The Effect of Changing the Substituent in the Sulphonyl Group in Base Catalysed Hydrolysis of 2,4-Dinitrophenyl Arylmethanesulphonate Esters in Aqueous Solution

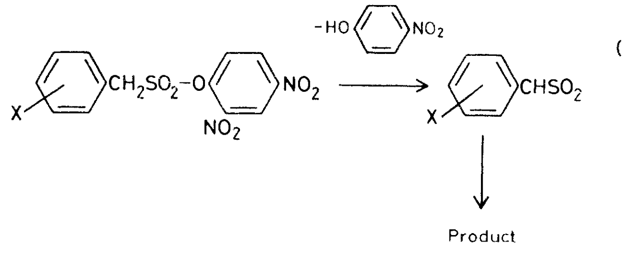
By **Sergio Thea** and **Andrew Williams,*** Istituto di Chimica Organica, Università di Genova, Genova, Italia, and University Chemical Laboratories, Canterbury, Kent

The base catalysed elimination of 2,4-dinitrophenyl arylmethanesulphonates to yield sulphene has been studied as a function of the aryl group. The Brønsted selectivity (β) *versus* the pK_a of the corresponding substituted phenol is -0.85 and -0.50, respectively, for pyridine and hydroxide ion. The change in effective charge on the sulphonate ester during sulphene formation indicates that build-up of charge on the α-carbon atom is not far advanced in the transition state; the change in β with change in strength of the base is consistent with an unsymmetrical transition-state where C–H bond cleavage is in advance of S–O fission. Assuming conservation of effective charge there is no significant change in charge on the sulphone moiety at the transition state during the elimination. The charge distribution in the transition state for the *E*1cB$_r$ mechanism indicates large changes at the sulphone, α-carbon, and leaving oxygen from the anionic ground state. Data drawn from the literature yields a charge distribution during attack of hydroxide on aryl phenyl sulphonates which provides further evidence for a concerted nucleophilic displacement process.

THERE is considerable interest in sulphenes as synthetic intermediates,[1] as models for theoretical study,[2] and in mechanistic considerations of sulphonyl group transfer reactions.[3] Sulphenes are part of a group of unsaturated species comprising the heterocumulenes which are of wide academic and commercial interest [4] and which we have been investigating for some time.

Previous studies from this laboratory [5] have provided good evidence for a change in mechanism for the hydrolysis of arylmethanesulphonates from *E*1cB$_i$ to *E*2 as the basicity of the leaving group decreases. There is good evidence that 2,4-dinitrophenyl phenylmethanesulphonate reacts with nucleophiles *via* the sulphene by base catalysed removal of the α-proton concerted with aryl oxide departure. The transition state is proposed to be unsymmetrical with C–H cleavage advanced over that for the S–O bond.

This study is aimed at providing data for the effect of substituents in the sulphyl group on base catalysed sulphene formation [equation (1)] to probe the charge distribution at the α-carbon atom. Coupled with the results of previous work on the substituent effect on the equilibrium constant for sulphonyl group transfer [6] we are able to describe the transition state in terms of effective charges on the constituent atoms.



(1)

EXPERIMENTAL

Materials.—Substituted-arylmethanesulphonyl chlorides were prepared from arylmethyl chlorides by first synthesising the *S*-arylmethylisothiouronium salt; the *S*-alkylisothiouronium salt was converted into the sulphonyl chloride by oxidation of the aqueous solution with chlorine.[5] The sulphonyl chloride product precipitated and was dried and recrystallised. The 2,4-dinitrophenyl esters of the sulphonic acids were prepared by reaction of the phenol and sulphonyl chloride in dichloromethane in the presence of an equivalent amount of triethylamine.

In the case of the 4-cyanophenylmethanesulphonate the chloride was not commercially available and the 4-cyanobenzyl bromide was converted into *S*-4-cyanophenylmethylisothiouronium acetate [7] prior to the chlorination procedure as the bromide gave an impure sulphonyl chloride. 4-Chloro-2-nitrobenzyl chloride was prepared by treating the corresponding alcohol (26.6 mmol) with thionyl chloride (53.2 mmol) at 0° for 1 h; the excess thionyl chloride was removed *in vacuo* and the residue poured onto crushed ice. Filtration afforded the chloride (m.p. 40—41°) recrystallised from ligroin (b.p. 40—60°) (the literature [8] method involving chlorination of the corresponding toluene gave an oil, b.p. 148—150° at 14 Torr).

Structures of the synthesised compounds were confirmed by analyses (carried out by Mr. G. Powell using a Hewlett–Packard model 185 CHN analyser) which are reported in Table 1, i.r. spectra (Perkin-Elmer 257 instrument), and by ^{1}H n.m.r. spectroscopy (carried out by Dr. D. O. Smith on a JEOL 100 MHz instrument). Other materials such as buffers and reagents were obtained commercially (Fisons or Aldrich) and were of analytical grade or were recrystallised or redistilled before use. Water was doubly distilled from glass. Deuterium oxide (99.7% D) and 35% deuterium chloride in D_2O (99% D) were obtained from Merck, Sharp and Dohme Ltd.

Methods.—Kinetics were followed spectrophotometrically using either a Unicam SP 500 or Beckman DBG instrument; both machines were equipped with linear–logarithmic converters and Servoscribe potentiometric recorders. A typical experiment involved adding a portion of a stock solution of substrate in ethanol (25λ) to 2.5 ml of the buffer in a silica cell in the thermostatted cell compartment of the spectrophotometer. The recorder was activated at the instant of addition and the change in absorption (*A*) at 400 nm recorded as a function of time. The pH of the solution was measured before and after the experiment in the case of buffered reactions using a radiometer digital pH-meter PHM 62 calibrated with E.I.L. standard buffer powders. In the case of reactions carried out in the absence of buffer the pH was monitored continuously and adjusted to a constant value using a Radiometer pH-Stat set; a special device (see later) was used to stir the contents of the silica cell in the cell compartment of the spectrophotometer.

The pK_w of the aqueous solutions under investigation was estimated from the pH of solutions with 0.01 and 0.1M-KOH buffers made up to 1M ionic strength with KCl and containing 4% (v/v) ethanol.

Pseudo-first-order rate constants were obtained by plotting $A_t - A_\infty$ *versus* time on two-cycle semilogarithmic graph paper. Values of A_∞ were determined from absorption measurements after at least seven half-lives. When it was established that a first-order rate law was obeyed A_∞ was calculated from equation (2).[9] Reliable values of the

$$A_\infty = (A_t - A_0)^2/(2A_t - A_{2t} - A_0) \qquad (2)$$

absorbance at infinite time could only be determined by this method for reactions where the rate had decreased by at least ten-fold (*i.e.* when the reaction had progressed to 90% of its total theoretical yield). Fitting curved plots of the rate constant *versus* buffer concentration was carried out according to the rate law (3). The fitting procedure utilised

$$k_{obs} = k^{max}[B]/(K + [BH]) \qquad (3)$$

a plot of log k_{obs} *versus* log [BH] and a normalised function analogous to the method of fitting used by Kezdy and and Brubacher [10a] and Hansen [10b] for estimating pK values from titration data.

Mechanical Stirring for Standard 3 *ml Silica Cells.*—Apparatus for stirring the contents of u.v.-visible cells during determinations of optical density has been described previously.[11] The reported designs require special cells and are specific for the make of spectrophotometer. We describe a cell block assembly which utilises the normal 3 ml 1 cm path length u.v.-visible cell; the assembly should fit most machines with cell compartments which can accommodate a block 7 × 5 × 7 cm³. The construction of the stirrer on the scale required gives rise to considerable technical difficulties; in particular the small clearance between the light path of most instruments and the base of the compartment necessitates a very thin drive mechanism for the magnetic stirrer.

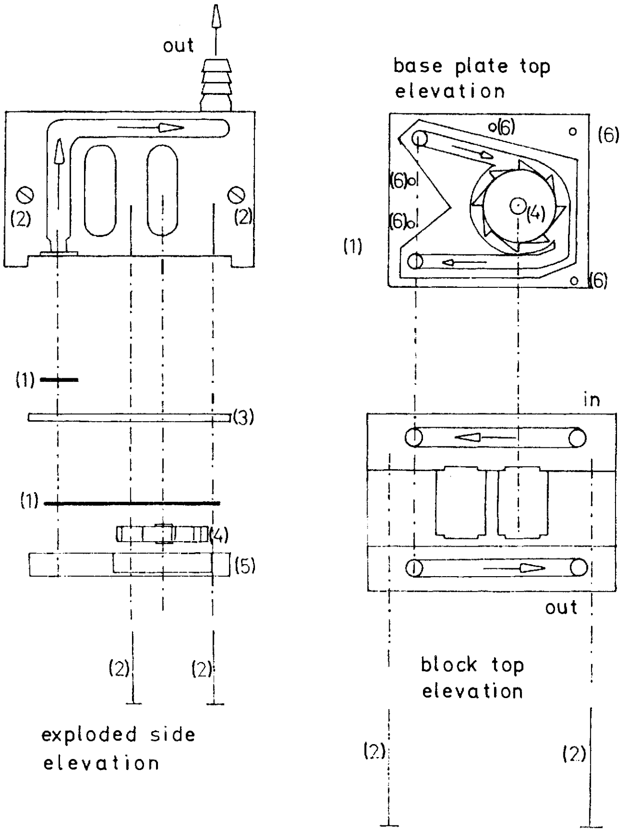


FIGURE 1 Cell holder with paddle wheel attachment for stirring the contents of 3 ml capacity, 1 cm path length cells: (1) rubber o rings for sealing block and base plate, (2) screws for retaining base plate and block, (3) base plate cover, (4) paddle wheel containing permanent magnet; wheel rotates on a stainless steel pin fixed to base plate, (5) base plate containing cavity for wheel and channels for water, (6) positions for retaining screws for base plate

The assembly (Figure 1) consists of a cell-holder block manufactured from brass and possessing channels for the passage of thermostatted water which also rotates a magnetic paddle wheel. The wheel is located at the base of the assembly so that it may be followed by a (bar) stirrer magnet in the normal u.v.-visible cell. Entry ports allow the nitrogen, titrant, and the pH-probe to enter the cell from

TABLE 1

Analytical and physical properties of 2,4-dinitrophenyl arylmethanesulphonates

Substituent [a]	M.p. (°C)	Found (%) C	H	N	Formula	Calculated (%) C	H	N
4-CH_3 [b]	101—102 [i]	47.3	3.2	7.9	$C_{14}N_{12}N_2SO_7$	47.7	3.4	8.0
3-CH_3 [c]	104—105	47.9	3.7	7.7	$C_{14}N_{12}N_2SO_7$	47.7	3.4	8.0
4-Cl [b]	118—119 [j]	41.8	2.0	7.4	$C_{13}H_9ClN_2SO_7$	41.9	2.4	7.5
3-Cl [b]	82—84 [g]	41.9	2.3	7.4	$C_{13}H_9ClN_2SO_7$	41.9	2.4	7.5
4-NO_2 [c]	176—177 [h]	40.9	2.2	11.2	$C_{13}H_9N_3SO_9$	40.7	2.4	11.0
3-NO_2 [c]	165—167 [k]	40.4	2.3	10.6	$C_{13}H_9N_3SO_9$	40.7	2.4	11.0
2-NO_2 [b]	134—135	40.7	2.4	10.9	$C_{13}H_9N_3SO_9$	40.7	2.4	11.0
4-CN [c]	158—159 [f]	46.3	2.6	11.7	$C_{14}H_9N_3SO_7$	46.3	2.5	11.6
3,5-$(NO_2)_2$ [d]	199—200	36.7	1.8	13.2	$C_{13}H_8N_4SO_{11}$	36.5	1.9	13.1
2-NO_2-4-Cl [e]	102—103	36.9	1.9	10.2	$C_{13}H_8ClN_3SO_9$	37.4	1.9	10.1
2-Cl-4-NO_2 [e]	131—132	37.4	2.1	9.8	$C_{13}H_8ClN_3SO_9$	37.4	1.9	10.1
2-Cl [e]	97—98	42.4	2.2	7.9	$C_{13}H_9ClN_2SO_7$	41.9	2.4	7.5

[a] An error is noted in the m.p. of the unsubstituted ester quoted by us previously;[5] the correct value is 113.5—115°. [b] Recrystallised from benzene–ligroin (b.p. 60—80°). [c] Recrystallised from benzene. [d] Recrystallised from acetone–ligroin (b.p. 60—80°). [e] Recrystallised from ethyl acetate. [f] Lit.,[l] 156—157°. [g] Lit.,[l] 82—83°. [h] Lit.,[l] 174—175°. [i] Lit.,[l] 98—100° [j] Lit.,[l] 117—118°. [k] Lit.,[l] 164—165°. [l] R. P. Beatson, Thesis, University of Western Ontario, 1975.

above and are adjusted so as not to project into the path of the light beam. The pH is adjusted by addition of mineral acid–base delivered in the present case by an autoburette ABU 11 controlled by a Radiometer pH-state set (REC 61 servograph, REA 160 titratigraph, and TTT 60 titrator) activated by signals from the cell probe through a digital pH meter (PHM 62).

The apparatus may be used to keep the pH of the u.v.–visible cell constant to obviate the use of buffers or to measure the pK_a of an absorbing acid by spectroscopy. The former technique obviates the extrapolation procedure to determine rate constants at zero buffer concentration and is especially useful where a reaction is strongly dependent on buffer concentration. The latter technique reduces the time period of a pK_a determination by eliminating buffer preparations and the accuracy is increased because the measurements of absorption are carried out on the same sample solution.

A relatively high initial surge of water pressure is required to start rotation of the paddle wheel in the thermostatted block. An ordinary thermostat circulator is not powerful enough and a Stuart Turner Centrigen CG80 circulating pump (26 lb in^{-2} at 18.3 m) was employed with a variable by-pass valve incorporated into the copper exit tube to enable the pressure of the circulating water to be reduced after the paddle wheel had started. It is important for the life of the pump bearings to ensure that the pump does not start against a high back pressure; the sequence of events is thus to open the by-pass valve, start the pump, close the by-pass valve till the paddle rotates, and open the by-pass valve till a relatively low pressure is attained consistent with paddle rotation.

RESULTS

The liberation of 2,4-dinitrophenol from the substrates in aqueous buffers obeyed good first-order kinetics over 80—90% of the total reaction. The rate constants varied in a non-linear function of pyridine buffer concentration and this is discussed in the preceding paper.[12] The data for the pyridine hydrolyses are given in Supplementary Publication No. SUP 22941 (7 pp.) * and the rate constants fit the rate law of equation (3). The initial slope of the plot of rate constant *versus* pyridine concentration gives the base catalysed rate constant (k_B); this value is obtained at low buffer molarity where the pH is held with the pH-stat apparatus (see Experimental section) and where curvature has not set in. The value of k_B could also be obtained from the parameter k^{max}/K from equation (3); the results agree with those from the initial slope method which is considered the more accurate. There is no catalysis by the acid form of the buffer [13] and stoicheiometry studies [13] indicate that S–O fission carries the major part of the reaction flux.

Values of k_{pyr}, k_{OH}, and k_{OH}^{max} are collected in Table 2 together with K. Brønsted plots of these parameters are illustrated in Figures 2 and 3.

At zero buffer concentration the rate constant for hydrolysis of the 2,4-dinitrophenyl esters is proportional to the hydroxide ion concentration (SUP 22941). It was impossible to measure the rate constant accurately from extrapolated points at finite buffer concentrations and all the data in Table 2 were obtained by the use of non-buffered solutions with the pH maintained and monitored by pH-stat.

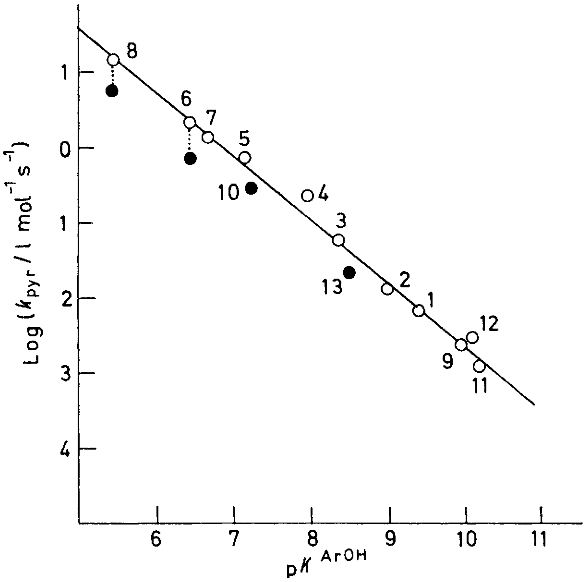


FIGURE 2 Dependence on pK_{ArOH} of k_{pyr}. The data are taken from Table 2. The line is theoretical and includes corrected points (see text) for 2-chloro-4-nitro- and 4-chloro-2-nitro-substituents; it has a slope β of −0.85. The full circles are omitted from the correlation as they have a steric hindrance

The buffer-independent rate constants (k^{max}) for hydrolysis of 2,4-dinitrophenyl 3-nitrophenylmethanesulphonate are proportional to the hydroxide ion concentration. Studies with other bases and esters [12] show that the proportionality

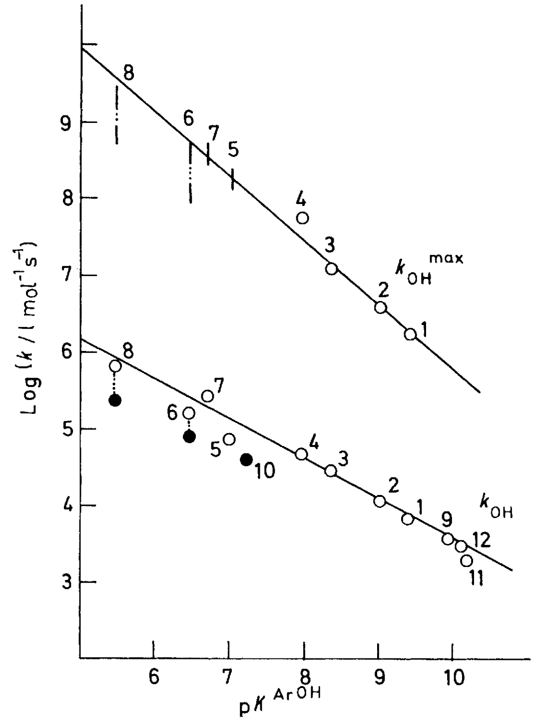


FIGURE 3 Dependence on pK_{ArOH} of k_{OH} and k_{OH}^{max}. The data are taken from Table 2 and the lines are theoretical (β −0.50 and −0.80, respectively). The lines include points for the 2-chloro-4-nitro, and 4-chloro-2-nitro-substituents corrected by the same amount as for the pyridine catalysis. The uncorrected values (filled circles) are not included in the correlation; values for substituents 5, 6, 7, and 8 for k_{OH}^{max} are uncertain within the ranges shown

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc,. Perkin Trans 2*, 1979, Index Issue.

holds for all the esters; the rate constants $k_{OH}^{max} = k^{max}/[OH^-]$ are recorded in Table 2.

TABLE 2

Kinetic parameters for the pyridine-catalysed hydrolysis of 2,4-dinitrophenyl-substituted phenylmethanesulphonates [a,c]

	Substituent	k_{pyr}/l mol^{-1} s^{-1}	K/mol l^{-1} [b]	10^{-6} k_{OH}^{max}/ l mol^{-1} s^{-1}	10^{-4} k_{OH}/ l mol^{-1} s^{-1}	pK_{ArOH}
1	4-Cl	6.11×10^{-3}	1.0	1.75	0.80	9.38
2	3-Cl	1.25×10^{-2}	1.1	4.01	1.35	9.02
3	3-NO_2	5.81×10^{-2}	0.56	12.6	3.5	8.35
4	4-CN	2.12×10^{-1}	0.8	58.1	5.67	7.95
5	4-NO_2	0.708	1.0	246	7.6	7.14
6	2-NO_2-4-Cl	0.682	0.37	83.2	9.00	6.46
7	3,5-$(NO_2)_2$	0.70	0.7	275	28.7	6.68
8	2-Cl-4-NO_2	5.4	0.34	479	28.6	5.45
9	Parent	2.3×10^{-3}	0.6	0.618	0.42	9.95
10	2-NO_2	0.265			4.7	7.23
11	4-CH_3	1.17×10^{-3}			0.23	10.19
12	3-CH_3	2.8×10^{-2}			0.35	10.08
13	2-Cl	2.08×10^{-2}	0.55	4.19		8.48

[a] In the preliminary communication (S. Thea and A. Williams, *J. Chem. Soc., Chem. Commun.*, **1979**, 715) we chose the wrong kinetic scheme to determine the pK values of the esters. The correct scheme given in the preceding paper [12] [equation (4)] and in the original communication does not allow the estimation of pK by kinetic means; the main conclusions of the original paper are, however, valid. [b] K is the value of the concentration of the conjugate acid of pyridine at $k_{obs} = \frac{1}{2}k^{max}$ and is discussed in the preceding paper.[12] [c] Conditions: 4% v/v ethanol–water, 25°, ionic strength made to 1M with KCl.

DISCUSSION

The reactions at low buffer concentration involve proton transfer in the rate-limiting step.[12] Figures 2 and 3 illustrate the dependence of log k_{pyr}, log k_{OH}, and log k_{OH}^{max} on the pK_a of the phenol with a substituent corresponding to that on the sulphonyl phenyl group of the substrate. Substrates with *meta*- and *para*-substituents fall on a relatively good straight line in each case. Groups giving high acidity when substituted into phenol (2-chloro-4-nitro,4-chloro-2-nitro) include *ortho*-substituents and these give low values for the parameters k_{pyr}, k_{OH}, and k_{OH}^{max} when measured against the *meta–para* line. The appearance of a break in the Brønsted plots consistent with a change in rate in limiting step is illusory because correction of the values for these electron-withdrawing groups for a steric effect computed from the deviation of the 2-nitrophenyl and 2-chlorophenyl species gives reasonably linear plots in all these cases (Figures 2 and 3). The final lines are taken through the corrected points but omit those of 2-nitro- and 2-chloro-derivatives. The small steric requirement is discussed in the following paper.[13]

The values of the Brønsted β agree with those calculated from King and Beatson's data [14] (−1.07 and −1.21) for reaction of pyridine and triethylamine respectively with 2,4-dinitrophenyl arylmethanesulphonate esters in 80% (v/v) dimethoxyethane–water. The relative magnitudes of the β values for k_{pyr} and k_{OH} are consistent with a 'Hammond effect,' *i.e.* the more basic species has a lower selectivity to substituent change on the phenyl group. King and Beatson [4] also observed Hammond behaviour for reaction of pyridine and triethylamine with the substituted phenylmethanesulphonates. Reference to the three-dimensional free energy diagram (Figure 4) representing cleavage of C–H and S–O bonds indicates the direction of movement expected for the transition state on changing the base strength. The reaction co-ordinate with an asymmetric transition state (with little S–O cleavage, A) should behave according to the Hammond postulate: as the base strength increases the movement is towards reactants causing a decrease in β; the change in stability of the top right corner does not affect the position of A.

In the case of the symmetrical transition state (B) an increase in base strength should cause a movement parallel and perpendicular to the reaction co-ordinate [15] as shown in Figure 4; this leads to a net cancelling of movement of the transition state along the C–H co-ordinate and to little change in β.

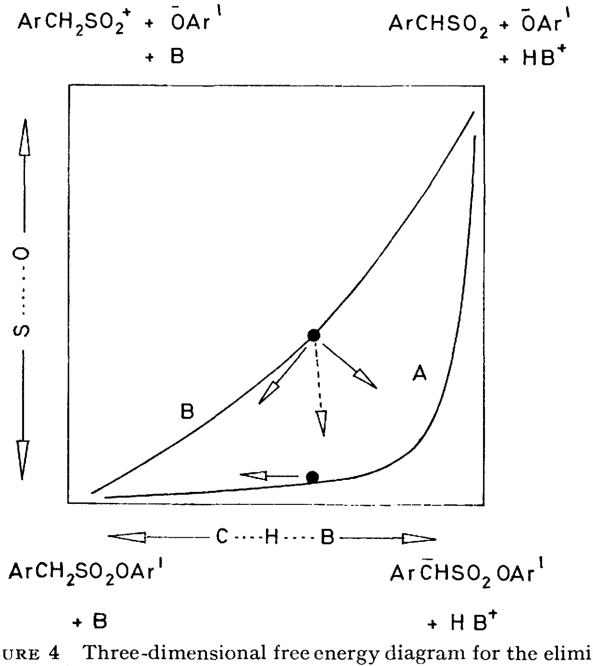


FIGURE 4 Three-dimensional free energy diagram for the elimination of phenol from an aryl arylmethanesulphonate. Free energy contours are omitted for clarity and details are given in the text. The filled circles represent transition states on the unsymmetrical path A and symmetrical path B

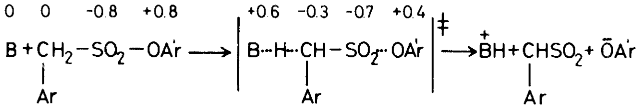
The 'effective charge' at the α-carbon in the transition state may be estimated provided we possess a standard substituent effect for generation of full negative charge on the system. The Brønsted β value for ionisation of substituted phenylmethanesulphones in dimethyl sulphoxide (DMSO) at 25° [equation (4)] [16a] is −2.9. With the assumption that the selectivity (β) in water is

$$ArCH_2SO_2CH_3 \rightleftharpoons Ar\bar{C}HSO_2CH_3 + H^+ \quad (4)$$

the same as that in DMSO this leads to an effective change of −0.29 and −0.17 units on the α-carbon for pyridine and hydroxide attack, respectively.

Bordwell [16b] finds that the acidities of carbon acids in DMSO and water are identical within a few p*K* units when extensive delocalisation as in acetone or nitromethane does not occur. Benzoic acids, where the p*K* in DMSO is larger than that in water, have a Hammett ρ of 2.4 in this solvent.[16c] We believe that the present assumption of similar selectivities is correct because the stabilisation of the carbanion is *via* an inductive effect from the sulphone group; if the assumption were not correct the Brønsted selectivity would be more negative. We could therefore regard the effective charge changes as being between −0.29 or −0.17 and zero for pyridine and hydroxide attack respectively. This will not alter the detailed charges (to be discussed later) to a significant extent.

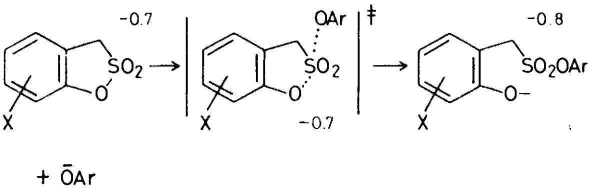
We may now build up a relatively detailed picture of the effective charge changes in the transition state for sulphene formation because the charge on the leaving oxygen may also be estimated. Previous work from this laboratory [6] has shown that the transfer of a phenolate ion to a sulphonyl group involves a total change in effective charge of +1.8 units (rounded average of two values) relative to unit change in charge on ionisation of a phenol. The attack of hydroxide ion on phenylmethanesulphonate esters where proton transfer is rate limiting (*E*1cB$_i$) [5] has a $\beta_{L.G.}$ of 0.4; thus the change in effective charge on the leaving oxygen is −0.4 units and the effective charge in the transition-state is +0.4 units [see equation (5)].



$$\overset{0}{B} + \underset{Ar}{\overset{0}{C}H_2}-\overset{-0.8}{SO_2}-\overset{+0.8}{OAr} \longrightarrow \left| \overset{+0.6}{B}\cdots H\cdots\underset{Ar}{\overset{-0.3}{C}H}-\overset{-0.7}{SO_2}\cdots\overset{+0.4}{OAr} \right|^{\ddagger} \longrightarrow \overset{+}{B}H + \underset{Ar}{\bar{C}H}SO_2 + \bar{O}Ar \quad (5)$$

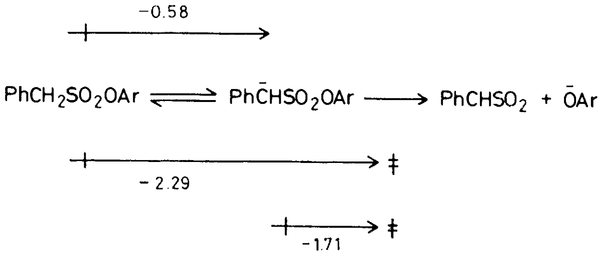
The effective charge on the base atom in the transition state is *ca.* +0.6 units and this leads to an imbalance which, if effective charge is conserved, is fed through to the sulphone moiety. The effective charge on the sulphone group (determined by difference) is not altered significantly from that in the ground state. The observation that the sulphone group appears to be ' intact ' during the reaction agrees with previous work on sulphonyl group transfer of sultones where the effective change on the sulphone moiety is unaltered during a concerted displacement [equation (6)].

There has been considerable discussion of the structure of the sulphone group concerning *d*-orbital participation and the existence of ionic or dative bonds. The present observations indicate that formation of a new bond to the sulphur atom results in a bond cleavage rather than a migration of a pair of electrons from the S–O bond to oxygen; if the latter were the case then the effective charge on the sulphone would increase.

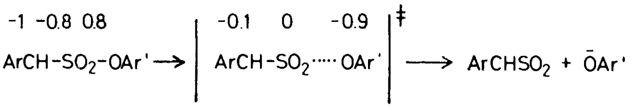


(6)

It is interesting that the effective charge distribution for the *E*1cB$_r$ mechanism may involve a large increase in positive charge on the sulphone in the transition state. Our recent work [17] indicates that the effect of substituents in the aryl group on the ionisation of a proton on the carbon α to the sulphone * has a Brønsted β value of −0.58 (plotting log K_{SH} *versus* pK_a of the phenol). The Brønsted β for attack of hydroxide on aryl phenylsulphonates (−2.29) [6] together with the ionisation β value indicate a $\beta_{L.G.}$ for the carbanion of −1.71 [equation (7)] which is consistent with an effective charge on the aryl oxygen of −0.9 units. The effective charge on the sulphone by difference is zero indicating an increase of +0.8 units [equation (8)].

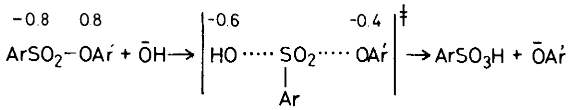


$$PhCH_2SO_2OAr \rightleftharpoons Ph\bar{C}HSO_2OAr \longrightarrow PhCHSO_2 + \bar{O}Ar \quad (7)$$



$$\overset{-1}{ArCH}-\overset{-0.8}{SO_2}-\overset{0.8}{OAr'} \longrightarrow \left| \overset{-0.1}{ArCH}-\overset{0}{SO_2}\cdots\overset{-0.9}{OAr'} \right|^{\ddagger} \longrightarrow ArCHSO_2 + \bar{O}Ar' \quad (8$$

The charge distribution in a displacement occuring at sulphur in a sulphonyl group transfer may be estimated from data drawn from the literature (Table 3). The attack of hydroxide ion on aryl benzenesulphonate esters has a Brønsted $\beta_{L.G.}$ of −2.1 and coupled with an equilibrium constant for sulphonate group transfer this leads to the distribution shown in equation (9). Extensive bond cleavage is indicated by the change in effective charge of −1.2 units from ground to transition state; this can only occur with a mechanism where there is a rate-limiting S–O bond cleavage step. An *E*1cB



$$\overset{-0.8}{ArSO_2}-\overset{0.8}{OAr'} + \bar{O}H \longrightarrow \left| \overset{-0.6}{HO}\cdots\underset{Ar}{SO_2}\cdots\overset{-0.4}{OAr'} \right|^{\ddagger} \longrightarrow ArSO_3H + \bar{O}Ar' \quad (9)$$

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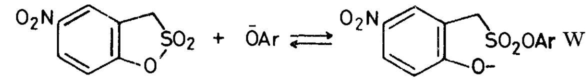
* The system $CH_3SO_2CH_2SO_2OAr \rightleftharpoons CH_3SO_2\bar{C}HSO_2OAr + H^+$ was studied using aqueous media.

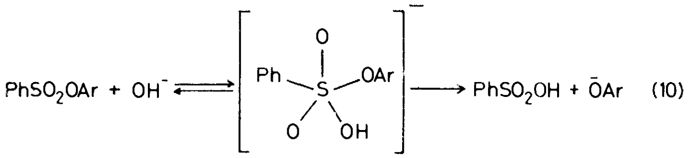
TABLE 3

Substituent effects for equilibria and base catalysed hydrolysis of aryl sulphonates

Reaction	Solvent composition	Temperature (°C)	β [a]	Reference
$ArCH_2SO_2Me \rightleftharpoons Ar\bar{C}HSO_2Me + H^+$	DMSO	25	−2.9	*b*
$ArCH_2SO_2O$-2,4-DNP [h] + C_5H_5N	80% DME–water; water	20, 25	−1.07, −0.82	*c,d*
$ArCH_2SO_2O$-2,4-DNP + NEt_3	80% DME–water	20	−1.21	*c*
$ArCH_2SO_2O$-4-NP [h] + NEt_3	80% DME–water	20	−0.24	*c*
$ArCH_2SO_2O$-2,4-DNP + ^-OH	Water, 1M ionic strength	25	−0.57,[k] −0.85 [i]	*d*
$ArCH_2SO_2OPh + {}^-OH$	70% Dioxan–water	40	−0.2	*e*
$PhCH_2SO_2OAr + {}^-OH$ ($E1cB_i$)	Water, 1M ionic strength	25	−0.4	*j*
$PhCH_2SO_2OAr + {}^-OH$ ($E1cB_r$)	Water, 1M ionic strength; 70% dioxan–water	25	−2.4, −2.29	*j,e*
	Water, 1M ionic strength	25	+1.83	*f*
$PhCH_2SO_2O$-2,4-DNP + B	Water, 1M ionic strength	25	+0.61	*d,j*
$ArSO_2OPh + {}^-OH$	70% Dioxan–water	50	−1.06	*g*
$PhSO_2OAr + {}^-OH$	70% Dioxan–water	50	−1.21	*g*

[a] The Brønsted β is measured *versus* the pK_a of the corresponding phenol. Where original data are in terms of a Hammett ρ value these are converted to a β value by division by 2.23 (A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 1961, 388). [b] The pK_a data are from F. G. Bordwell, personal communication. [c] From ref. 14. [d] From ref. 13. [e] R. V. Vizgert, I. M. Tuchapski, and Y. G. Skrypnik, *Reakstsionnaya Sposobnost. Org. Soedinenii*, 1975, **11**, 785. [f] Ref. 6. [g] R. V. Vizgert, *Zh. Obshch. Khim.*, 1958, **28**, 1877. [h] Abbreviations used are : 2,4-DNP = 2,4-dinitrophenyl; 4-NP = 4-nitrophenyl; DMSO = dimethyl sulphoxide; DME = dimethoxyethane. [i] Value for k_{OH}^{max}. [j] M. B. Davy, K. T. Douglas, J. S. Loran, A. Steltner, and A. Williams, *J. Am. Chem. Soc.*, 1977, **99**, 1196. [k] Value for k_{OH} at zero buffer concentration.

mechanism is not possible due to the absence of proton on an α-carbon atom and a stepwise addition–elimination (AE) mechanism is excluded because expulsion of the aryl oxide ion would be faster than expulsion of hydroxide [equation (10)]. The involvement of pseudo-rotational



$$PhSO_2OAr + OH^- \rightleftharpoons \left[Ph\overset{\overset{O}{|}}{\underset{O\ \ OH}{S}}OAr \right]^- \longrightarrow PhSO_2OH + \bar{O}Ar \quad (10)$$

AE mechanisms is also exluded by the requirement of extensive S–OAr bond cleavage in the rate-limiting step. These data together with the previous work with sultones provide good evidence for a concerted nucleophilic displacement at sulphonyl centres.

The data for the sulphonyl group transfer from reactions of sultones [5] indicate a relatively large coupled change in effective charges consistent with a coupled S_N2 concerted displacement; this is in contrast with the uncoupled concerted displacements recently discussed by Benkovic and his co-workers for phosphodiester displacements.[18] The present system is more akin to nucleophilic displacement at phosphate [19] which involves a coupled transition-state where $\beta_{L.G.}$ is dependent on the pK_a of the attacking nucleophile and the reaction may be concerted.[19] It is likely that displacements at the sulphate group [20] are like those at monosubstituted phosphates [21] and involve little coupling between entering and leaving groups.

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