Rate and product studies in the solvolyses of two arenesulfonic anhydrides
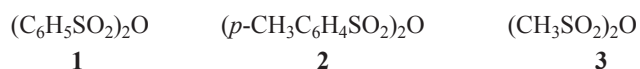
Dennis N. Kevill[a]* and Zoon Ha Ryu[b]

[a]Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, Illinois 60115-2862, USA

[b]Department of Chemistry, Dong-Eui University, 24 Kaya-dong, Busan-Jin-Gu, Busan 614-714, Korea

The specific rates of solvolysis of benzenesulfonic anhydride (**1**) and *p*-toluenesulfonic anhydride (**2**) have been measured conductometrically at –10°C in 34 solvents for **1** and 33 solvents for **2**. Studies at higher temperatures have allowed extrapolated values in additional solvents to be calculated. All of the values, for 35 solvents for **1** and for 37 solvents for **2**, have been used in an extended Grunwald–Winstein equation treatment using N_T and Y_{OTs} values. Activation parameters in several solvents and kinetic solvent isotope effects (MeOH/MeOD) have been determined for both substrates. Product selectivity values (*S*) have been determined for binary mixtures of water with ethanol, methanol, or 2, 2, 2-trifluoroethanol. The results from the kinetic and product studies are compared to those previously reported for methanesulfonic anhydride (**3**). An S_N2 mechanism is proposed for the solvolytic displacement reactions of the three substrates in all of the solvents used in the investigation.

Keywords: solvolysis, arenesulfonic anhydrides, Grunwald–Winstein equation, selectivity

We report a kinetic and product study of the solvolyses of two arenesulfonic anhydrides: benzenesulfonic anhydride (**1**) and *p*-toluenesulfonic anhydride (**2**). We have previously reported [1] a parallel study of the solvolyses of an alkanesulfonic anhydride: methanesulfonic anhydride (**3**).

$$(C_6H_5SO_2)_2O \qquad (p\text{-}CH_3C_6H_4SO_2)_2O \qquad (CH_3SO_2)_2O$$
$$\textbf{1} \qquad\qquad\qquad \textbf{2} \qquad\qquad\qquad \textbf{3}$$

There have only been a few mechanistic studies involving substitution reactions of sulfonic anhydrides,[1-5] some of which[1,3-5] involve their solvolysis reactions.

Christensen[3] showed that the solvolyses of arenesulfonic anhydrides in aqueous acetone and dioxane were 100–400 fold faster than the corresponding solvolyses of the arenesulfonyl chloride. The specific rates were conveniently determined by a stopped-flow technique. An extension to determine the kinetic isotope effect (k_{H_2O}/k_{D_2O}) in aqueous acetone and dioxane led to values in the range [2] of 1.2–1.4, significantly lower than values of 1.5–1.8 determined[6,7] for sulfonyl chlorides (RSO_2Cl) under similar conditions. The original[8] (simple) Grunwald–Winstein equation [eqn (1)] was applied and a low *m* value was taken to imply that the

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

mechanism was S_N2 in character in most solvents. However, an increase in *m* value to 0.72 for the solvolyses of **2** with 60–76% water was taken to indicate a change to a more S_N1-like mechanism. This interpretation was probably influenced by a slightly earlier claim that the hydrolyses of sulfonyl chlorides in water-rich aqueous dioxane proceed by the S_N1 mechanism.[9] In eqn (1), *k* and k_o represent the specific rates of solvolysis of the substrate in the solvent under consideration and in the standard solvent (80% ethanol), *m* is the sensitivity towards changes in solvent ionising power (*Y*), and *c* is a constant (residual) term. When nucleophilic participation by the solvent is an important factor, an extended form of the original Grunwald–Winstein equation, incorporating the sensitivity (l) to changes in solvent nucleophilicity (N) is recommended.[10-13] [eqn (2)].

$$\log(k/k_o) = l\ N + m\ Y + c \qquad (2)$$

Application of this equation to the solvolyses of methanesulfonic anhydride[1] and several sulfonyl chlorides[1,14,15] has given no evidence for a unimolecular pathway, and the appreciable *l* values obtained have provided good evidence for bimolecular character. Even in solvents of low nucleophilicity

* Correspondent. E-mail: dkevill@niu.edu

and high ionising power, incorporating high percentages of 2,2,2 – trifluoroethanol (TFE) or 1,1,1,3,3,3 – hexafluoro-2-propanol (HFIP), no evidence for a change to a unimolecular pathway was obtained.

In binary mixtures of hydroxylic solvents, R^1OH and R^2OH, selectivity values (*S*) can give useful information about reaction mechanism [eqn (3)]. Studies of the

$$S = \frac{[\text{Product from } R^1OH \text{ attack}]\ [R^2OH \text{ in solvent}]}{[\text{Product from } R^2OH \text{ attack}]\ [R^1OH \text{ in solvent}]} \qquad (3)$$
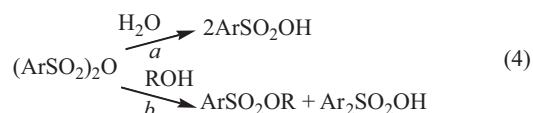
product partitioning can be especially useful if a change in the trend of *S* values during systematic variation of solvent composition is observed. This can be indicative of a change in mechanism and evidence of this type is considerably strengthened if changes in the sensitivities to variations in solvent nucleophilicity and ionising power (*l* and *m* values) are observed in the same region of solvent composition.[16,17]

Results

The specific rates of solvolysis were determined at –10.0°C in 34 solvents for **1** and in 33 solvents for **2**. The solvents consisted of ethanol, methanol and TFE and their binary mixtures with water, binary mixtures of water with acetone or HFIP, and TFE-ethanol mixtures. The values are reported in Table 1 together with one value for **1** and four values for **2** obtained for HFIP-water mixture by Arrhenius equation extrapolation of values (from Table 2) obtained at higher temperatures. Also contained within Table 1 are the solvent nucleophilicity (N_T)[12,13] and solvent ionising power (Y_{OTs})[11,18-20] values.

In addition to the specific rates at higher temperatures for four HFIP–water compositions, specific rates at temperatures other than –10.0°C are also reported in Table 2 for 100% and 80% ethanol, 100% methanol, and 100% and 97% TFE. The enthalpies and entropies of activation using the entries from Table 2 and (when determined at –10.0°C) from Table 1, are reported in Table 3.

The percentages of reaction with water and alcohol for solvolyses in water–alcohol mixtures can be estimated from the infinity acid titres. Reaction with water produces two equivalents of acid and with alcohol only one equivalent of acid [eqn (4)]. The percentages of reaction with water can be calculated by

$$(ArSO_2)_2O \begin{array}{c} \xrightarrow[a]{H_2O} 2ArSO_2OH \\ \xrightarrow[b]{ROH} ArSO_2OR + Ar_2SO_2OH \end{array} \qquad (4)$$

Table 1 Specific rates of solvolysis (k) of benzenesulfonic anhydride (**1**) and p-toluenesulfonic anhydride (**2**) at –10.0°C and N_T and Y_{OTs} values for the solvents[a]

Solvent[b]	$10^3k(\mathbf{1})$/s^{-1c}	$10^3k(\mathbf{2})$/s^{-1c}	N_T[d]	Y_{OTs}[e]
100% EtOH	5.15 ± 0.05	3.66 ± 0.08	0.37	–1.95
90% EtOH	13.9 ± 0.3	8.84 ± 0.19	0.16	–0.77
80% EtOH	21.9 ± 0.5	15.7 ± 0.8	0.00	0.00
70% EtOH	30.7 ± 1.1	19.8 ± 0.3	–0.20	0.47
60% EtOH	41.6 ± 1.3	33.5 ± 0.9	–0.38	0.92
50% EtOH	65.9 ± 0.1	48.3 ± 0.5	–0.58	1.29
40% EtOH	184 ± 10	108 ± 2	–0.74	1.97
100% MeOH	21.1 ± 0.3[f]	14.6 ± 0.1[g]	0.17	–0.92
90% MeOH	55.2 ± 1.9	38.2 ± 0.7	–0.01	–0.05
80% MeOH	126 ± 8	74.5 ± 0.8	–0.06	0.47
70% MeOH	242 ± 9	129 ± 5	–0.40	1.02
60% MeOH		217 ± 6	–0.54	1.52
95% Acetone	0.232 ± 0.005	0.103 ± 0.016	–0.49	–2.95
90% Acetone	0.602 ± 0.002	0.207 ± 0.008	–0.35	–1.99
80% Acetone	1.71 ± 0.03	0.680 ± 0.008	–0.37	–0.94
70% Acetone	4.13 ± 0.01[h]	1.62 ± 0.04[h]	–0.42	0.07
65% Acetone		2.35 ± 0.18	–0.48[i]	0.36[i]
60% Acetone	7.89 ± 0.06	3.97 ± 0.04	–0.52	0.66
50% Acetone	27.2 ± 0.7	10.3 ± 0.4	–0.70	1.26
40% Acetone	73.9 ± 0.7	25.8 ± 1.6	–0.83	1.85
30% Acetone	133 ± 4	103 ± 6	–0.96	2.50
100% TFE[j]	0.108 ± 0.001[k]	0.263 ± 0.005	–3.93	1.77
97% TFE[j]	0.286 ± 0.001	0.466 ± 0.012	–3.30	1.83
90% TFE[j]	0.790 ± 0.009	1.14 ± 0.01[k]	–2.55	1.90
80% TFE[j]	1.87 ± 0.03	2.44 ± 0.04	–2.19	1.94
70% TFE[j]	3.33 ± 0.08	3.89 ± 0.10	–1.98	2.00
50% TFE[j]	7.38 ± 0.05	7.33 ± 0.11	–1.73	2.14
97% HFIP[j]	0.0495[l]	0.102[l]	–5.26	3.61
90% HFIP[j]	0.148 ± 0.003	0.511[l]	–3.84	2.90
70% HFIP[j]	1.28 ± 0.02	1.72[l]	–2.94	2.40
50% HFIP[j]	2.64 ± 0.03	2.57[l]	–2.63	2.26
90T-10E[m]	1.76 ± 0.03	2.27 ± 0.06	–2.62[i]	1.32[i]
80T-20E[m]	3.31 ± 0.06	3.85 ± 0.04	–1.76	0.98
60T-40E[m]	6.81 ± 0.08	5.76 ± 0.09	–0.94	0.21
50T-50E[m]	8.48 ± 0.12	7.55 ± 0.04	–0.64[i]	0.14[i]
40T-60E[m]	9.61 ± 0.06	7.38 ± 0.11	–0.34	–0.44
20T-80E[m]	8.95 ± 0.13	6.37 ± 0.03	0.08	–1.18[i]

[a]Substrate concentration of 6.0×10^{-4} M for **1** and 1.5×10^{-4} M for **2** and unless otherwise indicated all runs performed at least in duplicate. [b]Unless otherwise indicated, on a volume–volume basis at 25.0°C, with the other component water (each solvent also contains 0.2% of CH_3CN). [c]With associated standard deviations. [d]From refs 12 and 13. [e]From refs 11, 18–20. [f]Also a value of 15.4 ± 0.1 in methanol-d (MeOD) for a k_{MeOH}/k_{MeOD} ratio of 1.37 ± 0.03. [g]Also a value of 10.4 ± 0.2 in methanol–d (MeOD) for a k_{MeOH}/k_{MeOD} ratio of 1.40 ± 0.03. [h]An Arrhenius equation extrapolation of data for 69.4% acetone at 15–42°C, from ref 3, leads to a value of 5.80 for **1** and of 1.95 for **2**. [i]Obtained by interpolation. [j]On a weight–weight basis. [k]Single run. [l]From Arrhenius equation, extrapolation of data from Table 2. [m] T–E are TFE–ethanol mixtures.

taking the excess titre over that for reaction in 100% ethanol (all pathway *b*) relative to the corresponding excess titre for solvolysis in 60% acetone (all pathway *a*). Values from duplicate experiments were recorded at 10, 15, and 20 half lives. Since no variation was observed over these time ranges, the values reported in Table 4 are based on the average of the six determinations for each binary composition. Determinations were carried out for solvolyses of both **1** and **2** in mixtures of water with ethanol, methanol, or TFE. Also reported in Table 4 are the *S* values calculated using equation (3).

Discussion

The speãfic rates of solvolysis of **1** and **2** at –10.0°C are higher than those previously measured for **3**.[1] This parallels the observation that, for solvolyses of sulfonyl chlorides at 25.0°C, the k_{Ph}/k_{Me} ratio has a value of 30 for ethanolysis and 17 for methanolysis.[21] Similarly, for the corresponding anhydrides, **1** and **3**, ethanolysis at 20.0°C gives a value for the ratio of 8.7 and methanolysis at 10.0°C gives a value of 17 (using data from Table 2 and ref. 1). The methanolysis ratios are essentially identical and the ethanolysis ratio for the anhydrides is about 3.4 times lower than for the chlorides. Caution is required in interpreting these comparisons since for the chlorides only the one organic grouping within the

sulfonyl chloride is varied but for the anhydrides there is also variation within the leaving group (benzenesulfonate or methanesulfonate in this case). However, the observation[18,19a] that over a wide variety of solvents, the adamantyl esters show k_{OTs}/k_{OMs} ratios in a narrow range of 0.5 to 2.1 suggests that the major factor determining the k_{Ph}/k_{Me} value is the influence of the organic group within the sulfonyl group at which the nucleophilic attack occurs, consistent with the similar ratios for chlorides and anhydrides.

In a comparison of the speãfic rates of solvolysis of **1** and **2** (Table 1) as a function of solvent composition, the relative rates are modestly solvent dependent. In ethanol, methanol and their aqueous mixtures and in aqueous acetone, **1** is consistently more reactive than **2**, by factors of up to three. However, in TFE and in aqueous TFE and aqueous HFIP, the situation is reversed and **2** becomes more reactive by factors of up to 3.5. In the five TFE–H$_2$O solvents studied, the value falls as the water content increases and in 50% TFE (w/w) the speãfic rates are essentially identical. Similarly, the values are almost identical in 50% HFIP (w/w). For TFE–ethanol mixtures, the full range of solvent composition could be studied and the ratio of 2.4, favouring **2** in 100% TFE gradually falls, as ethanol is added, to a value of 0.71 in 100% ethanol. Interpolation indicates that the speãfic rates of **1** and **2** would be identical at about 70% TFE–30%

Table 2 Specific rates of solvolysis of benzenesulfonic anhydride (**1**) and *p*-toluenesulfonic anhydride (**2**) at various temperatures[a]

Solvent[b]	T/°C	$10^3 k(1)/s^{-1c}$	$10^3 k(2)/s^{-1c}$
100% EtOH	−19.5	1.91 ± 0.01	
	0.0	14.7 ± 0.1	9.58 ± 0.20
	10.0	39.9 ± 0.5	22.9 ± 0.3
	20.0	97.7 ± 0.5	55.9 ± 0.4
80% EtOH	−20.0	6.93 ± 0.05[d]	5.56 ± 0.03
	0.0	58.1 ± 0.5	38.6 ± 1.0
	10.0	158 ± 2	105 ± 3
100% MeOH	−20.0	8.32 ± 0.02[d]	4.97 ± 0.01
	0.0	57.9 ± 0.5	41.2 ± 0.9
	10.0	161 ± 3	100 ± 1
100% TFE	0.0	0.240 ± 0.001	
	10.0	0.631 ± 0.001	
	20.0	1.36 ± 0.04	
	25.0	1.91 ± 0.03	
97% TFE	−20.0		0.163 ± 0.001
	0.0	0.700 ± 0.001	1.15 ± 0.01
	10.0	1.82 ± 0.01	2.66 ± 0.02
	20.0	3.96 ± 0.09	
	25.0	5.67 ± 0.01	
97% HFIP	0.0	0.128 ± 0.001	0.240 ± 0.004
	10.0	0.316 ± 0.010	0.570 ± 0.005
	20.0	0.696 ± 0.012	1.14 ± 0.02
	25.0	1.06 ± 0.01	
90% HFIP	0.0		1.35 ± 0.08
	10.0		3.33 ± 0.04
	20.0		7.72 ± 0.08
70% HFIP	0.0		4.98 ± 0.01
	10.0		13.3 ± 0.4
	20.0		32.2 ± 0.5
50% HFIP	0.0		7.60 ± 0.05
	10.0		20.3 ± 0.9
	20.0		52.8 ± 0.3

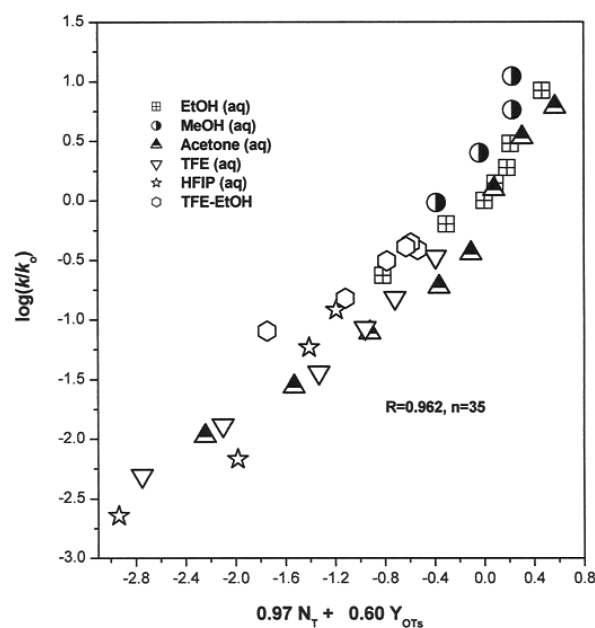[a]Substrate concentration of 3 × 10^{-3} M. [b]80% EtOH on volume–volume basis and other binary solvents on weight–weight basis, each solvent also contained 0.2% CH_3CN. [c]With associated standard deviations. [d]At −19.5°C.

ethanol (v/v). In all solvents, the differences are relatively small (a factor of 3.5 or less), consistent with the introduction into **1** of the electron-supplying *p*-methyl group, leading to **2**, having compensating influences on the breaking of the bond to the leaving group and the formation of the bond to the attacking nucleophilic solvent molecule.[22] The inversion of the relative reactivities in solvents rich in fluoroalcohol is consistent with a modest variation in an S_N2 transition-state structure on transfer from aqueous ethanol, methanol, or acetone to a weakly nucleophilic and highly electrophilic fluoroalcohol-rich medium. This modest influence of solvent variation suggests that small differences may be observed in the *l* and/or *m* values when eqn (2) is applied to the speãfic rates of solvolysis of the two substrates.

Fig. 1 Plot of log (k/k_o) for solvolyses of benzenesulfonic anhydride at −10.0°C against (0.97N_T + 0.60 Y_{OTs}).

The activation parameters (Table 3) are consistent with a bimolecular mechanism, with enthalpies of activation ranging from 11.9 kcal mol^{-1} for **2** in 97% HFIP to 14.9 kcal mol^{-1} for **2** in 50% HFIP. The entropies of activation are all appreãably negative, ranging from −31.6 cal mol^{-1}K^{-1} for **2** in 97% HFIP to −11.3 cal mol^{-1}K^{-1} for **1** in 80% EtOH. The enthalpy of activation for **1** in 97% HFIP is also quite low at 13.1 kcal mol^{-1} and the most unusual feature of the analyses is the low activation energies for the relatively slow solvolyses in 97% HFIP.

The extended Grunwald–Winstein equation [eqn (2)] has been applied to the speãfic rates of solvolysis in the solvents listed in Table 1 (35 solvents for **1** and 37 solvents for **2**). The analyses incorporate the listed N_T and Y_{OTs} values. Strictly speaking, for solvolyses of **1**, a scale based on the solvolyses of an adamantyl benzenesulfonate should be used, but values are not available and the Y_{OTs} values are considered to be a good substitute.[18] The *l* and *m* values and measures of the goodness of fit are reported in Table 5, together with corresponding values for solvolyses of **3** and of related sulfonyl chlorides. The *l* and *m* values obtained for solvolyses of **1** (Fig. 1) are essentially identical to those previously reported[1] for solvolyses of **3**. The *m* values are essentially identical for the solvolyses of **1**, **2**, and **3**. The major variation within the sensitivity values is a slightly reduced value of 0.85

Table 3 Enthalpies ($\Delta H^{\ddagger}$/kcal mol^{-1}) and entropies ($\Delta S^{\ddagger}$/cal mol^{-1}K^{-1}) of activation for the solvolyses of benzenesulfonic anhydride (**1**) and *p*-toluenesulfonic anhydride (**2**)[a,b]

Solvent	1		2	
	$\Delta H^{\ddagger}_{283.2}$	$\Delta S^{\ddagger}_{283.2}$	$\Delta H^{\ddagger}_{283.2}$	$\Delta S^{\ddagger}_{283.2}$
100% EtOH	14.3 ± 0.2	−14.7 ± 0.7	13.3 ± 0.2	−18.8 ± 0.7
80% EtOH	14.5 ± 0.3	−11.3 ± 1.1	13.3 ± 0.2	−16.0 ± 0.9
100% MeOH	13.8 ± 0.4	−13.4 ± 1.6	13.8 ± 0.2	−14.3 ± 0.7
100% TFE	12.5 ± 0.3	−28.9 ± 1.1		
97% TFE	12.9 ± 0.2	−25.6 ± 0.8	12.7 ± 0.2	−25.4 ± 0.7
97% HFIP	13.1 ± 0.1	−28.3 ± 0.4	11.9 ± 0.5	−31.6 ± 1.8
90% HFIP			13.3 ± 0.1	−22.8 ± 0.2
70% HFIP			14.3 ± 0.2	−16.6 ± 0.7
50% HFIP			14.9 ± 0.2	−13.7 ± 0.8

[a]Using the specific rate data of Table 2, plus (when available) the experimental value at −10.0°C from Table 1. [b]With associated standard errors.

Table 4 Selectivity values (S)[a] for solvolyses at –10.0°C of benzenesulfonic anhydride (**1**) and p-toluenesulfonic anhydride (**2**) in binary mixtures of water with ethanol, methanol, or 2,2,2-trifluorethanol and a comparison with S values from the solvolyses of methanesulfonic anhydride (**3**)

Solvent [b]	**1**			**2**			**3**[c]
	% Ester[d]		S	% Ester[d]		S	S
90% EtOH	81.7		1.6	91.8		4.0	1.2
80% EtOH	74.8		2.4	85.1		4.6	2.0
70% EtOH	63.3		2.4	80.5		5.7	2.1
60% EtOH				72.7[e]		5.7[e]	2.9
90% MeOH	92.4		3.0	92.6		3.1	3.7
80% MeOH	84.8		3.1	89.5		4.8	3.7
97% TFE	37.4		0.10				
90% TFE	22.4		0.18	21.2		0.17	0.06
80% TFE	10.6		0.17	11.2		0.17	0.12

[a]As defined in eqn. 3. [b]Aqueous ethanol and methanol on volume–volume basis at 25.0°C and aqueous TFE on weight–weight basis. [c]Values from ref. 1. [d]Molar percentage of $ArSO_2OR$ formed *in competition* with $ArSO_2OH$ (both formed in conjunction with an equimolar amount of $ArSO_2OH$). [e]At 0.0°C.

± 0.06 for *l* for solvolyses of **2** (Fig. 2), as compared to values for solvolyses of **1** of 0.97 ± 0.05 and of **3** of 0.95 ± 0.04. This reduction is consistent with the solvent-induced inversion of the relative rates for solvolyses of **1** and **2** mentioned earlier and with a reduced demand for external nucleophilic assistance in the presence of the electron-supplying *p*-methyl substituent.

The lower *l* values for **1**–**3** (0.85 to 0.97), relative to those presented for sulfonyl chlorides[1,14,15] in Table 5 (1.17 to 1.28), are consistent with a reduced demand for nucleophilic assistance in the presence of a sulfonate leaving group, which is a better leaving group than chloride.

For the methanolysis, the kinetic solvent isotope effect (KSIE) was studied by use of both methanol and methanol-*d*. The ratio k_{MeOH}/k_{MeOD} was 1.37 ± 0.03 for solvolyses of **1** and 1.40 ± 0.03 for solvolyses of **2** (Table 1). These values are very close to the value of 1.35 ± 0.02 reported[1] for **3**. Corresponding values for sulfonyl chlorides include values at 25.0°C of 1.62 for solvolyses of methanesulfonyl chloride[23] and 2.54 for solvolyses of 2-propanesulfonyl chloride.[24] Lower KSIE values for arenesulfonic anhydrides, than for the corresponding chloride, have also been observed for hydrolyses in water or deuterium oxide.[4,6,7] Again, the lower KSIE values observed for anhydrides are consistent with lowered demand for nucleophilic assistance in the presence of a better leaving group.

Selectivity values (S) have been measured (Table 4) using equation (3) for solvolyses in water–alcohol mixtures of both **1** and **2**. The values obtained for solvolyses of **1** parallel quite closely those previously reported[1] for solvolyses of **3**.

In aqueous ethanol, there is a slight increase in value with increasing water content and, in aqueous methanol (90 and 80%), the values are virtually identical. Low solubility for both **1** and **2** prevents the extension to highly aqueous mixtures. For **2**, the S values are somewhat larger in aqueous ethanol and methanol. For both **1** and **2** (and also for **3**) the S
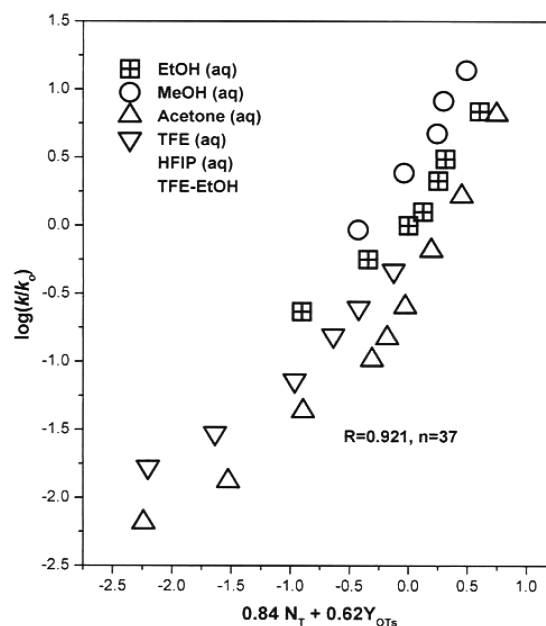
Fig. 2 Plot of log (k/k_0) for solvolyses of *p*-toluenesulfonic anhydride at –10.0°C against ($0.84N_T + 0.62Y_{OTs}$).

values are much lower in TFE–water mixtures, where attack by water is favoured over the considerably less nucleophilic TFE[12,13] by a factor of about 6. The S values are also very similar to those previously observed for solvolyses of sulfonyl chlorides with, in particular, a close resemblance in mixtures of water with ethanol or methanol to those observed[25] with *p*-methoxybenzenesulfonyl chloride as the substrate. In water–TFE mixtures there is a close resemblance to the S values seen in solvolyses of N, N-dimethylsulfamoyl chloride.[15]

Table 5 Coefficients from extended Grunwald–Winstein treatments [equation (2)] of the solvolyses of benzenesulfonic anhydride (**1**) and p-toluenesulfonic anhydride (**2**) and a comparison with coefficients previously obtained for solvolyses involving nucleophilic substitution at sulfur

Substrate	n[a]	l[b]	m[b]	c[b]	R[c]	F[d]
$(C_6H_5SO_2)_2O$	35	0.97 ± 0.05	0.60 ± 0.05	0.17 ± 0.06	0.959	196
$(p\text{-}CH_3C_6H_4SO_2)_2O$	37	0.84 + 0.06	0.62 + 0.06	0.06 + 0.06	0.921	95
$(MeSO_2)_2O$	41	0.95 + 0.04	0.61 + 0.03	-0.10 + 0.05	0.973	342
$p\text{-}MeC_6H_4SO_2Cl$[e]	33[f]	1.25 + 0.15	0.62 + 0.04	0.21 + 0.20[g]	0.967	216
$MeSO_2Cl$[h]	39[f]	1.17 + 0.04	0.49 + 0.02	0.23 + 0.05	0.981	454
Me_2CHSO_2Cl[i]	19[f]	1.28 + 0.05	0.64 + 0.03	0.18 + 0.06	0.988	333

[a]Number of data points. [b]With associated standard errors. [c]Multiple correlation coefficient. [d]F-test value. [e]From ref. 14. [f]No T-E solvents, not studied for *p*-toluenesulfonyl chloride and omitted from the correlation for methanesulfonyl and 2-propanesulfonyl chlorides. [g]Associated with the standard error of the estimate. [h]From ref. 1. [i]From ref. 15.

Conclusion

The solvolyses of the two arenesulfonic anhydrides, **1** and **2**, show characteristics very similar to those previously found for methanesulfonic anhydride, **3**. The speãfic rates of solvolysis are quite well correlated by an extended Grunwald–Winstein equation [eqn (2)], incorporating a term governed by solvent nucleophiliãty as well as the one governed by solvent ionising power. A slightly lower sensitivity to changes in solvent nucleophiliãty (*l* value) for **2** can be rationalised in terms of a reduced demand in the presence of the electron-supplying *p*-methyl substituent. A corollary of this difference is a reversal of the ordering of speãfic rates of solvolysis, with **1** being more reactive in the traditional aqueous alcohols and aqueous acetone and **2** being more reactive in solvents rich in fluoroalcohol.

The KSIE values for reaction in methanol relative to methanol-*d* are essentially identical, at 1.35 to 1.40, for solvolyses of **1**, **2**, and **3**. These values are somewhat lower than a literature value of 1.62 for methanolysis of methanesulfonyl chloride and considerably lower than a literature value of 2.5 for the methanolysis of 2-propanesulfonyl chloride. The lower values for anhydrides suggest less nucleophilic assistance from the solvent than in the methanolyses of the chlorides. Fully consistent with this explanation is the observation that the *l* values of 0.85 to 0.97 for **1**, **2**, and **3** are appreãably lower than the literature values of 1.17 to 1.28 for the three sulfonyl chlorides listed, for comparison, in Table 5.

The selectivity values (*S*), defined in equation (3), show preference for attack by the more nucleophilic component: ethanol and methanol in their aqueous mixtures and water in aqueous TFE. The values, espeãally for **1**, are similar to those previously reported for **3** and for sulfonyl chlorides such as *p*-methoxybenzenesulfonyl chloride and *N,N*-dimethylsulfamoyl chloride.

The observations from the different aspects of the investigation are all consistent with a concerted S_N2 mechanism across the full range of solvents for both substrates, but with a slight variation in transition-state structure favouring reduced bond formation to the nucleophilic solvent molecule both relative to the attack on sulfonyl chlorides and, also, as the solvent is varied, by use of solvents rich in fluoroalcohol, which have high electrophiliãty and low nucleophiliãty.

Experimental

The benzenesulfonic anhydride (TCI America) and *p*-toluenesulfonic anhydride (Aldrich, 97%) were used as received. The solvents were purified as previously described.[12] The product ratios were determined by titration of the aãd developed in experiments carried out separately from the kinetic runs. For solvolyses of **1**, duplicate determinations were carried out at –10.0°C by adding 0.40 ml of a 0.723 M stock solution of **1** in acetonitrile to 20 ml of the appropriate solvents and removing 5-ml samples at 10, 15, and 20 half-lives (determined from speãfic rates of Table 1) for titration of the developed aãd against a 2.25×10^{-3} M solution of sodium methoxide in methanol, as previously described.[12] The same procedure was used in the solvolyses of **2**, except that 0.45 ml of a 0.127 M stock solution was used and the determination in 60% ethanol was at 0.0°C.

The fraction of the overall reaction of the anhydride with water in an alcohol–water mixture is based on the increase in the aãd titre over that for the solvolysis in the pure alcohol relative to the corresponding increase in aãd titre for solvolysis in 60% acetone (100% hydrolysis) over that for solvolysis in the pure alcohol. Accordingly, the presence of either aãd impurity, such as that initially present in the substrate or formed during preparation of the concentrated stock solution, or inert impurity will not influence the determined product ratio and the derived *S* values.

When the six aãd titre determinations are averaged, the standard deviations are in the range of 0.2–0.7% of the average value. Other factors being equal, the *S* values will be most accurate when appreãable amounts of both reaction pathways are followed and the preãsion will fall considerably if one of the products is formed only in small amounts, due to the small difference between the two titres

now being assoãated with a relatively large error. We will consider the two extreme examples from within Table 4. In 90% methanol, only 7.4% of product is from reaction of **2** with water and the *S* value can be estimated as 3.11 ± 0.43 (the standard deviation being 14% of the value). For solvolysis of **1** in 97% TFE, 62.6% of reaction is with water and the *S* value can be estimated as 0.103 ± 0.008 (the standard deviation being 8% of the value).

The kinetic runs were followed using an apparatus which allows rapid response to changes in conductivity.[26] The apparatus used has been previously described.[27] Typically, the determinations involved the injection of 4.0 μl of a solution of the substrate in acetonitrile (0.30 M for **1** and 0.075 M for **2**) into 2.0 ml of the solvent under investigation. Speãfic rates (first-order rate coeffiãents) and the assoãated standard deviations were determined from a computer analysis (Guggenheim method[28]) of the plots of conductivity against time. The multiple regression analyses were carried out using commerãally available statistical packages.

References

1 (a) D.N. Kevill, Z.H. Ryu, M.A. Niedermeyer, F. Koyoshi and M.J. D'Souza, *J. Phys. Org. Chem.*, 2007, **20**, 431; (b) D.N. Kevill, Z.H. Ryu, M.J. D'Souza, L. Yaakoubd and F. Koyoshi, presented at the 18th International Conference on Physical Organic Chemistry, Warsaw, Poland, Aug. 20–25, 2006; Book of Abstracts, pp. 40-41.

2 (a) L.M. Litvinenko, N.T. Maleeva, V.A. Savelova and O.I. Butko, *J. Org. Chem. (USSR)*, 1973, **9**, 2139; (b) N.T. Maleeva, V.A. Savelova, I.V. Sh'anko and L.M. Litvinenko, *Reakts. Sosobn. Org. Soedin.*, 1974, **11**, 203; *Chem. Abstr.*,1975, **82**, 42581p; (c) L.M. Litvinenko, N.T. Maleeva and V.A. Savelova, *Reakts. Sosobn. Org. Soedin.*, 1974, **11**, 225; *Chem. Abstr.*,1975, **82**, 42583r.

3 N.H. Christensen, *Acta Chem. Scand.*, 1966, **20**, 1955.

4 N.H. Christensen, *Acta Chem. Scand.*, 1967, **21**, 899.

5 R.M. Laird and M.J. Spence, *J. Chem. Soc. (B)*, 1971, 1435.

6 R.E. Robertson and P.M. Laughton, *Can. J. Chem.*, 1957, **35**, 1319.

7 G. Geiseler, P. Hermann, K.H. Reps and R. Wüstner, *Z. Phys. Chem (Leipzig)*, 1962, **221**,185.

8 E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, 1948, **70**, 846.

9 R.V. Vizgert, *J. Gen. Chem. (USSR)*, 1962, **32**, 619.

10 S. Winstein, E. Grunwald and H.W. Jones, *J. Am Chem. Soc.*, 1951, **73**, 2700.

11 F.L. Schadt, T.W. Bentley and P.v.R. Schleyer, *J. Am. Chem. Soc.*, 1976, **98**, 7667.

12 D.N. Kevill and S.W. Anderson, *J. Org. Chem.*, 1991, **56**, 1845.

13 D.N. Kevill, in Advances in Quantitative Structure–Property Relationships, Vol. 1, ed. M. Charton, JAI Press, Greenwich, CT., 1996, pp 81-115.

14 D.N. Kevill and M.J. D'Souza, *Collect. Czech. Chem. Commun.*, 1999, **64**, 1790.

15 D.N. Kevill, B.-C. Park, K.-H. Park, M.J. D'Souza, L. Yaakoubd, S.L. Mlynarski and J.B. Kyong, *Org. Biomol. Chem.*, 2006, **4**, 1580.

16 (a) T.W. Bentley, H.C. Harris and I.S. Koo, *J. Chem Soc., Perkin Trans. 2*, 1988, 783; (b) T.W. Bentley and I.S. Koo, *J. Chem Soc., Perkin Trans. 2*, 1989, 1385; (c) T.W. Bentley and C.S. Shim, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1659.

17 D.N. Kevill and M.J. D'Souza, *J. Phys. Org. Chem.*, 2002, **15**, 881.

18 T.W. Bentley and G. Llewellyn, *Prog. Phys. Org. Chem.*, 1990, **17**, 121.

19 (a) T.W. Bentley and C.T. Bowen, *J. Chem Soc., Perkin Trans. 2*, 1978, 557; (b) T.W. Bentley and G.E. Carter, *J. Org. Chem*, 1983, **48**, 579; (c) B. Allard and E. Casadevall, *Nouv. J. Chim.*, 1985, **9**, 565; (d) D.N. Kevill and D.C. Hawkinson, *J. Org. Chem.*, 1989, **54**, 158.

20 (a) M. Fujio, M. Goto, T. Yoshino, K. Funatsu, Y. Tsuji, S. Ouchi and Y. Tsuno, *Mem. Fac. Sã. Kyushu Univ., Ser. C*, 1987, **16(1)**, 85; *Chem. Abstr.*,1988, **109**, 148671j; (b) M. Fujio, T. Susuki, M. Goto, Y. Tsuji, K. Yatsugi, Y. Saeki, S.H. Kim and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 2233.

21 F.P. Ballistreri, A. Cantone, E. Maccarone, G.A. Tomaselli and M. Tripolone, *J. Chem. Soc., Perkin Trans. 2*, 1981, 438.

22 T.H. Lowry and K.S. Richardson, *Mechanism and Theory in Organic Chemistry*, 3rd Ed., Harper and Row, New York, 1987, pp. 379-381.

23 I.S. Koo, K. Yang, S.K. An, C.-K. Lee and I. Lee, *Bull. Korean Chem. Soc.*, 2000, **21**, 1011.

24 I.S. Koo, K. Yang, H.B. Shin, S.K. An, J.P. Lee and I. Lee, *Bull. Korean Chem. Soc.*, 2004, **25**, 699.

25 I.S. Koo, T.W. Bentley, G. Llewellyn and K. Yang, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1175.

26 T.W. Bentley and R.O. Jones, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2351.

27 I. Lee, H.W. Lee, T.S. Uhm, D.D. Sung and Z.H. Ryu, *J. Korean Chem. Soc.*, 1988, **32**, 85.

28 (a) E.A. Guggenheim, *Philos. Mag.*, 1928, **2**, 538; (b) A.A. Frost and