Reaction Kinetics in the Ionic Liquid Methyltributylammonium Bis(trifluoromethylsulfonyl)imide. Pulse Radiolysis Study of 4-Mercaptobenzoic Acid

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Hydrogen-abstraction reactions of various radicals with 4-mercaptobenzoic acid (MB) to produce the 4-carboxyphenylthiyl radical have been studied by pulse radiolysis in aqueous solutions and in the ionic liquid methyltributylammonium bis(trifluoromethylsulfonyl)imide (R_4NNTf_2). The rate constants in aqueous solutions are in the range of $(1-3) \times 10^8$ L mol^{-1} s^{-1} for the reactions of MB with several alkyl radicals, are higher with reducing radicals (6.4×10^8 L mol^{-1} s^{-1} for $CH_3\dot{C}HOH$ and 1.4×10^9 L mol^{-1} s^{-1} for $(CH_3)_2\dot{C}OH$) and lower with oxidizing radicals ($\leq 10^7$ L mol^{-1} s^{-1} for $^{\bullet}CH_2COCH_3$). Because the bond dissociation energy for the S−H bond is much lower than that for the C−H bonds involved in these reactions, it appears that hydrogen abstraction from mercaptobenzoic acid is not controlled by the relative bond dissociation energies but rather by the electron density at the radical site through a polar transition state. The rate constants for similar reactions in alcohols are slightly lower than those in water, supporting a polar transition state. The rate constants in the ionic liquid are in the range of 10^7-10^8 L mol^{-1} s^{-1} and are essentially controlled by the diffusion rate; variations within this range appear to be due mainly to changes in viscosity. The $^{\bullet}CF_3$ radical reacts slightly more slowly (3.6×10^6 L mol^{-1} s^{-1}) with MB in the ionic liquid, in agreement with the low reactivity in water of radicals bearing electron-withdrawing groups.

Introduction

Room-temperature ionic liquids[1] serve as good solvents for various reactions, are nonvolatile and nonflammable, and have been proposed as "green solvents" for various processes. To understand the effects of these solvents on rates of chemical reactions, we have begun to study the rate constants for several elementary reactions in ionic liquids and to compare them with those in other solvents. We have determined the rate constants for several electron-transfer reactions in a number of ionic liquids: 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIPF_6$) and tetrafluoroborate ($BMIBF_4$),[2] *N*-butylpyridinium tetrafluoroborate ($BuPyBF_4$), *N*-butyl-4-methylpyridinium hexafluorophosphate ($BuPicPF_6$), and methyltributylammonium bis(trifluoromethylsulfonyl)imide (R_4NNTf_2).[3] The rate constants were generally lower in the ionic liquids than in water or alcohols. In a more recent study,[4] rate constants for addition and hydrogen abstraction reactions of $^{\bullet}CF_3$ radicals with several compounds in the ionic liquid R_4NNTf_2 were found to be only slightly lower than those in water and acetonitrile. In the present study, we examine hydrogen abstraction reactions from a thiol by various radicals. Most carbon-centered radicals abstract hydrogen from thiols relatively rapidly[5] because the S−H bond dissociation energy[6] is much lower than that of the C−H bond.[7] To simplify the detection of the thiyl radical produced and to avoid complications due to binding of $RS^{\bullet}$ to RS^-, we use an aromatic thiol in this study.

Pulse radiolysis experiments with thiophenol dissolved in the ionic liquid, in aqueous alcohol solutions and in neat organic solvents, demonstrated the radiolytic production of the $PhS^{\bullet}$ radical (λ_{max} 460 nm)[8,9] in all cases.[10] While attempting to measure the rate constants for reaction of thiophenol with various radicals, however, it was discovered that thiophenol is partially removed when the solution is purged with nitrogen. Therefore, we use 4-mercaptobenzoic acid (MB), which is much less volatile. To characterize the reactions of MB and the thiyl radical produced, we carried out first extensive experiments in aqueous solutions, where mechanisms of production of various radicals and their radiolytic yields are known with great detail, and then we compared rate constants measured in the ionic liquid to those in aqueous and in alcohol solutions.

Experimental Section[11]

Methyltributylammonium bis(trifluoromethylsulfonyl)imide (R_4NNTf_2) was prepared from methyltributylammonium chloride ($MeBu_3N^+Cl^-$) and lithium bis(trifluoromethylsulfonyl)imide ($(CF_3SO_2)_2N^-Li^+$) as described before.[3] The starting materials for this synthesis, as well as 4-mercaptobenzoic acid (MB), *tert*-butyl alcohol (t-BuOH), and *n*-butyl chloride (*n*-BuCl), were obtained from Aldrich. Most other organic solvents were from Mallinckrodt. Water was purified with a Millipore Super-Q system. Fresh solutions were prepared just prior to irradiation, were deoxygenated by bubbling with Ar or N_2 or saturated with the desired gas, and were used within an hour. The pH of the solutions was the natural pH obtained with MB; in aqueous solutions, the pH was generally between 3.6 and 3.8 (unless specified otherwise).

Reaction kinetics and transient spectra were determined by pulse radiolysis. Experiments were carried out with 0.1−1.5 μs pulses of 6 MeV electrons from a Varian linear accelerator; other details were as described before.[12] The dose per pulse was determined by thiocyanate dosimetry.[13] All measurements were performed at room temperature, (22 ± 2) °C. Rate

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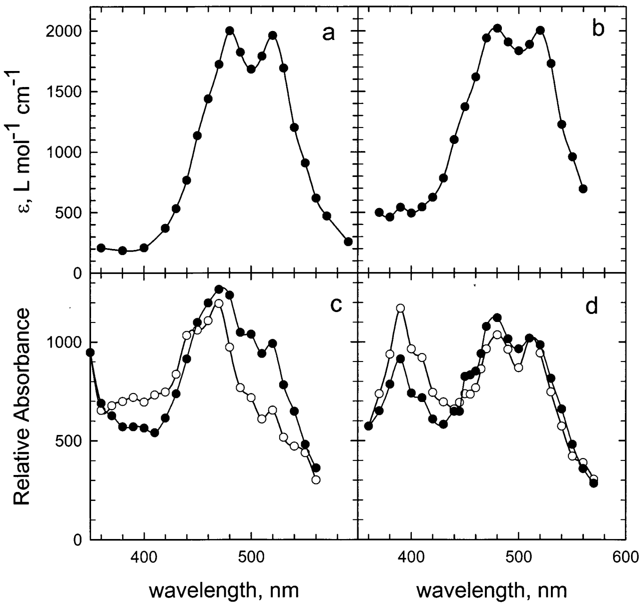

Figure 1. Transient absorption spectra monitored by pulse radiolysis of aqueous alcohol solutions containing 4-mercaptobenzoic acid (MB). (a) 20% v/v *i*-PrOH, 1 mmol L^{-1} MB, pH 3.8; saturated with N_2O, monitored 2 μs after the pulse. (b) 20% v/v *t*-BuOH, 3 mmol L^{-1} MB, pH 3.7, saturated with CH_3Cl, monitored 10 μs after the pulse. (c) 10% v/v *t*-BuOH, 1.2 mmol L^{-1} MB, pH 3.8, deoxygenated with N_2, monitored 1 (○) and 10 μs (●) after the pulse. (d) 10% v/v *t*-BuOH, 0.1 mol L^{-1} $HClO_4$, 1.1 mmol L^{-1} MB, monitored 1 (○) and 10 μs (●) after the pulse. The molar absorption coefficients in a and b were determined from thiocyanate dosimetry (taking a radiolytic yield of 0.6 μmol J^{-1} for $(CH_3)_2\dot{C}OH$ and 0.28 μmol J^{-1} for $^{\bullet}CH_2C(CH_3)_2(OH)$), and the relative absorbance scales in c and d are relative to those in a and b; molar absorption coefficients were not calculated for c and d because of the presence of a mixture of radicals.

constants and molar absorption coefficients are reported with their estimated overall standard uncertainties, taking into account the standard deviation of the kinetic measurements and estimated uncertainties in the values of the concentrations.

Results and Discussion

Pulse Radiolysis of 4-Mercaptobenzoic Acid in Aqueous Solutions. Pulse radiolysis of a N_2O-saturated aqueous solution containing 20% *i*-PrOH leads to production of one predominant radical, $(CH_3)_2\dot{C}OH$. The transient absorption spectrum monitored by pulse radiolysis of such a solution containing 1 mmol L^{-1} MB at its natural pH of 3.8 (Figure 1a) exhibits two peaks at 480 and 520 nm. By comparison with the spectrum of the phenylthiyl radical, which has a peak at 460 nm and a shoulder at 480 nm,[9] we ascribe the spectrum in Figure 1a to the 4-carboxyphenylthiyl radical, produced by reaction 4:

$$H_2O \rightsquigarrow e_{aq}^-, H^{\bullet}, {}^{\bullet}OH, H_2, H_2O_2, H^+ \quad (1)$$

$$e_{aq}^- + N_2O + H_2O \rightarrow N_2 + OH^- + {}^{\bullet}OH \quad (2)$$

$$H^{\bullet}/{}^{\bullet}OH + (CH_3)_2CHOH \rightarrow H_2/H_2O + (CH_3)_2\dot{C}OH \quad (3)$$

$$(CH_3)_2\dot{C}OH + HO_2CC_6H_4SH \rightarrow (CH_3)_2CHOH + HO_2CC_6H_4S^{\bullet} \quad (4)$$

The molar absorption coefficient of the 480 nm peak was determined from thiocyanate dosimetry by assuming the same radiolytic yield for production of $(SCN)_2^{\bullet-}$ in N_2O-saturated 0.01 mol L^{-1} SCN^- solution and production of $HO_2CC_6H_4S^{\bullet}$ under the conditions of Figure 1a. The value of 2000 ± 200 L mol^{-1} cm^{-1} determined for $HO_2CC_6H_4S^{\bullet}$ at 480 nm is slightly lower than the value of 2500 L mol^{-1} cm^{-1} reported for $C_6H_5S^{\bullet}$ at 460 nm .[8,9] When the solution is made alkaline (pH 9.5) so that the SH group is dissociated to S^- ($pK_a = 6.5$ for thiophenol), reaction 4 becomes too slow to detect in the pulse radiolysis experiment. This supports the H-abstraction mechanism for formation of the thiyl radical.

The spectrum of the $HO_2CC_6H_4S^{\bullet}$ radical was also recorded in the presence of *t*-BuOH and CH_3Cl (Figure 1b), where the radical is produced via the following reactions:

$$e_{aq}^- + CH_3Cl \rightarrow {}^{\bullet}CH_3 + Cl^- \quad (5)$$

$$^{\bullet}OH + (CH_3)_3COH \rightarrow {}^{\bullet}CH_2C(CH_3)_2(OH) + H_2O \quad (6)$$

$$^{\bullet}CH_3 + HO_2CC_6H_4SH \rightarrow CH_4 + HO_2CC_6H_4S^{\bullet} \quad (7)$$

$$^{\bullet}CH_2C(CH_3)_2(OH) + HO_2CC_6H_4SH \rightarrow (CH_3)_3COH + HO_2CC_6H_4S^{\bullet} \quad (8)$$

In these experiments, the primary radicals of water radiolysis are converted to two different carbon-centered radicals, both of which abstract H from the SH group. If the primary radicals are allowed to react with MB, different products are formed. In deoxygenated *t*-BuOH aqueous solutions, the spectrum of the $HO_2CC_6H_4S^{\bullet}$ radical is observed along with an additional overlapping absorption with a peak near 460 nm (Figure 1c), which is probably due to the electron adduct $(HO_2CC_6H_4SH)^{\bullet-}$ or its protonated form $(H_2O_2CC_6H_4SH)^{\bullet}$:[14]

$$e_{aq}^- + HO_2CC_6H_4SH \rightarrow (HO_2CC_6H_4SH)^{\bullet-} \quad (9)$$

The possibility that e_{aq}^- reacts also by eliminating SH^- cannot be ruled out because it would be difficult to observe the carboxyphenyl radical produced in such a reaction.[15] In the presence of *t*-BuOH and a strong acid, to convert e_{aq}^- into $H^{\bullet}$, the spectrum of the H adduct of MB is observed, with a peak at 390 nm (Figure 1d), along with the spectrum of the thiyl radical:

$$e_{aq}^- + H^+ \rightarrow H^{\bullet} \quad (10)$$

$$H^{\bullet} + HO_2CC_6H_4SH \rightarrow (HO_2CC_6H_5SH)^{\bullet} \quad (11)$$

Partial reaction of $^{\bullet}H$ atoms at the SH group to produce the thiyl radical cannot be ruled out. The experiments in Figure 1, parts c and d, are not meant to provide a complete description of the reactions of MB with primary radiolytic species but rather to indicate that such species must be scavenged by other solutes if quantitative formation of the thiyl radical is to be observed. Such conditions are used for measuring the thiyl radical formation kinetics.

The rate constant for reaction 4 was determined by following the formation of the thiyl radical absorption at 480 nm as a function of [MB]. The kinetic traces (a sample is in Figure 2a) were fitted to a first-order rate law to calculate k_{obs}, and a plot of k_{obs} vs [MB] (Figure 2c) yields a second-order rate constant $k_4 = (1.4 \pm 0.2) \times 10^9$ L mol^{-1} s^{-1}. Similar experiments with N_2O-saturated solutions containing MeOH, EtOH, *t*-BuOH, or *p*-dioxane gave the rate constants for reactions of MB with the radicals derived from these solutes (Table 1). The rate constant for $^{\bullet}CH_3$ radicals was determined in the presence of CH_3Cl and *t*-BuOH, where both $^{\bullet}CH_3$ and $^{\bullet}CH_2C(CH_3)_2(OH)$ are produced.[16] Only one step, forming a full yield of the MB radical,

TABLE 1: Rate Constants for Reactions of Radicals with 4-Mercaptobenzoic Acid in Aqueous and Organic Media

medium[a]	radical	k, L mol^{-1} s^{-1}
H_2O, 20% t-BuOH, N_2O	$^{\bullet}CH_2C(CH_3)_2OH$	$(1.4 \pm 0.2) \times 10^8$
t-BuOH, N_2O	$^{\bullet}CH_2C(CH_3)_2OH$	$(1.2 \pm 0.3) \times 10^8$
H_2O, 20% t-BuOH, CH_3Cl	$^{\bullet}CH_3 + {}^{\bullet}CH_2C(CH_3)_2OH$	$(1.9 \pm 0.3) \times 10^8$
	$^{\bullet}CH_3$[b]	$\approx 2.4 \times 10^8$
H_2O, 20% i-PrOH, N_2O	$(CH_3)_2\dot{C}OH$	$(1.4 \pm 0.2) \times 10^9$
H_2O, 20% i-PrOH, pH 0.7, N_2	$(CH_3)_2\dot{C}OH$	$(1.3 \pm 0.3) \times 10^9$
i-PrOH, N_2O	$(CH_3)_2\dot{C}OH$	$(1.2 \pm 0.2) \times 10^9$
H_2O, 20% EtOH, N_2O	$CH_3\dot{C}HOH$	$(6.4 \pm 1.0) \times 10^8$
EtOH, N_2O	$CH_3\dot{C}HOH$	$(4.9 \pm 0.8) \times 10^8$
H_2O, 20% MeOH, N_2O	$^{\bullet}CH_2OH$	$(3.0 \pm 0.5) \times 10^8$
MeOH, N_2O	$^{\bullet}CH_2OH$	$(1.8 \pm 0.3) \times 10^8$
H_2O, 10% *p*-dioxane, N_2O	$^{\bullet}CHOCH_2CH_2OCH_2$	$(4.1 \pm 0.6) \times 10^8$
p-dioxane, N_2O	$^{\bullet}CHOCH_2CH_2OCH_2$	$(2.3 \pm 0.4) \times 10^8$
H_2O, 20% acetone	$(CH_3)_2\dot{C}OH$	$(1.4 \pm 0.3) \times 10^9$
	$^{\bullet}CH_2COCH_3$	$\leq 1 \times 10^7$
H_2O, 20% $(CH_2OH)_2$, N_2O	$HOCH_2\dot{C}HOH$	$(1.5 \pm 0.2) \times 10^8$
H_2O, 20% $(CH_2OH)_2$, pH 0.7	$^{\bullet}CH_2CHO$	$\leq 1 \times 10^7$
H_2O, 20% t-BuOH, 1% acetone	$(CH_3)_2\dot{C}OH$	$(1.4 \pm 0.3) \times 10^9$
	$^{\bullet}CH_2C(CH_3)_2OH$	$(1.0 \pm 0.2) \times 10^8$
H_2O, 20% n-PrOH, N_2O	$CH_3CH_2\dot{C}HOH$	$(8.2 \pm 1.6) \times 10^8$
	$CH_3\dot{C}HCH_2OH$	$(6.8 \pm 1.3) \times 10^7$

[a] The fraction of the cosolvent is given in volume percent, and the mixture is saturated with the indicated gas. If no gas is indicated, the solution was deoxygenated by bubbling with Ar or N_2. The pH of the solution was the natural pH due to MB, generally between 3.6 and 3.8, unless noted otherwise. [b] Rate constant estimated from that measured for the mixture and for $^{\bullet}CH_2C(CH_3)_2OH$ alone.

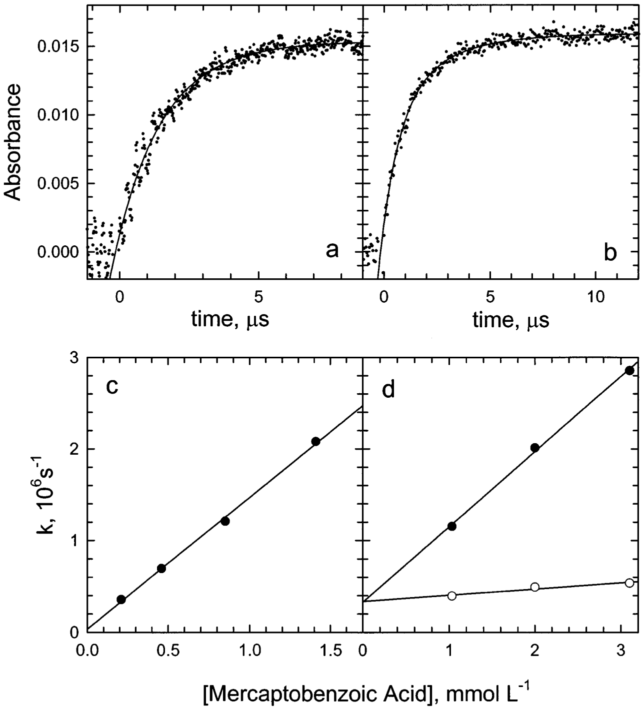

Figure 2. Rate constants for reaction of 4-mercaptobenzoic acid with the radicals derived from *i*-PrOH (a and c) and *n*-PrOH (b and d). a and b are sample kinetic traces at 480 nm recorded by pulse radiolysis of aqueous solutions containing 20% v/v of the alcohol and 0.5 or 1.0 mmol L^{-1} MB at pH 3.7 to 3.9. The trace in a is fitted to one exponent, and that in b is fitted to two exponents. The rate constants derived from such traces are plotted in c and d vs the concentration of MB to derive the second-order rate constants.

was observed, indicating that these two radicals react with similar rate constants. By comparing the rate constant determined for this mixture ($k = (1.9 \pm 0.3) \times 10^8$ L mol^{-1} s^{-1}) with that determined for $^{\bullet}CH_2C(CH_3)_2(OH)$ alone ($k = (1.4 \pm 0.2) \times 10^8$ L mol^{-1} s^{-1}) and because the yields of the two radicals are nearly equal, we estimate the rate constant for reaction of $^{\bullet}CH_3$ as $k \approx 2.4 \times 10^8$ L mol^{-1} s^{-1}.

In contrast with the *t*-BuOH/CH_3Cl system, where only one formation step was evident, a mixture of *t*-BuOH and acetone, to produce $^{\bullet}CH_2C(CH_3)_2(OH)$ by reaction 6 and $(CH_3)_2\dot{C}OH$ by reactions 12 and 13

$$e_{aq}^{-} + (CH_3)_2CO \rightarrow (CH_3)_2\dot{C}O^{-} \qquad (12)$$

$$(CH_3)_2\dot{C}O^{-} + H_2O \leftrightarrows (CH_3)_2\dot{C}OH + OH^{-} \qquad (13)$$

showed formation of the thiyl radical in more complex kinetics. The traces could not be fitted to one exponential formation and were fitted to two exponentials, from which we derive rate constants that are in good agreement with the rate constants for the two radicals determined independently (Table 1). This experiment was undertaken to test the validity of fitting the kinetic traces to two exponents. Such fits were then used to study the case of *n*-PrOH, where two radicals are formed with nearly equal yields ($\alpha/\beta = 54/46$),[17] $CH_3CH_2\dot{C}HOH$ and $CH_3\dot{C}HCH_2OH$. The results for *n*-PrOH are demonstrated in Figure 2, parts b and d, and the rate constants derived differ by an order of magnitude. By comparison with the results obtained for the radicals of *i*-PrOH, EtOH, and *t*-BuOH, we ascribe the faster rate constant of $(8.2 \pm 1.6) \times 10^8$ L mol^{-1} s^{-1} to $CH_3CH_2\dot{C}HOH$ and the slower rate constant of $(6.8 \pm 1.3) \times 10^7$ L mol^{-1} s^{-1} to $CH_3\dot{C}HCH_2OH$.

Experiment with CH_3Cl-saturated solutions containing 20% v/v *i*-PrOH permit observation of reactions 4 and 7 in parallel. By fitting the traces to two exponentials, we derived rate constants for reactions 4 and 7 that are identical to those given in Table 1. Attempts to determine the rate constant for $^{\bullet}CF_3$ radicals by using *t*-BuOH/CF_3Br or *t*-BuOH/CF_3Cl aqueous solutions failed because of the limited solubility of CF_3Br and CF_3Cl in this solvent mixture (only ≈ 5 mmol L^{-1}, even with higher % alcohol), which is not sufficient for scavenging a substantial fraction of the e_{aq}^{-} in competition with MB.

An attempt to determine the rate constant for $^{\bullet}CH_2COCH_3$ was made by using 0.2 volume fraction acetone to scavenge both e_{aq}^{-} and $^{\bullet}OH$, i.e., to produce $(CH_3)_2\dot{C}OH$ via reactions 12 and 13 and $^{\bullet}CH_2COCH_3$ via reaction 14:

$$^{\bullet}OH + CH_3COCH_3 \rightarrow H_2O + {}^{\bullet}CH_2COCH_3 \qquad (14)$$

The results gave the rate constant for $(CH_3)_2\dot{C}OH$ and indicated that the value for $^\bullet CH_2COCH_3$ is too low to be detected under these conditions (Table 1). To support the low reactivity of $^\bullet CH_2COCH_3$, we examined the $^\bullet CH_2CHO$ radical formed from ethylene glycol in acidic solutions.[18]

$$H^\bullet/^\bullet OH + HOCH_2CH_2OH \rightarrow H_2/H_2O + HOCH_2\dot{C}HOH \quad (15)$$

$$HOCH_2\dot{C}HOH \rightarrow H_2O + {}^\bullet CH_2CHO \quad (16)$$

Pulse irradiation of aqueous solutions containing 0.2 volume fraction ethylene glycol and various concentrations of MB at pH 3.6 to 3.8 gave a rate constant of 1.5×10^8 L mol^{-1} s^{-1} for the $HOCH_2\dot{C}HOH$ radical. At pH 0.7, where $HOCH_2\dot{C}HOH$ is rapidly converted into $^\bullet CH_2CHO$ by water elimination (reaction 16), <20% of the thiyl radical absorbance was formed rapidly, because of partial reaction of $HOCH_2\dot{C}HOH$ with MB occurring in parallel with reaction 16, but no reaction ascribable to $^\bullet CH_2CHO$ was observed. We estimate the rate constant for the reaction of the latter radical with MB to be $\leq 1 \times 10^7$ L mol^{-1} s^{-1}. It should be mentioned in this context that the reaction of $(CH_3)_2\dot{C}OH$ with MB took place with nearly the same rate constant at pH 0.7 as at pH 3.7. The oxidizing radical $^\bullet CH_2CHO$ can be produced also in alkaline solutions, but under these conditions (pH 12.3), it was found to react rapidly ($k = (1.6 \pm 0.3) \times 10^8$ L mol^{-1} s^{-1}) with MB to produce the thiyl radical. This reaction involves oxidation of the ionized form, $^-SPhCO_2^-$. On the other hand, the reducing radicals $(CH_3)_2\dot{C}OH$ and $(CH_3)_2\dot{C}O^-$ do not react with $^-SPhCO_2^-$ ($k \leq 1 \times 10^7$ L mol^{-1} s^{-1}).

The reactions of the various radicals with ArSH (Table 1) take place via hydrogen abstraction to form the $ArS^\bullet$ radical. This is clear from the facts that the reactions do not occur when ArSH is ionized to ArS^- and that ArS^-, but not ArSH, reacts rapidly with oxidizing radicals to form $ArS^\bullet$. By comparing the rate constants for hydrogen abstraction from MB by various substituted alkyl radicals in aqueous solutions (Table 1), we notice that reducing radicals ($CH_3\dot{C}HOH$ and $(CH_3)_2\dot{C}OH$) react more rapidly than simple alkyl radicals. The same trend was observed for the reactions of $^\bullet CH_3$, $^\bullet CH_2OH$, $CH_3\dot{C}HOH$, and $(CH_3)_2\dot{C}OH$ with aliphatic thiols.[19] The increased reactivity of the reducing radicals is in opposite direction to that expected on the basis of bond dissociation energies (BDE). Alpha C−H bonds in alcohols[20] and ethers have BDEs that are 10−20 kJ mol^{-1} lower than those in alkanes,[7] and thus, hydroxyalkyl and alkoxyalkyl radicals are expected to react more slowly than simple alkyl radicals in hydrogen abstraction reactions. The finding that they react more rapidly with MB indicates an additional effect that is more important than the thermodynamic driving force. The BDEs of the S−H bond in thiophenols are in the range of 325−335 kJ mol^{-1}.[6] The BDEs of the C−H bonds for the radicals in Table 1 vary from 440 kJ mol^{-1} for CH_3−H[7] to 395 kJ mol^{-1} for $(CH_3)_2C(OH)$−H.[20] Thus, the thermodynamic driving force is sufficiently large even for the weakest C−H bond to make the reaction very rapid. Possibly, the difference in the reactivity of the various radicals is due to differences in electron density at the radical site. Hydroxyl, alkoxyl, and alkyl groups at the alpha position increase the electron density at the radical site, thus increasing the reducing power of the radical. Reducing alkyl radicals react with MB faster than nonreducing alkyl radicals possibly because the higher electron density at the radical site facilitates formation of a polar −C···H···S− transition state. The slowness of the reaction of the oxidizing radicals $^\bullet CH_2COCH_3$ and $^\bullet CH_2CHO$ is probably due to an opposite effect, a lower electron density at the radical site because of electron withdrawing by the carbonyl group. The results with $^\bullet CF_3$ radicals in the ionic liquid described below suggest that electron withdrawing by the fluorine atoms also decreases the rate constant.

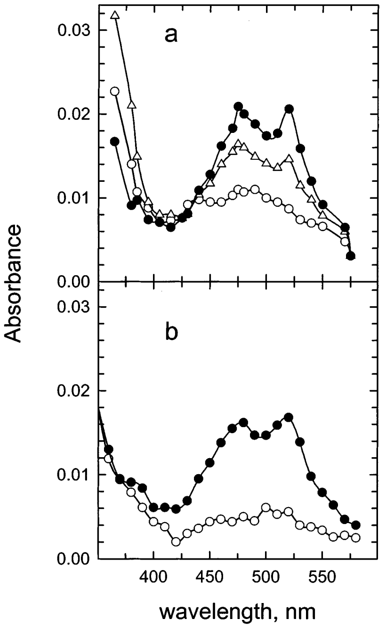

Figure 3. Transient absorption spectra monitored by pulse radiolysis of R_4NNTf_2 containing 4-mercaptobenzoic acid (MB). (a) 11 mmol L^{-1} MB, monitored 1 (○), 10 (△), and 90 *μ*s (●) after the pulse. (b) 11 mmol L^{-1} MB, saturated with CF_3Br, monitored 2 (○) and 90 *μ*s (●) after the pulse.

Rate constants for reactions of MB with the radicals derived from MeOH, EtOH, *i*-PrOH, *t*-BuOH, and *p*-dioxane were also measured in the respective organic solvents in the absence of water (Table 1). The rate constants are slightly lower in the organic solvents than in water/organic solvent mixtures, supporting a polar transition state for these H-abstraction reactions.

Pulse Radiolysis of 4-Mercaptobenzoic Acid in the Ionic Liquid. Radiolysis of neat R_4NNTf_2 leads to production of solvated electrons, protons, radical cations, and neutral radicals.The solvated electrons do not react with the solvent ions,

$$(R_4N)^+(NTf_2)^- \rightsquigarrow e_{solv}^-, H^+, R_4N^{\bullet 2+}, NTf_2^\bullet, R^\bullet \quad (17)$$

R_4N^+ and NTf_2^-, and can be scavenged by reactive solutes.[3] The oxidized species formed in reaction 17, and the excited species formed by geminate recombination, may undergo fragmentation or deprotonation. These fragment radicals include $^\bullet CF_3$.[4] Saturating the solutions with CF_3Br leads to production of additional $^\bullet CF_3$ radicals via reaction 18:[4]

$$e_{solv}^- + CF_3Br \rightarrow {}^\bullet CF_3 + Br^- \quad (18)$$

The transient absorption spectra recorded with MB solutions in R_4NNTf_2 in the presence and absence of CF_3Br (Figure 3) show a small absorbance in the 450−500 nm region within 1 *μ*s after the pulse, and this grows over 100 *μ*s to give a clear double-peak spectrum of the $HO_2CC_6H_4S^\bullet$ radical. In the absence of CF_3Br, there was also an initial absorbance below 400 nm, which decayed within 50 *μ*s and is probably associated with reaction of MB with solvated electrons. This absorbance was not characterized further because the solution does not transmit light at lower wavelengths.

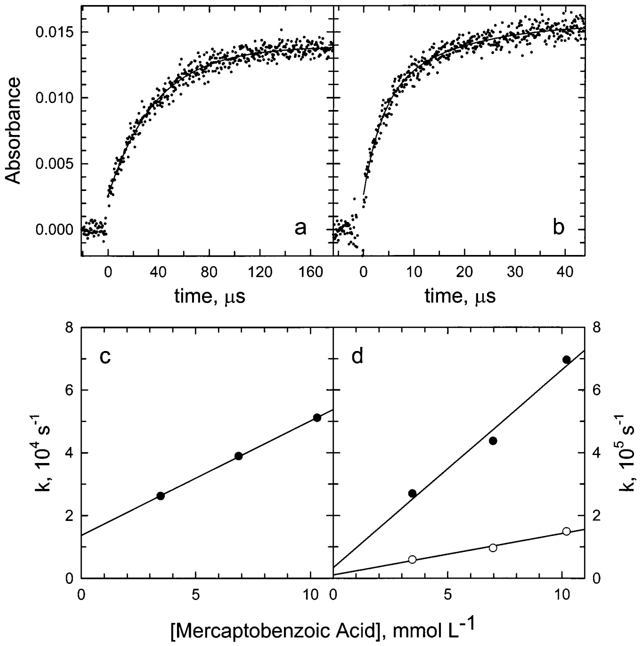

Figure 4. Rate constants for reaction of 4-mercaptobenzoic acid with radicals in irradiated R_4NNTf_2 saturated with CF_3Br (a and c) or CH_3Cl (b and d). a and b are sample kinetic traces at 480 nm recorded with 3.5 mmol L^{-1} MB; the trace in a is fitted to one exponent, and that in b is fitted to two exponents. The rate constants derived from such traces are plotted in c and d vs the concentration of MB to derive the second-order rate constants.

The formation kinetics of $HO_2CC_6H_4S^\bullet$ at 480 nm in the presence of CF_3Br obeys a clean first-order rate law (Figure 4a). This finding indicates that reactions of MB with other radicals derived from the solvent are negligible under these conditions. From the dependence of k_{obs} on [MB] (Figure 4c) we derive $k = (3.6 \pm 0.8) \times 10^6$ L mol^{-1} s^{-1} for reaction 19 in the ionic liquid:

$$^\bullet CF_3 + HO_2CC_6H_4SH \rightarrow CHF_3 + HO_2CC_6H_4S^\bullet \qquad (19)$$

In the absence of CF_3Br, MB reacts with $^\bullet CF_3$ and with other solvent radicals but only one kinetic process was discerned. A rate constant of 4.7×10^6 L mol^{-1} s^{-1} was determined in acidic solutions, and 1.0×10^7 L mol^{-1} s^{-1} was found when no strong acid was added. Because of the unknown mixture of radicals, derived from the solvent and also from MB upon reaction with solvated electrons or hydrogen atoms, we cannot ascribe the measured rate constants to specific reactions, but we use them as background information for subsequent experiments with other additives.

Addition of CH_3Cl to scavenge the solvated electrons leads to production of $^\bullet CH_3$ radicals and to the observation of two kinetic steps in the production of $HO_2CC_6H_4S^\bullet$. By fitting the kinetic traces to two exponents (Figure 4b), we derive two rate constants (Figure 4d): a slow reaction with $k = (9.6 \pm 2.3) \times 10^6$ L mol^{-1} s^{-1} is ascribed to the various solvent radicals, and a faster reaction with $k = (6.4 \pm 1.6) \times 10^7$ L mol^{-1} s^{-1} is ascribed to reaction with $^\bullet CH_3$ radicals (Table 2).

Similar results were obtained when *n*-BuCl was added instead of CH_3Cl. With 5% *n*-BuCl, the faster rate constant of 1.0×10^8 L mol^{-1} s^{-1}, ascribed to reaction of *n*-butyl radical, is slightly higher than that for methyl radical, but the slower rate constant of 2.7×10^7 L mol^{-1} s^{-1} is three times as fast as that determined with CH_3Cl. Because the slower step is expected to have a similar rate constant in both systems, we suspected that the higher value observed with 5% *n*-BuCl as compared with CH_3Cl-saturated solutions may be due to a lower viscosity of the former solution. Indeed, when we used only 1% *n*-BuCl, we obtained 2.5 times lower rate constants (Table 2), with the slow reaction now having a rate constant similar to that under CH_3Cl. The viscosity of the 5% *n*-BuCl solution was 0.288 Pa s, as compared with 0.527 Pa s for the 1% *n*-BuCl solution. Because the ratio of rate constants (2.5) in the two solutions is close to the ratio of viscosities (1.8), it is likely that these reactions are controlled in part by the diffusion.

TABLE 2: Rate Constants for Reactions of Radicals with 4-Mercaptobenzoic Acid in the Ionic Liquid

medium[a]	radical	*k*, L mol^{-1} s^{-1}
R_4NNTf_2, CF_3Br[b]	$^\bullet CF_3$	$(3.6 \pm 0.8) \times 10^6$
R_4NNTf_2, 0.2 mol L^{-1} acid	misc.	$(4.7 \pm 0.8) \times 10^6$
R_4NNTf_2	misc.	$(1.0 \pm 0.2) \times 10^7$
R_4NNTf_2, CH_3Cl[c]	$^\bullet CH_3$	$(6.4 \pm 1.6) \times 10^7$
	misc.	$(9.6 \pm 2.3) \times 10^6$
R_4NNTf_2, $N_2/CH_3Cl = 4/1$	$^\bullet CH_3$	$(6.1 \pm 1.6) \times 10^7$
	misc.	$(8.5 \pm 2.1) \times 10^6$
R_4NNTf_2, 5% *n*-BuCl	$^\bullet CH_2CH_2CH_2CH_3$	$(1.0 \pm 0.3) \times 10^8$
	misc.	$(2.7 \pm 0.9) \times 10^7$
R_4NNTf_2, 1% *n*-BuCl	$^\bullet CH_2CH_2CH_2CH_3$	$(4.0 \pm 1.3) \times 10^7$
	misc.	$(1.0 \pm 0.3) \times 10^7$
R_4NNTf_2, 5% acetone	$(CH_3)_2\dot{C}OH$	$(1.3 \pm 0.3) \times 10^8$
	misc.	$(2.6 \pm 0.7) \times 10^7$
R_4NNTf_2, 1% acetone	$(CH_3)_2\dot{C}OH$	$\approx 2 \times 10^7$
	misc.	$\approx 4 \times 10^6$

[a] The fraction of the cosolvent is given in volume percent, and the mixture is saturated with the indicated gas. If no gas is indicated, the solution was deoxygenated by bubbling with Ar or N_2. [b] The concentration of CF_3Br in saturated ionic liquid was estimated from the increase in weight to be ≈0.2 mol L^{-1}. [c] The concentration of CH_3Cl in saturated ionic liquid was estimated from the increase in weight (≈3.85 w%) to be ≈0.95 mol L^{-1}.

Because of the effect of *n*-BuCl concentration on the solution viscosity and the rate constant, we examined the effect of CH_3Cl concentration by comparing the results in CH_3Cl-saturated solutions with results in solutions saturated with a 4/1 mixture of N_2/CH_3Cl. The rate constants were found to be the same. This finding suggests that dissolution of CH_3Cl up to the saturation level of ≈4 wt % has no significant effect on the viscosity of R_4NNTf_2. We are not able to measure the viscosity of this mixture because of the loss of CH_3Cl during such measurements.

To determine the rate constant for reaction of MB with $(CH_3)_2\dot{C}OH$, we added acetone as an electron scavenger that will produce $(CH_3)_2\dot{C}OH$ via reactions 12 and 13. Two steps were observed, with rate constants that differ by a factor of 5. Although the rate constants with 1% acetone have greater uncertainties that those determined with 5% acetone, because of smaller signals, it was clear that the rate constants are significantly higher with 5% acetone than with 1%, again because of the decrease in viscosity (from 0.49 Pa s with 1% acetone to 0.21 Pa s with 5% acetone).

In summary, rate constants for reactions of MB in the ionic liquid R_4NNTf_2 can be determined for radicals that can be produced by reaction of a solute with solvated electrons. However, because radiolysis of the ionic liquid also produces other radicals that can react with MB, the desired reactions of solute-derived radicals take place in parallel with reactions of the solvent-derived radicals. This necessitates more complex kinetic calculations and increases the uncertainties of the rate constants. The overall standard uncertainties for these rate constants are estimated to be ±25% to 30%, whereas the overall standard uncertainties for the kinetic measurements in aqueous solutions were generally between 10% and 20%. Despite these uncertainties, it is clear that the rate constant for reaction of $^{\bullet}CH_3$ with MB in the ionic liquid is lower than that in aqueous solutions by a factor of 4 and that this difference may be due mainly to the diffusion limit in the viscous ionic liquid. The rate constant for the reaction of $(CH_3)_2\dot{C}OH$ with MB in the ionic liquid is 1 or 2 orders of magnitude lower than that in aqueous solutions, depending on the medium viscosity, again indicating a diffusion-controlled reaction. As a result of the diffusion limit, the rate constant for $(CH_3)_2\dot{C}OH$ in the ionic liquid is not found to be higher than the rate constants for $^{\bullet}CH_3$ and $^{\bullet}CH_2CH_2CH_2CH_3$, although the rate constant for $^{\bullet}CF_3$ radicals is significantly lower. The low reactivity of $^{\bullet}CF_3$, despite the high $H-CF_3$ BDE, is probably due to electron withdrawing by the F atoms which makes this radical behave like the other oxidizing radicals studied in aqueous solutions (but could not be studied in the ionic liquid). Thus, experimental rate constants for H abstraction from 4-mercaptobenzoic acid by alkyl radicals in the ionic liquid are lower than those in water or alcohols, mainly because of increased viscosity. Because the effect of solvent polarity on such reactions is relatively small, it is not possible to discern whether the ionic liquid behaves as a polar or nonpolar solvent. Rate constants for H-abstraction and addition reactions of $^{\bullet}CF_3$ radicals with several compounds other than MB, which are much lower than the diffusion-controlled limit, were found[4] to be lower than those in acetonitrile and aqueous solutions by a factor of ≤ 4. On the other hand, rate constants for electron-transfer reactions were found[3] to be one or more orders of magnitude lower in ionic liquids than in water or alcohols. All of these results are in line with the suggestion that ionic liquids behave as solvents of low polarity because of extensive association of their cations and anions.

Note Added in Proof. The order of reactivity of hydroxyalkyl radicals with thiols was also noted and given a detailed theoretical treatment by: Reid, D. L.; Shustov, G. V.; Armstrong, D. A.; Rauk, A.; Schuchmann, M.-N.; Akhlag, M. S.; von Sonntag, C. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2965.

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