Reactions of Organic Sulphur Compounds. Part I. The Hydrolysis of Arenesulphonyl Chlorides

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Rate constants have been determined for the hydrolyses of 27 substituted benzenesulphonyl chlorides in 1% dioxan. The results are discussed in terms of linear free energy relationships.

PRELIMINARY investigations of the kinetics of the reactions occurring in the benzenesulphonyl chloride promoted cross-linking reactions of gelatins,[1] showed the reactions to occur in the aqueous phase.[2] Wishing to predict the individual rates of hydrolysis of different aryl(chloro)sulphonyl groups present in a polymer, these groups having known Hammett σ values,[3] the work of Hedland[4] on the hydrolysis of benzenesulphonyl chlorides in water was extended to other substituents using 1% dioxan as solvent. During the course of this work, a number of other workers have made studies of this reaction in aqueous solution determining substituent effects for a limited number of substituents,[5-7] but also the effect of cosolvent,[7] volume of activation,[8] heat capacity of activation,[9] and solvent isotope effects.[10] As an interpretation of the reaction mechanism differing from those previously accepted[11-13] has been given[14] and curvature of the Hammett plot claimed,[5,6] this investigation of substituent effects was extended to clarify the position.

EXPERIMENTAL

Materials.—Solvents were purified as before.[15] The sulphonyl chlorides were purified by either crystallisation or vacuum distillation. When not commercially available, the chlorides were prepared from the sulphonic acid by treatment with thionyl chloride. Sulphanilic acid was acetylated to give *p*-acetamidobenzenesulphonic acid. *p*-Cyanobenzenesulphonic acid and the *m*-halogenobenzenesulphonic acids were obtained by a Sandmeyer reaction from sulphanilic and metanilic acids respectively.

Rate Measurements.—The hydrolyses of the sulphonyl chlorides in 1% dioxan were followed spectrophotometrically by the change in absorbance at an appropriate wavelength, as before on a Perkin-Elmer 139 spectrophotometer with a Honeywell VT 100 digital reactant.[16] For those compounds which gave no change in absorbance in the reaction (and also little change on ionisation of the sulphonic acid[17,18]), conductance measurements were done as before[15] using a Wayne-Kerr B641 autobalance universal bridge.

RESULTS

Rate constants, together with the wavelengths used, for the solvolyses of the sulphonyl chlorides are in Table 1 and

TABLE 1

Measured rate constants for the hydrolysis of arenesulphonyl chlorides in 1% v/v dioxan

p-Acetamidobenzenesulphonyl chloride at 290 nm

T/K	282·67	288·46	293·76	299·46
10^3k/s^{-1}	0·738	1·26	1·96	3·42
T/K	304·15			
10^3k/s^{-1}	5·25			

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TABLE 1 (*Continued*)

Benzenesulphonyl chloride at 276 nm

T/K	283·16	294·34	297·56	298·16
$10^{3}k/\mathrm{s}^{-1}$	0.897	2·25	2·75	2·94
T/K	304·15	307·56		
$10^{3}k/\mathrm{s}^{-1}$	4·68	5·96		

m-Bromobenzenesulphonyl chloride at 238 nm

T/K	286·55	290·76	292·98	297·66
$10^{3}k/\mathrm{s}^{-1}$	0·459	0·824	0·992	1·68
T/K	298·66	302·06		
$10^{3}k/\mathrm{s}^{-1}$	2·02	3·14		

p-Bromobenzenesulphonyl chloride at 252 nm

T/K	285·88	294·26	297·86	308·76
$10^{3}/\mathrm{s}^{-1}$	0·467	1·40	2·09	6·01
T/K	310·76			
$10^{3}/\mathrm{s}^{-1}$	7·14			

m-Chlorobenzenesulphonyl chloride at 284 nm

T/K	283·08	286·54	292·07	299·37
$10^{3}/\mathrm{s}^{-1}$	0·390	0·557	0·971	1·74
T/K	303·12	314·07		
$10^{3}/\mathrm{s}^{-1}$	2·25	7·66		

p-Chlorobenzenesulphonyl chloride at 248 nm

T/K	285·83	293·46	298·26	298·66
$10^{3}k/\mathrm{s}^{-1}$	0·551	1·40	2·02	2·16
T/K	302·16	304·15	312·46	
$10^{3}k/\mathrm{s}^{-1}$	3·01	3·50	7·25	

4-Chloro-2-methylbenzenesulphonyl chloride at 248 nm

T/K	285·48	295·06	297·86	302·56
$10^{3}k/\mathrm{s}^{-1}$	0·892	2·07	2·36	3·38
T/K	311·16			
$10^{3}k/\mathrm{s}^{-1}$	6·05			

2-Chloro-5-nitrobenzenesulphonyl chloride at 245 nm

T/K	285·84	290·66	294·67	300·27
$10^{3}k/\mathrm{s}^{-1}$	0·187	0·404	0·644	1·28
T/K	306·82	313·84		
$10^{3}k/\mathrm{s}^{-1}$	2·29	3·45		

4-Chloro-2-nitrobenzenesulphonyl chloride at 280 nm

T/K	282·26	292·56	297·16	302·56
$10^{3}k/\mathrm{s}^{-1}$	0·115	0·282	0·427	0·689
T/K	307·56			
$10^{3}k/\mathrm{s}^{-1}$	0·961			

4-Chloro-3-nitrobenzenesulphonyl chloride at 252 nm

T/K	285·96	288·26	292·56	301·97
$10^{3}k/\mathrm{s}^{-1}$	0·311	0·430	0·697	1·88
T/K	304·16	306·67	314·36	
$10^{3}k/\mathrm{s}^{-1}$	2·48	3·12	6·79	

p-Cyanobenzenesulphonyl chloride at 244 nm

T/K	291·41	294·06	300·66	304·16
$10^{3}k/\mathrm{s}^{-1}$	1·09	1·36	2·60	3·64
T/K	310·96			
$10^{3}k/\mathrm{s}^{-1}$	7·55			

3,4-Dichlorobenzenesulphonyl chloride at 247 nm

T/K	285·79	292·26	298·52	304·27
$10^{3}k/\mathrm{s}^{-1}$	0·361	0·776	1·62	2·77
T/K	308·16	316·98		
$10^{3}k/\mathrm{s}^{-1}$	4·26	7·01		

p-Fluorobenzenesulphonyl chloride at 240 nm

T/K	286·33	293·76	296·36	302·16
$10^{3}k/\mathrm{s}^{-1}$	0·443	1·11	1·28	2·57
T/K	304·26	307·96	312·36	
$10^{3}k/\mathrm{s}^{-1}$	3·21	4·56	8·47	

TABLE 1 (*Continued*)

m-Hydroxybenzenesulphonyl chloride at 290 nm

T/K	283·34	288·96	295·38	300·86
$10^{3}k/\mathrm{s}^{-1}$	0·536	0·649	1·84	3·43
T/K	308·16			
$10^{3}k/\mathrm{s}^{-1}$	7·68			

m-Iodobenzenesulphonyl chloride at 292 nm

T/K	284·24	288·88	300·82	311·96
$10^{3}k/\mathrm{s}^{-1}$	0·473	0·624	2·16	6·00

p-Iodobenzenesulphonyl chloride at 290 nm

T/K	285·88	288·46	292·56	299·16
$10^{3}k/\mathrm{s}^{-1}$	0·676	0·802	1·28	2·45
T/K	302·16	308·86		
$10^{3}k/\mathrm{s}^{-1}$	3·30	6·27		

Mesitylenesulphonyl chloride [a]

T/K	290·86	298·06
$10^{3}k/\mathrm{s}^{-1}$	1·88	3·51

p-Methoxybenzenesulphonyl chloride at 270 nm

T/K	282·54	287·16	288·46	294·24
$10^{3}k/\mathrm{s}^{-1}$	1·39	1·91	2·38	4·38
T/K	299·26	302·66		
$10^{3}k/\mathrm{s}^{-1}$	7·29	10·6		

2-Methyl-5-nitrobenzenesulphonyl chloride at 243 nm

T/K	285·66	293·64	297·36	304·15
$10^{3}k/\mathrm{s}^{-1}$	0·620	1·51	2·08	3·76
T/K	306·82			
$10^{3}k/\mathrm{s}^{-1}$	4·96			

Naphthalene-2-sulphonyl chloride [a]

T/K	291·46	298·06
$10^{3}k/\mathrm{s}^{-1}$	1·25	2·88

m-Nitrobenzenesulphonyl chloride at 325 nm

T/K	285·79	292·50	293·66	297·86
$10^{3}k/\mathrm{s}^{-1}$	0·243	0·591	0·906	1·00
T/K	298·91	302·66	307·96	
$10^{3}k/\mathrm{s}^{-1}$	1·36	1·84	5·14	

o-Nitrobenzenesulphonyl chloride at 280 nm

T/K	285·79	288·56	294·66	298·88
$10^{3}k/\mathrm{s}^{-1}$	0·184	0·241	0·458	0·694
T/K	303·06	308·34		
$10^{3}k/\mathrm{s}^{-1}$	1·03	1·68		

p-Nitrobenzenesulphonyl chloride at 250 nm

T/K	285·76	291·88	305·17	314·22
$10^{3}k/\mathrm{s}^{-1}$	0·668	1·39	4·47	10·9

o-Toluenesulphonyl chloride at 240 nm

T/K	285·54	285·86	291·66	293·06
$10^{3}k/\mathrm{s}^{-1}$	1·34	1·45	2·49	2·81
T/K	294·16	298·91	302·76	
$10^{3}k/\mathrm{s}^{-1}$	3·38	5·22	7·16	

p-Toluenesulphonyl chloride at 245 nm

T/K	278·96	282·96	289·16	293·46
$10^{3}k/\mathrm{s}^{-1}$	0·484	0·680	1·39	2·10
T/K	296·46	297·96	302·36	304·15
$10^{3}k/\mathrm{s}^{-1}$	2·82	3·42	4·28	5·28
T/K	308·96			
$10^{3}k/\mathrm{s}^{-1}$	9·34			

2,3,4-Trichlorobenzenesulphonyl chloride at 250 nm

T/K	285·66	288·16	294·26	298·91
$10^{3}k/\mathrm{s}^{-1}$	0·197	0·283	0·483	0·763
T/K	303·91	308·44		
$10^{3}k/\mathrm{s}^{-1}$	1·19	1·35		

2,4,5-Trichlorobenzenesulphonyl chloride at 250 nm

T/K	285·58	292·06	295·60	302·32
$10^{3}k/\mathrm{s}^{-1}$	0·187	0·393	0·568	1·03
T/K	310·70	316·71	318·54	
$10^{3}k/\mathrm{s}^{-1}$	2·20	4·27	4·68	

[a] By conductance.

TABLE 2

Arrhenius parameters and rate constants interpolated to 298·2 K for the hydrolysis of substituted benzenesulphonyl chlorides in 1% dioxan

Substituent	E/kJ mol^{-1}	log (A/s^{-1})	10^3k/s^{-1}
p-Methoxy	73·6 ± 2·8	10·7 ± 0·5	6·57
p-Methyl	69·5 ± 1·7	9·68 ± 0·31	3·25
Hydrogen	56·1 ± 0·7	7·31 ± 0·13	2·97
p-Acetamido	65·2 ± 1·4	8·9 ± 0·25	3·05
3,4-Benz	(93) [a]		2·88
p-Fluoro	82·1 ± 2·5	11·6 ± 0·4	1·70
m-Hydroxy	(82 ± 7	11·8 ± 1	2·5) [a]
p-Iodo	72·3 ± 1·4	10·02 ± 0·24	2·25
p-Chloro	70·8 ± 1·9	9·72 ± 0·34	2·03
p-Bromo	74·6 ± 0·8	10·40 ± 0·14	2·12
m-Iodo	69·3 ± 3·4	9·37 ± 0·43	1·70
m-Chloro	68·7 ± 3·3	9·26 ± 0·54	1·67
m-Bromo	86·9 ± 2·9	12·5 ± 0·51	1·91
3,4-Dichloro	80·3 ± 1·3	11·25 ± 0·23	1·49
p-Cyano	74·4 ± 2·3	10·4 ± 0·4	2·10
m-Nitro	94·4 ± 7·7	13·6 ± 1·3	1·27
p-Nitro	70·9 ± 2·1	9·80 ± 0·36	2·41
4-Chloro-3-nitro	82·9 ± 0·7	11·2 ± 0·1	1·28
	o-Substituted compounds		
o-Methyl	69·4 ± 1·1	9·8 ± 0·2	4·73
4-Chloro-2-methyl	54·7 ± 1·6	7·0 ± 0·3	2·45
2-Methyl-5-nitro	70·4 ± 1·7	9·7 ± 0·3	2·22
2,4,6-Trimethyl	(63) [a]		3·51
2,3,4-Trichloro	63·4 ± 3·9	7·9 ± 0·7	0·663
2,4,5-Trichloro	73·5 ± 1·2	9·7 ± 0·2	0·708
2-Chloro-5-nitro	86·7 ± 4·4	12·2 ± 0·7	0·932
o-Nitro	72·2 ± 0·3	9·45 ± 0·04	0·645
4-Chloro-2-nitro	61·3 ± 1·0	7·4 ± 0·2	0·462

[a] Values not used in subsequent correlations.

Arrhenius parameters and interpolated rate constants at 298·2 K are in Table 2. As the errors in k are a function of the total change in absorption in the reactions, the standard deviations of the Arrhenius parameters obtained by the unweighted least squares treatment are included in Table 2. From the standard errors of estimate of log k obtained from the Arrhenius plots, with the exception of the less accurate *m*-hydroxy- and *m*-nitro-compounds, the standard error in $\Delta G^{\ddagger}$ varies from ±0·5 to ±0·1 kJ mol^{-1}. The mean value of ±0·35 kJ mol^{-1} is similar to values obtained by other workers.[5-7] It is estimated that the precision of log k is doubled at temperatures below 300 K and that Hammett ρ values should be accurate to at least ±0·01.

TABLE 3

Rate constants for the hydrolysis of benzenesulphonyl chlorides in water at 298·2 K (10^3k/s^{-1})

Source Substituent	Ref. 4	Ref. 5	Ref. 6	Ref. 7	Ref. 9	This paper
p-Methoxy		5·25	5·25	6·86	6·529	6·57
p-Methyl	3·85	3·60	3·00	3·73	3·736	3·25
Hydrogen	3·07	3·10	3·06	3·08	3·095	2·97
p-Fluoro			1·85			1·70
p-Bromo		1·80			2·161	2·12
m-Nitro	1·44		1·46	1·35		1·27
p-Nitro	2·73	2·37	2·82	2·66	2·717	2·41

DISCUSSION

There is good agreement between our results in 1% dioxan (Table 2) and those obtained by other workers in more aqueous solvents (Table 3) in that the values are highly correlated with each other and that the

TABLE 4

Hammett $\rho\sigma$ type correlations for the hydrolysis of *m*- and *p*-substituted benzenesulphonyl chlorides against σ (or another free energy function) to give a Hammett ρ value (or a ratio) (r = correlation coefficient, n = number of reactions correlated, and s the standard error of estimate of log k from the calculated regression line value)

Function	T/K	Standard function		r	n	s
log k	298·2	σ [a]	−0·421 ± 0·014	0·965	13 [b]	0·038
log k	298·2	σ [a]	−0·438 ± 0·031	0·877	16 [c]	0·082
log k	298·2	σ^{n} [d]	−0·431 ± 0·072	0·699	13 [c]	0·10
log k	298·2	σ^{I} [e]	−0·359 ± 0·075	0·597	14 [c]	0·11
log k	298·2	σ^{+} [f]	−0·393 ± 0·015	0·941	14 [c]	0·059
log k	285·0	σ [a]	−0·603 ± 0·030	0·930	13 [b]	0·079
log k	285·0	σ [a]	−0·578 ± 0·041	0·874	16 [c]	0·109
log k	310·0	σ [a]	−0·272 ± 0·022	0·890	13 [b]	0·046
log k	310·0	σ [a]	−0·323 ± 0·035	0·779	16 [c]	0·089
log k	298·2	σ^{+} [f]	−0·333 ± 0·07	0·800	15	0·11
log k	298·2	σ^{-} [a]	−0·231 ± 0·09	0·556	15	0·15
log k	298·2	σ^{+} and σ^{-}	−0·763 +0·467	0·916	15	0·076
log k	298·2	log k $ArOSO_3^-$	−1·159 ± 0·021 [h]	0·983	8 [c]	0·062
pK_a ($ArSeO_3H$) [k]	298·2	pK_a $ArSO_3^-$ [g]	−1·18 ± 0·3 [h]	0·924	4	0·055
log k ($ArSeO_3H$) [k]	298·2	pK_a $ArSOCH_3$ [i]	−1·14 ± 0·08 [h]	0·989	7	0·049
log k	298·2	pK_a $ArSeO_3H$ [j]	−0·396 ± 0·07 [h]	0·720	10	0·11
log k	298·2	pK_a $ArSeO_3H$ [k]	−0·508 ± 0·02 [h]	0·977	8 [l]	0·032

[a] Refs. 3 and 19. [b] Excluding *p*-MeO, *p*-F, *p*-CN, and *p*-NO_2. [c] Excluding *p*-NO_2. [d] Ref. 20. [e] Ref. 21. [f] Ref. 22. [g] Ref. 23. [h] ρ Ratio. [i] Ref. 24. [j] Ref. 25. [k] Ref. 26. [l] Excluding *p*-MeO and *p*-NO_2.

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p-methoxy- and *p*-nitro-compounds are more reactive and the *p*-fluoro-compound less reactive than expected. The results of a statistical analysis of the results in terms of Hammett type relations are collected in Table 4.

The results in Table 4 may be summarised. (*a*) 13 Compounds follow the Hammett equation with high precision [3] but the *p*-MeO, *p*-F, *p*-CN, and *p*-NO_2 substituted compounds show significant deviations. (*b*) The trivariate correlation of *all* the compounds with σ^+ and σ^-,[3] but no other combination considered (Table 4), gives a statistically significant improvement over bivariate plots of *all* the compounds against σ^+ or σ^- but *not* over that using σ. (*c*) Better correlations are obtained with other sulphur reactions than with the standard σ values based on the ionisation of benzoic acids.

As the validity of the negative values for ρ found by us and other workers [4,7,9] has been disputed,[27] a consistent explanation of all the deviations from the Hammett plot is desirable. The good free energy correlations of the sulphonyl chloride hydrolyses with the arylsulphate hydrolyses [27] and the pK_a values of areneselenonic acids [26] (Table 4) fail to accommodate the *p*-NO_2 and the *p*-NO_2 and *p*-MeO compounds respectively and a unique σ scale for sulphur reactions as has been proposed for phosphorus reactions [28] is not indicated. That the deviations are not merely systematic differences in solute–solvent interactions of the type noted by Kevill and his co-workers [29] is shown by the magnitude of the free energy changes.

As correlation with σ^+ and σ^- values (Table 4) is improved by omission of the *p*-F compound, this correlation might be considered evidence for a two-step process. As the possibilities of concurrent unimolecular and bimolecular reactions,[4–6,30] an ion-pair intermediate [9,31] and acid catalysis [4,11] have all been rejected, then *a priori* this could be considered evidence for a two-step reaction involving the rate-determining decomposition of a five-co-ordinate addition compound [12,14,32,33] $ArSO_2(OH)Cl$. This scheme does not predict the found variation [4,5,7,11,12,34–43] in ρ values with change in solvent and is at variance with the conclusions of Ciuffarin and his co-workers [14] who claim from a study of leaving group tendencies that intermediate formation is rate determining. This approach has the problems discussed at length for bimolecular aromatic substitution reactions [44] and the recent study of leaving groups in phenyl chlorosulphate has led Buncel and his co-workers [45] to the conclusion that an intermediate is unlikely.

Only at the highest temperature, 310 K, is there evidence of curvature in the Hammett plots, a correlation ratio, 0·809, being calculated [46] for four arrays of log *k* and six arrays of σ.[3,19] The variance ratio, $F_{4,10} = 0{\cdot}87$, shows there is no evidence for rejecting a linear correlation in favour of a non-linear one required for a curved Hammett plot.[6,11,47]

An alternative description is to suggest that the *p*-MeO, *p*-CN, and *p*-NO_2 compounds showing positive deviations from the Hammett plots have substituents which donate electrons conjugatively to the increasingly positive sulphur atom and that the *p*-F compound has a negative deviation due to a decrease in or absence of conjugation. There is considerable evidence [48–50] that the sulphur atom in sulphonyl groups bears a considerable positive charge so that even the sulphonate ion group with a formal negative charge normally acts as an electron acceptor.[3,51] As the dipole interaction moments of sulphonyl fluorides,[52] the SO stretching frequency in sulphonyl chlorides,[53] the *p* absorption band [54] in arenesulphonyl halides,[52,55] and hydrogen-bond formation with phenol in a non-squeous solvent [56] all follow σ^+ values, an exalted value for the *p*-MeO compound due to conjugative electron release is ex-

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pected, as suggested by Rogne[57] for the reactions of benzenesulphonyl chlorides with amines.

N.q.r. evidence suggests that in the ground state,[58] the *p*-nitro-group acts as a conjugate electron donor to the chlorosulphonyl group. As the *p*-nitro-group can act as an electron-donor to the strongly electron-withdrawing *p*-diazonium group,[59] with σ 1·91,[60] there is little doubt that the *p*-nitro- and *p*-cyano-groups can act as conjugative electron donors to the electronegative chlorosulphonyl group in the ground state and hence at the positive reaction centre. As the standard σ^+ scale is based on an incipient carbonium ion reaction centre with a σ value both less than that of the trimethylammonium group with unit charge and $\sigma = 0{\cdot}8$ and similar to those of the *p*-NO_2 and *p*-CN groups, the σ^+ values for these groups are close to the standard σ values. Since the occurrence of negative values of r in the Yukawa and Tsuno equation[61] implies use of $\sigma_p - \sigma^+$ values for σ^- in the Yoshioka–Hamamoto–Kubota equation,[62] we have calculated for the three compounds a value of $0{\cdot}44 \pm 0{\cdot}04$ for r employing $\sigma_p - \sigma^-$ instead of σ^+ for the *p*-CN and *p*-NO_2 compounds. The assumption that σ_R^+ in the Yukawa–Tsuno type equations is unchanged by change in direction of electron flow is not established, but because in the ionisation of anilines σ^- values arise partly from regain of electrons donated to the NH_3^+ group, the equivalence of σ^- for the *p*-NO_2 group in *both* the defining series[63] seems at present to justify the assumption.

The *p*-fluoro-group as in the ionisation of the areneselenonic acids[26] and presumably the arenesulphonic acids[24] (Table 4) shows little conjugation in the ground state and is close to the σ^I value.[21] Further confirmation is obtained from the u.v. spectra in 1,2-dichloroethane and water; spectral shifts of 1·5 and 1 nm respectively were obtained and are evidence[55] for the absence of conjugative release in *p*-fluorobenzenesulphonyl chloride.

Considering the effect of change of temperature, of nucleophile, or of solvent in reducing the importance of bond breaking relative to bond forming as ρ changes sign, a reversal in the direction of conjugation for substituents deviating from the Hammett plot is expected. Thus σ^- values[3,64] hold not only for the hydrolysis of *p*-nitrobenzenesulphonyl chloride in 70% dioxan as shown by Vizgert and Savchuk,[5] but also for other nucleophilic sulphur reactions at a negative reaction centre (positive ρ values),[65] and for the solvolysis[4,5,7,9–12,40] and amine[6,57] reactions of benzenesulphonyl halides the predicted reversal of the deviations in the σ values is found. It is surprising to find σ^- values even with a positive ρ value when the sulphur atom in the transition state has, as for the sulphonate ion, a net positive charge.[3,51,66] However, sulphonate,[67] selonate,[26] and sulphonamide[68] can act as conjugative donors. Whether the σ^- values result mainly from conjugative electron release from the sulphonyl group or by loss of a negative charge in the initial state as suggested by the difference plots of Rogne[6] and Robertson and Rossall,[9] it is clear that the change at the reaction centre is large. Thus, if it is assumed that the chlorosulphonyl group in the initial state and associated with σ^+ substituents has a σ^- value, then the change in σ value at the sulphonyl group on entering the transition state must be comparable with that for the ionisation of phenol and the anilinium ion, the defining equilibria for σ^- values.

Although our work is done at constant volume composition, it is of interest to compare the isokinetic relation[69,70] deriving with values obtained by other workers.[7,9] As it has been pointed out that it is incorrect to draw inferences from a calculated regression between two dependant variables,[70,71] the statistical analysis of our results has been done by the method of Exner.[70,72] However, the traditional plots[69] like the two temperature plot of Exner,[70] indicate[73a–c,g] the separate character of the *p*-methoxy-compound. The Exner analysis gives a more precise estimate of $\beta = 337 \pm 5$ K than does the temperature dependence of ρ, 332 ± 31 and 345 ± 64 K * for the 13 well behaved and all 16 compounds respectively, and with s_0, s_∞, and b having values of 0·059, 0·078, and 0·421 respectively together with the plot of s_u, show that this is a reaction with compensation.[70] It can be stated that (*a*) the *p*-methoxy- and (*b*) the *o*-chloro- and *o*-nitro-compounds do not obey the relationship in having either a lower or a higher E : log A ratio respectively.

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* The expected result of the inclusion of temperature dependent σ values.[10,20,73f]

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The absence of kinetic evidence for steric effects for the *o*-methyl compounds is in agreement with the results for an amine displacement reaction at a mesityl ester.[74] The mesitylenesulphonyl chloride results (Tables 1 and 2) confirm the prediction of Tonnet and Hambly [7] that this compound also reacts by a bimolecular mechanism. The recent results of Ciuffarin and his co-workers [75] for the hydrolysis of this compound which were obtained by a flow method seem too high and resemble the results for a two-phase system [2] in which light scattering is observable [18] and a very low apparent E_a value is obtained.[40]

Steric hindrance has been most commonly detected by assuming either an identical,[76] or better, a non-attenuated value based on the *para*-substituent [63,76,77] to hold for the *ortho*-substituent and noting any differences. Within experimental uncertainty, a ρ value of $-0{\cdot}35$ is obtained for variation of *meta*- and *para*-substituents in both the *o*-chloro- and *o*-nitro-benzenesulphonyl chlorides. The predicted rate constant for *o*-chlorobenzenesulphonyl chloride, $2{\cdot}02 \times 10^{-3}$ s^{-1}, from this ρ value, is in agreement with the value, $2{\cdot}13 \times 10^{-3}$ s^{-1}, predicted from the phenylsulphate hydrolysis [23] (Table 4). This reduction in ρ values is the expected result for an additional electron-withdrawing group encouraging bond forming rather than breaking.

A ρ value of $-0{\cdot}91$ is obtained for the *ortho*-substituted compounds. The ratio of the *meta* and *para* ρ values relative to the *ortho*, 0·46, is in agreement with the attenuation, $0{\cdot}4 \pm 0{\cdot}05$, generally found.[3,73d,78] The departure of the *p*-nitro-compounds having different net conjugative effects [73e] from the phenylsulphate correlation [23] (Table 4), a correlation which accommodates the *o*-nitro-compounds in which steric distortions [79] prevent conjugation of the nitro-group with the benzene ring, also occurs in the correlation of *ortho*-substituted benzenesulphonyl chlorides with the corresponding *para*-compounds in their hydrolysis reaction. If, however, instead of the *para*-compound the non-conjugative *meta*-compound is used, a correlation corresponding to an *ortho* ρ value of $-0{\cdot}86$ is obtained and the less accurate three-point plots for both the *ortho*-substituted *p*-chloro- and *m*-nitro-compounds confirm that the *ortho* ρ value is $-0{\cdot}9 \pm 0{\cdot}1$.

Steric effects may be conveniently classified into those in which distortion of the *ortho*-group is caused by the nucleophile during formation of the transition state and more commonly [77] into those in which routes avoiding direct interaction with the *ortho*-group remain, although the number of routes to the transition state are reduced. To the latter type, characterised by a reduction in $\Delta S^{\ddagger}$ and a correlation of log k_o with σ_p [77] may be assigned the *o*-chloro- and *o*-nitro-compounds. Although there are difficulties in interpreting the effects of alkyl substituents,[80] it is noted that the greater reactivity of *o*-toluenesulphonyl chloride in comparison with the *para*-compound is also found for the pK_a values of the corresponding acids.[24]

Although most authors are agreed on a penta-co-ordinate transition state, the conformations of the initial states of arenesulphonyl derivatives in general [81] are uncertain except for cyclic compounds.[82] For the transition state, two of the three possibilities [83] have been discounted for nucleophilic displacements at the sulphonyl group, apical-equatorial being inconsistent with retention of optical activity [84] and equatorial-equatorial being inconsistent with kinetic evidence of steric hindrance.[85] For an apical-apical transition state although the leaving group is necessarily in the plane of the aryl ring for the hydrolysis of cyclic benzenesulphonic anhydrides,[85] it has been suggested [32,74] that the entering and leaving groups will generally be in a plane perpendicular to the benzene ring. In the light of the *X*-ray crystallographic evidence of distortion in the ground state [79,86] all that may be stated is there is no kinetic evidence for loss of transmission of electronic effects between the sulphur atom and the benzene ring as a result of out of plane rotation, a result characteristic of π–d bonding.[87]

As π–d conjugation tends to decrease as the charge on sulphur is reduced,[88] we have an explanation for the observation made by Rogne [89] and us [85] that selectivity increased with *increase* in reactivity for a number of sulphur reactions, since generally the faster the sulphur reaction the more important is bond forming in the transition state with a consequent decrease in positive charge at the sulphur atom.

A decrease in conjugative charge acceptance by the sulphonyl group is predicted for both the axial-axial displacement and the addition mechanisms, but this should be expected to be greater for the latter. Unless electron donation to sulphur from oxygen in the tran-

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sition state is proposed, the transition states will have a p orbital for the entering and leaving groups with a sulphur d orbital available for π–d conjugation with the benzene ring and a σ-type pd orbital respectively. In conclusion, as the stereochemistry is the same for both mechanisms, and in absence of evidence for an intermediate, it is suggested in agreement with other workers [6-11,45,90] that there is no reason at present to depart from the simplest hypothesis of a bimolecular displacement reaction for this and related reactions.

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