Identification of radiolytic products of [C4mim][PF6] under γ-irradiation Postprint

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Abstract

Trace water-soluble radiolysis products of pure 1-butyl-3-methylimidazolium hexafluorophosphate ([C4mim][PF6]) were identified by analyzing water-washed samples of γ-irradiated ionic liquids. HF and difluorophosphoric acid were confirmed as the primary radiolysis products of [C4mim][PF6], with their radiation chemical yields quantitatively determined via 19F NMR (G(F-) = 0.14 mol/J, G(HOP(O)F2) = 0.053 mol/J). [C4mim][PF6] demonstrated superior irradiation stability compared to [C4mim][NTf2].

Full Text

Preamble

Identification of Radiolytic Products of [C4mim][PF6] under γ-Irradiation

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Abstract. The trace water-soluble radiolytic products of neat 1-butyl-3-methylimidazolium hexafluorophosphate ([C4mim][PF6]) were identified by analyzing water-washed samples of γ-irradiated ionic liquids. HF and difluorophosphinic acid were confirmed as the main radiolytic products of

[C4mim][PF6], and their radiation chemical yields were quantified by ^{19}F NMR ($G(F^-) = 0.14$ μmol/J, $G(HOP(O)F_2) = 0.053$ μmol/J). Compared to [C4mim][NTf_2], [C4mim][PF6] shows better radiation stability.

Keywords: [C4mim][PF6], γ-irradiation, Radiolytic products, Radiation chemical yields
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Introduction

Room-temperature ionic liquids (RTILs) represent a new class of solvents with numerous attractive properties, particularly exceptional chemical stability and negligible vapor pressure, which offer significant advantages over traditional organic solvents. These characteristics have positioned RTILs as promising candidates for extracting radioactive isotopes from spent nuclear fuel (SNF) [1-6], a critical application in the nuclear industry where conventional volatile organic solvents are currently employed for reprocessing and recycling. The extraction of actinide metals using [C4mim][PF6] has demonstrated substantially enhanced metal ion partitioning compared to traditional solvents [7], and highly efficient Sr^{2+} extraction from aqueous solutions can be achieved when [C4mim][PF6] is combined with crown ether [8, 9]. However, γ-irradiation noticeably reduces Sr^{2+} partitioning in the crown ether/[C4mim][PF6] extraction system, an effect attributed to inhibition of the cation exchange mechanism and competition from radiation-generated hydrogen ions [10]. Conversely, γ-irradiation of [C4mim][PF6] shows no discernible influence on Sr^{2+} extraction from highly acidic nitric acid solutions [11], demonstrating the feasibility of using [C4mim][PF6] as an extraction solvent for SNF reprocessing.

Given that SNF extraction processes involve exposure to high radiation doses, both extracting agents and solvents must exhibit robust radiation resistance [12-14]. Consequently, investigating the radiation effects on RTILs is essential before their practical implementation in SNF reprocessing. Previous spectroscopic studies using Micro-FTIR, ^1H NMR, and ^{19}F NMR on [C4mim][PF6] irradiated at 550 kGy revealed no detectable changes in the spectra [14, 15], suggesting that radiolytic species were present only in trace quantities. Qi et al. reported that radiolysis of [C4mim][PF6] leads to increased UV-vis absorbance and decreased fluorescence intensity [13]. Electron paramagnetic resonance studies have confirmed radical species and degradation pathways for imidazolium ionic liquids under electron irradiation [16-18], while pulse radiolysis of dry [C4mim][PF6] observed the cation radical $C4mim^{+}\cdot$, neutral radical $C4mim\cdot$, and other potential species [19]. Nevertheless, few studies have focused specifically on identifying the radiolytic products of [C4mim][PF6].

The present work reports the identification of water-soluble radiolytic products of [C4mim][PF6] using Micro-FTIR, ^{19}F NMR, and ^{31}P NMR spectroscopy. Quantitative analysis by ^{19}F NMR enabled determination of the radiation chemical yields of these products.

Materials and Methods

Materials

[C4mim][PF6] (>99%) was purchased from Lanzhou Greenchem ILs, LICP, CAS, China. NMR analysis detected no impurities. Difluorophosphoric acid hemihydrate ($HOP(O)F_2 \cdot 5H_2O$, Strem Chemicals, Inc.) was obtained as a standard compound for product identification. CF_3COONa (Tokyo Chemical Industry Co., >98%) was used for quantitative analysis. All other solvents were analytical-grade reagents used without further purification.

Irradiation

Irradiation of [C4mim][PF6] ionic liquid was performed in air at (298 ± 2) K using a ^{60}Co source with an average dose rate of approximately 210 Gy/min (Department of Applied Chemistry, Peking University). The absorbed dose was measured using a Fricke dosimeter.

Identification of Radiolytic Products

Water-soluble radiolytic products were separated from the organic phase by contacting 0.5 mL of irradiated sample with 0.5 mL of deuterium oxide (D_2O) for approximately 10 minutes in a vibrating mixer, followed by centrifugation to ensure complete phase contact and separation. The aqueous phase from the washed [C4mim][PF6] was then analyzed by various spectroscopic methods.

Micro-FTIR: The aqueous phase was deposited onto a slide and dried at 40 °C for 30 minutes. Residual radiolytic products were analyzed using a Magna-IR 750 Thermo Scientific Micro Fourier transform infrared spectrometer in the spectral range of 4000–600 cm^{-1}.

NMR: The aqueous phase was analyzed using a Bruker 500 MHz Avance III NMR spectrometer. Chemical shifts were referenced to (−162.73 ppm) for ^{19}F NMR and H_3PO_4 (0 ppm) for ^{31}P NMR spectra. CF_3COONa dissolved in deuteroxide (50 mmol/L) served as an internal standard for quantitative analysis.

Results and Discussion

Micro-FTIR and ^1H NMR spectra of [C4mim][PF6] showed no discernible changes even after irradiation at 550 kGy [14], indicating that radiolytic species were present only in trace quantities. To separate these water-soluble products from the organic phase, irradiated [C4mim][PF6] was washed with D_2O and the aqueous phase (A-phase) was analyzed spectroscopically. As shown in [Figure 1: see original paper], the A-phase absorption exhibits changes compared to the unirradiated sample, with the latter attributed to residual [C4mim][PF6] ionic liquid. For the A-phase, an absorption band at 1521 cm^{-1} was assigned to a Lewis acid, as identified using pyridine as a molecular probe [10]. Bands

at 1299 cm^{-1} and 1140 cm^{-1} correspond to O-P-O bond vibrations [20, 21], indicating P-F bond cleavage and O-P-O bond formation during irradiation. The altered absorption band at 841 cm^{-1} suggests formation of a PF_2 group [21].

^{19}F NMR and ^{31}P NMR chemical shifts are highly sensitive to fluorine- and phosphorus-containing compounds, respectively. Analysis of the A-phase by ^{19}F NMR revealed that the unirradiated sample shows a duplicate peak at −71.70 ppm (J_F-P = 706.5 Hz) assigned to PF_6^-. The A-phase displays two new peaks at −82.60 ppm (duplicate, J_F-P = 960.8 Hz) and −129.58 ppm, attributed to radiolytic products [Figure 2: see original paper]. The chemical shift at −129.58 ppm corresponds to HF, previously identified as a main radiolytic product of [C4mim][NTf_2] [22, 23]. HF fumes were also detected during [C4mim][PF6] irradiation [12], confirming HF as a primary radiolytic product.

As shown in [Figure 3: see original paper], the ^{31}P NMR spectrum of the unirradiated sample exhibits a heptet at −145.01 ppm (J_F-P = 707.0 Hz) assigned to PF_6^-. A new triplet appears at −14.82 ppm in the A-phase. Combined with the ^{19}F NMR results, this triplet at −14.82 ppm (J_F-P = 959.7 Hz) shows the same coupling constant as the peak at −82.60 ppm in the ^{19}F NMR (J_F-P = 960.8 Hz), indicating that the radiolytic product contains a PF_2 group (PF_2-Gr). Lu et al. identified $[OP(O)F_2]^-$ as a hydrolysis product of [C4mim][PF6] [24], suggesting $HOP(O)F_2$ as a possible radiolytic product under γ-irradiation. A $HOP(O)F_2$ standard compound was obtained for confirmation, showing a duplicate peak at −82.64 ppm (J_F-P = 961.4 Hz) in ^{19}F NMR and a triplet at −14.85 ppm (J_F-P = 961.4 Hz) in ^{31}P NMR. These results definitively confirm the radiolytic product PF_2-Gr as $HOP(O)F_2$.

Based on these findings, HF and $HOP(O)F_2$ are confirmed as the main radiolytic products of [C4mim][PF6] under γ-irradiation. For quantitative analysis, the irradiated sample was washed four times with D_2O to ensure complete collection of acidic radiolytic products. After four washes, a neutral upper aqueous phase was obtained and analyzed by ^{19}F NMR using CF_3COONa in deuteroxide (50 mmol/L) as an internal standard. Compared to the unirradiated sample, the concentrations of main radiolytic products increased significantly with dose [Figure 4: see original paper]. The radiation chemical yields of the radiolytic products ($G = G(F^-) + G(HOP(O)F_2) = 0.14$ μmol/J + 0.053 μmol/J = 0.19 μmol/J) are close to the radiation chemical yield of the anion (0.18 μmol/J) of [C4mim][PF6] determined by ^{19}F NMR [25]. Compared to the radiation yields of acidic radiolytic products from [C4mim][NTf_2] , [C4mim][PF6] demonstrates superior radiation stability, indicating that stability is influenced by the anion' s chemical structure. The overall content of HF and $HOP(O)F_2$ was less than 0.7% for [C4mim][PF6] even after irradiation at 500 kGy.

Conclusion

Trace water-soluble acidic radiolytic products of [C4mim][PF6] were identified using Micro-FTIR, ^{19}F NMR, and ^{31}P NMR spectroscopy. The main radiolytic products (HF and $HOP(O)F_2$) were confirmed and quantified by ^{19}F NMR. The total concentration of non-volatile acidic radiolysis products remained below 0.7% for [C4mim][PF6] even at 500 kGy, demonstrating excellent radiation stability and promising potential for applications in nuclear fuel reprocessing extractions.

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Note: Figure translations are in progress. See original paper for figures.