NUCLEAR SCIENCE AND TECHNIQUES **26**, 030302 (2015)

Identification of radiolytic products of [C_4mim][PF_6] under γ-irradiation*

AO Yin-Yong (敖银勇),[1] XU Min (徐敏),[1] PENG Jing (彭静),[1]
LI Jiu-Qiang (李久强),[1] ZHAI Mao-Lin (翟茂林),[1,†] and WU Guo-Zhong (吴国忠)[2,‡]

[1]*Beijing National Laboratory for Molecular Sciences, Radiochemistry and Radiation Chemistry Key Laboratory for Fundamental Science, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*
[2]*Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China*

(Received August 15, 2014; accepted in revised form September 12, 2014; published online June 20, 2015)

The trace water-soluble radiolytic products of neat 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6]) were identified by analysing water-washed samples of γ-irradiated ionic liquids. HF and difluorophosphinic acid were confirmed as the main radiolytic products of [C_4mim][PF_6], and their radiation chemical yields were quantified by ^{19}F NMR ($\mathrm{G(F^-)} = 0.14\,\mu$mol/J, $\mathrm{G(HOP(O)F_2)} = 0.053\,\mu$mol/J). Compared to [$C_4$mim][$NTf_2$], [$C_4$mim][$PF_6$] shows better radiation stability.

Keywords: [C_4mim][PF_6], γ-irradiation, Radiolytic products, Radiation chemical yields

DOI: 10.13538/j.1001-8042/nst.26.030302

I. INTRODUCTION

The room-temperature ionic liquids (RTILs) are new-fashioned solvents and have too many attractive properties, especially in chemical stability and low vapour pressure, compared with traditional solvents. RTILs are considered promising solvents for the extraction of radioactive isotopes from spent nuclear fuel (SNF) [1–6]. This is an area of great significance to the nuclear industry, in which traditional volatile organic solvent extraction is currently used in SNF reprocessing and recycling. The solvent extractions of actinide metals were investigated using [C_4mim][PF_6], which showed that the use of [C_4mim][PF_6] greatly enhances metal ion partitioning, compared to using a traditional solvent [7]. A highly efficient extraction of Sr^{2+} from an aqueous solution can be achieved using [C_4mim][PF_6] in combination with crown ether [8, 9]. Sr^{2+} partitioning in the crown ether, combined with the [C_4mim][PF_6] extraction phase, decreased obviously after γ-irradiation [10]. The decline of the distribution ratio was attributed to the inhibition of the cation exchange mechanism and competition by radiation-formed hydrogen ions. However, γ-irradiation of [C_4mim][PF_6] showed no discernible influence on Sr^{2+} extraction from a nitric acid solution with high acidity [11]. This research show the feasibility of [C_4mim][PF_6] as an extracting solvent for the reprocessing of SNF.

In an extraction process involving SNF, there will be a requirement for extracting agents and solvents to be robust to high radiation doses [12–14]. Therefore, studies on the radiation effects of RTILs are of great importance before their practical application in SNF reprocessing and recycling. Micro-FTIR, ^{1}H NMR, and ^{19}F NMR spectra of [C_4mim][PF_6] irradiated at 550 kGy suggested that no discernible changes were found in these spectra [14, 15]. Qi *et al.* reported that the radiolysis of [C_4mim][PF_6] leads to an increase in UV-vis absorbance and a decrease in fluorescence intensity [12]. Radical generated species and different degradation pathways were proposed for imidazolium ionic liquids under electron irradiation and were confirmed by electron paramagnetic resonance [16–18]. The cation radical $C_4mim^{+}\cdot$, neutral radical $C_4mim\cdot$, and other potential species were observed by pulse radiolysis during the irradiation of dry [C_4mim][PF_6] [19]. However, as of now there are still few works focusing on the identification of radiolytic products of [C_4mim][PF_6].

In this work, the aim of the present study is to report the identification of water-soluble radiolytic products of [C_4mim][PF_6] by using Micro-FTIR, ^{19}F NMR, and ^{31}P NMR. ^{19}F NMR was employed to provide a quantitative study for the radiolytic products of [C_4mim][PF_6] and their radiation chemical yields were obtained.

II. MATERIALS AND METHODS

A. Materials

[C_4mim][PF_6] (>99%) was purchased from Lanzhou Greenchem ILs, LICP, CAS, China (Lanzhou, China). No impurities were detected by NMR analysis. Difluorophosphoric acid hemihydrate ($HOP(O)F_2 \cdot 5\,H_2O$, Strem Chemicals, Inc.) was obtained as a standard compound for the identification of radiolytic products of [C_4mim][PF_6]. CF_3COONa (Tokyo Chemical Industry Co, >98%) was used for quantitative analysis. Other solvents were analytical-grade reagents and used without further purification.

B. Irradiation

The irradiation of [C_4mim][PF_6] ionic liquid was carried out in air ((298 ± 2) K) using a ^{60}Co source with an average

---

[*] Supported by the National Natural Science Foundation of China (Nos. 91126014 and 11079007) and the Research Fund for the Doctoral Program of Higher Education of China (No. 20100001110021)

[†] mlzhai@pku.edu.cn
[‡] wuguozhong@sinap.ac.cn

dose rate of ca. 210 Gy/min (Department of Applied Chemistry of Peking University). The absorbed dose was traced by a Fricke dosimeter.

C. Identification of radiolytic products

The separation of water-soluble radiolytic products from the organic phase was conducted by contacting 0.5 mL of irradiated sample with 0.5 mL of deuterium oxide (D_2O) for about 10 min in a vibrating mixer, followed by centrifuging to ensure that the phases were fully contacted and separated. The aqueous phase from the wash of irradiated $[C_4mim][PF_6]$ was analysed by various spectroscopic methods.

Micro-FTIR: The aqueous phase was dropped onto a slide and dried at 40 °C for 30 min. Then, the residual radiolytic products on the slide were analysed by a Magna-IR 750 Thermo Scientific Micro Fourier transform infrared spectrometer (Micro-FTIR) in the spectral range of 4000–600 cm^{-1}.

NMR: The aqueous phase was analyzed by a Bruker 500 MHz Avance III NMR spectrometer. C_6F_6 (-162.73 ppm) for ^{19}F NMR and H_3PO_4 (0 ppm) for ^{31}P NMR spectra were used as references. CF_3COONa was dissolved in deuteroxide (50 mmol/L) and used as internal standard compound for quantitative analysis.

III. RESULTS AND DISCUSSION

Micro-FTIR and ^1H NMR spectra of $[C_4mim][PF_6]$ suggested that no discernible changes were found, even after irradiation at 550 kGy [14], which was an indication that the radiolytic species were very small in quantity. In order to separate water-soluble radiolytic products from the organic phase, the irradiated $[C_4mim][PF_6]$ was washed by D_2O and then the aqueous phase (A-phase) was analysed by various spectroscopic methods. As shown in Fig. 1, the absorption of A-phase shows some changes, compared to that of the unirradiated sample. The absorption of the unirradiated sample is attributed to $[C_4mim][PF_6]$ ionic liquid. For A-phase, an absorption band at 1521 cm^{-1} was attributed to a Lewis acid, which has been identified using pyridine as a molecular probe [10]. The absorption bands at 1299 cm^{-1} and 1140 cm^{-1} corresponded to the vibration of the O=P−O bonds [20, 21], which indicate that the P−F bond was broken and an O=P−O bond was formed during the irradiation of $[C_4mim][PF_6]$. The change of absorption band at 841 cm^{-1} indicated the formation of a PF_2 group [21].

^{19}F NMR and ^{31}P NMR chemical shifts are highly sensitive to fluorine-containing and phosphorus-containing compounds, respectively. The A-phase was also analysed by ^{19}F NMR and ^{31}P NMR. As shown in Fig. 2, the ^{19}F NMR of the unirradiated sample shows a duplicate peak at -71.70 ppm ($J_{\text{F-P}} = 706.5$ Hz) assigning to PF_6^-. The A-phase shows two new peaks at -82.60 (duplicate, $J_{\text{F-P}} = 960.8$ Hz) and -129.58 ppm, which were ascribed to the signals of the radiolytic products. The chemical shifts at -129.58 ppm can be assigned to the signal of HF, which has been identified as a main radiolytic product of $[C_4mim][NTf_2]$ [22, 23]. HF fumes were also detected during the irradiation of $[C_4mim][PF_6]$ [12], thus, HF was one of main radiolytic products of $[C_4mim][PF_6]$.

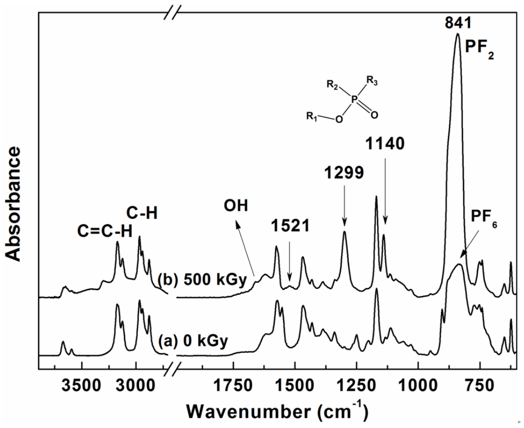

Fig. 1. Micro-FTIR spectra of unirradiated and irradiated $[C_4mim][PF_6]$ (The aqueous phase from the washing of unirradiated sample (a) and γ-irradiated sample (b)).

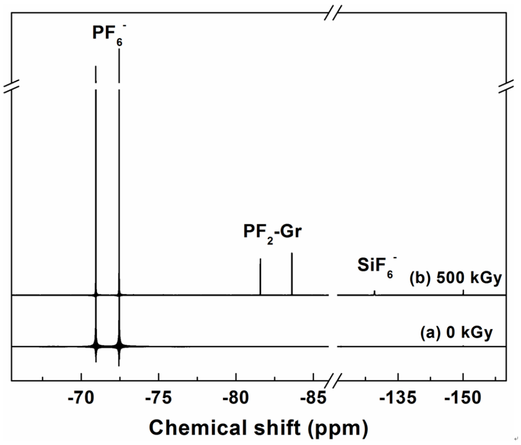

Fig. 2. ^{19}F NMR spectra of unirradiated and irradiated $[C_4mim][PF_6]$ (The aqueous phase from the washing of unirradiated sample (a) and γ-irradiated sample (b)).

As shown in Fig. 3, the ^{31}P NMR of an unirradiated sample shows a heptet at -145.01 ppm ($J_{\text{F-P}} = 707.0$ Hz) assigning to PF_6^-. A new triplet at -14.82 ppm is observed in the A-phase. Combined with the results of ^{19}F NMR, the triplet at -14.82 ppm ($J_{\text{F-P}} = 959.7$ Hz) has the same coupling constants as the peak at -82.60 ppm in ^{19}F NMR ($J_{\text{F-P}} = 960.8$ Hz), which indicates that the chemical structure of the radiolytic product contains a PF_2 group (PF_2-Gr). Lu *et al.* pointed out that $[OP(O)F_2]^-$ was one of the hydrolysis products of $[C_4mim][PF_6]$ [24]. $HOP(O)F_2$ is a possible radiolytic product when $[C_4mim][PF_6]$ is irradiated by γ-radiation. A $HOP(O)F_2$ standard compound was obtained for further identification. The $HOP(O)F_2$ shows a duplicate peak at -82.64 ppm ($J_{\text{F-P}} = 961.4$ Hz) in ^{19}F NMR and a

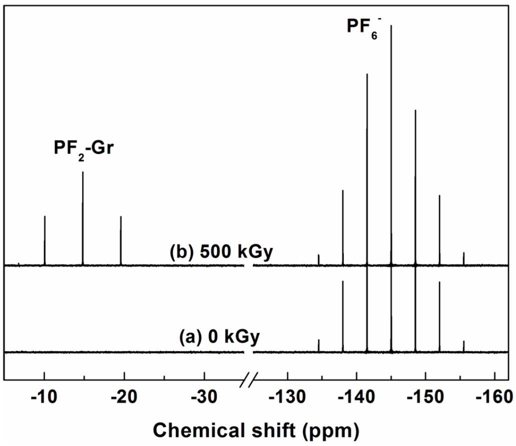

Fig. 3. ^{31}P NMR spectra of unirradiated and irradiated [C$_4$mim][PF$_6$] (The aqueous phase from the washing of unirradiated sample (a) and γ-irradiated sample (b)).

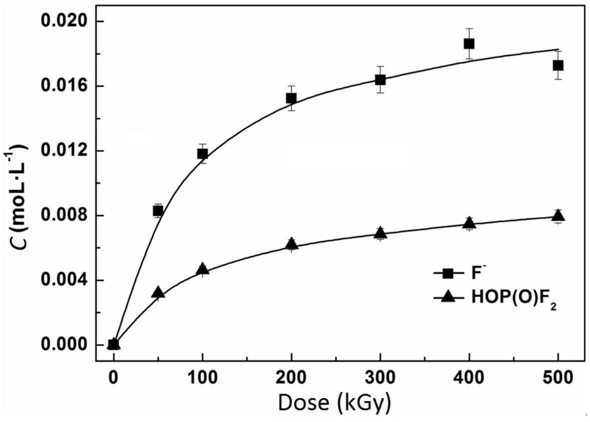

Fig. 4. The relationship between the concentration of radiolytic products and doses.

triplet at -14.85 ppm ($J_{\text{F-P}} = 961.4$ Hz) in ^{31}P NMR, we can conclude that the radiolytic product PF$_2$-Gr can be definitely confirmed as HOP(O)F$_2$.

According to the above results, HF and HOP(O)F$_2$ are confirmed as the main radiolytic products of [C$_4$mim][PF$_6$] under γ-irradiation. In order to realize a quantitative analysis of the radiolytic products of [C$_4$mim][PF$_6$] after γ-irradiation, herein, the irradiated sample was washed 4 times with D$_2$O before analysis to ensure that acidic radiolytic products were totally collected. After 4 washes, a neutral upper aqueous phase was obtained and analysed by ^{19}F NMR. CF$_3$COONa was dissolved in deuteroxide (50 mmol/L) and used as an internal standard compound for the quantitative analysis. Compared to the unirradiated sample, the amounts of main radiolytic products increased obviously with dose increases (Fig. 4). The radiation chemical yields of radiolytic products ($G = G(F^-) + G(HOP(O)F_2) = 0.14\,\mu$mol/J $+ 0.053\,\mu$mol/J $= 0.19\,\mu$mol/J) are close to the radiation chemical yields of the anion (0.18 μmol/J) of [C$_4$mim][PF$_6$] determined by ^{19}F NMR [25]. Compared to the radiation chemical yields of acidic radiolytic products of [C$_4$mim][NTf$_2$] (Table 1), the radiation stability of [C$_4$mim][PF$_6$] is better than that of [C$_4$mim][NTf$_2$] and is influenced by the chemical structure of the anion. HF and HOP(O)F$_2$ were identified as the main radiolytic products of PF$_6{}^-$ of [C$_4$mim][PF$_6$], and their overall contents were less than 0.7% for [C$_4$mim][PF$_6$], even when irradiated at 500 kGy.

TABLE 1. Radiation yields of radiolytic products and corresponding anions

RTILs	G(F$^-$)	Other products (μmol/J)	G(anion) (μmol/J)
[C$_4$mim][PF$_6$]	0.14	0.053	−0.18 [25]
[C$_4$mim][NTf$_2$]	0.20 [22]	0.151 [22]	−0.22 [25]

IV. CONCLUSION

The trace water-soluble acidic radiolytic products of [C$_4$mim][PF$_6$] were confirmed by using various spectroscopic methods, including Micro-FTIR, ^{19}F NMR, and ^{31}P NMR. The main radiolytic products (HF and HOP(O)F$_2$) of [C$_4$mim][PF$_6$] were identified and their amount was quantified by ^{19}F NMR. The overall concentration of nonvolatile acidic radiolysis products was less than 0.7% for [C$_4$mim][PF$_6$], even when irradiated at 500 kGy, which shows that [C$_4$mim][PF$_6$] has excellent radiation stability and is promising for the application of extractions in nuclear fuel reprocessing.

---

[1] Xu C, Yuan L Y, Shen X H, *et al.* Efficient removal of caesium ions from aqueous solution using a calix crown ether in ionic liquids: mechanism and radiation effect. Dalton T , 2010, **39**: 3897–3902. DOI: 10.1039/b925594j

[2] Binnemans K. Lanthanides and actinides in ionic liquids. Chem Rev, 2007, **107**: 2592–2614. DOI: 10.1021/Cr050979c

[3] Nakashima K, Kubota F, Maruyama T, *et al.* Feasibility of ionic liquids as alternative separation media for industrial solvent extraction processes. Ind Eng Chem Res, 2005, **44**: 4368–4372. DOI: 10.1021/ie049050t

[4] Binnemans K. Ionic liquid crystals. Chem Rev, 2005, **105**: 4148–4204. DOI: 10.1021/Cr0400919

[5] Tokuda H, Tsuzuki S, Susan M A B H, *et al.* How ionic are room-temperature ionic liquids? An indicator of the physicochemical properties. J Phys Chem B, 2006, **110**: 19593–19600. DOI: 10.1021/jp064159v

[6] Dietz M L, Jakab S, Yamato K, *et al.* Stereochemical effects on the mode of facilitated ion transfer into room-temperature ionic liquids. Green Chem, 2008, **10**: 174–176. DOI: 10.1039/B713750H

[7] Visser A E and Rogers R D. Room-temperature ionic liquids: new solvents for f-element separations and associated solution chemistry. J Solid State Chem, 2003, **171**: 109–113. DOI: 10.1016/S0022-4596(02)00193-7

[8] Visser A E, Swatloski R P, Reichert W M, *et al*. Traditional extractants in nontraditional solvents: Groups 1 and 2 extraction by crown ethers in room-temperature ionic liquids. Ind Eng Chem Res, 2000, **39**: 3596–3604. DOI: 10.1021/ie000426m

[9] Dai S, Ju Y H, Barnes C E. Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids. J Chem Soc Dalton, 1999, **8**: 1201–1202. DOI: 10.1039/A809672D

[10] Yuan L Y, Peng J, Xu L, *et al*. Influence of gamma-radiation on the ionic liquid [C_4mim][PF_6] during extraction of strontium ions. Dalton T, 2008, **45**: 6358–6360. DOI: 10.1039/B811413g

[11] Yuan L, Peng J, Xu L, *et al*. Radiation effects on hydrophobic ionic liquid [C_4mim][NTf_2] during extraction of strontium ions. J Phys Chem B, 2009, **113**: 8948–8952. DOI: 10.1021/jp9016079

[12] Allen D, Baston G, Bradley A E, *et al*. An investigation of the radiochemical stability of ionic liquids. Green Chem, 2002, **4**: 152–158. DOI: 10.1039/b111042j

[13] Qi M Y, Wu G Z, Chen S M, *et al*. Gamma radiolysis of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. Radiat Res, 2007, **167**: 508–514. DOI: 10.1667/rr0727.1

[14] Howett S E, Joseph J M, Noël J J, *et al*. Effect of gamma irradiation on gas-ionic liquid and water-ionic liquid interfacial stability. J Colloid Interface Sci, 2011, **361**: 338–350. DOI: 10.1016/j.jcis.2011.05.034

[15] Berthon L, Nikitenko S I, Bisel I, *et al*. Influence of gamma irradiation on hydrophobic room-temperature ionic liquids [BuMeIm]PF_6 and [BuMeIm]$(CF_3SO_2)_2N$. Dalton T, 2006, **21**: 2526–2534. DOI: 10.1039/b601111j

[16] Shkrob I A, Chemerisov S D, Wishart J F. The initial stages of radiation damage in ionic liquids and ionic liquid-based extraction systems. J Phys Chem B, 2007, **111**: 11786–11793. DOI: 10.1021/jp073619x

[17] Shkrob I A, Marin T W, Chemerisov S D, *et al*. Radiation induced redox reactions and fragmentation of constituent ions in ionic liquids. 2. imidazolium cations. J Phys Chem B, 2011, **115**: 3889–3902. DOI: 10.1021/jp200305b

[18] Shkrob I A, Marin T W, Chemerisov S D, *et al*. Radiation induced redox reactions and fragmentation of constituent ions in ionic liquids. 1. anions. J Phys Chem B, 2011, **115**: 3872–3888. DOI: 10.1021/Jp2003062

[19] Behar D, Gonzalez C, Neta P. Reaction kinetics in ionic liquids: Pulse radiolysis studies of 1-butyl-3-methylimidazolium salts. J Phys Chem A, 2001, **105**: 7607–7614. DOI: 10.1021/jp011405o

[20] Weil M, Puchberger M, Baran E J. Preparation and characterization of dimercury(I) monofluorophosphate(V), Hg_2PO_3F: crystal structure, thermal behavior, vibrational spectra, and solid-state ^{31}P and ^{19}F NMR spectra. Inorg Chem, 2004, **43**: 8330–8335. DOI: 10.1021/Ic048741e

[21] Matsumoto K and Hagiwara R. A new series of ionic liquids based on the difluorophosphate anion. Inorg Chem, 2009, **48**: 7350–7358. DOI: 10.1021/Ic9008009

[22] Ao Y Y, Peng J, Yuan L Y, *et al*. Identification of radiolytic products of [C_4mim][NTf_2] and their effects on the Sr^{2+} extraction. Dalton T, 2013, **42**: 4299–4305. DOI: 10.1039/c2dt32418k

[23] Ao Y Y, Zhou H Y, Yuan W J, *et al*. α-Radiolysis of ionic liquid irradiated with helium ion beam and the influence of radiolytic products on Dy^{3+} extraction. Dalton T, 2014, **43**: 5580–5585. DOI: 10.1039/c3dt53297f

[24] Lu Y C, King F L, Duckworth D C. Electrochemically-induced reactions of hexafluorophosphate anions with water in negative ion electrospray mass spectrometry of undiluted ionic liquids. J Am Soc Mass Spectrom, 2006, **17**: 939–944. DOI: 10.1016/j.jasms.2006.02.017

[25] Le Rouzo G, Lamouroux C, Dauvois V, *et al*. Anion effect on radiochemical stability of room-temperature ionic liquids under gamma irradiation. Dalton T, 2009, **31**: 6175–6184. DOI: 10.1039/b903005k