Limitations of the Transition State Variation Model. Part 2. Dual Reaction Channels for Solvolyses of 2,4,6-Trimethylbenzenesulphonyl Chloride

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Rate constants for solvolyses of 2,4,6-trimethylbenzenesulphonyl chloride (**1**) are reported for aqueous binary mixtures with acetone, acetonitrile, dioxane, ethanol and methanol. Kinetic solvent isotope effects in water and in methanol and product selectivities in alcohol–water mixtures are also reported. Additional Y_{Cl} values have been determined for aqueous acetonitrile and dioxane from rate constants for solvolyses of 1-adamantyl chloride. Contrary to earlier reports, correlations between logarithms of rate constants for solvolyses of **1** *vs.* Y or Y_{Cl} are approximately bilinear. From these plots the rate data are dissected into contributions from two competing reaction channels, and this interpretation is supported for alcohol–water mixtures by the trends of product selectivities, which show maxima close to the solvent compositions where there are breaks in the rate–rate profiles. Greater rate constants for 40% v/v ethanol–water than for 97% w/w trifluoroethanol–water (solvents of approximately equal ionizing power) show the importance of nucleophilic solvent assistance (S_N2 character) even for the reaction channel favoured in more polar media. Hence, in agreement with an earlier consensus, neither of the reaction channels corresponds to an S_N1 mechanism. From the kinetic solvent isotope effect of 1.68 in methanol, it is proposed that the reaction channel favoured in less polar media is general-base catalysed and/or is possibly an addition–elimination pathway.

Rate–rate profiles of solvent effects in aqueous binary mixtures have provided significant new insights into the reactivites and mechanisms of solvolyses of benzoyl chloride and substituted derivatives.[1,2] Solvent effects were analysed[1,2] (by the procedure outlined below) in terms of competing (dual) reaction channels rather than the transition state variation model currently in favour.[3] Competing reaction channels can be detected by means of rate–rate profiles if two conditions are met: (i) the reaction channels should differ in their sensitivities to changes in solvent ionizing power, and (ii) rate data for a suitable reference substrate should be available to model the behaviour expected for one of the reaction channels. A non-linear plot of logarithms of rate constants for the substrate under investigation *vs.* logarithms of rate constants for the model substrate, over a range of solvent compositions from alcohol to water, indicates a change in mechanism from predominantly one channel to the other.

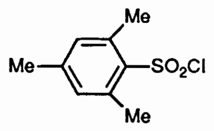
Our interpretation[1,2] was supported by the product selectivities in alcohol–water mixtures; in contrast, typical previous investigations in acetone–water or dioxane–water mixtures do not provide this additional information. In extending this work to the reactions of sulphonyl chlorides, we examined solvolyses of 2,4,6-trimethylbenzenesulphonyl chloride (**1**) and found that these too showed competing reaction channels.[4] A full account of this work is given here.

Results

Kinetic data for solvolyses of **1** are given in Table 1, and kinetic solvent isotope effects in water and methanol are in Table 2. Product selectivities (S), defined by eqn. (1) using molar

$$S = [\text{ester}]_{\text{prod}}[\text{water}]_{\text{solv}}/[\text{acid}]_{\text{prod}}[\text{alcohol}]_{\text{solv}} \quad (1)$$

concentrations,[1b] for solvolyses of **1** in alcohol–water mixtures are presented in Table 3. Kinetic data for solvolyses of 1-adamantyl chloride (**2**), used to obtain additional values of the modified Grunwald–Winstein parameter for solvent ionizing power Y_{Cl},[6] are given in Table 4.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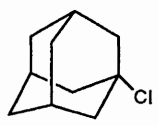
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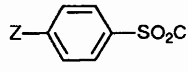
Discussion

Previous work.—Published work on solvolyses of sulphonyl chlorides has been concerned with substituent effects on reactivity,[5d,7] and solvent effects have been examined for mixtures of acetone–water[8a–c] and dioxane–water,[8d,e] ethanol–water and ethanol–trifluoroethanol,[9] and for aqueous sulphuric acid.[10] Typical results for *p*-substituted benzenesulphonyl chlorides (**3**) show approximately linear relationships between logarithms of rate constants and solvent ionizing power for acetone–water[8a,c] and dioxane–water.[8d,e] A tendency for rate constants to decrease in highly aqueous media ('downward curvature') was observed for solvolyses of *p*-nitrobenzenesulphonyl chloride **3** (Z = NO_2),[8d,e] and similar results have been explained by general base catalysis for solvolyses of *p*-nitrobenzoyl chloride **4** (Z = NO_2).[1b]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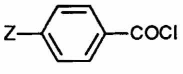
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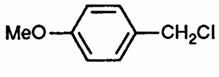
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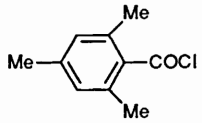
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Table 1 Rate constants k for solvolyses of 2,4,6-trimethylbenzenesulphonyl chloride **1** in aqueous binary mixtures at 25 °C[a]

Solvent % v/v	$k/10^{-3}$ s^{-1} Ethanol	Methanol	Acetone	Acetonitrile	Dioxane
100	0.154	1.04	—	—	—
90	0.355	2.02	0.072	—	—
80	0.617	3.14	0.115	0.092	0.053
70	0.934	5.08	0.199	—	0.213[b]
60	1.40	8.68	0.36	0.39	0.49
50	2.35	14.6	0.65	—	1.15[b]
40	5.33	23.7	1.92	1.70	3.04
30	14.4	35.2	4.39	4.46	—
20	33.1	46.2	17.9[c]	12.8	17.1
10	60.2[d]	69.0[e]	37.8[f]	38.7	35.9
Water[g]	85.2[h]	85.2[h]	85.2[h]	85.2[h]	85.2[h]

97% w/w trifluoroethanol–water, $k/10^{-3}$ s^{-1} = $(2.64 \pm 0.02) \times 10^{-2}$

[a] Determined conductimetrically in duplicate; average deviation < ±5%. [b] Extrapolated from data at 30–50 °C [ref. 5(*a*)]. [c] An independent set of measurements (each in duplicate) gave $k = (1.59 \pm 0.03) \times 10^{-2}$ s^{-1} at 25.0 °C and $(4.47 \pm 0.03) \times 10^{-2}$ s^{-1} at 40.0 °C; $\Delta H^\ddagger = 12.2$ kcal mol^{-1}, $\Delta S^\ddagger = -25.9$ cal mol^{-1} K^{-1} (1 cal = 4.184 J). [d] At 40.0 °C, $k = (1.70 \pm 0.01) \times 10^{-1}$ s^{-1}; $\Delta H^\ddagger = 12.2$ kcal mol^{-1}, $\Delta S^\ddagger = -23.1$ cal mol^{-1} K^{-1}. [e] At 40.0 °C, $k = (2.10 \pm 0.01) \times 10^{-1}$ s^{-1}; $\Delta H^\ddagger = 13.2$ kcal mol^{-1}, $\Delta S^\ddagger = -19.7$ cal mol^{-1} K^{-1}. [f] At 40.0 °C, $k = (1.11 \pm 0.02) \times 10^{-1}$ s^{-1}; $\Delta H^\ddagger = 12.7$ kcal mol^{-1}, $\Delta S^\ddagger = -22.4$ cal mol^{-1} K^{-1}. [g] Solvent contained 0.2–0.4% acetonitrile; this experiment requires dilute solutions and added cosolvent, because the sulphonyl chloride is 'quite insoluble' [ref. 5(*b*)] in water. [h] Literature value, $k = 81 \times 10^{-3}$ s^{-1} [ref. 5(*c*)]; also 83.4 (Table 2) and 3.5 [ref. 5(*d*)]; although the solvent contained 1% dioxane this latter result is almost certainly incorrect.

Table 2 Rate constants/s^{-1} and kinetic solvent isotope effects for solvolyses of 2,4,6-trimethylbenzenesulphonyl chloride **1**[a]

Solvent	Rate constant (SOH)	Rate constant (SOD)	KSIE
MeOH	$(1.02 \pm 0.01) \times 10^{-3}$	$(6.08 \pm 0.01) \times 10^{-4}$	1.68 ± 0.02
HOH	$(8.34 \pm 0.15) \times 10^{-2}$	$(6.22 \pm 0.02) \times 10^{-2}$	1.34 ± 0.03

[a] Determined conductimetrically in duplicate, in the order SOH, SOD, SOD, SOH.

Table 3 Product selectivities [S, eqn. (1)] for solvolyses of 2,4,6-trimethylbenzenesulphonyl chloride **1** in aqueous alcohols[a]

Alcohol (% v/v)	Methanol [ester]/[acid]	S	Ethanol [ester]/[acid]	S
95	9.4	1.1	12	0.8
90	7.6	1.9	4.2	1.5
80	4.3	2.4	3.1	2.5
70	3.3	3.2	2.2	3.0
60	2.35	3.6	1.7	3.8
50	1.7	3.9	1.3	4.1
40	1.3	4.4	0.95	4.6
30	0.87	4.5	0.46	3.4
20	0.43	3.9	0.24	3.1
10	0.18	3.5	0.10	2.9
5	0.076	3.3	0.04	2.5

[a] Determined at least in duplicate by HPLC analyses of two independent solutions; error estimate ± 5%.

In contrast, logarithms of rate constants for solvolyses of **1**, plotted *versus* Y_{Cl} in Fig. 1, show upward curvature and a strong dispersion into separate correlation lines for the various aqueous binary mixtures (*e.g.* acetone, ethanol and methanol). Two approximately linear regions of significantly different slope can be seen for acetone–water mixtures, and similar results were obtained in preliminary work for acetonitrile–water mixtures. Linear regions for ethanol– and methanol–water mixtures can be seen (Fig. 1) for solvent compositions of low ionizing power. It was reported previously that logarithms of rate constants for solvolyses of **1** in dioxane–water mixtures (within the range 70% v/v to water) plotted linearly[8e] or almost linearly[5c] with the original Grunwald–Winstein Y parameter for solvent ionizing power.[11] Our plot (Fig. 2) can be interpreted as a curve[5c] or as two approximately linear regions from 80% to 40% dioxane–water and from 20% dioxane to pure water. For this range of solvents, Y and Y_{Cl} are expected to be linearly related with little or no dispersion,[12] and the rate–rate profiles shown in Fig. 1 are unexpectedly complex.

Choice of Model Compounds for Rate–Rate Profiles.—Successful mechanistic applications of rate–rate profiles of solvent effects depend on appropriate choices of model compounds. Model compounds reacting by S_N1 mechanisms are usually chosen,[1,2,6] although substrates responding to a combination of solvent ionizing power and solvent nucleophilicity could also be employed.[1c] For solvolyses of carboxylic acid chlorides, the model compound was *p*-methoxybenzoyl chloride **4** (Z = OMe)[1a] and we have recently shown that almost identical results would have been obtained using *p*-methoxybenzyl chloride (**5**).[2] Conjugation between the carbocationic centre and the benzene ring has a significant effect on these rate–rate profiles,[2,13] and accounts for the poor correlation between solvolyses of **4** (Z = OMe) and Y_{Cl}.[14] However, for solvolyses of sulphonyl halides, conjugation between sulphur and the benzene ring is probably weak,* and the choice of Y_{Cl} (Fig. 1) can be justified by analogy.[2,13]

Unfortunately, the correct choice of model compound cannot be established directly because there is no known case of an S_N1 solvolytic reaction of a sulphonyl chloride.[5c,15] Sulphonyl cations are so unstable that strongly electron-donating substituents are required for them to be observed even in very weakly nucleophilic media,[16] whereas stable acylium ions can be isolated.[17] Also, sulphonyl chlorides are highly susceptible to nucleophilic attack. Because there is rotation of the SO_2Cl group,[18] nucleophilic attack by primary alcohols[19] or by amines[20a,b] is not greatly retarded by 2,6-dialkyl groups; 2,6-dimethyl and even 2,6-diisopropyl groups give rate retardations of less than ten-fold.[19b] *ortho*-Alkyl groups (methyl or isopropyl) accelerate rather than hinder substitution at sulphonyl sulphur in chloride exchange reactions.[20c]

Dissection of the Kinetic Data into Contributions from Competing Reaction Channels.—Quantitative dissection of the rate–rate profiles (Fig. 1) into contributions from the competing reaction channels was carried out by a similar method to that reported recently for solvolyses of benzoyl chloride,[1a] for which two linear regions could be seen clearly for each binary mixture. The dissected rate constants, calculated for the reaction channel dominant in more polar media, correlated (without significant dispersion) with rate constants for solvolyses of the model compound **4** (Z = OMe).[1a,2] A more approximate procedure was necessary to dissect the rate data for solvolyses of **1**, because the reaction channel dominant in more aqueous media is not so clearly visible (Fig. 1) and the choice of model compound is less clear-cut (see above). The dashed line (Fig. 1) is a least-squares fit to data points for nine non-alcoholic

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* The kinetic effect of substituting the *p*-methyl group in **1** by *p*-methoxy is only two- to six-fold in a range of solvents from ethanol to trifluoroethanol (I. S. Koo, unpublished results), and the slope of the dashed line (Fig. 1) is high (0.87)—see also later discussion.

Table 4 Rate constants k and Y_{Cl} values for solvolyses of 1-adamantyl chloride **2** in aqueous acetonitrile and dioxane[a]

Solvent composition (% v/v)	Acetonitrile		Dioxane	
	k/s^{-1}	Y_{Cl}	k/s^{-1}	Y_{Cl}
30	$(1.19 \pm 0.01) \times 10^{-5}$	3.17	$(7.55 \pm 0.01) \times 10^{-6}$	2.97
20	$(4.48 \pm 0.07) \times 10^{-5}$	3.75	$(4.15 \pm 0.03) \times 10^{-5}$	3.71
10	$(1.74 \pm 0.03) \times 10^{-4}$	4.34	$(1.37 \pm 0.03) \times 10^{-4}$	4.23

[a] Determined conductimetrically in duplicate; errors shown are average deviations.

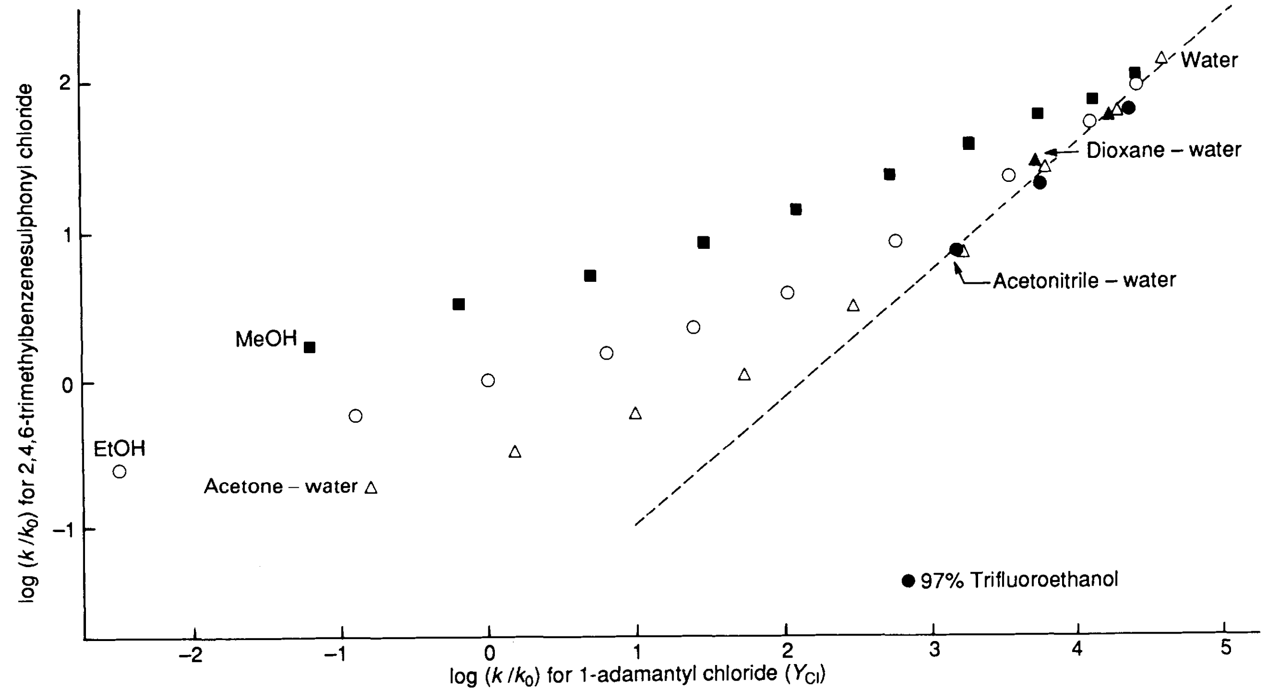


Fig. 1 Correlation of logarithms of rate constants for solvolyses of 2,4,6-trimethylbenzenesulphonyl chloride **1** with Y_{Cl}; kinetic data from Table 1 and Y_{Cl} values from ref. 6; solvent codes: ■, methanol–water; ○, ethanol–water; △, acetone–water; ▲, dioxane–water; ●, acetonitrile–water and trifluoroethanol–water. The correlations are: (*a*) the dashed line through the data points for water, 10–30% acetone–water and acetonitrile–water, and 10 and 20% dioxane–water: slope = 0.87 ± 0.05 (r = 0.9906); (*b*) the data points MeOH to 70% methanol–water: slope = 0.26 ± 0.01 (r = 0.9986); (*c*) the data points EtOH to 70% ethanol–water; slope = 0.24 ± 0.01 (r = 0.9994).

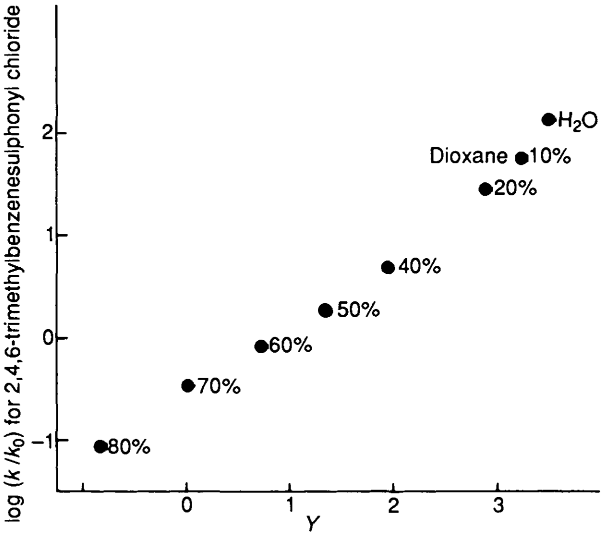


Fig. 2 Correlation of logarithms of rate constants for solvolyses of 2,4,6-trimethylbenzenesulphonyl chloride **1** with Y; kinetic data from Table 1 and Y values from ref. 6

solvents (*i.e.* water, 10–30% acetone–water and acetonitrile–water, and 10–20% dioxane–water), which appear on inspection of Fig. 1 to be close to linear. Data points for 10 and 20% ethanol–water also fit this line well; it is the line estimated for the rate–rate profile of the reaction channel dominant in more polar media. When the observed rate constant is greater than predicted from the dashed correlation line, the results may be explained by a mechanistic change involving additional contributions from a second reaction channel.

For each set of the binary mixtures (*e.g.* methanol–water), the solvent compositions corresponding to the proposed mechanistic change can be *predicted* from the rate–rate profile (Fig. 1), in contrast with the transition state variation model which generally operates retrospectively. The mechanistic change (50% contribution from each of the two reaction channels) occurs when the observed rate constants for solvolyses of **1** (Fig. 1) deviates by log 2 from the dashed line, in the 'vertical' direction. The predicted Y_{Cl} values for three of the binary mixtures are as follows: Y_{Cl} = 3.8 (*ca.* 30% methanol–water), Y_{Cl} = 3.0 (*ca.* 35% ethanol–water), and Y_{Cl} = 1.8 (*ca.* 50% acetone–water). For solvolyses of benzoyl chloride, the corresponding solvent compositions are 10–30% less aqueous (*e.g.* for benzoyl chloride, the mechanistic change occurs near to 60% methanol–water[1a] rather than 30%, as observed for solvolyses of **1**). Hence, these results reflect either properties of the substrates or a combination of properties of the substrate and the solvent (*i.e.* they are not solely properties of the solvent).

Because of ambiguities in the interpretation of Fig. 1, independent supporting evidence for the proposal of dual reaction channels was obtained from product selectivities. Maximum S values are observed (Table 3) for 30% methanol–water and for 40% ethanol–water mixtures, so the reversal in trend of product selectivities (Table 3) for alcohol–water occurs in almost identical solvent compositions to those predicted from interpretation of the rate–rate profiles. Although S_{max} is a good *guide* to the point of mechanistic change, the solvent composition for which S_{max} is observed is not expected to be the *exact* point of mechanistic change. For solvolyses of benzoyl chloride, S_{max} was observed in solvent compositions 15–20% less aqueous than the solvent composition at the true point of mechanistic change.[1a] Hence, there is satisfactory agreement between the solvent compositions where there are changes in slopes of rate–rate profiles (Fig. 1) and where there are S_{max} values (Table 3), consistent with solvolyses of **1**, proceeding *via* competing reaction channels.

Further evidence of mechanistic changes for carboxylic acid chlorides was available, because the reaction channel favoured in highly aqueous media showed a constant selectivity (explained by reaction *via* a solvent-separated ion pair).[1a] Solvolyses of **4** (Z = OMe) shows constant low selectivity (1.3 in methanol–water mixtures[1a]), but for solvolyses of **5**, S is larger and increases in more aqueous media to a value of >6 in methanol–water.[2] Therefore, solvolyses of **4** (Z = OMe) and **5** do not show the same product-determining steps, although they show almost identical solvent effects and kinetic solvent isotope effects and presumably similar rate-determining steps.[2] Hence, contrary to our initial expectations,[4] failure to achieve a constant and low S value (Table 3) cannot be interpreted in terms of the extent to which the changeover from one reaction channel to the other has taken place.

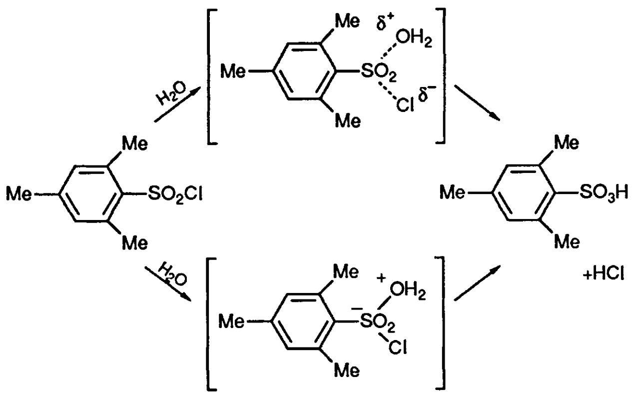
Mechanistic Assignments.—The data point for 97% w/w trifluoroethanol–water deviates by a factor of 200 from the hatched correlation line (Fig. 1), showing the importance of solvent nucleophilicity in these reactions.[21] It is now generally accepted that these solvolyses are not S_N1 processes.[5c,8c,15] The high slope (0.87) of the dashed line of the Y_{Cl} correlation (Fig. 1) including data for highly aqueous media, is consistent with the proposal of an unusually low degree of charge delocalisation from the sulphur atom to the benzene ring in the transition state of an S_N2 reaction. Also, from high level molecular orbital calculations, it has been suggested[22] that there is a formal positive charge of two on the sulphur atom of methanesulphonyl chloride. Such a high positive charge in the initial state is likely to lead to an unusual response to changes in solvent ionizing power.

Further work is in progress[23] on the rate–rate profiles for S_N2 reactions, which show the dispersion effects for the various binary mixtures having different solvent nucleophilicities.[21] This dispersion could further complicate the interpretation of rate–rate profiles for sulphonyl chlorides (*e.g.* Fig. 1) because, unlike solvolyses of carboxylic acid chlorides,[1a,2] the reaction channel favoured in more polar media may show dispersion. However, S_N2 reactions of benzyl halides do not show significant reversals in trends of S values,[23,24] so the S values (Table 3) are consistent with dual reaction channels.

Kinetic Solvent Isotope Effects.—If the reaction channel favoured in highly aqueous media is an S_N2 process, then a different mechanism is required for the second reaction channel favoured in less polar media. In ethanol- and methanol–water mixtures having a high alcohol content, the slopes (Fig. 1) of less than 0.3 are much lower than for the dashed line (0.87, Fig. 1). The kinetic solvent isotope effect (KSIE, Table 2) of 1.68 for solvolyses of **1** in methanol is greater than the value of 1.34 in water (Table 2). Hence, the KSIE results are consistent with a general-base catalysed displacement for the second reaction channel (alternatively, or *also*, it might be an addition–elimination process[5c,8b,8c]).

The KSIE value in water is less than the value of 1.405 observed for solvolyses of **3** (Z = OMe).[5b] Values in the range 1.405 to 1.822 for solvolyses of **3** (Z = OMe to NO_2) at 15 °C have been correlated with Hammett σ values.[5b] Also, the value of 1.34 for **1** is in the range expected for S_N2–S_N1 processes;[25] an almost identical value of 1.33 was observed for the hydrolysis of dimethylsulphamoyl chloride.[8c] Surprisingly, solvolyses of mesitoyl chloride **6** show KSIE values in the range 1.5–1.7,[26,27] although they appear to be S_N1 processes.[28] A four-centre transition state might explain values for the KSIE greater than 1.35, by analogy with a recent proposal for reactions of deuteriated aniline nucleophiles reacting with 1-phenylethyl benzenesulphonates, which show clean second-order kinetics and a primary kinetic isotope effect of *ca.* 2.[29]

The mechanisms of reactions discussed above refer to neutral or slightly acidic solutions. Solvolyses of benzenesulphonyl chloride **3** (Z = H) are not accelerated by acid above pH 1,[5a,10a,30] but solvolyses of benzenesulphonyl chlorides **3**[5b,30b] and even of **1** are strongly accelerated by hydroxide ion.[5c]



Scheme 1 Dual channel mechanism for hydrolysis of 2,4,6-trimethylbenzenesulphonyl chloride **1**—the addition–elimination pathway may alternatively (or also) involve general base catalysis

Conclusions

New insights into reactivity in aqueous solutions can be obtained from studies of binary aqueous mixtures. By examining a wide range of compositions of dioxane–water mixtures (Fig. 2), evidence for dual reaction channels (see Scheme 1) in solvolyses of **1** can be obtained. By examining several binary mixtures (Fig. 1) the appropriate choice of model compound can be judged, and a quantitative dissection of the dual (competing) reaction channels can be achieved. Important supporting evidence for dual reaction channels is provided by the trends of product selectivities [eqn. (1)] for alcohol–water mixtures, which increase and then decrease as water is added to alcohol.

A major limitation of the transition state variation model[3] is that, by assuming there is only one reaction channel, it is possible to explain many (possibly all) experimental observations *retrospectively*. This approach is so flexible and 'successful' that the possibility of competing reaction channels is receiving insufficient attention. There is now strong evidence for competing reaction channels for solvolyses of *p*-substituted benzoyl chlorides **4** (Z = Cl, H, Me),[1a] as well as for the electron rich sulphonyl chloride **1**. Ethanol–water mixtures provide a wide range of solvent ionizing power (Y_{Cl} values span seven powers of ten in rate[6]), making it possible to observe competing processes differing in response to changes in solvent ionizing power. Mechanistic changes could be sought over an even wider range of solvents of lower polarity (by studies of other alcohols) or of higher polarity (by studies of aqueous sulphuric acid mixtures[10]).

Experimental

2,4,6-Trimethylbenzenesulphonyl chloride **1** was a commercial sample (Aldrich), checked for purity by HPLC analysis of the methanolysis product. Rates and products were obtained as described previously.[12,28]

In an alternative, more convenient, method for obtaining standard solutions (*e.g.* of ethyl ester, methyl ester or sulphonic acid) for HPLC response calibrations, accurate mm^3 volumes of **1** in dilute (*ca.* 10%) solution in dry acetonitrile were injected carefully into 5.00 cm^3 of dry ethanol, dry methanol and 40% acetonitrile–water respectively and were left to react for 10 half-lives; (this alternative method is only suitable for producing sulphonic acid esters, which do not undergo significant S_N2 displacement at the ethyl or methyl groups). Reliable (±1%) HPLC injections (volumes *ca.* 10 mm^3) were then made using a Perkin-Elmer ISS 101 autosampler. Typical HPLC conditions were as follows: column, 15 cm × $\frac{1}{4}$ in, packed with 5 μm Spherisorb ODS2; eluent, 80% methanol–water, UV detection; λ = 260 nm, A = 0.1, ester/acid response factor = 1.8. Higher sensitivity and a more suitable ester/acid response ratio of 1.2 was achieved with λ = 230 nm (the wavelength was chosen after determining the UV spectra of the standard solutions), and this was used for studies of the more highly aqueous media. For product studies, small volumes (10 mm^3) of a 1% solution of **1** in dry acetonitrile were injected into 5 cm^3 of rapidly-stirred,[28] thermostatted solvent and after 10 half-lives the product ratio was obtained by HPLC.

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