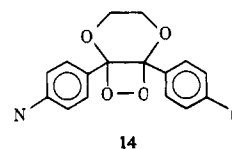


Product Analyses. Photooxygenations of solutions of **7** or **8** in dichloromethane (1.0×10^{-2} M) were carried out as described above. These samples were warmed to room temperature and allowed react for 5 h. The NMA yield in each sample was determined by fluorescence assay using the method of standard additions. The identifications and assays of benzophenone from **7** and benzaldehyde from **8** were by gas chromatography on a Hewlett-Packard Model 5730 chromatograph. Conditions were as follows: benzophenone, 25% SE-30 on Chromosorb P column at 230 °C, diphenylmethane as internal standard; benzaldehyde, 20% Carbowax 20M on Chromosorb P column at 130 °C, mesitylene as an internal standard. Yields of benzophenone and benzaldehyde, based on moles of NMA, were $100 \pm 10\%$.

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with $E_a = 19.7$ kcal/mol.¹⁶ The apparently lower activation energy for the electron-transfer step in the acridan compounds may reflect their greater conformational flexibility that allows close approach of the basic nitrogen to the peroxide bond.

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Solvolysis in 2,2,2-Trifluoroethanol–Water and 2,2,2-Trifluoroethanol–Ethanol Mixtures. Selectivity of the Intermediates and *N* Values

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Abstract: Solvolysis of 1-adamantyl bromide (**1-Br**) in eight TFE–EtOH mixtures gave a Grunwald–Winstein m_{GW} value of 1.50, and the ethyl (**1-OEt**) and trifluoroethyl (**1-OTFE**) ethers. The selectivity ratios for reaction with the solvent components k_{TFE}/k_{EtOH} are medium dependent, being 2.60–0.83. In TFE–H₂O, $m_{GW} = 0.56$ and the k_{TFE}/k_{H_2O} ratios increase with X_{H_2O} from 0.49 to 2.04. Solvolysis of 1-anisyl-2-methylpropen-1-yl tosylate (**2-OTs**) in TFE–EtOH gives $m_{GW} = 0.89$ and an average k_{TFE}/k_{EtOH} value of 0.086. Methyl tosylate was solvolyzed in several TFE–EtOH and TFE–H₂O mixtures and new values of the nucleophilic parameter *N* were determined. Products were derived from the free cation in the solvolysis of **2-OTs** and from the solvent-separated ion pair in the solvolysis of **1-Br**, and the selectivities of these species were analyzed. The nucleophilicities of TFE–H₂O and TFE–EtOH mixtures and the recent use of the comparison of TFE–H₂O and EtOH–H₂O mixtures for evaluating solvent participation in solvolysis reactions were discussed.

2,2,2-Trifluoroethanol (TFE) and aqueous TFE have been used frequently as media for solvolytic reactions during the last decade,^{1,2} owing to their high ionizing power. The analogous binary solvent mixtures TFE–EtOH were investigated much less and only recently.^{3–6} These two binary solvent mixtures are complementary to one another. By starting from

TFE ($\epsilon = 26.14$ at 25 °C)⁷ and increasing the dielectric constant by addition of water ($\epsilon = 78.54$ at 25 °C)⁸ the ionizing power of the medium increases, as judged by the increased solvolysis rate of *t*-BuCl at higher mole fraction of water (X_{H_2O}).² Simultaneously, the nucleophilicity of the medium also increases since water is more nucleophilic than TFE.⁹

Table I. Solvolysis of 1-Adamantyl Bromide in TFE-EtOH at 35 °C

% TFE (v/v)	X_{TFE}^a	$10^6 k_1, \text{s}^{-1}$	% 1-OEt	% 1-OTFE	[1-OTFE]/ [1-OEt]	$k_{\text{TFE}}/k_{\text{EtOH}}^b$
100	1.000	291 ± 0.6	0	100		
90	0.880	100 ± 0.3	5	95	19.00	2.60 ± 0.55
80	0.763	38.3 ± 0.3	18	82	4.56	1.42 ± 0.10
70	0.652	11.3 ± 0.2	31	69	2.23	1.19 ± 0.06
60	0.548	1.97 ± 0.01	50	50	1.00	0.83 ± 0.04
50	0.447	1.18 ± 0.02	58	42	0.72	0.90 ± 0.03
40	0.349	0.276 ± 0.010	67	33	0.49	0.92 ± 0.04
30	0.257	0.0956 ± 0.003	70	30	0.43	1.24 ± 0.04
20	0.168	0.0411 ± 0.003	78	22	0.28	1.40 ± 0.08
0	0	0.009 ^c				

^a Mole fraction of trifluoroethanol. ^b The errors were calculated by assuming a 1% error in the percentages of 1-OTFE and 1-OEt. ^c Calculated from ref 10 by using the Winstein-Grunwald equation.

Addition of EtOH ($\epsilon = 24.32$ at 25 °C)⁷ to TFE changes the dielectric constant very little, but, since ethanol is more nucleophilic than TFE,⁹ the nucleophilicity of the solvent increases, while the microscopic bulk of the solvent components changes relatively slightly.

Previous work on trifluoroethanol-ethanol mixtures investigated the reactions of *tert*-butyl chloride³ for defining the Y values and of methyl tosylate for evaluating the N values.³ The number of values obtained was limited to three N and three Y values. We added several new Y values by using the solvolysis of *p,p'*-dichlorobenzhydryl chloride as a secondary standard.⁶ However, it was of interest to have additional values which are derived from the same model compound in both TFE-H₂O and TFE-EtOH. We chose 1-adamantyl bromide (1-Br), a substrate for which there is extensive solvolysis data, which undoubtedly solvolyzes via S_N1,¹⁰ thus reducing the possibility of a nucleophilic component in the overall solvolysis. Moreover, in a plot of log k for 1-adamantyl bromide vs. $Y(t\text{-BuCl})$ in 22 solvents only the three points for aqueous TFE mixtures showed positive deviation from the linear relationship,¹¹ suggesting that the Y values which are based on *t*-BuCl are not measuring the heterolysis step of the C-Br bond alone. A recent probe for solvent participation in solvolysis reactions is based on the log k vs. log $k(1\text{-Br})$ plots in TFE-H₂O and EtOH-H₂O.^{1r}

A topic of recent interest is the selectivity of cationoid intermediates in binary solvent mixtures.¹²⁻¹⁶ The ratios of alcohols to ethyl ethers in the solvolyses of several alkyl halides in EtOH-H₂O mixtures of different compositions gave information on the selectivities of the intermediates toward ethanol and water. Selectivity-reactivity relationships were observed.¹⁷ Adamantyl systems were investigated as models for systems where products are formed from solvent-separated ion pairs.¹⁴⁻¹⁶ Selectivities in TFE-H₂O mixtures were studied

much less, although data derived from the solvolyses of several vinyl derivatives were reported.¹⁰ Selectivities in different compositions of TFE-EtOH were determined for the benzyl system³ and the *p,p'*-dichlorobenzhydryl system,⁶ whereas adamantyl derivatives carrying different leaving groups were studied in 50% EtOH-50% TFE.⁵

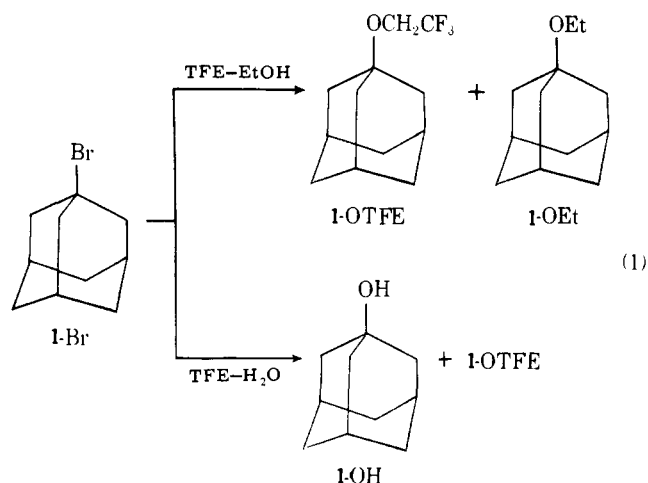
In order to obtain more information on the solvent parameters and on the selectivities of the intermediates, three different systems were studied. The saturated 1-adamantyl bromide (1-Br) was solvolyzed in TFE-EtOH giving the ethers 1-OEt and 1-OTFE and in TFE-H₂O giving 1-OTFE and 1-adamantanol (1-OH) (eq 1). The vinylic 1-anisyl-2-methylpropen-1-yl tosylate (2-OTs) was solvolyzed in TFE-EtOH giving the ethers 2-OEt and 2-OTFE and the solvolyses rates of the k_2 substrate¹⁸ methyl tosylate were studied in TFE-H₂O and TFE-EtOH.

Results

Solvolysis of 1-Adamantyl Bromide. A. In TFE-EtOH. The first-order rate constants for the solvolysis of 1-Br in TFE and in eight TFE-EtOH mixtures in the range 100% TFE-20% TFE-80% EtOH (v/v), together with the literature value for pure EtOH, are given in Table I. The k_1 value of $1.18 \times 10^{-6} \text{ s}^{-1}$ in 50% TFE-50% EtOH at 35 °C together with the single value of $8.63 \times 10^{-5} \text{ s}^{-1}$ at 75 °C reported by Ando and Tsukamoto⁵ give an activation enthalpy of 22.8 kcal mol⁻¹, which is similar to ΔH^\ddagger values in aqueous EtOH and aqueous TFE.¹¹ The rate coefficients remained constant during the reaction, giving no indication of common ion rate depression. The solvolysis products were 1-adamantyl ethyl ether (1-OEt) and 1-adamantyl 2,2,2-trifluoroethyl ether (1-OTFE). The pure compounds were prepared by solvolysis of 1-Br in aqueous acetone and in pure TFE buffered by triethylamine, respectively. The product distributions together with their ratio were obtained by gas chromatography and are given in Table I. Also given are the ratios of the second-order rate constants for the capture of the cationoid intermediate by the two solvents, $k_{\text{TFE}}/k_{\text{EtOH}}$, which were calculated by eq 2, which assumes that the capture rates are proportional to the solvent concentrations. These values first decrease between 90% TFE-10% EtOH and 60% TFE-40% EtOH and then increase. Our value of 0.90 in 50% TFE-50% EtOH at 35 °C is lower than the value of 1.48 reported for this mixture at 75 °C.⁵

$$k_{\text{TFE}}[\text{TFE}]/k_{\text{EtOH}}[\text{EtOH}] = [\text{1-OTFE}]/[\text{1-OEt}] \quad (2)$$

B. In TFE-H₂O. The first-order rate constants for the solvolysis of 1-Br in aqueous TFE are given in Table II. Common ion rate depression was not observed. Some data are available at other temperatures,^{14,11} and the interpolated two values from the work of Raber et al.¹¹ are in good agreement with our values. The values increase on increasing $X_{\text{H}_2\text{O}}$. The products are 1-adamantanol (1-OH), which is the main product when



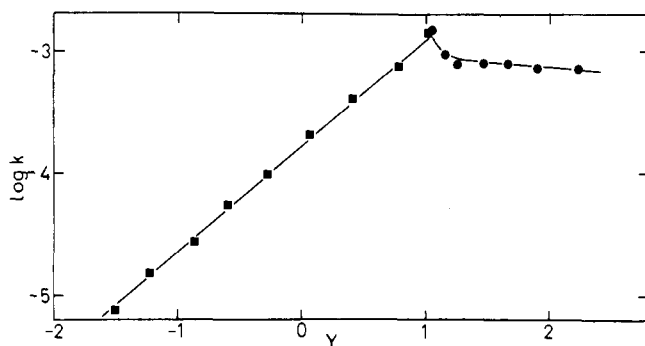


Figure 2. A $\log k$ vs. $Y(t\text{-BuCl})$ plot for 2-OTs in TFE-H₂O (●) and TFE-EtOH (■) at 35 °C.

Table IV. Solvolysis of Methyl Tosylate in Aqueous TFE and in TFE-EtOH at 50 °C

% TFE (w/w) in TFE-H ₂ O		$10^6 k_1, \text{s}^{-1}$	% TFE (v/v) in TFE-EtOH		$10^6 k_1, \text{s}^{-1}$
100		0.064 ± 0.007	100		0.064 ± 0.007
97		0.128^a	90		0.406 ± 0.015
94		0.317 ± 0.016	80		0.83^b
90		0.705 ± 0.008	70		1.74 ± 0.02
80		2.25 ± 0.11	60		2.48 ± 0.05
70		$4.40 \pm 0.22 (5.64)^a$	50		3.5^b
60		7.39 ± 0.14	40		4.63 ± 0.10
50		11.3^a	30		5.59 ± 0.10
40		17.7 ± 0.5	20		6.3^b
0		138^c	0		6.55^d

^a From ref 1p. ^b From ref 3. ^c From ref 20b. ^d From ref 20a.

three TFE-EtOH mixtures, but the solvolysis of 1-Br was not previously investigated. Our data for 1-Br in TFE-H₂O and TFE-EtOH (Tables I and II) are the most extensive available. Figure 1 shows that the $\log k$'s for 1-Br and *t*-BuCl are linearly correlated in contrast with the nonlinearity found for several α -anisylvinyl substrates in TFE-H₂O¹⁰ and for benzyl halides in TFE-EtOH.³ However, the data for the two solvent mixtures and the extrapolated data for the EtOH-H₂O mixture at 35 °C (dotted line) are not correlated by a single line. Each binary mixture gives a different line and, since the k 's for EtOH-H₂O are on the line with $m_{\text{GW}} = 1.20$ for the other solvents,¹¹ the rate in any TFE-containing solvent is higher than expected from this line. The slopes m_{GW} of the linear relationships at 35 °C differ significantly. The value of 0.56 for TFE-H₂O is relatively low and the value of 1.50 in TFE-EtOH is relatively high. The calculated rate for pure TFE is 14.6 times higher than the value for EtOH-H₂O at the same apparent Y value.

Two explanations for this behavior are possible. (a) The structures of 1-Br and of other substrates which solvolyze via k_c and show similar behavior^{1r} ensure a completely hindered nucleophilic solvation from the rear. Consequently, the electrophilic solvation from the front becomes more important than for *t*-BuCl. TFE is more acidic than EtOH or H₂O and is probably the most effective solvator for the leaving group, making 1-Br faster than expected from the $\log k$ - Y correlation in TFE-containing solvents. Addition of TFE to EtOH results in an increase both in Y and in the electrophilicity and in a consequent higher m_{GW} value. In contrast, on addition of water to TFE, both Y and the nucleophilicity increase simultaneously and the rate increase and the m_{GW} value are relatively low. Okamoto²² ascribed the similar rate acceleration in the solvolysis of 1-Br and 2-adamantyl tosylate in benzene-phenol mixtures to electrophilic acceleration due to hydrogen bonding with the phenol. The substantial rate acceleration of the acetylation of *t*-BuBr in 25% AcOH-75% CCl₄ by *p*-nitrophenol

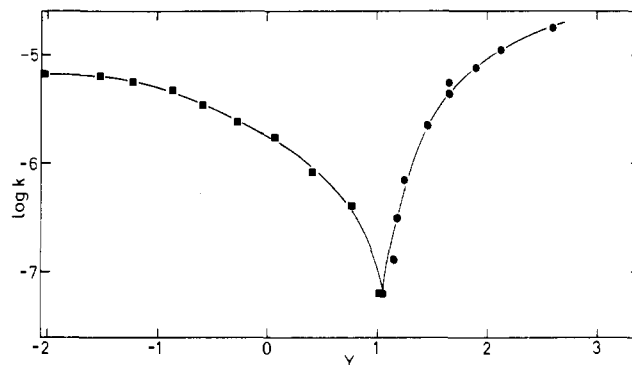


Figure 3. A $\log k$ vs. $Y(t\text{-BuCl})$ plot for MeOTs in TFE-H₂O (●) and TFE-EtOH (■).

is lost for *o*-nitrophenol, where intramolecular hydrogen bonding reduces intermolecular hydrogen bonding.²³

(b) An alternative is that *t*-BuCl is less reactive than expected in TFE-containing solvents. According to Harris^{1r} the Y values in TFE-H₂O do not reflect ionizing power alone since a nucleophilic component is present in the reaction of *t*-BuCl in TFE-H₂O. This conclusion is based on the $\log k$ plots for various substrates vs. $\log k(1\text{-Br})$. Compounds reacting without nucleophilic assistance (1-adamantyl chloride, 2-adamantyl tosylate, 2-norbornyl tosylate, and pinacolyl brosylate) gave a single line in both EtOH-H₂O and TFE-H₂O mixtures. Primary and secondary compounds, (MeOTs, *i*-PrOTs, cyclohexyl-OTs) which react via the solvent-assisted k_s route¹⁸ gave different lines in EtOH-H₂O and TFE-H₂O mixtures.^{1r} The appearance of two lines, one with higher k 's and a lower slope in EtOH-H₂O and another for TFE-H₂O, indicated a solvent-assisted process. Since two such lines were found for *t*-BuCl and *t*-BuBr, a nucleophilic component is indicated in $Y(\text{TFE-H}_2\text{O})$. Similar reasoning will apply to TFE-EtOH mixtures. This conclusion is not supported by analysis of Kopel and Palm's analysis²⁴ of the solvolysis of *t*-BuCl in terms of solvent polarity, electrophilicity, and nucleophilicity, which suggests that solvent nucleophilicity is unimportant. However, it is in line with the similar behavior of 1-Br and 1-adamantyl chloride^{1r} and with recent evidence for an S_N2 character for the solvolysis of *tert*-butyl halides.²¹

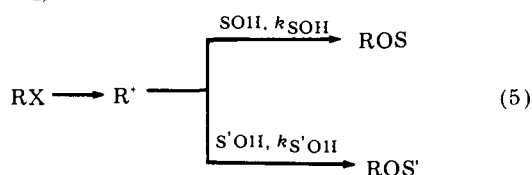
m_{GW} Values. If the $\log k$ values for three solvents are known and a linear $\log k$ vs. Y plot is expected, the three binary mixtures derived from these solvents will give either a single line or a triangle. In the latter case the three Grunwald-Winstein slopes m_{GW} will not be independent. We do not know of any example where such a relationship was observed. The expectation of a linear $\log k$ vs. Y relationship was fulfilled in the present work for 2-OTs in TFE-EtOH, but a nonlinear plot was observed in TFE-H₂O.¹⁰ Figure 1 for 1-Br is the best example of such behavior, although it is clear that for intersection of the TFE-H₂O and the EtOH-H₂O lines a nonlinearity of both plots is expected at the high $X_{\text{H}_2\text{O}}$ region.

Possible reasons for the observation of several lines rather than a single one are discussed above. Since 1-Br undoubtedly solvolyzes via k_c ^{10,11} the usual expectation is that all the m_{GW} values will be ca. unity or higher. This is true for the EtOH-H₂O and the TFE-EtOH mixtures, and the value of 1.50 in the latter binary mixtures is one of the highest known. In contrast, the value of 0.56 in TFE-H₂O is low for systems reacting via the k_c process. It was shown previously⁴ that the high slope of the linear relationship between the nucleophilicity parameter N and the ionizing power parameter Y can explain both high and low observed m_{GW} values in TFE-H₂O, but this treatment implicitly involves some contribution from a nucleophilic assisted process. An alternative is that different extents of ion-pair return affect the titrimetric rate constants

differently, but sufficient data on this question are not available.

In spite of the uncertainties concerning the source of the variation in the m_{GW} values there are two remarkable observations. First, the $\log k$ vs. Y plots are linear in TFE–EtOH for all the three k_c substrates studied (1-Br, 2-OTs, and *p,p'*-dichlorobenzhydryl chloride⁶). Second, the slopes in these cases are higher than those for the same substrates in other binary mixtures. Since the various TFE–EtOH mixtures are nearly isodielectric⁷ and nucleophilic solvent assistance is absent, a main contribution to the solvent effect is the higher electrophilic assistance to leaving-group expulsion by TFE. Whether this behavior is characteristic only of substrates strongly hindered to rearside attack requires further work.

Selectivity of the Cationoid Intermediates in Binary Solvent Mixtures. There is a recent interest in the selectivity of solvolitically generated cationoid intermediates toward the solvent components in binary solvent mixtures (SOH–S'OH), especially aqueous ethanol.^{12–16} From eq 5 where R^+ is the product-forming intermediate the selectivity ($k_{\text{SOH}}/k_{\text{S'OH}}$) is usually calculated from the product ratio $[\text{ROS}]/[\text{ROS}']$. It is assumed that the solvent components compete for R^+ in first-order reactions in both SOH and S'OH. The stoichiometric concentration ratio $[\text{SOH}]/[\text{S'OH}]$ and less frequently the corresponding activity coefficient ratio¹⁵ is being used (eq 6; cf. eq 2 when $S = \text{Et}$, $S' = \text{CF}_3\text{CH}_2$ and eq 3 when $S = \text{H}$, $S' = \text{CF}_3\text{CH}_2$).



$$k_{\text{SOH}}/k_{\text{S'OH}} = ([\text{ROS}]/[\text{ROS}'])([\text{S'OH}]/[\text{SOH}]) \quad (6)$$

The selectivity ratios should be invariant with the solvent composition. However, Pross and co-workers found that for octyl, benzyl, and diphenylmethyl derivatives¹² the selectivities in aqueous ethanol $k_{\text{EtOH}}/k_{\text{H}_2\text{O}}$ are >1 as expected, but increase with the increase of the Y values. They discussed three possible explanations.^{12,14} (a) An increased stabilization of the intermediate in the more polar medium gives a more selective species according to the reactivity–selectivity principle.¹⁷ (b) An increased proportion of a more dissociated and more selective intermediate is formed in the more polar medium. (c) A composition-dependent change in the nucleophilicities of SOH and S'OH is superimposed on their concentration change. In order to distinguish between the alternatives, the solvolysis of adamantyl derivatives, including 1-Br, was studied.¹⁴ The reasoning was that in this case the only product-forming intermediate is the solvent-separated ion pair, since nucleophilic approach from the rear either to the covalent material or to the intimate ion pair is sterically highly unlikely and formation of the free ion is energetically not feasible.

However, the solvolysis of the adamantyl derivatives differs from that of the other derivatives discussed above. First, a “negative selectivity”, i.e., that water is more nucleophilic than ethanol, was found for 1-Br. The $k_{\text{H}_2\text{O}}/k_{\text{EtOH}}$ ratios are 1.65–1.89 in 50–95% aqueous EtOH¹⁴ (or 2.15 ± 0.07 according to another source¹⁵) with a very small selectivity maximum at ca. 70–80% EtOH. The selectivities for 1-Br in 60% EtOH increased linearly with the percentage of added acetone which reduced the dielectric constant.¹⁴ It was concluded that for the adamantyl derivatives the relative nucleophilicities of water and ethanol change with the medium composition. The negative selectivity was ascribed to the fact that for most substrates the $k_{\text{H}_2\text{O}}/k_{\text{EtOH}}$ ratios represent rearside nucleophilicity, whereas for 1-Br collapse of the sol-

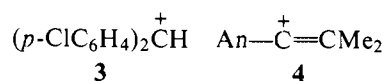
vent-separated ion pair is from the frontside.²⁵ Higher stabilization by hydrogen bonding to the leaving group of the water separated ion pair gives $k_{\text{H}_2\text{O}}/k_{\text{EtOH}} > 1$.

Harris and co-workers¹³ suggested that a different but constant selectivity, regardless of the stability, applies for attack on the neutral species, the intimate ion pair, and the free ion. Changes in the $k_{\text{EtOH}}/k_{\text{H}_2\text{O}}$ ratios therefore indicate either a shift to a more dissociated species or change in the stability of the solvent-separated ion pair.

In the present work we obtained $k_{\text{EtOH}}/k_{\text{TFE}}$ ratios for 1-Br and 2-OTs and $k_{\text{TFE}}/k_{\text{H}_2\text{O}}$ values for 1-Br. Together with the previous $k_{\text{EtOH}}/k_{\text{TFE}}$ ratios for *p,p'*-dichlorobenzhydryl chloride,⁶ substituted benzyl bromides,³ and 2-adamantyl arenesulfonates⁵ and the $k_{\text{TFE}}/k_{\text{H}_2\text{O}}$ values for 2-OTs and *t*-BuCl² some trends are discernible.

The $k_{\text{EtOH}}/k_{\text{TFE}}$ values in TFE–EtOH strongly depend on the nature of the cationoid species. The fastest solvolysis in this medium is that of *p,p'*-dichlorobenzhydryl chloride,⁶ and the observed common ion rate depression indicates that the product-forming intermediate is the free cation **3**, at least in the TFE-rich media. Hence, the $k_{\text{EtOH}}/k_{\text{TFE}}$ ratios of ca. 40 which do not show a large dependence on the medium composition represent selectivity values of a free cation toward the two alcohols, where ethanol is a superior nucleophile.

The results for 2-OTs are similar. The $k_{\text{EtOH}}/k_{\text{TFE}}$ ratios are ca. 12 and, although they are somewhat higher at lower X_{TFE} , the effect is small and may be due to experimental error. Common ion rate depression was not observed in TFE–EtOH, but since the corresponding bromide 2-Br shows common ion rate depression in aqueous TFE and gives similar product distributions to those from 2-OTs¹⁰ we believe that the solvolysis intermediate in TFE–EtOH is the free vinyl cation **4**. This is consistent with the intermediacy of free vinyl cations in the solvolyses of other β -substituted α -anisylvinyl systems.²⁶ The difference between the $k_{\text{EtOH}}/k_{\text{TFE}}$ ratios for the free cations **3** and **4** is in contrast with Ritchie's constant selectivity rule²⁷ for free cations, but we already noted²⁸ that such comparison is unjustified especially since steric effects play an important role in the capture process of **4**.



The $k_{\text{EtOH}}/k_{\text{TFE}}$ ratios of 0.4–1.2 for 1-Br show that trifluoroethanol is either more reactive or has a similar reactivity to EtOH toward the cationic intermediate. Similar ratios (0.58–1.2) were found by Ando and Tsukamoto for the solvolyses of 1- and 2-adamantyl arenesulfonates and bromides in 50% TFE–EtOH.⁵ Although the low value in 90% TFE may reflect a high error when 1-OEt is only a minor product, a maximum in the $k_{\text{EtOH}}/k_{\text{TFE}}$ ratios is clearly observed at $X_{\text{TFE}} \sim 0.5$. We note, however, that the ratios of 0.67 at 75 °C and 0.69 at 90 °C found in 50% TFE–50% EtOH⁵ are lower than our value of 1.1 at 35 °C in the same medium. Reasons for such discrepancies were discussed.¹⁵

The negative ($k_{\text{EtOH}}/k_{\text{TFE}} < 1$) or the zero selectivity ($k_{\text{EtOH}}/k_{\text{TFE}} \sim 1$) argues for the intermediacy of a cationoid species in the solvolysis of 1-Br which is different from the free ion. By Pross¹⁴ and Harris¹³ arguments this is the solvent-separated ion pair. The product distribution is then determined either by the relative stabilities of the EtOH-separated and the TFE-separated ion pairs or by their relative rate of collapse if this is slower than the exchange of the solvent molecule with the bulk solvent. The ion pairs are stabilized by hydrogen bonding of the SOH molecule to the leaving group, which will favor the TFE ion pair since TFE is a better hydrogen bond donor than EtOH. The EtOH-separated ion pair is favored by a better cation–oxygen lone pair interaction since EtOH is more basic. The collapse rates of the ion pairs are also governed by com-

compensation effects since hydrogen bonding to the leaving group increases the nucleophilicity of the less nucleophilic TFE. Apparently, this compensation is reflected by the low selectivity values.

A positive or a negative selectivity can be observed depending on the contribution of the effects discussed above and additional ones such as the bulk of the solvent molecule,²⁹ the number of hydrogen bonds that it forms with the leaving group¹⁶ and its acidity. However, it is difficult to predict if the collapse rate will become rate determining. A notable feature of the behavior in TFE-EtOH is that the negative selectivity for $X_{\text{TFE}} > 0.65$ and < 0.35 becomes positive at $X_{\text{TFE}} = 0.35-0.65$ and reaches a maximum at $X_{\text{TFE}} \sim 0.5$. This is not surprising since the assumption that the nucleophilicity of EtOH and TFE is independent of the medium composition is oversimplified. TFE-EtOH mixtures are far from being ideal and EtOH-EtOH and TFE-TFE dimers and the mixed species $\text{CF}_3\text{CH}_2\text{OH} \cdots \text{HOCH}_2\text{CH}_3$, which was shown to be the most stable in CCl_4 , are present in the solution.⁷ The concentrations of these species need not change linearly on changing the TFE or the EtOH concentration. This effect should be more important for the reaction with the free ions, but it should be also reflected for solvent-separated ion pairs where the intervening solvent molecule is mainly associated with the ion-pair partners. The selectivity maximum appears at the same solvent composition where the boiling point is at a maximum,⁷ indicating a connection between the solvent structure and its selectivity.

A support for a frontside capture for the adamantyl ion pair is shown by comparison with the less reactive benzyl bromides.³ No trifluoroethyl ether was obtained in the solvolysis of *m*- $\text{FC}_6\text{H}_4\text{CH}_2\text{Br}$ for $X_{\text{TFE}} < 0.76$ or of PhCH_2Br for $X_{\text{TFE}} < 0.45$, and the $k_{\text{EtOH}}/k_{\text{TFE}}$ ratios are 22 and 4.2 for benzyl bromide and its *p*-methyl derivative, respectively, at $X_{\text{TFE}} = 0.76$. The lower ratio for the more reactive substrate indicates product formation either from a nucleophilic assisted process or by attack on an earlier ion pair than the solvent-separated one. If Harris' discussion of the origin of the stability-selectivity relationship¹³ is applicable, the products in the benzyl bromides solvolysis are formed from at least two species. Consequently, the lowest selectivity (either positive or negative) is expected for reaction via a solvent-separated ion pair. This conclusion should be incorporated in Pross' analysis of the reasons for a change of the selectivity with the medium composition.¹⁴

Interpretation of the selectivities observed in aqueous TFE is more complicated. Since TFE is much less nucleophilic than water⁹ the $k_{\text{H}_2\text{O}}/k_{\text{TFE}}$ ratios for a capture of a free carbonium ion are expected to be much higher than unity. Previous studies revealed several experimental complications. The solvolysis of *t*-BuCl gives a nearly constant $k_{\text{H}_2\text{O}}/k_{\text{TFE}}$ ratio of 1.17 ± 0.12 for $X_{\text{TFE}} = 0.21-0.85$ but it includes an elimination component.² The ratios for the solvolyses of 2-methylpropenyl bromide (**2-Br**) and of **2-OTs** (which proceed at least partially via the free ion) decrease from 1.50 at $X_{\text{TFE}} = 0.85$ to 0.22 at $X_{\text{TFE}} = 0.07$ in the presence of Et_3N ,¹⁰ but the trifluoroethyl ether is unstable to hydrolysis at these conditions. However, the ratios at the same solvent compositions decrease steadily from 0.63 to 0.08 in the presence of 0.25 M NaOH.¹⁰ The $k_{\text{H}_2\text{O}}/k_{\text{TFE}}$ for *o*- $\text{MeOC}_6\text{H}_4\text{C}(\text{OTs})=\text{CMe}_2$, where the derived trifluoroethyl ether is stable under the reaction conditions, are also < 1 in the presence of both Et_3N and NaOH.¹⁰ Consequently, in contrast to expectations, TFE has a similar or a higher nucleophilicity than water toward the free vinyl cation, and the nucleophilicity of each solvent component is composition independent.

The new $k_{\text{TFE}}/k_{\text{H}_2\text{O}}$ ratios for **1-Br** are > 1 for $X_{\text{TFE}} = 0.85-0.29$, but they decrease steadily with the decrease in X_{TFE} except for the value for $X_{\text{TFE}} = 0.11$. Consequently, a negative

selectivity is observed for an extensive solvent range. To the extent that the dielectric constant measures the medium polarity, the medium-dependent reactivity-selectivity relationship is opposite to that found for other systems. Moreover, the selectivity decrease is even stronger than the accompanying increase in the solvolysis rate, which is presumed to be inversely proportional to the reactivity of R^+ . A 14% increase in the solvolytic reactivity between $X_{\text{TFE}} = 0.85$ and $X_{\text{TFE}} = 0.64$ is accompanied by a 35% decrease in the $k_{\text{H}_2\text{O}}/k_{\text{TFE}}$ values, whereas the 2.55-fold increase in the reactivity from 97% TFE ($X_{\text{TFE}} = 0.85$) to 60% TFE ($X_{\text{TFE}} = 0.21$) is accompanied by a 3.1-fold decrease in the $k_{\text{H}_2\text{O}}/k_{\text{TFE}}$ values. This is unusual since large changes in the reactivity are accompanied by minor changes in the selectivity in either TFE-EtOH or EtOH-H₂O. The solvent effect on the ionization rate of **1-Br** is composed of a general dielectric constant effect and an electrophilic assistance via hydrogen bonding to the leaving group. Both effects usually result in an appreciable rate increase on increasing $X_{\text{H}_2\text{O}}$ in a binary ROH-H₂O mixture. However, since TFE is more acidic than water³⁰ and by $E_{\text{T}}(1)$ measurements it is more polar,¹⁰ increasing $X_{\text{H}_2\text{O}}$ in TFE-H₂O mixtures increases the dielectric constant but reduces the electrophilicity of the medium, and the combination of the effects is a relatively small rate increase.

The product-forming intermediates are the TFE-separated and the H₂O-separated ion pairs. If their collapse to the solvolysis products is slower than exchange with the bulk solvent, the $k_{\text{H}_2\text{O}}/k_{\text{TFE}}$ values indeed measure the frontside nucleophilicities.²⁵ These should reflect the ratios toward free cations, modified by the interaction of the intervening solvent molecule with the leaving group. Since the hydrogen bond increases the electron density on the nucleophilic oxygen in the better hydrogen donor TFE, the $k_{\text{H}_2\text{O}}/k_{\text{TFE}}$ values will be reduced and a negative selectivity may be obtained. The dependence of the values on the solvent composition may result from a slower or similar rate of solvent relaxation around the ion compared with the rate of ion-pair collapse. Only very crude estimates for collapse/relaxation rates for similar systems are available.¹³

The dependence of the $k_{\text{H}_2\text{O}}/k_{\text{TFE}}$ ratios on the solvent composition is a failure of the assumption of a medium-independent nucleophilicity. This assumption seems a priori unjustified since TFE-H₂O mixtures are far from being ideal and species such as H₂O-H₂O and TFE-TFE dimers and the mixed species TFE-H₂O presumably have different nucleophilicities. Since equilibria between these species is established rapidly, their concentration dependency on the solvent will be more complicated than a first order. The overall result will be a medium dependency of the selectivity ratios.

The assumption of an independence of the nucleophilicity of the medium components on its composition calls for an additional result. Multiplication of the $k_{\text{TFE}}/k_{\text{H}_2\text{O}}$ ratios from the TFE-H₂O data by the $k_{\text{EtOH}}/k_{\text{TFE}}$ ratios from the EtOH-H₂O data at the same X_{TFE} ratios gives $k_{\text{EtOH}}/k_{\text{H}_2\text{O}}$ ratios for the corresponding X_{EtOH} values. These should be similar to the $k_{\text{EtOH}}/k_{\text{H}_2\text{O}}$ obtained from solvolysis in EtOH-H₂O if the above assumption is valid. In spite of the fact that the $k_{\text{TFE}}/k_{\text{EtOH}}$ and the $k_{\text{H}_2\text{O}}/k_{\text{TFE}}$ ratios were composition dependent it was of interest to find out if their product is not. The $k_{\text{EtOH}}/k_{\text{H}_2\text{O}}$ ratios calculated in this way are compared with those obtained by Karton and Pross¹⁴ and by Luton and Whiting¹⁵ in Table V. The differences between the calculated and the observed values argue against the unreserved use of eq 2 and 3.

Nucleophilicity of TFE-H₂O and TFE-EtOH Mixtures. The solvolysis of methyl tosylate was used by Schleyer and co-workers as a model reaction for calculating the nucleophilicity of various solvents, and nucleophilic parameters *N* were calculated for 97, 90, 70, 50, and 30% TFE-H₂O.⁹ Kevill and Lin recently suggested a solvent nucleophilicity scale based on

Table V. Calculated and Observed $k_{\text{EtOH}}/k_{\text{H}_2\text{O}}$ Ratios for the Solvolysis of **1-Br**

X_{TFE}	$k_{\text{TFE}}/k_{\text{EtOH}}$	$k_{\text{TFE}}/k_{\text{H}_2\text{O}}$	$k_{\text{EtOH}}/k_{\text{H}_2\text{O}}(\text{calcd})^a$	$k_{\text{EtOH}}/k_{\text{H}_2\text{O}}(\text{obsd})^b$
0.88	2.60			
0.85		0.49	0.19	
0.76	1.42			0.61 (0.49)
0.74		0.63	0.44	
0.65	1.19			
0.64		0.76	0.92	0.57
0.55	0.83			
0.45	0.90			0.53 (0.48)
0.44		0.78	0.87	
0.35	0.92			
0.29		0.88	0.96	
0.26	1.24			0.55 (0.45)
0.21		1.51	1.22	
0.17	1.40			
0.15		2.04	1.46	0.58 (0.45)

^a Calculated from $(k_{\text{TFE}}/k_{\text{H}_2\text{O}})/(k_{\text{TFE}}/k_{\text{EtOH}})$ at similar X_{TFE} values. ^b Values are from ref 14 and values in parentheses are from ref 15.

triethyloxonium ion in solvolysis and measured the corresponding nucleophilicity values N_{KL} for 97, 90, 70, and 50% TFE-H₂O (w/w).³¹ Solvolysis of MeOTs in 97% TFE at higher temperatures was recently investigated.³² N values were also obtained by da Roza, Andrews, and Keefer for 80, 50, and 20% TFE in TFE-EtOH (v/v)³ and an N value for pure TFE was estimated.⁹

From our solvolysis data of MeOTs in several additional TFE-H₂O and TFE-EtOH mixtures (Table IV) we calculated new N values, thus avoiding the necessity for interpolation and extrapolation from the previous data. The values are given in Table VI together with a list of Y values for the same solvent mixtures, as calculated from the solvolyses of *p,p'*-dichlorobenzhydryl chloride in TFE-EtOH⁶ and of *t*-BuCl in the two binary mixtures. We discussed previously the nearly linear relationship between the two parameters N and Y .⁴ In view of the recent use of TFE-H₂O and EtOH-H₂O binary mixtures for detecting nucleophilic assistance in the solvolysis,^{1r} and the possible use of TFE-EtOH mixture for similar purposes, the relationship between $\log k(\text{MeOTs})$ and Y (Figure 3) is of interest. Figure 3 is complementary to Figure 1 in showing the change of nucleophilicity in all the three mixtures. It demonstrates that the change in $\log k$ with Y is the steepest in TFE-H₂O and is positive; i.e., higher Y gives higher $\log k$. A very moderate increase in the same direction was observed in EtOH-H₂O, but in TFE-EtOH $\log k$ decreases when Y increases.

Use of EtOH-H₂O and TFE-H₂O Mixtures as a Probe for Nucleophilic Solvent Assistance. The behavior described by

Figure 1 serves as the basis for the "TFE-EtOH criterion" for detecting nucleophilic solvent assistance in solvolysis reactions suggested recently by Harris and co-workers.^{1r,33} Their assumptions are (a) absence of nucleophilic assistance in the solvolysis of **1-Br**; (b) strong dependence on the nucleophilicity in binary TFE-H₂O mixtures; (c) nearly constant nucleophilicity in EtOH-H₂O, which is higher than in any of the binary TFE-H₂O mixtures. Consequently, a plot of $\log k$ for the solvolysis of a substrate in EtOH-H₂O and TFE-H₂O mixtures vs. $\log k(\text{1-Br})$ in the same media can show two types of behavior. If nucleophilic assistance is unimportant, one correlation line will be obtained for the two binary mixtures. If solvent nucleophilicity is important, a different correlation line will be obtained for each binary mixture, with higher slope for the TFE-H₂O line but with higher overall reactivity for the EtOH-H₂O line. The solvolysis of several compounds showed linear $\log k$ - $\log k(\text{1-Br})$ relationships according to these predictions.^{1r}

An older criterion for nucleophilic solvent assistance which was suggested by Winstein and co-workers is the $(k_{\text{aq ROH}}/k_{\text{RCOOH}})_Y$ ratio.¹⁹ This is the ratio of the solvolysis rates at a certain Y value in a nucleophilic solvent (aqueous ROH) and in a relatively nonnucleophilic one (RCOOH). The ratio should be higher than unity for an extensive solvent assistance and close to unity for unassisted processes. The new criterion replaces the $Y = \log k(t\text{-BuCl})$ values by $\log k(\text{1-Br})$ values and used two linear relationships instead of a single point. Viewed in this way it seems superior to the more limited $(k_{\text{aq ROH}}/k_{\text{RCOOH}})_Y$ value.

However, there are some reservations concerning the new criterion. Obviously, if linearity is extended to more aqueous solvents, the TFE-H₂O and the EtOH-H₂O lines should intersect at the point for pure water, where the reactivity should be the highest. **1-Br** was not solvolyzed in pure water, but, since points in aqueous EtOH fit the correlation line for $\log k(\text{1-Br})$ vs. Y , extrapolation to pure water is possible. The calculated $\log k$ value is -2.26 at 25 °C. If the $\log k(\text{1-Br})$ vs. Y plot for the aqueous TFE mixture is used, the value for pure water is -2.75 . However, from the published plots of Harris, Raber, and co-workers^{1r} the intersection points for all the substrates are at more negative $\log k(\text{1-Br})$ values. They are -3.3 to -3.2 for methyl, cyclopentyl, and cyclohexyl tosylates and 2-propyl brosylate, -3.5 for the k_s process for 2-phenyl-1-propyl tosylate, and -2.7 for cycloheptyl and *endo*-2-norbornyl tosylates. Consequently, either the point for pure water deviates from the correlation line for **1-Br** vs. Y or the plots themselves are nonlinear as the solvent composition approaches pure water. In view of the linearity observed over an appreciable solvent range the first possibility seems more likely.

If the linearity of the two lines is indeed extended up to their intersection point in pure water, comparison of two points

Table VI. N and Y Values for TFE-EtOH and for TFE-H₂O Mixtures

% TFE (v/v) in TFE-EtOH	N (at 50 °C)	Y (at 25 °C) ^a	% TFE (w/w) in TFE-H ₂ O	N (at 50 °C)	Y (at 25 °C) ^b
100	-2.74	1.147 ^{b,c}	100	-2.74	1.045
90	-1.97	0.77	97	-2.59 ^d	1.245
80	-1.55 ^c	0.406 ^c	94	-2.20	1.461
70	-1.13	0.07	90	-1.87	1.659
60	-0.87	-0.27	80	-1.43	1.894
50	-0.63 ^c	-0.588 ^c	70	-1.20 ^d	2.229
40	-0.42	-0.87	60	-1.09	2.60
30	-0.23	-1.22	50	-0.93 ^d	
20	-0.09 ^c	-1.515 ^c	40	-0.88	
10		-1.69	0	-0.26 ^e	
0	+0.09 ^b	-2.033 ^c			

^a From ref 6. ^b From ref 2. ^c From ref 3. ^d From ref 1p. ^e From Bentley, T. W.; Schadt, F. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 992.

further away from this point gives the same information obtained from the full lines of the "TFE-EtOH criterion".^{1r} These points can be for the same Y values and their difference will show how much a point on the TFE-H₂O line is vertically away from the EtOH-H₂O line. Such comparisons which involve the solvent pairs 70% TFE or 50% EtOH and 97% TFE and 60% EtOH were used in the study of vinylic solvolysis.^{1e,m} This analysis is similar to that of Winstein¹⁹ except that aqueous TFE replaces RCOOH as the medium of low nucleophilicity. Another comparison is between the two pure solvents TFE and EtOH. If m is the slope of the EtOH-H₂O line and m' is the slope of the TFE-H₂O line, eq 7 applies.

$$\log(k_{\text{EtOH}}/k_{\text{TFE}}) = (m' - m) \log k(\text{1-Br})_{\text{H}_2\text{O}} + m \log k(\text{1-Br})_{\text{EtOH}} - m' \log k(\text{1-Br})_{\text{TFE}} \quad (7)$$

Using the values -3.2 , -9.06 , and -4.05 for $\log k(\text{1-Br})$ in H₂O, EtOH, and TFE, respectively, eq 8 is obtained.

$$\log(k_{\text{EtOH}}/k_{\text{TFE}}) = 0.85m' - 5.86m \quad (8)$$

One extreme case where solvent participation is absent is 1-Br itself, for which $m = m' = 1$ and $\log(k_{\text{EtOH}}/k_{\text{TFE}})$ is -5 . The other extreme is methyl tosylate, which reacts via the k_c route. Values of $m = 0.186$ and $m' = 3.4$ for MeOTs were calculated from the data of Raber, Harris, and co-workers,^{1r} and hence $\log(k_{\text{EtOH}}/k_{\text{TFE}}) = 1.8$. Consequently, the position of an observed $\log(k_{\text{EtOH}}/k_{\text{TFE}})$ ratio between -5 and 1.8 can serve as a measure of the extent of solvent participation in the solvolysis. The conclusions obtained from the divergence of the TFE-H₂O and the EtOH-H₂O lines and from the $\log(k_{\text{EtOH}}/k_{\text{TFE}})$ ratios are expected to be the same, and the use of the simpler $\log(k_{\text{EtOH}}/k_{\text{TFE}})$ ratios for deducing the presence or absence of solvent participation is therefore recommended.³⁴

Experimental Section

IR spectra were recorded with a Perkin-Elmer 337 instrument, UV spectra with a Perkin-Elmer 450 instrument, mass spectra with a MAT 311 instrument, and NMR with a T-60 or a A56/60 instrument and chemical shifts are given in δ units downfield from internal tetramethylsilane.

Solvents and Materials. Dry ethanol³⁵ and dry trifluoroethanol³⁶ were purified according to the literature and conductivity water was used for preparing the binary mixtures. 2,6-Lutidine was distilled from solid KOH. Methyl tosylate³⁷ and 1-anisyl-2-methylpropen-1-yl tosylate¹⁹ were prepared by literature procedures. Commercial 1-adamantyl bromide (Aldrich), mp 119 °C, was purified by recrystallization from pentane at -80 °C.

Kinetic Methods. The solvolysis of methyl tosylate was followed by potentiometric titration using a Radiometer TTT 1c instrument. The solvolysis of 1-anisyl-2-methylpropen-1-yl tosylate was followed by conductivity using a Pye conductivity bridge. The solvolyses of 1-adamantyl bromide were followed by potentiometric titration of the bromide ion with silver nitrate, after extraction of the unreacted 1-Br.

Solvolysis Products. 1-Anisyl-2-methylpropen-1-yl ethyl³⁸ and 2,2,2-trifluoroethyl¹⁹ ethers are known from previous work. 1-Adamantyl ethyl ether was obtained from solvolysis of 1-Br in pure ethanol.

1-Adamantyl 2,2,2-Trifluoroethyl Ether. A mixture of 1-adamantyl bromide (1.4 g, 6.5 mmol) and triethylamine (1 mL) in TFE (100 mL) was kept at 35 °C for 24 h with stirring. The dissociation was complete after 3 h. The solvent was evaporated, and the remainder was dissolved in ether (30 mL), washed with water, and dried (MgSO₄). The ether was evaporated, and distillation gave 1.3 g (85%) of 1-adamantyl 2,2,2-trifluoroethyl ether: bp 226 °C or 95 °C (19 mm); λ_{max} (EtOH) no absorption >210 nm; ν_{max} (KBr) no characteristic peaks; δ (CCl₄) 1.85, 1.92, 1.98 (12 H, 3 s, CH₂), 2.52 (3 H, broad s, CH), 3.95 (2 H, q, $J_{\text{H-F}} = 8$ Hz, CH₂); ¹⁹F NMR δ (CCl₄) 83.86 (upfield from CCl₃F; triplet, $J_{\text{H-F}} = 8$ Hz); m/e 234 (43%, M), 177 (100%, M - 3F), 135 (32%, adamantyl).

Anal. Calcd for C₁₂H₁₇F₃O: C, 61.53; H, 7.32; F, 24.33. Found: C, 61.71; H, 7.49; F, 24.15.

Product Analysis. The product distributions were determined by gas chromatography using SE-30 columns. The products were found to be stable to mutual interconversion at the analytical conditions used.

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- (25) A referee had correctly commented that, if the negative selectivity is due to a higher stability of the intermediate TFE-separated ion pair, it may be misleading to use the term nucleophilicity. He suggested discussing deviations from "intrinsic nucleophilicity" in this case. Following Pross and Karton¹⁴ we prefer to use the descriptive term "frontside nucleophilicities", since the intuitive "intrinsic nucleophilicities" are solvent dependent, as discussed in the paper.
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- (33) The use of the terms "ethanol-trifluoroethanol method" or "EtOH-TFE plots" for describing $\log k(\text{substrate})$ vs. $\log k(\text{1-Br})$ in aqueous TFE and

aqueous EtOH¹¹ is misleading since "TFE-EtOH" should be reserved for reactions in binary mixtures of the two alcohols.

- (34) The method of Raber, Harris, and co-workers¹¹ utilizes a statistical analysis of the slope, the intercept, and their uncertainties. Hence, it appears superior in certain cases to the more convenient "two-points" method. However, there is an arbitrary criterion which accompanies the statistical analysis. In our opinion, a parallel arbitrary criterion together with a quantitative use of the log ($k_{\text{EtOH}}/k_{\text{TFE}}$) values of -5 and 1.8 will make the

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Vinyl Cations from Solvolysis. 29.^{1,2} Solvolysis of 9-(α -Bromoarylidene)anthrones as a Probe to the Reactivity-Selectivity Relationship in Solvolysis Reactions

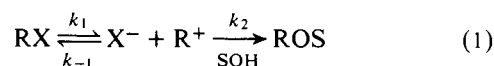
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Abstract: The solvolyses of 9-(α -bromoarylidene)anthrones **5a** (Ar = An), **5b** (Ar = Tol), **5c** (Ar = Ph), and **5d** (Ar = *o*-An) in 1:1 AcOH-Ac₂O/NaOAc and in TFE/2,6-lutidine and of **5a** in buffered AcOH and 80% EtOH were investigated. An extensive common ion rate depression by the formed or added Br⁻ ion was observed. Selectivity constants $\alpha = k_{\text{Br}^-}/k_{\text{AcO}^-}$ and $\alpha' = k_{\text{Br}^-}/k_{\text{TFE}}$ or $k_{\text{Br}^-}/k_{80\% \text{EtOH}}$ for competitive capture of the derived cations **14** by Br⁻ vs. AcO⁻ or the solvent were calculated. The α values in 1:1 AcOH-Ac₂O, the α' values in TFE, and the reactivities (k_t^0 values) are structure dependent and follow the order **5a** > **5d** > **5b**. The results for **5c** are not sufficiently accurate for reliable selectivity determination. The nature of the capturing nucleophile in AcOH-containing media is discussed and evidence for product formation nearly exclusively from a solvolytically generated *free* vinyl cation in AcOH, AcOH-Ac₂O, and TFE is given. Linear or nearly linear reactivity-selectivity relationships of log k_t^0 vs. log α or log α' for **5a**, **5b**, and **5d** were obtained, but the selectivity differences are moderate in 1:1 AcOH-Ac₂O and small in TFE. This behavior is discussed in relation to Ritchie's constant selectivity rule for stable cations and the linear reactivity-selectivity observed for less selective ions. It is suggested that the different selectivity relationships represent different regions of an overall nonlinear reactivity-selectivity plots for carbonium ion reactions. The merits and disadvantages of measuring selectivities by common ion rate depression are discussed.

A widely used relationship in mechanistic organic chemistry is the reactivity-selectivity relationship,³ according to which, in a family of closely related reactions, increased reactivity of a reactant or an intermediate is associated with a lower selectivity. Many cases of this relationship were reviewed,³ but serious questions concerning its validity were recently raised.^{4,5} An area where the relationship was observed is in solvolytic reactions involving carbonium ion intermediates.^{3a,6} Since the solvolytically generated cations are highly reactive and formed mostly in steady-state concentrations, direct kinetic measurements of their reactivities and selectivities are usually unavailable. Instead, the relative reactivities of a series of carbonium ions R⁺ are inferred from the solvolysis rates of their precursors, e.g., the halides RX. Hammond's postulate⁷ is being used in assuming that the faster the solvolysis of RX the more stable and less reactive is the formed carbonium ion. The relative selectivities of the ions were determined in two ways. First, competition of two nucleophiles for R⁺ gives two capture products and the selectivity ratio is obtained from their ratio by assuming that the capture rates are proportional to the concentrations of the nucleophiles. Applying this method for the competitions of N₃⁻ and H₂O^{6d,e} or for mixtures of two nucleophilic solvents, especially aqueous alcohols,^{6f-n} gave linear reactivity-selectivity relationships.

The second method is a kinetic one based on the phenomenon of common ion rate depression.^{6a,8} When products are formed from the *free* cations R⁺ (eq 1), capture by the solvent



SOH (k_2) competes with the recombination reaction of R⁺ and X⁻ (k_{-1}). From the decrease of the first-order solvolysis rate

constant by the X⁻ formed during the reaction or added externally, or by measuring the incorporation of labeled X⁻, the competition ratios k_X/k_{SOH} can be evaluated. A reactivity-selectivity relationship was observed by this method for the solvolysis of substituted benzhydryl halides.^{6a,c}

A contrasting behavior was discovered recently by Ritchie.^{5,9} A study of the combination reaction of anions with stable organic cations revealed a large difference in the relative reactivities of the cations but constant selectivities toward a large series of nucleophiles. A similar relationship holds also for reactions of nucleophiles with activated aromatic,¹⁰ carbonyl,¹¹ vinyllic,¹² and sulfonyl¹³ substrates.

A satisfactory explanation for this behavior is not available,¹⁴ and it raises the question: how could the contrasting "reactivity-selectivity" and "constant selectivity" relationships for reactions of organic cations mutually coexist? One explanation is that a reactivity-selectivity relationship holds for unstable cations but it reaches a plateau at higher selectivity for the more stable cations.¹⁵ Another explanation notes that a selectivity which is based on the product distribution reflects a weighted average of the selectivities of the product-forming ion pairs and free ions rather than the selectivity of a single species.^{5,16} Indeed, reactivity-selectivity relationships were used in the study of ion pairs formed in solvolysis.^{6f,g,i-o,17}

For evaluating this suggestion¹⁸ and for comparison of the selectivities of the solvolysis intermediates and the stable cations^{5,9} the solvolysis reaction should fulfill several prerequisites. First, it should be shown that the cationoid species involved in the selectivity measurements is a *free* carbonium ion. Second, the extents of ion pair and external ion returns^{8b,c} should be known so that the ionization rate constant would serve as a measure of the stability and the reactivity of R⁺. Third, a ki-