

Correlation of the Rates of Solvolysis of Allyl and Benzyl Arenesulphonates

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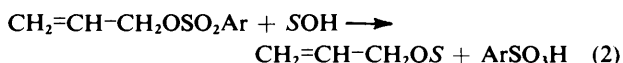
Analysis of the specific rates of solvolysis of allyl arenesulphonates in terms of the extended Grunwald–Winstein equation indicates a marked dependence on both the solvent nucleophilicity (high l value) and the solvent ionizing power (high m value). As the charge delocalization in the leaving group increases, both l and m values fall. For allyl toluene-*p*-sulphonate solvolysis in 28 solvents at 50.0 °C, values for l (0.83) and for m (0.63), based on the use of N_{KL} and Y values, are very similar to the equivalent values of 0.90 and 0.67 previously reported for benzyl toluene-*p*-sulphonate solvolysis. Related extended Grunwald–Winstein analyses are considered and the need for variety in the choice of solvents is emphasized.

Studies of the solvolyses of benzyl systems in terms of the extended Grunwald–Winstein equation (1) have indicated rather large values for both the sensitivity (l) to solvent

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

nucleophilicity (N) values and the sensitivity (m) to solvent ionizing power (Y) values; l and k_0 represent the specific rates of solvolysis in the solvent under consideration and in the standard (80% ethanol) solvent, respectively. For unsubstituted alkyl and cycloalkyl derivatives, there is a trend of decreasing l values as m values increase, and indeed a Q parameter scale^{1,3,4} has been devised for situating the solvolysis of a substrate intermediate between methyl and 2-adamantyl derivative solvolyses. For such a scale (with one parameter less than the extended Grunwald–Winstein equation) to operate, it is required that $m + 0.7l = 1$, where the N and Y values of equation (1) are based on studies of methyl and 2-adamantyl toluene-*p*-sulphonate (tosylate) solvolyses; for benzyl tosylate¹, $l = 0.75$ and $m = 0.64$, and the $(m + 0.7l)$ value of 1.17 is anomalously high.

In the present study, we apply equation (1) to the solvolyses of allyl arenesulphonates [equation (2)]. Allyl systems have been found to be similar to the corresponding benzyl systems



in their solvolytic behaviour. Insofar as differences do occur, allyl systems are usually considered to be somewhat less reactive and somewhat more dependent on solvent nucleophilicity.⁵

The specific rates of solvolysis of the unsubstituted allyl benzenesulphonate and several ring-substituted derivatives have been studied by Sendega and his co-workers in pure alcohols,⁶ aqueous dioxane,⁷ aqueous acetone,⁸ and aqueous methanol.⁹ As would one expect, detailed product studies^{10,11} in aqueous methanol showed that ether formation from reaction with the more nucleophilic methanol component is favoured over alcohol formation from reaction with the water component. The kinetic studies include measurements in pure water, and they are of special interest since very few studies of sulphonate ester solvolyses in aqueous–organic binary mixtures have been extended to the region of water-rich compositions.¹² It was found^{7–9} that, as the leaving group ability (Hammett σ value of substituent) increased, the m value of the simple Grunwald–Winstein equation [equation (1) without the lN term] tended to decrease, and one aim of the present investigation was to see how this decrease relates to

Table 1. Grunwald–Winstein parameters l and m for the solvolyses of allyl arenesulphonates^a

Substituent	30 °C			40 °C		
	l^b	m^c	r^d	l^b	m^c	r^d
<i>p</i> -CH ₃	1.07	0.70	0.989	1.10	0.70	0.987
None	1.07	0.68	0.989	1.08	0.68	0.989
<i>p</i> -Cl	0.97	0.63	0.992	0.98	0.63	0.992
<i>m</i> -NO ₂	0.86	0.55	0.994	0.88	0.54	0.993

^a Using the first seventeen solvents listed in Table 2. ^b The standard deviation for l values ranged from 10 to 15% of the value. ^c The standard deviation for m values ranged from 4 to 6% of the value. ^d Correlation coefficient.

corresponding changes in the l and the m values of the four-parameter equation (1). For most mixed solvent systems, either a decrease in the m value or an increase in the l value of the four-parameter equation would lead to a fall in the experimental m value of the two-parameter equation.² For 17 solvents for which both N_{KL} values² and Y values¹³ are available, these kinetic studies covered a range of Y values of 5.5 but a range of N_{KL} values of only 1.5. For allyl tosylate at 50 °C, we have determined specific solvolysis rates in 11 additional solvents and the extended data set covers a range of N_{KL} values of 2.8.

We wish to emphasize that it will frequently be necessary to extend the range of solvent nucleophilicity for which kinetic measurements are available if one wishes to get reasonably accurate l values for systems previously studied only in terms of the simple (two-parameter) Grunwald–Winstein equation.

Results

By using reported values of the first-order solvolytic rate coefficients^{6–9} for allyl benzenesulphonate and its *p*-CH₃, *p*-Cl, and *m*-NO₂ derivatives, the values for l and m [equation (1)] were calculated (Table 1). The N values used were based on triethyloxonium ion solvolysis² and the Y values on *t*-butyl chloride solvolysis.¹³ The data entered into equation (1) are summarized in the first seventeen entries of Table 2. For the unsubstituted and the *p*-methyl-substituted esters, the reported specific rates of solvolysis in pure water differed by up to 30% between the dioxane–water⁷ and the methanol–water⁹ studies; the more recent values⁹ were assumed to be the more accurate. For the solvolyses of allyl tosylate at 50 °C, specific solvolysis rates for the same seventeen solvents were either available^{6,7} or calculated using the reported Arrhenius parameters, obtained from a study at lower temperatures.^{8,9}

Table 2. Specific rates of solvolysis of allyl toluene-*p*-sulphonate, at 50.0 °C, in a variety of pure and mixed aqueous-organic solvents, and appropriate N_{KL} and Y values

Solvent ^a	$10^5 k_1/s^{-1}$	$[N_{KL}]^b$	Y^c
MeOH	16.06	+0.58	-1.09
EtOH	6.50	+0.46	-2.03
H ₂ O	977. ^d	-0.87	+3.49
90% Dioxane	0.457	-0.03 ^e	-2.03
70% Dioxane	9.40	-0.22	+0.01
40% Dioxane	143.9	-0.54	+1.95
20% Dioxane	589.	-0.71	+2.88
80% MeOH	50.1 ^d	+0.21	+0.38
60% MeOH	117. ^d	-0.18	+1.49
40% MeOH	249. ^d	-0.39	+2.39
20% MeOH	399. ^d	-0.75	+3.03
90% Acetone	0.836 ^d	-0.26	-1.86
80% Acetone	3.15 ^d	-0.29	-0.67
70% Acetone	7.36 ^d	-0.38	+0.13
60% Acetone	20.2 ^d	-0.44	+0.80
40% Acetone	65.0 ^d	-0.64	+1.98
20% Acetone	299. ^d	-0.76	+2.91
80% EtOH	30.3	0.00	0.00
60% EtOH	74.5	-0.29	+1.12
40% EtOH	169.	-0.52	+2.20
20% EtOH	521	-0.82	+3.05
97% TFE ^f	1.95	-2.22	+1.15
90% TFE	4.43	-1.67	+1.25
80% TFE	11.10	-1.40 ^e	+1.46
60% TFE	23.5	-1.05 ^e	+1.89
40% TFE	57.5	-0.88 ^e	+2.60
CH ₃ CO ₂ H	0.167	-1.34	-1.64
HCO ₂ H	34.2	-1.61	+2.05

^a Except where otherwise stated, mixed solvents were prepared on a volume to volume basis at 25 °C. ^b From ref. 2. ^c From ref. 13 or (for H₂O-TFE mixtures) ref. 14. ^d Obtained by extrapolation of values at 20, 30, and 40 °C. ^e Obtained by extrapolation or interpolation of values for other compositions. ^f TFE represents 2,2,2-trifluoroethanol and all H₂O-TFE mixtures were prepared on a weight to weight basis (see ref. 14).

A parallel analysis to that of Table 1 leads to values for l of 1.11 ± 0.17 and for m of 0.70 ± 0.04 ($r = 0.987$).

Allyl tosylate was prepared by the heterogeneous reaction for 2 days of a *ca.* 0.4M-solution of allyl bromide in pentane with an excess of silver tosylate. Reactant solutions in ethanol, 80% ethanol, and 60% ethanol were prepared by addition of 1.00 ml of this solution to 50.0 ml of the appropriate solvent. For other solvent systems, the solution in pentane was first converted into an equivalent solution in dioxane. The specific rates of solvolysis were then determined by removal of portions at suitable time intervals and titration of the acid developed; infinity titres were obtained after at least ten half-lives. The values obtained in aqueous ethanol, in aqueous 2,2,2-trifluoroethanol (TFE), in acetic acid, and in formic acid (always the average of at least two determinations) are reported in Table 2. For 60% ethanol, the specific rate measured after addition of 1.00 ml of a dioxane stock solution ($71.0 \times 10^{-5} s^{-1}$) was essentially identical with that obtained (Table 2) using a pentane stock solution and, for 40% ethanol, the specific rate using 1.00 ml of a pentane stock solution ($167 \times 10^{-5} s^{-1}$) was essentially identical with that obtained (Table 2) using a dioxane stock solution. For solvolysis in 100% ethanol (containing 1.96% added pentane), the specific solvolysis rate of $6.73 (\pm 0.14) \times 10^{-5} s^{-1}$ was in good agreement with the previously reported ⁶ value of $6.50 \times 10^{-5} s^{-1}$, indicating that no serious perturbation resulted from the presence of a small amount of co-solvent.

An extended Grunwald-Winstein equation treatment of the

complete 28 entries of Table 2, using N_{KL} and Y values, leads to a value for l of 0.833 ± 0.067 and a value for m of 0.632 ± 0.026 ($r = 0.980$).

Discussion

Table 1 shows that substitution within the leaving group leads to a fall in the values of both l and m as the nucleofugality of the leaving group is increased. The increased leaving group ability can be considered to arise from improved charge dispersal within the incipient anion, which in turn reduces the need for stabilization by solvation and, therefore, lowers the m value.¹⁵ A further influence of a better leaving group can be to reduce the need for nucleophilic assistance by the solvent, resulting in a lower value for l ; such a loosening of the transition state would in itself tend to increase the m value but this effect is apparently outweighed by the influences of the structural changes within the nucleofuge upon the m value.

In a study of benzyl systems, Young and Jencks¹⁶ have used data from the literature to calculate very approximate values of l and m for a series of *para*- and *meta*-substituted benzyl derivatives. Employing the Kaspi and Rappoport¹⁷ approach, they used the two experimental values for m (m^{exp}) obtained from simple Grunwald-Winstein equation treatments of solvolyses in water-ethanol and TFE-ethanol mixtures. The l values obtained increased from 0 for the *p*-methyl derivative to 1.5 for the *p*-nitro derivative. This was accompanied by a trend of decreasing m values (0.47 to 0.37). These observations appear to support the concept of variable transition state structure; however, in addition to the approximations inherent in the Kaspi and Rappoport approach, several m^{exp} values were estimated and, in particular, the nucleofuge was varied from *p*-bromobenzenesulphonate in the aqueous ethanol study to chloride in the TFE-EtOH system. In one instance, incorporating data of Harris, Shafer, Moffatt, and Becker,¹⁸ a calculation can be made restricted to only the assumptions inherent in this type of analysis, the principal assumption being that approximately linear relationships exist between solvent nucleophilicity and solvent ionizing power for both of these mixed solvent systems. For *p*-methylbenzyl chloride at 25 °C, an m^{exp} value of 0.63 for aqueous ethanol¹⁸ can be combined with the value of 0.47 for TFE-ethanol mixtures.¹⁶ The l and m values of 0.21 and 0.64 so obtained¹⁷ are quite different from the values of 0 and 0.47 calculated by Young and Jencks.¹⁶ While the actual values are obviously in some doubt, it appears that the very large differences in l values obtained by Young and Jencks must be meaningful, but it would be dangerous to place confidence in the much smaller variations within the m values.

The l and m values of 0.83 and 0.63, respectively, for allyl tosylate solvolysis are very similar to the values of 0.90 and 0.67 obtained,² using the same N and Y scales, for benzyl tosylate solvolysis at 25 °C, consistent with the generally held belief that allyl and benzyl derivatives exhibit similar solvolysis characteristics.⁵ The high value for l is not consistent with the conclusions reached by Sendega, Vizgert, and Mikhalevich⁶ that the solvolyses of allyl arenesulphonates are towards the S_N1 side of the S_N2 - S_N1 spectrum and the reactivity is 'determined mainly by the polarity of the C-O bond and to a smaller degree should depend on the nucleophilicity of the reagents.'

The restricted range of N values available from the measurements of Sendega and his co-workers⁶⁻⁹ was reflected in the standard deviation for l of 16% of its value. This was reduced to 8% when the data base (and range of N values) was enlarged by eleven additional solvents. The accompanying decrease in the standard deviation for the m value was from 5 to 4%. These changes were, however, accompanied by a slight decrease in

the correlation coefficient from 0.987 to 0.980. In contrast, and illustrating the need to consider solvent nucleophilicity, the m^{exp} values are, in the initial 17 solvents, 0.505 ± 0.045 ($r = 0.946$) and, in the expanded series of 28 solvents, 0.492 ± 0.060 ($r = 0.847$). Good correlations can be obtained with a much smaller data base provided the solvents are carefully selected to show a wide range of Y and N values. For example, in eight solvents (MeOH, EtOH, 80% EtOH, 60% EtOH, 97% TFE, 80% TFE, $\text{CH}_3\text{CO}_2\text{H}$, and HCO_2H) similar to the 'standard' solvents used in other studies,^{1,2,19} values are obtained of 0.871 ± 0.068 for l and of 0.620 ± 0.046 for m ($r = 0.989$).

The need for variety in the selection of solvents is illustrated by a reconsideration of an analysis by Nair and Nair,²⁰ using the N scale based on methyl tosylate solvolysis¹ and the Y scale based on *t*-butyl chloride solvolysis,¹³ of the specific rates of solvolysis of 2,2-dimethyl-1-phenylpropyl methanesulphonate, a compound with both a tertiary alkyl group and a phenyl group on the α -carbon atom. Such a compound would be expected to favour an ionization mechanism and, indeed, the solvolyses of 2-(1-adamantyl)ethyl tosylate, with a tertiary alkyl and a methyl group on the α -carbon atom, correlate very well⁴ with Y values based on 2-adamantyl tosylate solvolysis¹ (slope of 1.05 ± 0.04 and correlation coefficient of 0.998); using N values based on methyl tosylate solvolysis, a treatment in terms of the extended (four-parameter) Grunwald-Winstein equation leads to a value for l of 0.00 ± 0.04 and for m of 1.04 ± 0.05 ($r = 0.996$). Accordingly, it is, at first sight, surprising to see that Nair and Nair obtain values for the solvolysis of 2,2-dimethyl-1-phenylpropyl methanesulphonate of 1.55 for l and 0.76 for m ($r = 0.999$). The l value suggests an even greater dependence on solvent nucleophilicity than for the solvolysis of a methyl derivative. Linear free energy plots of their data against Y values for aqueous ethanol, aqueous methanol, aqueous acetone, and aqueous dioxane mixtures give plots very similar in character to those previously reported for diphenylmethyl chloride solvolysis.* The aqueous alcohols give a linear plot of slope (m^{exp}) 0.61 ± 0.03 ($r = 0.996$) and the other two mixed systems give a lower lying linear plot of slope 0.75 ± 0.03 ($r = 0.997$). The two specific rates measured in aqueous acetonitrile give points lying intermediate between these two lines. The excellent correlation of all the data using the extended Grunwald-Winstein equation follows from an artefact: all the aqueous methanol and aqueous ethanol mixtures have N values of -0.01 ± 0.06 , all the aqueous dioxane and aqueous acetone mixtures have N values of -0.45 ± 0.06 , and the two (intermediate lying) aqueous acetonitrile mixtures have N values of -0.24 ± 0.06 . For example, the average separation ($\Delta \log k/k_0$) between the two major plots is 0.65 and the N values differ (ΔN) by a constant 0.44 and, therefore, (in a strictly formal sense) $0.65 = 0.44 l$, and a value for l of 1.48 (value of 1.55 is reported²⁰) will compensate for the dispersion between the two (constant N value) branches of the simple Grunwald-Winstein plot.

The detailed shapes of the Grunwald-Winstein plots of the allyl arenesulphonate specific solvolysis rates against Y values are of interest in connection with the observation¹² that secondary alkyl tosylates, and to a lesser extent secondary alkyl methanesulphonates (mesylates), give plots which curve upwards in the high water content region, appreciably for aqueous ethanol and somewhat less markedly for aqueous acetone. This curvature was ascribed to differences in initial state solvation, including solvent sorting. For example, for tosylates in aqueous ethanol, the dominant feature causing curvature was believed to be that, relative to the chloride of

the *t*-butyl chloride standard, the tosylate group was more enriched by ethanol molecules than by water molecules. In the present study of allyl tosylate, similar behaviour is found and a linear region of from 100 to 40% ethanol is followed by an upward curvature (100–40% ethanol $m^{\text{exp}} = 0.33$; 40–0% ethanol $m^{\text{exp}} = 0.59$). The m^{exp} value can be estimated, in the manner previously discussed,² from the l and m values and the constant inter-relating the N_{KL} and Y scales for aqueous ethanol mixtures. The value of 0.43 so obtained is intermediate between the values obtained for the two ranges of solvent composition, confirming that for aqueous ethanol the m^{exp} values can be reasonably accurately estimated from the l and m values of the four-parameter equation.²

Sendega and Gorbatenko have observed similar behaviour for the solvolyses of several allyl arenesulphonates in aqueous acetone⁸ (allyl tosylate at 30 °C, 90–40% acetone $m^{\text{exp}} = 0.52$; 40–0% acetone $m^{\text{exp}} = 0.69$). Interestingly, however, plots for the same allyl arenesulphonates in aqueous methanol⁹ all curve downwards with the closest approach to linearity lying in the high water content region (allyl tosylate at 30 °C, 100–40% methanol $m^{\text{exp}} = 0.39$; 40–10% methanol $m^{\text{exp}} = 0.36$). If one accepts the argument based on preferential solvation previously put forward,¹² then an inverse behaviour requires the arenesulphonate group to be, relative to the chloride of *t*-butyl chloride, preferentially enriched by water molecules rather than by methanol molecules.

Previously observed reversals^{21,22} of the relative reactivities of *p*-NO₂ and *m*-NO₂ derivatives in the solvolyses of arenesulphonate esters, such that the *m*-NO₂ derivative with the lower Hammett σ value reacts the faster, have been explained²² in terms of solvent effects upon the substituent constants.²³ Sendega, Vizgert, and Mikhalevich⁶ have found identical behaviour for the solvolyses of *n*-propyl esters in six pure alcohols, including the previously discussed ethanol.²² However, for exactly parallel studies with allyl esters, they found for each solvent the behaviour one would expect based on Hammett σ values, with the *p*-NO₂ derivative reacting faster than the *m*-NO₂ derivative. Since the reversal had previously been observed in the ethanolyse of substrates ranging from model $S_{\text{N}}2$ (methyl esters)²¹ to model $S_{\text{N}}1$ (adamantyl esters),²² we cannot at present offer any convincing explanation for the absence of reversal in the ethanolyse of allyl esters.

Experimental

Materials.—The commercially available solvents were purified using previously outlined^{2,24} procedures. Pentane and allyl bromide were purified by distillation, and silver toluene-*p*-sulphonate (tosylate) was dried overnight at 120 °C and allowed to cool in a desiccator.

In a typical preparation of a stock solution of allyl tosylate, allyl bromide (0.884 g) was dissolved in pentane (20 ml) and kept for 2 days at room temperature in contact with a heterogeneous phase of silver tosylate (4.640 g). The excess of silver tosylate and the precipitated silver bromide were then removed by filtration. For conversion into an equivalent solution in dioxane, an excess of dioxane was added and the solution was allowed to evaporate, in the absence of water vapour, until the original volume was present.

Kinetic Procedures.—To the solvent under investigation (50.0 ml), maintained at 50.0 °C, was added a stock solution (1.00 ml) of allyl tosylate in pentane or dioxane. After shaking and a brief period for temperature equilibration, portions (5.00 ml) were removed at suitable time intervals. For runs in the aqueous-organic solvents, the portions were quenched by pipetting into acetone (20 ml) at -78 °C; otherwise the sampling, titration procedures, and calculation of first-order

* See, for example, Figure 13 of ref. 5.

solvolysis rate coefficients were as previously described.² All runs were performed, at least, in duplicate.

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