Aromatic Sulphonation. Part 91.[1] The Sulphonation of Anisole, Phenol, Phenyl Methanesulphonate, Potassium Phenyl Sulphate, and a Series of Methyl-, Bromo-, and Chloro-substituted Anisoles and Phenols in Concentrated Aqueous Sulphuric Acid

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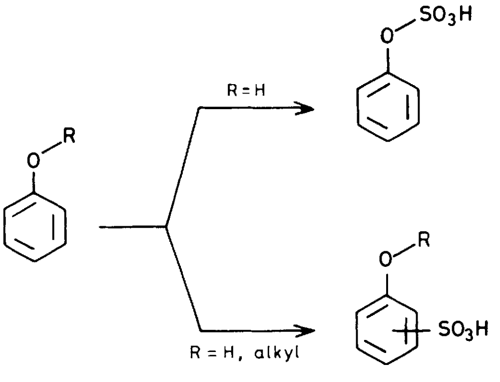
The (homogeneous) sulphonation of a number of aromatic ethers and alcohols, *viz.* anisole (**1**), 3-methyl- (**2**), 4-methyl- (**3**), 2-bromo- (**4**), 4-bromo- (**5**), 2-chloro- (**6**), and 4-chloro-anisole (**7**), phenol (**8**), 2-methyl- (**9**), 3-methyl- (**10**), 4-methyl- (**11**), 4-bromo- (**12**), 2-chloro- (**13**), and 4-chloro-phenol (**14**), phenyl methanesulphonate (**15**), and potassium phenyl sulphate (**16**) in concentrated aqueous sulphuric acid at 25.0 °C has been studied, and rates and isomer distributions have been determined. The sulphonation is first-order in the aromatic substrate, and from the rate measurements it is concluded that the species undergoing sulphonation in the phenyl ring is an *unprotonated* substrate species. In the lower acid concentrations the sulphonating entity is $H_3SO_4^+$. With increasing sulphuric acid concentration there is a gradual change-over in the sulphonating entity from $H_3SO_4^+$ to $H_2S_2O_7$. The acid concentrations of equal rate contribution by the two entities for anisole and phenol are 87 and 90 ± 1%, respectively. Sulphonation on the oxygen atom (*i.e.*, sulphation) does not occur. The *o/p*-ratios for (**1**) and (**8**) do not vary over the studied sulphuric acid range of 75—90% H_2SO_4. Partial rate factors for the 2- and 4-position of (**1**) and (**8**) are reported. The very low partial rate factors for the 4-substitution of (**1**) and (**8**) and the observed extreme suppression and compression of the reactivities of the substrates (**1**)—(**14**) are ascribed to hydrogen bonding of the substrates with the acidic solvent species present. It is tentatively suggested that the relatively high contents of sulphonation *ortho* to -OR with anisole (36%) and phenol (48%) are due to specific complexation of the substrates with the sulphonating electrophile.

Phenol and anisole are sulphonated with extreme ease in concentrated aqueous sulphuric acid. The sulphonation may take place at a ring carbon atom (*i.e.*, sulphonation) and in the case of a phenol also at the oxygen atom (*i.e.*, sulphation), as illustrated in Scheme 1. It has been reported[2–4] that these ambident substrates are protonated predominantly on the oxygen atom in concentrated aqueous sulphuric acid, in addition to being sulphonated, and that the protonation is governed by the H_0^{a}[5] acidity function.[3,4] Further, it has been proposed that phenol and anisole are present in strongly acidic media as hydrogen-bonded solvated species.[6–8]

It has been proposed that the quantitative mononitration of anisole[6] and phenol[7] by nitric acid in sulphuric acid containing 58—80% H_2SO_4 involves reaction with the nitronium ion (NO_2^+) at, or very close to, the encounter-controlled rate. The *o/p* product ratios from anisole and phenol change smoothly over the acid range of 61—83% H_2SO_4 from 1.6 to 0.7[6] and 1.9 to 0.9,[7] respectively. We were eager to learn whether such rate-limiting effects would be encountered in sulphonation and, in continuation of our earlier studies, we have therefore made a kinetic and product study of the sulphonation of the substrates (**1**)—(**16**) in concentrated sulphuric acid at 25.0 °C.

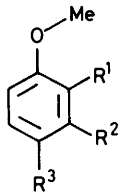
Quantitative data on the kinetically controlled sulphonation of compounds of this type are very sparse.[9] Phenol in 98% H_2SO_4 at 20 °C was reported to give 49% of the 2- and 51% of the 4-sulphonic acid.[10] 2-Methylphenol in 100% H_2SO_4 at 50 °C was reported to give 75% of the 4- and 25% of the 3-sulphonic acid,[11] but this result is in contrast with a more recent report that under these conditions the 4- and 4,6-di-sulphonic acids are formed in 57 and 36% yield, respectively.[12] 3-Methylphenol in concentrated sulphuric acid at 25 °C gives 63% of the 4- and 27% of the 6-sulphonic acid.[13] Sulphonation of 4-methylphenol leads to the 2-sulphonic acid.[14,15]



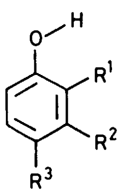
Scheme 1.

Results

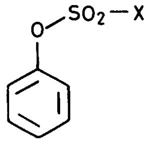
The isomer distribution and the kinetics of the (mono)-sulphonation of the substrates (**1**)—(**16**) have been studied in concentrated aqueous sulphuric acid by ^1H n.m.r. and u.v. spectroscopy. The sulphonation was carried out in a very large excess of sulphuric acid, so that the sulphuric acid concentration remained essentially constant during the reaction. The structures of the sulphonation products were assigned on the basis of their ^1H n.m.r. spectral data, collected in Table 1.



(1) $R^1 = R^2 = R^3 = H$
(2) $R^1 = R^3 = H$; $R^2 = Me$
(3) $R^1 = R^2 = H$; $R^3 = Me$
(4) $R^1 = Br$; $R^2 = R^3 = H$
(5) $R^1 = R^2 = H$; $R^3 = Br$
(6) $R^1 = Cl$; $R^2 = R^3 = H$
(7) $R^1 = R^2 = H$; $R^3 = Cl$



(8) $R^1 = R^2 = R^3 = H$
(9) $R^1 = Me$; $R^2 = R^3 = H$
(10) $R^1 = R^3 = H$; $R^2 = Me$
(11) $R^1 = R^2 = H$; $R^3 = Me$
(12) $R^1 = R^2 = H$; $R^3 = Br$
(13) $R^1 = Cl$; $R^2 = R^3 = H$
(14) $R^1 = R^2 = H$; $R^3 = Cl$



(15) X = Me
(16) X = O^-K^+

Table 1. ^1H N.m.r. spectral data on the mono- and di-sulphonic acids of (1) and (8)—(15)[a–c]

Substrate	H_2SO_4 (% w/w) (±0.1)	Position of SO_3H	δ(p.p.m.) Me[d]	OMe[d]	2-H	3-H	4-H	5-H	6-H
(1)	82.8	2		3.93(1)		7.76(m)[e]	7.05(m)[e]	7.56(t,d)	7.05(m)[e]
		4		3.89(1)	7.05(m)[e]	7.76(m)[e]		7.76(m)[e]	7.05(m)[e]
		2,4		4.04(1)		8.30(d)		8.10(d,d)	7.25(d)
(8)	82.8	2				7.80(m)[e]	7.13(m)[e]	7.54(t,d)	7.13(m)[e]
		4			7.13(m)[e]	7.80(m)[e]		7.80(m)[b]	7.13(m)[e]
		2,4				8.34(d)		8.07(d,d)	7.27(d)
(9)	81.6	4	2.31(2)			7.69(s)		7.66(d)	7.04(d)
		6	2.31(2)			7.54(m)[e]	7.04(m)[e]	7.54(m)[e]	
		4,6	2.37(2)			7.89(d)		8.09(d)	
(10)	81.6	2	2.56(3)				6.95(m)[e]	7.39(t)	6.95(m)[e]
		4	2.58(3)		6.90(m)[e]			7.86(d)	6.90(m)[e]
		6	2.34(3)		6.90(m)[e]		6.90(m)[e]	7.60(d)	
		4,6	2.66(3)		7.08(s)			8.25(s)	
(11)	81.6	2	2.31(4)			7.55(d)		7.38(d,d)	6.98(d)
		2,6	2.37(4)			7.83(s)		7.83(s)	
(12)	87.0	2				7.90(d)		7.68(d,d)	7.00(d)
(13)	87.0	4				7.97(d)		7.79(d,d)	7.23(d)
(14)	87.0	2				7.77(d)		7.56(d,d)	7.16(d)
(15)	90.2	4	3.98 ($MeSO_2O$–)		8.10(d)	8.62(d)		8.62(d)	8.10(d)

[a] The chemicial shifts (δ) of the sulphonic acids of (9)—(14), [(1) and (8)], and (15) are relative to 3-(trimethylsilyl)propane-1-sulphonic acid as internal, D_2O as external, and neat Me_4Si as external standard, respectively. [b] All the *ortho* and *meta* $J_{H,H}$ values were found to be 7.5—9.5 and 1.5—3.0 Hz, respectively. [c] For matters of convenience, the numbering of the substrates has been presented in the sulphonic acids. [d] The first datum gives the chemical shift of the methyl group and the one in parentheses is the position of the substituent. [e] Centre of unresolved multiplet.

The isomer distributions obtained with (1)—(16) are listed in Table 2. Notable is the constancy of the isomer distributions from both anisole (1) and phenol (8) over the whole sulphuric acid range studied.

The sulphonation reactions were found to follow first-order kinetics with respect to the aromatic substrate. The (pseudo)-stoicheiometric first-order rate coefficients, $_{ps}k_{stoich}$, are given in Table 3. The data for phenyl methanesulphonate (15), which is far less reactive than the other substrates, are collected in Table 4.

Discussion

The first-order rate coefficients increase strongly with increasing sulphuric acid concentration. To obtain information as to the sulphonating entity we sought a correlation between the observed rate constants and the activities of the two sulphonating entities previously established to be reactive in concentrated aqueous sulphuric acid, *viz.* $H_3SO_4^+$ and $H_2S_2O_7$.[17]

Anisole (1).—For (1) the graph of log $_{ps}k_{stoich}$ *versus* log $a_{H_2S_2O_7}$ has two linear parts, *viz.* at sulphuric acid concentrations below and above 83.5% H_2SO_4 with slopes of 0.51 and 0.56, respectively (Figure 1). The graph of log $_{ps}k_{stoich}$ *versus* log $a_{H_3SO_4^+}$ also has two linear parts, *viz.* at the acid regions below and above 85.5% H_2SO_4 with slopes 0.70 and 0.88, respectively (Figure 1). These observed slopes are somewhat smaller than those observed for the sulphonation of, for example, *o*- and *m*-xylene [the slopes d(log $_{ps}k$)/d(log $a_{H_3SO_4^+}$) of the linear graphs being 0.83[18]] and the halogenobenzenes [the slopes d(log $_{ps}k$)/d(log $a_{H_2S_2O_7}$) of the linear graphs being in between 0.88 and 0.93[17,19]]. The lower values of the slopes for anisole, as compared with the *non*-oxygen containing substrates, may be explained as resulting from protonation of the ether substrate (B). In fact it has been shown[2,4] that (1) is 'half-protonated' in 76.4% H_2SO_4. The positive charge will render the protonated species (BH^+) far less susceptible to electrophilic substitution than the unprotonated one. Also the absence of anisole-3-sulphonic acid from the

Table 2. Isomer distribution for the monosulphonation of (**1**)—(**16**) at 25.0 °C determined by ^{1}H n.m.r.

Substrate	H_2SO_4 (% w/w) (±0.1)	Isomer distribution (%) (±2)[a,b]		
(**1**)	75.7	2(36)	4(64)[c]	
	79.8	2(35)	4(65)[c]	
	82.8	2(37)	4(63)	
	85.2	2(36)	4(64)[c]	
	90.2	2(37)	4(63)	
(**8**)	73.5	2(48)	4(52)	
	75.7	2(48)	4(52)	
	79.8	2(51)	4(49)	
	82.8	2(47)	4(53)	
	85.5	2(48)	4(52)	
	90.2	2(48)	4(52)	
(**9**)	81.6	4(56)	6(44)	
(**10**)	81.6	2(17)	4(55)	6(28)
(**11**)	81.6	2(100)		
(**12**)	87.0	2(100)		
(**13**)	87.0	4(80)[d]		
(**14**)	87.0	2(100)		
(**15**)	85.5	4(100)		
	90.2	4(100)		
(**16**)	73.5	2(47)	4(53)	
	75.7	2(47)	4(53)	
	79.8	2(49)	4(51)	
	82.8	2(48)	4(52)	
	85.5	2(47)	4(53)	
	90.2	2(47)	4(53)	

[a] The actual recorded sulphonic acid yields were always >90% and with the majority of the substrates even >98%. [b] The first datum gives the position of the sulphonic substituent, the datum in parentheses the relative yield (%). [c] The isomer distribution has been determined u.v. spectroscopically, since the sulphonic acid isomers have no specific ^{1}H n.m.r. signals in this sulphuric acid concentration. [d] The reaction mixture contained 20% of another product, with a multiplet absorption between 7.70—7.90 p.p.m. and a multiplet absorption between 7.10—7.30 p.p.m. with an area ratio of 2:1, which is tentatively assigned to be the 6-sulphonic acid.

sulphonation products of anisole, which product would be formed (at least in part) with the $-O^+MeH$ substituent on the basis of the large $-I$ and the direct field effect, renders the sulphonation of protonated (**1**) in the sulphuric acid range under study very unlikely.*

The ratio of the concentrations of BH^+ and B is determined by equation (1),[21–24] where H_x stands for the appropriate

$$\log [BH^+]/[B] = pK_a - m\cdot H_x \qquad (1)$$

acidity function and m for the slope of the graph of log $[BH^+]/[B]$ *versus* H_x. The $[BH^+]/[B]$ ratios, calculated using $pK_a = -6.00$,[2,4] $m = 0.87$,[4] and the combined[25] $H_0{}^a$ scale,[5] are listed in Table 5.

Both the protonated and unprotonated species can, in principle, be sulphonated, but the sulphonation of the unprotonated species is expected to be much faster as argued above. Accordingly, although protonated (**1**) is the predominant species present above 76% H_2SO_4, the sulphonation will proceed predominantly *via* the unprotonated (**1**) (Scheme 2).

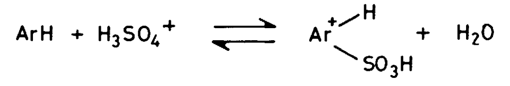
The rate of the sulphonation v is defined by equations (2) and (3), where ${}_{ps}k_{stoich}$ is the observed stoicheiometric first-order rate

$$v = {}_{ps}k_{stoich}([B] + [BH^+]) \qquad (2)$$

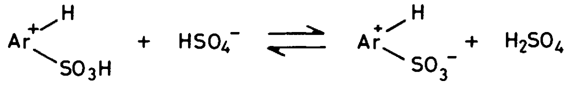
$$v = ({}_{ps}k_B[B] + {}_{ps}k_{BH^+}[BH^+]) \qquad (3)$$

$${}_{ps}k_B = {}_{ps}k_{stoich}([B] + [BH^+])/[B] \qquad (4)$$

coefficient, ${}_{ps}k_B$ and ${}_{ps}k_{BH^+}$ are the first-order rate coefficients for the species B and BH^+, respectively. Where ${}_{ps}k_{BH^+} \ll {}_{ps}k_B$, equation (4) follows from equations (2) and (3). The ${}_{ps}k_B$ values, calculated using equation (4), are also given in Table 5. The correlations of log ${}_{ps}k_B$ with log $a_{H_3SO_4^+}$ and log $a_{H_2S_2O_7}$ are shown in Figure 1. Both graphs have two linear parts, *viz.* below and above 83.5% H_2SO_4, with slopes of 0.88 and 1.20, respectively, for the $H_3SO_4^+$, and 0.63 and 0.79, respectively for the $H_2S_2O_7$ entity. Similar differences in slope between the two types of graphs were observed for toluene, isopropylbenzene, and the three isomeric xylenes,[17,18,26,27] and biphenyl.[28] Considering these slopes and the interpretation of the results for the alkylbenzenes,[17–29] we propose on the basis of the unit slope criterion† that the sulphonation of anisole in the lower sulphuric acid concentrations is effected by the species $H_3SO_4^+$ according to the sequence (5)—(7).[17]

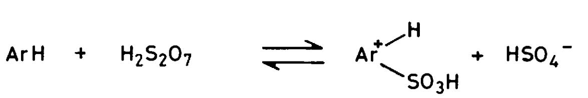


$$ArH + H_3SO_4^+ \rightleftharpoons Ar^+\!\!<^{H}_{SO_3H} + H_2O \qquad (5)$$



$$Ar^+\!\!<^{H}_{SO_3H} + HSO_4^- \rightleftharpoons Ar^+\!\!<^{H}_{SO_3^-} + H_2SO_4 \qquad (6)$$

$$Ar^+\!\!<^{H}_{SO_3^-} + HSO_4^- \longrightarrow ArSO_3^- + H_2SO_4 \qquad (7)$$



$$ArH + H_2S_2O_7 \rightleftharpoons Ar^+\!\!<^{H}_{SO_3H} + HSO_4^- \qquad (8)$$

With increasing sulphuric acid concentration there is a gradual change-over in the sulphonating entity from $H_3SO_4^+$ to $H_2S_2O_7$, with the latter species effecting the sulphonation according to the sequence (8), (6), (7).[17] The acid concentration of equal rate contribution by the two entities is 87 ± 1% H_2SO_4. The constancy in the 2- to 4-sulphonic acid isomer ratio over the whole sulphuric acid range studied (78—90% H_2SO_4) then infers that the *ortho* to *para* substitution ratio is the same for the $H_3SO_4^+$ and the $H_2S_2O_7$ sulphonation mechanisms. The currently observed slope of 0.88 for the graph of log ${}_{ps}k_B$ *versus* log $a_{H_3SO_4^+}$ accords well with the slopes for the reactive positions of aromatic hydrocarbons, *e.g.*, the 4-positions of *o*- and *m*-xylene and biphenyl, the slopes being 0.83,[18] 0.83,[18] and 0.95,[28] respectively.

Phenol (**8**), *Phenyl Methanesulphonate* (**15**), *and Potassium Phenyl Sulphate* (**16**).—The correlations of log ${}_{ps}k_{stoich}$ with log $a_{H_3SO_4^+}$ and log $a_{H_2S_2O_7}$ for phenol are shown in Figure 2. Each of the graphs has two linear parts below and above 85.5%

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* Between 97 and 100% H_2SO_4, the sulphonation of aniline occurs in part by electrophilic attack on the anilinium ion yielding 9—16% of the aniline-3-sulphonic acid.[20]

† From the relationship ${}_{ps}k = k_2 \cdot a_X$, where X is the entity that effects the sulphonation and k_2 the appropriate second-order rate coefficient, it follows that log ${}_{ps}k$ = log k_2 + log a_X. Consequently, a plot of log ${}_{ps}k$ *versus* log a_X will be linear with unit slope.

Table 3. First-order rate coefficients for the homogeneous sulphonation of (1)—(14) in concentrated sulphuric acid[a]

H_2SO_4 (% w/w) ($\pm$0.1)	$10^4 \cdot {}_{ps}k_{stoich}/s^{-1}$ ($\pm$5%)															
	(1)			**(2)**	**(3)**	**(4)**	**(5)**	**(6)**	**(7)**	**(8)**	**(9)**	**(10)**	**(11)**	**(12)**	**(13)**	**(14)**
		64.4 °C	84.5 °C													
60.1			0.42													
63.6			1.4													
64.3			1.6													
65.1		0.27	2.2													
70.3		1.6	14													
74.3	0.064	8.9	63													
76.3	0.20	21														
77.1	0.25			1.25												
78.2				2.2												
79.5	0.93	75														
79.8	1.16			7.0				0.153		2.4						
80.8				9.9												
80.9					1.24	0.25		0.22								
81.7	3.2			13.5		0.42						17.1	5.6			
82.8				26.7		0.66		0.63	0.153	6.3; 7.1[b]	7.6					
83.4	6.6			37	4.5											
84.1				57			0.31					47	9.9			
84.5										17						
84.7	15.3					2.1										
85.0														0.60	2.2	
85.1	17.5					2.2	0.52			20	18.4					0.71
85.2	18.9				13.3								22			
85.3					12.6		0.56	1.81	0.48							
87.0							1.30							1.61	7.3	1.25
87.1	39				35	5.1	1.58	4.5	1.18	42[c]	45	173	32			
88.0										76						
88.6	97					9.2										
88.7					82		3.0		2.50	124		182				
89.8										142[d]						
90.4	183					28	6.8	31	6.5	170; 220	109		104	6.6	35	6.7

[a] The reaction temperature is 25.0 °C, unless stated otherwise. [Substrate] usually 10^{-4}—10^{-5} mol dm^{-3}. [b] For this acid concentration at 36, 46, and 56 °C $10^4 \cdot {}_{ps}k_{stoich}$ is equal to 21, 52, and 125 s^{-1}, respectively. [c] [Phenol] varied between 1.3 × 10^{-4} and 0.6 mol dm^{-3}. [d] Value measured by Gore.[16]

Table 4. First-order rate coefficients for the homogeneous sulphonation of (15) in concentrated sulphuric acid at 25.0 °C

H_2SO_4 (% w/w) ($\pm$0.1)	$10^6 \cdot {}_{ps}k/s^{-1}$($\pm$5%)
89.1	1.3 $\pm$ 0.2
90.4	1.6
91.5	2.5
92.9	6.0
94.3	11.1
95.9	25.9
96.9	52
97.7	76
98.5	118
99.8	210

$H_2SO_4{}_+$; the slopes up to 85.5% H_2SO_4 are 0.58 and 0.40, respectively, and above 85.5% H_2SO_4 0.85 and 0.55, respectively.

Phenyl methanesulphonate (**15**) is far less reactive in sulphonation than phenol and anisole. The graphs of log ${}_{ps}k$ *versus* log $a_{H_3SO_4^+}$ and log $a_{H_2S_2O_7}$, shown in Figure 3, are linear in the acid range 91—97% H_2SO_4 with slopes of 1.29 and 0.77, respectively. With (**8**), the slopes are, just as with (**1**), somewhat smaller than observed with the non-OR (R = H, Me)-substituted benzenes.[17,18,28,29] The lower slopes of the OH-containing substrate (**8**) may be explained to result from oxygen protonation, just as with anisole (see before).

With phenol (**8**) in concentrated aqueous sulphuric acid, in addition to the *O*-protonated species, phenyl hydrogen sulphate

$PhOSO_2X$

(**17**) X = OH
(**18**) X = O^-

(**17**) and/or its anion (**18**), *i.e.*, the products of sulphation, could be present, which might also undergo sulphonation. This is highly unlikely in view of the following observations. First, the pseudo-first-order rate coefficient for the sulphonation in 90.4% H_2SO_4 is $>10^4$ times greater for (**8**) than for (**15**). Secondly, the monosulphonation isomer distributions of (**8**) and (**15**) are very different. With (**8**), over the whole sulphuric acid range studied, the 2- and 4-sulphonic acids are formed in constant relative yields of 48 and 52%, respectively, whereas with (**15**) the 4-sulphonic acid is formed exclusively (Table 2).* Thirdly, dissolution of (**16**) in 73.5—82.8% H_2SO_4 yields (**8**) as the only initial product (according to ^{1}H n.m.r.); the phenol (**8**) is then sulphonated. In fact, the ^{1}H n.m.r. spectra of the sulphonic acid mixtures obtained upon dissolving (**8**) and (**16**) in any given sulphuric acid concentration in 73.5—90.2% H_2SO_4 are fully superimposable (*cf.* Table 2). Furthermore, the observation that phenol-2- and phenol-4-sulphonic acid and the 4-sulphonic acid of (**15**) do not isomerize under the applied sulphonation conditions seems to rule out the possibility of initial sulphonation of (**17**), followed by a subsequent isomerization of

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* The absence of the formation of *o*-sulphonic acid in the sulphonation of phenyl methanesulphonate (**15**) excludes the hydrolysis of this substrate as any resulting phenol would yield 48% of *ortho*-substitution.

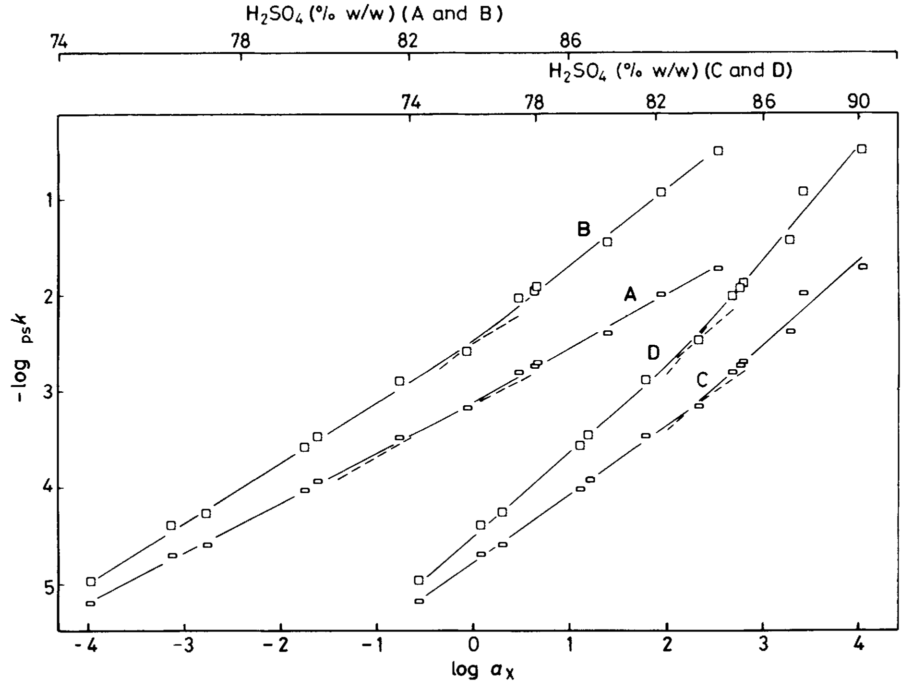
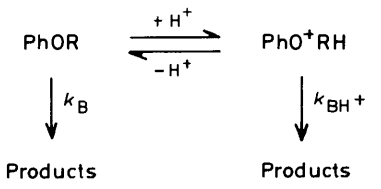


Figure 1. Sulphonation of anisole (1). Correlation of log $_{ps}k_{stoich}$ (A and C) and log $_{ps}k_B$ (B and D) with log a_X, where X = $H_2S_2O_7$ (A and B) and $H_3SO_4^+$ (C and D)



Scheme 2.

the resulting sulphonic acid mixture to yield the observed sulphonic acid isomer ratio. Fourthly, the observed reaction rates and the rate profiles of anisole (which cannot be sulphated) and phenol are very similar. Further, it seems relevant that the sulphonation of phenolic substrates for which sulphation plays a role (as with 4-hydroxy- and 4-methoxy-phenol)[30] never occurs *ortho* to the sulphate group.

The first-order-rate constants of unprotonated (**8**) ($_{ps}k_B$) were calculated from the stoicheiometric rate constants ($_{ps}k_{stoich}$), using relation (4) and the [BH$^+$]/[B] ratios calculated from equation (1) with pK_a = -6.40,[2–4] and m = 0.91;[4] the data are listed in Table 5. The graphs of log $_{ps}k_B$ *versus* both log $a_{H_3SO_4^+}$ and log $a_{H_2S_2O_7}$ have two linear parts, *viz.* below and above 85.5% H_2SO_4, the first with slopes of 0.83 and 1.11, and the latter with slopes of 0.48 and 0.80, respectively (Figure 2). By analogy with (**1**) (see before) and the alkylbenzenes,[17,29] we propose that (**8**) in the lower acid concentrations is sulphonated by the $H_3SO_4^+$ entity according to the sequence (5)—(7). With increasing sulphuric acid concentration there is a gradual change-over in the sulphonating entity from $H_3SO_4^+$ to $H_2S_2O_7$, with the latter species effecting the sulphonation according to the sequence (8), (6), (7).[17,*] The acid concentration of equal rate contribution by the two entities is 90 ± 1% H_2SO_4.

Table 5. [BH$^+$]/[B] ratios and first-order rate coefficients for the homogeneous sulphonation of unprotonated (**1**) and (**8**) in concentrated aqueous sulphuric acid at 25.0 °C

H_2SO_4 (% w/w) (±0.1)	[BH$^+$]/[B] (**1**)	[BH$^+$]/[B] (**8**)	$10^4\,_{ps}k_B$/s^{-1} (±10%) (**1**)	$10^4\,_{ps}k_B$/s^{-1} (±10%) (**8**)
74.3	0.64		0.105	
76.3	0.98		0.40	
77.1	1.13		0.54	
79.5	1.75		2.57	
79.8	1.90	0.85	3.3	4.4
81.7	2.78		12.3	
82.8		1.59		16.2
		1.59		18.2
83.4	3.90		32	
84.5		2.21		55
84.7	4.97		91	
85.1	5.38	2.51	109	71
85.2	5.49		123	
87.1	8.19	3.90	354	210
88.0		4.52		420
88.6	10.4		1 120	
88.7		5.23		760
89.8		6.59		1 070
90.4	15.9	7.79	3 100	1 510
		7.79		2 000

The sulphonic acid concentration of change-over in mechanism[17] appears to be higher with phenol (90 ± 1%) than with anisole (87 ± 1%). The σ^+ values for the 4-position of phenol and anisole are -0.92[8] and -0.78,[8] respectively,

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[*] It is noteworthy that the sulphonation of 2- and 4-phenol- and the corresponding anisole-sulphonic acids in 88—99% H_2SO_4 proceed by reaction of the *unprotonated* substrate species with $H_2S_2O_7$ as the sulphonating entity.[30] Further, it is striking that the plot of log $_{ps}k_{stoich}$ *versus* log $a_{H_2S_2O_7}$ for the sulphonation of 4-hydroxyazobenzene in 81—100.1% H_2SO_4, yielding the 4′-sulphonic acid, is linear up to 99.8% H_2SO_4 with a slope (0.79)[31] similar to those observed in the sulphonation of phenol, anisole, and their *o*- and *p*-sulphonic acids.

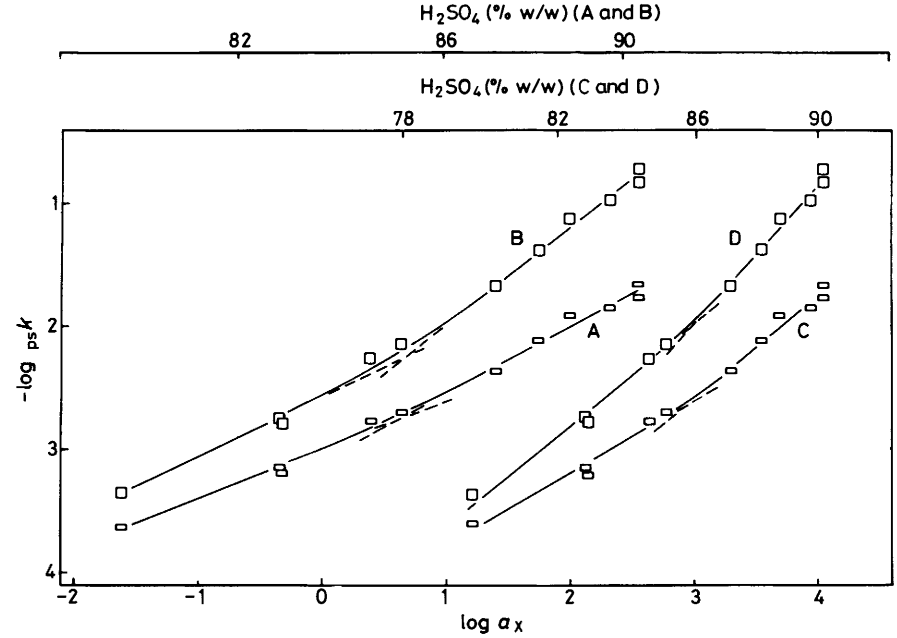


Figure 2. Sulphonation of phenol (**8**). Correlation of log $_{ps}k_{stoich}$ (A and C) and log $_{ps}k_B$ (B and D) with log a_X, where X = $H_2S_2O_7$ (A and B) and $H_3SO_4^+$ (C and D)

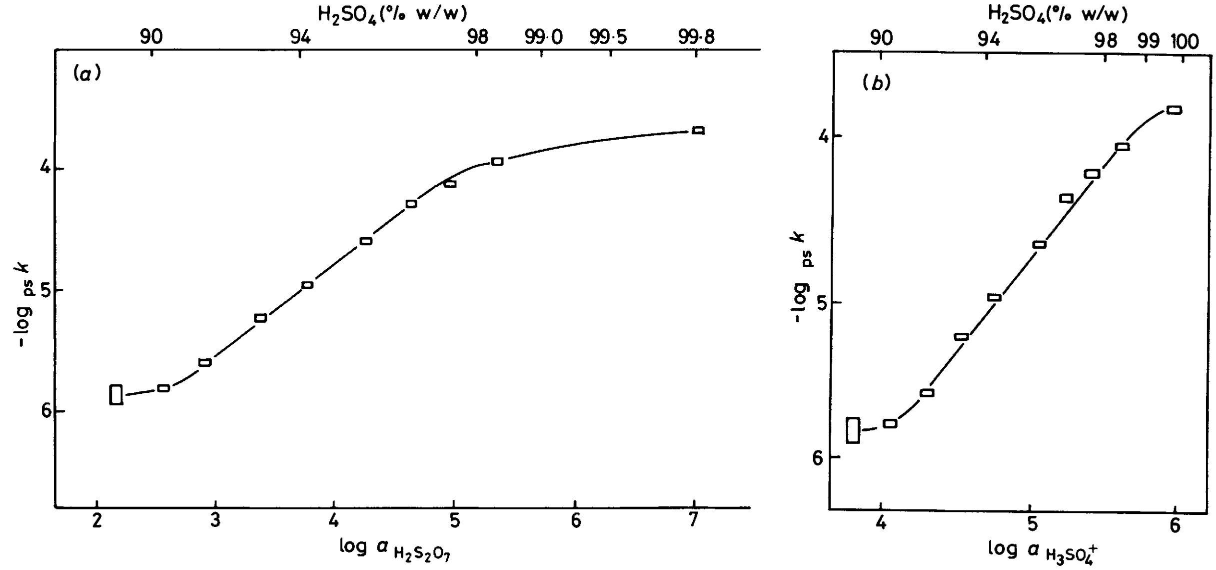


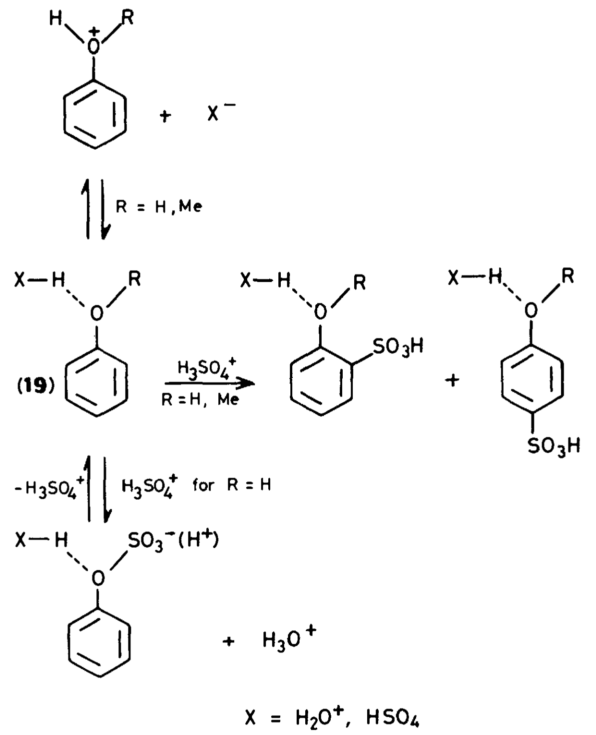
Figure 3. Sulphonation of phenyl methanesulphonate (**15**). Correlation of log $_{ps}k_{stoich}$ with log $a_{H_3SO_4^+}$ and log $a_{H_2S_2O_7}$

illustrating the higher reactivity of phenol as compared with anisole. Accordingly the present observation is consistent with earlier results for hydrocarbon substrates, which indicate that the acid concentration, at which the rate contributions by the entities $H_3SO_4^+$ and $H_2S_2O_7$ are equal, increases with increasing reactivity of the position at which substitution takes place.[17] Again with phenol the constancy of the product isomer ratios infers that the *ortho* to *para* substitution ratio is the same for the $H_3SO_4^+$ and the $H_2S_2O_7$ mechanisms.

The reaction possibilities of (**1**) and (**8**) in the lower acid concentrations are shown in Scheme 3, in which (**19**) is a substrate species which is hydrogen-bonded to an acidic solvent species.

Substrate Reactivity and the Reaction Mechanism.—The partial rate factors for the sulphonation in 77.8% H_2SO_4 at 25.0 °C of the 2- and 4-positions of anisole (**1**) and phenol (**8**) were calculated from the $_{ps}k_B$ values, the isomer distributions of (**1**) and (**8**), and the contribution to the rate constant for the sulphonation of benzene due to the $H_3SO_4^+$ mechanism in 77.8% H_2SO_4 [$= (3.55 \pm 1.0) \times 10^{-8}$ s^{-1}].[29,32] They are collected in Table 6 together with the partial rate factors of a series of hydrocarbon substrates.

The Hammett–Brown plot of these data is shown in Figure 4. The graph for the hydrocarbon positions is linear with a slope $\rho^+ = -9.3 \pm 0.3$. The points for the 4-positions of (**1**) and (**8**) are below this graph. A comparison of the actually observed partial rate factors for the 4-positions of anisole and phenol (log $^{OMe}f_4 = 3.85$ and log $^{OH}f_4 = 3.86$) with the extrapolated ones (log $^{OMe}f_4 = 7.25$ and log $^{OH}f_4 = 8.56$), shows that the



Scheme 3.

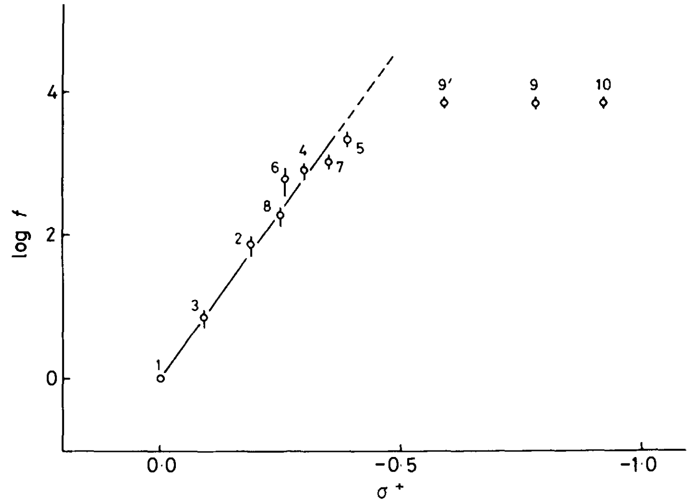


Figure 4. Hammett–Brown relation for the sulphonation by the entity $H_3SO_4^+$. (For the entries, see Table 6)

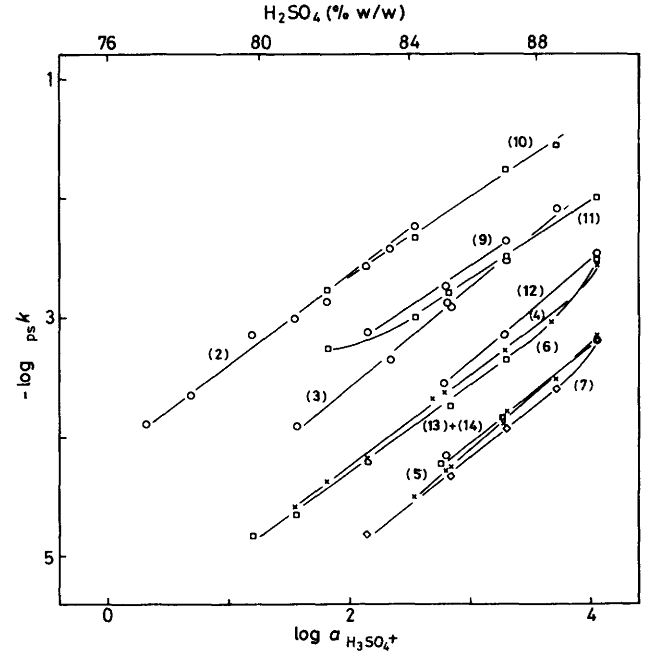


Figure 5. Correlation of $\log {}_{ps}k_{stoich}$ with $\log a_{H_3SO_4^+}$ for the sulphuric acid sulphonation of (2)—(7) and (9)—(14); the respective slopes are 0.76, 0.83, 0.77, 0.88, 0.73, 0.80, 0.66, 0.68, 0.66, 0.85, 0.82, and 0.82

Table 6. Partial rate factors for the sulphonation in concentrated aqueous sulphuric acid by the entity $H_3SO_4^+$ at 25.0 °C

Substrate	Position	f	$\sigma^{+\,a}$	Entry
Benzene	1	1	0	1
Toluene	2	69 ± 20[b]	−0.19[c]	2
	3	7 ± 2[b]	−0.09	3
	4	760 ± 200[b]	−0.30	4
o-Xylene	4	2 000 ± 500[b]	−0.39[d]	5
Biphenyl	4	600 ± 300[e]	−0.26[e]	6
Naphthalene	1	1 020 ± 250[f]	−0.35	7
	2	180 ± 50[f]	−0.25	8
Anisole	2	2 000 ± 250		
	4	7 100 ± 750	−0.78[g]	9
			−0.59[h]	9′
Phenol	2	3 400 ± 400		
	4	7 300 ± 800	−0.92[i]	10

[a] The σ^+ values were taken from reference 8, unless stated otherwise. [b] Reference 29. [c] Reference 33. [d] $\sigma^+ = \sigma^+(m\text{-Me}) + \sigma^+(p\text{-Me})$. [e] Reference 28. [f] Reference 34. [g] Reference 35. [h] This value refers to a –OMe substituent hydrogen-bonded to trifluoroacetic acid. [i] Reference 36.

sulphonation rates of these substrates are suppressed by factors of 3×10^3 and 5×10^4 respectively. For anisole a suppression of the reactivity has been reported previously: the protiodetritiation of [p-^{3}H]anisole in trifluoroacetic acid was found to be *ca.* 15 times slower than expected on the basis of the σ^+ and ρ^+ values.[8,37] This reduction of reactivity was ascribed to a hydrogen-bonding interaction between the substrate and acidic solvent species.[38–40]

The slopes of the graphs of $\log {}_{ps}k_{stoich}$ *versus* $\log a_{H_3SO_4^+}$ of the activated [(**2**), (**3**), (**9**)—(**11**)] and the deactivated [(**4**)—(**7**), (**12**)—(**14**)] derivatives of anisole and phenol are comparable with those of (**1**) and (**8**) (Figure 5). The reactivities of the substrates (**2**)—(**7**) and (**9**)—(**14**) to sulphonation also appear to be suppressed but not all to the same extent. The differences in the reactivities of the substrates towards the sulphonating entity are far less than expected on the basis of the additivity of the substituent effects,* and show in fact a very narrow band width. In addition to the suppression and compression of reactivity in this reaction, the constancy of product proportions for both (**1**)

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* For example, the sulphonation partial rate factor ratio in 90.4% H_2SO_4 for the 4-substitution of (**9**) and (**13**) was calculated from the ${}_{ps}k_{stoich}$ (Table 3) and the monosulphonic acid isomer ratios (Table 2) to be ${}^{(9)}f_4/{}^{(13)}f_4 = 2$. This value is very much smaller than the value of 8×10^3 calculated using $\rho^+ = -9.3 \pm 0.3$ and the σ^+ values for the 4-positions of (**9**) and (**13**) of −1.01 and −0.55, respectively. The latter two values have been calculated assuming additivity of the substituent effects; σ^+(4-position of (**9**)] = $\sigma^+(p\text{-OH}) + \sigma^+(m\text{-Me}) = -0.92^{36} + (-0.09)^8 = -1.01$ and σ^+(4-position of (**13**)] = $\sigma^+(p\text{-OH}) + \sigma^+(m\text{-Cl}) = -0.92^{36} + 0.40^{35} = -0.52$.

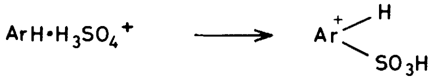
and (**8**) over ranges of acidity where, according to the kinetic analysis offered above, the proportions of reaction involving $H_3SO_4^+$ and $H_2S_2O_7$ as electrophiles vary is both noteworthy and surprising.

The following three possibilities may be considered in explanation of the special attributes of these reactions.

(i) *Diffusion control of reaction rate.* The second-order rate coefficients for the formation of the encounter complex $ArH{\cdot}H_3SO_4^+$ by step (10) have been calculated for (**1**) and (**8**) in 80.0% H_2SO_4 as follows. The first-order sulphonation rate coefficient of the unprotonated substrate species for the sequence of steps (9)—(11), followed by (6) and (7) is given by

$$H_2SO_4 + H^+ \rightleftharpoons H_3SO_4^+ \qquad (9)$$

$$ArH + H_3SO_4^+ \rightleftharpoons ArH{\cdot}H_3SO_4^+ \qquad (10)$$



$$ArH{\cdot}H_3SO_4^+ \longrightarrow Ar\overset{+}{<}\begin{matrix}H\\SO_3H\end{matrix} \qquad (11)$$

equation (12), and, when k_{10} is rate limiting, by (13). The test then is whether k_{10} approaches the diffusion-controlled rate coefficient of encounter k_{enc}, which depends on the viscosity of the solution and equals 0.36×10^9 mol^{-1} s^{-1} dm^3 for 80.0% H_2SO_4.[41] For a given sulphuric acid concentration $[H_3SO_4^+]$ is correlated with the acidity function H_0 by equation (14)[42] and $[H_3SO_4^+]$ is thence calculated to be 2.5×10^{-7} mol dm^{-3} for 80.0% H_2SO_4.

$$_{ps}k_B = k_{10}k_{11}[H_3SO_4^+]/(k_{10} + k_{11}) \qquad (12)$$

$$_{ps}k_B = k_{10}[H_3SO_4^+] \qquad (13)$$

$$\log [H_3SO_4^+] = -(H_0 + 13.95) \qquad (14)$$

Accordingly, for (**1**) and (**8**) in 80.0% H_2SO_4, using equation (13) k_{10} was calculated to be 0.14×10^4 and 0.15×10^4 mol^{-1} s^{-1} dm^3, respectively. Thus, provided the estimate of $[H_3SO_4^+]$ is correct, the observed rates are *ca.* 2×10^5 times smaller than the limiting rate caused by the $H_3SO_4^+$ ions and substrate molecules diffusing together. This situation is very different from that which occurs for nitration of reactive substrates in a similar medium.[43] It follows that this phenomenon does not provide an explanation for the suppression of reactivity observed.

(ii) *Hydrogen bonding.* It is to be expected that hydrogen bonding of the –OR substituent with the hydronium ion (H_3O^+) or other acidic species will lower the activating effect of the substituent. It has been suggested[6,7] for the nitration of these compounds that hydrogen bonding may be responsible for them reacting at a little below the encounter rate (by a factor of ≤ 2), which has been established with other substrates. If this is the case, the deactivating effect of the hydrogen bonding has been *ca.* 10^4 in rate, as these substrates would have been much more reactive had not encounter control intervened.[43] It is possible therefore that hydrogen-bonding effects can explain the rate suppression for (**1**) and (**8**). If this is also the explanation for the compression reactivity of their derivatives, the effect of hydrogen bonding must be somewhat greater in more activated substrates [*e.g.*, (**10**)] and smaller in some less activated substrates [*e.g.*, (**13**)]. The constancy of isomer proportions from (**1**) and (**8**) remains fortuitous.

(iii) *Complexation of substrate and electrophile.* It is possible that the electrophile would initially complex with the –OR substituent by hydrogen bonding, thus lowering the reactivity of the substrate to substitution in the ring. Formation of the products from this complex at least partially by intramolecular transfer of the SO_3H group *via* a six-membered ring transition state, could explain the relatively high degree of sulphonation *ortho* to the –OR substituent in the sulphonations in sulphuric acid of (**1**) and (**8**).*

Hydrogen-bond formation should be too fast to be the rate determining stage of reaction and so pre-equilibrium complex formation is implied. A minor proportion of the unprotonated substrate must be involved in this particular complex, the remainder being hydrogen bonded to other species in solution, or the acidity dependence of rate would not be as observed, assuming that intramolecular reaction is involved. A common intermediate for the two electrophilic species involved over the acidity range would provide an attractive explanation for the constancy of isomer ratios from (**1**) and (**8**). However, as the two electrophilic species $H_3SO_4^+$ and $H_2S_2O_7$ give observably different slopes for the acidity dependence of rate it is not possible for a common intermediate formed in a pre-equilibrium to be involved. It follows that the two electrophiles would have to form different hydrogen-bonded complexes and the constancy of isomer ratios remain fortuitous.

Experimental

Apparatus and Materials.—The ^1H n.m.r. spectra were recorded on a Varian XL-100-12 or a Jeol MH 100 spectrometer. The rate measurements were carried out with a Zeiss PMQ II, and a Pye Unicam SP 1800 and Perkin-Elmer 402 spectrophotometer with quartz cells with a path length of 10 mm. Sulphuric acid (AnalaR; *d* 1.84) was obtained from BDH Chemicals. This acid was diluted with demineralized water in order to obtain the solutions of the desired acid strength. Concentrations of dilute sulphuric acid solutions were determined from density measurements, or measurements of the rate coefficients of sulphonation of substrates for which the rate coefficients had been determined with high precision previously.[48]

Substrates (**1**)—(**14**) were redistilled or recrystallized commercial reagents.

Phenyl methanesulphonate[49] and potassium phenyl hydrogen sulphate[50] were synthesized by known procedures.

Procedures.—The structural assignments of the sulphonation products were made by ^1H n.m.r. spectroscopy and are based on the relative area ratios, the multiplicity of the various signals, the coupling constants, and the specific substituent shielding parameters. The compositions of the reaction mixtures were determined by multicomponent ^1H n.m.r. analysis.[51] The rate measurements were based on the differences in u.v. absorption of a substrate and its reaction products. The reaction rates were determined by measuring the absorbance at a given wavelength as a function of time. The wavelengths, chosen so as to allow a maximum variation in the extinction, were 255, 285, 235, 294, 240, 300, 241, 299, 225, 229, 230, 222, 295, 232, 294, and 270 nm for (**1**)—(**15**) respectively. The pseudo-first-order rate coefficients, $_{ps}k$, were derived from plots of log $|E - E_t|$ *versus* time, where E and E_t are the absorbances of the homogeneous reaction mixture at infinite time (final products), and time t, respectively. In all cases straight line plots over at least three half-lives were obtained.

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* The *o*/*p* ratios for the sulphonation of PhMe, PhEt, PhOH, and PhOMe with 80 (and 85)% H_2SO_4 at 25 °C are 0.36 (0.62),[43,44] (0.27),[44] 0.92, (0.92),[45] and 0.56 (0.56) (this paper), respectively, and with SO_3 in nitromethane at 0 °C 0.13,[46] unknown, ≤ 0.02,[47] and ≤ 0.02,[47] respectively.

Isomer Distributions.—The isomer distributions have been determined by ^{1}H n.m.r. 50 mg of a given substrate were added to 3.0 ml of the chosen sulphuric acid solution and after shaking or stirring to homogeneity, the resulting solution was transferred into a 5 mm n.m.r. tube and was subjected to multicomponent ^{1}H n.m.r. analysis.[51] With **(1)** and **(8)** in sulphuric acid that was $<87\%$ H_2SO_4 only a mixture of the 2- and 4-sulphonic acids is obtained and in $\geq 87\%$ H_2SO_4 the 2,4-disulphonic acid is obtained in addition. For sulphuric acid more concentrated than 87% H_2SO_4 the initial *ortho*:*para* sulphonation ratio of **(1)** and **(8)** has been determined from the content of the 2-, 4-, and 2,4-di-sulphonic acid, and the sulphonation rate constants of the former two sulphonic acids.[52] (These rate constants were used to estimate the relative content of the two monosulphonic acids from which the 2,4-disulphonic acid was formed.)

The activites of $H_3SO_4^+$ and $H_2S_2O_7$ in sulphuric acid that was $\leq 98.0\%$ H_2SO_4 were obtained with (15)[29] and (16)[19a]

$$\log a_{H_3SO_4^+} = \log a_{H_2SO_4} + \log a_{H_3O^+} - \log a_{H_2O} \qquad (15)$$

$$\log a_{H_2S_2O_7} = 2 \log a_{H_2SO_4} - \log a_{H_2O} \qquad (16)$$

respectively, using the reported[29] values for $a_{H_2SO_4}$, $a_{H_3O^+}$, and a_{H_2O}. The log $a_{H_2S_2O_7}$ values for sulphuric acid that was $>98.0\%$ H_2SO_4 were obtained by adding to the reported values for 114—97% H_2SO_4[53] 12.25, which is the constant difference between the log $a_{H_2S_2O_7}$ data calculated for 114—97% H_2SO_4[53] and for 78—100% H_2SO_4[29] in the overlapping range.

Acknowledgements

The award of an S.E.R.C. Research Grant is gratefully acknowledged (R. G. C. and G. P. T.).

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Received 18*th June* 1984; *Paper* 4/1048