

Reaction mechanism studies involving the correlation of the rates of solvolysis of benzoyl and *p*-nitrobenzoyl *p*-toluenesulfonates

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The solvolyses of benzoyl and *p*-nitrobenzoyl *p*-toluenesulfonates (tosylates) are considerably slower than those of the previously studied mixed anhydride of acetic and *p*-toluenesulfonic acids (acetyl tosylate), which, even with application of rapid-response conductivity, could only be studied at considerably reduced temperatures. For the presently studied compounds, the specific rates over a wide variety of solvents could be conveniently studied at $-10\text{ }^{\circ}\text{C}$. For solvolyses of benzoyl tosylate, application of the extended (two-term) Grunwald–Winstein equation gives sensitivities to changes in solvent nucleophilicity and solvent ionising power consistent with an ionisation (S_N1) pathway. Indeed, a good correlation is obtained against only solvent ionising power. For the solvolyses of the *p*-nitro-derivative, very different sensitivities are obtained, with an appreciable dependence on solvent nucleophilicity, and a dominant bimolecular pathway for the substitution is proposed for all of these solvolyses, except for those in solvents rich in fluoroalcohol. Studies of solvent deuterium isotope effects in methanolysis, of leaving-group effects relative to a halide and of temperature variation effects are consistent with the proposed mechanistic pathways.

Keywords: benzoyl *p*-toluenesulfonate, *p*-nitrobenzoyl *p*-toluenesulfonate, extended Grunwald–Winstein equation, nucleofugality, solvolysis, solvent isotope effect

Mixed anhydrides of carboxylic acids can be prepared by the silver salt method.¹ Reaction of an acyl chloride (RCOCl) with the silver salt of a monobasic oxyacid (Ag^+OY^-) leads to the formation of RCOOY. Examples include the formation of acetyl^{2,3} or benzoyl⁴ perchlorates by the interaction of the acid chloride with silver perchlorate. These mixed anhydrides of the carboxylic acid and perchloric acid, used in solution without isolation, were found to be excellent acylium ion donors, such as in Friedel–Crafts acylations. In a study highly relevant to the present investigation, Overberger and Sarlo⁵ prepared several mixed carboxylic sulfonic anhydrides by the interaction of a silver arenesulfonate with the appropriate acyl chloride. In this way, after removal of the solvent, extraction with ether, and lowering of the temperature, 40–60% yields of the mixed anhydrides, including the benzoyl *p*-toluenesulfonate (tosylate, **1**) and *p*-nitrobenzoyl tosylate (**2**) of the presently reported study, were obtained and characterised. The reaction of **2** with ethanol led to a 94% yield of ethyl *p*-nitrobenzoate, indicating solvolysis to occur at the benzoyl carbonyl group with loss of an OTs⁻ tosylate anion (Scheme 1).

A brief conductimetric study of the kinetics of solvolyses of acetyl and benzoyl benzenesulfonate has been reported.⁶ The substrates were prepared by the methods of Flavell and Ross⁷ and Overberger and Sarlo,⁵ respectively. Solvolyses in ethanol and methanol were studied, with the substrate added as a solution in diethyl ether, such that 6.7% of the ether was present in the mixed solvent.⁸ Due to high reactivity, studies were at considerably reduced temperature, in ranges of $-57\text{ }^{\circ}\text{C}$ to $-46\text{ }^{\circ}\text{C}$ for the acetyl benzenesulfonate and $-22\text{ }^{\circ}\text{C}$ to $+11\text{ }^{\circ}\text{C}$ for the benzoyl benzenesulfonate. Obtaining values at $-25\text{ }^{\circ}\text{C}$ from an Arrhenius equation treatment, the acetyl/benzoyl rate ratios

were 429 in methanol and 900 in ethanol. Laird and Spence⁶ concluded that a concerted displacement may be involved but the mechanism “must be considered unresolved”. The more probable reaction pathways for those solvolytic displacement reactions are shown (for displacement of chloride) in Scheme 2.

Recently we reported⁹ concerning the application of the extended Grunwald–Winstein equation to the solvolyses of acetyl *p*-toluenesulfonate, with consideration also of leaving-group effects and solvent deuterium isotope effects. This study is now extended to substrates with benzoyl and *p*-nitrobenzoyl groups associated with the *p*-toluenesulfonate leaving group.

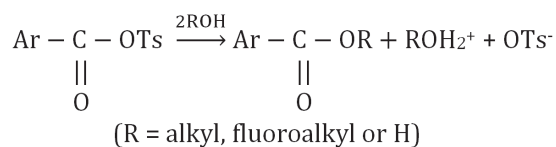
The original Grunwald–Winstein equation¹⁰ [Equation (1)] incorporated a solvent ionising power

$$\log(k/k_0)_{\text{RX}} = mY + c \quad (1)$$

scale (Y), based on the solvolysis of *tert*-butyl chloride ($m=1$) and a sensitivity factor (m) towards changes in Y for solvolyses of RX as the solvent is varied. The k and k_0 are the specific rate in a given solvent for RX solvolysis relative to the corresponding value in the standard solvent (arbitrarily chosen¹⁰ as 80% ethanol) and c is a constant (residual) term. The equation works quite well for unimolecular (S_N1+E1) solvolyses but, as one would expect, poorly for bimolecular (S_N2+E2) solvolyses and the introduction of a second term governed by the sensitivity (l) to changes in solvent nucleophilicity (N) was added¹¹ [Equation (2)]. The scale (N_T) usually chosen at the present time is based on the solvolyses of the *S*-methylidibenzothiophenium ion.¹²

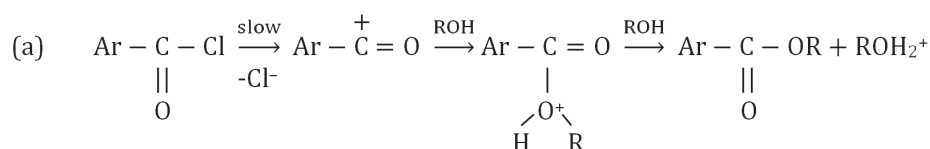
$$\log(k/k_0)_{\text{RX}} = lN + mY + c \quad (2)$$

Also, the original Y scale does not apply well when the nucleofuge is other than chloride and there is believed to be a nucleophilic component for solvolyses of *tert*-butyl derivatives, which is incorporated into the Y scale. The present usage involves a standard scale (Y_X) based on the solvolyses of 1- and/or 2-adamantyl derivatives with the appropriate leaving group X.¹³ The development and uses of the Grunwald–Winstein equations were recently, to mark the 60th anniversary of its introduction, the subject of a short review within this journal.¹⁴ More extensive reviews, with tables of values, are also available for solvent ionising power¹⁵ and solvent nucleophilicity¹⁶

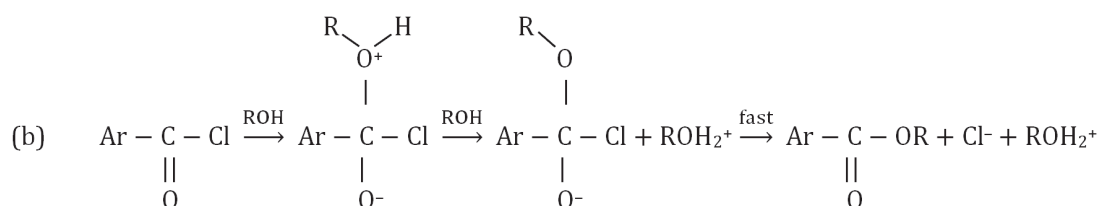


Scheme 1

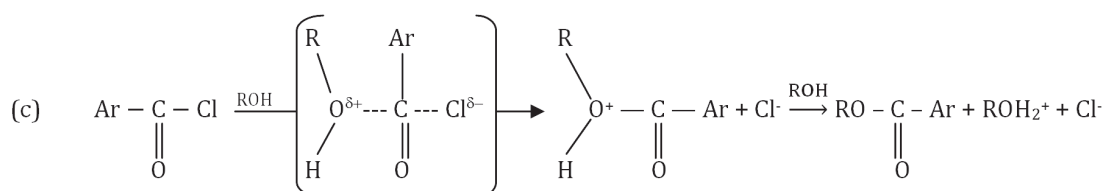
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An ionisation mechanism for solvolysis.



An addition-elimination mechanism for solvolysis.



Solvolysis by a concerted bimolecular displacement (S_N2).

Scheme 2

considerations. Equation (2), as applied in this study, can be written more specifically as Equation (3).

$$\log(k/k_0)_{\text{ArCO}_2\text{Ts}} = lN_{\text{T}} + mY_{\text{OTs}} + c \quad (3)$$

In addition to applying the Grunwald–Winstein equations to the solvolyses of **1** and **2**, we will also consider temperature variation parameters (especially the entropy of activation), leaving group effects, such as $k_{\text{OTs}}/k_{\text{Cl}}$ and $k_{\text{OTs}}/k_{\text{Br}}$,^{17–19} and solvent deuterium isotope effects for solvolyses in MeOH and MeOD,^{20,21} to assist in the assignment of mechanism.

The main reason for a change to *p*-toluenesulfonate as a leaving group from the benzenesulfonates studied by Laird and Spence⁶ is that an extensive range of Y_{OTs} values is available.¹⁵ The Y_{OTs} scale would be a reasonable approximation for the unavailable scale for the benzenesulfonate leaving group but, clearly, it is better to have a direct relationship to the scale. Additional secondary considerations include that both **1** and **2** have previously been prepared, isolated and adequately characterised⁵ and that since the solvolyses are quite rapid, the change to a poorer leaving group will allow measurements at somewhat higher and more convenient temperatures.

Results and discussion

Table 1 reports the first-order rate coefficients (specific rates) for solvolyses of **1** and **2** in hydroxylic solvents at –10.0 °C. For solvolyses of **1** directly determined values are reported for 36 solvents and for 95% acetone a value obtained by extrapolation of values at higher temperatures (Table S1 in the Electronic Supplementary Information, ESI), using the Arrhenius equation, is presented. For solvolyses of **2**, values are directly reported for 32 solvents and eight of the values are obtained as above from an extrapolation of values at higher temperatures (Table S2 in the ESI). Also, presented within Table 1 are the relevant N_{T} ,^{12,16} and Y_{OTs} ,^{15,22} values for use in applications of the Grunwald–Winstein equations.

Table 2 reports the values for the enthalpies and entropies of activation for the solvolyses. These are calculated, using the Eyring equation,²³ from the specific rates reported in Tables S1 and S2 at from three to five temperatures.

Table 3 reports comparisons of the reported specific rates at 25.0 °C, or values obtained at 25.0 °C by use of the Arrhenius equation, with literature values for chlorides or fluorides. For **1**, the comparison is with literature values for both chlorides^{24–29} and fluorides³⁰ and, for **2**, the values required for comparison are only available for chlorides.^{24,28,31–33}

In Table 4, the specific rates of solvolysis in methanol (k_{H}) and methan(ol-d) (k_{D}) are compared at –10 °C for the methanolyses of both **1** and **2**. Four additional temperatures, in the range of 0–25 °C, are also used for the solvolyses of **2**. A comparison of the studies of **1** and **2** shows appreciably different $k_{\text{H}}/k_{\text{D}}$ ratios.

Table 5 presents the l , m , and c parameters from multiple correlation analyses of specific rate data for **1** and **2**, from Table 1, against the literature N_{T} and Y_{OTs} values. The first entry, for solvolyses of **1**, involves application of the simple (one-term) equation. To assess the goodness-of-fit, the multiple correlation coefficient (simple for the first entry) and F-test values are also presented. To allow comparisons with formally related solvolyses, previous correlation analyses of the solvolyses of acetyl tosylate,⁹ benzoyl fluoride,³⁰ acetyl and monochloroacetyl chlorides,³⁴ benzoyl chloride and its *para*-nitro and *para*-methoxy derivatives,³² and phenyl chloroformate³⁵ are also presented within Table 5.

A major component of this investigation involves the application of the Grunwald–Winstein equations to the data of Table 1, which lists specific rates of solvolysis of **1** and **2** and the associated values of the solvent nucleophilicity and solvent ionising power. In previous Grunwald–Winstein analyses of the corresponding chlorides,³² it was shown that the parent benzoyl chloride was best analysed in terms of two distant regions, with a bimolecular pathway for substitution in solvents with relatively high nucleophilicities and only moderate

Table 1 Specific rates of solvolysis (k) of benzoyl (**1**) and *p*-nitrobenzoyl (**2**) *p*-toluenesulfonates^a at -10.0°C and the appropriate solvent nucleophilicity (N_T) and solvent ionising power (Y_{OTs}) values

Solvent ^b	$10^4 k/s^{-1}$ (1)	$10^4 k/s^{-1}$ (2)	N_T ^c	Y_{OTs} ^d
100% EtOH	1.33±0.01	1.71±0.01	0.37	-1.95
90% EtOH	5.30±0.03	13.9±0.4	0.16	-0.77
80% EtOH	13.3±0.7	21.7±0.5	0.00	0.00
70% EtOH	31.2±1.3	30.0±0.7	-0.20	0.47
60% EtOH	65.6±0.2	25.4±0.5 ^e	-0.38	0.92
50% EtOH	105±1	29.4±1.2 ^e	-0.58	1.29
40% EtOH	521±32	43.6±0.7 ^f	-0.74	1.97
100% MeOH	9.10±0.06	3.52±0.01	0.17	-0.92
90% MeOH	26.1±0.2	14.9±0.3	-0.01	-0.05
80% MeOH	75.1±0.4	26.0±1.1	-0.06	0.47
70% MeOH	198±7	35.6±0.5	-0.40	1.02
60% MeOH	545±1	38.1±0.4 ^e	-0.54	1.52
50% MeOH	1020±170	41.0±0.5 ^f	-0.57	2.00
40% MeOH		49.6±0.3 ^f	-0.87	2.43
100% MeOD	8.29±0.06	1.91±0.01		
1-PrOH		1.13±0.04		
2-PrOH		0.998±0.006		-2.83
95% Acetone	0.0732 ^g	4.72±0.05	-0.49	-2.95
90% Acetone	0.298±0.001	8.87±0.01	-0.35	-1.99
80% Acetone	1.32±0.01	12.2±0.3	-0.37	-0.94
70% Acetone	5.85±0.03	11.8±0.1 ^e	-0.42	0.07
65% Acetone	9.57±0.09	11.0±0.1 ^e	-0.48	0.36 ^h
60% Acetone	20.1±0.7	9.35±0.07 ^f	-0.52	0.66
50% Acetone	96.2±1.6	10.6±0.1 ^f	-0.70	1.26
40% Acetone	353±1	10.8±0.4 ^f	-0.83	1.85
100% TFE	186±2	0.0298 ^g	-3.93	1.77
97% TFE	212±7 ⁱ	0.0404 ^{g,i}	-3.30	1.83
90% TFE	273±2	0.100 ^g	-2.55	1.90
80% TFE	363±2	0.277±0.003	-2.19	1.94
70% TFE	441±8	1.65±0.03	-1.98	2.00
97% HFIP	3720±250	0.0453 ^g	-5.26	3.61
90% HFIP	2050±60	0.0467 ^g	-3.84	2.90
70% HFIP	872±14	0.241 ^g	-2.94	2.40
50% HFIP	783±10	0.617 ^g	-2.63	2.26
90T-10E	89.9±0.2	0.0522 ^g	-2.62	1.32 ^h
80T-20E	50.7±0.2	0.153±0.006	-1.76	0.98
60T-40E	18.8±0.9	0.313±0.005	-0.94	0.21
50T-50E	11.6±0.1	0.433±0.007	-0.64	0.14 ^h
40T-60E	8.01±0.03	0.812±0.002	-0.34	-0.44
20T-80E	3.30±0.01	1.13±0.04	0.08	-1.18

^aUnless otherwise stated at concentrations of $\sim 6.0 \times 10^{-4} \text{ mol L}^{-1}$ for solvolysis of **1** and $\sim 3.0 \times 10^{-4} \text{ mol L}^{-1}$ for solvolysis of **2**; with associated standard deviations.

^bBinary solvents on a volume–volume basis at 25°C except HFIP– H_2O and TFE– H_2O mixtures are on a weight–weight basis. When not specified, the second component is H_2O . T-E represent 2,2,2-trifluoroethanol-ethanol mixtures.

^cValues from refs 12 and 16.

^dValues from ref. 15.

^eSubstrate concentration of $1.0 \times 10^{-4} \text{ mol L}^{-1}$.

^fSubstrate concentration of $0.5 \times 10^{-4} \text{ mol L}^{-1}$.

^gFrom an Arrhenius equation extrapolation of values measured at higher temperatures (see Table 2).

^hInterpolated value.

ⁱ $k(40\text{EtOH})/k(97\text{TFE})$ value of 2.5 ± 0.2 .

^j $k(40\text{EtOH})/k(97\text{TFE})$ values of 1080 ± 90 .

Table 2 Calculated enthalpies (ΔH^\ddagger , kcal mol⁻¹) and entropies (ΔS^\ddagger , cal mol⁻¹ K⁻¹) of activation for solvolysis of benzoyl *p*-toluenesulfonate (**1**) and *p*-nitrobenzoyl *p*-toluenesulfonate (**2**) in various solvents^a

Substrate	Solvent	n^b	Temp/K ^c	ΔH^\ddagger ^d	ΔS^\ddagger ^d
1	100% EtOH	5	283.2	19.1±0.3	-3.6±1.2
	80% EtOH	4		20.8±0.2	7.8±0.9
	100% MeOH	4		18.0±0.1	-3.7±0.2
	95% Acetone	3		18.0±0.3	-13.5±1.1
	90% Acetone	3		19.5±0.2	-5.0±0.7
2	100% TFE	5	273.2	17.6±0.1	0.5±0.3
	97% TFE	5		19.2±0.2	6.9±0.8
	100% EtOH	5	283.2	13.7±0.1	-23.4±0.4
	80% EtOH	4		10.4±0.1	-32.4±0.4
	100% MeOH	5		14.7±0.2	-16.1±0.7
	100% MeOD	5		15.3±0.1	-21.7±0.4
	100% 1-PrOH	3	298.2	14.4±0.4	-27.6±1.4
	100% 2-PrOH	4	283.2	10.3±0.2	-33.7±0.7
	100% TFE	4		18.6±0.2	-12.9±0.7
	97% TFE	4		18.8±0.1	-11.5±0.4
	90% TFE	4		18.1±0.3	-12.3±1.1
	97% HFIP	4		17.6±0.2	-15.9±0.7
	90% HFIP	5		18.8±0.1	-11.3±0.4
	70% HFIP	5		17.7±0.3	-12.2±1.1
	50% HFIP	4		16.4±0.1	-15.2±0.2
90T-10E	4		18.3±0.3	-13.0±1.1	

^aUsing specific rates listed for various temperatures in Tables S1 and S2 of the supplementary data.

^bNumber of temperatures.

^cTemperature at which ΔH^\ddagger and ΔS^\ddagger values were calculated.

^dWith associated standard errors.

ionising power, such as aqueous ethanol, methanol, and acetone with low water content and with a unimolecular (ionisation) mechanism in these mixed solvents with higher water content and in fluoroalcohol-containing solvents and acetic and formic acids. A borderline region, with appreciable contributions from both mechanisms included 60% ethanol, 70% methanol, and 50% acetone.

Based on studies of a change from chloride to *p*-toluenesulfonate for alkyl and arylalkyl derivatives,^{17,18} one would predict that, for a given solvent, this change in nucleofuge would greatly increase the rate of the ionisation reaction and have only a moderate effect on the rate of bimolecular reaction. Accordingly, we would expect an expanded range of solvents for which the ionisation pathway is dominant for the solvolyses of **1**. Indeed, it would not be surprising to find that the ionisation pathway is dominant over most, if not all, of the range of solvents included in this study.

The analyses reported within Table 5 show that this is the case and, indeed, for solvolyses of **1** the full range of solvents can be well analysed using the simple Grunwald–Winstein equation [Equation (1)] with an m value of 0.73, correlation coefficient of 0.974 and an F-test value of 621 (Fig. 1). Use of the extended form [Equation (2)] leads to the introduction of a small l value of 0.11 ± 0.04 (with a 0.015 probability that the lN_T term is not statistically significant) accompanied by an m value of 0.80. There is only a very modest increase in the correlation coefficient, to 0.978, and the F-test value is now 364 (Fig. 2).

Also reported in Table 5 are correlations for the solvolyses of the *para*-nitro derivatives with chloride or tosylate as the leaving group. The chloride was studied in 35 solvents,³² and the extended Grunwald–Winstein equation gave a reasonably good correlation with values of 1.58 for l , 0.52 for m , 0.959 for the multiple correlation coefficient and 182 for the F-test

Table 3 Specific rates of solvolysis (k , s⁻¹) of benzoyl and *p*-nitrobenzoyl *p*-toluenesulfonates and chlorides in various solvents at 25.0 °C and leaving group ($k_{\text{OTs}}/k_{\text{X}}$) ratios, where X=Cl or F

Solvent ^a	$k(\text{C}_6\text{H}_5\text{CO}_2\text{Ts})^b$	$k(\text{C}_6\text{H}_5\text{COCl})^c$	$k_{\text{OTs}}/k_{\text{Cl}}$	$k_{\text{OTs}}/k_{\text{F}}^d$
100% Ethanol	1.20×10^{-2}	6.89×10^{-4} e	17.4	8.1×10^3
80% Ethanol	1.68×10^{-1} f	2.77×10^{-3} e,g	60.6	2.6×10^3
100% Methanol	5.88×10^{-2} f	4.27×10^{-3} e,g	13.8	4.8×10^3
95% Acetone	4.85×10^{-4}	5.51×10^{-5} h	8.81	6.1×10^3
90% Acetone	2.74×10^{-3}	1.7×10^{-4} i	16.1	4.7×10^3
100% TFE	1.08 f	1.96×10^{-3} j	551	
97% TFE	1.77 f	3.63×10^{-3} i,k	489	1.5×10^8

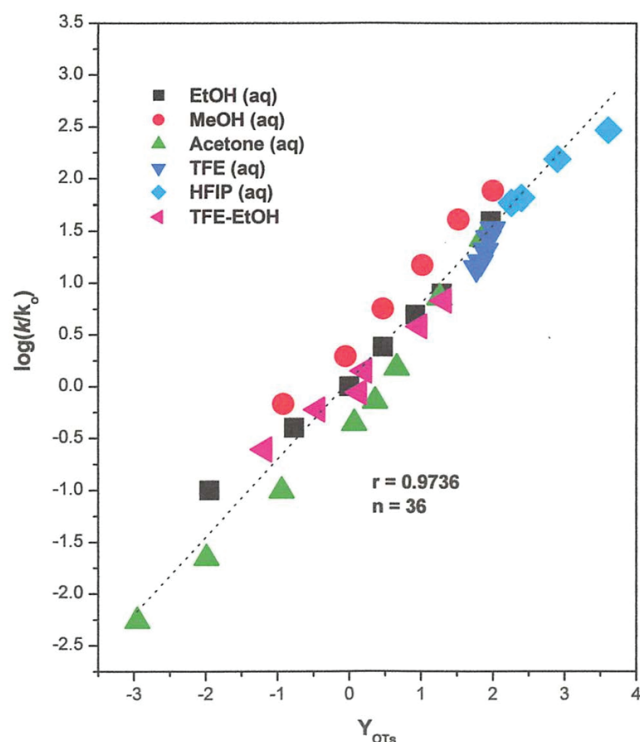
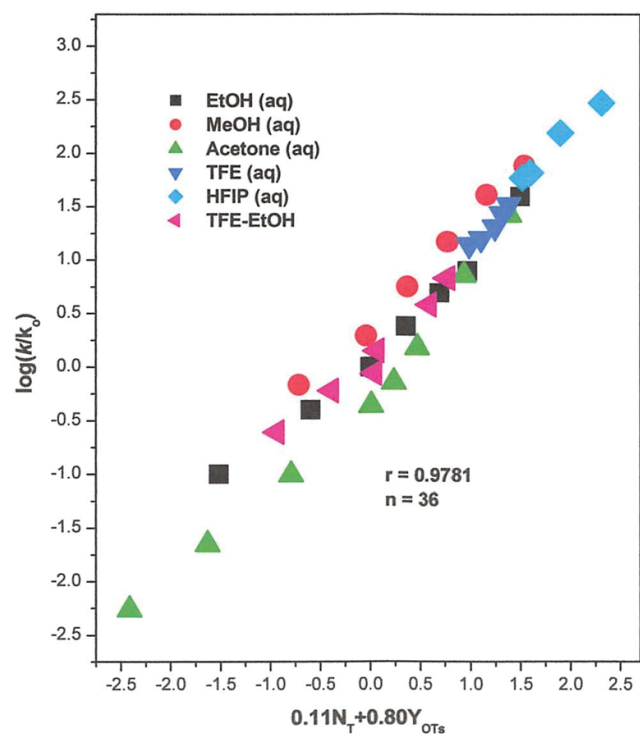
Solvent ^a	$k(p\text{NO}_2\text{C}_6\text{H}_4\text{CO}_2\text{Ts})^l$	$k(p\text{NO}_2\text{C}_6\text{H}_4\text{COCl})^c$	$k_{\text{OTs}}/k_{\text{Cl}}$
100% Ethanol	4.11×10^{-3}	2.15×10^{-2e}	0.19
80% Ethanol	2.33×10^{-2}	4.85×10^{-2e}	0.48
100% Methanol	1.06×10^{-2}	4.02×10^{-2e}	0.26
100% 2-Propanol	1.16×10^{-3}	1.20×10^{-3m}	0.99
100% TFE	2.22×10^{-4}	6.35×10^{-7n}	350
97% TFE	3.13×10^{-4}	9.9×10^{-6o}	31.6
90% TFE	6.66×10^{-4p}	6.6×10^{-5q}	10.1
97% HFIP	2.72×10^{-4}	1.77×10^{-6n}	154
90T-10E	3.22×10^{-4p}	4.7×10^{-5j}	6.85

^aSee footnote ^b to Table 1.^bValues from Table S1 or by an Arrhenius equation extrapolation of the values at other temperatures given within that table.^cLiterature values, source indicated by footnote.^dValues at 25.0 °C, k_{F} values from ref. 30.^eFrom ref. 24.^fExtrapolated value (Arrhenius equation).^gFrom ref. 25.^hFrom ref. 26.ⁱFrom ref. 27.^jFrom ref. 28.^kFrom ref. 29.^lUnless otherwise indicated, values from Table S2.^mFrom ref. 31.ⁿFrom ref. 32.^oFrom ref. 33.^pInterpolation (Arrhenius equation) within values of Table S2 at other temperatures.^qInterpolation within values at other solvent compositions at 25.0 °C by plotting $\log k$ against percentage by weight of TFE in the TFE-H₂O mixtures (values from Table 1 of ref. 28).**Table 4** Solvent deuterium isotope effects ($k_{\text{H}}/k_{\text{D}}$) for solvolyses of benzoyl *p*-toluenesulfonate (**1**) and *p*-nitrobenzoyl *p*-toluenesulfonate (**2**) in methanol and methan(ol-d) at various temperatures^a

(a)	Benzoyl <i>p</i> -toluenesulfonate (1)				
Temp/°C:	-10.0				
$k_{\text{H}}/k_{\text{D}}$ ^b	1.10 ± 0.01				
(b)	<i>p</i> -Nitrobenzoyl <i>p</i> -toluenesulfonate (2)				
Temp/°C	-10.0	0.0	10.0	20.0	25.0
$k_{\text{H}}/k_{\text{D}}$ ^b	1.84 ± 0.02	1.77 ± 0.03	1.75 ± 0.02	1.67 ± 0.02	1.59 ± 0.02

^aSpecific rate values at -10.0 °C from Table 1 and at other temperatures from Table S2.^bWith associated standard deviations.

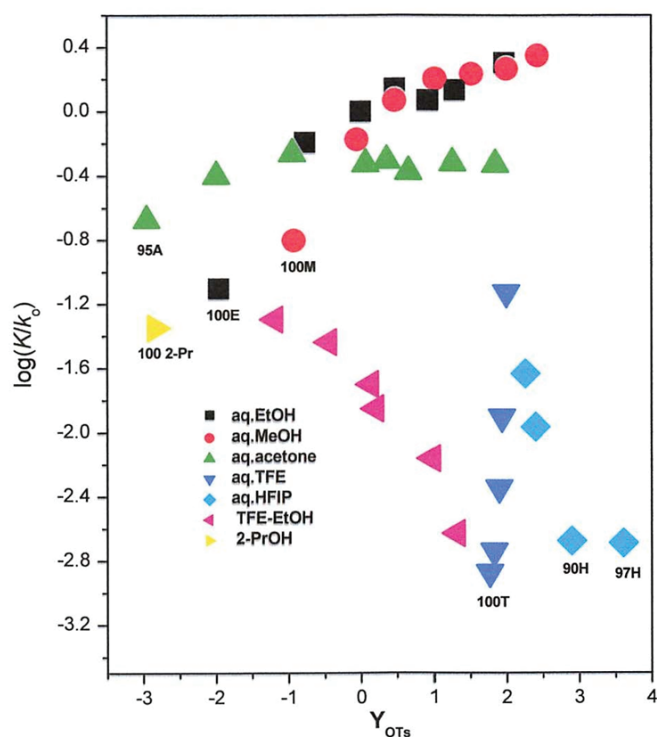
value. It could readily be seen that the 97% HFIP point lies above the plot, consistent with incursion of an appreciable component from an ionisation pathway for this solvent of lowest nucleophilicity and highest ionising power of the solvents used in the study. Omission of this data point from the correlation led to a modest increase to 1.78 in the l value and to essentially no change in the m value, with an increase in the correlation coefficient to 0.969 and in the F-test value to 237.

**Fig. 1** Plot of $\log(k/k_0)$ for solvolyses of benzoyl *p*-toluenesulfonate (**1**) in 36 solvents against Y_{OTs} values.**Fig. 2** Plot of $\log(k/k_0)$ for solvolyses of benzoyl *p*-toluenesulfonate (**1**) in 36 solvents against $(0.11 N_T + 0.80 Y_{\text{OTs}})$.

It is of interest to see whether there is any extension of this very limited range of solvent composition that has an appreciable contribution from an ionisation pathway when chloride is replaced by tosylate to give **2**. Application of the simple (one-term) equation (Fig. 3) leads to what is essentially a scatter plot (correlation coefficient of 0.294), suggesting that there is no far-reaching extension of the limited ionisation range and that a bimolecular reaction remains dominant. With

Table 5 Correlation of the specific rates of solvolysis of benzoyl and *p*-nitrobenzoyl *p*-toluenesulfonates (this study) and a comparison with literature values for other solvolyses at acyl carbon

Substrate/T°C	<i>n</i> ^a	<i>l</i> ^b	<i>m</i> ^b	<i>c</i> ^b	<i>l/m</i>	<i>R</i> ^c	<i>F</i> ^d
C ₆ H ₅ CO ₂ Ts (-10.0)	36 ^e		0.73±0.03	0.04±0.05		0.974	621
	36 ^e	0.11±0.04	0.80±0.04	0.11±0.06	0.14	0.978	364
<i>p</i> -NO ₂ C ₆ H ₄ CO ₂ Ts (-10.0)	37 ^e		-0.21±0.12	-0.76±0.19		0.294	3.3
	37 ^e	0.90±0.09	0.38±0.08	-0.18±0.11	2.37	0.880	58
	21 ^f	1.19±0.05	0.66±0.06	-0.13±0.06	1.80	0.983	265
C ₆ H ₅ COCl (25.0)	32 ^g	0.47±0.03	0.79±0.02	-0.49±0.17	0.59	0.990	680
	<i>p</i> -NO ₂ C ₆ H ₄ COCl (25.0)	35 ^h	1.58±0.08	0.52±0.05	0.00±0.46	3.04	0.959
34 ⁱ		1.78±0.08	0.54±0.04	0.11±0.37	3.30	0.969	237
<i>p</i> -MeOC ₆ H ₄ COCl (25.0)	37 ^h		0.72±0.03	-0.04±0.31		0.974	657
	37 ^h	0.31±0.05	0.81±0.02	0.08±0.21	0.38	0.989	738
CH ₃ CO ₂ Ts (-39.6)	13 ^j	0.56±0.10	0.61±0.05	-0.29±0.08	0.92	0.966	70
CH ₃ COCl (0.0)	30 ^k	0.83±0.06	0.72±0.04	0.00±0.07	1.15	0.953	134
	25 ^l	0.83±0.03	0.70±0.02	0.11±0.04	1.19	0.989	484
ClCH ₂ COCl (0.0)	34 ^k	1.40±0.05	0.40±0.03	0.11±0.05	3.50	0.978	342
PhOCOCl (25.0)	49 ^m	1.66±0.05	0.56±0.03	0.15±0.07	2.96	0.980	568
C ₆ H ₅ COF (25.0)	41 ⁿ	1.58±0.09	0.82±0.05	-0.09±0.10	1.93	0.953	186

^aNumber of solvents (data points).^bFrom equation (2), with associated standard errors, using Y_{OTs} or Y_{Cl} as appropriate.^cCorrelation coefficient.^dF-test value.^eUsing all available data points.^fOmitting the acetone–H₂O, TFE–ethanol, 100% TFE, and 97% HFIP data points.^gFrom ref. 32, using the solvolyses believed to follow an ionisation pathway (from the overall 47 measurements available).^hFrom ref. 32, using all solvents.ⁱFrom ref. 32, omitting the 97% HFIP data point.^jFrom ref. 9, using all solvents.^kFrom ref. 34, using all solvents.^lFrom ref. 34, omitting the five TFE–EtOH data points.^mFrom ref. 35, using all solvents.ⁿFrom ref. 30, using all solvents and Y_{Cl} values.**Fig. 3** Plot of $\log(k/k_0)$ for solvolyses of *p*-nitrobenzoyl *p*-toluenesulfonate (2) in 37 solvents against Y_{OTs} values.

application of the two-term equation (Eqn. (3)), using all 37 solvents, a poor correlation is obtained with an *l* value of 0.90, an *m* value of 0.38, a correlation coefficient of 0.880, and an F-test value of 58. Examination of a plot of $\log(k/k_0)$ against $(0.90N_T + 0.38 Y_{OTs})$ indicates that, as one would predict, the 97% HFIP, previously showing upward deviation for plots involving the corresponding chloride, also shows this deviation for the tosylate. With the tosylate, the 100% TFE point also shows a deviation. In addition, there are two mixed solvent systems that show considerable deviation. The TFE–EtOH mixtures lie below the plot. This is not surprising as this is commonly observed when bimolecular reactions are being treated in terms of the extended equation. This phenomenon has been discussed previously.³⁶

Somewhat more surprising, but not unprecedented,^{37,38} is the observation that the rates of solvolysis, and hence the $\log(k/k_0)$ values, show little change with variation in the composition of aqueous acetone solvents. Unexpected behaviour was observed earlier in a study by Halmann³⁹ of the solvolyses of chlorodipropylphosphine in ethanol–acetone mixture, where it was found that addition of acetone, expected to reduce the specific rates, actually led to *increases* in the values. It has been observed⁴⁰ in nucleophilic substitution reactions of 2-octyl sulfonates that acetone (and also dioxane) is capable of showing appreciable nucleophilicity and can initially compete with methanol or water during the substitution process. In acetone–methanol mixtures, the initial acetoxonium ion was

further converted into the alcohol, which would not have been formed if products were formed only by attack of the methanol component. Based on plots against Y_{OTs} values, larger than expected specific rates have also been found for solvolyses in acetone–water mixtures rich in acetone of 1-adamantyl picrate, 2-adamantyl trifluoromethanesulfonate and 2-adamantyl perchlorate.⁴¹

We have carried out further correlations, using Equation (3), of the rates of solvolysis of **2** with omission of the TFE–EtOH and/or aqueous acetone deviating solvent mixtures. Since the 97% HFIP plot was already deviant for the chloride; it would also be predicted to deviate from the two-term plot for the tosylate. It was found that the best plot (highest correlation coefficient and F-test value) was for 21 solvents, with those just mentioned plus 100% TFE omitted (Table 5 and Fig. 4). The m value of 0.66 is consistent with other determinations in the table believed to be bimolecular in nature, a value of 0.54 had previously been obtained³² for the corresponding chloride. The l value of 1.19 is, however, considerably lower than the 1.78 for the chloride.

One aspect to be considered is how good is the Y_{OTs} scale for solvolyses of **2** by the addition–elimination mechanism with the addition step rate-determining. Since the scale is rather different, in particular being condensed, from the Y_{Cl} scale and the Y_{Cl} scale has been found to be an acceptable scale for a process involving movement of the π electrons onto an oxygen atom, one would anticipate that the Y_{OTs} scale could be inferior in analysing this process. We have previously argued in a consideration of benzoyl fluoride solvolyses,³⁰ where no Y_{F} scale is available, that Y_{Cl} would be a good substitute when negative charge was developing on the atom that started in the reactants as the carbonyl oxygen (Scheme 2b). The Y_{OTs} scale, with the negative charge dispersed among the oxygens of the developing tosylate anion when the standard solvolyses of 1- and 2-adamantyl tosylate are studied, would not be predicted to

be a scale of choice when the charge is developing on a single atom.

The difference between Y_{Cl} and Y_{OTs} values is encouraging but differences alone are not sufficient for a meaningful consideration in terms of goodness-of-fit values. There is also a requirement that the two scales do not correlate with each other. In this regard, the scales have been plotted against each other in the review by Bentley and Llewellyn.¹⁵ Eleven solvents were included in the plot and it was found that ethanol and four ethanol–water mixtures gave a good correlation ($r=0.998$) and the plot of Y_{Cl} against Y_{OTs} had a slope of 1.28 ± 0.04 . However, water, formic acid, acetic acid, and trifluoroacetic acid lay below the plot and 97% HFIP and 97% TFE lay above the plot. We have extended the correlation and have plotted Y_{OTs} against Y_{Cl} for the 37 solvents used in the correlation of the solvolysis kinetics of **2** (listed in Table 1). We find a very good correlation, with a slope of 0.731 ± 0.014 , intercept of -0.146 ± 0.032 , correlation coefficient (r) of 0.994 and F-test value of 2874. The slope must be compared with the inverse of that from the Bentley and Llewellyn correlation.¹⁵ This value of 0.781 ± 0.024 is in very good agreement with the presently reported value.

Bentley, Carter and Roberts⁴² carried out a correlation of Y_{OTs} against Y_{Cl} using all of the paired data available at that time. For 34 paired data points they obtained a good correlation with a slope of 0.80 ± 0.02 . It is clear that the correlation of the two scales is very robust with all three correlations with from five to 37 data points giving almost identical slopes.

Accordingly, it appears that comparisons of correlations using Y_{Cl} or Y_{OTs} are not going to be helpful in assigning mechanism. It follows from the direct correlation of Y_{OTs} against Y_{Cl} that the goodness-of-fit parameters will be very similar and, if the two-term Grunwald–Winstein equation is used, so also will be the l values. The m values will differ such that the $m_{\text{OTs}}/m_{\text{Cl}}$ ratio will be the inverse of the $Y_{\text{OTs}}/Y_{\text{Cl}}$ ratio, so as to give identical mY contributions to Equation (2).

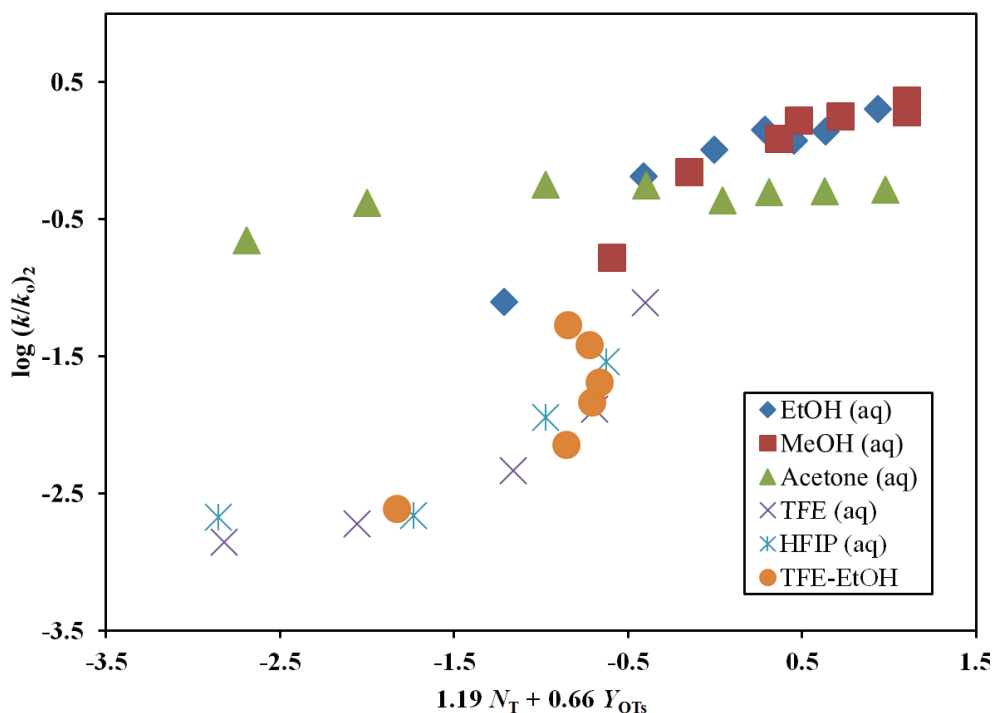


Fig. 4 Plot of $\log(k/k_0)$ for solvolyses of *p*-nitrobenzoyl *p*-toluenesulfonate (**2**) in 21 solvents against $(1.19 N_T + 0.66 Y_{\text{OTs}})$. The 16 data points for Acetone–H₂O, TFE–EtOH, 97% HFIP and 100% TFE are not included in the correlation; they are added to the plot to show the extent of their deviation from the regression line.

We have shown this to be the case for both compounds **1** and **2**, with use of both one and two term Grunwald–Winstein equations, and for varying combinations of solvents. For example, for compound **2** with use of all 37 solvents, a treatment using N_T and Y_{Cl} values leads to values for l of 0.92 ± 0.09 , for m of 0.29 ± 0.07 , for R of 0.876, and for the F -test value of 56. The l , R , and F values are very similar to those of Table 5, which are obtained with use of Y_{OTs} rather than Y_{Cl} values. The m value can be compared to a value of 0.38 ± 0.08 with use of Y_{OTs} for an m_{OTs}/m_{Cl} ratio of 1.31 ± 0.58 , in agreement with the correlation between Y_{OTs} and Y_{Cl} values. When solvolyses that deviate due to differences in behaviour from the standard systems (acetone–water and TFE–ethanol) or due to a change in mechanism in the more highly ionising and low nucleophilicity solvents are omitted, we are left with 21 solvents for which the solvolyses of **2** give a very good correlation using N_T and Y_{OTs} , with the results reported in Table 5. With Y_{Cl} values substituted for Y_{OTs} , the new correlations lead to values of 1.27 ± 0.06 for l , 0.51 ± 0.04 for m , 0.986 for R , and 312 for F . The l , R and F values are all very close to those reported in Table 5. The m_{OTs}/m_{Cl} ratio of 1.29 ± 0.22 is again in excellent agreement with the 1.37 ± 0.03 from the direct correlation of the two Y scales. The large errors for the ratio obtained from the correlations of **2** are mainly due to a large contribution to the multiple regression analysis from the lN_T term.

It is also possible to get useful but less reliable mechanistic information from a restricted number of solvents.¹⁵ Indeed, a comparison of the specific rates in only two solvents can give information concerning the extents of nucleophilic participation if the solvent ionising power values are similar and there are appreciable differences in the solvent nucleophilicity values. For example, 40% ethanol and 97% TFE have similar Y_{OTs} values (1.97 and 1.83) but very different N_T values (−0.74 and −3.30) and the ratio (k_{40EtOH}/k_{97TFE}) of specific rates of a solvolysis in the two solvents will increase with increasing nucleophilic participation. The values for 2-adamantyl tosylate (1.38) and 1-adamantyl chloride (0.83) are, for example, consistent with the well-documented absence of nucleophilic participation.¹⁵

In the present study, the k_{40EtOH}/k_{97TFE} ratios of 2.5 for benzoyl tosylate (**1**) and 1080 for *p*-nitrobenzoyl tosylate (**2**) (footnotes to Table 1) are nicely consistent with the proposed ionisation pathway for **1** and, for most solvents, an addition–elimination pathway for **2**.

There is, of course, the basic assumption that the mechanism does not change on going from 40% ethanol to 97% TFE and many examples of such a change in mechanism have been reported.³⁴ Changes of this nature would be obvious in Grunwald–Winstein treatments^{32,34} but not in comparisons using only two data points. Indeed, the ratio of 1080 for **2** may be somewhat low when considered in terms of the addition–elimination pathway because of the probability of a minor component from an essentially ionisation pathway towards the solvolysis in the low nucleophilicity 97% TFE. This is indicated by the k_{OTs}/k_{Cl} value of 32 as opposed to 350 and 154 in 100% TFE and 97% HFIP and values at the other extreme of 0.2 to 7 in pure alcohols, 80% ethanol and 90% TFE–10% ethanol.

The solvent deuterium isotope effect in methanolyses has been found to be useful for mechanistic investigations of the solvolyses of acyl halides. Those believed to be bimolecular, but with additional incursion of a second solvent molecule to give general-base catalysis, show quite large values, in the range of 2.1–4.0. A tabulation of literature values has been given.⁹ For reactions indicated by extended Grunwald–Winstein treatments to have only moderate sensitivities to changes in solvent nucleophilicity (l values), lower k_{MeOH}/k_{MeOD} values are

obtained, with a value of 1.29 for acetyl chloride.⁴³ For other aliphatic acyl chlorides, values in the range of 1.38 to 1.48 were observed.^{21,44} For acetyl tosylate, a value of 0.99 ± 0.04 was recorded⁹ at −39.6 °C. In the present investigation (Table 4), values very different to each other are obtained for **1** and **2**. At −10.0 °C, the value of 1.10 ± 0.01 for **1** suggests a methanolysis without general-base catalysis and with considerable ionisation character, as was proposed for the methanolyses of acetyl chloride and tosylate.⁹ However, the value of 1.84 ± 0.02 for **2**, reducing gradually to 1.59 ± 0.02 at 25.0 °C as the temperature is increased, suggests reaction through an addition–elimination mechanism, with the rate-determining addition being subject to general-base catalysis by a second methanol molecule.

The entropies of activation (tabulated in units of $\text{cal mol}^{-1} \text{K}^{-1}$, sometimes referred to as entropy units, e.u.) reported in Table 2 are for **1** fairly close to zero, with sometimes small negative and sometimes small positive values. For **2**, the corresponding values are uniformly negative, in the range of −11 to −32 $\text{cal mol}^{-1} \text{K}^{-1}$. Such behaviour, as observed for the solvolyses of alkyl halides and sulfonates, has been rationalised in terms of unimolecular and bimolecular solvolyses.^{45,46} In the present instance, the values are consistent with the conclusions from Grunwald–Winstein correlations and solvent deuterium isotope effects.

The use of leaving group effects can be useful in elucidating mechanisms of substitution reactions. The interpretation was initially only in terms of electronic effects^{17,18} but the situation became more complicated when it was realised⁴⁷ that the very large effects observed for crowded tertiary structures in S_N1 reactions reflected, to a major degree, the much greater relief of steric strain during the departure of a bulky tosylate group than during the departure of bromide in the determination of k_{OTs}/k_{Br} ratios. In the present consideration of the solvolyses of acyl derivatives with the substitution occurring at an sp^2 -hybridised carbon, with much reduced steric interactions, lower ratios would be expected than the 10^3 , or greater, values that have been recorded previously.¹⁹

For bimolecular S_N2 reactions, values have been close to unity, or even considerably lower, for attack by powerful nucleophiles. For the looser S_N2 transition state believed to be operative for the solvolyses of the acetyl derivatives in 90% acetone, a k_{OTs}/k_{Br} ratio of 1.4 was observed.⁹ Unfortunately, for the present investigation, although there is a wealth of values for the chlorides, the bromide corresponding to **2** does not seem to have been studied under the commonly used solvolytic conditions. There is, however, a study of several aryl bromides,⁴⁸ including the parent benzoyl bromide, undergoing solvolysis in a variety of pure and binary hydroxylic solvents. We can compare the specific rates of solvolysis of **1** with those of benzoyl bromide at −10.0 °C, to give k_{OTs}/k_{Br} ratios of 0.20 for 100% methanol, 0.47 for 90% methanol, and 1.1 for 80% methanol. At 25.0 °C, values are obtained of 0.20 for 100% ethanol and 0.084 for 90% acetone.

If we accept the claim⁴⁸ that benzoyl bromide, like the chloride, undergoes a change in mechanism induced by the variation of solvent, with a bimolecular mechanism dominating in solvents of relatively high nucleophilicity and relatively low electrophilicity, then the above mentioned k_{Br} values will relate to the bimolecular pathway. The Grunwald–Winstein treatments of **1** (Figs 1 and 2 and Table 5) strongly indicate a unimolecular pathway across the full range of k_{OTs} values for solvolyses of **1**.

It follows that the low k_{OTs}/k_{Br} experimental values reported above must be even lower for the bimolecular pathway for both the tosylate and bromide. The *p*-nitrobenzoyl tosylate

(2) was found (Fig. 4 and Table 5) to react by the bimolecular pathway in ethanol and methanol and the aqueous binary mixtures of each with appreciable alcohol content. Although, the *p*-nitro derivative was not included in the Liu study,⁴⁸ there was a study of the *p*-chloro derivative, which lies, as regards reactivity, between the parent and the *p*-nitro compound. In 100% methanol at 25.0 °C, the specific rate of solvolysis was $43.8 \times 10^{-2} \text{ s}^{-1}$, which can be taken as a minimum value for the faster reacting *p*-nitro derivative. Using this specific rate of methanolysis of *p*-chlorobenzoyl bromide as k_{Br} in the $k_{\text{OTs}}/k_{\text{Br}}$ ratio, with k_{OTs} being the value for the *p*-NO₂ derivative, leads to a maximum value of the ratio for methanolyses of the *p*-nitro derivatives of 0.024. Extrapolation of specific rates for benzoyl bromide and *p*-chlorobenzoyl bromide using a two-point Hammett plot leads to a *very* approximate specific rate for the *p*-nitrobenzoyl bromide at 25.0 °C of 8.2 and an approximate $k_{\text{OTs}}/k_{\text{Br}}$ for the *p*-nitrobenzoyl substrates of 0.0013. Although very approximate, there is no doubt that, as predicted, the ratio is considerably lower than the values in the range of 0.034 to 1.07 when experimental values (involving unimolecular and bimolecular pathways) are considered.

The indications from treatment using extended Grunwald–Winstein plots is that, in binary mixtures with water, a high ethanol, methanol, or acetone content leads to unimolecular solvolyses of **1** but to bimolecular solvolyses of the corresponding chloride. While ratios can be calculated they will not, as in the tosylate/bromide comparison, be directly relevant to reaction mechanism studies. The ratios are found to be quite small with values in the range of 8 to 60 for those considered in Table 3. In 100% TFE and 97% HFIP, both substrates are considered to react by the unimolecular pathway but with varying degrees of nucleophilic assistance (more for the chloride). Ratios of about 500 are now observed (Table 3), appreciable values but less than for the solvolyses of crowded tertiary alkyl structures.

For the *p*-nitrobenzoyl derivatives, both substrates are believed to solvolyse predominantly by the bimolecular mechanism in all but 97% HFIP for the chloride and in all but 100% TFE and 97% HFIP for the tosylate. The $k_{\text{OTs}}/k_{\text{Cl}}$ ratios are less than unity in ethanol, 80% ethanol, methanol and propan-2-ol (Table 3). Higher values, similar to those observed for solvolyses of the benzoyl derivatives, of 154 and 350 are observed in 97% HFIP and 100% TFE. The ratio of 350 in 100% TFE is similar to the value of 551 for solvolyses of the benzoyl derivatives in that solvent, consistent with both pairs of substrates (tosylate and chloride) solvolysing by the ionisation pathway in this solvent.

Conclusions

The mixed anhydrides of carboxylic and sulfonic acids undergo solvolyses with substitution at the carbonyl carbon and ejection of a sulfonate anion. The earlier studied⁹ acetic *p*-toluenesulfonic anhydride (acetyl tosylate) solvolysed rapidly and could only be studied in appropriate solvents at considerably reduced temperatures.⁹ Aroyl tosylates are less reactive. For example, in ethanol at –20 °C the benzoyl tosylate reacts 2.5×10^4 times more slowly than acetyl tosylate. At –10.0 °C a wide range of solvolyses could be studied using rapid-response conductivity measurements and other values were obtained from extrapolation of values obtained at several higher temperatures.

Grunwald–Winstein correlations were carried out (Table 5). For benzoyl tosylate (**1**), it was found that the original (one-term) equation gave a good correlation (Fig. 1) and the two-term equation gave only a slightly higher correlation coefficient and a considerably reduced F-test value (Fig. 2). The sensitivity *l* to

changes in solvent nucleophilicity of only 0.11 ± 0.04 , coupled with a sensitivity to changes in solvent ionising power (*m*) of 0.80 ± 0.04 , strongly indicates an ionisation mechanism with a weak nucleophilic solvation of the developing acylium ion.

For the correlations of the *p*-nitro derivative (**2**), very different behaviour was indicated by the Grunwald–Winstein treatments. Correlation against only Y_{OTs} for the solvolysis in 37 solvents led to a scatter plot (Fig. 3) with extremely low values for the correlation coefficient (0.294) and the F-test value (33). Application of the two-term equation gave an improved but still unacceptable correlation (Table 5). For 21 “well-behaved” solvolyses, values for *l* and *m* were consistent with an addition–elimination mechanism with addition rate-determining and the correlation coefficient (0.983) and F-test values (265) were considerably improved.

We also applied four additional criteria with results that were fully consistent with the conclusions from the Grunwald–Winstein correlations.

- Solvent deuterium isotope effects in the methanolyses of **1** and **2** in methanol or methan(ol-d) have been analysed in terms of $k_{\text{H}}/k_{\text{D}}$ ratios. At –10.0 °C, values were obtained of 1.10 ± 0.01 for **1** and 1.84 ± 0.02 for **2**. These are consistent with the proposed appreciable ionisation character for the methanolysis of **1** and the addition–elimination pathway, with the addition assisted by general-base catalysis within the rate-determining step, for the methanolysis of **2**.
- The entropies of activation of close to zero for solvolyses of **1** are in contrast to those for **2** which are uniformly negative, in the range of –11 to –32 cal mol^{–1} K^{–1}. Such behaviour has been rationalised in terms of unimolecular and bimolecular processes.^{45,46}
- The $k_{\text{OTs}}/k_{\text{Cl}}$ ratios for **1** and the corresponding chloride (Table 3) are in the range of 9 to 61 in ethanol, 80% ethanol, methanol and 95% or 90% acetone. In the more ionising and less nucleophilic 100% and 97% TFE, the values increase to about 500, consistent with an ionisation mechanism for *both* types of substrate. In the 100% TFE and 97% HFIP, compound **2** and the corresponding chloride show similar large values of 350 and 154 but lower ratios, consistent with the proposed addition–elimination pathway, of 0.2 to 32 are observed as the solvent changes from 100% ethanol to 97% TFE.
- The ratio for the solvolyses of a given substrate of $k_{40\% \text{EtOH}}/k_{97\% \text{TFE}}$ (specific rates of solvolysis in 40% ethanol and 97% TFE) can give an indication of the importance of changes in solvent nucleophilicity, since the ionising powers of the solvents are almost identical. Values of 2.5 for **1** and 1080 for **2** are consistent with the proposed ionisation pathway for **1** and addition–elimination pathway for **2**.

Experimental

The benzoyl *p*-toluenesulfonate (**1**) and *p*-nitrobenzoyl *p*-toluenesulfonate (**2**) were prepared by the method of Overberger and Sarlo.⁵ Equimolar amounts of the corresponding chloride and silver *p*-toluenesulfonate were reacted in dry acetonitrile. A very rapid precipitation of silver chloride occurred and the solution could be used directly as a source of the substrate. For **1**, a 0.3 M solution was prepared and 4.0 μL added to 2.0 mL of the appropriate solvent maintained in a conductivity cell at the required temperature, to give a $6.0 \times 10^{-4} \text{ mol L}^{-1}$ solution of the reactant. For **2**, a 0.03 M solution was prepared and 20 μL added to the 2.0 mL of solvent, to give a $3.0 \times 10^{-4} \text{ mol L}^{-1}$ solution. In a few instances, a different concentration of **1** or **2** was used, details of such instances are reported as footnotes to Table 1.

In some instances, **2** was isolated, with melting points in agreement with that measured⁵ earlier and with an excellent elemental analysis (C, H, N). When the 0.03 M stock solution in acetonitrile was prepared by redissolving the isolated solid, the observed kinetics were in excellent agreement with those obtained without intermediate isolation of the substrate. In a typical isolation, *p*-nitrobenzoyl chloride (9.2 g) was reacted with silver *p*-toluenesulfonate (13.9 g) in acetonitrile (40 mL) to give on workup⁵ (2 8.5 g, 61%), m.p. 166–167 °C (lit.⁵ 167–169 °C). Anal. calcd for C₁₄H₁₁NO₆S: C, 52.33; H, 3.45; N 4.36; found: C, 52.21; H, 3.38; N, 4.33% (PerkinElmer 2400 CHN elemental analyser).

The progress of the reaction was followed by following the conductivity changes as *p*-toluenesulfonic acid was produced, as previously described.⁹ Details of the conductivity apparatus and the computer procedure for calculation of the specific rates have previously been reported.^{49,50}

Since the variation of specific rates of solvolysis of **2** in aqueous acetone mixtures was considerably reduced from what had been observed for various acyl chlorides and chloroformate esters, we repeated the measurements, with new preparations of the mixed solvents and substrate. Excellent agreement was observed between the two sets of measurements. The multiple regression analyses were performed using commercially available statistical packages.

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Electronic Supplementary Information

Tables S1 and S2 available through stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data give the specific rates used in the Eyring equation calculations (Table 2) which are additional to those reported in Table 1.

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