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Decomposition of halophenols in room-temperature ionic liquids by ionizing radiation

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ABSTRACT

In this article, we report the reaction of halophenols with solvated electrons in room-temperature ionic liquids (RTILs) initiated by γ-ray and pulsed electron radiolyses. The decomposition *G*-values of *ortho*-chlorophenol (CP) in *N*-methyl-*N*-propylpyrrolidinium–bis(trifluoromethanesulfonyl)imide (TFSI), *N*-butyl-*N*-methylpyrrolidinium–TFSI and *N*-methyl-*N*-propylpiperidinium–TFSI were estimated to be 1.4, 1.6, and 1.7 molecules 10^{-2} eV^{-1} under γ-ray irradiation; these values were almost the same as the yield of solvated electron formation. The second-order rate constant for the reaction of CP with solvated electrons in diethylmethyl(2-methoxyethyl)ammonium (DEMMA)–tetrafluoroborate (BF_4) was one order of magnitude lower than that in DEMMA–TFSI although the *G*-values of CP decomposition and phenol formation in DEMMA-BF_4 were higher. The decomposition yield of *ortho*-iodophenol in DEMMA–TFSI was slightly higher than that of the other halophenol (*ortho*-fluorophenol, CP, and *ortho*-bromophenol), and the formation yield of phenol for the decomposition of only *ortho*-fluorophenol was lower.

1. Introduction

Room-temperature ionic liquids (RTILs) have received considerable attention as new functionalized media due to their unique properties, namely, nonflammability, low melting point, and high polarity, which are useful in the fields of chemistry, biology, environmental engineering, and mechanical engineering (Welton, 1999). Typical RTILs are composed of an organic cation such as immidazolium, ammonium, pyridinium, or phosphonium with a soft anion such as bis(trifluoromethanesulfonyl)imide (TFSI) or tetrafluoroborate (BF_4). Since the distribution coefficient of solutes in RTILs during liquid–liquid extraction can be controlled easily by changing the cations and anions, RTILs have been used as a solvent media in analytical applications (Liu et al., 2005). Moreover, the high ionic conductivity and wide electrochemical potential window of RTILs make them attractive media for redox reactions such as electrochemical and biological reactions (Inagi et al., 2008; Tsuda et al., 2008; Watarai et al., 2008; Wu et al., 2008). Much of this past research has been focused on finding more effective reactions between charged reactive species in RTILs, which have a Coulombic field. In addition, reactions in RTILs involving charged reactive species, particularly solvated electrons, have been studied by the techniques of radiation chemistry (Katoh et al., 2007; Takahashi et al., 2008; Wishart and Neta, 2003; Wishart et al., 2005; Yang et al., 2008; Asano et al., 2008). The behavior of the solvated electrons in RTILs have also been observed, and the *G*-values (molecules per 100 eV absorbed energy) of the solvated electrons in RTILs have been determined with picosecond pulse radiolysis systems (Wishart and Neta, 2003; Asano et al., 2008; Kondoh et al., 2009). These results suggested that RTILs might be a suitable medium for radiation-induced reduction; however, the mechanism of the reaction between organic solutes and the solvated electrons has not yet been elucidated.

The reaction rates of halogenated organic compounds (HOCs) with the solvated electrons are generally fast in water, and their reaction mechanisms have been investigated in many previous studies (Arbon and Mincher, 1996; Koster and Asmus, 1973; Getoff and Solar, 1986, 1988; Glowa and Mezyk, 1998; Mohan et al., 1992; Winarno and Getoff, 2002; Zona et al., 1999). HOCs, therefore, are good probes to study reactions involving solvated electrons in RTILs. Moreover, trace amount of HOCs in wastewater have acute, chronic, and reproductive toxicity, and are hazardous to aquatic animals. These chemicals are difficult to treat with aerobic-activated sludge systems due to their persistency and oxidation

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resistance. Trace amounts of these toxic and persistent organic compounds can be decomposed by ionizing radiation, an advanced oxidation method, which produces hydroxyl radicals homogeneously (Getoff, 1996, 2002; Kimura et al., 2004, 2006, 2007). However, commercial plants based on this method are not yet viable since the toxic and persistent organic compounds cannot be completely treated on a large scale. By elucidating the mechanism of HOC reduction, RTILs could potentially be utilized as a media for new water treatment methods, in which HOCs are extracted from wastewater into RTILs and then reduced by ionizing radiation.

In our previous work, we investigated the decomposition of *ortho*-chlorophenols (CP) by γ-ray and pulsed electron irradiation in RTILs that were composed of various cations and anions (Kimura et al., 2008). We also investigated the effect of viscosity on the decomposition of CP by changing the anions used in combination with diethylmethyl(2-methoxyethyl)ammonium (DEMMA), and the reactivity of CP with solvated electrons was found to be enhanced in RTILs having higher viscosity. The cations used with TFSI affected the decomposition of CP, and CP was decomposed effectively in DEMMA–TFSI by ionizing radiation but not in 1-butyl-3-methylimidazolium (BMI)–TFSI. Solvated electrons were not detected in BMI–TFSI in pulse radiolysis experiments and were considered to be scavenged by BMI due to its aromaticity. γ-ray radiolysis experiments on *ortho*-, *meta*-, and *para*-chlorophenols in RTILs and aliphatic alcohols suggested that the substitution site of chlorine affects neither the decomposition rate of CP nor the formation rate of phenol.

In order to facilitate the application of RTILs in the field of environmental technology, the reaction behavior of halophenols and the effects on halophenol decomposition of various cations and anions in RTILs were investigated by γ-ray and pulse radiolysis in the present study. Decomposition of CP by γ-ray and pulsed electron irradiation was carried out in DEMMA–TFSI, *N*-methyl-*N*-propylpyrrolidinium (P13)–TFSI, *N*-butyl-*N*-methylpyrrolidinium (P14)–TFSI, and *N*-methyl-*N*-propylpiperidinium (PP13)–TFSI to investigate the contribution of solvated electrons to the decomposition of CP. Furthermore, the rate constants for the reaction of CP with solvated electrons in DEMMA–TFSI and DEMMA–BF_4 were measured in the pulse radiolysis experiments to study the effects of the anion on the reaction of CP with solvated electrons. Decomposition of halophenols in DEMMA–TFSI was also investigated in γ-ray and pulse radiolysis experiments. Various halogen atoms of the halophenols were assumed to affect their decomposition yield in RTILs upon treatment with ionizing radiation.

2. Experimental

DEMMA–TFSI, P13–TFSI, P14–TFSI, and PP13–TFSI were purchased from Kanto Chemical Co., Inc., Japan. The chemical structures of the RTILs are shown in Fig. 1. These RTILs were washed 10 times with pure water and dried in an oven overnight before sample preparation. DEMMA–BF_4 was used just after drying because of its high water absorptivity. The water amount in the RTILs was measured by Karl Fischer titration (Kyoto Electronics Manufacturing Co., Ltd., MKC-501) and maintained at less than 0.7%. The viscosities of the RTILs were measured with a viscometer (CBC Co., Ltd., Viscomate VM-10A). Reichardt's dye (90%, Aldrich) was used to estimate the $E_T(30)$ values of the RTILs (Reichardt, 2003) which were the polarity values. *ortho*-Chlorophenol (CP, Wako Pure Chemical Industries, Ltd., >99.7 wt%, HPLC grade), *ortho*-fluorophenol (FP, Wako, 97.0 wt%), *ortho*-bromophenol (BP, Tokyo Chemical Industry Co., Ltd., guaranteed reagent (GR) grade), and *ortho*-iodophenol (IP, Wako, 97.0 wt%) were dissolved at 10–40 mmol dm^{-3} in each RTILs and then saturated with nitrogen, oxygen, or nitrous oxide.

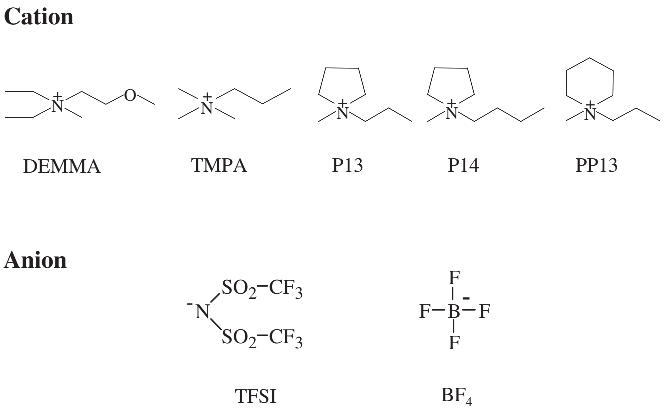

Fig. 1. Chemical structures of cations and anions of room-temperature ionic liquids used in this study.

The samples were poured into a plastic tube (volume: $\phi 5\times 30$ mm; thickness: <1 mm) and placed in a sealed glass vial (volume: $\phi 8\times 30$ mm; thickness: 1 mm). The samples in the sealed glass vials were irradiated with ^{60}Co γ-rays at doses ranging from 5000 to 20,000 Gy at 298 K. The sample solutions before and after irradiation were analyzed by HPLC (Agilent Technologies, 1100 series) using a reversed-phase column (C18 silica, Shodex, RSpak DE-613) at 313 K with an 80 vol% methanol (Wako, >99.7 wt%, HPLC grade) aqueous solution as eluent. The concentration of each halophenol (FP, CP, BP, and IP) and its irradiation products was measured with absorption (Waters, 2487 Dual Wavelength Absorbance Detector) and fluorescence detectors (Waters, 2475 Multi Wavelength Fluorescence Detector), respectively. The absorbance was observed at 280 nm. The emission intensity was monitored at 310 nm with excitation at 280 nm. The irradiation products were also analyzed by an ion chromatography (Metrohm, 761 Compact IC) with an ion exchange column (Shodex, IC SI-90 4E). Dosimetric experiments were carried out with an ethanol (Wako, >99.7 wt%, HPLC grade)–chlorobenzene (Aldrich, 99.9%, HPLC grade) dosimeter (Mahesk, 1985). The dosimeter was irradiated with γ-rays at 298 K and analyzed using the ion chromatography to determine the amount of chlorinated ion released in the solution, from which the absorbed doses were estimated.

Pulse radiolysis was performed with an *L*-band linear accelerator at the Institute of Scientific and Industrial Research, Osaka University. The prepared samples were poured into 1-cm quartz cells and saturated with nitrogen. The experimental setup was the same as described previously in the literature (Asano et al., 2008; Yang et al., 2008; Kimura et al., 2008; Kondoh et al., 2009). The absorbed dose was estimated to be 110 Gy/pulse by using the extinction coefficient of $(SCN)_2^-$ ($\varepsilon=7600\,dm^3\,mol^{-1}\,cm^{-1}$ at 475 nm) in aqueous KSCN solution and the *G*-value of 2.7 for hydroxyl radicals (Bugaenko et al., 1996; Kojima et al., 2004).

3. Results and discussion

3.1. Decomposition of CP in DEMMA–TFSI, P13–TFSI, P14–TFSI, and PP13–TFSI by γ-rays and pulsed electrons

The contribution of the solvated electrons to the decomposition of CP was investigated in γ-ray and pulse radiolysis experiments in DEMMA–TFSI, P13–TFSI, P14–TFSI, and PP13–TFSI; the *G*-values of solvated electrons in these RTILs have been determined previously (Kondoh et al., 2009). The *G*-value of solvated electrons $G(e^-)$ in DEMMA–TFSI, P13–TFSI, P14–TFSI, and PP13–TFSI was estimated