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Correlation of the Rates of Solvolysis of the Benzhydryldimethylsulfonium Ion. Application of the Aromatic Ring Parameter[1]

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Values for the specific rates of solvolysis of the benzhydryldimethylsulfonium ion in 34 solvents have been analyzed using various forms of the extended Grunwald−Winstein equation. The specific rates are insensitive toward changes in solvent nucleophilicity (N_T) values, and they correlate best against a combination of Y^+ values (based on the solvolyses of the 1-adamantyldimethylsulfonium ion) and aromatic ring parameter (I) values. Common-molecule return is observed, being especially powerful in solvents rich in fluoro alcohol; the logarithm of the associated mass law constant correlates inversely with the solvent N_T values. The product selectivities in ethanol−water mixtures are also consistent with an S_N1 mechanism for the solvolyses.

Recently we developed,[2] from a consideration of the differences in response to solvent variation of the specific rates of solvolysis of the (*p*-methoxybenzyldimethyl)sulfonium ion and the 1-adamantyldimethylsulfonium ion (Y^+ values[3]), a scale of aromatic ring parameter (I) values for the treatment of the dispersion involved in Grunwald−Winstein plots of the specific rates of solvolysis of benzylic derivatives proceeding with, at the transition state, appreciable development of positive charge. The one-term Grunwald−Winstein equation (1)[4] is thus expanded to eq 2. When solvent nucleophilicity changes

$$\log (k/k_o)_{RX} = mY_X + c \qquad (1)$$

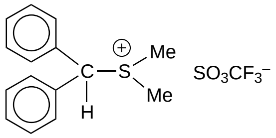
$$\log (k/k_o)_{RX} = mY_X + hI + c \qquad (2)$$

also partially control the variations of specific rates with solvent, an lN_T term can be added[5,6] to give eq 3. In eqs

$$\log (k/k_o)_{RX} = lN_T + mY_X + hI + c \qquad (3)$$

1−3, k and k_o are the specific rates of solvolysis of RX in the solvent under consideration and in the standard solvent, 80% ethanol; l is the sensitivity to changes in solvent nucleophilicity, best expressed as N_T values;[6] m is the sensitivity to changes in solvent ionizing power (Y_X) values;[7] h is the sensitivity to changes in aromatic ring parameter (I) values;[2] and c is a constant (residual) quantity.

Specific rates of solvolysis of benzylic,[8,9] naphthylmethyl,[10,11] anthrylmethyl,[12] and benzhydryl[10,13] derivatives with anionic leaving groups (RX substrates) have been successfully correlated using eq 2 or, occasionally, eq 3.[2,14−16] Even allylic and propargylic substrates[9] show improved correlations of their specific rates of solvolysis when the hI term is incorporated, but with reduced h values relative to benzylic substrates.[2] Recently, support for the incorporation of the hI term, based on molecular orbital studies using the AM1 method, has been put forward.[17a] However, there have been very few studies of the effect of solvent variation on the solvolyses of α-aryl-substituted derivatives with neutral molecule leaving groups (RX^+ substrates). Accordingly, we have carried out a study of the solvolysis of the benzhydryldimethylsulfonium ion (**1**), as the trifluoromethanesulfonate salt, in a wide variety of solvents.



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From a similarity model consideration,[17b] the unimolecular solvolyses of $RSMe_2^+$-type substrates should give good correlations when the scales applied are the I scale,[2]

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developed using the solvolyses of p-MeOC$_6$H$_4$CH$_2$SMe$_2^+$ (**2**), in conjunction with the Y^+ scale[3] (from a study of the solvolyses of the 1-adamantyldimethylsulfonium ion) and, when eq 3 is employed, the N_T scale developed from a consideration of the specific rates of solvolysis of the S-methyldibenzothiophenium ion.[6] Although, when eq 3 was applied, solvolyses of benzhydryl bromides[10] with moderately electron-withdrawing substituents showed l values of very close to zero and large probabilities that the lN_T term was statistically insignificant, the presence of the more powerfully electron-withdrawing p-NO$_2$ substituent led to an appreciable l value of 0.31 ± 0.09 with only a very low (0.01) probability that the lN_T term was statistically insignificant.[16] Accordingly, it is important in the study of the solvolyses of **1** to see whether here also an lN_T term needs to be incorporated into the extended Grunwald–Winstein treatment.

As an alternative to the use of the hI term in conjunction with the mY_X term, one can develop a series of similarity models for use as the Y scale when the solvolyses under study involve substrates with α-aryl substituents. Several scales of this type (Y_{BnX}) have been developed by Liu and co-workers,[8,18–23] and Bentley has suggested the use of p-methoxybenzyl chloride[9,24] for correlations of benzylic chlorides. It has been recognized[10] that additional similarity model scales are needed when two aromatic rings are in conjugation with the charge developing at the α-carbon.

It has been demonstrated[2,14–16] in terms of eq 2 (or eq 3) that the important consideration is not similarity in structure but similarity in the h/m ratio for the solvolyses of the substrate under investigation and the solvolyses of the substrate chosen as the similarity model. It has been shown that the h value of the ratio increases in value not only on introduction of a second aromatic ring at the α-carbon but also on introduction at this carbon of an electron-withdrawing group or on introduction within the aromatic ring of an electron-supplying substituent.

Although one would expect a similarity model that is closely related to the substrate undergoing solvolysis, in regard to both h/m ratio and actual structure, to give excellent correlations, it has been shown[2,14–16] that in almost all instances the improvements relative to use of the appropriate Y_X scale[7] in conjunction with the I scale[2] are marginal. It follows that the considerable extra effort involved in first establishing what would be a good similarity model (no nucleophilic component and similar h/m ratio) and then, if necessary, experimentally determining the Y_{BnX} scale would only rarely[25] be justifiable.

In the present paper, we report on the solvolyses of **1** with respect to specific rates of solvolysis in a wide range of solvents, temperature effects on the specific rates of ethanolysis, product partitioning in aqueous ethanol mixtures, and common-molecule retardation (including studies with initially added dimethyl sulfide). The specific rates of solvolysis are found to be very well correlated using I and Y^+ values within eq 2.

Table 1. Specific Rates of Solvolysis of the Benzhydryldimethylsulfonium Ion[a] at 25.0 °C

solvent[b]	10^4k, s^{-1} [c]	solvent[b]	10^4k, s^{-1} [c]
100% EtOH	4.60 ± 0.06[d]	95% dioxane	0.75 ± 0.01[e]
80% EtOH	2.30 ± 0.04	80% dioxane	1.02 ± 0.08
60% EtOH	1.77 ± 0.04	60% dioxane	1.08 ± 0.04
40% EtOH	1.66 ± 0.12	40% dioxane	1.02 ± 0.03
20% EtOH	2.03 ± 0.15	20% dioxane	1.41 ± 0.08
100% H$_2$O	2.19 ± 0.08	100% TFE	27.3 ± 1.7[f]
100% MeOH	7.88 ± 0.13	97% TFE	20.8 ± 1.4[g]
80% MeOH	4.53 ± 0.09	90% TFE	15.6 ± 1.1[h]
60% MeOH	3.16 ± 0.17	70% TFE	9.25 ± 0.19
40% MeOH	2.61 ± 0.09	50% TFE	6.39 ± 0.26
20% MeOH	2.38 ± 0.15	97% HFIP	57 ± 6[i]
95% acetone	3.16 ± 0.15	70% HFIP	40.3 ± 2.9[j]
90% acetone	2.81 ± 0.06	50% HFIP	24.1 ± 1.6[j]
80% acetone	2.29 ± 0.06	80T-20E	20.1 ± 0.9
70% acetone	1.70 ± 0.08	60T-40E	13.5 ± 1.1
60% acetone	1.62 ± 0.03	40T-60E	7.62 ± 0.20
40% acetone	1.40 ± 0.03	20T-80E	6.37 ± 0.21
20% acetone	1.58 ± 0.07		

[a] As the trifluoromethanesulfonate salt and at a concentration of 0.003–0.005 M, except the concentration was *ca.* 0.01 M in HFIP-containing solvents. [b] Prepared on a volume–volume basis at 25.0 °C, except for TFE–H$_2$O and HFIP–H$_2$O mixtures, which were prepared on a weight–weight basis. [c] All runs performed in duplicate, and all of the integrated values are used to obtain an average value and the associated standard deviation. [d] Also values for $10^4\ k$ (s^{-1}) of 21.1 ± 1.2 at 35.0 °C, 0.91 ± 0.04 at 15.0 °C, and 0.067 ± 0.003 at 0.0 °C; from the four determinations at different temperatures, $\Delta H^{\ddagger}_{298} = 26.6 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ddagger}_{298} = 15.3 \pm 0.2$ eu. [e] Not used in the correlations (no N_T value available). [f] Substrate concentration of 0.0050 M in the presence of 0.0045 M pyridine and using eq 5 with an α value of 600; in the absence of pyridine an equilibrium was established at 20.0 ± 0.8% reaction. [g] Substrate concentration of 0.0050 M and using eq 5 with an α value of 130; equilibrium was established at 92 ± 1% reaction. [h] No evidence for fall-off of experimental integrated first-order rate coefficients, and equilibrium was established at 97 ± 1% reaction. [i] Average value of determinations with 0.0100 M substrate and 0.0076, 0.0151, and 0.0227 M pyridine present (six runs) and using eq 5 with an α value of 1500; in the absence of pyridine an equilibrium was established at 11.9 ± 1.1% reaction. [j] In the absence of pyridine and using eq 5 with an α value of 200 for 70% HFIP and an α value of 150 for 50% HFIP.

Results

Kinetic Studies. All kinetic studies were carried out with 0.003–0.006 M concentration of **1**, except for a *ca.* 0.01 M concentration being used in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)-containing solvents. The solvents were prepared, at 25.0 °C, on a volume–volume basis, except for 2,2,2-trifluoroethanol (TFE)–H$_2$O and HFIP–H$_2$O mixtures, which were prepared on a weight-weight basis.

Specific rates of solvolysis, determined at 25.0 °C, are reported in Table 1 for 35 solvents. For determinations in water, ethanol, and methanol and in aqueous mixtures with ethanol, methanol, acetone, and dioxane, as well as in TFE–ethanol mixtures, the values reported are average values of integrated first-order rate coefficients from duplicate runs. Similar analyses were possible for solvolyses in 70% and 50% TFE.

Runs in other fluoro alcohol-containing solvents needed analyses taking into account an appreciable common-molecule rate depression. Also, the runs in 100% TFE

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Table 2. Effect of Added Pyridine and Dimethyl Sulfide upon the Specific Rate of Solvolysis of the Benzhydryldimethylsulfonium Ion[a] in 100% TFE at 25.0 °C

[pyridine], M	[Me_2S], M	10^4k^{expt}, s^{-1} [b]	10^4k, s^{-1} [c]
0.00453[d]			27.3 ± 1.7
0.00650			25.0 ± 1.5
0.00905[d]			29.4 ± 2.2
0.01300			30.0 ± 2.2
0.01359[d]			31.0 ± 1.7
0.00453	0.0025		24.9 ± 1.1
0.00453	0.0050		28.0 ± 1.4
0.00453	0.0100	3.68 ± 0.14	31.6 ± 1.0
0.00453	0.0200	1.65 ± 0.07	23.7 ± 1.2
0.00453	0.0400	0.91 ± 0.04	25.0 ± 1.6

[a] As the trifluoromethanesulfonate salt and concentration of *ca.* 0.005 *M*. [b] Integrated first-order rate coefficients fall off appreciably with increasing extent of reaction, except at the higher [Me_2S] concentrations. [c] Calculated on a point-by-point basis from the experimental integrated first-order rate coefficients according to eq 5, with an α value of 600. [d] Infinity acid titer of 95 ± 3%, 91 ± 3%, and 85 ± 3% of maximum possible with [pyridine] of 0.004 53, 0.009 05, and 0.013 59 M, respectively.

Table 3. Effect of Added Pyridine and Dimethyl Sulfide upon the Specific Rate of Solvolysis of the Benzhydryldimethylsulfonium Ion[a] in 97% HFIP at 25.0 °C

[pyridine], M	[Me_2S], M	10^4k, s^{-1} [b]
0.0076		56 ± 6[c]
0.0151		51 ± 4
0.0227		63 ± 6
0.0076	0.0200	55 ± 6[c]
0.0076	0.0400	69 ± 6[c,d]

[a] As the trifluoromethanesulfonate salt and concentration of *ca.* 0.010 M. [b] Calculated on a point-by-point basis from the experimental integrated first-order rate coefficients according to eq 5, with an α value of 1500. [c] Followed to 40–50% of possible acid formation. [d] Experimental first-order rate coefficient value of 1.07 (±0.10) × 10^{-4} s^{-1}, showing slight fall-off with increasing extent of reaction.

Table 4. Effect of Added Dimethyl Sulfide upon the Experimental Specific Rate of Solvolysis of the Benzhydryldimethylsulfonium Ion[a] at 25.0 °C

solvent	[Me_2S], M	10^4k^{expt}, s^{-1}	α^b (M^{-1})
95% acetone	0.0000	3.00 ± 0.04[c]	
	0.0500	2.67 ± 0.05	2.47
	0.1000	2.40 ± 0.05	2.50
95% dioxane	0.0000	0.750 ± 0.012	
	0.0500	0.701 ± 0.007	1.40
	0.1000	0.666 ± 0.012	1.26

[a] As the trifluoromethanesulfonate salt and concentration of *ca.* 0.005 M. [b] Calculated from eq 4. [c] An additional determination, independent of the one reported in Table 1.

Table 5. Illustrative Run for Solvolysis of 0.00621 M Benzhydryldimethylsulfonium Ion[a] in 100% TFE, at 25.0 °C in the Presence of 0.00650 M Pyridine

t (min)	0	3.79	7.08	9.67	12.55	15.38	18.47	1620
10^3x, M	1.05	2.26	3.00	3.25	3.57	3.98	4.20	6.01
10^4k^{expt}		12.3	11.8	10.2	9.4	9.7	9.1	
10^4k^b		25.0	27.2	24.6	23.8	26.1	25.4	
10^4k^{expt} (calcd)		12.2	11.2	10.2	9.6	9.4	8.9	

[a] Footnotes as in Table 3, plus *x* represents extent of formation of acid. [b] Using α = 600 in eq 5 (with *c* = 0).

and 97% HFIP reached early equilibria, which could be avoided by addition of at least 1 equiv of pyridine (Tables 2 and 3). The infinity acid titers then approached the theoretical values but remained somewhat less in 100% TFE, presumably because of some capture by pyridine to give the benzhydrylpyridinium ion (without acid development); the percentages of the theoretical infinity titer in the presence of up to 0.0136 M pyridine are reported as a footnote to Table 2.

The common-molecule rate depression is very small in 95% acetone or 95% dioxane, and it can be detected as a modest retardation only in the presence of a large excess (0.05–0.10 M) of added dimethyl sulfide (Me_2S). The specific rates and the mass law constants (α), calculated according to eq 4, are presented in Table 4. In eq 4, k^{expt}

$$k = k^{expt}(1 + \alpha c) \qquad (4)$$

is the specific rate determined in the presence of a concentration *c* of Me_2S and *k* is the experimental value in the absence of added Me_2S.

In contrast, extremely large common-molecule retardations are observed for solvolyses, even in the absence of initially added Me_2S, in 100% TFE and 97% HFIP. In these solvents, a very pronounced initial fall-off in integrated first-order rate coefficient values is followed by a series of fairly constant values, which could, erroneously, be averaged to give an apparent (but much too low) *k* value. When concentrations of added Me_2S are not in large excess, the k^{expt} values fall with extent of reaction and the true *k* values are given by eq 5, where *a* is the

$$k + \frac{\alpha x}{t} = k^{expt}[1 + \alpha(a + c)] \qquad (5)$$

initial concentration of substrate and *x* represents the extent of solvolysis at time *t*. The *k* values, calculated according to eq 5, are given in Tables 2 and 3, which also show the essentially negligible effect of variation of the pyridine concentration. The *k* values are obtained from the k^{expt} values by determining the best fit value for the mass law constant (α), and this α value is then used in the estimation (eq 5 with *c* = 0) of the *k* values reported in Table 1. For runs in 97% TFE and 70% and 50% HFIP, the α value is smaller and the variation in k^{expt} values during the solvolyses in the absence of added Me_2S can be analyzed directly to get the best fit value for α and the appropriate *k* value. An illustrative run and the accompanying analysis for the solvolysis of **1** in 100% TFE is presented in Table 5.

In the consideration of the specific rates of ethanolysis of **1**, values were also determined at 35, 15, and 0 °C and these values, together with the enthalpy and entropy of activation values obtained from an Arrhenius equation treatment of the four measurements, are presented in footnote d of Table 1.

Determination of Selectivities in Aqueous Ethanol. From a gas chromatographic determination of the relative amounts of benzhydrol and benzhydryl ethyl ether formed, one can determine selectivity values (*S*), defined in eq 6, where the ratio of the concentrations of

$$S = \frac{k_E}{k_W} = \frac{[(C_6H_5)_2CHOEt]}{[(C_6H_5)_2CHOH]} \cdot \frac{[H_2O]}{[EtOH]} \qquad (6)$$

benzhydryl derivatives is determined after, at least, 10 half-lives of reaction, and the concentrations of water and ethanol are those present in the solvent mixture. Determinations were carried out with from 96 to 20% (volume-volume) of ethanol in the binary solvent. The selectivities are reported in Table 6, together with (for comparison) previously determined values for benzhydryl bromide,[26] chloride,[26–29] 2,4-dinitrobenzoate,[28] and *p*-nitrobenzoate.[28]

Discussion

Specific Rates for Solvolysis of 1. From the Arrhenius plot of the specific rates of ethanolysis at 0−35 °C, one can calculate a value of 1.6×10^{-2} s^{-1} at 50 °C, about 200 times greater than the value for the (*p*-methoxybenzyl)dimethylsulfonium ion (**2**) at that temperature.[2] A linear free energy relationship (LFER) plot of the specific rates of solvolysis of **1** at 25.0 °C against the corresponding specific rates of solvolysis of **2** at 50.0 °C gives, for 34 solvents, a linear plot with a slope of 1.01 ± 0.02, intercept of 0.01 ± 0.07, correlation coefficient of 0.991, and *F*-test value of 1843.

As in two previous studies of solvent effects upon the specific rates of solvolysis of substrates believed to solvolyze by the S_N1 mechanism and involving dimethyl sulfide as the leaving group, the highest specific rate for the series of solvents studied was in 97% HFIP and the lowest was in 95% dioxane. The ratio of the specific rates in these solvents was 76 (at 25.0 °C), compared to 50 for solvolyses of **2** (at 50.0 °C)[2] and 5 for solvolyses of the 1-adamantyldimethylsulfonium ion (at 70.4 °C).[3] A very small variation of the specific rate of solvolysis with solvent variation has also been found[30,31] for the solvolyses of the 1-adamantylpyridinium ion. This once again illustrates the larger variation observed, due to differences in solvation changes in going from the ground state to the transition state, upon the introduction of α-aryl substituents.[2,9,22,32,33] Variations with solvent of the extent of ion-pair (in this case, ion-molecule) return have also been considered as a possible source of dispersion.[13,23,34,35]

In almost all instances the reaction proceeded essentially to completion, but as indicated in the footnotes to Table 1, an equilibrium was established in solvents rich in fluoro alcohol. With a substrate concentration of 0.005 M, the solvolysis proceeded to 20% in 100% TFE, 92% in 97% TFE, and 97% in 90% TFE. With a substrate concentration of 0.0100 M, the solvolysis proceeded to 12% in 97% HFIP.

Effect of Added Pyridine. In order to follow the kinetics of solvolysis with reasonable precision, uncomplicated by a movement toward equilibrium, pyridine was added to the solvolyses in 100% TFE and 97% HFIP. In both of these solvents essentially unchanged specific rates were obtained after addition of up to 2.5 equiv of pyridine (Tables 2 and 3). A second-order component involving attack by pyridine is not to be expected because it has been shown[36] that additions of a moderate concentration of pyridine do not significantly increase the rates of solvolysis of *N*-isopropyl-, *N*-2-pentyl-, or *N*-3-pentylquinolium salts in 100% TFE or 100% HFIP, cations containing secondary alkyl groups that are much more susceptible to nucleophilic attack than the benzhydryl group.

While the *N*-benzhydrylpyridinium ion will not be formed via a concerted bimolecular route, it can be formed by capture of the intermediate carbocation, in competition with solvolysis. A competition of this type was found to be present when pyridine was added to solvolyses of the (*p*-methoxybenzyl)dimethylsulfonium ion.[2] For solvolyses of **1** in 100% TFE, the infinity titers were 95, 91, and 85% of the theoretical value with additions of pyridine of 0.0045, 0.0090, and 0.01359 M, respectively (Table 2, footnote d). These observations correspond to k_N/k_S ratios of 12, 11, and 13 M^{-1}, where k_N is the second-order rate coefficient for capture of the carbonium ion by pyridine and k_S is the first-order rate coefficient for capture by solvent. The constancy of the value obtained is consistent with the proposed mechanism, and the average value corresponds to a selectivity value (*S*) for capture by a pyridine molecule relative to a TFE molecule of 160.

Common Molecule Return and the Effect of Added Dimethyl Sulfide. In 95% acetone and 95% dioxane, although no fall-off in values could be detected during kinetic runs in the absence of additives, the specific rates could be depressed to a lower, essentially constant, value by the addition of a fairly large excess of dimethyl sulfide (Table 4). Defining the mass law constant (α) in the usual way, as the k_{-1}/k_1 ratio within eq 7, one arrives at a rate equation at any instant as

$$\mathrm{Ph_2CHSMe_2}^{+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ph_2CH}^{+} + \mathrm{SMe_2} \xrightarrow[k_s]{\mathrm{SOH}} \mathrm{Ph_2CHOS} + \mathrm{SOH_2}^{+} + \mathrm{X}^{-} \quad (7)$$

expressed in eq 8, where *a* is the initial concentration of

$$\frac{\mathrm{d[Ph_2CHOS]}}{\mathrm{d}t} = k^{\mathrm{inst}}(a - \mathrm{x})(1 + \alpha x)^{-1} \quad (8)$$

substrate, *x* is the amount of solvolysis product that has been formed at time *t*, and k^{inst} is the instantaneous rate coefficient for development of solvolysis product. With a large excess of added dimethyl sulfide, integration leads to eq 4 with, using the data of Table 4, α values of 2.5 ± 0.3 M^{-1} in 95% acetone and 1.3 ± 0.2 M^{-1} in 95% dioxane. The value in 95% acetone corresponds to slightly less external return than for the corresponding solvolysis of the (*p*-methoxybenzyl)dimethylsulfonium ion (α value of 4.8 ± 0.6, at 50.0 °C).

In solvents rich in fluoro alcohol, the nucleophilicity of the solvent is considerably reduced relative to 95% acetone or dioxane[6] and, accordingly, in the competition for the benzhydryl carbocation between solvolysis and return of dimethyl sulfide the extents of return are considerably magnified.

Under these conditions, the integrated first-order rate coefficients fall off with extent of reaction, as dimethyl sulfide accumulates. An illustrative run with 0.0062 M substrate in 100% TFE is presented in Table 5. The fall-off in values for k^{expt} can be reproduced using an initial value (zero [Me_2S]) of 25.4 ± 1.2 s^{-1} for k^{expt} and an α value of 600 M^{-1}, with the analysis in terms of eq 5 and *c* (the added [Me_2S] concentration) being zero. The addition of equimolar pyridine is to prevent an early

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Table 6. Selectivity Values (k_E/k_W) for the Solvolysis of the Benzhydryldimethylsulfonium Ion in Aqueous Ethanol at 25.0 °C and Comparison with Determinations for the Corresponding Solvolyses of Other Benzhydryl Derivatives (Ph_2CHX)

	k_E/k_W values										
	% EtOH (v/v) in aqueous EtOH										
X	96	95	90	86	80	70	60	50	40	30	20
SMe_2^+ [a]	2.6		2.3	2.7	2.7		2.5		4.3		4.0
Br[b]		3.1	3.3		3.7	4.1					
Cl[b]		2.3	2.5		2.8	3.3[c]					
Cl[d,e]			2.2		2.6	3.0	3.2	3.8			
Cl[e,f]			2.5		2.8	3.3	3.7	4.0	4.4	4.6	
DNB[d,g]					2.3	2.8	3.2	3.8			
PNB[d,h]					2.2	2.6	3.3	3.8			

[a] This work. [b] At 25.0 °C, from ref 26. [c] A value of 5.0 has also been reported (ref 27). [d] From ref 28. [e] At 25.0 °C. [f] From ref 29. [g] The 2,4-dinitrobenzoate ester at 100 °C. [h] The *p*-nitrobenzoate ester at 100 °C.

Table 7. Mass-Law Constant (α) for Solvolyses of 1 in Solvents of Varying Solvent Nucleophilicity (N_T) Values at 25.0 °C

solvent[a]	α, M^{-1}	log α	N_T[b]
97% HFIP	1500[c]	3.18	−5.26
70% HFIP	200	2.30	−2.94
50% HFIP	150	2.18	−2.49
100% TFE	600	2.78	−3.93
97% TFE	130	2.11	−3.30
95% acetone	2.5	0.40	−0.49

[a] On a weight−weight basis, except for 95% acetone, which is on a volume−volume basis at 25.0 °C. [b] Values from ref 6. [c] Calculated, using eq 5, from runs in presence of an excess of dimethyl sulfide.

(20%) equilibrium. This pyridine concentration would not be expected to seriously perturb the kinetics since interpolation within data presented as footnote d in Table 2 leads to an infinity titer of 93% of theoretical. This indicates that pyridine at this concentration competes only weakly with the solvent, in contrast to dimethyl sulfide, which competes very effectively. The effectiveness of the dimethyl sulfide intervention is indicated by the observation (Table 5) that, when the initial titer is at 17% solvolysis and a subsequent titer at 38% solvolysis, the calculated $k^{\rm expt}$ value is only 50% of the true initial value.

When dimethyl sulfide is added initially to solvolyses in 100% TFE at 25.0 °C, the fall-off in specific rates is dramatic. With 0.01 M additive, the specific rate is about 12% of the value in the absence of dimethyl sulfide, and with 0.04 M additive the corresponding ratio is only about 4%. Using the previously estimated α value of 600 M^{-1} one can convert, using eq 5, the observed $k^{\rm expt}$ values to the unperturbed specific rates of solvolysis (Table 2).

In 97% HFIP, the common-molecule rate depression is even more pronounced, and it was not possible to obtain even an approximately accurate value for α from runs in the absence of added dimethyl sulfide. An enormous fall-off in rate with development of the first small amounts of dimethyl sulfide was observed. The α value could, however, be accurately estimated (at a value of 1500 M^{-1}) from the very slow runs in the presence of initially added dimethyl sulfide. To illustrate this retardation, in the presence of 0.040 M dimethyl sulfide, the true solvolysis rate (in the absence of perturbation by dimethyl sulfide) was reduced by 98.5%. The α value obtained from these experiments was then applied, using eq 5, to solvolyses in the absence of initially added dimethyl sulfide. A value for the specific rate of solvolysis in the absence of any perturbation induced by dimethyl sulfide of about 60×10^{-4} s^{-1} (at 25.0 °C) was obtained both for runs in the absence of initially added dimethyl sulfide and for runs when up to 0.04 M dimethyl sulfide was added (Table 3).

The α values obtained for solvolyses in six solvents, varying in solvent nucleophilicity (N_T) values from −0.49 (95% acetone) to −5.26 (97% HFIP),[6] are reported in Table 7. It is found that the log α values are quite well correlated with solvent nucleophilicity values, with a slope of −0.58 ± 0.08, intercept of 0.39 ± 0.30, and correlation coefficient of −0.960. It could be considered as rather surprising that the correlation is this precise, because the k_{-1}/k ratio, which α represents, is dependent not only on solvent nucleophilicity but also upon the nucleophilicity of dimethyl sulfide, which one would expect to be solvent dependent. However, the nucleophilicity of the dimethyl sulfide will be to a large degree influenced by the ability of the solvent to interact electrophilically with the sulfur atom, and these reductions in sulfide nucleophilicity will be approximately related to the reductions in solvent nucleophilicity.

Extended Grunwald−Winstein Equation Treatment with Application of the Aromatic Ring Parameter (*I*) Scale. For 34 of the 35 solvents listed in Table 1 (N_T value not available for 95% dioxane), the variation in specific rate with solvent composition has been analyzed in terms of eqs 1, 2, and 3, and, also, in terms of linear regression against *I* values and regression against a combination of Y^+ and N_T scales. The results of these five analyses are presented in Table 8.

It can be seen, from analyses either in terms of Y^+ and N_T scales ($l = -0.01 \pm 0.10$) or Y^+, *I*, and N_T scales ($l = 0.03 \pm 0.02$), that the specific rates of solvolysis are insensitive to changes in solvent nucleophilicity. For linear regression analyses, it is found that correlation against Y^+ values is unsatisfactory ($r = 0.795$; *F*-test value of 55) and correlation against *I* values is considerably superior ($r = 0.935$; *F*-test value of 224).

The best results (see Figure 1) are obtained by multiple regression analysis against a combination of Y^+ and *I* values ($R = 0.991$; *F*-test value of 897). In this correlation, the *m* value of 1.35 ± 0.10 and *h* value of 0.99 ± 0.04 are essentially identical to those for the solvolysis of the (*p*-methoxybenzyl)dimethylsulfonium ion at 50.0 °C [*h* value of 1.00 (standard system) and *m* value of 1.3].[2] This correspondence in *h* and *m* values is consistent with the previously discussed good LFER plot with unit slope for the specific rates of the two solvolyses. It appears that, for solvolyses of the $RSMe_2^+$ derivative, the two phenyl substituents within the benzhydryl(diphenylmethyl) group have the same influence upon the changes in the specific rates of solvolysis, as they result from variation of both Y^+ and *I*, as the *p*-methoxyphenyl substituent within the *p*-methoxybenzyl (*p*-methoxyphenyl)methyl group.

Product Selectivity in Aqueous Ethanol. For solvolyses of **1** at 25.0 °C in aqueous ethanol mixtures, the product partitioning between benzhydrol and benzhydryl ethyl ether has been determined and converted into selectivity values (*S*), defined as k_E/k_W, where k_E and k_W are the second-order rate coefficients for capture by ethanol and water, respectively. The previously noted absence of any sensitivity of the specific rates of solvolysis toward changes in solvent nucleophilicity suggests that the capture is of a carbocation previously formed in the

Table 8. Correlation of the Specific Rates of Solvolysis, in 34 Solvents at 25.0 °C,[a] of the Benzhydryldimethylsulfonium Ion, Using the Grunwald–Winstein Approach and Various Combinations of Y^+, N_T, and I Parameters

scale(s)[b]	l[c]	m[c]	h[c]	c[d]	R[e]	F[f]
Y^+		2.71 ± 0.37		−0.17 ± 0.31	0.795	55
I			1.30 ± 0.09	0.21 ± 0.18	0.935	224
Y^+, N_T	−0.01 ± 0.10 (0.89)	2.60 ± 0.85		−0.17 ± 0.31	0.795	27
Y^+, I		1.35 ± 0.10	0.99 ± 0.04	0.00 ± 0.07	0.991	897
Y^+, I, N_T	0.03 ± 0.02 (0.20)	1.56 ± 0.19	1.00 ± 0.04	0.00 ± 0.07	0.992	612

[a] Data from Table 1. [b] Values from refs 3, 6, and 7. [c] With associated standard error; values in parentheses are the probabilities that the term is not statistically significant (recorded if greater than 0.005). [d] Residual (constant) term, accompanied by the standard error of the estimate. [e] Correlation coefficient. [f] The F-test value.

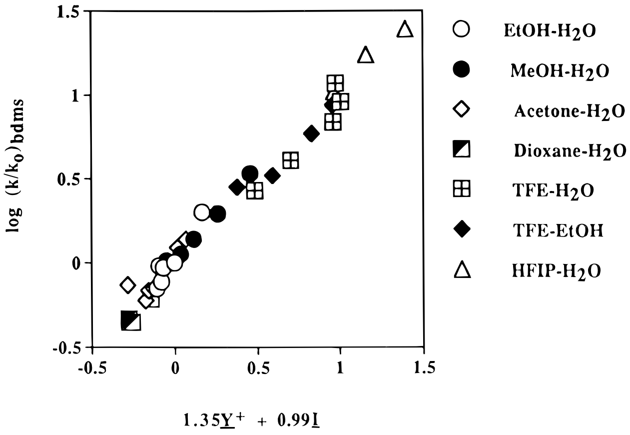

Figure 1. Plot of log (k/k_o) for **1** against ($1.35Y^+ + 0.99I$).

rate-determining step. The modest preference for reaction with the more nucleophilic ethanol component (Table 6) suggests capture of a free carbocation, and the somewhat larger S value in the more aqueous solvents is consistent with previously observed[29,37] trends for such a capture. In contrast, capture at a solvent-separated ion pair is usually accompanied by a modest preference for reaction with the water and an S value of below unity. Similar behavior was observed for the product partitioning both from the 1-adamantyldimethylsulfonium ion and from 1-adamantyl derivatives with anionic leaving groups, suggesting that capture at a solvent-separated ion-molecule stage has very similar characteristics to capture at a solvent-separated ion pair stage.[3]

If the capture is at the free carbocation stage then the competition must be independent of the source of the carbocation, and not surprisingly, the selectivities observed for **1** parallel closely those previously observed, and listed in Table 6, for the corresponding bromides,[26] chlorides,[26,28,29] 2,4-dinitrobenzoates,[28] and p-nitrobenzoates.[28]

Conclusions

The logarithms of the specific rates of solvolysis of **1** in 34 hydroxylic solvents of widely varying character can be very well correlated against a combination of Y^+ and I parameters ($R = 0.991$). It is found that the sensitivity of the specific rates of solvolysis toward changes in solvent nucleophilicity (N_T) values is essentially zero, consistent with the considerable evidence for S_N1 solvolyses of benzhydryl derivatives. The ion **1** undergoes ethanolysis at 50.0 °C about 200 times faster than the (p-methoxybenzyl)dimethylsulfonium ion, but the sensitivities toward changes in both Y^+ and I are virtually identical, and it appears that, within these correlations, the influence of two phenyl groups mimics that of a p-methoxyphenyl group. The utility of the aromatic ring parameter (I) in these correlations gives yet further evidence for its generality in correcting for dispersion in Grunwald–Winstein plots for the solvolyses of benzylic and related derivatives.

Common-molecule return is found. While it constitutes a weak effect in 95% acetone (detectable only on addition of appreciable concentrations of dimethyl sulfide), the effect is considerably magnified in solvents rich in fluoro alcohol. In 97% HFIP, the rate depression is so pronounced that an accurate value for the mass law constant (α) can be obtained only from runs carried out in the presence of a fairly large initial concentration of dimethyl sulfide. The log α values, available for six solvents, correlate quite well with N_T values ($r = -0.960$).

Selectivity values (k_E/k_W) in aqueous ethanol show a small preference for reaction with ethanol, and they rise slightly in value in the water-rich solvents. This pattern of behavior is usually taken to indicate competition for a free carbocation, and it contrasts with that for capture at the solvent-separated ion-pair (or ion-molecule) stage, which is usually accompanied by a slight preference for reaction with the less nucleophilic water.

Experimental Section

Materials. The purification of acetone, dioxane, ethanol, and methanol were as described previously.[38] The purifications of 1,1,1,3,3,3-hexafluoro-2-propanol[39] and 2,2,2-trifluoroethanol[40] also used previously reported procedures. Benzhydryl chloride, dimethyl sulfide, and silver trifluoromethanesulfonate were used without further purification. Pyridine was refluxed over barium monoxide and then fractionally distilled.[41] Benzhydrol (Aldrich) was recrystallized from ligroin (bp 60–80 °C), with decolorization using Norit (activated carbon), to give white needles. Benzhydryl ethyl ether was prepared using the method previously reported for the preparation of 1-adamantyl ethyl ether[38] but with benzhydryl chloride replacing 1-adamantyl iodide: bp 122–122.5 °C (1.4 mmHg) [lit.[42] bp 128–132 °C (1.3 mmHg)].

Benzhydryldimethylsulfonium Trifluoromethanesulfonate. The procedure followed was identical to that previously used[2] to prepare the (p-methoxybenzyl)dimethylsulfonium salt, but with benzhydryl chloride substituted for

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p-methoxybenzyl chloride. A 73% yield of white crystals was obtained: mp 117.5−121.5 °C;[43] IR (KBr disk) 3010, 2930, 1490, 1420, 1270, 1160, 1030, 640 cm^{-1}; PMR (CD_3CN) δ 2.71 (s, 6H), 5.76 (s, 1H), 7.2−7.7 (m, 10H). Anal. Calcd for $C_{16}H_{17}F_3O_3S_2$: C, 50.78; H, 4.53; S, 16.94. Found: C, 50.64; H, 4.57; S, 16.88.

Kinetic Procedures. The kinetic runs and subsequent multiple regression analyses were performed as previously described.[2]

Determination of Product Composition. The product division between benzhydrol and benzhydryl ethyl ether was determined for solvolysis at 25.0 °C in seven aqueous ethanol mixtures by use of a response-calibrated GLPC analysis with nitrogen as the carrier gas and a 3.1 m × 6 mm glass column packed with OV-17 (3%) on 80−100 mesh DMCS-treated Chromosorb W (non-acid-washed) at a programmed temperature span of 100−200 °C, 5° per min, temperature held initially at 100 °C for 10 min. A Packard instrument (Model GC-430), with flame ionization detector and microprocessor integrator, was used. All solutions were allowed to react for a little over 10 half-lives, and determinations were at least in duplicate, with an error of ± 5% estimated for the product ratio.

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