resulting thiol was purified and counted as before. The ether layer containing the sulfenamide was washed several times and dried over anhydrous sodium sulfate. After evaporation of the solvent the solid was reduced with Zn–H$_2$SO$_4$ at reflux. The thiol was purified and counted.

In check experiments it was proved that these methods of separation of the unequivalent sulfur atoms for both thiolsulfinate and thiolsulfonate do not induce any appreciable scrambling.

Kinetic Procedure. Aliquots of the reaction mixture were sealed under nitrogen in glass ampoules and placed in a thermostated bath from which they were withdrawn at time intervals. Temperature control was ±0.05°. The reaction was followed by uv spectroscopy at 300 mμ with a Unicam SP 800 or a Beckman DU spectrophotometer. The runs in the presence of DPPH were followed between 350 and 520 mμ according to the concentration of DPPH. All the solutions containing DPPH were prepared, sealed in ampoules, and decomposed in the dark due to the instability of DPPH in the presence of light in solutions of thiolsulfinates.

Quantitative Analysis of the Disproportionation Products. The decomposition products of phenyl benzenethiolsulfinite were identified and quantitatively assessed by glc analysis of the reaction mixture. In the presence of styrene the formation of about 30% of at least six addition products with styrene made impossible a clean separation of disulfide and thiolsulfonate by column chromatography. The gas chromatographic analysis was critical and required carefully controlled conditions. A 50-cm column filled with 2.5% XE 60 (Perkin-Elmer) on Chromosorb 80–100 mesh was used. The disulfide was determined at 165° with tetracosane (C$_{24}$) as internal standard. The thiolsulfonate was determined at 180° without any internal standard by carefully controlling the amount of solution injected using a special Hamilton syringe.

The decomposition mixture of phenyl benzenethiolsulfinate in benzene was checked for acidity by stirring with water with a magnetic stirrer and titrating with 0.01 N NaOH. The mixture was also checked for the presence of sulfinic acid with a standard solution of KNO$_2$. The test was negative.

The Role of Solvent in the Solvolysis of *t*-Alkyl Halides[1]

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Abstract: In the Winstein–Grunwald relationship for solvolysis reactions, $\log k/k_0 = mY$, Y is a parameter taken to represent "solvent ionizing power" and not the nucleophilicity of the solvent or its ability to promote rate-determining elimination. Using *t*-butyl chloride, the reference compound chosen by Winstein and Grunwald to evaluate Y, it is impossible to rule out these other mechanistic contributions. In order to assess the role of solvent, rate constants for solvolysis of 1-adamantyl bromide in fourteen solvents were determined; data for eight additional solvents were obtained from the literature. In such a bridgehead substrate, backside nucleophilic solvent attack and elimination are both impossible. In general, an excellent correlation between data for *t*-butyl chloride and 1-adamantyl bromide is found indicating that *t*-butyl chloride, in most instances, solvolyzes by a limiting mechanism, free from nucleophilic solvent participation and from rate-determining elimination. Significant dispersion is found for aqueous trifluoroethanol solvent systems; this deviation is discussed in terms of specific substrate and leaving group effects.

The Winstein–Grunwald relationship for solvolysis reactions, $\log k/k_0 = mY$, affords a useful although not entirely precise tool for the calculation of solvolysis rates.[3] The parameter m is taken to be a measure of the susceptibility of a substrate to changes in Y, "the measure of the ionizing power of the solvent";[3c] k and k_0 are rate constants for solvolysis in the solvent in question and the standard solvent, respectively. While there are many possible modes of solvent interaction during solvolysis,[4] these are generalized into two factors of overriding importance: solvent nucleophilicity and ionizing power. "Solvent nucleophilicity" refers to the ability of the solvent acting as nucleophile to displace the leaving group, while "solvent ionizing power" concerns the ability of the medium to solvate ions and thus to facilitate their separation.[5] Since tertiary compounds have been assumed to solvolyze by a limiting mechanism free from nucleophilic solvent participation, Winstein and Grunwald[3] chose *t*-butyl chloride as the reference compound for the mY relationship and defined its m value as unity. Y values were then assigned by measuring the solvolysis rates of *t*-butyl chloride in various solvents. It was reasoned that the Y values thus obtained should be a function of solvent ionizing power only. The good agreement between Y and other measures of solvent polarity[6] (*e.g.*, Z,[7] a parameter determined from the effect of solvent on charge-transfer absorptions, which is presumably independent of solvent nucleophilicity) lends support to this contention.

Recently, however, we have shown that large rate enhancements may be ascribed to solvent participation in the solvolysis of secondary derivatives.[8,9] In the

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(3) (a) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 70, 846 (1948); (b) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, 73, 2700 (1951); (c) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(4) (a) C. D. Ritchie in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969; (b) S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Amer. Chem. Soc.*, **79**, 4146 (1957).

(5) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962.

(6) For a recent review of the various solvent parameters see: C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, 4, 29 (1965).

(7) E. M. Kosower, *J. Amer. Chem. Soc.*, 80, 3253 (1958).

(8) C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91**, 4291 (1969); C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *ibid.*, **91**, 4294 (1969); C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91**, 4296 (1969); P. v. R. Schleyer and C. J. Lancelot, *ibid.*, **91**, 4297 (1969).

course of this work, several possible inconsistencies (see below) concerning the specific role of solvent in the solvolysis of tertiary substrates were also encountered. Misgivings about the choice of *t*-butyl chloride as the standard for limiting solvolysis prompted the work reported here. As *t*-butyl chloride is the least substituted of all tertiary groups it might also be the most susceptible to nucleophilic solvent participation. Similarly, *t*-butyl chloride is capable of undergoing concerted elimination to isobutylene with involvement of solvent in the rate-determining step. To the extent that solvent is involved in either rate-determining nucleophilic displacement or rate-determining elimination, Y must reflect the nucleophilicity and proton-abstracting power of the solvent in addition to its ionizing power. A variety of experimental observations are discussed below which give some support to these possibilities.

Discussion

The susceptibility of *t*-butyl derivatives to direct displacement reactions has been the subject of some debate; although steric hinderance should certainly decrease the S$_N$2 rate of a *t*-butyl derivative, it is not clear that this process is not competitive.[10] A number of "S$_N$2 rate constants" for *t*-butyl bromide have been reported,[10b–d] but Winstein[10e] provided evidence that the rate increases observed in the presence of added nucleophile were the result of salt effects rather than bimolecular substitution reactions. On the other hand, while discussing the mechanistic implications of the mY relationship with regard to solvolysis of *t*-butyl and other limiting substrates Winstein suggested[3b] that the first intermediate or ion pair ". . . may nevertheless have some covalent character to the interaction between a solvent molecule and the central carbon atom . . . ." It is just this sort of solvent participation to which we have ascribed large rate enhancements in the solvolysis of secondary derivatives.[8,9]

The m value of a compound appears to reflect the mechanism by which it solvolyzes.[5,9a] Table I shows that the m values for a series of simple alkyl bromides increase sharply in going from the nonlimiting primary and secondary compounds to the presumably limiting tertiary derivatives. However the m values for both 1-adamantyl bromide and 1-bicyclo[2.2.2]octyl bromide are greater than those of either *t*-butyl chloride or *t*-butyl bromide. To the extent that this indicates more limiting character in the solvolysis of bridgehead derivatives, reaction of the *t*-butyl derivatives may proceed with nucleophilic solvent participation.

Table I. m Values for Alkyl Halides[a]

Substrate	m
Methyl bromide	0.22
Ethyl bromide	0.34 (55°)
Isopropyl bromide	0.43
t-Butyl bromide	0.94
t-Butyl chloride	1.00
1-Bicyclo[2.2.2]octyl bromide	1.03
1-Adamantyl bromide	1.20[b]

[a] Aqueous ethanol, 25°; unless otherwise indicated m values were taken or calculated from literature data as summarized in ref 9a. [b] This work. Our former value (1.08)[9a] was based on data in only two aqueous ethanol solvent systems.

A second measure of limiting behavior in solvolysis is the ratio of rate constants in acetic acid and in an aqueous solution with the same ionizing power: $(k_{\mathrm{EtOH}}/k_{\mathrm{AcOH}})_Y$.[5,9a] Since Y should not reflect nucleophilicity, this ratio is expected to be unity for limiting solvolysis. However, as aqueous ethanol is highly nucleophilic, the ratio should be considerably larger than unity for compounds which solvolyze with nucleophilic solvent assistance. Several examples have been reported, however, of alkyl tosylates (*e.g.*, 2-adamantyl tosylate, 0.13, and 1-adamantyl tosylate, 0.16) for which this ratio is less than unity.[9a] While $(k_{\mathrm{EtOH}}/k_{\mathrm{AcOH}})_Y$ is certainly sensitive to changes in leaving group, the possibility again arises that the solvolysis rate of *t*-butyl chloride in aqueous ethanol is enhanced by nucelophilic solvent participation.

The rate constants of other presumably limiting substrates show a dispersion effect when their logarithms are plotted against Y.[11] For example, α-phenylethyl bromide has an overall m value of 1.03, but the m value in aqueous ethanol is 0.82.[11] While Winstein's suggestion[11] that this effect arises from the inability of a simple linear free-energy relationship to account for differential solvation of transition- and ground-state molecules seems plausible, it is difficult to rule out mechanistic changes involving varying amounts of nucleophilic solvent assistance in ionization.

The problem of bimolecular elimination in *t*-butyl solvolyses is similarly unresolved. Thornton[12] studied the solvolysis of deuterated *t*-butyl chloride in several solvents, and the observed isotope effects and product distributions indicated that bimolecular elimination was not a major pathway. However, Shiner's[13] recent observation of an appreciable amount of olefin formation (30%) accompanied by a large β-deuterium isotope effect in the trifluoroethanolysis of *t*-butyl chloride ". . . strongly suggests that elimination from an ion pair in this solvent may be rate determining . . . ."[13]

In light of these ambiguities, we have attempted to clarify the role of solvent in *t*-butyl chloride solvolyses by the indirect method of comparison with a compound (1-adamantyl bromide) for which elimination and backside solvent participation are impossible. Elimination in the 1-adamantyl nucleus is highly unlikely due to the large amount of strain which would be present in the resulting bridgehead olefin;[14,15] product studies of the solvolysis of 1-adamantyl derivatives have failed to reveal any evidence of olefin formation.[15] Nucleophilic participation by solvent is even more

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(9) (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, *ibid.*, **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).

(10) (a) C. G. Swain and R. B. Mosely, *ibid.*, **75**, 4627 (1953); (b) L. J. Le Roux and E. R. Swart, *J. Chem. Soc.*, 1475 (1955); (c) P. B de La Mare, *ibid.*, 3180 (1955); (d) E. D. Hughes, C. K. Ingold, and J. D. H. Mackie, *ibid.*, 3173 (1955); (e) S. Winstein, S. Smith, and D. Darwish, *Tetrahedron Lett.*, No. **16**, 24 (1959).

(11) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 1602 (1957).

(12) G. J. Frisone and E. R. Thornton, *ibid.*, **90**, 1211 (1968).

(13) V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *ibid.*, **91**, 4838 (1969).

(14) J. March, "Advanced Organic Chemistry," McGraw-Hill, New York, N. Y., 1968; R. B. Gagosian, J. C. Dalton, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4754 (1970).

(15) (a) R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); (b) J. E. Nordlander, S. P. Jindal, and D. K. Kitko, *Chem. Commun.*, 1136 (1969).

unlikely as the cage structure completely blocks the rear side of the reaction center. Another bridgehead system (1-bicyclo[2.2.2]octyl bromide) has been studied,[16] but the number of solvents examined (five) was not sufficient to allow a definitive conclusion.

The kinetic results for solvolysis of 1-adamantyl bromide (including several literature values) are presented in Table II. The wide range of both nucleophilicity and ionizing power for the solvents examined should allow considerable opportunity for mechanistic variation. A plot of the logarithms of the rate constants (at 25°) for 1-adamantyl bromide *vs.* Y is shown in Figure 1. The correlation between the rates of 1-adamantyl bromide and *t*-butyl chloride is reasonably good; the only points which deviate significantly are those for aqueous trifluoroethanol (TFE).

Table III presents a summary of the correlations between log k for 1-adamantyl bromide and Y for different groups of solvents; these data afford a measure of the dispersion between different solvent families. When the points for aqueous trifluoroethanol are omitted the correlation improves markedly: the standard deviation is decreased from 0.069 to 0.036 and the correlation coefficient is raised from 0.972 to 0.992. Thus, although the aqueous trifluoroethanols show considerable dispersion, this effect is much less for the other solvent families, which are accommodated well by a single line (Figure 1).

The linear free-energy relationship established between *t*-butyl chloride and 1-adamantyl bromide solvolyses suggests that these compounds react *via* highly similar mechanisms in most solvents. (As a corollary nothing intrinsically "unusual" is indicated for the solvolysis of bridgehead compounds.) On the assumption that elimination and backside solvent participation are ruled out for 1-adamantyl bromide, these processes should also be absent for the solvolysis of *t*-butyl chloride in these solvents. Even the deviation of the line for aqueous trifluoroethanol cannot be a consequence of elimination or solvent participation in *t*-butyl chloride solvolysis; the line lies above the main line in Figure 1, and this is inconsistent with any process causing rate enhancement of *t*-butyl chloride. We therefore concur with Winstein's earlier conclusion[4b] that in the solvolysis of *tertiary* alkyl halides the role of solvent with regard to the central carbon atom is one of electrostatic stabilization rather than of specific solvation.

The anomalies discussed earlier with regard to the mY relationship are clearly not a consequence of either rate-determining elimination or backside solvent participation in the solvolysis of *t*-butyl chloride; they must originate as the result of specific substrate and leaving group characteristics. Three phenomena may be of general importance in this respect: (1) the extent of charge dispersal in the transition state,[9a] (2) the amount of ion pair return,[4b,17] and (3) hydrogen bonding of the leaving group.[4b,18]

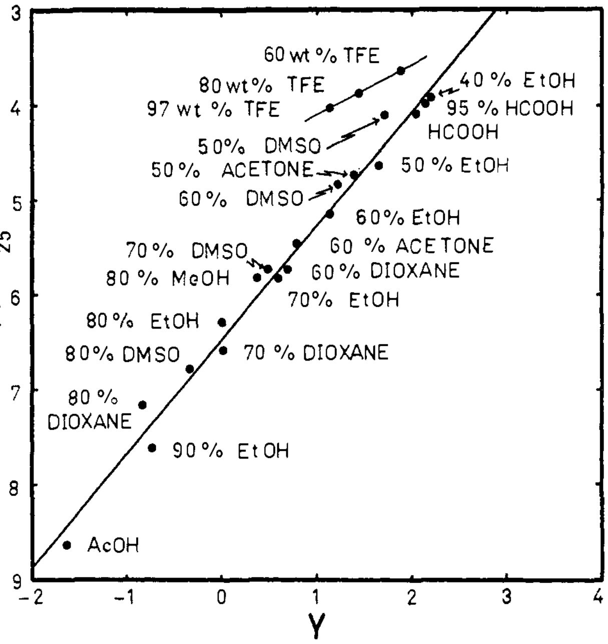

Figure 1. Plot of $-\log k$ (25°) for solvolysis of 1-adamantyl bromide *vs.* Y. The line represents the least-squares fit for all solvents except the aqueous trifluoroethanols.

The sensitivity of the magnitude of m to the degree of charge dispersal in the transition state is quite pronounced.[9a] For example, substrates known to solvolyze with predominant neighboring group participation have m values in the range 0.4–0.8.[19] A similar effect should be operative for the leaving group. The ability of leaving groups to disperse developing negative charge is expected to decrease in the order tosylate > bromide > chloride; m values decrease in the reverse order.[9a,18] Similarly, the generally larger m values of bridgehead derivatives (compared to those of acyclic analogs) may arise from the exclusion of solvent at the rear side of the reaction center, thus decreasing electrostatic solvation. Such solvation could partially disperse positive charge in the acyclic substrates.

"Abnormal" $(k_{\mathrm{EtOH}}/k_{\mathrm{AcOH}})_Y$ ratios[9a,4b] may be in part a consequence of ion-pair return and hydrogen bonding to the leaving group. Internal return appears to be less for sulfonates than for halides[20a] and is also less in ethanol than in acetic acid.[20] Similarly, hydrogen bonding to the leaving group[4b,18] apparently is more important in acetic acid than in ethanol and increases in the leaving group order Br < Cl < OTs. Either or both of these effects could be responsible for the lower values of $(k_{\mathrm{EtOH}}/k_{\mathrm{AcOH}})_Y$ observed for tosylates relative to halides.[4b,9a]

Since $(k_{\mathrm{EtOH}}/k_{\mathrm{AcOH}})_Y$ is to some extent a measure of dispersion between the lines for aqueous ethanol and acetic acid–formic acid, ion-pair return and hydrogen bonding to the leaving group may also contribute to the general dispersion of lines found with 1-adamantyl bromide, 1-adamantyl tosylate,[21] and other

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(16) M. Finkelstein, Ph.D. Thesis, Yale University, New Haven, Conn., 1955; although this work has been cited in the review literature,[5,15a] it has never been published.

(17) A. F. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 1904 (1968).

(18) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1608 (1957).

(19) *Cf.* S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961); see also ref 4b and 18.

(20) (a) S. Winstein, B. Appel, R. Baker, and A. Diaz, Special Publication No. 19, The Chemical Society, London, 1965, p 109; (b) A. F. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 4300 (1969).

(21) D. N. Kevill, F. L. Weitel, and V. M. Horvath have carried out a similar kinetic study with 1-adamantyl tosylate: Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, PETR 055. We thank Professor Kevill for providing us with a manuscript prior to publication.

Table II. Solvolysis Rates of 1-Adamantyl Bromide[a]

Solvent	T, °C	k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
40% EtOH[b]	25	1.21×10^{-4}	21.0	−6.2
50% EtOH[b]	25[c]	2.86×10^{-5}	22.6	−3.9
60% EtOH[d,e]	50.4	$1.41 \pm 0.07 \times 10^{-4}$	21.8	−8.8
	77.8	$2.17 \pm 0.04 \times 10^{-3}$		
	25[c]	7.19×10^{-6}		
70% EtOH[d,e]	50.2	$3.72 \pm 0.02 \times 10^{-5}$	23.6	−5.9
	78.1	$7.49 \pm 0.04 \times 10^{-4}$		
	25[c]	1.54×10^{-6}		
80% EtOH[d,e]	77.8	$1.76 \pm 0.03 \times 10^{-4}$	22.4	−12.3
	100.9	$1.36 \pm 0.02 \times 10^{-3}$		
	25[c]	5.10×10^{-7}		
90% EtOH[b]	25[c]	2.47×10^{-8}	27.0	−2.9
97% (w/w) TFE[d]	25.15	$9.66 \pm 0.01 \times 10^{-5}$	19.3	−12.3
	51.50	$1.47 \pm 0.01 \times 10^{-3}$		
	25[c]	9.50×10^{-5}		
80% (w/w) TFE[d]	25.00	$1.31 \pm 0.01 \times 10^{-4}$	19.8	−9.9
	51.50	$2.18 \pm 0.01 \times 10^{-3}$		
60% (w/w) TFE[d]	25.00	$2.28 \pm 0.01 \times 10^{-4}$	20.8	−5.3
	51.50	$4.38 \pm 0.01 \times 10^{-3}$		
60% dioxane[d]	50.4	$3.95 \pm 0.02 \times 10^{-5}$	22.5	−9.3
	78.0	$6.71 \pm 0.05 \times 10^{-4}$		
	25[c]	1.85×10^{-6}		
70% dioxane[d]	78.0	$1.22 \pm 0.02 \times 10^{-4}$	23.3	−10.4
	100.6	$9.80 \pm 0.05 \times 10^{-4}$		
	25[c]	2.72×10^{-7}		
80% dioxane[f]	75.0	$1.22 \pm 0.02 \times 10^{-5}$	20.6	−22.2
	100.2	$9.75 \pm 0.32 \times 10^{-5}$		
	25[c]	7.11×10^{-8}		
50% acetone[d]	50.4	$2.86 \pm 0.04 \times 10^{-4}$	20.1	−12.9
	75.1	$2.82 \pm 0.03 \times 10^{-3}$		
	25[c]	1.84×10^{-5}		
60% acetone[d]	50.4	$6.53 \pm 0.25 \times 10^{-5}$	21.2	−12.3
	75.1	$7.38 \pm 0.10 \times 10^{-4}$		
	25[c]	3.57×10^{-6}		
AcOH–NaOAc[f]	74.9	$2.33 \pm 0.01 \times 10^{-6}$	27.8	−4.7
	100.1	$3.78 \pm 0.10 \times 10^{-5}$		
	25[c]	2.38×10^{-9}		
HCO_2H–NaO_2CH[f]	24.7	$7.93 \pm 0.12 \times 10^{-5}$	22.3	−2.4
	10.10	$1.08 \pm 0.01 \times 10^{-5}$		
	25[c]	8.25×10^{-5}		
80% MeOH[d]	50.45	$3.84 \pm 0.08 \times 10^{-5}$	23.7	−5.8
	74.90	$5.47 \pm 0.01 \times 10^{-4}$		
	25[c]	1.53×10^{-6}		
95% HCO_2H[g]	25[c]	1.13×10^{-4}	17.6	−17.6
50% DMSO[h,i]	25[c]	7.99×10^{-5}	20.5	−8.7
60% DMSO[h,i]	25[c]	1.46×10^{-5}	21.1	−9.9
70% DMSO[h,i]	25[c]	1.83×10^{-6}	22.1	−10.8
80% DMSO[h,i]	25[c]	1.68×10^{-7}	23.4	−11.0

[a] All solvents are volume per cent unless otherwise noted. [b] J. Delhoste, G. Lamaty, and P. Pajanacci, *C.R. Acad. Sci.*, **266**, 508 (1968). [c] Calculated from data at other temperatures. [d] Determined conductometrically. [e] Agreement with literature data[b] for these solvents is satisfactory; also *cf.* ref 15a. [f] Determined titrimetrically. [g] F. N. Stepanov and G. I. Danilenko, *J. Org. Chem. U.S.S.R.*, **2**, 1607 (1966). [h] J. Delhoste, G. Gomez, and G. Lamaty, *C. R. Acad. Sci.*, **266**, 1468 (1968). [i] Y values were obtained by interpolation of the data of K. Heinonen and E. Tommila, *Suom. Kemistilehti B*, **38**, 9 (1965); 50% DMSO, $Y = 1.720$; 60% DMSO, $Y = 1.230$; 70% DMSO, $Y = 0.500$; 80% DMSO, $Y = -0.330$.

Table III. Correlation of the Logarithms of the Rate Constants for Solvolysis of 1-Adamantyl Bromide with Y for Different Groups of Solvents

Solvents (no.)	Slope (m)	Intercept	Standard dev	Corr coeff
All (22)	1.27	−6.380	0.069	0.972
TFE excluded (19)	1.20	−6.450	0.036	0.992
Aqueous ethanol (6)	1.20	−6.532	0.064	0.994
Aqueous dioxane (3)	0.91	−6.451	0.143	0.988
Aqueous dimethyl sulfoxide (4)	1.29	−6.371	0.038	0.999
Aqueous trifluoroethanol (3)	0.51	−4.618	0.031	0.998
Aqueous acetone (2)	1.18	−6.389		
Acids (3)	1.23	−6.607	0.005	1.000

limiting substrates.[4b,11,18] Leaving group effects alone cannot account for this dispersion as the effect is also observed with limiting chlorides.[4b,18]

Although *t*-butyl chloride appears to be an excellent model for limiting solvolysis in the commonly used solvents, the possibilities of rate-limiting elimination and nucleophilic solvent participation in other media cannot be ignored. For this reason we propose that for future determination of Y values, serious consideration should be given to the use of 1-adamantyl bromide as the reference compound,[22] or at least that 1-adamantyl bromide be used as a check on the results

(22) On this basis Y_{Ad} values can be calculated for the aqueous mixtures of trifluoroethanol: 60% (w/w) TFE, 2.65; 80% (w/w) TFE, 2.41; and 97% (w/w) TFE, 2.27.

obtained with *t*-butyl chloride. The choice of reference compound may be dictated by the nature of the experimental system of interest.

Experimental Section

Purification of Chemicals. 1-Adamantyl Bromide. Commercial 1-adamantyl bromide (Aldrich) was sublimed at 105 (10 mm) and 95° (0.15 mm), and was then recrystallized from pentane at −80°, mp 118.8–119.2° (lit. 119–120°).[23]

Ethanol. Ethanol was distilled from magnesium ethoxide as described by Lund and Bjerrum.[24]

Methanol. Methanol was distilled from magnesium methoxide as described by Lund and Bjerrum.[24]

Acetone. Commercial acetone was allowed to reflux with potassium permanganate, dried with Drierite, and distilled through a 24-in. Vigreux column.[25]

Dioxane. Dioxane was purified by the method of Fieser.[25] The purified solvent was stored over sodium and distilled shortly before use.

Formic Acid. The crude formic acid (Eastman, 97%) was stirred with an excess of boric anhydride for 1 week and distilled through a 24-in. Vigreux column, bp 33–34° (45 mm).[26]

Acetic Acid. Glacial acetic acid (1 l.) was refluxed with 100 ml of acetic anhydride and several milliliters of concentrated sulfuric acid. The dry acetic acid was then distilled under nitrogen through a 24-in. vacuum-jacketed column packed with glass helixes, bp 118° (1 atm).

Trifluoroethanol. Commercial 2,2,2-trifluoroethanol (Matheson Colemen and Bell) was distilled from aqueous potassium carbonate, dried with phosphorus pentoxide, and fractionally distilled through a 24-in. vacuum-jacketed column packed with glass helixes, bp 73.5–74.5°.[13]

Kinetic Methods. Rates in the aqueous solvents were determined conductometrically with a Wayne-Kerr Model B331 Impedence Bridge, capable of 0.1% accuracy. The conductivity cells used had bright platinum electrodes, cell constants of 0.2–0.4, and a volume of approximately 25 ml. In a typical experiment, enough 1-adamantyl bromide to make a 10^{-3} *M* solution was placed in the conductivity cell and 20 ml of solvent was added. The cell was then sealed and equilibrated with stirring for 5 min in the constant temperature bath. The usual number of measurements taken was 12. The raw conductance data were then fitted to the first-order rate equation by means of a least-squares computer program. The solvents used for conductivity measurements give linear conductivity–concentration plots within the limits of experimental error;[27] a possible exception to this may be 80% dioxane in which the rates obtained conductometrically were faster than the titrimetric rates by almost a factor of two. The titrimetric rate constant was used for analysis of the data.

Rate constants in acetic acid and formic acid were determined by Volhard titration of hydrogen bromide, preceded by extraction of unreacted 1-adamantyl bromide as described by Winstein and Fainberg.[30] This method was also used to check the conductometric measurements in 97% trifluoroethanol at 25°.

Acknowledgment. We thank Dr. T. W. Bentley for helpful discussions.

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[23] S. Landa and S. Hala, *Collect. Czech. Chem. Commun.*, **24**, 93 (1959).

[24] H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

[25] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath, Boston, Mass., 1941.

[26] S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120 (1952).

[27] *Cf.* B. L. Murr, Jr., Ph.D. Dissertation, Indiana University, 1961.

The Reaction of Trityl Carbonium Ion with Water

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Abstract: The reversible reaction of trityl fluoroborate with water in acetonitrile solvent has been studied using nmr line broadening. The reaction is moderately fast on the nmr time scale ($\tau \approx 10^{-2}$ sec, 0.1 *M* cation and water) at room temperature and is approximately first order in water and zero order in cation under these conditions. The kinetic results and ^{19}F nmr studies are consistent with a model involving extensive aggregation.

The rate constants for attack of nucleophiles on carbonium ions are of considerable interest. Since in many carbonium ion reactions, relative rates such as the ratio of attack of solvent to ion-pair return or internal rotation are known,[2] the measurement of an absolute rate would generate a great deal of useful information. For the most part, owing to the high reactivity of carbonium ions, such direct measurements have been limited to relatively stable species such as highly substituted trityl ions. Early work by Grunwald[3] and Turgeon and LaMer[4] established the rates of attack of water and hydroxide ion in aqueous media on crystal violet and closely related derivatives. These reactions were slow (k_1 *ca.* 10^{-4} sec^{-1}) and could be followed by conventional spectroscopic means. More recently, the development of stopped-flow techniques has made measurement of faster reactions accessible. Taft[5] has measured the rates of reactions of a series of substituted trityl ions with water. Pseudo-first-order rate constants as rapid as 10^3 sec^{-1} were recorded for the mono-*p*-methoxytrityl cation. Ritchie[6] has studied the rates of attack on crystal violet and related ions by a large number of nucleophiles both in aqueous and nonaqueous media. Again, rapid rates were observed, especially in the nonaqueous systems. Hill[7] has recently measured the rates of reaction of water, ammonia, and hydroxide ion with tris-*p*-methoxytrityl cation by stopped flow. Nicholson and Wyatt[8] also measured

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[2] For a general review, see A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1968.

[3] E. F. J. Duynstee and E. Grunwald, *J. Amer. Chem. Soc.*, **81**, 4542 (1959).

[4] V. C. Turgeon and V. K. LaMer, *ibid.*, **74**, 5988 (1952).

[5] R. A. Diffenback, K. Sano, and R. W. Taft, *ibid.*, **88**, 4747 (1966).

[6] C. D. Ritchie, G. A. Skinner, and V. G. Badding, *ibid.*, **89**, 2063 (1967).

[7] E. A. Hill and W. J. Mueller, *Tetrahedron Lett.*, 2565 (1968).