oil with a yellow tint that crystallized immediately (69 mg). Infrared analysis showed this sample to be essentially all starting material (85% recovery). Column chromatography of the entire sample on silica gel separated 4 mg of a carbonyl compound which had an infrared spectrum similar to that of the corresponding amide of 2-quinolinecarbontrile.

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Solvolyses of Secondary Sulfonates in Aqueous Ethanol and Acetone. Nonlinear *mY* Relationships due to Leaving Group and Medium Effects

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Solvolytic rate constants for secondary mesylates and tosylates in aqueous ethanol and in aqueous acetone are correlated with Winstein–Grunwald Y values. Curvature of these plots is greatest for tosylates in aqueous ethanol, especially for 2-adamantyl. Because mesylates show little or no curvature, it is argued that the results cannot be explained by mechanistic changes but by solvation effects of the leaving group in the mixed solvents. The parameter, m, measuring response to solvent ionizing power varies from 0.68 for isopropyl to 1.21 for 2-adamantyl mesylate in aqueous acetone at 25 °C. An alternative solvent ionizing power parameter for tosylates, Y_{OTs}, and the solvent nucleophilicity parameter, N_{OTs}, are evaluated for 20% ethanol/water, 20% acetone/water, and 40% acetone/water. It is proposed that solvolyses of substrates having the same (or very similar) leaving group should be compared if reliable mechanistic information (e.g., nucleophilic solvation effects) is required. The tendency for "dispersion" of correlation lines for various binary mixed solvents appears to be due to both leaving-group effects and to variations in solvent nucleophilicity. By helping to account for curvature and dispersion in mY correlations, this work supports recent work in which mechanistic information was deduced from similar correlations.

The relative rates of solvolyses of primary, secondary, and tertiary substrates are markedly dependent on solvent.[2] Recent studies of the dependence of solvent on the solvolytic reactivity of secondary substrates have provided important new insights into the mechanisms of these reactions.[3-5] Solvolysis rates of both secondary[3-5] and tertiary[6] tosylates can be correlated by two-parameter linear free energy relationships based on 2-adamantyl tosylate (I, R = p-$CH_3C_6H_4$) as a model compound for a scale of solvent ionizing power designated Y_{OTs}.[3b] This solvent scale now appears to be much more suitable for tosylates than the usual Y scale based on *tert*-butyl chloride, but the reasons for the inadequacies of Y values require further investigation.

The Y scale of solvent ionizing power is based on solvolyses of *tert*-butyl chloride [$m = 1$ at 25 °C, eq 1, where

$$\log (k/k_0)_{\mathrm{RX}} = mY \tag{1}$$

k/k_0 is the rate of solvolysis in any solvent (k) relative to the rate of solvolysis in 80% v/v ethanol/water (k_0)] and was introduced in 1978 to correlate other S_N1-like solvolyses.[7a] Subsequently it was discovered that even S_N2 solvolyses of primary arenesulfonates in aqueous ethanol mixtures correlated quite well with Y values.[8,9] This now appears to be at least partly because mixtures of ethanol and water have similar nucleophilicities.[3b,10] During the course of our earlier work,[3a] we were surprised to find that solvolyses of secondary tosylates in the full range of aqueous ethanol mixtures did not correlate well with Y values. While good linear correlations were found for a range of solvents from ethanol to 50% v/v ethanol/water, there was upward curvature between data points for 50% v/v ethanol/water and pure water.[11] Because curvature of free-energy relationships is often associated with mechanistic changes,[12] we investigated this phenomenon in more detail.

Hydrolysis rate constants for many alkyl halides and methyl, ethyl, and isopropyl sulfonates have been determined in water[13] and in alcohol–water, acetone–water, and

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[1] (a) University College of Swansea, supported by the Science Research Council (London). (b) Purdue University. (c) Postdoctoral research associate on Project No. AT(11-1) 70 supported by the Atomic Energy Commission.

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Table I. Solvolytic Rate Constants for Secondary Alkyl Sulfonates

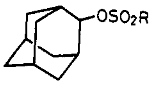
alkyl group	leaving group[a]	solvent[b]	temp, °C	k,[c] s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{OTs}/k_{OMs}
isopropyl	OMs	20% A	0.0[d]	2.05×10^{-6}			
			25.0[d]	7.04×10^{-5}	22.3	−2.7	
cyclopentyl	OMs	80% A	0.0[d]	9.4×10^{-8}			
			25.0[d]	2.7×10^{-6}	21.2	−13	
cyclohexyl	OMs	20% A	0.0[d]	2.87×10^{-6}			
			25.0[d]	9.36×10^{-5}	22.0	−3.2	1.48[e]
cyclohexyl	OMs	80% E	75.1[f]	$(2.62 \pm 0.01) \times 10^{-4}$	23.1	−9.1	1.26[h]
			50.0[g]	$(1.83 \pm 0.07) \times 10^{-5}$			
	OMs	50% E	75.18[g]	$(2.54 \pm 0.10) \times 10^{-3}$	21.4	−9.4	1.08[h]
			50.01[f]	$(2.13 \pm 0.01) \times 10^{-4}$			
	OTs	40% E	74.98[f]	$(5.75 \pm 0.13) \times 10^{-3}$			
			49.95[f]	$(4.54 \pm 0.07) \times 10^{-4}$	22.1	−5.6	
			24.90[f]	$(2.30 \pm 0.05) \times 10^{-5}$			
	OTs	20% E	49.93[f]	$(3.49 \pm 0.03) \times 10^{-3}$			
			24.90[f]	$(2.40 \pm 0.04) \times 10^{-4}$	19.9	−8.5	1.47[i]
	OTs	40% A	50.26[f]	$(2.67 \pm 0.03) \times 10^{-4}$			
			25.0[j]	$(1.45 \pm 0.2) \times 10^{-5}$	21.5	−8.6	1.20[k]
exo-norbornyl	OMs	20% A	25.0[f]	$(7.26 \pm 0.03) \times 10^{-2}$	(17.9)[l]	(−3.0)[l]	
endo-norbornyl	OMs	20% A	0.0[d]	1.30×10^{-6}			
			25.0[d]	3.50×10^{-5}	20.8	−9.3	
2-adamantyl	OMs	60% E	75.02[f]	$(1.77 \pm 0.01) \times 10^{-4}$	26.7	0.7	0.85[h]
			50.02[f]	$(8.29 \pm 0.06) \times 10^{-6}$			
	OMs	50% E	75.0[f]	$(4.39 \pm 0.05) \times 10^{-4}$	24.6	−3.5	0.84[h]
			50.31[f]	$(2.70 \pm 0.06) \times 10^{-5}$			
	OMs	60% A	90.05[f]	$(2.78 \pm 0.07) \times 10^{-4}$			
			75.06[f]	$(5.43 \pm 0.10) \times 10^{-5}$	26.0	−3.7	
			49.98[m]	2.83×10^{-6}			
	OTs	60% A	75.05[f,n]	$(5.2 \pm 0.1) \times 10^{-5}$			0.96
	OTs	40% A	75.1[f]	$(5.5 \pm 0.2) \times 10^{-4}$			
			50.02[f]	$(3.9 \pm 0.2) \times 10^{-5}$	23.2	−7.0	1.13[o]

[a] OMs = mesylate, OTs = tosylate. [b] A = v/v acetone/water; E = v/v ethanol/water. [c] In some cases calculated from data at other temperatures. [d] Determined titrimetrically. [e] Tosylate data from Table II. [f] Determined conductometrically in duplicate; errors shown are average deviations. [g] Determined conductometrically in triplicate. [h] Tosylate data from ref 3a. [i] Mesylate data from Table III. [j] Average of four conductimetric runs, including two carried out independently by Miss G. E. Carter (Swansea), giving $k = (1.24 \pm 0.04) \times 10^{-5}$ s^{-1}. [k] Mesylate data from Table II. [l] Activation parameters calculated from the following data, referring to *approximately* 20% acetone/water (k, temp, °C): $(5.71 \pm 0.05) \times 10^{-3}$, 0.22; $(1.97 \pm 0.03) \times 10^{-2}$, 10.36; $(3.43 \pm 0.07) \times 10^{-2}$, 14.99; $(9.74 \pm 0.14) \times 10^{-2}$, 25.15. [m] One measurement of rate constant. [n] In agreement with published kinetic data.[19a] [o] At 25 °C, data from Table II.

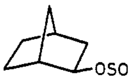
dioxane–water mixtures.[14] Many solvolyses of sulfonates have been examined in mixtures of water and cosolvent in which the volume of cosolvent (acetone, ethanol, dioxane) predominates,[15] but few solvolyses of sulfonates in the highly aqueous media required for the present investigation have previously been reported. Presumably this is because of the poor solubility expected for alkyl sulfonates in highly aqueous media. In related work quaternary sulfonates have recently been used as water-soluble leaving groups,[16] and mesylates with alkyl groups up to C_7 have been showed to dissolve quite rapidly in water.[4,17] As mesylates have very similar solvolytic reactivity to tosylates, and tosylate/mesylate rate ratios do not appear to depend markedly on the substrate,[18] we have carried out a systematic study of tosylates and mesylates in highly aqueous media. We selected acetone and ethanol as the cosolvents because they are probably the two most frequently employed.

Results

Solvolyses for which activation parameters have been obtained are shown in Table I. Results for aqueous acetone at 25 °C along with additional data from the literature are summarized in Table II and results for aqueous ethanol at 25 °C are summarized in Table III. Initial kinetic work was carried out by using titrimetric techniques at Purdue,[4] and additional kinetic data were obtained by using conductometric techniques at Swansea.[18] Where direct comparisons between the two techniques can be made, agreement is usually within 5 or 10% (e.g., *endo*-norbornyl mesylate (III, R = CH_3) in aqueous acetone, Table II). Even for relatively rapid solvolyses in pure water, where the higher concentrations required for titrimetric studies (ca. 10^{-2} M in comparison with ca. 10^{-4} M for conductometric studies) might lead to difficulties, agreement between the two methods is surprisingly good; e.g., for *exo*-norbornyl mesylate (II, R = CH_3) in water at 0 °C $k = 1.40 \times 10^{-2}$ s^{-1} (titrimetric) and $k = 1.48 \times 10^{-2}$ s^{-1} (conductometric). Only for solvolyses of cyclopentyl mesylate in water is there a serious discrepancy (ca. 50%) between the two methods. Difficulties arise if sparingly soluble compounds do not dissolve sufficiently rapidly in



(I)



(II)

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Table II. Rate Constants for Solvolyses of Secondary Alkyl Sulfonates in Aqueous Acetone at 25 °C[a]

	10^6k, s^{-1}, in solvent				
sulfonate	H_2O	20% A	40% A	60% A	80% A
isopropyl (OMs)	201[b]	70.4[c]	15.5[d]	2.78[b]	0.292[d]
isopropyl (OTs)	411[e]		(18)[f,g]		0.34[h]
cyclopentyl (OMs)	5460[e]	(2450)[d,i]	(317)[d,j]	34.9[b]	2.71[c]
cyclopentyl (OTs)	(11500)[k]				(3.5)[l,m]
cyclohexyl (OMs)	426[e]	93.6[c]	12.1[d]	1.23[b]	0.073[d]
cyclohexyl (OTs)	(895)[k]	139[g]	14.5[c]		(0.1)[n]
pinacolyl (OMs)	1330[e]	284[g]	44[g]		
exo-norbornyl (OMs)	326000[e,o]	72600[c,p]	10600[g,q]	800[g]	37[g,r]
endo-norbornyl (OMs)	133[b]	35.0[d]	5.55[d]	0.63[b]	0.059[d]
	128[e]	32.8[g]	5.0[g]		
2-adamantyl (OMs)	150[e]	20.6[g]	1.50[g]	(0.087)[s]	
2-adamantyl (OTs)	(315)[k]	27[t]	1.7[s]	(0.11)[u]	

[a] Abbreviations for solvents and leaving groups as in Table I. [b] Reference 4. [c] From Table I. [d] Determined titrimetrically. [e] Reference 18. [f] Calculated from the rate constant at 50 °C (3.4×10^{-4} s^{-1}), assuming $\Delta H^{\ddagger} = 22$ kcal/mol. [g] Determined conductometrically. [h] Huckel, W.; Tomopulos, K. *Justus Liebigs Ann. Chem.* **1957**, *610*, 78 (extrapolated from higher temperatures). [i] Calculated from the rate constant at 0 °C (1.02×10^{-4} s^{-1}), assuming $\Delta H^{\ddagger} = 20$ kcal/mol. [j] Calculated from the rate constant at 0 °C (1.32×10^{-5} s^{-1}), assuming $\Delta H^{\ddagger} = 20$ kcal/mol. [k] Calculated from the rate constant for hydrolysis of the mesylate, assuming OTs/OMs = 2.1; see ref 18. [l] Assuming $\Delta H^{\ddagger} = 21$ kcal/mol and calculated from data at 50 °C (6.04×10^{-5} s^{-1}). Reich, H. I.; Renga, J. M. *Tetrahedron Lett.* **1974**, 2747. [m] A significantly higher value is obtained from the rate constant at 40 °C (2.92×10^{-5} s^{-1}) given in the reference cited in footnote *h* above. [n] Estimated from data at 40 °C (5.6×10^{-7} s^{-1}) and 50 °C (2.3×10^{-6} s^{-1}), given in the reference cited in footnote *h*, but assuming $\Delta H^{\ddagger} = 22$ kcal/mol rather than the highly unlikely value of 27.8 kcal/mol required by these data. [o] We repeated our previous work and obtained $k = (3.19 \pm 0.08) \times 10^{-1}$ s^{-1} for two kinetic runs. [p] Titrimetric data at 0 °C, $k = 5.2 \times 10^{-3}$ s^{-1}. [q] Titrimetric data at 0 °C, $k = 7.2 \times 10^{-4}$ s^{-1}. [r] Titrimetric data at 0 °C, $k = 1.4 \times 10^{-6}$ s^{-1}. [s] Extrapolated from data given in Table I. [t] We thank Miss G. E. Carter (Swansea) for this result. [u] Extrapolated from data given in ref 19a.

Table III. Rate Constants for Solvolyses of Secondary Alkyl Sulfonates in Aqueous Ethanol at 25 °C[a]

	10^6k, s^{-1}, in solvent				
sulfonate	20% E	40% E	50% E	60% E	80% E
isopropyl (OMs)			17.3[b]		2.62[b,c]
isopropyl (OTs)			15.4[d]		2.99[d]
cyclohexyl (OMs)	165[e]		12.1[f]		0.83[f]
cyclohexyl (OTs)	243[f]	23.4[f]	8.6[d]	3.46[d]	0.75[d]
2-adamantyl (OMs)	38.3[e]		(0.96)[f]	(0.23)[f]	ca. 0.024[g]
2-adamantyl (OTs)	50.6[e]		(0.47)[d]	(0.2)[d]	(0.024)[d]

[a] Abbreviations for solvents and leaving groups as in Table I; data for water in Table II. [b] Reference 18. [c] Assuming for 25 °C $k_{OTs}/k_{OMs} = 1.14$, observed at 50 °C. [d] Reference 3a. [e] Determined conductometrically. [f] Calculated from data at other temperatures; see Table I. [g] Assuming $k_{OTs}/k_{OMs} \simeq 1$.

aqueous media. Although good first-order kinetics can be observed over several half-lives, low "infinity" values may be observed, followed by upward drift at longer reaction times. Such solutions may contain aggregates or possibly micelles. Satisfactory solutions can be obtained relatively quickly by first dissolving the substrate in the organic solvent before adding water. In contrast, addition of substrate to a premixed organic solvent may require hours or days before satisfactory kinetics are observed. Acceptable kinetic runs showed a high-precision fit to first-order kinetics (<0.3% for conductimetric runs) and insignificant drift of infinity conductances. Therefore it is *unlikely* that formation of micelles[19b] or other aggregates of molecules significantly affected the results reported here. However, by an unfortunate combination of circumstances, it is conceivable in isolated cases that substrates could dissolve completely *during* the first one or two half-lives, giving good first-order kinetics and good infinity titers along with inaccurate first-order rate constants. Duplicate kinetic runs might reproduce such systematic errors, so as additional verification, agreement between rate constants calculated from data for 50% reaction and the rate constants calculated from the full run (3-4 half-lives and infinity) was established. Another test for reliability of the kinetic data is that reasonable activation parameters are obtained over a temperature range of about 25 °C for which there should be a major change in the relative rates of formation of truly homogeneous solutions and of solvolysis. Careful preparation of homogeneous solutions was particularly important for solvolyses of tosylates because they dissolve much less rapidly than mesylates. Other difficulties associated with conductimetric studies of sparingly soluble substrates have been discussed by Robertson.[13b]

Tosylate/mesylate rate ratios are shown in Table I, and others are readily calculated from data in Table II and III.

Discussion

Figure 1 shows that the nonlinearity of mY correlations for secondary tosylates in aqueous ethanol is most marked for 2-adamantyl tosylate—the compound most likely to react by an S_N1 process! The *least* curved plot is shown for isopropyl tosylate, for which nucleophilic solvent assistance (S_N2 character) is greatest.[3b] (Linearity of this plot for 74 °C from ethanol to ca. 30% ethanol/water has been noted recently,[20] but we have found that the data

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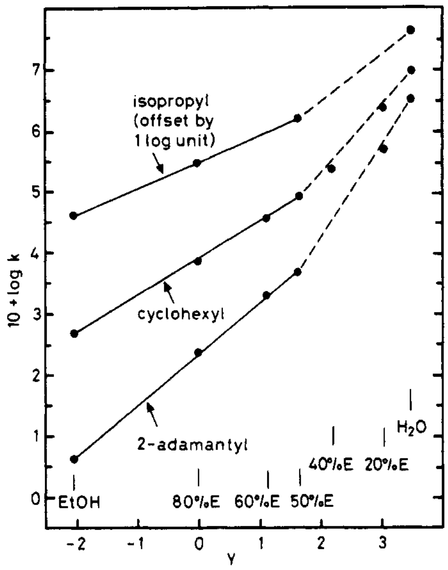

Figure 1. Correlation of logarithms of solvolysis rate constants at 25 °C for secondary tosylates in aqueous ethanol against *Y*. Kinetic data from Table II and III and *Y* values from ref 7b.

Table IV. Rate Constants for Solvolysis of Secondary Alkyl Sulfonates in Methanol at 25 °C

alkyl group	$10^6 k$, s^{-1}		k_{OTs}/k_{OMs}
	tosylate[a]	mesylate[b]	
isopropyl	0.118	0.0663	1.78
cyclopentyl	0.985	0.558	1.77
cyclohexyl	0.0159	0.0097	1.64

[a] Reference 4. [b] This work.

point for water (extrapolated from lower temperatures) is off the correlation line.) This trend is exactly the reverse of what one would expect from the definition of *Y* values, based on S_N1 reactions. The extent of nonlinearity of Figure 1 is such that extrapolation of each of the three lines through ethanol—50% ethanol data points to *Y* values of about 5—is required to accommodate the points for water (the accepted *Y* value for water is 3.49).[7b] Alternatively, by use of fixed points for pure ethanol and pure water, an 8-fold increase in rate for solvolysis of 2-adamantyl tosylate in 50% ethanol would be required for a linear correlation (along with smaller increases for the other compositions).

A clue to the cause of these anomalous results comes from comparisons of rate data for tosylates and mesylates. The rate ratio k_{OTs}/k_{OMs} varies from 2.1 in water[18] to about 0.5 for 2-adamantyl tosylate in 50% ethanol/water at 25 °C (Table III). Data for pure ethanol are not available but the ratio increases again to about 1.7 in pure methanol (Table IV). Thus a decrease in k_{OTs}/k_{OMs} rate ratio appears to occur in mixed solvents with the largest change occurring for about 50% ethanol/water. Satisfactory, although probably slightly curved, mY correlations are observed for mesylates in aqueous ethanol and in aqueous acetone (Figure 2). Also k_{OTs}/k_{OMs} rate ratios in aqueous acetone exceed 1. Consequently the anomalous behavior is mainly associated with tosylates in aqueous ethanol and to a lesser extent with tosylates in aqueous acetone; some mesylates also tend to give slightly curved plots.

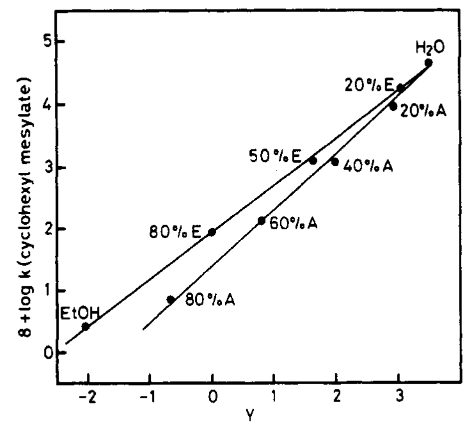

Figure 2. Correlation of logarithms of solvolysis rate constants at 25 °C for cyclohexyl mesylate in aqueous ethanol and in aqueous acetone against *Y*. Data for cyclohexyl mesylate in ethanol estimated from data for the tosylate,[3a] assuming a tosylate/mesylate rate ratio of 1.7.

Table V. Corrections Using Equation 1 for Solvolysis Rates of Mesylates in Aqueous Acetone at 25 °C[a]

alkyl group	slope, *m*	solvent range	number of data points
isopropyl	0.68	0–80% v/v	5
cyclopentyl	0.81[b]	0–80% v/v	5
cyclohexyl	0.87[c]	0–80% v/v	5
endo-norbornyl	0.81	0–80% v/v	5
exo-norbornyl	0.94[d]	0–80% v/v	5
pinacolyl	0.98	0–40% v/v	3
2-adamantyl	1.21[e]	0–60% v/v	4

[a] *Y* values from ref 7b; other data from Table II. [b] Titrimetric data at 0 °C gives 0.86. [c] See Figure 3. [d] Titrimetric data at 0 °C gives 0.96. [e] These results would be better accommodated by shallow curve.

Because of the similar solvolytic reactivities of tosylates and mesylates, it seems unlikely that mechanistic changes are responsible for the nonlinear correlations (Figure 1). As mesylates show little if any of this anomalous behavior, it does not appear to reflect another deficiency of the *Y* scale of solvent ionizing power.[2b] The anomalous results may be due to variations in initial-state solvation,[21] possibly including "solvent sorting";[22] e.g., the solvation shell of the tosylate leaving group may be enriched by ethanol rather than by water molecules because tosylates provide a more hydrophobic environment than mesylates. This could lead to a less polar environment for tosylates, causing a decrease in reactivity relative to mesylates.

It is also known that alkyl groups are better solvated than aryl groups in water.[23] This is explained by the aryl group causing greater disruption of the highly developed solvent structure than an alkyl group. On this basis the tosylate (aryl) anion might be expected to disrupt the solvent structure to a greater extent than the smaller mesylate (alkyl) anion. Both would be expected to disrupt the water structure more than the chloride anion because of their larger size. It is to be expected that this difference in solvation between aryl and alkyl groups should be greatly reduced in binary solvents where solvent structure breaking is not so important. Compared to the k_{OTs}/k_{OMs} rate ratio of ca. 2 observed in water, a ratio closer to unity is indeed observed in binary solvents (Table I). However, this solvation effect cannot be the sole contributing effect to k_{OTs}/k_{OMs} rate ratios since in methanol, solvation differences between aryl and alkyl groups are reduced[23] but the k_{OTs}/k_{OMs} rate ratio remains high (Table IV).

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Table VI. Additional Solvent Parameters for Tosylates[a]

solvent	methyl tosylate, $k \times 10^5$, s^{-1} (50 °C)	Y_{OTs}	N_{OTs}
water[b]	13.8	4.1	−0.44
20% acetone/water	7.6[c]	3.05	−0.38
40% acetone/water	3.3[c]	1.85	−0.38
60% acetone/water[d]	1.38	0.66	−0.41
20% ethanol/water	10.0[e]	3.32	−0.34
50% ethanol/water[d]	4.41	1.29	−0.09

[a] For definitions see ref 3b; kinetic data from Tables II and III and from ref 3b. [b] Reference 18. [c] Calculated from kinetic data for ethyl benzenesulfonate (ref 14a) as described in ref 3b. [d] Reference 3b. [e] Calculated by interpolation of data for water and 50% ethanol/water, plotting log *k* vs. *Y*.

Correlations using eq 1 for solvolysis rates of mesylates in aqueous acetone at 25 °C are shown in Table V. The slopes of the correlations parallel those observed previously for the corresponding secondary tosylates in solvents having a wider range of nucleophilicities.[3-5] The relatively low slope for *endo*-norbornyl and the high slope for 2-adamantyl are particularly noteworthy.

Ambiguities due to solvation of leaving groups can arise if solvolysis rates of substrates other than chlorides are correlated with *Y* values. Differences between tosylates and mesylates have been discussed above, and similar effects can be seen when tosylates are studied in solvents of different acidities, e.g., acetic acid and aqueous ethanol.[3a] Consequently it is preferable to compare tosylates with tosylates or mesylates with mesylates. The scale of solvent ionizing power based on 2-adamantyl tosylate (Y_{OTs}) can now be extended, using the new kinetic data (Tables II and III). Additional Y_{OTs} and N_{OTs} parameters are shown in Table VI. These data could be used to extend the range of solvents for correlations using eq 2, in which the lN term accounts explicitly for sensitivity of a substrate to solvent

$$\log (k/k_0)_{ROTs} = mY_{OTs} + lN_{OTs} \qquad (2)$$

nucleophilicity.[3b] The additional solvents show a wide variation in the ionizing-power parameter (Y_{OTs}) and a relatively small change in the nucleophilicity parameter (N_{OTs})—the latter changes more from water to 50% ethanol/water (a change of 0.35) than from 50% ethanol to pure ethanol (a change of 0.09). While eq 2 would be expected to lead to improved correlations, it is better to apply it when there are larger changes in N_{OTs}.

Improvements in correlations for solvolyses of substrates having the same leaving groups can be seen by comparing Figures 2 and 3. Substantial "dispersion"[7c] between lines for ethanol/water and acetone/water are observed (Figures 2) when cyclohexyl mesylate is correlated with *Y* values (i.e., *tert*-butyl chloride). The dispersion is reduced considerably when 2-adamantyl mesylate is used as the reference substrate instead of *tert*-butyl chloride (Figure 3). As solvolyses of cyclohexyl substrates are sensitive to solvent nucleophilicity,[3] the dispersion between the two correlation lines in Figure 3 may be explained at least partly by the greater nucleophilicity of ethanol/water mixtures than acetone/water mixtures (Table VI). Also some of the correlations for mesylates with *Y* values appear on close examination to be slightly curved (e.g., aqueous acetone data in Figure 2) but no such curvature is apparent in Figure 3.

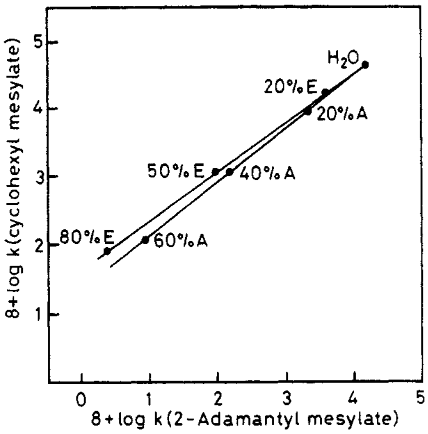

Figure 3. Correlation of logarithms of solvolysis rate constants at 25 °C for cyclohexyl mesylate in aqueous ethanol and in aqueous acetone against logarithms of solvolysis rate constants for 2-adamantyl mesylate.

Recently, there has been considerable discussion of comparisons of rate data in ethanol/water with trifluoroethanol/water mixtures as mechanistic probes of nucleophilic solvent assistance.[5,24] These papers include comparisons for tosylates with *Y* values based on *tert*-butyl chloride and with logarithms of rate constants for solvolysis of 1-adamantyl bromide. Comparisons should preferably be made between substrates having the same leaving group. A convenient mechanistic probe for tosylates is the ratio of rates of solvolysis in 40% v/v acetone/water and in 97% w/w trifluoroethanol/water; fortuitously these two solvents have almost the same Y_{OTs} values (1.85 and 1.83 respectively), and comparisons could be made between various tosylates and 2-adamantyl tosylate.[3] Nonlinear correlations (Figure 1) also account for some of the inconsistencies noted when rate data for tosylates in ethanol/water and in trifluoroethanol/water are extrapolated to pure water.[24]

Conclusion

Nonlinear correlations of solvolysis rate constants for secondary tosylates in aqueous ethanol against *Y* do not appear to be caused by mechanistic changes nor by a major deficiency of the *Y* scale of solvent ionizing power. The nonlinearity is much less significant for mesylates than for tosylates and may be caused by different solvation of the leaving groups (mesylate and tosylate) in the initial states and/or in the transition states. Improved correlations are obtained when solvolyses having the same leaving group are compared. By accounting for the anomalous curvature of some correlations, this work supports recent studies[3-6,25] in which mechanistic information was deduced from similar correlations.

Experimental Section

Both preparations of chemicals and kinetic methods were carried out as described previously.[4,18] For tosylates it was often necessary to dissolve the substrate in ethanol or acetone before adding water. More recently we have found that formation of satisfactory solutions is aided by immersing the solution in an ultrasonic bath.

Registry No. I (R = Me), 31616-68-9; I (R = p-MeC_6H_4), 25139-43-9; II (R = Me), 28627-77-2; III (R = Me), 28627-78-3; isopropyl mesylate, 926-06-7; cyclopentyl mesylate, 16156-57-3; cyclohexyl mesylate, 16156-56-2; cyclohexyl tosylate, 953-91-3; isopropyl tosylate, 2307-69-9; cyclopentyl tosylate, 3558-06-3; cyclohexyl tosylate, 953-91-3; pinacolyl mesylate, 75767-76-9.

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