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Reaction Kinetics in Ionic Liquids: Pulse Radiolysis Studies of 1-Butyl-3-methylimidazolium Salts

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Radiolysis of liquid 1-butyl-3-methylimidazolium (BMI^+) salts leads to formation of several species with similar absorption spectra. To identify and characterize these species, experiments were carried out with BMI^+ in solution under various conditions. BMI^+ is reduced by e_{aq}^- very rapidly ($k = 1.9 \times 10^{10}$ L mol^{-1} s^{-1}) but not by $(CH_3)_2\dot{C}O^-$ radicals ($k \leq 1 \times 10^5$ L mol^{-1} s^{-1}). The reduced species exhibits an absorption peak at 323 nm ($\epsilon = 5.9 \times 10^3$ L mol^{-1} cm^{-1}). It decays via radical−radical reactions but does not react with O_2 or with methyl viologen. BMI^+ reacts rapidly also with OH radicals ($k = 3.7 \times 10^9$ L mol^{-1} s^{-1}) to produce a mixture of isomeric OH-adducts. The spectrum of these adducts is similar to that of the reduced species, it exhibits a peak at 322 nm ($\epsilon = 2.5 \times 10^3$ L mol^{-1} cm^{-1}) but with a pronounced shoulder at 380 to 420 nm. The adducts react with O_2 and with OH^-. In the latter reaction they lose H^+ to form a hydroxylated analogue of the electron adduct. Irradiation of liquid BMI^+ salts produces $BMI^\bullet$, $BMI^{\bullet 2+}$, and various radical adducts. In the presence of CCl_4 and O_2, $CCl_3O_2^\bullet$ radicals are formed and these radicals oxidize Trolox and chlorpromazine with rate constants of (1 to 3) × 10^7 L mol^{-1} s^{-1}. Even after correcting for the effect of viscosity, the rate constants are much lower than those determined in aqueous solutions and close to those measured in low-polarity organic solvents. The low rate constants in $BMIPF_6$ and $BMIBF_4$ probably indicate a high degree of ion-association in these ionic liquids. On the other hand, the activation energy of the reaction is close to that measured in aqueous solutions but higher than that in alcohols. This is discussed in terms of highly structured solvent/solute domains.

Introduction

Ionic liquids[1] are a class of organic salts that are liquid at or near room temperature. They serve as good solvents for various thermal and electrochemical reactions, are nonvolatile and nonflammable, and can be easily recycled. Therefore, they have been proposed as “green solvents” for chemical reactions and separation processes. Ionic liquids have been shown to enhance the rates of certain reactions and to affect product distribution.[1] To compare reaction rate constants in ionic liquids with those in other solvents we chose to begin with the reactions of $CCl_3O_2^\bullet$ radicals with Trolox and chlorpromazine, which have been studied in a wide variety of solvents.[2] It has been shown that $CCl_3O_2^\bullet$ radicals can be produced by radiolysis of practically any solvent or solvent mixtures containing CCl_4 and O_2. Herein, we report on their production in ionic liquids, the rate constants for some of their reactions, and the mechanism by which these radicals are produced. In this manuscript we describe first the radiolytic reactions of the 1-butyl-3-methylimidazolium cation, to establish the mechanism by which the peroxyl radicals are produced in this ionic liquid, while the rate constants for reactions of the peroxyl radicals with solutes in the ionic liquid are presented and discussed in the last section.

Experimental Section[3]

1-Butyl-3-methylimidazolium (BMI^+) chloride was prepared by reacting *N*-methylimidazole with *n*-butyl chloride, as described before.[4] The product was purified by repeated extractions of the remaining starting materials with ethyl acetate (until no *N*-methylimidazole was detected spectrophotometrically at 275 nm in the ethyl acetate fraction). After the last extraction, the remaining ethyl acetate was removed at 70 °C under vacuum. The product was solid at room temperature. Two room-temperature ionic liquids were prepared from BMICl by replacing the chloride ion with a hexafluorophosphate or a tetrafluoroborate ion. $BMIPF_6$ was prepared by mixing equimolar amounts of BMICl and KPF_6, each predissolved in a similar weight of water. $BMIPF_6$ is insoluble in water and is readily separated, thoroughly washed with water, and dried in a vacuum at 70 °C. $BMIBF_4$ is soluble in water and was prepared by the method described by Fuller et al.[5] by mixing BMICl and NH_4BF_4 in acetonitrile.

Various compounds were used to probe reduction and oxidation reactions: benzoquinone, duroquinone (tetramethylbenzoquinone), methyl viologen (1,1′-dimethyl-4,4′-bipyridinium dichloride), chlorpromazine (ClPz) (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 using mainly $BMIPF_6$; a few comparative experiments in $BMIBF_4$ gave very similar results. The radiolytic reactions of BMI^+ ions were also studied in solution by using $BMIPF_6$ or BMICl in various solvents. 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.[6] The dose per pulse was determined by thiocyanate dosimetry[7] and was varied between 2 and 20 Gy. Unless stated otherwise, the measurements were performed at room temperature, (21 ± 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, with a nominal gap of 0.7 mm. Tests were performed between shear rates of

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$0.1\ s^{-1}$ to $10\ s^{-1}$, and the fluid showed no signs of non-Newtonian behavior. The change in the gap with thermal expansion has been measured to be $(1.75 \pm 0.10)\ \mu m\ K^{-1}$ and a correction has been applied to the data taken above room temperature to account for this change in the geometry. The reported viscosity is the mean of 3 to 5 values determined at different shear rates and the standard uncertainty of the mean varied from about 1% at room temperature to about 3% at the higher temperatures. Measurements were carried out with neat $BMIPF_6$ and after addition of 1% CCl_4. The liquids were equilibrated with air.

Results and Discussion

Preliminary pulse radiolysis experiments with neat liquid $BMIPF_6$ showed production of transient species that exhibit optical absorption with a peak at 325 nm. In the presence of CCl_4 and O_2, the organic reductants Trolox and chlorpromazine were oxidized to their respective radicals. To investigate the mechanism of the radiolytic oxidation of these compounds and to characterize the species formed by the radiolysis of $BMIPF_6$, we carried out pulse radiolysis studies both with neat BMI^+ salts and with their solutions under various conditions. Essential information for understanding the radiation chemistry of the neat ionic liquids was obtained from experiments in solution and these are described first.

Pulse Radiolysis of BMI^+ Salts in Solution. Most experiments were carried out in aqueous solutions using BMICl, which is very soluble in water, and $BMIPF_6$, which is much less soluble. The radiolytic reactions of BMI^+ were studied under conditions that the anion is unreactive (see below).

The radiolysis of water produces mainly hydrated electrons and hydroxyl radicals with small amounts of hydrogen atoms and molecular products. The rate constants for reactions of e_{aq}^- were determined by following the decay of its optical absorption at 600 nm in aqueous solutions containing $0.1\ mol\ L^{-1}$ methanol at pH 9. The methanol serves as a scavenger of the $H^•$ and $^•OH$ radicals and the alkaline pH is used to prevent the reaction of e_{aq}^- with H^+. The second-order rate constant for reaction of e_{aq}^- with BMI^+, determined from the dependence of k_{obs} upon $[BMI^+]$, was $k_1 = (1.9 \pm 0.3) \times 10^{10}\ L\ mol^{-1}\ s^{-1}$, identical to the value reported for 1-methylimidazolium ion[8]

$$BMI^+ + e_{aq}^- \rightarrow BMI^• \qquad (1)$$

It is known that e_{aq}^- does not react with Cl^- and we have determined that e_{aq}^- does not react with PF_6^- either. The rate of e_{aq}^- decay was not changed upon addition of up to $0.1\ mol\ L^{-1}$ KPF_6, from which we estimate $k \le 1 \times 10^5\ L\ mol^{-1}\ s^{-1}$.

The $BMI^•$ radical exhibits an absorption spectrum with $\lambda_{max} = 323$ nm (Figure 1). From thiocyanate dosimetry,[7] and assuming that the radiolytic yield of $BMI^•$ is equal to that of e_{aq}^- and that $G(e_{aq}^-)$ in $1.3\ mol\ L^{-1}$ 2-PrOH solution is $3.2 \times 10^{-7}\ mol\ J^{-1}$, we calculate its molar absorption coefficient $\epsilon = (5.9 \pm 0.7) \times 10^3\ L\ mol^{-1}\ cm^{-1}$. This spectrum was monitored $<1\ \mu s$ after the pulse with a deoxygenated aqueous solution containing $2\ mmol\ L^{-1}$ BMICl and $1.3\ mol\ L^{-1}$ 2-PrOH at pH 7.[9] No further buildup of absorption was detected at longer times. However, when $[BMI^+]$ was increased above $10\ mmol\ L^{-1}$, a slower buildup step was observed that may be due to reaction of BMI^+ with the $(CH_3)_2\dot{C}OH$ radicals. The rate constant for this second reaction was determined from experiments with $[BMI^+] = (0.05$ to $0.1)\ mol\ L^{-1}$ at pH 10 and found to be $(2.7 \pm 0.7) \times 10^5\ L\ mol^{-1}\ s^{-1}$. This rate constant is in the same range as those reported for other imidazolium ions.[10] The spectrum of the product radical, however, is different from that of $BMI^•$; its peak is shifted to 335 nm. Therefore, we suggest that the reaction of the $(CH_3)_2\dot{C}OH$ radicals with BMI^+ takes place via addition, not via electron transfer, as reported before for several other heterocycles.[11] When the pH was raised to 13, to convert $(CH_3)_2\dot{C}OH$ into the stronger reductant $(CH_3)_2\dot{C}O^-$, no reaction was observed. It is concluded, therefore, that the addition reaction becomes slower when the radical is ionized and the electron-transfer reaction is still very slow, $k < 1 \times 10^5\ L\ mol^{-1}\ s^{-1}$. This indicates that the reduction potential of BMI^+ is more negative than that of $(CH_3)_2\dot{C}O^-$, which is -2.1 V.[12]

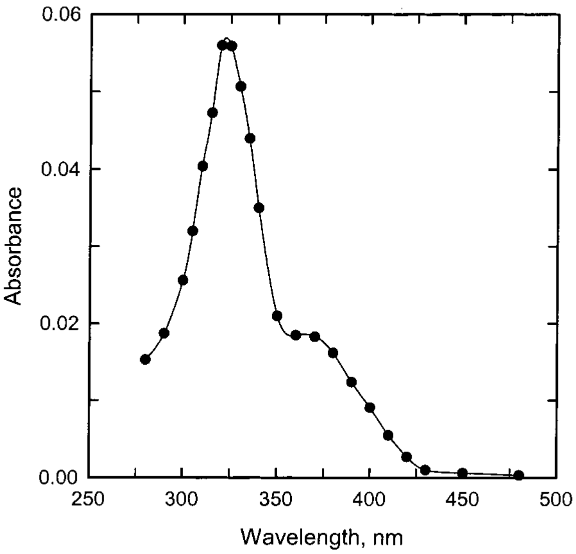
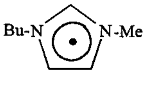


Figure 1. Transient absorption spectrum of the radical produced by reaction of BMI^+ with e_{aq}^-. Determined by pulse radiolysis of deoxygenated aqueous solutions containing $1.3\ mol\ L^{-1}$ 2-PrOH and $2\ mmol\ L^{-1}$ BMICl at pH 7, buffered with $10\ mmol\ L^{-1}$ phosphate, monitored $0.2\ \mu s$ after the pulse.

$BMI^•$ radicals were found to decay by second-order processes over 50 ms but did not react rapidly with O_2 ($k \ll 1 \times 10^7\ L\ mol^{-1}\ s^{-1}$), CCl_4 ($k \ll 1 \times 10^5\ L\ mol^{-1}\ s^{-1}$), *p*-benzoquinone ($k \ll 1 \times 10^7\ L\ mol^{-1}\ s^{-1}$), or methyl viologen ($k < 5 \times 10^4\ L\ mol^{-1}\ s^{-1}$). Because the reduction potential of BMI^+ is estimated to be near -2 V, it is generally expected that its one-electron reduction product will transfer an electron to oxygen and quinones rapidly. The finding that such reactions are slow indicate that $BMI^•$ is not a typical electron adduct. The possibility that the slow electron transfer is due to the presence of a dimeric $(BMI)_2^{•+}$ rather than a monomeric $BMI^•$ is not likely because the spectrum remained unchanged between $1 \times 10^{-3}\ mol\ L^{-1}$ and $0.1\ mol\ L^{-1}$ BMI^+.

Electron adducts of nitroaromatic compounds have been found to transfer an electron to O_2 and other compounds much more slowly than is expected on the basis of their reduction potentials.[13] This behavior was ascribed to a large difference in geometry between the radical anion, in which the ring and the nitro group are locked in the same plane, and the neutral compound, where the nitro group can rotate freely. This is also expressed as a very slow self-exchange rate for $ArNO_2/ArNO_2^{•-}$.[14] We speculate that addition of an electron to BMI^+ also results in considerable change in geometry, i.e., that $BMI^•$ cannot be formulated as a planar structure **1**. Possibly, the two nitrogens and C_2 form an allylic structure that is not conjugated with the $C_4{=}C_5$ double bond (structure **2**) and the ring is puckered.

Another possibility is that the unpaired electron density is located mainly on the nitrogens, because nitrogen-centered



1

2

radicals are generally unreactive toward O_2. However, such radicals are oxidants rather than reductants, but we found that $\mathrm{BMI}^{\bullet}$ does not oxidize TMPD rapidly ($k < 1 \times 10^7$ L mol^{-1} s^{-1}) and, thus, conclude that it is a very weak oxidant, if at all.

To examine these suggestions we carried out ab initio molecular orbital calculations on the imidazolyl, 1-methylimidazolyl, and 1,3-dimethylimidazolyl radicals. Full geometry optimizations were performed with density functional theory, DFT, using Becke's three-parameter hybrid exchange functional and the gradient corrected correlation functional developed by Lee, Yang, and Parr, B3LYP,[15] together with the double-ζ plus polarization 6-31G* basis set.[16] Analytical vibrational frequency calculations carried out at the same level of theory confirmed that the optimized structures are minima, characterized by exhibiting 3N-6 positive vibrational frequencies, where N is the total number of atoms. All calculations were carried out with the Gaussian 98 suite of programs.[17] The optimized geometrical parameters (Table 1) indicate that indeed all structures are nonplanar and that they exhibit a sizable degree of puckering in the ring (9° to 10°). This puckering does not seem to be dependent on substitution on the nitrogen atoms given that even in the imidazolyl radical a puckering angle of approximately 10° is observed. The central carbon and the two adjacent nitrogen atoms seem to form an allylic structure that does not conjugate with the C=C double bond (see Table 1). From the spin density results (Table 2) it is clear that the unpaired electron is localized in the region comprised by central carbon and the two nitrogen atoms and that the major fraction of the spin density is on the central carbon. These findings confirm the above suggestion that $\mathrm{BMI}^{\bullet}$ can be represented more closely by structure **2** rather than **1** and explain its lack of reactivity as an electron donor.

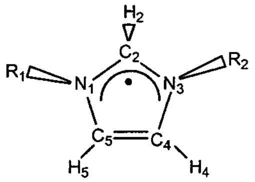
Hydroxyl radicals react with imidazoles very rapidly via addition.[8,18] Addition of $^{\bullet}\mathrm{OH}$ to BMI^+ is expected to take place at all three carbon atoms to produce three isomeric adducts, whereas H-abstraction from the alkyl side chains should make a minor contribution. The spectrum of the OH-adducts, monitored by pulse radiolysis of N_2O-saturated aqueous solutions containing 2 mmol L^{-1} BMICl and 10 mmol L^{-1} phosphate buffer at pH 7, exhibits a peak at 322 nm, similar to that of the electron adduct but with a pronounced shoulder at 360 to 440 nm (Figure 2a). The spectrum is similar to those observed before for OH-adducts of other imidazoles.[8,18] The effective molar absorption coefficient of this isomeric mixture is $\epsilon = (2.5 \pm 0.3) \times 10^3$ L mol^{-1} cm^{-1}, assuming that all $^{\bullet}\mathrm{OH}$ radicals reacted via addition and correcting for the contribution of H-adducts (see below).

The rate constant for reaction of $^{\bullet}\mathrm{OH}$ radicals with BMI^+ was determined in N_2O-saturated aqueous solutions at pH 7 (5 mmol L^{-1} phosphate buffer) from the rate of absorption buildup at 325 nm as a function of [BMI^+]

$$\mathrm{BMI}^+ + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{HO{-}BMI}^{\bullet} \qquad (2)$$

We measured $k_2 = (3.7 \pm 0.5) \times 10^9$ L mol^{-1} s^{-1}, only slightly lower than the value reported for the N-methylimidazolium cation (5×10^9 L mol^{-1} s^{-1}).[8]

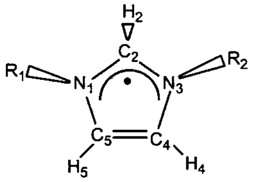
TABLE 1: Geometrical Parameters[a] Optimized at the B3LYP/6-31G* Level of Theory



parameter[b]	R_1=H, R_2=H	R_1=CH_3, R_2=H	R_1=CH_3, R_2=CH_3
R(C_2−N_3)	1.429	1.430	1.424
R(N_3−C_4)	1.404	1.405	1.397
R(C_4−C_5)	1.347	1.349	1.351
R(C_5−N_1)	1.404	1.397	1.398
R(N_1−C_2)	1.429	1.423	1.424
R(H_2−C_2)	1.094	1.095	1.096
R(H_5−C_5)	1.081	1.081	1.081
R(H_4−C_4)	1.081	1.081	1.081
R(R_1−N_1)	1.015	1.449	1.449
R(R_2−N_3)	1.015	1.015	1.449
∠(C_4−N_3−C_2)	107.7	107.5	107.7
∠(C_5−C_4−N_3)	107.7	108.6	108.9
∠(N_1−C_5−C_4)	108.8	109.1	108.9
∠(C_2−N_1−C_5)	107.7	107.9	107.7
∠(H_2−C_2−N_3)	116.6	116.9	116.6
∠(R_1−N_1−C_2)	117.6	120.5	120.3
∠(R_2−N_3−C_2)	117.6	117.4	120.4
∠(H_5−C_5−C_4)	129.6	129.7	129.7
∠(H_4−C_4−C_5)	129.6	129.6	129.7
τ(C_2−N_1−C_5−C_4)	10.3	8.6	8.9
τ(C_2−N_3−C_4−C_5)	10.3	10.4	8.9
τ(R_1−N_1−C_5−C_4)	147.0	156.3	155.4
τ(R_2−N_3−C_4−C_5)	147.0	146.3	155.7
τ(H_2−C_2−N_3−C_4)	146.0	144.9	144.4
τ(H_5−C_5−C_4−N_3)	174.4	174.8	175.7
τ(H_4−C_4−C_5−N_1)	174.4	175.3	175.7

[a] Some redundant coordinates have been included for sake of clarity. [b] Distances R(X−Y) in Å, and angles ∠(X−Y−Z) and torsions τ(X−Y−Z−K) in degress.

TABLE 2: Spin Density on Atomic Centers on the Ring Computed at the B3LYP/6-31G* Level of Theory



atom center	R_1=H, R_2=H	R_1=CH_3, R_2=H	R_1=CH_3, R_2=CH_3
N_1	0.1408	0.1501	0.1504
C_2	0.6646	0.6378	0.6127
N_3	0.1407	0.1411	0.1503
C_4	0.0048	0.0221	0.0048
C_5	0.0046	−0.0110	0.0058
R_1	0.0112	−0.0056	−0.0056
R_2	0.0113	0.0111	−0.0058
H_2	0.0189	0.0216	0.0238
H_4	0.0016	0.0008	0.0012
H_5	0.0016	0.0020	0.0012

The OH-adducts react rapidly with O_2. The rate constant, estimated from the decay of the transient absorption in solutions saturated with N_2O/O_2 mixtures, is ~1×10^9 L mol^{-1} s^{-1}, and the reaction probably yields peroxyl radicals. In the absence of O_2 the OH-adducts undergo further reactions and then second-order decay.

The initial spectrum of the OH-adducts monitored at pH 7 (Figure 2a) and pH 3.2 undergoes slight changes over 75 μs before it decays. In alkaline solutions, however, as the pH was gradually increased from 8 to 12, the spectral changes became increasingly more pronounced and occurred more rapidly. A sample spectrum at pH 9.8 is shown in Figure 2b, where the initial absorbance is seen to increase in intensity by more than a factor of 2 and to change in shape, though still retaining the peak at nearly the same position. The rate constant of this spectral change, determined at 330 nm between pH 8.4 and pH 12, was found to increase with [OH^-] but not linearly. Linear

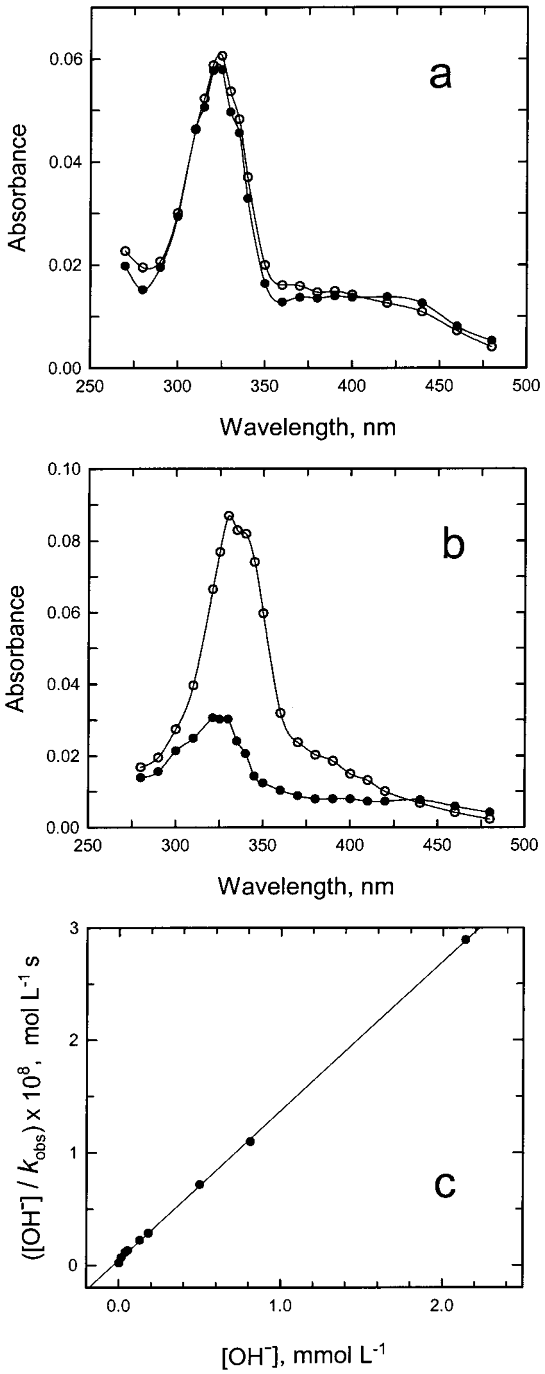


Figure 2. Transient absorption spectra and kinetics of the radicals produced by reaction of BMI^+ with $^{\bullet}OH$ radicals. (a) Spectra monitored with N_2O-saturated aqueous solution containing 2 mmol L^{-1} BMICl at pH 7, buffered with 10 mmol L^{-1} phosphate, monitored 0.2 (●) and 75 (○) μs after the pulse. (b) Spectra monitored under similar conditions but at pH 9.8 (unbuffered), 0.2 (●) and 80 (○) μs after the pulse. (c) Dependence of the rate of spectral transformation on the concentration of OH^- according to the equation $k_{obs} = k_4K_3[OH^-]/(1 + K_3[OH^-])$.

dependence was found when $[OH^-]/k_{obs}$ was plotted vs $[OH^-]$ (Figure 2c). Such dependence suggests an equilibrium reaction of the initial radical with OH^- followed by a first-order process. We propose, therefore, that the OH-adducts undergo ionization followed by rearrangement

$$HO{-}BMI^{\bullet} + OH^- \leftrightarrows {}^-O{-}BMI^{\bullet} + H_2O \qquad (3)$$

$${}^-O{-}BMI^{\bullet} \rightarrow \text{Product} \qquad (4)$$

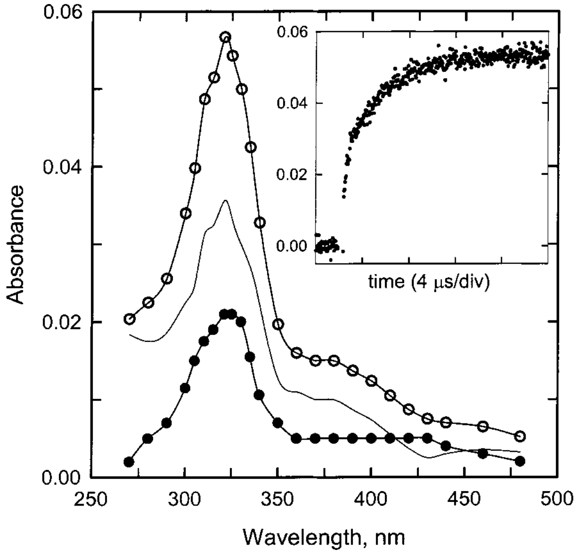
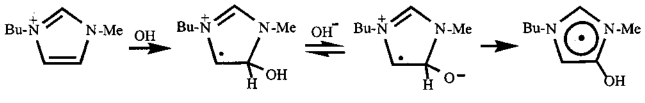


Figure 3. Transient absorption spectra of the radicals produced by reaction of BMI^+ with $^{\bullet}OH$ radicals and $H^{\bullet}$ atoms in acidic solutions. Determined in deoxygenated aqueous solution containing 1.1 mmol L^{-1} $BMIPF_6$ and 0.1 mol L^{-1} $HClO_4$, monitored 0.2 (●) and 20 (○) μs after the pulse. The early spectrum is mainly that of the OH-adducts, the final spectrum is the sum of the OH-and H-adducts and the middle line is the spectrum of the H-adducts obtained from the difference between the two spectra. The insert shows a typical trace taken at 325 nm demonstrating the fast formation step followed by the slow formation step.

This mechanism leads to the dependence

$$k_{obs} = k_4K_3[OH^-]/(1+K_3[OH^-]) \qquad (5)$$

and a linear plot of $[OH^-]/k_{obs}$ vs $[OH^-]$ permits the calculation of k_4 from the slope and K_3 from the intercept. From such a plot (Figure 2c) we calculate $k_4 = (7.5 \pm 0.8) \times 10^4\ s^{-1}$ and estimate $K_3 \approx 1.7 \times 10^6$. The latter value is a rough approximation due to a large uncertainty in the value of the small intercept. From this value, we estimate that the OH-adducts have $pK_a \approx 8$ and the ionized forms undergo a first-order reaction to form different products. The spectrum of these products has $\lambda_{max} = 330$ nm with $\epsilon = (5.8 \pm 0.8) \times 10^3$ L mol^{-1} cm^{-1} (after correcting for the small contribution of the H-adducts, see below). We propose that these products are formed by the following process, where the radicals **3**, **4**, and **5** represent one of three possible isomers



BMI⁺ **3** **4** **5**

Thus, the sum of reactions 2, 3, and 4 is to convert BMI^+ in alkaline solutions into radical **5**, which is a hydroxylated analogue of $BMI^{\bullet}$. This mechanism is plausible in view of the great stability of $BMI^{\bullet}$. The main peak of radical **5** is red shifted by 7 nm as compared with that of $BMI^{\bullet}$ and the molar absorption coefficients of the two radicals are practically identical.

Further experiments were carried out in acidic solutions to observe the H-adducts and the radical cation of BMI^+. Pulse radiolysis of deoxygenated solutions of $BMIPF_6$ at pH 1 showed a rapid formation of the OH-adducts and then a slower formation of the H-adduct (Figure 3). The spectrum of the OH-adduct, monitored <1 μs after the pulse, is identical to that recorded at pH 3.2 and pH 7 (Figure 2a). The spectrum of the H-adducts is

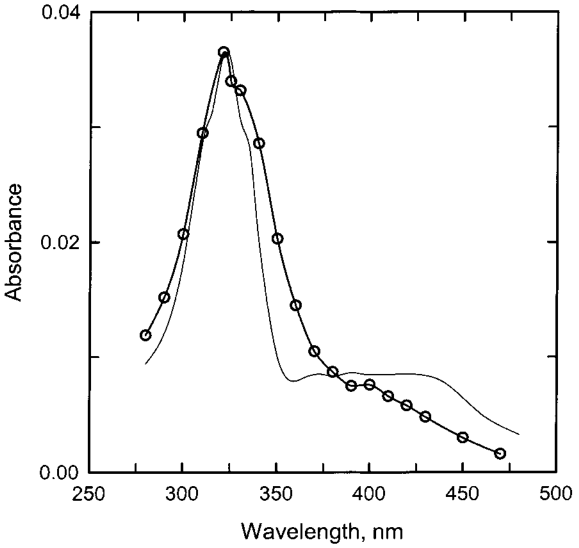


Figure 4. Transient absorption spectrum of the radical cation produced by reaction of BMI^+ with $SO_4^{\bullet-}$ radicals. Monitored with deoxygenated aqueous solution containing 0.025 mol L^{-1} $Na_2S_2O_8$, 0.16 mol L^{-1} *t*-BuOH, and 2 mmol L^{-1} $BMIPF_6$ at pH 4.7, 5 μs after the pulse. A normalized spectrum of the OH-adducts (faint line) is shown for comparison.

different in the shape of the shoulder at 380 nm but has a similar peak at 322 nm and a higher absorption coefficient, $\epsilon = (4.1 \pm 0.7) \times 10^3$ L mol^{-1} cm^{-1}. The rate constant for reaction of $H^\bullet$ atoms with BMI^+, determined from the rate of formation at 322 nm as a function of $[BMI^+]$, was found to be $k_6 = (2.5 \pm 0.4) \times 10^8$ L mol^{-1} s^{-1}

$$BMI^+ + H^\bullet \rightarrow H{-}BMI^\bullet \tag{6}$$

The above experiments were carried out with $BMIPF_6$, not with BMICl, because Cl^- ions react rapidly with $^\bullet OH$ radicals at low pH to form $Cl_2^{\bullet-}$ radicals. $Cl_2^{\bullet-}$ absorb strongly at 340 nm and can mask the absorbance of the BMI^+ products. The possibility that $Cl_2^{\bullet-}$ oxidize BMI^+ rapidly was ruled out in separate experiments with excess Cl^-, which gave an upper limit of $k < 2 \times 10^5$ L mol^{-1} s^{-1} for reaction of $Cl_2^{\bullet-}$ with BMI^+.

To produce the radical cation of BMI^+, we used the stronger oxidant $SO_4^{\bullet-}$ (produced by reaction of e_{aq}^- with $S_2O_8^{2-}$)

$$BMI^+ + SO_4^{\bullet-} \rightarrow BMI^{\bullet 2+} + SO_4^{2-} \tag{7}$$

The rate constant for reaction 7 was estimated from the rate of absorption buildup to be $\sim 1 \times 10^9$ L mol^{-1} s^{-1}. The spectrum of the species formed by reaction 7 (Figure 4) has a peak at 320 nm with $\epsilon = (4.9 \pm 0.7) \times 10^3$ L mol^{-1} cm^{-1}, calculated by taking into account the small contributions of the reactions of H atoms with persulfate and with BMI^+. Although the peak of the radical cation absorption is similar to that of the OH-adducts, careful comparison of the spectra (Figure 4) shows clear differences.

The spectra of the OH-adducts at pH 7 and pH 1 are identical but the spectrum of the radical cation is quite different. Therefore, we conclude that the OH-adducts are not converted into the radical cation at pH 1. The radical cation of *N*-methylimidazole has been reported to be converted into the OH-adduct at pH >9.[19] The spectrum of $BMI^{\bullet 2+}$, however, remained unchanged up to pH 11. This lack of reaction with OH^- may be due to an increased stability of $BMI^{\bullet 2+}$ by charge delocalization over two nearly equivalent quaternary nitrogens, whereas in the radical cation of *N*-methylimidazole only one of the nitrogens is quaternary.

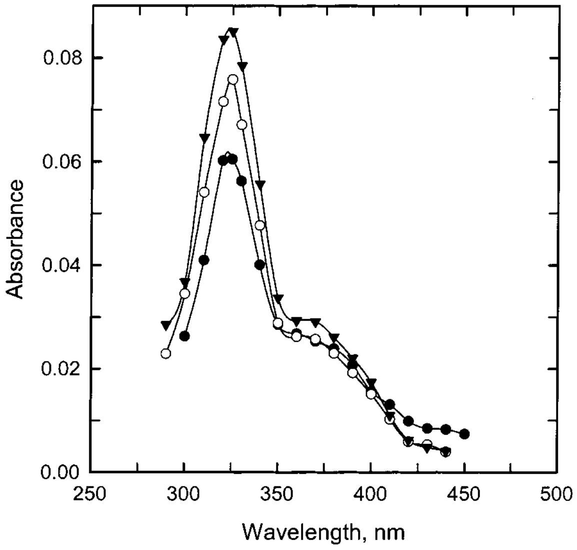


Figure 5. Transient absorption spectra recorded upon pulse irradiation of deoxygenated neat $BMIPF_6$, monitored 1 (●), 4 (○), and 90 (▼) μs after the pulse.

Because BMI^+ was not oxidized by $Cl_2^{\bullet-}$ radicals, an attempt was made to oxidize it by $Cl^\bullet$ atoms, which are known to be formed as one of the primary species in irradiated CH_2Cl_2.[20] Pulse radiolysis experiments with 0.1 mol L^{-1} BMICl in CH_2Cl_2 indicated that $Cl^\bullet$ atoms reacted preferentially with Cl^- to produces $Cl_2^{\bullet-}$, which was identified through its spectrum at 350 nm and which decayed without producing any $BMI^{\bullet 2+}$. With 0.04 mol L^{-1} $BMIPF_6$ in CH_2Cl_2, where $Cl_2^{\bullet-}$ is not formed (due to the absence of Cl^-), we observed only a tail of absorption extending from 270 to 400 nm with no apparent peak near 320 nm, indicating that $Cl^\bullet$ atoms did not react with BMI^+ under these conditions. It was not possible to increase the degree of scavenging of $Cl^\bullet$ atoms by BMI^+ because the concentration of $BMIPF_6$ in CH_2Cl_2 was near its limit. Therefore, from the known lifetime of $Cl^\bullet$ atoms in this solvent,[20] we can only estimate an upper limit of $<1 \times 10^9$ L mol^{-1} s^{-1} for the reaction of BMI^+ with $Cl^\bullet$. Because BMI^+ is oxidized rapidly by $SO_4^{\bullet-}$ ($E = 2.43$ V)[21] and less rapidly, if at all, by $Cl^\bullet$ atoms ($E = 2.41$ V),[22] we estimate that the oxidation potential of BMI^+ lies within this range. Thus, BMI^+ is electrochemically inactive from -2.1 V to $+2.4$ V vs. NHE in water and the ionic liquids $BMIPF_6$ and $BMIBF_4$ can serve as inert electrolytes or electrochemical solvents over this wide range.[1]

Pulse Radiolysis of $BMIPF_6$ as an Ionic Liquid. The spectra recorded upon pulse irradiation of deoxygenated liquid $BMIPF_6$ exhibit a peak at 325 nm and a shoulder near 370 nm. The absorbance at 325 nm increases with time in two distinct steps and the exact shape of the spectrum also changes. The changes occurring over 4 μs and 90 μs are shown in Figure 5. On the basis of the results obtained in solution, the species produced in neat $BMIPF_6$ and absorbing at 325 nm may include $BMI^\bullet$, $BMI^{\bullet 2+}$, and various radical adducts. In the radiolysis of $BMIPF_6$, the energy deposited in the liquid will be absorbed in BMI^+ (~53%) and PF_6^- (~47%) according to their relative electron densities. In both cases, the first step is expected to be ionization, forming a thermalized electron and the remaining radical

$$BMI^+ \rightsquigarrow BMI^{\bullet 2+} + e^- \tag{8}$$

$$PF_6^- \rightsquigarrow PF_6^\bullet + e^- \qquad (9)$$

Geminate recombination of the primary species leads to formation of excited states and consequently to various bond dissociations. The most likely bond dissociations in excited BMI^+ may occur at the benzylic type C$-$H bonds on the methyl and butyl groups, forming $H^\bullet$ atoms and the remainder radicals ($^\bullet R-MI^+$). In addition, C$-$C bond dissociation may produce various alkyl radicals (from $^\bullet CH_3$ to $^\bullet C_4H_9$), and additional $^\bullet R-MI^+$ of different structures. From the $PF_6^\bullet$ moiety one can envision formation of PF_5 and $F^\bullet$, and from excited PF_6^- one may expect PF_5 and F^-.

After these primary steps, in which the thermal electron may or may not be solvated, the e^- and $H^\bullet$ will react rapidly with BMI^+, according to reactions 1 and 6, and $F^\bullet$ is expected to react very rapidly, possibly via addition to the ring or oxidation. These processes will be complete within <10 ns and their products are observed immediately at the end of the microsecond pulse (Figure 5). These species include $BMI^\bullet$, $BMI^{\bullet 2+}$, and the three isomeric H-adducts, all of which are known to exhibit a peak near 325 nm, and possibly some F-adducts, which may have a similar absorption. The increase in absorbance occurring over 4 μs (Figure 5) is ascribed to the reactions of various alkyl radicals ($R^\bullet$ as well as $^\bullet R\text{-}MI^+$) with BMI^+, which are estimated to take place with rate constants $\approx 10^5$ L mol^{-1} s^{-1}

$$BMI^+ + R^\bullet \rightarrow R-BMI^{\bullet +} \qquad (10)$$

The finding that the increase in absorbance in the 300 to 350 nm region is accompanied by a decrease in the 400 to 450 nm region indicates that the latter absorbance may be due to benzylic type radicals, which decay during this process (because simple $R^\bullet$ and nonbenzylic $^\bullet R\text{-}MI^+$ are not expected to absorb in this range). The second increase of absorbance occurring ≈20 times more slowly (Figure 5) may be ascribed to slower reactions of BMI^+ with certain radicals, for example, the H-adducts, which may lead to dimeric radicals absorbing in the same range. Finally, all the radicals decay by various second-order processes leading to products that do not absorb at 325 nm.

Pulse Radiolysis of Liquid $BMIPF_6$ Containing Additives. Irradiation of O_2-saturated $BMIPF_6$ leads to production of species with a lower absorbance at 325 nm and a rapid decrease in absorbance over 5 μs after the pulse. The spectrum remaining after 5 μs is similar to that in Figure 5 but the absorbance at 325 nm was lower (42%). O_2 cannot compete with the large excess of BMI^+ for the primary radicals. As shown from the results in aqueous solutions, O_2 does not react with $BMI^\bullet$ and $BMI^{\bullet 2+}$. On the other hand, it is known to react rapidly with carbon-centered radicals. It is suggested, therefore, that the observed decay, much of it occurring during the pulse, is due to reaction of O_2 with the various alkyl radicals and adducts, whereas the remaining absorbance is due to $BMI^\bullet$ and $BMI^{\bullet 2+}$. A very small increase in absorbance was observed over the next 50 μs, which may be due to addition of some of the peroxyl radicals to BMI^+, and this process was followed by radical$-$radical decay.

Irradiation of liquid $BMIPF_6$ containing 0.1 mol L^{-1} CCl_4 leads to production of species which also absorb at 325 nm but with a lower absorbance (34% as compared with that in the absence of CCl_4) and with no subsequent decrease of absorbance. Some of the radicals, probably the carbon-centered radicals, react with CCl_4 and this reaction is completed within the pulse to produce the nonabsorbing $^\bullet CCl_3$ radicals. Subsequently, a considerable (40%) increase in absorbance was observed to take place over 80 μs, which may be due to addition of $^\bullet CCl_3$ radicals to BMI^+. At the concentrations used in these experiments, CCl_4 was found to be a more effective radical scavenger than O_2, suggesting that in air-saturated 0.1 mol L^{-1} CCl_4 solutions most reducing radicals will react preferentially with CCl_4 and subsequently a reaction of $^\bullet CCl_3$ radicals with O_2 will produce $CCl_3O_2^\bullet$ radicals. The reactions of these species with other additives are discussed in the next section.

Pulse radiolysis of liquid $BMIPF_6$ containing chlorpromazine (ClPz) was carried out to estimate the yield of oxidizing species. Production of the $ClPz^{\bullet +}$ radical cation was monitored at 525 nm. With 0.01 mol L^{-1} ClPz, the absorbance was quite low and it increased with [ClPz] by a factor of ~3, leveling off at 0.1 mol L^{-1}. From thiocyanate dosimetry in aqueous solutions, after correcting for the higher energy absorption by $BMIPF_6$ as compared with dilute aqueous thiocyanate (by a ratio of 743/556 from the electron density), and by assuming that the molar absorption coefficient of $ClPz^{\bullet +}$ in $BMIPF_6$ is similar to that in water (1.07×10^4 L mol^{-1} cm^{-1}),[23] the yield of $ClPz^{\bullet +}$ is calculated to be $G = (1.8 \pm 0.2) \times 10^{-7}$ mol J^{-1}. This oxidation of ClPz to its radical cation took place within the pulse. The rate of oxidation could not be determined because when [ClPz] was decreased below 0.02 mol L^{-1} the yield of $ClPz^{\bullet +}$ was dramatically decreased. This indicates that ClPz is oxidized by a very short-lived species that is practically absent after the end of the pulse. Because the $BMI^{\bullet 2+}$ radical cation was found to be relatively long-lived in water, this cannot be the species that is oxidizing ClPz. The other primary species formed by the radiolysis of $BMIPF_6$ is formed from the PF_6^- moiety and is probably $PF_6^\bullet$. This is expected to be a short-lived, strongly oxidizing radical, which may oxidize ClPz within the duration of the pulse. Alternatively, $PF_6^\bullet$ decays rapidly to produce PF_5 and $F^\bullet$ and the latter also is a short-lived strong oxidant that may oxidize ClPz. Thus, the G value of 1.8×10^{-7} mol J^{-1} probably represents only the oxidizing species formed from PF_6^-. Because energy absorption by the BMI^+ moiety is slightly higher (by a factor of 77/69) than that by the PF_6^- moiety, the initial yield of $BMI^{\bullet 2+}$ radical cations is expected to be $G = (2.0 \pm 0.3) \times 10^{-7}$ mol J^{-1}. Thus, the sum of primary yields is estimated to be 3.8×10^{-7} mol J^{-1} oxidizing species and a similar amount of solvated electrons, close to the primary yields in water.[24]

In an attempt to determine the total yield of oxidizing species, we carried out pulse radiolysis experiments with TMPD in $BMIPF_6$ because TMPD has a much lower oxidation potential than ClPz. Indeed, at low concentrations of TMPD (2 to 7 mmol L^{-1}) we observed formation of $TMPD^{\bullet +}$, with its typical peaks at 565 and 610 nm, in two steps. A very small initial absorbance was found immediately after the pulse, and was followed by a slow formation process. The rate constant for the slow reaction was determined to be $(5 \pm 1) \times 10^7$ L mol^{-1} s^{-1} and may be ascribed to oxidation of TMPD by $BMI^{\bullet 2+}$

$$BMI^{\bullet 2+} + TMPD \rightarrow BMI^+ + TMPD^{\bullet +} \qquad (11)$$

Such a reaction was not observed with ClPz. From the increase in absorbance during the slow formation process, we estimate the yield of $BMI^{\bullet 2+}$ that escape the spur and reach the homogeneous phase as $(0.65 \pm 0.1) \times 10^{-7}$ mol J^{-1} (assuming that the molar absorption coefficient of $TMPD^{\bullet +}$ in $BMIPF_6$ is similar to that in water). This yield is only $^1/_3$ of the total primary yield of $BMI^{\bullet 2+}$ estimated above and suggests that a major fraction of the primary $BMI^{\bullet 2+}$ recombine with electrons within the spur to produce excited states and subsequently carbon-centered radicals. When the concentration of TMPD was increased, the initial absorbance after the pulse increased and reached values >0.1, which correspond to a yield ≈2 × 10^{-7} mol J^{-1}. However, the maximum yield of oxidizing species could not be determined in this system because the small amounts of $TMPD^{\bullet+}$ produced from TMPD during the experiment became significant at high TMPD concentrations and an additional process of a rapid decrease in [$TMPD^{\bullet+}$] became apparent.

It is not possible to estimate the yield of solvated electrons in $BMIPF_6$ by adding an electron scavenger because the electrons react with BMI^+ very rapidly, as determined above in aqueous solutions. We added millimolar concentrations of duroquinone to detect other reducing species in irradiated $BMIPF_6$. We detected the characteristic spectrum of durosemiquinone at 445 nm formed with a second-order rate constant ∼1 × 10^8 L mol^{-1} s^{-1}, which may be ascribed to reaction with some of the carbon-centered radicals produced in $BMIPF_6$. The typical absorption of the other radicals at 325 nm was also present and no reduction of duroquinone by $BMI^{\bullet}$ is expected (based on the above results in aqueous solutions).

Kinetics of Oxidation in Liquid $BMIPF_6$. From the above experiments with CCl_4 and O_2, it was concluded that $CCl_3O_2^{\bullet}$ radicals can be formed in irradiated $BMIPF_6$ containing both of these solutes. Addition of millimolar concentrations of ClPz to air-saturated $BMIPF_6$ containing 0.1 mol L^{-1} CCl_4 resulted in the slow formation of $ClPz^{\bullet+}$ radical cations after the radiation pulse. At the same concentrations, practically no $ClPz^{\bullet+}$ was detected in the absence of CCl_4, indicating that the observed formation is due to reaction 12

$$CCl_3O_2^{\bullet} + ClPz \rightarrow CCl_3O_2^{-} + ClPz^{\bullet+} \qquad (12)$$

The rate of formation was monitored at 525 nm as a function of ClPz concentration and from the linear plot of k_{obs} vs [ClPz] we derived $k_{12} = (1.2 \pm 0.2) \times 10^7$ L mol^{-1} s^{-1}.

An attempt to determine the rate of oxidation of Trolox by the same method failed because of limited solubility in neat $BMIPF_6$. Sufficient solubility was obtained in $BMIPF_6$ containing 10% 2-PrOH (1.3 mol L^{-1}) and 0.1 mol L^{-1} CCl_4. Therefore, we determined the rate constants for oxidation of both ClPz and Trolox by $CCl_3O_2^{\bullet}$ in this solvent mixture and found (2.9 ± 0.4) × 10^7 and (9.4 ± 1.6) × 10^6 L mol^{-1} s^{-1}, respectively. The rate constant for Trolox was also determined in $BMIBF_4$ under similar conditions and found to be (6 ± 1) × 10^6 L mol^{-1} s^{-1}.

Rate constants for oxidation of ClPz and Trolox have been determined before in a wide variety of solvents.[2] They were found to be close to 1 × 10^9 L mol^{-1} s^{-1} in water and decreased to ∼1 × 10^7 L mol^{-1} s^{-1} as the solvent polarity decreased. The present results in the ionic liquids suggest that these solvents are closer in behavior to alcohols than to water, despite the fact that they are composed of ions. However, before accepting this conclusion we have to consider the high viscosity of the ionic liquids, which may be the cause of the low rate constants.

We measured the viscosity of $BMIPF_6$ containing a volume fraction of 1% CCl_4 at 22 °C to be (0.298 ± 0.003) Pa s (0.319 Pa s without CCl_4). From this value we estimate the diffusion-controlled rate constant (k_{diff}) by using the approximation[25]

$$k_{diff} = 8000RT/3\eta \qquad (13)$$

where R is the gas constant (8.3144 J K^{-1} mol^{-1}), T the absolute temperature, and η the viscosity (in Pa s). The value of k_{diff} was found to be 2.2 × 10^7 L mol^{-1} s^{-1} at 22 °C. The experimental rate constant of reaction 12 (k_{exp}) was then corrected for the effect of the diffusion-controlled limit (k_{diff}) to derive the activation-controlled rate constants (k_{act})[25]

$$k_{act}^{-1} = k_{exp}^{-1} - k_{diff}^{-1} \qquad (14)$$

The value of k_{act} was found to be 2.6 × 10^7 L mol^{-1} s^{-1}.

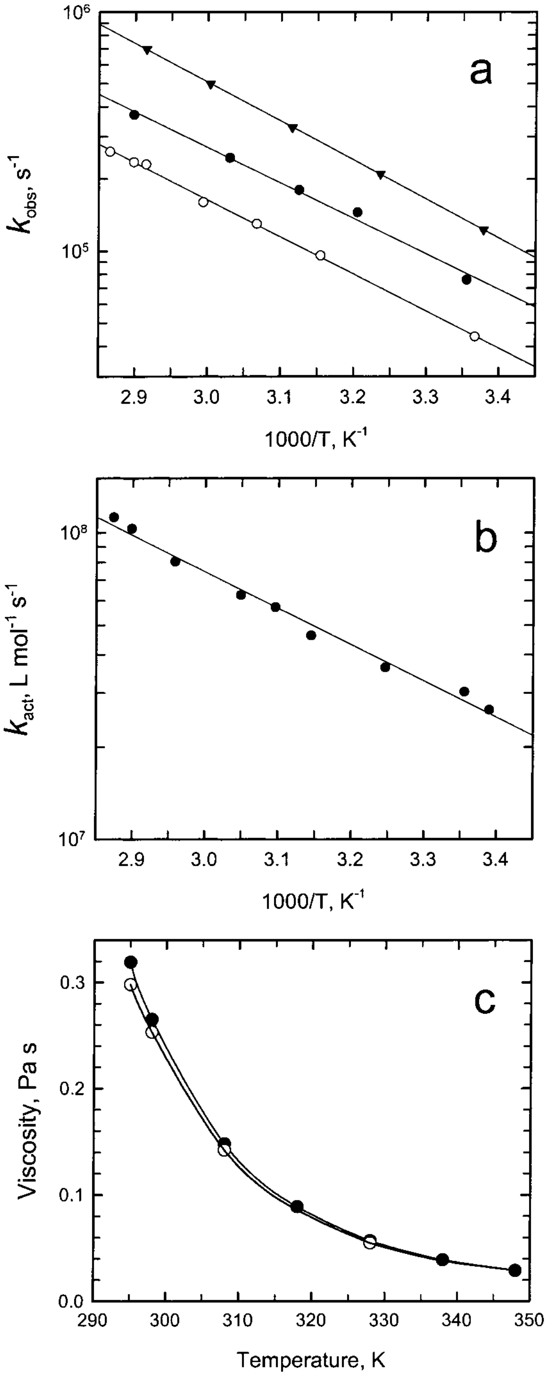


Figure 6. Rate constant for oxidation of chlorpromazine by $CCl_3O_2^{\bullet}$ radicals in $BMIPF_6$ and solvent viscosity as a function of temperature. (a) Arrhenius plots of the observed rate constants determined by pulse radiolysis of $BMIPF_6$ containing 0.1 mol L^{-1} CCl_4, air saturated, and 3 concentrations of chlorpromazine, [ClPz] = 3.3 (○), 5.6 (●), 9.6 (▼) mmol L^{-1}. (b) Arrhenius plot of the calculated k_{act} (see text). (c) Viscosity of $BMIPF_6$ neat (●) and containing 0.1 mol L^{-1} CCl_4 (○) as a function of temperature, measured under air.

The viscosity and rate constant were also determined as a function of temperature (Figure 6). The experimental rate constants at three ClPz concentrations give linear Arrhenius plots (Figure 6a). The second-order rate constant for reaction 12 (k_{exp}), derived from the results in Figure 6a, varies from 1.2×10^7 to 7.9×10^7 L mol^{-1} s^{-1} upon increasing the temperature from 22 to 75 °C. The values of k_{diff} at the different temperatures were estimated (using eq 13) from the viscosity measurements between 22 and 75 °C (Figure 6c) and vary from 2.2×10^7 to 2.7×10^8 L mol^{-1} s^{-1}. The values of k_{act}, calculated from these results according to eq 14, varied from 2.6×10^7 to 1.12×10^8 L mol^{-1} s^{-1} in the same temperature range and give a linear Arrhenius plot (Figure 6b) from which we calculate an activation energy $E_a = (22.7 \pm 2.0)$ kJ mol^{-1} and a preexponential factor $\log A = 11.4$. (The measured activation energy of k_{exp} is (30.3 ± 2.0) kJ mol^{-1} and of k_{diff} (40.5 ± 2.0) kJ mol^{-1}).

The activation-controlled rate constant at 295 K, $k_{12} = 2.6 \times 10^7$ L mol^{-1} s^{-1}, is 42 times lower than that measured in water, 3 times lower than in methanol, slightly lower than in 2-PrOH, and somewhat higher than the rate constants in *t*-BuOH or acetone.[2] Thus, the ionic liquid BMIPF$_6$ exerts a similar effect as weakly polar organic solvents rather than water. This result is in agreement with a recent measurement of the rate constant for electron transfer from excited Ru(bpy)$_3^{2+}$ to methyl viologen in BMIPF$_6$,[26] which was found to be similar to that in acetonitrile and 2 orders of magnitude lower than that in water. One measure of the solvent effect on reactivity is derived from the solvatochromic effect of the solvent on the spectra of certain dyes.[27] Recent measurements[28−30] indicate that the solvatochromic effect of BMIPF$_6$ is much lower than that of water and is close to that of ethanol.

The values of E_a and $\log A$ can be compared to the values determined for the same reaction in various water/2-PrOH/CCl$_4$ mixtures.[31] Both E_a and $\log A$ were found to decrease with the polarity of the solvent mixture. The values determined in the present study in BMIPF$_6$ are close to those found before in a mixture containing 70% to 80% water and higher than the values found in 10% water or in neat organic solvents. In this respect, BMIPF$_6$ appears to behave as a considerably more polar medium than the alcohols. As has been discussed before,[2] polarity is not the only parameter that determines the solvent effect on the rate constant. Because reaction requires separation and reassembly of solvent molecules, the rate constants were better correlated with the solvent cohesive energy density.[2] In addition, it has been suggested[2] that electron transfer to CCl$_3$O$_2^{\bullet}$ radicals is concerted with proton transfer to produce CCl$_3$O$_2$H and that the rate constant depends on the ability of the insipient anion (CCl$_3$O$_2^-$) to receive a proton from the solvent or the reducing molecule. It may be speculated that in this ionic liquid protons are not readily available to the insipient anion. Because the solvent is composed of ions, each molecule and each site of a large molecule may be surrounded by different ions. For example, although the ammonium tail of ClPz may be solvated by PF$_6^-$ anions, the aromatic part may be solvated by the imidazole ring or the butyl groups of BMI$^+$. Thus, the CCl$_3$O$_2^{\bullet}$ radical may easily penetrate the domain of the central ring of ClPz to accept an electron from the sulfur atom but because the proton source is solvated by PF$_6^-$ ions in a different microdomain, the electron transfer reaction is not readily completed and the reactants may separate without reacting (or by undergoing a back electron transfer). Because the solvent and solutes are highly ordered, the activation energy for the reaction is high because it is necessary to break the order of the medium to bring all the necessary components to the reaction site. Furthermore, if the solvent and solute molecules are highly ordered in ionic liquids, we speculate that the observed solvatochromic effect describes the medium in the immediate vicinity of the dye molecule but not necessarily the bulk medium.[28]

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