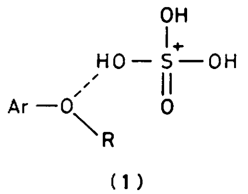
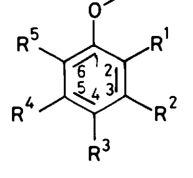
Aromatic Sulphonation. Part 92.[1] Sulphonation of the Three Methylphenols and the Six Dimethylphenols in Concentrated Aqueous Sulphuric Acid; and the Isomerization of Some of the Resulting Sulphonic Acids and of *m*-Xylene-2- and *o*-Xylene-3-sulphonic Acid

Hans J. A. Lambrechts,† Zwaan R. H. Schaasberg-Nienhuis, and Hans Cerfontain *
Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

The isomer distributions for the mono- and di-sulphonation of the three methylphenols in 81.6—90.0% sulphuric acid and of the six dimethylphenols in 84.9% sulphuric acid at 35 °C have been determined by means of ^1H n.m.r. spectroscopy. Products that would result from demethylation, disproportionation, or *ipso*-substitution have not been observed. The monosulphonation isomer distribution of each of the three methylphenols is independent of the sulphuric acid concentration. 2,4-Dimethylphenol in 84.9% H_2SO_4 yields 19% 5- and 79% 6-sulphonic acid, and 2,6-dimethylphenol yields 28% 3- and 72% 4-sulphonic acid. With the phenols (**2**), (**3**), (**5**), and (**7**), which have positions both *ortho* and *para* to the -OH substituent available for sulphodeprotonation, the yield of *ortho*-substitution is relatively high, *viz.* 44, 45, 36, and 27%, respectively. The mono- and di-sulphonic acids of which the sulpho group is between the -OH and an -Me group are unstable under the reaction conditions employed, with the exception of the 3,5-dimethylphenol-2-sulphonic acid. It is proposed that their isomerization proceeds by protiodesulphonation followed by resulphonation to yield the more stable sulphonic acid isomer(s). From a kinetic analysis of the calculated first-order rate coefficients for protiodesulphonation, it is concluded that the *unprotonated* substrate species is the entity undergoing the protiodesulphonation.

Anisole and phenol in concentrated aqueous sulphuric acid are protonated predominantly on the oxygen.[2–4] The actual species undergoing the sulphonation in concentrated aqueous sulphuric acid are, however, the *unprotonated* substrates with $H_3SO_4^+$ and $H_2S_2O_7$ as the sulphonating entities, which are the predominant reacting species in sulphuric acid below 83 and above 88% H_2SO_4, respectively.[1] The partial rate factors for the 4-position of anisole, $^{OMe}f_4$, and phenol, $^{OH}f_4$, are *ca.* 10^4 times smaller than expected on the basis of the substituent effects. This was explained tentatively in terms of a specific complexation of the oxygen lone pair of the substrate by the $H_3SO_4^+$ reagent, as shown in (**1**).[1]


(1)



(2) R^1 = Me ; $R^2 = R^3 = R^4 = R^5$ = H
(3) R^2 = Me ; $R^1 = R^3 = R^4 = R^5$ = H
(4) R^3 = Me ; $R^1 = R^2 = R^4 = R^5$ = H
(5) $R^1 = R^2$ = Me ; $R^3 = R^4 = R^5$ = H
(6) $R^1 = R^3$ = Me ; $R^2 = R^4 = R^5$ = H
(7) $R^1 = R^4$ = Me ; $R^2 = R^3 = R^5$ = H
(8) $R^1 = R^5$ = Me ; $R^2 = R^3 = R^4$ = H
(9) $R^2 = R^3$ = Me ; $R^1 = R^4 = R^5$ = H
(10) $R^2 = R^4$ = Me ; $R^1 = R^3 = R^5$ = H

Following on from these studies,[1,3,4] we now report a sulphonation product study of the three methylphenols (**2**)—(**4**), the six dimethylphenoles (**5**)—(**10**), and their sulphonic acids in concentrated aqueous sulphuric acid at 35 °C.

Apart from a recent report regarding the sulphonation of 2-methylphenol (**2**) in sulphuric acid that was 100% H_2SO_4 producing the 2- and the 2,6-di-sulphonic acids in 57.2 and 36.3% yield, respectively,[5] the reported data on the sulphonation of the substrates (**2**)—(**10**) in concentrated aqueous sulphuric acid are dated.[6–13]

As regards the nitration of these type of substrates, the reaction of (**2**)—(**4**) by nitric acid in 58—80% sulphuric acid involves reaction with NO_2^+ at or very close to the encounter-controlled rate.[14] The nitration of (**3**) in sulphuric acid of 68—72% H_2SO_4 involves *ca.* 40% *ipso*-substitution at C-4, followed by a subsequent rearrangement of the 4-methyl-4-nitrocyclohexa-2,5-dienone formed to yield 4-methyl-2-nitrophenol.[14] More recently,[15] 6-methyl-6-nitrocyclohexa-2,4-dienones were isolated in $\geqslant 60\%$ yield upon treating (**2**), (**5**), (**6**), and (**7**) with nitric acid in acetic anhydride. These dienones were found to undergo a regiospecific 1,3-nitro shift to give exclusively the corresponding 2-nitro-6-methylphenols. This was explained in terms of a bonding interaction between the oxygen atom of the substrate and the migrating nitro group.

Halogenation of phenols and anisoles proceeds, in general, *ortho* and *para* to the -OR group.[16–18] Addition of bromine to a solution of the phenols (**4**), (**6**), (**8**), and (**9**) in superacid solvents

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† *Present address:* Quaker Chemical (Holland) B.V., Industrieweg 3-13, 1422 AH Uithoorn, The Netherlands.

Table 1. ^{1}H N.m.r. data of the mono- and di-sulphonic acids of **(2)**—**(10)**[a,b]

Substrate	H_2SO_4 (% w/w) (±0.1)	Position(s) of SO_3H	δ (p.p.m.) Me	Me	2-H	3-H	4-H	5-H	6-H
(2)	84.9	4	2.31(2)			7.70(d)		7.66(d)	7.04(d)
		6	2.31(2)			7.41(d)	7.01(t)	7.58(d)	
		4,6	2.38(2)			7.90(d)		8.19(d)	
(3)	84.9	2	2.56(3)				6.95(m)[c]	7.39(t)	6.95(m)[c]
		4	2.58(3)		6.95(m)[c]			7.94(d)	6.95(m)[c]
		6	2.42(3)		6.95(m)[c]		6.95(m)[c]	7.59(d)	
		2,4	2.99(3)					8.11(d)	6.95(m)[c]
		4,6	2.68(3)		7.10(s)			8.46(s)	
(4)	84.9	2	2.33(4)			7.59(d)		7.40(d)	7.03(d)
		2,6	2.41(4)			7.94(s)		7.94(s)	
(5)	84.9	4	2.29(2)	2.61(3)				7.82(d)	6.97(d)
		6	2.27(2)	2.27(3)			6.97(d)	7.55(d)	
		4,6	2.35(2)	2.69(3)				8.36(s)	
(6)	84.9	5	2.39(2)	2.64(4)		7.31(s)			7.61(s)
		6	2.39(2)	2.39(4)		7.37(d)		7.52(d)	
(7)	84.9	4	2.27(2)	2.61(5)		7.76(s)			6.93(s)
		6	2.31(2)	2.61(5)		7.26(d)	6.86(d)		
		4,6	2.31(2)	2.31(5)		7.99(s)			
(8)	84.9	3	2.66(2)	2.42(6)			7.70(d)	7.30(d)	
		4	2.42(2)	2.42(6)		7.69(s)		7.69(s)	
(9)	84.9	2	2.62(3)	2.35(4)				7.46(d)	6.96(d)
		6	2.35(3)	2.35(4)	6.99(s)			7.59(s)	
		2,6	2.76(3)	2.35(4)				7.98(s)	
(10)	84.9	2	2.59(3)	2.33(5)			6.74(s)		6.96(s)

[a] The chemical shifts (δ) are relative to external [$^2H_2$]O. [b] The *ortho* and *meta* $J_{H,H}$ values were all found to be 7.5—9.5 and 1.5—3.0 Hz, respectively. The substrate concentrations were *ca.* 0.5 mol dm^{-3}. [c] Centre of unresolved multiplet.

Table 2. Reaction of the substrates **(2)**—**(10)** with concentrated aqueous sulphuric acid

Substrate	H_2SO_4 (% w/w) (±0.1)	Reaction time	Temperature (°C)	Product distribution (%) (±2)[a,b]					Initial monosulphonation isomer distribution (%) (±2)[c]		
(2)	81.6[d]				4(56)	6(44)				4(56)	6(44)
	84.9	24 h	30		4(54)	6(21)	4,6(25)			4(58)	6(42)
	90.0	12 min	35		4(58)	6(35)	4,6(7)			4(58)	6(42)
(3)	81.6[d]	36 min	35	2(17)	4(55)	6(28)			2(17)	4(55)	6(28)
	84.9	18 min	35	2(16.5)	4(53.5)	6(26.5)	4,6(2.5)		2(19)	4(53.5)	6(26.5)
	90.0	5 min	35	2(17)	4(53)	6(23)	2,4(3)	4,6(4)	2(20)	4(53)	6(27)
(4)	81.6[d]			2(100)					2(100)		
	84.9	24 h	30	2(93)			2,6(7)		2(100)		
	90.0	25 min	35	2(93)			2,6(7)		2(100)		
(5)	84.9	17 min	35	4(61)	6(32)	4,6(7)			4(64)	6(36)	
(6)	84.9[d]	24 h	30	5(19)	6(79)[e]				3(2)	5(19)	6(79)
(7)	84.9	17 min	35	4(73.5)	6(17)	4,6(9.5)			4(73.5)	6(26.5)	
(8)	84.9	3 h	35	3(28)	4(72)				3(28)	4(72)	
(9)	84.9	19 min	35	2(17)	6(78)	2,6(5)			2(21)	6(79)	
(10)	84.9	48 h	30	2(100)					2(100)		

[a] The first datum gives the position of the sulphonate substituents; the datum in parentheses the yield (%). [b] In this paper, the numbering of the substrates has been preserved in the products for reasons of convenience. [c] Extrapolated data. [d] Taken from reference 1. [e] The mixture contained 2% of another compound. On the basis of the singlet absorption at 8.00 p.p.m. it is tentatively assigned to be the 3,5-disulphonic acid.

leads, however, exclusively to bromination *meta* to the –OH substituent.[19,20]

Electrophilic benzylation of 2,6-dimethylphenol (**8**) and 2,6-dimethylanisole (**11**) yields *ca.* 40% of the 3- and *ca.* 60% of the 4-substituted product.[21]

Results and Discussion

The sulphonic acid products obtained on reaction of **(2)**—**(10)** in concentrated aqueous sulphuric acid at 35 °C were assigned on the basis of their ^{1}H n.m.r. spectral data, listed in Table 1. The sulphonic acid product compositions are compiled in Table 2.

Products that would result from demethylation, from disproportionation, or from *ipso*-substitution at a carbon bearing a methyl- or hydroxy-group, have never been observed.

Methylphenols.—When 2-methylphenol (**2**) is dissolved in sulphuric acid varying in concentration from 81.6 to 90.0% H_2SO_4, the initial products are the 4- and 6-sulphonic acids formed in a yield of 58 and 42 ± 2%, respectively, which are subsequently sulphonated relatively slowly to yield quantitatively the 4,6-disulphonic acid. Dissolution of 4-methylphenol (**4**) in sulphuric acid of the same acid range affords initially the 2-sulphonic acid, which is eventually sulphonated

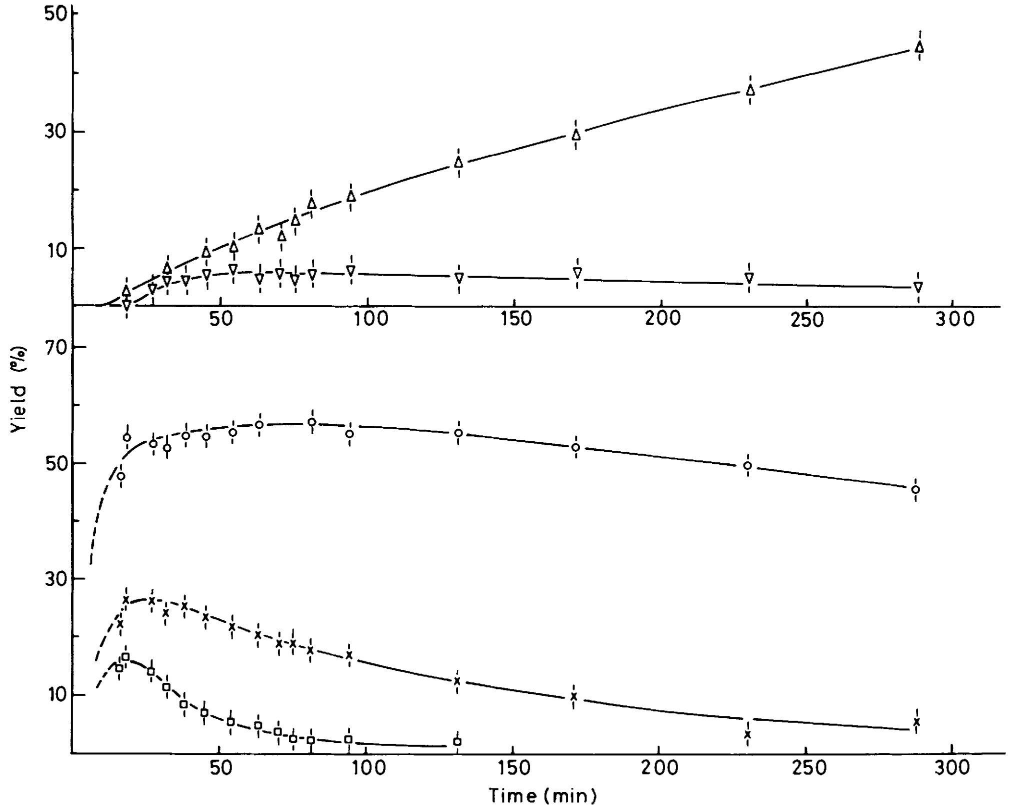

Figure 1. Variation of the composition of the sulphonation mixture resulting from 3-methylphenol (**3**) in 84.9% H_2SO_4 with the reaction time at 35 °C. □, 2-Sulphonic acid; ○, 4-sulphonic acid; ×, 6-sulphonic acid; ▽, 2,4-disulphonic acid; △, 4,6-disulphonic acid

slowly to yield exclusively the 2,6-disulphonic acid (*cf.* Table 2).

3-Methylphenol (**3**) after 18 min in 84.9% H_2SO_4 gives a mixture of the 2-, 4-, 6-, and 4,6-di-sulphonic acid in yields of 16, 54, 27, 3, and ± 2%, respectively. With increasing reaction time the 2,4-disulphonic acid is also formed. From a plot of the relative contents of the sulphonic acids *versus* the reaction time (Figure 1), it appears that the 2-, the 4-, the 6-, and the 2,4-disulphonic acid are all converted again. The final product after 1 month is the 4,6-disulphonic acid. Since the rate of conversion of the 2-sulphonic acid is $\geqslant 10$ times the rate of isomerization of the 2,4- into the 4,6-disulphonic acid, it follows that the greater part of the 2-sulphonic acid isomerizes to the 4- and 6-monosulphonic acids.* The sulphonation of (**3**) in 84.9% H_2SO_4, to the 4,6-disulphonic acid as the ultimate exclusive product, may then be represented as in Scheme 1. A similar isomerization was found with *m*-xylene-2-sulphonic acid, which upon dissolution in sulphuric acid that was 75—99% H_2SO_4 at 25 °C yields initially *m*-xylene-4-sulphonic acid, which is subsequently sulphonated to *m*-xylene-4,6-disulphonic acid.[22]

With the substrates (**2**)—(**4**) the monosulphonic acid isomer distribution appears to be invariable in the sulphuric acid range studied, 81.6—90.0% H_2SO_4, a behaviour which is similar to that observed with both anisole and phenol.[1]

Dimethylphenols.—Dissolution of 2,3-dimethylphenol (**5**) in 84.9% H_2SO_4 affords the 4- and 6-sulphonic acids, 64 and 36% respectively, which are both eventually sulphonated to the 4,6-disulphonic acid.

2,4-Dimethylphenol (**6**) in 84.9% H_2SO_4 yields 19% of the 5-, 79% of the 6-sulphonic acid, and 2% of another product, which is probably the 3,5-disulphonic acid. Of note is the formation of 19% of the 5-sulphonic acid, in which the sulpho substituent is *meta* to -OH. The introduction of a methyl group at the 2-position of 4-methylphenol (**4**) apparently activates the 5-position to such an extent that the sulphonation *meta* to -OH becomes comparable in rate to that *ortho* to -OH.

Sulphonation of 2,5-dimethylphenol (**7**) with sulphuric acid that was 84.9% H_2SO_4 after 17 min yielded the 4-, 6-, and 4,6-di-sulphonic acids, 75.5, 17.0, and 9.5%, respectively. The 6- and 4,6-di-sulphonic acids are unstable under the reaction conditions and are both converted into the 4-sulphonic acid. The contents of the various sulphonic acids are plotted *versus* the reaction time in Figure 2. The graphs indicate that the 6-sulphonic acid is converted predominantly into the 4,6-disulphonic acid, which is relatively slowly protiodesulphonated to the 4-sulphonic acid. The sulphonation of (**7**) thus proceeds as represented in Scheme 2.

Dissolution of 2,6-dimethylphenol (**8**) in 84.9% H_2SO_4 affords the 3- and 4-sulphonic acids in yields of 28 and 72%, respectively. The isomer ratio remains constant for 3 h; thereafter the 4-sulphonic acid starts to precipitate from the reaction mixture.

To account for the high degree of 3-substitution in the sulphuric acid sulphonation of (**8**) three explanations may be considered. First, the sulphonation proceeds *via* the sulphate as intermediate; secondly, the 3-sulphonic acid results from sulphonation of the oxygen protonated species of (**8**), and thirdly, the substantial substitution at the 3-position is due to electronic and steric effects (inhibition of resonance). The first

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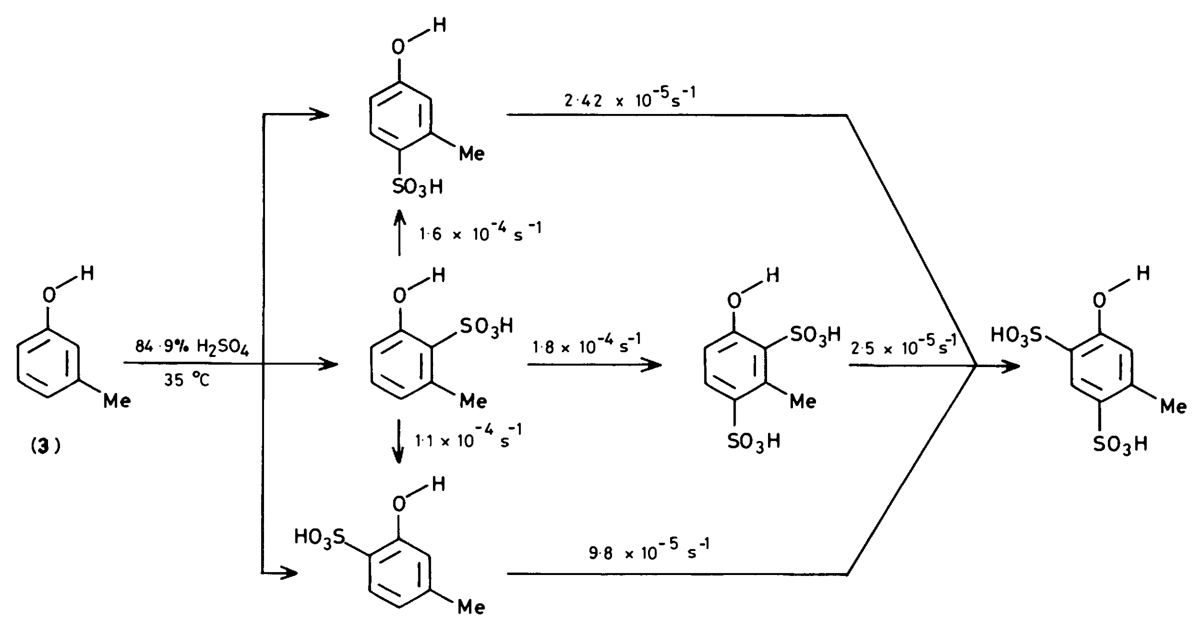
* When an 88:12% mixture of the potassium salts of the 4- and 6-sulphonic acid is dissolved in 84.9% H_2SO_4, both acids are sulphonated to the 4,6-disulphonic acid, which is eventually the only product observed in the ^1H n.m.r. spectrum.



Scheme 1.

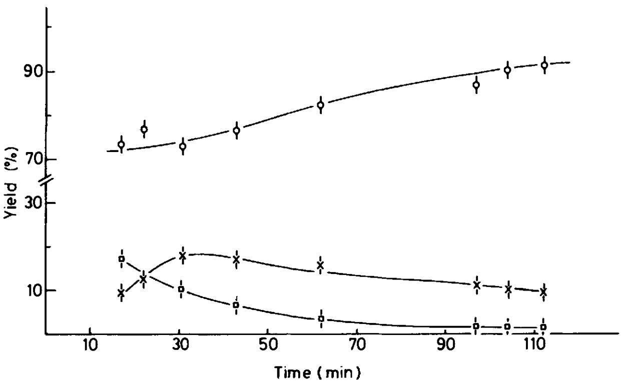
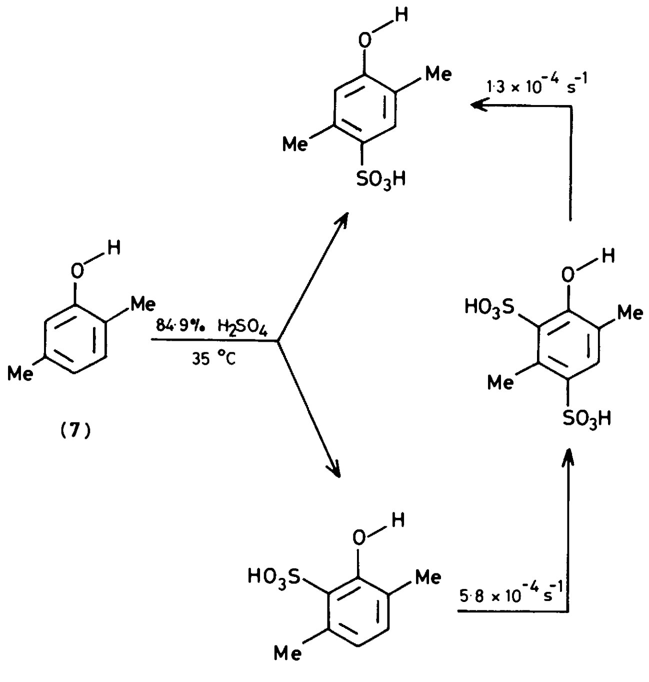


Figure 2. Variation of the composition of the sulphonic acid mixture, resulting from 2,5-dimethylphenol (**7**) in 84.9% H_2SO_4, with reaction time at 35 °C. ○, 4-Sulphonic acid; □, 6-sulphonic acid; ×, 4,6-disulphonic acid

explanation is rendered unlikely, as (*i*) 2,6-dimethylanisole (**11**) (the sulphation of which is impossible), in 84.5% H_2SO_4 is mainly sulphonated at the 3-position,[23] and (*ii*) phenyl methanesulphonate (**12**) (which is an analogue of phenyl hydrogen sulphate) in 86—99% H_2SO_4 yields exclusively the 4-sulphonic acid.[1] The second explanation can also be refuted, as it has been shown previously that a large number of *ortho*- and *para*-substituted phenols and anisoles are sulphonated *via* the *unprotonated* species, which is very much more reactive than the *protonated* species (which is the predominant substrate species present).[1] This leaves the third explanation of steric inhibition of resonance.[24] A detailed mechanistic study of the sulphonation of 2,6-disubstituted phenols and (**11**) under protic and aprotic conditions will be reported elsewhere.[23]

3,4-Dimethylphenol (**9**) in 84.9% H_2SO_4 after 19 min gives the 2-, 6-, and 2,6-di-sulphonic acids in yields of 17, 78, and 5%, respectively. With increasing reaction time the yield of the 2,6-disulphonic acid increases to a maximum content of 6.5%. The 2- and 2,6-di-sulphonic acids are unstable and after 1 month the 6-sulphonic acid appears to be the exclusive product present.

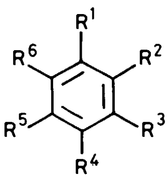


Scheme 2.

Since the rate of conversion of the 2-sulphonic acid is ≫ 10 times the rate of sulphonation of the 6- to the 2,6-di-sulphonic acid, it follows that the greater part of the 2-sulphonic acid, if not all, isomerizes to the 6-sulphonic acid. In fact, in 82.0% H_2SO_4 the 2,6-disulphonic acid is not observed as an intermediate product, which infers that the 2-sulphonic acid exclusively isomerizes to the 6-sulphonic acid. The sulphonation of (**9**) in 84.9% H_2SO_4 thus proceeds as represented in Scheme 3.

3,5-Dimethylphenol (**10**) in 84.9% H_2SO_4 yields exclusively the 2-sulphonic acid, which was found to be stable for one week.

Substrates which allow a choice between substitution *ortho* and *para* to the –OR (R = H, Me) substituent, are, for example,



(11) R^1 = OMe; $R^2 = R^6$ = Me; $R^3 = R^4 = R^5$ = H
(12) $R^1 = OSO_2Me$; $R^2 = R^3 = R^4 = R^5 = R^6$ = H
(13) R^1 = OH; $R^2 = SO_3H$; R^3 = Me; $R^4 = R^5 = R^6$ = H
(14) R^1 = OH; $R^2 = SO_3H$; $R^3 = R^4$ = Me; $R^5 = R^6$ = H
(15) $R^1 = R^2$ = Me; $R^3 = SO_3H$; $R^4 = R^5 = R^6$ = H
(16) $R^1 = R^3$ = Me; $R^3 = SO_3H$; $R^4 = R^5 = R^6$ = H
(17) R^1 = OH; $R^2 = SO_3H$; $R^3 = R^4 = R^5 = R^6$ = H

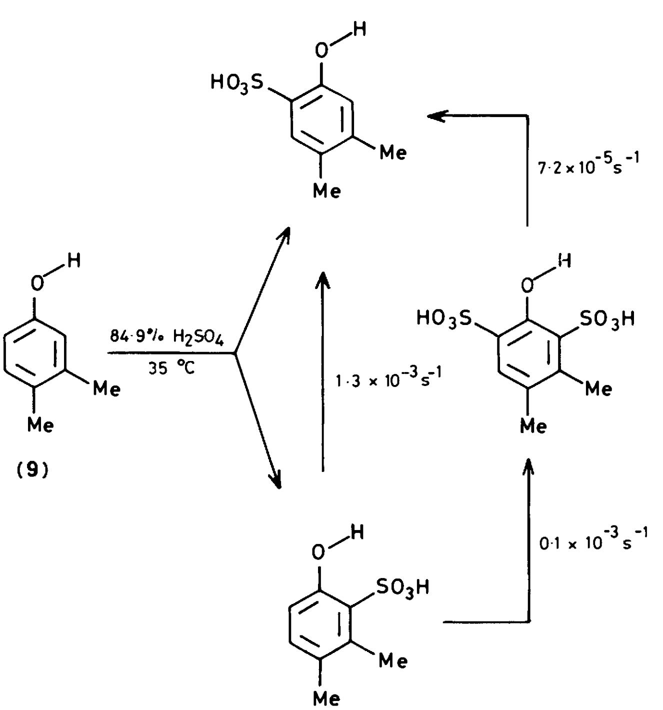
Table 3. Stoicheiometric rate coefficients of disappearance (${}_{ps}k$) and of protiodesulphonation (k_{des}) for the substrates (**13**)—(**16**) in concentrated aqueous sulphuric acid

Substrate	H_2SO_4 (% w/w) (±0.1)	Temperature (°C)	$10^5\,{}_{ps}k/s^{-1}$	$10^5 k_{des}/s^{-1}$
(**13**)	89.0	35	10.1	6.4
	84.9		44.4	32.8
	88.0		89	58
(**14**)	84.9	35	140	130
(**15**)	74.0	80		0.35[a]
	86.5			8.3[a]
	90.3			17[a]
(**16**)	75.2	25		0.13[a]
	96.8			6.5[a]
	98.9			7.6[a]
	99.6			14[a]

[a] Taken from reference 22.

(**2**), (**3**), (**5**), (**7**), phenol, and anisole, which have a relatively high degree of substituion *ortho* to –OR, *viz.* 44, 45, 36, 27, 48,[1] and 36%,[1] respectively. The relatively high degree of *ortho*-sulphonation with phenol and anisole was explained in terms of complexation of the substrate by the sulphonating entity $H_3SO_4^+$ as a result of hydrogen bonding between one of the $H_3SO_4^+$ hydrogens with the oxygen of the substrate [see (**1**)].[1] Intramolecular transfer of SO_3H in the complex (**1**) *via* a six-membered ring transition state then leads to a high degree of the *o*-sulphonic acid. The high specific *ortho* preference for the sulphonation of phenol is also apparent from a comparison of the monosulphonic acid isomer ratios resulting from 2,4- (**6**) and 2,6-dimethylphenol (**8**) (see Table 2).

Isomerization and Protiodesulphonation of the Arenesulphonic Acids.—The isomerizations of the 3-methylphenol-2- (**13**) and 3,4-dimethylphenol-2-sulphonic acid (**14**) were found to be first-order in the substrate for at least two half-lives. The stoicheiometric first-order rate coefficients of the isomerization are listed in Table 3. The isomerization of arenesulphonic acids in concentrated aqueous sulphuric acid can be regarded as an intermolecular (protio)desulphonation and subsequent sulphonation process.[*,13,22,25–27] Accordingly, the isomerization of a given methylphenolsulphonic acid, *i*-MP-*p*-S, into the corresponding *q*- and *r*-sulphonic acids proceeds by reactions (1)—(3). The rate of sulphonation of the phenols and their monosulphonic acids is high compared with the rates of the protiodesulphonation of their respective mono- and di-sulphonic acids. Accordingly, the first-order desulphonation rate coefficient of a given isomer *i*-MP-*p*-S, ${}_ik_p$, is related to the first-order rate coefficients of the isomerization of that isomer into the corresponding *q*- and *r*-isomers, ${}_ik_{pq}$ and ${}_ik_{pr}$, by equations (4) and (5).



$$i\text{-MP-}p\text{-S} \underset{{}_ik_q}{\overset{{}_ik_p}{\rightleftharpoons}} i\text{-MP} \quad (1)$$

$$i\text{-MP} \xrightarrow{{}_ik_{-q}} i\text{-MP-}q\text{-S} \quad (2)$$

$$i\text{-MP} \xrightarrow{{}_ik_{-q}} i\text{-MP-}r\text{-S} \quad (3)$$

$${}_ik_p = {}_ik_{pq}/{}_iS_q \quad (4)$$

$${}_ik_p = {}_ik_{pr}/{}_iS_r \quad (5)$$

where $${}_iS_q = {}_ik_{-q}/({}_ik_{-p} + {}_ik_{-q} + {}_ik_{-r})$$

and $${}_iS_r = {}_ik_{-r}/({}_ik_{-p} + {}_ik_{-q} + {}_ik_{-r}).$$

The rate coefficients for the protiodesulphonation of 3-methylphenol-2-sulphonic acid (**13**) and 3,4-dimethylphenol-2-sulphonic acid (**14**) were calculated from equations (4) and (5) using the first-order stoicheiometric rate coefficients of isomerization (Table 3) and the sulphonation isomer distribution data (Table 2). They are collected in Table 3 together with the protiodesulphonation rate constants of *o*-xylene-3-sulphonic acid (**15**) and *m*-xylene-2-sulphonic acid (**16**).[22] The correlation of the logarithm of the protiodesulphonation rate coefficients of (**13**), (**15**), and (**16**) with the H_{c}[28] acidity function, which governs the protonation on the aromatic carbons,[28] is shown in Figure 3. The graphs are linear with slopes of 0.54, 0.49, and 0.43 for (**13**), (**15**), and (**16**), respectively. For an *A*1 and an *A*-S_E2 mechanism for the protiodesulphonation of arene-

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[*] It should be realized that 2,5-dimethylphenol-6-sulphonic acid isomerizes predominantly *via* initial sulphonation and subsequent desulphonation.

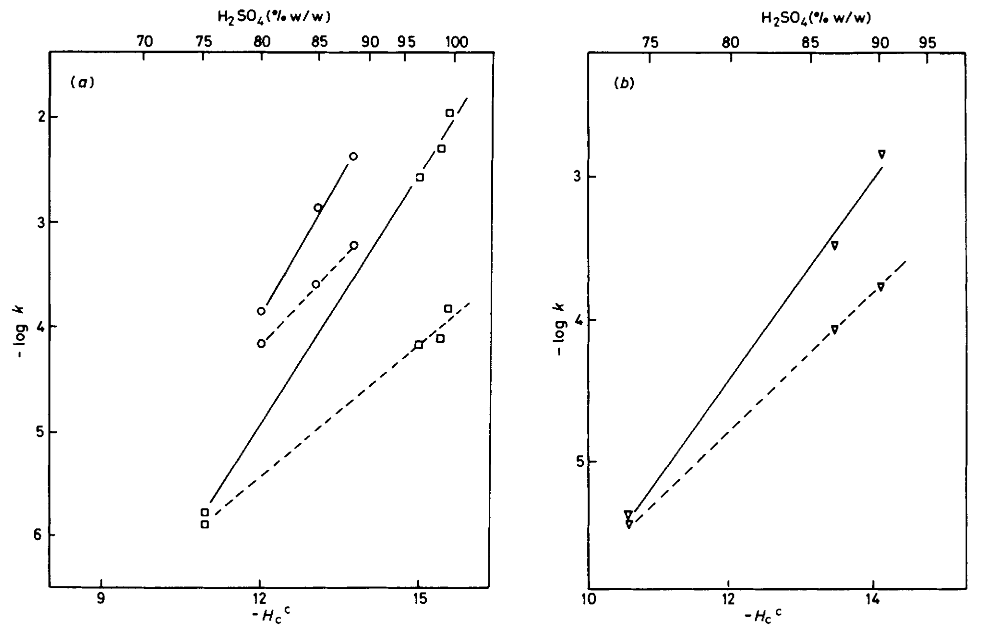

Figure 3. Correlation of log $_{ps}k_{des}$ (broken lines) and log $_{ps}k_{des}^{B}$ (full lines) with the H_c^{c} acidity function; the slopes of the respective graphs are given in parentheses. (*a*) ○, 3-Methylphenol-2-sulphonic acid, 35 °C (0.54; 0.88); □, *m*-xylene-2-sulphonic acid, 25 °C (0.43; 0.80). (*b*) ▽, *o*-Xylene-3-sulphonic acid, 80 °C (0.49; 0.72)

Table 4. $[BH^+]/[B]$ ratios and protiodesulphonation rate coefficients for the sulphonate anions of the substrates (**13**)—(**15**) in concentrated aqueous sulphuric acid

H_2SO_4 (% w/w)	$[BH^+]/[B]$			$10^5k_{des}^{B}/s^{-1}$		
(±0.1)	(**13**)	(**15**)	(**16**)	(**13**)	(**15**)	(**16**)
74.0		0.18			0.41	
75.2			0.25			0.16
80.0	1.02			13		
84.9	3.0			132		
86.5		2.95			32.8	
88.0	6.0			410		
90.3		7.2			140	
96.8			38.9			260
98.9			64.6			500
99.6			77.6			1 100

sulphonic acids the slopes should be unity.[29,30] However, the currently observed slopes are far less than unity. This is ascribed to the occurrence of reactions (6)[22,29,30] and (7).[1] For with

$$ArSO_3^- + H^+ \rightleftharpoons ArSO_3H \qquad (6)$$

$$ArOR + H^+ \rightleftharpoons ArO^+RH \qquad (7)$$

increasing sulphuric acid strength the fraction of the far less reactive protonated substrate species $ArSO_3H$ and ArO^+RH will strongly increase at the expense of that of the much more reactive unprotonated species $ArSO_3^-$ and ArOR. Since these unprotonated species B are much better nucleophiles than the protonated species BH^+, it seems very likely that the protiodesulphonation proceeds mainly *via* B. This infers that the observed rate coefficient, k_{des}, is very much smaller than the actual rate coefficient of the free base B, k_{des}^{B}. The relation between k_{des} and k_{des}^{B} is given by equation (8).[1] The ratio $[BH^+]/[B]$ may be obtained using equation (9),[31–33] where H_x

$$k_{des}^{B} = k_{des}([B] + [BH^+])/[B] \qquad (8)$$

$$\log[BH^+]/[B] = pK_a - mH_x \qquad (9)$$

stands for the appropriate acidity function and *m* for the slope of the graph of log $[BH^+]/[B]$ *versus* H_x. The $[BH^+]/[B]$ ratios for (**13**), (**15**), and (**16**), calculated using the pK_a values of −6.26,* −6.50,* and −6.41,* respectively, $m = 1.0$, and the combined[39] H_0^{a}[40],† acidity scale, are listed in Table 4.

The correlations of the log k_{des}^{B} values with the H_c[28] acidity function are shown in Figure 3. The graphs are linear with slopes of 0.88, 0.72, and 0.80 for (**13**), (**15**), and (**16**), respectively. With the *sulphonation* at the 4-position of 3-methylphenol, *o*-xylene, and *m*-xylene in concentrated aqueous sulphuric acid, the slopes of the linear graphs of the logarithms of the sulphonation rate coefficients of the unprotonated substrate species *versus* log $a_{H_3SO_4^+}$ have similar values, *viz.* 0.81,[41] 0.83,[42] and 0.83,[42] respectively.

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* The pK_a values of (**13**), (**15**), and (**16**) were calculated as follows. 3-Methylphenol-2-sulphonic acid (**13**) can be regarded as being built up from phenol-2-sulphonic acid (**17**) with a methyl at the 3-position. The pK_a of $-SO_3H$ of (**17**) is −6.4;[3] that of $-O^+H_2$ of (**17**) is not accurately known, but it is < -9.0.[34] This infers that with (**13**) the $[BH^+]/[B]$ ratio will mainly be determined by reaction (6). The result of introduction of a methyl *ortho* to a sulphonic acid group is given by the difference between the pK_a values of benzenesulphonic acid (−6.61[35,36]) and toluene-2-sulphonic acid (−6.55[35]), *i.e.*, −0.06. Thus $pK_a^{SO_3H}$ (**13**) = −6.4 + 0.06 = −6.34.

o-Xylene-3-sulphonic acid (**15**) can be regarded as being built up from toluene-2-sulphonic acid with a methyl at the 6-position, *i.e.*, *meta* to SO_3H. Thus $pK_a^{SO_3H}$ (**15**) = −6.55[35] − $(\sigma_{m\text{-Me}} \times \rho_{SO_3H})$ = −6.55 − (−0.07[37] × 0.7[38]) = −6.50.

m-Xylene-2-sulphonic acid (**16**) can be regarded as being built up from toluene-2-sulphonic acid with a methyl at the 3-position. Thus $pK_a^{SO_3H}$ (**16**) = −6.55[35] + 0.06 = −6.49.

† The protonation on oxygen of the $-SO_3$[39] and $-OH$[3] substituent is governed by the H_0^{a} acidity function.

Experimental

Apparatus and Materials.—^{1}H N.m.r. spectra were recorded on a Varian XL-100-12 spectrometer. Sulphuric acid (AnalaR; *d* 1.84) was obtained from BDH Chemicals. This acid was diluted with demineralized water in order to obtain solutions of the desired acid strength. The substrates **(2)**—**(10)** were obtained from Aldrich. A mixture of potassium 3-methylphenol-4- and some -6-sulphonate was obtained by reaction of 3-methylphenol with 1 equivalent of SO_3 in $MeNO_2$ according to a described procedure;[43] the resulting crystalline material consisted of the 4- and 6-sulphonate in a ratio of 88:12%.

Procedures.—The sulphonation was performed by adding sulphuric acid (2.0 ml) to the substrate (1.0 mmol) and shaking of the resulting mixture to homogeneity. The solubility of **(6)** and **(8)** in concentrated aqueous sulphuric acid that was 84.9% H_2SO_4 appeared to be very low. After adding the sulphuric acid to these substrates and vigorous shaking of the resulting mixtures for *ca.* 5 min, the unreacted material [*ca.* 50% for **(6)** and *ca.* 80% for **(8)**] was filtered off.

The progress of the reaction was followed by examining the sulphuric acid solution directly by ^{1}H n.m.r. at 35 °C (probe temperature) using neat $[^2H_2]O$ as an external standard. The structural assignments of the sulphonation products were made by ^{1}H n.m.r. spectroscopy and are based on the absorption 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 ^{1}H n.m.r. analysis.[44]

The first-order rate coefficients were derived from plots of the logarithm of the relative amount of the substrate under scrutiny *versus* the reaction time. In all cases straight lines over at least three half-lives were obtained.

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