Aromatic Sulphonation. Part XL.[1] Rates of Sulphonation *ortho, meta,* and *para* to a Sulphonic Acid Group in Methyl Substituted Benzenesulphonic Acids

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Rates and isomer distributions for the sulphonation of benzenesulphonic acid and sixteen (poly)methyl derivatives in fuming sulphuric acid have been determined. With 3-methyl- and 3,5-dimethyl-benzenesulphonic acid sulphonation partly *ortho* to the SO_3H group was observed. The isomer distributions are dependent on the sulphuric acid concentration, but approach a constant ratio at acid concentrations below 104 and above 115% H_2SO_4. It is suggested that the substrate species undergoing sulphonation in $\geqslant$115% H_2SO_4 is $ArSO_3H_2^+$. Positional relative rates for sulphonation in weak oleum at 25·0° have been calculated. The observed rate order is explained in terms of steric and electronic effects of the methyl substituents on the rates of formation and decomposition of the intermediate σ complex. The low reactivity of the higher methylated sulphonic acids is ascribed to buttressing of the substituent *ortho* to the reaction centre by the function *ortho* to that group, *i.e. meta* to the reaction centre.

We have previously reported the rates of sulphonation of benzenesulphonic acid and various methyl substituted benzenesulphonic acids.[2] With 2- and 4-methyl-, 2,3-dimethyl-, 3,4-dimethyl-, and 2,4-dimethyl-benzenesulphonic acid, sulphonation occurs *meta* with respect to the original sulpho-group.[2c] With benzene- and 2,5-dimethylbenzene-sulphonic acid, some additional substitution *para* to the sulpho-group is observed.[2c]

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[1] Part XXXIX, H. Cerfontain, *Internat. J. Sulfur Chem.*, in the press.

[2] (*a*) H. Cerfontain, *Rec. Trav. chim.*, 1961, **80**, 296; (*b*) *ibid.*, 1965, **84**, 551; (*c*) A. J. Prinsen, A. Koeberg-Telder, and H. Cerfontain, *Tetrahedron*, 1970, **26**, 1953; (*d*) H. Cerfontain, Z. R. H. Nienhuis, and W. A. Zwart Voorspuy, *J.C.S. Perkin II*, 1972, 2087.

Substitution *ortho* to the sulpho-group was recently observed with some *meta*-halogenobenzenesulphonic acids.[3] It was therefore thought that it would be of interest to extend the earlier studies[2] to other (poly)-methylbenzenesulphonic acids for which sulphonation could be expected to take place, at least in part, *ortho* and/or *para* to the sulpho-group. A further aim was to compare the rates of substitution at the various positions of these polymethylbenzenesulphonic acids.

RESULTS

The experimental pseudo-first-order rate constants of sulphonation of the various methylbenzenesulphonic acids are given in Table 1. 2,6-Dimethylbenzenesulphonic acid in an excess of $\leqslant$98·9% H_2SO_4 isomerizes to the 2,4-dimethyl acid, whereas in 104% H_2SO_4 it is sulphonated directly to 2,4-dimethylbenzene-1,3-disulphonic acid.[4] By n.m.r. spectroscopy it was shown that the lowest acid concentration at which only sulphonation and no isomerization occurs is 99·996% H_2SO_4. This acid concentration was therefore used for rate measurements of this substrate.

TABLE 1

Rates of sulphonation at 25·0°

H_2SO_4 (%)	Methyl substituted benzenesulphonic acid	λ/nm [a]	$10^4k_1/s^{-1}$
99·996 ± 0·001	2,6-Me_2	283	157
100·04 ± 0·03 [b]	4-Me	279	2·90
	2,5-Me	290	6·4
100·07 ± 0·01 [b]	2-Me	275	51·2
	2,3,4,6-Me_4	310	134
104·0 ± 0·1 [b]	3-Me	285, 290	91·2
	3,5-Me_2	300	161
	3,4,5-Me_3	260	30
	2,3,4,5-Me_4	260	22·4
	2,3,5,6-Me_4	280, 320	173

[a] Wavelength at which the rate measurement was made. [b] For each sulphuric acid concentration, all rate measurements were made in sulphuric acid originating from the same stock solution.

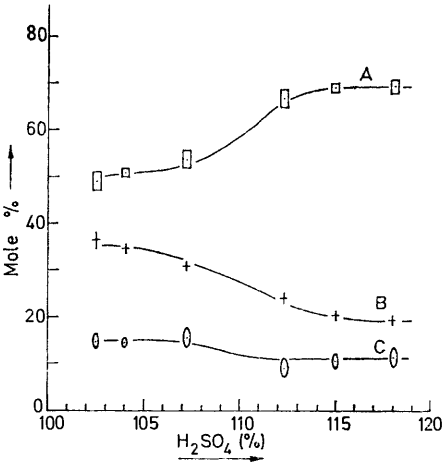


FIGURE 1 Sulphonation of 3-methylbenzenesulphonic acid at 25°; dependence of isomer distribution on sulphuric acid concentration. Products: A, 5-Me-1,3-diacid; B, 2-Me-1,4-diacid; C, 4-Me-1,2-anhydride

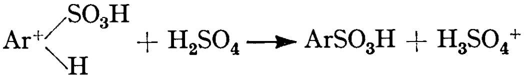
The isomeric composition of the disulphonic acid products was determined from the n.m.r. spectra of the sulphuric acid reaction mixtures; the results are given in Table 2. The isomer distributions are dependent on the sulphuric acid concentration, as is shown for 3-methylbenzenesulphonic acid in Figure 1. The graphs show that a constant isomer ratio is approached both at low and high sulphuric acid concentration. A similar type of dependence on the sulphuric acid concentration has been observed with 3-fluorobenzenesulphonic acid.[5]

The temperature dependence of the isomer distribution for 3-methyl- and 2,6-dimethyl-benzenesulphonic acid and the activation parameter differences are given in Table 3. With 3-methylbenzenesulphonic acid in 104·0% H_2SO_4 at 100°, the isomer ratio of the 2-Me-1,4-, 4-Me-1,2-, and 5-Me-1,3-disulphonic acids varies from 41·1 : 7·6 : 51·4 for a reaction time of 1 min to a constant ratio of 37·7 : 14·3 : 48·0 for $\geqslant$70 min.

DISCUSSION

Sulphonation in Weak Oleum.—The sulphonation of mono- and di-substituted benzene derivatives in weak oleum up to 104% H_2SO_4 proceeds by the two step mechanism (1) and (2) in which k_{-1} and k_2 are of the same order of magnitude.[6] The rate of sulphonation is then given by equation (3). With arenesulphonic acids in fuming sulphuric acid protonation[7] and/or sulphur trioxide complex formation of the sulphonic group must be considered,[2a] as the reactive species in the sulphonation up to 109% H_2SO_4 is the sulphonic acid proper, the protonated sulphonic acid being regarded as far less reactive.[2a,b,6a] As an approximation it will be assumed that the degree of protonation and complex formation for a given sulphuric acid concentration is the same for the various polymethylbenzenesulphonic acids under study.*

$$ArH + H_3S_2O_7^+ \rightleftharpoons Ar^{+}\!\!<^{SO_3H}_{H} + H_2SO_4 \qquad (1)$$



$$Ar^{+}\!\!<^{SO_3H}_{H} + H_2SO_4 \longrightarrow ArSO_3H + H_3SO_4^+ \qquad (2)$$

$$v = k_1k_2[ArH][H_3S_2O_7^+]/(k_{-1} + k_2) \qquad (3)$$

For benzene- and 3-methylbenzene-sulphonic acid in 100·2—104% H_2SO_4 and for 2- and 4-methylbenzenesulphonic acid in 98—100·5% H_2SO_4 it was observed that the relative rates of sulphonation of the sulphonic acids is independent of the sulphuric acid concentration. Furthermore, the sulphonation isomer distribution is

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* The substituent effect on the pK_a of the deprotonation equilibrium $ArSO_3H \rightleftharpoons ArSO_3^- + H^+$ is small, the Hammett ρ value being 0·7 ± 0·2.[8]

[3] H. Cerfontain, A. Koeberg-Telder, and W. A. Zwart Voorspuy, *Canad. J. Chem.*, 1972, **50**, 1574.

[4] A. Koeberg-Telder, A. J. Prinsen, and H. Cerfontain, *J. Chem. Soc.* (*B*), 1969, 1004.

[5] A. Koeberg-Telder, C. Ris, and H. Cerfontain, to be published.

[6] (*a*) C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, 1970, **88**, 1298; (*b*) H. Cerfontain and C. W. F. Kort, *Internat. J. Sulfur Chem. C*, 1971, **6**, 123.

[7] R. J. Gillespie, *Rev. Pure Appl. Chem.*, 1959, **9**, 1.

[8] H. Cerfontain and B. W. Schnitger, *Rec. Trav. chim.*, 1972, **91**, 199.

almost independent of the sulphuric acid concentration over the range of 101—104% H_2SO_4 (Table 2). Accordingly, a comparison of the positional rates of sulphonation in weak oleum $\leqslant$104% H_2SO_4 can be made (Table 4).

TABLE 2

Sulphonation isomer distribution at 25°

Methyl substituted benzenesulphonic acid	H_2SO_4 (%)	Isomer distribution (%) [a] 2-	3-	4-	5-	6-	Ref.
None	101·2		48·3 ± 0·3	3·4 ± 0·5	48·3 ± 0·3		1*c*
None	104·4		48·8 ± 0·3	2·4 ± 0·5	48·8 ± 0·3		1*c*
None	109		48·5 ± 0·3	2·9 ± 0·5	48·5 ± 0·3		1*c*
None	115		49·0 ± 0·3	2·0 ± 0·5	49·0 ± 0·3		
2-Me	104·4		0·8 ± 0·4		99·2 ± 0·4		
3-Me	102·5			36·4 ± 2·0	49·0 ± 2·0	14·6 ± 2·0	
3-Me	104			34·7 ± 1·0	50·9 ± 1·0	14·4 ± 1·0	
3-Me	107·2			31·0 ± 1·0	53·6 ± 0·2	15·4 ± 2·0	
3-Me	112·3			24·2 ± 1·0	66·9 ± 2·0	9·1 ± 2·0	
3-Me	115			20·3 ± 1·0	69·2 ± 1·0	10·5 ± 1·2	
3-Me	118·1			19·2 ± 1·0	69·4 ± 1·5	11·4 ± 1·5	
4-Me	104·4	$\leqslant$0·3	50		50	$\leqslant$0·3	
2,3-Me_2	103				100	$\leqslant$0·5	
2,4-Me_2	104·4		$\leqslant$0·5		100		1*c*
2,5-Me_2	101·2		92·1 ± 0·5	7·9 ± 0·5		$\leqslant$0·3	1*c*
2,5-Me_2	104·4		92·8 ± 0·7	7·2 ± 0·7		$\leqslant$0·3	1*c*
2,5-Me_2	107·2		93·1 ± 0·5	6·9 ± 0·5		$\leqslant$0·3	
2,5-Me_2	109		93·6 ± 0·5	6·4 ± 0·5		$\leqslant$0·3	1*c*
2,5-Me_2	115		96·2 ± 0·6	3·8 ± 0·6		$\leqslant$0·3	
2,6-Me_2	99·97 ± 0·03		50	$\leqslant$0·03	50		
2,6-Me_2	104·4		50	$\leqslant$0·3	50		
3,4-Me_2	104·0				100	$\leqslant$0·5	
3,5-Me_2	104·0	13·6 ± 0·3		72·8 ± 0·5		13·6 ± 0·3	
2,3,4-Me_3	104·0				100	$\leqslant$0·3	
2,4,5-Me_3	104·0		100			$\leqslant$0·3	
2,4,6-Me_3	110		50		50		
3,4,5-Me_3	107	50				50	
2,3,4,5-Me_4	107					100	
2,3,4,6-Me_4	107				100		
2,3,5,6-Me_4	107			100			

[a] The upper limits were estimated from the absence of specific, in general methyl, n.m.r. absorption peaks.

TABLE 3

Temperature dependence of isomer distributions in 104·0% H_2SO_4

Methyl substituted benzene-sulphonic acid	Temp. °C	Disulphonic acid isomer distribution (%) 1,2-	1,6-	1,4-	1,5-	$\Delta H_p - \Delta H_m$ (kcal mol⁻¹)	$\Delta H_p - \Delta H_o$ [a] (kcal mol⁻¹)	$\Delta S_p - \Delta S_m$ (cal mol⁻¹ K⁻¹)	$\Delta S_p - \Delta S_o$ [a] (cal mol⁻¹ K⁻¹)
3-Me	0·0		19·2	29·5	51·3	0·7 ± 0·1	2·9 ± 0·1	1·4 ± 0·5	11·5 ± 1·0
	25·0 [b]		14·4	34·7	50·9				
	100 [b]		6·5	41·8	51·7				
3,5-Me_2	0·0	14·8 [5]	14·8 [5]	70·3			0·4 ± 0·1		4·5 ± 0·2
	25·0	13·6 [5]	13·6 [5]	72·7					
	62	13·2 [5]	13·2 [5]	73·5					
	98	12·8	12·8	74·4					
	150	12·3 [5]	12·3 [5]	75·3					
None [2c]						2·2 ± 0·2		1·3 ± 0·7	$\geqslant$5 [c]
2,5-Me_2 [2c]						2·4 ± 0·1		3·0 ± 0·4	

[a] The indices refer to the position of substitution relative to the sulpho-group. [b] Isomer distribution data obtained by extrapolation to zero reaction time. [c] Calculated from k_p/k_o on the assumption that $\Delta H_p = \Delta H_o$.

Substitution meta *to* SO_3H.—The rate of substitution *meta* to the sulpho-group is strongly enhanced upon introduction of a methyl group in the molecule *ortho* to the reaction centre. This rate enhancement is smaller if this methyl group is flanked by a sulpho than by a methyl group (compare 3-methyl- with 3,4-dimethyl- on the one hand and 2,5-dimethyl-benzenesulphonic acid on the other). Introduction of a second methyl group *ortho* to the reaction centre leads only to a *small* increase in rate, if this second methyl group is flanked by a 'free' sulpho-group, *i.e.* with a hydrogen atom in the *ortho* position (*cf. e.g.* 2,5-dimethyl- and 2,4,5-trimethylbenzenesulphonic acid). Introduction of a second methyl group *ortho* to the reaction centre even leads to a significant decrease in rate, if this methyl group is flanked by a sulpho-group with a methyl group at the other *ortho*-position (*cf.* both 2,4- and 2,6-dimethyl- with 2,4,6-trimethyl-benzenesulphonic acid).

Introduction of a methyl group *para* to the reaction centre leads to an increase in rate by a factor of *ca.* 10^4 if the reaction centre has two hydrogens in the *ortho*-positions, to an increase of *ca.* 2 × 10^3 if there is one methyl group in an *ortho*-position and to no increase in rate for the case of two *o*-methyl groups.

The steric hindrance for substitution *ortho* to a methyl group which has no substituent at the other *ortho*-position corresponds to an entropy change of 9 ± 4 cal mol^{-1} K^{-1}.[1c] The large increase in the overall rate of sulphonation upon introduction of a methyl group *ortho* (or *para*) to the reaction centre is ascribed to a large increase in the rate of reaction (1), mainly as a result of hyperconjugative electron release by the methyl group to the reaction centre in the transition state. The introduction of the second methyl group *ortho* to the reaction centre is expected to lead to a further increase in rate of reaction (1). The observed lower overall reactivity must then be ascribed mainly to a large decrease in the rate of reaction (2). This decrease in rate is due to the overcrowding occuring in the resulting 2,4-dimethylbenzene-1,3-disulphonic acid or methyl derivative. Evidence supporting this explanation is first the observed higher overall enthalpy of activation for the sulphonation of 2,4,6-trimethyl- as compared with that of 2,4-dimethyl-benzenesulphonic acid,[1c] and secondly the observed substantial geometric deformations in the molecular structure of dipotassium 2,4,6-trimethylbenzene-1,3-disulphonate.[9]

TABLE 4

Positional relative rates of sulphonation in weak oleum $\leqslant 104\%$ H_2SO_4

Methyl substituted benzenesulphonic acid	k_{rel} [a]				
	2-	3-	4-	5-	6-
None	$\leqslant 0.5 \times 10^{-3}$	1	4.8×10^{-2}	1	$\leqslant 5 \times 10^{-3}$
2-Me		67		8200	
3-Me			7.6	11	3.1
4-Me	$\leqslant 1$	250		250	$\leqslant 1$
2,3-Me_2			$\leqslant 600$	1.2×10^5	
2,4-Me_2		$\leqslant 4300$		8.5×10^5	
2,5-Me_2		1020	79		$\leqslant 3$
2,6-Me_2		1.1×10^5	$\leqslant 700$	1.1×10^5	
3,4-Me_2				1.4×10^4	$\leqslant 70$
3,5-Me_2	5.2		28		5.2
2,3,4-Me_3				1.4×10^6	$\leqslant 4000$
2,4,5-Me_3		2.3×10^4			$\leqslant 7000$
2,4,6-Me_3		1.1×10^4		1.1×10^4	
3,4,5-Me_3	3.6				3.6
2,3,4,5-Me_4					5.3
2,3,4,6-Me_4				2.2×10^4	
2,3,5,6-Me_4			41		

[a] Rate constant of sulphonation relative to that of one *meta*-position of benzenesulphonic acid.

Substitution para *and* ortho *to* SO_3H.—For sulphonation *para* to the sulpho-group the same general phenomena regarding the overall rate are observed as for *meta* substitution (*cf.* benzene- with 3-methylbenzenesulphonic acid *vs.* 3-methyl- with 2,5-dimethyl- and 3,5-dimethyl-benzenesulphonic acid). As for sulphonation *ortho* to SO_3H, introduction of a methyl group *ortho* to the reaction centre, *i.e.* in fact introduction of the second *ortho*-substituent, leads, as was expected, only to a small increase (*cf.* 3-methyl- with 3,5-dimethyl-benzenesulphonic acid).

Activation Parameters for 104·0% H_2SO_4.—The activation entropy data $\Delta S_p - \Delta S_o$ (Table 3) illustrate that there is a substantial steric hindrance for substitution *ortho* to the SO_3H substituent. The difference in entropy of activation for substitution *para* and *meta* to the SO_3H group is small. The probably significant difference may be explained in terms of a higher degree of solvation of the transition state for *meta*- than of that for *para*-substitution.

Sulphonation in Oleum $>104\%$ H_2SO_4.—For sulphonation in 104—109% H_2SO_4 the sulphonating entity is $H_2S_4O_{13}$,[6] whereas in 112—118% H_2SO_4 it may be $H_2S_4O_{13}$ or a higher polysulphuric acid. The isomer distribution of 3-methylbenzenesulphonic acid is independent of the sulphuric acid concentration from 115—118% H_2SO_4. In that acid concentration the degree of substitution *meta* to the sulpho-group is greater than in weak oleum, for which acid range the substrate species undergoing substitution is the sulphonic acid proper.[6] It is suggested that the sulphonation in $\geqslant 115\%$ H_2SO_4 proceeds for the greater part *via* the protonated [*] (or sulphur trioxide complexed) arenesulphonic acid. For it is expected that the degree of *meta*-substitution will be greater for the $SO_3H_2^+$ (or S_2O_6H) than for the SO_3H substituent. The alternative explanation that the sulphonation in 115—118% H_2SO_4 proceeds by sulphonation of the unprotonated sulphonic acid substrate by means of a polysulphuric acid entity different from $H_2S_4O_{13}$ or by sulphur trioxide proper cannot, however, be rigorously excluded.

EXPERIMENTAL

Spectrometers.—U.v. measurements were made with a Zeiss PMQ2 spectrophotometer. N.m.r. spectra were

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[*] In 115% H_2SO_4 (H_0 −14·9 [10]), the ratio of protonated to unprotonated, *e.g.* 3-methylbenzenesulphonic acid (pK_a −12·2 [2a,11]) is equal to 500.

[9] M. A. M. Meester, and H. Schenk, *Rec. Trav. chim.*, 1972, **91**, 213.

[10] R. J. Gillespie, T. E. Peel, and E. A. Robinson, *J. Amer. Chem. Soc.*, 1971, **93**, 5083.

[11] M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, 1963, **85**, 878.

recorded with a Varian HA 100 spectrometer, equipped with a time averaging computer. Sodium 2,2-dimethyl-2-silapentane-5-sulphonate was used as an internal standard for the D_2O solutions and tetramethylsilane–carbon tetrachloride (1 : 1 v/v) as an external standard for the sulphuric acid solutions. Unless stated otherwise, the solutions for n.m.r. contained 100 mg of the sample per ml.

Materials.—Potassium 3,4,5-*trimethylbenzenesulphonate.* 1,2,3-Trimethylbenzene (1·0 ml) and 98% H_2SO_4 (2·0 ml) were shaken at 30—50° till the hydrocarbon had dissolved. Then 69·9% H_2SO_4 (9·0 ml) was added and the resulting homogeneous 74% H_2SO_4 solution, containing mainly the 2,3,4-trimethyl acid, was heated at 140° for 17 h. After cooling, the precipitated 3,4,5-trimethyl acid was filtered off and taken up in ethanol, and ethanolic potassium hydroxide was added until the solution became slightly alkaline. The precipitate, containing potassium sulphate and some sulphonate, was filtered off, dried, and extracted with ethanol. From the filtrate which contained the sulphonate together with some potassium sulphate the solvent was removed and the dried residue was extracted with ethanol. The two ethanolic solutions were combined, the solvent removed, and the residual crude sulphonate recrystallized three times from ethanol and three times from methanol–diethyl ether (yield 0·4 g), δ (D_2O; 50 mg ml^{-1}) 7·42, (s, 2,6-H_2), 2·26 (s, 3,5-Me_2), and 2·11 (s, 4-Me).

Potassium 2-*methylbenzene*-1,4- *and* 5-*methylbenzene*-1,3-*disulphonate.* These were obtained by adding 115% H_2SO_4 (15 ml) to potassium 3-methylbenzenesulphonate (4·8 g) and heating the mixture with stirring at 155° for 4 h. After cooling, the mixture was poured on ice (200 g), and the solution made alkaline with concentrated aqueous potassium hydroxide. Fractional crystallization afforded the 1,3-disulphonate (2·0 g), δ (D_2O) 8·01 (s, 2-H), 7·82 (s, 4,6-H_2), and 2·46 (s, Me); and the 1,4-disulphonate (1·0 g), δ (D_2O) 7·78 (s, 3-H), 8·00 (AB, *J* 13 Hz, 6-H), 7·74 (AB, *J* 13 Hz, 5-H), and 2·68 (s, 1-Me).

Potassium 4-*methylbenzene*-1,2-*disulphonate.* This was obtained by treating the corresponding diacid chloride (Fluka, purum) with saturated ethanolic potassium hydroxide, δ (D_2O) 7·95 (s, 3-H), 7·99 (AB, *J* 8 Hz, 6-H), 7·43 (AB, *J* 8 Hz, 5-H), and 2·40 (s, Me).

Potassium 2,3,4,5-, 2,3,4,6-, *and* 2,3,5,6-*tetramethylbenzenesulphonate.* These were prepared *via* the reaction of the corresponding hydrocarbons with chlorosulphuric acid.[12]

Sodium 2,5-dimethylbenzenesulphonate was obtained from Eastman. The preparation of the other sulphonates has been described.[13] The preparation of purified fuming sulphuric acid free from sulphur dioxide has been described previously.[2a,6a]

Procedures and Analysis.—The rate constants of sulphonation were determined by u.v. measurements according to standard procedures.[13a]

The sulphonation product composition was determined by multicomponent n.m.r. analysis of the reaction mixture (*cf.* refs. 3 and 14). The mixtures were obtained by adding the alkali arenesulphonate (100—200 mg) to liquid sulphuric acid (2·0 ml) at 25°, except for 2,6-dimethylbenzenesulphonate, for which compound only 2·3 mg was used.

The assignment of the polymethylbenzenedisulphonic acids was based upon the following observations. First, upon the introduction of a sulpho-group into a (polymethyl)-benzene, the hydrogens *ortho-*, *meta*, and *para* to the sulpho-substituent undergo a downfield shift of 0·44, 0·17, and 0·29 p.p.m. respectively.[15] Secondly, the methyl groups *ortho*, *meta*, and *para* to the sulpho-group introduced undergo a downfield shift of 0·3, <0·1, and <0·1 p.p.m. respectively.[15] Thirdly, the effect of a second sulpho-group is additive.[15] Fourthly, arene-1,2-disulphonic acids in fuming sulphuric acid are readily converted into intramolecular anhydrides. The chemical shifts of the hydrogens at the 3- and 6-position are 0·11 p.p.m. greater for benzene-1,2-disulphonic acid than for the corresponding anhydride. Finally, for benzene-1,2-disulphonic anhydride, the chemical shift of the hydrogens at the 3- and 6-positions is equal to that of the hydrogens at the 4- and 5-positions.

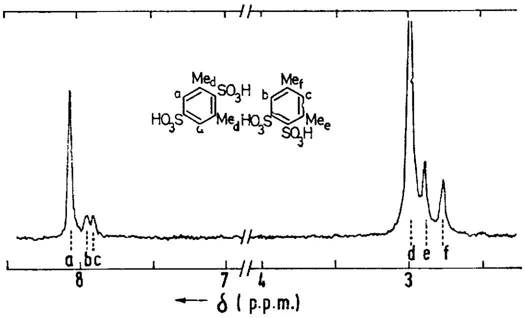

FIGURE 2 N.m.r. spectrum of reaction mixture of 3,5-dimethylbenzenesulphonic acid in 104% H_2SO_4

The assignment of the typical n.m.r. spectrum of the sulphonation mixture of 3,5-dimethylbenzenesulphonic acid is shown in Figure 2. With 3-methylbenzenesulphonic acid as substrate, the n.m.r. spectral assignment of the sulphonation mixture, made on the principles outlined above, was proved to be correct by comparison with the spectra of test mixtures of 3-Me-1,4-, 4-Me-1,2-, and 5-Me-1,3-disulphonic acid in fuming sulphuric acid.[16]

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[2/2267 *Received, 2nd October,* 1972]

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[14] A. Koeberg-Telder and H. Cerfontain, *Rec. Trav. chim.*, 1972, **91**, 22.

[15] C. Ris, Thesis, University of Amsterdam, 1973.

[16] H. Cerfontain, A, Koeberg-Telder, C. Krak, and C. Ris, *Analyt. Chem.*, in the press.