Radiation-induced reactivity in ionic liquids

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Ionic liquids are fascinating materials whose remarkable and tunable properties profoundly alter radiation-induced reactivity patterns in comparison to conventional molecular solvents.

1   Introduction

In little over a decade, ionic liquids (ILs) have moved from being relatively obscure laboratory curiosities to being subjects of widespread and intense interest[1,2]. There are good reasons why this has occurred. First, the ability to combine an extremely wide variety of cations and anions creates a tremendously diverse pool of ionic liquids with properties that are tunable in nearly any direction desired. Second, due to the unusual compositional features of ionic liquids, their physical properties often extend beyond the range of normal liquids in useful ways.

Among these exceptional properties are (in certain cases): very low vapor pressure, high conductivity, wide electrochemical windows, and the ability to solubilize polar and non-polar materials in the same solvent. The latter property is a consequence of the micro-heterogeneous coexistence of polar ionic domains and non-polar domains formed by the aggregation of alkyl side chains. On top of all the variety generated by simply mixing cations and anions, functional groups may be attached to the ions to provide centers for specific interactions or reactivity (so-called "task-specific" ionic liquids) [3,4]. The fascinating collection of properties afforded by ionic liquids has made them a favorite new media for advanced fundamental studies in many areas of physical chemistry[5–7].

However interesting their fundamental physical chemistry, ionic liquids also have a lot of practical importance[1,2,8]. They are beginning to be used in real-World applications, such as media for homogeneous reactions and phase-transfer catalysis[2,9], in dye-sensitized solar cells[10,11], electrodeposition[12], and advanced batteries and supercapacitors[13]. In addition, ionic liquids have many desirable properties for the design of advanced new systems to recycle spent nuclear fuel[14]. This could potentially have a very positive impact on the World's electricity supply by reducing the environmental impact and long-term waste disposal burdens of nuclear power, thus allowing it to expand responsibly and sustainably as a substitute for a substantial portion of fossil fuel-based power generation.

Successful use of ionic liquids in the applications mentioned above, and many others, depends on being able to understand how the unique environments within ionic liquids affect chemical reactions and the movement of electrical charge across short and long distance scales. Pulse radiolysis and radiation chemistry have proven to be excellent tools for studying these types of processes in conventional solvents. Historically, this was only possible after the identities and reactivities of radiolytically-produced transient species were adequately characterized in a particular solvent. Similar fundamental characterization work has been going on in the field of ionic liquids for a decade among a relatively small group of investigators, but the scope of the task is much larger due to the wide variety of ionic liquids in common use, not to mention the infinite possible combinations. Each family of ionic liquid cations and anions has a characteristic reactivity profile in isolation, however that reactivity is affected by the particular counter ions present in the ionic liquid.

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It is also very important to understand the fundamental radiation chemistry of ionic liquids as it affects their potential use as nuclear fuel recycling media, due to the resulting direct exposure to ionizing radiation. In this context one must consider not only the reactive species produced from radiolysis of the ionic liquid, but also their reactions with possible solutes and co-solvents, such as extractants, metal ions, water and mineral acids. Accordingly, comprehension of all these facets is a tremendous challenge. Nevertheless, much progress has been made already in advancing our understanding toward practical applications[14,15].

2   Primary events in IL radiolysis

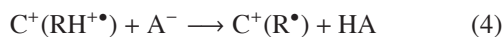### 2.1   Initial radiolysis events and their products

Even the purest ionic liquids are complex binary mixtures of cations C^+ and anions A^-, each having various pendant functional groups. Therefore, ionization events (Eqns.1 and 2) create a variety of initial products that must be accounted for.

$$C^+ \longrightarrow C^{++\bullet} + e^- \qquad (1)$$

$$A^- \longrightarrow A^\bullet + e^- \qquad (2)$$

The oxidized species $C^{++\bullet}$ and $A^\bullet$ contain electron vacancies commonly referred to as holes h^+. In the case of anions, some may form quasi-stable intermediates $A^\bullet$ that could be strong oxidants[16,17], some may fragment into reactive radicals observed in product studies[18–20], while others (e.g., halides and pseudohalides like SCN^- and $N(CN)_2^-$) react with a second anion to produce a dimer as shown in Eqn.3 [16,17,21–23].

$$A^\bullet + A^- \longrightarrow A_2^{-\bullet} \qquad (3)$$

When fully aliphatic cations are ionized, the alkyl radical cations thus formed can rapidly transfer a proton to a nearby anion, thus forming a pair of neutral species: an alkyl radical and a protonated anion[16].

$$C^+(RH^{+\bullet}) + A^- \longrightarrow C^+(R^\bullet) + HA \qquad (4)$$

The HA thus formed may subsequently scavenge excess electrons, leading to elevated yields of H_2[24].

If instead the cation is aromatic, for example an imidazolium or pyridinium cation, ionization may result in oxidation of the heterocyclic ring. The resulting ring-dications would be very strong oxidants, however Behar et al. have plausibly demonstrated the existence of C_4mim^{++} as an absorption transient in neat butylmethylimidazolium hexafluorophosphate C_4mim PF_6[25].

2.2   Excess electrons: solvation and reactivity

We will first consider the case of ionic liquids consisting of ions that do not readily react with excess electrons. These include tetraalkylammonium and tetraalkylphosphonium salts of many anions, and other variations too numerous to list here.

On the reducing sides of equations 1 and 2, ionization produces excess electrons with a range of kinetic energies, leading to a distribution of electron-hole distances. Geminate recombination of the electron-hole pair proceeds, but with significant differences from regular neutral solvents. First, the high concentration of ions in ionic liquids (2-5 M) effectively shields the hole and electron from each other, so that the recombination process is simply diffusive with no electrostatic attraction component. Furthermore, by the time they recombine the oxidizing and reducing equivalents may no longer be oppositely charged. In addition, the viscosities of ionic liquids are 10-1000 times higher than those of conventional solvents, so the diffusion rate of the solvated electron, which behaves as if it were an IL anion, is typically reduced by a factor of 100. Thus, the inhomogeneous electron-hole recombination processes that run for several nanoseconds in water may take hundreds of nanoseconds in ionic liquids. These processes may be seen by following solvated electron absorption decay in sufficiently-purified ionic liquids with saturated cations, such as methyl-butyl-pyrrolidinium bis(trifluoro-methyl-sulfonyl)amide C_4mpyrr NTf_2[26].

One of the largest distinctions between radiation chemistry in ionic liquids versus ordinary solvents is the importance of pre-solvated electron reactivity. This is due to the fact that solvation processes take much longer in ionic liquids as a consequence of their higher viscosity[27]. Consequently, it takes an ionic liquid 100 to 1000 times longer to completely respond to the injection of an excess electron compared to a normal liquid like water or methanol. Average solvation times in common ionic liquids range from hundreds of picoseconds to tens of nanoseconds[28–30]. The result is that the excess electrons spend much more

time in weakly-trapped pre-solvated (or "dry") states, in which they are more mobile and reactive. This makes pre-solvated electron scavenging much more important than in regular solvents and leads to product distributions that significantly differ from mechanistic predictions based on rate constants for solvated electron scavenging[14,15,31,32]. Efficient pre-solvated electron scavenging in ionic liquids has been observed with a wide variety of scavengers[31,33–38].

The high reactivity of pre-solvated electrons in ionic liquids takes on even more importance because the reactions of solvated electrons are much slower than one would expect, as alluded to above. In general, reported diffusion-limited rate constants for reactions with arenes[31,38], imidazolium cations[36] and bis(oxalato)borate anions[37] in a variety of ILs are on the order of $1\text{-}6 \times 10^8 \ M^{-1}s^{-1}$, about 100 times slower than in regular solvents. It is likely that the solvated electrons occupy anion vacancies surrounded by cations and that their diffusion requires collective motion of the local environment akin to anion diffusion. In comparison, small neutral species like hydrogen atoms $H^\bullet$ diffuse ten times faster than solvated electrons[32].

The fact that ionic liquids show fast and significant pre-solvated electron reactivity and slow solvated electron reactivity means that a great deal of information is needed to predict what will happen when complex mixtures, such as those found in nuclear fuel recycling systems, are irradiated.

2.3 Aromatic cation reduction and reactivity

In ionic liquids with aromatic cations such as imidazolium or pyridinium salts, excess electrons are very rapidly captured by the cations to produce neutral radicals.

$$C^+ + e^- \longrightarrow C^\bullet \qquad (5)$$

Evidence is still tentative, but the best estimate is that this process is complete within a few picoseconds. On nanosecond to microsecond timescales the spectra of the imidazoyl Rmim$^{\bullet}$[16,21,25] and pyridinyl Rpy$^{\bullet}$[39] radicals have been observed in the neat ionic liquids.

Addition of an electron to a imidazolium cation causes in significant out-of-plane distortion at the C(2) carbon between the nitrogen atoms of Rmim$^\bullet$ (Fig. 1), resulting in a reactive radical center that may be capable of forming a C(2)-C(2) adduct with an imidazolium cation to form Rmim$_2^{+\bullet}$ under certain circumstances[16,40].
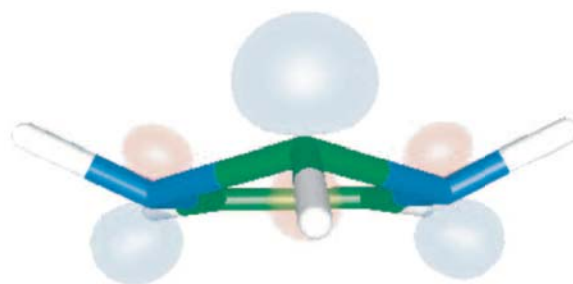

Fig. 1 Optimized structure for the Cs symmetrical σ-radical (2A') of im$^\bullet$, which serves as the minimal model of Rmim$^\bullet$. Adapted with permission from Ref.16. Copyright 2009 American Chemical Society.

In contrast, the relatively stable pyridinyl radical Rpy$^\bullet$ remains planar and unreactive towards protonation[40]. Both Rmim$^\bullet$ and Rpy$^\bullet$ can act as reducing agents. Intermolecular electron transfer reactions of Rpy$^\bullet$ have been studied in pure and mixed ionic liquid systems[39,41]. Recent work on the radiolytic production of gold nanoparticles in ionic liquids shows that Rmim$^\bullet$ can operate as an electron shuttle between the radiolysis event and the reduction of $AuCl_4^-$[42].

The ability of the aromatic cations to accept and, in some cases, reversibly release excess electrons holds promise for the design of ionic liquid systems that can minimize the irreversible damaging effects of radiolyic energy deposition.

3 Conclusion and future directions

This short review covers only the early stages of radiation-induced reactivity in ionic liquids. Readers are asked to consult other recent publications for more detail[14,15,17,26,40,43]. Much work remains to be done in characterizing the primary radiation chemistry of ionic liquids. However, enough is known at this point about early radiolysis products and their reactivity to begin to use ionic liquids in the same way that we use pulse radiolysis in ordinary solvents - as a tool for initiating reactions to study general questions of chemical reactivity. Electron transfer and redox-induced reactions will be important areas to investigate in ionic liquids because of their many potential applications involving such reactions.

Work continues in trying to characterize the reactivity of pre-solvated electrons with a wide variety of scavengers.

At BNL's LEAF picosecond pulse radiolysis facility we have a new "Optical Fiber Single-Shot" instrument for measuring picosecond kinetics on small volumes of samples[44], which is well suited for such studies.

It is also important to better identify the transient radical species observed in the pulse radiolysis of ionic liquids using methods that are structurally specific, such as vibrational spectroscopy. At the LEAF facility we are installing a transient absorption experimental system[45] that will cover a large portion of the mid-infrared to permit more definitive identification of radiolytic transients, including those that are difficult to observe or identify in the UV-vis-NIR region.

It is hoped that this brief account will stimulate interest in the challenges of describing and characterizing the wide array of reactions that can occur during the radiolysis of these diverse and interesting materials.

4 Acknowledgment

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