123.4 (C-7), 123.7 (C-10), 127.2 (2 C, Ph), 127.5 (C-8), 127.7 (C-9), 128.8 (2 C, Ph), 128.9 (Ph), 129.0 (C-4), 132.70 (C-2 or C-5), 132.74 (C-5 or C-2), 133.6 (C-γ), 139.4 (Ph), 150.4 (C-3), 154.5 (C-α); IR (CCl_4) 3045, 1630, 1228 cm^{-1}; MS *m/z* (rel intensity) 269 (M$^+$, 100). Anal. Calcd for $C_{20}H_{15}N$: C, 89.19; H, 5.61, N, 5.20. Found: C, 88.96; H, 5.36; N, 5.14.

Reaction of 20a with Dimethyl Acetylenedicarboxylate (DMAD). A solution of **20a** (95 mg, 0.275 mmol) and DMAD (394 mg, 2.77 mmol) in toluene (2 mL) was heated under reflux for 4 h. After removal of the solvent in vacuo, the residue was separated by TLC on silica gel using hexane–ethyl acetate (3/1) as a developer to give the adduct **27** (113 mg, 99%).

27: mp 170–171 °C (from MeOH); ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.44 (1 H, d, J = 5.3 Hz), 2.38 (1 H, d, J = 5.3 Hz), 4.14 (3 H, s), 4.22 (3 H, s), 4.37 (1 H, dd, J = 5.6, 2.3 Hz), 5.66 (1 H, dd, J = 5.5, 2.4 Hz), 6.39–6.55 (2 H, m), 7.30–7.60 (11 H, m), 8.10–8.25 (2 H, m); IR ($CHCl_3$) 1715, 1270 cm^{-1}; MS *m/z* (rel intensity) 487 (M$^+$, 63), 428 (100). Anal. Calcd for $C_{32}H_{25}NO_4$: C, 78.83; H, 5.17; N, 2.87. Found: C, 78.65; H, 5.39; N, 2.86.

Reaction of [(Tributylphosphoranylidene)amino]benzene (28) with 16a. To a solution of **28**, prepared in situ from azidobenzene (54 mg, 0.45 mmol) and tributylphosphine (145 mg, 0.72 mmol) in toluene (3 mL), was added **16a** (203 mg, 0.98 mmol), and the mixture was heated under reflux for 26 h. The reaction mixture was concentrated, and the residue was chromatographed on silica gel using benzene as an eluent to eliminate tributylphosphine oxide. The fractions were concentrated in vacuo and separated by TLC on silica gel using benzene–hexane (2/1) as a developer to give chalcone anil **29** (116 mg, 91%): mp 96–98 °C (from ether) (lit.[17] mp 99–101 °C); ^{1}H NMR (90 MHz, $CDCl_3$) δ 6.62–7.50 (15 H, m), 7.69–7.80 (2 H, m).

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Registry No. 1, 2443-46-1; **5**, 134858-12-1; **6**, 137594-06-0; **7**, 15825-92-0; **8x**, 134858-17-6; **8y**, 137594-07-1; **9x**, 137594-08-2; **9y**, 137594-09-3; **10**, 115163-02-5; **12**, 137594-10-6; **13**, 137594-11-7; **14**, 137594-12-8; **15**, 137594-13-9; **16a**, 94-41-7; **16b**, 956-02-5; **16c**, 956-04-7; **16d**, 625-33-2; **16e**, 42858-38-8; **16f**, 768-03-6; **19a**, 137594-14-0; **19b**, 137594-15-1; **19c**, 137594-16-2; **20a**, 137594-17-3; **20a**·picrate, 137594-18-4; **20b**, 137594-20-8; **20b**·picrate, 137695-53-5; **20c**, 137594-21-9; **20c**·picrate, 137594-22-0; **20d**, 137594-23-1; **20d**·picrate, 137594-24-2; **20e**, 137594-25-3; **20f**, 137594-26-4; **26a**, 137594-27-5; **26f**, 137594-28-6; **27**, 137594-29-7; **29**, 64723-86-0; DMAD, 762-42-5; triphenylphosphine, 603-35-0; carbon disulfide, 75-15-0; tributylphosphine, 998-40-3; 3-cyclododecenone, 42858-38-8; azidobenzene, 622-37-7.

Supplementary Material Available: ^{1}H NMR and ^{13}C NMR spectra of azido[10]annulenes **5** and **6**, methanocyclodeca[*b*]pyridines **20a–d,f**, and **26a,f** and ^{1}H NMR spectra of isothiocyanates **14** and **15** and methanocyclodeca[*b*]pyridine **20e** (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

On the Importance of Reactions of Carbocation Ion Pairs in Water: Common Ion Inhibition of Solvolysis of 1-(4-Methoxyphenyl)-2,2,2-trifluoroethyl Bromide and Trapping of an Ion-Pair Intermediate by Solvent

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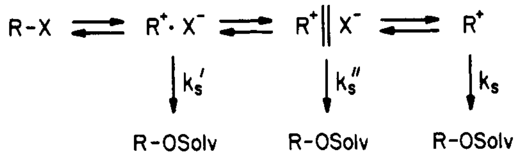
The effect of added bromide ion on the reactivity of 1-(4-methoxyphenyl)-2,2,2-trifluoroethyl bromide in water at 25 °C and I = 6.00 ($NaClO_4$) has been determined. The pseudo-first-order rate constant for this reaction decreases 300-fold as [NaBr] is increased from 0–5.00 M, which shows that ≥99.7% of the solvolysis reaction proceeds through the free carbocation intermediate, whose concentration is reduced by mass action of added bromide ion. At high [NaBr], the observed rate constants show a significant positive deviation from the rate law for a reaction in which solvolysis products are derived solely from capture of the free carbocation. This deviation is consistent with a second pathway for the formation of solvolysis products, by direct attack of solvent on an ion-pair intermediate. The limiting velocity through this pathway, approached at high concentrations of bromide ion, is estimated to be 0.06% of that through the liberated carbocation. It is concluded that the capture of ion-pair intermediates of solvolysis reactions by solvent water is normally an unimportant reaction.

Introduction

At least three intermediates may form in an S_N1 ($D_N + A_N$)(1) nucleophilic substitution reaction (Scheme I): the intimate ion pair, the solvent-separated ion pair, and the free ions.(2) In nonpolar solvents, the stabilizing electrostatic interactions between ions are relatively strong, so that solvent and other nucleophilic reagents may react directly with ion pair intermediates at a rate that is competitive with the dissociation of the ion pair to give free ions. In water, ion pairs are much more unstable and undergo rapid dissociation to give free ions. The capture of ion pair intermediates by this solvent will not be a significant reaction when the rate of dissociation of the intimate ion pair to form free ions is much faster than the capture of the ion pair by water.(3–5)

Scheme I



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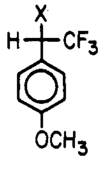
The reaction of water with a free carbocation can be distinguished from reaction with ion-pair intermediates by an examination of common ion inhibition of the solvolysis reaction.[6,7] The common ion (X^-) will act by mass action to convert the free carbocation (R^+, Scheme I) to substrate, and the resultant decrease in the concentration of R^+ leads to a reduction in the velocity of solvolysis. However, the common ion should have little or no effect on the rate of reaction of solvent with R^+ that is already paired with the leaving group ion. Therefore, large concentrations of X^- that reduce the concentration of R^+ to close to zero will either cause the velocity for the solvolysis reaction to approach zero, if the solvent reacts only with R^+, or to level off at a constant value, if the solvent also captures an ion pair intermediate(s).

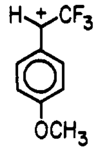
Carbocations form as reaction intermediates only when they are stabilized by hydrophobic substituents, but these substituents also render the neutral substrates sparingly soluble in water. The low solubility, in water, of substrates that react by an S_N1 ($D_N + A_N$)[1] reaction mechanism makes it extremely difficult to monitor the progress of their reaction. Consequently, there have been few investigations in water of ion-pair intermediates of $D_N + A_N$ solvolysis reactions.

1-(4-Methoxyphenyl)-2,2,2-trifluoroethyl bromide (**1-Br**) is well suited for this study. This compound is sufficiently soluble in water for its reaction to be followed by UV spectroscopy. Nucleophilic substitution reactions at **1-Br** proceed by the $D_N + A_N$ mechanism. The 1-(4-methoxyphenyl)-2,2,2-trifluoroethyl carbocation intermediate of this reaction (**2**) shows an unusual kinetic stability for a carbocation which is destabilized by the strongly electron-withdrawing α-CF_3 substituent, and the capture of this intermediate by added bromide ion results in strong common ion inhibition of the reaction of **1-Br**.[5]

I report here the results of a study of bromide common ion inhibition of the solvolysis of **1-Br** in water at $I = 6.00$, maintained with $NaClO_4$. The pseudo-first-order rate constant, k_{obsd}, for this reaction decreases by 99.7% as [Br^-] is increased from 0–5.00 M, which shows that the reaction of solvent with [$2\cdot Br^-$] ion pairs is relatively unimportant. However, at high concentrations of bromide ion, the values of k_{obsd} show a positive deviation from the rate law for a reaction in which solvent captures only the free carbocation. The positive deviation is attributed to the contribution of a second reaction pathway to k_{obsd}, representing the direct addition of solvent to a carbocation-bromide ion pair.



1-X



2

Experimental Section

Materials. Reagent-grade inorganic salts were used without further purification. The water used for kinetic studies was distilled and then passed through a Milli-Q water purification system. **1-Br** and **1-I** were prepared by published procedures.[5]

Table I. Bromide Common-Ion Inhibition of the Reaction of 1-Br in Water[a]

[NaBr], M	$k_{obsd}/10^{-3}$, s^{-1}	[NaBr], M	$k_{obsd}/10^{-3}$, s^{-1}	$k_{calc}/10^{-3}$,[b] s^{-1}	$(k_{obsd} - k_{calc})/10^{-3}$, s^{-1}
0	49	2.00	0.357	0.316	0.041
0.0067	33	2.50	0.291	0.253	0.038
0.013	23.4	3.00	0.233	0.211	0.022
0.027	16.3	3.50	0.215	0.181	0.034
0.040	12.3	4.00	0.191	0.159	0.032
0.053	9.92	4.50	0.171	0.141	0.030
0.067	7.99	5.00	0.164	0.127	0.037
0.093	5.97			(0.074)[c]	(0.090)[c]
0.13	4.31				
0.20	2.85				
0.27	2.25				
0.40	1.67				
0.53	1.32				
0.80	0.81				
1.00	0.68				
1.50	0.445				

[a] At 25 °C and $I = 6.00$ ($NaClO_4$). [b] Calculated from eq 1 with $k_{solv} = 0.049\ s^{-1}$ and $k_{Br}/k_s = 77\ M^{-1}$ (see text). [c] Corrected for the estimated specific bromide ion salt effect on k_{calc} (see text).

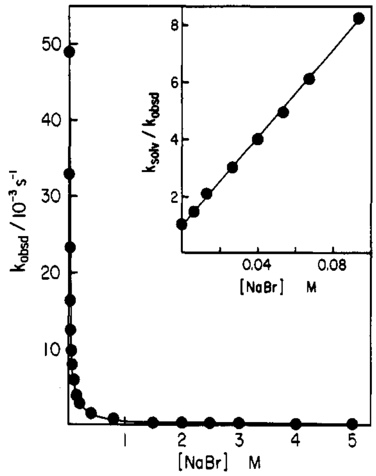


Figure 1. Effect of added NaBr on the pseudo-first-order rate constants, k_{obsd}, for solvolysis of **1-Br** in water at 25 °C and $I = 6.00$ ($NaClO_4$). The inset shows the linear replot of the data according to eq 1 of the text.

Methods. Kinetic Analyses. These studies were in water at 25 °C and $I = 6.00$ maintained with $NaClO_4$. The progress of the reactions of **1-Br** and **1-I** was followed by monitoring the decrease in absorbance at 280 nm on a Perkin-Elmer λ-4B spectrophotometer. The substrates were prepared as solutions in acetonitrile and the reactions were initiated by making a 100-fold dilution into the aqueous solution. There is a decrease in the solubility of **1-Br** in solutions of increasing concentrations of NaBr. The final concentration of **1-Br** was 4×10^{-5} M for reactions at [NaBr] = 0–1.00 M and was reduced to 1×10^{-5} M for reactions at [NaBr] = 1.33–5.00 M. The reactions at the lower concentration of **1-Br** were monitored in cuvettes with a 6-cm path length, instead of the standard 1 cm cells. The final concentration of **1-I** was 6×10^{-6} M.

Pseudo-first-order rate constants for these reactions were determined as the slope of a semilogarithmic plot of reaction progress against time. The plots were linear for ≥3 halftimes of the reaction. The rate constants were reproducible to ±5%.

HPLC Product Analyses. The products of the reaction of solvent and azide ion with **1-Br** were separated by HPLC and detected spectrophotometrically at 271 nm as described in earlier work.[4,5] The rate constant ratio for the reaction of **1-Br** with azide ion and solvent was determined from the ratio of the yields of the azide and solvent adducts.[4,5]

Results

Table I and Figure 1 show the effect of increasing concentrations of bromide ion on the pseudo-first-order rate

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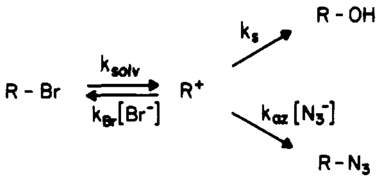
Scheme II



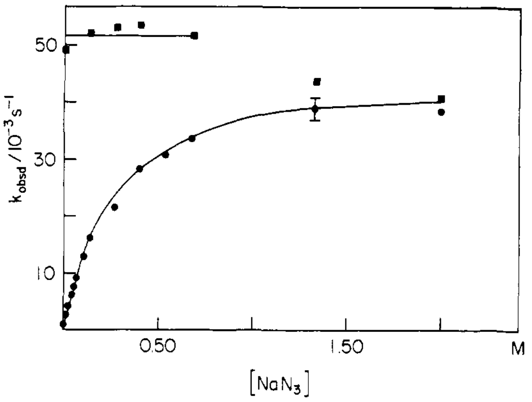


Figure 2. Effect of added NaN_3 on the pseudo-first-order rate constants, k_{obsd}, for reaction of **1-Br** in water at 25 °C and I = 6.00 ($NaClO_4$). (■) Reactions in the absence of NaBr. (●) Reactions at [NaBr] = 1.00 M.

constant k_{obsd} for the reaction of **1-Br** in water at 25 °C and I = 6.00 ($NaClO_4$). The inset in Figure 1 shows the fit to eq 1, derived for Scheme II, of the data at low [NaBr]:

$$k_{solv}/k_{obsd} = 1 + (k_{Br}/k_s)[Br^-] \qquad (1)$$

k_{solv} in eq 1 is k_{obsd} at [NaBr] = 0 M. The data define a line of slope $k_{Br}/k_s = 77\ M^{-1}$, where k_{Br} and k_s are the rate constants for the capture of **2** by bromide ion and solvent, respectively.

Increasing $[N_3^-]$ causes little change in k_{obsd} (■, Figure 2) for the reaction of **1-Br** in water at 25 °C and I = 6.00 ($NaClO_4$), but at the highest $[N_3^-]$ the yield of the azide adduct is >99%. Under the same conditions, but at [NaBr] = 1.00 M, the addition of azide ion causes large increases in k_{obsd} (●, Figure 2). The apparent bimolecular reaction of azide ion with **1-Br** observed at low $[N_3^-]$ can be explained by reference to Scheme II. At [NaBr] = 1.00 M, the trapping of **2** by bromide ion is very fast, so that the rate-determining step for the reaction of **1-Br** is the capture of **2** by nucleophilic reagents ($k_{Br}[Br^-] \gg k_s$). The capture of **2** by azide ion causes an increase in the velocity of the rate-determining step, which results in a larger pseudo-first-order rate constant for the disappearance of **1-Br**.

The data at low $[N_3^-]$ from Figure 2 show a good fit (Figure 3, ●) to eq 2, derived for Scheme II, with the condition that $k_{Br}[Br^-] \gg (k_s + k_{az}[N_3^-])$: k_0 in eq 2 is k_{obsd} for the reaction of **1-Br** at [NaBr] = 1.00 M and [NaN_3] = 0 M. The slope of the line in Figure 3 (●) is k_{az}/k_s =

$$k_{obsd}/k_0 = 1 + (k_{az}/k_s)[N_3^-] \qquad (2)$$

187 M^{-1}, where k_{az} is the rate constant for the capture of **2** by azide ion. Figure 3 (■) shows data at a fixed [NaBr] = 5.00 M and increasing [NaN_3] (I = 6.00, $NaClO_4$) which has been fit with a slope $k_{az}/k_s = 140\ M^{-1}$.

The pseudo-first-order rate constant for the reaction of **1-Br** in water with no salt (I = 0) is $1.24 \times 10^{-2}\ s^{-1}$. This rate constant decreases 15-fold to $8.2 \times 10^{-4}\ s^{-1}$ for reaction in the presence of 1.0 M NaBr.

The pseudo-first-order rate constant for solvolysis of **1-I** in water at 25 °C and I = 6.00 ($NaClO_4$) is $k_{obsd} = 4.3 \times 10^{-3}\ s^{-1}$. This decreases to $k_{obsd} = 2.5 \times 10^{-3}\ s^{-1}$ at [NaBr] = 5.00 M and I = 6.00 ($NaClO_4$). The major product of the reaction at [NaBr] = 5.00 M is **1-Br**, which is stable on the time scale for the reaction of **1-I** (Table I).

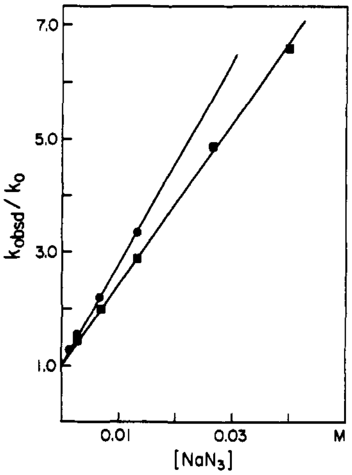


Figure 3. Linear replot, according to eq 2 of the text, of data for reactions of **1-Br** at a fixed concentration of NaBr and increasing concentrations of NaN_3. (●) Replot of data from Figure 2 for the reaction of **1-Br** at [NaBr] = 1.00 M. (■) Replot of data (not shown) for the reaction of **1-Br** at [NaBr] = 5.00 M.

A product rate constant ratio[4,5] of $k_{az}/k_s = 220\ M^{-1}$ was determined from the yields of the azide and solvent adducts obtained from reaction of **1-Br** at [NaN_3] = 6.67×10^{-3} M and I = 6.00 ($NaClO_4$).

Discussion

Simple Conclusions. The observation of strong bromide common ion inhibition (Figure 1) and of the formation of **1-N₃** by a reaction zero-order in $[N_3^-]$ (Figure 2) show that the reaction of **1-Br** in water proceeds by the same S_N1 ($D_N + A_N$)[1] mechanism (Scheme II) previously reported for the reaction of this compound in 50:50 (v/v) trifluoroethanol/water[5] and in 20% acetonitrile in water.[8] The reaction of azide ion with **2**, the carbocation intermediate of the reaction of **1-Br**, is diffusion limited with an estimated rate constant $k_{az} = 5 \times 10^9\ M^{-1}\ s^{-1}$.[5,9] Combining this value for k_{az} with k_{az}/k_s (M^{-1}) determined from the data in Figure 3 or from product analysis gives k_s = 2.3×10^7 and $3.6 \times 10^7\ s^{-1}$ for reaction of **2** with solvent at [NaBr] = 0 M and [NaBr] = 5.00 M, respectively.

When sodium perchlorate is omitted from the reaction there is a 15-fold decrease in k_{obsd} for the reaction of **1-Br** as the concentration of sodium bromide is increased from 0 to 1.0 M. This shows that bromide common-ion inhibition is not induced by perchlorate ion.[6b]

There is a 300-fold decrease in k_{obsd} for the reaction of **1-Br** as the concentration of bromide ion is increased from 0 to 5.00 M (Table I). The decrease in the rate of the solvolysis reaction shows that at least 99.7% of the reaction products are formed by the reaction of solvent with the liberated intermediate **2**, whose concentration can be reduced by mass action of bromide ion. The value of 99.7% is a lower limit because 5.00 M NaBr does not completely suppress the reaction through free **2**, as shown by the decrease in k_{obsd} observed even at the highest concentration of NaBr (Table I). I conclude that >99.7% of the solvolysis reaction of **1-Br** in water at I = 6.00 ($NaClO_4$) pro-

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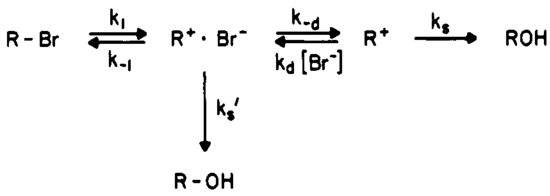
Scheme III



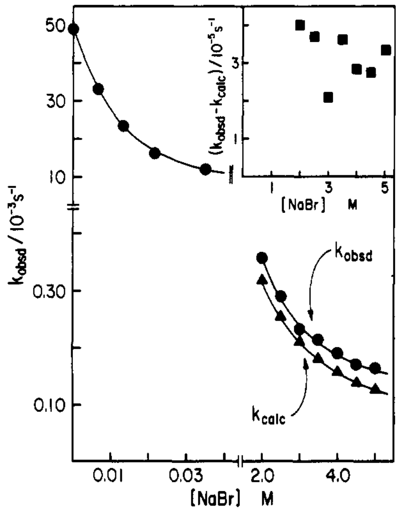


Figure 4. Expansion of the plot in Figure 1, where k_{obsd} is the observed rate constant for the reaction of **1-Br**, and k_{calc} is the value calculated from eq 1, as described in the text. The inset shows a plot of $(k_{obsd}-k_{calc})$ against the concentration of bromide ion.

ceeds through the liberated intermediate **2** and <0.3% through an ion pair intermediate.

The data provide experimental support for the proposal that stepwise solvolysis reactions in water will generally proceed through the *liberated* carbocation intermediate.[3-5] The low (<0.3%) yield of products from the reaction of solvent with an ion-pair intermediate shows that the *irreversible* dissociation of this species to give the free ions is much faster than its direct capture by solvent ($k_{-d} > 300\ k_s'$, Scheme III).

Complex Interpretations. The inset in Figure 1 shows the fit to eq 1 of the data for reaction of **1-Br** at [NaBr] = 0–0.10 M with $k_{solv} = 0.049$ s^{-1} and $k_{Br}/k_s = 77$ M^{-1}. These values were substituted into eq 1 to obtain calculated rate constants (k_{calc}, Table I) for the reaction of **1-Br** at [NaBr] = 2.00–5.00 M. Figure 4 shows that the values of k_{obsd} for the reaction of **1-Br** at [NaBr] = 2.00–5.00 M are larger than the values of k_{calc}. At [NaBr] = 5.00 M, $(k_{obsd}-k_{calc})$ is 22% of k_{obsd}. This is significantly larger than the estimated experimental error in k_{obsd} of ±5%.

There are at least two explanations for the failure of eq 1 to fit the data for the reaction of **1-Br** at high concentrations of sodium bromide.

(*1*) *The positive deviation of k_{obsd} might be due to a specific salt effect that arises from the replacement of NaBr by NaClO$_4$.* This is very unlikely. Perchlorate ion acts to stabilize carbocations relative to neutral substrates,[10] so that the substitution of NaBr for NaClO$_4$ should destabilize **2** relative to **1-Br**. At high concentrations of sodium bromide, the rate-limiting step for solvolysis of **1-Br** is the capture of **2** by solvent (k_s, Scheme II). Substitution of Br$^-$ for ClO$_4^-$ should destabilize the carbocation-like transition state for this step relative to the starting neutral substrate, so that this would lead to a *negative*, rather than positive, deviation of k_{obsd} from eq 1. The following effects of the replacement of ClO$_4^-$ by Br$^-$ on the observed rate constants for related reactions are consistent with the proposal that bromide ion destabilizes **2** relative to **1-X**.

(a) The decrease in the observed rate constant for solvolysis of 4-MeOArCH(CF$_3$)I (**1-I**) from 4.3×10^{-3} s^{-1} at [NaBr] = 0 M to 2.5×10^{-3} s^{-1} at [NaBr] = 5.00 M and I = 6.00 (NaClO$_4$) is consistent with a specific salt effect that destablilizes the carbocation-like transition state for solvolysis relative to **1-I**.

(b) The increase in k_s for the capture of **2** by solvent from 2.3×10^7 s^{-1} at [NaBr] = 0 M to 3.6×10^7 s^{-1} at [NaBr] = 5.00 M is consistent with a specific salt effect that destabilizes this carbocation relative to the solvent adduct.

(*2*) *The positive deviation represents the contribution of a second pathway for the formation of the solvent adduct.* Scheme III is an expansion of Scheme II which includes an ion-pair intermediate that is captured by solvent with a rate constant k_s'. The ion pair in Scheme III includes both the initimate and solvent-separated ion pairs from Scheme I. No attempt is made here to distinguish between the reaction of solvent with the two types of ion pairs, because this distinction cannot be made from the experimental results. The rate law for Scheme III is given in eq 3. The first and second terms in the numerator

$$k_{obsd} = \frac{k_1 k_{-d} k_s + k_1 k_s'(k_s + k_d[\mathrm{Br}^-])}{k_s(k_{-1} + k_s' + k_{-d}) + k_d[\mathrm{Br}^-](k_{-1} + k_s')} \qquad (3)$$

of eq 3 describe, respectively, the contribution to k_{obsd} of the pathways which proceed through the free carbocation (k_s, Scheme III) and the ion-pair intermediates (k_s'). At low [Br$^-$] the reaction of **1-Br** proceeds largely through the free carbocation intermediate **2** and the second term in the numerator of eq 3 is not significant ($k_{-d} \gg k_s'$, see below). The values of k_{calc} in Table I, calculated from data at low [Br$^-$] where the reaction proceeds by capture of free **2**, provide an estimate for the contribution of this pathway to k_{obsd} for reactions at high [Br$^-$]. The difference between k_{obsd} for the reaction of **1-Br** and k_{calc} calculated for the reaction of **1-Br** only through free **2** (Table I and Figure 4) is consistent with a second pathway for the reaction of **1-Br** involving direct reaction of solvent with [**2**·Br$^-$].

The difference $(k_{obsd}-k_{calc})$ is a measure of the first-order rate constant for the reaction of **1-Br** that proceeds through the k_s' step. This is given by the second term in the numerator of eq 3 and is written separately as eq 4 (k_d[Br$^-$] $\gg k_s$, see below). The estimated rate constant for diffusional encounter is $k_d = 5 \times 10^9$ M^{-1} s^{-1},[5,9] the rate constant for separation of the ion pair to give free ions is $k_{-d} \approx 1.6 \times 10^{10}$ s^{-1},[11] and bromide ion is much more reactive than solvent toward **2** (k_{Br}/k_s = 77 M^{-1}) so that $k_{-1} \gg k_s$. At high [Br$^-$], eq 4 reduces to eq 5, because $k_s = 4 \times 10^7$ s^{-1} and $k_s' < k_s$ (see below) are negligible in comparison with k_d[Br$^-$], k_{-d} and k_{-1}. The average value of $(k_{obsd}-k_{calc})$ over [NaBr] = 2.00–5.00 M is $(3 \pm 1) \times 10^{-5}$ s^{-1} (inset, Figure 4). This is an estimate for the limiting

$$k_{obsd} - k_{calc} = \frac{k_1 k_s' k_d[\mathrm{Br}^-]}{k_s(k_{-1} + k_s' + k_{-d}) + k_d[\mathrm{Br}^-](k_{-1} + k_s')} \qquad (4)$$

$$k_{obsd} - k_{calc} = k_1 k_s'/k_{-1} \qquad (5)$$

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velocity of the reaction of 1-**Br** at infinite [Br^-], where the solvolysis reaction would proceed solely by the capture of the ion-pair intermediate [$2{\cdot}Br^-$]. This limiting velocity is only 0.06% (±0.02%) of the value of $k_{solv} = 0.049\ s^{-1}$ for the solvolysis reaction of 1-**Br** in the absence of bromide ion.

The substitution of bromide ion for perchlorate ion is expected to destabilize **2** relative to 1-**Br** because of the specific bromide ion salt effect (see above). This would be expected to lead to a decrease in k_{calc} for the reaction of 1-**Br** through the carbocation intermediate **2**. There is a 42% decrease in the observed first-order rate constant for the solvolysis of 1-**I** when 5.00 M NaBr is substituted for $NaClO_4$ at $I = 6.00$ ($NaClO_4$). If there were a similar specific bromide ion salt effect on k_{calc} (Table I), then (k_{obsd}–k_{calc}) would be increased to $9.0 \times 10^{-5}\ s^{-1}$.

The magnitude of (k_{obsd}–k_{calc}) at a given concentration of bromide ion depends on the association constant for formation of the ion pair from free ions ($K_{ass} = k_d/k_{-d}$) and on the relative reactivities of the free carbocation and the ion pair toward solvent (k_s/k_s'). Equation 6 gives a simple relationship between $K_{ass}(k_s'/k_s)$ and kinetic parameters determined in this work: $k_{solv} = 0.049\ s^{-1} = k_1k_{-d}/(k_{-1} + k_{-d})$; $k_{Br}/k_s = 77\ M^{-1} = k_dk_{-1}/[k_s(k_{-1} + k_{-d})]$. Substitution

$$\frac{k_{obsd} - k_{calc}}{k_{solv}/(k_{Br}/k_s)} = (3 \times 10^{-5}\ s^{-1})/(6.4 \times 10^{-4})\ M = (k_s'/k_s)K_{ass} \quad (6)$$

of an estimated[11] value of $K_{ass} = 0.3\ M^{-1}$ into eq 6 gives $k_s'/k_s = 0.16$, using the average value of ($k_{obsd} - k_{calc}$) = $3 \times 10^{-5}\ s^{-1} = k_1k_s'/k_{-1}$ (Figure 4), and $k_s'/k_s = 0.4$, using ($k_{obsd} - k_{calc}$) = $9.0 \times 10^{-5}\ s^{-1}$ obtained by correcting for the estimated bromide ion salt effect on k_{calc}.

The values of ($k_{obsd} - k_{calc}$) in Figure 4 are consistent with a reaction in which the ion-pair intermediate [$2{\cdot}Br^-$] is slightly less reactive toward water than the free carbocation **2** (k_s'/k_s = 0.16–0.4). A value of $k_s'/k_s = 0.33$ can be calculated from data of Ritchie, based on the 3-fold difference in the rate constants for the addition of water to a trityl carbocation with an *o*-sulfonyl methyl ester substituent and the analogous intramolecular trityl carbocation–sulfonate ion pair.[12]

Summary

The solvolysis reaction of 1-**Br** proceeds through the highly unstable carbocation intermediate **2**, which has an estimated half-life in water of ca. 30 ns. In spite of the high reactivity of **2**, the ion-pair intermediate [$2{\cdot}Br^-$] of the reaction of 1-**Br** escapes to form free ions before there is a significant reaction of solvent ($k_d > 300k_s'$, Scheme III). The Winstein model for solvolysis reactions includes three types of carbocation intermediates, each of which may be captured by solvent.[2] The present results show that the reaction of solvent with an ion pair of the highly reactive carbocation **2** is normally not an important reaction. They are consistent with the proposal that, for solvolysis reactions in water, nucleophilic reagents generally react with the *liberated* carbocation intermediates.[3-5]

In the following exceptional cases a direct reaction between solvent and an ion-pair intermediate of a solvolysis reaction may be observed experimentally: (1) when the addition of large concentrations of the leaving group ion acts, by mass action, to convert a large fraction of the free carbocation to the ion pair; and (2) when $k_s' \geq k_{-d}$ (Scheme III), the ion pair will react directly with solvent, before there is significant escape to form free ions. The rate constant for capture of the 1-(4-methylphenyl)ethyl carbocation by 50:50 (v/v) trifluoroethanol/water is estimated to be $k_s = 6 \times 10^9\ s^{-1}$.[11] The reactions of 1-(4-methylphenyl)ethyl derivatives in this solvent generate ion-pair intermediates whose capture by solvent accounts for ~ 30% of the solvolysis reaction products, and the data are consistent with $k_{-d} \approx 1.6 \times 10^{10}\ s^{-1}$ for diffusional separation of the ion-pair intermediate to free ions.[11]

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N-Fluorobis[(perfluoroalkyl)sulfonyl]imides: Reactions with Some Olefins via α-Fluoro Carbocationic Intermediates[1]

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N-Fluorobis[(perfluoroalkyl)sulfonyl]imides are a new class of electrophilic fluorinating agents. Reaction of $(CF_3SO_2)_2NF$ (**1**) with olefins gave various products, depending on the reaction conditions and the structure of the substrate. In solvents of higher nucleophilicity such as H_2O, acetic acid, aqueous HCl, and $(HF)_nPy$, α-fluorohydrins or their acetates, α,β-chlorofluoro- and α,β-difluoroalkanes were obtained. In acetic acid, *trans*-stilbene and tetraphenylethylene produced the rearranged, nonfluorinated aldehyde and ketone. Evidence is presented for the reactions proceeding via a one-electron transfer mechanism involving α-fluorocarbocationic intermediates.

Selectively fluorinated organic compounds are of current interest due to the rapidly increasing number of examples of useful biological activity.[2] Strategic fluorinations using a variety of electrophilic fluorination reagents including F_2,[3] CF_3OF,[4] C_2F_5OF,[5] RCO_2F,[6] R_fCO_2F,[7] XeF_2,[8] and

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(1) Part of this work was presented at 12th International Symposium on Fluorine Chemistry, Santa Crutz, CA, Aug 7–12, 1988; Abstract No. 416.

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