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Preparation of Ions. Cyanocarbenium ions and propargyl cations were prepared from the progenitor cyanohydrins and propargyl alcohols as described earlier.[12,14]

The ^{13}C NMR spectroscopic studies were carried out at 50 MHz on a Varian XL-200 superconducting NMR spectrometer equipped with a variable-temperature broad-band probe. The ^{13}C–^{13}C coupling constants in the ^{13}C-enriched ions and the progenitors were directly measured from their proton-noise-decoupled ^{13}C NMR spectra. The coupling constants in the other neutral model compounds reported in Table II were measured from the ^{13}C satellite spectra by using the INADEQUATE[6] pulse sequence: $90°\ (x)–\ \tau–180°\ (\pm y)–\ \tau–90°\ (x)–\ \Delta–90°\ (\phi)\simeq\text{Acq.}\ (\psi)$, where $\tau \simeq (2n + 1)/4J_{CC}$, Δ is a very short delay ($\sim 10\ \mu s$) needed to reset the radiofrequency phase during which time double-quantum coherance evolves and ϕ and ψ are the phase of the last 90° "read" pulse and the receiver, respectively.

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Essentially Solvent-Independent Rates of Solvolysis of the 1-Adamantyldimethylsulfonium Ion. Implications Regarding Nucleophilic Assistance in Solvolyses of *tert*-Butyl Derivatives and the N_{KL} Solvent Nucleophilicity Scale[1]

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Abstract: Rearside nucleophilic solvation of the developing carbocation is severely hindered during the solvolysis of the 1-adamantyldimethylsulfonium ion (1-AdSMe$_2^+$). For variation in the composition of binary solvent systems, the ion always shows a variation of the specific rate in the opposite direction to that observed for the *tert*-butyldimethylsulfonium ion (*t*-BuSMe$_2^+$); these observations are rationalized in terms of a dominant nucleophilic solvation at the transition state for *t*-BuSMe$_2^+$ solvolysis and a dominant nucleophilic stabilization of the reactant for 1-AdSMe$_2^+$ solvolysis. These systems are compared to the corresponding alkyl halides. Corrections applied in setting up the N_{KL} scale of solvent nucleophilicities would be better based on 1-AdSMe$_2^+$ solvolyses. However, the insensitivity of 1-AdSMe$_2^+$ solvolyses to solvent variation (specific rates in 41 solvents, at 70.4 °C, vary by less than a factor of seven) allows $\log (k/k_0)_{\mathrm{Et_3O^+}}$ values to be taken as a good measure of solvent nucleophilicity. For solvolyses of 1-AdSMe$_2^+$ in aqueous ethanol (≥60% ethanol), the S value (favoring reaction with water) is 1.35 at both 70.6 and 100.1 °C.

Considerable interest centers around the extent to which specific rates of solvolysis of *tert*-butyl chloride are influenced by the nucleophilicity of the solvent. Evidence for[2-10] and against[11-16] detectable interaction of the solvent has been presented. The original Grunwald–Winstein equation[17] (eq 1) defines a scale of

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

solvent ionizing power (Y) in terms of the specific solvolysis rates of *tert*-butyl chloride in a given solvent (k) and in 80% ethanol (k_0), with m assigned a value of unity. Accordingly, the detailed mechanism has important implications both as regards the significance of the Y scale and as regards the types of substrates for which it can logically be used in correlation analysis.

In a discussion of solvation effects upon S$_N$1 and E1 reactions, Ingold stated[18] "in the unimolecular substitution of an alkyl halide, both of the ions, which are formed in the initial heterolysis, have to be solvated". While the nucleophilic solvation of a developing bridgehead carbocation will necessarily be relatively weak, appreciable rearside solvation is possible for a developing *tert*-butyl carbocation.[19,20] In accord with the description of Ingold, we have considered[8] the solvolysis of *tert*-butyl chloride to involve carbenium ion formation, with the need to consider solvation of *both* of the incipient ions. Bentley and co-workers[7,9] have viewed the mechanism in a slightly different way and have formulated it as an example of an S$_N$2 (intermediate) mechanism.[21] Other workers[13-16] have, however, proposed that changes in the specific solvolysis rate, accompanying changes in the solvent, can be rationalized without the need to consider the nucleophilicity of the solvents.

If our view of the solvation process[8,18] is accepted, the original Y scale[17] is valid as a scale of solvent ionizing power. However, it should be used within eq 1 only for the correlation of solvolyses within which a similar (relatively small) contribution from nu-

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cleophilic solvation accompanies a dominant contribution resulting from electrophilic solvation and solvent dipolarity/polarizability effects. For example, a linear correlation of the logarithms of the specific rates of solvolysis of benzoyl chloride against Y values in solvents of high Y and/or low N values was considered[22] to reflect a nucleophilic contribution similar to that claimed[8,9] for *tert*-butyl chloride solvolysis.

For S_N2 solvolyses with an appreciable dependence upon solvent nucleophilicity, a two-term equation (the extended Grunwald–Winstein equation) has been proposed (eq 2).[23] The additional

$$\log (k/k_0) = lN + mY \qquad (2)$$

lN term involves a scale of solvent nucleophilicity[24,25] (N) and the sensitivity (l) of the substrate solvolysis to this property. Ideally, all nucleophilic contributions are governed by the lN term, and any inclusion of nucleophilic properties within the Y scale is undesirable. Alternative Y scales have been developed based upon the solvolyses of adamantyl derivatives, where nucleophilic contributions are minimized.[26] When a Y_{Cl} scale, based on 1-adamantyl chloride solvolysis, is used within eq 2, a l value of ca. 0.3 (based upon N_{OTs} values[24]) can be calculated for *tert*-butyl chloride.[9] The validity of this analysis has been questioned. It has been suggested[15,16] that the moderate differences in response to the solvent variation observed for the specific rates of solvolysis of 1-adamantyl chloride and *tert*-butyl chloride could result not from a higher response to changes in the solvent nucleophilicity for *tert*-butyl chloride but from a higher response to changes in the solvent electrophilicity for 1-adamantyl chloride. Although the explanation in terms of nucleophilicity conforms nicely to a comparison of bridgehead and acyclic substrates, the strong covariences[8,27] often observed between N and Y values, for a given mixed solvent system, make the choice between the two explanations a nontrivial one. However, the value interrelating the N and Y scales varies considerably for different binary systems, and the covarience problem can be overcome by a careful choice of standard solvents.[9,24,28]

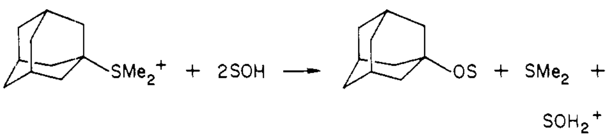
Support for the absence of a nucleophilic component comes from an alternative linear free-energy relationship (LFER) treatment of *tert*-butyl chloride solvolysis in terms of solvatochromatic properties (π^*, α, and β).[29] It was found[15] that the specific rates could be correlated against π^* and α, without the need to include a term relating to solvent basicity (β values). Similarly, a treatment[16] in terms of the Koppell-Palm equation,[13] with inclusion[30] of the Hildebrand parameter, did not require a term relating to basicity or nucleophilicity.

A problem with multiparameter equations is that inclusion of a minor contributor will not meaningfully improve the correlation if its contribution is significantly less than the sum of the deviations associated with the other parameters. For *tert*-butyl chloride, it is generally agreed that solvent-induced rate variations are governed primarily by electrophilicity and dipolarity/polarizability changes (for aqueous ethanol, a contribution of 10% being governed by nucleophilicity changes was estimated[8]). While multiparameter LFER treatments are needed for estimating the relative importance of electrophilicity and dipolarity/polarizability effects during *tert*-butyl chloride solvolysis, we believe that for solvolysis of *tert*-butyl derivatives, the best approach toward estimating the importance of ***nucleophilicity*** is not to try to improve the LFER treatment (such as by incorporation of additional terms) but to change the leaving group in a way which eliminates or minimizes those other contributions which are dominant in the solvolysis of *tert*-butyl chloride. A convenient type of substrate for such a study is with an initially positively charged leaving group, which leaves as a neutral molecule (eq 3). We have shown

$$\text{R-X}^+ \rightarrow \text{R}^+ + \text{:X} \qquad (3)$$

previously[8] that specific solvolysis rates for the *tert*-butyldimethylsulfonium ion (t-BuSMe$_2^+$) correlate with N_{KL} solvent nucleophilicity values,[25] with an l value of ca. 0.35. For studies in aqueous ethanol, a brief comparison was made with specific solvolysis rates of the 1-adamantyldimethylsulfonium ion (1-AdSMe$_2^+$).

In the present paper, we present full details of our study of the solvolysis of the 1-AdSMe$_2^+$ ion (eq 4). It will be shown that the hindrance to rear-side solvation, due to the cage structure, leads to the specific solvolysis rates at a given temperature being almost independent of the composition of the solvent. For S_N2-reacting R–X$^+$ substrates, the corrections which must be applied to the logarithmic rate ratio term in the establishment of an N scale are discussed. Product ratios in aqueous ethanol are determined and compared to those for neutral adamantyl substrates.[31-36] The ratios of t-BuSMe$_2^+$ to 1-AdSMe$_2^+$ specific solvolysis rates in aqueous 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) solvents are obtained and compared with the low ratios previously reported[9] for the corresponding solvolyses of the chlorides.



(4)

Results

Solvolyses in Dry Alcohols, Water, Acetic Acid, and 80% Ethanol. Rates of solvolysis were determined at four or five temperatures in the 50–90 °C range. Runs in *tert*-butyl alcohol were carried out in the presence of a 5% excess of pyridine.[37] In acetic acid, the reaction appeared to come to an equilibrium (paralleling observations[38] for the acetolysis of the *tert*-butylethylmethylsulfonium ion) and theoretical infinity titers were used in the calculations; for example, for a 0.0063 M solution of 1-AdSMe$_2^+$OTf$^-$ in acetic acid at 90.1 °C, a mean of experimental infinity titers from six independent kinetic runs corresponded to an acid development which was 68.6 ± 0.8% of the theoretical. Addition of a 15% excess of sodium acetate prevented the establishment of an equilibrium and, at 70.4 °C, a specific acetolysis rate of 3.19 (± 0.25) × 10^{-6} s^{-1} was observed, a value 19% higher than that estimated (from data at other temperatures) in the absence of sodium acetate.

Constant integrated values for the first-order rate coefficients were obtained throughout each run. All the values for, at least, duplicate runs were averaged, and these averages are reported in Table I, together with values for Y^+ (calculated by using eq 1 with $m = 1$) for 1-AdSMe$_2^+$ solvolysis. These Y^+ values establish a scale analogous to the solvent ionizing power scale for neutral substrates. The activation parameters (at 70.4 °C), obtained from a treatment of the data of Table I in terms of the Eyring equation, are reported in Table II.

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Table I. First-Order Rate Coefficients for the Solvolysis of 1-Adamantyldimethylsulfonium Trifluoromethanesulfonate[a,b] and Y^+ Values[c]

	10^6k, s^{-1}						
temp, °C	80% EtOH	MeOH	EtOH	*i*-PrOH	*t*-BuOH	AcOH	H_2O
49.9	0.0770	0.0996	0.0765[d]	0.0583[d]	0.0331		
50.6			0.0802	0.0638[d]			0.174
60.3	0.461	0.520	0.423	0.346	0.226	0.479	0.911
70.4	2.27	2.47	2.15	1.68	1.09	2.45[e]	4.10
80.1	10.6	12.0	10.3	7.41	4.94	9.69	16.4
90.4	45.8			34.0	18.5	39.8	
Y^+	0.000	0.037	−0.024	−0.131	−0.319	0.072	0.257

[a] Concentration of 0.0060–0.0065 M. [b] Standard deviations for k were within 5% of the reported values. [c] $\log (k/k_0)_{1\text{-AdSMe}_2^+}$ at 70.4 °C, where k_0 refers to the specific rate in 80% ethanol. [d] Single determination. [e] At 69.8 °C; use of the Arrhenius equation leads to a value of 2.68×10^{-6} s^{-1} at 70.4 °C.

Table II. Enthalpies ($\Delta H^{\ddagger}$) and Entropies ($\Delta S^{\ddagger}$) of Activation for Solvolysis of 1-Adamantyldimethylsulfonium Trifluoromethanesulfonate[a]

solvent	$\Delta H^{\ddagger}_{343.6}$, kcal/mol	$\Delta S^{\ddagger}_{343.6}$, eu
80% ethanol[b]	36.2 ± 0.2	20.9 ± 0.6
methanol	35.2 ± 0.8	17.9 ± 2.6
ethanol	36.1 ± 0.6	20.3 ± 1.8
2-propanol	36.0 ± 0.4	19.6 ± 1.1
tert-butyl alcohol	35.8 ± 0.6	18.2 ± 2.0
acetic acid	34.4 ± 0.9	15.7 ± 2.9
water	34.2 ± 0.4	16.2 ± 1.3

[a] Calculated by using the data of Table I, with associated standard errors. [b] On a volume–volume basis at 25.0 °C.

Table III. First-Order Rate Coefficients for the Solvolysis of the 1-Adamantyldimethylsulfonium Ion[a,b] in Pure and Binary Solvents[c,d] at 70.4 °C and Y^+ Values[e]

solvent	10^6k, s^{-1}	Y^+	solvent	10^6k, s^{-1}	Y^+
60% EtOH	2.57	0.054	95% acetone	3.16[h]	0.144
40% EtOH	2.87	0.102	90% acetone	3.11	0.137
20% EtOH	3.56	0.195	80% acetone	3.02	0.124
80% MeOH	2.79	0.090	60% acetone	2.90	0.106
60% MeOH	2.85	0.099	40% acetone	3.08	0.133
40% MeOH	3.01	0.123	20% acetone	3.41	0.177
20% MeOH	3.21	0.150	95% dioxane	1.32	−0.235
100% TFE	6.49	0.456	90% dioxane	1.69	−0.128
97% TFE	5.58	0.391	80% dioxane	1.76	−0.111
90% TFE	5.27	0.366	70% dioxane	2.07	−0.040
70% TFE	4.97	0.340	60% dioxane	2.29	0.004
50% TFE	4.43	0.290	40% dioxane	2.30	0.006
97% HFIP	7.09[f]	0.495	20% dioxane	2.71	0.077
90% HFIP	6.97	0.487	80% T–20% E[c]	4.88	0.332
70% HFIP	5.15	0.356	60% T–40% E	3.47	0.184
50% HFIP	4.87	0.332	40% T–60% E	3.00	0.121
100% HCO_2H	2.46[g]	0.035	20% T–80% E	2.59	0.057

[a] Concentration of 0.0060–0.0065 M. [b] Standard deviations for k were within 6% of the reported values. [c] Other component water, except for TFE–EtOH (T–E) mixtures. [d] On a volume–volume basis at 25.0 °C, except for TFE–H_2O and HFIP–H_2O mixtures which are on a weight–weight basis. [e] For definition, see footnote c of Table I. [f] Value of 0.304×10^{-6} s^{-1} s 49.7 °C. [g] Obtained by extrapolation to zero [HCO_2Na] of three duplicate determinations with added sodium formate; with [HCO_2Na] of 0.0040, 0.0086, and 0.0171 M, 10^6k values were 2.49, 2.59, and 2.66 s^{-1}. [h] With initial [Me_2S] of 0.050 and 0.10 M, 10^6k values were 3.09 and 2.94 s^{-1}.

Solvolyses in Solvents of Varying Ionizing Power. A study was made at 70.4 °C in formic acid, 2,2,2-trifluoroethanol (TFE)–ethanol mixtures and in mixtures of water with ethanol, methanol, acetone, TFE, dioxane, and HFIP. For solvolysis in 100 and 97% TFE and in 97 and 90% HFIP, a 5% excess of pyridine was added, to prevent the establishment of an equilibrium. Those values not previously reported in Table I are reported in Table III. All runs were performed, at least, in duplicate.

For solvolysis in 95% acetone, the effect upon the specific solvolysis rate of initially added dimethyl sulfide, in concentrations of up to 0.1 M, was found to be negligible (Table III).

In formic acid, a rather early equilibrium could be avoided by the addition of sodium formate. Specific rates in the presence of three concentrations of sodium formate were linearly extrapolated to zero concentration (Table III).

Product Studies. The products from the solvolysis of 1-$AdSMe_2^+OTf^-$ in aqueous ethanol mixtures containing from 96 to 20% ethanol were studied by GLPC at 70.6 and 100.1 °C. A 10% excess of pyridine was added in order to prevent acid-catalyzed equilibration of the alcohol and ethyl ether products, which had been observed for the corresponding solvolyses of other adamantyl derivatives.[32,33] No evidence was obtained for any 1-adamantyl methyl sulfide formation, which would have been expelled during substitution reaction at a methyl group. The percentages of 1-adamantanol formation are reported in Table IV.

The small percentages of 1-adamantanol found after solvolysis in 100% ethanol were ascribed as being due to contamination of the substrate. In the calculation of the selectivity values (S), reported in Table IV, the percentage of 1-adamantanol found after solvolysis in 100% ethanol was subtracted from each of the values reported for the solvolysis in aqueous ethanol before insertion into eq 5.

$$S = \frac{[\text{adamantanol}][\text{ethanol}]}{[\text{adamantyl ethyl ether}][\text{water}]} \qquad (5)$$

Effect upon the Ethanolysis of Added Tetraethylammonium Chloride. Addition of 0.16 M tetraethylammonium chloride to the ethanolysis of 0.0062 M 1-$AdSMe_2^+OTf^-$, at 70.4 °C, severely perturbed both the kinetics and the product formation. The specific rates of acid formation, based upon theoretical infinity titers, fell in value during the run. The development of acid reached a maximum value of ca. 45% of the theoretical after 8 days, and it then fell slowly in value to about 30% of the theoretical after 78 days. A GLPC analysis of the products indicated the absence of 1-adamantyl chloride and the presence of a 60% yield of 1-adamantyl methyl sulfide.

Solvolysis of *tert*-Butyldimethylsulfonium Trifluoromethanesulfonate in HFIP-H_2O Mixtures. Our previous studies[8,39] of the solvolysis of this salt have been extended to 97–50% HFIP at 49.7 and 70.1 °C. The specific solvolysis rates are reported in Table V, together with ratios for the reactivity of this substrate relative to the reactivity of 1-$AdSMe_2^+OTf^-$ in identical solvolyses (using specific rates from Table III).

Discussion

Although the 1-$AdSMe_2^+$ ion does not appear to have been previously reported, there are two reports of the preparation of the 1-adamantylethylmethylsulfonium ion.[38,40] It was claimed[38] that no detectable acetolysis occurred after 138 h at 50 °C. Based on an extrapolated specific rate for 1-$AdSMe_2^+$, from the data of Table I, and applying a rate ratio of 4.2 (obtained from a comparison, at this temperature, of the rates of *t*-$BuSMeEt^+$[38] and *t*-$BuSMe_2^+$[8,41] acetolyses), it can be predicted that ca. 16% reaction should have been observed.

A striking observation (Tables I and III) is that the rates of solvolysis of the 1-$AdSMe_2^+$ ion are, at a given temperature, almost

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Table IV. Percentage of Product Present[a] as 1-Adamantanol after the Solvolysis of 1-Adamantyldimethylsulfonium Trifluoromethanesulfonate[b,c] in Aqueous Ethanol and Selectivity Values (S)[d]

	70.6 °C				100.1 °C			
%EtOH[e]	AdOH	S	AdOH	S	AdOH	S	AdOH	S
100	3.6[f]		7.8[f]		1.6[f]		7.8[f]	
96	19.9	1.47			16.3	1.27	21.5	1.26
90			38.6	1.36	34.5	1.36	40.2	1.47
88	42.8	1.51			40.8	1.46	41.0	1.24
86	47.3	1.53			45.1	1.46	43.7	1.27
84					49.5	1.50	47.6	1.20
82			49.7	1.14	51.5	1.41	53.4	1.34
80			55.0	1.26	52.3	1.28	59.8	1.56
70			67.2	1.27	64.0	1.22	68.6	1.36
60			75.2	1.22	73.3	1.21	77.1	1.37
40			87.0	1.22	85.3	1.15	85.9	1.11
20			94.1	1.11				

[a] Only 1-adamantanol and 1-adamantyl ethyl ether detected as products. [b] Concentration of 0.01 M. [c] A 10% excess of pyridine was present. [d] Ratio of specific rate constants for reaction of intermediate ionic species with water and ethanol, respectively (see text). [e] On a volume–volume basis at 25.0 °C. [f] Corresponds to percentage of 1-adamantanol impurity in the substrate.

Table V. First-Order Rate Coefficients for the Solvolysis of the *tert*-Butyldimethylsulfonium Ion[a] in 1,1,1,3,3,3-Hexafluoro-2-propanol–Water Mixtures and a Comparison with Corresponding Values[b] for the 1-Adamantyldimethylsulfonium Ion

		10^6k, s^{-1}		
%HFIP[c]	N[d]	49.7 °C	70.4 °C	$k_{t\text{-BuSMe}_2^+}/k_{1\text{-AdSMe}_2^+}$[e]
97	−5.55	0.823	18.4	2.60 (2.71)[f]
90	−3.78	1.28	26.2	3.76
70	−2.81	1.67	35.3	6.81
50	−2.48	1.82	43.1	8.85

[a] Trifluoromethanesulfonate salt; concentration of 0.0065 M and all runs performed in duplicate. [b] From Table III. [c] By weight. [d] Solvent nucleophilicity based upon the specific rates of solvolysis of the S-methyldibenzothiophenium ion (ref 45). [e] At 70.4 °C. [f] At 49.7 °C.

independent of the solvent composition. At 70.4 °C, for 41 different solvent compositions, the rates vary only by a factor of less than 7, from 1.09 × 10^{-6} s^{-1} in *tert*-butyl alcohol to 7.09 × 10^{-6} s^{-1} in 97% HFIP. Such a small variation in rate at a given temperature would be a remarkable coincidence unless the activation parameters were also virtually identical. Temperature effects were measured for seven solvents (Table I), and the values for both activation parameters were found to be, as expected, almost solvent-independent (Table II). A large temperature dependence is reflected in the high enthalpies of activation, of ca. 35 kcal/mol. Reasonable rates are observed only because of a compensating entropy of activation of ca. +18 eu.

The observation of almost constant specific rates of solvolysis is relevant to the proposal[16,42,43] that a "cavity term" should be included in the LFER for solvolyses of a substrate. This term relates to the energy changes associated with the change in the size of the cavity within the solvent, when the substrate is converted to the transition state. While the present observations do not rule out the influence of such a term upon the kinetics, they do strongly indicate, at least for 1-AdSMe$_2^+$ solvolyses, that little variation in the magnitude of any cavity-term contribution accompanies a change in the solvent composition.

A scale of solvent nucleophilicity, based upon the solvolysis of the triethyloxonium ion (a R–X$^+$-type substrate), has been defined[25] by eq 6. This equation parallels eq 2 (with $l = 1$), except that the scale of the solvent ionizing power (Y) is replaced by a

$$\log (k/k_0)_{\mathrm{Et_3O^+}} = N + mY^+ \qquad (6)$$

Y^+ scale, governing the kinetic influence of the solvent at an initially positively charged leaving group, relative to the influence of the standard solvent (80% ethanol). More precisely, it can be considered to govern, for a R–X$^+$ substrate, all contributions toward changes in the reaction rate resulting from a change in the solvent other than those resulting from changes in solvent nucleophilicity.

Initially the t-BuSMe$_2^+$ ion was chosen as the standard for the Y^+ scale.[25] This paralleled the choice of *tert*-butyl chloride as the standard for the Y scale,[17] and it had the advantage that several values were available.[41] Other Y^+ values were estimated by using eq 7. However, a subsequent experimental extension to other

$$Y^+ = -0.09Y \qquad (7)$$

solvents[8] strongly indicated that the dominant factor controlling the variations in specific solvolysis rates of t-BuSMe$_2^+$ with changes in solvent composition was not the partial transfer of the positive change from sulfur to carbon but nucleophilic solvation of the incipient carbenium ion. Further, these observations indicated that t-BuSMe$_2^+$ solvolysis was a poor choice for establishing a Y^+ scale for use within eq 6. Indeed, the mY^+ corrections that had been made, fortunately rather small, were in the wrong direction. By analogy with the use of initially neutral adamantyl derivatives to establish Y scales,[26] an appropriate Y^+ scale for use within eq 6 could be based upon 1-AdSMe$_2^+$ solvolysis, and Y^+ values are included within Tables I and III. These values vary only from −0.319 to +0.495, and accepting that an m value of 0.55 is appropriate[25] for triethyloxonium ion solvolysis, the mY^+ contribution varies only from −0.175 to +0.272. To a reasonable approximation, these contributions can be neglected compared to the much larger variations in $\log (k/k_0)_{\mathrm{Et_3O^+}}$, and an N scale[44] can be defined as in eq 8. Within Table V, four N values are included which are similarly calculated from the rates of solvolysis of the S-methyldibenzothiophenium ion.[45]

$$\log (k/k_0)_{\mathrm{Et_3O^+}} = N_{\mathrm{Et_3O^+}} \qquad (8)$$

By comparison with literature data, it can be predicted that an S_N2 attack at a methyl group with expulsion of 1-adamantyl methyl sulfide will proceed much slower than S_N1 attack with expulsion of dimethyl sulfide. At 100 °C, the specific hydrolysis rate of the trimethylsulfonium ion[46] is 12.8 × 10^{-10} s^{-1}. From the data of Table I, an extrapolated value of 24.7 × 10^{-5} s^{-1} for hydrolysis of 1-AdSMe$_2^+$, at 100 °C, can be calculated, a value greater than that for the trimethylsulfonium ion by a factor of 1.9 × 10^5. The differing structures of the leaving sulfide molecules would be expected to lead to only modest rate differences. For solvolyses in aqueous ethanol, confirmation of the prediction of no significant attack at a methyl group came from the failure to

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(42) Kamlet, M. J.; Carr, P. W.; Taft, R. W.; Abraham, M. H. *J. Am. Chem. Soc.* **1981**, *103*, 6062.

(43) Abraham, M. H.; Kamlet, M. J.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1982**, 923.

(44) These $N_{\mathrm{Et_3O^+}}$ values can be found within ref 25 and 39, where they are the first column of values within the Table I of both references.

(45) A full range of N values, based upon this substrate, has been determined. These values will be reported elsewhere (Kevill, D. N.; Anderson, S. W., unpublished results).

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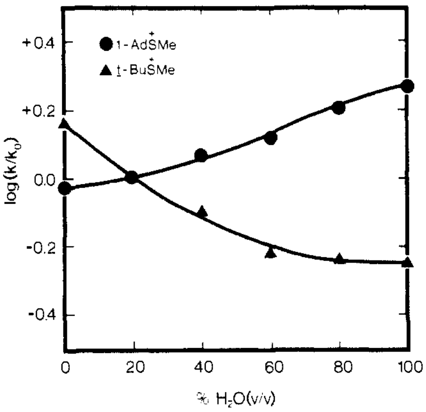

Figure 1. Logarithmic plots of the specific rates of solvolysis of 1-AdSMe$_2$$^+OTf^-$ (at 70.4 °C) and *t*-BuSMe$_2$$^+Cl^-$ (at 50.4 °C) as a function of the composition of an aqueous–ethanol solvent.

observe by GLPC any 1-adamantyl methyl sulfide within the products.[47]

Experiments carried out in the presence of a substantial concentration of tetraethylammonium chloride would, however, be expected to show a competing S$_N$2 attack by chloride ion. A second-order rate coefficient of 7.3 × 10^{-5} L mol^{-1} s^{-1} has been reported[48] for the bimolecular decomposition of trimethylsulfonium chloride in ethanol at 100 °C, corresponding to an initial specific rate in the presence of a 0.16 M chloride ion of 1.17 × 10^{-5} s^{-1}. A specific rate of ethanolysis of 1-AdSMe$_2$$^+$ at 100.1 °C of, 16.4 × 10^{-5} s^{-1} can be obtained by an Arrhenius extrapolation of the data of Table I. Since the leaving groups differ, the specific rate of attack by chloride ion on the trimethylsulfonium ion can be considered as only a rough estimate of its specific rate of attack on 1-AdSMe$_2$$^+$. Nonetheless the data do suggest that some attack is to be expected, especially at lower temperatures. Solvolyses carried out in the presence of 0.16 M tetraethylammonium chloride did lead to the formation of 1-adamantyl methyl sulfide, coupled with a fall off in the solvolytic specific rate with increasing extent of reaction. These are observations that would be expected to be a feature of S$_N$2 attack by chloride ion at a methyl group. Consistent with observations previously made for the ethanolysis of 1-adamantyl *p*-toluenesulfonate,[37] no 1-adamantyl chloride, which would have resulted from capture of the carbenium ion by chloride ion, was observed within the products.

The S$_N$2 attack of the halide ion at a methyl group becomes the major pathway in a dipolar aprotic solvent, such as acetonitrile, and reaction of 1-AdSMe$_2$$^+$ with tetra-*n*-butylammonium bromide in acetonitrile was used to prepare the 1-adamantyl methyl sulfide needed for GLPC calibration.

For seven binary solvent systems, the rates of solvolysis of both 1-AdSMe$_2$$^+$ and *t*-BuSMe$_2$$^+$ have been determined over a wide range of solvent composition. The rates of solvolysis of the 1-AdSMe$_2$$^+$ ion always vary in exactly the opposite manner to those reported, in Table V and elsewhere,[8,39,41] for the rates of solvolysis of the *t*-BuSMe$_2$$^+$ ion; several examples are given in Figures 1 and 2. Also, it can be seen that the rate variations accompanying changes in solvent composition are considerably lower for the 1-AdSMe$_2$$^+$ ion.

The marked differences in response to solvent variation of *t*-BuSMe$_2$$^+$ and 1-AdSMe$_2$$^+$ solvolysis rates are consistent with the claim[8] that the variations in *t*-BuSMe$_2$$^+$ solvolysis rates are controlled primarily by solvent nucleophilicity considerations. In contrast, for 1-AdSMe$_2$$^+$ solvolysis, where specific rear-side nucleophilic solvation is not possible, one can consider the rate variations in terms of nonspecific solvation. The Hughes–Ingold approach[49] can be used but with nucleophilic solvation being considered as the dominant effect rather than the ill-defined concept of polarity. Increased nucleophilic solvation will stabilize the more intensely charged initial state rather than the charge-dispersed transition state, leading to a reduction in the solvolysis rate. However, as discussed previously,[8] it has been suggested[30] that S$_N$1 reactions in protic solvents have a very late transition state with 80–90% bond heterolysis. Under these conditions, R–X$^+$ substrates will have appreciable transfer of charge and relatively little charge dispersion. Therefore, it is not surprising that as the solvent is varied, the rate changes are modest. The same modest effect must also operate in the solvolyses of *t*-BuSMe$_2$$^+$. However, for this substrate, it is swamped out by the stronger effect of stabilization of the incipient *tert*-butyl carbocation by specific nucleophilic solvation, an effect which has an opposite influence upon the reaction rate.

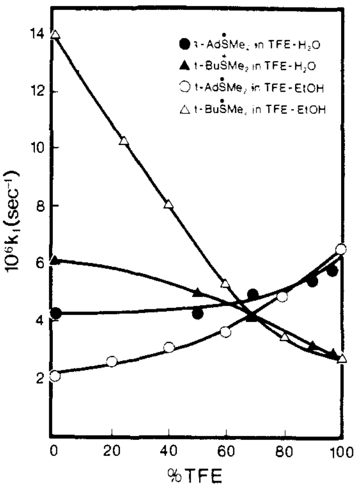

Figure 2. Plots of the specific rates of solvolysis of 1-AdSMe$_2$$^+OTf^-$ (at 70.4 °C) and *t*-BuSMe$_2$$^+OTf^-$ (at 50.0 °C) as a function of the composition of aqueous–TFE and TFE–EtOH solvents.

In his extensive investigation of *t*-BuSMe$_2$$^+$ solvolysis,[50] Hyne found[50d] poor correlations of solvent-induced rate changes with Grunwald-Winstein *Y* values, Kosower *Z* values, or the bulk dielectric constant. He recognized that specific solute–solvent interactions, other than those based on polarity and solvating power, must play a critical role. In a discussion of solvolyses in *N*-methylformamide–water mixtures,[50d] a nucleophilic role for *N*-methylformamide involving covalent bond formation to the α-carbon was actually proposed.[51] Surprisingly, Hyne and Jensen did not take the logical next step: to consider whether solvent nucleophilicity was also the general answer as to the nature of the proposed specific solute–solvent interactions.

The observation of almost solvent-independent activation parameters for 1-AdSMe$_2$$^+$ solvolyses is consistent with data for *tert*-butyldialkylsulfonium ion solvolyses. Almost constant activation parameters were observed for *t*-BuSEtMe$^+$ solvolyses in ethanol, acetic acid, and 50% acetic acid–acetic anhydride.[47] The solvolyses of both *t*-BuSMe$_2$$^+$ and (α-phenylethyl)dimethylsulfonium ion in water and three aqueous–ethanol mixtures had activation parameters within narrow ranges: $\Delta H^‡$ from 32.4 to 33.0 kcal/mol and $\Delta S^‡$ from 15 to 18 eu.[52] In direct comparisons, activation parameters for hydrolysis of 1-AdSMe$_2$$^+$ of 34.2 kcal/mol and 16.2 eu (Table II) can be compared with values for *t*-BuSMe$_2$$^+$ of 32.4 kcal/mol and 17.7 eu[53] or of 31.6 kcal/mol and 15.7 eu.[54] Values of 36.2 kcal/mol and 20.9 eu for solvolysis

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[47] Similarly, a careful study of the products after the acetolysis of *t*-BuSMeEt$^+$ indicated the absence of both *t*-BuSMe and *t*-BuSEt: Darwish, D.; Tourigny, G. *J. Am. Chem. Soc.* **1972**, *94*, 2191.

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[51] A similar nucleophilic role for formamides in *tert*-alkyl halide solvolyses had previously been proposed; see ref 2.

[52] Hyne, J. B.; Golinkin, H. S. *Can. J. Chem.* **1963**, *41*, 3139.

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[54] Leffek, K. T.; Robertson, R. E.; Sugamori, S. *J. Am. Chem. Soc.* **1965**, *87*, 2097.

of 1-AdSMe$_2^+$ in 80% ethanol can be compared with values for *t*-BuSMe$_2^+$ of 32.1 kcal/mol and 18.2 eu.[53] It appears that the specific nucleophilic solvation of the incipient carbenium ion, which increases the rates of *t*-BuSMe$_2^+$ solvolyses over those of corresponding 1-AdSMe$_2^+$ solvolyses, is accompanied by a reduction in the activation energy and by little change in the entropy of activation. Possibly, the solvent molecules involved in rear-side solvation of the transition state are already suitably positioned at the initial state.

In 95% aqueous acetone, the unchanged solvolysis kinetics in the presence of up to 0.1 M dimethyl sulfide (Table III) indicates the absence of any appreciable external return. This is consistent with the lack of retardation upon addition of *p*-toluenesulfonate ion to the ethanolysis of 1-adamantyl *p*-toluenesulfonate[37] and the lack of external capture of 1-adamantyl carbocations by chloride[37] or azide ions[55] in competition with capture by protic solvents.

In highly nucleophilic solvents, the specific rate of solvolysis of the *t*-BuSMe$_2^+$ ion[8,39,41] is considerably in excess of that of the 1-AdSMe$_2^+$ ion. For example, a ratio of 210 is observed for ethanolysis at 50.5 °C. As the nucleophilicity of the solvent is decreased, the rates of *t*-BuSMe$_2^+$ solvolysis decrease and those of 1-AdSMe$_2^+$ solvolysis increase slightly. If these trends were to continue indefinitely, a situation would eventually be reached, in low nucleophilicity solvents, where the *t*-BuSMe$_2^+$ solvolysis was the slower. This situation can be avoided if the *t*-BuSMe$_2^+$ solvolysis abandons the specific nucleophilic assistance and solvolyzes by a mechanism essentially identical with that followed by 1-AdSMe$_2^+$ solvolyses.

In a comparison of *tert*-butyl bromide and 1-adamantyl bromide solvolyses,[7] it was found that as the solvent nucleophilicity decreased, the rates became very similar and, in 97% HFIP at 25 °C, the rate ratio was only 2.56. It has, however, been suggested[15,16] that the variation in the rate ratio can alternatively be explained in terms of 1-adamantyl bromide being more sensitive to solvent electrophilicity than *tert*-butyl bromide; in this case, the low ratio in 97% HFIP is due not to its low nucleophilicity but to its high electrophilicity.

The comparison of *t*-BuSMe$_2^+$ and 1-AdSMe$_2^+$ specific solvolysis rates is of interest not only in its own right but also because it can help to decide between the two competing theories for the corresponding alkyl chloride solvolyses. The observation in 97% HFIP of low ratios for the specific solvolysis rates, 2.60 at 70.4 °C and 2.71 at 49.7 °C (Table V), gives strong support to the description for the halides based on solvent nucleophilicity.[9] Solvent electrophilicity is not an important factor in the solvolyses of R–X$^+$-type substrates, as illustrated by the essentially solvent-independent 1-AdSMe$_2^+$ specific solvolysis rates. The observation of a ratio *identical* with that for the alkyl bromide solvolyses is probably coincidental.

Based on studies in solvents of low polarity (such as methylene halide[56]) or in the gas phase,[57] it has been found that, in the absence of solvation, the 1-adamantyl carbocation is actually more stable than the *tert*-butyl carbocation.

If a higher sensitivity toward nucleophilicity for *t*-BuX and not a higher sensitivity toward electrophilicity for 1-AdX is indeed the dominant factor determining variations in the rate ratio, one might expect that in low nucleophilicity solvents, it might be possible to reduce the *t*-BuX/1-AdX ratio to below unity. This has not been observed,[58] and it might be an unrealistic goal in hydroxylic solvents since, even in the absence of specific nucleophilic solvation, one would expect longer range dipolarity/polarizability effects[15] to be more effective in stabilizing the incipient carbocation when they can operate at the rear side of a nonbridgehead system.

In 96–60% aqueous ethanol, product studies (Table IV) show a constant selectivity, with average *S* values (eq 5) of 1.35 ± 0.15 at 70.6 °C and 1.35 ± 0.11 at 100.1 °C. Below 60% ethanol content, a slight fall off in the *S* values was observed. The values are slightly lower than the values of 1.5 to 2.6 which have previously been observed in the same solvent mixtures for 1- and 2-adamantyl bromides and arenesulfonates,[32,33] 1-adamantyl picrate,[33] 2-adamantyl perchlorate,[34] and 2-adamantyl trifluoromethanesulfonate.[36] Values have also been reported outside of this range: slightly lower for 1-adamantyl bromide[35] and higher for 2-adamantyl arenesulfonates.[31]

The preference for reaction with water rather than with ethanol remains on going from the initially neutral leaving groups to the initially positively charged leaving group. The preference for reaction with the less nucleophilic water has been explained in terms of the relative abilities to hydrogen bond to the departed anion within a solvent-separated ion pair[31] and in terms of a bulk effect, with the smaller water molecule better able to insert itself into the solvent-separated ion pair.[59] More recent experiments[32,33] have not confirmed the reported[31] variation of *S* with hydrogen bonding ability of the anion, and for aqueous ethanol at least,[35] the bulk theory would appear to present the simpler explanation. The bulk theory would also appear to offer the simplest explanation of the *S* value being greater than unity in the aqueous–ethanol solvolyses of 1-AdSMe$_2^+$, with the need to consider the separation by the solvent of an ion and a molecule.

Experimental Section

Materials. The purifications of acetone, *tert*-butyl alcohol, dioxane, ethanol, methanol, and 2-propanol were as previously described.[37] The purifications of acetic acid,[41] acetonitrile,[60] formic acid,[61] 1,1,1,3,3,3-hexafluoro-2-propanol,[62] and 2,2,2-trifluoroethanol[63] were also prepared by use of previously reported procedures. The 1-adamantyl iodide was prepared from 1-adamantanol and hydriodic acid as previously described.[37] Silver trifluoromethanesulfonate (Aldrich) and methyl sulfide (Aldrich) were used without further purification.

1-Adamantyldimethylsulfonium Triflate. Methyl sulfide (1.78 mL) was added to a solution of 6.06 g of 1-adamantyl iodide in 100 mL of nitromethane. After 2 h, a solution of 5.94 g of silver triflate in 100 mL of nitromethane was added. An immediate precipitate of silver iodide occurred, and after stirring for 22 h, the mixture was filtered through a fine sintered glass funnel. The precipitate was washed with acetonitrile. Concentration of the total filtrate (rotary evaporator) gave a clear brown oil, which solidified to a tan paste. Repeated washing with ether led to a fine white powder (5.62 g, 70.3%): mp 112–118.5 °C;[64] IR (KBr disc) 3023, 2925, 2913, 2860, 1255, 1171, 1149, 1031, 1004, 639 cm^{-1}; PMR (CDCl$_3$) δ 2.85 (s, CH$_3$, 6 H) 2.32 (s, γ-H, 3 H), 2.07 (d, β-H, 6 H, *J* = 2.3 Hz), 1.81 (d, δ-H, 6 H, *J* = 2.3 Hz). Anal. Calcd for $C_{13}H_{21}F_3O_3S_2$: C, 45.07; H, 6.11; S, 18.51. Found: C, 45.01; H, 6.19; S, 18.37. Complete ethanolysis of a tared sample, in a sealed tube at 75 °C for 480 h, led to a titration against NaOMe in MeOH corresponding to 100.3% of the theoretical value.

***tert*-Butyldimethylsulfonium Triflate.** This salt was prepared as previously described:[39] mp 128–137 °C dec [lit.[39] mp 173–175 °C dec).[64] The PMR data were identical with those previously reported.[39] Anal. Calcd for $C_7H_{15}F_3O_3S_2$: C, 31.34; H, 5.64; S, 23.90. Found: C, 31.34; H, 5.47; S, 23.74.

1-Adamantyl Methyl Sulfide. Tetra-*n*-butylammonium bromide (1.33 g, Fluka) and 1-adamantyldimethylsulfonium triflate (0.95 g) were reacted in refluxing acetonitrile for 24 h. Removal of solvent (rotary evaporator) gave a clear amber oil, which was partitioned between ether (25 mL) and water (25 mL). The aqueous layer was extracted with ether (3 × 25 mL) and the combined ether extracts were washed with water

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(3 × 25 mL) and dried over anhydrous $MgSO_4$. Removal of solvent (rotary evaporator) gave 0.34 g of crude product. Distillation under reduced pressure afforded 0.18 g (36%) of a clear, colorless liquid: bp 68-69 °C (0.55 mmHg); PMR ($CDCl_3$) δ 2.01 (s, CH_3 + γ-H, 6 H), 1.86 (d, β-H, 6 H, J = 2.4 Hz), 1.70 (d, δ-H, 6 H, J = 2.4 Hz); IR (neat) 2910, 2860, 1655, 1450, 1345, 1300, 1045 cm^{-1}. Anal. Calcd for $C_{11}H_{18}S$: C, 72.46; H, 9.95. Found: C, 72.36; H, 10.06.

Kinetic Procedures. Each run was carried out by using nine sealed Kimble Neutraglas ampules. For runs with HFIP-containing solvents, each ampule contained 1 mL of solution, and for all other runs, each ampule contained 5 mL of solution. For runs in water, alcohols, and aqueous-organic mixtures, ampules were removed from the constant temperature bath at suitable time interals, quenched in an ice bath, and the contents rinsed with acetone into 25 mL of acetone, containing Lacmoid (resorcinol blue) indicator, cooled within a solid CO_2-acetone slush bath. The acid produced was titrated against a standardized solution of sodium methoxide in methanol. The titration procedures for runs in acetic acid and formic acid and the calculation of the first-order solvolytic rate coefficients were as previously described.[25]

Product Studies. Ampules containing a ca. 0.01 M solution of 1-$AdSMe_2^+OTf^-$ in ethanol or the appropriate aqueous-ethanol solvent were allowed to react for at least ten half-lives at 70.6 or 100.1 °C. The products were directly analyzed by response-calibrated GLC, as previously described.[34] Only 1-adamantanol and 1-adamantyl ethyl ether were detected as products; in particular, no 1-adamantyl methyl sulfide was detected. The 1-adamantyl methyl sulfide was, however, detected after reaction in ethanol in the presence of a large excess of anhydrous[60] tetraethylammonium chloride.

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Geometries and Energies of the Fluoroethylenes

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Abstract: The geometries of the fluorinated ethylenes have been gradient optimized at the SCF level with a double-ζ plus polarization function on carbon (DZ+D_C) basis set. The C=C and C—F bond lengths for C_2H_4, C_2H_3F, CH_2CF_2, *cis*-CHFCHF, *trans*-CHFCHF, and C_2F_4 have been optimized at the configuration-interaction level, including all single and double excitations (CI-SD). Good agreement with the original electron diffraction work was found. The values for r(C=C) and r(C—F) are found to decrease with increasing fluorine substitution. Correction factors to the SCF values are discussed and an estimated structure for C_2HF_3 is given. Isodesmic reaction ethalpies for the fluoroethylenes have been calculated with (DZ+D_C) and double-ζ plus polarization function (DZ+P) basis sets. Both basis sets gave comparable results in satisfactory agreement with experiment. The calculated heats of formation of *cis*- and *trans*-CHFCHF are −71.0 and −70.0 kcal/mol, respectively, which compare to the experimental values of −70.8 ± 3.1 and −69.4 ± 3.1 kcal/mol. Ionization potentials and dipole moments of the fluoroethylenes also have been calculated and are compared to experimental data.

Fluoroethylenes are very simple compounds and are extremely important monomers, but their structures are not unequivocally established.[1] In a systematic electron diffraction study, Bauer and co-workers[2] found that the C=C bond length decreases as fluorines are substituted for hydrogen in ethylene. The C=C bond length of 1.315 Å in CH_2CF_2 from a microwave study[3a] agrees with an electron diffraction value of 1.316 Å.[2] The bond distances in C_2H_3F as determined by microwave[3b] and electron diffraction were also in good agreement. Recently, however, the structures of the fluoroethylenes have been redetermined by using a combination of electron diffraction and microwave data,[4-8] and the results did not show the expected general trend for a decrease in the value of r(C=C) with increasing substitution of fluorine. In fact, the C=C bond lengths in CH_2CH_2, CH_2CF_2, and $CHFCF_2$ were reported to be identical within experimental error.[7,8] The similarity in values for r(C=C) and r(C–F) further complicated the analysis of the electron diffraction data.

As part of our general theoretical study of fluorocarbons, we have optimized the structures of the fluoroethylenes at the SCF level using a double-ζ (DZ) basis set augmented by polarization functions on carbon (DZ+D_C). To obtain accurate geometries and resolve the discrepancies among the experimental measurements, we subsequently optimized the C=C and C—F bonds for C_2H_4, C_2H_3F, the difluoroethylenes, and C_2F_4 with correlated wave functions starting from the optimum SCF structures. The results are compared with those from previous ab initio calculations.

To further test the reliability of the DZ+D_C basis set, the total energies of the fluoroethylenes were computed and used to calculate isodesmic reaction enthalpies, which are known experimentally. Ionization potentials and dipole moments also were calculated and compared to experiment.

Calculations. The calculations were performed with the HONDO program[9] package on DEC VAX/11-780 and IBM 3083 computers. Geometries were optimized at the SCF level with the use of gradient techniques.[10] The correlated wave

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