(12) G. Cauquis and G. Reverdy, *Tetrahedron Lett.*, 1493 (1967).

(13) Photolysis of **1** in cyclohexene also gives **41.**

(14) W. J. Baron, M. E. Hendrick, and M. Jones, Jr., *J. Am. Chem. Soc.*, **95**, 6286 (1973).

(15) The thermal conversion of **51** to **52** may involve a diradical intermediate or a concerted $[_{\sigma}2 + {}_{\sigma}2]$ cycloreaction. See J. E. Baldwin and M. W. Grayston, *J. Am. Chem. Soc.*, **96**, 1629, 1630 (1974).

(16) Alkene **59** was prepared by treating 9-xanthone with 1,2-dimethyl-1-propenyllithium to form 9-(1,2-dimethyl-1-propenyl)-9-hydroxyxanthene (39%); the latter compound reacts with trimethylaluminum to give **59** (58%) (see Experimental Section).

(17) This method has been used previously by (a) L. W. Christensen, E. E. Waali, and W. M. Jones, *J. Am. Chem. Soc.*, **94**, 2118 (1972); (b) D. Seyferth, J. Y. P. Mui, and R. Damrauer, *ibid.*, **90**, 6182 (1968); (c) I. H. Sadler, *J. Chem. Soc. B*, 1024 (1969).

(18) When a 54:46 mixture of **17**a:**17d** is subjected to the photolysis conditions and workup, the cyclopropanes are recovered in a 51:49 ratio.

(19) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

(20) J. Hine, "Physical Organic Chemistry", 2nd ed . McGraw-Hill, New York, 1962, pp 405, 432, and 470.

(21) J. R. Shelton and C. K. Liang, *J. Org. Chem.*, **38**, 2301 (1973).

(22) M. Swarc, C. H. Leigh, and A. N. Sehon, *J. Chem. Phys.*, **19**, 657 (1951).

(23) P. Carmella, R. Huisgen, and B. Schmolke, *J. Am. Chem. Soc.*, **96**, 2997 (1974).

(24) (a) Photolysis of **1** in *cis*-propenylbenzene at −78 °C in ethyl ether gives 9-xanthone azine as the principal product. (b) Cyclopropanes **18** and **19** were analyzed by ^{1}H NMR methods; because of the limitations of the ^{1}H NMR method, small amounts of **18** or **19** in admixture with its geometric isomer could not be determined.

(25) (a) Diarylcarbenes such as diphenylmethylene and **61** show reactions in mixed singlet and triplet states. Styrenes, however, are excellent triplet scavengers and may siphon off **4** much faster than **3**. (b) Reference 10a, pp 73–84. (c) G. Cauquis and G. Reverdy, *Tetrahedron Lett.*, 3491 (1972).

(26) On the basis that **2** apparently reacts with double bonds via triplet **4** to give cyclopropanes, the fact that **2** undergoes such intimate allylic C–H insertion (without double-bond migration) is interestingly subtle. It may very well be that there are abstraction-recombination reactions of sterically unencumbered triplet carbenes on allylic C–H which occur without double-bond migration.

(27) M. J. Aroney, G. M. Hoskins, and R. LeFevre, *J. Chem. Soc. B*, 980 (1969).

(28) S. V. McKinley, P. A. Grieco, A. E. Young, and H. H. Freedman, *J. Am. Chem. Soc.*, **92**, 5900 (1970).

(29) Z. M. Holubec and J. Jonas, *J. Am. Chem. Soc.*, **90**, 5986 (1968).

(30) S.-I. Murahashi, O. Moritani, and M. Nishino, *J. Am. Chem. Soc.*, **89**, 1257 (1967).

(31) J. A. Elvidge, in "Nuclear Magnetic Resonance for Organic Chemistry", Part 2, D. W. Mathieson, Ed., Academic Press, New York, 1967, Chapter 3.

(32) For further discussion of the nonequivalence in an isopropyl group due to molecular asymmetry see G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 2628 (1964).

(33) (a) R. Meyer and J. Szanecki, *Chem. Ber.*, **33,** 2577 (1900); (b) T. C. Holton, Ph.D. Dissertation, The Ohio State University, 1970.

(34) None of the spiro[2-arylcyclopropane-1,9'-xanthenes] rearranges and/or decomposes during chromatography on silica gel.

(35) Dixanthyl ether was identified by comparison with a standard sample; F. Gordnwy, K. Jones, and A. M. Ward, *J. Chem. Soc.*, 535 (1930).

(36) The photolysis apparatus consisted of a Pyrex well having a 450-W Hanovia high-pressure quartz mercury-vapor lamp and a reaction vessel (140 mL). The vessel had a nitrogen inlet for purging oxygen and for stirring the solution, a magnetic stirring bar, and a nitrogen outlet. All solutions were nitrogen purged for 15 min before and during a photolysis. The apparatus was cooled in dry ice–2-propanol and water (5 °C) was circulated through the jacket cooling the lamp.

(37) (a) The stereochemical assignments of **18** and **19** were made in accord with the general observation that for cyclopropanes cis is larger than trans *vicinal* coupling,[37b–d] and in agreement with the Karplus rule which predicts J_{trans} never to be larger than J_{cis} for any given pair of cyclopropane isomers.[37e,f] (b) H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **40**, 875 (1962). (c) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963). (d) G. L. Closs and R. A. Moss, *ibid.*, **86**, 4042 (1964). (e) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959). (f) L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed., Pergamon Press, Oxford, 1969, pp 286–287.

(38) **Note Added** in **Proof:** H. Dürr, S. Fröhlich, B. Schley, and H. Weisgerber, *J. Chem. Soc., Chem. Commun*, 843 (1977), report that photolysis of **6** in ether yields **8** (15%) and **9** (7%) as separable products.

Solvent Nucleophilicity. A Scale Based on Triethyloxonium Ion Solvolysis[1]

Dennis N. Kevill* and Gloria Meichia L. Lin

Contribution from the Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115.

Received December 12, 1978

Abstract: First-order rate coefficients have been obtained for the solvolysis of triethyloxonium hexafluorophosphate in a variety of organic and aqueous-organic solvents. These have been used to set up a scale of solvent nucleophilicities based upon the four-parameter (two-term) Grunwald–Winstein equation. The required corrections for variation in solvent influence upon the leaving group were estimated from data available for *tert*-butyldimethylsulfonium ion solvolysis. A previously established scale, based upon methyl *p*-toluenesulfonate solvolysis, can be brought into good agreement with this scale if a revised value is used for methyl *p*-toluenesulfonate sensitivity to the electrophilic influence of the solvent. The scale is applied to previously studied solvolyses of alkyl *p*-toluenesulfonates and chlorides.

Determination of solvent nucleophilicities is complicated by concurrent solvent influence upon the leaving group. Previous attempts to establish a nucleophilicity scale for solvolytic reactions have used data from initially neutral substrates;[2,3] to a first approximation, the overall influence of the solvent could be considered as a nucleophilic push at the α carbon and an electrophilic pull at the leaving group. Two-term (four-parameter) equations have been proposed[2,4] for the combination of these two effects within a linear free energy relationship. Subsequent work[3,5–8] has favored the earlier formulation,[4] expressed in the equation

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

In eq 1, k represents the specific rate in a given solvent, k_0 the specific rate in 80% ethanol, and, for a given substrate, l and m represent the sensitivities of the solvolysis to N and Y, the solvent nucleophilicity and the solvent ionizing power. The equation was developed as an extension of the more familiar one-term (two-parameter) Grunwald–Winstein equation[9] (eq 2) from S_N1 to S_N2 solvolyses.

$$\log (k/k_0) = m'Y \qquad (2)$$

Peterson and Waller[5] attempted to overcome the problem of variable influence upon the leaving group by studying nucleophilicities toward cyclic halonium ions in a large excess of liquid sulfur dioxide. Because the carboxylic acids studied have similar dimer $\rightleftharpoons$ monomer equilibrium constants[10] (favoring the dimer), the observed three-halves-order kinetics could be approximately related to the relative nucleophilicities of individual solute molecules. For alcohols, which show complex aggregation behavior in relatively low polarity solvents,[11] the more complex kinetic patterns could not readily

0002-7863/79/1501-3916$01.00/0

be interpreted.[12] Further, it has been shown that the nucleophilicities of acetic and formic acids relative to water[8] and the relative nucleophilicities of the components of ethanol–water mixtures[13] are solvent dependent and relative nucleophilicities measured at low concentration in a constant solvent are probably not a reliable measure of true solvent nucleophilicities.

Schadt, Bentley, and Schleyer[3] have calculated solvent nucleophilicities from measurements of, or literature data for, methyl *p*-toluenesulfonate specific solvolysis rates. Adjustments for the differing solvent influences upon the leaving group were made using eq 1. Scales of solvent ionizing power (Y) based on solvolysis of either *tert*-butyl chloride[9,14] or 2-adamantyl *p*-toluenesulfonate[3,15,16] were available but it was also necessary to estimate the sensitivity (m) of the standard substrate to this factor. The m value chosen (0.3) was based upon the rather dubious assumption that the equal nucleophilicities for acetic and formic acids in liquid sulfur dioxide[5] can be carried over to the pure solvents.[17] Since any uncertainty in the mY term is reflected as a corresponding uncertainty in the scale of solvent nucleophilicities, we have minimized the electrophilicity term, and associated errors, by choice of an initially positively charged substrate which will show charge dispersal (rather than charge development) on going to the transition state. For example, on transfer of the solvolysis from ethanol to water, *tert*-butyl bromide shows a 1450-fold rate variation (increase) and *tert*-butyldimethylsulfonium ion only a threefold variation (decrease).[18] The solvolysis of the *tert*-butyldimethylsulfonium ion has previously been studied in several pure and mixed solvents at 50.4 °C and log (k/k_0) values have been reported.[19] We use these as Y^+ values and obtain further values by interpolation. Values for other solvents can be roughly estimated, using *tert*-butyl chloride Y values,[14] from the equation

$$Y^+ = -0.09Y \tag{3}$$

Other factors being equal, the contributions from the mY term and the errors associated with choice of an appropriate value for m will, for an initially positively charged substrate, be less than 10% of those for an initially neutral substrate.

Since methyl *p*-toluenesulfonate has been chosen previously as a standard substrate (l = 1), a methyl derivative would be the obvious choice for an initially positively charged substrate. Dimethyl sulfide and trimethylamine are much poorer leaving groups than *p*-toluenesulfonate ion[20] and trimethylsulfonium and tetramethylammonium ions would solvolyze too slowly even at elevated temperatures. On the other hand, the trimethyloxonium ion solvolyzes in hydroxylic solvents too rapidly for measurement by conventional sampling techniques at 0 °C; rates have been measured[21] at lower temperatures (<−20 °C) but such low temperatures would severely limit the range of solvents which could be studied. We have chosen, instead, to study the slower reacting[22] triethyloxonium ion, supplied as the hexafluorophosphate. When a good leaving group is considered, the methyl and ethyl derivatives usually solvolyze at very similar rates[23] and the appreciable rate difference between the two oxonium ions is almost certainly a consequence of the differing ether molecule leaving groups.

A S_N2 mechanism for triethyloxonium ion solvolyses is indicated by the previously drawn conclusions that ethyl perchlorate[23] and ethyl trifluoromethanesulfonate,[24] containing groups with leaving ability comparable to a dialkyl ether,[21] solvolyze by a S_N2 mechanism, even in solvents of relatively high ionizing power.

Table I. Solvolysis Data for Triethyloxonium Hexafluorophosphate, Y^+, N_{KL}, and $0.83N_{m=0.5}$ Values

solvent, vol %[a]	log (k/k_0),[b] 0.0 °C	Y^+ [c]	N_{KL} [d]	$0.83N_{m=0.5}$ [e]
EtOH–H_2O				
100	+0.55	+0.16	+0.46	+0.41
80	0.00	0.00	0.00	0.00
60	−0.35	−0.10	−0.29	−0.31
40	−0.64	−0.22	−0.52	−0.56[f]
20	−0.95	−0.24	−0.82	−0.77[f]
H_2O	−1.01	−0.25	−0.87	−0.79
MeOH–H_2O				
100	+0.64	+0.11	+0.58	+0.18
80	+0.19	−0.04	+0.21	−0.08
60	−0.25	−0.13	−0.18	−0.35
40	−0.49	−0.19	−0.39	−0.53[f]
20	−0.88	−0.23	−0.75	−0.70[f]
Me_2CO–H_2O				
95	−0.23	+0.36	−0.43	
90	−0.12	+0.26	−0.26	−0.04[g]
80	−0.22	+0.13	−0.29	−0.31
70	−0.36	+0.04	−0.38	−0.42
60	−0.46	−0.03	−0.44	−0.51
40	−0.71	−0.12	−0.64	−0.70[f]
20	−0.86	−0.19	−0.76	−0.83[f]
CH_3COOH	−1.42[h]	−0.14	−1.34	−1.44
Dioxane–H_2O				
80	−0.10	+0.07	−0.14	−0.22
70	−0.24	0.00	−0.24	−0.35
60	−0.34	−0.06	−0.31	−0.46
40	−0.60	−0.18	−0.50	−0.66[f]
20	−0.80	−0.26	−0.66	−0.80[f]
CF_3CH_2OH–H_2O[i]				
97	−2.28	−0.10	−2.22	−2.33
90	−1.73	−0.11	−1.67	−1.98[f]
70	−1.28	−0.15	−1.20	−1.19
50	−1.05	−0.20	−0.94	−1.17
HCOOH	−1.71[h]	−0.18	−1.61	−2.03

[a] Volume % (at 25.0 °C) of component other than water, except where otherwise stated; solvent is 98% (by volume) that indicated and 2% CH_3CN. [b] Decimal logarithm of the first-order rate coefficient for Et_3O^+ solvolysis at 0.0 °C relative to first-order solvolysis rate coefficient (0.74×10^{-3} s^{-1}) in 80% ethanol. [c] Decimal logarithm of first-order solvolysis rate coefficient for $Me_3CS^+Me_2$ in indicated solvent at 50.4 °C relative to that in 80% ethanol. For entries up to and including acetic acid, value is obtained directly or by interpolation (extrapolation for 95% acetone) from ref 19. Other entries are roughly estimated as $-0.09Y$. [d] $N_{KL} = \log(k/k_0) - 0.55Y^+$. [e] Values from data for MeOTs contained within Table I of ref 3b; N recalculated, using the *tert*-butyl chloride Y scale, with $m = 0.5$ rather than $m = 0.3$. [f] The required value for log $(k/k_0)_{CH_3OTs}$ obtained by interpolation of a plot vs. percent solvent composition. [g] Value suspect since it is based on a log (k/k_0) value which does not correlate with corresponding data in dioxane–water mixtures. The correlation requires a value of −1.25 for log $(k/k_0)_{MeOTs}$ which leads to a $0.83N_{m=0.5}$ value of −0.27. [h] Obtained from Arrhenius plot of rate coefficients at higher temperatures; acetic acid, 0.347×10^{-3} s^{-1} at 25.1 °C and 1.93×10^{-3} s^{-1} at 45.1 °C; formic acid, 0.190×10^{-3} s^{-1} at 25.0 °C and 1.13×10^{-3} s^{-1} at 45.1 °C. [i] Weight % of CF_3CH_2OH.

Results and Discussion

In Table I are reported kinetic measurements, in terms of acid production, which have been carried out using an approximately 0.01 M solution of triethyloxonium hexafluorophosphate.

$$Et_3O^+PF_6^- + SOH \rightarrow EtOS + Et_2O + HPF_6$$

The log (k/k_0) value at 0 °C for acetonitrile is a very low −2.70 (the imidoyl cation, $CH_3CNC_2H_5^+$, titrates as acid[21]) and reactant solutions were prepared by addition of a concentrated acetonitrile solution.

One possible complication would be if the specific solvolysis rates were concentration dependent. Trimethyloxonium flu-

Table II. Parameters for Alkyl *p*-Toluenesulfonate Solvolyses for Use with N_{KL} and Ordinary Y Values[a]

substrate	l	m	r[b]	$(m - 0.24l)$	m'_{expt}[c]
MeOTs[d]	1.20	0.50	0.984	0.21	0.22
EtOTs[e]	1.00[f]	0.55	0.987	0.31	0.26
$C_6H_5CH_2OTs$[g]	0.90	0.67	0.999	0.45	0.49[h]
i-PrOTs[i]	0.50	0.55	0.990	0.43	0.43
c-C_5H_9OTs[j]	0.25	0.56	0.999	0.50	0.49
c-$C_6H_{11}OTs$[i]	0.18	0.60	0.997	0.56	0.61
2-AdOTs[k]	0.00	0.81	0.999	0.81	0.78

[a] The eight "standard" solvents are 50, 80, and 100% EtOH, MeOH, 70 and 97% CF_3CH_2OH, CH_3COOH, and HCOOH (rate coefficients from ref 3 and 16). [b] Correlation coefficient. [c] For aqueous ethanol, from ref 16. [d] In the standard solvents. [e] In the standard solvents but excluding the two trifluoroethanol solvents (experimental data not available). [f] By definition. [g] In 50, 60, 70, 80, and 100% EtOH and in CH_3COOH; HCOOH data available but excluded. [h] From J. Delhoste, *Bull. Soc. Chim. Fr.*, 133 (1974). [i] In the standard solvents but excluding HCOOH. [j] Based only on 80% EtOH, EtOH, and CH_3COOH (HCOOH data available but excluded). [k] Based on data for 50, 60, 80, and 100% EtOH, MeOH, and 60% acetone.

oroborate has been shown[25] to solvolyze in trifluoroacetic acid at 29.9 °C with a specific rate which fell in value by about 600-fold as the substrate concentration was increased from 0.01 to 1.39 M. Complications due to aggregation would be most marked, within our study, for solvolyses in acetic acid[26] and, at 25.1 °C, the first-order rate coefficients for 0.0050, 0.0100, and 0.0200 M triethyloxonium hexafluorophosphate were respectively $0.338\ (\pm 0.026) \times 10^{-3}$, $0.347\ (\pm 0.014) \times 10^{-3}$, and $0.310\ (\pm 0.018) \times 10^{-3}\ s^{-1}$. These values are essentially constant and, for our region of <0.01 M substrate, the concentration dependence is within experimental error.

Initially, the substrate sensitivity (m) to changes in Y^+ values was taken as 0.4 (the value reported[3] for ethyl *p*-toluenesulfonate sensitivity to Y values) and this was refined to 0.55 by reapplying the generated preliminary solvent nucleophilicities to the ethyl *p*-toluenesulfonate data. The solvent nucleophilicity values (N_{KL}) reported in Table I were then calculated by the use of the equation

$$N_{KL} = \log (k/k_0)_{Et_3O^+} - 0.55Y^+ \qquad (4)$$

These values differ appreciably from $0.83N_{m=0.3}$ values based on reported[3] $N_{m=0.3}$ values and the reported[3b] l value for ethyl *p*-toluenesulfonate, but the agreement becomes extremely good if the N values are recalculated using a m value of 0.5 (Table I).

For extensive ranges of solvent composition of several of the commonly studied aqueous-organic mixtures, the logarithms of the solvolysis rate coefficients for the triethyloxonium ion are linearly related to the Y values,[14] with slopes (m' values of eq 2) of -0.343 ± 0.007 for 100-40% aqueous methanol, -0.283 ± 0.005 for 100-40% aqueous ethanol, -0.191 ± 0.006 for 80-20% aqueous dioxane, and -0.163 ± 0.009 for 90-20% aqueous acetone. The larger (two-parameter) m' value for solvolysis of ethyl benzenesulfonate in aqueous dioxane[27] or aqueous acetone[28] (0.41) relative to that in aqueous alcohols[4] (0.28) can now be seen to arise from larger variations within the nucleophilic contribution for the aqueous alcohol mixtures.

The agreement between N_{KL} and $0.83N_{m=0.5}$ values supports the view[8] that a common scale of nucleophilicities can be applied to solvolyses of both RX- and RX^+-type substrates. However, a more rigid test of this hypothesis is the ability of the scale based upon triethyloxonium ion solvolysis to correlate solvolysis rates for neutral substrates.

The N_{KL} and "traditional" Y values[14] have been used to correlate solvolysis rates, available from compilations within the literature for alkyl *p*-toluenesulfonates[3,16] and alkyl halides,[4,9] by use of eq 1. The appropriate l and m values and the correlation coefficients are listed in Tables II and III. Also, in several of the commonly studied aqueous-organic mixtures (for example, in aqueous ethanol), the N and Y values are linearly related,[7,29,30] resulting in a linear plot for the two-parameter Grunwald-Winstein equation (eq 2). Combining eq 2 and eq 1:

$$m'Y = mY + lN$$

and for aqueous ethanol

$$N_{KL} = -0.24Y$$

such that

$$m'Y = (m - 0.24l)Y$$

In both Tables II and III, $(m - 0.24l)$ values can be seen to be in excellent agreement with previously reported[4,16] experimental m' values for aqueous ethanol mixtures.

The general trends of the l and m values are the same as previously obtained[3] but from methyl to cyclohexyl the range of l values has widened (over and above that due to choice of ethyl rather than methyl as standard substrate) and the range of m values has considerably compressed; indeed, for methyl, ethyl, and secondary substrates, the m values vary only by 0.1 units. It is gratifying to find that the same l values can be used for both *p*-toluenesulfonates and halides, consistent with this parameter governing the sensitivity to S_N2-type attack at the α carbon of the alkyl group. As Streitwieser pointed out several years ago,[31] whether the series of $l > 0$ values is considered to reflect a single mechanism or a range of mechanisms is a question of definition, not of meaning. Esters of *p*-toluenesulfonic acid are usually less sensitive than alkyl halides to solvent changes when leaving-group effects are considered because the *p*-toluenesulfonate can disperse developing negative charge internally while the halide can only disperse it through solvation.[32,33] The generally higher m values for the halides relative to the corresponding *p*-toluenesulfonate can be considered to reflect this situation.

For the reported solvents, the correlations are very good to excellent (Tables II and III). For the secondary and benzyl *p*-toluenesulfonates, the available data in formic acid were excluded from the correlations; for formic acid the log (k/k_0) values calculated by eq 1 are 0.6-1.0 units lower than the ex-

Table III. Parameters for Alkyl Halide Solvolyses for Use with N_{KL} and Ordinary Y Values[a]

substrate	(temp, °C)	l	m	r[b]	$(m - 0.24l)$	m'_{expt}[c]
MeBr	(50)	1.20	0.55	0.972	0.26	0.26
EtBr	(55)	1.00	0.60	0.998	0.36	0.34
$C_6H_5CH_2Cl$[d]	(50)	0.90	0.65	0.996	0.43	0.43
i-PrBr	(50)	0.50	0.65	0.998	0.53	0.54
t-BuBr[e]	(25)	0.00	0.91	0.999	0.91	0.92[f]

[a] In EtOH, 80% EtOH, 50% EtOH, and H_2O (rate coefficients from ref 4). [b] Correlation coefficient. [c] For aqueous ethanol, from ref 4. [d] Data in MeOH replacing data in H_2O. [e] From ref 9, using the data in 60, 80, 90, and 100% EtOH. [f] Data for aqueous-acetone mixtures included in the calculation.

perimental values. Schadt, Bentley, and Schleyer[3b] have previously found that trifluoroacetolyses of secondary substrates correlate rather poorly with other solvolyses and significant changes in their l and m values occurred when trifluoroacetolysis was included; again, the calculations underestimated the experimentally observed value. We believe that these deviations for formic and trifluoroacetic acid solvolyses are due to the superimposition of a dominant $\mathrm{S_N}1$ mechanism.[34] Indeed, convincing evidence has been presented showing that the solvolyses of secondary p-toluenesulfonates in trifluoroacetic acid are $\mathrm{S_N}1$ processes.[3,35] By definition, a $\mathrm{S_N}1$ process has a l value of zero and the previous inclusion[3b] of data obtained in trifluoroacetic acid on plots for secondary p-toluenesulfonate solvolyses governed by l values of 0.4 (isopropyl) and 0.23 (cyclohexyl) is in direct conflict with the evidence for limiting $\mathrm{S_N}1$ character discussed elsewhere in the same paper.

For the $\mathrm{S_N}1$ solvolyses[15] of 2-adamantyl p-toluenesulfonate ($l = 0$), in addition to data in formic acid, it was necessary to omit the data in acetic acid and the two aqueous–trifluoroethanol solvents; however, data in these three solvents correlates well in the other ($l > 0$) solvolyses. One possible explanation for this dichotomy is that the specific electrophilic assistance at the p-toluenesulfonate, believed to operate in these acidic solvents,[36] occurs to a large extent at the intimate ion-pair stage of the $\mathrm{S_N}1$ reaction, so as to prevent internal return.[37,38] An assistance of this type could not operate for the synchronous ($l > 0$) $\mathrm{S_N}2$ reactions.

Experimental Section

Materials. Triethyloxonium hexafluorophosphate (Cationics) was found to be suitable for use as received. The purifications of acetonitrile,[39] acetic acid,[19] acetone,[40] dioxane,[36] ethanol,[41] formic acid,[42] methanol,[41] and 2,2,2-trifluoroethanol[43] were carried out using previously reported procedures.

Kinetic Procedures. To 49 mL of the solvent under investigation, maintained at the appropriate temperature, was added 1 mL of a stock solution of $\mathrm{Et_3O^+PF_6^-}$ in acetonitrile, also maintained at the appropriate temperature. After a brief vigorous shaking and temperature reequilibration, 5-mL portions were removed at suitable time intervals.

Runs in water, alcohols, and aqueous-organic mixtures were carried out at 0 °C and portions were quenched by pipetting into 20 mL of a saturated solution of lithium chloride in acetone. Unreacted triethyloxonium ion was converted to ethyl chloride and diethyl ether and the previously produced acid could then be titrated against a standardized solution of sodium methoxide in methanol, using resorcinol blue (Lacmoid) as indicator.

For acetic and formic acids (solids at 0 °C), rate coefficients obtained at 25 and 45 °C were extrapolated to 0 °C by use of the Arrhenius equation. For runs in acetic acid, portions were pipetted into 10 mL of acetic acid and immediately titrated against a standard solution of sodium acetate in acetic acid, using bromophenol blue as indicator.[44] For runs in formic acid, portions were pipetted into 20 mL of purified dioxane[36] and immediately titrated against a standard solution of sodium acetate in acetic acid, using bromocresol green as indicator.[45]

First-order solvolysis rate coefficients (k) were calculated from the equation

$$k = \frac{1}{t}\ln\frac{(V_\infty - V_0)}{(V_\infty - V_t)} \qquad (5)$$

In eq 5, V_0 is the titer at time zero (when first portion is removed), V_t is the titer at time (t) of removal of a subsequent portion, and V_∞ is the titer for a portion removed after at least 10 half-lives. For very slow runs, V_∞ can also be obtained by addition of a portion to 10 mL of methanol and, after at least 30 min, titration in the usual way. The standard deviation of the mean value for each run was typically 2–4% but it ranged up to 8% for some of the faster runs and for runs in acetic and formic acids. All runs were performed, at least, in duplicate.

Reference and Notes

(1) Abstracted, in part, from the Ph.D. Thesis of G.M.L.L., Northern Illinois University, Dec 1978.

(2) C. G. Swain, R. B. Mosely, and D. E. Bown, *J. Am. Chem. Soc.*, 77, 3731 (1955).

(3) (a) T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 992 (1972); (b) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *ibid.*, **98**, 7667 (1976); (c) T. W. Bentley and P. v. R. Schleyer, *Adv. Phys. Org. Chem.*, **14**, 1 (1977).

(4) S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951).

(5) P. E. Peterson and F. J. Waller, *J. Am. Chem. Soc.*, **94**, 991 (1972).

(6) D. A. da Roza, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **95**, 7003 (1973).

(7) J. Kaspi and Z. Rappoport, *Tetrahedron Lett.*, 2035 (1977).

(8) P. E. Peterson, D. W. Vidrine, F. J. Waller, P. M. Henrichs, S. Magaha, and B. Stevens, *J. Am. Chem. Soc.*, **99**, 7968 (1977).

(9) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

(10) (a) H. A. Pohl, M. E. Hobbs, and P. M. Gross, *J. Chem. Phys.*, **9**, 408 (1941); (b) A. A. Maryott, M. E. Hobbs, and P. M. Gross, *J. Am. Chem. Soc.*, **71**, 1671 (1949); (c) J. T. Harris, Jr., and M. E. Hobbs, *ibid.*, **76**, 1419 (1954).

(11) (a) R. F. Hudson and G. W. Loveday, *J. Chem. Soc. B*, 766 (1966); (b) R. F. Hudson, G. W. Loveday, S. Fliszar, and G. Salvadori, *ibid.*, 769 (1966).

(12) C. Neblett, M.S. Thesis, University of South Carolina, 1977, cited in ref 8.

(13) A. Pross, H. Aronovitch, and R. Koren, *J. Chem. Soc., Perkin Trans. 2*, 197 (1978).

(14) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

(15) 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).

(16) T. W. Bentley and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 7658 (1976).

(17) For example, it has since been shown (ref 8) that, on transfer from liquid $\mathrm{SO_2}$ to water, the nucleophilicities of acetic and formic acids toward cyclic halonium ions move apart by 0.4 log units.

(18) N. S. Isaacs, "Reactive Intermediates in Organic Chemistry", Wiley, New York, 1974, p 108.

(19) C. G. Swain, L. E. Kaiser, and T. E. C. Knee, *J. Am. Chem. Soc.*, **80**, 4092 (1958).

(20) E. R. Thornton, "Solvolysis Mechanisms", Ronald Press, New York, 1964, p 165.

(21) D. N. Kevill and G. M. L. Lin, *Tetrahedron Lett.*, 949 (1978).

(22) For solvolysis at 11.7 °C in acetonitrile (to give a nitrilium ion) the triethyloxonium ion has a specific rate of 7.86 ($\pm$0.24) $\times 10^{-6}$ s^{-1} and the trimethyloxonium ion has a specific rate of 3.18 ($\pm$0.18) $\times 10^{-4}$ s^{-1}, a difference by a factor of 40. For solvolysis in methanol at −23.4 °C, the corresponding values are 2.04 ($\pm$0.03) $\times 10^{-4}$ and 3.08 ($\pm$0.22) $\times 10^{-3}$ s^{-1}, a difference by a factor of 15.

(23) D. N. Kevill and B. Shen, *Chem. Ind.* (*London*), 1466 (1971).

(24) (a) A. Streitwieser, Jr., C. L. Wilkins, and E. Kichlmann, *J. Am. Chem. Soc.*, **90**, 1598 (1968); (b) G. A. Dafforn and A. Streitwieser, Jr., *Tetrahedron Lett.*, 3159 (1970).

(25) F. J. Slama, Ph.D. Thesis, St. Louis University, St. Louis, Mo., 1969; we wish to thank Professor P. E. Peterson for bringing this work to our attention.

(26) A. I. Popov in "The Chemistry of Non-Aqueous Solvents", Vol. III, J. J. Lagowski, Ed., Academic Press, New York, 1970, p 241.

(27) E. Tommila and E. Merikallio, *Suom. Kemistil. B*, **26**, 79 (1953).

(28) E. Tommila and J. Jutila, *Acta Chem. Scand.*, **6**, 844 (1952).

(29) C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965).

(30) P. R. Wells, "Linear Free Energy Relationships", Academic Press, New York, 1968, p 67.

(31) A. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill, New York, 1962, pp 64–65.

(32) H. M. R. Hoffmann, *J. Chem. Soc.*, 6753, 6762 (1965).

(33) D. N. Kevill and R. F. Sutthoff, *J. Chem. Soc. B*, 366 (1969).

(34) It was suggested (ref 3b) that the faster than predicted rates for secondary *p*-toluenesulfonates in trifluoroacetic acid were due to an unusually high degree of electrophilic solvation. However, the Y values used were those based upon 2-adamantyl *p*-toluenesulfonate solvolysis, a scale which was specifically designed to compensate for the influence of such effects upon a *p*-toluenesulfonate leaving group (ref 16). A much more probable explanation is the superimposition of a new pathway requiring correlation parameters appropriate for $\mathrm{S_N}1$ (not $\mathrm{S_N}2$) solvolyses.

(35) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *Tetrahedron Lett.*, 2335 (1974).

(36) D. N. Kevill, K. C. Kolwyck, and F. L. Weitl, *J. Am. Chem. Soc.*, **92**, 7300 (1970).

(37) S. Winstein, A. Fainberg, and E. Grunwald, *J. Am. Chem. Soc.*, **79**, 4146 (1957).

(38) It has been proposed that in adamantyl systems very little internal return occurs within the intimate ion pair.[16] On the other hand, it has been shown that the 2-adamantyl carbonium ion is highly reactive and extremely unselective [D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **93**, 4821 (1971)]. It is difficult to see why such a highly reactive unselective species would consistently fail to react with the ideally situated counterion within an intimate ion pair.

(39) D. N. Kevill and J. E. Dorsey, *J. Org. Chem.*, **34**, 1985 (1969).

(40) S. Winstein, S. G. Smith, and A. H. Fainberg, *J. Am. Chem. Soc.*, **83**, 618 (1961).

(41) H. Lund and J. Bjerrum, *Chem. Ber.*, **64**, 210 (1931).

(42) S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1126 (1956).

(43) V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rupp, *J. Am. Chem. Soc.*, **91**, 4838 (1969).

(44) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948).

(45) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).