having the same range of basicity (0.75^1). The gradually curving solid line in Figure 1 was computed using a value of $\Delta G^{\ddagger}_0 = 10$ kcal in the Marcus expression for proton transfer.[1,11-13] This degree of curvature is approximately the amount expected for a "Hammond postulate" type of change in transition state structure, judging from isotope effect[14,15] and other[16] data. The thiol anion data are more similar to this curve than are the oxy anion data both in β value and in degree of curvature.

These observations, along with the fact that cyanide ion fits well with the thiol anion data rather than with the oxy anion data, support the solvation effect argument used to explain Brønsted plot curvature for the oxy anions.[1] According to this argument, oxy anions can benefit from a solvation shell in the transition state because the charge stabilization is great enough to offset the unfavorable effect of leaving solvent molecules in position after proton transfer. Cyanide and thiol anions would benefit less from such charge stabilization and would, in addition, have to pay a larger energetic price for the construction of the solvation shell. It is therefore reasonable that the rate constants for these catalysts are smaller and that the β value measured more closely reflects the degree of proton transfer in the transition state.

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Solvolysis of Cyclopentyl *p*-Bromobenzenesulfonate in Aqueous Hexafluoroisopropyl Alcohol. Deuterium Rate Effects, Stereochemistry of Substitution and Elimination, and Reaction Mechanism

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Abstract: In 90% hexafluoroisopropyl alcohol–10% water cyclopentyl *p*-bromobenzenesulfonate solvolyzes at 25 °C with a half-life of 26 min. The yield of cyclopentene is 80% and syn elimination is favored over anti by a factor of about 4. The α-*d* rate effect is large (1.23), indicating that the intimate ion pair is reversibly formed and that nucleophilic attack to give cyclopentanol is not rate determining or partially rate determining. The cis-β-*d* rate effect (1.35) is larger than the trans-β-*d* effect (1.22). The β-*d₄* rate effect (2.86) is large and greater than the square of the product of the cis-β-*d* and the trans-β-*d* rate effects (2.71). It is concluded that the reaction mechanism involves reversible formation of the intimate ion pair which further reacts mainly by two irreversible, competitive processes: (1) removal of the cis-β proton by the leaving group to give cyclopentene and (2) conversion to the solvent-separated ion pair. The solvent-separated ion pair gives cyclopentanol and possibly some additional cyclopentene. These results are briefly compared with results published earlier for the solvolysis of cyclopentyl *p*-bromobenzenesulfonate in ethanol–water, dioxane–water, and trifluoroethanol–water solvents.

Introduction

In earlier papers[1-4] α- and β-deuterium rate effects,[1,2] product distributions,[1,2] and the stereochemistry of elimination[3] and substitution[4] in the solvolysis of cyclopentyl *p*-bromobenzenesulfonate (1) in various solvents have been reported. It was concluded that in 70–100% ethanol–water (E–W) solvents both elimination and substitution products were predominantly derived by rate-determining solvent attack on the reversibly formed intimate ion pair, A. The evidence also strongly suggests that in 70% 2,2,2-trifluoroethanol–water (70 TFE–W) elimination and substitution take place after the rate-determining step, most probably from the solvent-separated ion pair (B), the formation of which via rate constant k_2 is rate determining. However, in 97 TFE–W the evidence

strongly supports the incursion of still another reaction, rate-determining syn elimination of the β proton in the intimate ion pair by the leaving group;[4] this process competes with rate-determining formation of the solvent-separated ion pair, which in turn leads to additional elimination and substitution (k_{6e} and k_{6s}).[4] In 80% dioxane–water (80 D–W)[2] it appears that rate-determining product formation at the intimate ion pair stage competes with rate-determining formation of the solvent-separated ion pair, and products are formed by solvent attack on both ion pairs.

It appeared to us to be of interest to examine the solvolysis of 1 in a solvent even less nucleophilic than TFE to establish more firmly, if possible, the occurrence of rate-determining syn elimination by the leaving group at the intimate ion pair

Table I. First-Order Rate Constants and Deuterium Isotope Effects in Solvolysis of Cyclopentyl p-Bromobenzenesulfonate (1)[a] in 90 and 97 wt % Hexafluoroisopropyl Alcohol–Water Mixtures at 25 °C

| | 90 wt % alcohol | | | 97 wt % alcohol | | |
compd	$k \times 10^5$, s^{-1} [b]	k_H/k_D	k_H/k_D (cor)[c]	$k \times 10^{-5}$, s^{-1} [a]	k_H/k_D	k_H/k_D (cor)[c]
1	27.46 ± 0.06			62.85 ± 0.19		
1-*1*-d	22.28 ± 0.03	1.232	1.232	50.28 ± 0.15	1.25	1.25
cis-1-2-d	20.42 ± 0.06	1.345	1.353	46.24 ± 0.21	1.36	1.37
trans-1-2-d	22.40 ± 0.03	1.226	1.222	51.61 ± 0.04	1.22	1.22
1-β-d_4	10.00 ± 0.02	2.746	2.864	20.96 ± 0.04	3.00	3.14

[a] The initial ester concentrations were ~0.003 M and the reactions were followed for ~2 half-lives. [b] Uncertainties are differences between duplicate measurements. [c] Corrected to 100% composition of the indicated isotopic isomer. Mass spectral analyses done on the precursor alcohols showed 1-*1*-d to be 100% pure; 1-β-d_4 is 96% isotopically pure; *cis*-1-2-d contains 98% d_1 and 2% d_0 molecules; *trans*-1-2-d contains 3.4% d_0, 91.8% d_1, and 4.8% d_2 molecules. The latter by ^{2}H NMR analysis is apparently the 1-*trans*-2-dideutero compound.

stage. Since the solvolysis of I in buffered trifluoroacetic acid (TFA) is too fast for accurate rate measurement by our techniques, and because the addition of TFA to cyclopentene occurs rapidly enough to complicate product analysis,[5] we selected 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) for these studies. Dowd[6] and Fisher[7] examined the utility of HFIP for solvolytic reactions, but because its low dissociative capacity for electrolytes seemed to limit the accuracy of conductance measurements in it, we have not generally used it in the study of deuterium rate effects and solvolysis mechanisms. Schleyer et al.[8] have more recently published results using HFIP for solvolysis and favor it as an alternative to TFA for high solvolytic ability and low nucleophilicity. The recent development in our laboratories of an automated spectrophotometric method for the precise determination of solvolysis rates (see Experimental Section) now makes it possible for us to use HFIP for the study of secondary deuterium rate effects.

Results and Discussion

The required 1-*1*-d, *cis*-1-2-d, *trans*-1-2-d, and 1-2,2,5,5-d_4 were prepared from the corresponding alcohols[1,9,10] by the Tipson procedure.[11] In Table I are given the solvolysis rate constants in both 90 and 97 wt % HFIP–W measured spectrophotometrically and the corresponding isotope rate effects. Since the products from solvolysis in 97 HFIP–W have not been analyzed, we will first discuss the results for the reaction in 90 HFIP–W. In this solvent neither common ion rate depression nor special salt effect was detected; 0.032 M added sodium perchlorate increased the solvolysis rate by ~8%, while ~0.008 M sodium brosylate increased the rate by ~4%. The α-d effect in 90 HFIP–W is high, equal to the value obtained earlier in 70 and 97 TFE–W and characteristic of either k_2 or k_{5c} being the rate-determining step but not consistent with k_1, k_{5s}, or k_{6s} being in any significant part rate determining. Therefore, the 20% substitution product (see below) must be formed via solvent attack at the solvent-separated ion pair stage. The trans-β-d effect (1.22) is very close to the trans-β-d effects observed earlier[1] for reactions where k_2 is rate determining or where k_{5c} is rate determining (1.20–1.21), and trans elimination did not contribute significantly; on the other hand, the cis-β-d effect (1.35) is significantly larger and indicates that elimination of this proton (or deuteron) contributes significantly to the rate-determining step. This last conclusion is also supported strongly by the observation of a β-d_4 effect (2.86) which is large and which exceeds the square of the product of the cis-β-d and the trans-β-d effects (2.73). The β-d_4 effect is larger and the noncumulative character is more pronounced in 97 HFIP–W solvent as would be expected if the olefin fraction were larger.

Table II gives the relative yields (totaled to 100%) of cyclopentene-*1*-d, cyclopentene-*3*-d, and undeuterated cyclopentene obtained by the mass spectrometric and ^{2}H NMR analysis method described previously,[3] for the cyclopentene

samples isolated from solvolysis of *cis*-1-2-d and *trans*-1-2-d in 90 HFIP–W. Under the assumption that the isotope effects for anti and syn elimination are equal, we derive the conclusion that syn elimination is favored over anti by a factor of 4.2. Qualitatively, it is impressive that the yield of undeuterated cyclopentene from *cis*-1-2-d is ~25%, while that from *trans*-1-2-d is only about 5%. Much more deuterium is lost in elimination from the cis than from the trans isomer. Thus, the product analysis provides a striking confirmation of the conclusion reached from the β-deuterium rate effects that it is the cis hydrogen (or deuterium) that is predominantly eliminated. The isotope effects indicate further that cis-β-proton loss is at least partly rate determining, and it seems reasonable to conclude that the mechanism involves abstraction of this proton in the intimate ion pair by the p-bromobenzenesulfonate anion leaving group. This reaction would be favored by default in the relatively nonnucleophilic, nonbasic, low dielectric constant HFIP–W solvent.

In Table III we show the relative yield of *cis*- and *trans*-cyclopentan-2-d-ols isolated after ~10 half-lives of solvolysis of *trans*-1-2-d in 90 HFIP–W. These results were obtained by the ^{2}H NMR analysis described previously.[4] The cyclopentanol, which GLC analysis shows to be formed to the extent of about 14% of the total yield, is 85% inverted and 15% retained in configuration at the reacting carbon relative to the starting material. This is a greater degree of retention than that obtained in 80 TFE–W[4] or 90 TFE–W[4] and indicates that the alcohol is formed mainly from the solvent-separated ion pair; solvent sorting seems to favor inversion but by a much smaller factor than that which seems to apply in TFE–W mixtures. The 4% yield of cyclopentyl hexafluoroisopropyl ether was too small to allow it to be readily isolated for ^{2}H NMR analysis.

Because of the apparent shift in mechanism from k_2 rate determining in 70 TFE–W to rate-determining internal elimination competing with k_2 in 97 TFE–W as well as in 90 HFIP–W, we thought it desirable to use the more precise conductance method to check some of the key deuterium rate effects determined earlier in the TFE–W solvents by the titrimetric procedure. The new results are given in Table IV and entered in Table V where they can be directly compared with the earlier experiments. The results of the two methods are seen generally to agree to within the ±1% standard error expected of the titrimetric procedure.
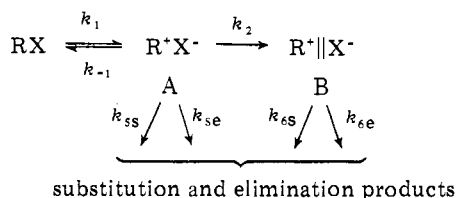
Table V contains a summary of all of the results obtained to date for the solvolysis of 1 in various solvents.

We believe that the isotope effects of Table V can be explained reasonably completely by the assumption that the observed effect depends primarily on which step (or steps) in the mechanism is rate determining, and that very similar isotope effects for each step apply in all of these solvents. The effects which we suggest apply for each of the single steps in Scheme 1 being rate determining can be calculated by deriving various steady-state equations which correlate the isotope rate

Table II. Olefin Yields[a] in Solvolysis of Cyclopentyl p-Bromobenzenesulfonate in 90 wt % Hexafluoroisopropyl Alcohol-Water at 25 °C

reactant				
cis-1-2-*d*[b]	obsd	15.2	59.6	25.2
	cor	13.1	61.9	25.1
trans-1-2-*d*[c]	obsd	48.6	43.0	8.4
	cor	47.8	46.9	5.3
k_e anti/k_e syn	(calcd)	0.24		

[a] Expressed as percentage of total olefin. Determinations were made on olefins isolated from 90 wt % hexafluoroisopropyl alcohol-water in the presence of 2,6-lutidine. [b] Contains 2% d_0 and 98% d_1 (7% is *trans*-2-*d*). [c] Contains 3.5% d_0, 91.8% d_1, and 4.8% d_2.

Scheme I

$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{A}{R^+X^-} \overset{k_2}{\longrightarrow} \underset{B}{R^+\|X^-}$$

substitution and elimination products

effects and the product yields within the framework of Scheme I. The parameters are then optimized to achieve a quantitative fit of the observed data through the use of the versatile simplex method of optimization.[12] These single-step isotope effects can then be combined to give the overall effects which apply when one particular step is rate determining as shown in Table VI. The effects for k_2 rate determining are those that are generated by the equilibrium formation of the intimate ion pair (k_1/k_{-1}), the assumption being that further separation of the ions toward the solvent-separated ion pair has little additional influence. These isotope effects are very close to those that are obtained for 70 TFE-W (Table V), a fairly polar, nonnucleophilic solvent. Very similar *secondary* effects apparently apply if k_{5e} is rate determining, since elimination has little influence on the α-*d* effect.[13] The primary isotope effect applies in k_{5e} when the isotopic atom is being eliminated. This manifests itself for the predominantly cis elimination in 97 TFE-W and in 90 HFIP-W (but *not* in 70 TFE-W!) in the following manner: (1) the cis-β-*d* effect is larger than 1.21 but the trans-β-*d* effect is not; (2) the β-d_4 effect is larger than 2.14; and (3) since the cis monodeuterated compound can eliminate the opposite cis proton, the isotope effects are not cumulative in that the square of the product of the cis-β-*d* and the trans-β-*d* effects is less than the β-d_4 effect. Of course, these effects are larger for larger fractions of elimination, and, although the observed β-d_4 effects in 97 TFE-W (2.474) and 90 HFIP-W (2.86) are significantly larger than the purely secondary effect of 2.21, they are not as large as the product of primary and secondary β-*d* effects (3.21). Also, to the extent that some elimination can arise from the solvent-separated ion pair, the β-d_4 effect will be smaller; this explains why it is significantly less in 97 TFE-W than in 90 HFIP-W.

For k_{5s} rate determining the partial attachment of the nucleophilic oxygen in the transition state reduces the α-*d* and β-*d* effects which are caused by equilibrium intimate ion-pair formation. These effects are very close to those which are observed in 100 E and 96 E-W; the small amounts of elimination by k_{5e} (solvent) cause some increase in all three β effects but most noticeably for the β-d_4 compound. This trend is amplified for 80 E-W and 70 E-W, which show larger olefin fractions. In these solvents, however, the olefin fraction is not large enough to cause significant noncumulative character. In D-W solvents[2] all information points to a mixed mechanism wherein

Table III. ²H NMR Analysis[a] of β-Deuterated Cyclopentanols

cyclopentanols	relative integrals		inversion %[b]
	cis-β-*d* τ 9.04[c]	trans-β-*d* τ 8.86[c]	
starting cis alcohol[d]	0.93	0.07	
trans alcohol[e]		1.00	
solvolysis product[f] from *trans*-1-2-*d*	0.85	0.15	85

[a] Varian HR-220 spectrometer operating at 33.8 MHz (²H NMR). [b] Error is approximately 3%. [c] In parts per million with Me₄Si-d_{12} as the external standard and using a Hewlett-Packard white noise decoupler centered at 220 002 587 Hz. Concentrations were about 1 M in CHCl₃. [d] Original sample of *cis*-cyclopentanol-2-*d* from which *cis*-1-2-*d* p-bromobenzenesulfonate used in solvolysis was prepared; starting alcohol contains 2% d_0 and 98% d_1 according to mass spectral analysis. [e] Original sample of *trans*-cyclopentanol-2-*d*; sample contained 3.4% d_0, 91.8% d_1, and 4.8% d_2 according to mass spectral analysis. [f] Isolated by GLC after 10 half-lives of solvolysis of *trans*-1-2-*d* in 90 HFIP-W at 25 °C.

Table IV. First-Order Rate Constants[a] and Deuterium Isotope Effects in Solvolysis of Cyclopentyl p-Bromobenzenesulfonate (1) in 2,2,2-Trifluoroethanol-Water at 25 °C

compd	97 TFE-W			70 TFE-W		
	$k \times 10^5$, s⁻¹	k_H/k_D (obsd)	k_H/k_D (cor)[b]	$k \times 10^5$, s⁻¹	k_H/k_D (obsd)	k_H/k_D (cor)[b]
1	10.544			32.671		
1-*1*-*d*	8.637	1.221	1.221			
cis-1-2-*d*	8.284	1.273	1.285	26.969	1.211	1.216
trans-1-2-*d*	8.747	1.205	1.201	27.024	1.209	1.205
1-β-d_4	4.418	2.387	2.474			

[a] Measured using the precise conductometric method. [b] Corrected to 100% deuteration according to mass spectral analyses given in footnote c, Table I.

k_{5e}, k_{5s}, and k_2 all compete nearly equally and product is derived by solvent attack on both ion pairs. The situation is intermediate between that in E-W solvents and that in TFE-W solvents.

Thus, cyclopentyl p-bromobenzenesulfonate reacts in all solvents studied through the reversibly formed intimate ion pair. It is instructive to compare for each solvent the ratio of the solvolysis rate of the cyclopentyl ester to that of the corresponding 3,3-dimethyl-2-butyl ester, since the latter does not undergo internal return or S$_N$2 attack. These ratios are shown in Table VII. Even though cyclopentyl p-bromobenzenesulfonate undergoes a significant amount of internal return in all solvents studied, in TFE-W and E-W solvents it reacts faster than does the 3,3-dimethyl-2-butyl analogue. This must be because the relief of initial state eclipsing strain accelerates ionization. Eclipsing strain also seems to make backside S$_N$2 attack in pure ethanol too slow to be of significance, even though this mechanism dominates in the ethanolysis of isopropyl p-bromobenzenesulfonate.[14] Further, eclipsing apparently operates to keep nucleophilic attack on the intimate ion pair from being faster than internal return, again in contrast to the behavior of the isopropyl ester in some E-W solvents.[7]

The solvolysis rate of cyclopentyl p-bromobenzenesulfonate decreases relative to that of the 3,3-dimethyl-2-butyl ester in the sequence of solvents listed in Table VII; in the transition from 100 E and 70 E-W to 70 TFE-W, the rate of nucleophilic attack by solvent is slowed and the polarity increases, so that conversion of the intimate ion pair to the solvent-separated ion pair replaces nucleophilic attack in the intimate ion pair as the rate-determining step. In 97 TFE-W the lower polarity slows the k_2 rate and causes syn elimination by the leaving group to become competitive with formation of the solvent-separated

Table V. Solvolysis of Cyclopentyl *p*-Bromobenzenesulfonates

| solvent | *t*, °C | isotope rate effects (cor)[a] | | | | | % alkene[d] | A/S[e] | % inversion[b] | |
		$\alpha - d$	cis-β-*d*	trans-β-*d*	$c^2 \times t^2$ [c]	β-*d*₄			alc	ether
100 E	40	1.15	1.10	1.14	1.57	1.58	11.8	1.20		99
96 E-W	40	1.15	1.13	1.16	1.72	1.63	17.0			
90 E-W	40	1.14	1.13	1.15	1.69	1.67	23.3	1.35		
80 E-W	40	1.15	1.13	1.18	1.78	1.77	26.7	1.44	100	96
70 E-W	40	1.18	1.14	1.17	1.78	1.84	21.9		99	100
80 D-W	40	1.20 ± 0.05	1.15 ± 0.05	1.20 ± 0.05		1.80 ± 0.05	31.4	0.80	92	
70 D-W	40	1.17	1.15	1.17	1.81	1.84	31.6			
60 D-W	40	1.19	1.14	1.18	1.81	1.89	31.4			
70 TFE-W	30	1.23	1.21	1.23	2.22	2.22	41.8			
70 TFE-W[f]	25		1.216	1.205	2.15					
80 TFE-W	30							0.36	100	92
97 TFE-W	30	1.25	1.26	1.19	2.25	2.49	76.4	0.22		91
97 TFE-W[f]	25	1.221	1.285	1.201	2.382	2.474				
90 HFIP-W	25	1.23	1.35	1.22	2.73	2.86	80.0	0.24	85	
97 HFIP-W	25	1.25	1.37	1.22	2.79	3.14				

[a] Corrected to 100% isotopic purity of indicated starting cyclopentyl *p*-bromobenzenesulfonate ester. For analysis, see footnote *c*, Table 1. [b] % inversion of configuration in product alcohols and ethers; balance to 100% is retention. [c] Product of the square of the cis-β-*d* and the square of the trans-β-*d* rate effects. (Compare with β-*d*₄ effects.) [d] Yield of cyclopentene from undeuterated reactant. [e] Ratio of rate of anti elimination to rate of syn elimination. [f] Results repeated in this work using the more precise conductometric method.

Table VI. Deuterium Isotope Rate Effects for Different Rate-Determining Steps in Solvolysis of Cyclopentyl *p*-Bromobenzenesulfonate at 25–40 °C

rate-determining step[a]	α-*d*	cis-β-*d*	trans-β-*d*	β-*d*₄
k_{5s}	1.135	1.10	1.13	1.54
k_2	1.24	1.21	1.23	2.21
k_{5e} (secondary)[b]	1.24	1.21	1.23	2.21
k_{5e} (primary)[b]		2.16	2.28	3.22[c]

[a] All steps prior to this are assumed to be reversible, and the isotope effect is relative to the initial state. Effects calculated from single-step isotope effects which were determined to give the best overall fit of the results to the indicated mechanism.[12] [b] Including the secondary effects on the ionization step. [c] Product of primary and secondary effects for β-*d*₄ compound.

Table VII. First-Order Solvolysis Rate Constants[a] for Cyclopentyl and 3,3-Dimethyl-2-butyl *p*-Bromobenzenesulfonate at 25 °C

solvent	$k_{cyclopentyl}$	$k_{3,3\text{-dimethyl-2-butyl}}$	$k_{cyclopentyl}/k_{3,3\text{-dimethyl-2-butyl}}$
70 E-W	27.8	1.735[c]	16
70 TFE-W	32.67	10.64[b]	3.1
97 TFE-W	10.54	7.98[b]	1.3
90 HFIP-W	27.46	49.28	0.56
98 TFA-W[d]	278	474	0.59

[a] Units are 10^{-5} s⁻¹. [b] Reference 14. [c] Reference 7. [d] Alkyl *p*-toluenesulfonates.

ion pair. In the HFIP–W and TFA–W solvents, the further decrease in polarity effectively eliminates conversion to the solvent-separated ion pair, and internal elimination dominates the reaction. Internal return is at its maximum, and the rate is less than that of the pinacolyl ester.

In work which will be published later, this qualitative analysis of the reaction pathways, isotope effects, and relative rates is subjected to a detailed quantitative treatment.

Experimental Section

Spectra. ²H NMR spectra were recorded using a Varian 220 spectrometer operating at 33.8 MHz. Chemical shifts were determined relative to tetramethylsilane-*d*₁₂. ²H NMR analyses of deuterium orientation in the β position in the cyclopentanol⁴ samples were accomplished using a Hewlett-Packard white noise decoupler centered at 220 002 587 MHz. Concentrations were about 1 M in CHCl₃. ²H NMR spectra and calculations of anti/syn elimination ratios were done in the manner described previously.³ Mass spectra were taken with slow scan on an AEI MS-9 double-focusing mass spectrometer. Olefins were analyzed at 10 V and alcohols at 12 V ionizing potential.

Deuterated Cyclopentanols. Specifically deuterated *cis*-cyclopentanol-*2*-*d* (**1**), *trans*-cyclopentanol-*2*-*d* (**2**), cyclopentanol-*1*-*d* (**3**), and cyclopentanol-*2,2,5,5*-*d*₄ (**4**) were prepared as described previously.[1,9,10] Mass analyses are given in Table 1, footnote *c*.

Isolation of Elimination and Substitution Products. The isolation and subsequent mass spectral and ²H NMR analyses of cyclopentenes were accomplished in the manner described previously.³ The procedure used in the isolation and ²H NMR analysis of cyclopentanol substitution product was identical with that used for 80 vol % ethanol-water solvent.⁴

Solvent Purification. 1,1,1,3,3,3-Hexafluoroisopropyl alcohol (HFIP) used for solvolysis was distilled from K₂CO₃ (20 g/L of HFIP), redistilled from P₂O₅ (3 g/L of HFIP) through a vacuum-jacketed 90 × 2 cm column filled with ³/₁₆-in. glass helices. The product was collected at 58.2 °C (740 mm) at a reflux ratio of 50:1. The water used in the preparation of 90 HFIP–W mixtures was purified in the manner used for water conductometric measurements.[15,16]

Kinetic Measurements. Rate measurements were made using a Cary 118A spectrophotometer. The reactions were carried out in stoppered 1-cm² quartz cells, which fitted closely into a specially constructed brass block cell holder. The brass block and the cell compartment were maintained at constant temperature by the circulation of water from a constant-temperature bath through internal channels. The bath temperature was controlled by a Princo thermoregulator, relay and immersion heater to the preset temperature determined to be necessary to maintain the temperature of a solution within the cell, as measured by a thermistor at 25.000 ± 0.003 °C. The spectrophotometer absorbance output was measured by a Hewlett-Packard Model 3450A digital voltmeter (HP). The BCD output of the HP and the output from an Atec Model 2503 crystal controlled time internal meter were sampled automatically at preset time intervals. The data were collected and stored by a Texas Instruments Computer Model 980 B operated "on line." The data were transferred at the end of each reaction to the CDC 6600 computer for batch processing with a program which fitted the observations to the first-order rate equation with a doubly weighted nonlinear least-squares routine. Further details of the method will be published elsewhere.[17] The cyclopentyl *p*-bromobenzenesulfonate solutions were ca. 0.003 M in 90% HFIP–10% water and were measured at ~267 nm. Generally 200–300 data points were collected for each reaction through about 2.5 half-lives. Standard errors in the rate constants were about ±0.1%, and the reproducibility was about ±0.3%. The rate constants are tabulated in Table 1.

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Contrasting Responses in Aqueous Trifluoroethanol and Aqueous Ethanol as a Probe for Nucleophilic Solvent Assistance in Solvolysis

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Abstract: Aqueous trifluoroethanols are much less nucleophilic solvents than aqueous ethanols. As a consequence, solvolysis reactions proceeding without nucleophilic solvent assistance (k_c and k_Δ processes) and solvolysis reactions proceeding with nucleophilic solvent assistance (k_s processes) show totally different responses to changes from the aqueous ethanol system to the aqueous trifluoroethanol system. These contrasting responses for k_s and for k_c and k_Δ processes are precisely defined in the present work by examining solvolyses of substrates which are readily classified either as k_s or as k_c or k_Δ. The result is a new method for determining the involvement of solvent nucleophile in solvolysis reactions.

The molecularity of the rate-determining step of a solvolysis reaction is difficult to determine because first-order kinetics are observed for both unimolecular and nucleophilically assisted bimolecular reactions (Schemes I and II). In the present work a method for detecting the presence of nucleophilic solvent assistance in these reactions is developed[2-4] by considering the responses of model unimolecular substrates (k_c or k_Δ reactions)[5] (Scheme I) and model bimolecular substrates (k_s reactions)[5] (Scheme II) to changes in water concentration in aqueous trifluoroethanol (TFE) and aqueous ethanol (EtOH).

The effects of solvent variation on solvolysis reactions can be effectively predicted by use of empirical equations which consider solvent ionizing power (Y) and solvent nucleophilicity (N), eq 1, as the only solvent parameters.[6-8]

$$\log (k/k_0) = lN + mY \qquad (1)$$

In this equation l and m represent respectively substrate response to variation in solvent nucleophilicity and ionizing power, k_0 is the rate constant in 80% aqueous ethanol, and k is the rate constant in some other solvent of nucleophilicity N and ionizing power Y. A model unimolecular substrate should show a negligible response to solvent nucleophilicity ($l \simeq 0$) and a large response to solvent ionizing power ($m \simeq 1$); in contrast a model bimolecular substrate should show a large response to solvent nucleophilicity ($l \simeq 1$) but only a moderate response to solvent ionizing power ($m \simeq 0.5$). Aqueous TFE

Scheme I
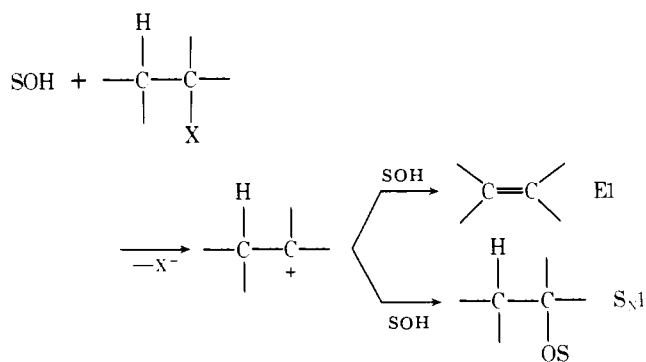
Scheme II
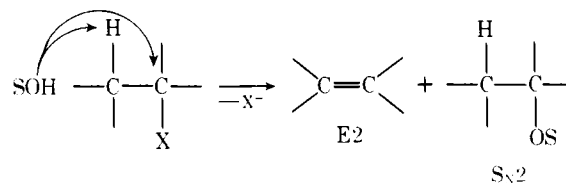
and aqueous ethanol are quite different solvent systems. Ethanol and water are both highly nucleophilic, but water has a much greater ionizing power; consequently, for aqueous eth-