Application of the Grunwald–Winstein equation to the solvolysis of the 2-adamantyl *p*-(trimethylammonio)benzenesulfonate (amsylate) cation. Absence of significant perturbation by a remote positive charge

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The solvolyses of 2-adamantyl *p*-(trimethylammonio)benzenesulfonate (amsylate) trifluoromethanesulfonate (**1**) in 37 pure and binary solvents proceed more rapidly than the corresponding solvolyses of 2-adamantyl toluene-*p*-sulfonate (2-AdOTs) used to establish the Y_{OTs} scale, and a Hammett σ value for a p-NMe_3^+ group of 0.77 ± 0.05 (in ethanol at 25 °C) is indicated. Despite the leaving group from **1** being a zwitterion, an excellent Grunwald–Winstein correlation with Y_{OTs} values is observed, with an m value of 0.92 ± 0.02 (correlation coefficient of 0.990). The appreciable solubility of amsylates in highly aqueous solvents suggests that **1** would be a good substitute substrate for establishing Y_{OTs} values for such solvents, in which 2-AdOTs is only very sparingly soluble.

For almost 50 years, the Grunwald–Winstein equation (1)[1] has

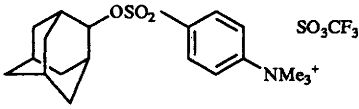
$$\log (k/k_o) = mY + c \qquad (1)$$

been a very useful tool in the investigation of unimolecular solvolysis reactions. In eqn. (1), k and k_o represent the specific rates of solvolysis of a substrate in a given solvent of ionizing power Y and in the standard solvent (80% ethanol), respectively, m is a measure of the sensitivity of the specific rate of solvolysis of the substrate under investigation to changes in the Y value [the slope of the plot of log (k/k_o) against Y value], and c is the intercept of the plot.

The initial Y scale[1,2] was based on the solvolysis of *tert*-butyl chloride; this scale has been shown to contain a component based on the nucleophilic characteristics of the solvent[3] and it has been recommended[4] that this component be eliminated by choosing as the standard substrate a 1-adamantyl or, for the better leaving groups, a 2-adamantyl derivative. We have very briefly reviewed these scales[5] and a detailed review of Y_X scales for an anionic X^- leaving group (with several tables of values) has appeared.[6]

Studies have also been made of the kinetic influences of solvent variation upon the solvolyses of R–X^+ substrates, where the positive charge is adjacent to the α-carbon and the leaving group is a neutral molecule. Among alkyldimethylsulfonium cations ($X = SMe_2$) which have been studied are several which are believed to solvolyse by an S_N1 mechanism, such as 1-adamantyl,[7] benzhydryl[8] and *p*-methoxybenzyl[9,10] derivatives. As with *tert*-butyl chloride solvolysis, a small nucleophilic component is believed to be present in the solvolysis of the *tert*-butyl derivative.[7,11] For the S_N1 solvolyses of this type of substrate in hydroxylic solvents, the effect on the specific rate of solvolysis of variation in the solvent composition is very small; extremely small relative to the large effects observed in S_N1 solvolyses of initially neutral RX substrates.[6]

The solvolyses of R–X^+ substrates where the charge is remote, such that the leaving group is a zwitterion, have been less extensively studied.[5,12–14] Several [2]betylates [$ROSO_2(CH_2)_2NMe_3^+$] have been prepared and shown to be good water-soluble alkylating agents.[12,14] We have shown[5] that, when the R group is 2-adamantyl (2-Ad), the 2-(2-adamantyloxysulfonyl)-*N*,*N*,*N*-trimethylethanaminium cation [$2AdOSO_2(CH_2)_2NMe_3^+$] undergoes solvolysis with a good Grunwald–Winstein correlation [eqn. (1)] using the Y_{OTs} scale[4,6,15] (based on 2-adamantyl toluene-*p*-sulfonate solvolysis rates). We now report specific rates of solvolysis of the 2-adamantyl (*p*-trimethylammonio)benzenesulfonate (amsylate) cation [prepared as the trifluoromethanesulfonate (triflate) salt, **1**], which can be directly compared in a linear free energy plot with the corresponding Y_{OTs} values. Further, it is shown that the data can be used to obtain a secondary Hammett σ value, in ethanol, for the *p*-trimethylammonio group.[16,17]



(2-AdOAm$^+$OTf$^-$, **1**)

Results and discussion

The specific rates of solvolysis of **1** have been determined in mixtures of water with ethanol, methanol, dioxane, 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). Determinations have also been made in TFE–ethanol mixtures. The first-order rate coefficients (specific rates) are reported, together with calculated Y_{OAm} values [eqn. (2)] and

$$Y_{OAm} = \log (k/k_o)_{2AdOAm^+} \qquad (2)$$

Y_{OTs} values from the literature[4,6,15] in Table 1; the Y_{OTs} values based on 1-adamantyl toluene-*p*-sulfonate solvolysis rates have been adjusted in the manner recommended by Allard and Casadevall.[5,15]

Inspection of Table 1 shows that the Y_{OAm} values closely resemble the Y_{OTs} values, slightly less so for the aqueous dioxane solvents, and a plot of the Y_{OAm} values against the Y_{OTs} values, for 37 solvents, is close to linear (Fig. 1) with a slope of 0.92 ± 0.02 and correlation coefficient of 0.990. Complete correlation data for these analyses, together with those for individual binary solvent systems, are presented in Table 2. The trend in values for the different binary systems (highest m value in aqueous HFIP and lowest m value in aqueous acetone) is similar to that previously reported[5] for corresponding correlations of the specific rates of solvolysis of the 2-adamantyl [2]betylate cation ($Y_{2Ad[2]B}$ values). Indeed, an excellent correlation is also observed in the plot of Y_{OAm} values against the 26 available[5] $Y_{2Ad[2]B}$ values: $m = 0.91 \pm 0.02$, $c =$

Table 1 First-order rate coefficients for the solvolysis of the 2-adamantyl *p*-(trimethylammonio)benzenesulfonate cation[a] in pure and binary solvents at 25.0 °C and the Y_{OAm} and corresponding Y_{OTs} values

Solvent[b,c]	$k/10^{-6}$ s^{-1}	Y_{OAm}[d]	Y_{OTs}[e]
90% EtOH	0.189 ± 0.006	−0.69	−0.58
80% EtOH	0.930 ± 0.020	0.00	0.00
70% EtOH	3.44 ± 0.07	0.57	0.47
60% EtOH	9.87 ± 0.19	1.03	0.92
50% EtOH	29.6 ± 0.8	1.50	1.29
40% EtOH	103 ± 3	2.04	1.97
30% EtOH	412 ± 18	2.65	2.84
100% MeOH	0.0838 ± 0.0020	−1.05	−0.92
90% MeOH	0.554 ± 0.007	−0.23	−0.17
80% MeOH	2.38 ± 0.07	0.41	0.47
70% MeOH	8.14 ± 0.18	0.94	1.02
60% MeOH	23.8 ± 0.6	1.41	1.52
40% MeOH	204 ± 8	2.34	2.43
90% Acetone	0.0298 ± 0.0011	−1.49	−1.70
80% Acetone	0.254 ± 0.005	−0.56	−0.79
70% Acetone	1.10 ± 0.03	0.07	−0.01
60% Acetone	3.76 ± 0.09	0.61	0.66
50% Acetone	13.3 ± 0.5	1.16	1.26
40% Acetone	59.5 ± 1.7	1.81	1.85
30% Acetone	215 ± 10	2.37	2.50
90% Dioxane	0.0277 ± 0.0007	−1.52	−2.06
80% Dioxane	0.254 ± 0.005	−0.56	−1.10
70% Dioxane	1.14 ± 0.05	0.09	−0.42
60% Dioxane	4.03 ± 0.06	0.64	0.30
50% Dioxane	16.6 ± 0.2	1.25	
40% Dioxane	59.5 ± 1.2	1.81	
30% Dioxane	209 ± 11	2.35	
100% TFE	47.7 ± 2.5	1.71	1.80
97% TFE	43.3 ± 1.3	1.67	1.83
90% TFE	41.4 ± 2.8	1.65	1.90
80% TFE	40.3 ± 2.2	1.64	1.94
70% TFE	42.6 ± 1.3	1.66	2.00
97% HFIP	4230 ± 190	3.66	3.53
90% HFIP	793 ± 40	2.93	2.90
80% HFIP	261 ± 16	2.45	2.57
70% HFIP	179 ± 11	2.28	2.41
80T–20E	6.76 ± 0.09	0.86	0.98
60T–40E	1.12 ± 0.04	0.08	0.21
40T–60E	0.224 ± 0.007	−0.62	−0.44
20T–80E	0.0600 ± 0.0018	−1.19	−1.18

[a] As the trifluoromethanesulfonate salt and with a concentration of *ca.* 4×10^{-3} mol dm^{-3}; rate coefficients presented with associated standard deviations. [b] With water as other component, except for TFE–EtOH (T–E) mixtures. [c] On a volume–volume basis, at 25 °C, except for TFE–H_2O and HFIP–H_2O mixtures, which are on a weight–weight basis. [d] log (k/k_o) for 2-AdOAm, where k_o is the first-order rate coefficient in 80% EtOH. [e] From refs. 6 and 15.

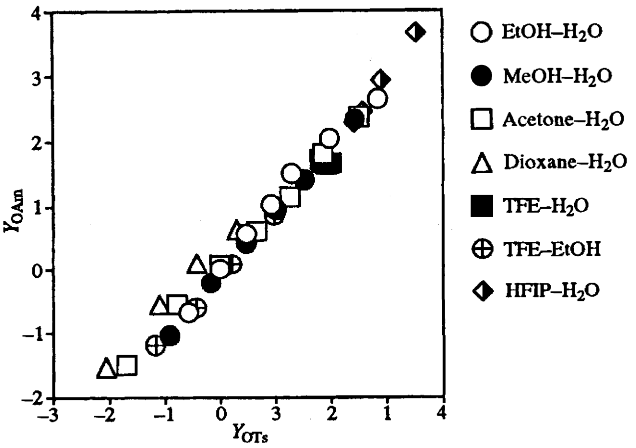


Fig. 1 Comparison of Grunwald–Winstein solvent ionizing power scales: plot of Y_{OAm} against Y_{OTs}

0.12 ± 0.11, $r = 0.996$, $F = 2864$ (symbols defined in footnotes to Table 2).

A major problem in obtaining Y_{OTs} values for highly aqueous media has been the low solubility of 2-adamantyl toluene-*p*-sulfonate. This problem has been countered by substituting the more soluble methanesulfonate ester and applying estimated toluene-*p*-sulfonate/methanesulfonate rate ratios to obtain the corresponding specific rate of solvolysis of the toluene-*p*-sulfonate.[6,18] The excellent linear relationship between the Y_{OAm} and Y_{OTs} scales coupled with the relatively high water solubility of betylate and amsylate salts suggests the use of **1** as an attractive alternative to the use of the methanesulfonate.

The close similarity in kinetic behaviour for the solvolyses of 2-adamantyl toluene-*p*-sulfonate and **1** is paralleled by the almost identical product-partitioning[19] in 70% TFE–30% ethanol, suggesting that both the rate-determining ionization stage and the product-determining carbocation capture stage are essentially identical in character, irrespective of whether the *para*-substituent is an uncharged methyl group or a positively charged trimethylammonio group.

The absence of perturbation by the remote positive charge is consistent with the interpretation that the *mY* equation primarily probes those solvation changes between initial and transition states which are close to the reaction site. Considerable differences in initial state solvation effects are to be expected depending upon whether the *para*-substituent of the benzenesulfonate aromatic ring is charged or uncharged. It appears, however, that the present study presents a further example of the situation recently discussed[20] in which these differences are also present at the transition state, such that, remote from the reaction site, differences in solvation between initial and transition states are small. Further, while the Y_x scales are determined primarily by the relative specific rates of ionization, they are also governed to a minor extent by the solvent dependence of the extent of ion-pair return[21] and it would appear that, for a given solvent, the extents of ion-pair return must be very similar, irrespective of whether the leaving group is an anion or a zwitterion.

A modest Grunwald–Winstein extrapolation using the parameters obtained for solvolyses in 90–30% ethanol (Table 2) allows the specific rate in 100% ethanol to be estimated as 0.0224×10^{-6} s^{-1}, essentially identical with the corresponding value[22] of 0.0238×10^{-6} s^{-1} for solvolysis of 2-adamantyl *m*-nitrobenzenesulfonate, indicating that in ethanol at 25.0 °C the *p*-NMe_3^+ and *m*-NO_2 groups have essentially identical Hammett σ values. In an analysis of the ethanolyses of a variety of arenesulfonate esters at temperatures in the range 15–75 °C, the σ value required for the *m*-NO_2 group was remarkably constant[22] at 0.78 ± 0.01. Correction for the very small specific rate difference allows the σ value for the *p*-NMe_3^+ group to be estimated as 0.77. An estimated standard error of ±0.05 can be obtained, based on estimates of ±0.02 from the Grunwald–Winstein extrapolation to 100% ethanol and ±0.03 based on the standard error associated with the Hammett ρ value (1.86 ± 0.07) for the solvolyses of a series of 2-adamantyl arenesulfonates in ethanol at 25.0 °C.[22]

Jaffé reported[16a] seven determinations of the Hammett σ value for a *p*-NMe_3^+ group, with a lower limit of 0.664, higher limit of 1.112, and mean value (with standard deviation) of 0.859 ± 0.149, and values tabulated more recently[17a] include 0.82[17b] and 0.96.[17c] In a detailed consideration of the applicability of the Hammett equation in the presence of charged substituents, Wepster and co-workers[17d] found a large variation of the σ values from reaction to reaction. For a *p*-NMe_3^+ group, a continuous range of from 0.7 to 2.2 was reported. It was demonstrated that the data could be very well treated by a modified Hammett equation involving the addition of a Bjerrum term to separate out the field (electrostatic effect)

Table 2 Correlation of Y_{OAm} values with Y_{OTs} values[a]

System	(*n*)[b]	*m*[c]	*c*[d]	*r*[e]	*F*[f]
90–30% EtOH	(7)	0.99 ± 0.05	0.04 ± 0.15	0.9927	340
100–40% MeOH	(6)	1.00 ± 0.01	−0.09 ± 0.03	0.9997	6960
90–30% Acetone	(7)	0.91 ± 0.02	0.07 ± 0.06	0.9991	2834
90–60% Dioxane	(4)	0.92 ± 0.04	0.42 ± 0.07	0.9980	490
97–70% HFIP	(4)	1.24 ± 0.04	−0.71 ± 0.04	0.9987	777
(100–20%T)-E	(5)	0.99 ± 0.03	−0.10 ± 0.07	0.9986	1106
All[g]	(37)	0.92 ± 0.02	0.07 ± 0.19	0.9901	1737
All (no dioxane)	(33)	0.97 ± 0.02	−0.02 ± 0.13	0.9947	2897

[a] Values from Table 1 and using the equation $Y_{\mathrm{OAm}} = mY_{\mathrm{OTs}} + c$. [b] Number of solvent systems studied. [c] With associated standard error. [d] Accompanied by the standard error of the estimate. [e] Correlation coefficient. [f] *F*-test value. [g] All the above listed solvents plus 97–70% TFE (four compositions).

and this led, for the *p*-NMe_3^+ group, to a 'normal' σ value of 0.53 ± 0.08. Our value of 0.77 ± 0.05 is towards the lower end of the range of experimental values obtained and it suggests that, during the ethanolysis of **1**, a dominant inductive effect of the substituent is accompanied by only a relatively small perturbation due to field effects.

Experimental

Materials

The purifications of acetone, dioxane, ethanol and methanol were as previously described.[23] The purifications of 2,2,2-trifluoroethanol[24] and 1,1,1,3,3,3-hexafluoropropan-2-ol[25] were also carried out using previously reported procedures. The adamantan-2-ol (Aldrich), sulfanilic acid (Aldrich), dimethyl sulfate (Aldrich) and methyl trifluoromethanesulfonate (Aldrich) were used without further purification.

2-Adamantyl *p*-(trimethylammonio)benzenesulfonate trifluoromethanesulfonate (1)

The procedure of Bergman and co-workers[26] was used to prepare *p*-dimethylaminobenzenesulfonyl chloride *via* the sodium salt of the corresponding acid; mp 110.0–111.0 °C (lit.,[27] 110.5–111.5 °C). This material was then reacted with adamantan-2-ol, following the procedure used by Schleyer and Nicholas to prepare the toluene-*p*-sulfonate,[28] but with a doubling of the reaction time, to give 2-adamantyl *p*-dimethylaminobenzenesulfonate as a white solid; mp (crude material) 95.0–95.5 °C; $\delta_H(CDCl_3)$ 7.72 (d, 2 H, J = 9 Hz), 6.67 (d, 2 H, J = 9 Hz), 4.59 (s, 1 H, $CHOSO_2$), 3.06 (s, 6 H) and 2.2–1.3 (m, 14 H); ν_{max}(KBr)/cm^{-1} includes strong peaks at 2912, 2860, 1600, 1352, 1165, 1099, 924, 855, 814, 676 and 650. Without further purification, 1.0 g of this material was reacted with methyl trifluoromethanesulfonate (0.5 cm^3), following the general procedure of King *et al.*,[14] and the product was recrystallized from dichloromethane to give 0.61 g of a white solid (41%); mp 158–165 °C (decomp.); $\delta_H(CD_3CN)$ 8.16 (d, 2 H, J = 9 Hz), 8.00 (d, 2 H, J = 9 Hz), 4.81 (s, 1 H, $CHOSO_2$), 3.59 (s, 9 H) and 2.1–1.5 (m, 14 H); ν_{max}(KBr)/cm^{-1} includes strong peaks at 2936, 2920, 2860, 1602, 1352, 1254, 1188, 1160, 1018, 910 and 628 (Found: C, 48.0; H, 5.65; N, 2.8; S, 13.05. Calc. for $C_{20}H_{28}F_3NO_6S_2$: C, 48.10; H, 5.61; N, 2.80; S, 12.83%).

Kinetic procedures

These were as previously described.[5] For runs with half-lives above 24 h (specific rate less than 8×10^{-6} s^{-1}) the time to the infinity titre was reduced by addition of a portion to 5 cm^3 of water and allowing the mixture to stand for an appropriate time at 50 °C prior to the addition of the 25 cm^3 of acetone and titration. This procedure was essential for the slower runs; for example, the solvolysis in 90% acetone at 25 °C was followed over 8 months, at which time it was only 55% complete.

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