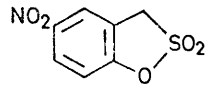
Reaction of 2-Hydroxy-5-nitrotoluene-α-sulphonic Acid Sultone with Nucleophiles

By **Timothy Deacon, Alex Steltner,** and **Andrew Williams,*** University Chemical Laboratories, Canterbury, Kent CT2 7NH

The title sultone is cleaved in the presence of nucleophiles in aqueous solution *via* general base-catalysed and nucleophilic pathways. The sensitivity of the nucleophilic reactivity to reagent structure (β_N) suggests extensive bond formation in the transition state. Proton transfer for nucleophilic attack by amines occurs after the S–N bond forming process is complete.

Reactions involving cleavage of the S–O bond in 2-hydroxy-5-nitrotoluene-α-sulphonic acid sultone (I) are interesting because the very favourable *E*1cB mechanism exhibited in the alkaline hydrolysis and aminolysis of

aryl toluene α-sulphonates (II) [1] is not followed.[2,3a] Kaiser and his co-workers [3a] have indicated that the lability of the S–O bond in (I) is due to release of ring



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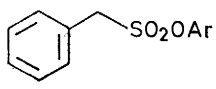


(II)

strain as in the hydrolysis of analogous five-membered cyclic phosphyl [3b] and sulphate esters.[3a]

This paper deals with the detailed nature of the transition state for cleavage of the S–O bond in the sultone (I) and provides an explanation for the mechanistic pathway taken during substitution. A preliminary account of part of this work has appeared.[1a]

EXPERIMENTAL

Materials.—Amines were purified by recrystallisation of their hydrochlorides or by distillation and other buffer species were either of analytical reagent grade or were recrystallised. 2-Hydroxy-5-nitrotoluene-α-sulphonic acid sultone was prepared from the parent sultone by nitration and recrystallised from ethanol, m.p. 149—150° (lit.,[4] 148°). Deuterium oxide (99.8%) was obtained from Prochem and doubly distilled water was used throughout. Acetonitrile was purified by distillation from P_2O_5 and then from calcium hydride; analytical reagent grade dioxan was used after percolating through activated alumina to purge from peroxides.

Methods.—Reactions were followed spectrophotometrically using the release of 4-nitrophenol at 350 nm for pH values below 6.5 and 400 nm for more alkaline solutions. A typical procedure involved introducing 25 μl of a stock solution of the sultone in alcohol or acetonitrile on the tip of a glass ' plumper ' into buffered reagent (2.475 ml) in a quartz cell in the thermostatted cell compartment of a Beckman DBG spectrophotometer. The absorption was monitored continuously with a Servoscribe (Smith's Industries) recording potentiometer *via* a linear–logarithmic converter and a ' back-off ' attachment. First-order rate constants were calculated using infinity readings taken after 5—6 half lives.

Fast reactions were measured at 400 nm with a stopped-flow apparatus constructed in this laboratory. The mixing chamber, observation tube, and supply syringes (2.5 ml) are encased in a massive brass jacket kept at the required temperature with a flow of thermostatted water. An SP 500 monochromator provided the light source which was detected with a photomultiplier (IP 28) powered by a Farnell E1 stabilised EHT power supply; the signal was amplified by the oscilloscope (Telequipment DM 64) which possessed a fluorescent storage screen. In these experiments the change in transmission was adjusted to be small and was therefore proportional to the concentration change. The rate constants were estimated using a capacitance–resistance discharge device developed by Crooks *et al.*[5] which was calibrated by photographing the oscilloscope trace with a Polaroid CR-9 Land camera and a type 105 Land film. The voltage *versus* time was measured by use of a photographic enlarger to project the negative trace onto graph paper. A plot of $\log_{10} V_t - V_\infty$ *versus* time gave the rate constant for the particular setting of the variable resistance.

The pH of the reaction solutions was measured after each run with a Pye-Dynacap instrument calibrated with E.I.L. standard buffers; pD was measured using the pH-meter reading and the equation pD = meter reading + 0.37 determined for solutions of 1M ionic strength.[6a]

Deuterium oxide buffers were made up in the case of 4-picoline and acetate from the free base and standard DCl but in the case of ethyl glycinate using the protio hydrochloride and NaOD. In the latter the protio content was not increased by more than 0.3%.

Product Analysis.—The kinetics were carried out with *ca.* 10^{-4}M-sultone making it difficult to estimate products under the reaction conditions; solubility in 1M ionic strength solutions prevents higher concentrations of substrate to be employed so that product analysis was carried out using dioxan–water solvent (50 : 50, v/v). Evaporation of the product, acidification to pH 4, extraction with chloroform, and weighing the residue enabled a crude estimate of the yield to be made. Analysis of the recrystallised material was also carried out (n.m.r. with a Perkin-Elmer R-10 machine and elemental analysis with a Hewlett-Packard 185 CHN analyser by Mr. G. M. Powell of this laboratory). The *piperidide*, recrystallised from ethanol, had m.p. 178—181° (Found: C, 47.9; H, 5.2; N, 9.0. $C_{12}H_{16}N_2O_5S$ requires C, 48.0; H, 5.3; N, 9.3%), δ ([$^2H_6$]-DMSO) 1.5br (6 H, CH_2), 3.15br (4 H, CH_2N), 6.5 (2 H, s, CH_2Ph), 7—8.5 (3 H, m, ArH), and 11.8br (1 H, ArO*H*). The *ethoxycarbonylmethylamide*, recrystallised from methanol, had m.p. 227—230° (Found: C, 41.3; H, 4.3; N, 8.9. $C_{11}H_{14}N_2SO_7$ requires C, 41.5; H, 4.4; N, 8.8%), δ ([$^2H_6$]-DMSO) 1.2 (3 H, t, CH_3), 3.8 (2 H, s, CH_2N), 4.2 (4 H, m, CH_2Ph and CH_2O), and 7.8—8.8br (5 H, m, ArH, ArOH, NH).

Molecular Orbital Calculations.—The programme for CNDO/2 calculations described by Pople and Beveridge [6b] was used to provide a check on previous calculations and to give information about the structure of the carbanion from a sulphonate ester. Angles and bond lengths are those derived from crystallographic data for analogous compounds and no attempt is made to minimise parameters. Calculations were carried out using the University of London Computer Centre's CDC 7600 machine *via* the University of Kent Computer Centre.

RESULTS

Kinetics.—Previous kinetic work with the title sultone has shown a pronounced solvent effect which disappears as the ionic strength exceeds *ca.* 0.4M.[7] We therefore

[1] (*a*) A. Williams, K. T. Douglas, and J. S. Loran, *J.C.S. Chem. Comm.*, 1974, 689; (*b*) J. F. King and R. P. Beatson, 7th Internat. Symposium on Sulphur Chemistry, Bangor, 1974, Abstract B20.

[2] (*a*) P. Müller, D. F. Mayers, O. R. Zaborsky, and E. T. Kaiser, *J. Amer. Chem. Soc.*, 1969, **91**, 6732; (*b*) O. R. Zaborsky and E. T. Kaiser, *ibid.*, 1970, **92**, 860.

[3] (*a*) E. T. Kaiser, *Accounts Chem. Res.*, 1970, **3**, 145; (*b*) F. H. Westheimer, *ibid.*, 1968, **1**, 70.

[4] W. Markwald and H. H. Frahne, *Ber.*, 1898, **31**, 1854.

[5] J. E. Crooks, M. S. Zetter, and P. A. Tregloan, *J. Phys.* (*E*), 1970, **3**, 73.

[6] (*a*) A. Williams, *J.C.S. Perkin II*, 1975, 947; (*b*) J. A. Pople and D. L. Beveridge, ' Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

[7] E. T. Kaiser, Kwok-Wing Lo, K. Kudo, and W. Berg, *Bio-organic Chemistry*, 1971, **1**, 32.

carried out all our kinetic investigations using 1M ionic strength aqueous solutions made up with sodium chloride.

The increase is absorption at 350 or 400 nm in reactions of the sultone in aqueous buffers was first order over *ca.* 90% of the total progress curves and the first-order rate constants were found to be proportional to the concentration of the total buffer species (Figure 1). No catalysis of the

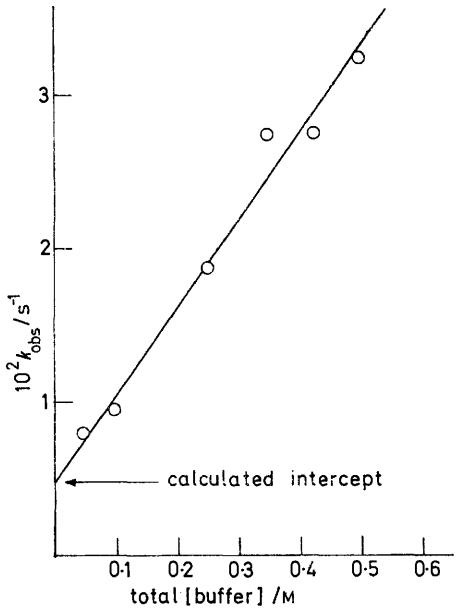


FIGURE 1 Plot of k_{obs} *versus* total ethylamine concentration at pH 8.23, Tris buffer at 0.1M (not included in the abscissa), ionic strength maintained at 1.0M with NaCl, 25°. Intercept, calculated from pH and total Tris base, is 5.1×10^{-3} s^{-1} (hydroxide contributes 2.4×10^{-3} s^{-1}). Value of k_B for ethylamine is calculated as shown in the text

reaction of buffer with sultone was observed as evidenced for example by an increase in rate constant to buffer concentration ratio as the buffer concentration increased. For buffer species with high pK_a such as ethylamine rate constants were measured at relatively low pH using Tris buffer and plots of rate constant *versus* nucleophile concentration therefore gave intercepts at zero concentration due to the action of the buffering material. These intercepts agreed with those estimated from the parameters for Tris (Table 1) and hydroxide knowing the buffer concentration and pH.

The basic form of the buffer was found to be responsible for the cleavage for a few selected examples (Table 1) by a plot of the slope of the observed rate constant against the total buffer concentration versus the fraction of base in the buffer. Figure 2 shows data for ethyl glycinate and in all cases the intercept on the ' acid ' limb was < *ca.* 5% of that on the ' basic ' axis. The other buffer species were investigated at a single pH usually the pK_a of the system and k_B estimated assuming only the base species was involved.

Second-order rate constants (k_B) for reaction of the base species with sultone are listed in Table 1 and plotted in a Brønsted type plot in Figure 3. The values for imidazole, *N*-methylimidazole, and hydroxide ion agree well with those previously determined by Kaiser and his co-workers.[7a]

Solvent deuterium oxide isotope effects were observed for ethyl glycinate, acetate, and 4-picolinate buffers and are recorded in Table 1.

Piperidine buffers gave the corresponding amide in stoicheiometric quantity within the error of the rather crude method (estimated to be *ca.* ±15%). In all the kinetic experiments the change in absorbance was almost the same for a given concentration of sultone for all the nucleophiles

TABLE 1

Reactivities of buffers with 2-hydroxy-5-nitrotoluene α-sulphonic acid sultone [a]

	Nucleophile	pK_a [b]	k_B/l mol^{-1} s^{-1} [c,f]
(1)	Ethyl β-alaninate	9.25	1.0
(2)	Morpholine	8.32	1.6
(3)	Ethyl glycinate	7.65	1.2×10^{-1} ($k_B^D = 8.6.10^{-2}$, $k_H/k_D = 1.37$)
(4)	β-Alanine	10.25	7.6
(5)	Ethylamine	10.88	25
(6)	Aniline	4.75	3.0×10^{-3}
(7)	Aminoacetonitrile	5.56	4.8×10^{-3}
(8)	Ammonia	9.49	1.3
(9)	Hydroxide	15.6	1 400 [e]
(10)	Methoxyamine	4.54	1.5×10^{-2}
(11)	Acetate	4.55	2.7×10^{-3} ($k_B^D = 2.7.10^{-3}$, $k_H/k_D = 1.0$)
(12)	Hydroxylamine	5.97	16
(13)	Piperazine H^+ [d]	5.68	8.1×10^{-3}
(14)	Semicarbazide	3.65	6.1×10^{-4}
(15)	Hydrazine	8.1	12
(16)	Phenylhydrazine	5.24	2.0×10^{-2}
(17)	Trimethylamine oxide	4.88	2.7×10^{-4}
(18)	Phosphate dianion	6.34	4.9×10^{-2}
(19)	Formate	3.35	1.3×10^{-3}
(20)	Chloroacetate	2.79	2.0×10^{-4}
(21)	Maleic acid dianion	5.76	1.0×10^{-2}
(22)	Methylamine	11.0	92
(23)	Diethylamine	10.82	0.67
(24)	Triethylamine	9.86	10^{-2}
(25)	Piperidine	11.35	120
(26)	Imidazole	7.21	2.7×10^{-3}
(27)	*N*-Methylimidazole	7.20	2.4×10^{-3}
(28)	Pyridine	5.17	1.9×10^{-4}
(29)	4-Picoline	6.02	1.0×10^{-3} ($k_B^D = 5.8.10^{-4}$, $k_H/k_D = 1.8$)
(30)	2,6-Lutidine	6.60	2.9×10^{-4}
(31)	Tris [g,h]	8.23	5.5×10^{-2}
(32)	Phenol	9.95	62
(33)	Methoxyacetic acid	3.27	1.1×10^{-3}
(34)	n-Butylamine	10.59	20
(35)	n-Propylamine	10.53	11
(36)	Cyclohexylamine	10.64	3.8
(37)	t-Butylamine	10.55	0.47

[a] Ionic strength made up to 1.0M with NaCl; 25°; 1% of either acetonitrile or ethanol (from stock substrate solution). [b] Values of pK_a taken from A. Williams and W. P. Jencks, *J.C.S. Perkin II*, 1974, 1753; W. P. Jencks and J. Regenstein, ' Handbook of Biochemistry,' ed. H. A. Sober, Chemical Rubber Co., Cleveland, Ohio, 1970, 2nd edn., pp. J-150—189, or are as determined from pH values of the various buffer solutions used in this study. [c] These values have an uncertainty of not more than ±10% from the maximum and minimum possible slopes through the experimental points (see Figure 2); the quoted values are for the best lines. [d] Monoprotonated form of piperazine is acting as the base species. [e] Pseudo-first-order rate constants were linear in hydroxide ion concentration up to pH 11; measurements of rate constant at high pH with the stopped-flow apparatus. [f] Values for k_A (see Figure 2) are only upper limits and are: 1, 10^{-2}, 10^{-4}, 5×10^{-4}, and 1 l mol^{-1} s^{-1} for species (2), (3), (11), (13), and (1) respectively. [g] Tris = trishydroxymethylaminomethane. [h] Reference to the value of k_B for t-butylamine reveals that although less reactive than expected for primary amines Tris is slightly more reactive than is to be expected since it has a more sterically hindered nitrogen than t-butylamine (see Figure 3). This enhanced rate constant could be due to participation of the Tris oxyanion present to a small extent.

depending on the wavelength employed, indicating that phenol was being released.

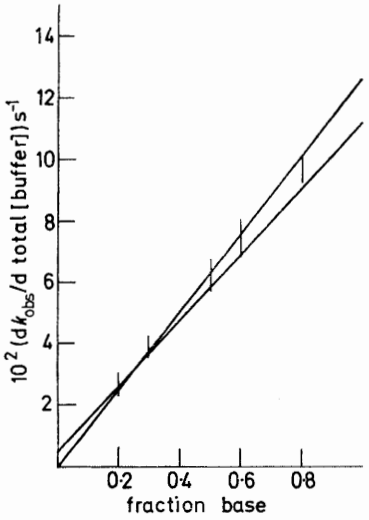


FIGURE 2 Plot of dk_{obs}/d[buffer] against the fraction of buffer present as base (fr B). In all the test cases examined the intercept at fr B = 0, quoted as k_A in Table 1, is an upper limit only

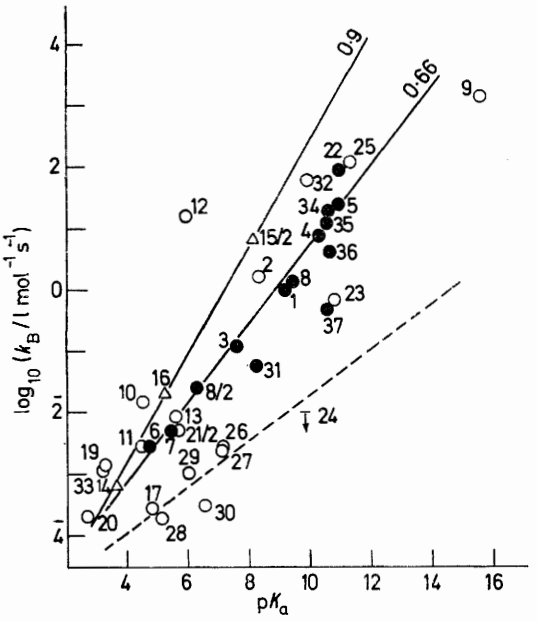


FIGURE 3 Brønsted type plot of $\log_{10}(k_B$/l mol^{-1} s^{-1}) *versus* pK_a (HB); identification of points as in Table 1; ● = primary amines, △ = hydrazine derivatives. The rate constants for symmetrical dibasic species are halved but the pK_a values are not corrected

DISCUSSION

Alkaline hydrolysis of the sultone has been shown, *via* oxygen-18 labelling, to involve S–O cleavage.[8] The product of reaction with amines indicates nucleophilic attack at sulphur and in other cases the absorption change is used as a measure of product since Ar–O fission would not yield 4-nitrophenol.

Before we discuss details of the transition-state for cleavage it is essential to decide whether the reaction with the base species of the buffer involves nucleophilic attack or general base catalysis of hydrolysis. Figure 3 indicates that although base species with similar structures obey good linear free energy relationships there is little correlation over a wide range of structures; together with the product analysis this confirms that nucleophilic attack at sulphur is occurring. We may extend this conclusion to other base species using the deuterium oxide solvent isotope effect (acetate, 1.0; ethyl glycinate, 1.37); the latter certainly involves some secondary effect due to substitution on the nitrogen. However, imidazole and *N*-methylimidazole have solvent isotope effects 4.2 and 3.5 respectively [7] and we find 4-picoline has $k_{H/D}$ 1.8; these values are above the minimal expected for general base catalysis.[9] Presumably pyridine also acts *via* this pathway. It was possible to measure an upper limit for trimethylamine (Table 1) so that a general base line including imidazole, *N*-methylimidazole, pyridine, and 4-picoline must lie close to or below this point. All points coming above this line will be due to a nucleophilic reaction and not general base catalysed hydrolysis. At low pK_a presumably the two pathways will compete on an equal footing but this will occur only near pK_a *ca.* 2. It is very unlikely that such a scattered diagram could arise totally from general base catalysis which is known not to possess stringent steric or structural requirements [10] except when the base is exceptionally hindered as with 2,6-lutidine.[10c]

The swing from nucleophilic to general base attack has been observed before for similar reagents and has been attributed to steric effects, less bulky bases tending to act as nucleophiles.[11] Similar explanations have been proposed for analogous reactions of aryl diphenylphosphinates.[12] It is interesting that phosphate dianion, normally considered to be a poor nucleophile, is in our system at least 30-fold more nucleophilic than imidazole.* It is a moot point whether the steric requirements for nucleophilic attack on the sulphur atom in the sultone are any more stringent than those in the open chain compounds studied by Kice.[11]

S_N2(S) versus E1*cb Mechanisms*.—The *E*1cB mechanism for hydrolysis would involve the ionisation of an α-proton (pK_a in DMSO solvent of the parent phenyl

* K. T. Douglas (Ph.D. Thesis, University of Kent, 1973) has observed a similar reversal of the normal nucleophilic propensities of phosphate dianion and imidazole in their reactions with 4-nitrophenyl dimethylphosphinate.

[8] O. R. Zaborsky, Ph.D. Thesis, University of Chicago, 1968.
[9] (*a*) S. L. Johnson, *Adv. Phys. Org. Chem.*, 1967, **5**, 237; (*b*) P. M. Laughton and R. E. Robertson, 'Solute–Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Dekker, New York and London, 1969, p. 399.
[10] (*a*) A. R. Butler and V. Gold, *J. Chem. Soc.*, 1961, 4362; (*b*) V. Gold and E. G. Jefferson, *ibid.*, 1953, 1409; (*c*) F. Covitz and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1963, **85**, 1773.
[11] (*a*) J. L. Kice, C. A. Walters, and S. B. Burton, *J. Org. Chem.*, 1974, **39**, 346; (*b*) J. L. Kice and J. D. Campbell, *ibid.*, 1971, **36**, 2291.
[12] A. Williams and R. A. Naylor, *J. Chem. Soc.* (*B*), 1971, 1967.

sultone is 15.6 [13a]) to yield a carbanion (III) or (IV). There is at present considerable doubt as to the configuration of a sulphonyl carbanion [13b] but at least in the open chain case there seems to be some preference for

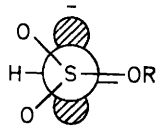
TABLE 2

Some selectivity values for substitution at sulphonyl centres

Substrate	Nucleophile	Selectivity [a]	Ref.
$(XC_6H_4SO_2)_2$	Et_3N, OH^-, F^-	ρ 4.3, 3.6, 5.0	*b*
$(C_6H_4SO_2)_2$	Various	0.9	*c*
$XC_6H_4SO_2Cl$	Pyridines	ρ 0.3—0.89 0.41—0.56	*d*, 9*c*
	Anilines	ρ 0.44—1.14 ρ 0.65—0.93	*e*
	H_2O (varying solvent)	ρ 0.1—1.7	*f*
$XC_6H_4SO_2F$	OH^-, H_2O	ρ 2.79	*g*
	H_2O	ρ 1.8	*h*
$PhSO_2Cl$	RCO_2^-	0.33	*i*
Dansyl chloride	RNH_2	0.52	*j*
$PhSO_2Cl$,Br,I	RNH_2, OH^-	Minimal element effect	*k*
OSO_2OpNp [a]	ArS^-	0.05	*l*
OSO_2OpNp [a]	RNH_2	0.13	*m*
$OSO_2OC_6H_4X$	H_2O	β_L −1.2	*n*
CH_2NSO_2OpNp [a]	RNH_2	0	*p*
$PhCHSO_2OpNp$ [a]	RNH_2	0	*q*
$PhSO_2OAr$	OH^-	β_L −0.93	*r*
$XC_6H_4SO_2OPh$	OH^-	ρ 2.24	*r*
$XC_6H_4SO_2OpNp$ [a]	PhS^-	ρ 1.18	*s*

[a] Except where stated the selectivity refers to β_N; *p*Np = 4-nitrophenyl. [b] J. L. Kice, *J. Org. Chem.*, 1972, **37**, 1865; J. L. Kice and G. J. Kaspereck, *J. Amer. Chem. Soc.*, 1970, **92**, 3393; J. L. Kice, G. J. Kaspereck, and D. Patterson, *ibid.*, 1969, **91**, 5516; there is doubt about the path involved in the NEt_3 catalysis.[4a] [c] J. L. Kice and E. Legan, *J. Amer. Chem. Soc.*, 1973, **95**, 3912; an explicit β_N is not calculated in this paper and nucleophilic attack is compared with attack at the acyl centre. [d] O. Rogne, *J. Chem. Soc.* (*B*), 1970, 727. [e] O. Rogne, *J. Chem. Soc.* (*B*), 1970, 1056; 1971, 1855; *J.C.S. Perkin II*, 1972, 472. [f] F. E. Jenkins and A. N. Hambly, *Austral. J. Chem.*, 1961, **14**, 190. [g] Ref. 19*a*. [h] M. E. Amberlin and C. A. Bunton, *J. Org. Chem.*, 1970, **35**, 1825. [i] Reported by A. R. Houghton and R. M. Laird in 'Hydrogen-bonded Solvent Systems,' eds. A. K. Covington and P. Jones, Taylor and Francis, London, 1968, p. 347. [j] B. S. Hartley, *Biochem. J.*, 1970, **119**, 805; dansyl = 5-dimethylamino-naphthalene-1-sulphonyl. [k] E. Ciuffarin, L. Senatore, and M. Isola, *J.C.S. Perkin II*, 1972, 468. [l] T. Kurusu, W. Tagaki, and S. Oae, *Bull. Chem. Soc. Japan*, 1970, **43**, 1553. [m] S. J. Benkovic and P. A. Benkovic, *J. Amer. Chem. Soc.*, 1966, **88**, 5505. [n] E. J. Fendler and J. H. Fendler, *J. Org. Chem.*, 1968, **33**, 3852. [p] A. Williams and K. T. Douglas, *J.C.S. Perkin II*, 1974, 1727. [q] A. Williams, K. T. Douglas, J. S. Loran, and A. Steltner, to be submitted. [r] R. V. Vizgert, *Zhur. obshchei Khim.*, 1958, **28**, 1873; *Russ. Chem. Rev.*, 1963, **32**, 1. [s] S. Oae, Y. Yoshikawa, and W. Tagaki, *Bull. Chem. Soc. Japan*, 1969, **42**, 2899.

the tetrahedral form corresponding to structure (IV). Molecular orbital calculations using the CNDO/2 programme indicate that the parent sulphene CH_2SO_2 prefers the planar configuration to the 'perpendicular' by a factor of *ca.* 35 kcal mol^{-1}.[14] The transition-state for the elimination of the phenolate anion from structures (III) or (IV) would be expected to resemble the perpendicular form of the sulphene and therefore provide a much less favourable pathway for



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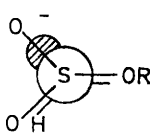
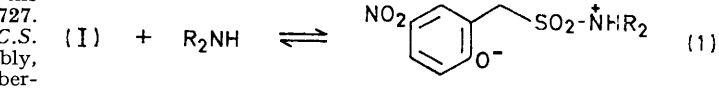


(IV)

substitution than the *E*1cB mechanism for the open-chain form [1a] which presumably involves a planar incipient sulphene in the transition-state. This perpendicular pathway would be expected to be suppressed below the S_N2 process because in the open-chain derivative the latter mechanism is *ca.* 10^3-fold less effective than the elimination pathway.[1a]

Transition State for Nucleophilic Attack.—Owing to scatter in Figure 3 it is not possible to utilise all the nucleophilic data in one Brønsted relationship and we can consider only series of nucleophiles of similar structure. Primary amines and hydrazines fit good lines of slope $\beta_N = 0.66$ and 0.90 respectively; these selectivities suggest considerable positive charge on the nitrogen in the transition state implying advanced S–N bond formation. Any conclusions as to the extent of bonding in the transition state must be tempered by the fact that we use as a model the acid dissociation constant of the buffer species rather than the equilibrium for the overall reaction [equation (1)]. The disadvantages of using the acid



(1)

dissociation constant are discussed by Jencks [15] and Fersht.[16] Table 2 collects some data for Brønsted type selectivities for attack of nucleophiles at sulphonyl sulphur. The effect of variation of substituents on the sulphur portion seems to indicate build up of charge on sulphur consistent with considerable bond formation in the transition state. Variation of nucleophile structure yields Brønsted type sensitivities which range from 0.33 for carboxylate attack on benzenesulphonyl chloride to 0.93 for anilines on 4-nitrobenzenesulphonyl chloride. Our conclusions concerning transition state structure must clearly be confined to the substrate in hand.

The Hammett δ^- dependence for attack of hydroxide ion on substituted 2-hydroxytoluene-α-sulphonic acid sultones [17] implies that the S–O bond is partially broken in the transition-state and if we assume that a similar situation holds for amine attack then, using the data reported here, we are able to construct a picture of the transition-state (V) as in equation (2).

[13] (*a*) D. F. Mayers and E. T. Kaiser, personal communication; (*b*) M. Gresser, *Mechanisms Reactions Sulphur Compounds*, 1969, **4**, 29.

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Our results do not allow a clear distinction to be made between a concerted process or a stepwise one with a pentacovalent intermediate.[3a,17] If the latter were involved, proton transfer would occur after cleavage of the S–O bond [*via* path A in equation (3)] otherwise it would have to be involved in a rate-determining step in order for there to be a high β_N. This requirement leads to the conclusion that proton transfer from the intermediate (a strong acid [18]) is *slower* than the fission of an S–OAr bond (*via* path B). Although this is an unlikely situation, it is not impossible; the concerted process with transition-state as in (V) does not have this objection and we feel that the present evidence is slightly in favour of a concerted process. There is at present considerable doubt over concerted *versus* stepwise processes at sulphonyl sulphur [19] and it is difficult to come to any firm conclusion in this work except as to the extent of bond formation in the transition state of the rate determining step.

We are unable to say anything more about the general base catalysed step [equation (4)] except that the extent of bond formation to the base from the proton is less than in the nucleophilic case (from the electrophilic sulphur). The absence of general base catalysis for any of the more powerful nucleophiles would suggest the existence of a continuum of mechanism from (VI) to (V) as the nucleophile gets stronger but no catalysis of the reaction of the weakest amines with the sultone has been observed.

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