

# 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 ( $R_4NNTf_2$ ), *N*-butylpyridinium tetrafluoroborate ( $BuPyBF_4$ ), and *N*-butyl-4-methylpyridinium hexafluorophosphate ( $BuPicPF_6$ ) leads to formation of solvated electrons and organic radicals. In  $R_4NNTf_2$  the solvated electrons do not react rapidly with the solvent and were reacted with several solutes, including  $CCl_4$ , 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  $R_4NNTf_2$  ( $k = 2 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ ) is much lower than that measured in water ( $k = 2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ) due to the high viscosity of the ionic liquid. Rate constants for electron transfer from the solvent-derived butylpyridinyl radicals in  $BuPyBF_4$  and  $BuPicPF_6$  to several compounds ( $k$  of the order of  $10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ ) 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  $BuPyBF_4$  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  $CCl_4$  and  $O_2$  leads to formation of  $CCl_3O_2^\bullet$  radicals, which oxidize chlorpromazine (CIPz) with rate constants near  $1 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ , 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.<sup>1</sup> Recently we have compared reaction rate constants in ionic liquids with those in other solvents by studying the reactions of  $CCl_3O_2^\bullet$  radicals with chlorpromazine and Trolox in 1-butyl-3-methylimidazolium hexafluorophosphate ( $BMIPF_6$ ) and tetrafluoroborate ( $BMIBF_4$ ).<sup>2</sup> 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  $BMIPF_6$  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  $BMIPF_6$  because  $BMI^+$  reacts very rapidly with solvated electrons and the  $BMI^\bullet$  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  $e_{\text{sol}}^-$ , 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  $e_{\text{aq}}^-$ , and is a salt of the asymmetric cation ( $n\text{-C}_4\text{H}_9$ )<sub>3</sub>N(CH<sub>3</sub>)<sup>+</sup> and the anion ( $CF_3SO_2$ )<sub>2</sub>N<sup>-</sup> (abbreviated as  $R_4NNTf_2$ ). The second type is based on the *N*-alkylpyridinium cation, which is known to react with  $e_{\text{aq}}^-$  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  $PF_6^-$  and  $BF_4^-$  as the anions. Rate constants were measured in these ionic liquids for several oxidation and reduction reactions.

## Experimental Section<sup>3</sup>

Methyltributylammonium bis(trifluoromethylsulfonyl)imide ( $R_4NNTf_2$ ) was prepared by reacting equimolar amounts of methyltributylammonium chloride ( $MeBu_3N^+Cl^-$ ) with lithium bis(trifluoromethylsulfonyl)imide ( $(CF_3SO_2)_2N^-Li^+$ ) in aqueous

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 (Biotech grade, purity >99.9%, packaged under N<sub>2</sub>) 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 tetrafluoroborate (BuPyBF<sub>4</sub>) ionic liquid was prepared by mixing 1 equiv of *N*-butylpyridinium chloride with 1.5 equiv of NH<sub>4</sub>BF<sub>4</sub> in acetonitrile. The compounds are not soluble, but after mixing for 5 days most of the NH<sub>4</sub>Cl 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 neutral alumina to remove opacity due to remaining NH<sub>4</sub>Cl 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 N<sub>2</sub>) 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 PF<sub>6</sub> 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 KPF<sub>6</sub>, each dissolved in water. The organic PF<sub>6</sub> 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 (AQS<sup>-</sup>), methyl viologen (MV<sup>2+</sup>, 1,1'-dimethyl-4,4'-bipyridinium dichloride), *p*-nitroacetophenone (*p*-NAP), *p*-nitrobenzoic acid (*p*-NBA), chlorpromazine (CIPz, 2-chloro-10-(3-dimethylaminopropyl)phenothiazine), N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD), and Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid, a Vitamin E analogue). These compounds, the starting materials for the syntheses, and the various solvents and additives were of the purest grade available from Aldrich, Baker, or Mallinckrodt. Water was purified with a Millipore Super-Q system.

Reaction kinetics in ionic liquids were determined by pulse radiolysis. Experiments were carried out with (0.1 to 1.5) μs pulses of 6 MeV electrons from a Varian linear accelerator; other details were as described before.<sup>4</sup> The dose per pulse was determined by thiocyanate dosimetry.<sup>5</sup> Unless stated otherwise, the measurements were performed at room temperature, (22 ± 2) °C. Rate constants and molar absorption coefficients are reported with their estimated standard uncertainties.

Viscosity measurements at different temperatures were carried out in steady shear between 50 mm diameter parallel plates using a Rheometric Scientific, Inc. ARES rheometer. Tests were performed at shear rates between 0.1 and 10 s<sup>-1</sup> (referenced to the outer radius of the plates), and none of the fluids tested showed any signs of non-Newtonian behavior. Small gaps of 0.7 mm or less were used to minimize the sample size and the rate of rotation needed to achieve higher shear rates. The change in the gap with thermal expansion has been measured to be

(1.75 ± 0.10) μm K<sup>-1</sup>, and a correction has been applied to the data taken above room temperature to account for this change in the test geometry. The reported viscosity is the mean of 3–10 values determined at different shear rates, and the relative standard uncertainty of the mean viscosity was less than 5%, except for BuPyBF<sub>4</sub> with added water. For those fluids, the viscosity decreases rapidly with added water, and the relative standard uncertainty of the mean viscosity increased from 2% to 10% with increasing water volume fraction. Measurements were carried out with neat ionic liquids and after addition of 1% CCl<sub>4</sub>, 1% TEA, or other major additives as used in the kinetic measurements. The liquids were equilibrated with air in the rheometer.

## Results and Discussion

In general, radiolysis of a liquid leads initially to production of solvated electrons and solvent radical cations. The solvated electrons may react with the solvent and, if this reaction is slow, they may react with solutes. The radical cations may oxidize solutes or may undergo deprotonation or fragmentation and the products then react with solutes differently. Geminate recombination of the solvated electrons and radical cations can produce excited species, which may undergo fragmentation to form radicals. Despite this complexity it is often possible to observe clean reduction or oxidation reactions in many solvents due to rapid conversion of primary species and selective reactions. Some of the mechanisms may be predicted on the basis of reaction rates in other solvents. For the ionic liquids under study, it is known that the BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> anions and tetrabutylammonium cations do not react with solvated electrons, whereas the pyridine ring is quite reactive.<sup>6</sup> In the next section we discuss the radiolysis of each ionic liquid more specifically.

**Radiolysis of the Neat Ionic Liquids.** *R<sub>4</sub>NNTf<sub>2</sub>*. Radiolysis of neat R<sub>4</sub>NNTf<sub>2</sub> leads to production of solvated electrons, protons, radical cations, and neutral radicals.



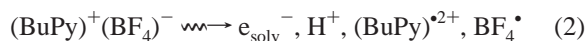
The solvated electrons do not react with R<sub>4</sub>N<sup>+</sup>.<sup>6</sup> Their reactivity with NTf<sub>2</sub><sup>-</sup> is unknown and was, therefore, examined in aqueous solutions. We found no effect of up to 27 mmol L<sup>-1</sup> LiN(SO<sub>2</sub>-CF<sub>3</sub>)<sub>2</sub> on the lifetime of e<sub>aq</sub><sup>-</sup> in deoxygenated aqueous alcohol solutions at pH 10.1,<sup>7</sup> from which we estimate an upper limit for the rate constant of NTf<sub>2</sub><sup>-</sup> with e<sub>aq</sub><sup>-</sup> of *k* < 1 × 10<sup>6</sup> L mol<sup>-1</sup> s<sup>-1</sup>. 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<sup>•</sup> atoms and •OH radicals are very slow for (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> but the rate constant increases with chain length<sup>8</sup> and it appears that only the hydrogens at the α-position are highly deactivated by the N<sup>+</sup> site. The rate constant for reaction of •OH radicals with (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup> was reported to be very high, 5 × 10<sup>9</sup> L mol<sup>-1</sup> s<sup>-1</sup>.<sup>8</sup> Therefore, R<sub>4</sub>N<sup>•2+</sup> 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 (•C<sub>4</sub>H<sub>8</sub>NR<sub>3</sub><sup>+</sup>). 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 N<sub>2</sub>O-saturated aqueous solutions at pH 7

and detected a transient species with a weak absorption at 330 nm ( $\epsilon = 450 \text{ L mol}^{-1} \text{ cm}^{-1}$ , assuming  $G = 0.58 \mu\text{mol J}^{-1}$ ) 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  $\text{NTf}_2\cdot$ .<sup>9</sup> This product may have a finite lifetime and may react by accepting an electron or a hydrogen atom.<sup>10</sup> In addition, fragmentation of excited states may form  $\cdot\text{CF}_3$  or  $\text{CF}_3\text{SO}_2\cdot$  fragments. The various fragments formed from the anion and the cation are represented by  $\text{R}\cdot$  in reaction 1. Most of these radicals are neither oxidants nor reductants but some of them can react with  $\text{O}_2$  to form oxidizing peroxy radicals.

Pulse radiolysis of neat  $\text{R}_4\text{NNTf}_2$  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  $\text{R}_4\text{NNTf}_2$  are discussed in later sections.

**BuPyBF<sub>4</sub> and BuPicPF<sub>6</sub>.** Radiolysis of *N*-butylpyridinium tetrafluoroborate ( $\text{BuPyBF}_4$ ) and *N*-butyl-4-methylpyridinium hexafluorophosphate ( $\text{BuPicPF}_6$ ) leads to production of solvated electrons, protons, radical cations, and neutral radicals, e.g.,



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



The most likely product is the benzylic radical, although other isomers cannot be ruled out. Such radicals are not oxidants but can react with  $\text{O}_2$  to form oxidizing peroxy radicals.



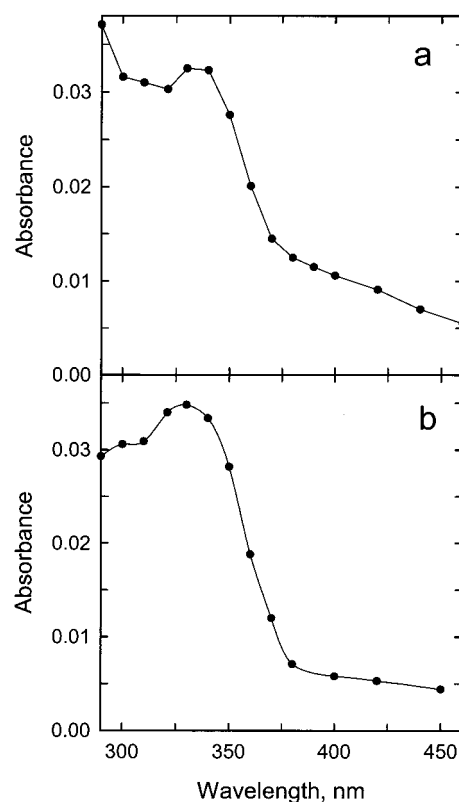
The solvated electrons formed in reaction 2 react very rapidly with the pyridinium cation to form the neutral butylpyridinyl radical.



We measured the rate constant for this reaction in deoxygenated aqueous solutions containing  $0.2 \text{ mol L}^{-1} \text{ MeOH}$  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.<sup>6</sup> The spectrum of the *N*-butylpyridinyl radical,  $\text{BuPy}\cdot$ , was recorded by pulse radiolysis of a deoxygenated aqueous solution containing  $0.1 \text{ mol L}^{-1} t\text{-BuOH}$  and shows a weak absorption at 340 nm ( $\epsilon = 850 \text{ L mol}^{-1} \text{ cm}^{-1}$ , assuming  $G = 0.29 \mu\text{mol J}^{-1}$ ) (Figure 1a). The spectrum recorded upon irradiation of neat  $\text{BuPyBF}_4$  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.

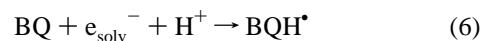
**Radiolytic Reduction in the Ionic Liquids.** In this section we discuss the radiolytic reduction of quinones, benzophenone, methyl viologen, and nitroaromatic compounds in various ionic liquids, the electron transfer from the benzophenone ketyl radicals to duroquinone, and the electron transfer between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

**Reduction Reactions in  $\text{R}_4\text{NNTf}_2$ .** Irradiation of deoxygenated  $\text{R}_4\text{NNTf}_2$  containing BQ or DQ ( $\approx 6 \text{ mmol L}^{-1}$ ) led to reduction

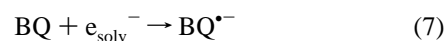


**Figure 1.** Transient absorption spectra monitored by pulse radiolysis of (a) deoxygenated aqueous solution containing  $0.1 \text{ mol L}^{-1} t\text{-BuOH}$  and  $1 \text{ mmol L}^{-1} \text{ BuPyBF}_4$ , recorded  $5 \mu\text{s}$  after the pulse, and (b) deoxygenated neat  $\text{BuPyBF}_4$ , recorded  $10 \mu\text{s}$  after the pulse.

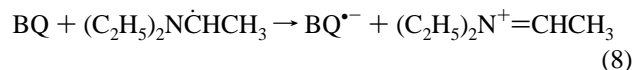
of these compounds by solvated electrons and by organic radicals derived from the solvent. From the absorption maxima of the radicals produced ( $\approx 410$  and  $420 \text{ nm}$ , respectively) we conclude that the semiquinone radicals were protonated under these conditions,<sup>11</sup> the proton being produced by the radiolysis (reaction 1).



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



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.  $\text{BQ}^{\cdot -}$  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  $20 \mu\text{s}$  ( $k \approx 1 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ ). The fast step is due to reaction 7 as well as reaction 8 of BQ with the reducing radical derived from TEA.



Both reactions 7 and 8 are known to have very high rate constants in aqueous solutions ( $k > 3 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ).<sup>6,12</sup> 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.<sup>13</sup>



A slightly different pattern was observed in the reduction of duroquinone. The  $\text{DQ}^{\bullet-}$  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 ( $k < 2 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ ) 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 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<sup>-1</sup>) in deoxygenated  $\text{R}_4\text{NNTf}_2$  solutions containing TEA produced initially the radical anion  $\text{BP}^{\bullet-}$ , which has an absorption peak in water at 610 nm<sup>14,15</sup> and in the ionic liquid at  $\approx 700 \text{ nm}$ . This species was converted within 10  $\mu\text{s}$  into  $\text{BPH}^{\bullet}$ , which has an absorption peak at 545 nm both in water<sup>14,15</sup> 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  $\text{BP}^{\bullet-}$  undergoes protonation under these conditions while  $\text{BQ}^{\bullet-}$  and  $\text{DQ}^{\bullet-}$  are not protonated is in line with the higher  $\text{p}K_{\text{a}}$  value in aqueous solution of  $\text{BPH}^{\bullet}$  (9.2)<sup>14,15</sup> as compared with those of the semiquinones (reactions 4 and 5).<sup>11</sup> From the measured absorbance of  $\text{BPH}^{\bullet}$  at 545 nm we can estimate the yield of solvated electrons in this ionic liquid by assuming that the molar absorption coefficient of  $\text{BPH}^{\bullet}$  in  $\text{R}_4\text{NNTf}_2$  is similar to that in aqueous solutions ( $5.5 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ).<sup>15</sup> By using thiocyanate dosimetry and correcting for the difference in electron density between the aqueous thiocyanate 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  $0.9 \times 10^{-7} \text{ mol J}^{-1}$  and approximately twice as high as that in the presence of TEA.

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

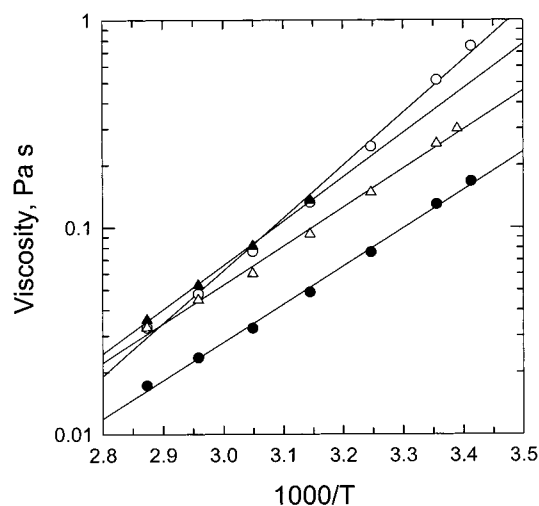


The rate constant was determined at room temperature by following the formation of  $\text{DQ}^{\bullet-}$  at 445 nm and found to be  $(2.0 \pm 0.3) \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ . Similar measurements were carried out in alcohol and aqueous solutions for comparison (Table 1). The rate constant determined in 2-PrOH solutions containing similar concentrations of TEA, BP, and DQ was  $(1.7 \pm 0.2) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$  and the rate constant in aqueous solutions, containing 25% 2-PrOH to permit sufficient solubility, was  $(2.2 \pm 0.3) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ . 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,  $(4 \pm 1) \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ .

**TABLE 1: Rate Constant for Reduction of DQ by  $\text{BPH}^{\bullet}$  (Reaction 11) in Various Solvents at Room Temperature**

solvent	$k_{\text{exp}}, \text{L mol}^{-1} \text{ s}^{-1}$	$k_{\text{diff}},^a \text{L mol}^{-1} \text{ s}^{-1}$
$\text{R}_4\text{NNTf}_2$	$(2.0 \pm 0.3) \times 10^7$	$1.5 \times 10^7$
2-PrOH	$(1.7 \pm 0.2) \times 10^8$	$\sim 3 \times 10^9$
$\text{H}_2\text{O}/2\text{-PrOH}$ (3/1)	$(2.0 \pm 0.4) \times 10^9$	$\sim 3 \times 10^9$ <sup>b</sup>
glycerol	$(4 \pm 1) \times 10^6$	$\sim 5 \times 10^6$

<sup>a</sup> 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).  
<sup>b</sup> This value was estimated by taking the viscosity of water with 25 v % 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).



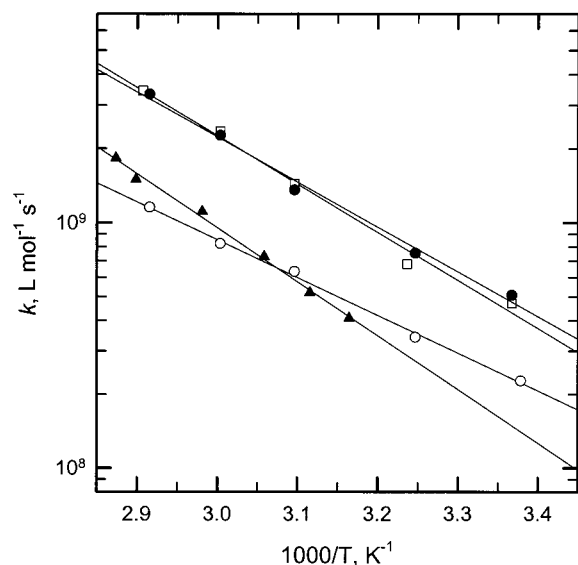
**Figure 2.** Viscosities of the neat ionic liquids at different temperatures (between 20 °C and 75 °C), shown as Arrhenius plots, for  $\text{R}_4\text{NNTf}_2$  (○),  $\text{BuPyBF}_4$  (●),  $\text{BuPicPF}_6$  (△). Sample numerical values (in Pa s) are:  $\text{R}_4\text{NNTf}_2$ : 0.75 at 20 °C, 0.52 at 25 °C.  $\text{BuPyBF}_4$ : 0.17 at 20 °C, 0.13 at 25 °C.  $\text{BuPicPF}_6$ : 0.14 at 45 °C.

These measured values should be compared to the diffusion-controlled rate constants, which can be estimated from the viscosities.

The viscosity of the neat ionic liquid was determined at various temperatures and the results are presented in the form of an Arrhenius plot (Figure 2). From the viscosity we can estimate the diffusion-controlled rate constant ( $k_{\text{diff}}$ ) by using the approximation,<sup>16</sup>

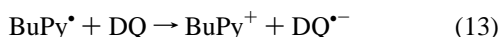
$$k_{\text{diff}} = 8000RT/3\eta \quad (12)$$

where  $R$  is the gas constant ( $8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $T$  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  $\text{R}_4\text{NNTf}_2$  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  $\sim 20$  times lower than  $k_{\text{diff}}$ . This comparison suggests that  $\text{R}_4\text{NNTf}_2$  behaves in this case as a polar solvent, which facilitates electron transfer, similar to water or glycerol and more polar than 2-PrOH.



**Figure 3.** Arrhenius plots for the rate constants for reduction by the pyridinyl radicals in the ionic liquids. In BuPyBF<sub>4</sub>: BuPy<sup>•</sup> + DQ (●), BuPy<sup>•</sup> + MV<sup>2+</sup> (○), BuPy<sup>•</sup> + *p*-NBA (□). In BuPicPF<sub>6</sub>: BuPic<sup>•</sup> + DQ (▲).

*Reduction Reactions in BuPicPF<sub>6</sub> and BuPyBF<sub>4</sub>.* 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  $k < 1 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$  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<sub>4</sub>NNTf<sub>2</sub>. We measured, however, the rate constants for reduction of various compounds by the butylpyridinyl radical (e.g., reaction 13).



Rate constants were measured for the reduction of duroquinone, methyl viologen, *p*-nitrobenzoic acid, and *p*-nitroacetophenone by the butylpyridinyl radical in these ionic liquids. Since the absorption of BuPy<sup>•</sup> 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,<sup>11</sup> 400 and 605 nm for MV<sup>2+</sup>,<sup>17</sup> 330 nm for *p*-NBA,<sup>18</sup> and 370 nm for *p*-NAP.<sup>14</sup> For each reactant, rate constants were measured at several concentrations and several temperatures, between 22 and 75 °C. Reactions in BuPicPF<sub>6</sub> 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<sup>•</sup> can reach the organic substrate without the need for complete diffusion of a specific BuPy<sup>•</sup> 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<sub>4</sub><sup>-</sup> 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<sup>-1</sup> for BuPicPF<sub>6</sub> and 37.6 kJ mol<sup>-1</sup> for BuPyBF<sub>4</sub>. 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<sup>2+</sup> is slightly lower due to its solvation with anions as discussed above.

The radiolytic yield for production of MV<sup>•+</sup> was determined by measuring the absorbance of this radical at 605 nm in deoxygenated BuPyBF<sub>4</sub> solutions containing 0.8 mmol L<sup>-1</sup> MV<sup>2+</sup> and using aqueous thiocyanate dosimetry.<sup>5</sup> By assuming that the molar absorption coefficient of MV<sup>•+</sup> in BuPyBF<sub>4</sub> is similar to that in water ( $1.3 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ )<sup>17</sup> and correcting for the differences in electron densities between water and BuPyBF<sub>4</sub> (668/556) we find  $G(\text{MV}^{\bullet+}) = (1.8 \pm 0.2) \times 10^{-7} \text{ mol J}^{-1}$ . The radiolytic yield in BuPyBF<sub>4</sub> 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<sup>•-</sup> in aqueous solutions was reported to be 17600 L mol<sup>-1</sup> cm<sup>-1</sup> at 350 nm and 2900 L mol<sup>-1</sup> cm<sup>-1</sup> at 545 nm.<sup>14</sup> We monitored the absorbance at 545 nm to avoid interference by the absorbance of the solvent radicals. To ascertain that *p*-NAP<sup>•-</sup> does not undergo protonation to form *p*-NAPH<sup>•</sup>, which has lower absorbance, we added TEOA as a base. From the absorbance at 545 nm observed with deoxygenated BuPyBF<sub>4</sub> containing 0.06 mol L<sup>-1</sup> TEOA and 0.6 mmol L<sup>-1</sup> *p*-NAP, we estimate the total yield of radicals  $G = (4.8 \pm 0.5) \times 10^{-7} \text{ mol J}^{-1}$ . This value is much higher than that determined with MV<sup>2+</sup> 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<sup>•</sup> and by the radicals derived from TEOA.



**TABLE 2: Rate Constants for Reduction Reactions in Various Solvents**

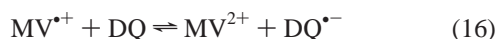
reaction	solvent	<i>T</i> , °C	<i>k</i> <sub>exp</sub> , L mol <sup>-1</sup> s <sup>-1</sup>	<i>E</i> <sub>a</sub> , <sup>a</sup> kJ mol <sup>-1</sup>	log <i>A</i>	<i>k</i> <sub>diff</sub> , <sup>b</sup> L mol <sup>-1</sup> s <sup>-1</sup>
BuPic <sup>•</sup> + DQ	BuPicPF <sub>6</sub>	43	(4.1 ± 0.6) × 10 <sup>8</sup>	42	15.6	5 × 10 <sup>7</sup>
BuPy <sup>•</sup> + DQ	BuPyBF <sub>4</sub>	24	(4.4 ± 0.7) × 10 <sup>8</sup>	34.9	14.8	5 × 10 <sup>7</sup>
BuPy <sup>•</sup> + MV <sup>2+</sup>	BuPyBF <sub>4</sub>	23	(2.3 ± 0.7) × 10 <sup>8</sup>	29.5	13.6	5 × 10 <sup>7</sup>
BuPy <sup>•</sup> + <i>p</i> -NBA <sup>c</sup>	BuPyBF <sub>4</sub>	24	(4.7 ± 0.8) × 10 <sup>8</sup>	39.8	15.6	5 × 10 <sup>7</sup>
BuPic <sup>•</sup> + DQ	2-PrOH <sup>d</sup>	22	(1.3 ± 0.3) × 10 <sup>9</sup>			3 × 10 <sup>9</sup>
BuPic <sup>•</sup> + DQ	H <sub>2</sub> O <sup>e</sup>	22	(3.3 ± 0.5) × 10 <sup>9</sup>			7 × 10 <sup>9</sup>
BuPy <sup>•</sup> + DQ	H <sub>2</sub> O <sup>e</sup>	22	(3.1 ± 0.5) × 10 <sup>9</sup>			7 × 10 <sup>9</sup>
BuPy <sup>•</sup> + MV <sup>2+</sup>	H <sub>2</sub> O <sup>f</sup>	22	(4.0 ± 0.5) × 10 <sup>9</sup>			7 × 10 <sup>9</sup>
BuPy <sup>•</sup> + <i>p</i> -NBA <sup>c</sup>	H <sub>2</sub> O <sup>e</sup>	22	(5.4 ± 0.8) × 10 <sup>9</sup>			7 × 10 <sup>9</sup>

<sup>a</sup> Activation energies have been determined with an overall estimated standard uncertainties of less than ±10%. <sup>b</sup> See footnote a in Table 1. <sup>c</sup> The rate constant in the ionic liquid was determined with *p*-nitrobenzoic acid but in water with *p*-nitrobenzoate anion since the acid is insoluble in water. <sup>d</sup> 1% TEA was added as a base to prevent protonation of DQ<sup>•-</sup> into DQH<sup>•</sup>. <sup>e</sup> 0.2 mol L<sup>-1</sup> *t*-BuOH was added as an OH radical scavenger. <sup>f</sup> 1 mol L<sup>-1</sup> *t*-BuOH was added as an OH radical scavenger.

The observed formation of *p*-NAP<sup>•-</sup>, however, appeared to take place in one step, with a rate constant of (2.2 ± 0.4) × 10<sup>8</sup> L mol<sup>-1</sup> s<sup>-1</sup>.

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<sup>•</sup> radical in deoxygenated aqueous solutions containing 0.2 mol L<sup>-1</sup> *t*-BuOH, 11 mmol L<sup>-1</sup> BuPyBF<sub>4</sub>, 5 mmol L<sup>-1</sup> phosphate buffer at pH 7, and between 0.07 and 0.2 mmol L<sup>-1</sup> *p*-NAP, but no TEOA, was determined to be *k*<sub>14</sub> = (6.2 ± 0.9) × 10<sup>9</sup> L mol<sup>-1</sup> s<sup>-1</sup>. In the absence of *t*-BuOH but with 0.07 mol L<sup>-1</sup> TEOA in N<sub>2</sub>O-saturated aqueous solutions (to convert e<sub>aq</sub><sup>-</sup> 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*<sub>15</sub> = (3.2 ± 0.6) × 10<sup>9</sup> L mol<sup>-1</sup> s<sup>-1</sup>, i.e., about half the value of *k*<sub>14</sub>.<sup>19</sup> 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 butylpyridinyl 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 BuPyBF<sub>4</sub> solutions containing MV<sup>2+</sup> (0.7 to 4 mmol L<sup>-1</sup>) and duroquinone (0.05 to 5 mmol L<sup>-1</sup>).

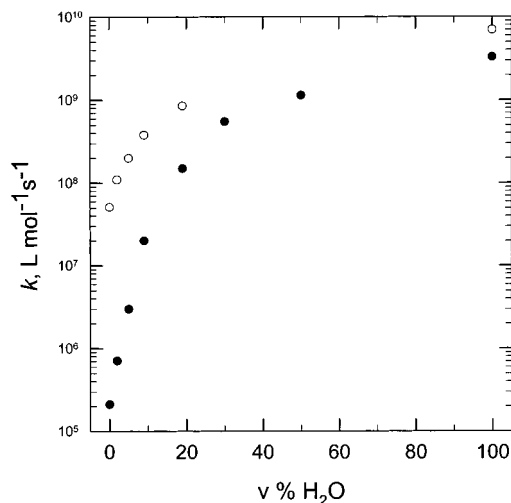


From the rate of decay of the MV<sup>•+</sup> absorption at 400 nm as a function of DQ concentration we derive *k*<sub>16</sub> = (1.4 ± 0.2) × 10<sup>5</sup> L mol<sup>-1</sup> s<sup>-1</sup>. This rate constant is 2 orders of magnitude lower than *k*<sub>diff</sub>, unlike the rate constant for reaction 13, which was an order of magnitude higher than *k*<sub>diff</sub>. For comparison, we also determined the rate constant for reaction 16 in aqueous solutions containing 10% 2-PrOH and found *k*<sub>16</sub> = (3.3 ± 0.5) × 10<sup>9</sup> L mol<sup>-1</sup> s<sup>-1</sup>, i.e., *k*<sub>16</sub> is 4 orders of magnitude lower in the ionic liquid than in water. We then measured *k*<sub>16</sub> in several BuPyBF<sub>4</sub>/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). From comparing with the values of *k*<sub>diff</sub> estimated from the viscosities (Figure 4), it is seen that in predominantly aqueous solutions the experimental *k*<sub>16</sub> is about 50% of *k*<sub>diff</sub> but as the fraction of ionic liquid approaches 1 the value of *k*<sub>16</sub> decreases below 1% of *k*<sub>diff</sub>. This comparison suggests that additional factors contribute to the decrease in *k*<sub>16</sub>, most likely a change in the equilibrium constant *K*<sub>16</sub> due to the change in the nature of the solvent. It is known that the reduction potential of MV<sup>2+</sup> is considerably more positive in alcohol solutions than in water,<sup>20</sup> while the reduction potentials of quinones are more negative in alcohols.<sup>21</sup> It is also known that in aqueous solutions

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

reaction	solvent	<i>T</i> , °C	<i>k</i> <sub>exp</sub> , L mol <sup>-1</sup> s <sup>-1</sup>
MV <sup>•+</sup> + DQ	BuPyBF <sub>4</sub>	25	(1.4 ± 0.3) × 10 <sup>5</sup>
MV <sup>•+</sup> + DQ	BuPyBF <sub>4</sub> , 2 v % H <sub>2</sub> O	25	(7.1 ± 1.1) × 10 <sup>5</sup>
MV <sup>•+</sup> + DQ	BuPyBF <sub>4</sub> , 5 v % H <sub>2</sub> O	25	(3.0 ± 0.5) × 10 <sup>6</sup>
MV <sup>•+</sup> + DQ	BuPyBF <sub>4</sub> , 9 v % H <sub>2</sub> O	25	(2.0 ± 0.3) × 10 <sup>7</sup>
MV <sup>•+</sup> + DQ	BuPyBF <sub>4</sub> , 19 v % H <sub>2</sub> O	25	(1.5 ± 0.3) × 10 <sup>8</sup>
MV <sup>•+</sup> + DQ	BuPyBF <sub>4</sub> , 30 v % H <sub>2</sub> O	25	(5.5 ± 0.8) × 10 <sup>8</sup>
MV <sup>•+</sup> + DQ	BuPyBF <sub>4</sub> , 50 v % H <sub>2</sub> O	25	(1.1 ± 0.1) × 10 <sup>9</sup>
MV <sup>•+</sup> + DQ	H <sub>2</sub> O, 10 v % 2-PrOH	25	(3.3 ± 0.5) × 10 <sup>9</sup>
DQ <sup>•-</sup> + MV <sup>2+</sup>	2-PrOH, 5 v % TEOA	25	(1.7 ± 0.4) × 10 <sup>9</sup>
AQS <sup>2-</sup> + MV <sup>2+</sup>	BuPyBF <sub>4</sub> , 2 v % H <sub>2</sub> O <sup>a</sup>	22	(4.0 ± 0.8) × 10 <sup>6</sup>
MV <sup>•+</sup> + AQS <sup>-</sup>	H <sub>2</sub> O, 2 v % 2-PrOH <sup>b</sup>	22	(6.1 ± 0.9) × 10 <sup>9</sup>
AQS <sup>2-</sup> + MV <sup>2+</sup>	2-PrOH, 15 v % water <sup>a</sup>	22	(1.5 ± 0.3) × 10 <sup>9</sup>

<sup>a</sup> A small amount of water was necessary to permit sufficient dissolution of AQS<sup>-</sup>. <sup>b</sup> 2-PrOH was used as a scavenger for H<sup>•</sup> and •OH radicals; the solution was neutral, unbuffered.

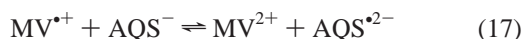


**Figure 4.** Rate constant for electron transfer from MV<sup>•+</sup> to DQ measured in different BuPyBF<sub>4</sub>/water mixtures (●) and the corresponding values of *k*<sub>diff</sub> (○) estimated from the measured viscosities by using eq 12.

reaction 16 has a driving force of about -0.21 V,<sup>22</sup> but in 2-PrOH the reaction is driven in the opposite direction.<sup>23</sup> To confirm this trend we followed reaction 16 in 2-PrOH solutions, and indeed, we found it to proceed to the left, with *k*<sub>-16</sub> = (1.7 ± 0.4) × 10<sup>9</sup> L mol<sup>-1</sup> s<sup>-1</sup> (Table 3). We also attempted to determine the equilibrium constant for reaction 16 in 2-PrOH but could only estimate *K* > 10<sup>4</sup> at the most extreme concentration ratio that was experimentally practical. Thus the driving force for reaction 16 changes from -0.21 V in water to at least 0.2 V in 2-PrOH. Therefore, we suggest that the driving force in BuPyBF<sub>4</sub> is intermediate between these values and thus the

reaction occurs much more slowly. It is also possible that reaction 16 in neat BuPyBF<sub>4</sub> is near equilibrium and that it is pulled to the right due to protonation of DQ<sup>•-</sup>. Irradiation of the solution produces protons (reaction 2), which are not neutralized under these conditions and can react with DQ<sup>•-</sup> to form DQH<sup>•</sup>. Since DQH<sup>•</sup> has a shorter lifetime than DQ<sup>•-</sup> and cannot transfer an electron to MV<sup>2+</sup>, 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<sup>•-</sup> to MV<sup>2+</sup> was observed in the presence of pyridine, with a rate constant  $k_{-16} \approx 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ , and the decay of MV<sup>•+</sup> occurred much more slowly than in the absence of pyridine. Thus reaction 16 proceeds in BuPyBF<sub>4</sub> 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<sup>2+</sup> and AQS<sup>-</sup>.



In aqueous solutions reaction 17 proceeds to the right with  $k_{17} = (6.1 \pm 0.9) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  while in 2-PrOH the direction is reversed<sup>23</sup> and  $k_{-17} = (1.5 \pm 0.3) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  (Table 3). In BuPyBF<sub>4</sub> the reaction proceeds to the left as in 2-PrOH, with  $k_{-17} = (4.0 \pm 0.8) \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$  (Table 3). Upon addition of 2 v% pyridine, to minimize the extent of protonation of AQS<sup>•2-</sup> to AQSH<sup>•-</sup>,  $k_{-17}$  increased to  $(2.7 \pm 0.5) \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ . These results clearly indicate the reversal of the driving force upon going from water to BuPyBF<sub>4</sub> 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  $\approx 3 \text{ mol L}^{-1}$  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<sub>3</sub>O<sub>2</sub><sup>•</sup> radicals produced in the presence of CCl<sub>4</sub>.

**Oxidation Reactions in R<sub>4</sub>NNTf<sub>2</sub>.** The radiolytic yield of oxidation in R<sub>4</sub>NNTf<sub>2</sub> 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<sub>4</sub>NNTf<sub>2</sub> containing 6 mmol L<sup>-1</sup> TMPD produced TMPD<sup>•+</sup> 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 μs after the pulse and an additional absorbance was formed within 100 μs, indicating the existence of at least two oxidizing species. The radiolytic yield of the fast oxidation step was  $1.1 \times 10^{-7} \text{ mol J}^{-1}$ , and the total yield was  $1.7 \times 10^{-7} \text{ mol J}^{-1}$ .<sup>24</sup> When a similar solution was irradiated under air, an additional formation step took place over 2 ms and the total yield increased to  $2.1 \times 10^{-7} \text{ mol J}^{-1}$ . 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<sup>•+</sup>, monitored at 525 nm, was very small, corresponding to only  $0.3 \times 10^{-7} \text{ mol J}^{-1}$ , and the

total yield of oxidation under air was only  $0.9 \times 10^{-7} \text{ mol J}^{-1}$ .<sup>25</sup> The different oxidation yields of these two compounds indicate that some radicals formed in this solvent can oxidize TMPD ( $E = 0.26 \text{ V vs NHE}$ )<sup>22</sup> but do not react rapidly with CIPz ( $E = 0.8 \text{ V}$ ).<sup>22</sup> Alkylperoxy 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<sub>2</sub>N<sup>•</sup>, 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<sub>3</sub>O<sub>2</sub><sup>•</sup> and R<sub>3</sub>N<sup>+</sup>CR<sub>2</sub>O<sub>2</sub><sup>•</sup>, are formed and these can oxidize CIPz.

Irradiation of various solvents containing CCl<sub>4</sub> and O<sub>2</sub> is known to produce CCl<sub>3</sub>O<sub>2</sub><sup>•</sup> radicals, which are strong oxidants. This is due to the fact that CCl<sub>4</sub> can form <sup>•</sup>CCl<sub>3</sub> radicals when it reacts with solvated electrons as well as with various organic radicals. Recently<sup>2</sup> we have studied the rate constant for oxidation of CIPz by CCl<sub>3</sub>O<sub>2</sub><sup>•</sup> radicals in another ionic liquid, BMIPF<sub>6</sub>.



In the present study we determined the rate constant for the same reaction in R<sub>4</sub>NNTf<sub>2</sub> by pulse radiolysis of oxygenated solutions containing 1% CCl<sub>4</sub> and various concentrations of CIPz. The rate of formation of CIPz<sup>•+</sup> was monitored at 525 nm as a function of CIPz concentration, and the value of  $k_{18}$  was derived from a linear plot of  $k_{\text{obs}}$  vs [CIPz]. However, unlike the earlier case of BMIPF<sub>6</sub>, where oxidation of CIPz took place to a significant extent only in the presence of CCl<sub>4</sub> and O<sub>2</sub>, in R<sub>4</sub>NNTf<sub>2</sub> there was oxidation of CIPz even in the absence of CCl<sub>4</sub>, as discussed above. Therefore, we measured the rate constant for oxidation of CIPz in oxygenated solutions of R<sub>4</sub>NNTf<sub>2</sub> both in the presence and absence of CCl<sub>4</sub>. The absorbance observed in the presence of CCl<sub>4</sub> was about twice as high as that observed in the absence of CCl<sub>4</sub>, 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<sup>26</sup> CF<sub>3</sub>O<sub>2</sub><sup>•</sup> and R<sub>3</sub>N<sup>+</sup>CH(R)O<sub>2</sub><sup>•</sup>. By assuming that the rate constant measured in the presence of CCl<sub>4</sub> ( $4.3 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ ) is the weighted average for the reactions with CCl<sub>3</sub>O<sub>2</sub><sup>•</sup> and with the other radicals (measured separately as  $3.7 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ ), we estimate that the rate constant for reaction 18 is  $5 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ .

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<sub>4</sub>. The activation energies are summarized in Table 4. The experimental rate constants ( $k_{\text{exp}}$ ) were then corrected for the effect of the diffusion-controlled limit ( $k_{\text{diff}}$ ) to derive the activation-controlled rate constants ( $k_{\text{act}}$ ).<sup>16</sup>

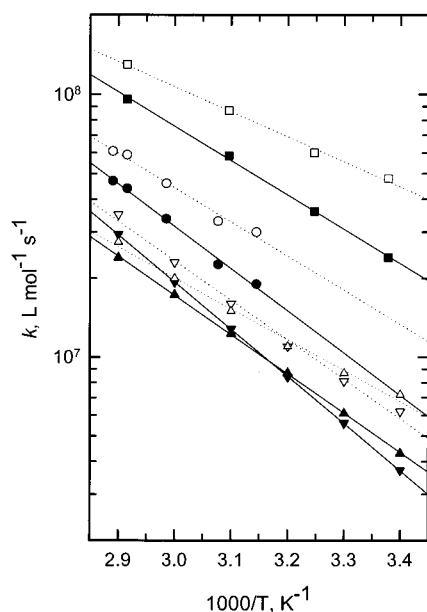
$$k_{\text{act}}^{-1} = k_{\text{exp}}^{-1} - k_{\text{diff}}^{-1} \quad (19)$$

The values of  $k_{\text{diff}}$  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  $k_{\text{act}}$  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<sub>4</sub> than those in its absence. Although the activation energy for reaction 18 derived in this complex manner is approximate,

**TABLE 4: Rate Constants for Oxidation Reactions in Ionic Liquids**

reaction	solvent	$T$ , °C	$k_{\text{exp}}$ L mol <sup>-1</sup> s <sup>-1</sup>	$E_a^a$	log $A$	$k_{\text{diff}}^b$ L mol <sup>-1</sup> s <sup>-1</sup>	$k_{\text{act}}$ L mol <sup>-1</sup> s <sup>-1</sup>	$E_a^a$	log $A$
CCl <sub>3</sub> O <sub>2</sub> <sup>•</sup> + CIPz <sup>c</sup>	R <sub>4</sub> NNTf <sub>2</sub>	21	$(4.3 \pm 0.6) \times 10^6$	29	11.8	$1.1 \times 10^7$	$7.2 \times 10^6$	22.6	10.8
RO <sub>2</sub> <sup>•</sup> + CIPz <sup>d</sup>	R <sub>4</sub> NNTf <sub>2</sub>	21	$(3.7 \pm 0.6) \times 10^6$	34	12.7	$9.2 \times 10^6$	$6.2 \times 10^6$	28.8	11.9
CCl <sub>3</sub> O <sub>2</sub> <sup>•</sup> + CIPz	BuPicPF <sub>6</sub>	45	$(1.9 \pm 0.3) \times 10^7$	30.8	12.3	$5.2 \times 10^7$	$3.0 \times 10^7$	25.0	11.6
CCl <sub>3</sub> O <sub>2</sub> <sup>•</sup> + CIPz	BuPyBF <sub>4</sub>	23	$(2.4 \pm 0.4) \times 10^7$	25.2	11.9	$4.8 \times 10^7$	$4.8 \times 10^7$	18.2	10.9
CCl <sub>3</sub> O <sub>2</sub> <sup>•</sup> + CIPz	BMIPF <sub>6</sub> <sup>e</sup>	22	$(1.2 \pm 0.2) \times 10^7$	30.3	12.4	$2.2 \times 10^7$	$2.6 \times 10^7$	22.7	11.4
CCl <sub>3</sub> O <sub>2</sub> <sup>•</sup> + CIPz	BMIPF <sub>6</sub> <sup>ef</sup>	22	$(2.9 \pm 0.4) \times 10^7$			$6.1 \times 10^7$	$5.5 \times 10^7$		
CCl <sub>3</sub> O <sub>2</sub> <sup>•</sup> + Trolox	BMIPF <sub>6</sub> <sup>ef</sup>	22	$(9.6 \pm 1.6) \times 10^6$			$6.1 \times 10^7$	$1.1 \times 10^7$		
CCl <sub>3</sub> O <sub>2</sub> <sup>•</sup> + Trolox	BMIBF <sub>4</sub> <sup>e</sup>	22	$(6 \pm 1) \times 10^6$			$6.7 \times 10^7$	$6.6 \times 10^6$		
CCl <sub>3</sub> O <sub>2</sub> <sup>•</sup> + Trolox	BuPyBF <sub>4</sub>	23	$(9 \pm 1) \times 10^6$	24.2	11.1	$4.8 \times 10^7$	$1.1 \times 10^7$	22.8	11.0
CCl <sub>3</sub> O <sub>2</sub> <sup>•</sup> + CIPz	H <sub>2</sub> O <sup>g</sup>	25	$1.2 \times 10^9$	23.7	13.2	$7 \times 10^9$			
CCl <sub>3</sub> O <sub>2</sub> <sup>•</sup> + CIPz	2-PrOH	22	$3.1 \times 10^7$ <sup>h</sup>	8.7 <sup>i</sup>	9.4 <sup>i</sup>	$3 \times 10^9$			

<sup>a</sup> Activation energies (in kJ mol<sup>-1</sup>) have been determined with an overall estimated standard uncertainties of less than  $\pm 10\%$ . <sup>b</sup> Estimated from the viscosities that were measured with identical solutions. <sup>c</sup> This reaction took place in parallel with reactions of solvent derived peroxy radicals with CIPz (see text) and the processes could not be separated. <sup>d</sup> Reaction involving several solvent radicals but excluding CCl<sub>3</sub>O<sup>•</sup> (see text). <sup>e</sup> Results from ref 2. <sup>f</sup> These solutions also contained 10 v% 2-PrOH. <sup>g</sup> Solution contained 10% 2-PrOH; results from ref 27. <sup>h</sup> From ref 28. <sup>i</sup> From ref 27 for 2-PrOH solutions containing 9% water.



**Figure 5.** Arrhenius plots for the rate constants for reaction of CCl<sub>3</sub>O<sub>2</sub><sup>•</sup> radicals with CIPz in ionic liquids. The solid symbols are for the measured  $k_{\text{exp}}$  and the open symbols are for the calculated  $k_{\text{act}}$ . The solvents are BuPyBF<sub>4</sub> (■), ByPicPF<sub>6</sub> (●), R<sub>4</sub>NNTf<sub>2</sub> with CCl<sub>4</sub> (▲), and R<sub>4</sub>NNTf<sub>2</sub> without CCl<sub>4</sub> (▼).

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<sub>6</sub> and BuPyBF<sub>4</sub>.** The radiolytic oxidation yield in BuPyBF<sub>4</sub> was determined by using TMPD solutions, as described above with R<sub>4</sub>NNTf<sub>2</sub>. The yield was  $1.5 \times 10^{-7}$  mol J<sup>-1</sup>, slightly lower than the yield in R<sub>4</sub>NNTf<sub>2</sub>.

The rate constants for oxidation of CIPz and Trolox by the CCl<sub>3</sub>O<sub>2</sub><sup>•</sup> radicals were determined in oxygenated ionic liquid solutions containing 1% CCl<sub>4</sub>. No significant oxidation was detected in these ionic liquids in the absence of CCl<sub>4</sub>. In all cases examined the rate constants at room temperature (Table 4) are close to  $10^7$  L mol<sup>-1</sup> s<sup>-1</sup>. 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<sub>3</sub>O<sub>2</sub><sup>•</sup> radicals in the various ionic liquids (Table 4) are all within a factor of 2 of  $1 \times 10^7$  L mol<sup>-1</sup>

s<sup>-1</sup>. 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 1.5–2 and remain close to  $1 \times 10^7$  L mol<sup>-1</sup> s<sup>-1</sup>. These values are clearly lower than the rate constant measured for this reaction in water<sup>27,28</sup> and close to the values measured in alcohols.<sup>28</sup> 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 fraction is  $\approx 0.5$  in the ionic liquids,  $\approx 0.2$  in water, and only  $\approx 0.01$  in 2-PrOH (Table 4) and other less polar organic solvents.<sup>28</sup> 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<sub>3</sub>O<sub>2</sub><sup>•</sup> radicals have been suggested to involve an electron transfer and a proton transfer occurring in concert,<sup>29</sup> so that the insipient CCl<sub>3</sub>O<sub>2</sub><sup>-</sup> anion is immediately converted to the more stable CCl<sub>3</sub>O<sub>2</sub>H. 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.<sup>27,28</sup> 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.<sup>28</sup>



## Summary and Conclusions

Pulse radiolysis of ionic liquids (BMIPF<sub>6</sub>, BMIBF<sub>4</sub>, BuPicPF<sub>6</sub>, BuPyBF<sub>4</sub>, and R<sub>4</sub>NNTf<sub>2</sub>) 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 CCl<sub>3</sub>O<sub>2</sub><sup>•</sup> 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<sub>4</sub>NNTf<sub>2</sub> 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<sub>4</sub>NNTf<sub>2</sub>, solvated electrons produced in imidazolium or pyridinium ionic liquids are rapidly scavenged by the solvent cations. In the case of BMI<sup>+</sup> the electrons are completely trapped, as discussed before,<sup>2</sup> but with BuPy<sup>+</sup> and BuPic<sup>+</sup> 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, whereby 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 couples, 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<sup>2+</sup>/MV<sup>•+</sup> couple and the AQS<sup>-</sup>/AQS<sup>•2-</sup> couple reverses direction upon going from water to 2-PrOH.<sup>23</sup> We confirm these findings and show that the equilibrium between the MV<sup>2+</sup>/MV<sup>•+</sup> couple and the DQ/DQ<sup>•-</sup> 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<sub>4</sub> 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 negative or positive 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

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