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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.

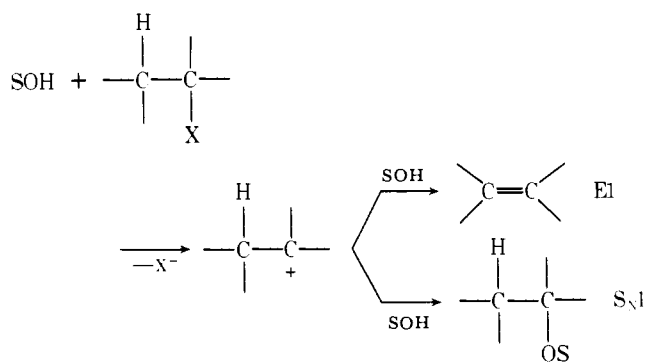
The molecularity of the rate-determining step of a solvolysis reaction is difficult to determine because first-order kinetics are observed for both unimolecular and nucleophilically assisted bimolecular reactions (Schemes I and II). In the present work a method for detecting the presence of nucleophilic solvent assistance in these reactions is developed²⁻⁴ 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

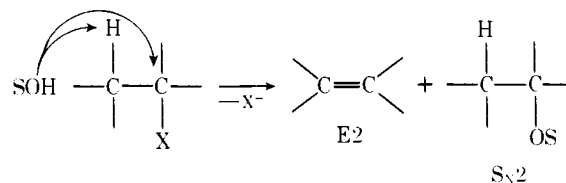
$$\log(k/k_0) = lN + mY \quad (1)$$

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 ($l \approx 0$) and a large response to solvent ionizing power ($m \approx 1$); in contrast a model bimolecular substrate should show a large response to solvent nucleophilicity ($l \approx 1$) but only a moderate response to solvent ionizing power ($m \approx 0.5$). 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-

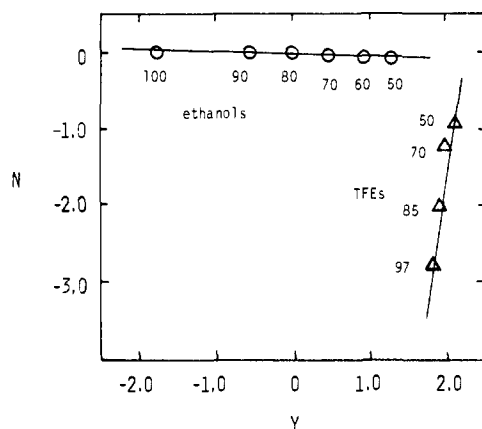


Figure 1. A plot of solvent nucleophilicity (N) against solvent ionizing power (Y , based on 2-adamantyl tosylate) for aqueous ethanol and aqueous trifluoroethanol. The numbers near the points refer to the percentage of the nonaqueous component in the solvent mixtures. The data are taken from ref 6b. In all figures in this paper circles are used to designate aqueous ethanols and triangles are used to designate aqueous trifluoroethanols.

anol increasing ethanol content produces a sharp decrease in ionizing power accompanied by essentially unchanged nucleophilicity. In contrast, water is far more nucleophilic than TFE, although both solvents have high ionizing power; consequently, an increase in TFE content for aqueous TFE produces a sharp decrease in nucleophilicity accompanied by essentially unchanged ionizing power. These relationships are clearly illustrated by Figure 1,⁹ where solvent nucleophilicity N is plotted as a function of solvent ionizing power Y .

The above reasoning indicates that bimolecular and unimolecular substrates should show sharply contrasting behavior in the aqueous ethanol and aqueous TFE solvent families. For example, the solvolysis of a bimolecular substrate in an aqueous TFE medium should show a large rate response to increasing the amount of water in the medium because this component provides the nucleophilic or basic solvent assistance to which this substrate responds. However, in aqueous ethanol both components have high nucleophilicity and the small variation in rate expected with changes in solvent composition should be primarily a function of the modest changes in ionizing power. Thus to a first approximation the behavior of the bimolecular substrate should be dependent on both N and Y in aqueous TFE but only on Y in aqueous ethanol. In contrast the behavior of a unimolecular substrate will be independent of N in both cases. It is this different dependence on N for the two substrates in the different solvent families which provides information on the molecularity of the solvolysis reaction.

The differing responses of the bimolecular and unimolecular substrates can be effectively demonstrated by examining logarithmic plots of rate constants for solvolysis in aqueous TFE and aqueous ethanol for the substrates in question as a function of the corresponding rate constants for a model unimolecular substrate. For any substrate that solvolyzes by a unimolecular mechanism (Scheme 1) the plot of the rate constants against those of the model substrate should result in a single straight line for both the aqueous ethanol and aqueous TFE solvent families. However, if nucleophilic participation or elimination is important in the rate-determining step then a single line should not be adequate for correlation of the data obtained in two such different families of solvents.

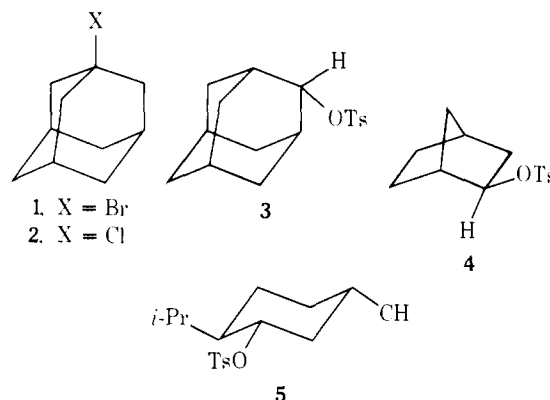
In the present paper we develop the method described above (henceforth described as the ethanol-TFE method) by constructing logarithmic plots for the solvolytic rate constants of well-understood substrates in aqueous TFE and aqueous ethanol as a function of the rate constants for 1-adamantyl bromide, a model unimolecular substrate.

Results and Discussion

Definitions. Solvolysis reactions proceeding by bimolecular rate-determining steps are of two mechanistic types: S_N2 (substitution and nucleophilic bimolecular) and E2 (elimination bimolecular). The designation k_s has also been used frequently to describe solvolytic processes in which there is nucleophilic solvent assistance.⁵ This nucleophilic solvent assistance includes nucleophilicity toward both carbon and hydrogen (Scheme II), so both S_N2 and E2 mechanisms are included in the k_s designation. Solvolysis reactions proceeding by unimolecular rate-determining steps are also of two mechanistic types: S_N1 (substitution nucleophilic unimolecular) and E1 (elimination unimolecular);¹⁰ unimolecular ionization may also be assisted by neighboring-group participation. The designation k_c has been assigned to processes in which ionization is not assisted,¹¹ and the designation k_{Δ} has been assigned to those processes in which unimolecular ionization is assisted by neighboring-group participation.⁵ It is frequently observed that neighboring group assisted (k_{Δ}) and nucleophilic solvent assisted (k_s) processes are competitive.^{5,12} Solvolyses in which there is no nucleophilic solvent assistance have also been described as "limiting" solvolyses, and include both k_c and k_{Δ} processes.^{5,11}

There also have been attempts to include in the mechanistic designation the extent to which ion pairing is involved.¹³ However, the method which is developed in the present work is not concerned with the identification of ion pairs, so these more informative but more complicated mechanistic labels will not be used here. Our goal is simply to determine the presence or absence of nucleophilic solvent assistance.

Model Unimolecular or Limiting Substrates. For the purpose of developing the ethanol-TFE method we have examined five substrates for which there is considerable evidence that reaction occurs via rate-determining unimolecular ionization. These substrates are 1-adamantyl bromide (**1**) and chloride



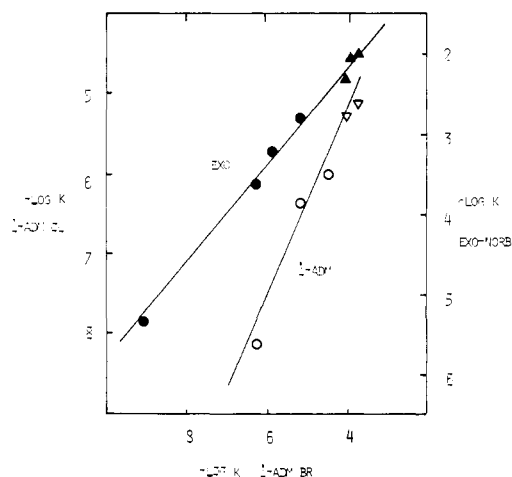
(**2**), 2-adamantyl tosylate (**3**), *exo*-2-norbornyl tosylate (**4**), and menthyl tosylate (**5**). Another substrate which might have been included in this list is *tert*-butyl chloride, since it has been proposed as a model limiting substrate,^{7,14} but we have excluded it on the basis of its unusual behavior in aqueous TFE.² In the following paragraph we review the evidence for the limiting nature of the solvolyses of these compounds proposed as limiting models.

The solvolyses of 1-adamantyl bromide and chloride, as of most bridgehead derivatives,¹⁵ must be k_c processes since it is sterically impossible for a nucleophile to approach the backside of the reaction center and elimination to form a bridgehead alkene is not energetically feasible.¹⁴ The solvolyses of 2-adamantyl derivatives have been studied extensively,^{5,6,16-20} and these substrates clearly react with little or no nucleophilic solvent assistance. As with 1-adamantyl derivatives, backside approach to the reaction center of the 2-adamantyl system is sterically hindered (although not totally

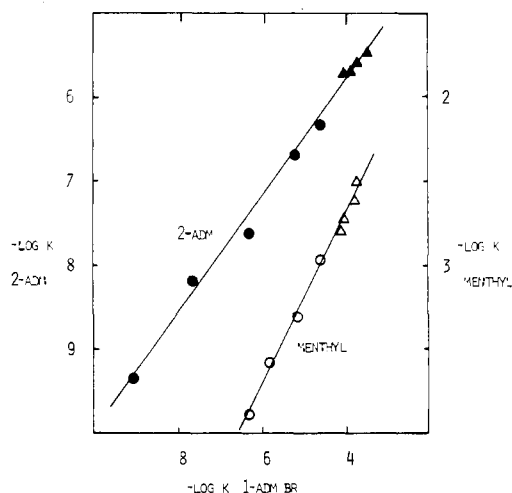
Table I. Solvolysis Rates ($-\log k$) for Alkyl Derivatives in Various Solvents at 25 °C^a

substrate	100E	90E	80E	70E	60E	50E	97T	85T	70T	60T	50T
1-adamantyl ^b bromide	9.06	7.61	6.29	5.81	5.14	4.54	4.02	3.97	3.75	3.64	3.46
1-adamantyl chloride			8.12 ^c		6.36	6.04 ^d	5.27 ^d		5.13 ^d		
2-adamantyl ^b tosylate	9.37	8.19	7.62		6.70	6.33	5.71	5.70	5.64		5.47
<i>exo</i> -2-norbornyl ^b tosylate	5.35		3.64	3.22	2.80		2.32	2.06	2.03		
menthyl tosylate			6.75	6.49	6.18		5.36	5.37	5.32	5.21	
methyl tosylate		5.89			5.41	5.31	8.06 ^e	7.37 ^e	6.29 ^e		6.16 ^e
2-propyl ^b brosylate	5.71	5.20	4.84			4.40	5.68		4.94		4.55
cyclopentyl ^f brosylate		3.50	3.14	2.84			3.45 ^g		2.93 ^g		
cyclohexyl tosylate			6.12 ^h	5.65	5.46 ^h	5.07 ^h	5.77	5.68	5.29		4.88
cycloheptyl brosylate			3.67	3.27	3.13		3.50	3.34	3.16	3.02	
2-phenyl-1-propyl tosylate		7.75	7.54 ⁱ	7.37	7.05	6.59	6.28	6.46	6.48		6.50
<i>endo</i> -2-norbornyl brosylate ^b	7.23		5.70	5.46	5.16	4.74	4.86	4.80	4.73	4.57	

^a E = aqueous ethanol; T = aqueous trifluoroethanol. Ethanols are volume percent, trifluoroethanols are weight percent. ^b Reference 4. ^c P. v. R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961). ^d P. v. R. Schleyer and T. W. Bentley, unpublished results. ^e Reference 2b. ^f Reference 34a; 40 °C. ^g Estimation from rates at 30 °C (ref 34a) by multiplying by a factor of 2. ^h Reference 6a. ⁱ Reference 39.

**Figure 2.** The EtOH-TFE plot for (a) 1-adamantyl chloride (open symbols) and (b) *exo*-2-norbornyl tosylate (filled symbols).

as with 1-adamantyl) and elimination is again strongly disfavored. The importance of neighboring carbon participation in 2-adamantyl tosylate solvolysis is, as usual,^{21,22} difficult to assess. This substrate does react to give minor amounts of rearranged products with the stereochemistry expected for intermediacy of a bridged intermediate,^{18,20} but none of the several possible interpretations¹⁹ of these results is consistent with nucleophilic solvent assistance. The solvolysis of *exo*-2-norbornyl derivatives gives only *exo*-2-norbornyl substitution products, thus eliminating a k_s mechanism which would require inversion of configuration at the reaction center.²¹ Again the major mechanistic uncertainty is the extent to which the unimolecular ionization is assisted by neighboring carbon.²² Menthyl tosylate (**5**) solvolysis is interesting in that studies of stereochemistry and β -deuterium isotope effects indicate that it reacts by a limiting mechanism; other cyclohexyl compounds react primarily by a k_s mechanism.²³⁻²⁵ For nucleophilic attack on carbon or for elimination by an E2 process to be favorable for menthyl tosylate, it would be necessary for the molecule to adopt conformation **5b** (Scheme III) or possibly a twist boat conformation;²³⁻²⁶ however, the experimental evidence does not support such a possibility. For example, Sunko and his co-workers studied the solvolysis of menthyl tosylate in 70% aqueous ethanol and 70% TFE and found that the products which would be expected for a solvent-assisted reaction (whether direct displacement or elimination) constitute only a small proportion of the total products.²³ Whether or not this ionization may be assisted by neighboring σ participation is not known.

**Figure 3.** The EtOH-TFE plot for (a) 2-adamantyl tosylate (filled symbols) and (b) menthyl tosylate (open symbols).

In Table I are presented rate constants at 25 °C in several aqueous ethanol and trifluoroethanol mixtures for the substrates considered in the present work. Rate constants at temperatures other than 25 °C and experimental errors are presented in Table II. As would be expected on the basis of the previous discussion, logarithmic rate-rate plots for any pair of the limiting substrates presently under consideration should yield linear correlations for all solvents considered. This is easily shown by further consideration of eq 1; for limiting substrates l will be zero and $\log k$ for each substrate will be linearly related to the ionizing power Y . A plot of $\log k$ vs. $\log k$ for two limiting substrates must therefore be linear. Since solvent assistance and elimination must be at an absolute minimum for 1-adamantyl bromide we have utilized this compound as our reference standard.^{14,27} The plots for compounds **2-5** are shown in Figures 2 and 3, and all of the plots show good linearity.

Some of the deviations from linearity exhibited in these plots are due to solvent effects on leaving-group abilities.^{6,28} For example, several of the substrates examined later in this study are brosylates, and brosylate/tosylate rate ratios show the following solvent dependencies: OBs/OTs = 5.0 in aqueous ethanol and 3.0 in aqueous trifluoroethanol and formic and acetic acids.²⁸ However, plots for substrates with the same leaving group are not perfectly linear.⁴ There are several readily identifiable contributors to this continued nonlinearity. First, reactant solvation has been demonstrated²⁹ to be a major contributor to solvent effects on ionization processes, and this

Table II. Solvolysis Rates Determined in This Study

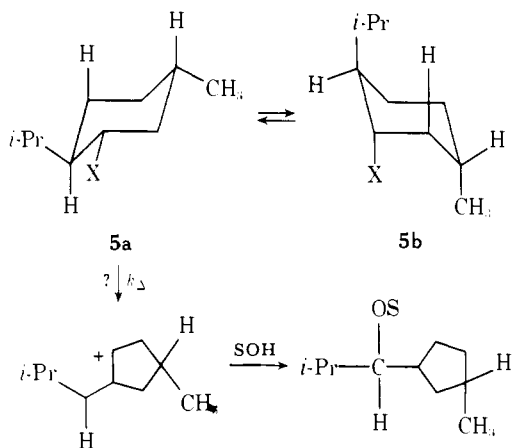
compd	solvent	<i>t</i> , °C	<i>k</i> , s ⁻¹	Δ <i>H</i> [‡] , kcal/mole	Δ <i>S</i> [‡] , eu
cycloheptyl OBs	80% EtOH	50.2	3.24 ± 0.01 × 10 ⁻³	20.1	-7.8
		30.5	3.98 ± 0.01 × 10 ⁻⁴		
		25.0 ^a	2.12 × 10 ⁻⁴		
	70% EtOH	50.2	5.54 ± 0.24 × 10 ⁻³		
		30.5	9.23 ± 0.12 × 10 ⁻⁴		
		25.0 ^a	5.38		
	50% EtOH	25.0	7.45 ± 0.09 × 10 ⁻⁴		
		50.2	4.29 ± 0.03 × 10 ⁻³		
	97% TFE	30.5	5.78 ± 0.02 × 10 ⁻⁴		
		25.0 ^a	3.16 × 10 ⁻⁴		
	85% TFE	50.2	6.43 ± 0.04 × 10 ⁻³		
		30.5	8.48 ± 0.03 × 10 ⁻⁴		
	70% TFE	25.0	4.61 × 10 ⁻⁴		
		25.0	6.98 ± 0.02 × 10 ⁻⁴		
	60% TFE	25.0	9.47 ± 0.18 × 10 ⁻⁴		
25.0		1.08 ± 0.01 × 10 ⁻³			
menthyl OTs	80% EtOH	95.2	1.08 ± 0.01 × 10 ⁻³	26.5	-0.5
		75.7	1.29 ± 0.06 × 10 ⁻⁴		
		25.0 ^a	1.72 × 10 ⁻⁷		
	70% EtOH	95.2	2.20 ± 0.07 × 10 ⁻³		
		75.7	2.66 ± 0.07 × 10 ⁻⁴		
		25.0 ^a	3.22 × 10 ⁻⁷		
	60% EtOH	95.2	4.17 ± 0.06 × 10 ⁻³		
		75.7	4.85 ± 0.33 × 10 ⁻⁴		
		25.0 ^a	6.64 × 10 ⁻⁷		
	50% EtOH	75.7	1.07 ± 0.04 × 10 ⁻³		
		75.7	1.63 ± 0.01 × 10 ⁻³		
	97% TFE	50.2	1.05 ± 0.02 × 10 ⁻⁴		
		25.0 ^a	4.40 × 10 ⁻⁶		
	85% TFE	75.7	1.81 ± 0.04 × 10 ⁻³		
		50.2	1.08 ± 0.01 × 10 ⁻⁴		
70% TFE	25.0 ^a	4.23 × 10 ⁻⁶			
	75.7	2.46 ± 0.02 × 10 ⁻³			
60% TFE	50.2	1.36 ± 0.00 × 10 ⁻⁴			
	25.0 ^a	4.76 × 10 ⁻⁶			
50% EtOH	75.7	3.18 ± 0.14 × 10 ⁻³			
	50.2	1.78 × 0.02 × 10 ⁻⁴			
97% TFE	25.0 ^a	6.10 × 10 ⁻⁶			
	25.0 ^a	2.68 ± 0.04 × 10 ⁻³			
methyl tosylate	50% EtOH	100.0	2.68 ± 0.04 × 10 ⁻³	17.9	-22.7
		74.9	4.37 ± 0.04 × 10 ⁻⁴		
		25.0 ^a	4.87 × 10 ⁶		
	60% EtOH	100.0	2.14 ± 0.02 × 10 ⁻³		
		75.0	3.53 ± 0.04 × 10 ⁻⁴		
		25.0 ^a	3.92 × 10 ⁻⁶		
	90% EtOH	100.0	1.04 ± 0.02 × 10 ⁻³		
		75.0	1.54 ± 0.02 × 10 ⁻⁴		
		25.0 ^a	1.28 × 10 ⁻⁶		
	70% EtOH	75.0	6.62 ± 0.12 × 10 ⁻⁴		
		50.0	4.77 ± 0.02 × 10 ⁻⁵		
		25.0 ^a	2.23 × 10 ⁻⁶		
	97% TFE	50.0	3.35 ± 0.04 × 10 ⁻⁵		
		75.0	4.33 ± 0.13 × 10 ⁻⁴		
		25.0 ^a	1.70 × 10 ⁻⁶		
85% TFE	50.0	5.53 ± 0.26 × 10 ⁻⁵			
	75.0	9.21 ± 0.12 × 10 ⁻⁴			
	25.0 ^a	2.09 × 10 ⁻⁶			
70% TFE	50.0	1.11 ± 0.01 × 10 ⁻⁴			
	75.0	1.56 ± 0.01 × 10 ⁻³			
	25.0 ^a	5.07 × 10 ⁻⁶			
50% TFE	50.0	2.53 ± 0.02 × 10 ⁻⁴			
	75.0	3.21 ± 0.18 × 10 ⁻⁴			
	25.0 ^a	1.31 × 10 ⁻⁵			
2-phenyl-1-propyl OTs	90% EtOH	100.0	3.89 ± 0.04 × 10 ⁻⁵	22.0	-20.1
		125.0	2.68 ± 0.11 × 10 ⁻⁴		
		25 ^a	1.77 × 10 ⁻⁸		
	70% EtOH	100.0	1.55 ± 0.01 × 10 ⁻⁴		
		125.0	1.22 ± 0.01 × 10 ⁻³		
		25 ^a	4.21 × 10 ⁻⁸		
	60% EtOH	100.0	2.64 ± 0.03 × 10 ⁻⁴		
		125.0	1.96 ± 0.04 × 10 ⁻³		
		25 ^a	8.91 × 10 ⁻⁸		
	50% EtOH	100.0	4.49 ± 0.05 × 10 ⁻⁴		
		125.0	2.92 ± 0.12 × 10 ⁻³		
		25 ^a	2.54 × 10 ⁻⁷		

Table II (Continued)

compd	solvent	<i>t</i> , °C	<i>k</i> , s ⁻¹	Δ <i>H</i> [‡] , kcal/mole	Δ <i>S</i> [‡] , eu
	97% TFE	75.0	7.53 ± 0.06 × 10 ⁻⁵	19.8	-20.7
		100.0	5.51 ± 0.29 × 10 ⁻⁴		
		25.0 ^a	5.25 × 10 ⁻⁷		
	85% TFE	75.0	8.25 × 10 ⁻⁵	21.9	-14.6
		100.0	7.38 ± 0.02 × 10 ⁻⁴		
		25.0 ^a	3.49 × 10 ⁻⁷		
	70% TFE	75.0	9.20 ± 0.11 × 10 ⁻⁵	22.6	-12.5
		100.0	8.76 ± 0.04		
		25.0 ^a	3.32 × 10 ⁻⁷		
	50% TFE	75.0	1.18 ± 0.01 × 10 ⁻⁴	23.8	-8.6
		100.0	1.26 ± 0.01 × 10 ⁻³		
		25.0 ^a	3.78 × 10 ⁻⁷		

^a Calculated from rates at other temperatures.

Scheme III. Menthyl Tosylate Solvolysis



process is a function of molecular size and shape,³⁰ both of which vary somewhat for the substrates under consideration. Second, solvation of the highly polar transition states for these apparently simple ionization processes is a function both of position of the transition state on the reaction coordinate (i.e., the extent of charge development) and, as has recently been indicated,^{31,32} also of the manner in which the developing positive charge is delocalized. A third factor contributing to the observed nonlinearity is extrapolation error which results from comparison of rates determined at different temperatures. All of these factors vary for the five limiting substrates. Thus a minimum requirement for obtaining a perfectly linear correlation for plots such as those of Figures 2 and 3 would be to match substrates having the same leaving group, similar rates and positions of the transition state on the reaction coordinate, and similar sizes and shapes; but even this degree of matching might not be sufficient.

The limitation on linearity does not, however, introduce any serious problems. Plots such as those in Figures 2 and 3 are indicative of reaction having little or no involvement of solvent as nucleophile, and as long as different results are obtained with *k_s* substrates, the ethanol-TFE method will serve to detect the presence of nucleophilic solvent assistance.

Model *k_s* Substrates. Primary substrates have been convincingly demonstrated to solvolyze by nucleophilic displacement (S_N2) processes, which in certain instances, such as for neopentyl derivatives, may be in competition with neighboring group assisted processes.^{12,13} The solvolysis of secondary derivatives is much more complicated, but simple, acyclic compounds such as 2-propyl derivatives seem clearly to react by a simple nucleophilic displacement mechanism.^{6,13} Consequently, methyl tosylate and 2-propyl brosylate provide non-

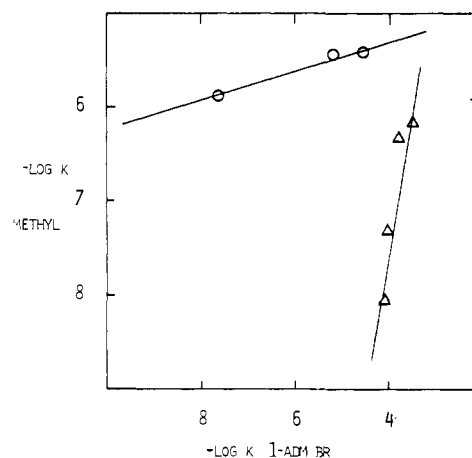


Figure 4. The EtOH-TFE plot for methyl tosylate.

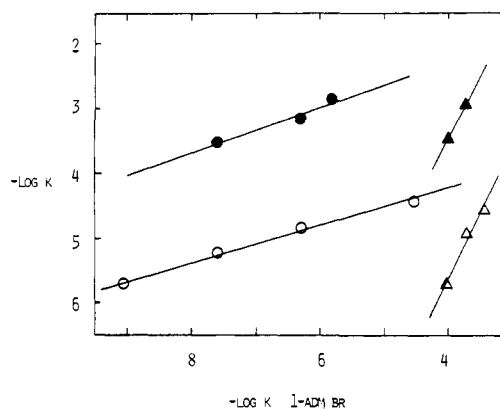


Figure 5. The EtOH-TFE plot for (a) 2-propyl brosylate (open symbols) and (b) cyclopentyl brosylate (filled symbols).

controversial examples of *k_s* substrates. Logarithmic rate-rate plots for these two compounds (again using 1-adamantyl bromide as the reference substrate) produce plots (Figures 4 and 5a) in which the TFE and ethanol points are not correlated by a single straight line.

This can be understood more clearly by further consideration of eq I, which, although empirical, should be capable of predicting the solvolysis rate for any substrate reacting via a single pathway. Note that the reference substrate (1-adamantyl bromide, which cannot benefit from nucleophilic solvent assistance) must have an *l* value which is effectively zero; the rates of the reference compound therefore depend only on solvent ionizing power. In contrast, the rate of solvolysis for a *k_s* substrate must be dependent on both solvent nucleophil-

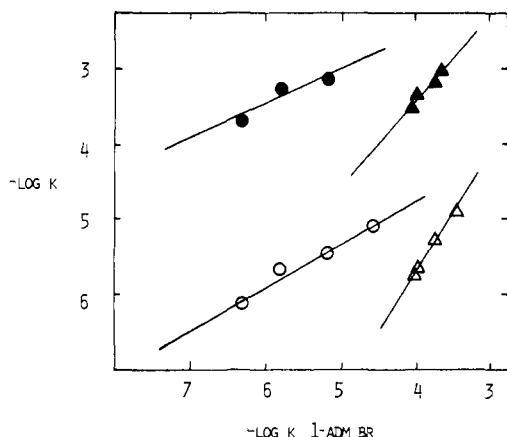


Figure 6. The EtOH-TFE plot for (a) cyclohexyl tosylate (open symbols) and (b) cycloheptyl brosylate (filled symbols).

icity and solvent ionizing power. For the aqueous ethanols the solvent nucleophilicity remains nearly constant and a linear correlation with the data for 1-adamantyl bromide is anticipated. However, the solvent nucleophilicity varies greatly for the aqueous trifluoroethanols, and inspection of Figure 1 suggests that the TFE data points for a k_s substance should not fall on the same line as the aqueous ethanol points. In fact the fortuitous linearity of N as a function of $Y^{9,33}$ demands that the TFE data points form a second straight line, and this is precisely the behavior observed for the model k_s substrates (Figures 4 and 5a).

Cyclopentyl, cyclohexyl, and cycloheptyl derivatives are also regarded as compounds which solvolyze by a k_s mechanism. Shiner and his co-workers have extensively studied the stereochemistry of elimination and substitution as well as the kinetic effects of α and β deuteria to assign the mechanism of cyclopentyl brosylate with an uncommon degree of detail.³⁴ That substitution for cyclopentyl brosylate is a k_s process is indicated by the α -deuterium isotope effect (α - d) of 1.15 (significantly less than the maximum of 1.22 found for k_c processes) and the formation of totally inverted substitution product. The elimination process is indicated to be rate determining by the observation of noncumulative β -deuterium isotope effects (β - d).^{34a,35} Whether or not solvent is involved as base in this elimination process cannot be determined from Shiner's work, but this would certainly be a reasonable supposition.³⁶ Bentley and Schleyer have also applied their measure of nucleophilic solvent assistance (see discussion below) to the solvolysis of cyclopentyl tosylate^{6a} and have concluded that the aqueous ethanolysis of this compound is a k_s process. Shiner and his co-workers have also examined the aqueous trifluoroethanolysis of cyclopentyl brosylate³⁴ and reaction by a k_c process was suggested on the basis of the α - and β -deuterium isotope effects and the formation of 16–20% racemic trifluoroethyl ether (although the alcohol produced was 100% inverted).^{34c} However, our results (Figure 5b: two distinct lines are observed) strongly suggest that solvent is involved in the rate-limiting steps of solvolysis of cyclopentyl derivatives in both solvent families; in the absence of solvent assistance it would be difficult to explain the large rate increase as the aqueous component of the TFE solvent system is increased.

The solvolysis of cyclohexyl derivatives has also been extensively examined. The Schleyer probes indicate weak but definite nucleophilic solvent assistance in solvents such as aqueous ethanols.^{6a} Also, the acetolysis of cyclohexyl tosylate has been shown to give noncumulative β - d 's²⁶ consistent with rate-determining elimination, and inverted substitution product²⁵ consistent with a k_s process. The only piece of evidence which is inconsistent with cyclohexyl solvolysis by a k_s

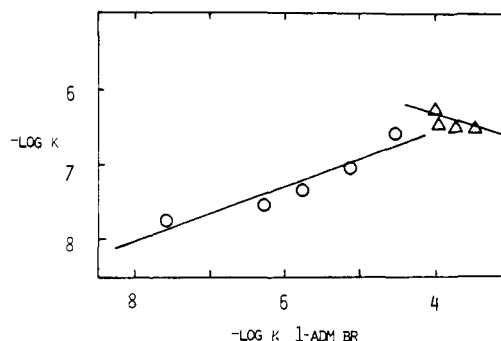
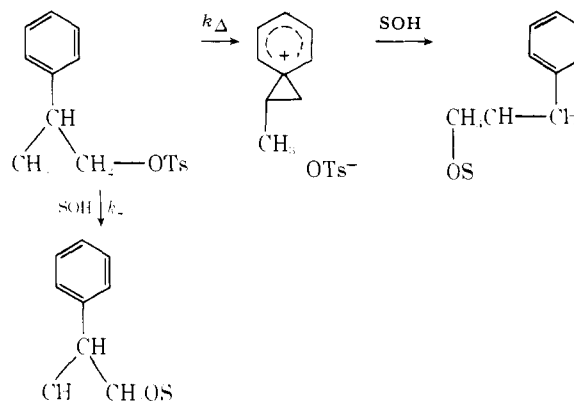


Figure 7. The EtOH plot for 2-phenyl-1-propyl tosylate (25 °C).

Scheme IV. Discrete Pathways for k_s and k_Δ in the Solvolysis of 2-Phenyl-1-propyl Tosylate (6)



mechanism in nucleophilic solvents is the α - d for acetolysis of 1.22,^{26b} which is of the magnitude expected for a k_c process.³⁴ However, it has been suggested that the α - d may, in some instances, fail as a satisfactory probe for the involvement of a nucleophile in the rate-determining step.^{13,37,38} The EtOH-TFE plot for cyclohexyl brosylate (Figure 6a) is similar to that for the k_s substrates discussed previously, with ethanol and TFE points lying on different lines. Cycloheptyl brosylate would be expected to be similar to the cyclopentyl and cyclohexyl derivatives, and its ethanol-TFE plot (Figure 6b) again shows the two lines observed for other k_s substrates.

Dissection of k_s and k_Δ Processes. Another test of the ethanol-TFE method is provided by examination of 2-phenyl-1-propyl tosylate (**6**) solvolysis, a reaction known³⁹ to proceed by competitive k_s and k_Δ processes. The relative amounts of the k_s and k_Δ processes will vary with solvent composition because of changes in solvent nucleophilicity and solvent ionizing power. As might be expected for a reaction in which the proportion of k_s and k_Δ processes varies, the ethanol-TFE plot for **6** is not linear (Figure 7).

The actual values of k_s and k_Δ can be determined by means of product studies, since different products are formed in the two pathways as shown in Scheme IV.

Since the reactions are not reversible, the k_s/k_Δ rate ratio corresponds to the ratio of primary to secondary products.³⁹ Therefore

$$k_s = \left(\frac{\% \text{ primary product}}{100} \right) k_{\text{obsd}} \quad (2)$$

and

$$k_\Delta = \left(\frac{\% \text{ secondary product}}{100} \right) k_{\text{obsd}} \quad (3)$$

The product distributions for solvolysis of **6** are reported in Table III together with the kinetic data calculated from eq 2

Table III. Products, Observed Rates, and Calculated k_s and k_{Δ} Constants for the Solvolysis of 2-Phenyl-1-propyl Tosylate at 125 °C

solvent	% sec ^a ROEt	% prim ^a ROEt	% sec ^a ROH	% prim ^a ROH	−log k_{obsd}^b	−log k_s^c	−log k_{Δ}^c
90E	53.4	10.6	32.2	3.8	3.57	4.41	3.64
80E	39.9	6.8	48.8	5.4	3.27 ^d	4.18	3.32
70E	29.8	2.9	63.0	4.5	2.92	4.05	2.95
60E	22.9	2.0	72.1	3.1	2.71	4.00	2.73
50E	15.9	0.4	81.1	2.8	2.53	4.03	2.55
97T	65.8		32.8	1.3	2.50	4.39	2.51
85T	23.7	0.1	75.7	0.6	2.30	4.45	2.30
70T	14.1	0.5	83.4	2.1	2.20	3.78	2.21
50T	18.3		80.8	0.9	2.00	4.04	2.00

^a Products determined by gas chromatography. ^b From the data in Table II. ^c Calculated using eq 2 and 3. ^d Reference 39.

and 3. Rate data at 125 °C rather than 25 °C were used to minimize extrapolation error when comparing product data (determined at 125 °C) with the kinetic data. Ethanol-TFE plots of the derived k_s and k_{Δ} rate constants (Figure 8a) demonstrate that while a single line can adequately correlate all of the k_{Δ} data, the same is not true for the k_s process. The observation of two distinct lines for the k_s process confirms the validity of our use of the ethanol-TFE method as a sensitive means of detecting nucleophilic solvent assistance.

Sensitivity of the Method. Comparison of Figures 2, 3, and 8b (typical k_c and k_{Δ} plots) with Figures 4–6 and 8 (typical k_s plots) demonstrates that the ethanol-TFE method has utility for determination of nucleophilic solvent assistance in solvolysis reactions. Next we will consider the magnitude of solvent assistance necessary for detection by this method. Insight into this question is provided by consideration of the Schleyer k_s/k_c ratio^{6a} for estimating the magnitude of nucleophilic solvent assistance:

$$k_s/k_c = [k(\text{ROTs})/k(2\text{-AdOTs})]_{\text{any solvent}} / [k(\text{ROTs})/k(2\text{-AdOTs})]_{\text{CF}_3\text{CO}_2\text{H}} \quad (4)$$

The basic assumptions in this ratio are that all secondary substrates react by limiting or near-limiting mechanisms in trifluoroacetic acid, that 2-adamantyl tosylate reacts by a limiting mechanism in all solvents, and that the m values for all limiting substrates are approximately the same. The result is a measure of nucleophilic solvent assistance received by a substrate in a particular solvent relative to that nucleophilic solvent assistance (approximately zero) received by the same substrate in trifluoroacetic acid.

The lowest k_s/k_c ratio among the model k_s substrates considered above is the value of 61 for cyclohexyl brosylate in 50% ethanol. The 50% ethanol point for this system lies on the line defined by the other ethanol points, so we can conclude that the ethanol-TFE method still gives two clearly separate lines when nucleophilic solvent assistance is as low as a factor of approximately 60. There are no well-studied compounds with lower k_s/k_c ratios for us to use to further define the limitations of the ethanol-TFE method, but in view of the ease with which assistance of a factor of 60 is detected (i.e., Figure 6a) the method must be capable of detecting assistance significantly below this limit. (For further discussion on this point, see the following paper.)

It should be noted, as Schleyer has pointed out,^{6a} that the k_s/k_c ratio is not a simple quantitative measure of the importance of nucleophilic solvent attack on carbon. The ratio measures, as does our method, both nucleophilic solvent assistance and the solvent acting as a base to promote elimination when either of these processes is kinetically significant. For example, the k_s/k_c ratio of 28 for acetolysis of cyclohexyl tosylate^{6a} may be as much the result of elimination as of nucleophilic attack on carbon; there is 80% elimination for this reaction,^{25a} and rate-determining elimination is indicated for this reaction by the noncumulative β -d.²⁶

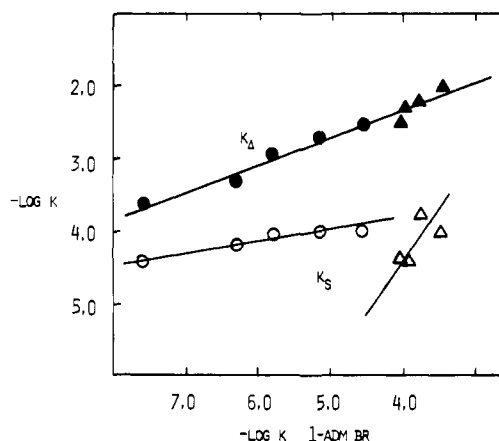


Figure 8. The EtOH-TFE plot of calculated k_s (open symbols) and k_{Δ} (filled symbols) rate constants at 125 °C.

Probably the greatest limitation of the k_s/k_c measure comes from the involvement of k_{Δ} processes, because significant dispersal of positive charge occurs in these transition states, resulting in low m values. The k_s/k_c ratio is intended to be applied only to k_s systems and it is assumed, as noted above, that as nucleophilic solvent assistance is removed from these reactions (i.e., as they become limiting) they will have m values close to unity. However, k_{Δ} processes are limiting processes with m values significantly less than unity. This distortion of k_s/k_c values can be illustrated with the acetolysis of 3-methyl-2-butyl tosylate, a known k_{Δ} system.⁴⁰ For 2-adamantyl and 3-methyl-2-butyl tosylates the m values (based on 2-adamantyl Y values)^{6b} are 1.0 and 0.70,⁴⁰ respectively, and for acetic and trifluoroacetic acids the Y values are −0.61 and 4.57, respectively.^{6b} Substitution into eq 1 affords the following dependence on m :

$$\log [k_{\text{AcOH}}/k_{\text{TFA}}] = -5.18m \quad (5)$$

Rearrangement of eq 4 permits the k_s/k_c relationship to be expressed as

$$k_s/k_c = [k_{\text{AcOH}}/k_{\text{TFA}}]_{3\text{-Me-2-Bu}} / [k_{\text{AcOH}}/k_{\text{TFA}}]_{2\text{-Ad}} \quad (6)$$

and substitution using eq 5 affords

$$k_s/k_c = 10^{-3.63} / 10^{-5.18} = 35 \quad (7)$$

The k_s/k_c ratio of 35 results simply because of the differences in m values, not from nucleophilic solvent assistance. The experimental value of the k_s/k_c for this acetolysis reaction is 41.7.⁴⁰ Obviously, little of this experimental ratio results from nucleophilic solvent assistance.

A further indication of the limitations of the ethanol-TFE method is provided by examination of the ethanol-TFE plot

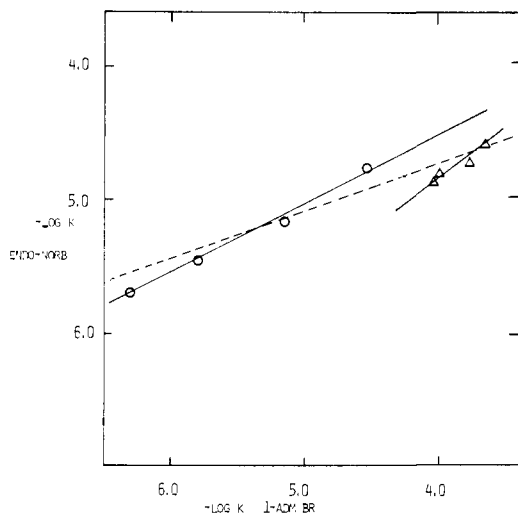
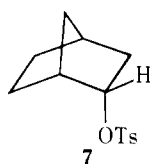


Figure 9. The EtOH-TFE plot for *endo*-2-norbornyl brosylate.



of *endo*-2-norbornyl brosylate (**7**) (Figure 9). There is a significant amount of evidence showing that this substrate reacts with *weak* nucleophilic solvent assistance⁴ (e.g., $k_s/k_c = 30$ for acetolysis), and indeed Figure 9 suggests that the ethanol and TFE points might best be considered to lie on slightly separate lines (although the points are adequately correlated by a single line). This correlation would seem to extend the sensitivity of the ethanol-TFE method beyond the k_s/k_c value of 60 cited above. This possibility is further emphasized by comparison with the data for *exo*-2-norbornyl tosylate (**4**). The latter compound has a k_s/k_c value of 8 for acetolysis,⁴¹ a value which must again result from factors other than solvent assistance since its limiting nature is well established.^{21,22} The k_s/k_c ratio of the *endo* isomer therefore exceeds that of the limiting *exo* isomer by only a factor of 4. Since both isomers react largely via the same carbocation, it might be argued that the factor of 4 should actually represent the lower limit for detection of solvent assistance by the ethanol-TFE method. However, close examination of the rate-rate plot for *exo*-2-norbornyl tosylate (Figure 3b) reveals a close similarity to that of the *endo* isomer; that is, separate lines can again be drawn for the ethanol and TFE points even though a single line correlates all the data quite well. Consequently, we interpret plots such as the *endo*-norbornyl plot (Figure 9) as representing the limit of the ethanol-TFE method; i.e., as indicative either of no nucleophilic solvent assistance or of assistance which is too weak to be detected by this method.

Statistical Evaluation. Although clear-cut choices regarding the presence or absence of solvent assistance are generally possible by qualitative examination of plots such as those in Figures 2-9, the fact that we are looking for *linear* plots suggests that simple statistical analysis should provide more objective criteria for making mechanistic assignments. Linear regression analysis of any set of experimental points affords four parameters (slope, intercept, correlation coefficient, and standard deviation) which can be used, and criteria may be established for each of these which will allow a mechanistic assignment. These criteria are discussed below and are summarized in Table IV.

1. Slope. In the case of a limiting process the slopes of both the ethanol and TFE lines are expected to be the same (within experimental error), whereas for a k_s process the ethanol points

Table IV. Statistical Criteria

parameter	k_s	limiting
slope	slope (E) < slope (T)	slope (E) = slope (T)
intercept	int (E) < int (T)	int (E) = int (T)
correlation coefficient	$R(E) - R(E + T) \geq 0.30$	$R(E) - R(E + T) \leq 0.01$
standard deviation	SD (E + T) > SD (E) and > SD (T) and ≥ 0.20	(a) SD (E + T) < SD (E) and < SD (T) or (b) SD (E + T) ≤ 0.10

should afford a line with a slope less than that for the TFE points.

2. Intercept. As in the previous case all the points for a limiting process should fall on the same line and both the ethanol points and the TFE points should yield straight lines with the same intercept (within experimental error). In contrast the intercepts should be different for a k_s substrate, that for TFE being less than that for ethanol.

3. Correlation Coefficient. For both k_s and limiting substrates the set of experimental points for ethanol and the set for TFE should each show correlation coefficients near unity. When the experimental points for both solvent families are considered together, the correlation coefficient should still be near unity for a limiting substrate, but for a k_s substrate (where the two sets of points should not fall on a single line) a drastic decrease in the correlation coefficient should result. In fact these estimates are too optimistic since we are dealing with data sets having relatively few experimental points in each case. Moreover, the rate-rate plots are empirical relationships and "perfect" linearity should not be expected. This is particularly true for the case of limiting substrates in TFE where there is little change in rate as the solvent composition is varied; consequently, we have chosen not to consider the correlation coefficient of the TFE points as a reliable criterion. A more meaningful criterion results from observing the effect of deleting the TFE points on the correlation coefficient for combined data sets. Our arbitrary⁴² criterion for a k_s process is that the correlation coefficient for the set of ethanol points exceed that for the combined data sets by at least 0.30. The criterion⁴² for a limiting substrate is that the correlation coefficient for all data points together will be within 0.01 unit of that for the ethanol points.

4. Standard Deviation. The standard deviation provides a measure of the difference between the observed experimental values and the values corresponding to the least-squares line. As in the case of the correlation coefficient, the inherent experimental errors are important, and we have again chosen some arbitrary limits to aid in the decision-making process. The assigned criterion⁴² for a k_s substrate is that the standard deviation for the data set including all the points (ethanol and TFE) be at least 0.20 and be larger than each of the standard deviations calculated for the ethanol and TFE data sets alone. In contrast we have set the criterion⁴² for a limiting substrate as having a standard deviation for the set of all data points which is either less than 0.1 log unit (corresponding to a "typical" uncertainty of $\pm 25\%$ in the extrapolated values of the actual rate constants) or does not exceed both of the standard deviations calculated for the ethanol and TFE data sets individually.⁴²

It is possible for each of these criteria that a particular substrate might not fall into either the k_s or limiting category. Since experimental errors are at times substantial, and since we are considering statistical analysis of a small number of data points, we believe that some data sets will simply be anomalous and that in such cases it is preferable that selection of one of these two categories not be required.

The results of the statistical analyses are reported in Table V, and application of the statistical criteria of Table IV yields

Table V. Statistical Analyses and Mechanistic Conclusions^a

compd	criterion	ethanol	TFE	E + T	mechanistic assignment
1-adamantyl chloride	<i>n</i>	3	2	5	
	<i>m</i>	1.23 ± 0.25	0.52	1.17 ± 0.10	
	<i>b</i>	0.27 ± 1.35	3.19	0.62 ± 0.49	
	<i>R</i>	0.98		0.99	lim
	SD	0.32		0.20	lim
2-adamantyl tosylate	<i>n</i>	5	4	9	
	<i>m</i>	0.66 ± 0.03	0.43 ± 0.06	0.70 ± 0.02	
	<i>b</i>	3.35 ± 0.24	4.01 ± 0.23	3.03 ± 0.13	
	<i>R</i>	1.00	0.98	1.00	lim
	SD	0.13	0.03	0.13	lim
<i>exo</i> -2-norbornyl tosylate	<i>n</i>	4	3	7	
	<i>m</i>	0.65 ± 0.02	0.79 ± 0.78	0.63 ± 0.02	lim
	<i>b</i>	-0.51 ± 0.14	-0.96 ± 3.05	-0.34 ± 0.11	lim
	<i>R</i>	1.00	0.71	1.00	lim
	SD	0.06	0.16	0.09	lim
menthyl tosylate	<i>n</i>	3	4	7	
	<i>m</i>	0.49 ± 0.02	0.37 ± 0.12	0.59 ± 0.02	lim
	<i>b</i>	3.64 ± 0.13	3.90 ± 0.47	3.04 ± 0.10	lim
	<i>R</i>	1.00	0.91	1.00	lim
	SD	0.02	0.04	0.06	lim
methyl tosylate	<i>n</i>	3	4	7	
	<i>m</i>	0.19 ± 0.004	3.16 ± 1.15	-0.26 ± 0.30	<i>k_s</i>
	<i>b</i>	4.44 ± 0.03	-5.03 ± 4.38	7.58 ± 1.43	<i>k_s</i>
	<i>R</i>	1.00	0.89	0.37	<i>k_s</i>
	SD	0.01	0.51	1.03	<i>k_s</i>
2-propyl brosylate	<i>n</i>	4	3	7	
	<i>m</i>	0.29 ± 0.02	2.01 ± 0.40	0.12 ± 0.09	<i>k_s</i>
	<i>b</i>	3.06 ± 0.12	-2.47 ± 1.51	4.37 ± 0.54	<i>k_s</i>
	<i>R</i>	1.00	0.98	0.51	<i>k_s</i>
	SD	0.06	0.16	0.48	<i>k_s</i>
cyclopentyl brosylate	<i>n</i>	3	2	5	
	<i>m</i>	0.35 ± 0.07	1.93	0.06 ± 0.10	<i>k_s</i>
	<i>b</i>	0.88 ± 0.49	-4.29	2.87 ± 0.58	<i>k_s</i>
	<i>R</i>	0.98	1.00	0.30	<i>k_s</i>
	SD	0.10		0.33	<i>k_s</i>
cyclohexyl tosylate	<i>n</i>	4	4	8	
	<i>m</i>	0.56 ± 0.08	1.59 ± 0.07	0.25 ± 0.12	<i>k_s</i>
	<i>b</i>	2.54 ± 0.46	-0.65 ± 0.26	4.33 ± 0.58	<i>k_s</i>
	<i>R</i>	0.98	1.00	0.64	<i>k_s</i>
	SD	0.11	0.03	0.33	<i>k_s</i>
cycloheptyl brosylate	<i>n</i>	3	4	7	
	<i>m</i>	0.45 ± 0.17	1.14 ± 0.17	0.11 ± 0.08	<i>k_s</i>
	<i>b</i>	0.75 ± 1.00	-1.12 ± 0.65	2.80 ± 0.38	<i>k_s</i>
	<i>R</i>	0.93	0.98	0.51	<i>k_s</i>
	SD	0.14	0.05	0.21	<i>k_s</i>
2-phenyl-1-propyl tosylate	<i>n</i>	5	4	9	
	<i>m</i>	0.36 ± 0.07	-0.28 ± 0.20	0.38 ± 0.04	
	<i>b</i>	5.12 ± 0.44	7.48 ± 0.76	5.02 ± 0.22	
	<i>R</i>	0.94	0.70	0.96	
	SD	0.17	0.09	0.17	
<i>endo</i> -2-norbornyl tosylate	<i>n</i>	5	4	9	
	<i>m</i>	0.54 ± 0.01	0.66 ± 0.15	0.47 ± 0.03	lim
	<i>b</i>	2.31 ± 0.08	2.20 ± 0.59	2.83 ± 0.16	lim
	<i>R</i>	1.00	0.95	0.99	lim
	SD	0.04	0.05	0.14	
2-phenyl-1-propyl tosylate (<i>k_{obsd}</i> ^{125°C})	<i>n</i>	5	4	9	
	<i>m</i>	0.35 ± 0.04	0.77 ± 0.18	0.36 ± 0.03	<i>k_s</i>
	<i>b</i>	0.92 ± 0.21	-0.69 ± 0.70	0.87 ± 0.13	<i>k_s</i>
	<i>R</i>	0.99	0.95	0.98	lim
	SD	0.08	0.08	0.10	lim
2-phenyl-1-propyl tosylate (<i>k_s</i> ^{125°C})	<i>n</i>	5	4	9	
	<i>m</i>	0.13 ± 0.03	0.82 ± 0.65	0.05 ± 0.06	<i>k_s</i>
	<i>b</i>	3.34 ± 0.18	1.06 ± 2.47	3.90 ± 0.30	lim
	<i>R</i>	0.93	0.66	0.30	<i>k_s</i>
	SD	0.07	0.29	0.23	lim
2-phenyl-1-propyl tosylate (<i>k_Δ</i> ^{125°C})	<i>n</i>	5	4	9	
	<i>m</i>	0.37 ± 0.04	0.78 ± 0.19	0.38 ± 0.13	<i>k_s</i>
	<i>b</i>	0.86 ± 0.23	-0.71 ± 0.74	0.81 ± 0.13	<i>k_s</i>
	<i>R</i>	0.99	0.94	0.98	lim
	SD	0.09	0.09	0.10	lim

^a Where *n* is the number of solvents used in the linear regression analysis, *m* is the slope, *b* is the intercept, *R* is the correlation coefficient, and SD is the standard deviation.

the conclusions which are reported in the last column of Table V. While the agreement with the conclusions based on Figures 2-9 is not surprising, the consistency is dramatic. For all of the model limiting substrates as well as all of the model k_s substrates there is not a single instance of an "incorrect" mechanistic assignment, although there are instances in which application of one of the statistical criteria predicts neither k_s nor limiting mechanisms. This success is encouraging and indicates that the ethanol-TFE method can be objectively applied to the study of substrates whose mechanism is in doubt.

The only example of a substrate in which the different criteria are not consistent is provided by 2-phenyl-1-propyl tosylate (**6**), which has some unusual features. The assignment of the overall solvolysis reaction at 125 °C (" k_{obsd} ") as both k_s and limiting by the different criteria is not disturbing since the reaction is in fact proceeding by a combination of these two pathways. The assignment of the " k_s pathway" as limiting according to the *intercept* and *standard deviation* criteria is readily understood on the basis of the large errors (e.g., an intercept of 1.06 ± 2.47) for the TFE data. This undoubtedly results from the uncertainties in the fraction of primary solvolysis product. The experimental values determined by gas chromatography range from 0.9 to 2.6%, and for such small fractions the uncertainties may approach the magnitude of the experimental values themselves. Similarly, the assignment of the " k_{Δ} pathway" as a k_s process according to the *slope* and *intercept* criteria appears to be a consequence of the uncertainty in the product determinations. These results point out the limitations of applying statistical methods to small numbers of data points and emphasize the importance of subjective evaluation of the rate-rate plots (i.e., Figure 8).

The assignment of *endo*-2-norbornyl brosylate solvolysis to the limiting (*slope*, *intercept*, *correlation coefficient*) category does not appear to result from experimental error. The standard deviations for both the ethanol and TFE data sets are small (0.04 and 0.05, respectively), but the standard deviation increases to 0.14 when all the points are considered together. As in the case of visual analysis of the rate-rate plot (Figure 9), no clear-cut decision can be made. These results again are consistent with *weak* solvent assistance in the solvolysis of the *endo*-2-norbornyl system, and again indicate that this compound reacts with solvent assistance which is at or below the limits of detection by the ethanol-TFE method.

Experimental Section

The arenesulfonates used in this work are known compounds and were prepared by standard procedures.⁴³ Rates were determined conductometrically as reported previously,¹⁴ and solvents were prepared as previously described.¹⁴ Product analysis of 2-phenyl-1-propyl tosylate solvolyses were carried out by gas chromatography as in earlier work.³⁹ Authentic samples of the secondary ethers were prepared by solvolysis of the corresponding secondary tosylate³⁹ in the appropriate aqueous alcohol. Samples of the primary ethers were prepared by reaction of the primary tosylate (**6**) with aqueous ethanol and with the sodium salt of trifluoroethanol in trifluoroethanol.

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