

was dissolved in 50 mL of ether and cooled to 0 °C. A stream of ammonia gas was passed through the solution for 10 min, the solids were filtered, and the filtrate was washed with 50 mL of 10% aqueous HCl, 80 mL of saturated ammonium chloride, and 2 × 50 mL of water. The solution was dried (MgSO₄) and the solvents were removed under reduced pressure. Distillation of the oily residue gave 7.8 g (30.1 mmol, 57%) of **4b**: bp 178–180 °C (20 mm/Hg) [lit.¹⁹ bp 130–133 °C (1 mmHg)]; ¹H NMR (CDCl₃) δ 0.20–0.80 (m, 4 H), 0.80–1.45 (m, 1 H), 1.50 (d, 3 H, *J* = 6.0 Hz), 4.15–4.80 (m, 1 H), and 7.15 (s, 3 H); IR (neat, film) 3085, 3020, 3000–2880, 1735, 1580, 1565, 1435, 1280, 1150, 1050, 930, 850, 800, and 780 cm⁻¹.

A total of 2.60 g (10.0 mmol) of **4b** in 10 mL of piperidine was heated for 25 h in a sealed tube at 130 °C. On cooling, some piperidine hydrobromide was filtered, and the filtrate was dissolved in 30 mL of 10% HCl solution and washed with ether. The aqueous phase was basified with NaOH and extracted with 3 × 100 mL of ether. The ether extracts were dried (Na₂SO₄) and filtered, and the solvents were removed under reduced pressure. The resulting oil contained piperidine but no trace of substitution products.

1-Cyclopropyl-1-ethanol 2,4,6-Trimethylbenzoate (4c). A solution of 6.3 g (77.6 mmol) of **4a** in 5 mL of pyridine and 15 mL of ethanol-free CHCl₃ was added to 20 mL of a solution of 14.3 g (78.3 mmol) of mesityl chloride²⁰ in ethanol-free chloroform, at 0 °C. The solution was stirred at ambient temperature for 13 h and quenched with 20 mL of water. The organic phase was washed with 2 × 50 mL of water, 50 mL of 10% aqueous HCl,

and 50 mL of 5% aqueous NaHCO₃. The solution was dried (MgSO₄), and the solvents were removed under reduced pressure. Distillation of the resultant oil through a 15-cm Vigreux column gave 14.4 g (62.0 mmol, 80%) of **4c**: bp, 160–162 °C (7 mmHg) [lit.¹⁹ bp 145–147 °C (2 mmHg)]; ¹H NMR (CDCl₃) δ 0.20–0.75 (m, 4 H), 0.75–1.30 (m, 1 H), 1.37 (d, 3 H, *J* = 6.0 Hz), 2.23 (s, 9 H), 4.10–4.73 (m, 1 H), and 6.65 (s, 2 H); IR (neat, film): 3080, 3020, 3000–2865, 1725, 1615, 1450, 1270, 1170, 1085, 1050, 930, and 850 cm⁻¹.

Subsequent reaction of 2.30 g (9.90 mmol) of **4c** with 10 mL of piperidine at 130 °C for 25 h gave, after the workup described for **4b**, an oil containing piperidine but no trace of substitution products.

Kinetic Studies of 1 with Amines. A total of 14.903 g (0.1 mol) of **1a** and 8.515 g (0.1 mol) of piperidine; or 17.709 g (0.1 mol) of **1e** and 8.515 g (0.1 mol) of piperidine; or 17.709 g (0.1 mol) of **1e** and 7.314 g (0.1 mol) of diethylamine was dissolved in 100 mL of dry benzene and heated at 55 °C in an oil bath. At intervals 2.0 mL of each solution was removed via syringe and titrated with 0.1 N HCl solution with a methyl orange indicator, following the method of Young.¹⁰ Each reaction was allowed to proceed through three half-lives and the data is presented in Figure 1. A similar experiment with **1a** and diethylamine failed to give data from which a straight-line plot could be made.

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Leaving Group and Solvent Effects on S_N1 Reactions of Adamantyl Substrates. Contributions from Electrostatic, Electrophilic, and Lipophilic Effects

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Solvolytic rate constants are reported for reactions of 1-adamantyl picrate, 2-adamantyl trifluoromethanesulfonate (triflate), and 2-adamantyl perchlorate in binary aqueous mixtures of ethanol, methanol, acetone, trifluoroethanol, and hexafluoroisopropyl alcohol. Logarithms of solvolysis rates for various compositions of a binary mixture (aqueous ethanol, methanol, or acetone) are correlated with the solvent ionizing power (e.g., logarithms of solvolysis rates for 2-adamantyl tosylate). Variations in slopes of the correlations for picrates are attributed primarily to electrostatic effects—more extensive delocalization of negative charge in the anionic leaving group reduces the sensitivities of the solvolyses to changes in solvent ionizing power. The discussion includes previous work on chlorides, bromides, and iodides. Deviations from the correlation lines for aqueous alcohol mixtures provide a measure of electrophilic assistance in acidic and fluorinated solvents. Triflates may be the only exceptions to the general pattern that electrophilic assistance by carboxylic acid solvents depends on the electronegativity of the atom(s) of the leaving group on which charge develops. Only triflates show similar deviations for fluorinated alcohol solvents. Perchlorates and picrates show enhanced reactivities in high percentage acetone/water mixtures, but it is suggested from a plot of *Y*₁ vs. *Y*_{Pic} that lipophilic effects may not cause these deviations.

Both 1-adamantyl (**1**) and 2-adamantyl (**2**) substrates react by S_N1 reactions,¹ and the rates of solvolysis of sulfonates show almost identical responses to changes in solvent ionizing power.² The tertiary adamantyl tosylate (**1**, X = OTs) reacts about 10⁵ times faster than the secondary tosylate (**2**, X = OTs).²⁻⁴ Consequently it is

possible to examine systematically leaving group and solvent effects over a wide range of solvolytic reactivity, using the adamantyl framework as a relatively constant alkyl group. To aid such studies, the experimentally accessible range of reactivity has been extended to conductometric studies of relatively rapid reactions (*t* < 1 s) of sparingly soluble substrates,^{2,5} which can be studied con-

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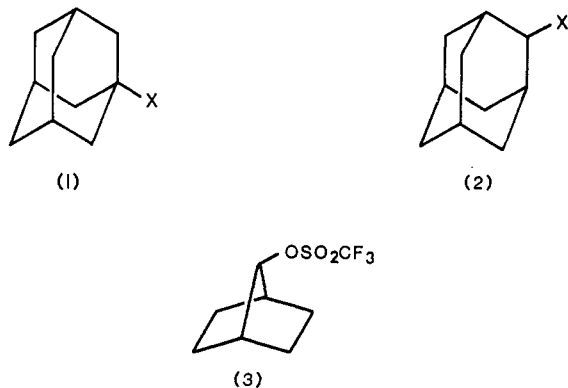
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veniently with acceptable precision. Slightly slower reactions but with half-lives as short as 3 s can be studied with high precision,^{5b} and these studies do not require apparatus specially designed for fast reactions.

We recently reported a comparison of solvent effects on the reactivity of 1-adamantyl chloride, bromide, iodide, and tosylate in protic solvents.⁶ Other workers examined solvolyses of 1-adamantyl picrate (1, X = *O*-2,4,6-tri-



nitrobenzene),⁷ 2-adamantyl perchlorate (2, X = OClO_3),⁸ and 2-adamantyl trifluoromethanesulfonate (2, X = OSO_2CF_3 or triflate).⁹ Data for 7-norbornyl triflate (3) have also been obtained recently.¹⁰ We now report additional kinetic data for 1-adamantyl picrate and 2-adamantyl perchlorate and triflate, so extensive kinetic data for solvolyses of adamantyl substrates for seven dissimilar leaving groups (chloride, bromide, iodide, tosylate, picrate, perchlorate, and triflate) are now available. Hence, we can evaluate the relative importance of electrostatic, electrophilic (e.g., hydrogen bonding), lipophilic, and other contributions to solvent effects on $\text{S}_{\text{N}}1$ reactivity.

Results

All of our solvolyses were carried out conductimetrically in dilute solutions ($<10^{-3}$ M). Solvolytic kinetic data for 1-adamantyl picrate (1, X = *O*-2,4,6-trinitrobenzene) are shown in Table I, for 2-adamantyl triflate (2, X = OSO_2CF_3) are shown in Table II, and for 2-adamantyl perchlorate (2, X = OClO_3) are shown in Table III. All three compounds were dissolved in dry dioxane to give 1–10% solutions before injecting rapidly into the thermostatted solvents in the conductivity cell. Consequently, the reaction medium usually contained 0.1–1% v/v dioxane, which has a small but detectable rate retarding effect (e.g., for 1-adamantyl picrate in 40% EtOH/ H_2O there is a 6% decrease in rate for solvent with 1% dioxane compared with 0.1% dioxane). To compare our results for 2-adamantyl perchlorate (2, X = OClO_3) with those of previous workers,⁸ we added 2% dioxane in the study of 80% acetone/water, and the effect of changing from 0.4% to 2.0% dioxane was to reduce the rate constant by 6%. Even a 10% rate effect changes the derived logarithmic solvent parameters only by 0.04, so no corrections for the effects of added dioxane have been attempted. When

Table I. Rate Constants for Solvolyses of 1-Adamantyl Picrate (1, X = *O*-2,4,6-trinitrobenzene)^a

solvent ^b	temp, °C	k , s ⁻¹	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
80% EtOH	50.0 ^f	$(5.01 \pm 0.04) \times 10^{-3}$		
	49.1 ^c	4.50×10^{-3}		
	49.1 ^k	4.52×10^{-3}		
50% EtOH	25.0 ^e	$(1.93 \pm 0.01) \times 10^{-4}$	24.3	6.0
	50.0 ^{d,j}	$(3.93 \pm 0.01) \times 10^{-2}$		
	49.1 ^c	3.53×10^{-2}		
	49.1 ^l	3.48×10^{-2}		
	25.0 ^g	$(1.59 \pm 0.03) \times 10^{-3}$	24.0	9.0
	49.1 ^{e,i,m}	$(3.35 \pm 0.20) \times 10^{-2}$	23.5 ⁿ	7.6 ⁿ
40% EtOH	49.1 ^{e,j}	$(3.33 \pm 0.03) \times 10^{-2}$		
	48.5 ^{e,i}	$(3.0 \pm 0.2) \times 10^{-2}$	23.2 ⁿ	6.5 ⁿ
	25.0 ^d	$(3.67 \pm 0.02) \times 10^{-3}$		
30% EtOH	25.0 ^{g,i}	$(3.46 \pm 0.06) \times 10^{-3}$		
	25.0 ^{g,i}	$(6.5 \pm 0.5) \times 10^{-3}$		
20% EtOH	25.0 ^g	$(1.84 \pm 0.08) \times 10^{-2}$		
	80% MeOH	$(50.0)^{e,h}$	$(6.56 \pm 0.10) \times 10^{-3}$	25.5
60% MeOH	25.0 ^e	$(2.17 \pm 0.10) \times 10^{-4}$		
	25.0 ^e	$(9.8 \pm 0.2) \times 10^{-4}$		
40% MeOH	25.0 ^f	$(5.35 \pm 0.13) \times 10^{-3}$		
	30% MeOH	$(25.0)^{g,h}$	$(5.6 \pm 0.1) \times 10^{-3}$	
80% (CH ₃) ₂ CO	50.0 ^{e,h}	$(2.70 \pm 0.02) \times 10^{-3}$		
	25.0 ^e	$(9.78 \pm 0.01) \times 10^{-5}$	24.8	6.3
60% (CH ₃) ₂ CO	50.0 ^{e,h}	$(1.43 \pm 0.15) \times 10^{-2}$		
	25.0 ^e	$(5.36 \pm 0.06) \times 10^{-4}$	24.5	8.8
40% (CH ₃) ₂ CO	25.0 ^g	$(2.70 \pm 0.03) \times 10^{-3}$		
	30% (CH ₃) ₂ CO	25.0 ^e	$(5.7 \pm 0.4) \times 10^{-3}$	
20% (CH ₃) ₂ CO	25.0 ^{g,h}	$(1.27 \pm 0.14) \times 10^{-2}$		
	10% (CH ₃) ₂ CO	25.0 ^{g,h}	$(3.1 \pm 0.2) \times 10^{-2}$	
97% CF ₃ CH ₂ OH	40.0 ^d	$(1.83 \pm 0.02) \times 10^{-2}$		
	25.0 ^d	$(3.24 \pm 0.01) \times 10^{-3}$	20.8	-0.2
70% CF ₃ CH ₂ OH	25.0 ^{d,h}	$(4.26 \pm 0.15) \times 10^{-3}$		
	50% CF ₃ CH ₂ OH	25.0 ^f	$(5.20 \pm 0.01) \times 10^{-3}$	

^a Determined conductimetrically in duplicate except where noted otherwise; errors shown are average deviations. ^b Percent EtOH refers to percent ethanol/water (v/v); percent MeOH refers to methanol/water (v/v); percent (CH₃)₂CO refers to acetone/water (v/v); percent CF₃CH₂OH refers to percent trifluoroethanol/water (w/w); percent (CF₃)₂CHOH refers to percent hexafluoroisopropyl alcohol/water (w/w). ^c Calculated from data at other temperatures. ^d Solvent also contained 0.1% v/v dioxane. ^e Solvent also contained 0.2–0.3% v/v dioxane. ^f Solvent also contained 0.4–0.5% v/v dioxane. ^g Solvent also contained 1% v/v dioxane. ^h Triplicate measurement of rate constant. ⁱ Quadruplicate measurement of rate constant. ^j Single measurement of rate constant. ^k Interpolated from a literature value (ref 7b) for $m = 0.612$ between Y values of -0.93 and 0.3 (eq 1) at 49.1 °C. ^l Interpolated from a literature value (ref 7b) for $m = 0.695$ between Y values of 1.17 and 1.98 (eq 1) at 49.1 °C. ^m Solution also contained up to 10^{-3} M 2,6-lutidine. ⁿ Probably less reliable than value quoted above.

2-adamantyl perchlorate dissolved in pentane was injected into 60% methanol/water, the conductance readings drifted upwards, presumably because of inadequate miscibility. Alternative solvents for injections (e.g., acetone, acetonitrile) may provide more rapid mixing than dioxane (mp 12 °C), particularly at low temperatures, but stringent drying would be required because 2-adamantyl triflate (and probably perchlorate) react rapidly with traces of moisture even in the “dry” dioxane.

For solvolyses of 1-adamantyl picrate in 50% ethanol/water, the kinetic effects of added 2,6-lutidine (up to 10^{-3} M) were undetectable. This supports the application of the conductivity method particularly in showing that there is no change in the degree of dissociation of the picric acid produced during the solvolyses. It seems likely that all three acids (picric, triflic, and perchloric) are completely dissociated in the dilute aqueous solutions ($<10^{-3}$ M).

The reliability of the rate data was examined by three criteria for individual kinetic runs: (i) precision of fit to

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Table II. Rate Constants for Solvolyses of 2-Adamantyl Triflate (2, X = OSO_2CF_3)^a

solvent ^b	temp, °C	k , s ⁻¹	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
80% EtOH	25.0 ^d	$(1.70 \pm 0.01) \times 10^{-2}$	21.7	6.3
	0.0 ^d	$(5.42 \pm 0.3) \times 10^{-4}$		
50% EtOH	25.0 ^g	$(3.79 \pm 0.09) \times 10^{-1}$		
	0.0 ^g	$(1.37 \pm 0.01) \times 10^{-2}$	21.0	10.0
30% EtOH	-10.0 ^g	$(2.98 \pm 0.02) \times 10^{-3}$		
	25.0 ^k	$(1.3 \pm 0.1) \times 10^{-1}$		
20% EtOH	-5.0 ^g	$(4.5 \pm 0.1) \times 10^{-1}$		
	25.0 ^k	13 ± 3		
MeOH	25.0 ^d	$(2.73 \pm 0.02) \times 10^{-3}$		
	0.0 ^d	$(5.61 \pm 0.02) \times 10^{-2}$	20.9	5.9
80% MeOH	25.0 ^d	$(2.03 \pm 0.01) \times 10^{-3}$		
	0.0 ^d	$(5.78 \pm 0.06) \times 10^{-1}$		
60% MeOH	25.0 ^e	$(2.35 \pm 0.01) \times 10^{-2}$	20.2	8.1
	0.0 ^g	$(5.49 \pm 0.03) \times 10^{-3}$		
40% MeOH	-10.0 ^g	$(4.70 \pm 0.07) \times 10^{-2}$		
	0.0 ^{g,i}	$(2.0 \pm 0.3) \times 10^{-1}$	20.7	14.3
30% MeOH	10.0 ^g	$(8.3 \pm 0.2) \times 10^{-1}$		
	25.0 ^c	5.5		
80% (CH ₃) ₂ CO	-10.0 ^g	$(1.0 \pm 0.1) \times 10^{-1}$		
	25.0 ^k	10 ± 2		
60% (CH ₃) ₂ CO	25.0 ^d	$(1.86 \pm 0.01) \times 10^{-2}$	20.0	0.8
	0.0 ^d	$(7.71 \pm 0.04) \times 10^{-4}$		
40% (CH ₃) ₂ CO	25.0 ^d	$(1.81 \pm 0.02) \times 10^{-1}$	19.5	3.5
	0.0 ^d	$(8.13 \pm 0.01) \times 10^{-3}$		
30% (CH ₃) ₂ CO	-10.0 ^g	$(2.48 \pm 0.01) \times 10^{-2}$	18.3	4.0
	0.0 ^g	$(9.29 \pm 0.14) \times 10^{-2}$		
97% CF ₃ CH ₂ OH	25.0 ^c	1.7		
	-10.0 ^g	$(7.37 \pm 0.08) \times 10^{-2}$		
97% (CF ₃) ₂ CHOH	25.0 ^m	5 ± 1		
	-10.0 ^{d,i}	$(2.1 \pm 0.1) \times 10^{-3}$		
97% (CF ₃) ₂ CHOH	10.0 ^d	$(2.69 \pm 0.18) \times 10^{-2}$	18.3	-0.9
	25.0 ^c	1.5×10^{-1}		
97% (CF ₃) ₂ CHOH	-10.0 ^{g,i}	$(9 \pm 3) \times 10^{-2}$		
	-5.0 ^{g,i}	$(5 \pm 3) \times 10^{-1}$		
97% (CF ₃) ₂ CHOH	0.0 ^{g,i}	$(9 \pm 3) \times 10^{-1}$		
	25.0 ⁿ	ca. 8		

^{a-j} As for Table I. ^k Estimated from data at lower temperatures assuming $\Delta H^\ddagger = 20 \pm 1$ kcal/mol. ^l Five measurements of rate constant. ^m Estimated from data at lower temperatures assuming $\Delta H^\ddagger = 18.3 \pm 1$ kcal/mol. ⁿ Calculated from the rate constant at 0 °C assuming $\Delta H^\ddagger = 13$ kcal/mol (see text) to obtain what is probably a lower limit to the true value.

first-order kinetics usually better than 0.1%; (ii) agreement between rate constants calculated for 50% reaction and for the full kinetic run (ca. 90% reaction); (iii) lack of drift of infinity conductances.^{3a} A major problem is that the substrate may dissolve during the kinetic run.^{3a} To detect this source of error, averages of two kinetic runs at a particular temperature were then compared with data at other temperatures to see if reasonable activation parameters were obtained. A good example, illustrating the reliability of such measurements even for relatively fast solvolytic reactions, is 2-adamantyl triflate in 60% methanol/water studied at -10, 0, and 25 °C (Table II). This additional reliability check proved to be valuable for 1-adamantyl picrate in 50% ethanol/water at 25 °C—our early results obtained by injecting more concentrated solutions gave $k \sim 1 \times 10^{-4}$ s⁻¹ (with $\Delta S^\ddagger > 20$ eu) compared with the more reliable value of 1.59×10^{-4} (Table I). This source of error was much less significant in studies at 50 °C, presumably because of the increased solubility of the picrate. However, an increase in temperature is not always beneficial because the reaction may become inconveniently rapid.

A further or alternative check on the reliability of the data for highly aqueous alcohols or acetone is the effect of reducing the proportions of organic cosolvent. In such

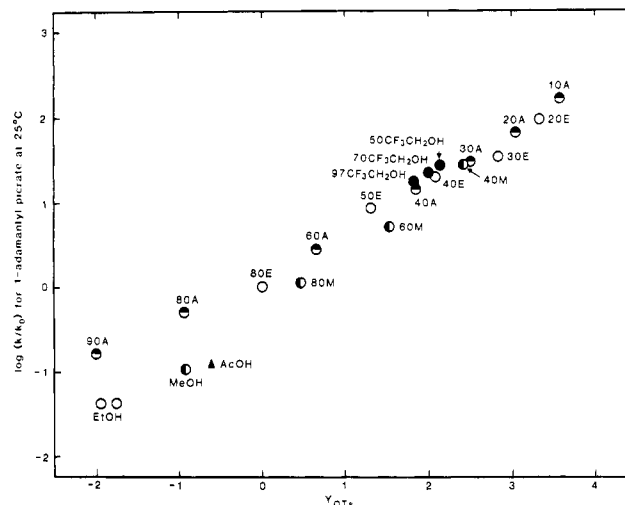


Figure 1. Logarithms of rate constants for solvolyses of 1-adamantyl picrate (1, X = O-2,4,6-trinitrobenzene) vs. Y_{OTs} ; picrate data from Table III and Y_{OTs} values from ref 2, 8, and 13a.

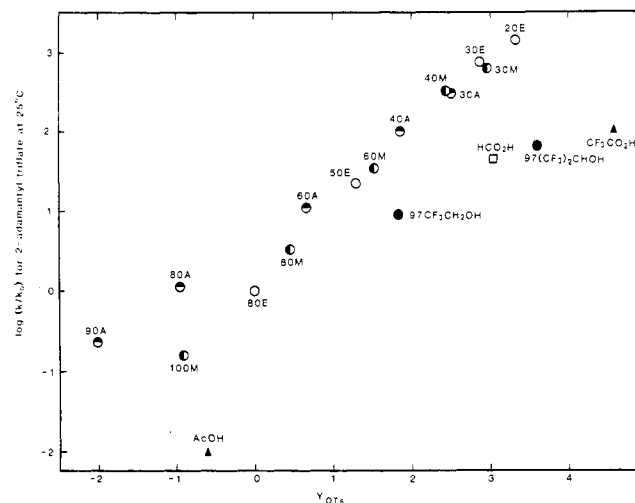


Figure 2. Logarithms of rate constants for solvolyses of 2-adamantyl triflate (2, X = OSO_2CF_3) vs. Y_{OTs} ; triflate data from Table III and Y_{OTs} values from ref 2, 8, and 13a.

media the picrate was extremely insoluble. Our rate constant for the picrate in 30% methanol/water is anomalously low (although it is reproducible), being only marginally faster than the value for 40% methanol/water (Table I). Because this value seems to be incorrect, it has been excluded from further consideration (e.g., in Figure 1 and Table IV). Also because of experimental difficulties and the unexpectedly low response to added water, the results for 2-adamantyl perchlorate in 10% (v/v) acetone/water may be inaccurate (see Figure 3). Further experiments are planned to try to improve the experimental procedure, hopefully without reducing its simplicity and convenience.

Despite considerable effort we were unable to obtain reliable rate constants and activation parameters for the solvolyses of 2-adamantyl triflate and perchlorate in 97% hexafluoroisopropyl alcohol (HFIP). The triflate solvolyses rapidly ($k \sim 1$ s⁻¹ at 0 °C), but our results at lower temperatures show an unexpectedly large temperature dependence (Table II). The results for both triflate and perchlorate were variable, and the precision of fit to first-order kinetics was much worse than expected even with injections corresponding to 5% (v/v) dioxane (though this did give some improvement). It appears that these

Table III. Rate Constants for Solvolyses of 2-Adamantyl Perchlorate (2, X = OClO₃) at 0.0 °C^a and a Summary of Y_X Values of Solvent Ionizing Power

solvent ^b	10 ⁴ k, s ⁻¹		solvent ionizing power		
	this work	ref 8	Y _{OClO₃} ^k	Y _{Pic} ^l	Y _{AdOTf} ^m
EtOH		0.0055 ⁿ	-1.83	-1.37 ^o	
80% EtOH	17.2 ± 0.1 ^p	14.9 ^{n,p}	0.00 ^q	0.00	0.00
50% EtOH	12.7 ± 0.3 ^{e,h}	33.9 ⁿ	1.53	0.92	1.35
40% EtOH	77.3 ± 1.1 ^g		2.32	1.28	2.13 ^r
30% EtOH	440 ± 20 ^g		3.07	1.53	2.9
20% EtOH	982 ± 61 ^{g,h}		3.42	1.98	3.1
MeOH		0.0541 ⁿ	-0.84	-0.97 ^s	-0.79
80% MeOH	1.46 ± 0.01 ^e	2.04 ⁿ	0.59	0.05	0.52
60% MeOH	20.7 ± 0.6 ^d	44.5 ⁿ	1.74	0.71	1.53
40% MeOH	201 ± 6 ^{g,h}		2.73	1.44	2.51
30% MeOH	426 ± 8 ^g		3.06		2.8
20% MeOH	654 ± 30 ^g		3.24		
90% (CH ₃) ₂ CO		0.541 ⁿ	0.16	-0.79 ^t	-0.64 ^u
80% (CH ₃) ₂ CO	2.13 ± 0.01 ^f		0.76	-0.29	0.04
	2.00 ± 0.01 ^{j,n}	2.36 ⁿ			
60% (CH ₃) ₂ CO	19.0 ± 0.4 ^e	21.6 ⁿ	1.71	0.44	1.03
40% (CH ₃) ₂ CO	145 ± 3 ^d		2.59	1.15	2.00
30% (CH ₃) ₂ CO	456 ± 2 ^g		3.09	1.47	2.5
20% (CH ₃) ₂ CO	890 ± 10 ^g		3.38	1.82	
10% (CH ₃) ₂ CO	1110 ± 50 ^g		3.47	2.21	
97% CF ₃ CH ₂ OH	13.1 ± 0.4 ^{d,h}	7.35 ⁿ	1.55	1.22	0.95
	272 ± 7 ^{d,p,v}				
70% CF ₃ CH ₂ OH	45.2 ± 0.1 ^{d,j}		2.08	1.34	
	42.5 ± 0.6 ^{g,j}	43.8 ⁿ			
50% CF ₃ CH ₂ OH	72 ± 2 ^{d,i}	71.5 ⁿ	2.29	1.43	
97% (CF ₃) ₂ CHOH	1700 ± 300 ^{g,i}		3.7		1.8 ^{w,x}
	7600 ± 1500 ^{g,i,y}				
AcOH		0.0148 ^z	-1.40	-0.90 ^{aa}	-2.0 ^w
HCO ₂ H					1.65 ^w
CF ₃ CO ₂ H					2.0 ^w

^{a-j} As for Table I. ^k Based on solvolyses of 2-adamantyl perchlorate (2, X = OClO₃) at 0.0 °C (eq 2); kinetic data from the adjacent columns. ^l Based on solvolyses of 1-adamantyl picrate (1, X = 0-2,4,6-trinitrobenzene) at 25.0 °C (eq 2); kinetic data from Table I. ^m Based on solvolyses of 2-adamantyl triflate (2, X = OSO₂CF₃) at 25.0 °C (eq 2); kinetic data from Table II. ⁿ Solvent also contained 2% (v/v) dioxane. ^o Calculated from data at 55 °C (ref 7a), assuming that ΔH[‡] = 25.9 kcal/mol, as observed for methanol. ^p At 25 °C. ^q Based on a rate constant of 3.73 × 10⁻⁵ s⁻¹ for solvolysis of 2-adamantyl perchlorate at 0 °C in 80% ethanol/water containing 2% dioxane. ^r Interpolated from the equation Y_{AdOTf} = 1.02 Y_{OTs} + 0.01. ^s Extrapolated from data at 45-65 °C (ref 7a). ^t Calculated from data at 50 °C (ref 7b), assuming that ΔH[‡] = 25.9 kcal/mol as observed for methanol; the solvent composition is volume percent (see correspondence quoted in Table III of ref 8). ^u Estimated from data at 25.4 °C (ref 9a). ^v Activation parameters: ΔH[‡] = 19.1 kcal/mol, ΔS[‡] = -1.8 eu. ^w Estimated from data for Y_{OTf} based on solvolyses of 7-norbornyl triflate, by adding 10% to previous values (ref 10) to allow for the greater *m* value of 2-adamantyl triflate. ^x Our approximate rate constant for 2-adamantyl triflate gives Y_{AdOTf} = 2.7. ^y At 10.0 °C. ^z Solvent also contained 2% (v/v) pentane. ^{aa} Interpolated from data at 24.6 and 45.1 °C (ref 7c).

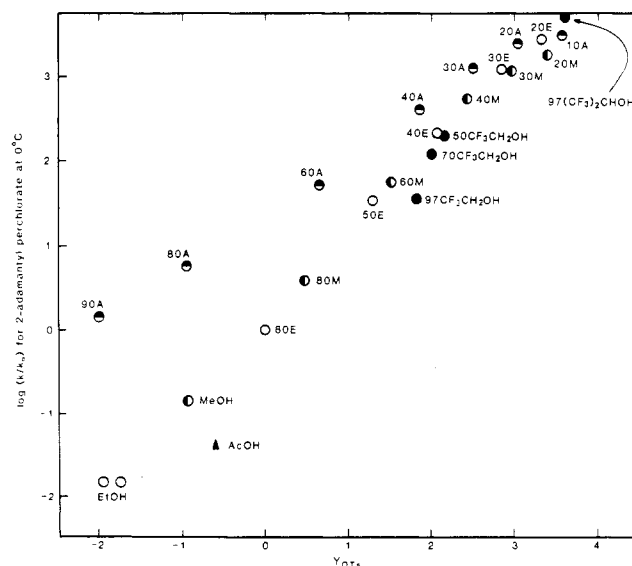
Table IV. Slopes of Correlations of Rate Data for 1-Adamantyl Picrate (Y_{Pic}), 2-Adamantyl Triflate (Y_{AdOTf}), and 2-Adamantyl Perchlorate (Y_{OClO₃}) with Data for 2-Adamantyl Tosylate^a

solvent ^b	Y _{Pic}	Y _{AdOTf}	Y _{OClO₃}
ethanol/water	0.57 ± 0.04 ^c	0.96 ± 0.06 ^{d,e}	1.04 ± 0.04 ^{c,d}
methanol/water	0.71 ± 0.02	0.95 ± 0.03 ^{d,f}	0.99 ± 0.05 ^d
acetone/water	0.55 ± 0.02	0.69 ± 0.02 ^{d,g}	0.65 ± 0.04 ^d

^a Data from Table III; see also Figures 1-3. ^b The data points are those given in Table III, and the range of compositions differ slightly for various binary mixtures and for the different leaving groups. ^c Excluding data for 100% ethanol. ^d Curvature in highly aqueous media. ^e If the data point for 20% ethanol/water is excluded, the slope becomes 1.02 ± 0.01. ^f If the data point for 30% methanol/water is excluded, the slope becomes 0.98 ± 0.02. ^g Slopes for 90% acetone/water to 60% acetone/water to 30% acetone/water are 0.63 and 0.78 respectively.

two substrates were dissolving during the kinetic run, even when there were no visible signs of inhomogeneity. This has been a problem in other studies with HFIP⁶ and is difficult to avoid if the reaction is too fast to provide time for ultrasonic destruction of the aggregates of molecules which we assume are present in the solution. Even with ultrasonic treatment of the "solutions", our studies of 1-adamantyl picrate in 97% HFIP were unsuccessful.

Comparisons with Published Data. Previous studies of 1-adamantyl picrate have been carried out by continuous

**Figure 3.** Logarithms of rate constants for solvolyses of 2-adamantyl perchlorate (2, X = OClO₃) vs. Y_{OTs}; perchlorate data from Table III and Y_{OTs} values from ref 2, 8, and 13a.

monitoring spectrophotometrically, a convenient rapid-response and sensitive technique for reactions above 0 °C.⁷ Our conductimetric results for 1-adamantyl picrate in 80%

and 50% ethanol/water at 49.1 °C agree well with those obtained by interpolation from previously published values in other ethanol/water mixtures (Table I). We have extended previous work⁷ to studies of more aqueous solvents at 25 °C, but the scope and reliability of the data was adversely affected by the extremely low solubility of 1-adamantyl picrate. In contrast, 2-adamantyl triflate appeared to dissolve rapidly and gave good conductimetric kinetic data, but the scope of our data for aqueous alcohols was affected by the high reactivity of the triflate and by the freezing of 20% v/v organic solvent/water mixtures at about -10 °C. To obtain data at 25 °C, we have assumed that values of enthalpies of activation (ΔH^\ddagger) for 30% EtOH, 20% EtOH, 30% MeOH, and 30% (CH₃)₂CO are the same as those for less aqueous mixtures. This appears to be true within ± 1 -2 kcal/mole for solvolyses of tosylates.^{2,3a,3c} Enthalpies of activation for solvolyses of 1-adamantyl and 2-adamantyl tosylates differ by ca. 8 kcal/mole (ref 2, Table III). Activation parameters for solvolyses of 2-adamantyl tosylate^{3,4a} and 2-adamantyl triflate also show consistent trends; the enthalpies of activation for the triflate are lower by an average of 5 kcal/mole, and the entropies of activation are higher by about 10 eu. If we assume that this trend is maintained for 97% HFIP, we obtain an enthalpy of activation of 13 kcal/mole for 2-adamantyl triflate (see also Table II, footnote n).

Other workers have studied solvolyses of 2-adamantyl triflate and perchlorate in binary aqueous mixtures of low ionizing power by titrimetric analyses of quenched aliquots.^{8,9} For the perchlorate only five of the eight direct comparisons (Table III) show satisfactory agreement; there are three cases of discrepancies of ca. 100%; all three of these solvents (50% EtOH, 60% MeOH, and 97% CF₃CH₂OH) are expected from previous work with other leaving groups to give good conductimetric kinetic data. Also we obtain a linear plot for logarithms of rate constants for solvolyses of 2-adamantyl perchlorate in methanol and methanol/water mixtures up to 40% versus Y_{OTs} (Table IV).

Discussion

Y_X Scales for Solvent Effects on Reactivity. Solvolytic rate data can be correlated with data for a "standard" compound with the aid of the Grunwald-Winstein equation 1.¹¹ Allowance is made for different

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

$$\log(k/k_0)_{RX} = mY_X \quad (2)$$

leaving groups (X) in equation 2. In eq 1 and 2, k refers to rates of solvolysis in any solvent relative to rates in 80% (v/v) ethanol/water (k_0). Y (eq 1) is the solvent ionizing power defined by $m = 1.000$ at 25 °C for solvolyses of *tert*-butyl chloride,¹¹ which is now thought to react with weak but significant nucleophilic solvent assistance.¹² Y_X values for each leaving group (X) have recently been defined by $m = 1.00$ (eq 2) for solvolyses of 1- and 2-adamantyl substrates (1, X = Cl,^{12a} Br,^{12a} I⁶, and Pic (picrate));⁸ 2, X = OTs^{2,13} and OCIO₃⁸). Additional Y_{OTs}

values have been obtained from solvolyses of 1, X = OTs,^{2,8} and Y_{OTf} values for triflates have been obtained from solvolyses of 7-norbornyl triflate (3).¹⁰ This range of Y_X values is needed to ensure that specific effects of leaving group solvation do not interfere with mechanistic deductions (e.g., the role of nucleophilic solvent assistance^{12a}).

All Y_X values have been defined either directly from experimental data or by interpolation or by minor extrapolation from other experimental data (e.g., at other temperatures or in other compositions of binary mixtures). Also all Y_X values are defined at 25 °C except for Y_{OCIO_3} values; because an extensive data set was initially defined at 0 °C,⁸ our additional perchlorate data (Table III) were also obtained at 0 °C. Previously calculated Y_{Pic} values referred to 49.1 °C,⁸ but as this data set was very limited, we have redetermined all of the Y_{Pic} values at 25 °C (Table III). Although the above definitions are important for precision and uniformity of data, the effects of changes in temperature on relative rates are usually too small to interpret mechanistically.

The choice of alkyl group also influences Y_X values slightly. Y_{OTs} values were originally defined from data for 2-adamantyl tosylate,^{13a} but for solvents having $Y_{OTs} < 0$, there are likely to be significant errors in extrapolations from data at higher temperatures. Alternative Y_{OTs} values can be obtained from data for 1-adamantyl tosylate,^{2,4a,8} and for ethanol both Y_{OTs} values are shown in Figures 1 and 3. Another reference substrate for sulfonates is 2-*endo*-norbornyl mesylate, which is particularly useful in highly aqueous media;^{13b} in this case allowance must be made for the low m value (0.7,^{13b} eq 2) including the possibility that this substrate is susceptible to nucleophilic assistance.¹⁴ Eight Y_{OTf} values have been calculated from solvolyses of 7-norbornyl triflate (3),¹⁰ which also has a lower m value than 2-adamantyl triflate (2, X = OSO₂CF₃).¹⁵ It may be mechanistically significant that m values decrease in the order: 1-adamantyl ($m = 1.06 \pm 0.03$),² 2-adamantyl ($m = 1.00$ by definition), and 7-norbornyl ($m = 0.9$);¹⁵ an early mechanistic proposal that 7-norbornyl systems solvolyse with anchimeric assistance^{16a} (and hence with an increase in charge delocalisation which reduces m values^{3b,14a}) has recently been rejuvenated.^{16b} Hence, previously reported Y_{OTf} values based on solvolyses of 7-norbornyl triflate are not directly comparable with the Y_{AdOTf} values given in Table III.

Sufficient data is now available to evaluate trends in the various Y_X values. Correlations of Y_{Pic} , Y_{AdOTf} , and Y_{OCIO_3} vs. Y_{OTs} (Figures 1-3) illustrate the effect of maintaining a constant charge-bearing atom (oxygen) while changing the extent of charge delocalization in the leaving group. Details of slopes are shown in Table IV and the nonlinearity of correlations for aqueous acetone is discussed below (see lipophilic effects).

Y_{OTf} values correlate with Y_{OTs} values (Figure 2) with close to unit slope and with little dispersion of correlation lines over the following ranges of binary mixtures: methanol to 30% methanol/water; 80% ethanol/water to 20% ethanol/water; 40% and 30% acetone/water. Data for less aqueous acetone/water mixtures deviate substantially and give a much lower m value (0.63, eq 2), in satisfactory

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(12) (a) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* 1982, 104, 5741. (b) Kevill, D. N.; Kamil, W. A.; Anderson, S. W. *Tetrahedron Lett.* 1982, 4635. (c) Bunton, C. A.; Mhala, M. M.; Moffatt, J. R. *J. Org. Chem.* 1984, 49, 3639.

(13) (a) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1976, 98, 7667. (b) Allard, B.; Casadevall, E. *Nouv. J. Chim.* 1983, 7, 569.

(14) (a) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1981, 103, 5466. (b) Banert, K.; Kirmse, W. *Ibid.* 1982, 104, 3766.

(15) An m value of 0.9 is estimated from data in the range 100% EtOH to 50% EtOH/H₂O—see Table II and ref 10.

(16) (a) Winstein, S.; Gadiant, F.; Stafford, E. T.; Klinedinst, P. E., Jr. *J. Am. Chem. Soc.* 1958, 80, 5895; but see also: Miles, F. B. *Ibid.* 1968, 90, 1265 and Sunko, D. E.; Vancik, H.; Deljac, V.; Milun, M. *Ibid.* 1983, 105, 5364. (b) Gassman, P. G.; Hall, J. B. *Ibid.* 1984, 106, 4267.

agreement with the value of 0.60 (eq 1) reported previously.^{9a} Similarly low m values have been discussed for solvolyses of 7-norbornyl triflate (3) in correlations with Y_{OTs} .¹⁰ If correlations for a wide range of solvents (e.g., ethanol/water mixtures having low Y_{OTs} values, fluorinated alcohols, and carboxylic acids) are attempted with eq 2 when the leaving groups differ (e.g., see Figure 2), imprecise correlations and atypical m values may result. More reliable m values can be determined from similar solvents of varying ionizing power e.g., ethanol/water mixtures (m_{EW} ^{3b}) or acetic and formic acids (m_{AF} ^{3b}). Whiting has pointed out that the choice of ethanol/water mixtures for extensive solvolytic studies was unfortunate because of nonideality.^{7b} Methanol/water mixtures give more closely linear correlations (based on eq 2) than ethanol/water mixtures.^{3a,6,12a} Therefore, we suggest that the best guide to m values may be obtained from a wide range of compositions of methanol/water (i.e., m_{MW} values). A disadvantage of this suggestion is that the solubilities of many organic compounds are less in methanol/water than in corresponding v/v ethanol/water mixtures.

In previous correlations of solvolysis rates for 2-adamantyl perchlorate,⁸ downward curvature for aqueous trifluoroethanol mixtures was observed, in agreement with our results (Figure 3); other binary aqueous mixtures were reported to curve upwards in correlations with Y (eq 1). Our results for Y_{OTs} (Figure 3) show a consistent pattern of downward curvature for all binary aqueous mixtures, but particularly for aqueous trifluoroethanol as data for all binary aqueous mixtures should converge towards the value for pure water (expected to be close to the data points for 20E, 20M, and 10A in Figure 3).^{12a,17}

The dispersion of results for various solvent compositions, particularly carboxylic acid solvents, fluorinated alcohols, and high percentage acetone/water mixtures (Figures 1–3) provides further justification for the selection of individual Y_X values for each combination of solvent and leaving group.^{6,8,9b,10,12a} A more fundamental approach would require explicit, quantitative consideration of several contributing effects, discussed qualitatively below.

Electrostatic Solvation Effects. It has long been recognized as a general qualitative principle that a more polar solvent will accelerate or retard a reaction depending on whether the transition state is more or less polar than the initial state.^{18,19} More quantitative extensions of this principle include: (i) the suggestion that the solvation effects of polar solvents are expected to decrease with increasing dispersal of charge;¹⁹ (ii) extensive discussion of m values (eq 1) as probes of the extent of charge delocalization in transition states;¹ (iii) the effects of added salts on reactions of different charge types.²⁰

The great importance of electrostatic effects is apparent from comparisons of solvolyses of substrates having neutral leaving groups with those having anionic leaving groups. Many heterolytic reactions of salts (e.g., trialkyl sulfonium salts, having neutral dimethyl sulfide as the leaving group) show the expected very small rate effects of an increase in solvent polarity. However, not all these reactions show the expected slight decrease in rate.^{12b} Heterolytic reactions of neutral substrates having anionic leaving groups

show large rate increases as solvent polarity increases (e.g., Table III). The effect of changes in dispersal or delocalization of charge is most evident for picrates (Figure 1, Table IV), because the negative charge can be delocalized from the phenolic oxygen atom onto the three nitro groups, each of which are separated by three carbon atoms. A similar, but less marked, effect was noted for the series chloride, bromide, and iodide.^{6,21}

If we assume that the anomalous behaviour of acetone/water mixtures (Table IV) is a specific solvation effect (see below), the changes in electrostatic effects can be based on data for alcohol/water mixtures. Slopes of correlations vs. Y_{Cl} (slope 1.00, by definition) would then be: for Y_{Br} (vs. 0.96⁶); Y_I (0.85⁶); Y_{OTs} (0.80⁶); Y_{AdOTf} (0.77); Y_{OCIO_3} (0.82). The similarity of slopes for the latter four Y_X scales is surprising and raises the hopeful and attractive prospect that slopes for S_N1 reactions involving other leaving groups (e.g., carboxylates, phosphates, and phosphonates) will also be similar. Considerable electrostatic stabilization may be provided in an ion pair transition state by interactions between the cation and the anion. Such effects have been proposed to account for the polar character of gas phase reactions.²³ In solution the charges will be greater but the stabilization energy will be reduced (because of the dielectric constant of the solvent), which may help to account for the similar slopes of correlations for the various leaving groups.

In the following two sections we will discuss deviations from the correlation lines for alcohol/water mixtures in terms of specific solvation (nonelectrostatic) effects and/or mechanistic changes. It will be assumed that for all solvents the electrostatic effects of charge delocalization in each of the various leaving groups are correlated by the slope of the appropriate line for alcohol/water mixtures. As this assumption is only approximate, deviations less than ca. twofold in rate from the expected correlation lines will not be considered to be significant.

Electrophilic Solvation Effects. The most well established electrophilic effects on the rates of nucleophilic substitutions are those caused by acids or by metal ions.²⁴ However, because hydrogen bonding to anions is also well established, it might at first be considered self-evident that Y_X values (Table III) will be affected by such electrophilic effects.^{25c} The situation is not so straightforward. Y_X values represent perturbations of reactivity relative to data for 80% ethanol/water. Also these changes are due to differences in solvation between initial and transition states. Hence a large solvation effect on the initial state will not affect reactivity if it is unchanged in magnitude in the transition state. Even if there is a large difference in solvation between initial and transition states, Y_X values will be unchanged if the change in solvation is the same as for 80% ethanol/water. Furthermore we have questioned alternative approaches to this problem based on solvatochromism, as a probe of solvent effects on reactivity; there are significant complications attributed to destabilization of the electronically excited states, which con-

(21) For a recent discussion of the solvation of halide ions see ref 22.

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(17) The exact shape of the graph in this region requires further study, particularly the small change in rate observed from 20% acetone/water to 10% acetone/water.

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Table V. Solvolytic Rate Data for Adamantyl Substrates at 25 °C and Leaving Group Effects on Reactivity

solvent ^a	1-AdOMs ^b	OTs/ OMs ^c	1-AdOTs ^d	OTs/Cl ^e	OTs/Br ^e	OTs/I ^f	OTs/Pic ^g	2-AdOTs ^h	OTs/ OTf ⁱ	OTs/ OCIO ₃ ^j
EtOH			4.4×10^{-5}	1.8×10^6	4.4×10^4	1.2×10^4	5.3	4.3×10^{-10}		1.4×10^{-5}
80% EtOH	4.17×10^{-3}	1.2	4.0×10^{-3a}	5×10^5	1.4×10^4	6.9×10^3	21	2.4×10^{-8}	1.4×10^{-6}	1.4×10^{-5}
50% EtOH	1.86×10^{-1}	0.5	9.3×10^{-2}	1.1×10^5	4.4×10^3	2.6×10^3	58	4.7×10^{-6}	1.2×10^{-5}	
MeOH	2.81×10^{-4}	1.7	4.8×10^{-4}	9.6×10^5	2.3×10^4	5.7×10^3	23	2.9×10^{-9}	1.1×10^{-6}	1.3×10^{-5}
80% (CH ₃) ₂ CO			4.6×10^{-4}	3.8×10^5	7.7×10^3	1.2×10^3	4.7	3.1×10^{-9l}	1.7×10^{-7}	
20% (CH ₃) ₂ CO	5.0	1.3	6.5	1.4×10^5	5.0×10^3	3.6×10^3	512	2.7×10^{-5m}		
97% CF ₃ CH ₂ OH	3.5×10^{-1}	1.4	4.9×10^{-1n}	9.1×10^4	5.2×10^3	5.1×10^3	151	1.6×10^{-6p}	1.1×10^{-5}	5.9×10^{-5}
97% (CF ₃) ₂ CHOH		0.78 ^o	27	2.8×10^4	3.0×10^3	6.8×10^3		9.7×10^{-5p}	1.2×10^{-5}	
AcOH			5.1×10^{-4}	2.6×10^6	2.4×10^5	1.4×10^5	21	5.9×10^{-9}	3.5×10^{-5}	1.2×10^{-4}
HCO ₂ H			6.7	5.2×10^5	8.1×10^4	2.7×10^5		2.7×10^{-5}	3.6×10^{-5}	
CF ₃ CO ₂ H			282	9.4×10^5				9.0×10^{-4}	5.3×10^{-4}	

^a Solvent codes as footnote b, Table I. ^b Rate constants (s⁻¹) for solvolyses of 1-adamantyl mesylate at 25 °C—data from ref 2. ^c Tosylate/mesylate rate ratios, assumed to depend slightly on the solvent, but not on the alkyl group in the substrate—see reference 3a. ^d Rate constants (s⁻¹) for solvolyses of 1-adamantyl tosylate at 25 °C—data from reference 4a when $k \leq 10^{-3}$ s⁻¹ and from OTs/OMs rate ratios when $10^{-3} \leq k \leq 10^{-1}$ s⁻¹; other values from eq 3. ^e Kinetic data for 1-adamantyl chloride and bromide, and Br/Cl rate ratios given in ref 12a. ^f Kinetic data for 1-adamantyl iodide and I/Br rate ratios given in ref 6. ^g Kinetic data for 1-adamantyl picrate from Table I and Table III. ^h Rate constants (s⁻¹) for solvolyses of 2-adamantyl tosylate at 25 °C—data from ref 13a. ⁱ Kinetic data for 2-adamantyl triflate from Tables II and III. ^j Kinetic data for 2-adamantyl perchlorate from Table III and ref 8. ^k Slightly higher values are predicted from the OTs/OMs rate ratio—other data: $k = 4.24 \times 10^{-3}$ s⁻¹ (ref 29a) and $k = 5.73 \times 10^{-3}$ s⁻¹ (ref 29b). ^l Calculated from eq 3. ^m Reference 3a. ⁿ Data extrapolated from -10 °C gives $k = 9.2 \times 10^{-1}$ s⁻¹ (ref 29c). ^o Reference 5a. ^p Lower rate constants have been obtained spectrophotometrically; for 97% CF₃CH₂OH $k = 1.02 \times 10^{-6}$ (ref 29d) and for 97% (CF₃)₂CHOH $k = 8.68 \times 10^{-5}$ (ref 14a and 7.97×10^{-5} (ref 29d).

tribute substantially to the observed solvent effects.^{6,25}

Electrophilic solvation effects might be considered to be likely contributors to the Y_X values of carboxylic acids and of fluorinated alcohols (trifluoroethanol and HFIP have high α values for hydrogen bond donation^{25c}). However, we reported recently that Y_{Cl}, Y_{Br}, Y_I, and Y_{OTs} values did not show significant effects of solvent electrophilicity for the fluorinated alcohols.⁶ Only carboxylic acid solvents showed significant deviations: e.g., when compared with Y_{Cl}, tosylates reacted slightly faster than expected whereas bromides and iodides reacted more slowly than expected.⁶ Although adamantyl fluorides have not yet been examined, there is good evidence that electrophilic effects for fluorides are even greater than for tosylates.^{11b} This consistent order of susceptibility to electrophilic effects F > OTs > Cl > Br > I can be explained by differences of electronegativity between the atoms on which the negative charge is developing.^{1a} In the present work (Figures 1–3), this atom is kept constant and charge develops on negatively charged oxygen. Hence the effect of other groups close to the reaction site but within the leaving group can be examined. The results for picrates (acetic acid and 97% CF₃CH₂OH, Figure 1) and perchlorates (acetic acid, 97% CF₃CH₂OH, and HFIP, Figure 3) show only one small but significant deviation from the expected correlations (acetic acid, Figure 3). These results imply that electrophilic effects are determined largely by the electronegativity of the atom on which charge develops.

There may be a major exception to the above generalization. Y_{AdOTf} (Figure 2) shows major deviations for fluorinated alcohols and carboxylic acids—the largest deviations encountered in the whole series of Y_X values. It was proposed¹⁰ that the decreased rates of triflate solvolyses may reflect reduced electrophilic catalysis in loss of the weakly basic triflate group. While this argument is plausible, it is perhaps surprising that the deviations for perchlorates are very much smaller (perchlorate ion is also weakly basic). There are at least two other possible explanations. There may be a destabilizing solvation effect between part of the triflate anion (e.g., the CF₃ group) and acidic solvents. Such solvation effects, corresponding to rate factors of three, have been proposed for mesylates and tosylates in alcohol/water mixtures^{3a} (see also Table V). Alternatively 2-adamantyl triflate may undergo significant ion pair return, whereas the very low nucleophilicity of perchlorate is thought to prevent ion pair return (e.g., the

special salt effect²⁶). Further it could be argued that the results in Figure 3 support our previous evidence that Y_{OTs} is not significantly affected by ion pair return.^{3b,14a} The small deviations from Figure 3 (e.g., for acetic acid) are in the opposite direction from those expected if ion pair return were affecting Y_{OTs}.

A more complex alternative explanation is that the deviations of electrophilic solvents from Figure 2 may be due to both internal return and reduced electrophilic assistance. It may then be argued that (i) Y_{OCIO₃} values are anomalously low because of reduced electrophilic assistance—e.g., see minor deviations of AcOH and 97% CF₃CH₂OH from Figure 3; (ii) Y_X values other than Y_{OCIO₃} and Y_{AdOTf} include small and similar⁶ contributions from electrophilic assistance in fluorinated alcohols. If electrophilic solvation helps to reduce the magnitude of ion pair return,^{1b} and this solvation is reduced for triflates, they may be unusually susceptible to ion pair return in strongly electrophilic (weakly nucleophilic) solvents. This could account for the exceptionally high k_a/k_t ratio observed for solvolyses of PhCH(OTf)CF₃ in HFIP.²⁷

Lipophilic Solvation Effects. Perchlorate ion has a much higher lipophilicity than tosylate, bromide, or chloride ion.^{8,28} For solvolyses of 2-adamantyl perchlorate it has been proposed that the deviation of the acetone/water correlation line from the alcohol/water correlation line (Figure 3) may be due to lipophilic effects.⁸ However, the picrate anion has an even higher lipophilicity than perchlorate ion,⁸ yet shows much smaller deviations (Figure 1). In the region 60–90% acetone/water, deviations of data points are similar for triflate (Figure 2) and picrate (Figure 1). It appears that these deviations may be due to anomalous behaviour of tosylates. This is supported by the absence of deviations in a plot of Y_{Pic} vs. Y_I (Figure 4). However, iodide is much more lipophilic than chloride,

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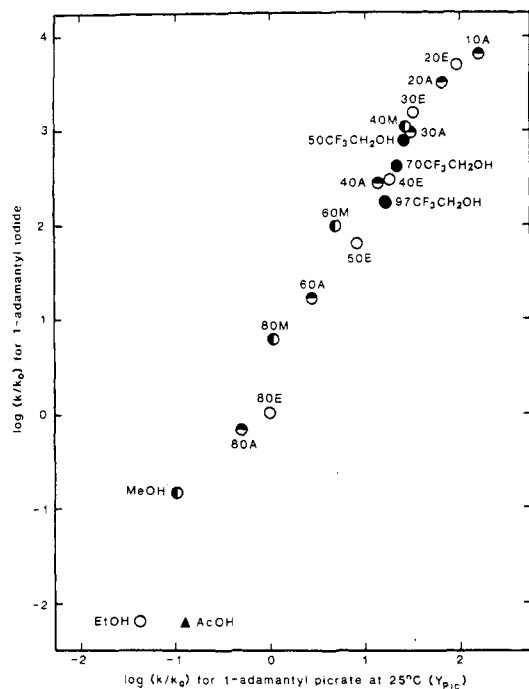


Figure 4. Logarithms of rate constants for solvolyses of 1-adamantyl iodide (1, X = I) vs. logarithms of rate constants for solvolyses of 1-adamantyl picrate; data from ref 6 and Table III.

bromide, or tosylate.²⁸ More convincing evidence would require Y_{Cl} and Y_{Br} values for high percentage acetone/water (e.g., 80%), but at present only extrapolated values are available.^{12a}

The high reactivity of perchlorates in aqueous acetone accounts at least in part for deviations from Figure 3. As this solvent is partially aprotic, it may provide less electrophilic assistance than aqueous alcohols. This could lead to small contributions from ion pair return for all adamantyl substrates except perchlorate. Alternatively there may be a specific solvation effect for perchlorates, one example of a potentially general situation arising "when leaving groups of differing solvation requirements are compared in solvent systems in which the two solvent components cannot play equivalent roles in interaction with an incipient anion."^{7a}

Leaving Group Effects. Relative rates of solvolyses of adamantyl substrates (Table V) show large effects of changes in solvent (ca. 100-fold). Some of the data is referred to 25 °C by extrapolations from data at higher or lower temperatures, and by short extrapolations based on eq 1 (for similar solvents) and on the relationship between the reactivity of 1- and 2-adamantyl tosylate (eq 3).² A consequence of the slope term in eq 3 (1.06 ± 0.03) is that

$$\log(k/k_0)_{1-AdOTs} = 1.06 \log(k/k_0)_{2-AdOTs} \quad (3)$$

the ratios given in Table V are slightly dependent on whether the tosylate data is derived from 1- or 2-adamantyl. Steric differences between secondary and tertiary systems also contribute significantly to OTs/Br rate ratios^{30a} and probably to other ratios.^{30b}

Conclusion

The main solvent effects on the reactivity of adamantyl chlorides, bromides, iodides, picrates, perchlorates, and tosylates can be rationalised by three generalizations:

(1) The major effects are electrostatic and depend on the degree of charge delocalization in the anionic leaving group.

(2) For carboxylic acid solvents there are significant contributions from electrophilic effects, which depend on the electronegativity of the atoms in the leaving group on which charge develops, i.e., O^- (tosylates, perchlorates, picrates) $> Cl^- > Br^- > I^-$.

(3) For fluorinated alcohols, expected from α values to show large effects of hydrogen bond donation,^{25c} there are no significant deviations from the expected correlations. This generalization further supports our previous arguments^{12a,14a} that fluorinated alcohols influence relative rates by showing lower nucleophilic effects than other alcohols (rather than showing greater electrophilic effects).

Major deviations from the expected correlations are shown by triflates in fluorinated alcohols and in carboxylic acids. Less substantial deviations for perchlorates (anomalously rapid) and tosylates (anomalously slow) in high percentage acetone/water mixtures may possibly be due to lipophilic effects, but evidence to the contrary is that the most lipophilic leaving group (picrate) shows a smaller effect than perchlorate. There are other, more subtle, solvation effects. Hence for mechanistic investigations we emphasise that comparative studies of solvent effects on heterolytic reactivity should be restricted to substrates having the same leaving group.

Experimental Section

Chemicals. 1-Adamantyl picrate (1, X = O-2,4,6-trinitrobenzene), prepared from 1-adamantanol (1, X = OH) and picryl fluoride in the presence of DABCO, was recrystallized from dichloromethane and was checked for purity by TLC; mp 148–151 °C (lit.^{7c} mp 149–150.5 °C). Picryl fluoride was obtained in 20% yield of purified product under slightly different reaction conditions from those previously reported^{7c}—we nitrated 2,4-dinitrofluorobenzene at 144 °C for 24 h. 2-Adamantyl perchlorate (2, X = OClO₃) was prepared as described previously,⁸ and stored in dioxane solution at room temperature in a Wheaton bottle fitted with a Mininert valve. After storage for over six months, a kinetic study in 80% ethanol/water at 25 °C showed about 50% decomposition to rapidly ionizing product(s), followed by excellent first order kinetics in agreement with the rate constant obtained with fresh substrate (Table III). 2-Adamantyl triflate was prepared in ca. 50% yield by literature methods^{9a} and stored at -4 °C in frozen dioxane or as a solid alone; mp about 20 °C; ¹H NMR in CCl₄ gave $\delta = 5.1$ (not 5.9^{9a}). The samples turned from yellow-brown to dark brown on cold storage over 4 mo and solvolyses in 80% acetone/water at 25 °C (repeated periodically) showed gradual decomposition to rapidly ionizing product(s). Samples, removed from storage weekly and kept in sample tubes at room temperature, decomposed much more rapidly. Solvents were obtained and/or purified as described previously.⁶

Kinetic Methods. Substrates dissolved in dioxane were injected rapidly into rapidly stirred thermostatted solutions (a method of mixing currently *not* superior to the manually operated, shaker technique previously described²). Conductimetric data were collected by a computer-controlled, high precision, digital voltmeter (SOLARTRON 7066), as described in detail elsewhere.^{5b} Experimental techniques have now been adapted so that kinetic data for fast reactions can be obtained with small volumes of solution (2–3 mL).

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Registry No. 1 (X = O-2,4,6-trinitrobenzene), 21623-87-0; 1 (X = OH), 768-95-6; 2 (X = OSO₂CF₃), 61242-41-9; 2 (X = OClO₃), 83187-55-7; picryl fluoride, 364-44-3.

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