Reaction Kinetics in the Ionic Liquid Methyltributylammonium Bis(Trifluoromethylsulfonyl)imide. Pulse Radiolysis Study of $^{\bullet}CF_3$ Radical Reactions

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Received: January 17, 2002; In Final Form: March 19, 2002

The reactions of trifluoromethyl radicals with pyrene, phenanthrene, crotonic acid, and 2-propanol (2-PrOH) in the ionic liquid methyltributylammonium bis(trifluoromethylsulfonyl)imide (R_4NNTf_2) are studied by pulse radiolysis. Radiolysis of R_4NNTf_2 leads to formation of solvated electrons and organic radicals, including $^{\bullet}CF_3$. The solvated electrons do not react rapidly with the solvent and are reacted with CF_3Br to produce additional $^{\bullet}CF_3$ radicals. The rate constants for addition of $^{\bullet}CF_3$ radicals to pyrene and phenanthrene are determined to be $(1.1 \pm 0.1) \times 10^7$ L mol^{-1} s^{-1} and $(2.6 \pm 0.4) \times 10^6$ L mol^{-1} s^{-1}, respectively. By competition kinetics, the rate constant for reaction of $^{\bullet}CF_3$ radicals with crotonic acid is determined to be $(2.7 \pm 0.4) \times 10^6$ L mol^{-1} s^{-1}, and the reaction is predominantly addition to the double bond. Competition kinetics with 2-PrOH in the absence of CF_3Br gives a rate constant of $(4 \pm 1) \times 10^4$ L mol^{-1} s^{-1} for H-abstraction from 2-PrOH, but in the presence of CF_3Br, the rate constant cannot be determined because a chain reaction develops through the reduction of CF_3Br by the $(CH_3)_2\dot{C}OH$ radical. The rate constants for reactions of $^{\bullet}CF_3$ radicals in acetonitrile solutions are slightly higher, by a factor of 2.3 for pyrene and phenanthrene and a factor of 1.3 for crotonic acid. The rate constant for pyrene in aqueous acetonitrile (30% water) solutions is 4 times higher than that in the ionic liquid. Rate constants for H-abstraction and addition reactions of $^{\bullet}CF_3$ radicals in the ionic liquid are of the same order of magnitude as in water and acetonitrile, whereas electron-transfer reactions were reported to be one or more orders of magnitude slower in ionic liquids than in water or alcohols.

Introduction

Room-temperature ionic liquids[1] serve as good solvents for various thermal and electrochemical reactions, are nonvolatile and nonflammable, and have been proposed as "green solvents" for various industrial 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, mainly because of the high viscosity of the ionic liquids. Some of the rate constants in the ionic liquids were close to the diffusion-controlled limit in those solvents, and in the case of electron transfer from the butylpyridinyl radical to various solutes in $BuPyBF_4$, the rate constants were higher than the diffusion limit, suggesting electron hopping through solvent cations. In this study, we examine two other types of reaction, addition and hydrogen abstraction. For this purpose, we chose the ionic liquid R_4NNTf_2. Solvated electrons produced by the radiolysis of R_4NNTf_2 do not react rapidly with this solvent and can be scavenged by alkyl halides to produce alkyl radicals. In the present study, we examine the reactions of $^{\bullet}CF_3$ radicals with pyrene, phenanthrene, crotonic acid, and 2-propanol (2-PrOH) and compare the rate constants in the ionic liquid with those in acetonitrile and in aqueous acetonitrile solutions.

Experimental Section[4]

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%). The starting materials for this synthesis were obtained from Aldrich. Phenanthrene, crotonic acid ($CH_3CH{=}CHCO_2H$), valeric acid ($CH_3CH_2CH_2CH_2CO_2H$), and triethylamine (TEA) were also from Aldrich, pyrene from Eastman, and acetonitrile and 2-propanol from Mallinckrodt. Ultrahigh purity nitrogen and bromotrifluoromethane were obtained from Matheson. Water was purified with a Millipore Super-Q system.

Reaction kinetics and transient spectra in ionic liquids 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.[5] The dose per pulse was determined by thiocyanate dosimetry.[6] All measurements were performed at room temperature, 22 ± 2 °C. Rate 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.

10.1021/jp020165p

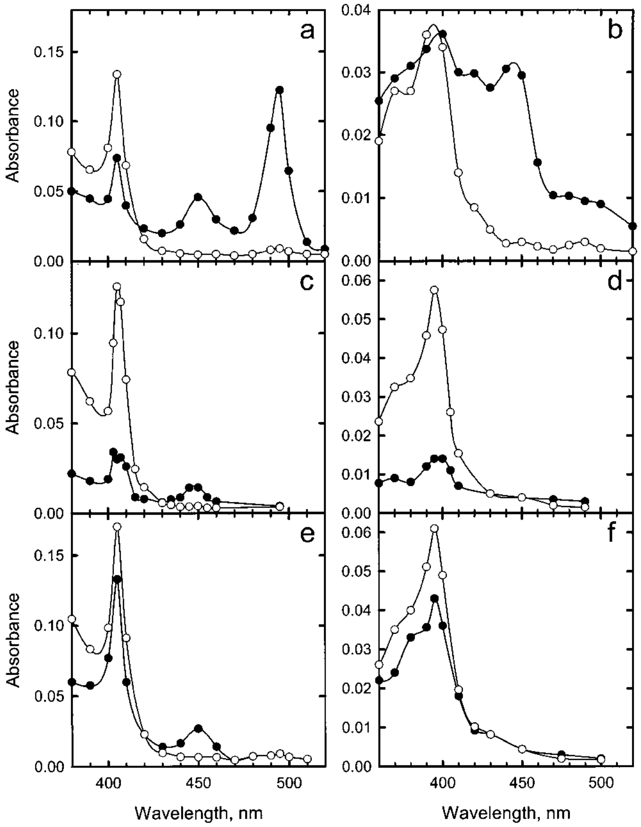

Figure 1. Transient absorption spectra monitored by pulse radiolysis of deoxygenated R_4NNTf_2 containing pyrene or phenanthrene: (a) 18 mmol L^{-1} pyrene; (b) 17 mmol L^{-1} phenanthrene; (c) 6 mmol L^{-1} pyrene saturated with CF_3Br; (d) 16 mmol L^{-1} phenanthrene saturated with CF_3Br; (e) 20 mmol L^{-1} pyrene with 0.2 mol L^{-1} $HClO_4$ added; (f) 19 mmol L^{-1} phenanthrene with 0.2 mol L^{-1} $HClO_4$ added. The spectra were recorded 1−2 (●) and 50−90 μs (○) after the pulse.

Results and Discussion

Pulse Radiolysis of Pyrene and Phenanthrene. Radiolysis of neat R_4NNTf_2 leads to production of solvated electrons, protons, radical cations, and neutral radicals.

$$(R_4N)^+(NTf_2)^- \rightsquigarrow e^-_{solv}, H^+, R_4N^{\bullet 2+}, NTf_2^{\bullet}, R^{\bullet} \tag{1}$$

The solvated electrons do not react with the solvent ions, R_4N^+ and NTf_2^-, and can be scavenged by reactive solutes.[3] The oxidized species formed in reaction 1, and excited species formed by geminate recombination, may undergo fragmentation or deprotonation. These fragment radicals include $^{\bullet}CF_3$.[7] In the present study, we saturate the solutions with CF_3Br to produce additional $^{\bullet}CF_3$ radicals via reaction 2.

$$e^-_{solv} + CF_3Br \rightarrow {}^{\bullet}CF_3 + Br^- \tag{2}$$

The rate constant for reaction 2 is diffusion-controlled in aqueous solutions[8] and is expected to be high in the ionic liquid as well. The reactions of $^{\bullet}CF_3$ radicals with several solutes were studied by pulse radiolysis.

Pulse irradiation of deoxygenated R_4NNTf_2 containing pyrene leads to rapid production of several species with optical absorption peaks at 405, 450, and 495 nm, and after 50 μs only the 405 nm peak remains and is more intense (Figure 1a). The 495 nm peak is clearly ascribable to the pyrene radical anion[9,10] and its decay may be due to protonation[11] by traces of water or oxidation by other transient species.

$$e^-_{solv} + Pyr \rightarrow Pyr^{\bullet -} \tag{3}$$

$$Pyr^{\bullet -} + H^+ \rightarrow {}^{\bullet}PyrH \tag{4}$$

The 450 nm peak is partly due also to the pyrene radical anion[9,10] and partly to the pyrene radical cation,[10,12] the latter species decaying probably via hydroxylation by traces of water or reduction by other transient species. The 405 nm peak is ascribed to the pyrene H-adduct (i.e., the protonated pyrene radical anion), part of which is produced rapidly and part of which is produced during the protonation of the radical anion (reaction 4). In addition, it is expected that $^{\bullet}CF_3$ radicals formed from the solvent would add to pyrene and produce a CF_3-adduct with a spectrum that may be similar to that of the H-adduct. This suggestion is confirmed below.

Pulse radiolysis of a similar pyrene solution saturated[13] with CF_3Br (Figure 1c) does not produce the radical anion absorption at 495 nm because the solvated electrons are captured by CF_3Br (reaction 2). The absorption peak at 450 nm is observed (Figure 1c) but is less intense than that in the absence of CF_3Br (Figure 1a), indicating that both the radical anion and the cation contribute to the 450 nm absorption. The final absorption peak at 405 nm, however, remains as intense in the presence of CF_3Br (Figure 1c), indicating that $^{\bullet}CF_3$ radicals indeed react with pyrene to produce an adduct that absorbs at 405 nm.

$$Pyr + {}^{\bullet}CF_3 \rightarrow {}^{\bullet}PyrCF_3 \tag{5}$$

In support of these assignments, we found that the 495 nm peak ascribed to the pyrene radical anion was greatly diminished in the presence of other electron scavengers, such as O_2 or N_2O[8] but was not affected by 2-PrOH or TEA. The 450 nm peak, which is due in part to the radical cation, was diminished by TEA as well as by O_2.

The spectrum recorded by pulse radiolysis of a deoxygenated pyrene solution containing 0.2 mol L^{-1} $HClO_4$ lacks the 495 nm absorption (Figure 1e). This result may be due either to a very rapid protonation of the anion radical by the acid (reaction 4) or to competition of the acid for the solvated electrons,[8] which prevents formation of the pyrene radical anion. In either case, $Pyr^{\bullet -}$ is replaced by $^{\bullet}PyrH$, and this is evident from the intense initial absorbance at 405 nm due to $^{\bullet}PyrH$ (Figure 1e). Additional absorbance at 405 nm is formed more slowly due to reaction of $^{\bullet}CF_3$ radicals with pyrene (reaction 5). It should be pointed out that addition of 0.2 mol L^{-1} $HClO_4$ does not result in 0.2 mol L^{-1} of H^+ in the solution. Because the anion of this ionic liquid is a weaker acid ($pK_a = 1.7$),[14] most of the added H^+ will protonate the solvent anion to form $HN(SO_2CF_3)_2$, and it is the reactions of this acid with the pyrene radical anion or with solvated electrons that will determine the outcome of this system. The results of the present study, however, are independent of the relative importance of these two reactions.

Several additional findings support the assignments of the 405 nm peak to $^{\bullet}PyrH$: (a) The H-adduct of pyrenesulfonic acid, observed by pulse radiolysis in acidic aqueous solutions containing *t*-BuOH, has an absorption peak at 415 nm, close to that found for the H-adduct of pyrene in the ionic liquid. (b) The H-adduct of pyrene in acetonitrile solutions containing 0.1 mol L^{-1} $HClO_4$ exhibits a peak at 405 nm, exactly as the peak observed in the ionic liquid. In the absence of acid, the 495 nm peak of $Pyr^{\bullet -}$ was observed. The H-adduct of pyrene in methanolic solutions was reported to have a peak at 400 nm.[15] (c) Addition of propene to the acidic ionic liquid pyrene solution greatly diminishes the intensity of the 405 nm peak. Because

TABLE 1: Rate Constants for Reactions of $^{\bullet}CF_3$ Radicals

reactant	medium	k, L mol^{-1} s^{-1}
pyrene	R_4NNTf_2, CF_3Br	$(1.1 \pm 0.15) \times 10^7$
	R_4NNTf_2, acidic	$(1.3 \pm 0.25) \times 10^7$
phenanthrene	R_4NNTf_2, CF_3Br	$(2.6 \pm 0.4) \times 10^6$
	R_4NNTf_2, acidic	$(3.2 \pm 0.6) \times 10^6$
crotonic acid	R_4NNTf_2, CF_3Br	$(2.9 \pm 0.5) \times 10^6$ [a]
		$(2.5 \pm 0.5) \times 10^6$ [b]
valeric acid	R_4NNTf_2, CF_3Br	$\leq 1 \times 10^4$ [a]
2-propanol	R_4NNTf_2, acidic	$(4 \pm 1) \times 10^4$ [a]
pyrene	acetonitrile, CF_3Br	$(2.7 \pm 0.4) \times 10^7$
phenanthrene	acetonitrile, CF_3Br	$(7.1 \pm 1.2) \times 10^6$
crotonic acid	acetonitrile, CF_3Br	$(3.4 \pm 0.7) \times 10^6$ [a]
acetonitrile	acetonitrile, CF_3Br	$\leq 5 \times 10^3$
pyrene	acetonitrile/water (7/3), CF_3Br	$(5.0 \pm 0.8) \times 10^7$
2-propanal	water, CF_3Br	9.2×10^4 [c]

[a] Determined by competition with pyrene. [b] Determined by competition with phenanthrene. [c] From ref 19.

propene is a good H-atom scavenger but does not react with solvated electrons, this finding indicates that $^{\bullet}$PyrH in acidic solutions is formed mainly by reaction of pyrene with H$^{\bullet}$ atoms, not by protonation of Pyr$^{\bullet-}$.

Parallel experiments were carried out with phenanthrene in R_4NNTf_2, and the results (Figure 1b,d,f) are very similar to those obtained with pyrene. The phenanthrene H-adduct ($^{\bullet}$PhenH) and CF_3-adduct ($^{\bullet}PhenCF_3$) exhibit an absorption peak at 395 nm, while the radical anion (Phen$^{\bullet-}$) has a peak at 445 nm and additional absorptions over most of the range recorded.[10,16] The H-adduct of phenanthrene, with a peak at 395 nm, was also observed by pulse radiolysis in methanolic solutions, both neutral (formed by protonation of the radical anion) and acidic (formed also by reaction with H$^{\bullet}$ atoms). The H-adduct in acidic acetonitrile solutions exhibited a peak at 375 nm.

Rate Constants for Reactions of $^{\bullet}CF_3$ Radicals. The rate constant for reaction of $^{\bullet}CF_3$ radicals with pyrene in R_4NNTf_2 was determined in neutral solutions saturated with CF_3Br (as in Figure 1c) and in acidic solutions without CF_3Br (as in Figure 1e). The results in the former case are more precise because the change in absorbance is greater than in the latter case. By following the rate of formation of the 405 nm absorption at three or four pyrene concentrations between 2 mmol L^{-1} and 8 mmol L^{-1}, we derive a second-order rate constant, $k_5 = (1.1 \pm 0.15) \times 10^7$ L mol^{-1} s^{-1} from experiments in the presence of CF_3Br and $(1.3 \pm 0.25) \times 10^7$ L mol^{-1} s^{-1} from experiments in the presence of acid (Table 1). The rate constant for reaction of phenanthrene with $^{\bullet}CF_3$ radicals was determined in a similar manner and found to be $(2.6 \pm 0.4) \times 10^6$ L mol^{-1} s^{-1} from experiments in the presence of CF_3Br (Figure 2a,c) and $(3.2 \pm 0.6) \times 10^6$ L mol^{-1} s^{-1} from experiments in the presence of acid (Figure 2b,d). The similarity of the rate constants determined in the presence of CF_3Br and in the presence of acid also indicates that the slow reaction observed in acidic solutions is due mainly to $^{\bullet}CF_3$ radicals. The intercepts of the linear plots in Figure 2c,d and similar plots obtained for pyrene are due to reaction of $^{\bullet}CF_3$ radicals with the solvent and to radical−radical reactions. From these intercepts, we estimate that the rate constant for reaction with the solvent (R_4NNTf_2) is $\leq 2 \times 10^4$ s^{-1} or $\leq 7 \times 10^3$ L mol^{-1} s^{-1}. The rate constants determined in the present study are summarized in Table 1.

By using the absolute rate constants for reactions of $^{\bullet}CF_3$ radicals with pyrene and phenanthrene, we can determine by competition kinetics the rate constants for other reactants that do not form readily observable species. We examined 2-PrOH and valeric acid, which react via H-abstraction, and crotonic acid, which reacts mainly via addition.

Competition kinetics with crotonic acid were performed using both pyrene and phenanthrene as the reference reactant in R_4NNTf_2 solutions saturated with CF_3Br. After varying the concentration of pyrene from 0 to 5.5 mmol L^{-1} and the concentration of crotonic acid from 0 to 26 mmol L^{-1} and monitoring the absorbance at 405 nm, we plotted the competition in a manner that takes into account the contribution of the solvent:

$$A_0/A = (k_{\mathrm{solv}} + k_{\mathrm{ref}}[\mathrm{ref}] + k_{\mathrm{crot}}[\mathrm{crot}])/(k_{\mathrm{ref}}[\mathrm{ref}]) \qquad (6)$$

where A_0 is the limiting absorbance at high pyrene concentrations in the absence of crotonic acid, A is the absorbance measured at the experimental concentrations of pyrene, [ref], and crotonic acid, [crot], k_{ref} and k_{crot} are the second-order rate constants for reaction of $^{\bullet}CF_3$ radicals with pyrene and crotonic acid, and k_{solv} stands for the first-order rate constant of the solvent and other side reactions. The limiting value A_0 was determined from extrapolation of the results obtained with various concentrations of pyrene in the absence of crotonic acid. The values of k_{solv} and k_{ref} were also determined from those results. By plotting $(A_0/A - k_{\mathrm{solv}}/(k_{\mathrm{ref}}[\mathrm{ref}]) - 1)$ vs [crot]/[ref], we obtained a straight line with a slope equal to $k_{\mathrm{crot}}/k_{\mathrm{ref}} = 0.267$ (Figure 3, solid circles). From $k_{\mathrm{pyrene}} = (1.1 \pm 0.15) \times 10^7$ L mol^{-1} s^{-1}, determined under similar conditions, we calculate $k_{\mathrm{crot}} = (2.9 \pm 0.5) \times 10^6$ L mol^{-1} s^{-1}. Similar experiments with phenanthrene as the reference (Figure 3, open circles) gave a slope of 0.964 and $k_{\mathrm{crot}} = (2.5 \pm 0.5) \times 10^6$ L mol^{-1} s^{-1}, in reasonable agreement.

Because crotonic acid can react with $^{\bullet}CF_3$ radicals via addition to the double bond and via H-abstraction from the methyl group, we carried out similar measurements with the saturated valeric acid to estimate the contribution of H-abstraction. By using pyrene as the reference compound and adding 0.46 mol L^{-1} valeric acid, we found only a small decrease in absorbance and increase in rate constant (5% to 10%). To observe a substantial degree of competition, it is necessary to increase the valeric acid concentration to much higher values, and this will lead to a considerable change in the nature of the solvent. Therefore, we only estimate $k_{\mathrm{val}} \leq 1 \times 10^4$ L mol^{-1} s^{-1}. Because abstraction from the CH_3 group is generally much slower than that from CH_2 groups, we conclude that crotonic acid reacts at least 99% via addition to form two isomeric radicals.

$$CH_3CH{=}CHCO_2H + {}^{\bullet}CF_3 \rightarrow CH_3CH(CF_3)\dot{C}HCO_2H + CH_3\dot{C}HCH(CF_3)CO_2H \qquad (7)$$

Further competition experiments were carried out with 2-PrOH, in which H-abstraction from the CH group, further activated by the OH group, is known to occur more rapidly than that from saturated carboxylic acids.[8] Competition experiments were attempted both in neutral ionic liquid solutions saturated with CF_3Br and in deoxygenated acidic solutions. In solutions saturated with CF_3Br, however, the absorbance did not decrease in relation to the concentration of 2-PrOH and the rate of formation became lower rather than higher. This is interpreted to be the result of a chain reaction, propagated by electron transfer from the $(CH_3)_2\dot{C}OH$ radical to CF_3Br,

$$^{\bullet}CF_3 + (CH_3)_2CHOH \rightarrow CHF_3 + (CH_3)_2\dot{C}OH \qquad (8)$$

$$(CH_3)_2\dot{C}OH + CF_3Br \rightarrow (CH_3)_2CO + H^+ + {}^{\bullet}CF_3 + Br^- \qquad (9)$$

whereby the $^{\bullet}CF_3$ radicals produced by reaction 9 react either

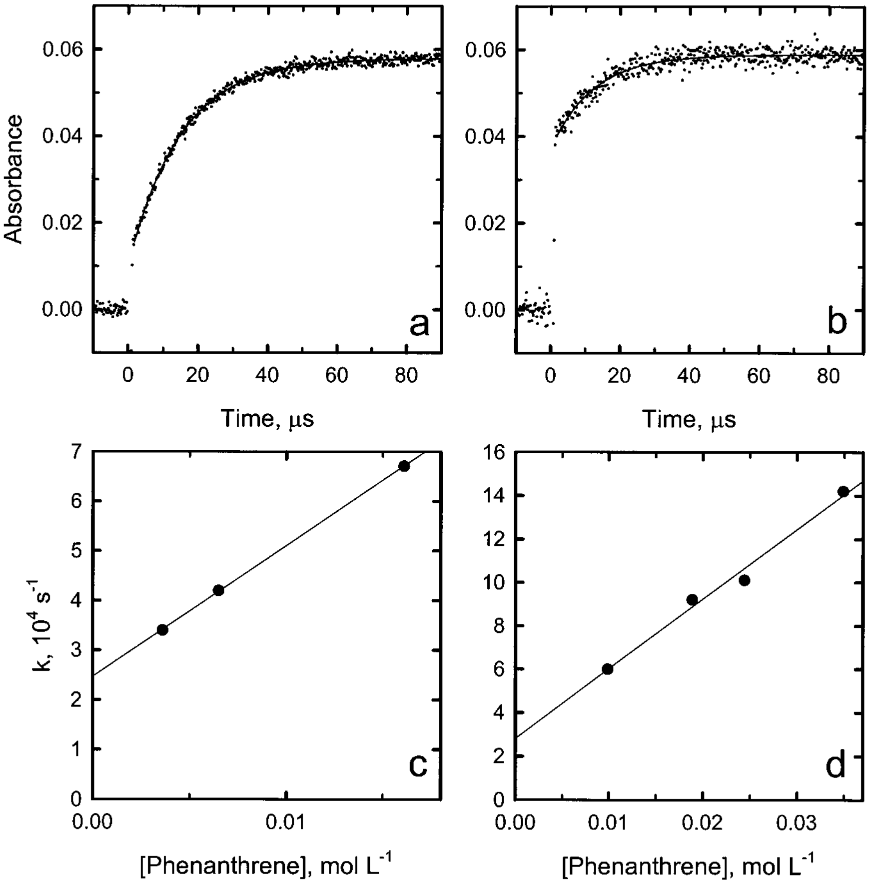

Figure 2. Reaction of $^{\bullet}CF_3$ radicals with phenanthrene. Kinetic traces at 395 nm were recorded by pulse radiolysis of R_4NNTf_2 solutions containing (a) 0.016 mol L^{-1} phenanthrene saturated with CF_3Br (0.1−0.2 mol L^{-1}) and (b) 0.019 mol L^{-1} phenanthrene and 0.2 mol L^{-1} acid (see text). Dependence of the observed rate constant on phenanthrene concentration in the presence of CF_3Br (c) and in the presence of acid (d) are shown.

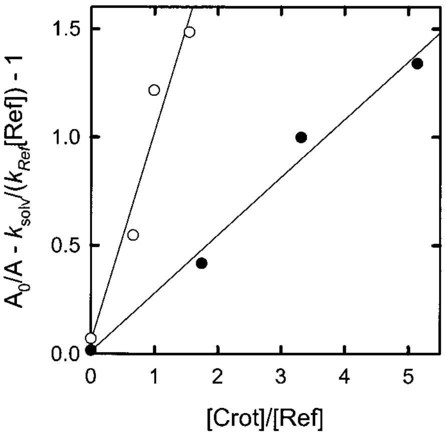

Figure 3. Competition plot to determine the rate constant for reaction of $^{\bullet}CF_3$ radicals with crotonic acid by using pyrene and phenanthrene as reference compounds. The results are plotted according to eq 6 (see text), where ref stands for pyrene (●) or phenanthrene (○).

with pyrene (reaction 5) or with 2-PrOH (reaction 8).[17] The rate constant for reaction 9 is unknown, but we can assume that it will be in the same range as the rate constants for the parallel reactions with $CF_3CHClBr$ (~6 × 10^7 L mol^{-1} s^{-1}) and CCl_4 (~10^8 L mol^{-1} s^{-1}) in aqueous solutions.[18] When 2-PrOH was replaced with methanol, where both reaction 8 and reaction 9 are expected to be slower,[18] competition with pyrene also indicated a chain reaction.

To avoid the chain reaction described above, competition experiments between pyrene and 2-PrOH were carried out in acidic R_4NNTf_2 solutions (in the absence of CF_3Br) by monitoring the absorbance at 405 nm. Because at this wavelength the absorbance is formed in two steps, it is necessary to determine the partial absorbance that is formed in the second step only, which is due to reaction of $^{\bullet}CF_3$ radicals. When we kept the pyrene concentration near 7 mmol L^{-1} and added 10% 2-PrOH (1.17 mol L^{-1}), we found that the absorbance decreased by about 60%. However, addition of only 2% 2-PrOH did not decrease the absorbance at all, and addition of a smaller concentration actually increased the absorbance. This effect must be due to scavenging by 2-PrOH of other radicals formed in the pulse, thus preventing their reactions with $^{\bullet}CF_3$ radicals. Because of this effect and because great variations in 2-PrOH concentrations change the nature of the solvent and its radiolytic yields, we performed the competition experiment by using a constant concentration of 2-PrOH and varying the concentration of pyrene. The results calculated from the absorbance suffer from large uncertainties due to the need to subtract the initial absorbance from the final absorbance and the uncertainty in the value of the initial absorbance. From these results, the rate constant varied between 2.5 × 10^4 and 7 × 10^4 L mol^{-1} s^{-1}. Better results were obtained from the kinetic data, which are not affected by the value of the initial absorbance. The rate of formation at 405 nm was determined as a function of pyrene concentration in the presence of 0%, 3%, and 5% 2-PrOH (Figure 4a). In these linear plots, the slope gives the rate constant for reaction of pyrene and the intercept represents the reaction of $^{\bullet}CF_3$ radicals with 2-PrOH and with any other species except pyrene. The slopes indicate an increase of approximately 7% and 15% in k_{pyrene} upon addition of 3% and 5% 2-PrOH, respectively, probably due to solvent effect on the rate constant.

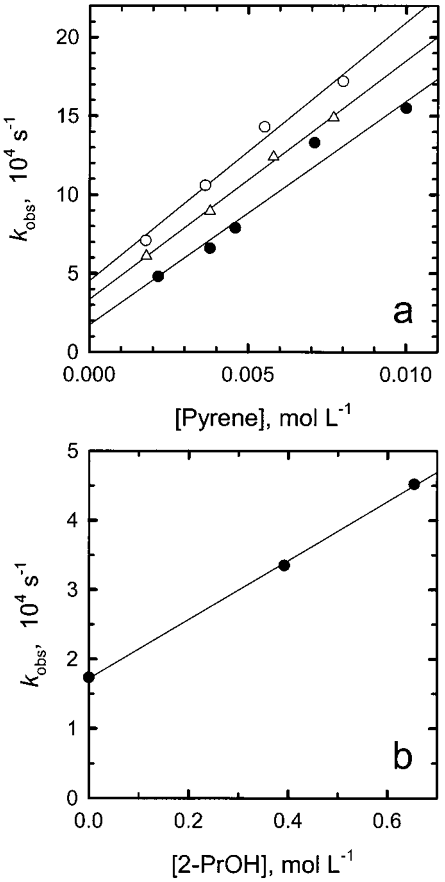

Figure 4. Kinetic experiments to determine the rate constant for reaction of $^{\bullet}CF_3$ radicals with 2-PrOH: (a) observed rate constant for the slower formation step at 405 nm as a function of [pyrene] in the presence of varying [2-PrOH] of 0 (●), 0.39 (△), and 0.65 (○) mol L^{-1}; (b) plot of the intercepts from panel a vs [2-PrOH].

By plotting the value of the intercept as a function of 2-PrOH concentration (Figure 4b), we obtained a straight line. The slope of this line gives the rate constant for 2-PrOH, $k_{PrOH} = (4 \pm 1) \times 10^4$ L mol^{-1} s^{-1} (Table 1).

For comparison with the rate constants determined in the ionic liquid, there are several values reported for reactions of $^{\bullet}CF_3$ radicals in aqueous solutions,[18] and we have determined several values in acetonitrile solutions. We chose acetonitrile because CF_3Br can be reduced by radiolysis in this solvent with a substantial radiolytic yield and because $^{\bullet}CF_3$ radicals do not react rapidly with this solvent. Very few solvents fulfill both of these requirements.

Pulse radiolysis of pyrene and phenanthrene in CF_3Br-saturated acetonitrile solutions led to production of transient species with optical absorption spectra practically identical to those observed in the ionic liquid, indicating production of the same CF_3-adduct radicals. The rate constants for the formation reactions for pyrene and phenanthrene, determined in the same manner, are shown in Table 1 and are a factor of ~2.3 higher than in the ionic liquid. The rate constant for crotonic acid was determined by competition with pyrene and is only slightly higher than that found in the ionic liquid (Table 1). We also attempted to determine the rate constant for pyrene in aqueous acetonitrile solutions, but because of limited solubility, we were able to measure this value only with $\leq$30% water (by volume). The rate constant was found to be nearly twice as high as that in neat acetonitrile solutions (Table 1). The difficulty in measuring this rate constant in water is not only the solubility of the compound but also the fact that the solubility of CF_3Br in water is much lower than that in organic solvents and, at the concentrations of reactants necessary to observe the $^{\bullet}CF_3$ reaction, the reactant will compete for the solvated electrons and prevent the formation of $^{\bullet}CF_3$. For this reason, it is not possible to determine the rate constant for reaction of pyrenesulfonic acid or crotonic acid with $^{\bullet}CF_3$ radicals in water because these compounds react rapidly with e^-_{aq}. The rate constant for 2-PrOH can be measured in aqueous solutions, and this was reported to be 9.2×10^4 L mol^{-1} s^{-1},[19] about twice the value in the ionic liquid. The rate constant for MeOH in aqueous solutions was estimated to be an order of magnitude lower than that of 2-PrOH.[19]

Ionic liquids generally are much more viscous than water or organic solvents, and thus, reaction rates in ionic liquids may be restricted by the rate of diffusion. The diffusion-controlled rate constant (k_{diff}) in R_4NNTf_2 was estimated from the measured viscosity to be $\sim 1.5 \times 10^7$ L mol^{-1} s^{-1} or slightly higher.[3] The experimental rate constant for the reaction of $^{\bullet}CF_3$ radicals with pyrene (Table 1) is close to the estimated k_{diff} and may be affected by this limit. The rate constant for phenanthrene is 4 times slower and thus would be affected by k_{diff} to a much smaller extent. The same reactions have experimental rate constants that are 2.3 times higher in acetonitrile than in the ionic liquid. The rate constants in acetonitrile clearly are not affected by the diffusion limit because k_{diff} in acetonitrile is $\sim 2 \times 10^{10}$ L mol^{-1} s^{-1}, that is, 3 orders of magnitude higher than that in R_4NNTf_2. The finding that the ratio k_{pyr}/k_{phen} is 4.0 ± 0.2 both in acetonitrile and in the ionic liquid suggests that the measured rate constants in the ionic liquid are not significantly restricted by the diffusion. If one accepts this suggestion, the rate constants for addition of $^{\bullet}CF_3$ radicals to the aromatic ring are nearly twice as high in acetonitrile and four times as high in aqueous acetonitrile solutions than in the ionic liquid. Because the radical adduct produced in this reaction and its transition state are more polar than the reactants and because rate constants for such reactions are expected to increase with solvent polarity, it may be concluded that R_4NNTf_2 behaves as a solvent of slightly lower polarity than water and acetonitrile. However, the effect is small in the present case, and the reaction cannot be examined in a wide variety of solvents because of the restrictions mentioned above (solubilities of reactants and reactivity of solvent toward $^{\bullet}CF_3$ radicals). For crotonic acid, where the reactant also is polar, the rate constant in acetonitrile is only slightly higher than that in R_4NNTf_2. For 2-PrOH, where the reaction is via H-abstraction, the rate constant reported[19] for aqueous solutions is twice as high as that measured in the ionic liquid (Table 1). In summary, experimental rate constants for the H-abstraction and addition reactions of $^{\bullet}CF_3$ radicals in the ionic liquid examined in this study are slightly lower than those in water or acetonitrile, while rate constants for electron-transfer reactions were reported to be one or more orders of magnitude lower in ionic liquids than in water or alcohols.[3] This is probably a general trend for these types of reactions. Other examples of H-abstraction and addition reactions are currently under study to examine the generality of this trend.

References and Notes

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(4) The mention of commercial equipment or material does not imply recognition or endorsement by the National Institute of Standards and

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