Vinylic Cations from Solvolysis. XVIII.[1,2] Unusual Solvent Effects and External Ion Return in the Solvolysis of Several Vinylic Compounds in Aqueous Trifluoroethanol

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Abstract: The solvolyses of 1-(*o*-methoxyphenyl)-2-methylpropen-1-yl tosylate (**1-OTs**) and of 1-(*p*-methoxyphenyl)-2-methylpropen-1-yl bromide (**3-Br**), chloride (**3-Cl**), tosylate (**3-OTs**), and brosylate (**3-OBs**) were studied in aqueous trifluoroethanol (TFE) buffered by 2,6-lutidine or Et_3N. The products were the corresponding vinyl ethers and ketones (from the ketonization of the enols) and the capture-rate ratios of the intermediates by the solvent components k_{H_2O}/k_{TFE} were 1.2 ± 0.1 for **1-OTs** and 1.4 ± 0.1 for **3-OTs** at 80–97% TFE (w/w). On adding water to the TFE, the rate coefficient k_1 for the solvolysis of **1-OTs** decreased, showed a minimum at molar fraction of water $X_{H_2O} \sim 0.7$, and then increased up to $X_{H_2O} = 0.995$, while k_1 of **3-OTs** decreased up to $X_{H_2O} = 0.85$. A strong common ion rate depression within a run or by added halide ion was observed for **3-Cl** and **3-Br** and $\geq 92\%$ of the products from **3-Br** in TFE arise from "dissociated" cations. The selectivity constants of the intermediate vinyl cation (α) decreased on increasing X_{H_2O}. The rate coefficient for **3-Br** in the absence of external ion return (k_1^0) showed a minimum in aqueous TFE at $X_{H_2O} \sim 0.4$. The following reactivity ratios were found in 100% TFE: k_1(**3-OBs**)/k_1(**3-OTs**) = 2.82, k_1^0(**3-Br**)/k_1^0(**3-Cl**) = 21, and k_1(**3-OTs**)/k_1(**1-OTs**) = 8, and they fit the SN1 mechanism. The unusual log k_1 *vs.* X_{H_2O} profiles were ascribed to opposing effects, of k_1 increasing on the one hand with the dielectric constant, and on the other, decreasing with the decrease in the amount of TFE, which is superior to water in the electrophilic assistance to the ionization. The higher solvating ability of TFE is supported by the transition energies ($E_T(1)$) of the internal charge-transfer band of 1-(*p*-hydroxyphenyl)-2,4,6-triphenylpyridinium betaine which decreases linearly with increasing X_{H_2O} in aqueous TFE. Involvement of ion pairs may contribute to the observed phenomena. The decrease of α on increasing X_{H_2O} was discussed in terms of changes in the bulk dielectric constant, the concentrations and the nucleophilicities of the nucleophilic solvent species, and the possible intervention of ion pairs. The "ionization power" Y of aqueous TFE mixtures was discussed and it was suggested that a better model than *t*-BuCl is required for defining these parameters.

Trifluoroethanol (TFE) and aqueous TFE mixtures became popular solvolytic media in recent years[3–19] due to the combination of low nucleophilicity[5,7] and high ionizing ability[4,5,10] of TFE which result from its high acidity[20] and dielectric constant.[21] These are reflected in the high solvolysis rates, the extensive neighboring group participation,[14,15,17,19] the rearrangements,[5,14,15,17,19] the ion pair return,[4,8,15] and the secondary isotope effects[4,9,12] which show that many of the solvolysis reactions are "limiting" [22a] in TFE. On the other hand, only the solvolysis of *t*-BuCl was studied in sufficient detail in aqueous TFE mixtures[4] and Y values[22] are available for 40–100% (w/w) TFE.[4] Usually, only the binary mixtures 97% TFE and 70% TFE (w/w) for which the ionization power parameters Y are similar to those of 60% EtOH and 50% EtOH, respectively, are used. Recently, Sunko and coworkers[16] collected literature data which show that "a number of systems of different geometry, secondary as well as tertiary, open chain and cyclic, show relatively low m values in TFE." Inspection of their data suggests that the Grunwald–Winstein m values[22] in aqueous TFE are 0.45–0.76 unit lower than in aqueous EtOH.

SN1 solvolysis of vinylic substrates RX (X = Br, OTs, etc.)[23] gives m values[18a,24–27] and k_{OTs}/k_{Br}

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ratios[26,28] which are lower than those for saturated substrates. The low *m* values were explained as partially due to reduced solvation at the vicinity of R^+, while the solvation of X^- is less hindered. Indeed, the solvolysis of 1-(*p*-methoxyphenyl)-2-methylpropen-1-yl tosylate gives a lower value in the nucleophilic aqueous acetone mixtures than in the electrophilic AcOH–HCOOH mixtures.[2,28] This solvent effect should also contribute to the k_{OTs}/k_{Br} ratios. Consequently, it was of interest to study vinylic solvolysis in aqueous TFE mixtures, where addition of water reduces the electrophilicity of the medium. Moreover, if Sunko's observation[16] is general, very low and even negative *m* values are expected for vinylic compounds in aqueous TFE, although certain vinyl triflates (trifluoromethanesulfonates) show a rather high response to the solvent change in aqueous TFE.[14]

Another interesting feature of the vinylic solvolysis is extensive common ion rate depression by X^-,[24b–d,29–31] and the formation of the bulk of the products from "dissociated" ions even in AcOH—a solvent of low dielectric constant. Aqueous TFE is an attractive solvent to investigate these phenomena since the change of the selectivity of the carbonium ion can cover an extensive solvent range, and we already found that α-phenyl-β,β-diarylvinyl cations which are formed in the trifluoroethanolysis of the bromides are highly selective.[31]

For study we selected the solvolyses of 1-(*p*-methoxyphenyl)- and 1-(*o*-methoxyphenyl)-2-methylpropen-1-yl substrates in aqueous TFE, since information on the *m* values,[2,28] ion return,[32] k_{OTs}/k_{Br},[28] and k_{OBs}/k_{OTs} ratios[33] is available for them in several solvents.

Results

1-(*o*-Methoxyphenyl)-2-methylpropen-1-yl tosylate (**1-OTs**) and its *p*-methoxy isomer **3-OTs** were prepared from the corresponding bromides and silver tosylate in acetonitrile. The bromides (*e.g.*, **3-Br**) were obtained by bromination of the corresponding 1-methoxyphenyl-2-methylpropenes.

Solvolysis of **1-OTs** in aqueous TFE was of the first order and the rates enabled the study of the solvolysis up to a very high mole fraction of water (X_{H_2O} = 0.995, 97.5% TFE (w/w)). In unbuffered TFE k_1 was higher than in the presence of 2,6-lutidine or Et_3N. Base was added in most of the runs in order to avoid undesired reactions with the liberated *p*-toluenesulfonic acid. The reaction was usually followed spectrophotometrically in the presence of Et_3N, but k_1 in 100% TFE was identical with the conductometrically measured value in the presence of 2,6-lutidine.

Table I. Solvolysis of **1-OTs**, **3-OTs**, and **3-OBs** (RX)[a] in Aqueous TFE[b]

Compd	Base[c]	Concn, *M*	% TFE (w/w) in TFE–H_2O	Temp, °C	10^4k_1, sec^{-1}
1-OTs	*d*		100	35	2.29 ± 0.03
	Lut[e]	0.085	100	35	1.68 ± 0.01
	Lut	0.14	100	35	1.70 ± 0.01
	TEA[f]	0.1	100	35	1.70 ± 0.01
	TEA[g]	0.096	100	35	0.47 ± 0.02
	TEA[f]	0.1	97	35	1.56 ± 0.005
	TEA[f]	0.1	94	35	1.41 ± 0.007
	TEA[f]	0.1	90	35	1.31 ± 0.006
	TEA[f]	0.1	80	35	1.07 ± 0.04
	TEA[f]	0.1	70	35	0.985 ± 0.004
	TEA[f]	0.1	60	35	1.16 ± 0.03
	TEA[f]	0.1	50	35	1.15 ± 0.03
	TEA[f]	0.1	40	35	1.34 ± 0.004
	TEA[f]	0.1	30	35	1.73 ± 0.005
	TEA[f]	0.1	20	35	3.09 ± 0.02
	TEA[f]	0.1	15	35	4.19 ± 0.01
	TEA[f]	0.1	10	35	5.29 ± 0.25[h]
	TEA[f]	0.1	5	35	6.11 ± 0.32[h]
	TEA[f]	0.1	2.5	35	7.84 ± 0.05
3-OTs	*i*		100	35	18.0 ± 0.5
	i		100	35	17.9 ± 0.1
	d		100	35	16.0 ± 0.1
	Lut[j]		100	35	11.6 ± 0.03
	Lut	0.04	100	35	13.4 ± 0.004
	Lut	0.12	100	35	11.7 ± 0.05
3-OTs	Lut	0.04	100	35	13.5 ± 0.05
	Lut	0.04	100	35	13.7 ± 0.04[h]
	Lut	0.04	100	15	1.45 ± 0.01
	Lut	0.06	97	35	9.33 ± 0.08
	Lut	0.06	90	35	7.73 ± 0.01
	Lut	0.06	80	35	7.97 ± 0.10
	Lut	0.06	70	35	7.90 ± 0.08
	Lut	0.06	60	15	0.667 ± 0.008
	Lut	0.06	60	35	7.16 ± 0.03
	Lut	0.06	50	35	7.13 ± 0.05
3-OBs	Lut	0.04	100	15	4.10 ± 0.01
	Lut	0.08	60	15	2.10 ± 0.06

[a] [RX] = 0.007–0.01 mol $l.^{-1}$ unless otherwise stated. [b] Runs without base or with 2,6-lutidine were followed conductometrically. Runs with Et_3N were followed spectrophotometrically. [c] Lut = 2,6-lutidine; TEA = triethylamine. [d] [RX] = 0.002 mol $l.^{-1}$. [e] [RX] = 0.008 mol $l.^{-1}$. [f] [RX] = 0.0001 mol $l.^{-1}$. [g] [RX] = 0.059 mol $l.^{-1}$. The reaction was followed by nmr in the presence of 0.36 mol $l.^{-1}$ of Et_4NOTs. [h] Average of two measurements. [i] [RX] = 0.02 mol $l.^{-1}$. [j] In the presence of 0.024 mol $l.^{-1}$ of Et_4NBr. The reaction was followed by potentiometric titration of the bromide ion.

The first-order rate coefficients k_1 (Table I) decrease moderately from 100 to 70% TFE ($X_{H_2O} \sim 0.7$) and then increase more strongly at higher X_{H_2O} values. Due to a combination of low solubility and high reactivity at the latter region, the k_1 values are somewhat less accurate than in the other X_{H_2O} regions and the average values from several experiments are given. The k_1 value extrapolated to pure water is 8.7 × 10^{-4} sec^{-1}, 5.1 times higher than k_1 in pure TFE. Plots of log k_1 *vs.* X_{H_2O} or the ionization power parameters, *Y*,[22] are

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Table II. Solvolysis Products of **1-OTs** in Aqueous TFE at 35° [a]

% TFE (w/w) in TFE–H_2O	X_{H_2O} [b]	Products in the presence of 0.25 *M* 2,6-lutidine: **1-OR** (%)	**2** (%)	k_{H_2O}/k_{TFE} [c]	Products in the presence of 0.25 *M* Et_3N: **1-OR** (%)	**2** (%)	k_{H_2O}/k_{TFE} [c]	Products in the presence of 0.25 *M* NaOH: **1-OR** (%)	**2** (%)	k_{H_2O}/k_{TFE} [c]
100	0.00	100	0		100	0				
97	0.15	81.5	18.5	0.83	86	14	0.93			
94	0.26	71	29	1.16	77	23	0.85			
90	0.355	60	40	1.20	65.5	34.5	0.96	88	12	0.25
90	0.355	57.5 [d]	42.5 [d]	1.35						
90	0.355	58.5 [e]	41.5 [e]	1.28						
80	0.555	44.5	55.5	1.00	51.5	48.5	0.76			
70	0.705	38	62	0.69	43	57	0.56			
50	0.93	26	74	0.22	30	70	0.18	53.5	46.5	0.07

[a] Product distributions were determined after 7–8 half-lives and are accurate to ±2%. [b] Mole fraction of water. [c] Capture ratios of the carbonium ion by the solvent components. Calculated from eq 3. [d] After 1 half-life. [e] After 3 half-lives.

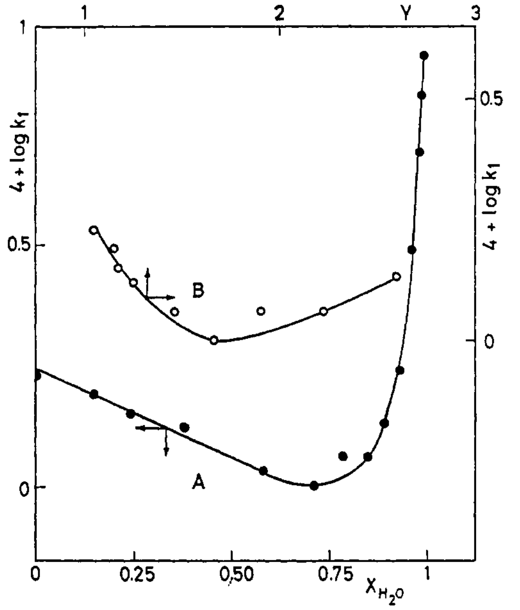


Figure 1. Plots of log k_1 for **1-OTs**: (A) *vs.* X_{H_2O} (right and lower scale), and (B) *vs.* *Y* (*t*-BuCl) (left and upper scale). *Y* values are defined only for 40–100% TFE (w/w) (ref 4).

given in Figure 1. The log k_1 *vs.* X_{H_2O} plot is linear in 70–100% TFE and 2.5–30% TFE and the (d log k_1/dX_{H_2O}) values are −0.35 for X_{H_2O} = 0–0.7 and 10 at X_{H_2O} = 0.96–1.0.

Reaction of 0.059 *M* **1-OTs** in the presence of 0.36 *M* Et_4NOTs in 100% TFE was followed by nmr and gave a k_1 value which is 3.6 times lower than the k_1 value in the absence of salt. This common ion rate depression was treated in terms of eq 1, where k_1 is the heterolysis rate coefficient, k_{-1} and k_2 are the second-order and the pseudo-first-order coefficients, and R^+ is a "dissociated" vinyl cation.[34b,c] The selectivity of the ion to capture by the leaving group *vs.* capture by the solvent, $\alpha = k_{-1}/k_2$, was determined from eq 2, where k_d is the rate

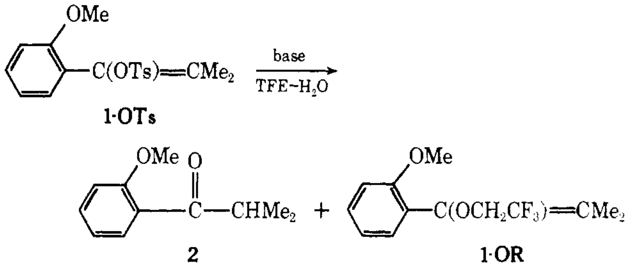
$$\text{R-X} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{R}^+ + \text{X}^- \xrightarrow[\text{SOH}]{k_2} \text{ROS} + \text{H}^+ \qquad (1)$$

$$\text{X} = \text{Br, OTs; S} = \text{H, CF}_3\text{CH}_2$$

$$k_d = k_1^0/(1 + \alpha[\text{X}^-]) \qquad (2)$$

coefficient in the presence of the added ion X^-, and k_1^0 is the k_1 value in the absence of the added salt.[34] The α value (not corrected for salt effect) is 7.3 and at least 73% of the product arises from the "dissociated" α-*o*-methoxyphenyl-β,β-dimethylvinyl cation.

The solvolysis products in aqueous TFE are *o*-methoxy-α-methylpropiophenone (**2**) and 1-(*o*-methoxyphenyl)-2-methylpropen-1-yl 2,2,2-trifluoroethyl ether (**1-OR**), but only the ether (>99% by vpc and nmr) was obtained in pure TFE in the presence of 2,6-lutidine or Et_3N. The product distributions at X_{H_2O} = 0–0.93 were studied in the presence of 2,6-lutidine, Et_3N, and occasionally with NaOH. **1-OR** is



stable to hydrolysis to **2** (*cf.* the product distribution in 90% TFE after 1, 3, and 7 half-lives) (Table II). The amount of the ether increases with the base strength, especially in the presence of NaOH.

Competition factors k_{H_2O}/k_{TFE} for the capture of the carbonium ion R^+ by water and by TFE were calculated from eq 3 and the data of Table II. They are

$$k_{H_2O}/k_{TFE} = [\mathbf{2}][\text{TFE}]/[\mathbf{1\text{-}OR}][\text{H}_2\text{O}] \qquad (3)$$

rather constant (1.2 ± 0.1) up to X_{H_2O} = 0.55 and start to decrease when X_{H_2O} > 0.55. The small difference between the values with 2,6-lutidine and Et_3N, and their near constancy at X_{H_2O} = 0.15–0.55, suggest that they reflect capture only by TFE and water. The lower values in the presence of NaOH probably reflect also capture by OH^- and $CF_3CH_2O^-$ ions, since $CF_3CH_2O^-$ is a stronger nucleophile than OH^- toward acetyl-4-methylpyridinium cation,[35a] or 2,4-dinitrofluorobenzene.[35b] Some capture by the anions, even in the reactions in the presence of the amines, is possible at lower X_{H_2O} where the k_{H_2O}/k_{TFE} ratios are lower.

The solvolysis of 1-(*p*-methoxyphenyl)-2-methylpropen-1-yl tosylate (**3-OTs**) and brosylate (**3-OBs**) in 100% TFE containing 2,6-lutidine gave only the ketone

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Table III. Solvolysis Products of AnC(X)=CMe$_2$ in Aqueous TFE at 35° [a]

X	% TFE (w/w) in TFE–H$_2$O	X_{H_2O} [b]	Products in the presence of 0.25 *M* Et$_3$N % 3-OR	% 4	k_{H_2O}/k_{TFE} [c]	Products in the presence of 0.25 *M* NaOH % 3-OR	% 4	k_{H_2O}/k_{TFE} [c]
OTs	100	0.00	100	0		100	0	
OTs	97	0.15	79	21	1.50	90	10	0.63
OTs	94	0.26	66.5	33.5	1.43	87.5	12.5	0.41
OTs	90	0.355	59.5	40.5	1.25	86	14	0.30
Br	90	0.355	57	43	1.37			
OTs	80	0.555	39	71	1.45	72	28	0.31
OTs	70	0.705	35	65	0.78	68	32	0.20
Br	70	0.705	35	65	0.78			
OTs	50	0.93	23	77	0.25	49.5	50.5	0.077
Br	50	0.93	26	74	0.22			

[a] Product distributions were determined after 7–8 half-lives and are accurate to ±2%. [b] Mole fraction of water. [c] Capture ratios of the carbonium ion by the solvent components. Calculated from an equation similar to eq 3.

4 after 10 half-lives and a H$_2$O–dilute HCl–NaHCO$_3$ work-up. However, vpc before work-up showed the formation of both **4** and the trifluoroethyl ether **3-OR**. Only **3-OR** was present in the presence of Et$_3$N before the work-up, but only **4** was obtained after neutralization with dilute HCl.

$$\underset{\textbf{3-OTs}}{\text{AnC(OTs)=CMe}_2} \xrightarrow{\text{aq TFE}} \underset{\textbf{4}}{\text{AnCOCHMe}_2} + \underset{\textbf{3-OR}}{\text{AnC(OCH}_2\text{CF}_3\text{)=CMe}^2}$$

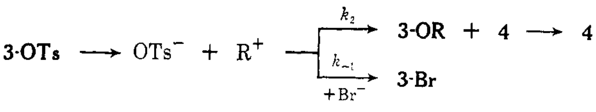
$$\text{An} = p\text{-MeOC}_6\text{H}_4\text{–}$$

The ether was found to be unstable to hydrolysis in the presence of weak bases such as pyridine, 2,6-lutidine, and morpholine, where even in 100% TFE both **3-OR** and **4** are formed. The product distributions were therefore determined in the presence of Et$_3$N or NaOH before work-up, conditions at which **3-OR** is stable.

The product distributions (Table III) show similar behavior to those described for **1-OTs**. The k_{H_2O}/k_{TFE} ratios were similar for **1-OTs** and **3-OTs** with NaOH, and for **1-OTs** with 2,6-lutidine and **3-OTs** with Et$_3$N.

The solvolysis in aqueous TFE was followed conductometrically in the presence of 2,6-lutidine, and the unbuffered trifluoroethanolysis of **3-OTs** was *ca.* 1.3 times faster than in the buffered solvent. A threefold increase in the base concentration had only a minor effect on the first-order coefficient which remained unchanged for >90% reaction. For solubility reasons the reaction could be followed only in 50–100% TFE (w/w), and k_1 decreased on increasing X_{H_2O}, giving a nonlinear log k_1 *vs.* X_{H_2O} curve (Figure 2). The change in k_1 for 50–90% TFE is small and may be within the limit of accuracy. The reactivity ratios k_1(**3-OTs**)/k_1(**1-OTs**) are slightly solvent dependent, being 7 ± 1 at 50–100% TFE.

Solvolysis of 0.02 *M* **3-OTs** in 100% TFE containing 1.2 molar excess of Et$_4$NBr and a molar equivalent of 2,6-lutidine was followed by titration of the Br$^-$. It gave an excellent first-order plot for the disappearance of the inorganic bromide ion (correlation coefficient r = 0.9993) with a rate coefficient which was 14% lower than k_1 in the absence of Br$^-$. After 5 half-lives, the composition of the mixture was: **3-OTs**, 5 ± 1%; **3-Br**, 83 ± 2%; and **4**, 12 ± 2%. By using eq 4, and neglecting the solvolysis of **3-Br** to give **4** which constitutes ≤1% of the reaction under our conditions, the steady-state treatment gives eq 5 where b = [**3-OTs**]$_0$,



$$\textbf{3-OTs} \longrightarrow \text{OTs}^- + \text{R}^+ \begin{cases} \xrightarrow{k_2} \textbf{3-OR} + \textbf{4} \longrightarrow \textbf{4} \\ \xrightarrow[+\text{Br}^-]{k_{-1}} \textbf{3-Br} \end{cases} \qquad (4)$$

$$\alpha = k_{-1}/k_2 = \ln\,(b/(b - X_t))/Y_t \qquad (5)$$

X_t = [**3-Br**]$_t$, and Y_t = [**4**]$_t$. The α value obtained by inserting the above values is 470 ± 100 which is comparable to the values calculated below from the common ion rate depression in the solvolysis of **3-Br**.

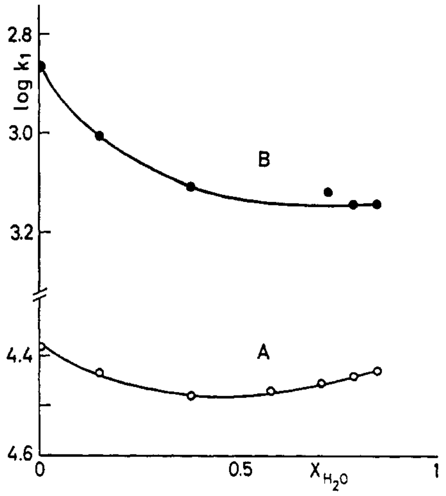


Figure 2. Plots of log k_1 *vs.* X_{H_2O}: (A) for **3-Br**; (B) for **3-OTs**.

The first-order solvolysis of **3-OBs** was also slower in the more aqueous solvent (k_1(100% TFE)/k_1(60% TFE) = 1.95). The k_1(**3-OBs**)/k_1(**3-OTs**) ratios are 2.82 (100% TFE) and 3.14 (60% TFE) at 15°.

In the solvolysis of 0.005–0.037 *M* 1-(*p*-methoxyphenyl)-2-methylpropen-1-yl bromide (**3-Br**) in aqueous TFE, the first-order rate coefficient falls during the kinetic runs due to common ion rate depression by the formed Br$^-$ (eq 1, $k_{-1} \gg k_2$). The corresponding rate equation is 6,[34] where x_0 = [Br$^-$]$_0$, $x + x_0$ = [Br$^-$]$_t$, and

$$dx/dt = k_1(a - x)/(1 + \alpha[x_0 + x]) \qquad (6)$$

a = [RX]$_0$. k_1 and $\alpha = k_{-1}/k_2$ were calculated by two methods. (a) The integrated rate coefficient k_1 was determined at ≤3% reaction where the external ion return[34] is negligible. By using this k_1 value, the amount of bromide ion $(\Delta x)_1$ formed at a short time interval $(\Delta t)_1$ = ($10^{-3}/k_1$ sec) was evaluated by eq 7,

$$(\Delta x)_1 = (\Delta t)_1[k_1(a - x)/(1 + \alpha(x + x_0))] \qquad (7)$$

Table IV. Solvolysis of $AnC(X){=}CMe_2$ (RX) in Aqueous TFE in the Presence of 2,6-Lutidine (Lut)

X	10^2[RX], mol l.$^{-1}$	10^2[Lut], mol l.$^{-1}$	Temp, °C	% TFE (w/w) in TFE–H_2O	$10^5k_1^0$, sec^{-1}	k_1^0/k_1^{50} [a]	α, l. mol^{-1}
Cl	1.67	5.1[b]	35	100	0.198 ± 0.038		337 ± 166
Br	3.65		35	100	4.61 ± 0.20	*b*	326 ± 43
Br	1.57	12.3	35	100	4.13 ± 0.23	2.84	394 ± 42
Br	1.50	2.28	35	100	4.21 ± 0.10	2.58	356 ± 24
Br	0.78	3.75	35	100	4.18 ± 0.04	1.92	450 ± 23
Br	1.43		45	100	14.4 ± 1.1	2.71	356 ± 51
Br	1.05	8.60	45	100	11.1 ± 0.3	2.10	290 ± 22
Br	0.50	6.15	45	100	13.1 ± 0.1	1.73	413 ± 32
Br	1.73	7.10	35	97	3.70 ± 0.20	2.30	225 ± 33
Br	1.57	12.30	35	90	3.30 ± 0.02	1.54	110 ± 5
Br	1.68	6.60	35	80	3.40 ± 0.03	1.12	27 ± 2
Br	1.65	6.50	35	70	3.51 ± 0.02	1.05	11 ± 3
Br	1.06	8.60	45	70	9.14 ± 0.02	1.04	12 ± 1
Br	1.68	7.44	35	60	3.63 ± 0.03	1.04	9 ± 3
Cl	1.97	4.48[c]	35	60	0.050 ± 0.001		<10[d]
Br	1.43	7.20	35	50	3.65 ± 0.01	1.02	8 ± 1

[a] k_1^0 and k_1^{50} are the values of the integrated k_1 of the equation $k_1t = 2.3 \log (a/(a - x))$ at 0 and at 50% reaction. [b] Reaction followed only up to 30%. $k_1^0/k_1^{25} = 2.20$. [c] Based on the calculated infinity. [d] No rate depression was observed during a run when the calculated infinity was used.

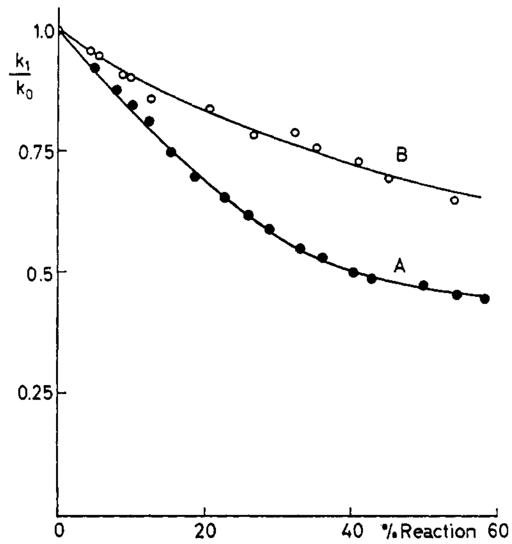


Figure 3. Plots of the relative decrease of k_1 of the first-order equation (expressed as k_1/k_1^0) with the progress of the reaction of **3-Br**. The points are experimental and the lines were calculated from eq 8: (A) 0.0105 mol l.$^{-1}$ of **3-Br** in 100% TFE at 45° with $\alpha = 290$; (B) 0.0157 mol l.$^{-1}$ of **3-Br** in 90% TFE at 35° with $\alpha = 110$.

and the values of $(\Delta x)_n$ for further time intervals $(\Delta t)_n$ were calculated with the aid of a computer program by substituting $(a - x)$ by $(a - x - (\Delta x)_{n-1})$ and $(x + x_0)$ by $(x + x_0 + (\Delta x)_{n-1})$ in eq 7. This gave theoretical [Br$^-$] *vs.* time curves whose shapes were dependent on the value of α, and the program found the α which gave the best fit of the experimental points to the theoretical plot. The fit is demonstrated for two solvent compositions in Figure 3, which shows a plot similar to Ingold's[34a] for the decrease of the experimental k_1/k_1^0 values during the reaction, and the theoretical curves which use the α values obtained from the above treatment. (b) Integration of eq 6 gives eq 8 when $x_0 = 0$

$$t/\ln [a/(a - x)] = 1/k_1 + (\alpha/k_1)[(a - x)/\ln (a/(a - x))] \quad (8)$$

and a plot of $t/\ln [a/(a - x)]$ *vs.* $[(a - x)/\ln (a/(a - x))]$ was indeed linear with a slope of α/k_1 and an intercept of $1/k_1$. This yielded k_1 and α values identical with those obtained by procedure (a).

The k_1^0 and the α values are summarized in Table IV. The ratios of the rate coefficient at 0% to that at 50% reaction according to the first-order equation without return (k_1^0/k_1^{50}) are given for comparison with previous work. They demonstrate the larger fall of k_1 within a run at higher initial concentrations of **3-Br**.

The common ion rate depression was verified by solvolyzing **3-Br** in the presence of added Et_4NBr. With 0.03 *M* [Br$^-$] a first-order behavior was obtained, k_1 was 11.7 times lower than k_1^0, and α was calculated by eq 2. At lower [Br$^-$] the extrapolated k_1 value at zero reaction time was again lower than k_1^0 and k_1 fell during the run. In these cases, the same results were obtained either by using the points at low reaction percentages for calculating k_d of eq 2, or by using procedure (a) above. The α values of Table V are in reasonable agreement with those of Table IV. A plot of k_1^0/k_d *vs.* [Br$^-$] for the four points of Table V is linear (*cf.* eq 2) with a slope $\alpha = 360 \pm 40$ ($r = 0.988$). From the maximum k_1^0/k_d ratios[34b] we calculated that at least 92% of the solvolysis products arise from "dissociated" α-*p*-methoxyphenyl-β,β-dimethylvinyl cations. The actual value is probably higher, since a limit to the rate depression was not achieved, and no correction for the positive salt effect on the heterolysis rate was introduced.

An appreciable rate depression in 60% TFE was found with the highest [Br$^-$] which could be studied. The α value was in good agreement with that of Table IV and at least 20% of the products are derived from dissociated cations.

The α values decrease with the increase in X_{H_2O} up to 50% TFE. Their near constancy at 50–70% TFE may be real, but these α values correspond to a very small return, and this, coupled with the low solubility of **3-Br**, makes α less accurate at this solvent range. Higher α values are observed for runs with lower concentrations of **3-Br** at a certain solvent mixture, as previously observed in AcOH.[36]

By assuming that the reactivities of Br$^-$, TFE, and H_2O toward the vinyl cation are only concentration

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(36) Y. Apeloig and Z. Rappoport, unpublished results.

Table V. Solvolysis of **3-Br** in the Presence of Added Bromide Ion at 35°

10^2[**3-Br**], mol l.$^{-1}$	10^2[Lut],^{a} mol l.$^{-1}$	10^2[Et_4NBr], mol l.$^{-1}$	% TFE (w/w)	$10^5k_1{}^0$, sec^{-1}	$k_1{}^0/k_1{}^{50}$	α, l. mol^{-1}
1.50	2.28		100	4.21	2.58	356 ± 24
1.69	2.87	0.72	100	1.30	1.71	302
1.65	3.20	1.52	100	0.55	1.08	430
1.69	3.12	2.99	100	0.36	1.00	350
1.68	7.44		60	3.63	1.04	9.4
1.76	3.55	3.06	60	2.89	1.00	8.5

^{a} Lut = 2,6-lutidine.

dependent, and that capture by OH^- and $CF_3CH_2O^-$ ions is negligible, eq 9 and 10, where $\alpha_1 = k_{-1}/k_{TFE}$ and

$$dx/dt = k_1(a - x)/(1 + \{k_{-1}/(k_{TFE}[TFE] + k_{H_2O}[H_2O])[Br^-]\}) \quad (9)$$

$$1/\alpha = [TFE]/\alpha_1 + [H_2O]/\alpha_2 \quad (10)$$

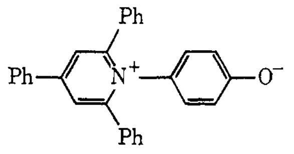
$\alpha_2 = k_{-1}/k_{H_2O}$ are two selectivity factors, replace eq 8. Application of a computer program to obtain the best α_1 and α_2 values gave the following results: for 80–100% TFE, $1/\alpha_1 = (-7.24 \pm 35.7) \times 10^{-5}$, $1/\alpha_2 = (3.11 \pm 0.68) \times 10^{-3}$ ($r = 0.918$); for 50–97% TFE, $1/\alpha_1 = (-7.60 \pm 6.37) \times 10^{-4}$, $1/\alpha_2 = (4.82 \pm 0.36) \times 10^{-3}$ ($r = 0.9763$); and for 50–100% TFE, $1/\alpha_1 = (-4.04 \pm 4.98) \times 10^{-4}$, $1/\alpha_2 = (4.69 \pm 0.33) \times 10^{-3}$ ($r = 0.9775$). The magnitude of the error and the sign of $1/\alpha_1$ suggest that this procedure gives only meaningful α_2, which are 321 ± 70, 207 ± 15, and 214 ± 15 for the three solvent regions, respectively. The data in 100% TFE were therefore used to calculate an α_1 value of 5000. Application of eq 10 by plotting $1/\alpha$ − [TFE]/5000 *vs.* [H_2O] for the region 50–100% TFE gives $\alpha_2 = 206 \pm 18$ ($r = 0.9817$), but this procedure is unsatisfactory since close inspection reveals a sigmoid rather than a linear relationship.

A plot of $k_1{}^0$ values for **3-Br** *vs.* X_{H_2O} (Figure 2) is similar to that observed for **1-OTs**: $k_1{}^0$ reaches a minimum and then increases slowly in the region of 50–80% TFE. Figure 2 differs from Figure 1 in the position of the minimum which is at $X_{H_2O} \sim 0.4$, and in the more moderate increase of $k_1{}^0$(**3-Br**) at higher X_{H_2O} values: $k_1{}^0$ changes by only 7% between 50 and 80% TFE.

The distributions of the solvolysis products of **3-Br** (Table III) in 90, 70, and 50% TFE in the presence of Et_3N are very similar to those from **3-OTs** in the same solvent mixtures.

Solvolysis of 1-(*p*-methoxyphenyl)-2-methylpropen-1-yl chloride (**3-Cl**) was slow and was followed conductometrically only up to 30% reaction. From the "calculated" infinities, which are based on the conductivity of 2,6-lutidinium hydrochloride in TFE, k_1 was calculated. The common ion rate depression in 100 and in 60% TFE gave similar α values to those for **3-Br** (Table IV). This similarity in α values was noted with other vinylic systems,[30b,36] and suggests that the errors in the infinity values are small. The k_{Br}/k_{Cl} ratios are 21 in 100% TFE and 73 in 60% TFE.

Spectra of 1-(*p*-Hydroxyphenyl)-2,4,6-triphenylpyridinium Betaine in Aqueous TFE. In order to find out whether the unusual properties of aqueous TFE as a solvolytic medium are reflected in other properties we investigated the position of the internal charge-transfer band of 1-(*p*-hydroxyphenyl)-2,4,6-triphenylpyridinium betaine (**5**, Dimroth's betaine **1**).[37] This is one of a large series of betaines which were studied by Dimroth, *et al.*,[37] as a probe to solvent properties.



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Only a high-intensity solvent insensitive maximum at 307–310 nm was observed in aqueous TFE. Since the absence of the charge-transfer band may be due to protonation of **5** by TFE, the spectra were investigated in the presence of base. We found that addition of 0.1 *M* Et_3N to **5** does not affect the λ_{max} of the charge-transfer band in EtOH (465 nm with and without Et_3N; lit.[37] 467 nm), *i*-PrOH (503 nm with and without Et_3N; lit.[37] 501 nm), and water (411 nm with Et_3N; 411.5 nm without Et_3N; lit.[37] 412 nm). In the presence of Et_3N (0.1 *M*) the low wavelength maximum of **5** is shifted to 305–307 nm, and a solvent-sensitive charge-transfer band of low intensity appears at 390–411 nm. Its position is unchanged in the presence of NaOH.

The position of the band (Table VI) is shifted to *higher* wavelengths (lower energies) with the increase of X_{H_2O}. A plot of the transition energies $E_T(1)$ (which are designated in analogy to Dimroth's $E_T(30)$ for his

Table VI. Spectral Data for 1-(*p*-Hydroxyphenyl)-2,4,6-triphenylpyridinium Betaine in Aqueous TFE

% TFE in TFE–H_2O (w/w)	$\lambda_{max}{}^a$ (ϵ)			$E_T(1)$
	In the absence of Et_3N	In the presence of 0.1 *M* Et_3N		
100	309 (34,900)	307 (36,800)	390 (2900)	73.2
97	310 (34,600)	306 (36,500)	392 (2800)	73.0
94	310 (33,500)	307 (35,500)	394 (2700)	72.6
90	309 (31,200)	307 (33,000)	396.5 (2450)	72.1
80	309 (35,000)	307 (36,500)	401.5 (2700)	71.3
70	309 (30,600)	306 (32,000)	404 (2400), 403.5^b	70.8
50	310 (30,600)	307 (32,200)	407.5 (2400)	70.2
30	309	306	412^c (411^b)	69.4
20	308	306	412^c	69.4
10	307	305	411^c	69.5
0	306	305	411 (411.5,^{d} 412^e)	69.5

^{a} Accurate to ±0.5 nm. ^{b} In the presence of 0.1 *M* NaOH. ^{c} Accurate to ±1 nm. ^{d} In the absence of Et_3N. ^{e} Literature value.[37]

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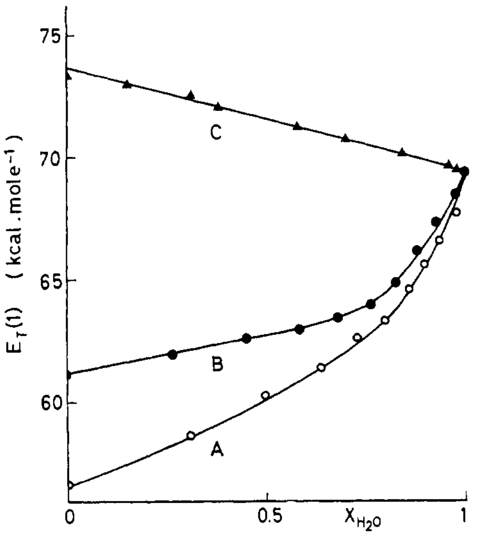

Figure 4. Plots of $E_T(1)$ *vs.* X_{H_2O} for: (A) aqueous acetone; (B) aqueous EtOH; (C) aqueous TFE.

betaine **30**)[37] *vs.* X_{H_2O} is linear within the accuracy of the determination of $E_T(1)$ (0.2 kcal mol^{-1}) while the $E_T(1)$ values for aqueous acetone and aqueous EtOH give nonlinear plots (Figure 4). The data for the latter solvents were calculated from Dimroth's results[37] except for $E_T(1)$ for acetone which we measured. The ϵ values in aqueous TFE of high X_{H_2O} were not determined due to the low solubility of **5**.

Discussion

The appearance of a minimum in a log k_1 *vs.* Y plot has only one precedent in the solvolysis of *t*-BuCl and 7-methyl-7-norbornyl tosylate (MNBOTs) in aqueous 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP).[38] A rate decrease on changing the solvent from 100% TFE to aqueous TFE with $X_{H_2O} \geq 0.36$ characterizes **1-OTs**, **3-OTs**, **3-OBs**, **3-Cl**, **3-Br**, and other compounds.[39] This unusual behavior can be attributed neither to an electrophilic addition–elimination (AdE-E, eq 11a),[40] since **3-OTs** solvolyzes in the more acidic CF_3COOH[33] and AcOH–HCOOH mixtures[28] *via* SN1, nor to a nucleophilic addition–elimination (AdN-E, eq 11b)[41] due to

$$\begin{tikzcd}
 & \mathrm{Ar\overset{+}{C}(X){-}CHMe_2} \arrow[r, "\mathrm{RO^-}"] & \mathrm{ArC(X)(OR){-}CHMe_2} \arrow[dd, "-\mathrm{HX}"'] \\
\mathrm{ArC(X){=}CMe_2} \arrow[ur, "(a)\ +\mathrm{H^+}"] \arrow[dr, "(b)\ +\mathrm{RO^-}\ \text{or}\ \mathrm{ROH}"'] & & \\
 & \mathrm{ArC(X)(OR){-}\bar{C}Me_2} \arrow[r, "-\mathrm{X^-}"] & \mathrm{ArC(OR){=}CMe_2}
\end{tikzcd} \qquad (11)$$

the insensitivity to the base concentration. Attack on sulfur[42] cannot account for the similar behavior of **3-Br** and **3-OTs** and for the formation of **1-OR** and **3-OR**. The unprecedented[41] in-plane k_s route[43] should show an increase in log k_1 *vs.* Y, and is prevented by the geometry of the crowded system.

The kinetics and the capture experiments fit the SN1 mechanism. The k_{Br}/k_{Cl} ratios of 21–73 and the k_{OBs}/k_{OTs} ratios of 2.8–3.1 for system **3** are similar to the ratios for saturated[44] and vinylic systems,[24,25,36] and differ from those observed for other routes ($k_{OBs}/k_{OTs} \sim 0.3$,[40a] $k_{Br}/k_{Cl} = 0.23$–0.56[40d] (AdE-E); $k_{Br}/k_{Cl} \sim 1$[41] (AdN-E)). The k_{OTs}/k_{Br} ratios in system **3** are much lower than the ratios found for saturated compounds which solvolyze *via* SN1,[39a,45] but they are similar to those for other vinylic systems,[24b,26,28] and they are discussed elsewhere.[26,39a] The $k_{3\text{-OTs}}/k_{1\text{-OTs}}$ ratio of 7 is much lower than the $k_{p\text{-MeO}}/k_{o\text{-MeO}}$ ratios observed for vinyl cation formation *via* electrophilic addition to acetylenes,[46] and fit the decrease of the ratios with the increased bulk of substituents around the incipient carbonium ion center.[46,47]

The Y values for aqueous TFE, which are based on *t*-BuCl, are an inappropriate measure of the ionizing power[4,48] (see below), and we therefore use the mole fraction of water (X_{H_2O}) as a solvent parameter in our discussion.

Log k_1 *vs.* X_{H_2O} Relationships. Three possible explanations for the unusual solvent effects on k_1 are in terms of (a) opposing effects on k_1, (b) ion pairing, and (c) solvent structure.

(a) Opposing Effects on k_1. The simplest explanation is that the curves of Figures 1 and 2 result from a combination of two opposing effects on k_1 of eq 1. Increased ionization rate is anticipated for an increase in the bulk dielectric constant (ϵ), but at high ϵ values specific effects are important,[49] and k_1 would be highly responsive to electrophilic assistance by hydrogen bonding to the departure of the leaving group. Electrophilic assistance would decrease on increasing X_{H_2O} since pK_a (TFE) < pK_a (H_2O),[20] and anion solvation in TFE is enhanced compared with that in water.[50] However, since the n → π shifts of acetone suggest that H_2O and TFE are similar hydrogen bond donors,[51] while

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[50] D. F. Evans, J. A. Nads, and M. A. Matesich, *J. Phys. Chem.*, **75**, 1708 (1971).

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other spectral evidence suggests that water is the better donor,[52] we studied the solvatochromic shifts of the betaine **5** as a model for solvation of our dipolar transition state. Table VI and the linearity of the $E_T(1)$ *vs.* H_2O plot (Figure 4C) substantiate the conclusion of a reduced solvation at higher X_{H_2O}.[52a] In contrast, k_1 and $E_T(1)$ increase with X_{H_2O} in aqueous acetone and EtOH mixtures (Figure 4).

The shape of the curves for different substrates would depend on the extent of "TFE sorting" around the leaving group in the transition state,[53] and on the presence of TFE–π (C=C) hydrogen bonds as observed for related compounds.[55]

The strong increase in k_1 at high X_{H_2O} may reflect reduced electrophilic assistance at high ϵ values,[56] but it is likely that the presence of ion pairs contributes to the observed shape of the k_1(**1-OTs**) *vs.* X_{H_2O} plot (see below).

(b) Ion Pairing. The intermediacy of ion pairs was suggested in the solvolysis of several saturated systems,[4,8,15] and of vinyl triflates[18] in TFE and in aqueous TFE, but the extent of the internal return as a function of X_{H_2O} is unknown.

Dissociated cations are not responsible for the shape of the curves, since the shapes of log $k_1{}^0$(**3-Br**) and log k_1(**1-OTs**) *vs.* X_{H_2O} plots are similar, although $k_1{}^0$ values are free from external ion return. For a scheme which involves a reversibly formed ion pair R^+X^- (eq 12), the rate equation is eq 13, where k_t and k_{ion} are the rate constants for product formation and for ionization, respectively. When account is taken of the external ion return, eq 14 is obtained, where $F = k_2/(k_{-1} + k_2)$ is the fraction of ion pairs which give the free cation.

$$RX \underset{k_{-\text{ion}}}{\overset{k_{\text{ion}}}{\rightleftharpoons}} R^+X^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R^+ + X^- \xrightarrow[\text{SOH}]{k_3} ROS \qquad (12)$$

$$k_t = k_{\text{ion}} \Big/ \left[1 + \frac{k_{-1}}{k_2}\left(1 + \frac{k_{-2}[X^-]}{k_{-3}}\right)\right] \qquad (13)$$

$$k_t{}^0 = k_{\text{ion}}k_2/(k_{-1} + k_2) = k_{\text{ion}}F \qquad (14)$$

F and k_{ion} would show opposite responses to a change in the blend of dissociating and ionizing power with X_{H_2O}. Ion pair dissociation constants increase with ϵ,[57] and F should increase with X_{H_2O} in a concave curve which reaches a plateau when $F = 1$. Due to electrophilic solvation, k_{ion} would decrease on increasing X_{H_2O} at least when $X_{H_2O} \ll 1$. The product of the two curves may give under certain conditions a k_t *vs.* X_{H_2O} plot with a minimum.[58] Figure 5 shows that if the shape of Figure 1 is to be obtained while the F *vs.* X_{H_2O} curve approaches a plateau, k_{ion} should initially give a sharp decrease with X_{H_2O}, in contradiction to the expected "TFE sorting" which would moderate such a decrease. Even if a plateau is obtained in the k_{ion} – X_{H_2O} plot at low X_{H_2O} values, the increase of k_t at high X_{H_2O} values should still be moderate.[59] We conclude that even if ion pairs are involved, k_{ion} should still show a minimum in aqueous TFE. The steep increase in k_t at high X_{H_2O}, and analogies with other systems,[36] suggest that ion pairs are indeed involved in the solvolysis, and the different k_t *vs.* X_{H_2O} plots for different substrates partially reflect a difference in the F and k_{ion} terms.

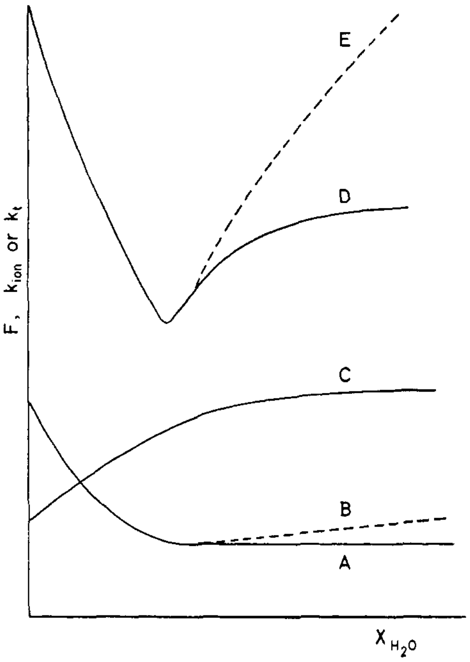

Figure 5. Schematic plots of: (A) k_{ion} with plateau *vs.* X_{H_2O}; (B) k_{ion} with shallow minimum *vs.* X_{H_2O}; (C) F *vs.* X_{H_2O}; (D) the product A·C *vs.* X_{H_2O}; (E) the product B·C *vs.* X_{H_2O}.

(c) Solvent Structure. The minimum in the log k *vs.* X_{H_2O} curves in the solvolyses of *t*-BuCl and MNBOTs in aqueous HFIP appears at $X_{H_2O} = 0.67$.[38] It was suggested that a HFIP·2H$_2$O species with a lower solvating power than either HFIP or water is formed.[38]

We reject a similar explanation for our TFE–H$_2$O mixtures for the following reasons. (a) There is no independent support for the formation of TFE·2H$_2$O, and even if a hypothetical hydrate TFE·2H$_2$O (**6**) is formed with a maximum number of linear hydrogen bonds, it still contains an acidic hydrogen which makes

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[52] C. N. R. Rao, G. K. Goldman, and A. Balasubramanian, *Can. J. Chem.*, **38**, 2508 (1960).

[52a] Note Added in Proof. P. Burri and H. Zollinger found recently a maximum in the rate of dediazoniation of benzenediazonium tetrafluoroborate in aqueous TFE. This reaction, which presumably takes place *via* phenyl cation–molecular nitrogen pair, is of an opposite charge type to our reaction, and a similar "preferential solvation" explanation may hold also in this case. We thank Professor Zollinger for communicating to us these unpublished results.

[53] In the solvolysis of substituted benzyl halides $ZC_6H_4CH_2X$ in the nearly isodielectric TFE–EtOH mixtures, log k for Z = *p*-Me increases with Y, and for Z = *m*-F log k decreases with Y. This was suggested to reflect the extent to which solvent is involved as an electrophile (mainly TFE) or nucleophile (mainly EtOH) in the rate-determining step.[54]

[54] D. A. da Roza, L. J. Andrews, and R. M. Keefer, *J. Amer. Chem. Soc.*, **95**, 7003 (1973).

[55] R. West, *J. Amer. Chem. Soc.*, **81**, 1614 (1959).

[56] Our explanation suggests a similar behavior for solvolysis in aqueous AcOH and aqueous HCOOH mixtures, where ϵ increases with X_{H_2O} and the specific solvation may be even more pronounced. We are not aware of any report of such behavior. Likewise, it is not clear why *t*-BuCl shows a monotonic increase in the log k *vs.* X_{H_2O} plot.

[57] M. Szwarc in "Ions and Ion Pairs in Organic Reactions," Vol. 1, M. Szwarc, Ed., Wiley-Interscience, New York, N. Y., 1972, Chapter 1.

[58] A similar explanation was given for the *maximum* observed for k_t for the acetolysis of *threo*-3-anisyl-2-butyl *p*-bromobenzenesulfonate, in AcOH–Ac$_2$O mixtures, on increasing X_{Ac_2O} (S. Winstein, R. Baker, and S. Smith, *J. Amer. Chem. Soc.*, **86**, 2072 (1964)). A maximum could be obtained from a product of a linear k_{ion} *vs.* X_{Ac_2O} plot with a negative slope, and a linear F *vs.* X_{Ac_2O} plot with a positive slope.

[59] Although Figure 5 represents a specific example of the response of F and k_{ion} to X_{H_2O}, inspection of similar plots reveals that other situations which retain our basic assumptions (*e.g.*, when the decrease of k_{ion} with X_{H_2O} is more moderate) result in $k_{\text{ion}}F$ *vs.* X_{H_2O} plots which much less resemble that of Figure 1.

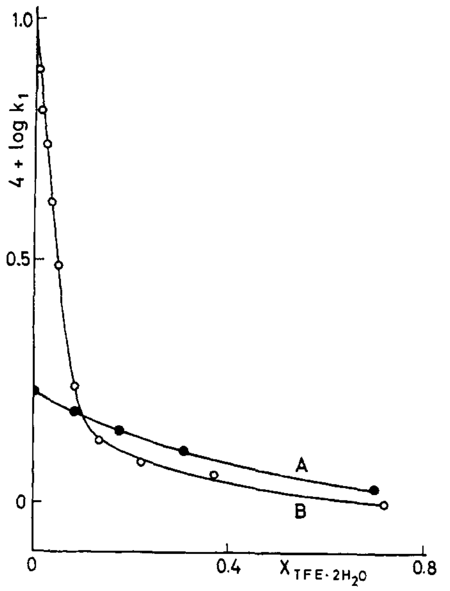
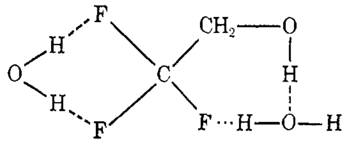


Figure 6. A plot of log k_1 *vs.* $X_{\mathrm{TFE \cdot 2H_2O}}$ in binary mixtures of TFE·2H₂O with TFE (A) and with water (B) for **1-OTs**.



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it a better hydrogen-bond donor than water. (b) Many solvolyzing substrates do not show a minimum in aqueous TFE, and k_t for *t*-BuCl[4] and for MNBOTs[38] behave differently at $X_{\mathrm{H_2O}} = 0.67$. (c) The $E_T(1)$ *vs.* $X_{\mathrm{H_2O}}$ plot shows no break at $X_{\mathrm{H_2O}} = 0.67$ or 0.33. (d) The minima for **1-OTs**, **3-OTs**, and **3-Br** should all be at $X_{\mathrm{H_2O}} = 0.67$. Figure 6 is a plot of log k_1 *vs.* $X_{\mathrm{TFE \cdot 2H_2O}}$ for **1-OTs**, calculated by assuming a high equilibrium constant for the formation of **6**, for the binary solvent mixtures TFE–TFE·2H₂O and TFE·2H₂O–H₂O. The assumption that a TFE·2H₂O species is less reactive than water or TFE can be applied here since k_1 decreases on increasing $X_{\mathrm{TFE \cdot 2H_2O}}$ from *ca.* 0.1 to 0.7, and k_1 increases strongly only at high $X_{\mathrm{H_2O}}$ values. However, the minimum for **3-Br** appears at $X_{\mathrm{H_2O}}$ of *ca.* 0.4, and it does not appear up to $X_{\mathrm{H_2O}} = 0.85$ for **3-OTs**.

Common Ion Rate Depression in Aqueous TFE. α-Arylvinyl derivatives (RX) frequently show strong common ion rate depression by the anion X^-. This was previously observed for Ar = Ph[31] or *p*-MeOC$_6$H$_4$–,[24b–d,28–30,36,40d,60] for X = Cl,[30,36,40d] Br,[24d,30,32,36] I,[29] OSO$_2$Me,[36] and OTs[24b,26] in aqueous DMF,[29] aqueous acetone,[24b,26] aqueous EtOH,[36] TFE,[31] AcOH,[24,28,30b,32,36] and AcOH–HCOOH mixtures.[30a,36,60] This phenomenon was observed now for **3-Br** in TFE and in aqueous TFE. Since a limit to the rate depression was not achieved, ≥92% of the solvolysis products in TFE, and a large fraction of them in aqueous TFE, are formed from "dissociated"[34b] vinyl cations.

The dependence of α on the solvent, in the case where both solvent components react with R$^+$, was not hitherto studied and is considered now. α will increase on enhanced cation solvation, which makes R$^+$ more stable and selective. α should be decreased by the following factors: (a) by enhanced anion solvation which reduces the nucleophilicity of $X^-(k_{-1})$; (b) by increase in ϵ since the recombination rate of R$^+$ with the anion X^- would decrease more than that with the neutral SOH;[61b] (c) by increase in the "ionic strength," and this effect will be more pronounced when ϵ is lower;[62] (d) by replacing the less nucleophilic solvent in a binary mixture by the more nucleophilic one; (e) by increasing the molar concentration of the nucleophilic solvent, since k_2 is a pseudo-first-order constant; (f) by capture of R$^+$ by the lyate ion (SO$^-$) which is more nucleophilic than SOH; (g) by the appearance of an ion pair which does not give products between RX and R$^+$. The relationship between the observed α (α_{app}) of eq 12 and α of eq 1 is then given by eq 15, and α will decrease since F

$$\alpha_{\mathrm{app}} = k_{-1}k_{-2}/k_3(k_{-1} + k_2) = \alpha(1 - F) \qquad (15)$$

increases with ϵ. When the ion pair gives products, the effect of the medium on α is more complicated.

Previous analysis of the decrease of α in aqueous acetone with $X_{\mathrm{H_2O}}$ for $(p\text{-MeC}_6\text{H}_4)_2\text{CHCl}$[62] and for Ph$_2CCl_2$[61] was mainly in terms of (b) and (c), and factor e was dismissed since "the mass law effect was presumed to be independent of the water content".[34a] Kohnstam and coworkers corrected for (c) by calculating α^0 values at zero ionic strength for Ph$_2$CCl$_2$, and predicted and observed a linear relationship between log α^0 and $1/\epsilon$.[61b] However, factor e cannot be dismissed, since, by assuming that α changes only due to it, we calculated a nearly constant dimensionless α for Ph$_2$CCl$_2$. Differential solvent effects have been mentioned previously,[61b] and the implications of ion pairing have been discussed by Winstein,[63] Kohnstam,[61b] and Ritchie.[64]

Increasing $X_{\mathrm{H_2O}}$ should increase α in our system since TFE increases anion solvation and water increases cation solvation,[50] while factor b would reduce α. Factor c should be negligible since there is no upward drift in k_1 for **1-OTs** and **3-OTs** by the formed 2,6-lutidinium tosylate, and the average α values were similar in the presence of the low [Br$^-$] formed and the high [Br$^-$] added in the capture experiments of **3-OTs** and **3-Br**.[65] By using the $k_{\mathrm{H_2O}}/k_{\mathrm{TFE}}$ ratios of Table III, which measure the capture ratio of the free cation from either **3-Br** or **3-OTs**, and eq 17 (which is derived from eq 16) we calculated k_3/k_{TFE} ratios, which were used to

$$k_3 = k_{\mathrm{TFE}}[\mathrm{TFE}] + k_{\mathrm{H_2O}}[\mathrm{H_2O}] \qquad (16)$$

$$k_3/k_{\mathrm{TFE}} = [\mathrm{TFE}] + (k_{\mathrm{H_2O}}/k_{\mathrm{TFE}})[\mathrm{H_2O}] \qquad (17)$$

correct the α values in terms of (d) and (e) together. Table VII gives the corrected values (α_{cor}) and shows that the correction is not large since α_{cor} values still decrease sevenfold from 100 to 80% TFE. As discussed above, the product distribution suggests that factor f is unimportant in the presence of 2,6-lutidine or Et$_3$N.[66]

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(60) Z. Rappoport and Y. Apeloig, *Tetrahedron Lett.*, 1817 (1970).

(61) (a) B. Bensley and G. Kohnstam, *J. Chem. Soc.*, 3408 (1955); (b) G. Kohnstam and B. Shillaker, *ibid.*, 1915 (1959).

(62) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

(63) S. Winstein, M. Hojo, and S. Smith, *Tetrahedron Lett.*, 12 (1960).

(64) For a review, see C. D. Ritchie, *Accounts Chem. Res.*, 348 (1972).

(65) If the different k_1^0 and α values at different initial concentrations of **3-Br** and 2,6-lutidine are due to ionic strength effects, HBr assists the ionization (k_1^0) more than 2,6-lutidinium bromide, and α is higher for a smaller decrease of the ionic strength per run, as predicted.

(66) Our $k_{\mathrm{H_2O}}/k_{\mathrm{TFE}}$ ratios for capture of a free cation are surprising in view of the much lower nucleophilicity of TFE compared with water.

Table VII. Calculated and Observed α Values

% TFE (w/w)	[TFE], M	[H_2O], M	k_{H_2O}/k_{TFE}[a]	ϵ[b] (35°)	k_3/k_{TFE}[c]	α,[d] l. mol^{-1}	α_{cor},[e] l. mol^{-1}	α_{cal},[f] l. mol^{-1}	$\alpha_{cal'}$,[g] l. mol^{-1}	$\alpha_{cal''}$,[h] l. mol^{-1}	$\alpha_{cal'''}$,[i] l. mol^{-1}	$\alpha_{cal^{iv}}$,[j] l. mol^{-1}
100	13.3	0		23.0	13.3	373	373	290	360	316	351	447
97	12.8	1.7	1.49	25.0	15.3	225	260	245	218	269	285	272
90	11.6	5.6	1.23	30.0	18.5	110	153	160	80	181	158	104
80	10.0	11.1	1.45	36.5	26.1	27	53	85	33	102	45	44
70	8.5	16.7	0.78	42.0	(21.4)[k]	11	(18)[k]	39	19	54		26
50	5.7	27.8	0.25	64.5	(12.8)[k]	8	(8)[k]	−66	5.5	−56		8

[a] From Table III. [b] Average of $\epsilon(30°)$ and $\epsilon(40°)$ values from ref 21 were used to calculate $\epsilon(35°)$. A plot of these $\epsilon(35°)$ values *vs.* X_{H_2O} gave the reported values by interpolation. [c] From eq 17. [d] From Table IV. [e] $\alpha_{cor} = \alpha(k_3/k_{TFE})/13.3$. [f] Calculated from the equation: $\alpha = 12{,}725/\epsilon - 263.5$ for six points ($r = 0.9047$). [g] Calculated from the equation: $\log \alpha = 65.31/\epsilon - 0.274$ for six points ($r = 0.9770$). [h] Calculated from the equation: $\alpha_{cor} = 13{,}306/\epsilon - 262.8$ for six points ($r = 0.9433$). [i] Calculated from the equation: $\alpha_{cor} = 19{,}092/\epsilon - 478$ for the first four points ($r = 0.9895$). [j] Calculated from the equation: $\log \alpha_{cor} = 62.74/\epsilon - 0.0768$ for six points ($r = 0.9844$). [k] These values probably contain a contribution from reaction with the lyate ions.

Factor b was evaluated by plotting α, α_{cor}, $\log \alpha$, or $\log \alpha_{cor}$ *vs.* $1/\epsilon$,[67] and comparing α and α_{cor} with the calculated values (α_{cal}) (Table VII). The plot of $\log \alpha$ for all six points, or of α_{cor} for the first four points, gives a similar reasonable fit. Hence, factor b alone, or in combination with (a), (d), and (e) can explain the trend in the α values. However, factor g, *i.e.*, decreased ion pair return on increasing X_{H_2O}, would also be a satisfactory explanation, in combination with (b), (d), and (e).

The reactivity–selectivity principle fails when comparing saturated and vinylic systems,[29] and although benzhydryl bromide is more reactive than **3-Br**, our α(TFE) is much higher than the α for benzhydryl bromide in aqueous acetone.[68] Reasons for the high selectivity of the vinyl cations were discussed previously,[24d, 30b, 32] and include charge stabilization by the anisyl group, increased lifetime of R^+ by steric hindrance to approach of the nucleophile, and ground-state stabilization of the vinylic precursor.

Ritchie found that anions show a constant selectivity toward several cations, as summarized in eq 18,[64] where

$$\log (k_n/k_{H_2O}) = N_+ \qquad (18)$$

k_n and k_{H_2O} are the rate constants for the reaction of the nucleophile n and water with a cation, and N_+ is the nucleophilic constant of n. Equation 18 predicts the same α for different substrates at each solvent composition, and is apparently not obeyed, since α(**3-Br**)/$\alpha(Ph_2C{=}C(Br)Ph)$ = 8.3 in TFE/2,6-lutidine.[31] This ratio is reminiscent of the $\alpha(\alpha\text{-An})/\alpha(\alpha\text{-Ph})$ ratios of ≥ 15 for triarylvinyl tosylates in 70% acetone,[26] and 5.3 for *p*-methoxybenzhydryl halides in 85% acetone.[68] On the other hand, α(**3-Br**) at 45°/α $(An_2C{=}C(Br)An)$ at 90° is *ca.* 5 in TFE,[36] although in AcOH α increases with the increased bulk of the β substituents.[24d, 30b] A different extent of ion pair formation can resolve this discrepancy.

If we assume that the average k_{H_2O}/k_{TFE} ratio of 1.40 for the $AnC^+{=}CMe_2$ cation as found for $X_{H_2O} < 0.56$ also applies when $X_{H_2O} \sim 1$, Table VII yields the competition ratios $k_{Br^-}/k_{TFE} = 4520$ and $k_{Br^-}/k_{H_2O} = 3230$. A lower limit for N_+ for Br^- in TFE will be 3.51.[69] Data for comparison with this value are not available.

Comments on Aqueous TFE as a Solvolyzing Media. The increased use of aqueous TFE as solvolyzing media raises the questions whether the behavior demonstrated in Figures 1 and 2 is general, and what are the "Ionizing Power" parameters which should be used in aqueous TFE?

Sunko and coworkers[16] observed that for several substrates which solvolyze by the SN1 route *m*(aqueous TFE) ≪ *m*(aqueous EtOH). However, inspection of Sunko's *k vs.* *Y* curve for MNBOTs for which he reports[16] *m*(aqueous TFE) = 0.062 also shows a minimum between 80 and 97% TFE. Indeed, except for *t*-BuCl[4] (and probably *t*-BuBr),[3] initial decrease in *k vs.* X_{H_2O} plots was observed whenever more than four aqueous TFE compositions were investigated. Table VIII summarizes the literature data known to us and shows that for cyclic vinyl triflates[14] and for secondary substrates[6] *m*(aqueous TFE) ≫ *m*(aqueous EtOH). Secondary substrates which react *via* the k_s route[43] should show a high response to the solvent nucleophilicity,[70, 71] but it is not clear whether this factor contributes to the high "*m*" values for cyclic vinyl triflates. We want to emphasize that most of the *m* values are based on measurements in only 2–3 solvent compositions. If the shapes of the *k vs.* X_{H_2O} curves for these substrates resemble those for **1-OTs** or **3-Br**, the magnitude and even the sign of *m* will be determined by the solvent compositions used and the position of the mimimum. Caution should be exercised in discussing *m* values before more data will be available.

Data on secondary isotope effects for the solvolysis of *t*-BuCl[4, 73] and on the addition of HCl to isobutene

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We may speculate that the solvation shell above and below the double bond of RX and of R^+ is enriched in TFE due to hydrogen bonding with the π system.[55] In this case, our discussion regarding solvent effects is related only to an in-plane solvation of the p orbital.

(67) The linearity predicted[61b] between $\log \alpha^0$ and $1/\epsilon$ was based on the Debye–Hückel relationship. Since the logarithmic relationship between $\log k$ and the ionic strength which is based on the Debye–Hückel relationship is inferior in comparison with the "normal salt effect," *i.e.*, the linear *k vs.* [salt] plot (A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2763 (1956)), we tried the α *vs.* $1/\epsilon$ plot.

(68) T. H. Bailey, J. R. Fox, E. Jackson, G. Kohnstam, and A. Queen, *Chem. Commun.*, 122 (1966).

(69) It will be the exact value if $F = 1$ and all the products are formed from free cations.

(70) It is suggested that the *m* values in aqueous TFE for substrates reacting with nucleophilic solvent assistance are abnormally high, and that comparison of *m*(aqueous EtOH) with *m*(aqueous TFE) should provide a probe into the role of solvent in solvolysis (J. M. Harris, D. J. Raber, W. C. Neal, Jr., and M. D. Dukes, *Tetrahedron Lett.*, in press. We thank Professor Raber for a preprint.).

(71) TFE is less nucleophilic than EtOH. The nucleophilic constants N_{BS} (T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 992 (1972)) are EtOH (0.09), and TFE (*ca.* −3.8,[19] −3.10 according to extrapolation based on MeOTs, and −2.1 based on extrapolation from ref 54[72]).

(72) F. L. Schadt, personal communication.

(73) V. J. Shiner, Jr., in "Isotope Effects in Chemical Reactions," C. J. Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold, New York, N. Y., 1970, p 90.

Table VIII. *m* Values for Solvolysis in Aqueous EtOH and in Aqueous TFE

				m in TFE based on			
Substrate	Temp, °C	TFE–H_2O (w/w) compositions studied	n^{a}	*t*-BuCl	Pinacolyl brosylate^{b}	*m* in aqueous EtOH	Ref
2-Adamantyl tresylate^{c}	25	97, 70	2	0.476	2.02		13, 16
1-Adamantyl bromide	25	97, 80, 70	3	0.427	1.95	1.187	6, 16
Pinacolyl brosylate	25	97, 70, 50	3	0.280	1.00	0.727	6, 16
7-Methyl-*anti*-7-norbornenyl *p*-nitrobenzoate				0.213			16
7-Methyl-7-norbornyl tosylate	20	100, 97, 80, 70 (50)	4(5)	0.062^{d}	0.22	0.684	16
tert-Butyl chloride	25	100–40	9	1.00	3.60	1.00	4, 22a
tert-Butyl bromide	25	100, 98.2, 97, 78	4	1.00^{e}	3.60	0.94	3, 22b
p-Methylbenzyl chloride	25	97, 94, 70	3	0.80	2.85	0.57	4, *g*
Isopropyl brosylate	25	50, 70	2	0.70	2.00	0.41	6, *h*
	45	97, 70	2	1.62	6.90		6
sec-Butyl brosylate	25	97, 70	2	1.33	5.65		6
3-Methyl-2-butyl brosylate	25	97, 70	2	0.67	2.85		6
Cyclohexyl brosylate	25	97, 70	2	1.02	4.34		6
2-Methylcyclohexenyl triflate^{f}	125	97, 70	2	1.61	6.85	0.30	14
2,3-Dimethylcyclohexenyl triflate^{f}	100	97, 70	2	1.01	4.30	0.67	14
	125	97, 70	2	1.10	4.68	0.42	14
Cycloheptenyl triflate^{f}	75	97, 70	2	0.99	4.22	0.75	14
	100	97, 70	2	1.15	4.90	0.66	14
Cyclooctenyl triflate^{f}	75	97, 70	2	0.96	4.08	0.64	14
	100	97, 70	2	1.08	4.60	0.65	14
Δ-$^{1(9)}$-Octalin 1-triflate^{f}	100	97, 70	2	1.00	4.25	0.76	14

[a] Number of solvent mixtures investigated. [b] See text. [c] Tresylate = 2,2,2-trifluoroethanesulfonate. [d] The point at 50% TFE was not used for the calculation. [e] Calculated by assuming that the point for 98.2% TFE deviates. $m = 1.14$ assuming that the point for pure TFE deviates. [f] Triflate = trifluoromethanesulfonate. [g] S. C. J. Olivier, *Recl. Trav. Chim. Pays-Bas*, **49**, 697 (1930); A. G. Evans and S. D. Hamman, *Trans. Faraday Soc.*, **47**, 25 (1951). [h] S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120 (1952).

Table IX. *Y* Values^{a} for Aqueous TFE, Defined for Several Model Compounds

	Y values based on						
Aqueous TFE (w/w)	*t*-BuCl^{g}	1-Adamantyl bromide^{h}	2-Adamantyl tosylate^{i}	Pinacolyl brosylate^{j}	MNBOTs^{b,k}	3-OTs^{c}	$E_T(1)$
100	1.045				1.72	0.96 (1.06)^{f}	4.30
97	1.148	2.27	1.83	1.10		0.79	4.25
90	1.245				1.65	0.71	4.05
80	1.461	2.41		1.16^{e}	1.72	0.72	3.90
70	1.659	2.53^{e}	2.00	1.22	1.86	0.72	3.80
60	1.894	2.65		1.32^{e}		0.68	
50	2.229 (2.23)^{d}			1.42	1.94	0.68	3.70

[a] Based on $Y = 0$ for 80% EtOH. [b] Log *k* values were taken from a plot and are approximate. [c] A value of $E_a = 24$ kcal mol^{-1}, as found for **3-OTs** in 80% EtOH,[28] was used. All the values are in the presence of 2,6-lutidine. [d] D. J. Raber, M. D. Dukes, and J. Gregory, *Tetrahedron Lett.*, 667 (1974). [e] Interpolated value. [f] In the absence of 2,6-lutidine. [g] Reference 4. [h] Reference 10. [i] Reference 72. [j] Reference 6. [k] Reference 16.

in TFE[48] suggest a rate-determining dissociation of a *reversibly formed* tight ion pair in the trifluoroethanolysis of *t*-BuCl. Since the extent of the ion pair return probably depends on the solvent composition, *Y* values which are based on *t*-BuCl do not measure the true "ionizing power" of the media. The need for another model becomes apparent by the recent use of *Y*(97% TFE) = 0.93 which is based on cycloheptenyl or cyclooctenyl triflates[18a] (*cf.* Table VIII for comparison of the solvent effects on these *vs.* other compounds), and by the use of *Y*(TFE) = 1.87,[19] and from Table IX which gives calculated *Y*'s based on different models. One such model, 1-adamantyl bromide, gives an excellent *mY* plot with *t*-BuCl except for aqueous TFE[10] but gives a relatively high *Y*(97% TFE) value. 2-Adamantyl tosylate behaves similarly but gives somewhat lower values.[72] Another model, pinacolyl brosylate, where ion pair return presumably does not interfere with the kinetics,[6] gives a good agreement with *Y*(*t*-BuCl) in 97% TFE but not in 50% TFE, and *m* values which are based on it are also recorded in Table VIII. The spread in the *Y* values further increases if **3-OTs** or MNBOTs are used for defining the *Y* values.

A possible model which avoids the problem of ion pair return is based on the solvatochromic changes of a betain,[37] *e.g.*, **5**. The two monotonic curves for $E_T(1)$ *vs.* *Y*(*t*-BuCl) for aqueous EtOH and aqueous acetone coincide at high *Y* values (Figure 7). By extrapolating the line and by using the $E_T(1)$ values of Table VI we obtained much higher *Y* values for aqueous TFE mixtures than those reported from the solvolysis studies (see Table IX). While we feel that these *Y* values are too high, they fit the assumption that TFE is a better ionizing solvent than water, and show dramatically the dependence of Y on the model.

Tables VIII and IX show that any result could be justified by choosing an arbitrary model for defining Y(aqueous TFE) values. We therefore suggest that any use of Y(aqueous TFE) values, or of the $(k_{\text{aq TFE}}/k_{\text{aq EtOH}})_Y$ ratios as mechanistic probes,[18a] should involve justification of the model used.

Experimental Section

Melting points are uncorrected. Ir spectra were recorded with a Perkin-Elmer 337 spectrophotometer, uv spectra with Perkin-Elmer 450 and Cary-17 instruments, mass spectra with a MAT 311 instrument, and nmr spectra with a Varian T-60 spectrometer. The nmr data are given in δ units downfield from tetramethylsilane. Vpc was conducted with Varian Aerograph 90-P and Becker 420 instruments.

Materials. 2,2,2-Trifluoroethanol (Halocarbon) was refluxed for 2 hr over anhydrous $CaSO_4$ and K_2CO_3 (8 : 1) and fractionated, and the fraction, bp 73–74°, was used. The aqueous TFE (w/w) mixtures were prepared from triply distilled water. Tetraethylammonium bromide (Fluka) and tosylate (Aldrich) and the betaine **5** (Eastman) were dried before use. Literature methods were used to prepare 1-(*o*-methoxyphenyl)-2-methylpropan-1-one (**2**),[74] 1-(*p*-methoxyphenyl)-2-methylpropen-1-yl chloride and bromide (**3-Cl** and **3-Br**),[40d] and 1-(*p*-methoxyphenyl)-2-methylpropan-1-one (**4**).[75]

1-(*o*-Methoxyphenyl)-2-methylpropen-1-yl Bromide (1-Br). To 1-(*o*-methoxyphenyl)-2-methylpropene[76] (7.5 g, 46.5 m*M*) in chloroform (50 ml), bromine (7.5 g, 46.5 mM) was added slowly with stirring at 0°. The solvent was evaporated, potassium *tert*-butoxide (5.8 g, 50 m*M*) in *tert*-butyl alcohol (150 ml) was added, and the mixture was shaken for 20 hr at 20°. Water (500 ml) was added; the mixture was extracted with ether (4 × 100 ml), dried ($MgSO_4$), filtered, and evaporated, and the remaining oil was distilled *in vacuo*, giving 8.1 g (73%) of crude **1-Br**, bp 176° (36 mm). A sample was purified by vpc on 1 m of 15% SE-30 on 60–80 Chromosorb W column operating at 140° (injector and detector at 250°), He flow 25 ml/min, retention time, 4 min: λ_{max} (C_6H_{12}) 282 nm (ϵ 3800) and 285 (3800); λ_{max} (EtOH) 283 nm (ϵ 3500); ν_{max} (neat) 2920, 2850, 1260, 740 cm^{-1} (all s); $\delta(CDCl_3)$ 1.53 (3 H, s, Me), 1.98 (3 H, s, Me), 3.68 (3 H, s, MeO), 6.68–7.33 (4 H, m, Ar); *m*/*e* 242, 240 (M, 80), 161 (M − Br, 70), 146 (M − Br − Me, B), 131 (M − Br − 2Me, 46), 121 (methoxytropylium ion, 5).

Anal. Calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43; Br, 33.14. Found: C, 55.00; H, 5.61; Br, 32.82.

1-(*o*-Methoxyphenyl)-2-methylpropen-1-yl Tosylate (1-OTs). 1-(*o*-Methoxyphenyl)-2-methylpropen-1-yl bromide (6.7 g, 28 m*M*) and silver tosylate (8 g, 28.5 m*M*) were refluxed in acetonitrile (100 ml) for 1 hr. The silver bromide was filtered, the solvent was evaporated, and the residue was dissolved in acetone, filtered, and evaporated. The remaining oil was crystallized from cold methanol, giving 3 g (33%) of **1-OTs**: mp 97°; λ_{max}(EtOH) 224 nm (ϵ 21,200); $\nu_{max}(CS_2)$ 3000–2850 (m), 1360, 1280, 1250, 1190, 1080, 1050, 1030, 990, 825, 810 cm^{-1} (all s). $\delta(CDCl_3)$ 1.60 (3 H, s, Me), 1.88 (3 H, s, Me), 2.33 (3 H, s, $OSO_2C_6H_4Me$), 3.60 (3 H, s, MeO), 6.45–7.45 (4 H, m, Ar); *m*/*e* 332 (M, 7%), 177 (M − SO_2Ar, B), 162 (M − SO_2Ar − Me, 5), 161 (M − OSO_2Ar, 4), 135 ($AnCO^+$, 33), 121 (methoxytropylium ion, 68).

Anal. Calcd for $C_{18}H_{20}O_4S$: C, 65.01; H, 6.37; S, 9.64. Found: C, 65.18; H, 6.22; S, 9.68.

1-(*p*-Methoxyphenyl)-2-methylpropen-1-yl Tosylate and Brosylate (3-OTs and 3-OBs). To **3-Br**[39d] (2.0 g, 8.3 m*M*) in acetonitrile (10 ml), silver tosylate (2.3 g, 8.3 m*M*) in acetonitrile (30 ml) was added. The mixture was refluxed for 10 min, and work-up similar to that for **1-OTs** gave 1.35 g (50%) of **3-OTs**; mp 73° (from MeOH); $\lambda_{max}(C_6H_{12})$ 225 nm (ϵ 17,800), 244 (12,400); $\delta(CDCl_3)$ 1.73 (3 H, s, Me), 1.87 (3 H, s, Me), 2.35 (3 H, s, $OSO_2C_6H_4Me$), 3.78 (3 H, s, MeO), 6.60, 6.76, 7.40, 7.56 (4 H, AA′BB′ q, $OSO_2C_6H_4Me$), 6.86, 7.02, 7.15, 7.31 (4 H, AA′BB′ q, C_6H_4OMe); *m*/*e* 332 (M, 10), 177 (M − SO_2Ar, 9), 162 (M − SO_2Ar − Me, 4), 161 (M − OSO_2Ar, 8), 149 ($AnCMe_2^+$, B), 135 ($AnCO^+$, 68), 121 (methoxytropylium ion, 15).

Anal. Calcd for $C_{18}H_{20}O_4S$: C, 65.01; H, 6.37; S, 9.64. Found: C, 65.07; H, 6.22; S, 9.78.

The brosylate (**3-OBs**), mp 108° (from MeOH), was prepared similarly in 50% yield by using AgOBs: $\lambda_{max}(C_6H_{12})$ 235.5 nm (ϵ 27,200); $\delta(CDCl_3)$ 1.76 (3 H, s, Me), 1.95 (3 H, s, Me), 3.83 (3 H, s, MeO), 6.65, 6.80, 7.04, 7.19 (4 H, AA′BB′ q, An), 7.47 (4 H, s, OBs).

Anal. Calcd for $C_{17}H_{17}BrO_4S$: C, 51.39; H, 4.31; Br, 20.12; S, 8.07. Found: C, 51.28; H, 4.40; Br, 19.87; S, 8.16.

1-(*o*-Methoxyphenyl)-2-methylpropen-1-yl 2,2,2-Trifluoroethyl Ether (1-OR). A mixture of **1-OTs** (200 mg, 0.6 m*M*) and triethylamine (70 mg, 0.7 m*M*) was kept at 35° in TFE (10 ml) for 18 hr. The solvent was evaporated, chloroform (10 ml) was added, the mixture was washed with water (90 ml), dried, and evaporated, and methylene chloride was added. Vpc showed formation of >95% of **1-OR** and <5% of the ketone **2**. A sample of the colorless **1-OR** was isolated by vpc under the conditions used for isolating **1-Br**: λ_{max}(EtOH) 243 nm (ϵ 3600) and 279 (3500); ν_{max} (neat) 2920, 1490, 1460, 1300, 1225, 760 cm^{-1} (all s); $\delta(CCl_4)$ 1.43 (3 H, s, Me), 3.67 (2 H, q, J = 9 Hz, CH_2), 3.79 (3 H, s, MeO), 6.76–7.41 (4 H, m, Ar); *m*/*e* 260 (M, 40), 230 (M − 2Me, 7), 218 (M − CMe_2, 13), 189 (12), 161 (M − OCH_2CF_3, 14), 150 (11), 146 (M − OCH_2CF_3 − Me, B), 135 (*o*-$MeOC_6H_4CO^+$, 50), 132 (35), 121 (methoxytropylium ion, 24).

Anal. Calcd for $C_{13}H_{15}F_3O_2$: C, 59.99; H, 5.81; F, 21.90. Found: C, 60.13; H, 5.61; F, 21.70.

1-(*p*-Methoxyphenyl)-2-methylpropen-1-yl 2,2,2-Trifluoroethyl Ether (3-OR). This ether was prepared and purified similarly to **1-OR**, except that the reaction time was 2 hr: λ_{max} (EtOH) 249 nm (ϵ 1400); ν_{max} (neat) 2920, 1500, 1450, 1270, 830 cm^{-1} (all s); $\delta(CCl_4)$ 1.63 (3 H, s, Me), 1.82 (3 H, s, Me), 3.69 (2 H, q, J = 8 Hz, CH_2), 3.77 (3 H, s, MeO), 6.92 (4 H, center of AA′BB′ q, J = 9 Hz, Ar); *m*/*e* 260 (M, B), 259 (M − H, 50), 246 (M − CH_2, 17), 230 (M − 2Me or M − CH_2O, 30), 218 (M − CMe_2, 16), 161 (M − OCH_2CF_3, 38), 150 (75), 146 (M − OCH_2CF_3 − Me, 25), 121 (methoxytropylium ion, 43).

Anal. Calcd for $C_{13}H_{15}F_3O_2$: C, 59.99; H, 5.81; F, 21.90. Found: C, 60.10; H, 5.60; F, 21.61.

Product Analysis. The product distributions were determined by vpc on a 2-m SE-30 column (20%) on Chromosorb W 60–80, with injector and detector at 220°. With column at 180° the retention times were **1-OR**, 4.2 min and **2,** 6 min; with column at 200°, the retention times were **3-OR**, 3.8 min and **4,** 4.2 min.

Products Stabilities. (a) Ketone **4** (100 mg) was dissolved in TFE (1 ml) containing Et_3N (100 mg) and the mixture was kept 60 min at 35°. Vpc of the mixture before work-up showed only the presence of **4**. (b) A mixture of **3-OTs** (70 mg) and Et_3N (100 ml) in TFE (1 ml) was kept at 35° for 60 min. Vpc before work-up or after addition of water showed the formation of only **3-OR**.

Kinetic Measurements. Conductivity measurements were with a Pye instrument, and control experiments showed that at our conditions, the conductance was linear with the concentrations of the 2,6-

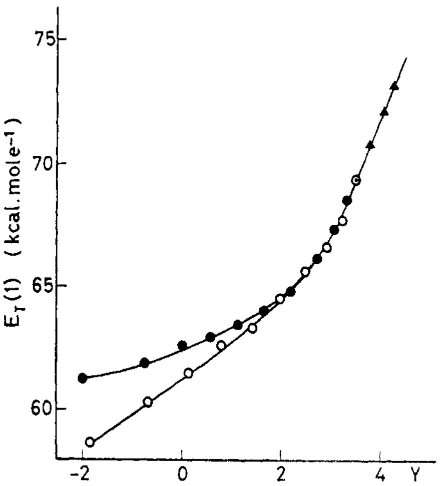

Figure 7. A plot of $E_T(1)$ *vs.* Y for aqueous acetone (○) and aqueous EtOH (●), and extrapolated values for aqueous TFE (▲).

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lutidinium bromide or tosylate. The solubility of HBr in TFE is low, and in the unbuffered solvolysis of **3-Br** the cell had to be carefully sealed in order to avoid evaporation of the HBr. The spectrophotometric measurements were conducted with a Gilford 2400-S spectrophotometer at 228 nm, where the difference in the absorptions of the starting materials and products is the largest. The rate constants for the first-order reaction were calculated by the KINDAT program.[77]

Reaction of 3-OTs with Br$^-$. A mixture of 0.021 *M* **3-OTs,** 0.021 *M* 2,6-lutidine, and 0.025 *M* Et_4NBr in TFE was kept at 35°. Samples were quenched with aqueous AcOH, and the Br$^-$ was titrated potentiometrically. After 40 min a sample was cooled, quenched with water, extracted (CH_2Cl_2), washed with water, $AgNO_3$ solution, dilute AcOH, and $NaHCO_3$ solution, and dried. The solvent was evaporated, and nmr analysis (CCl_4) by integration of the Me and MeO signals gave **3-Br** ($83 \pm 2\%$), **3-OTs** ($5 \pm 2\%$), and **4** ($12 \pm 2\%$).

Reaction of 1-OTs with OTs$^-$. A mixture of 0.059 *M* **1-OTs,** 0.096 *M* triethylamine, and 0.36 *M* Et_4NOTs in TFE was kept at 35°. Samples were poured into a 1 : 1 mixture of CCl_4 and water. The organic layer was separated, washed (water, AcOH, dilute $NaHCO_3$ solution), dried ($MgSO_4$), and evaporated. The remainder was analyzed by nmr in CCl_4. The progress of the reaction was evaluated from the ratios of the following signals: (a) Me (δ 1.43) [**1-OR**]/Me (δ 1.60) [**1-OTs**]; (b) MeO (δ 3.79) [**1-OR**]/MeO (δ 3.60) [**1-OTs**]; (c) Me (δ 2.33) [**1-OTs**]/overall Me or overall MeO. These ratios differed by $\leq 2\%$ and their average was used.

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Reactions of Primary and Secondary Alkoxy Radicals Derived from Hypochlorites[1]

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Abstract: By the use of suitable chlorine atom traps, *e.g.*, trichloroethylene, primary and secondary alkyl hypochlorites may be used as effective radical chlorinating agents, and the chemistry of the corresponding alkoxy radicals examined. The amount of β scission, in competition with reaction with cyclohexane, decreases roughly 100-fold in the order tertiary alkoxy > secondary alkoxy > primary alkoxy (for loss of the same radical, R_1) with a corresponding increase in activation energy, the order correlating with decreasing π-bond energy of the carbonyl compound formed. Within the same class of alkoxy radical, ease of β scission parallels stability of the radical R_1 formed. β scission also shows a marked polar effect (for substituted benzyl radical loss $\rho^+ = -1.04$). In reaction with substrates (both selectivity between primary, secondary, and tertiary hydrogen and in the competition between olefin substitution and addition) primary, secondary, and tertiary alkoxy radicals show only small differences, but polar additions of primary and secondary hypochlorites are difficult to suppress.

The chemistry of the *tert*-butoxy (and other tertiary alkoxy) radicals has been investigated extensively, for the most part *via* either the decomposition of suitable peroxides or study of radical chain chlorinations using the corresponding hypochlorites.[2] Primary and secondary alkoxy radicals are less readily accessible, and chain chlorinations with primary and secondary hypochlorites are greatly complicated by induced decomposition suggested[3] as occurring *via* chlorine atom chains, *e.g.*

$$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot \qquad (1)$$

$$\begin{aligned} &X\cdot\ (Cl\cdot \text{ or } RO\cdot) + RCH_2OCl \longrightarrow \\ &\qquad HX\ (HCl \text{ or } ROH) + R\dot{C}HOCl \end{aligned} \qquad (2)$$

$$R\dot{C}HOCl \longrightarrow RCHO + Cl\cdot \qquad (3)$$

$$HCl + RCH_2OCl \longrightarrow RCH_2OH + Cl_2 \qquad (4)$$

Chlorine atom chains are also occasional complications in the decomposition of tertiary hypochlorites, but here they can be successfully repressed by the use of negatively substituted olefins (which react readily with halogen atoms, but not with alkoxy radicals) as chlorine atom traps,[4,5] *e.g.*

$$Cl\cdot + CHCl{=}CCl_2 \longrightarrow CHCl_2\dot{C}Cl_2 \qquad (5)$$

$$CHCl_2CCl_2 + ROCl \longrightarrow CHCl_2CCl_3 + RO\cdot \qquad (6)$$

Some time ago it occurred to us that the same technique could be applied to minimize induced decomposition and eliminate chlorine atom chains in the reactions of primary and secondary hypochlorites, and we have shown that in the presence of di- and trichloroethylene, those with long side chains can be converted to δ-chloro alcohols *via* intramolecular chlorination in high, and sometimes almost quantitative, yield.[6]

This paper describes application of the same technique to short-chain hypochlorites, aimed at investigating the ease of β scission and selectivity in reaction of a number of primary and secondary alkoxy radicals derived from the corresponding hypochlorites.

Results and Discussion

β Scission of Alkoxy Radicals. In the radical chain decomposition of alkyl hypochlorites in the presence

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[1] Taken from the Ph.D. Thesis of R. T. Clark, University of Utah, 1973. Support of this work by grants from the National Science Foundation (GP 24300 and GP 36620) is gratefully acknowledged.

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