The SN2–SN1 Spectrum. 1. Role of Nucleophilic Solvent Assistance and Nucleophilically Solvated Ion Pair Intermediates in Solvolyses of Primary and Secondary Arenesulfonates

T. William Bentley and Paul v. R. Schleyer*

Contribution from the Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP, United Kingdom, and the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received January 5, 1976*

Abstract: Rates of solvolysis of 2-adamantyl tosylate in acetic acid, formic acid, trifluoroacetic acid, and mixtures of ethanol and water are compared with those for simple primary and secondary substrates: methyl, ethyl, 2-propyl, 2-butyl, 2-pentyl, 3-pentyl, 4-heptyl, cyclopentyl, and cyclohexyl. Application of various mechanistic criteria (m, m_{AF}, $[k_{EtOH/H_2O}/k_{RCO_2H}]_Y$, α-deuterium isotope effect) shows that there is a gradation or merging of mechanism and reactivity from methyl to 2-adamantyl tosylate. The sensitivity to solvent ionizing power, m, decreases *proportionately* as the sensitivity to solvent nucleophilicity $[k_{EtOH/H_2O}/k_{RCO_2H}]_Y$ increases. Solvolysis rates of 2-adamantyl tosylate are shown to be insensitive to solvent nucleophilicity and ion pair partitioning effects, and the mechanism probably involves rate-determining formation of an intimate ion pair intermediate (SN1). Ionization of the minimally hindered methyl tosylate is strongly nucleophilically assisted, and no ion pair intermediates are formed (i.e., concerted SN2 mechanism). Merging of mechanism between these two substrates probably proceeds by rate-determining heterolysis with varying amounts of nucleophilic solvent assistance (Scheme I), depending largely on steric factors, and may involve nucleophilically solvated intimate ion pair intermediates. If there is evidence for an intermediate as well as evidence for nucleophilic solvent assistance, the mechanism is designated by the new term SN2 (intermediate). Alternative mechanisms, which do not consider nucleophilic solvation of ion pair intermediates (e.g., Sneen et al., 1969; Shiner et al., 1969) are discussed and criticized.

The solvolysis of simple secondary substrates[1] has always been difficult to fit into the SN1–SN2 framework.[2a,3-7] Although these reactions exhibit carbenium ion character, there is overwhelming evidence that free, dissociated carbenium ions are not involved in solvents such as ethanol, water, and acetic and formic acids. Common ion rate depression is not observed,[8] and the products depend on the leaving group.[9] Direct substitution by solvent is now known to proceed with the complete inversion of configuration characteristic of SN2 reactions.[11-13] Therefore competition between SN1 and SN2 processes, which could lead to partial racemization, is difficult to justify. A spectrum of behavior between SN1 and SN2 possibly involving intermediate mechanisms seems most likely.[4,14] While the role of ion pair intermediates has recently received much attention,[6,15-19] and these may well be present, we believe instead that varying degrees of nucleophilic solvent assistance[20] to ion pair formation provide the key to the solution of the problem.[21-23]

Sneen and co-workers[15] have proposed a unification of SN1 and SN2 mechanisms, all proceeding via intimate ion pair intermediates (not nucleophilically solvated). In the extremes, nucleophilic attack on such ion pairs may be rate limiting (SN2) or may be rapid relative to ion pair return (SN1). This would demand that in SN2 reactions return to covalent starting material (internal return) occurs much more rapidly than nucleophilic attack.[15b,24] However, Sneen's interpretations and his evidence have been criticized extensively,[6b,6c,6e,13c,22g,25] and his conclusions appear to be invalid for simple primary and secondary substrates.

Shiner and co-workers[16,17] have also suggested that solvolyses of simple secondary substrates may proceed through intimate ion pair intermediates (again not nucleophilically solvated), which preferentially collapse to covalent starting material much more rapidly and much more often than they dissociate or react with nucleophiles. Because of the "tightness" of this ion pair, such internal return would not be detected by standard techniques such as racemization of, or ^{18}O exchange in, sulfonates recovered after partial reaction;[19] hence the term "hidden return" has been proposed. A new mechanism for anchimeric assistance involving such "hidden return" has been postulated: titrimetric rates (i.e., the observed rates of formation of strong acid) are not enhanced by participation during intimate ion pair formation but by rapid rearrangement of the ion pair preventing hidden return.[15c,17c,18] Shiner's evidence for hidden return and his mechanistic conclusions have also been criticized.[6b,6c,22j,25d]

In order to understand the rates and mechanisms of secondary solvolyses, it is necessary to evaluate the importance of nucleophilic solvent assistance[20] and hidden ion pair return. We have done this by studying the effect of solvents of varying nucleophilicity and ionizing power on solvolysis rates. Our approach has the advantage that the abilities of the two explanations to account for experimental data are compared directly. Also a study of solvent effects involves small and potentially continuous changes in the reaction under investigation.

Results

We studied solvolyses of some of the simplest acyclic and alicyclic arenesulfonates, i.e., methyl, ethyl, 2-propyl, 2-butyl, 2-pentyl, 3-pentyl, 4-heptyl, cyclopentyl, and cyclohexyl in trifluoroacetic acid, formic acid, acetic acid, and mixtures of ethanol and water. New data for solvolyses in ethanol/water and formic acid are given in Table I. Previously reported data for 2-adamantyl, our model system, have been checked independently and revised for solvolysis in formic acid and 50% v/v ethanol/water (Table II). The rate of solvolysis of 2-adamantyl tosylate in trifluoroacetic acid, originally obtained by conductivity[22c] (a questionable procedure), was redetermined by Hall[22f] by ultraviolet spectroscopy; his revised value (about four times slower) is preferred to the earlier one. Much of the required data has already been reported by others and is reviewed critically here (Table III). Data for methyl and ethyl tosylate are collated in the following paper.[26]

* Address correspondence to the Institute für Organische Chemie, Universität Erlangen-Nürnberg, Henkestr. 42, 8520 Erlangen, West Germany.

Table I. Solvolysis Rate Constants of Secondary Alkyl Tosylates[a]

Substrate	Solvent[b]	T, °C	k, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
2-Propyl	80% EtOH	75.4[d]	6.88×10^{-4}		
		49.65[d]	5.30×10^{-5}	21.7	−11.1
		25[c]	2.99×10^{-6}		
		25[c,e,f]	2.94×10^{-6}	21.7	−11.1
	50% EtOH	49.65[g]	$(2.82 \pm 0.03) \times 10^{-4}$	21.9	−7.0
		30.14[g]	$(2.94 \pm 0.04) \times 10^{-5}$		
		25[c]	1.54×10^{-5}		
		25[e]	1.47×10^{-5}	22.3	−6.0
	HCO_2H	24.94[d]	$\sim 2.1 \times 10^{-5}$		
		24.94[h,i]	$(2.25 \pm 0.04) \times 10^{-5}$		
		25[c]	2.28×10^{-5}		
		25[j]	2.38×10^{-5}		
2-Butyl	80% EtOH	75.0	$(8.48 \pm 0.06) \times 10^{-4}$		
		49.65[i]	$(6.80 \pm 0.15) \times 10^{-5}$	21.7	−10.6
		30.06	$(7.10 \pm 0.05) \times 10^{-6}$		
		25[c]	3.81×10^{-6}		
	50% EtOH	49.65	$(4.24 \pm 0.01) \times 10^{-4}$	22.2	−5.2
		29.95	$(4.28 \pm 0.08) \times 10^{-5}$		
		25[c]	2.23×10^{-5}		
2-Pentyl	80% EtOH	75.4[g]	$(7.40 \pm 0.13) \times 10^{-4}$		
		49.65	$(5.68 \pm 0.07) \times 10^{-5}$	21.8	−10.6
		30.07[d]	5.91×10^{-6}		
		29.95[d]	5.7×10^{-6}		
		25[c]	3.12×10^{-6}		
	50% EtOH	49.65	$(3.45 \pm 0.04) \times 10^{-4}$	21.8	−7.1
		29.95	$(3.57 \pm 0.04) \times 10^{-5}$		
		25[c]	1.93×10^{-5}		
3-Pentyl	80% EtOH	75.4	$(1.22 \pm 0.04) \times 10^{-3}$		
		49.65	$(1.04 \pm 0.01) \times 10^{-4}$	21.0	−12.0
		30.06	$(1.21 \pm 0.03) \times 10^{-5}$		
		25[c]	6.34×10^{-6}		
	50% EtOH	49.65	$(6.69 \pm 0.02) \times 10^{-4}$	21.0	−8.3
		29.95	$(7.51 \pm 0.04) \times 10^{-5}$		
		25[c]	4.14×10^{-5}		
4-Heptyl	80% EtOH	75.0[g]	$(9.64 \pm 0.07) \times 10^{-4}$		
		49.65	$(7.72 \pm 0.11) \times 10^{-5}$	21.5	−10.8
		30.06	$(8.35 \pm 09) \times 10^{-6}$		
		25[c]	4.47×10^{-6}		
	50% EtOH	49.65	$(4.75 \pm 0.02) \times 10^{-4}$		
		30.06	$(5.15 \pm 0.01) \times 10^{-5}$	21.5	−7.2
		29.95	$(5.00 \pm 0.05) \times 10^{-5}$		
		25[c]	2.74×10^{-5}		
Cyclohexyl	80% EtOH	75.05[d]	3.26×10^{-4}		
		49.65	$(1.96 \pm 0.06) \times 10^{-5}$		
		29.95[d,k]	1.48×10^{-6}		
		25[c]	7.54×10^{-7}		
		30[c]	1.51×10^{-6}	24.4	−4.6
		30[l]	1.65×10^{-6}	22.8	−10
	60% EtOH	75.1	$(1.36 \pm 0.05) \times 10^{-3}$		
		49.65	$(8.15 \pm 0.4) \times 10^{-5}$		
		29.95[d,k]	6.83×10^{-6}		
		25[c]	3.46×10^{-6}		
		30[c]	6.85×10^{-6}	24.0	−3.2
		30[l]	7.2×10^{-6}	22.9	−8.0
	50% EtOH	75.2	$(2.76 \pm 0.02) \times 10^{-3}$		
		49.66	$(1.84 \pm 0.02) \times 10^{-4}$		
		30.20	$(1.70 \pm 0.02) \times 10^{-5}$		
		25[c]	8.58×10^{-6}	23.1	−4.2

[a] Determined conductometrically in duplicate, except where noted otherwise. [b] Volume percent. [c] Calculated from data at other temperatures. [d] One measurement of rate constant. [e] Reference 60a. [f] Reference 22g. [g] Average rate constant for four independent measurements. [h] Determined by potentiometric titration with 0.028 M sodium acetate in acetic acid. [i] Average rate constant for three independent measurements. [j] Reference 23b. [k] Determined by titration of 0.13 M solution with NaOH. [l] D. D. Roberts, *J. Org. Chem.*, **33**, 118 (1968).

Discussion

Solvent Effect on Relative Rates. It is common to discuss the solvent effect on relative rates using the mY equation of Winstein and Grunwald:[4,27]

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

The fixed parameter, Y, the "ionizing power" of the solvent is defined by $m = 1$ for solvolysis of *tert*-butyl chloride at 25 °C; 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).[28]

When solvolysis rates for different binary mixtures of solvents are correlated by eq 1, the well-known phenomenon of

Table II. Solvolysis Rate Constants of 2-Adamantyl Tosylate[a]

Solvent[b]	T, °C	k, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
80% EtOH	49.65[d]	8.55×10^{-7}		
	49.65[d,e]	8.24×10^{-7}		
	50[c,f]	8.82×10^{-7}	26.9	−3.0
	25[c,f]	2.41×10^{-8}		
60% EtOH	100.90[d]	2.25×10^{-3}		
	84.43	$(4.45 \pm 0.06) \times 10^{-4}$		
	75.15	$(1.51 \pm 0.03) \times 10^{-4}$	26.7	+0.5
	49.67	$(6.89 \pm 0.06) \times 10^{-6}$		
	25[c]	2.0×10^{-7}		
	25[c,f]	$[2.49 \times 10^{-7}]$	[25.7]	[−2.4]
50% EtOH	100.4[g]	$>4.7 \times 10^{-3}$		
	100[c]	5.3×10^{-3}		
	84.43[d]	1.04×10^{-3}		
	75.16	$(3.77 \pm 0.07) \times 10^{-4}$	26.8	+2.3
	49.65[h]	$(1.63 \pm 0.07) \times 10^{-5}$		
	25[c]	4.7×10^{-7}		
	25[c,f]	$[7.7 \times 10^{-7}]$	[24.8]	[−3.4]
90% EtOH	100.9[d,e]	8.32×10^{-5}		
	75.2[d,e]	5.33×10^{-6}	27.0	−5.6
	25[c]	6.4×10^{-9}		
EtOH	25[c,i]	4.3×10^{-10}	29.6	−2.2
HCO_2H	49.67[j]	$(7.00 \pm 0.22) \times 10^{-4}$		
	24.94[j]	$(2.63 \pm 0.04) \times 10^{-5}$	24.8	+3.6
	24.94[d]	2.5×10^{-5}		
	25[c,j]	2.65×10^{-5}		
	25[k]	2.75×10^{-5}		
	25[c,f,l]	$[1.16 \times 10^{-5}]$	[25.9]	[+5.6]
CF_3CO_2H	25[m]	9.0×10^{-4}		
	25[f,l]	$[3.67 \times 10^{-3}]$	[16.6]	[−13.9]
CH_3CO_2H	25[c,f,n]	5.9×10^{-9}	28.1	−2.1

[a] Determined conductometrically in duplicate, except where otherwise noted. [b] Volume percent. [c] Calculated from data at other temperatures. [d] One measurement of rate constant. [e] Determined by titration of 0.13 M solution with NaOH (phenolphthalein). [f] Reference 22c. [g] Rate constant inaccurate due to short half-life and poor solubility. [h] Measurement of rate constant triplicated—low solubility caused small drift of infinity. [i] D. N. Kevill, K. C. Kolwyck, D. M. Shold, and C. Kim, *J. Am. Chem. Soc.*, **95**, 6022 (1973). [j] Determined by potentiometric titration with 0.028 M sodium acetate in acetic acid. [k] G. Yamagami, A. Sera, and K. Maruyama, *Bull. Chem. Soc. Jpn.*, **47**, 881 (1974). [l] Determined by unreliable conductivity technique. [m] Reference 22f; determined spectrophotometrically. [n] Determined titrimetrically.

Table III. Solvolysis Rate Constants of Arenesulfonates (25 °C)

Substrate[a]	10^5k, s^{-1}					
	CF_3CO_2H	HCO_2H	AcOH	50% EtOH	80% EtOH	EtOH
2-Propyl-OTs	2.49[b,c,d]	2.38[b,e]	0.0077[g]	1.47[h]	0.294[h]	0.039[i]
2-Butyl-OTs	14.6[b,c]	5.50[b]	0.0134[g]	2.23[h]	0.381[h]	*j*
2-Pentyl-OTs	19.0[b,c]	5.35[b,f]	0.011[g]	1.93[h]	0.312[h]	*j*
3-Pentyl-OTs	76.8[b,c]	14.08[b]	0.0234[g]	4.14[h]	0.634[h]	0.067[k]
4-Heptyl-OTs	115[b,c]	13.2[b]	0.0209[g]	2.74[h]	0.447[h]	
Cyclohexyl-OTs	27[l,c]	3.98[m]	0.00488[m]	0.858[h]	0.075[h]	0.0046[n]
Cyclopentyl-OTs	240[l,c]	72.2[o]	0.165[o]		2.91[o]	0.269[o]
2-Adamantyl-OTs	90[p,q]	2.65[p]	0.00059[p]	0.047[p]	0.0024[p]	0.000043[p]
Pinacolyl-OBs	1230[r]	85.8[s]	0.0695[t]	10.11[u]	0.636[u]	
Pinacolyl-OTs	409[r]	31.8[c]	0.0191[t]			

[a] Tosylates except pinacolyl brosylate. [b] Reference 23b. [c] Buffered with 0.125 M sodium trifluoroacetate. [d] $k = 2.14 \times 10^{-5}$ (0.06 M buffer): J. E. Nordlander and W. J. Kelly, *J. Am. Chem. Soc.*, **91**, 996 (1969); 2.27×10^{-5}: A. Streitwieser, Jr., and G. A. Dafforn, *Tetrahedron Lett.*, 1263 (1969). [e] $k = 2.28 \times 10^{-5}$ (this work, Table I). [f] $k = 5.3 \times 10^{-5}$: E. S. Lewis and C. E. Boozer, *J. Am. Chem. Soc.*, **76**, 791 (1954). [g] Reference 21b and J. J. Harper, Ph.D. Thesis, Princeton University, 1968. Rates from W. Pritzkow and K. W. Schoppler, *Chem. Ber.*, **95**, 834 (1962), are slightly higher. [h] From Table I. [i] Calculated from the benzenesulfonate, P. M. Laughton and R. E. Robertson, *Can. J. Chem.*, **33**, 1207 (1955), in agreement with eq 1 and reference 27a; the extrapolated value from W. Huckel and K. Tomopulos, *Justus Liebigs Ann. Chem.*, **610**, 78 (1957), appears to be unreliable. [j] Rates calculated at 50 °C from eq 1, using experimental data for 50 and 80% ethanol, do not agree with published experimental values—W. Huckel and Y. Riad, *ibid.*, **678**, 19 (1964); A. K. Colter and R. D. Johnson, *J. Am. Chem. Soc.*, **84**, 3289 (1962); see also *i* and *k*. [k] W. Huckel and O. Honecker, *Justus Liebigs Ann. Chem.*, **678**, 10 (1964)—eq 1 is satisfactory. [l] D. D. Roberts and W. Hendrickson, *J. Org. Chem.*, **34**, 2415 (1969). [m] H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78**, 2735 (1956). [n] S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955). [o] D. D. Roberts, *J. Org. Chem.*, **33**, 118 (1968). [p] Table II. [q] Unbuffered. [r] Estimated from the tosylate ($k = 4.09 \times 10^{-3}$, 0.06 M buffer, ref 35), assuming OBs/OTs = 3 (see also ref 36). [s] Reference 39a. [t] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952); A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2780 (1956). [u] Reference 17c. [c] A. Sera, C. Yamagami, and K. Muruyama, *Bull. Chem. Soc. Jpn.*, **46**, 3864 (1973)—other data in formic acid at 25 °C: 10^5 $k = 2.47$ (2-propyl), 6.04 (2-butyl), and 13.1 (3-pentyl).

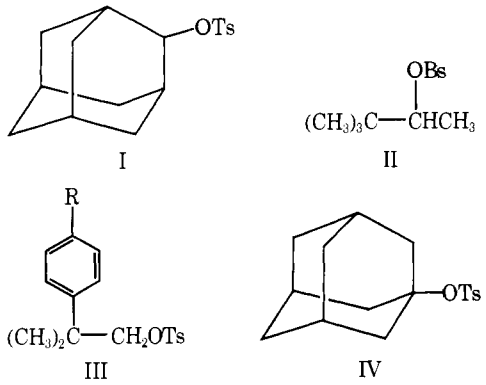
Table IV. Summary of Mechanistic Criteria for Proposed Models for SN1 Solvolyses of Arenesulfonates[a]

Substrate	Criteria[a]			
	m_{EW}	m_{AF}	$[k_{EW}/k_{AcOH}]_Y$	$[k_{EW}/k_{HCO_2H}]_Y$
p-MeO-neophyl (III, R = OMe)[b,c]	0.42 (0.54)	0.59 (0.59)	0.50 (1.44)	0.10
Neophyl-OTs (III, R = H)[c,d]	0.39 (0.51)	0.59 (0.59)	0.37 (0.79)	0.07
1-Adamantyl-OTs (IV)[b,e]	0.97 (1.23)		0.18 (1.20)	
2-Adamantyl-OTs (I)[b,f]	0.78 (1.0)	1.0 (1.0)	0.2 (1.0)	0.04
Pinacolyl-OBs (II)[b,f,g]	0.73 (0.93)	0.84 (0.84)	0.59 (2.45)	0.23

[a] Data in parentheses calculated from Y values based on 2-adamantyl tosylate (see also eq 1 and ref 26). [b] 25 °C. [c] Reference 32. [d] 75 °C. [e] Reference 31. [f] Data from Table III. [g] Solvolysis may involve nucleophilic solvent assistance, see text.

"dispersion" is often observed, and lines or curves of slightly different slopes or intercepts are observed.[29] While some of these deviations are small, there are often large differences between the correlations for mixtures of ethanol/water on the one hand and the carboxylic acids, formic and acetic, on the other. The slope of the ethanol/water correlation line designated m_{EW} is Winstein's original m value, and the slope for acetic and formic acids, m_{AF}, is Winstein's apparent m.[3] The dispersion between the two lines is conveniently discussed in terms of the rate ratios in two solvents having the same values of Y, $[k_{EW}/k_{AcOH}]_Y$ and $[k_{EW}/k_{HCO_2H}]_Y$. These ratios and the m_{AF} and m_{EW} values are useful criteria of mechanism (see Figure 1).

It is first necessary to establish the values of and the trends in these mechanistic criteria for substrates believed to solvolyze without nucleophilic solvent assistance *and* internal return. Values of m_{EW}, m_{AF}, $[k_{EW}/k_{AcOH}]_Y$, and $[k_{EW}/k_{HCO_2H}]_Y$ for SN1 solvolyses[30] of various arenesulfonates are shown in Table IV. Neophyl and *p*-methoxyneophyl tosylates (III) are thought to solvolyze by aryl participation without nucleophilic solvent participation *and* internal return.[32] Because the rearside is severely hindered, the bridgehead 1-adamantyl tosylate (IV) is not susceptible to rearside nucleophilic solvent



assistance;[31] pinacolyl (3,3-dimethyl-2-butyl) brosylate (II) is thought to solvolyze by "rate-determining formation of tight ion pair", which, Shiner proposes, rapidly rearranges and does not undergo internal return.[17c]

Ideally $[k_{EW}/k_{AcOH}]_Y$ and $[k_{EW}/k_{HCO_2H}]_Y$ values should be unity for limiting (SN1) solvolyses. In fact, these ratios are substantially less than unity due to a leaving group effect. Arenesulfonate transition states appear to be specifically solvated (e.g., by hydrogen bonding) in carboxylic acids to a greater extent (compared with ethanol/water mixtures) than that expected from the Y values based on *tert*-butyl chloride.[29d] Y values based on arenesulfonates[21h,26] correct this situation and lead to the second set of data shown in parentheses in Table IV.

The magnitude of $[k_{EW}/k_{RCO_2H}]_Y$ has been established as a measure of the importance of nucleophilic solvent assistance.[3] *We now* propose that $[k_{EW}/k_{AcOH}]_Y$, in substrates solvolyzing

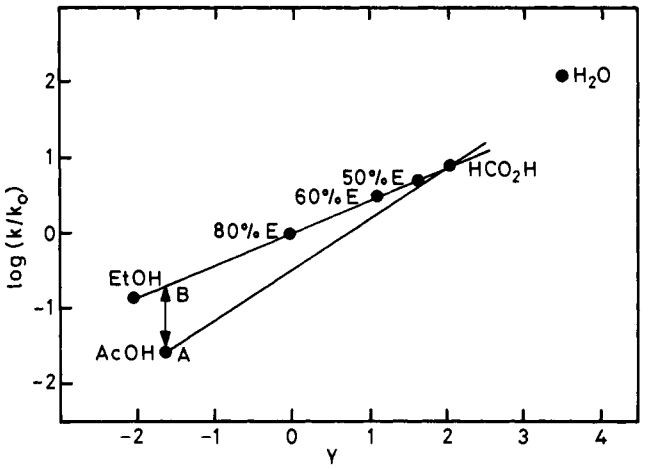


Figure 1. Solvolysis rate constants for 2-propyl tosylate vs. Y (eq 1). Illustration of mechanistic criteria: slopes m_{EW} and m_{AF}; also log $[k_{EW}/k_{AcOH}]_Y$ = B − A; data (25 °C) from Table III and ref 60.

without nucleophilic solvent assistance (SN1), can detect internal ion pair return *if it is significant* (rate constants k refer to total or titrimetric rate constants; see Appendix). Values of $[k_{EW}/k_{AcOH}]_Y \sim 0.3$–$0.5$ and $[k_{EW}/k_{HCO_2H}]_Y \sim 0.04$–$0.1$ are observed for solvolyses of arenesulfonates occurring without nucleophilic solvent assistance *and* internal return; alternatively if Y values are based on 2-adamantyl tosylate, values of $[k_{EW}/k_{AcOH}]_Y \sim 1.0$ are expected and observed (Table IV).[33] *Since solvolyses of 1- and 2-adamantyl tosylates also give low values of* $[k_{EW}/k_{RCO_2H}]_Y$, *we conclude that internal ion pair return is not significant in these substrates in acetic acid, formic acid, and ethanol/water.*

Assuming that pinacolyl arenesulfonates solvolyzed without internal return, Shiner and Fisher[34] and Nordlander et al.[35] proposed that ion pair partitioning in 2-adamantyl influenced the relative rates of solvolysis of 2-adamantyl and pinacolyl arenesulfonates. The logarithms of solvolysis rate constants of 2-adamantyl tosylate and pinacolyl brosylate are compared in Figure 2, and *the linear correlation confirms that internal return is not appreciable even in trifluoroacetic acid and trifluoroethanol.* The slight dispersion (a factor of 3 in rate) between ethanol/water and carboxylic acid correlation lines is at least partly due to the comparison of a brosylate with a tosylate—OBs/OTs ratios are slightly dependent on solvent electrophilicity.[36] If the remaining dispersion is significant, it is in the direction expected for nucleophilic solvent assistance in pinacolyl solvolyses.[37] This possibility has been considered previously[22j,39] and explains the slightly high values of $[k_{EW}/k_{RCO_2H}]_Y$ and slightly low m_{EW} and m_{AF} values (Table IV).

Mechanism of Solvolysis. As 2-adamantyl tosylate is a secondary substrate which solvolyzes with <1% rearrangement,[40] does not undergo an SN2 reaction with azide ion,[22g] gives large α-deuterium isotope effects,[22f,34] and shows other

Table V. Summary of Mechanistic Criteria. Comparison of Simple Primary and Secondary Tosylates with 2-Adamantyl

Substrate	Criteria[a]			
	m_{EW}	m_{AF}	$[k_{EW}/k_{AcOH}]_Y$	$[k_{EW}/k_{HCO_2H}]_Y$
2-Adamantyl	0.78[b]	1.0	0.2	0.04
Cyclohexyl	0.61[c]	0.79	1.6[f]	0.37
Cyclopentyl	0.49[c]	0.72	2.5	0.40
4-Heptyl	0.48[b]	0.76	3.5	0.32
3-Pentyl	0.485[c]	0.75	4.4	0.46
2-Pentyl	0.48[b]	0.73	4.6	0.56
2-Butyl	0.46[b]	0.71	5.0	0.62
2-Propyl	0.43[c]	0.68	7.6	0.92
Ethyl (50 °C)[d,e]	0.26	0.44	80	18
Methyl (50 °C)[e]	0.22[c,g]	0.30	130	64

[a] 25 °C except where stated otherwise; for explanation of symbols see text and Figure 1. [b] From 80 and 50% ethanol/water. [c] From least-squares line for 100, 80, and 50% ethanol/water. [d] Reference 3, Table 29. [e] Data summarized in reference 26. [f] Earlier value (4.3, ref 22a, Table I) is incorrect, due to extrapolation errors. [g] Curved line would accommodate the data better.

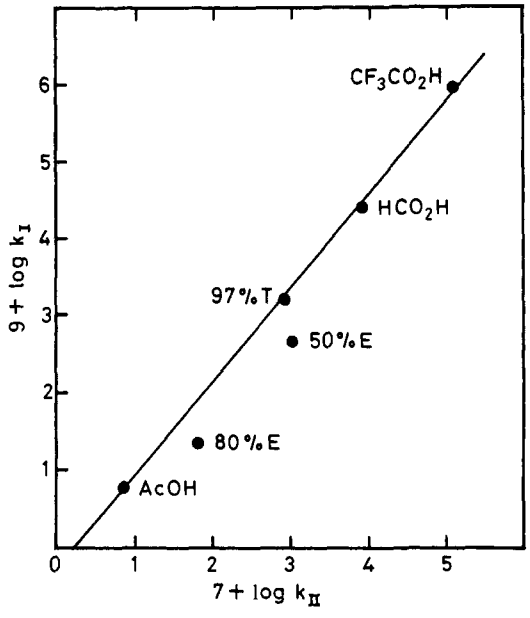


Figure 2. Solvolysis rate constants for 2-adamantyl tosylate (k_I) vs. pinacolyl brosylate (k_{II}); data at 25 °C from Table III. Correlation line (four points), slope = 1.21 ± 0.01, correlation coefficient = 0.9996.

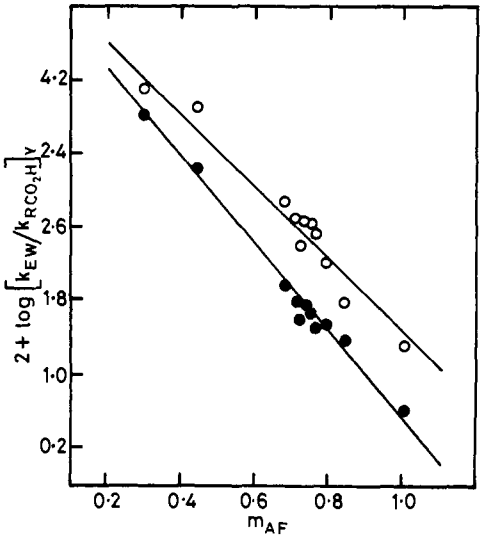


Figure 3. Interdependence of mechanistic criteria: (●) m_{AF} vs. log $[k_{EW}/k_{HCO_2H}]_Y$, slope = −4.75 ± 0.17, correlation coefficient = 0.993; (○) m_{AF} vs. log $[k_{EW}/k_{AcOH}]_Y$, slope = −4.1 ± 0.25, correlation coefficient = 0.982; data from Table V (25 °C).

mechanistic criteria (Table IV) characteristic of limiting, SN1 substrates, it is a suitable model with which to compare the solvolyses of primary and other secondary substrates.[41] The m values and $[k_{EW}/k_{RCO_2H}]_Y$ ratios are summarized in Table V. The most important feature of the data in Table V is the *interrelationship* between the m values and $[k_{EW}/k_{RCO_2H}]_Y$ ratios. The m values decrease as the $[k_{EW}/k_{RCO_2H}]_Y$ ratios increase, and the relationship is shown graphically in Figure 3, which includes solvolyses of ethyl and methyl substrates. *We propose that the linear relationship observed (Figure 3) is due to different extents of nucleophilic solvent participation which decreases m values and also increases* $[k_{EW}/k_{RCO_2H}]_Y$ *ratios.* Other quantitative correlations confirm the gradation of mechanism and reactivity from methyl to 2-adamantyl tosylates.[26] To interpret the correlation mechanistically, it is necessary to consider the mechanisms of solvolysis of methyl and 2-adamantyl tosylates.

The reactions of methyl substrates are known to be highly sensitive to solvent nucleophilicity,[3] and it seems safe to conclude that the nucleophile (solvent) attacks covalent substrate in a concerted SN2 reaction. This conclusion is supported by the following evidence. (i) Substitution almost certainly occurs with inversion of configuration, since this is found for primary[43] and secondary substrates,[3,11-13] although direct stereochemical studies on solvolyses of methyl substrates have not been carried out. (ii) There is no convincing evidence for a reactive intermediate.[3] (iii) α-Deuterium isotope effects (k_H/k_D) ratios) are close to unity.[16] (iv) There is satisfactory agreement between the two scales of solvent nucleophilicity, N_{BS} and N_{PW} constants.[22h,23c] N_{BS} constants are defined from solvolyses of methyl tosylate (eq 2),[22h,26]

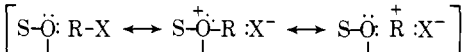
$$N_{BS} = \log (k/k_0)_{CH_3OTs} - 0.3Y \qquad (2)$$

and N_{PW} constants are determined from bimolecular reactions of carboxylic acids as nucleophiles with tetramethylenechloronium ions in liquid SO_2.[23c] It would be remarkable fortuity if the behavior of ion pairs from methyl tosylate and tetramethylenechloronium ions in the different solvents were very similar. (v) Formation of an ion pair from methyl substrates is most unfavorable energetically, since methyl is one of the least stable cations. Abraham showed that the energy required for formation of the methyl ion pair (assuming no partial covalent bonding between the anion and the methyl cation) was 40 kcal/mol greater than the experimentally observed activation energy for solvolysis.[25c] As Hammett has pointed out,[44] ion pairs probably have covalent character and may be described as cationoid,[45] but the great discrepancy between observed and calculated activation energies suggests to us that

nucleophilic stabilization by both solvent and leaving group is occurring. Sneen's conclusions[15] for simple primary and secondary substrates are based on a spectacular generalization of one possible interpretation of the solvolysis of 2-octyl mesylate in 25 and 30% aqueous dioxane. At present we are not aware of any satisfactory evidence for, nor any plausible argument in favor of, an alternative to the classical SN2 mechanism for solvolyses of methyl substrates.[25]

The solvolysis of 2-adamantyl substrates appears to be similar to unactivated tertiary substrates,[10,14] as the products can depend markedly on the leaving group,[9b] and there is a slight preference for substitution with retention of configuration.[46] As we have argued above that internal return is absent, we assume that solvolysis of 2-adamantyl tosylate is due to rate-determining formation of intimate ion pair, possibly σ-bridged.[42]

The transition state or first intermediate for solvolysis can be represented by the three resonance forms V–VII:[4]



V VI VII

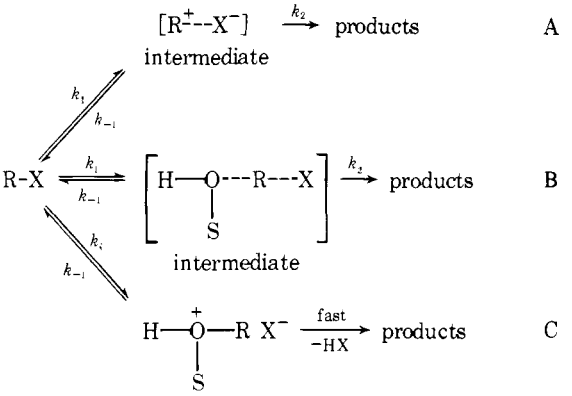
In 2-adamantyl the transition state is represented as a hybrid of V and VII. In other systems, as the importance of resonance form VI (i.e., nucleophilic solvation) in the transition state increases, the ratio $[k_{EW}/k_{RCO_2H}]_Y$ increases because mixtures of ethanol and water are more nucleophilic than carboxylic acids.[3,47] Also the charge is more dispersed with increased importance of resonance form VI (nucleophilic solvation) in the transition state, which explains why the m value decreases.[2c] Thus nucleophilic solvent assistance provides a simple explanation of the proportional decrease in m as log $[k_{EW}/k_{RCO_2H}]_Y$ increases (Figure 3).

It is emphasized that the regular gradation of the magnitude of the mechanistic criteria from 2-adamantyl to methyl tosylates in solvents from formic acid to ethanol (Figure 3) suggests that one effect causes the gradation throughout the series. As the solvolysis of methyl tosylate involves nucleophilic solvent assistance and the solvolysis of 2-adamantyl tosylate does not, it is attractive to attribute the gradation of solvent effect on rates mainly or exclusively to nucleophilic solvent assistance. We cannot evaluate or exclude *small* kinetic effects caused by more complex ion pairing, e.g., those revealed by ^{18}O equilibration.[19b] It is also possible, though unlikely, that large unknown effects are present, but not detected because they are either constant or proportional to solvent nucleophilicity.

In 2-adamantyl solvolyses we have proposed that the first intermediate is the intimate ion pair, whereas in methyl solvolyses there is no reaction intermediate. As there is a gradation of behavior between these two substrates, *it seems likely that there are weakly nucleophilically assisted processes in which a nucleophilically solvated intimate ion pair corresponds to an energy minimum, i.e., an intermediate.* An intermediate of this type has been postulated by Doering and Zeiss[14] and by Winstein and co-workers;[19b,48] it explains the SN2 character, the variety of ion pair effects, and the spectrum of products observed from these "borderline" solvolyses. The three possibilities, shown in Scheme I, may be regarded as ion pair interpretations of the three mechanisms discussed by Hughes and Ingold (i.e., SN2, borderline, and SN1).[49] We suggest the name "SN2 (intermediate)" for reactions (e.g., B, Scheme I) where there is evidence for nucleophilic assistance by solvent or other external nucleophile *and* evidence for a reaction intermediate.

While the variable character of SN2 reactions has long been recognized,[4,50,51] much confusion has been caused by the various interpretations of both the theoretical and operational

Scheme I. Spectrum of Solvolysis Mechanisms Postulated for Simple Unactivated Primary and Secondary Substrates ($k_2 \gg k_{-1}$)[a]



A, SN1, transition state leading to intermediate intimate ion pair is not nucleophilically solvated
B, SN2, (intermediate), via nucleophilically solvated transition state leading to a nucleophilically solvated ion pair intermediate
C, SN2, no intermediate

[a] Solvation by hydrogen bonding to the leaving group and general solvation has been omitted.

definitions of SN1 and SN2 reactions. We have adopted Ingold's theoretical definitions[30,52] but believe that the operational definitions have been overemphasized. According to Ingold's theoretical definition, SN2 reactions need not necessarily proceed by attack by nucleophile on covalent substrate leading directly to product—the requirement for an SN2 reaction is that two molecules "necessarily undergo covalency change during the rate determining step". Thus Sneen's "ion pair SN2" and the "SN2 (intermediate)" are alternative mechanisms of bimolecular nucleophilic substitution and could be called "SN2" reactions. But as it is so well established in current thinking, we suggest that the term "SN2" or "classical SN2" should continue to signify displacement on covalent substrate leading directly to product. The term "SN2 (intermediate)" emphasizes the possibility that an SN2 reaction may proceed via a nucleophilically solvated ion pair intermediate,[48] which is energetically more feasible than Sneen's ion pair SN2 mechanism.

Nucleophilically solvated ion pairs may possibly be frequent intermediates in solvolyses. Doering and Zeiss[14] pointed out that in some cases stabilization by covalent (nucleophilic) solvation in the rear may only become significantly effective *after* the transition-state configuration has been passed. Thus, nucleophilically solvated ion pairs may be intermediates in SN1 reactions, and nucleophilic solvation may constitute a significant (though probably small) barrier to the reverse reaction and thus help to prevent internal return. At present, we are unable to test this tenuous proposal experimentally, but it is feasible that nucleophilically solvated ion pairs are intermediates in SN1 reactions.[55]

Evidence against Internal Return in Weakly Nucleophilic Solvents. Shiner and co-workers have proposed that internal return influences solvent effects on relative rates of simple secondary substrates in weakly nucleophilic solvents (e.g., acetic acid, formic acid, trifluoroacetic acid, and trifluoroethanol), but agree that solvent can attack covalent substrate nucleophilically in ethanol/water mixtures.[16,17c] Unfortunately, the basis upon which Shiner made this proposal is founded, in part, on experimental errors and incorrect assumptions. In a recent communication, we have criticized extensively Shiner's interpretation[22j] and suggested that internal return is not appreciable in solvolyses of simple secondary substrates. Our interpretation is now supported by additional, independent evidence from $[k_{EW}/k_{RCO_2H}]_Y$ ratios

Table VI. Solvent Dependence of Ion Pair Partitioning

Substrate	$F^{a,b}$ EtOH	AcOH	HCO_2H
1-Phenyl-2-propyl-OTs[a,c]	~1.0	0.19	1.0
p-MeO-2-phenylethyl-OTs[a,d]	0.89	0.27	1.0
2-*exo*-Norbornyl-OBs[b]	0.34[e]	0.22[f]	
threo-3-Anisyl-2-Bu-OBs[b,g]	0.79	0.25, 0.22[h]	(0.92[j])
threo-3-Phenyl-2-Bu-OTs[b,g]	0.49	0.22	0.85
2-Phenylethyl-OTs[a,k]	~1[l]	0.27	0.95

[a] $F = k_2/(k_{-1} + k_2)$ in Scheme II, calculated from carbon scrambling in starting material extrapolated to zero time. [b] $F = k_t/k_\alpha$, calculated from the polarimetric rate constant ($k_\alpha = k_1$, Scheme II) in symmetrical systems. [c] A. F. Diaz and S. Winstein, *J. Am. Chem. Soc.*, **91**, 4300 (1969). [d] E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958). [e] S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1154 (1952). [f] S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *ibid.*, **87**, 376 (1965). [g] S. Winstein and G. G. Robinson, *ibid.*, **80**, 169 (1958); S. Winstein, R. Baker and S. Smith, *ibid.*, **86**, 2072 (1964), and ref 19a. [h] Tosylate. [j] In 25% formic acid/acetic acid. [k] I. L. Reich, A. F. Diaz, and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2256 (1972), and references there cited. [l] A. Diaz, I. Lazdins, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 6546 (1968).

(Table IV) and comparison of 2-adamantyl and pinacolyl arenesulfonates (Figure 2), discussed above.

However, one could argue that for secondary substrates, m_{AF} is reduced because internal return is greater in formic acid than acetic acid. From comparison of 2-propyl brosylate with pinacolyl brosylate II, Shiner and co-workers[17c] stated that, "Attack by formic acid appears slower (more internal return, smaller ratio) than attack by acetic acid, *as expected*" (our italics). We believe that this argument is incorrect. Acetic acid and formic acid are almost equally nucleophilic,[22h,23c,26] and as formic acid has a much higher "ionizing power" than acetic acid, one would expect that internal return would be *less* in formic acid than acetic acid in contrast to Shiner's assumption. Internal return measured from *F* values (Table VI) is greater in acetic acid than formic acid, although ^{18}O-scrambling studies indicate that acetic and formic acids behave similarly.[19b] Therefore if internal return were occurring, solvolyses in acetic acid would behave similarly to formic acid or would be slowed more than in formic acid; hence, if internal return increased relative to solvent capture, m_{AF} would remain constant or increase as $[k_{EW}/k_{RCO_2H}]_Y$ ratios increased. Figure 3 shows that m_{AF} actually *decreases* as $[k_{EW}/k_{RCO_2H}]_Y$ ratios increase. Therefore, we propose that internal return does not appreciably influence interpretation of any of the data in Table V and Figure 3.

Conclusions

2-Adamantyl tosylate I solvolyzes without detectable nucleophilic solvent assistance (i.e., SN1) and internal ion pair return and is the best model for which data are currently available for comparison with solvolyses of primary and other secondary tosylates. The magnitude of nucleophilic solvent assistance[20] increases in importance from solvolyses of 2-adamantyl to methyl tosylates, resulting in a decrease in *m* value, an increase in $[k_{EW}/k_{RCO_2H}]_Y$ ratio, and a decrease in α-deuterium isotope effect.[16,26] The good linear relationship (Figure 3) between m_{AF} and log $[k_{EW}/k_{RCO_2H}]_Y$, including solvolyses of methyl, ethyl, 2-propyl, cyclohexyl, pinacolyl, and 2-adamantyl, indicates a merging of mechanism due to a change in sensitivity of the substrate to solvent nucleophilicity. This establishes "normal" behavior for the SN2–SN1 spectrum of solvolyses.

We propose that reaction proceeds by rate-determining heterolysis with varying amounts of nucleophilic solvent assistance,[20] mainly depending on steric factors. The highly hindered 2-adamantyl tosylate solvolyzes by rate-determining heterolysis without detectable nucleophilic solvent assistance to an intimate ion pair (SN1), whereas the minimally hindered methyl tosylate solvolyzes directly to substitution product (SN2). Some solvolyses, in between these two, may involve nucleophilically solvated ion pairs [SN2(intermediate), Scheme I] which can undergo side reactions in competition with substitution with inversion of configuration.[11-13]

This interpretation suggests a variation in the magnitude of nucleophilic solvent assistance in SN2 transition states with a clear *theoretical* distinction between SN2 and SN1 reactions;[50b] few solvolyses should be classified as "borderline"—i.e., which, at present, cannot be classified *operationally* and convincingly as either SN2 or SN1, because nucleophilic solvent assistance is either small or negligible. The changing character of SN2 reactions as the magnitude of nucleophilic solvent assistance varies removes the necessity to postulate many competitive (i.e., simultaneous) SN1 and SN2 solvolysis reactions. However, if nucleophilic solvent assistance is very small (<1 kcal/mol), it is conceivable that the overall reaction proceeds via significant proportions of both nucleophilically assisted (SN2) and unassisted (SN1) transition states, but the two processes blend into one another with loss of operational distinction.

Experimental Section

Purification of Chemicals. Tosylates. All tosylates, prepared by reacting the alcohol with tosyl chloride in pyridine at 0 °C, were purified by crystallization (or separation) from pentane. 2-Pentyl tosylate was obtained as a yellow oil, further purified by column chromatography (silica gel). Purified 2-propyl, 2-butyl, 2-pentyl, and 4-heptyl tosylates were obtained as colorless oils and their purity checked by thin-layer chromatography and NMR—refractive indices were in agreement with literature values.[57] 3-Pentyl, cyclohexyl, and 2-adamantyl tosylates were obtained as white solids, with melting points in agreement with literature values.[26,57]

Solvents. Ethanol was heated under reflux with magnesium ethoxide and distilled through a 24-in. Vigreux column.[58] Crude formic acid (Eastman, 97%) was stirred at room temperature for 1 week with an excess of boric anhydride and distilled through a 12-in. Vigreux column, bp 30 °C (40 mm).[39a] Distilled water was passed through an ion exchange column before use. Aqueous ethanol solutions were prepared using accurately calibrated volumetric flasks and pipets.

Kinetic Methods. Conductance measurements were made in cells with bright platinum electrodes and cell constants 0.2–0.4 using approximately 25 ml of 10^{-3} M solution. Readings were taken with a Wayne-Kerr Model B331 Impedance Bridge, capable of 0.1% accuracy. Solvolyses were followed by taking at least 12 readings approximately equally spaced in conductance over at least 3 half-lives. The raw conductance data were then fitted to the first-order rate equation by means of a least-squares computer program (modified LSKIN),[59] and the precision of the fit to first-order kinetics was satisfactory over at least 3 half-lives for solvolyses in 80% v/v and 50% v/v ethanol/water. In a typical experiment, where the substrate is readily soluble, enough tosylate to make a solution approximately 10^{-3} M was added to the cell containing 20–25 ml of the solvent. The cell was then sealed and equilibrated by shaking in the constant temperature bath for at least 3 min and usually considerably longer.

The low solubility of tosylates caused difficulties with 60 and 50% ethanol/water solutions. The precision of the fit to first-order kinetics was lower than usual and the experimentally determined conductivity at the "infinity point" drifted higher than that calculated from the initial rate constant. We found that more homogeneous solutions could be prepared by first dissolving the tosylate (1–10 mg) in dry ethanol (50 ml). For 50% ethanol, deionized water (10 ml) was slowly added to ethanol solution (10 ml), using the same pipet, to give 10^{-3}–10^{-4} M solutions. 60% ethanol solutions were prepared similarly using matched 10-ml and 15-ml pipets. This procedure could be carried out accurately and reproducibly, e.g., rates for 2-propyl tosylate in 50% ethanol were in good agreement with the titrimetric measurements of Robertson[60a] (Table I). Revised data for 2-adamantyl tosylate in 60 and 50% ethanol are shown in Table II—extrapolation errors in the original calculated value[22c] for solvolysis in 50% ethanol at 25 °C were reduced by making more reliable measurements over a greater range of temperature.

Although formic acid has a high dielectric constant, we have found that rate constants derived from conductivity measurements in this solvent are not always reliable. For *tert*-butyl chloride at 25 °C our measurements were reproducible and in good agreement (<2% higher) with those of Fainberg and Winstein,[28] but for 1-adamantyl chloride the conductivity at the "infinity point" drifted downwards. For 2-adamantyl tosylate some drift was noted but the rate constant was in reasonable agreement with, but lower than, our independent measurements using potentiometric titration (Table II). Similar results were obtained for 2-propyl tosylate (Table I), and our potentiometric value is in good agreement with independent measurements (Table III). In earlier work using conductivity techniques, formolysis of 2-propyl[21b,22c] and 2-adamantyl tosylates[22c] gave significantly different values (Table II), which we now regard as being of doubtful accuracy.

Acknowledgments. The ideas and conclusions expressed in this paper have evolved from numerous discussions in Princeton. We thank in particular R. C. Bingham, J. L. Fry, C. J. Lancelot, J. M. Harris, and D. J. Raber for their contributions. This work was supported by grants from the National Science Foundation, the Donors of the Petroleum Research Fund, administered by the American Chemical Society, Hoffmann-La Roche, Inc., Nutley, N.J., and a NATO Postdoctoral Fellowship (to T.W.B., Princeton, 1969-71), administered by the Science Research Council, London. Also we are most grateful to M. H. Abraham, Z. Rappoport, and F. L. Schadt for providing helpful comments.

Appendix

Solvent Effects on Ion Pair Partitioning. While the response of different solvents to systems undergoing hidden internal return cannot be measured directly, we assume that the solvent effects will parallel or at least be in the same direction as those noted for internal return from bridged ions and ^{18}O scrambling in other sulfonates. Table VI presents a summary in the form of F values, the fraction of intimate ion pairs proceeding to product rather than returning $k_2/(k_{-1} + k_2)$; see Scheme II. These F values are always significantly lower in acetic acid than in ethanol—no exception is known to us—in participating systems where nucleophilic solvent assistance cannot be involved. Therefore in SN1 solvolyses where internal return is occurring one would expect $[k_{EW}/k_{AcOH}]_Y$ ratios to be greater than in solvolyses where internal return is absent. For SN1 substrates the rate of ion pair formation (k_1 in Scheme II) and the rate of internal return (k_{-1}) should depend on solvent ionizing power. However, further reaction of the intimate ion pair (k_2) depends on solvent nucleophilicity even in bridged ions where attack from the rear cannot occur. Solvents of higher nucleophilicity with similar ionizing power intercept the ion pair more efficiently (Table VI). This should be even more so when nucleophilic attack at the rear is possible; e.g., ^{18}O scrambling of 2-octyl brosylate in methanol is seven times less than in acetic acid.[19b]

The results in Table VI strongly support our implicit assumption, in this and the following paper,[26] that the extent of hidden return should depend on the solvent. Therefore, if hidden return is appreciable, it should be detectable by the methods discussed here.

Scheme II. Formation and Reactions of Intimate Ion Pairs. Abbreviated Ion Pair Scheme (Excluding All Solvation)

$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+X \xrightarrow{k_2}$$

where $k_t = k_1k_2/(k_{-1} + k_2)$ and k_t is the overall (total or titrimetric) rate constant, k_1 is the rate constant for formation of intimate ion pair (R^+X^-) from covalent substrate (RX), k_{-1} is the rate constant for internal return (collapse to covalent RX), and k_2 is the rate constant for attack by nucleophile on intimate ion pair or the rate constant for dissociation of intimate ion pair to solvent separated ion pair.

References and Notes

(1) We apply the term simple secondary substrates to saturated secondary alkyl groups, which do not yield resonance stabilized carbenium ions and do not undergo neighboring group participation.
(2) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2d ed, Cornell University Press, Ithaca, N.Y., 1969, (a) pp 433, 455; (b) p 428; (c) p 459.
(3) A. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill, New York, N.Y., 1962.
(4) S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951).
(5) (a) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom", Elsevier, New York, N.Y., 1963, Chapter 1; (b) S. R. Hartshorn, "Aliphatic Nucleophilic Substitution", Cambridge University Press, London, 1973, Chapter 1.
(6) For recent reviews of the mechanism of solvolysis and ion pair formation, see (a) D. J. Raber and J. M. Harris, *J. Chem. Educ.*, **49**, 60 (1972); (b) J. M. Harris in "Progress in Physical Organic Chemistry", Vol. 11, A. Streitwieser, Jr., and R. W. Taft, Ed., Wiley-Interscience, New York, N.Y., 1974, pp 89–173; (c) D. J. Raber, J. M. Harris, and P. v. R. Schleyer in "Ions and Ion Pairs in Organic Reactions", Vol. 2, M. Szwarc, Ed., Wiley, New York, N.Y., 1974, pp 247–374; (d) P. v. R. Schleyer in "Reaction Transition States", J. E. Dubois Ed., Gordon and Breach, New York, N.Y., 1972, pp 197–210; (e) T. W. Bentley and P. v. R. Schleyer, *Adv. Phys. Org. Chem.*, **14**, 1–67 (1976).
(7) (a) J. Hine, "Physical Organic Chemistry", McGraw-Hill, 2d ed, New York, N.Y., 1962, pp 137–139; (b) J. March, "Advanced Organic Chemistry", McGraw-Hill, New York, N.Y., 1968, pp 261–263; (c) E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York, N.Y., 1959, p 252; (d) M. C. Whiting, *Chem. Br.*, **2**, 482 (1966); (e) R. Breslow, "Organic Reaction Mechanisms", 2d ed, W. A. Benjamin, New York, N.Y., 1969, pp 67–79.
(8) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Am. Chem. Soc.*, **78**, 328 (1956).
(9) (a) V. J. Shiner, Jr., and W. Dowd, *J. Am. Chem. Soc.*, **93**, 1029 (1971); (b) J. M. Harris, A. Becker, J. F. Fagan, and F. A. Walden, *ibid.*, **96**, 4484 (1974); (c) J. M. Harris, D. C. Clark, A. Becker, and J. F. Fagan; *ibid.*, **96**, 4478 (1974); (d) This is true even for solvolyses of some tertiary substrates.[10]
(10) M. Cocivera and S. Winstein, *J. Am. Chem. Soc.*, **85**, 1702 (1963); D. Darwish and G. Tourigny, *ibid.*, **94**, 2191 (1972).
(11) (a) H. Weiner and R. A. Sneen, *J. Am. Chem. Soc.*, **84**, 3599 (1962); (b) H. Weiner and R. A. Sneen, *ibid.*, **85**, 2181 (1963); (c) H. Weiner and R. A. Sneen, *Tetrahedron Lett.*, 1309 (1963); (d) H. Weiner and R. A. Sneen, *J. Am. Chem. Soc.*, **87**, 287 (1965).
(12) A. Streitwieser, Jr., and T. D. Walsh, *Tetrahedron Lett.*, 27 (1963); (b) A. Streitwieser, Jr., T. D. Walsh and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, **87**, 3682 (1965); (c) A. Streitwieser, Jr., and T. D. Walsh, *ibid.*, **87**, 3686 (1965); see also (d) N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc. B*, 355 (1968); (e) M. Pankova, J. Sicher, M. Tichy, and M. C. Whiting, *ibid.*, 365 (1968), (f) J. B. Lambert, G. J. Putz and C. E. Mixan, *J. Am. Chem. Soc.*, **94**, 5132 (1972); (g) J. B. Lambert and G. J. Putz, *ibid.*, **95**, 6313 (1973); (h) J. E. Nordlander and T. J. McCrary, Jr., *ibid.*, **94**, 5133 (1972).
(13) (a) A. Streitwieser, Jr., and A C. Waiss, Jr., *J. Org. Chem.*, **27**, 290 (1962); (b) E. D. Hughes, C. K. Ingold, and S. Masterman, *J. Chem. Soc.*, 1196 (1937); (c) K. Humski, V. Sendijarević, and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **95**, 7722 (1973).
(14) W. von E. Doering and H. H. Zeiss, *J. Am. Chem. Soc.*, **75**, 4733 (1953).
(15) (a) R. A. Sneen, *Acc. Chem. Res.*, **6**, 46 (1973); (b) R. A. Sneen and J. W. Larsen, *J. Am. Chem. Soc.*, **91**, 362 (1969); (c) R. A. Sneen and J. W. Larsen, *ibid.*, **91**, 6031 (1969); (d) H. Weiner and R. A. Sneen, *ibid.*, **87**, 292 (1965).
(16) V. J. Shiner, Jr., in "Isotopes Effects in Chemical Reactions", C. J. Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold, New York, N.Y., 1970, (a) pp 91–159; (b) pp 120–135.
(17) (a) V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *J. Am. Chem. Soc.*, **91**, 4838 (1969); (b) V. J. Shiner, Jr., and W. Dowd, *ibid.*, **91**, 6528 (1969); (c) V J. Shiner, Jr., R. D. Fisher, and W. Dowd, *ibid.*, **91**, 7748 (1969).
(18) (a) W. M. Schubert and P. H. LeFevre, *J. Am. Chem. Soc.*, **91**, 7746 (1969);

(b) W. M. Schubert and W. L. Henson, *ibid.*, **93,** 6299 (1971); (c) W. M. Schubert and P. H. LeFevre, *ibid.*, **94,** 1639 (1972).
(19) (a) S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, **No. 19,** 109–130 (1965); (b) A. F. Diaz, I. Lazdins, and S. Winstein, *J. Am. Chem. Soc.*, **90,** 1904 (1968).
(20) We define nucleophilic solvent assistance as kinetically significant involvement of the solvent as nucleophile or base by partial bonding (as distinct from general electrostatic solvation) to any atom of the substrate (e.g., α-carbon, β-hydrogen, etc.).
(21) (a) C. J. Lancelot and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **91,** 4291 (1969); (b) C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *ibid.*, **91,** 4294 (1969); (c) C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91,** 4296 (1969); (d) P. v. R. Schleyer and C. J. Lancelot, *ibid.*, **91,** 4297 (1969); (e) J. M. Harris, F. L. Schadt, P. v. R. Schleyer, and C. J. Lancelot, *ibid.*, **91,** 7508 (1969); (f) H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *ibid.*, **92,** 5244 (1970); (g) D. J. Raber, J. M. Harris, and P. v. R. Schleyer, *ibid.*, **93,** 4829 (1971); (h) F. L. Schadt and P. v. R. Schleyer, *ibid.*, **95,** 7860 (1973).
(22) (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92,** 2538 (1970); (b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92,** 2540 (1970); (c) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92,** 2542 (1970); (d) S. H. Liggero, J. J. Harper, P. v. R. Schleyer, A. P. Krapcho, and D E. Horn, *ibid.*, **92,** 3789 (1970); (e) J. M. Harris, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92,** 5729 (1970); (f) J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93,** 2551 (1971); R. E. Hall, A. B. Thesis, Princeton University, 1970; (g) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **93,** 4821 (1971); (h) T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *ibid.*, **94,** 992 (1972); (i) J. L. Fry, E. M. Engler, and P. v. R. Schleyer, *ibid.*, **94,** 4628 (1972); (j) T. W. Bentley, S. H. Liggero, M. A. Imhoff, and P. v. R. Schleyer, *ibid.*, **96,** 1970 (1974); (k) F. L. Schadt, P. v. R. Schleyer, and T. W. Bentley, *Tetrahedron Lett.*, 2335 (1974).
(23) (a) P. E. Peterson, *J. Am. Chem. Soc.*, **82,** 5834 (1960); (b) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *ibid.*, **87,** 5169 (1965); (c) P. E. Peterson and F. J. Waller, *ibid.*, **94,** 991 (1972).
(24) (a) J. M. W. Scott, *Can. J. Chem.*, **48,** 3807 (1970); (b) J. Koskikallio, *Acta Chem. Scand.*, **26,** 1201 (1972); (c) J. M. W. Scott and R. E. Robertson, *Can. J. Chem.*, **50,** 167 (1972).
(25) (a) B. J. Gregory, G. Kohnstam, A. Queen, and D. J. Reid, *Chem. Commun.*, 797 (1971); (b) D. J. McLennan, *J. Chem. Soc., Perkin Trans. 2*, 1577 (1972); (c) M. H. Abraham, *ibid.*, 1893 (1973); (d) K M. Koshy, R. E. Robertson, and W. M. J. Strachan, *Can. J. Chem.*, **51,** 2958 (1973); (e) A. R. Stein, *J. Org. Chem.*, **38,** 4022 (1973); (f) G. A. Gregoriou, *Tetrahedron Lett.*, 233 (1974); (g) E. Grunwald and A. Effio, *J. Am. Chem. Soc.*, **96,** 423 (1974); (h) D. J. McLennan, *J. Chem. Soc., Perkin Trans. 2*, 481 (1974); (i) V. F. Raaen, T. Juhlke, F. J. Brown, and C. J. Collins, *J. Am. Chem. Soc.*, **96,** 5928 (1974); (j) P. J. Dais and G. A. Gregoriou, *Tetrahedron Lett.*, 3827 (1974); (k) D. J. McLennan, *Tetrahedron Lett.*, 4689 (1975); *Acc. Chem. Res.*, **9,** 281 (1976).
(26) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, following paper in this issue.
(27) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70,** 846 (1948).
(28) For a tabulation of *Y* values, see A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78,** 2770 (1956).
(29) (a) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **79,** 1597 (1957); (b) A. H. Fainberg and S. Winstein, *ibid.*, **79,** 1602 (1957); (c) A. H. Fainberg and S. Winstein, *ibid.*, **79,** 1608 (1957); (d) S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, **79,** 4146 (1957); (e) L. Wilputte-Steinert and P. J. C. Fierens, *Bull. Soc. Chim. Belg.*, **64,** 287 (1955).
(30) Molecularity is defined as the number of molecules necessarily undergoing covalency change during the rate-determining step(s).[2b,5,7d] Thus, if solvent behaves as kinetically significant nucleophile, the reaction is bimolecular (SN2). If solvent does not behave as kinetically significant nucleophile, the reaction is unimolecular (SN1). According to these definitions, both SN2 and SN1 reactions may proceed via intermediate ion pairs;[7a,15a] in SN1 reactions of unactivated tertiary substrates these are well documented,[10,14] and the notion (e.g., ref 6a and many textbooks) that SN1 reactions necessarily proceed via dissociated carbenium ions is slowly disappearing.[5b,7e]
(31) D. N. Kevill, K. C. Kolwyck, and F. L. Weitl, *J. Am. Chem. Soc.*, **92,** 7300 (1970).
(32) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83,** 618 (1961); A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90,** 6546 (1968).
(33) In support of these proposals, the scale of ionizing power based on 2-adamantyl tosylate[2,1h] is in agreement with the neophyl scale.[32]
(34) V. J. Shiner, Jr., and R. D. Fisher, *J. Am. Chem. Soc.*, **93,** 2553 (1971).
(35) J. E. Nordlander, R. E. Gruetzmacher, and F. Miller, *Tetrahedron Lett.*, 927 (1973).
(36) D. D. Roberts, *J. Org. Chem.*, **37,** 1510 (1972).
(37) Thornton[38] has pointed out that an intermediate with nucleophilic stabilization <0.6 kcal/mol could not be specifically detected because of thermal agitation of the molecules at 25 °C.
(38) E. R. Thornton, "Solvolysis Mechanisms", Ronald Press, New York, N.Y., 1964, pp 96–101.
(39) (a) S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74,** 1120 (1952); (b) A. Pross and R. Koren, *Tetrahedron Lett.*, 1949 (1974).
(40) M. L. Sinnott, H. J. Storesund, and M. C. Whiting, *Chem. Commun.*, 1000 (1969); M. L. Sinnott and M. C. Whiting, *J. Chem. Soc., Perkin Trans. 2*, 1446 (1975); H. J. Storesund and M. C. Whiting, *ibid.*, 1452 (1975); also see ref 42d.
(41) Solvolysis of 2-adamantyl tosylate may involve at most only weak anchimeric assistance.[42]
(42) (a) J. A. Bone and M. C. Whiting, *Chem. Commun.*, 115 (1970); (b) D. Lenoir, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96,** 2138 (1974); (c) D. Lenoir, D. J. Raber, and P. v. R. Schleyer, *ibid.*, **96,** 2149 (1974); (d) D. Lenoir, P. Mison, E. Hyson, P. v. R. Schleyer, M. Saunders, P. Vogel, and L. A. Telkowski, *ibid.*, **96,** 2157 (1974); (e) J. R. Pritt and M. C. Whiting, *J. Chem. Soc., Perkin Trans. 2*, 1458 (1975).
(43) L. Tenud, S. Farooq, J. Seibl, and A. Eschenmoser, *Helv. Chim. Acta*, **53,** 2059 (1970); A. Streitwieser, Jr., and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, **81,** 4912 (1959), and references there cited.
(44) L. P. Hammett, "Physical Organic Chemistry", 2d ed, McGraw-Hill, New York, N.Y., 1970, pp 206–208.
(45) H. C. Brown, private communication.
(46) C. Cloke, J. R. Pritt, and M. C. Whiting, *J. Chem. Soc., Perkin Trans. 1*, 2648 (1972); J. A. Bone, J. R. Pritt, and M. C. Whiting, *J. Chem. Soc., Perkin Trans. 2*, 1447 (1975).
(47) This argument would be valid even if rate-limiting nucleophilic attack occurs on covalent substrate or on an ion pair intermediate.
(48) (a) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74,** 1147 (1952); (b) S. Winstein, D. Darwish, and N. J. Holness, *ibid.*, **78,** 2915 (1956); see also (c) J. C. Martin and R. J. Basalay, *ibid.*, **95,** 2572 (1973), references there cited, and ref 6b; (d) R. C. Dougherty, J. Dalton, and J. D. Roberts, *Org. Mass Spectrom.*, **8,** 77 (1974); (e) F. G. Bordwell et al., *J. Am. Chem. Soc.*, **97,** 118, 123, 127, 132 (1975).
(49) (a) M. L. Dhar, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2058 (1948); (b) M. L. Bird, E. D. Hughes, and C. K. Ingold, *ibid.*, 634 (1954).
(50) (a) C. G. Swain and W. P. Langsdorf, Jr., *J. Am. Chem. Soc.*, **73,** 2813 (1951); (b) see also V. Gold, *J. Chem. Soc.*, 4633 (1956); (c) M. H. Abraham and G. F. Johnston, *J. Chem. Soc. A*, 1610 (1971).
(51) K. J. Laidler, *Suom. Kemistil. A*, **33,** 44 (1960).
(52) Alternative viewpoints that SN1 and SN2 reactions are polymolecular[53] or termolecular[54] are valid but less useful.[2b,5]
(53) J. Steigman and L. P. Hammett, *J. Am. Chem. Soc.*, **59,** 2536 (1937).
(54) C. G. Swain, *J. Am. Chem. Soc.*, **70,** 1119 (1948); C. G. Swain and R. W. Eddy, *ibid.*, **70,** 2989 (1948).
(55) Recent work by Grob and co-workers[56] has shown that intramolecular nucleophilic attack on tertiary chlorides is not too difficult sterically; also see ref 48e.
(56) C. A. Grob, K. Seckinger, S. W. Tam, and R. Traber, *Tetrahedron Lett.*, 3051 (1973).
(57) J. J. Harper, Ph.D. Thesis, Princeton University, 1968.
(58) H. Lund and J. Bjerrum, *Chem. Ber.*, **64,** 210 (1931).
(59) D. F. Detar and C. E. Detar in "Computer Programs for Chemistry", Vol. 1, D. F. Detar, Ed., W. A. Benjamin, New York, N.Y., 1968, pp 126–173; W. Sliwinski, Ph.D. Thesis, Princeton University.
(60) (a) R. E. Robertson, *Can. J. Chem.*, **31,** 589 (1953); (b) K. T. Leffek, R. E. Robertson, and S. E. Sugamori, *ibid.*, **39,** 1989 (1961).