

Ionic Liquids: Novel Media for Characterization of Radical Ions

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The novel application of ionic liquids as media for radiolytic generation and UV–vis–NIR spectroscopic characterization of radical ions is described. The redox properties of neat 1-butyl-3-methylimidazolium salts and their aqueous solutions have been investigated by means of pulse radiolysis. Furthermore, ionic liquids prove to be ideal media for the simultaneous generation of radical cations and anions. The radical cations generated from 1-methyl-1,4-dihydronicotinamide, a structural analogue of NADH, have been spectroscopically characterized under matrix conditions for the first time.

Introduction

Ionic liquid is now a commonly accepted term for low melting salts (melting point typically <100 °C). These materials are prepared by combining bulky organic cations, such as 1-butyl-3-methylimidazolium, with a wide variety of anions. The great interest in ionic liquids which has developed in recent years is closely related to their utilization as novel solvents for organic synthesis and their potential use in a variety of commercial applications.^{1–3} In general, ionic liquids can replace conventional media in a wide range of chemical processes. More specifically, there are some interesting recent examples of use of these solvents as media for photochemical reactions.^{4,5} We therefore decided to test the applicability of ionic liquids in the study of reactive species induced by ionizing radiation. The reactive nature of radical ions and radicals requires not only special techniques for their generation and detection but also appropriate solvents. One of the most successful methods applied for this purpose is combination of radiolytic generation of radical ions with matrix-isolation techniques for their spectroscopic characterization.^{6–8} However, many substrates are insufficiently soluble in the solvents generally used for the formation of glassy matrixes suitable for these studies, thus limiting the range of systems that may be studied. Since many ionic liquids form transparent, good-quality glasses on freezing at 77 K, they can be used as matrixes over a wide range of temperatures in combination with the UV–vis–NIR spectroscopy for detection of reactive species generated. Furthermore, ionic liquids are good solvents for a wide range of organic and inorganic materials.

Despite extensive research on ionic liquids, much of their basic chemistry remains to be explored. Indeed, understanding of some of their basic properties is of general importance for applications of ionic liquids, particularly in the fields of radiation chemistry and photochemistry.

Experimental Section

Starting Materials. 1-Methylimidazole and 1-bromobutane (Aldrich) were distilled before use. A 70% w/w hexafluorophosphoric acid solution (Fluorochem), lithium bis(trifluoromethylsulfonyl)imide (3M), and compounds used as the solutes (Aldrich) were used as received.

Compounds. 1-Butyl-3-methylimidazolium bromide (BMIM⁺Br⁻) and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM⁺[PF₆]⁻) were prepared following the method of Huddleston et al.⁹ The identity of the salts was confirmed by ¹H NMR. When initially formed, the bromide salt is a pale yellow viscous oil, but on extended storage the salt tends to crystallize to form a white solid. The oily phase may be re-formed by heating the salt to above its melting point. 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM⁺[N(SO₂CF₃)₂]⁻) was prepared from BMIM⁺Br⁻ and Li[N(SO₂CF₃)₂] following the method of Bonhôte et al.¹⁰

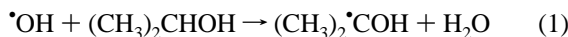
1-Methylnicotinamide, Chloride salt (MNA⁺Cl⁻). The iodide (MNA⁺I⁻) was prepared via reaction of nicotinamide with methyl iodide in methanol at room temperature, and then converted to the chloride salt by shaking its aqueous solution with freshly precipitated silver chloride. mp 243 °C.

1-Methyl-1,4-dihydronicotinamide (MNAH). To a stirred, degassed solution of sodium dithionite (6 g) and sodium carbonate (2 g) in 50 mL of water, 3 g (17.4 mmol) of MNA⁺Cl⁻ was added during a 20-min period. The solution was extracted with chloroform (3 × 100 mL), the extract was dried with anhydrous MgSO₄, and the solvent was removed on a rotary evaporator. The residual oil was pumped out and dried over P₂O₅ to give a yellow solid (60% yield). ¹H NMR (Bruker 250 MHz, CDCl₃) δ ppm: 2.94 (s, 3H, CH₃), 3.05 (m, 2H, CH₂), 4.73 (m, 1H), 5.68 (m, 1H), 7.01 (s, 1H).

Radiolysis in Solution. The pulse radiolysis of water produces three highly reactive species: H₂O → e_{aq} (2.6), •OH (2.7), and H• (0.6) (numbers in parentheses are the *G* values, i.e., yields of radicals per 100 eV of energy absorbed).¹¹

To study the reaction of BMIM⁺ cations with e_{aq} without any interference from the other products of radiolysis of water, it is necessary to scavenge the •OH radicals using *tert*-butyl or isopropyl alcohols (0.1–1 M) in the N₂-saturated aqueous solutions. Isopropyl alcohol also scavenges the H• atoms effectively.^{12,13}

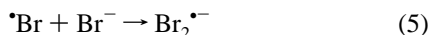
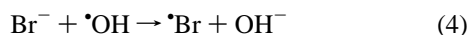
The radical produced from the reaction of •OH with *tert*-butyl alcohol is inert with regard to further reactions but the acetone ketyl radical formed via reactions 1 and 2



may act also as a reducing agent. The reduction of BMIM⁺ by acetone ketyl radical was tested in aqueous solutions containing 1 M isopropyl alcohol saturated with N₂O which converts e_{aq}⁻ into $\cdot\text{OH}$ radicals with a rate constant on the order of 10¹⁰ M⁻¹ s⁻¹.



The reaction of BMIM⁺ cations with Br₂^{•-} was carried out in N₂O-saturated aqueous solutions of BMIM⁺Br⁻ (5 × 10⁻² M).^{12,13}



The concentration of solute was kept in the range of (1–10) × 10⁻³ M.

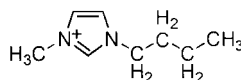
The pulse radiolysis system based on a linear electron accelerator delivering a dose of 10–50 Gy per pulse (17 ns) was described earlier.¹⁴

Experiments in Cryogenic Glasses. The glassy samples of ionic liquids were prepared by immersing air-saturated room-temperature solutions in liquid nitrogen. The samples were 1–3 mm thick and were placed in a temperature-controlled, liquid helium or nitrogen cooled cryostats (Oxford Instruments). The desired temperature (10–100 K) was achieved by proper helium flow and/or automatically controlled heating. The optical absorption spectra were measured on a Cary 5 (Varian) spectrophotometer.

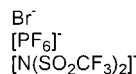
The samples mounted in a cryostat were irradiated with 4 μs electron pulses from an ELU-6 linear accelerator. Details of the pulse radiolysis system are given elsewhere.^{14,15}

Results and Discussion

Redox Properties of Ionic Liquids. Three different salts were the subject of our investigation. All of them contain the 1-butyl-3-methylimidazolium cation (BMIM⁺), but three dif-



BMIM⁺



ferent counterions were used: [PF₆]⁻, [N(SO₂CF₃)₂]⁻, and Br⁻. All of these salts form transparent glasses on freezing at 77 K, and therefore they can be used over a wide range of temperatures for optical measurements.

The redox properties of salts depend both on the cation and anion. The redox properties of anions are already widely reported.^{12,16–19} Much less information is available on the redox properties of BMIM⁺ cation, although some similarities to the reactivity of protonated imidazole can be expected. Indeed, pulse radiolysis of investigated salts in aqueous solution leads to the formation of quite stable intermediate characterized by a relatively strong transient absorption spectrum (see Figure 1) with a maximum at 320 nm and a shoulder around 400 nm, as well as a weaker band at 250 nm. The extinction coefficient at 320 nm was estimated as ε = 3.2 × 10³ M⁻¹ cm⁻¹. The

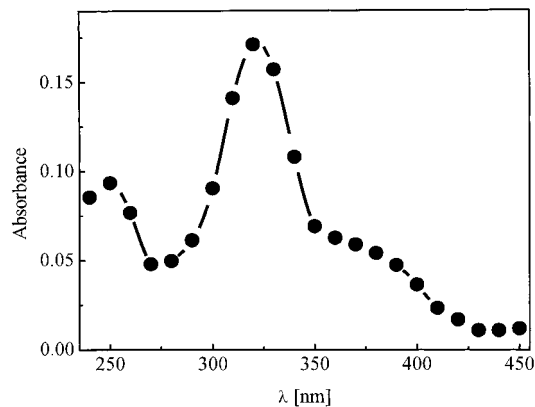
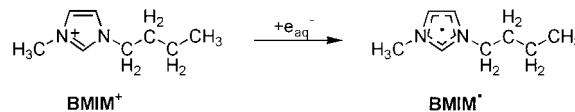


Figure 1. Electronic absorption spectrum of BMIM[•] radical obtained on reduction of BMIM⁺Br⁻ (<0.005 M) by pulse radiolysis in an N₂-saturated aqueous solution containing *tert*-BuOH (1 M). The spectrum was measured 1 μs after the electron pulse. The sample was 1 cm thick and received a radiation dose of 60 Gy.

SCHEME 1



formation of this transient product correlates with the rate of the decay of an electron absorption and therefore can be assigned to the process of electron capture and formation of the corresponding radical (BMIM[•], Scheme 1).

The rate of this reaction was determined by monitoring the decay kinetics of the electron absorption at 700 nm. This was carried out in the presence of *tert*-butyl alcohol (1 M), which scavenges the very reactive $\cdot\text{OH}$ radicals produced on pulse radiolysis of water (see Experimental Section for further details). The bimolecular rate constant determined at different concentrations of BMIM⁺ is 1.5 × 10¹⁰ M⁻¹ s⁻¹, slightly higher than that obtained for the unsubstituted imidazolium cation but in perfect agreement with the rate of reduction of the 2-methylimidazolium ring.^{20,21} The presence of different counterions seems to have no effect on this process.

In our recent work on the reactivity of N-substituted pyridinium salts, we have found very fast reactions not only with electrons, but also with acetone ketyl radicals (CH₃)₂•COH (*k* = (0.7–1) × 10¹⁰ M⁻¹ s⁻¹).²² Complete reduction was achieved in aqueous solutions containing 2-propanol (1 M) saturated with N₂O. The reaction of acetone ketyl radical with BMIM⁺ was not, however, observed under these conditions. Previous work of Bakac et al. indicated that the substituted imidazolium cations do indeed react very slowly with acetone ketyl radicals (*k* = 10⁴–10⁶ M⁻¹ s⁻¹).²³ This originates from the lower reducibility of the imidazolium compared to pyridinium cations. The reduction of these cations by e_{aq}⁻ with close to the diffusion-controlled rate completely masks this significant difference in reducibility (for example, the difference in reduction potential of 1-ethyl-3-methylimidazolium and *N*-butylpyridinium chlorides in CH₃CN is ca. 0.8 V⁴).

On pulse radiolysis of pure ionic liquids under ambient conditions, relatively strong absorption spectra of BMIM[•] were also observed, as can be seen in Figure 2A,B. This indicates that electrons ejected from the solvent molecules can be effectively trapped by BMIM⁺ cations with the rather high yield of *G* = 3.5 (yield of radicals generated per 100 eV of energy absorbed).⁸ Upon radiolysis of the salts, electrons can be ejected from the BMIM⁺ cations or the counterions. Removal of an

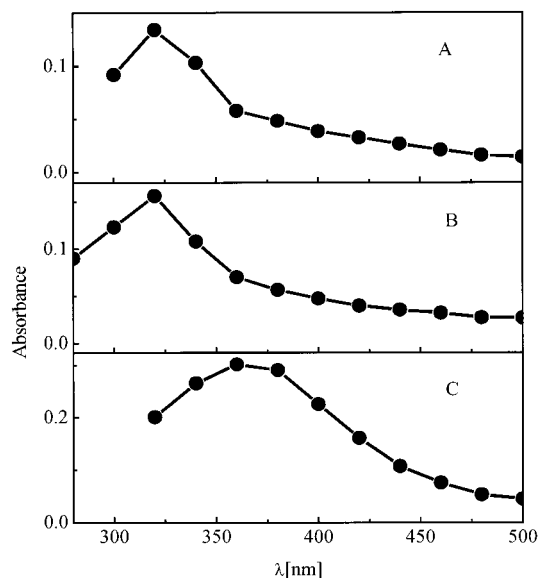


Figure 2. Transient absorption spectra measured 200 ns after the electron pulse irradiation of pure ionic liquids under ambient conditions: (A) $\text{BMIM}^+[\text{PF}_6]^-$; (B) $\text{BMIM}^+[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$; (C) BMIM^+Br^- . The samples were 1 cm thick and received a radiation dose of 60 Gy.

electron from BMIM^+ cation results in formation of the radical dication BMIM^{2+} . A similar radical species generated from the imidazolium cation was previously characterized by Neta and Schuler by means of ESR spectroscopy²⁴ and by Parsons et al. using UV-vis optical spectroscopy.²⁵ Ionization of anions leads to strongly oxidizing radical species which can further form appropriate radical anions such as $\text{Br}_2^{\bullet-}$ and $[\text{N}(\text{SO}_2\text{CF}_3)_2]_2^{\bullet-}$ (by analogy to the dithiocyanate radical anion $(\text{SCN})_2^{\bullet-}$, which displays an absorption band around 500 nm) with a rate constant close to that of diffusion control.^{26,27} These radical anions are still strong oxidants (for example, the redox potential of $\text{Br}_2^{\bullet-}/2\text{Br}^-$ is 1.6 V vs NHE, or $(\text{SCN})_2^{\bullet-}/2\text{SCN}^-$ is 1.31 V vs NHE)¹² and are capable of oxidizing the imidazolium cation. However, the reaction of $\text{Br}_2^{\bullet-}$ with protonated imidazole is very slow. We have also found that the BMIM^+ cation reacts with $\text{Br}_2^{\bullet-}$ very slowly. The second-order rate constant $k = 2.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for this reaction was determined by pulse radiolysis experiments of N_2O -saturated aqueous solutions of BMIM^+Br^- (0.2 M). This reaction does not take place in viscous pure BMIM^+Br^- . The radical anion $\text{Br}_2^{\bullet-}$ can be easily identified by its strong absorption at 360 nm (see Figure 2C), and in the pure ionic liquid this decays by a second-order reaction with a low rate constant, $k = 2.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. Interestingly, the radical anion $\text{Br}_2^{\bullet-}$ is also formed in the glassy matrix of pure BMIM^+Br^- at 77 K, which indicates that bimolecular reactions are still possible in this rigid environment.

Ionic Liquids as Solvents. The high yield of electrons and holes generated by radiolysis of pure ionic liquids and further trapped by BMIM^+ or anions indicates that these solvents should be excellent media for the generation of radical ions. Moreover, as the ionic liquids show a tendency for supercooling, resulting in formation of more viscous liquids and finally transparent glasses without crystallization even on slow cooling, they can be used for the generation and spectroscopic characterization of solute radical ions.

On pulse radiolysis of ionic liquids containing solute molecules of high electron affinity, such as tetracyanoethene (TCNE) or tetracyanoquinodimethane (TCQM) at concentration of 0.1–1 M, most of the electrons generated are effectively trapped by solute molecules both under ambient conditions and

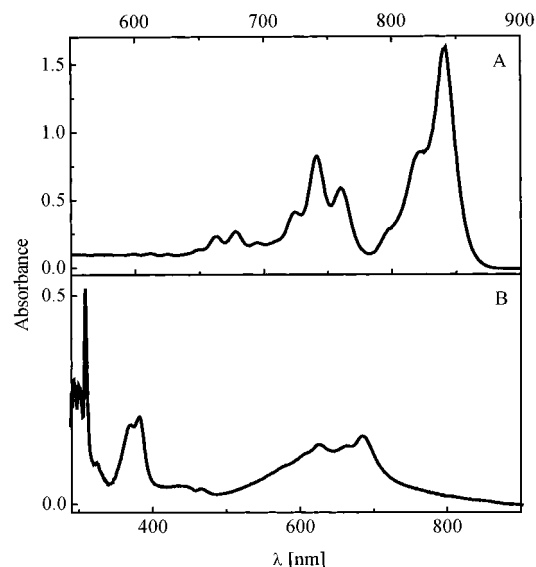


Figure 3. Electronic absorption spectra of the radical anion of TCQM (A) and the radical cation of naphthalene (B) obtained after irradiation of TCQM (0.1 M) and naphthalene (0.1 M), respectively, in glassy $\text{BMIM}^+[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$ at 77 K. The spectrum before irradiation was subtracted. The samples were 1 mm thick and received a radiation dose of 2.5 kGy.

in glasses at 77 K. The BMIM^+ cations do not effectively compete in the capture of electrons in the matrix as a result of their low reducibility.

The spectrum of the radical anion of TCQM in glassy $\text{BMIM}^+[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$ presented in Figure 3A illustrates the excellent properties of this matrix, such as high transparency and spectral resolution.⁸ At lower solute concentrations, the radiation yield of radical anions decreases, but for a typical concentration used in the glassy matrix techniques, i.e., 0.01–0.02 M, the radiation yield of $G = 1$ is still reasonably high. Under the conditions of radical ion generation by radiolytic methods, low concentrations of solute molecules of the order of 0.01–0.1 M ensure that the direct effect of radiation on the solute molecules can be ignored. This is one of the major requirements for successful use of radiolytic methods for generating radical ions. At ambient temperatures the bimolecular rate constant for electron capture by, for example, 2-methylanthraquinone (2-MAQ) (0.01 M) in the very viscous BMIM^+Br^- is $1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and the lifetime of the radical anion formed is $\tau = 8 \times 10^{-5} \text{ s}$. Under cryogenic conditions the radical anion is stable and only thermal annealing resulting in softening of the matrix can trigger its decay via bimolecular reactions.

Besides radical anions, radical cations can also be generated in glassy ionic liquids. Naphthalene can be used as an example (see Figure 3B). Under ambient conditions the radical cation of naphthalene is formed in a very fast process and the subsequent process of dimerization is also fast under these conditions ($k = 1.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). Thus, dimerization can effectively compete with the decay of radical ions due to recombination processes ($\tau = 5 \times 10^{-5} \text{ s}$ in $\text{BMIM}^+[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$). Under cryogenic conditions the dimerization can be observed only on annealing of the glass.

In Figure 4 the yield of formation of naphthalene radical cation is presented as a function of solute concentration. It is evident from this plot that the yield of radical cations formed in glassy matrices is lower than the yield of radical anions and reaches a saturation value of $G \approx 0.9$ at concentrations above 0.1 M. The addition of electron scavengers such as TCNE (1

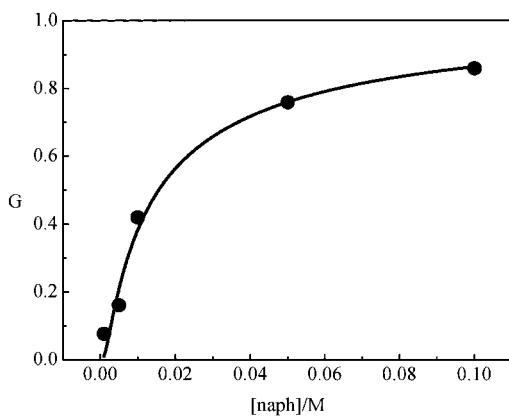


Figure 4. Radiation yield G of naphthalene radical cation formation in a glassy BMIM⁺[PF₆]⁻ at 77 K as a function of naphthalene concentration.

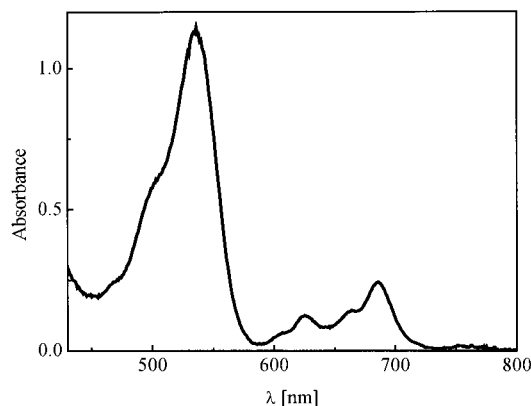


Figure 5. Electronic absorption spectrum of the radical anion of 2-MAQ and the radical cation of naphthalene obtained after irradiation of a mixture of 2-MAQ (0.01 M) and naphthalene (0.01 M) in glassy BMIM⁺[PF₆]⁻ at 77 K. The spectrum before irradiation was subtracted. The sample was 2.5 mm thick and received a radiation dose of 2 kGy.

M) does not increase this yield. Some of the holes are effectively captured by the matrix and do not reach the solute molecules. In the case of the very viscous BMIM⁺Br⁻, the radical cation of naphthalene was not observed at ambient temperatures (even at a naphthalene concentration of up to 1 M), although the strongly oxidizing Br₂^{•-} was effectively formed and long-lived. In the other two salts good-quality spectra of the naphthalene radical cation were observed under cryogenic conditions (see Figure 3B). An important feature is the observation that, even at low concentrations of solute (10⁻³ M), the spectrum of the radical cation remains of good quality without noticeable interference from other byproducts of radiolysis.

Finally, in Figure 5 we present a spectrum of the radical cation of naphthalene and the radical anion of 2-MAQ generated in the same glassy sample containing a mixture of both these solutes in BMIM⁺[PF₆]⁻ at 77 K. At first sight the possibility of simultaneous generation of radical anions and cations in the same matrix seems a disadvantage, since in some cases both these species can be generated from the same solute molecules. This, however, can be easily overcome by addition of appropriate electron or hole scavengers. Undoubtedly the advantage of this feature is that radical anions and radical cations can be characterized in the same environment. Moreover, some interesting photochemical processes, which require the presence of both types of radical ions, can be conveniently investigated.

Ionic Liquids as Media for the Characterization of Previously Unobserved Radical Cations. The group of ionic liquids investigated here have already allowed spectroscopic

SCHEME 2: Species Identified and Reactivity Observed in Glassy Ionic Liquids on Ionization of MNAH or Reduction of MNA⁺

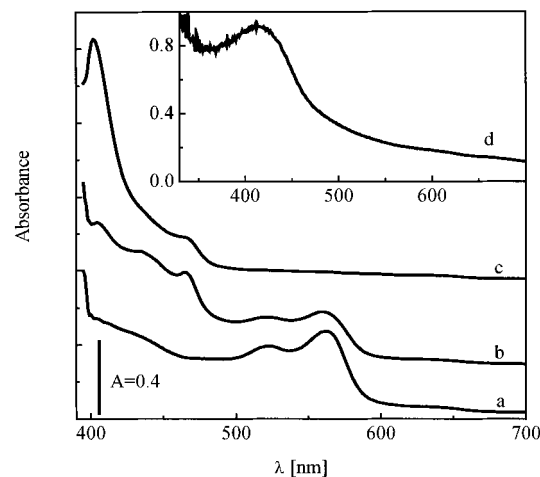
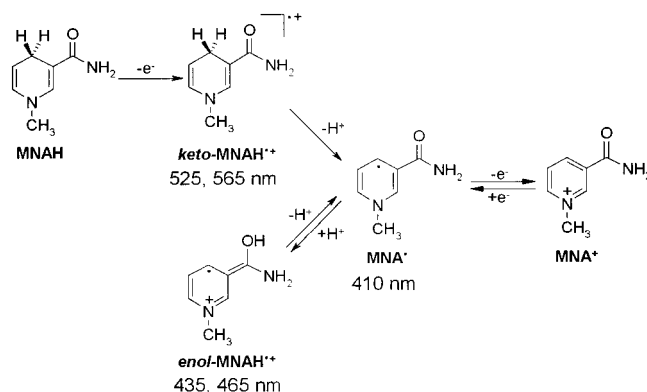


Figure 6. Electronic absorption spectra obtained on electron impact ionization of MNAH (saturated solution) in glassy BMIM⁺[PF₆]⁻ at 77 K (spectrum a). The sample was 1.5 mm thick and received a radiation dose of 7.2 kGy. Spectra b and c show the change of spectrum a on thermal relaxation of the sample for 1 h at 150 and 200 K, respectively. Inset: spectrum d obtained on irradiation of MNA⁺ (saturated solution). The spectrum before irradiation was subtracted. The sample was 2.5 mm thick and received a radiation dose of 2.6 kGy

characterization of radicals generated from 1-methyl-1,4-dihydronicotinamide (MNAH), a structural analogue of NADH. In our previous studies, we were unable to characterize the radical cations generated from MNAH (see Scheme 2) owing to its poor solubility in conventional organic solvents, which form transparent glasses on freezing.^{22,28–30} This was, however, possible in BMIM⁺[PF₆]⁻. For example, on ionization of MNAH embedded in this matrix at 77 K the radical cation in keto form is observed (*keto*-MNAH^{•+}, λ_{max} = 525 and 565 nm; see Figure 6, spectrum a). On annealing, this species deprotonates and a neutral radical MNA• (λ_{max} = 410 nm) is formed. Simultaneously the radical cation in enol form can be formed (*enol*-MNAH^{•+}, λ_{max} = 435 and 465 nm), most likely via bimolecular reactions (Figure 6b,c).²² As these solvents can be used as media for generation of species by oxidation or reduction, the neutral radical MNA• was also characterized in the same matrix on reduction of the salt MNA⁺Cl⁻ (Figure 6d).

We believe that an appropriate matrix for the generation of ionization products directly from NADH could also be selected from the large variety of ionic liquids now available. Moreover, since the very viscous environment of glassy ionic liquids inhibits the recombination processes, it seems realistic to

imagine that one could be found whose properties will allow for the generation and stabilization of radical ions even at ambient temperatures.

Conclusions

The ionic liquids used here are excellent media for the generation and spectral characterization of radical ions of solute molecules. We have shown that radical ions of interest can be generated under cryogenic conditions and their reactivity can be monitored on thermal annealing of the solvent up to ambient temperatures. Most notably, the possibility exists for the generation of both radical cations and anions in the same experiment. Furthermore, we have been able to identify previously unseen radical cation intermediates formed on pulse radiolysis of MNAH. This novel application of ionic liquids could be of very wide use especially in characterizing biologically important compounds with low solubility in conventional organic matrixes. As the properties of ionic liquids can be controlled to a large extent by variation of both the cation or the anion, the desired features can be reached by appropriate design and synthesis.

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