Reaction Kinetics in Ionic Liquids as Studied by Pulse Radiolysis: Redox Reactions in the Solvents Methyltributylammonium Bis(trifluoromethylsulfonyl)imide and N-Butylpyridinium Tetrafluoroborate

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Rate constants for several reduction and oxidation reactions were determined by pulse radiolysis in three ionic liquids and compared with rate constants in other solvents. Radiolysis of the ionic liquids methyltributylammonium bis(trifluoromethylsulfonyl)imide (R₄NNTf₂), N-butylpyridinium tetrafluoroborate (BuPyBF₄), and N-butyl-4-methylpyridinium hexafluorophosphate (BuPicPF₆) leads to formation of solvated electrons and organic radicals. In R₄NNTf₂ the solvated electrons do not react rapidly with the solvent and were reacted with several solutes, including CCl₄, benzophenone, and quinones. In the pyridinium ionic liquids the solvated electrons react with the pyridinium moiety to produce a pyridinyl radical, which, in turn, can transfer an electron to various acceptors. The rate constant for reduction of duroquinone by the benzophenone ketyl radical in R₄NNTf₂ (k = 2 × 10⁷ L mol⁻¹ s⁻¹) is much lower than that measured in water (k = 2 × 10⁹ L mol⁻¹ s⁻¹) due to the high viscosity of the ionic liquid. Rate constants for electron transfer from the solvent-derived butylpyridinyl radicals in BuPyBF₄ and BuPicPF₆ to several compounds (k of the order of 10⁸ L mol⁻¹ s⁻¹) also are lower than those measured in water and in 2-PrOH but are significantly higher than the diffusion-controlled rate constants estimated from the viscosity, suggesting an electron hopping mechanism through solvent cations. Electron transfer between methyl viologen and quinones takes place 3 or 4 orders of magnitude more slowly in BuPyBF₄ than in water or 2-PrOH and the direction of the electron transfer is solvent dependent. The driving force reverses direction on going from water to 2-PrOH and is intermediate in the ionic liquid. Radiolysis of ionic liquid solutions containing CCl₄ and O₂ leads to formation of CCl₃O₂ radicals, which oxidize chlorpromazine (CIPz) with rate constants near 1 × 10⁷ L mol⁻¹ s⁻¹, i.e., much lower than in aqueous solutions and close to rate constants in alcohols. On the other hand, the experimental rate constants in the ionic liquids and in water are close to the respective diffusion-controlled limits while the values in alcohols are much slower than diffusion-controlled.

Introduction

Room-temperature ionic liquids serve as good solvents for various thermal and electrochemical reactions, are nonvolatile and nonflammable, and have been proposed as “green solvents” for various processes.¹ Recently we have compared reaction rate constants in ionic liquids with those in other solvents by studying the reactions of CCl₃O₂ radicals with chlorpromazine and Trolox in 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF₆) and tetrafluoroborate (BMIBF₄).² The rate constants were found to be close to those measured in nonpolar organic solvents and much lower than those determined in aqueous solutions. The low rate constants in BMIPF₆ were only partially due to the high viscosity of the solutions and were interpreted to indicate a high degree of ion-association in this ionic liquid. On the other hand, the activation energy was found to be closer to that in water than in alcohols. The results were suggested to be due to specific solvation of the reactants by different components of the ionic liquid and the need for proton transfer to occur along with the electron transfer in this particular oxidation reaction. Reduction reactions could not be studied in BMIPF₆ because BMI⁺ reacts very rapidly with solvated electrons and the BMI⁺ radical produced is very unreactive with respect to electron-transfer reactions to other compounds. In this study we utilize two other ionic liquids, one that does not react with solvated electrons, thus permitting reduction of solutes by eaq⁻, and one that does react with solvated electrons but produces a radical that can reduce other solutes. The first ionic liquid is based on a tetraalkylammonium cation, which is known to be unreactive toward eaq⁻, and is a salt of the asymmetric cation (n-C₄H₉)₄N(CH₃)⁺ and the anion (CF₃SO₂)₂N⁻ (abbreviated as R₄NNTf₂). The second type is based on the N-alkylpyridinium cation, which is known to react with eaq⁻ rapidly, but produces a pyridinyl radical that can transfer an electron to many solutes. Several ionic liquids of the second type were prepared, with N-butylpyridinium (BuPy) and N-butyl-4-methylpyridinium (BuPic) as the cations and with PF₆⁻ and BF₄⁻ as the anions. Rate constants were measured in these ionic liquids for several oxidation and reduction reactions.

Experimental Section³

Methyltributylammonium bis(trifluoromethylsulfonyl)imide (R₄NNTf₂) was prepared by reacting equimolar amounts of methyltributylammonium chloride (MeBu₃N⁺Cl⁻) with lithium bis(trifluoromethylsulfonyl)imide ((CF₃SO₂)₂N⁻Li⁺) in aqueous

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solutions at room temperature. The viscous ionic liquid separated from the aqueous phase. The product was purified by repeated extractions of the LiCl and the unreacted materials with water and then dried at 70 °C under vacuum (yield 88%).

N-Butylpyridinium chloride was prepared by adding 1.1 equiv of 1-chlorobutane (HPLC grade, purity >99.5%) to 1 equiv of pyridine (Biotage grade, purity >99.9%, packaged under N₂) and gently refluxing for 4 days under a dry atmosphere. The solid product was precipitated after cooling, filtered and washed several times with ethyl acetate in a dry atmosphere (because it is highly hygroscopic), and then dried at 90 °C under vacuum (yield 70%). The N-butylpyridinium tetrabromoborate (BuPyBF₄) ionic liquid was prepared by mixing 1 equiv of N-butylpyridinium chloride with 1.5 equiv of NH₄BF₄ in acetonitrile. The compounds are not soluble, but after mixing for 5 days most of the NH₄Cl precipitated. This was filtered and the acetonitrile was removed from the liquid phase by distillation under vacuum. The ionic liquid product was passed through a column of alumina to remove opacity due to remaining NH₄Cl and then dried in a vacuum at 100 °C (yield >95%).

N-Butyl-4-methylpyridinium bromide was prepared by adding 1.1 equiv of 1-bromobutane (purity >99%) to 1 equivalent of 4-picoline (freshly distilled under N₂) in ethanol solution and gently refluxing for 24 h. The solid product precipitated after cooling, was filtered and washed several times with ethyl acetate in a dry atmosphere, and then dried at 90 °C under vacuum (yield 50%). The PF₆ salts of the pyridinium ions are not liquid at room temperature. Their melting points are 38–39 °C for the N-butyl-4-picolinium and about 67 °C for the N-butylpyridinium. They were prepared by mixing equimolar amounts of the halide salt with KPF₆, each dissolved in water. The organic PF₆ salts immediately precipitated and were filtered, washed several times with ethyl acetate, and dried in a vacuum at 100 °C (yield 86%).

Various compounds were used to probe reduction and oxidation reactions: benzophenone (BP), benzoquinone (BQ), duroquinone (DQ, tetramethylbenzoquinone), 9,10-anthraquinone-2-sulfonate (AQSO⁻), methyl viologen (MV₂⁺), 1,1′-dimethyl-4,4′-bipyridinium dichloride), p-nitroacetonitrile (p-NAP), p-nitrobenzoic acid (p-NBA), chlorpromazine (ClPz, 2-chloro-10-p-chlorophenyl-1,2,3,4-tetrahydro-1,2-dihydro-1-naphthylamine (TMPD), and Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid, a Vitamin E analogue). The oxidized species formed in reaction 1, and excited species of neat R₄NNTf₂ leads to production of solvated electrons, protons, radical cations, and neutral radicals.

\[
(R_4N)^+(NTf_2^-) \rightarrow e_{\text{solv}}^-, H^+, R_4N^{2+}, \text{NTf}_2^-, R^- \quad (1)
\]

The solvated electrons do not react with R₄N⁺. Their reactivity with NTf₂⁻ is unknown and was, therefore, examined in aqueous solutions. We found no effect of up to 27 mmol L⁻¹ LiN(SO₂CF₂)₂ on the lifetime of eₘ⁻ in deoxygenated aqueous alcohol solutions at pH 10.1, from which we estimate an upper limit for the rate constant of NTf₂⁻ with eₘ⁻ of k ≈ 1 × 10⁶ L mol⁻¹ s⁻¹. Therefore, the solvated electrons in this ionic liquid are expected to react with the protons and with other reactive solutes, as demonstrated in a later section.

The oxidized species formed in reaction 1, and excited species formed by geminate recombination, may undergo fragmentation or deprotonation. Concerning the quaternary ammonium ion, it is known that hydrogen abstraction reactions by H⁺ and OH radicals are very slow for (CH₃)₄N⁺ but the rate constant increases with chain length and it appears that only the hydrogens at the α-position are highly deactivated by the N⁺ site. The rate constant for reaction of OH radicals with (n-C₄H₉)₄N⁺ was reported to be very high, 5 × 10¹³ L mol⁻¹ s⁻¹. Therefore, R₄N⁺ is likely to deprotonate at one of the more remote C–H bonds of the butyl groups to form alkyl radicals with a tetraalkylammonium moiety (C₅H₁₁N⁺). Fragmentation of an excited state may lead to C–C bond rupture as well and thus to alkyl radicals with and without the ammonium moiety. Concerning the species formed from the bis(trifluoromethylsulfonyl)imide anion, we examined the reaction of this anion with OH radicals in N₂O-saturated aqueous solutions at pH 7.
and detected a transient species with a weak absorption at 330 nm \((\varepsilon = 450 \text{ L mol}^{-1} \text{ cm}^{-1})\), assuming \(G = 0.58 \text{ mmol} \text{ J}^{-1}\) formed with a rate constant of \(\approx 1.2 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}\). The most likely reaction is oxidation of \(\text{NTf}_2^-\) with \(^\cdot\text{OH}\) to form \(\text{NTf}_2^\cdot\).\(^9\) This product may have a finite lifetime and may react by accepting an electron or a hydrogen atom.\(^{10}\) In addition, fragmentation of excited states may form \(^\cdot\text{CF}_2\) or \(^\cdot\text{CF}_2\text{SO}_2^\cdot\) fragments. The various fragments formed from the anion and the cation are represented by \(R^\cdot\) in reaction 1. Most of these radicals are neither oxidants nor reductants but some of them can react with \(O_2\) to form oxidizing peroxyl radicals.

Pulse radiolysis of neat \(R_4\text{NNTf}_2\) produced species with only a weak tail of absorption from 300 to 400 nm. This absorption is due to a mixture of the radicals discussed above. We cannot identify these radicals from the present results, but we can examine the outcome of their reactions with solutes. Radiolytic reduction and oxidation of various reactants dissolved in \(R_4\text{-NNTf}_2\) are discussed in later sections.

**BuPyBF\(_4\) and BuPicPF\(_6\).** Radiolysis of \(N\)-butylpyridinium tetrafluoroborate (BuPyBF\(_4\)) and \(N\)-butyl-4-methylpyridinium hexafluorophosphate (BuPicPF\(_6\)) leads to production of solvated electrons, protons, radicals, and neutral radicals, e.g.,

\[
(\text{BuPy})^+ (\text{BF}_4^-) \rightarrow e_{\text{solv}}^-, H^+, (\text{BuPy})^{2+}, \text{BF}_4^-. \tag{2}
\]

\((\text{BuPy})^{2+}\) and BF\(_4^\cdot\) (or BuPic\(^{2+}\) and PF\(_6^\cdot\)) may act as oxidants or undergo fragmentation. \((\text{BuPy})^{2+}\) is likely to lose a proton from the butyl group to form a pyridylalkyl radical.

\[
(C_2H_5Py)^{2+} \rightarrow C_2H_5Py^+ + H^+ \tag{3}
\]

The most likely product is the benzylic radical, although other isomers cannot be ruled out. Such radicals are not oxidants but can react with \(O_2\) to form oxidizing peroxyl radicals.

\[
C_2H_5Py^+ + O_2 \rightarrow OOC_2H_5Py^+ \tag{4}
\]

The solvated electrons formed in reaction 2 react very rapidly with the pyridinium cation to form the neutral butylpyridinyl radical.

\[
\text{BuPy}^+ + e_{\text{aq}}^- \rightarrow \text{BuPy}^\cdot \tag{5}
\]

We measured the rate constant for this reaction in deoxygenated aqueous solutions containing 0.2 mol L\(^{-1}\) \(\text{MeOH}\) at pH 11 and found \(k_5 = (4 \pm 1) \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}\), in line with rate constants for similar compounds.\(^6\) The spectrum of the \(N\)-butylpyridinyl radical, BuPy\(^\cdot\), was recorded by pulse radiolysis of a deoxygenated aqueous solution containing 0.1 mol L\(^{-1}\) \(\text{t-BuOH}\) and shows a weak absorption at 340 nm \((\varepsilon = 850 \text{ L mol}^{-1} \text{ cm}^{-1})\), assuming \(G = 0.29 \text{ mmol} \text{ J}^{-1}\) (Figure 1a). The spectrum recorded upon irradiation of neat BuPyBF\(_4\) shows a similar weak peak (Figure 1b), as expected if the main absorbing species is the same pyridinyl radical. This radical is expected to transfer an electron to compounds with higher electron affinity, such as quinones, as demonstrated in the next section.

**Radiolytic Reduction in the Ionic Liquids.** In this section we discuss the radiolytic reduction of quinones, benzophenone, methyl viologen, and nitroaromatic compounds in various ionic liquids, the electron transfer from the benzophenone ketyl radicals to duroquinone, and the electron transfer between quinones and methyl viologen, and compare the rate constants with values measured in other solvents.

**Reduction Reactions in \(R_4\text{NNTf}_2\).** Irradiation of deoxygenated \(R_4\text{NNTf}_2\) containing BQ or DQ (\(\approx 6 \text{ mmol L}^{-1}\)) led to reduction of these compounds by solvated electrons and by organic radicals derived from the solvent. From the absorption maxima of the radicals produced (\(\approx 410\) and 420 nm, respectively) we conclude that the semiquinone radicals were protonated under these conditions,\(^11\) the proton being produced by the radiolysis (reaction 1).

\[
\text{BQ} + e_{\text{solv}}^- + H^+ \rightarrow \text{BQH}^+ \tag{6}
\]

Addition of 0.07 mol L\(^{-1}\) triethylamine (TEA), to capture the protons, led to production of the semiquinone radical anions, with absorption maxima at 420 and 445 nm for BQ and DQ, respectively.\(^11\)

\[
\text{BQ} + e_{\text{solv}}^- \rightarrow \text{BQ}^- \tag{7}
\]

The yields of both radical anions were much higher in the presence of TEA because TEA quenches excited states and oxidizing radicals to produce additional reducing radicals. BQ\(^-\) was produced in two distinct steps; approximately half the absorbance was formed immediately after the pulse \((k > 1 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1})\) and the other half within 20 \(\mu\)s \((k \approx 1 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1})\). The fast step is due to reaction 7 as well as reaction 8 of BQ with the reducing radical derived from TEA.

\[
\text{BQ} + (C_2H_5)_2N\text{CHCH}_3 \rightarrow \text{BQ}^- + (C_2H_5)_2N=CHCH_3 \tag{8}
\]

Both reactions 7 and 8 are known to have very high rate constants in aqueous solutions \((k \approx 3 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1})\).\(^5,12\) The slower step may be due to reaction of BQ with various alkyl radicals formed from the solvent. Such reactions have been observed in aqueous solutions and found to occur via addition.
of the radical to the ring of BQ and subsequent electron transfer from the adduct to another BQ.\textsuperscript{13}

\[
\text{BQ} + R^* \rightarrow R\text{-BQ}^* \quad (9)
\]

\[
R\text{-BQ}^* + BQ \rightarrow [R\text{-BQ}^*] + BQ''^- \quad (10)
\]

A slightly different pattern was observed in the reduction of duroquinone. The DQ\textsuperscript{--} radical anion was produced in three distinct steps, a very rapid step due to reaction with solvated electrons, a slower step (\(k \approx 6 \times 10^7 \text{ L mol}^{-1} \text{s}^{-1}\)) presumably due to reaction with the TEA radical, and a much slower step (\(k < 2 \times 10^3 \text{ L mol}^{-1} \text{s}^{-1}\)) probably due to reactions parallel to reactions 9 and 10. The increase of absorbance produced in the last step was very small, and the process was probably incomplete because of radical–radical reactions. Therefore, its observed rate constant is considered to be an upper limit. If this last step indeed involves addition of the radicals to the ring (as in reaction 9), it is not surprising that its rate constant is much lower for DQ than for BQ because of the steric hindrance of the four methyl groups on the ring.

Reduction of benzophenone (0.04 to 0.09 mol L\(^{-1}\)) in deoxygenated R\(_4\)NNTf\(_2\) solutions containing TEA produced initially the radical anion BP\textsuperscript{--}, which has an absorption peak in water at 610 nm\textsuperscript{14,15} and in the ionic liquid at \(\approx 700\) nm. This species was converted within 10 \(\mu\)s into BPH\textsuperscript{+}, which has an absorption peak at 545 nm both in water\textsuperscript{14,15} and in the ionic liquid. After this rapid initial production of the radical, a slower increase in absorbance, with \(k \approx 1 \times 10^6 \text{ L mol}^{-1} \text{s}^{-1}\), was observed, probably due to reduction of BP by the TEA radical. The finding that BP\textsuperscript{--} undergoes protonation under these conditions while BQ\textsuperscript{--} and DQ\textsuperscript{--} are not protonated is in line with the higher \(pK_a\) value in aqueous solution of BPH\textsuperscript{+} (9.2)\textsuperscript{14,15} as compared with those of the semiquinones (reactions 4 and 5).\textsuperscript{11} From the measured absorbance of BPH\textsuperscript{+} at 545 nm we can estimate the yield of solvated electrons in this ionic liquid by assuming that the molar absorption coefficient of BPH\textsuperscript{+} in R\(_4\)NNTf\(_2\) is similar to that in aqueous solutions (5.5 \(\times 10^3\) L mol\(^{-1}\) cm\(^{-1}\)).\textsuperscript{15} By using thioacetate dosimetry and correcting for the difference in electron density between the aqueous thioacetate solution and the ionic liquid (646/556), we estimate that the radiolytic yield of solvated electrons captured by BP in the absence of TEA is 0.9 \(\times 10^{-7}\) mol J\(^{-1}\) and approximately twice as high as that in the presence of TEA.

Electron transfer from BPH\textsuperscript{+} to DQ (reaction 11) was examined in R\(_4\)NNTf\(_2\) solutions containing 70 mmol L\(^{-1}\) TEA, 90 mmol L\(^{-1}\) BP, and various concentrations of DQ between 0.15 and 1.2 mmol L\(^{-1}\).

\[
\text{BPH}^+ + \text{DQ} \rightarrow \text{BP} + \text{H}^+ + \text{DQ}''^- \quad (11)
\]

The rate constant was determined at room temperature by following the formation of DQ\textsuperscript{--} at 445 nm and found to be \((2.0 \pm 0.3) \times 10^7\) L mol\(^{-1}\) s\(^{-1}\). Similar measurements were carried out in alcohol and aqueous solutions for comparison (Table 1). The rate constant determined in 2-PrOH solutions containing similar concentrations of TEA, BP, and DQ was \((1.7 \pm 0.2) \times 10^8\) L mol\(^{-1}\) s\(^{-1}\) and the rate constant in aqueous solutions, containing 25% 2-PrOH to permit sufficient solubility, was \((2.2 \pm 0.3) \times 10^6\) L mol\(^{-1}\) s\(^{-1}\). Thus, the measured rate constant of this electron-transfer reaction in the ionic liquid is much lower than that in alcohol or aqueous solutions. This effect must be due in part to the high viscosity of the ionic liquid. For comparison, we measured the same rate constant in glycerol and found it to be even lower, \((4.1 \pm 1) \times 10^6\) L mol\(^{-1}\) s\(^{-1}\).

\[ k_{\text{diff}} = 8000RT/3\eta \quad (12) \]

where \(R\) is the gas constant (8.3144 J K\(^{-1}\) mol\(^{-1}\)), \(T\) the absolute temperature, and \(\eta\) the viscosity (in Pa s). The values of \(k_{\text{diff}}\) for the respective conditions (Table 1) were estimated from the viscosity measured under those conditions (i.e., with solutions containing all the main components, not just with neat solvents). It is seen that the rate constant for reaction 11 measured in R\(_4\)NNTf\(_2\) is approximately the same as the estimated \(k_{\text{diff}}\). The measured values in glycerol and in water/2-PrOH are also close to the corresponding value of \(k_{\text{diff}}\). On the other hand, the measured rate constant in 2-PrOH is \(~20\) times lower than \(k_{\text{diff}}\). This comparison suggests that R\(_4\)NNTf\(_2\) behaves in this case as a polar solvent, which facilitates electron transfer, similar to water or glycerol and more polar than 2-PrOH.

<table>
<thead>
<tr>
<th>solvent</th>
<th>(k_{\text{exp}}) L mol(^{-1}) s(^{-1})</th>
<th>(k_{\text{diff}}) L mol(^{-1}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(_4)NNTf(_2)</td>
<td>((2.0 \pm 0.3) \times 10^7)</td>
<td>(1.5 \times 10^7)</td>
</tr>
<tr>
<td>2-PrOH</td>
<td>((1.7 \pm 0.2) \times 10^8)</td>
<td>(~3 \times 10^8)</td>
</tr>
<tr>
<td>H(_2)O/2-PrOH (3/1)</td>
<td>((2.0 \pm 0.4) \times 10^6)</td>
<td>(~3 \times 10^9)</td>
</tr>
<tr>
<td>glycerol</td>
<td>((4 \pm 1) \times 10^6)</td>
<td>(~5 \times 10^6)</td>
</tr>
</tbody>
</table>

* The values of the diffusion-controlled rate constants, \(k_{\text{diff}}\), were estimated from the viscosity by using eq 12 and are considered to be lower limits. They may be higher by up to 50% depending on the exact shapes of the reactants (Edwards, J. T. J. Chem. Ed. 1970, 47, 261).

This value was estimated by taking the viscosity of water with 25% 2-PrOH as 0.002 Pa s, based on values given in the literature (Landolt-Börnstein. Numerical Data and Functional Relationships in Science and Technology; Springer-Verlag: Berlin, 1969; Vol. 2, Part 5a, pp 366–367) for water/EtOH and water/1-PrOH mixtures (the viscosity of water/alcohol mixtures is higher than that of either solvent alone).

![Figure 2. Viscosities of the neat ionic liquids at different temperatures (between 20 °C and 75 °C), shown as Arrhenius plots, for R\(_4\)NNTf\(_2\) (○), BuPyBF\(_4\) (●), BuPicPF\(_6\) (▲), and BMIPF\(_6\) (△). Sample numerical values (in Pa s) are: R\(_4\)NNTf\(_2\): 0.75 at 20 °C, 0.52 at 25 °C, BuPyBF\(_4\): 0.17 at 20 °C, 0.13 at 25 °C, BuPicPF\(_6\): 0.14 at 45 °C.](image-url)
of rate constants were derived from the concentration dependence Arrhenius plots for the rate constants for reduction by the pyridinyl radicals in the ionic liquids. In BuPyBF$_4$: BuPy$^+$ + DQ (●), BuPy$^+$ + MV$^{2+}$ (○), BuPy$^+$ + p-NBA (□). In BuPicPF$_6$: BuPic$^+$ + DQ (▲).

**Reduction Reactions in BuPicPF$_6$ and BuPyBF$_4$.** Solutes in these ionic liquids are not reduced by the radiolytically produced solvated electrons since $e_{\text{solv}}^-$ is rapidly scavenged by the pyridinium cations (reaction 5). Therefore, the main reducing species in these ionic liquids is the butylpyridinyl radical. This radical does not reduce benzophenone (an upper limit of $k < 1 \times 10^6$ L mol$^{-1}$ s$^{-1}$ was estimated in 2-PrOH/water solutions), and we could not measure the rate of reduction of quinones by the benzophenone ketyl radical in these ionic liquids as we did in R$_2$NNTf$_2$. We measured, however, the rate constants for reduction of various compounds by the butylpyridinyl radical (e.g., reaction 13).

$$\text{BuPy}^+ + \text{DQ} \rightarrow \text{BuPy}^+ + \text{DQ}^-$$

(13)

Rate constants were measured for the reduction of duroquinone, methyl viologen, $p$-nitrobenzoic acid, and $p$-nitrocatechol by the butylpyridinyl radical in these ionic liquids. Since the absorption of BuPy$^+$ is weak, the rate constants for its reactions with these reactants were determined by following the buildup of absorption of the radicals produced from the other reactants: 445 nm for DQ,$^{11}$ 400 and 605 nm for MV$^{2+},^{17}$ 330 nm for $p$-NBA,$^{18}$ and 370 nm for $p$-NAP.$^{14}$ For each reactant, rate constants were measured at several concentrations and several temperatures, between 22 and 75 °C. Reactions in BuPicPF$_6$ were measured only between 43 and 75 °C since the melting point of this ionic liquid is 38–39 °C. Second-order rate constants were derived from the concentration dependence of $k_{\text{obs}}$. The values at the different temperatures give good Arrhenius plots (Figure 3) and the results are summarized in Table 2.

The rate constants for the same reactions were also determined in aqueous solutions and the rate constants are compared in Table 2. In all cases, the rate constants are about an order of magnitude higher in water than in the ionic liquid. In the case of DQ the rate constant was also measured in 2-PrOH and found to have an intermediate value between those in water and in the ionic liquid.

Table 2 also shows the values of the diffusion-controlled rate constants estimated from the viscosities by using eq 12. The viscosities of the ionic liquids were measured (Figure 2) and those of water and 2-PrOH were taken from the literature. In water and 2-PrOH, the electron-transfer rate constants are somewhat lower than the values of $k_{\text{diff}}$, as observed before for many other reactions. In contrast, all the rate constants measured in the ionic liquids are about an order of magnitude higher than the calculated $k_{\text{diff}}$. This unexpected observation may be explained by an electron-transfer mechanism that involves hopping of the electron between solvent cations so that the unpaired electron of BuPy$^+$ can reach the organic substrate without the need for complete diffusion of a specific BuPy$^+$ radical to the substrate. This is particularly facilitated when the neutral substrate is solvated by the pyridinium cations, which can channel the electron. The positively charged methyl viologen is expected to be solvated partly by the BF$_4^-$ anions and thus the rate of electron transfer, although higher than $k_{\text{diff}}$, is not as high as with the neutral solutes (Table 2).

The measured electron-transfer rate constants in the ionic liquids were found to increase with temperature as shown by Arrhenius plots (Figure 3) and their activation energies are summarized in Table 2. For comparison, we calculated $k_{\text{diff}}$ at the different temperatures and derived the activation energy for $k_{\text{diff}}$: 43.6 kJ mol$^{-1}$ for BuPicPF$_6$ and 37.6 kJ mol$^{-1}$ for BuPyBF$_4$. These values are very close to the activation energies for the reactions of DQ and $p$-NBA in both ionic liquids (Table 2). This finding is in line with the hopping mechanism suggested above if we assume that increased diffusion rate (a) facilitates encounters between solvent cations by faster repositioning of the solvent ions, thus enhancing the electron hopping, and (b) increases the probability of encounters between the radical and the solute, thus requiring fewer hopping steps. The activation energy for the reaction of MV$^{2+}$ is slightly lower due to its solvation with anions as discussed above.

The radiolytic yield for production of MV$^{+}$ was determined by measuring the absorbance of this radical at 605 nm in deoxygenated BuPyBF$_4$ solutions containing 0.8 mmol L$^{-1}$ MV$^{2+}$ and using aqueous thiocyanate dosimetry.$^{5}$ By assuming that the molar absorption coefficient of MV$^{+}$ in BuPyBF$_4$ is similar to that in water ($1.3 \times 10^4$ L mol$^{-1}$ cm$^{-1}$)$^{17}$ and correcting for the differences in electron densities between water and BuPyBF$_4$ (668/556) we find G(MV$^{+}$) = (1.8 ± 0.2) × 10$^{-7}$ mol J$^{-1}$. The radiolytic yield in BuPyBF$_4$ was also determined by measuring the yield of reduction of $p$-NAP and assuming that the absorption coefficient of its radical anion is similar to that in water. The molar absorption coefficient of $p$-NAP$^-$ in aqueous solutions was reported to be 17600 L mol$^{-1}$ cm$^{-1}$ at 350 nm and 2900 L mol$^{-1}$ cm$^{-1}$ at 545 nm.$^{14}$ We monitored the absorbance at 545 nm to avoid interference by the absorbance of the solvent radicals. To ascertain that $p$-NAP$^-$ does not undergo protonation to form $p$-NAPH, which has lower absorbance, we added TEOA as a base. From the absorbance at 545 nm observed with deoxygenated BuPyBF$_4$ containing 0.06 mol L$^{-1}$ TEOA and 0.6 mmol L$^{-1}$ $p$-NAP, we estimate the total yield of radicals $G = (4.8 \pm 0.5) \times 10^{-7}$ mol J$^{-1}$. This value is much higher than that determined with MV$^{2+}$ in the absence of TEOA and indicates that most of the initial oxidizing species are converted into reducing radicals by the TEOA, as discussed above for TEA. Therefore, $p$-NAP is reduced by both BuPy$^+$ and by the radicals derived from TEOA.

$$\text{BuPy}^+ + p\text{-NAP} \rightarrow \text{BuPy}^+ + p\text{-NAP}^-$$

(14)

$$\text{(HOCH}_2\text{CH}_3\text{)}_2\text{NCHCH}_2\text{OH} + p\text{-NAP} \rightarrow$$

$$\text{(HOCH}_2\text{CH}_3\text{)}_2\text{N}^+\text{CHCH}_2\text{OH} + p\text{-NAP}^-$$

(15)
The observed formation of p-NAP−, however, appeared to take place in one step, with a rate constant of (2.2 ± 0.4) × 10¹² L mol⁻¹ s⁻¹.

In an attempt to clarify the role of TEOA in the reduction of p-NAP, we conducted experiments in aqueous solutions. The rate constant for reduction of p-NAP by the BuPy⁺ radical in deoxygenated aqueous solutions containing 0.2 mol L⁻¹ t-BuOH, 11 mmol L⁻¹ BuPyBF₄, 5 mmol L⁻¹ phosphate buffer at pH 7, and between 0.07 and 0.2 mmol L⁻¹ p-NAP, but no TEOA, was determined to be $k_{16} = (6.2 ± 0.9) × 10^9$ L mol⁻¹ s⁻¹. In the absence of t-BuOH but with 0.07 mol L⁻¹ TEOA in N₂O-saturated aqueous solutions (to convert e₆O⁻ into OH⁻ so that all the primary species are converted into TEOA radicals), at pH 9.4, the reduction of p-NAP took place with $k_{16} = (3.2 ± 0.6) × 10^9$ L mol⁻¹ s⁻¹, i.e., about half the value of $k_{16,19}$. In the ionic liquid, reactions 14 and 15 took place in parallel and it was not possible to distinguish two steps of reduction.

**Electron Transfer between Methyl Viologen and Quinones.**

In addition to the electron transfer from the solvent butyrylpyridinyl radicals to various solutes, we studied secondary electron transfer from a solute radical to a different solute. First, we measured the rate constant for reaction 16 by pulse radiolysis of deoxygenated BuPyBF₄ solutions containing MV²⁺ (0.7 to 4 mmol L⁻¹) and duroquinone (0.05 to 5 mmol L⁻¹).

$$\text{MV}^+ + \text{DQ} \rightleftharpoons \text{MV}^{2+} + \text{DQ}^- $$

From the rate of decay of the MV⁺ absorbance at 400 nm as a function of DQ concentration we derive $k_{16} = (1.4 ± 0.2) × 10^9$ L mol⁻¹ s⁻¹. This rate constant is 2 orders of magnitude lower than $k_{diff}$, unlike the rate constant for reaction 13, which was an order of magnitude higher than $k_{diff}$. For comparison, we also determined the rate constant for reaction 16 in aqueous solutions containing 10% 2-ProH and found $k_{16} = (3.3 ± 0.5) × 10^9$ L mol⁻¹ s⁻¹, i.e., $k_{16}$ is 4 orders of magnitude lower in the ionic liquid than in water. We then measured $k_{16}$ in several BuPyBF₄/water mixtures. The results (Table 3) show a large increase in rate constant upon addition of small amounts of water and then a slower approach to the aqueous solution value (Figure 4).

**Table 3: Rate Constants for Electron Transfer between Quinones and Methyl Viologen**

<table>
<thead>
<tr>
<th>reaction</th>
<th>solvent</th>
<th>T, °C</th>
<th>$k_{exp}$, L mol⁻¹ s⁻¹</th>
<th>$E_{a,exp}$, kJ mol⁻¹</th>
<th>log A</th>
<th>$k_{diff}$, L mol⁻¹ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>MV⁺ + DQ</td>
<td>BuPyBF₄</td>
<td>25</td>
<td>(1.4 ± 0.3) × 10⁹</td>
<td>34.9</td>
<td>14.8</td>
<td>5 × 10⁹</td>
</tr>
<tr>
<td>MV⁺ + DQ</td>
<td>BuPyBF₄, 2 v % H₂O</td>
<td>25</td>
<td>(7.1 ± 1.1) × 10⁹</td>
<td>34.9</td>
<td>14.8</td>
<td>5 × 10⁹</td>
</tr>
<tr>
<td>MV⁺ + DQ</td>
<td>BuPyBF₄, 5 v % H₂O</td>
<td>25</td>
<td>(3.0 ± 0.5) × 10⁹</td>
<td>34.9</td>
<td>14.8</td>
<td>5 × 10⁹</td>
</tr>
<tr>
<td>MV⁺ + DQ</td>
<td>BuPyBF₄, 9 v % H₂O</td>
<td>25</td>
<td>(2.0 ± 0.3) × 10⁹</td>
<td>34.9</td>
<td>14.8</td>
<td>5 × 10⁹</td>
</tr>
<tr>
<td>MV⁺ + DQ</td>
<td>BuPyBF₄, 19 v % H₂O</td>
<td>25</td>
<td>(1.5 ± 0.3) × 10⁹</td>
<td>34.9</td>
<td>14.8</td>
<td>5 × 10⁹</td>
</tr>
<tr>
<td>MV⁺ + DQ</td>
<td>BuPyBF₄, 30 v % H₂O</td>
<td>25</td>
<td>(5.5 ± 0.8) × 10⁹</td>
<td>34.9</td>
<td>14.8</td>
<td>5 × 10⁹</td>
</tr>
<tr>
<td>MV⁺ + DQ</td>
<td>BuPyBF₄, 50 v % H₂O</td>
<td>25</td>
<td>(1.1 ± 0.1) × 10⁹</td>
<td>34.9</td>
<td>14.8</td>
<td>5 × 10⁹</td>
</tr>
<tr>
<td>MV⁺ + DQ</td>
<td>H₂O, 10 v % 2-ProH</td>
<td>25</td>
<td>(3.3 ± 0.5) × 10⁹</td>
<td>34.9</td>
<td>14.8</td>
<td>5 × 10⁹</td>
</tr>
<tr>
<td>DQ⁻ + MV²⁺</td>
<td>2-ProH, 5 v % TEOA</td>
<td>25</td>
<td>(1.7 ± 0.4) × 10⁹</td>
<td>34.9</td>
<td>14.8</td>
<td>5 × 10⁹</td>
</tr>
<tr>
<td>AQS⁻⁻ + MV²⁺</td>
<td>BuPyBF₄, 2 v % H₂O</td>
<td>22</td>
<td>(4.0 ± 0.8) × 10⁹</td>
<td>34.9</td>
<td>14.8</td>
<td>5 × 10⁹</td>
</tr>
<tr>
<td>MV⁺ + AQS</td>
<td>H₂O, 2 v % 2-ProOH</td>
<td>22</td>
<td>(6.1 ± 0.9) × 10⁹</td>
<td>34.9</td>
<td>14.8</td>
<td>5 × 10⁹</td>
</tr>
<tr>
<td>AQS⁻⁻ + MV²⁺</td>
<td>2-ProH, 15 v % water</td>
<td>22</td>
<td>(1.5 ± 0.3) × 10⁹</td>
<td>34.9</td>
<td>14.8</td>
<td>5 × 10⁹</td>
</tr>
</tbody>
</table>

A small amount of water was necessary to permit sufficient dissolution of AQS⁻⁻. 2-ProOH was used as a scavenger for H⁺ and OH radicals; the solution was neutral, buffered.

![Figure 4. Rate constant for electron transfer from MV⁺ to DQ measured in different BuPyBF₄/water mixtures (●) and the corresponding values of $k_{diff}$ (○) estimated from the measured viscosities by using eq 12.](image-url)
reaction occurs much more slowly. It is also possible that reaction 16 in neat BuPyBF$_4$ is near equilibrium and that it is pulled to the right due to protonation of DQ$^-$. Irradiation of the solution produces protons (reaction 2), which are not neutralized under these conditions and can react with DQ$^-$ to form DQH$^*$. Since DQH$^*$ has a shorter lifetime than DQ$^-$ and cannot transfer an electron to MV$^2+$, reaction 16 can be driven to the right. In confirmation of this suggestion we found that addition of 2 v% pyridine to neutralize part of the protons led to reversal of the direction of reaction 16. Electron transfer from DQ$^-$ to MV$^2+$ was observed in the presence of pyridine, with a rate constant $k_{16} \approx 10^6$ L mol$^{-1}$ s$^{-1}$, and the decay of MV$^+$ occurred much more slowly than in the absence of pyridine. Thus reaction 16 proceeds in BuPyBF$_4$ in the same direction as in 2-PrOH and in opposite direction to that in water.

This reversal of the reaction driving force was demonstrated more clearly in similar experiments with MV$^2+$ and AQS$^-$. 

\[
\text{MV}^+ + \text{AQS}^- \rightleftharpoons \text{MV}^2+ + \text{AQS}^2- \quad (17)
\]

In aqueous solutions reaction 17 proceeds to the right with $k_{17} = (6.1 \pm 0.9) \times 10^9$ L mol$^{-1}$ s$^{-1}$ while in 2-PrOH the direction is reversed and $k_{17} = (1.5 \pm 0.3) \times 10^9$ L mol$^{-1}$ s$^{-1}$ (Table 3). In BuPyBF$_4$ the reaction proceeds to the left as in 2-PrOH, with $k_{17} = (4.0 \pm 0.8) \times 10^8$ L mol$^{-1}$ s$^{-1}$ (Table 3). Upon addition of 2 v% pyridine, to minimize the extent of protonation of AQS$^2-$ to AQSH$^-$, $k_{17}$ increased to $2.7 \pm 0.5 \times 10^5$ L mol$^{-1}$ s$^{-1}$. These results clearly indicate the reversal of the driving force upon going from water to BuPyBF$_4$ and emphasize the similarity between the ionic liquid and the alcohol.

Most of the reactions discussed in this study involve at least one uncharged species and thus their rates are not affected by the ionic strength of the medium to any appreciable extent. Only reaction 17 involves two charged species in both directions. The reverse direction, involving two doubly charged species with opposite signs, is decelerated at increased ionic strength. Although $k_{17}$ measured in the ionic liquid is much smaller than that measured in 2-PrOH, this decrease is due to at least in part to changes in reduction potentials and it is not possible to assess whether the ionic liquid exerts the ionic strength effect expected from $\approx 3$ mol L$^{-1}$ salt concentration.

**Radiolytic Oxidation in the Ionic Liquids.** In this section we discuss the oxidation of TMPD and CIPz in the neat ionic liquids, from which we estimate the total oxidation yields, and the rate constants for oxidation of CIPz and Trolox by the CCl$_4$O$_2^+$ radicals produced in the presence of CCl$_4$.

**Oxidation Reactions in R$_4$NNTf$_2$.** The radiolytic yield of oxidation in R$_4$NNTf$_2$ was determined by using TMPD and CIPz. These compounds are oxidized to produce long-lived radical cations, which have strong absorption peaks with known molar absorption coefficients in various solvents. Pulse radiolysis of deoxygenated R$_4$NNTf$_2$ containing 6 mmol L$^{-1}$ TMPD produced TMPD$^{++}$ with two absorption peaks at 565 and 613 nm. The absorbance at 565 nm was produced in two steps, one part was formed within 1 $\mu$s after the pulse and an additional absorbance was formed within 100 $\mu$s, indicating the existence of at least two oxidizing species. The radiolytic yield of the fast oxidation step was $1.1 \times 10^{-7}$ mol J$^{-1}$, and the total yield was $1.7 \times 10^{-7}$ mol J$^{-1}$.

When a similar solution was irradiated under air, an additional formation step took place over 2 ms and the total yield increased to $2.1 \times 10^{-7}$ mol J$^{-1}$. This increase is due to oxidation of TMPD by peroxy radicals. Similar experiments with CIPz gave lower yields. The initial step of rapid formation of CIPz$^{++}$, monitored at 525 nm, was very small, corresponding to only $0.3 \times 10^{-7}$ mol J$^{-1}$, and the total yield of oxidation under air was only $0.9 \times 10^{-7}$ mol J$^{-1}$. The different oxidation yields of these two compounds indicate that some radicals formed in this solvent can oxidize TMPD ($E = 0.26$ V vs NHE) but do not react rapidly with CIPz ($E = 0.8$ V). Alkylperoxyl radicals are known to exhibit such behavior and they are produced in the present system when irradiated under air. The radicals produced in deoxygenated solutions include Tf$_2$N$^*$, which is probably the strong oxidant that leads to the rapid oxidation step, and various fragments that are weaker oxidants. In oxygenated solutions, it is possible that the peroxy radicals, such as CF$_3$O$_2$ and R$_3$N$^+$CR$_2$O$_2^*$, are formed and these can oxidize CIPz.

Irradiation of various solvents containing CCl$_4$ and O$_2$ is known to produce CCl$_3$O$_2^+$ radicals, which are strong oxidants. This is due to the fact that CCl$_4$ can form CCl$_3$ radicals when it reacts with solvated electrons as well as with various organic radicals. Recently we have studied the rate constant for oxidation of CIPz by CCl$_3$O$_2^+$ radicals in another ionic liquid, BMIPF$_6$.

\[
\text{CCl}_3\text{O}_2^+ + \text{CIPz} \rightarrow \text{CCl}_3\text{O}_2^- + \text{CIPz}^{++} \quad (18)
\]

In the present study we determined the rate constant for the same reaction in R$_4$NNTf$_2$ by pulse radiolysis of oxygenated solutions containing 1% CCl$_4$ and various concentrations of CIPz. The rate of formation of CIPz$^{+}$ was monitored at 525 nm as a function of CIPz concentration, and the value of $k_{18}$ was derived from a linear plot of $k_{obs}$ vs [CIPz]. However, unlike the earlier case of BMIPF$_6$, where oxidation of CIPz took place to a significant extent only in the presence of CCl$_4$ and O$_2$, in R$_4$NNTf$_2$ there was oxidation of CIPz even in the absence of CCl$_4$, as discussed above. Therefore, we measured the rate constant for oxidation of CIPz in oxygenated solutions of R$_4$NNTf$_2$ both in the presence and absence of CCl$_4$. The absorbance observed in the presence of CCl$_4$ was about twice as high as that observed in the absence of CCl$_4$ but the rate constants were similar, and it was not possible to determine different rate constants for different processes. This is not surprising if the solvent derived radicals include the strong oxidants CF$_3$O$_2^+$ and R$_3$N$^+$CH(R)O$_2^*$. By assuming that the rate constant measured in the presence of CCl$_4$ ($4.3 \times 10^8$ L mol$^{-1}$ s$^{-1}$) is the weighted average for the reactions with CCl$_3$O$_2^+$ and with the other radicals (measured separately as $3.7 \times 10^8$ L mol$^{-1}$ s$^{-1}$), we estimate that the rate constant for reaction 18 is $5 \times 10^5$ L mol$^{-1}$ s$^{-1}$.

We also measured the rate constants as a function of temperature from 21 to 75 °C and found slightly different temperature dependences in the presence and absence of CCl$_4$.

The activation energies are summarized in Table 4. The experimental rate constants ($k_{exp}$) were then corrected for the effect of the diffusion-controlled limit ($k_{diff}$) to derive the activation-controlled rate constants ($k_{act}$).

\[
k_{act}^{-1} = k_{exp}^{-1} - k_{diff}^{-1} \quad (19)
\]

The values of $k_{act}$ as a function of temperature were estimated from the viscosity measured at different temperatures (Figure 2) according to eq 12. Arrhenius plots for the calculated $k_{act}$ values are shown in Figure 5 and the results from these plots are also summarized in Table 4. It is seen that the experimental rate constants are approximately the same near 43 °C and that the Arrhenius plots diverge from there, giving an activation energy and a preexponential factor that are lower in the presence of CCl$_4$ than those in its absence. Although the activation energy for reaction 18 derived in this complex manner is approximate,
its value is within the range of the activation energies determined in a more direct manner in the other ionic liquids (see below).

Oxidation Reactions in BuPicPF$_6$ and BuPyBF$_4$. The radiolytic oxidation yield in BuPyBF$_4$ was determined by using TMPD solutions, as described above with R$_4$NNTf$_2$. The yield was $1.5 \times 10^{-7}$ mol J$^{-1}$, slightly lower than the yield in R$_4$NNTf$_2$.

The rate constants for oxidation of CIPz and Trolox by the CCl$_3$O$_2^-$ radicals were determined in oxygenated ionic liquid solutions containing 1% CCl$_4$. No significant oxidation was detected in these ionic liquids in the absence of CCl$_4$. In all cases examined the rate constants at room temperature (Table 4) are close to $10^7$ L mol$^{-1}$ s$^{-1}$. The rate constants were also measured at different temperatures to derive the activation energies (Table 4). The experimental data were then corrected for the effect of $k_{\text{diff}}$ to derive $k_{\text{act}}$. Arrhenius plots of $k_{\text{act}}$ are shown in Figure 5, and the results calculated from these plots are also summarized in Table 4.

Oxidation Rate Constants. The experimental rate constants for oxidation of CIPz by CCl$_3$O$_2^-$ radicals in the various ionic liquids (Table 4) are all within a factor of $2$ of $1 \times 10^7$ L mol$^{-1}$ s$^{-1}$. The diffusion-controlled rate constants estimated from the viscosities measured under the same conditions are about twice as high, as listed in Table 4, or possibly as much as three times as high (see footnote a in Table 1). The values of $k_{\text{act}}$, estimated from $k_{\text{exp}}$ and $k_{\text{diff}}$, are higher than $k_{\text{exp}}$ by a factor of $1.5$ to $2$ and remain close to $1 \times 10^7$ L mol$^{-1}$ s$^{-1}$. These values are clearly lower than the rate constant measured for this reaction in water$^{27,28}$ and close to the values measured in alcohols.$^{28}$ On the other hand, the activation energies are closer to those measured in aqueous solutions and higher than those in alcohols (Table 4). On this basis, we cannot equate the solvent effect of the ionic liquids on reaction 18 with that of either alcohols or water. Furthermore, if we compare the rate constants for reaction 18 in the different solvents not on an absolute basis but as a fraction of the diffusion-controlled limit, we find that this reaction is approximately 0.5 in the ionic liquids, approximately 0.2 in water, and only approximately 0.01 in 2-ProH (Table 4) and other less polar organic solvents.$^{28}$ This comparison indicates that the correction of $k_{\text{exp}}$ to derive $k_{\text{act}}$ is small for water and negligible for alcohols but very large for the ionic liquids, where $k_{\text{exp}}$ and $k_{\text{diff}}$ are close. As a result, the calculated values of $k_{\text{act}}$ in the ionic liquids are extremely sensitive to the exact value of $k_{\text{diff}}$. The above comparison shows, however, that encounters between reactants in water and ionic liquids are much more likely to result in reaction than encounters in alcohols and nonpolar organic solvents. Possibly, encounters in ionic liquids take place in more organized microenvironments, where the reactants remain in the same domain for longer periods and have a higher probability of reacting. The reactions of CCl$_3$O$_2^-$ radicals have been suggested to involve an electron transfer and a proton transfer occurring in concert,$^{29}$ so that the insipient CCl$_3$O$_2^-$ radical is immediately converted to the more stable CCl$_4$O$_2^-$. If the proton is supplied from the ammonium tail of CIPz (or from the phenolic OH of Trolox), lengthening the time of encounter between the reactants will also increase the probability for the proton transfer.

The rate constants for oxidation of Trolox in the ionic liquids (Table 4) are slightly lower than those for oxidation of CIPz, as noted before for the same reactions in other solvents.$^{27,28}$ This is due to the fact that Trolox is a neutral phenol and only the deprotonated form undergoes rapid oxidation. Therefore, the solvent effect on reaction with Trolox includes as an additional parameter the ability of the solvent to remove a proton from Trolox. This point was discussed in detail previously.$^{28}$
Summary and Conclusions

Pulse radiolysis of ionic liquids (BMIPF$_6$, BMIBF$_4$, BuPicPF$_6$, BuPyBF$_4$, and R$_n$NNTf$_2$) permits production of a variety of radicals and measurement of absolute rate constants for reduction and oxidation of various molecules. The experimental rate constants for oxidation of CIPz and Trolox by CC$_1$O$_2^+$ radicals in the ionic liquids (Table 4) are much lower than rate constants for the same reactions in aqueous solutions and closer to rate constants measured in alcohols. This comparison suggests that the ionic liquids do not behave as highly polar solvents. However, from comparison of the experimental rate constants with the diffusion-controlled limits estimated from the viscosities of the solvents, it is concluded that encounters between reactants in ionic liquids are more fruitful than encounters in water and much more than those in nonpolar solvents.

Solvated electrons that are radiolytically produced in R$_n$NNTf$_2$ do not react rapidly with the solvent and can react with solutes. Thus it was possible to reduce benzophenone to its ketyl radical and to determine the rate constant for electron transfer from this radical to duroquinone. Although the experimental rate constant is relatively low, it is close to the diffusion-controlled limit in this solvent. The rate constants for the same reaction in water and in glycerol are also close to the respective diffusion-controlled limits, but the value is much lower in 2-PrOH. In contrast with R$_n$NNTf$_2$, solvated electrons produced in imidazolium or pyridinium ionic liquids are rapidly scavenged by the solvent cations. In the case of BMI$^+$ the electrons are completely trapped, as discussed before, but with BuPy$^+$ and BuPic$^+$ it is possible to follow the electron transfer from the solvent radicals to various solutes. Surprisingly, several such reductions occur with rate constant that are significantly higher than the diffusion-controlled limit, unlike the rate constants for the same reactions in water and 2-PrOH, which are slower than the diffusion-controlled limit. This very fast reaction is interpreted as an electron hopping mechanism, where the electron reaches its final destination via intervening pyridinium groups without requiring the diffusion of a specific radical to approach a reactant molecule.

Ionic liquids also affect the reduction potentials of certain species, e.g., by preferential solvation of the reduced or oxidized species as compared with the solvation of these species in other solvents. It has been demonstrated that the equilibrium between the MV$^{2+}$/MV$^{4+}$ couple and the AQ$^+$/AQ$^{2-}$ couple reverses direction upon going from water to 2-PrOH.$^{23}$ We confirm these findings and show that the equilibrium between the MV$^{2+}$/MV$^{4+}$ couple and the DQ/DQ$^-$ couple also reverses direction upon going from water to 2-PrOH. In all cases the electron transfer rate constants are fairly high. On the other hand, these electron transfer reactions are much slower in BuPyBF$_4$ and the direction of the equilibrium is the same as in 2-PrOH and opposite that in water. The slowness of the electron transfer is partly due to the high viscosity and partly due to a lower driving force for the reaction, leading to a very large solvent effect on the rate constant. The change in driving force, i.e., the shift in equilibrium 16 and 17, appears to be due to enhanced solubility of species with fewer positive or negative charges. This may be taken as another indication that this ionic liquid is highly associated, thus solubilizing neutral species better than ionic species. The effect of the microenvironment on the reduction potentials of the reactants is demonstrated by the finding that addition of small amounts of water to the ionic liquid has a very large effect on the electron transfer rate constant.

References and Notes

(3) The mention of commercial equipment or material does not imply recognition or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified are necessarily the best available for the purpose.
(7) Radiolysis of water produces hydrated electrons along with hydroxyl radicals and small amounts of hydrogen atoms. The alcohol serves as a scavenger for the OH radicals and permits observation of the reaction of the hydrated electrons with other solutes. The use of high pH is for preventing the reaction of hydrated electrons with protons that are also formed in the radiolysis.
(9) (CF$_3$SO$_2$)$_2$NH is a strong acid, with $pK_a$ = 1.7 (Foropoulous, J., Jr.; DesMarreau, D. I. Inorg. Chem. 1984, 33, 3720).
(19) In the aqueous TEOA solutions, when the concentration of p-NAP was reduced below 0.3 mmol L$^{-1}$, the kinetic traces indicated two formation steps. The slower step became more pronounced as the concentration of TEOA, (HOCH$\cdot$CH$_2$)$_2$NC$\cdot$NAP was decreased and its rate constant was estimated to be $4 \times 10^{-4}$ L mol$^{-1}$ s$^{-1}$. We interpret this observation by considering that two radicals can be from TEOA, (HOCH$_2$CH$_2$)$_2$NCH$_2$OH and (HOCH$_2$CH$_2$)$_2$NCH$_2$CHOH, both reducing p-NAP with very similar rate constants, but the second radical can undergo base-catalyzed elimination of (HOCH$_2$CH$_2$)$_2$NCH$_2$CHOH to yield CH$_3$CHO (Gilbert, B. C.; Larkin, J. P.; Norman, R. O. C. J. Phys. Chem., Perkin Trans. 2 1972, 794. Steenken, S. J. Phys. Chem. 1979, 83, 595) while the first radical cannot do so. As the concentration of p-NAP is decreased the rate of reduction is accordingly decreased, permitting a more substantial fraction of the second radicals to undergo elimination. This results in a decrease in the contribution of the fast step and an increase in the contribution of the slow step. Since CH$_3$CHO is not a reducing radical, the slow step probably involves reaction with p-NAP via addition, as do various other radicals (Jagannadham, V.; Steenken, S. J. Am. Chem. Soc. 1984, 106, 6642; 1988, 110, 2188).
(24) Calculated from thiocyanate dosimetry by correcting for the difference in electron density of the solutions and assuming that the molar absorption of TMPD$^+$ is $1.2 \times 10^4$ L mol$^{-1}$ cm$^{-1}$, similar to that determined in CCl$_4$ solutions by Burrows, H. D.; Greatorex, D.; Kemp, T. J. J. Phys. Chem. 1972, 76, 20.
(25) Calculated by assuming that the molar absorption coefficient of CIP$^+$ in MIBNTf$_2$ is similar to that in water (1.07 $\times 10^4$ L mol$^{-1}$ cm$^{-1}$); Pelizzetti, E.; Meisel, D.; Mulac, W. A.; Neta, P. J. Am. Chem. Soc. 1979, 101, 6954.