

Classical Carbonium Ions. Part 11.¹ Solvent Effects on Solvolysis Rates: the Grunwald–Winstein Equation

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Although originally proposed for 'limiting' solvolyses in any solvent, the Grunwald–Winstein equation accurately fits the reactions of 1-methylethyl toluene-*p*-sulphonate in water–ethanol mixtures, which are known to be non-limiting. Solvolyses of 1-adamantyl derivatives (picrate and toluene-*p*-sulphonate) cannot involve nucleophilic assistance, yet in solvent systems like methanol–tetramethylene sulphone or ethanol–chloroform, seriously non-linear Grunwald–Winstein plots are observed. In an alternative treatment of the data, the solvolysis of 1-adamantyl picrate in methanol–tetramethylene sulphone is shown, by the remarkable insensitivity to solvent composition of its rate and its entropy of activation, to be a particularly simple process mechanistically. The relationship between the activity of the alcohol component and the solvolysis rate indicates that in the other three systems studied, the alcohol molecules participate stoichiometrically in hydrogen bonding to the incipient anion. Criteria for linear Grunwald–Winstein plots can therefore be suggested.

THE Grunwald–Winstein equation (1),² where k and k_0 are rates of solvolysis of a substrate in a given solvent

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

and in 80% ethanol, respectively, m is a constant characteristic of the substrate, and Y is $\log k/k_0$ for *t*-butyl chloride at 25 °C, is one of the most widely used extrathermodynamic relationships in organic chemistry. Its original derivation assumed that the solvolysis of the substrate was 'limiting', that is, that a small change in the solvent would affect the rate only by varying the tendency of the substrate to ionise. Nevertheless, solvolysis of 2-bromopropane and the corresponding *p*-bromobenzenesulphonate in water–alcohol mixtures of varying composition, although regarded as non-limiting, in fact fitted the generalisation quite well.^{2,3a} Although at first it was hoped that m would be independent of the solvent, later work^{3b} showed that each binary solvent system gave, for a given substrate, its own m value; this is called 'dispersion'. Most tests of linearity, within any one binary system, have been undemanding, in that few solvent mixtures, covering only a limited range of rates, have been used. We have therefore measured rates of solvolysis for the solvent system originally preferred, water–ethanol, over a wide composition range but with a substrate, 1-methylethyl toluene-*p*-sulphonate, which was always believed not to be limiting and is now known to undergo solvolysis with substantial and measurable (21 ± 4 kJ mol⁻¹)⁴ nucleophilic assistance. We followed the reaction spectrophotometrically at 74 °C, using 0.005M-substrate and 0.01M-sodium acetate (Table 1); Robertson's⁵ titrimetric results (0.015M-

substrate, no buffer salt; extrapolated from 25 and 50 °C) are added. The spectrophotometric results define an almost perfect straight line when plotted against Y ($\rho = 0.99987$; standard deviation of $\log k = 0.0111$, assuming completely accurate data for *t*-butyl chloride, with $m = 0.433$, cf. 0.408 for the *p*-bromobenzenesulphonate at 70 °C^{3a}). Incorporation of the titrimetric data changes these figures only to $\rho = 0.99986$, standard deviation of $\log k = 0.0126$, and $m = 0.429$. Trivially, agreement between the two methods increases confidence in our spectrophotometric technique; more significantly, the exact agreement with the linearity predicted by the Grunwald–Winstein equation over rate ranges of 10² and 10^{4.6} for the two reactions compared reinforces the view that in aqueous ethanol nucleophilic assistance varies linearly with ionising power.²

The original use of *t*-butyl chloride as reference substrate² was a matter of convenience; 1-adamantyl derivatives, or similar bridgehead compounds in which the absence of nucleophilic assistance is assured, would surely have been employed if then available.⁶ In aqueous dimethyl sulphoxide^{7a} and aqueous ethanol^{7b} at 50 °C solvolysis rates of 1-bromoadamantane were studied, the latter giving a good linear plot against Y with $m = 1.16$. In a wide range of solvent systems rates for this substrate were well correlated with Y , giving $m \approx 1.2$ (although in aqueous trifluoroethanol the plot was a straight line of much lower slope).⁶ Similarly, solvolysis of 1-adamantyl toluene-*p*-sulphonate in a variety of solvents gives a series of straight lines for binary mixtures, showing some dispersion but with an overall slope near to 1.⁸ We have reported good proportionality to Y for rates in water–ethanol mixtures for 1-adamantyl picrate at 74 °C and for the 2,4-dinitrophenolate at 119.6 °C.⁹ It follows that if any one of these 1-adamantyl derivatives were used to replace *t*-butyl chloride in defining a solvent parameter similar to Y , as has been suggested,^{6,8} the other three would undergo solvolysis at rates well correlated by the Grunwald–Winstein relationship in aqueous ethanol, and in some similar systems. The observed m values, however, vary widely; for the toluene-*p*-sulphonate, picrate, bromide, and 2,4-dinitrophenolate in water–ethanol they

TABLE 1

Solvolysis of 1-methylethyl toluene-*p*-sulphonate at 74 °C in aqueous ethanol

mol % H ₂ O	Y	10 ⁶ k/s^{-1}
86.9	2.59	939 ± 14 ^a
68.4	1.12	207 ± 3 ^a
54.4	0.35	98.2 ^a
39.1	-0.23	54.7 ^a
17.9	-1.12	23.4 ^a
'50% EtOH'	1.65	342 ^b
0.0	-2.03	9.46 ^b

^a This work. ^b Ref. 5, extrapolated from 25 and 50 °C.

are 0.965, 0.564, 1.16, and 0.602, in order of diminishing rate over most of the solvent range. One must explain these by assuming solvation of the incipient anion which, for any one anion, varies in energy in proportion to the solvent ionising power.

The advantages *a priori* of 1-adamantyl derivatives prompted an investigation of a relationship of Grunwald-Winstein type in solvent systems unlike those for which it was developed; these are overwhelmingly mixtures of water with various organic solvents, but also include the formic-acetic acid system. We chose pairs consisting of an alcohol and a dipolar inert component: methanol-tetramethylene sulphone (tetrahydrothiophen 1,1-dioxide), and ethanol-chloroform. In the former pair dielectric constants are similar (32.6 and 44) and the non-volatility of the sulphone renders activity coefficients easy to determine; in the latter there is a significant difference in dielectric constant (24.3 and 4.6,

TABLE 2

Rates of solvolysis at 55 °C in methanol-tetramethylene sulphone

mol % MeOH	a_{MeOH}	a_s	$10^4 k$ (Tos)/s ⁻¹	$10^4 k$ (Pic)/s ⁻¹
100	1.000	0.000	143	12.3
94.2	0.958	0.202	167	12.8
93.4	0.952	0.220	187	18.4
88.0	0.925	0.282	180	21.0
80.5	0.884	0.360	158	22.6
69.5	0.835	0.426	89.9	24.5
56.8	0.750	0.515	53.0	26.0
33.9	0.513	0.692	20.4	21.9
18.1	0.310	0.825	7.50	18.5
11.3	0.202	0.889	3.15	15.4
7.8	0.145	0.926	1.53	15.0
0.0*	0.000	1.000	<0.5	13.2

* *ca.* 0.1 mol % of water present.

TABLE 3

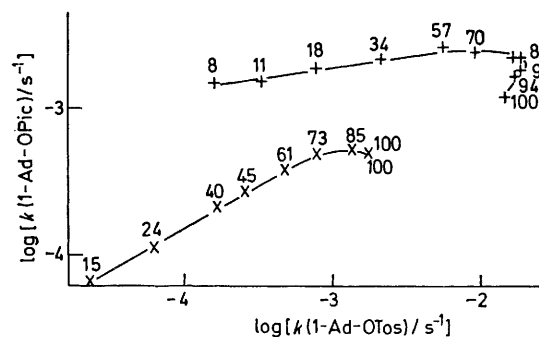
Rates of solvolysis at 55 °C in ethanol-chloroform

mol % EtOH	a_{EtOH}	a_{CHCl_3}	$10^5 k$ (Tos)/s ⁻¹	$10^5 k$ (Pic)/s ⁻¹
100	1.000	0.000	170	49.2
			±2	±0.6
91.9	0.919	0.143		55.7
88.0	0.880	0.215		49.9
				±1.6
85.7	0.857	0.257		51.5
84.7	0.847	0.277	133	52.8
79.5	0.797	0.375		55.5
72.7	0.733	0.490	75.9	(49.0)
			±1.6	
69.5	0.711	0.533		47.3
61.4	0.657	0.617	46.8	38.3
51.6	0.601	0.698		31.4
				±0.3
49.0	0.588	0.717	25.4	(27.5)
39.6	0.525	0.775	16.3	(21.4)
38.2	0.516	0.781		21.2
				±0.1
24.4	0.435	0.845	6.25	(11.2)
23.0	0.425	0.852		10.3
22.5	0.421	0.855		10.2
17.0	0.370	0.882		8.14
				±0.19
14.8	0.342	0.894	2.27	(6.60)
13.1	0.320	0.901		5.04
11.3	0.296	0.915		4.45
8.8	0.259	0.931		3.23
6.0	0.209	0.949		1.88

* Data in parentheses are interpolated.

respectively) and activity coefficients are published.¹⁰ Reasonably reactive substrates were needed, so the toluene-*p*-sulphonate and picrate were chosen, reactions being followed at 55 °C in the presence of a small amount of 2,6-lutidine. The observed rates are listed in Tables 2 and 3, and are disconcerting. The picrate shows a nearly constant reaction rate, varying only by a factor of about two, in the first system, and in both a rate maximum is observed, at *ca.* 65% methanol and at *ca.* 92% ethanol. The toluenesulphonate also shows a rate-maximum in the first system, and possibly in the second. When, for either solvent pair, $\log k$ for one substrate is plotted against $\log k$ for the other, a wandering curve is obtained (Figure). Plainly the Grunwald-Winstein equation fails in these cases, and an alternative treatment is required.

We began by checking products, by g.l.c.; these were simply the 1-adamantyl ether, except for 'pure' sulphone, when 1-adamantanol was the only product, presumably from the *ca.* 10⁻²M-water present, a concen-



Rates of solvolysis of 1-adamantyl derivatives; ×, ethanol-chloroform, +, methanol-tetramethylene sulphone; values on data points represent mol % of alcohol component

tration exceeding that of the organic substrate. We measured activation parameters for 1-adamantyl picrate at five compositions, and for the toluenesulphonate for one mixture, in the methanol-tetramethylene sulphone system (Table 4). Finally, we determined activity coefficients in the latter, on the basis that the sulphone would have a negligible partial pressure at 55 °C in mixtures, as it does as neat solvent, using the Gibbs-Duhem equation.¹¹

Qualitatively, the most remarkable result is the rapid solvolysis of the picrate in tetramethylene sulphone. The high rate, positive entropy of activation, and insensitivity of rate to the addition of methanol in concentrations large enough to overwhelm the small water content in trapping the cationic intermediate, all point to the simplest mechanism possible. Rate-determining heterolysis gives a 1-adamantyl cation and a picrate anion, initially solvated only by sulphone molecules incapable of any covalent interaction, as a classical Bjerrum ion pair. Even when the water content is only 10⁻²M, reaction with water, to give a water-separated ion pair, must be more rapid than the return of the Bjerrum ion pair to starting material. The water-separated ion pair, or the methanol-separated ion pair

TABLE 4
Activation parameters in methanol-tetramethylene sulphone, 1-adamantyl-X

Mol % MeOH	X	T/ °C	$10_4k/s^{-1}$	$\Delta H/kJmol^{-1}$	$\Delta S/JK^{-1} mol^{-1}$
100	OPic	65.2	42		
		54.7	12.3	108.3 ± 1.6	29 ± 5
		45.0	3.43		
100	OTos *			86.9 ± 1.3	-18 ± 4
80.0	OPic	65.0	66.9		
		55.5	21.8	104.5 ± 1.3	21 ± 3
69.5	OPic	45.3	6.36		
		66.8	91.0		
		53.0	18.4	104.5 ± 0.4	22 ± 1
7.77	OPic	43.1	5.3		
		64.6	47.6		
		55.3	15.5	108.3 ± 0.4	30 ± 1
7.77	OTos	40.8	2.38		
		55.4	23.4		
		54.9	23.3		
		44.4	7.63	85.7 ± 2.5	-53 ± 10
0.00	OPic	42.1	6.52		
		37.3	3.52		
		64.0	39.9		
		55.2	13.5	112.9 ± 1.3	44 ± 3
		45.5	3.64		

* Ref. 8, based on rates at 15–45.9 °C.

formed when methanol is present, rapidly collapses to product. Transference to pure methanol does not change the mechanism significantly, although weak hydrogen-bonding to picrate anion when almost fully formed is possible; as there is little change in dielectric constant either, the reaction rate hardly varies over the whole range of compositions.

Solvolysis of the picrate in ethanol-chloroform is a less straightforward process; the direct heterolysis in chloroform is at least a hundred-fold slower than in tetramethylene sulphone, and cannot be observed. At the other extreme, in pure ethanol the reaction is only 2.5 times slower than in pure methanol, and probably can be represented as a simple heterolysis. At low concentrations of ethanol in chloroform the rate is sensitive to ethanol concentration, and $\log k$ is (roughly) linearly related to $\log a_{EtOH}$ (a = activity) with, however, a non-integral slope, 2.6.

Solvolysis of the toluenesulphonate in methanol-tetramethylene sulphone could not be followed to pure sulphone, as the maximal estimate of $5 \times 10^{-5} s^{-1}$ recorded refers to a process which did not follow a first-order law. Addition of small amounts of methanol resulted in a marked increase in rate, $d(\log k)/d(\log a_{MeOH}) = 2.05$. The simple interpretation of this as the result of the need for two molecules of methanol to solvate the incipient toluene-*p*-sulphonate ion at the transition state seems reasonable, and it appears to be the dominant process over the range 8–50% (molar) methanol, that is, up to 20% w/w. The markedly negative entropy of activation, contrasting with the positive entropy observed for the picrate, attests a

severe loss of freedom to, for example, two solvent molecules.

The toluenesulphonate in ethanol-chloroform showed much the sharpest dependence of solvolysis rate on solvent composition. A plot of $\log k$ versus $\log a_{EtOH}$ had a slope of about 4.6. The difference in the slope of $\log k$ versus $\log a_{alcohol}$ for the toluenesulphonate and picrate was thus about 2 units in each system. Again, a very simple picture comes to mind; that in arenesulphonate solvolysis in a solvent of high dielectric constant, two alcohol molecules are needed to form hydrogen bonds to the two oxygen atoms of the SO_2Ar group in the incipient anion, whereas none is needed for a potential picrate anion. In a solvent of much lower dielectric constant, *e.g.* chloroform, an additional alcohol molecule is required, to form a hydrogen bond to the oxygen atom still partially linked to the adamantyl residue in either picrate or toluenesulphonate. Furthermore, the heterolysis is accelerated by an increase in solvent polarity, the effect amounting to about a 1.6 power relationship to ethanol activity. [Here, as usual, 'solvent polarity' cannot be closely related to bulk dielectric constant (D), as plots¹² of $\log(k/a_{EtOH}^n)$ versus D or $(D-1)(2D+1)$ using various integral values of n for 1-adamantyl toluenesulphonate and picrate in ethanol-chloroform mixtures were curved over the whole solvent-composition range]. Our results allow, but do not, of course, rigidly require, these reasonable hypotheses.

Attempts to correlate solvolysis rates with the composition of binary mixtures of solvents, using various substrates, have been numerous, and so have the theoretical treatments used to rationalise the results; they have been reviewed.¹³ In particular, Swain's 'push-pull' mechanism¹⁴ has emphasised the electrophilic solvation of incipient anions, as no less important than nucleophilic interactions with incipient cations. This is not weakened by our demonstration, in a special case, of a solvolysis requiring neither 'push' nor 'pull'; 1-adamantyl picrate may indeed be a useful probe for solvolysis mechanisms, although other bridgehead derivatives with very 'soft' leaving groups should share its advantages. We have tried to find more or less empirical relationships between reaction rate and solvent activity; for example, the solvolysis rate for 1-adamantyl picrate in tetramethylene sulphone-methanol is very accurately reproduced over the whole range by equation (2), where k_s and k_m are the rates observed in

$$k = (k_s a_s + k_m a_m)(a_s + a_m)^2 \quad (2)$$

pure sulphone and pure methanol, while a_s and a_m are the activities of sulphone and methanol in the solution in which the observed rate is k . Unfortunately it is difficult either to relate this expression to any theory of the immediate environment of the reacting molecule, or to find equally good related expressions for the other three cases examined over the whole solvent-composition range; we therefore refer the reader to a thesis¹³ for further details.

The Grunwald-Winstein equation fails even for 1-adamantyl derivatives when leaving groups of differing solvation requirements are compared in solvent systems in which the two solvent components cannot play equivalent roles in interaction with an incipient anion. We would of course expect a similar failure when such solvent systems are used with substrates having similar or identical leaving groups, but incipient cations of markedly different susceptibility to interaction with one of the solvent components. With mixtures like water-ethanol, however, the two components are interchangeable in each role and their efficiency in each appears to be proportional to their effect on overall polarity. If insight into the process of solvolysis is needed, solvent systems tailored to respond unambiguously to the three main types of interaction (nucleophilic, electrophilic, electrostatic) have major advantages, and (like ethanol-trifluoroethanol¹⁵) methanol-tetramethylene sulphone is such a system. Equally, if interest is focused on cation-solvent interaction, leaving groups like picrate or dinitrophenolate have the important merit of minimising anion-solvent interaction, and therefore minimising the consequences of earlier or later transition states when leaving groups are held constant.

We tabulate some solvolysis rates in ethanol-chloroform determined for benzhydryl chloride (Table 5); these allow calculation of $d(\log k)/d(a_{\text{EtOH}}) = 4.0$, and are mainly important as showing the spectrophotometric method to be convenient even with optically unhelpful leaving groups.

TABLE 5

Solvolysis of benzhydryl chloride in ethanol-chloroform

mol % EtOH	a_{EtOH}	a_{CHCl_3}	$10^5 k/s^{-1}$
100	1.000	0.000	145
61.4	0.657	0.617	102
24.4	0.435	0.845	18.0
13.1	0.320	0.901	5.61

EXPERIMENTAL

Ethanol was dried by distillation through a Vigreux column from magnesium ethoxide, and typically had a water content of 0.008% (Karl Fischer); methanol, similarly dried, had a water content of 0.012%. Chloroform was washed with concentrated sulphuric acid, then water, dried over calcium chloride, distilled, and stored only briefly at 0 °C in the dark before mixing with ethanol. Tetramethylene sulphone was distilled under reduced pressure, dissolved in water, and treated with potassium permanganate at 60 °C until an excess remained for 30 min. Oxalic acid was added and the solution was extracted with methylene chloride; the extract was dried (CaCl₂, MgSO₄), evaporated and distilled *in vacuo*; the sulphone then had m.p. 28.2° and a water content of 0.013% (*ca.* 10⁻²M). All mixed solvents were prepared gravimetrically.

1-Adamantyl picrate and toluene-*p*-sulphonate were prepared by methods previously described.¹⁶ Solvolyses were followed spectrophotometrically, using a Unicam SP 800 or Cary 14 spectrophotometer and cuvettes capped by septa held in a block through which water was circulated from a thermostatically heated bath. Reaction temperatures were measured in a 'dummy' cell, a thermocouple measuring the

difference between cell and bath temperatures. Optical densities were recorded at a chosen wavelength during 2.5–3.5 half-lives at equal time intervals, and least-squares Guggenheim slopes were computed, together with (in a few cases) standard errors for slopes. For picrates, a trace of 2,6-lutidine was added to deprotonate the picric acid formed, in most cases, the reaction then being followed at 400 nm; with rather less precision the reaction could be followed at 330 nm in the absence of lutidine, the two methods giving for 1-adamantyl picrate values of 1.26 and $1.24 \times 10^{-3} \text{ s}^{-1}$ when run in adjacent cells at about 55 °C. The toluenesulphonate solvolysis in ethanol was followed either by observing the decrease in covalent OTs absorption at 273 nm, at 0.01M concentration in the presence of 0.05M-KOAc, or by observing the increase in absorption (ϵ 3 500 \rightarrow 7 500) as 2,6-lutidine is protonated; here 0.000 2M-substrate and 0.000 3M-base were needed, and direct comparison with the former technique gave rates of 1.71 ± 0.02 and $1.69 \pm 0.01 \times 10^{-3} \text{ s}^{-1}$. The solvolysis of benzhydryl chloride (0.000 2M) was carried out in the presence of 0.000 3M-1,8-bisdimethylaminonaphthalene, a particularly non-nucleophilic amine,¹⁷ the rate observed (370 nm) in ethanol ($1.45 \times 10^{-3} \text{ s}^{-1}$) being directly comparable with that (0.03M) determined by halide analysis^{3c} ($1.48 \times 10^{-3} \text{ s}^{-1}$).

Vapour pressures (*P*) of methanol-tetramethylene sulphone mixtures were measured at 55 °C with an isoteniscope and mercury thermometer, giving values of 550 mmHg for pure methanol (*P*₀) and 0.0 mmHg for pure sulphone. The activities of methanol (a_{MeOH}) in mixtures were taken as *P*/*P*₀. Activities of tetramethylene sulphone were calculated from the Gibbs-Duhem equation in the form (3),

$$\log \gamma_s = \int \frac{X_{\text{MeOH}}}{X_s} d(\ln \gamma_{\text{MeOH}}) \quad (3)$$

where γ_s and γ_{MeOH} are the activity coefficients of sulphone and methanol, and X_s and X_{MeOH} are the corresponding molar fractions. A smooth curve was drawn by hand through a plot of (X_{MeOH}/X_s) versus $\ln \gamma_{\text{MeOH}}$. For any value x of (X_{MeOH}/X_s), γ_s was then $\exp[\int (X_{\text{MeOH}}/X_s) d(\ln \gamma_{\text{MeOH}})]$, the area being measured by weighing. Table 6 gives our results.

TABLE 6

Vapour pressures and activities, methanol-tetramethylene sulphone

mol % MeOH	V.p./mmHg	a_{MeOH}^a	a_s^b
100	505	1.000	0.000
94.2	481	0.952	
90		(0.928)	0.266
80.4	444	0.880	
80		(0.880)	0.363
70		(0.837)	0.422
69.3	421	0.834	
60		(0.775)	0.487
56.4	377	0.747	
50		(0.683)	0.566
40		(0.583)	0.646
33.5	250	0.495	
30		(0.465)	0.728
20		(0.338)	0.806
17.7	158	0.314	
10		(0.175)	0.902
7.6	66	0.131	
0	0	0.000	1.000

^a Values in parentheses by interpolation. ^b From Gibbs-Duhem equation.

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