10 Ionic Liquid Radiation Chemistry

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ABSTRACT

Many potential uses of ionic liquids, such as recycling of used nuclear fuel, aerospace applications, and radiation processing, involve exposure to ionising radiation. Radiation chemistry provides powerful tools for studying redox reaction mechanisms, charge transport processes, and the reactivity of highly energetic species, including the electrochemical processes that occur in ionic liquid-based energy storage devices. This chapter provides an introduction to radiation chemistry and its relevance to the expanding field of ionic liquids. It discusses what happens to ionic liquids when they are irradiated and evaluates whether some ionic liquids would be stable enough to use in nuclear fuel separations. It presents some practical aspects of using ionic liquids in radiolysis studies and nanoparticle synthesis, and concludes with prospects for future work.

10.1 INTRODUCTION: WHAT IS RADIATION CHEMISTRY?

Nowadays, the term "radiation chemistry" is unfamiliar to many chemists; however, it is the name applied to the chemistry induced by ionising radiation. Ionising radiation is all around us and it has important medical and industrial applications, including medical diagnostics, imaging and therapeutic treatment, the sterilisation of medical supplies and foodstuffs, the production of high-performance materials, industrial and construction inspection, and the removal of pollutants from waste water. Radiation chemistry is therefore very important to our daily lives, yet scientific interest in radiation chemistry has seen

several ups and downs since the field was inaugurated by Pierre and Marie Curie eleven decades ago [1].

From the Second World War up to the 1980s, international interest and effort in the study of radiation chemistry was very strong for two main reasons. First, the radiation chemistry of water and aqueous solutions is fundamentally important for comprehending radiation biology and medicine, including the effects of radiation on the human body and on the genetic code. Second, the effects of radiation as a product and a by-product of peaceful uses of the atom, including nuclear power, industrial applications, and medicine, needed to be understood. The radiation chemists of that era were an extremely talented and resourceful group who tackled many of the basic questions, such as the identification and reaction chemistry of the reactive transient species produced in water and other liquids by radiation, often using clever methods and chemistries that extended their mechanistic insights well beyond the range of the equipment of the time.

Consequently, by the 1980s and 1990s, many of the core issues had been addressed to some degree of satisfaction, and the emphasis of the field shifted to investigation of the radiation chemistry of organic solvents and to applying radiation chemistry techniques to other mechanistic investigations, most notably electron-transfer reactions, biochemistry, and radiation biology. Pulse radiolysis, the time-resolved kinetic measurement of reactions initiated by a pulse of radiation, is particularly useful for the mechanistic study of redox and redox-induced reactions. Financial support for the field also generally waned due to the global retreat away from nuclear power development, which had been a natural justification for stewardship of radiation chemistry expertise.

These trends have reversed during the last decade because of several factors. A new generation of ultra-fast accelerators for pulse radiolysis [2–4], triggered by and synchronised with versatile laser systems, have allowed direct observation of early-time processes that determine the distribution of the radiolytically produced primary transient species, whose chemistry determines all subsequent events. The development of advanced computational equipment and methods now permits detailed simulation of early events in radiation chemistry to support and extend the power of experimental observations. Societal concerns about the need to expand non-carbon-based energy sources have revived worldwide interest in nuclear power development, with an emphasis on responsible and sustainable management of the nuclear fuel cycle [5]. Recognition of the central role of radiation chemistry in the successful implementation of this programme has provided renewed support for the field.

In addition, new types of "neoteric" media, ionic liquids and supercritical solvents, became important targets of radiation chemistry studies in recent years. Supercritical water is of particular interest because of its use in advanced oxidation processes, and for its potential use as the primary coolant in one type of Generation IV nuclear reactor, scheduled for start-up around the year 2030. However, the gamut and operating ranges of known supercritical solvents are limited and experimentally restrictive, so from a certain perspective, there is only so much that can be learned from them. On the other hand, ionic

liquids present an infinitely diverse array of materials to investigate for their radiolytic behaviour. Furthermore, the unusual properties of ionic liquids that distinguish them from conventional solvents, such as (1) their inherent binary nature, (2) their molecular-scale polar/non-polar heterogeneity combined with a degree of short-range order, and (3) their dynamical timescales extending over three to five orders of magnitude longer than normal liquids, make them particularly useful for studying fundamental radiation chemistry that is difficult to observe with regular solvents. These areas include the mechanisms of radiolytic energy deposition, the spatial distribution of primary radiolysis products, and the atypical reactivity and mobility of transient species in unrelaxed solvation states as compared with equilibrated ones.

Ionic liquids thus provide the opportunity to pick up and advance many of the fundamental mechanistic questions that had lain fallow since the early, "golden" years of radiation chemistry. This is not merely an issue of intellectual curiosity—due to the vast diversity of ionic liquids available to choose from—understanding the process of radiolytic product formation permits the control of product speciation through ionic liquid design. Such control by design can be extremely important for potential applications of ionic liquids in recycling spent nuclear fuel, for example [6, 7], where radiation exposure is unavoidable but radiation damage and loss of efficiency can be mitigated by the proper choice of materials.

10.2   THE RELEVANCE OF RADIATION CHEMISTRY TO IONIC LIQUID SCIENCE AND APPLICATIONS

The connections between ionic liquids and radiation chemistry rest on three pillars:

(a) Understanding the effects of cumulative radiation exposure on ionic liquid-based systems used in radiation fields, such as those experienced in processing nuclear materials, or in outer space applications (which could include propellants [8], instrumentation, or even lunar telescope mirrors [9]).

(b) The use of ionic liquids for the radiolytic preparation of advanced materials such as polymers and nanoparticles, often attempting to use the inherent local structural order of ionic liquids to create materials with specific morphologies.

(c) The application of pulse radiolysis techniques to the general study of reactivity in ionic liquids, as has been done successfully for many years in conventional solvents where chemistries have been devised to cleanly generate reducing or oxidising species to initiate desired reactions.

The fundamental knowledge needed to support these pillars is essentially the same: the identification of primary ionic liquid radiolysis products and the characterisation of their reactivities, as functions of ionic liquid composition.

This knowledge can be used to direct reaction pathways to produce well-defined intermediate species for the following:

1. The diversion of radiolytic damage into benign end points.
2. Polymerisation [10], polymer grafting [11], or nanoparticle growth [12].
3. The production of desired reducing, oxidising, or radical species for chemical kinetics studies.

The last point has far-reaching implications because many important future technologies using ionic liquids involve reactions that transfer charge [13], including dye-sensitised solar cells, batteries, electromechanical actuators, electrochromic displays, sensors, and catalysis. Pulse radiolysis provides a powerful technique to initiate charge-transfer reactions sometimes inaccessible by photochemical or electrochemical routes.

10.3   A BRIEF DESCRIPTION OF FUNDAMENTAL RADIATION CHEMISTRY AND IONIC LIQUIDS

A thorough description of radiation chemistry and its experimental techniques is well beyond the scope of this chapter. The interested reader is referred to several recent books on the subject [14–17], and to previous chapters and articles on its relationship to ionic liquids [7, 18–22].

Ionising radiations, in the form of photons (X- and gamma-rays) or energetic particles (electrons, alpha particles, heavy ions such as carbon C^{6+}, neutrons, etc.), deposit energy in materials (liquids, gases, or solids) through several types of physical interactions. The nett effect of these interactions is to excite the constituent molecules or atoms, often to the point of ejecting an electron into the surrounding medium, thus "ionising" the molecule and creating a "hole," or electron vacancy, on it.*

The incident radiation deposits its energy in increments of thousands to tens of thousands of $kJ \cdot mol^{-1}$ per interaction along its path, creating a track of ionised molecules. Secondary electrons generated by the ionisations often create their own ionisation track or spur, branched off the main track, creating a dendritic pattern of localised energy deposition. Away from the track, the medium is unaffected. This is a key point—radiolytic energy deposition is non-uniform and locally dense, depending on the type of incident radiation. Cross-reactions between initial radiolytic products depend on the density of species formed, and they determine the ultimate product yields. Consequently, product yields will be different for electrons compared with alpha particles since the latter deposit more energy per unit length of travel through a medium.

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* In conventional radiation chemistry of neutral molecules, the hole is usually called a cation because it is positively charged. That usage will not be employed here in the context of ionic liquids to avoid confusion.

When electrons are ejected from their molecules, they have excess kinetic energy, which they lose through interactions with the surrounding medium until they come to rest. At that point, the molecules of the medium begin to reorient to solvate the introduced excess negative charge. In normal liquids, the solvation process is complete within a few picoseconds, but due to the slow dynamics of ionic liquids, the process can take a thousand times longer. During that time, the energetic, weakly localised pre-solvated electrons can react in ways that are energetically or dynamically inaccessible to the localised, solvated electrons they are evolving into. The relative importance of pre-solvated electron reactivity in ionic liquids is a major distinction with conventional solvents. The details and implications of this fact have been treated several times before, and for the sake of brevity here the reader is referred to the previous discussions [7, 18–24]. To summarise, pre-solvated electron reactivity dictates different reactivity profiles and product distributions than predicted from solvated electron reactivity. However, on the useful side, it can be exploited to control those distributions and to overcome the kinetic limitations of slow reactant diffusion in ionic liquids. In addition, the distributed dynamical properties of ionic liquids dilate the electron solvation timescale so that the mechanisms of the electron scavenging processes, which have been controversial subjects for decades, are exposed for detailed analysis with modern picosecond pulse radiolysis instrumentation [22, 25].

The fate of radiolytically induced holes is a very important aspect of radiation chemistry as well. In general, holes may recombine with their geminate electrons, extract electrons by oxidising solute molecules or other constituents of the ionic liquid, form radical dimers, or undergo bond scission due to loss of a valence electron. The chemistry of the holes formed by ionic liquid radiolysis is even more complex than that of normal solvents because of the enormous variety of cations and anions that can be used to make ionic liquids. Hole chemistry is often harder to follow as well since few hole species have conveniently accessible transient optical absorption spectra (most are in the UV). Some exceptions are bromide and thiocyanate ionic liquids, which form observable dimer radical anions $[Br_2]^-$ and $[(SCN)_2]^-$ [26, 27], and imidazolium cations [28, 29], which form ring-centred radical dications. To address this general deficiency, detailed electron spin resonance studies of a wide variety of irradiated ionic liquid glasses have been undertaken to determine the radical species produced and to pinpoint the sites where radiolytic damage occurs in different families of ionic liquids [7, 30–32]. The chemistry of a particular cation or anion can even be altered by the choice of counterion [33, 34]. Easily oxidisable anions, such as thiocyanate, can reductively quench holes that were initially formed on cations, effectively eliminating precursors to permanent damage fixation in favour of a relatively stable and reversible redox species.

Radiolysis product studies using analytical methods (such as electrospray mass spectral analysis) are extremely useful for connecting primary radiation chemistry studied by the time-resolved and cryogenic experiments described

earlier to the quantitative accumulation of radiation damage in ionic liquid systems. The group of Moisy has pioneered this approach by examining gamma-irradiated salts of the $[C_4mim]^+$ cation with the $[NTf_2]^-$, $[OTf]^-$, $[PF_6]^-$, and $[BF_4]^-$ anions [35, 36], as well as $[N_{1\,4\,4\,4}][NTf_2]$ [37]. They have identified major fragmentation pathways, as well as the addition of the anion-derived fragments $–CF_3$ and $–F$ to the $[C_4mim]^+$ cation, another example of the counterion effects mentioned earlier. The product analysis results generally agree with the expectations based on the radicals observed in the irradiated ionic liquid glasses [7, 30–34], but some observed products have yet to be identified.

10.4   WOULD IONIC LIQUIDS BE STABLE ENOUGH FOR SPENT NUCLEAR FUEL RECYCLING?

The description of fundamental aspects of ionic liquid radiation chemistry given earlier underscores the complexity of the problem when one attempts to put all ionic liquids in one neat bundle. While it was commonplace during the early years of expansion in ionic liquid research to make broad generalisations about the properties, behaviour, and merits of ionic liquids, it is now abundantly clear to the field that exceptions are the rule [8, 38]. The term "ionic liquids" is almost as generic as "solvents." This is actually a sign of how robust the field has become. Despite this awareness, it is all too common to find publications on ionic liquid radiation chemistry that attempt to draw broad conclusions from investigations of one or two ionic liquids. Frequently, these liquids are known bad actors such as $[PF_6]^-$ and $[BF_4]^-$ salts, which are now understood to undergo hydrolysis to produce hydrofluoric acid (HF) [39, 40].

One such area where generalities should be avoided concerns the radiation stability of ionic liquids, which is a concern for spent nuclear fuel processing and space applications. However, it is important to remember that all materials will degrade to some extent under ionising radiation; the ultimate objective is to identify specific ionic liquids that can outperform the materials currently in use for a particular application, for example, making a more robust and efficient separation process. Various groups of researchers have applied different techniques to evaluate radiation stability, including nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MS), and hydrogen gas evolution. The results present a reasonably coherent picture over the limited range of ionic liquids that have been studied so far, and have pointed to new families of ionic liquids to be next investigated.

The baseline study of ionic liquid radiation stability was published in 2002 by a large group of authors from the United Kingdom [41]. They studied the effect of alpha, beta (electron), and gamma radiation on $[C_4mim][NO_3]$, $[C_2mim]Cl$, and $[C_6mim]Cl$, and compared the ionic liquid results with those of the standard tributylphosphate/kerosene mixture used in the PUREX process to separate plutonium and uranium from spent nuclear fuel. Using

NMR spectroscopy to quantify the extent of radiation damage at a dose of 400 kGy (1 Gy = 1 J kg^{-1}), they were unable to observe degradation products above the estimated detection threshold of 1%, whereas the PUREX mixture shows 15% conversion to radiolysis products at that dose level. They concluded that the ionic liquids they studied were "relatively radiation resistant," particularly with respect to the PUREX mixture.

This resistance was attributed to the aromatic nature of the imidazolium cation since it is known from "classical" radiation chemistry that aromatic organic liquids are resistant to ionisation because a much larger portion of the radiolytic energy is absorbed as molecular excitations rather than ionisations. This difference can be quantified by measuring the radiolytic yield (called the G-value) of molecular hydrogen per unit of energy absorbed. For benzene, $G(H_2) = 3.8 \times 10^{-9}$ mol J^{-1} [42], while $G(H_2)$ is much larger in aliphatic liquids, $5–6 \times 10^{-7}$ mol J^{-1} [43], demonstrating that the effect of aromaticity has a strong stabilising effect.

Tarabek et al. [44] recently explored the influence of aromaticity on radiolytic stability over a representative sample of aromatic (imidazolium and pyridinium), aliphatic (pyrrolidinium and phosphonium), and protic ionic liquids, all with the same [NTf$_2$]$^-$ anion, by measuring H$_2$ yields under electron radiolysis. The results presented in Table 10.1 fit well with the aromaticity interpretation. The imidazolium and pyridinium ionic liquids have the lowest $G(H_2)$ values, substantially larger than benzene but comparable with butylbenzene, thus allowing for effect of the side chains of the cations. The aliphatic pyrrolidinium and protic triethylammonium ionic liquids have higher H$_2$ yields, indicating slightly higher radiation sensitivity, while the phosphonium ionic liquid with very long side chains exhibits a very large, hydrocarbon-like $G(H_2)$. It is therefore clear that incorporating aromaticity into ionic liquids for spent

TABLE 10.1   Radiolytic Yields of Molecular Hydrogen in Ionic and Molecular Liquids

Liquid	$G(H_2)/10^{-8}$ mol·J^{-1}	Reference
C$_6$mim][NTf$_2$]	2.6	[44]
[C$_6$(dma)$_7$py][NTf$_2$]^a	2.6	[44]
[C$_4$mpyr][NTf$_2$]	6.5	[44]
[HN$_{2\,2\,2}$][NTf$_2$]	7.2	[44]
[P$_{8\,8\,8\,14}$][NTf$_2$]	25	[44]
[C$_4$mim][NO$_3$]	6.5^b	[41]
[C$_6$mim]Cl	7.2^b	[41]
Benzene	0.38	[42]
Benzene (alpha radiolysis)	2.0^b	[42]
Butylbenzene	2.6	[43]
Aliphatic hydrocarbons	50–60	[43]

Yields are for electron or gamma radiolysis unless otherwise noted.
^{a} [C$_6$(dma)$_7$py]$^+$ stands for 1-hexyl-4-dimethylaminopyridinium cation.
^{b} Radiolysis using ~6 MeV alpha particles.

fuel recycling would help stabilise them towards ionising radiation. In addition to raising the cross section for excitation at the expense of ionisation, aromatic cations can also reduce the effects of ionisation by serving as relatively stable electron and hole traps, raising the probability of electron–hole recombination to avoid radiolytic damage.

As shown in Table 10.1, Allen et al. [41] measured $G(H_2)$ values for [C$_4$mim][NO$_3$] and [C$_6$mim]Cl, but those yields are significantly higher than that for [C$_6$mim][NTf$_2$] because alpha particles were used instead of electrons. Heavy ion radiations deposit more energy per unit length than electron and gamma radiations, and the higher density of reactive intermediates thus generated results in more cross-reactions to form molecular hydrogen, among other things. The $G(H_2)$ in benzene is also significantly elevated under those conditions (Table 10.1). Alpha radiolysis of ionic liquids is an important subject to study because many of the isotopes relevant to spent fuel reprocessing are alpha emitters; however, the appropriate instrumentation for steady-state and time-resolved alpha radiolysis is relatively scarce.

The group of Moisy has done extensive work using high-performance liquid chromatography (HPLC), NMR and electrospray MS to quantify gamma radiation damage by measuring the loss of cations and anions from [C$_4$mim]$^+$ ionic liquids with [NTf$_2$]$^-$, [OTf]$^-$, [PF$_6$]$^-$, and [BF$_4$]$^-$ anions [36]. They obtained $G(-[C_4mim]^+)$ yields in the range of 2.8–3.7 $\times$ 10^{-7} mol J^{-1} and $G(-anion) =$ 1.0–2.2 $\times$ 10^{-7} mol J^{-1}, using doses of up to 2 MGy. In an earlier report [37], they obtained $G(-[N_{1\,4\,4\,4}]^+) = 3.8 \times 10^{-7}$ mol J^{-1} and $G(-[NTf_2]^-) =$ 2.5 $\times$ 10^{-7} mol J^{-1} for [N$_{1\,4\,4\,4}$][NTf$_2$]. (Parenthetically, it is also possible to calculate a yield of $G([NO_2]^-) = 1.5 \times 10^{-7}$ mol J^{-1} for the formation of nitrite ion during gamma radiolysis of [C$_4$mim][NO$_3$] from the data in Allen et al. [41].) The magnitudes of these radiation damage yields are similar to those observed in polar liquids, which would seem to indicate that the stabilities of these particular ionic liquids are comparable with other solvents and not significantly superior. It is notable, however, that Moisy's group reported only very weak radiolysis product NMR signals (<0.5%) at doses up to 1.2 MGy [35] and needed 2 MGy doses to obtain quantifiable electrospray ionisation (ESI)-MS data for yield estimation [36, 37]. Their overall conclusion from this work, taking into account that actual spent fuel processing systems are exposed to doses of 0.1–1.0 MGy, is that the ionic liquids they studied are suitable for nuclear applications and may have benefits in terms of their low production of hydrogen gas [36].

10.5   SUITABILITY OF IONIC LIQUID PREPARATIONS FOR RADIATION CHEMISTRY STUDIES

Due to the nature of their formation, the primary species formed during the radiolysis of any material, not just ionic liquids, tend to be extremely energetic, unstable, and reactive. It has always been important for the study of chemical kinetics that the materials used should be free of any contaminants that could

interfere with or catalyse a reaction, but radiolysis studies can be particularly sensitive due to the reactivity of the intermediates with contaminants. This presents a particular challenge for studying kinetics in ionic liquids because some of the standard solvent purification techniques, such as distillation and chromatography, are difficult or impossible.

Unlike conventional solvents, where it is normal to commercially obtain very pure materials with complete analytical data, the situation with commercial ionic liquids is uneven, with no broadly accepted purity standards set by industry or some governing body. Although the policies of some ionic liquid suppliers may be more thorough, stated ionic liquid purity criteria have largely focussed exclusively on water and halide content. Nonetheless, other serious contaminants could include unreacted starting materials, side products, fine particles or compounds extracted out of columns, and solvents used in processing, including for the removal of water. Stories of experimental troubles caused in ostensibly pure ionic liquids by lithium ion [45], alumina [45,46], silica [46], methylimidazole [47], and dichloromethane (used to remove water but inadequately pumped off) circulate among researchers in the field.

The situation is also complicated for those who choose to, or of necessity must, prepare their own ionic liquids. If one is up on the literature, it is possible to use the best recommended synthesis and purification techniques, and one has the advantage of knowing all the reagents and solvents used in the preparation. However, adequate analytical instrumentation or the time to use it may not be available for the individual principal investigator. One approach that is being taken by many people to address this is to collaborate in larger groups that share materials and the expertise to properly characterise them. These large collaborations are definitely a boon to the field and should be encouraged. From my observations, however, widespread distribution of common research materials does not guarantee that the quality of those materials is adequate.

For non-aromatic ionic liquids, one useful empirical criterion of ionic liquid purity for radiation chemistry purposes is the lifetime of the solvated electron, which is a very reactive species that can be scavenged by acids, aromatics, haloalkanes, and protonated amines. Figure 10.1 shows the decay kinetics of the solvated electron in 1-butyl-1-methylpyrrolidinium bis{(trifluoromethyl) sulfonyl}amide, followed by its optical absorption at 900 nm measured at the BNL Laser-Electron Accelerator Facility (LEAF) pulse radiolysis facility [2]. The four lots of "high purity" ionic liquid came from two suppliers, as listed in the legend. The samples from Supplier 1, lot "A" and Supplier 2 show simple pseudo-first-order electron decays, indicating the presence of a significant amount of adventitious scavenger, in the case of "A," a very large amount. After these data were shown to a representative of Supplier 1 at a conference, the supplier sent lot "B," which contained much less scavenger, as indicated in the figure. The next batch ordered, lot "C," showed even more ideal behaviour. The true form of the electron decay will look much like a second order reaction, but it is actually inhomogeneous electron–hole recombination within the radiation track. Preparations of $[C_4mpyr][NTf_2]$ made in our laboratories
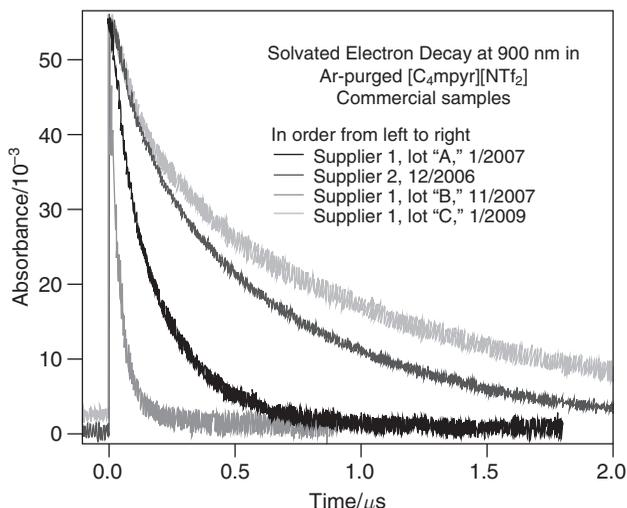
Figure 10.1 Electron pulse radiolysis kinetic traces monitored at 900 nm, showing the decay of solvated electrons in four commercial lots of 1-butyl-1-methylpyrrolidinium bis{(trifluoromethyl)sulfonyl}amide. The peak absorbances have been normalised for easier comparison of the kinetics. Samples synthesised in our own laboratory fall between lots "B" and "C."

show behaviours between lots "B" and "C". To my colleagues in ionic liquid radiation chemistry, I would suggest that if your aliphatic ionic liquid electron decays look like "A" and not "B" or "C," you should be concerned.

This story shows that ionic liquids suppliers will work with customers to provide the quality of materials they need, but because of the range of science being done, they cannot necessarily anticipate those needs. Nevertheless, it is important for the quality of research in the field—which ultimately will determine the outcome between success and failure—to establish baseline performance criteria for ionic liquid products intended for certain types of research and applications, just as with conventional solvents. The various research communities, physical chemists, electrochemists, catalysis researchers, and so on, should make their group needs known to industry, and explain these needs in terms of a business case that will satisfy all parties. On the bottom line, better research will lead to more business.

10.6 PRACTICAL IMPORTANCE: APPLYING FUNDAMENTAL IONIC LIQUID RADIATION CHEMISTRY TO NANOPARTICLE SYNTHESIS

Thanks to their unusual combinations of properties, ionic liquids are enabling exciting new areas of physical chemistry to be explored, including aspects of

fundamental radiation chemistry that were previously inaccessible. Such basic knowledge is important for understanding how our world works, but it is especially gratifying if it can be directly applied to accomplishing a purpose such as the production of advanced materials.

Radiation chemistry has been applied to metal nanoparticle synthesis in conventional solvents for many decades. It has helped to explain and ultimately to perfect the mechanisms of silver photographic image formation [48], and it allows an exquisite level of control over nanoparticle synthesis, including bimetallic core/shell versus alloy composition and the growth of specific morphologies and complex three-dimensional structures [49]. Nanoparticles in ionic liquids are currently a topic of intense interest, so it comes as no surprise that radiolytic nanoparticle synthesis has been tried in ionic liquids. However, results can vary widely from one ionic liquid to another (changing cations or anions) due to basic differences in the radiation chemistries of different families of ionic liquids, which must be understood for proper application.

An interesting example of the impacts of different radiation chemistry mechanisms on radiolytic nanoparticle synthesis in ionic liquids was recently published by Kuwabata and coworkers [12], who examined gold nanoparticle synthesis in three ionic liquids, $[C_4mim][NTf_2]$, $[N_{1\,4\,4\,4}][NTf_2]$, and $[C_1C_3pip]$ $[NTf_2]$. Using gamma and electron beam radiolysis of 0.5 mmol l^{-1} NaAuCl$_4$ •2H$_2$O in each of the three ionic liquids and radiation doses of 6 or 20 kGy, gold nanoparticles were only observed in the imidazolium salt and not in the ammonium ones (except for a very small amount in $[C_1C_3pip][NTf_2]$ at the highest dose and dose rate).

The results are not adequately explained in the original report, but from our understanding of primary ionic liquid radiation chemistry, we know that radiolytically produced excess electrons would be rapidly captured by imidazolium cations to form neutral radicals [24, 28, 29], which may form dimers by reacting with an additional cation [7, 31, 32], whereas the electron does not react with the cations in quaternary ammonium ionic liquids, and instead becomes a solvated species [23, 50, 51]. However, the diffusion-limited rate constant for solvated electron scavenging in $[N_{1\,4\,4\,4}][NTf_2]$ at room temperature is $\leq 2 \times 10^8$ l mol^{-1}·s^{-1} [23], resulting in an effective lifetime for the electrons (in the absence of other reactions) of at least 10 microseconds at the gold concentration used. In practice, the electrons will not survive nearly that long because they will react either with inadvertent scavengers, or if the ionic liquid is very pure, by geminate recombination with transient species produced from the radiolytically formed holes on the timescale of a couple of microseconds.

Thus, it comes as no surprise that gold reduction will not be competitive in the ammonium ionic liquids under the conditions that were used. However, the remarkable feature of these experiments is that the reduction product of the imidazolium cation (whose exact form is unknown but the subject of active investigation [34]) is indeed capable of efficiently reducing tetrachloroaurate(III) anions to form gold nanoparticles. The final product of the imidazolium-derived species after gold reduction is not yet characterised, nor

is the yield of metallic gold per unit of radiolytic energy absorbed. Supporting this analysis, another study showed that gold nanoparticles were successfully formed in a quaternary ammonium ionic liquid when the $Zn^{2+/+}$ couple was used as an electron shuttle, even though the gold concentration was five times lower [52].

The established knowledge base on ionic liquid radiation chemistry also suggests that radiolytic nanoparticle synthesis should proceed efficiently in pyridinium ionic liquids, since the pyridinium cation captures electrons to form a relatively stable pyridinyl radical that undergoes facile redox processes [53, 54]. As of this writing, no published information could be found on such studies. Ultimately, advanced radiolytic nanoparticle synthesis in ionic liquids may involve mixtures of two or more cations or anions, with certain ions selected for their radiolysis and redox properties, and others chosen to control nanoparticle growth and morphology through interactions with the particle surface [55].

10.7   FUTURE PROSPECTS

There are vast areas of radiation chemistry research to be explored using ionic liquids and vice versa. Ionic liquids provide a new and adaptable medium to test theories concerning the early events in radiolytic energy deposition and the effects of solvent relaxation on transient species energetics and reactivity. The potential for transfer of radiolytic damage (holes and electrons) between cations and anions makes each combination of ions a new chapter in the story. Ultimately, we wish to elucidate chemistries for particular families of ionic liquids that will convert the chaos of the initial radiolysis events into known yields of specific products, so that pulse radiolysis in ionic liquids can be used to study electron transfer, catalysis, charge transport through advanced devices, nanomaterial synthesis, durability in extreme environments, carbon fixation, clean fuel generation, nuclear separations, and many other technologies that are important for creating a sustainable world infrastructure.

ACKNOWLEDGEMENTS

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