11130 *J. Phys. Chem. A* **2002,** *106,* 11130−11134

Formation and Reaction of $Br_2^{\bullet-}$ Radicals in the Ionic Liquid Methyltributylammonium Bis(trifluoromethylsulfonyl)imide and in Other Solvents

J. Grodkowski[†] **and P. Neta***

Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8381

Received: June 26, 2002; In Final Form: August 20, 2002

Reaction of solvated electrons with $BrCH_2CH_2Br$ produces Br^- and $^{\bullet}CH_2CH_2Br$, which decomposes rapidly into $CH_2{=}CH_2$ and $Br^{\bullet}$. Reaction of $Br^{\bullet}$ with Br^- forms $Br_2^{\bullet-}$. The stability of $Br_2^{\bullet-}$ is much greater in the ionic liquid and in acetonitrile than in water or alcohols. The rate constant for oxidation of chlorpromazine by $Br_2^{\bullet-}$ radicals decreases upon changing the solvent from water ($\approx 6 \times 10^9$ L mol^{-1} s^{-1}) to methanol (2.8×10^9 L mol^{-1} s^{-1}), ethanol (1.2×10^9 L mol^{-1} s^{-1}), isopropyl alcohol (1.2×10^9 L mol^{-1} s^{-1}), 1-propanol (7.5×10^8 L mol^{-1} s^{-1}), *tert*-butyl alcohol (3.0×10^8 L mol^{-1} s^{-1}), acetonitrile (2.0×10^7 L mol^{-1} s^{-1}), *N*,*N*-dimethylformamide (5.3×10^6 L mol^{-1} s^{-1}), the ionic liquid methyltributylammonium bis(trifluoromethylsulfonyl)imide (1.1×10^6 L mol^{-1} s^{-1}), and hexamethylphosphoramide ($\leq 8 \times 10^4$ L mol^{-1} s^{-1}). The rate constants show poor correlation with typical solvent polarity parameters, but reasonable correlations with hydrogen bond donor acidity and with anion-solvation tendency parameters. From the good correlation with the free energy of transfer of Br^- ions from water to the various solvents, it is suggested that the change in the energy of solvation of Br^- in the different solvents is the main factor that affects the rate constant of the reaction through its effect on the reduction potential of $Br_2^{\bullet-}$ and the driving force of the reaction.

Introduction

Because of the potential importance of room-temperature ionic liquids as solvents for various industrial processes,[1] we have begun a systematic study of their effects on rate constants of representative elementary reactions, including electron transfer,[2,3] addition,[4] and H-abstraction[4,5] reactions. In the present study, we examine the effect of the ionic liquid methyltributylammonium bis(trifluoromethylsulfonyl)imide (R_4NNTf_2) on the stability constant of the complex radical anion $Br_2^{\bullet-}$:

$$Br^{\bullet} + Br^- \leftrightarrows Br_2^{\bullet-} \quad (1)$$

and on the rate constants of oxidation of chlorpromazine ($ClPz^+$) by $Br_2^{\bullet-}$:

$$Br_2^{\bullet-} + ClPz^+ \rightarrow 2Br^- + ClPz^{\bullet 2+} \quad (2)$$

$Br_2^{\bullet-}$ has been studied extensively in aqueous solutions,[6] where it is produced by reaction of $^{\bullet}OH$ radicals with Br^- to form $Br^{\bullet}$, followed by reaction 1.[7] The stability constant of reaction 1 in water is $K_1 = 1.1 \times 10^5$ L mol^{-1}, and thus at $[Br^-] > 0.01$ mol L^{-1}, the ratio of the concentrations $[Br_2^{\bullet-}]/[Br^{\bullet}]$ is $>10^3$. To increase the yield of $Br_2^{\bullet-}$ in irradiated aqueous solutions, the solutions are saturated with N_2O, which converts e_{aq}^- into $^{\bullet}OH$. In the ionic liquid and in organic solvents, reaction of Br^- with $^{\bullet}OH$ (or $RO^{\bullet}$) radicals is not practical as a source of $Br_2^{\bullet-}$ because the solvents react with these radicals. However, another route was reported[8,9] to produce $Br_2^{\bullet-}$ efficiently, namely, reaction of solvated electrons with 1,2-dibromoethane:

$$e_{sol}^- + BrCH_2CH_2Br \rightarrow Br^- + {}^{\bullet}CH_2CH_2Br \quad (3)$$

which is followed by the rapid decomposition ($k \approx 3 \times 10^6$ s^{-1} in water):

$${}^{\bullet}CH_2CH_2Br \rightarrow CH_2{=}CH_2 + Br^{\bullet} \quad (4)$$

and then by reaction 1. Reaction 4 has been demonstrated also in photochemical experiments using several organic solvents.[10] The radiolytic method is applicable with organic solvents that do not capture the solvated electrons rapidly. We have used it with alcohols (MeOH, EtOH, n-PrOH, i-PrOH, t-BuOH), acetonitrile (MeCN), *N*,*N*-dimethylformamide (DMF), the ionic liquid R_4NNTf_2, and hexamethylphosphoric triamide (hexamethylphosphoramide, HMPA), and we estimate that the stability of $Br_2^{\bullet-}$ increases roughly in that order and the rate constant for oxidation of chlorpromazine by $Br_2^{\bullet-}$ decreases in that order by a large factor.

Experimental Section[11]

Methyltributylammonium bis(trifluoromethylsulfonyl)imide (R_4NNTf_2) was prepared as described before.[3] High-purity organic solvents and inorganic salts were obtained from Baker or Mallinckrodt, and water was purified with a Millipore Super-Q system. 1,2-Dibromoethane (DBE) and hexamethylphosphoramide (HMPA) were from Aldrich, and chlorpromazine (2-chloro-10-(3-dimethylaminopropyl)phenothiazine hydrochloride, $ClPz^+$) was from Sigma. As the source of bromide ions, we used NaBr in aqueous and methanol solutions, where it is sufficiently soluble, but in all other solvents we used hexyltriethylammonium bromide (from Aldrich). Deoxygenated solutions containing DBE in various solvents, with or without bromide ions, were studied by pulse radiolysis, using 0.1 μs pulses of 6 MeV electrons from a Varian linear accelerator; other details were as described before.[12] The dose per pulse was generally in the range of 2−4 Gy, as determined by thiocyanate dosimetry.[13] The formation and decay of $Br_2^{\bullet-}$ were

---

[†] On leave from the Institute of Nuclear Chemistry and Technology, Warsaw, Poland.

10.1021/jp021498p CCC: $22.00

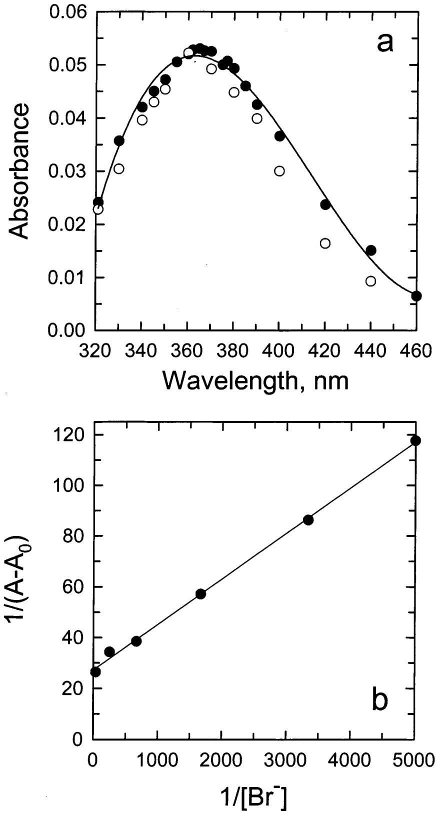

Figure 1. (a) Transient optical absorption spectra of $Br_2^{\bullet-}$ in the ionic liquid and in methanol. Recorded by pulse radiolysis of deoxygenated R_4NNTf_2 (●, 0.13 mol L^{-1} DBE) and MeOH (○, 0.01 mol L^{-1} DBE, 0.03 mol L^{-1} KBr). (b) Competition kinetic plot of the absorbance at 360 nm recorded by pulse radiolysis in deoxygenated MeOH solutions containing 0.01 mol L^{-1} DBE and concentrations of KBr varying from 0.2 to 28 mmol L^{-1}.

monitored at 360 nm, and the spectrum of $Br_2^{\bullet-}$ was recorded with representative solutions. The oxidation of ClPz by $Br_2^{\bullet-}$ radicals was followed at 530 nm with various ClPz concentrations, and the spectrum of the ClPz radical cation was recorded in several cases to confirm the identity of the species produced. 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.

Results and Discussion

Radiolysis of alcohols, MeCN, DMF, HMPA, and R_4NNTf_2 produces solvated electrons and other unstable intermediates. The solvated electrons do not react very rapidly with these solvents and thus can react with DBE when this solute is present, leading to production of Br^- and then $Br^\bullet$ (reactions 3 and 4). To examine the formation of $Br_2^{\bullet-}$ radicals, we carried out pulse radiolysis experiments with deoxygenated solutions containing DBE in the various solvents, with and without added Br^-. The spectrum of $Br_2^{\bullet-}$ has a peak at 360−365 nm in all the solvents studied, similar to the peak position in aqueous solutions. The spectra recorded in MeOH (○) and in the ionic liquid (●) are shown in Figure 1a as examples. The radiolytic yield of $Br_2^{\bullet-}$ depends on the concentration of added bromide, and this dependence is strongly affected by the solvent. For example, the yield of $Br_2^{\bullet-}$ in the ionic liquid was practically the same in the absence and presence of added Br^- while in methanol it increased dramatically with increasing $[Br^-]$. This dependence is due to competition between reaction 1 and the decay of $Br^\bullet$ atoms via other routes, such as dimerization to Br_2 or reaction with the solvent, for example, with methanol:

$$Br^\bullet + CH_3OH \rightarrow HBr + {}^\bullet CH_2OH \tag{5}$$

To derive the ratio of rate constants (k_5/k_1) in MeOH, we plotted the dependence of the absorbance at 360 nm on $[Br^-]$ in the form of a linear plot of $1/(A - A_0)$, where A is the absorbance measured at a given $[Br^-]$ and A_0 is the absorbance measured in the absence of added Br^-, vs $1/[Br^-]$ (Figure 1b). From the slope of this plot, we derive $k_5/k_1 = 2.7 \times 10^{-5}$, practically the same as the ratio derived in aqueous solutions ($k_5/k_1 = 2.5 \times 10^{-5}$).[9] Such measurements could not be done in the ionic liquid because a full yield of $Br_2^{\bullet-}$ was obtained even in the absence of added Br^- (estimated from the absorbance at 360 nm and assuming a molar absorption coefficient for $Br_2^{\bullet-}$ similar to that in aqueous solutions, $\approx 1 \times 10^4$ L mol^{-1} cm^{-1}).[14] These results indicate that in the ionic liquid the $Br^\bullet$ atom formed in reaction 4 reacts predominantly with the Br^- ion formed in reaction 3 rather than with the solvent even when $[Br^-] < 10^{-5}$ mol L^{-1}.

The rate of decay of $Br_2^{\bullet-}$ was also dependent on the solvent. The decay observed in DBE solutions is due not only to the $Br_2^{\bullet-} + Br_2^{\bullet-}$ reaction but also to reactions of the organic radicals, produced from the solvent, with $Br_2^{\bullet-}$ or with $Br^\bullet$. Moreover, reactions of $Br^\bullet$ atoms with the solvent also can contribute to the observed decay. Thus, in aqueous solutions containing 2 mol L^{-1} t-BuOH, 0.01 mol L^{-1} DBE, and 0.01 mol L^{-1} KBr, we find an overall decay rate of $2k/\epsilon \approx 4 \times 10^5$ s^{-1}, while in MeOH solutions containing 0.01 mol L^{-1} DBE and 0.03 mol L^{-1} NaBr we find a higher decay rate, $2k/\epsilon \approx 3 \times 10^6$ s^{-1}. In contrast, decay of $Br_2^{\bullet-}$ in the ionic liquid was much slower, $2k/\epsilon \approx 3 \times 10^3$ s^{-1}. If we assume that the latter decay is due only to $Br_2^{\bullet-} + Br_2^{\bullet-}$ reaction and assume for $Br_2^{\bullet-}$ $\epsilon \approx 1 \times 10^4$ L mol^{-1} cm^{-1}, we calculate $k \approx 1.5 \times 10^7$ L mol^{-1} s^{-1}, which is close to the diffusion-controlled limit in this viscous solvent.[3] This indicates that there is no significant decay due to reaction of $Br^\bullet$ or $Br_2^{\bullet-}$ with the ionic liquid.

The rate constant for oxidation of chlorpromazine by $Br_2^{\bullet-}$ radicals was determined in various solvents containing DBE and Br^- by following the formation of the ClPz radical cation absorption at 530 nm at different ClPz concentrations. The added ClPz can react with $Br_2^{\bullet-}$ (reaction 2) and also with $Br^\bullet$ atoms. The latter reaction takes place in competition with reaction 1 and leads to a decrease in the yield of $Br_2^{\bullet-}$. This effect was minimized by using $[Br^-] \gg [ClPz]$ whenever possible. From the linear dependence of k_{obs} upon [ClPz] (Figure 2), we derived the second-order rate constants summarized in Table 1. The rate constants reported for aqueous solutions are given for comparison. The lowest value is found in HMPA, where only an upper limit of the rate constant could be estimated. The value in the ionic liquid could be accurately measured as $k_2 = (1.1 \pm 0.1) \times 10^6$ L mol^{-1} s^{-1}. The rate constants in all other solvents are higher. The highest rate constant is that reported for aqueous solutions and is close to the diffusion-controlled limit in water. The rate constants in the other solvents are significantly lower than the respective diffusion-controlled limits estimated from the viscosities (by a factor of 3−5 in the alcohols, by 3 orders of magnitude in MeCN, DMF, and HMPA, and by an order of magnitude in the ionic liquid).

The values of k_2 in the different solvents vary over 4 orders of magnitude. The variations do not correlate with solvent polarity; for example, the rate constants in MeCN and DMF are much lower than those in MeOH and 2-PrOH while the

TABLE 1: Rate Constants for Oxidation of Chlorpromazine by $Br_2^{\bullet-}$ Radicals in Various Solvents and Selected Solvent Parameters

solvent	k_2, L mol^{-1} s^{-1}	η^a	ϵ^b	$E_T{}^c$	$\delta_H{}^d$	π^{*e}	α^e	$A_j{}^f$	$B_j{}^f$	$\Delta_tG(Br^-)^g$
H_2O	$(7.7^h, 5.0^i) \times 10^9$	0.89	78.4	63.1	47.9	1.09	1.17	1.00	1.00	0
MeOH	$(2.8 \pm 0.3) \times 10^9$	0.55	32.7	55.4	29.6	0.60	0.93	0.75	0.50	11.1
EtOH	$(1.2 \pm 0.3) \times 10^9$	1.08	24.6	51.9	26.0	0.54	0.83	0.66	0.45	18.2
i-PrOH	$(1.2 \pm 0.3) \times 10^9$	2.07	19.9	48.4	23.5	0.48	0.76	0.59	0.44	
n-PrOH	$(7.5 \pm 1.1) \times 10^8$	1.96	20.3	50.7	24.3	0.52	0.78	0.63	0.44	22
t-BuOH	$(3.0 \pm 0.4) \times 10^8$	5.12	12.5	43.3	21.7	0.41	0.68	0.45	0.50	
MeCN	$(2.0 \pm 0.3) \times 10^7$	0.34	37.5	45.6	24.3	0.75	0.19	0.37	0.86	31.3
DMF	$(5.3 \pm 0.8) \times 10^6$	0.80	36.7	43.8	24.8	0.88	0	0.30	0.93	36.2
R_4NNTf_2	$(1.1 \pm 0.1) \times 10^6$	470					$(0)^j$	$(0.20)^j$	$(1.04)^j$	$(\approx 39)^j$
HMPA	$\leq 8 \times 10^4$	3.25	30	40.9	21.5	0.87	0	0	1.07	46

[a] Viscosity at 25 °C, in 10^{-3} Pa s, from ref 20. The viscosity of R_4NNTf_2 is from ref 3. [b] Dielectric constant, from ref 20. [c] Reichardt's solvent polarity parameter from ref 15. [d] Hildebrand's solubility parameter, or cohesive energy density, from ref 17. [e] Solvent dipolarity/polarizability parameter π^* and solvent hydrogen bond donor acidity parameter α from ref 16. [f] Solvent anion-solvating tendency ("acity"), A_j, and solvent cation-solvating tendency ("basity"), B_j, from ref 15. [g] Free energy of transfer, in kJ mol^{-1} at 25 °C, for the transfer of Br^- from water to the indicated solvent, from ref 20. [h] Rate constant from ref 21. [i] Rate constant from ref 22. [j] Estimated, see text.

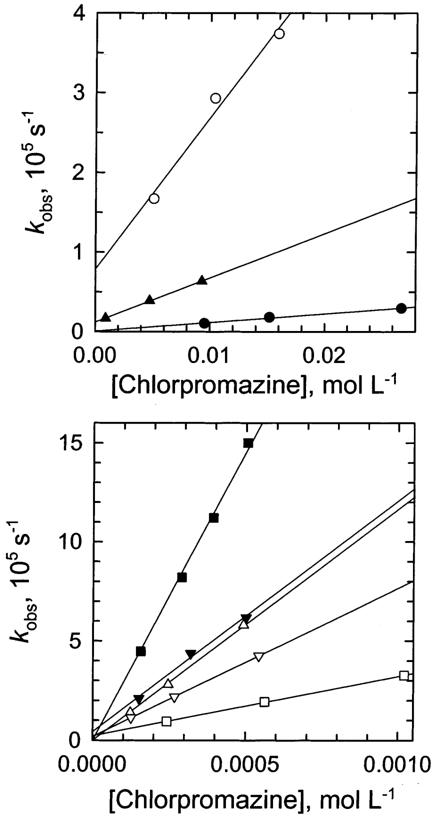

Figure 2. Plots of the observed rate constants for reaction 2 vs chlorpromazine concentration in various solvents: R_4NNTf_2 (●), DMF (▲), MeCN (○), t-BuOH (□), i-PrOH (△), n-PrOH (▽), EtOH (▼), MeOH (■).

dielectric constants are higher (Table 1). Correlation with empirical solvent polarity parameters, such as E_T[15] or π^*,[16] is also poor and so is a correlation with the solvent cohesive energy density δ_H.[17] The latter parameter gave a reasonable correlation with the rate constants for oxidation of ClPz by the $CCl_3O_2^\bullet$ radicals,[18] and we find poor correlation between those values and the rate constants for oxidation of ClPz by $Br_2^{\bullet-}$ ($r^2 = 0.54$). These poor correlations and the observation that k_2 is significantly higher in protic solvents than in aprotic solvents suggest that hydrogen bonding may be an important factor affecting the rate constant of reaction 2. Therefore, we attempted to correlate the rate constants with the empirical parameters π^* (solvent dipolarity/polarizability)[16] and α (solvent hydrogen bond donor acidity).[16] Correlation with these two parameters gives a better fit ($r^2 = 0.904$) of the calculated and experimental rate constants (Figure 3a) according to: $\log k = (6.73 \pm 0.62) + (3.40 \pm 0.42)\alpha - (0.83 \pm 0.74)\pi^*$. This result shows that the effect of hydrogen bonding (α) is significant but the correlation with solvent polarity (π^*) is very poor. Indeed, correlation with α alone is as good (Figure 3b) ($r^2 = 0.906$). These correlations were performed for the solvents listed in Table 1, except for the ionic liquid, for which the solvent parameters are unknown. However, based on the value of α for other solvents and since the ionic liquid has no acidic protons, we can assume a value of $\alpha = 0$ for this solvent and include this point in Figure 3b. This correlation with α is reasonable if we consider that reaction 2 involves doubling of the total number of charges and thus better hydrogen bonding with the solvent favors the products and can increase the rate constant.

Better correlation ($r^2 = 0.988$, Figure 3c) was obtained between the rate constants and the anion- and cation-solvating tendency parameters,[15] A_j and B_j, respectively (Table 1). The correlation is $\log k = (7.043 \pm 0.236) + (4.569 \pm 0.214)A_j - (1.842 \pm 0.244)B_j$. This result shows that increased tendency to solvate anions increases the rate constant while increased tendency to solvate cations decreases the rate constant but has a smaller effect. From this correlation, we can estimate a pair of values for the ionic liquid. For example, the pair $A_j = 0.20$ and $B_j = 1.04$ are in line with the values for the other solvents (Table 1).

The reaction under study involves an electron transfer from $Br_2^{\bullet-}$ to $ClPz^+$, and thus its rate constant depends on the difference between the reduction potential of the $Br_2^{\bullet-}/2Br^-$ couple (1.62 V vs NHE in water)[19] and that of the $ClPz^{\bullet 2+}/ClPz^+$ (0.78 V vs NHE in water).[19] The reduction potentials in aqueous solutions differ by 0.84 V, and thus reaction 2 is very rapid. In the organic solvents listed in Table 1, it is assumed that the energy of solvation of the various ions decreases, from its value in water, approximately in the listed order. However, the solvation energy of the small Br^- ion is expected to decrease to a greater extent than the solvation energy of the larger $Br_2^{\bullet-}$ radical ion. This difference leads to an increase in the stability constant K_1 and a decrease in the reduction potential of $Br_2^{\bullet-}/2Br^-$, leading to a slower reaction 2. This effect will be accentuated by the changes in the solvation energies of $ClPz^{\bullet 2+}$ and $ClPz^+$, although the effect is probably much smaller than that on the bromine couple due to the larger size and the organic core of these ions.

The effect of ion solvation can be assessed more quantitatively by using the values of $\Delta_tG°$ reported for Br^- ions[20] (Table 1). These values are the standard molar Gibbs free energy of transfer

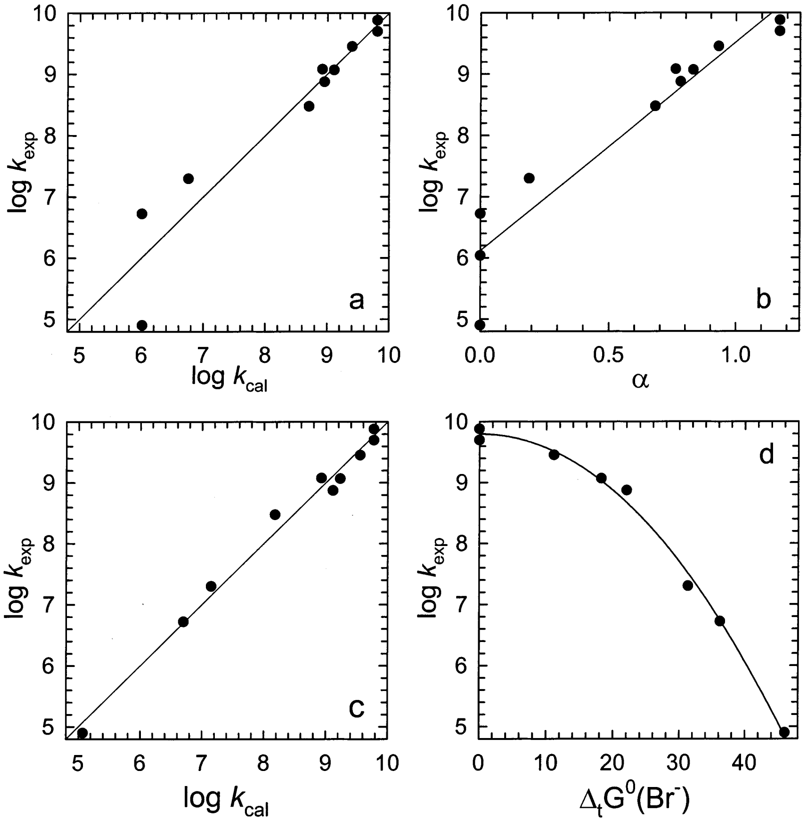

Figure 3. Correlation of the experimental rate constants for reaction 2 (k_{exp}) with solvent parameters: (a) correlation with π^* and α (see text); (b) correlation with α alone; (c) correlation with A_j and B_j (see text); (d) correlation with $\Delta_tG°$.

of the bromide ion from water to the various solvents, i.e., the difference between the energy of solvation in the specific solvent and that in water. The values of $\Delta_tG°$ for $Br_2^{\bullet-}$ are not known but are expected to be much lower than those for Br^- or even negative (as are the values for I_3^- in Table 6.8 of ref 20). The values of $\Delta_tG°$ for $ClPz^+$ and $ClPz^{\bullet 2+}$ are also estimated to be negative (based on results for other organic cations in Table 6.8 of ref 20) and probably not very different for these two bulky cations. Correlation of log k_2 with $\Delta_tG°$ is shown in Figure 3d and is clearly better than the other correlations. From this plot, we estimate for the ionic liquid $\Delta_tG° \approx 39$ kJ mol^{-1} for Br^-. This plot is reminiscent of the Marcus relation between the electron-transfer rate constant and the driving force of the reaction and suggests that the observed variations in rate constants are due mainly to the change in driving force resulting from the change in Br^- solvation energy. If the value of $\Delta_tG°$ is the main contributor to the change in the driving force of reaction 2, it can be estimated that the driving force will decrease by about 0.5 V, i.e., from 0.8 to 0.3 V. The finding that the rate constant in HMPA is immeasurably slow suggests that the driving force of reaction 2 in this solvent may be closer to 0, due to changes in solvation energies of the other ions. However, we could not detect any evidence that reaction 2 is driven in the opposite direction in HMPA.

In conclusion, the energy of solvation of bromide ions, and probably all small inorganic anions, is much smaller in the ionic liquid than in water or alcohols. The energy of solvation of the larger, complex anions such as $Br_2^{\bullet-}$ or I_3^- may be similar or slightly larger than that in water. As a result, the stability constants of such complexes are higher in the ionic liquid than in water and alcohols and the reduction potential of $Br_2^{\bullet-}$ is much lower in the ionic liquid than in water or alcohols. The present results demonstrate the need for measurements of solvation energies and reduction potentials in ionic liquids as predictors for various reaction rates and equilibria.

References and Notes

(1) Welton, T. *Chem. Rev.* **1999**, *99*, 2071, and references cited therein. Brennecke, J. F.; Maginn, E. J. *AIChE J.* **2001**, *47*, 2384.

(2) Behar, D.; Gonzalez, C.; Neta, P. *J. Phys. Chem. A* **2001**, *105*, 7607.

(3) Behar, D.; Neta, P.; Schultheisz, C. *J. Phys. Chem. A* **2002**, *106*, 3139.

(4) Grodkowski, J.; Neta, P. *J. Phys. Chem. A* **2002**, *106*, 5468.

(5) Grodkowski, J.; Neta, P. *J. Phys. Chem. A* **2002**, *106*, 9030.

(6) See compilation by Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027.

(7) Sutton, H. C.; Adams, G. E.; Boag, J. W.; Michael, B. D. In *Pulse Radiolysis*; Ebert, M., Keene, J. P., Swallow, A. J., Baxendale, J. H., Eds.; Academic Press: London, 1965; p 61. Cercek, B.; Ebert, M.; Gilbert, C. W.; Swallow, A. J. In *Pulse Radiolysis*; Ebert, M., Keene, J. P., Swallow, A. J., Baxendale, J. H., Eds.; Academic Press: London, 1965; p 83. Matheson, M. S.; Mulac, W. A.; Weeks, J. L.; Rabani, J. *J. Phys. Chem.* **1966**, *70*, 2092. Zehavi, D.; Rabani, J. *J. Phys. Chem.* **1972**, *76*, 312. Mamou, A.; Rabani, J.; Behar, D. *J. Phys. Chem.* **1977**, *81*, 1447.

(8) Lal, M.; Mönig, J.; Asmus, K.-D. *Free Radical Res. Commun.* **1986**, *1*, 235.

(9) Merényi, G.; Lind, J. *J. Am. Chem. Soc.* **1994**, *116*, 7872.

(10) Scaiano, J. C.; Barra, M.; Calabrese, G.; Sinta, R. *J. Chem. Soc., Chem. Commun.* **1992**, 1418. Scaiano, J. C.; Barra, M.; Krzywinski, M.; Sinta, R.; Calabrese, G. *J. Am. Chem. Soc.* **1993**, *115*, 8340. Scaiano, J. C.; Barra, M.; Krzywinski, M.; Hancock, T.; Calabrese, G.; Sinta, R. *Chem. Mater.* **1995**, *7*, 936.

(11) The mention of commercial equipment or material does not imply recognition or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified are necessarily the best available for the purpose.

(12) Grodkowski, J.; Neta, P. *J. Phys. Chem. A* **2000**, *104*, 4475.

(13) Schuler, R. H.; Patterson, L. K.; Janata, E. *J. Phys. Chem.* **1980**, *84*, 2088.

(14) In support of the high stability of $Br_2^{\bullet-}$ in the ionic liquid, we found a high stability for I_3^-. The stability constants of I_3^- in water and methanol were determined spectrophotometrically and found to be 6.7×10^2 L mol^{-1} and 2.5×10^4 L mol^{-1}, respectively, in agreement with literature values

(Palmer, D. A.; Ramette, R. W.; Mesmer, R. E. *J. Solution Chem.* **1984**, *13*, 673. Olsson, L.-F. *Inorg. Chem.* **1985**, *24*, 1398. Benoit, R. L.; Guay, M.; Desbarres, J. *Can. J. Chem.* **1968**, *46*, 1261). Similar measurements in MeCN and in R_4NNTf_2, however, showed much higher stabilities for I_3^-. The concentration of I_3^- was identical to that of the component used at the lower concentration, either I_2 or I^-, indicating stability constants much greater than 10^5 L mol^{-1}. For MeCN, the stability constant was estimated by other methods to be close to 10^7 L mol^{-1} (Barraque, C.; Vedel, J.; Tremillon, B. *Anal. Chim. Acta* **1969**, *46*, 263).

(15) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH: Weinheim, 1988.

(16) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

(17) Barton, A. F. M. *Chem. Rev.* **1975**, *75*, 731. Barton, A. F. M. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press: Boca Raton, FL, 1983.

(18) Alfassi, Z. B.; Huie, R. E.; Neta, P. *J. Phys. Chem.* **1993**, *97*, 7253.

(19) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637. Stanbury, D. *Adv. Inorg. Chem.* **1989**, *33*, 69.

(20) Marcus, Y. *Ion Solvation*; Wiley: New York, 1985; p 168.

(21) Bahnemann, D.; Asmus, K.-D.; Willson, R. L. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1661.

(22) Davies, A. K.; Land, E. J.; Navaratnam, S.; Parsons, B. J.; Phillips, G. O. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 22.