovalent iron or FeO (9.60 mmol) were introduced into the gold vessel, and the reactor was pressurized to 0.60 MPa with argon and sealed. Because $[Me_3PrN][(CF_3SO_2)_2N]$ is insoluble in water at room temperature and the density is 1.43 $g\text{ cm}^{-3}$, the droplet of colorless $[Me_3PrN][(CF_3SO_2)_2N]$ sunk on the bottom of the vessel.

The reactor was placed in an oven, and the reactor temperature was raised to the desired value (246–376 °C). After a specified time passed (e.g., 6 h), the reactor was quickly cooled to room

temperature, and the reaction solution was subjected to ion chromatography and high-performance liquid chromatography/mass spectrometry (LC–MS). The gas phase was collected with a sampling bag and subjected to gas chromatography/mass spectrometry (GC–MS) and GC, and the solid phase (iron-based reducing agent) was subjected to X-ray diffractometry (XRD). We also conducted control experiments in the absence of an iron-based reducing agent, as well as under O_2 instead of argon.

2.3. Analysis

An ion-chromatography system (IC-2001, Tosoh, Tokyo, Japan) consisting of an automatic sample injector (30- μL injection volume), a degasser, a pump, a guard column (TSKguard column Super IC-A, 4.6-mm i.d., 1.0-cm length, Tosoh), a separation column (TSKgel Super IC-Anion, 4.6-mm i.d., 15-cm length, Tosoh), a column oven (40 °C), and a conductivity detector with a suppressor device was used to measure the F^- concentrations. The mobile phase was an aqueous solution containing $Na_2B_4O_7$ (6 mM), H_3BO_3 (15 mM), and $NaHCO_3$ (0.2 mM); and the flow rate was 0.8 $mL\text{ min}^{-1}$.

The concentrations of the anionic moiety, $[(CF_3SO_2)_2N]^-$, were quantified by means of an ion-chromatography system (IC-2010, Tosoh). The separation column was a Tosoh TSKgel Super Anion HS column (4.6-mm i.d., 10-cm length); the mobile phase was an aqueous solution containing acetonitrile (39%), $NaHCO_3$ (7 mM), and Na_2CO_3 (7 mM); and the flow rate was 0.8 $mL\text{ min}^{-1}$. An LC–MS system (LCMS-2010 EV, Shimadzu, Kyoto, Japan) with a separation column (TSKgel ODS-80TSQA) was used to identify the intermediates in the reaction solutions. The mobile phase was a 1:1 (v/v) mixture of methanol and aqueous CH_3COONH_4 (1 mM, adjusted to pH 4.0 with acetic acid), and the flow rate was 0.2 $mL\text{ min}^{-1}$. Analyses were carried out in negative-ion mode, and the electrospray probe voltage was 4.50 kV.

The gas-phase products were analyzed by GC–MS (QP2010 SE, Shimadzu) with a fused silica capillary column (RT-Q-BOND, Restek, Bellefonte, PA, USA). The carrier gas was helium, and the injection temperature was held constant at 120 °C. The sample gas was introduced into the instrument in split mode (ratio, 20/1) and analyses were conducted in full-scan mode (m/z 2.0–200). The oven temperature was kept at 30 °C for 5 min, raised to 200 °C at a rate of 20 °C min^{-1} , and held at that temperature for 20 min. A GC system (GC 323, GL Sciences) consisting of an injector (150 °C), a column oven (110 °C), and a thermal conductivity detector (130 °C) was used to quantify H_2 . The column was an active carbon column (60/80 mesh, 2.17-mm i.d., 2-m length), and the carrier gas was argon.

Changes in iron-based reducing agents that occurred during the reactions were determined by XRD with Cu $K\alpha$ radiation (Multi-flex, Rigaku, Tokyo, Japan).

3. Results and discussion

3.1. Reactions in subcritical and supercritical water under various conditions

The results for reactions of $[Me_3PrN][(CF_3SO_2)_2N]$ in subcritical water (342–345 °C) and supercritical water (375–376 °C) at a constant reaction time of 6 h are summarized in Table 1. When the reaction was carried out in pure subcritical water at 342 °C, that is, under argon without any additive (entry 1), almost all (99%) of the initial $[(CF_3SO_2)_2N]^-$ remained after the reaction, and the F^- yield $\{=(\text{moles of } F^- \text{ formed})/(\text{moles of fluorine content in initial } [Me_3PrN][(CF_3SO_2)_2N])\}$ was only 1%. This result indicates that the $[(CF_3SO_2)_2N]^-$ in $[Me_3PrN][(CF_3SO_2)_2N]$ was stable in pure subcritical water, reflecting the anion's high thermal and chemical

Download English Version:

<https://daneshyari.com/en/article/1313574>

Download Persian Version:

<https://daneshyari.com/article/1313574>

[Daneshyari.com](https://daneshyari.com)