Correlation of the rates of solvolysis of 2,1-benzoxathiol-3-one-1, 1-dioxide (2-sulfobenzoic acid cyclic anhydride)

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Solvolysis of acyclic mixed carboxylic–sulfonic anhydrides in hydroxylic solvents is known to involve displacement at the carbonyl carbon to produce a carboxylic acid (water as the nucleophile) and/or an ester (alcohol as the nucleophile) plus the anion of the sulfonic acid. Parallel solvolyses of the cyclic mixed anhydride 2-sulfobenzoic anhydride (structurally similar to phthalic anhydride but with one carbonyl group replaced by a sulfonyl group) involve expulsion from the carbonyl carbon of a sulfonate anion that remains attached as an *ortho*-substituent in the benzoic acid and/or benzoate ester produced. This complicates the choice of a solvent-ionising-power scale for use in an extended Grunwald–Winstein equation treatment. The Y_{OTs} scale, previously recommended as a good general purpose scale, is chosen and used in conjunction with the N_T solvent nucleophilicity scale. An acceptable correlation is obtained, which is improved when the two solvents rich in the highly ionising 1,1,1,3,3,3-hexafluoro-2-propanol are excluded. As the solvent is varied, the sensitivities to the changes induced in the two scales are low, consistent with an early transition state, but their ratio has a value which is typical for a pathway involving addition–elimination, with addition rate-determining. Earlier reports, supporting aspects of the proposed mechanism, are reviewed.

Keywords: 2-sulfobenzoic acid cyclic anhydride, Grunwald-Winstein equation, solvolysis, addition-elimination, ring-opening

We have previously reported on the solvolyses of acyclic mixed carboxylic acid–sulfonic acid anhydrides. These studies, in a wide variety of solvents, involved the solvolyses of acetyl *p*-toluenesulfonate (acetic *p*-toluenesulfonic anhydride)¹ and a similar study of the slower reacting benzoyl and *p*-nitrobenzoyl *p*-toluenesulfonates.² In addition to linear free energy relationship (LFER) treatments with use of the extended Grunwald–Winstein equation,^{3,4} there were also considerations of deuterium isotope effects, of leaving-group effects relative to halide, and of the activation parameters.

We now report on the solvolyses of 2-sulfobenzoic acid cyclic anhydride [SBA, 2-(or o-) sulfobenzoic anhydride,^{5,6} systematic name: 2,1-benzoxathiol-3-one-1,1-dioxide]. Solvolyses were in a pure or binary hydroxylic solvent, designated as ROH, where R is hydrogen, alkyl, or fluoroalkyl. The overall reaction is shown in Scheme 1.

The SBA is readily available from several sources and it has a wide variety of important applications both in the laboratory and in industry. It can be considered as being formally related to phthalic acid with one of the carbonyl groups replaced by a sulfonyl group. In the laboratory, for example, it has been used in the synthesis of a catalyst for enantioselective Michael additions⁷ and as a capping agent in solid phase peptide synthesis.⁸

In industrial applications, SBA has been proposed as an additive to lithium ion batteries to control swelling,⁹⁻¹¹ as a reagent for the preparation of proton-conducting fuel cell membranes,^{12,13} as a reagent for the preparation of sulfonate-bearing polysiloxanes for household and health-care formulations,¹⁴ for use in the synthesis of stabilisers in emulsion polymerisation¹⁵ and for use in the synthesis of well-defined diblock copolymers.¹⁶

In the previously studied ^{1,2,17} acyclic carboxylic acid–sulfonic acid anhydrides (Scheme 2) solvolysis leads to two products, whereas (Scheme 1) only one results from solvolysis, with ring-opening, of a cyclic anhydride.

Earlier studies have looked at the rates of solvolysis of both cyclic^{5,6,17} and acyclic^{1,2,17} mixed sulfonic–carboxylic anhydrides.



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Laird and Spence^{5,6,17} studied a wide variety of substrates in only a few solvents, primarily alcohols containing 6.7% ether or aqueous dioxane with, by volume, 10-20% H₂O (or D₂O) and some of the determinations of the specific rates were made at several temperatures, allowing activation parameters to be calculated.

In contrast, our more recent studies concentrated on three acyclic substrates. These were studied in a wide variety of solvents, with consideration of the influence upon the specific rates of the solvent nucleophilicity and the solvent ionising power. Parallel applications of the extended Grunwald–Winstein equation,^{3,4} are in this communication used to correlate the specific rates of solvolysis of SBA.

The extended Grunwald–Winstein equation¹⁸⁻²⁰ can be expressed as in Eqn (1), where a substrate RX is undergoing solvolysis and *k* and *k*₀ are the specific rates of solvolysis in the solvent under investigation and in a standard solvent (chosen²¹ as 80% ethanol). The *l* value represent the sensitivity to change in solvent nucleophilicity (N_T),^{22,23} the *m* value represents the sensitivity to changes in solvent ionising power (*Y*_X for a leaving group X)^{24,25} and *c* is a constant (residual) term.

$$\log \left(k/k_0\right)_{\rm RX} = l N_{\rm T} + mY_{\rm X} + c \tag{1}$$

Results and discussion

Table 1 reports the first-order rate coefficients for the solvolysis of SBA in a variety of hydroxylic solvents at -10.0 °C. Also presented within Table 1 are those $N_{\rm T}$ and $Y_{\rm OTS}$ values that are

Table 1 Specific rates of solvolysis (*k*) of 2-sulfobenzoic cyclic anhydride (SBA)^a at -10.0°C and the appropriate solvent nucleophilicity (N_{T}) and solvent ionising power (Y_{OTs}) values

	010		
Solvent ^b	10 ⁴ k/s ⁻¹	N _T ^c	Y_{OTs}^{d}
100% EtOH	80.1±0.7⁰	0.37	-1.95
90% EtOH	343±16	0.16	-0.77
80% EtOH	652±18	0.00	0.00
100% MeOH	187±2°	0.17	-0.92
95% Acetone	23.2±0.4	-0.49	-2.95
90% Acetone	108±1	-0.35	-1.99
100% TFE	0.81±0.02	-3.93	1.77
97% TFE	3.84±0.15	-3.30	1.83
90% TFE	13.6±0.2	-2.55	1.90
80% TFE	35.0±0.4	-2.19	1.94
70% TFE	88.1±1.0	-1.98	2.00
97% HFIP	3.02±0.04	-5.26	3.61
90% HFIP	16.7±0.7	-3.84	2.90
90T-10E	17.5±0.2	-2.62	1.32
80T-20E	28.1±0.6	-1.76	0.98
60T-40E	51.4±0.8	-0.94	0.21
50T-50E	64.5±0.4	-0.64	0.14
40T-60E	73.5±0.4	-0.34	-0.44
20T-80E	94.1±0.6	0.08	-1.18

^a Determined conductimetrically after injection of 20 μ L of a 0.10 mol dm⁻³ solution of the substrate in dry acetonitrile into 2.0 mL of the indicated solvent (concentration of SBA of *ca* 1.0×10⁻³ mol dm⁻³). Specific rates, averaged from duplicate runs, reported together with standard deviations.

^b Binary solvents on a volume-volume basis at 25.0°C, except for TFE-H₂0 and HFIP-H₂0 mixtures, which are on a weight-weight basis. When not specified the second component is H₂0. T-E represents 2,2,2-trifluoroethanol-ethanol mixtures.

 $^{\circ}$ Values from refs 22 and 23.

^d Values from ref. 25.

 $^{\rm e}$ For solvents also containing 6.7% diethyl ether, values of 54.9×10⁻⁴ s⁻¹ and of 191×10⁻⁴ s⁻¹ can be calculated from the Arrhenius parameters given in Table 3 of ref. 6 for solvolyses at –10.0°C in ethanol and methanol, respectively.

needed for the application of the extended Grunwald–Winstein equation to the experimental specific rates. The choice of a Y_x scale is a difficult one for ring-openings of cyclic anhydrides. In the present instance, the sulfonate anion produced is leaving from the α -carbon but it is not leaving from the product formed (Scheme 1). Since different arenesulfonate leaving groups have for most solvents, similar Y_x scale values,²⁵ the use of Y_{OTs} values is a reasonable compromise. Indeed, Bentley and Llewellyn recommend the use of Y_{OTs} as a general-purpose scale of solvent ionising power for cases where the appropriate Y_x scale is not available.²⁵

For solvolyses in all of the types of solvent used in the present study, it was earlier concluded that benzoyl p-toluenesulfonate solvolysed by an S_N^1 pathway with only minor assistance from nucleophilic solvation,² acetyl p- toluenesulfonate solvolysed by an S_N1 pathway with an increased assistance from nucleophilic solvation (or by a loose $S_N 2$ process, which would be expected to show similar characteristics in an extended Grunwald-Winstein correlation),¹ and *p*-nitrobenzoyl *p*-toluenesulfonate showed very different characteristics in the correlation, such that a bimolecular process was indicated² in all solvents except those rich in the highly ionising 2,2,2-trifluoroethanol (TFE) or 1,1,1,3,3,3-hexafluoro-2 propanol (HFIP). The results from these earlier studies of acyclic mixed carboxylic-sulfonic acid anhydrides, together with those for solvolyses of several carboxylic acid halides^{26,27} and a chloroformate ester,²⁸ are compared, in Table 2, to those for the presently reported mixed carboxylic-sulfonic acid anhydride, SBA. Since the magnitudes of the paired $N_{\rm T}$ and $Y_{\rm CI}$, values tabulated for use in Eqn (1) are not normalised, the magnitudes of the sensitivity values (l and m) do not directly relate to the relative contributions to the LFER from the terms governed by the nucleophilicity and by the ionising power of the solvents [Eqn (2)]. The ratio of the values, l/m, has, however, been found to be a useful indicator of the *relative* importance of the two terms for a series of substrates undergoing solvolysis.^{29,30} The l/m ratios are, therefore, also tabulated in Table 2.

The data from the analysis for solvolyses of SBA reported in Table 2 show an improved correlation when the two solvents rich in HFIP are excluded. This situation usually results from an ionisation mechanism, which is making a negligible contribution towards rate-determining nucleophilic attack mechanisms in the other solvents, becoming a significant contributor in the low nucleophilicity-high ionising power solvents rich in HFIP. The correlation in the 19 studied solvents is shown in Fig. 1, where the deviation of the two HFIP-containing solvents from the correlation line can be noted. Figure 2 shows a simple Grunwald–Winstein plot against Y_{ors} values [use of Eqn (2) without the $l N_{\text{T}}$ term]. It can be seen that, due to multicollinearity, reasonable correlation is very poor.

The solvolyses of phenyl chloroformate²⁷ can be taken as a standard for an addition–elimination (A–E) reaction with the addition process rate-determining (Scheme 3). A variant would involve attack by a pre-associated ROH dimer and the collapse of the first two forward steps into one.

For solvolyses of phenyl chloroformate,²⁸ values are obtained of 1.66 for *l* and 0.56 for *m*, with the *l/m* ratio at a value of 2.96. Similar values are obtained for the solvolyses of *p*-nitrobenzoyl chloride of 1.78, 0.54, and 3.30, respectively.²⁶ For the solvolyses of *p*-nitrobenzoyl tosylate, with the *p*-nitro group disfavouring the ionisation with loss of the tosylate anion, values are obtained of 1.19, 0.66 and 1.80, respectively, believed to indicate essentially the same mechanism but with somewhat less involvement of the nucleophile at the transition state.² For the chlorides, replacement

Table 2 Correlations using the extended Grunwald–Winstein equation of the specific rates of solvolysis of SBA and a comparison with literature values for other solvolyses at acyl carbon

Substrate (T°C)	nª	ľ	mb	C ^b	l/m	R°	F ^d
SBA (-10.0)	19°	0.65±0.09	0.30±0.08	-0.38±0.12	2.17	0.922	46
	17 ^f	0.74±0.08	0.31±0.07	-0.32±0.11	2.39	0.945	58
C ₆ H ₅ CO ₂ Ts (-10.0)	36 ^g	0.11±0.04	0.80±0.04	0.11±0.06	0.14	0.978	364
$p - NO_2C_6H_4CO_2Ts$ (-10.0)	21 ^h	1.19±0.05	0.66±0.06	-0.13±0.06	1.80	0.983	265
CH ₃ CO ₂ Ts (-39.6)	13 ⁱ	0.56±0.10	0.61±0.05	-0.29±0.08	0.92	0.966	70
p-MeOC ₆ H ₄ COCI (25.0)	37 ^j	0.31±0.05	0.81±0.02	-0.08±0.21	0.38	0.989	738
C ₆ H ₅ COCI (25.0)	32 ^k	0.47±0.03	0.79±0.02	-0.49±0.17	0.59	0.990	680
$p - NO_2C_6H_4COCI$ (25.0)	34 ¹	1.78±0.08	0.54±0.04	0.11±0.37	3.30	0.969	237
C ₆ H ₅ COF (25.0)	41 ^m	1.58±0.09	0.82±0.05	-0.09±0.10	1.93	0.953	186
C ₆ H ₅ OCOCI (25.0)	49 ⁿ	1.66±0.05	0.56±0.03	0.15±0.07	2.96	0.980	568

^a Number of solvents (data points).

^b From Eqn (1), with associated standard errors, using N_{T} and Y_{0TS} for first four entries and N_{T} and Y_{CI} for last five entries.

° Correlation coefficient.

^d F-test value.

^e Using all available data points.

^f Omitting the data points for the two HFIP-containing solvents.

⁹ From ref. 2, using all solvents.

^h From ref. 2, omitting acetone-H₂O, TFE-ethanol, 100% TFE and 97% HFIP data points.

ⁱ From ref. 1, using all solvents.

^j From ref. 26, using all solvents.

^k From ref. 26, using the solvolyses believed to follow an ionisation pathway (from a total of 47 measurements).

¹ From ref. 26, omitting the 97% HFIP data point.

^m From ref. 27, using all solvents.

ⁿ From ref. 28, using all solvents.





Fig. 1 Plot of $\log(k/k_0)$ for solvolyses of 2-sulfobenzoic cyclic anhydride (SBA) in 19 solvents against (0.65 $N_{\rm T}$ + 0.30 $Y_{\rm OTe}$).

of the strongly electron-withdrawing *p*-nitro group by the strongly electron-supplying *p*-methoxy group leads to a major change in solvolysis mechanism as indicated by corresponding values of 0.31, 0.81 and 0.36, consistent with extensive ionisation character and only a rather weak nucleophilic assistance within the rate-determining step (Scheme 4).²⁶

Fig. 2 Plot of $\log(k/k_0)$ for solvolyses of 2-sulfobenzoic cyclic anhydride (SBA) in 19 solvents against $Y_{_{OTs}}$ values.

An alternative picture of the process in Scheme 4 would involve a very loose concerted S_N^2 process, with at the transition state rather weak bonding from the carbon at the reaction centre to both the incoming and outgoing nucleophilic species (Scheme 5). Such a process is proposed by Bentley for the solvolyses of acetyl chloride.^{1,31}



 $(Ar = p-CH_3OC_6H_4)$

Scheme 4 Ionisation (assisted by solvation of the developing cation).

+ Cl



Scheme 5

Although we willsubsequently refer to an ionisation reaction when the correlations show a significant l value but a low l/m ratio, it is possible that the detailed pathway could be as in Scheme 5, with the positive charge at the transition state dispersed.

The solvolyses of benzoyl chloride are delicately balanced²⁶ in the solvents used for the investigation with concurrent operation of both ionisation and A–E mechanisms. For the solvent region favouring ionisation, values are obtained of 0.47 for *l*, 0.79 for *m*, and 0.59 for the *l/m* ratio. The corresponding tosylate,² with a leaving group stabilised by resonance, solvolysed by an ionisation mechanism for the full range of solvents with values of 0.11 for *l* and 0.80 for *m*, such that the *l/m* ratio is 0.14. Indeed, an excellent correlation for these solvolyses was obtained² when only solvent ionising power was considered.

To give a measure of the specific solvolysis rates relative to earlier studied mixed carboxylic–sulfonic acid anhydrides, we can look at specific rates measured (or estimated using the Arrhenius equation) at -10.0 °C in 95% acetone. Relative values are: SBA (1.0), acetyl tosylate (99),¹ benzoyl tosylate (0.0032)² and *p*-nitrobenzoyl tosylate (0.20).² The solvolysis of SBA is appreciably slower than for the open-chain aliphatic substrate and faster than for the open-chain aromatic substrates, which are appreciably stabilised by the interaction of the aromatic ring with the carbonyl group.

An extended Grunwald-Winstein treatment of the solvolyses of SBA leads, for all 19 solvents, to values for l of 0.65 and for mof 0.30, with a rather low correlation coefficient of 0.922 (Table 2). Inspection of the plot (Fig. 1) of log k/k_0 against 0.65 N_T + $0.30Y_{CI}$ [using Eqn (1)] shows that the two points for HFIP-H₂O mixtures lie above the plot. Omission of these two points, leads to a moderate improvement of the correlation with an lvalue of 0.74 and m value of 0.31, with a correlation coefficient of 0.945. As can be seen by a comparison with the data for the solvolysed related compounds given in Table 2, this correlation, although marginally acceptable, is significantly inferior to the other correlations within the table. This is consistent with the observation earlier that the ring-opening leads to the breaking of one bond to the sulfonyl group but the formed sulfonate ion is still bonded as an ortho-substituent to the formed acid or ester group (Scheme 1).

The values for both l and m are lower than for related solvolyses believed to follow the addition–elimination pathway, with addition rate-determining, but the l/m ratio of 2.39 is consistent with such a pathway. One way of rationalising the low values, coupled with an l/m ratio compatible with an A–E pathway, is to assume that a much earlier transition state is present along the reaction pathway for the solvolyses of the cyclic SBA.

In an earlier study, a consideration of the effect of a substituent in the 4- or 5- position of the aromatic ring of SBA

was considered.⁶ A Hammett equation³² treatment was carried out with the substituent (Cl, Br, I, NO₂) in the 4-position (*para* to the carboxyl group and *meta*- to the sulfonyl group). For a chlorine substituent, a study was also carried out with the substituent in the 5-position. Remarkably, at -25° C, the specific rates for the two isomeric substrates (4-chloro- and 5-chloroderivatives of SBA) were essentially identical to each other for the solvolyses in methanol, ethanol, 1-propanol, and 2-propanol. Unfortunately, the influence of the other substituents was only studied when in the 4-position and it would be dangerous to generalise from this one observation.

A common situation, in applications of the Hammett equation, is to have two (or more) aromatic ring substituents and such situations can be considered as additive as regards the σ values of the substituents.³² A much less common situation is to have one substituent but two reaction sites, as in the study here under consideration. Laird and Spence⁶ attempted to analyse this situation using an Hammett-equation³² approach. The extended form used involved two terms.^{33, 34} These govern the influence of the substituent for each of the two directions leading into the anhydride ring, which is *ortho*-fused to the benzene ring [Eqn (2)].

$$\log(k/k_0) = \rho_1 \sigma_1 + \rho_2 \sigma_2 + c \tag{2}$$

It is the $\rho\sigma$ terms that are additive and they represent the sensitivities of the specific rates towards the changes at the two "reaction sites" of the substrate: in this instance, to the changes taking place at the carbonyl carbon and at the developing sulfonate anion during the heterolytic ring-opening process.

It was found⁶ that the two ρ values obtained from the multiregression analysis approach were considerably lower than the values for addition to the carbonyl group of substituted benzaldehydes35 and for the ethanolysis of ethyl arenesulfonates.³⁶ It was concluded that an early transition state was present with bond making running ahead of bond breaking. This conclusion is consistent with the A-E mechanism presently suggested by the extended-Grunwald-Winstein treatment. It should, however, be mentioned that six data points are considerably less than the number recommended for a two-term regression analysis.³⁷ Also, this seems to be a type of situation where second-order effects, involving a third term of the $\rho_{12}\sigma_{1}\sigma_{2}$ form might make a noticeable contribution. In contrast, when a series of substituents are in two aromatic rings, one in the attacking nucleophile and one in the substrate, then only a very small contribution from a cross-interaction term of this type is observed.38-40

A study of solvent deuterium isotope effects⁵ in the solvolyses of SBA in 90% dioxane–10% H₂O (or D₂O) showed no trend in the $k_{\rm H_2O}/k_{\rm D_2O}$ value at three temperatures in the range of 9.7– 17.2 °C, and an average value of 1.45±0.05 was observed. This value is slightly higher than for the corresponding solvolyses of benzenesulfonic anhydride (1.20) and methanesulfonic anhydride (1.22) at 23.0 °C. For the cyclic 3-sulfopropionic anhydride at 10.2 °C, a $k_{\rm H_2O}/k_{\rm D_2O}$ ratio of 1.27 was observed.¹⁷ These ratios indicate similar solvent deuterium isotope effects for sulfonic anhydrides and cyclic mixed sulfonic–carboxylic anhydrides, with slightly higher values for the cyclic mixed anhydrides.

Due to slower reactions, studies with carboxylic anhydrides have been made with more aqueous dioxane– H_2O mixtures. These reactions are subject to acid catalysis and many of the numerous studies have been of this catalysis.⁴¹⁻⁴³ The deuterium isotope effect values are appreciably larger than those for SBA, with values in the range of 2.7–3.9 having been recorded for

spontaneous (no acid catalysis) solvolyses of acyclic⁴⁴ and cyclic^{45,46} carboxylic anhydrides in water at 25 °C.

One possible explanation for the higher values in water than in 90% dioxane–10% H_2O could be that dioxane is to some degree replacing H_2O as a general-base assisting the hydrolysis. Both dioxane and acetone have been shown to be able to function as nucleophiles in their mixtures with water⁴⁷ and, presumably, they could also function as bases. However, the observation that runs in 60% dioxane–40% water give⁴⁸ essentially the same solvent deuterium isotope effect for hydrolyses of acetic anhydride and glutaric anhydride as their values in 100% H_2O would argue against this suggestion. A more probable explanation could be that the more reactive mixed carboxylic sulfonic anhydride, SBA, is less selective as regards whether it reacts with H_2O or D_2O than the less reactive acylic or cyclic carboxylic acid anhydrides.

In the earlier study⁵ of the solvolyses of SBA, the effect on the specific rate of temperature variation was reported in terms of activation energies and frequency factors for dioxane-water (or D₂O) and five alcohols (containing 6.7% ether). The frequency factors correspond to entropy of activation (ΔS^{\ddagger}) values from -10 cal mol⁻¹ K⁻¹ (in 2-propanol) to -29 cal mol⁻¹ K⁻¹ (in 90% dioxane-10% H₂O). These values are similar to the values of -23 cal mol⁻¹ K⁻¹ in ethanol and -16 cal mol⁻¹ K⁻¹ in methanol for the solvolyses of *p*-nitrobenzoyl tosylate, solvolyses believed to be following an addition-elimination pathway, with the addition rate-determining.² The values are much more negative than the values of -3 cal mol⁻¹ K⁻¹ in ethanol and -4 cal mol⁻¹ ¹ K⁻¹ in methanol for benzoyl tosylate solvolyses, believed to follow an ionisation pathway.² Johnson⁴⁹ has proposed that large negative entropies of activation coupled with appreciable solvent deuterium isotope effects can be considered as giving excellent support to claims that general-base catalysis is operating.

The solvolysis of the cyclic carboxylic anhydride, succinic anhydride, in 60% dioxane⁴⁸ also involves an appreciably negative entropy of activation of -31 cal mol⁻¹ K⁻¹ and the appreciably slower reaction follows mainly from an enthalpy of activation of 14 kcal mol⁻¹, somewhat higher than the 11.5 kcal mol⁻¹ for solvolysis of SBA in 90% dioxane.⁵ This difference is consistent with a favourable lowering of the electron density at the carbonyl carbon when it is attached to a sulfonate group rather than when attached to a carboxylate group: the Hammett σ_m values are 0.31 for COMe and 0.65 for SO₂Me.³³

Conclusions

Application of the extended Grunwald–Winstein equation to the solvolyses of the mixed cyclic anhydride 2-sulfobenzoic anhydride (SBA; systematic name: 2,1,benzoxathiol-3-one-1,1-dioxide) leads to sensitivities towards changes in solvent nucleophilicity (*l* value) and towards change in solvent ionising power (*m* value) that are lower than those for previously studied acyclic mixed anhydrides of carboxylic and sulfonic acids. The *l/m* ratio was, however, within the range previously observed for reactions believed to follow an addition–elimination (association–disassociation) pathway, with the addition ratedetermining (Table 2).

An earlier extended Hammett treatment of the parent and 4-substituted (*para* to the carbonyl group and *meta* to the sulfonyl group) derivatives gave what were considered to be low ρ values for the influences at these two reaction centres.⁶ An early transition state was proposed in which bond making had proceeded further than bond breaking, consistent with the conclusion reached from the Grunwald–Winstein treatment.

A previous study⁵ of the solvent deuterium isotope effect for hydrolysis $(k_{\rm H_2O}/k_{\rm D_2O})$ of SBA leads to a value in 90% dioxane–10% H_2O (or D_2O) at 9.7 to 17.2°C of 1.45, which is appreciably lower than the range of 2.7 to 3.9⁴⁴⁻⁴⁶ observed for the solvolyses of cyclic carboxylic anhydrides in more aqueous solvents. While alternative explanations are possible, this is consistent with the higher reactivity of the mixed anhydrides leading to a lower selectivity as regards reaction with H_2O or D_2O .

The bimolecular (or higher) nature of the solvolyses of SBA is supported by studies at several temperatures leading to frequency factors⁵ which convert to entropies of activation in the -10 to -29 cal mol⁻¹ K⁻¹ range. These values are similar into those obtained for *p*-nitrobenzoyl tosylate solvolysis¹ and considerably more negative than those for benzoyl tosylate solvolysis,¹ consistent with an addition–elimination pathway, rather than an ionisation pathway, for the solvolyses of SBA.

Experimental

The 2-sulfobenzoic acid cyclic anhydride (SBA, TCI >95%) was used as-received. For determination of the specific rates of solvolysis, a 0.1 M solution of SBA in dry acetonitrile was prepared and 20 μ L at room temperature was added to 2 mL of the appropriate solvent contained within a conductivity cell at –10.0 °C to give a 1×10⁻³ mol L⁻¹ solution of the reactant.

The progress of the reaction was monitored by following the increases in conductivity as the mixed diacid (reaction with water) and/ or carboxylic acid ester derivative of the diacid (reaction with alcohol) were produced (Scheme 1), as previously described.¹ Details of the conductivity apparatus and the computer procedure for calculation of the specific rates have previously been reported.^{50,51} The multiple regression analyses were performed using commercially available statistical packages.

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