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Solvolysis of the (*p*-Methoxybenzyl)dimethylsulfonium Ion. Development and Use of a Scale to Correct for Dispersion in Grunwald–Winstein Plots[1]

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The specific rates of solvolysis of the (*p*-methoxybenzyl)dimethylsulfonium ion have been found to vary only modestly over a wide range of solvents and previous claims of a dependence on water nucleophilicity during hydrolysis are questioned. The variations in specific rate are somewhat greater than those previously recorded for the 1-adamantyldimethylsulfonium ion and the differences are used to establish values for an aromatic ring parameter (I). Application of the parameter removes dispersion from Grunwald–Winstein plots and the need to choose from within a matrix of similarity models, which are now recommended only as regards the leaving group. The requirements for a good similarity model are discussed in terms of the I parameter. It is shown that either a neglect of the term including I or an overcompensation when using the alternative similarity model approach can be reflected as an apparent relationship between the specific rate and solvent nucleophilicity.

Introduction

The primary aim of the reported investigation is to develop a treatment of the dispersion frequently observed in Grunwald–Winstein plots. A new scale is developed, which is then used as the basis for a term which can be added to the linear free energy relationship. We believe that this approach is preferable to the ongoing development of a large number of similarity model scales for solvolysis of an RX substrate, which have to be based not only on the identity of the leaving group X but also on the detailed identity of the R group. Values for a parameter with the desired properties are obtained for a wide range of solvents and applied with a very high degree of success to remove dispersion from several previously analyzed solvolyses.

The specific rates of solvolysis of the 1-adamantyldimethylsulfonium ion (1-AdSMe$_2^+$) have been shown[2] to be almost independent of solvent composition over a wide range of pure and binary solvents. This supports the use of methyl and primary RX$^+$ substrates, such as the triethyloxonium ion[3] and the *S*-methyldibenzothiophenium ion,[4] as standard substrates for the development of scales of solvent nucleophilicity.[5–8]

In general, dispersion effects in unimolecular solvolyses[9,10] (believed to be due to variations in the detailed nature of solvation changes in going from the ground state to the transition state in the presence of substituents containing π electrons[11–13]) make a smaller contribution to the overall linear free energy relationship (LFER) than solvent nucleophilicity effects in bimolecular solvolyses. Any attempt to develop a treatment of dispersion in Grunwald–Winstein plots[14,15] (eq 1) by

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

addition of a term governing the dispersion will parallel the approach used to treat superimposed nucleophilic assistance from the solvent using the extended Grunwald–Winstein equation (eq 2),[16] except that the considerable advantages of minimizing leaving-group effects by use of an RX$^+$ substrate (previously discussed[3,4,7,8]) rather than a neutral RX substrate[13] are even more pronounced.

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

In eqs 1 and 2, k and k_0 are the specific rates of solvolysis in a given solvent and in the standard solvent, 80% ethanol, and l and m are the sensitivities of the specific rate of solvolysis to changes in solvent nucleophilicity (N) and solvent ionizing power (Y), respectively.

The hydrolysis of the (*p*-methoxybenzyl)dimethylsulfonium ion (**1**) has previously been shown to proceed at a convenient rate at temperatures in the 60–70 °C range[17,18] and, especially since the corresponding chloride has recently been given attention[11,13] as a standard

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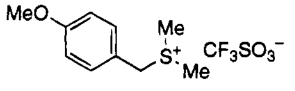
substrate for a similarity model[19] Y scale, this ion was chosen as the standard substrate for the establishment of a scale of values for what we term the "aromatic ring parameter (I)", developed for use within two- or three-term Grunwald–Winstein treatments (involving addition of an hI term to eq 1 or eq 2). A major goal of this approach is to remove or, at least, minimize the proliferation of similarity model scales (Y_{sim}). Ideally, as an alternative, it will be possible to carry out multiple-regression analysis incorporating the appropriate Y_x scale (based on adamantyl derivative solvolyses)[15] in conjunction with the aromatic ring scale (I). Further, these analyses allows us to quantify the requirements for two differently constituted benzylic groups to be considered as "similar" within the framework of the similarity model treatment of solvolytic reactions.[20]

A secondary aim of the study is to extend previous investigations of the hydrolysis of **1**,[17,18,21] with emphasis on the influence of solvent variation. Based on the influence of added azide ion upon rate and products[17] and on a consideration of sulfur isotope effects,[18] it has been proposed that there is appreciable nucleophilic assistance toward the hydrolysis. This is in conflict with results for the corresponding chloride, which strongly suggest an S_N1 mechanism,[11,13] and with the observation of common-ion rate depression in the solvolyses of the bromide in aqueous dioxane.[22] It will be demonstrated that claims of nucleophilic assistance from the solvent toward hydrolysis of **1** are considerably weakened by concerns about either the theoretical analysis[17] or the experimental procedures.[18]



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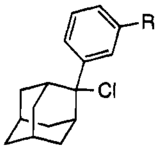

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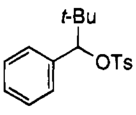

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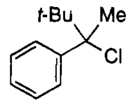

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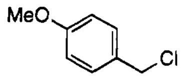

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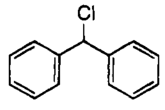

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Results

Solvolyses of 1 at 50.0 °C. Specific rates of solvolysis of **1** as the trifluoromethanesulfonate (triflate) salt were obtained in the pure solvents ethanol, methanol, water, and 2,2,2-trifluoroethanol (TFE), in binary mixtures of water with the three organic solvents mentioned above as well as with acetone, dioxane, and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), and in TFE-ethanol mixtures (Table 1). Attempts to measure specific rates of acetolysis and formolysis[23] were abandoned because of the apparent establishment of an early equilibrium, at 22% of possible solvolysis in acetic acid, which was followed in formic acid by a slow increase in the extent of acid formation.

Table 1. Specific Rates of Solvolysis of the (*p*-Methoxybenzyl)dimethylsulfonium Ion[a] (*k*), at 50.0 °C, and the Associated Aromatic Ring Parameter (*I*)

solvent[b]	$10^5 k$, s^{-1} [c]	$\log(k/k_o)$[d]	I[e]
100% EtOH	7.94 ± 0.19	0.17	0.20
80% EtOH	5.37 ± 0.08	0.00	0.00
60% EtOH	4.51 ± 0.25	−0.08	−0.15
40% EtOH	4.20 ± 0.06	−0.11	−0.24
20% EtOH	4.44 ± 0.29	−0.08	−0.33
100% H_2O	4.15 ± 0.07	−0.11	−0.45
100% MeOH	15.5 ± 0.8	0.46	0.41
80% MeOH	9.72 ± 0.50	0.26	0.14
60% MeOH	6.86 ± 0.35	0.11	−0.02
40% MeOH	5.79 ± 0.28	0.03	−0.13
20% MeOH	4.71 ± 0.27	−0.06	−0.26
95% acetone	6.19 ± 0.12	0.06	−0.13
90% acetone	5.50 ± 0.20	0.01	−0.17
80% acetone	4.59 ± 0.07	−0.07	−0.23
70% acetone	4.10 ± 0.08	−0.13	−0.29
60% acetone	3.87 ± 0.21	−0.14	−0.28
40% acetone	3.54 ± 0.13	−0.18	−0.35
20% acetone	3.65 ± 0.30	−0.17	−0.40
95% dioxane	2.51 ± 0.15	−0.33	−0.02
90% dioxane	2.72 ± 0.11	−0.29	−0.12
80% dioxane	2.87 ± 0.07	−0.27	−0.13
60% dioxane	2.80 ± 0.10	−0.28	−0.29
40% dioxane	2.95 ± 0.11	−0.26	−0.27
20% dioxane	3.76 ± 0.18	−0.15	−0.25
100% TFE[f,g]	49.2 ± 3.2	0.96	0.37
97% TFE[f,g]	53.6 ± 3.1	1.00	0.49
90% TFE[f,g]	47.9 ± 3.1	0.95	0.47
80% TFE[f,g]	28.7 ± 0.4	0.73	0.28
70% TFE[f,g]	26.5 ± 1.5	0.69	0.25
50% TFE[g]	15.9 ± 0.9	0.47	0.09
80T−20E[f]	47.8 ± 2.5	0.95	0.52
60T−40E	35.9 ± 1.5	0.83	0.59
40T−60E	21.0 ± 1.1	0.59	0.43
20T−80E	13.0 ± 0.4	0.38	0.31
97% HFIP[h]	(125)[i]	1.37	0.73
90% HFIP[h]	91.6 ± 6.2[j]	1.23	0.60
70% HFIP	75.9 ± 2.4[k]	1.15	0.69
50% HFIP	49.4 ± 2.8	0.96	0.53

[a] As the triflate salt and concentration of 0.0045−0.0055 M, except for HFIP−H_2O mixtures (0.0095 M); all runs performed, at least, in duplicate. [b] 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. [c] With associated standard deviation. [d] k_o is the specific rate of solvolysis in 80% ethanol. [e] The I value is defined as $\log(k/k_o) - 1.3Y^+$ (where Y^+ values are $\log(k/k_o)$ values for 1-adamantyldimethylsulfonium ion solvolysis at 70.4 °C and are listed in ref 2.) [f] Runs carried out in the presence of 0.0051 M pyridine; in absence of pyridine, specific rates averaged over the first 20% of reaction in 97% TFE gave value of $43.9(\pm 2.2) \times 10^{-5}$ s^{-1} and, over first 50% of reaction, values of $39.7(\pm 2.2) \times 10^{-5}$ s^{-1} in 90% TFE and $19.3(\pm 1.0) \times 10^{-5}$ s^{-1} in 70% TFE. [g] Comparison of final titer (10 half-lives) in absence of pyridine to the infinity titer obtained after standing for 10 half-lives following addition to equal volume of methanol, indicated equilibrium positions of 48(±1)% (3 detmn) in 97% TFE, 80% in 90% TFE, 95% in 70% TFE, and 98.4% in 50% TFE. [h] In presence of 0.0076 M pyridine. [i] Extrapolated value (estimated standard deviation ±20%), values fall during reaction but calculated V_∞ is attained; in absence of pyridine, final titration corresponds to 11.6(±0.3)% (2 detmn) of this value. [j] Slight falloff, value is averaged from 4 runs within the first 25% of reaction; in absence of pyridine, final titer indicates equilibrium at 48% reaction. [k] No falloff over 65% of reaction.

The positions of equilibria in aqueous TFE were established by comparison of the titer at 10 half-lives with the corresponding acid titer obtained after initial

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Table 2. Specific Rates of Solvolysis of the (*p*-Methoxybenzyl)dimethylsulfonium Ion[a] at Various Temperatures and Enthalpies ($\Delta H^{\ddagger}$) and Entropies ($\Delta S^{\ddagger}$) of Activation[b]

	10^6k, s^{-1} [c]		
temp, °C	EtOH	80% EtOH[d]	H_2O
14.8	0.298 ± 0.013	0.152 ± 0.006	
16.3			0.173 ± 0.003
25.0	1.48 ± 0.02	0.762 ± 0.023	0.964 ± 0.019
35.0	8.21 ± 0.10	4.83 ± 0.08	4.68 ± 0.17
60.0	312 ± 5	225 ± 3	190 ± 5[f]
$\Delta H_{298}^{\ddagger}$ (kcal/mol)[e]	29.0 ± 0.4	30.6 ± 0.6	29.7 ± 0.5
$\Delta S_{298}^{\ddagger}$ (eu)[e]	12.1 ± 1.3	15.8 ± 1.9	13.4 ± 1.7

[a] As the triflate salt and concentration of 0.0047–0.0055 M. [b] Specific rates at 50.0 °C (from Table 1) also included in the calculation. [c] With associated standard deviations (averages combining both series of integrated values from duplicate runs). [d] On a volume-volume basis at 25.0 °C. [e] With associated standard error. [f] Values have been reported (ref 17) of 178(±1) × 10^{-6} s^{-1} for the perchlorate salt and 179(±3) × 10^{-6} s^{-1} for the nitrate salt.

addition to an equal volume of methanol (which closely corresponded to the theoretical infinity titer). For 100–70% TFE, the specific rates reported in Table 1 were determined in the presence of sufficient pyridine to avoid the acid-catalyzed reverse reaction. In 97, 90, and 70% TFE, averaged specific rates obtained during the early stages of runs carried out in the absence of pyridine were 20–35% lower than those obtained over a larger extent of reaction in the presence of pyridine.

In 97 and 90% HFIP, the position of equilibrium was established by comparison of the developed acid with the infinity titer obtained in the presence of pyridine. In 90% HFIP, because of a modest falloff in the value of the integrated specific rate in the presence of pyridine with extent of reaction, the 12–14 values were accumulated and averaged from the first 25% of four runs rather than the usual first 60–70% of duplicate runs. In 97% HFIP, the corresponding falloff was considerably more pronounced and an initial value was estimated from a plot of *k* against extent of reaction for duplicate runs. The falloff is probably associated with common-molecule rate depression and/or some degree of capture by the added pyridine to give a slower reacting[24] (*p*-methoxybenzyl)pyridinium ion. Unfortunately, attempts to prepare (*p*-methoxybenzyl)pyridinium triflate for a study of its possible involvement led only to unstable oils.

Determination of Activation Parameters. In addition to the determination of the specific rates at 50.0 °C, the solvolyses in ethanol, 80% ethanol, and water were also studied at four other temperatures (Table 2). The specific rates at all five temperatures were used to calculate the reported entropies and enthalpies of activation.

Effect of Added Pyridine or Dimethyl Sulfide. The effect upon the specific rate of solvolysis in 95% acetone at 50.0 °C was studied for additions of up to 0.1 M pyridine or dimethyl sulfide (Table 3). Addition of dimethyl sulfide depressed the rate but led to the predicted infinity titer. Addition of pyridine increased the specific rate of reaction and the observed acid production at 10 half-lives was reduced. For these reactions, the observed titer was used as the infinity titer, assuming the percentage of the overall reaction proceeding with acid formation remained constant throughout each run.

Table 3. Effect of Added Pyridine and Dimethyl Sulfide upon the Specific Rates of Reaction of the (*p*-Methoxybenzyl)dimethylsulfonium Ion[a] in 95% Acetone, at 50.0 °C

$[C_5H_5N]$, M	$[Me_2S]$, M	10^5k, s^{-1} [b]	% solvolysis[c]
0.0000		6.19 ± 0.12	99.8
0.0502		7.28 ± 0.19	73.4
0.1004		8.89 ± 0.27	51.0
	0.0360	5.31 ± 0.15[d]	99.4
	0.0720	4.58 ± 0.10[d]	98.8

[a] As the tosylate salt and concentration of 0.005 M. [b] With associated standard deviation (using all of the points from duplicate runs). [c] Comparison of theoretical and observed (10 half-lives) infinity titers. [d] Retardation corresponds to a mass-law constant of 4.6 ± 0.9 M^{-1} with 0.036 M Me_2S and 4.9 ± 0.8 M^{-1} with 0.072 M Me_2S.

Discussion

Specific Rates and Equilibrium Considerations for the Solvolyses of 1. In the study of the solvolyses of **1** at 50 °C in 37 pure or binary solvents (Table 1), the specific rates of solvolysis were found to vary only by a factor of 50. While small, this value is nonetheless larger than the corresponding factor of slightly less than seven for the specific rates of solvolysis of the 1-$AdSMe_2^+$ ion.[2] As with the 1-$AdSMe_2^+$ solvolyses, the faster reactions are in solvents rich in fluoro alcohol, the least nucleophilic solvents of the study, and clearly solvent nucleophilicity cannot be the dominant factor in causing the small rate variations. This difference in behavior between **1** and 1-$AdSMe_2^+$ can be assigned to the same source as that leading to dispersion in Grunwald–Winstein plots for neutral substrate in the presence of substituents containing π electrons.[10–13] This dispersion is usually ascribed as being due to differences in the solvation changes when going from the ground state to the transition state in the presence or absence of aryl substituents.[10,13] Variations in the solvent dependence of differences in the extent of ion-pair return have also been considered as a possible source of dispersion.[9,20,25,26]

The early equilibrium for solvolyses in acetic acid resembles those previously observed for the *tert*-butylethylmethylsulfonium ion[27] and the 1-$AdSMe_2^+$ ion.[2] Equilibria are also observed in solvents rich in fluoro alcohol (see footnotes to Table 1). In TFE, an equilibrium at 48% reaction in 97% TFE moves to 95% reaction in 70% TFE and to essentially complete reaction with 50%

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water present. Similarly, in aqueous HFIP, a value of 12% reaction for 97% HFIP becomes 48% in 90% HFIP, and the reaction is essentially complete in 70% HFIP. These observations are, however, in conflict with a report[21] than an equilibrium is established during hydrolysis in pure water. Earlier studies of the hydrolysis[17,18] have made no mention of an equilibrium and indeed we find, contrary to what would be expected if equilibria were involved, a constant infinity titer for solvolyses in water, ethanol, and methanol, remaining unchanged for solvolyses in mixtures of water with ethanol, methanol, acetone, or dioxane. Further, this experimental infinity titer was in all instances within 2% of the theoretical value for 100% solvolysis.

A study of the variation of the specific rate of solvolysis with temperature in water, ethanol, and 80% ethanol indicated (Table 2) a high activation energy (ca. 30 kcal/mol) and an appreciably positive entropy of activation (12−16 eu), both values somewhat less than for 1-AdSMe$_2^+$ solvolysis (*ca.* 35 kcal/mol and 16−21 eu). The activation parameters for hydrolysis can be used to estimate a specific rate at 80 °C of 2.5×10^{-3} s^{-1}, in exact agreement with the value (abstracted from their Figure 2) measured by Buckley and Oppenheimer[21] for the chloride salt. Our experimental value of 1.90×10^{-4} s^{-1} at 60 °C is in good agreement with previously reported values of 1.78×10^{-4} s^{-1} for the perchlorate salt and 1.79×10^{-4} s^{-1} for the nitrate salt.[17]

A third previous study of the hydrolysis, by Friedberger and Thornton,[18] reports a value at 68.7 °C of 375×10^{-6} s^{-1}, considerably less than our extrapolated value of 588×10^{-6} s^{-1}. The good agreement between the values obtained from the present data and two previously reported studies[17,21] suggests that this experimental value is probably in error. The measurement was one portion of parallel studies of the specific rates of hydrolysis and sulfur isotope effects within the leaving group. The measured sulfur isotope effects showed little variation with change of the substituent within the benzyldimethylsulfonium ion. This was especially puzzling for **1**, since the *p*-methoxy substituent would be expected to favor increased S$_N$1 character and a larger S^{32}/S^{34} isotope effect. They concluded that the hydrolysis of **1** had more S$_N$2 character than previously thought. This conclusion has been questioned and a lack of sensitivity of the sulfur isotope effect to position along the S$_N$1−S$_N$2 spectrum proposed as an alternative rationalization.[28]

In their report, Friedberger and Thornton outline some experimental difficulties, suggested as being associated with the limited solubility of the *p*-methoxybenzyl alcohol product in water. Indeed, they specifically mention that in some experiments anomalously low isotope effects were associated with anomalously low specific rates of solvolysis. They claimed that this problem was bypassed by restricting analyses to the first 25% of reaction. It now appears that, as regards specific rates at least, the problem was not resolved. Applying the recommended[18] criterion of rejecting sulfur isotope effects as being low if they are associated with low specific rates, it appears that the observation of a sulfur isotope effect for hydrolysis of **1** essentially the same as for other derivatives of the benzyldimethylsulfonium ion was probably fortuitous, and the true S^{32}/S^{34} ratio should be higher than that reported, possibly moving into the range consistent with an S$_N$1 hydrolysis.

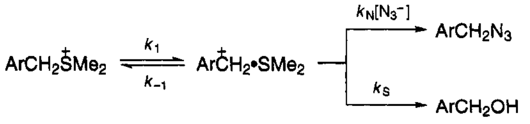
Table 4. Reconsideration of the Influence of Azide Ion on the Kinetics and Products for Reaction of the (*p*-Methoxybenzyl)dimethylsulfonium Ion (RSMe$_2^+$) in Water at 60 °C

	experimental[a]		calcd (Sneen)		calcd (S$_N$1−S$_N$2)[c]	
[NaN$_3$], M	10^4k, s^{-1}	%RN$_3$	10^4k, s^{-1} [a]	%RN$_3$[b]	10^4k, s^{-1}	%RN$_3$[d]
0.000	1.79					
0.030		51.5		59.0		50.7
0.060		71.3		74.2		70.2
0.070	2.64	76.5	3.06	77.1	2.80	75.1
0.090		79.6		81.2		80.0
0.100	3.25	82.0	3.23	82.8	3.23	82.1
0.120	3.50	84.5	3.30	85.2	3.51	85.6

[a] From ref 17. [b] Calculated as $100/[1 + (m[N_3^-])^{-1}]$, with *m* value ($k_N/k_s$) from ref 17 of 48.0 M^{-1}. [c] Assuming $k = k_o + k_2[N_3^-]$, with k_2 determined as 14.4×10^{-4} M^{-1} s^{-1}, such that the fraction of total product as azide due to the S$_N$2 component (*y*) is $[k_2[N_3^-]/(k_2[N_3^-] + k_o)]$, where k_o is the specific rate in absence of azide ion. The fraction of total product as azide within the S$_N$1 component is then determined by competition between $k_N[N_3^-]$ and k_s pathways and can be expressed as $(1 - y)/[1 + (m[N_3^-])^{-1}]$, with a best fit value for *m* of 21.1 M^{-1}. [d] Sum of percentages from S$_N$1 and S$_N$2 components.

Effect on Specific Rate of Added Pyridine and Dimethyl Sulfide. Additions of up to 0.1 M pyridine modestly increase the rate of reaction (Table 3) and the percentage of solvolysis is decreased due to formation of the (*p*-methoxybenzyl)pyridinium ion, which is to be expected to solvolyze much slower than **1**.[24] The increases in the specific rate of overall reaction in 95% acetone at 50.0 °C are consistent with a second-order rate coefficient for bimolecular reaction of **1** with pyridine of $2.5(\pm0.2) \times 10^{-4}$ L mol^{-1} s^{-1}. Multiplying the overall specific rates by the percentage of overall reaction proceeding by solvolysis, one obtains specific rates of solvolysis of $5.34(\pm0.14) \times 10^{-5}$ s^{-1} at 0.0502 M pyridine and $4.53(\pm0.14) \times 10^{-5}$ s^{-1} at 0.1004 M pyridine. Assuming the reductions below the $6.19(+0.12) \times 10^{-5}$ s^{-1} obtained in the absence of pyridine are due to interception of a *p*-methoxybenzyl carbocation intermediate by pyridine, we can calculate sensitivities (*S*) for capture of the carbocation by a pyridine molecule as opposed to capture by a water molecule of 8.8 ± 2.1 for 0.0502 M pyridine and 10.1 ± 1.4 for 0.1004 M pyridine.

Sneen[17] has investigated the influence of additions of up to 0.12 M azide ion to the hydrolysis in 100% water in terms of eq 3. An ion-molecule pair was assumed to be formed which can either return to reactant or proceed to products by reaction with either azide ion or water. Using a best fit parameter of 1.19 for k_{-1}/k_s, and estimated values of 48.0 M^{-1} for k_N/k_S (termed the *m* value) and 3.90×10^{-4} s^{-1} for k_1, the fit of calculated and experimental specific rates is not especially good and the calculated percentages of azide product deviate markedly from experimental measurements at the lower azide ion concentration (Table 4).



(3)

Sneen acknowledged that the data could be rationalized in terms of a competitive S$_N$1−S$_N$2 scheme but qualified that statement with the phrase "albeit only with

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[28] Harris, J. M.; Mount, D. L.; Smith, M. R.; Neal, W. C., Jr.; Dukes, M. D.; Raber, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 8147.

difficulty". In fact, a treatment paralleling the one outlined above for pyridine addition, assuming concurrent S_N1 and S_N2 processes, gives an excellent fit to the data (Table 4), superior to the fit obtained with the application of the unifying mechanism proposed by Sneen.[29] The fit to the S_N1–S_N2 scheme requires a k_2 value for reaction of azide ion with **1** in water at 60 °C, of 14.4×10^{-4} L mol^{-1} s^{-1} and a k_N/k_S value, within the S_N1 component, of 21.1 M^{-1}; taking the concentration of water in pure water at 60 °C to be 54.7 M, this corresponds to a selectivity value (*S*) for capture by an azide ion relative to captive by a water molecule of 1150. An independent determination of this k_N/k_S value does not seem to have been made but Richard[30] has reported values in the range of 140–220 M^{-1} for the 1-(*p*-methoxyphenyl)-2,2,2-trifluoroethyl carbocation (similar to that formed from **1** but with an α-trifluoromethyl substituent introduced) after formation from the bromide in the presence of 6 M salt (varying amounts of NaBr and $NaClO_4$) at 25 °C in 100% H_2O containing azide ion.

Additions of dimethyl sulfide to the solvolysis in 95% acetone at 50 °C lead to modest reductions in the specific rate of solvolysis. Similar reductions of the specific rates of solvolysis of the benzhydryldimethylsulfonium ion were ascribed[8] to common-molecule return, indicative of product formation at the free ion stage. Since the concentrations of initially added Me_2S are considerably in excess of the substrate concentration, the kinetic influences of the Me_2S produced during reaction can be neglected and the common-molecule rate depression can be analyzed in terms of eq 4, where k is the specific rate

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

of formation of the free carbocation (considered to be the specific rate of reaction in the absence of added Me_2S), k^{expt} is the measured specific rate of product (acid) formation in the presence of an added concentration (c) of Me_2S, and α is the mass-law constant, the ratio of the capture of the carbenium ion by dimethyl sulfide ion in unit concentration relative to its rate of capture by the solvent water.[31] Averaging the two determinations (Table 3), we obtain an α value of 4.8 ± 0.6 M^{-1}. This value is similar to the value of 2.5 ± 0.3 M^{-1} obtained from an analysis of corresponding data[1] at 25 °C for Me_2S additions to the solvolysis of the benzhydryldimethylsulfonium ion. The α value corresponds to a selectivity value (*S*) for reaction of the carbocation from **1** with a Me_2S molecule relative to reaction with a water molecule within the 95% acetone of 13.3 ± 1.7; this value is very slightly higher than the weighted average value of 9.6 ± 1.3 obtained when pyridine, rather than Me_2S, was in competition with the solvent.

Development of a Scale of Values for the Aromatic Ring Parameter (*I*). In early discussions of dispersion in the Grunwald–Winstein plot (eq 1) for solvolysis of an RX substrate, it was recognized that the delocalization of charge made possible by the presence of α-aryl groups,[10] the variations in specificity for differing leaving groups,[25] and any disturbances arising from ion-pair return[9] were all important considerations for S_N1 reactions, with additional disturbances due to superimposed solvent nucleophilicity effects for S_N2 reactions.[16,25]

Effects due to solvent nucleophilicity have been treated by use of the extended Grunwald–Winstein equation (eq 2)[5–8] and effects due to variation in the leaving group by a similarity model approach involving establishment of a series of Y_x scales.[15] In consideration of the other factors, Bentley[11] and Liu[32] have suggested that the major cause of dispersion arising from structural aspects of the R group which are not present in the standard substrate is solvation differences between aromatic rings and alkyl groups. Bunton[33] has also favored differential solvation rather than ion-pair return effects as the dominant influence and, supporting this view, it has been shown[34] that the collapse/solvolysis ratio for 1-adamantyl chloride ion-pairs formed by loss of carbon dioxide from 1-adamantyl chloroformate shows relatively little change with variation in solvent. It is, however, difficult to distinguish between ion-pair return and aromatic ring solvation effects and it has been pointed out that their operation could be linked.[20] In the following analysis what, for lack of a better term, we label as the aromatic ring parameter could well be governed to some degree by perturbations due to variations in ion-pair return.

In their consideration of aromatic ring solvation effects as a cause of dispersion in Grunwald–Winstein plots, Bentley and Mayr[13] favored the similarity model approach[19] and they tabulated, for a constant chloride ion leaving group, scales for an assortment of R groups,[11,13] including one developed by Liu[12,32] based on the specific rate of solvolysis of 2-chloro-2-(*m*-chlorophenyl)adamantane (**2**), termed the Y_{BnCl} scale. The similarity model approach can be useful but we have argued[20] that, for routine applications of the Grunwald–Winstein equation, the dispersion which is associated with the detailed structure of R is not a major problem and, if possible, a proliferation of scales, such as would be involved in the matrix of scales required for choosing *both* a similar R and a similar X, should be avoided. Such rigid restrictions would be a strong disincentive to general application of the Grunwald–Winstein equation, especially in the absence of firm guidelines as to how best to choose from among the available similarity models.

We prefer, and here develop, an alternative treatment, retaining the similarity model approach for consideration of the leaving group (selection of an appropriate Y_x scale) but incorporating a multiparameter approach (paralleling that used to treat solvent nucleophilicity) for a quantitative treatment of the dispersion caused by differential solvation and/or ion-pair return effects.

It is not obvious that such an approach will be successful but some observations in the literature are encouraging; for example, deviations are greater for benzhydryl chloride (two aromatic rings) than for α-phenylethyl chloride (one aromatic ring).[9] Generalizing, Bentley and Mayr[13] concluded that the dispersions were larger the greater the number of π electrons and they demonstrated that plots of $[\log(k/k_o)_{\text{RCl}} - \mathrm{Y}]$ against Y, in acetone–water mixtures for four substrates with π-electron-containing substituents on the α-carbon, showed

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(29) For accounts in favor of and opposed to the unifying mechanism, see (a) Sneen, R. A. *Acc. Chem. Res.* **1973**, *6*, 46 and (b) McLennan, D. J. *Acc. Chem. Res.* **1976**, *9*, 281, respectively.

(30) Richard, J. P. *J. Org. Chem.* **1992**, *57*, 625.

(31) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1969; pp 483–484.

(32) Liu, K.-T.; Sheu, H.-C.; Chen, H.-I.; Chiu, P.-F.; Hu, C.-R. *Tetrahedron Lett.* **1990**, *31*, 3611.

(33) Bunton, C. A.; Mhala, M. M.; Moffatt, J. R. *J. Org. Chem.* **1984**, *49*, 3639.

(34) Kevill, D. N.; Kyong, J. B.; Weitl, F. L. *J. Org. Chem.* **1990**, *55*, 4304.

differing extents of dispersion but otherwise very similar characteristics.

The principle of the approach is to add an hI term to eqs 1 and 2 to give eqs 5 and 6, where the symbols are as in the earlier equations, plus h represents the sensitivity of the specific rates of solvolysis to changes in the aromatic ring parameter (I). Within the actual multiple regression analyses, a constant term (c) is also included.

$$\log(k/k_o) = mY + hI \tag{5}$$

$$\log(k/k_o) = lN + mY + hI \tag{6}$$

The establishment of an I scale based on eq 5 has obvious similarities to the establishment of an N scale based on eq 2 and one can profit from previous considerations. A standard substrate of the RX^+ type is to be preferred to a neutral standard substrate.[3,4,7,8] However, even so, the situation where contributions from the lN term swamp out those from mY^+ (Y^+ being $\log(k/k_o)$ for 1-$AdSMe_2^+$ solvolysis[2]), such that $\log(k/k_o)$ for the standard substrate can be taken as the solvent nucleophilicity scale, will not be paralleled in the establishment of the I scale; the specific rates of solvolysis of **1** show variations larger than, but not enormously larger than, those for 1-$AdSMe_2^+$.

Accordingly, we express the required scale as in eq 7, where m_s represents the sensitivity of the specific rate of solvolysis of the standard substrate to changes in Y^+. In order to arrive at a value for m_s, we recall that, for a substrate RX, the initially elusive sensitivity of the specific rate of solvolysis of methyl tosylate toward changes in solvent ionizing power (eq 2) could be obtained in principle by studying the solvolyses of an RX substrate, where X was other than tosylate. One could carry out multiple regression analysis of $\log(k/k_o)_{RX}$ against N_{OTs}, as calculated for any arbitrarily chosen m_s value [which could be zero, when N_{OTs} would be $\log(k/k_o)_s$], Y_{OTs}, and Y_x.[35] Two Y scales, if both involve anionic leaving groups, will show a fairly strong correlation[15] and this approach was not pursued. In the present case, however, if we consider the combination of a neutral RX and an RX^+ standard, the scales involved will be Y_x and Y^+, which show only a very weak correlation, and this approach becomes feasible.

$$I = \log(k/k_o)_s - m_sY^+ \tag{7}$$

Since we wish to avoid any possible lN term contribution, we have chosen adamantane derivatives for the RX substrates.[15] Liu has studied,[12] in a reasonably wide selection of solvents, **2** and the corresponding unsubstituted 2-chloro-2-phenyladamantane (**3**). Combining eqs 5 and 7, the specific rates of solvolysis are analyzed using eq 8, a variant of the equation previously presented,[35] to obtain h and hm_s (and hence m_s) as the sensitivities toward variations of $\log(k/k_o)_s$ and Y^+ [$\log(k/k_o)_s$ values from Table 1 and Y_{Cl} and Y^+ values[2,15] from the literature]. For compound **2** (20 solvents), one obtains $m = 1.00 \pm 0.05$, $h = 1.76 \pm 0.27$, $hm_s = 2.30 \pm 0.87$, and $c = 0.19 \pm 0.27$ (correlation coefficient of 0.9913). For compound **3** (15 solvents), one obtains $m = 0.96 \pm 0.03$, $h = 1.67 \pm 0.12$, $hm_s = 2.19 \pm 0.42$, and $c = -0.05 \pm 0.12$ (correlation coefficient of 0.9979). The m_s values obtained are 1.31 ± 0.53 and 1.31 ± 0.27, respectively. We have taken the m_s value for insertion into eq 7 as 1.3 but the scales of I values and the correlations obtained when I is used in conjunction with the Y_x scale, or both Y_x and N_T scales, are virtually unchanged if a value of 1.2 is taken for m_s. Even with a value for m_s of 0.8, the correlations are only marginally inferior. However, the correlations become noticeably inferior if m_s is taken as zero, which corresponds to the assumption that the mY^+ term makes a negligible contribution relative to the hI term.

$$\log(k/k_o)_{RCl} = mY_{Cl} + h\log(k/k_o)_s - hm_sY^+ + c \tag{8}$$

Table 5. Correlation of the Specific Rates of Solvolysis of Benzylic Derivatives, without[a] and with[b] the Aromatic Ring Parameter

substrate (n)[c]	m[d]	h[d]	c[d]	r[e]
2 (19)	1.02 ± 0.07		0.28 ± 0.54	0.9621
	0.98 ± 0.04	1.75 ± 0.24	0.18 ± 0.27	0.9912
3 (15)	0.95 ± 0.08		0.01 ± 0.48	0.9591
	0.96 ± 0.02	1.67 ± 0.11	−0.05 ± 0.11	0.9980
4 (23)	0.98 ± 0.05		0.03 ± 0.30	0.9763
	0.96 ± 0.02	0.86 ± 0.07	0.04 ± 0.11	0.9972
5 (12)	0.79 ± 0.06		−0.05 ± 0.27	0.9688
	0.75 ± 0.05	0.89 ± 0.26	0.06 ± 0.19	0.9866
6 (28)	0.79 ± 0.03		−0.16 ± 0.28	0.9842
	0.85 ± 0.02	0.99 ± 0.18	−0.14 ± 0.19	0.9930
7 (18)	0.83 ± 0.07		−0.05 ± 0.49	0.9507
	0.87 ± 0.03	1.61 ± 0.22	−0.02 ± 0.23	0.9896

[a] $\log(k/k_o)_{RX} = mY_x + c$. [b] $\log(k/k_o)_{RX} = mY_x + hI + c$, with I values from Table 1. [c] For identity of substrate, see text; n is the number of solvents studied. [d] With associated standard error; error presented with c is the standard error of the estimate. [e] Correlation coefficient.

Values for I obtained using eq 9 are presented in Table 1, for essentially the same solvents as were previously used[2] to determine Y^+ values.

$$I = \log(k/k_o)_1 - 1.3Y^+ \tag{9}$$

Application of the I Scale to Solvolyses Displaying Dispersion in Grunwald–Winstein Plots. To illustrate the use of the I parameter we have chosen six substrates whose solvolyses have previously been found to show dispersion in Grunwald–Winstein plots and which have been studied in a reasonably wide range of solvent type. These included **2** and **3**,[12] already used in the determination of the sensitivity of the specific rates of solvolysis of **1** to changes in Y^+ value, α-(*tert*-butyl)benzyl tosylate (**4**),[36] α-(*tert*-butyl)-α-methylbenzyl chloride (**5**),[32] *p*-methoxybenzyl chloride (**6**),[11] and benzhydryl chloride (**7**).[9,33] The LFER values obtained from multiple regression analysis of the factors influencing the $\log(k/k_o)$ value for these compounds are reported for use of eq 5 in Table 5 and for use of eq 6 in Table 6. Grunwald–Winstein treatments involving eqs 1 and 2, with N_T and the appropriate Y_x scales, have previously been reported[20] for all except **4**. For compounds **2**, **3**, and **5**–**7**, the solvents are as previously used,[20] except that 40% acetone (an extrapolated value) is removed from the analyses of **2** and aqueous acetonitrile mixtures are removed from analyses of **6** and **7** plus acetic acid from analysis of **7** (no I values available). For these five substrates the statistical analyses using eq 1, reported in Table 5, are essentially the same as previously reported.[20] For compound **4**, the solvents are the first 25 listed in Table 1 of

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(35) Kevill, D. N.; Rissmann, T. J. *J. Org. Chem.* **1985**, *50*, 3062.

(36) Tsuji, Y.; Frijio, M.; Tsuno, Y. *Tetrahedron Lett.* **1992**, *33*, 349.

Table 6. Correlation of the Specific Rates of Solvolysis of Benzylic Derivatives, with Inclusion of the Solvent Nucleophilicity Parameter and without[a] and with[b] the Aromatic Ring Parameter

substrate $(n)^c$	$l^{d,e}$	m^d	h^d	c^d	r^f
2 (19)	−0.25 ± 0.16(0.14)	0.89 ± 0.11		0.15 ± 0.52	0.9672
	0.05 ± 0.10(0.61)	1.00 ± 0.06	1.83 ± 0.28	0.20 ± 0.28	0.9913
3 (15)	−0.22 ± 0.17(0.22)	0.85 ± 0.11		−0.10 ± 0.47	0.9642
	0.00 ± 0.05(0.99)	0.96 ± 0.03	1.67 ± 0.12	−0.05 ± 0.12	0.9980
4 (23)	−0.20 ± 0.06(0.00)	0.84 ± 0.05		−0.01 ± 0.23	0.9860
	0.08 ± 0.04(0.05)	1.01 ± 0.03	1.04 ± 0.11	0.06 ± 0.10	0.9977
5 (12)	−0.17 ± 0.10(0.12)	0.68 ± 0.09		−0.05 ± 0.25	0.9768
	0.00 ± 0.10(0.96)	0.75 ± 0.07	0.87 ± 0.36[g]	0.06 ± 0.20	0.9866
6 (28)	0.10 ± 0.11(0.38)	0.81 ± 0.04		−0.13 ± 0.28	0.9847
	0.30 ± 0.05(0.00)	0.93 ± 0.02	1.26 ± 0.13	−0.06 ± 0.13	0.9969
7 (18)	0.11 ± 0.17(0.53)	0.87 ± 0.07		−0.09 ± 0.53	0.9547
	0.30 ± 0.07(0.00)	0.98 ± 0.03	1.98 ± 0.17	0.10 ± 0.16	0.9959

[a] $\log(k/k_o)_{RX} = lN_T + mY_x + c$. [b] $\log(k/k_o)_{RX} = lN_T + mY_x + hI + c$, with I values from Table 1. [c] For identity of substrate, see text; n is the number of solvents studied. [d] With associated standard error; error presented with c is the standard error of the estimate. [e] Value in parentheses is the probability that the lN_T contribution is not statistically significant. [f] Correlation coefficient. [g] A 0.04 probability that the hI term is not statistically significant.

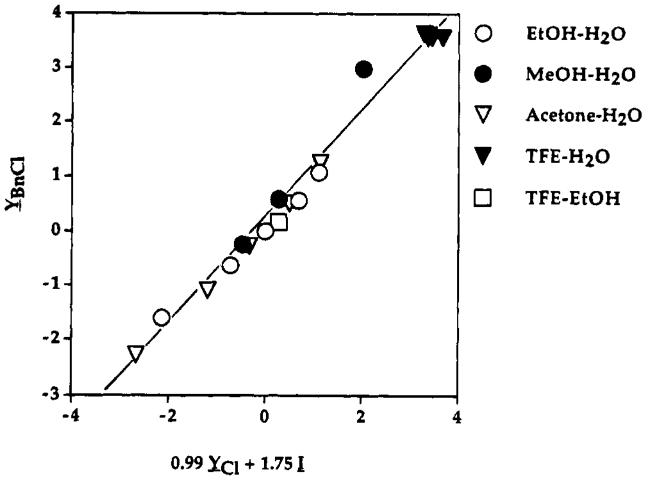

Figure 1. Plot of $\log(k/k_o)$ for **2** (corresponding to Y_{BnCl}) against ($0.99Y_{Cl} + 1.75I$).

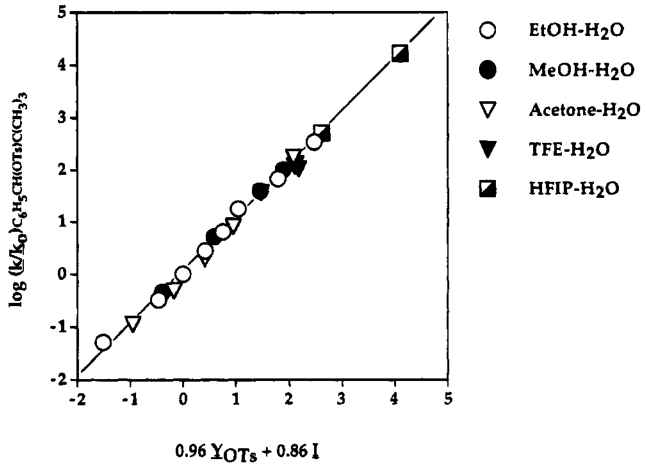

Figure 2. Plot of $\log(k/k_o)$ for **4** against ($0.96Y_{OTs} + 0.86I$).

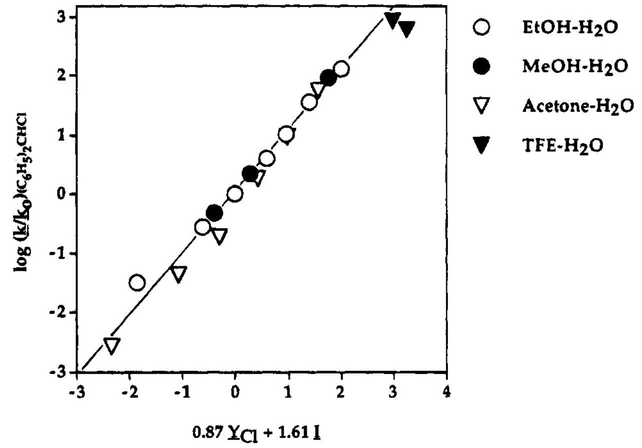

Figure 3. Plot of $\log(k/k_o)$ for **7** against ($0.87Y_{Cl} + 1.61I$).

ref 36 but with the exclusion (I values not available) of 40 and 30% TFE.

The elimination of the dispersion observed in simple Grunwald–Winstein plots by use of eq 5, eq 1 with the hI term added, can clearly be seen by comparing the two entries for each substrate in Table 5. The m and c values are little changed after removal of dispersion, but in all cases the associated standard errors are substantially reduced. Appreciable h values are obtained and, for all analyses, the probability that the hI term does not contribute significantly to the LFER is less than 0.005. The correlation coefficients of from 0.951 to 0.984 in the absence of the hI term improve to 0.987 to 0.998 in its presence. The largest increases in correlation coefficient value are shown by **3** (0.959 to 0.998) and **7** (0.951 to 0.990) and the smallest is shown by **6** (0.984 to 0.993), not surprising since this gives a fairly good correlation in the absence of the hI term.

Figures 1–3 show the LFER plots (using eq 5) for **2**, **4**, and **7**. Compounds **2** and **4** were chosen because the plots can be compared to plots in the literature[20,36] against Y_{Cl} and Y_{OTs}, respectively. The plot for **7** shows that even with two aromatic rings present, eq 5 leads to a good linear plot.

In multiple regression analysis, one always needs to consider the possibility of multicollinearity. For 31 solvents for which not only I values are available but also experimentally determined, or interpolated, Y_{Cl} and N_T values, eqs 9–11 are found to hold. Fortunately, there is essentially zero correlation between I and Y_{Cl} values,

$$I = -0.18(\pm 0.05)N_T - 0.07(\pm 0.32);\ r = 0.552 \quad (9)$$

$$I = 0.00(\pm 0.03)Y_{Cl} + 0.15(\pm 0.39);\ r = 0.004 \quad (10)$$

$$I = -0.33(\pm 0.06)N_T - 0.13(\pm 0.03)Y_{Cl} - 0.03(\pm 0.26);\ R = 0.749 \quad (11)$$

with the scatter being reflected in the large standard error associated with the constant term. A rather weak correlation is observed between I and N_T, which, surprisingly, improves considerably when correlation is against a combination of N_T and Y_{Cl} scales.

Only **4** was studied in aqueous HFIP solvents; these solvolyses tend to be very fast for those neutral S_N1-reacting substrates which solvolyze at a convenient rate in aqueous alcohols. Excluding the three aqueous HFIP solvents from the multicollinearity considerations leads to a slightly modified relationship between I and N_T (eq 12). In a recent review[20] we mentioned several examples

$$I = -0.13(\pm0.06)N_T - 0.05(\pm0.32); r = 0.394 \quad (12)$$

of modestly negative l values when benzylic derivatives were correlated against N_T and Y_x scales and four such values appear in Table 6. It can now be seen that it is the neglect of the hI term which leads to solvolyses having true l values of close to zero giving apparently negative values. For neutral substrates the hI term makes only a small contribution to the overall LFER and, therefore, the approximate nature of the equation interrelating I and N_T leads to only a fairly modest lowering of the overall correlation coefficient when a dependence on I is actually analyzed as a dependence on N_T. The h, m, c, and r values listed in Table 5 for **2** and **3** are identical to those calculated earlier, together with the desired m_s values. Accordingly, the values obtained using I and Y_x in the correlation could alternatively be obtained without the need for an I scale, by correlation (eq 8) against Y_x, $\log(k/k_o)_s$, and Y^+ values. The treatment is, however, simpler and easier to visualize with the use of the I parameter, rather than incorporation of both of the $\log(k/k_o)_s$ and Y^+ scales.

An alternative way to show that the negative l values arise from neglect of the hI term is to add the term to eq 2, so as to get eq 6. For a meaningful correlation against three variables, a large data set, including a selection of solvents with very different characteristics, is required. Even in the absence of any correlation between parameters, chance correlation becomes increasingly possible with increase in the number of variables.[37]

In Table 6, it can be seen that, for compounds **2**–**5**, the otherwise negative l values rise to essentially zero upon incorporation of the hI term and the correlations are essentially as reported in Table 5, where the lN_T term was excluded from the correlations. The l values also rise for **6** and **7** (Figure 4) but now from a value of 0.1 to a value of 0.3, comparable to that observed for solvolyses of *tert*-butyl chloride,[8,38–40] where the positive value is believed to reflect nucleophilic solvation of the developing carbocation. We are, however, somewhat apprehensive about the significance of the l value calculated for **6** and **7** because the mix of solvents is not very good with, in particular, very few fluoro alcohol-containing solvents included. However, such l values are not implausible. The solvolyses of p-methoxybenzyl halides show[41] a superimposed nucleophile-assisted component upon addition of fairly strong nucleophiles, giving indirect support to the concept of nucleophilic solvation during carbocation formation from **6**, and nucleophilic participation by the solvent toward solvolyses of **7** has been proposed based on a slower reaction in acetic acid than in the aqueous-ethanol mixture of identical Y value[9] and on differences in product formation from direct solvolysis of the p-nitrobenzoate ester and from the reaction of diphenyldiazomethane with p-nitrobenzoic acid.[29b,42]

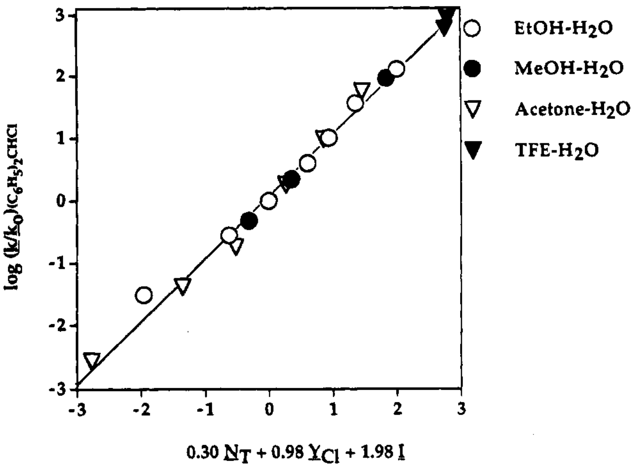

Figure 4. Plot of $\log(k/k_o)$ for **7** against $(0.30N_T + 0.98Y_{Cl} + 1.98I)$.

Table 7. Correlation of the Specific Rates of Solvolysis of Allyl and Propargyl Derivatives, without[a] and with[b] the Aromatic Ring Parameter

substrate (n)[c]	m[d]	h[d]	c[d]	r[e]
8 (17)	0.82 ± 0.01		−0.03 ± 0.09	0.9989
	0.84 ± 0.01	0.35 ± 0.10	−0.02 ± 0.07	0.9994
9 (16)	0.80 ± 0.01		0.00 ± 0.12	0.9977
	0.85 ± 0.01	0.58 ± 0.14	−0.01 ± 0.08	0.9990
6 (17)	0.79 ± 0.03		−0.12 ± 0.28	0.9886
	0.88 ± 0.02	1.50 ± 0.15	−0.07 ± 0.10	0.9985

[a–e] See footnotes to Table 5.

Bentley and Mayr[13] in their consideration of similarity models showed in a semiquantitative way that, when the number of π electrons within the α-substituent was reduced by replacing the aryl group by an acetylenic or a vinyl group, the extent of dispersion was reduced but the general pattern of the dispersion was essentially unchanged. In an attempt to quantify these observations we have analyzed, in terms of eq 5, the data reported for α,γ-dimethylallyl chloride (**8**) and 4-chloro-4-methylpent-2-yne (**9**) and have compared the results with an analysis of the corresponding solvolysis of **6** in the same limited range of solvents (Table 7).

Unfortunately, the results cannot be expected to be of high precision because the solvent types are very limited: mixtures of water with ethanol, methanol, or acetone (plus 20% dioxane). In particular, none of the important fluoro alcohol-containing solvents were included. Indeed, attempts to apply eq 6 to the data led to the computer program issuing a warning concerning multicollinearity within the data set. From the data reported within Table 7, it can be seen that the h value of 1.50 ± 0.15 for **6** is reduced to 0.58 ± 0.14 for the propargylic **9** and to 0.35 ± 0.10 for the allylic **8**, nicely consistent with the earlier[13] conclusions.

What are the Requirements for a Good Similarity Model Scale? The requirements for a good similarity model scale can be addressed in terms of eq 5 as applied

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to solvolysis of an RX substrate (eq 13). Similarly, for

$$\log(k/k_o)_{RX} = m_{RX}Y_x + h_{RX}I \qquad (13)$$

the standard substrate used to develop the similarity model scale, we can write eq 14. Substituting for Y_x from

$$Y_s = m_sY_x + h_sI \qquad (14)$$

eq 14 within eq 13 leads to eq 15. In order to be able to

$$\log(k/k_o)_{RX} = m_{RX}m_s^{-1}Y_s + m_s^{-1}(h_{RX}m_s - h_sm_{RX})I \qquad (15)$$

express this LFER as a one-term Grunwald–Winstein equation (eq 1), there is the requirement that $h_{RX}m_s = h_sm_{RX}$, or $h_s/m_s = h_{RX}/m_{RX}$, such that, ideally, the *h*/*m* ratio for the solvolyses of the chosen standard substrate should be identical to the ratio for the RX substrate under investigation.

Previously proposed standard substrates can be reevaluated in terms of their *h*/*m* ratio, and correlation features which could not be fully explained in a recent review commentary[20] can now be rationalized.

Liu has developed Y_{BnX} scales based on the solvolyses of 2-X-2-(*m*-chlorophenyl)adamantane derivatives for use in Grunwald–Winstein equation studies of benzylic derivatives.[12,32,43] These would, at first sight, appear to be excellent substrates for such an enterprise, both containing the required α-aryl group and being structurally closely related to the adamantyl derivatives used to establish Y_x scales. The derivative with X = *p*-toluenesulfonate was, however, too reactive to be used for establishing the X_{BnOTs} scale.[44] It was found[20,45,46] that, except for substrates very similar in structure to the standard, such Y_{BnX} scales usually represented only a marginal improvement over the Y_x scale.

The *h*/*m* ratios for compounds **2**–**7** (Table 5) are 1.79, 1.74, 0.90, 1.19, 1.16, and 1.85, respectively. The Y_{BnCl} scale, based on the solvolysis of **2**, shows a relatively large value for the ratio, which, is virtually the same as that for **3** (identical to **2** except for removal of the *m*-chloro substituent), and **3** does indeed show an excellent LFER (r = 0.997) against Y_{BnCl} values.[20] The *h*/*m* value is higher than for the other monoaryl derivatives and, indeed, it is comparable to that for (diaryl) benzhydryl chloride, which, accordingly, also correlates[20] considerably better with Y_{BnCl} values (r = 0.986 with Y_{BnCl} and 0.954 with Y_{Cl}). Compounds **4**–**6** correlate about equally well with either Y_{Cl} or Y_{BnCl} because their *h*/*m* values of around unity are only a little closer to the value of 1.75 for the Y_{BnCl} scale than to the value of zero for the Y_{Cl} scale.

To summarize this aspect of the study, the Y_{BnCl} scale tends to overcompensate for aromatic ring effects when used as a similarity model scale for monoaryl benzylic chlorides and, indeed, it constitutes a good model for solvolyses of benzhydryl chloride. The observation[20] that the scale proposed by Bentley,[11,13] based on solvolyses of **5** frequently gave better correlations than Y_{BnCl} can now be seen to be a consequence of it having a more typical *h*/*m* value.

To simplify the above discussion, the possibility of an lN_T term being required was ignored. If needed, it would be added to eq 13 and it would carry over to eq 15. The argument would then relate to this equation simplifying to eq 2, and the requirements would be identical to those presented and discussed above.

Aromatic Ring Effects Disguised as Solvent Nucleophilicity Effects. For a solvolysis reaction believed to have a true *l* value of close to zero, it has already been mentioned that the negative *l* values frequently observed when the N_T scale[20,45,46] (or N_{OTs} scale[44]) is used in the LFER, in conjunction with Y_x values, can be a consequence of the neglect of the *hI* term coupled with an approximately linear relationship between the *I* and N_T scales (eq 12). The observed negative *l* values disappear when the *hI* term is added to the LFER (eq 6 and entries for **2**–**5** in Table 6).

Alternatively, the similarity model approach can be applied, with the Y_x scale replace by a Y_{sim} scale. As, with change of standard substrate, the associated h_s/m_s value rises from the value of zero for the Y_x scale toward the h_{RX}/m_{RX} value, the apparent *l* value will also rise, reaching zero when the ratios are equal. However, if one overcompensates, such as by using the Y_{BnCl} scale for solvolyses of most other monoaryl benzylic chlorides, then the apparent *l* value will continue to rise and positive values will result. Several claims made for a weak nucleophilic assistance based on fairly small positive *l* values, resulting from the use of a solvent nucleophilicity scale in conjunction with Y_{BnX} values, are reassessed below.

The increases in the observed *l* values for the solvolyses of a series of ring-substituted cumyl derivatives, as the substituent became more electron-withdrawing,[47,48] have been accepted previously[45,46] as evidence for a weak nucleophilic solvation. Recently, it has been found[49] that the h_{RX}/m_{RX} value falls as the substituent becomes more electron-withdrawing (consistent with the observation[13] that the dispersion decreases as the number of π elections adjacent to the site of reaction is reduced). Accordingly, the already overcompensating Y_{BnCl} scale becomes increasingly less appropriate for use as the similarity model scale and the ($h_s/m_s - h_{RX}/m_{RX}$) gap increases, resulting in an increase in the apparent *l* value calculated using eq 2.

Conclusions

A comparison of the specific rates of solvolysis of the (*p*-methoxybenzyl)dimethylsulfonium ion and the 1-adamantyldimethylsulfonium ion has been used to develop a scale of aromatic ring effects (*I*) for a wide variety of solvents. This scale can be used in conjunction with Y_x values (based on specific rates of solvolyses of adamantyl derivatives with the appropriate leaving group) as an alternative to developing a matrix of similarity model *Y* scales for an RX substrate, involving consideration of suitable models for both R and X.

For a unimolecular solvolysis, the linear free energy relationship will be as in eq 5, where *m* and *h* are sensitivities of the solvolysis to changes in solvent ionizing power (Y_x) and aromatic ring parameter (*I*). It is demonstrated that the magnitude of the *h* value is a

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function of the π electron density adjacent to the reaction site. For reactions believed to also involve nucleophilic assistance from the solvent, an lN_T term can be added to eq 5, where l is the sensitivity of the solvolysis to changes in solvent nucleophilicity (N_T).

A good similarity model for use as the Y scale in Grunwald–Winstein correlations (hI term excluded) has the requirement that the h/m ratio for solvolyses of the standard be close (ideally, identical) to that for solvolyses of the substrate under investigation. Choice of a standard substrate that overcompensates in terms of the h/m ratio can lead for S_N1 reactions ($l = 0$) to an apparent sensitivity toward solvent nucleophilicity changes, when analyses are in terms of the extended Grunwald–Winstein equation (eq 2).

Claims that the hydrolysis of the (*p*-methoxybenzyl)dimethylsulfonium ion proceeds with appreciable nucleophilic assistance from the solvent are shown to be based on questionable theoretical interpretation or experimental procedure.

Experimental Section

Materials. The purification of acetone, dioxane, ethanol, and methanol were as described previously.[50] The purifications of 1,1,1,3,3,3-hexafluoro-2-propanol[51] and 2,2,2-trifluoroethanol[52] were also using previously reported procedures. Dimethyl sulfide, *p*-methoxybenzyl chloride, pyridine, and silver trifluoromethanesulfonate (Aldrich) were used without further purification.

(*p*-Methoxybenzyl)dimethylsulfonium Triflate. Dimethyl sulfide (1.06 mL) and *p*-methoxybenzyl chloride (2.14 g) were added to 2 mL of nitromethane and stirred for 30 min at ice bath temperature. A solution of silver triflate (3.52 g) in 20 mL of nitromethane was then added dropwise over a 10 min period. Acetonitrile (20 mL) was added and the stirring continued for 30 min. Filtration through Celite (Johns-Manville) and removal of solvent (rotary evaporator) gave a viscous brown liquid, which crystallized at ice bath temperature. Filtration and washing with small portions of pentane and ether led to 1.5 g (33%) of white crystals: mp 77–79 °C; IR (KBr disc) 3020, 2920, 1610, 1440, 1250, 1160, 1030, 840 cm^{-1}; PMR (CD_3CN) δ 2.70 (s, 6H), 3.82 (s, 3H), 4.48 (s, 2H), 7.02 (d, 2H, $J = 8.6$ Hz), 7.37 (d, 2H, $J = 8.6$ Hz). Anal. Calcd for $C_{11}H_{15}F_3O_4S_2$: C, 39.75; H, 4.55; S, 19.29. Found: C, 39.65; H, 4.53; S, 19.26.

Kinetic Procedures. All runs were performed at least in duplicate. The usual procedure involved withdrawal of 5 mL aliquots from 50 mL of bulk solution maintained at the desired temperature and, after quenching by addition to 15 mL of acetone at solid-CO_2 temperature, titration against a standardized solution of sodium methoxide in methanol (ca. 3.9×10^{-3} M) to a resorcinol blue (Lacmoid) endpoint. Runs in HFIP-containing solvents were carried out by pipetting 1 mL aliquots from 10 mL of solution, of somewhat increased concentration, into 10 mL of cooled acetone and titrating against a 0.90×10^{-3} M solution of sodium methoxide in methanol.

All of the integrated first-order rate coefficients from duplicate runs were averaged (except for a few runs with fall off in values, where the averaging was restricted to initial stages). For some of the runs in solvents rich in 2,2,2-trifluoroethanol, infinity titers were obtained after addition to an equal volume of methanol.

Multiple regression analyses were performed using the ABSTAT statistical program (Anderson-Bell, Arvada, CO).

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