Aromatic Sulphonation. Part 94.[1] Sulphonation and Sulphation of the Three 2- and 4-Hydroxy- and 2- and 4-Methoxy-benzenesulphonic Acids in Concentrated Sulphuric Acid

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The sulphonation of 2-methoxy- (1) and 4-methoxy-benzene sulphonate (2) and 1- (3), 3- (4), and 4-hydroxybenzenesulphonate (5) in 86.9—98.5% H_2SO_4 at 25 °C has been studied. Substrates (1)—(3) and (5) all yield the corresponding 2,4-disulphonic acid as the exclusive product, whereas (4) yields a mixture of 2-hydroxybenzene-1,4- and 4-hydroxybenzene-1,2-disulphonic acid. 3- and 4-Hydroxybenzenesulphonic acids in sulphuric acid (>87% H_2SO_4) are present in part as their hydrogen sulphates and the sulphuric acid concentration of 50% sulphation is 97.5 and 100.5 ± 0.2% H_2SO_4. The sulphonation is first order in the aromatic substrate. From the rate dependence on the sulphuric acid concentration it is concluded that the substrate species undergoing ring sulphonation is the $^-O_3SC_6H_4OR$ (R = H; Me) species with $H_2S_2O_7$ as the sulphonating entity. From the observed proportionality between $[^-O_3SC_6H_4OSO_3H]/[^-O_3SC_6H_4OH]$ and a_{SO_3} it is concluded that the aromatic species undergoing sulphation is again $^-O_3SC_6H_4OH$.

Anisole and phenol in concentrated aqueous sulphuric acid are protonated to a substantial degree very predominantly on oxygen.[2-4] The sulphuric acid sulphonation, however, proceeds by substitution of the *unprotonated* substrate species.[5] Below 85% H_2SO_4 the main sulphonating species is $H_3SO_4^+$ and above 90% H_2SO_4 it is predominantly $H_2S_2O_7$.[5] Sulphonation of both anisole and phenol in sulphuric acid ranging from 80—90% H_2SO_4 at ambient temperature leads initially to a mixture of the 2- and 4-sulphonic acids (the respective ratios being 36:64 and 48:52 respectively[5]) and eventually to the 2,4-disulphonic acids.[3,5]

In continuation of our studies[1-5] we have made a kinetic study on the sulphonation of the substrates (1)—(5) in concentrated aqueous sulphuric acid. Previously we established[3] that the sulphonates (1)—(3) and (5) in aqueous sulphuric acid more concentrated than 85% H_2SO_4 are protonated very predominantly on one of the oxygen atoms of the sulphonate group or/and on OR (R = H; Me) (Scheme 1), and that these protonations are governed by the $H_0^{'6}$ acidity function.

Results

The kinetics of the sulphonation of substrates (1)—(5) in concentrated aqueous sulphuric acid containing 86.9—98.5% H_2SO_4 at 25.0 °C have been studied by u.v. spectroscopy. The sulphonation was carried out in a very large excess of sulphuric acid, so that the acid concentration remained essentially constant during the reaction. The sulphonation products have been assigned on the basis of their ^1H n.m.r. data which are listed in Table 1. The methoxybenzenesulphonic (anisole-sulphonic) acids (1) and (2) and the hydroxybenzenesulphonic (phenolsulphonic) acids (3) and (5) in 86.9—98.5% H_2SO_4 are sulphonated to the corresponding anisole- (6) and phenol-2,4-disulphonic acid (7), respectively. Phenol-3-sulphonate (4) in 89.1—98.5% H_2SO_4 yields initially both phenol-2,5- (8) and phenol-3,4-disulphonic acid (9). With increasing reaction time, (9) was found to be unstable and was eventually fully converted into the 2,5-disulphonic acid isomer (8).

All the sulphonations were found to follow first-order kinetics with respect to the aromatic substrate. The stoicheiometric first-order rate coefficients, $_{ps}k_{stoich}$, are compiled in Table 2. In sulphuric acid ⩾105% H_2SO_4 (4) and (5) are fully converted
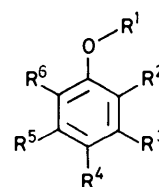
(1) R^1 = Me, R^2 = $SO_3^-K^+$, R^3 = R^4 = R^5 = R^6 = H

(2) R^1 = Me, R^2 = R^3 = R^5 = R^6 = H, R^4 = $SO_3^-K^+$

(3) R^1 = R^3 = R^4 = R^5 = R^6 = H, R^2 = $SO_3^-K^+$

(4) R^1 = R^2 = R^4 = R^5 = R^6 = H, R^3 = $SO_3^-K^+$

(5) R^1 = R^2 = R^3 = R^5 = R^6 = H, R^4 = $SO_3^-K^+$

(6) R^1 = Me, R^2 = R^4 = SO_3H, R^3 = R^5 = R^6 = H

(7) R^1 = R^3 = R^5 = R^6 = H, R^2 = R^4 = SO_3H

(8) R^1 = R^3 = R^4 = R^6 = H, R^2 = R^5 = SO_3H

(9) R^1 = R^2 = R^5 = R^6 = H, R^3 = R^4 = SO_3H

(10) R^1 = R^3 = SO_3H, R^2 = R^4 = R^5 = R^6 = H

(11) R^1 = R^4 = SO_3H, R^2 = R^3 = R^5 = R^6 = H
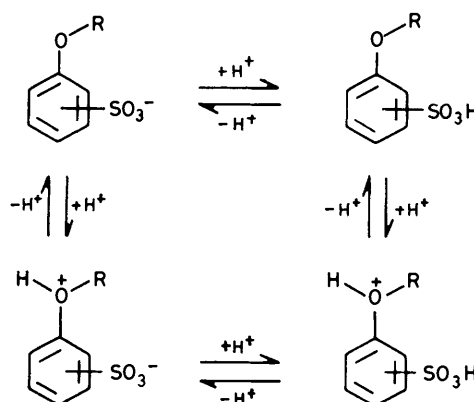
Scheme 1.

Table 1. [1]H N.m.r. data of (1)—(11)[a,b]

| Substrate | H_2SO_4 (wt %; ±0.1) | δ | | | | | |
		OMe	H (2)	H (3)	H (4)	H (5)	H (6)
(1)	82.8	3.93 (1)		7.76 (m)[c]	7.05 (m)[c]	7.56 (t,d)	7.05 (m)[c]
(2)	82.8	3.89 (1)	7.05 (m)[c]	7.76 (m)[c]		7.76 (m)[c]	7.05 (m)[c]
(3)	82.8			7.80 (m)[c]	7.13 (m)[c]	7.54 (t,d)	7.13 (m)[c]
(4)	89.1		7.72 (d)		7.65 (m)[c]	7.65 (m)[c]	7.41 (d,br)
(5)	82.8		7.13 (d)	7.80 (d)		7.80 (d)	7.13 (d)
	95.9		7.20 (d)	7.95 (d)		7.95 (d)	7.20 (d)
(6)	82.8	4.04 (1)		8.30 (d)		8.10 (d,d)	7.25 (d)
(7)	82.8			8.34 (d)		8.07 (d,d)	7.27 (d)
(8)	92.9				7.75 (m)[c]	7.73 (m)[c]	8.12 (d)
(9)	92.9		8.10 (s)			8.27 (d)	7.70 (m)[c]
(10)	92.9		7.97 (s)		7.80 (m)[c]	7.80 (m)[c]	8.01 (d)
(11)	95.9		7.62 (d)	8.09 (d)		8.09 (d)	7.62 (d)

[a] The chemical shifts (δ) of the sulphonic acids were calculated from the proton signal of the external reference [[2]H$_2$]O which was taken to be δ 4.60. [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] Centre of unresolved multiplet.

Table 2. First-order rate coefficients for the homogeneous sulphonation of (1)—(5) in concentrated aqueous sulphuric acid at 25.0 °C

| H_2SO_4 (wt %; ±0.1) | $10^5 \, _{ps}k_{stoich} \, s^{-1}$ (±5%) | | | | |
	(1)	(2)	(3)	(4)	(5)
86.9	5.8		6.0		
88.0	9.1	0.35			0.53
89.1	14.1	0.50	14.1	3.3×10^{-3}	0.68
90.4	22.9	0.72	22.4		1.00
91.5	43.7	1.17	37.2		1.55
92.9	76	2.09	66	10.7×10^{-3}	2.34
94.3	135	2.63	126		3.39
95.9	288	5.0	229		4.27
96.9	460	7.1	407		5.62
97.7	810	9.6	580		7.6
98.5	1 450	17.4	1 290	40.8×10^{-3}	8.9

into their hydrogen sulphates (10) and (11), respectively (Scheme 2), but in 90% H_2SO_4 only for 2 and 9%, respectively. On plotting the ratios of $[(10)]/\{[(4)] + [(10)]\}$ and $[(11)]/\{[(5)] + [(11)]\}$ versus the sulphuric acid concentration, sigmoidal curves are obtained (Figure 1); the acid concentrations of half-sulphation for (4) and (5) are 97.5 and 100.5 ± 0.2% H_2SO_4, respectively.

Discussion

Ring Sulphonation.—The first-order sulphonation rate coefficients increase strongly with increasing sulphuric acid concentration. In order to obtain information as to the reacting substrate species and the sulphonating entity, the first-order rate coefficients have been correlated with the activities of $H_3SO_4^+$ and $H_2S_2O_7$, the two sulphonating entities reactive in concentrated aqueous sulphuric acid.[7a] For the substrates (1)—(3) and (5) the graphs of log $_{ps}k_{stoich}$ versus log $a_{H_3SO_4^+}$ are curved, thus rendering it a priori unlikely that $H_3SO_4^+$ is the sulphonating entity.

For (1)—(5) the graphs of log $_{ps}k_{stoich}$ versus log $a_{H_2S_2O_7}$ are linear in the acid region of 91—98% H_2SO_4 with slopes of 0.65, 0.50 (Figure 2) and 0.60, 0.30, and 0.30 (Figure 3) respectively. The observed slopes in this instance are significantly smaller than those observed for benzene,[8] the halogenobenzenes (which are in between 0.83 and 0.93),[7] and the three biphenylsulphonic acids (which are 0.74 ± 0.01).[9] The lower values of the slopes for (1)—(3) and (5) as compared with those for benzene and the halogenobenzenes may be explained to result from protonation
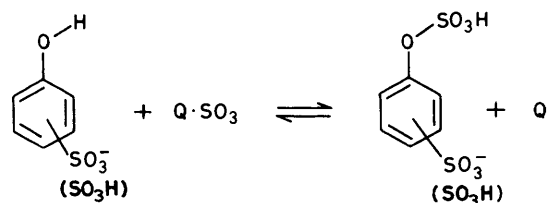
Scheme 2.
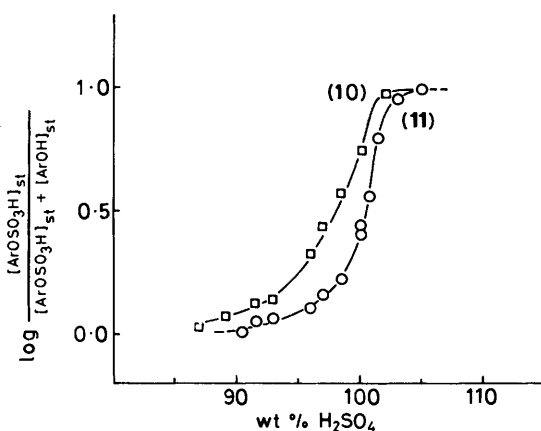
Figure 1. Relative content of 3- (10) and 4-sulphophenyl hydrogen sulphate (11) as a function of the sulphuric acid concentration

of the substrates (Scheme 1). With (5) the slope may also be lowered as a result of the formation of the hydrogen sulphate (11) which is far less reactive than (5)[5] (see later). In fact, it was shown[3] that (1)—(3) and (5) are protonated very predominantly on one of the oxygen atoms of SO_3^- and on OR (R = H; Me) (Scheme 1) and that these protonations are governed by the H_0^R[6] acidity function. The H_0^R values at half-protonation are compiled in Table 3. The positive charge of O^+RH (R = H; Me) and the neutral SO_3H will render the substrate species BH_2^+ [$= HO_3SC_6H_4O^+RH$ (R = H, Me)] far less susceptible towards electrophilic substitution than the substrate species BH^{OS} ($= HO_3SC_6H_4OR$) and BH^{OR} ($= \,^-O_3SC_6H_4O^+RH$) which in their turn will be far less reactive than the substrate species B^- ($= \,^-O_3SC_6H_4OR$). A similar explanation was advanced to explain the observed sulphonation kinetics of the

wt % H_2SO_4

88·0 90·0 92·0 94·0 96·0 98·0 99·0
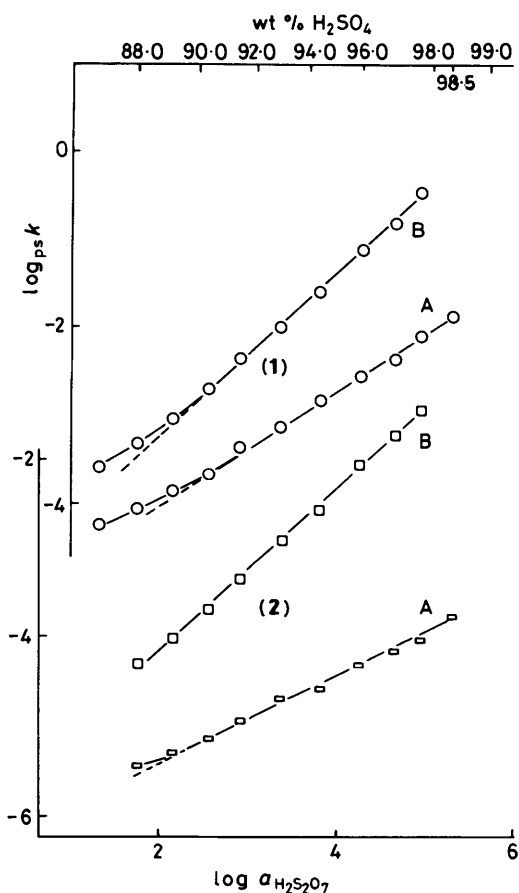
Figure 2. Sulphonation of anisolesulphonic acids; correlation of log $_{ps}k_{stoich}$ (A) and log $_{ps}k_{B^-}$ (B) with log $a_{H_2S_2O_7}$. ○, Anisole-2-sulphonic acid (1); □, anisole-4-sulphonic acid (2)

OR-containing substrates anisole (R = Me) and phenol (R = H)[5] and the SO_3^--containing biphenylmonosulphonates.[9]

The ratios $[BH^{OS}]/[B^-]$ and $[BH^{OR}]/[B^-]$ are governed by equations (1) and (2), respectively[12–15] in which H_0^R is the

$$\log [BH^{OS}]/[B^-] = pK_a(1) - m \cdot H_0^R \qquad (1)$$

$$\log [BH^{OR}]/[B^-] = pK_a(2) - m \cdot H_0^R \qquad (2)$$

acidity function that governs[3,4] the ionization of both O^+RH (R = H; Me) and SO_3H and m the slope of the graph of log. $\{[BH^{OS}]/[B^-]\}$ and log $\{[BH^{OR}]/[B^-]\}$ versus H_0^R. The $[BH^{OS}]/[B^-]$ and $[BH^{OR}]/[B^-]$ ratios of (1)—(5) were calculated using the pK_a* and m values listed in Table 3 and the combined[16] H_0^R scale[6] under the presumption that the concentration of the species BH_2^+ in <98.5% H_2SO_4 is negligably small; the data are listed in Tables 4 and 5. In principle both the protonated and unprotonated substrate species can be sulphonated, but the unprotonated one will react very much faster, as it is the far better nucleophile. Accordingly, although the substrate species $HO_3SC_6H_4OR$ and $^-O_3SC_6^-$ H_4O^+RH are in general the predominant entities present in sulphuric acid >83% H_2SO_4, the sulphonation will proceed predominantly via species B^- (Scheme 3).

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* The pK_a values of the O^+MeH of (1) and the O^+H_2 of (3) are both < −9.0 (cf. Table 3). Accordingly, for the ortho-sulphonic acids (1) and (3), $[BH^{OS}]/[BH^{OR}] = 10^{>2.6}$ and $10^{>2.34}$, respectively; thus $[BH^{OR}]$ is very small relative to $[BH^{OS}]$.

wt % H_2SO_4

88·0 90·0 92·0 94·0 96·0 98·0 99·0
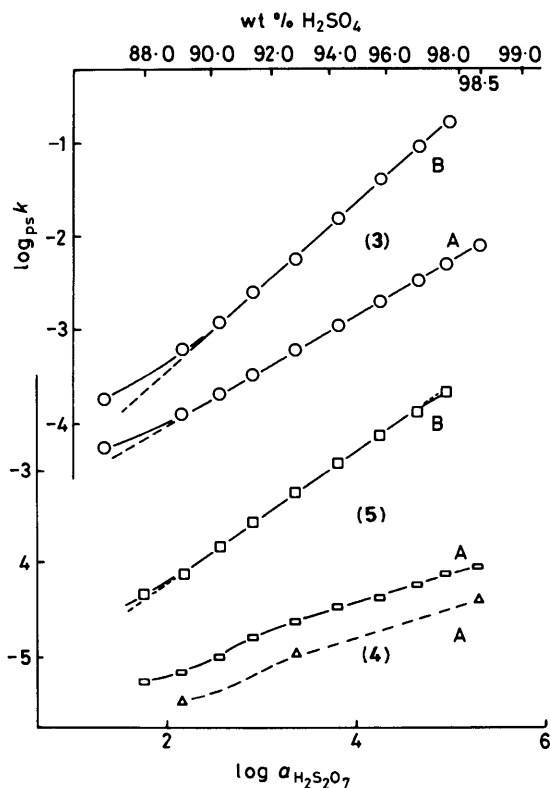
Figure 3. Sulphonation of phenolsulphonic acids; correlation of log $_{ps}k_{stoich}$ (A) and log $_{ps}k_{B^-}$ (B) with log $a_{H_2S_2O_7}$. ○, Phenol-2-sulphonic acid (3); △, phenol-3-sulphonic acid (4), log $_{ps}k_{stoich}$ + 2; □, phenol-4-sulphonic acid (5)

Table 3. Protonation of substrates (1)—(5)[a]

Substrate	Substituent being protonated	$-H_0^R$ at half-protonation	wt % H_2SO_4 at half-protonation	m
(1)	SO_3^-	6.4 ± 0.1	80.6 ± 1	0.9
	OMe	>9.0[b]		
(2)	OMe	6.34 ± 0.05	80.0 ± 0.5	0.81
	SO_3^-	6.5 ± 0.1	81.5 ± 0.5	1.5
(3)	SO_3^-	6.66 ± 0.01	83.3 ± 0.1	0.97
	OH	>9.0[b]		
(4)	OH	6.53	82.0	1.0
	SO_3^-	6.69	83.5	1.0
(5)	OH	6.57 ± 0.05	82.4 ± 0.5	0.83
	SO_3^-	6.42 ± 0.05	80.8 ± 0.5	0.94

[a] The values of (1)—(3) and (5) are taken from ref. 3. Those of (4) were calculated using pK_a (benzenesulphonic acid) = −6.61,[3] ρ($SO_3H \rightleftharpoons SO_3^-$) = 0.7,[10] σ(m-OH) = −0.12,[11] and pK_a (phenol) = −6.40,[3] ρ($-OH_2^+ \rightleftharpoons -OH$) = 0.5,[4] σ(m-$SO_3H$) = 0.57.[10][b] The variations in the ^{13}C chemical shifts of C(1) and C(4) of both (1) and (3) over the acid range of 29—91% H_2SO_4 are both ≤0.4 ± 0.2 p.p.m. and the graphs of the chemical shifts of these carbons versus the H_0^R acidity function are linear. This infers[3] that the –OR (R = H; Me) group is not protonated to any significant extent in that acid region. Consequently the pK_a values of both OH and OMe are at least 1.5 units in H_0^R smaller than the H_0^R of 91.0% H_2SO_4 (= −7.5), and thus both < −9.0.
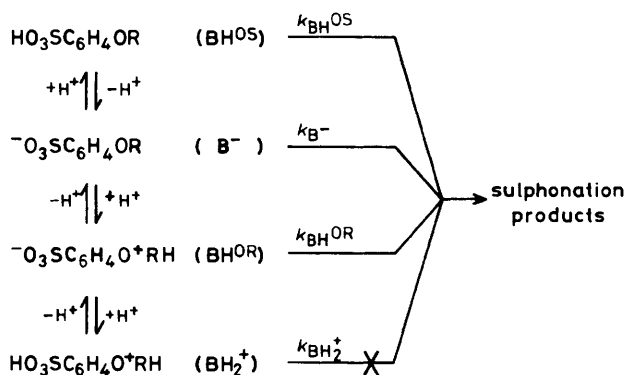

Anisole-2- (1), *Anisole-4-* (2), *and Phenol-2-sulphonate* (3).— The rate of the sulphonation v of (1)—(3) is defined by equations (3) and (4), where $_{ps}k_{stoich}$ is the observed stoicheiometric first-order rate coefficient, and $_{ps}k_{B^-}$, $_{ps}k_{BH^{OS}}$, and $_{ps}k_{BH^{OR}}$ the first-order rate coefficients for the species B^-, BH^{OS}, and BH^{OR}

Table 4. $[BH^{OS}]/[B^-]$ and $[BH^{OR}]/[B^-]$ ratios and first-order rate coefficients for the homogeneous sulphonation of the B^- species of (1)—(3) in concentrated aqueous sulphuric acid at 25.0 °C

H₂SO₄ (wt %, ±0.1)	$[BH^{OS}]/[B^-]$			$[BH^{OR}]/[B^-]$	$10^5\, {}_{ps}k_{B^-}/s^{-1}$ (±10%)		
	(1)	(2)	(3)	(2)	(1)	(2)	(3)
86.9	3.78		2.34		27.5		20.0
88.0	4.63	9.1		4.45	51	5.0	
89.1	5.82	13.3	3.74	5.5	96	10.0	68
90.4	7.6	20.9	5.0	7.0	200	20.9	135
91.5	9.6	30.6	6.4	8.5	457	46.8	275
92.9	12.5	47.9	8.5	10.9	1 020	125	630
94.3	18.2	89	12.8	15.2	2 570	275	1 740
95.9	26.4	166	19.1	21.3	7 940	930	4 570
96.9	33.9	251	24.9	26.6	15 800	2 000	10 500
97.7	41.7	355	31.2	32.1	34 700	3 720	18 600

Table 5. Ratios of entities and first-order rate coefficients for the homogeneous sulphonation of the B^- species of (4) and (5) in concentrated sulphuric acid at 25.0 °C

H₂SO₄ (wt %; ±0.1)	$[BH^{OS}]/[B^-]$		$[BH^{OR}]/[B^-]$		$[ArOSO_3H]_{stoich}/\{[B^-] + [BH^{OS}] + [BH^{OR}]\}$		$[ArOSO_3H]_{stoich}/[B^-]$		$10^5\, {}_{ps}k_{B^-}/s^{-1}$ (±10%)	
	(4)	(5)	(4)	(5)	(4)	(5)	(4)	(5)	(4)	(5)
86.9	3.24		2.24		0.03		0.20			
88.0		4.75		2.97		<0.01		0.09		4.6
89.1	5.3	6.0	3.63	3.67	0.09	0.01	0.77	0.12	0.035	7.3
90.4		8.0		4.70		0.02		0.31		14.0
91.5	9.1	10.1	6.3	5.8	0.15	0.03	2.46	0.54		27.1
92.9	12.3	13.4	8.5	7.4	0.16	0.05	3.55	1.18	0.27	54
94.3		19.8		10.5		0.09		2.72		115
95.9	28.2	29.3	19.5	14.8	0.49	0.14	24.0	6.2		218
96.9	37.2	38.0	25.7	18.6	0.79	0.18	50.2	10.6		383
97.7		47.1		22.5		0.24		16.5		660

$HO_3SC_6H_4OR$ (BH^OS) — $k_{BH}{}^{OS}$

$+H^+ \updownarrow -H^+$

$^-O_3SC_6H_4OR$ (B^-) — k_{B^-}

$-H^+ \updownarrow +H^+$

$^-O_3SC_6H_4O^+RH$ (BH^OR) — $k_{BH}{}^{OR}$

$-H^+ \updownarrow +H^+$

$HO_3SC_6H_4O^+RH$ (BH₂^+) — $k_{BH_2^+}$ ✗

→ sulphonation products

Scheme 3.

respectively. For sulphuric acid concentrations where ${}_{ps}k_{BH^{os}}$ ≪ ${}_{ps}k_{B^-}$ and ${}_{ps}k_{BH^{os}}$ ≪ ${}_{ps}k_{B^-}$, equation (5) follows from (3) and (4). The ${}_{ps}k_{B^-}$ values for (1)—(3), calculated with (5), are listed

$$v = {}_{ps}k_{stoich}\{[B^-] + [BH^{OS}] + [BH^{OR}]\} \qquad (3)$$

$$v = {}_{ps}k_{B^-}[B^-] + {}_{ps}k_{BH^{os}}[BH^{OS}] + {}_{ps}k_{BH^{os}}[BH^{OR}] \qquad (4)$$

$${}_{ps}k_{B^-} = {}_{ps}k_{stoich}\{[B^-] + [BH^{OS}] + [BH^{OR}]\}/[B^-] \qquad (5)$$

in Table 4. The graphs of log ${}_{ps}k_{B^-}$ versus log $a_{H_2S_2O_7}$, for (1) and (2) (Figure 2) and (3) (Figure 3) are all linear in the acid range 90—98.5% H_2SO_4 with slopes of 0.92, 0.92, and 0.91, respectively. Considering these slopes and the interpretation of

the results for benzene,[8] the halogenobenzenes[7] and biphenyl-3- and -4-sulphonic acid,[9] we propose on the basis of the unit-slope criterion that the sulphonation of the substrates (1)—(3) in the acid range 90—98.5% H_2SO_4 is effected by the $H_2S_2O_7$ entity according to the sequence (6)—(8),[7a,8a] in which Ar =

$$ArH + H_2S_2O_7 \rightleftharpoons Ar^+\!\!\begin{array}{c}H\\ \diagdown SO_3H\end{array} + HSO_4^- \qquad (6)$$

$$Ar^+\!\!\begin{array}{c}H\\ \diagdown SO_3H\end{array} + HSO_4^- \rightleftharpoons Ar^+\!\!\begin{array}{c}H\\ \diagdown SO_3^-\end{array} + H_2SO_4 \qquad (7)$$

$$Ar^+\!\!\begin{array}{c}H\\ \diagdown SO_3^-\end{array} + HSO_4^- \rightleftharpoons ArSO_3^- + H_2SO_4 \qquad (8)$$
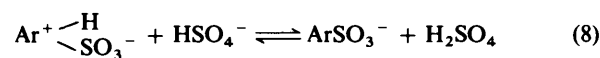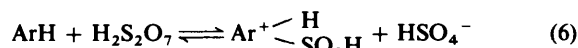
$^-O_3SC_6H_4OR$ (R = H; Me). The slopes observed here of the graphs of log ${}_{ps}k_{B^-}$ versus log $a_{H_2S_2O_7}$, compare very well with those of 0.90 and 0.91, observed for the sulphonation of the biphenyl-3- and -4-sulphonic acid, respectively.[9]

Phenol-3- (4) *and Phenol-4-sulphonate* (5).—With (4) and (5) in addition to the protonation of the SO_3^- and OH substituents, the OH group is sulphated to yield the hydrogen sulphates (10) and (11), respectively (Scheme 2), which compounds are far less reactive towards sulphonation than (4) and (5) proper.[5] The sulphonation of (4) and (5) will thus also proceed predominantly via species B^- (see earlier). Accordingly, the rate of sulphonation v is given by equations (9) and (10), where ${}_{ps}k_{ArOSO_3H_{stoich}}$ is the first-order rate coefficient for $ArOSO_3H_{stoich}$. For sulphuric acid concentrations where ${}_{ps}k_{BH^{os}}$, ${}_{ps}k_{BH^{os}}$, and ${}_{ps}k_{ArOSO_3H_{stoich}}$ are all much smaller than ${}_{ps}k_{B^-}$ equation (11) follows from (9) and (10).

$$v = {}_{ps}k_{stoich}\{[B^-] + [BH^{OS}] + [BH^{OR}] + [ArOSO_3H_{stoich}]\} \quad (9)$$

$$v = {}_{ps}k_{B^-}[B^-] + {}_{ps}k_{BH^{os}}[BH^{OS}] + {}_{ps}k_{BH^{or}}][BH^{OR}] + {}_{ps}k_{ArOSO_3H_{stoich}}[ArOSO_3H_{stoich}] \quad (10)$$

$${}_{ps}k_{B^-} = {}_{ps}k_{stoich}\{[B^-] + [BH^{OS}] + [BH^{OR}] + [ArSO_3H_{stoich}]\}/[B^-] \quad (11)$$

The ratios of $[BH^{OR}]/[B^-]$ and $[BH^{OS}]/[B^-]$, calculated using equations (1) and (2), are given in Table 5. The ratios of the stoicheiometric concentrations of the hydrogen sulphates (10) and (11) and the sum of the concentrations of the non-sulphated species (i.e. B^-, BH^{OR}, and BH^{OS}) were determined from Figure 1 and are compiled in Table 5. The ratios $[B^-]/\{[B^-] + [BH^{OR}] + [BH^{OS}]\}$ were calculated from the $[BH^{OR}]/[B^-]$ and $[BH^{OS}]/[B^-]$ ratios listed in Table 5. From these two calculated ratios, the $[ArOSO_3H_{stoich}]/[B^-]$ ratios were obtained (see Table 5). The $_{ps}k_{B^-}$ values, calculated with equation (11), are compiled in Table 5. The plot of log $_{ps}k_{B^-}$ versus log $a_{H_2S_2O_7}$, shown in Figure 3, is linear in the acid range 90—97% H_2SO_4 with a slope of 0.71. This value is somewhat less than observed with (1)—(3) (0.91—0.93), the halogenobenzenes (0.83—0.93),[8] and biphenyl-3- and -4-sulphonate (0.90—0.91),[9] respectively. The origin of the lower slope with (5) is as yet unexplained.

The deviations from linearity of the plots of log $_{ps}k_{B^-}$ versus log $a_{H_2S_2O_7}$, at low (upward curvature) and high sulphuric acid concentration (downward curvature), apparent in Figures 2—4, were also observed for a number of other substrates and are thought to be significant. The deviations at low acidity are ascribed to a changeover from $H_2S_2O_7$ to $H_3SO_4^+$ as the sulphonating entity, whereas the deviations at high acidity are thought to be the result of the sharp decrease in the concentration of the HSO_4^- ion, leading to a decrease in the rate of the proton-removing step (8), which will then become in part rate limiting.

Hydrogen Sulphate Formation.—Hydrogen sulphate formation occurs upon dissolving (4) and (5) in sulphuric acid more concentrated than 86% H_2SO_4 but not with the ortho-isomer (2). The sulphation of (4) and (5) is represented by equations (12) and (13) in which Q stands for the various entities in sulphuric acid, which may form complexes with SO_3, such as H_2O, H_3O^+, H_2SO_4, $H_3SO_4^+$, and $H_2S_2O_7$. It can now be shown that the hydrogen sulphate to phenol ratio is given by equation (14). The plot of log $\{[ArOSO_3H]/[ArOH]\}$ versus

$$Q + SO_3 \rightleftharpoons Q\cdot SO_3 \quad (12)$$

$$Q\cdot SO_3 + ArOH \rightleftharpoons ArOSO_3H + Q \quad (13)$$

$$\log\{[ArOSO_3H]/[ArOH]\} = \log a_{SO_3} + \log K_{12}\cdot K_{13} \quad (14)$$

log a_{SO_3} should thus be linear with unit slope. The graphs of log $\{[(10)_{stoich}]/[(4)_{stoich}]\}$ and log $\{[(11)_{stoich}]/[(5)_{stoich}]\}$ versus log a_{SO_3} are in fact strongly curved (Figure 4). The deviation from unit slope may be explained to result from the difference in the sulphation reactivities of the species B^-, BH^{OS}, and BH^{OR}. The neutral SO_3H and the positive charge of O^+H_2 will render the substrate species BH^{OS} and BH^{OR} far less susceptible towards sulphation than B^- ($= {}^-O_3SC_6H_4OH$) which is the far more reactive nucleophile. The effective sulphation reaction will then be (15) and accordingly equation (16) would apply rather than (14). The plots of log $\{[(10)_{stoich}]/[B^-]\}$ and log $\{[(11)_{stoich}]/[B^-]\}$ (cf. Table 5) versus log a_{SO_3} are linear with slopes of 0.91 and 0.90 respectively (see Figure 4).* These slopes are very
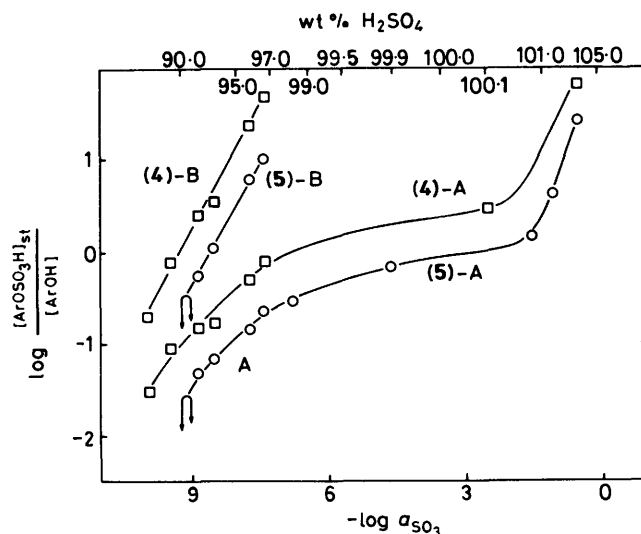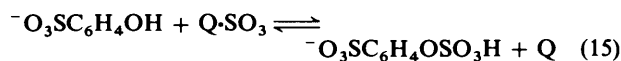

Figure 4. Sulphation of phenol-3- (4) and -4-sulphonic acid (5). Correlation of log $\{[(10)_{stoich}]/[(4)_{stoich}]\}$ [(4)-A], log $\{[(10)_{stoich}]/[(4)_{B^-}]\}$ [(4)-B], log $\{[(11)_{stoich}]/[(5)_{stoich}]\}$ [(5)-A], and log $\{[(11)_{stoich}]/[(5)_{B^-}]\}$ [(5)-B], all with log a_{SO_3}

$${}^-O_3SC_6H_4OH + Q\cdot SO_3 \rightleftharpoons {}^-O_3SC_6H_4OSO_3H + Q \quad (15)$$

$$\log\{[{}^-O_3SC_6H_4OSO_3H]/[B^-]\} = \log a_{SO_3} + \log K_{12}\cdot K_{15} \quad (16)$$

similar to those observed in the same acid region for the ring sulphonation by $H_2S_2O_7$ as sulphonating entity of anisole-2- (0.92) and -4-sulphonate (0.92), phenol-2-sulphonate (0.91) (see before), and biphenyl-3- (0.90) and -4-sulphonate (0.91).[9] This similarity then seems to infer that the sulphation equilibrium is correctly described by reaction (15). The very predominant sulphate species in the acid range of 86—97% H_2SO_4 are apparently m- and p-${}^-O_3SC_6H_4OSO_3H$. This implies that pK_a (p-$HO_3SC_6H_4OSO_3H$) $\leqslant pK_a(p$-$HO_3SC_6H_4OH)$-2 $= 8.42.$[3] The lower pK_a value of the carbon-bonded sulphonic acid moiety of the hydrogen sulphate as compared with that of the corresponding phenol is due to the electron-withdrawing effect of the oxygen-bonded SO_3H group.

Experimental

Procedures.—The structural assignments of the sulphonation products were made by [1]H n.m.r. spectroscopy and are based on the relative area ratios, the multiplicity of the various signals,

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* Unfortunately the plot cannot be extended to acid concentrations >97% H_2SO_4, since the H_0^* acidity function, which is required to calculate $[B^-]$, is not known beyond that sulphuric acid concentration.[6,16]

the coupling constants, and the specific substituent shielding parameters.[20] The compositions of the reaction mixtures were determined by multicomponent ^1H n.mr. analysis.[20] 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 u.v. extinction at a given wavelength as a function of time. The wavelengths, chosen for (1)—(3) and (5) so as to allow a maximum variation in the extinction, were 240, 280, 235, and 280 nm respectively. The first-order rate coefficients, $_{ps}k_{stoich}$, were derived from plots of log $(E_\infty - E_t)$ versus time, where E_∞ and E_t are the extinction 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.

The activities of $H_2S_2O_7$ in sulphuric acid $<98.0\%$ H_2SO_4 were calculated with equation (17),[7b] using the reported[8a] values for $a_{H_2SO_4}$ and a_{H_2O}, and setting the arbitrary constant c, equal to zero. The log $a_{H_2S_2O_7}$ values for $>98.0\%$ H_2SO_4 were obtained by adding to the reported[21] values for 114—97% H_2SO_4[20] 12.25, which is the (constant) difference between the log $a_{H_2S_2O_7}$ data calculated for 114—97% H_2SO_4[21] and for 78—100% H_2SO_4 in the overlapping range (cf. ref. 22). The activities of SO_3 were calculated from equation (18), using the reported[21] log $a_{H_2S_2O_7}$ and log $a_{H_2SO_4}$ values, and setting the arbitrary constant c_2 equal to zero.

$$\log a_{H_2S_2O_7} = 2 \log a_{H_2SO_4} - \log a_{H_2O} + c_1 \quad (17)$$

$$\log a_{SO_3} = \log a_{H_2S_2O_7} - \log a_{H_2SO_4} + c_2 \quad (18)$$

Sulphation of (4) *and* (5).—To the sulphuric acid solution (3.0 ml) of the desired strength was added (4) or (5) (50 mg) and after shaking to homogeneity, the resulting solution was transferred into a 5 mm n.m.r. tube and subjected immediately to multicomponent ^1H n.m.r. analysis[20] in order to determine the proportion of the hydrogen sulphates.

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