Aromatic Sulphonation. Part 63.[1] Sulphonation of *m*-Aminobenzenesulphonic Acid in Fuming Sulphuric Acid. Formation of an Overcrowded Tetrasulphonic Acid

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m-Aminobenzenesulphonic acid upon sulphonation in fuming sulphuric acid at elevated temperatures yields a mixture of anilinium-2,5-di-, -2,4,5-tri-, and -2,3,4,6-tetra-sulphonic acids. The degree of polysubstitution increases with increasing (fuming) sulphuric acid concentration. The ratio of di-, tri-, and tetra-sulphonic acids is thermodynamically controlled. Substitution takes place *ortho* and/or *para* to the ammonium substituent. It is proposed that the reaction proceeds *via* a rate-limiting conversion of the ammonium group into a sulphamic acid group. The resulting sulphamic acid is then sulphonated in its *N*-unprotonated form. In aqueous sulphuric acid at room temperature the overcrowded aniline-2,3,4,6-tetrasulphonate is readily desulphonated (with release of steric strain) to yield the 2,4,5-trisulphonate.† From the orientation it is concluded that the reaction takes place *via* a species in which the amino-group is unprotonated. In highly concentrated sulphuric acid the steric compression in the tetrasulphonic acid is decreased by intramolecular anhydride formation.

A FEW studies of the sulphonation of *m*-aminobenzenesulphonic acid in fuming sulphuric acid have been reported. At room temperature no reaction takes place, not even in 115% H_2SO_4.[2] Sulphonation does, however, occur at elevated temperatures, *e.g.* at 180 °C.[3] Although the evidence appears conflicting, sulphonation was assumed to yield the anilinium-2,5-disulphonic acid [4] and not the -3,4-disulphonic acid.[5] No attempt was made to establish whether the formation of the disulphonic acid was kinetically or thermodynamically controlled. *o*- and *p*-Aniliniumsulphonic acids are reported to isomerize in concentrated aqueous sulphuric acid at 180 °C.[6]

RESULTS

Sulphonation of m-*Aminobenzenesulphonic Acid*.—*m*-Aminobenzenesulphonic acid (0.3—0.5M) has been sulphonated in 99—107% H_2SO_4 at temperatures between 100 and 180 °C. At 100 °C the conversion is very slow, *e.g.* the half-life in 105.5% H_2SO_4 is 1 day, whereas it is *ca.* 0.5 h at 140 °C; at 180 °C in 104% H_2SO_4 complete conversion was obtained within 5 min. The sulphonation products are anilinium-2,5-di-, -3,4-di- (always $<3\%$), -2,4,5-tri-, and -2,3,4,6-tetrasulphonic acids. Anilinium-3,5-disulphonic acid is not formed.

The product composition is thermodynamically controlled. For example in 105.5% H_2SO_4 at 140 °C the same product distribution [*viz. ca.* 2% anilinium-2,5-di- + -3,4-di-, (78 ± 2) %-2,4,5-tri-, and (20 ± 2)% -2,3,4,6-tetrasulphonic acid] was obtained from *m*-aminobenzenesulphonic acid or anilinium-2,5-di-, -3,4-di-, or -2,4,5-trisulphonic acid. The product composition is strongly dependent on the sulphuric acid concentration (Table 1). The 2,5-disulphonic acid is formed in substantial amounts in $>99\%$ H_2SO_4 and so is the 2,4,5-trisulphonic acid in $>100\%$ H_2SO_4 and the 2,3,4,6-tetrasulphonic acid in $>102\%$ H_2SO_4.

m-Trimethylammoniobenzenesulphonate and anilinium-3,5-disulphonic acid in 107% H_2SO_4 at 140 °C are not sulphonated.

Desulphonation of Dicalcium Aniline-2,3,4,6-*tetrasulphonate at* 25 °C.—Upon addition at room temperature of *m*-aminobenzenesulphonic acid and the salts of anilinium-2,5-di-, -3,4-di-, and -2,4,5-tri-sulphonic acids to aqueous or fuming sulphuric acid no desulphonation or sulphonation is observed.

Aniline-2,3,4,6-tetrasulphonate in a large excess of 3.0—90.0% H_2SO_4 at 25 ± 1 °C is desulphonated to yield the 2,4,5-trisulphonate. The reaction is first-order with respect to the substrate for at least three half-lives. The observed rate of desulphonation reaches a maximum at 40—45% H_2SO_4 (Table 2) which is just beyond the acid concentration of half-protonation (see later). For 3.0—45.3% H_2SO_4 the graph of log k_1 *versus* log $c_{H_3O^+}$ is linear with a slope of 0.77 ± 0.05 (*r* 0.978, 6 points, Figure 1). In $>50\%$ H_2SO_4 the observed rate constant decreases less rapidly than the water activity: the slope of the graph log k_1 *versus* log a_{H_2O} decreases from *ca.* 1.0 in the acid range 52.5—69.5% H_2SO_4 to *ca.* 0.5 in 80.0—90.0% H_2SO_4 (Figure 2).

The protonation of dicalcium aniline-2,3,4,6-tetrasulphonate was studied by monitoring u.v. absorption at 345 nm. At this wavelength the unprotonated form (B)

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† In this paper for convenience, the amino-group is always taken to be at position 1.

[1] Part 62, T. A. Kortekaas and H. Cerfontain, *J.C.S. Perkin II*, accepted for publication.

[2] A. Koeberg-Telder, C. Ris, and H. Cerfontain, *J.C.S. Perkin II*, 1974, 98.

[3] C. M. Suter, 'Organic Chemistry of Sulphur,' Wiley, New York, 1944, p. 248.

[4] S. C. J. Olivier, *Rec. Trav. chim.*, 1920, **39**, 499.

[5] H. Limpricht, *Ber.*, 1876, **9**, 553.

[6] Z. J. Allan and Z. Vrba, *Coll. Czech. Chem. Comm.*, 1969, **34**, 272.

TABLE 1

Sulphonation products of *m*-aminobenzenesulphonic acid (0.25—0.5M) in 99—107% H_2SO_4

H_2SO_4 [a] (%)	Temp. (°C)	Aniliniumsulphonic acids (%) [b] *meta*	3,4-di-	2,5-di-	2,4,5-tri-	2,3,4,6-tetra-
99.9 (99)	140	44		56		
100.1 (99.5)	120	17	1	82		
100.5 (100)	120		1	70	29	
102.3 (101.5)	140		2	56	42	
104.0 (102)	140			6	84	10
107.0	140				76	24
108.3 (106.5)	140				67	33

[a] The data in parentheses refer to the eventual sulphuric acid concentration after the sulphonation as determined from the position of the ^1H n.m.r. solvent peak relative to external tetramethylsilane (see ref. 19). [b] Determined by ^1H n.m.r. spectroscopy.

TABLE 2

First-order rate constants for desulphonation of dicalcium aniline-2,3,4,6-tetrasulphonate in aqueous sulphuric acid at 25 ± 1 °C

H_2SO_4 (±0.1%)	$-\log k_1$ [a]	$\log c_{H_3O^+}$ [b]	$-\log a_{H_2O}$ [c]
3.0	5.87	−0.43	
6.2	5.66	−0.10	
14.8	5.45	0.31	
30.0	5.10	0.67	
39.2	4.89	0.81	
45.3	4.87	0.90	0.31
52.5	5.04	0.97	0.52
69.5	5.66	1.11	1.31
80.0	6.30		2.27
84.8	6.61		2.88
90.0	6.88		3.63

[a] k_1/s^{-1} (±10%) as determined by u.v. spectroscopy (see Experimental section). [b] Taken from H. Chen and D. E. Irish, *J. Phys. Chem.*, 1971, **75**, 2672. [c] Taken from W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, *J. Amer. Chem. Soc.*, 1960, **82**, 62.

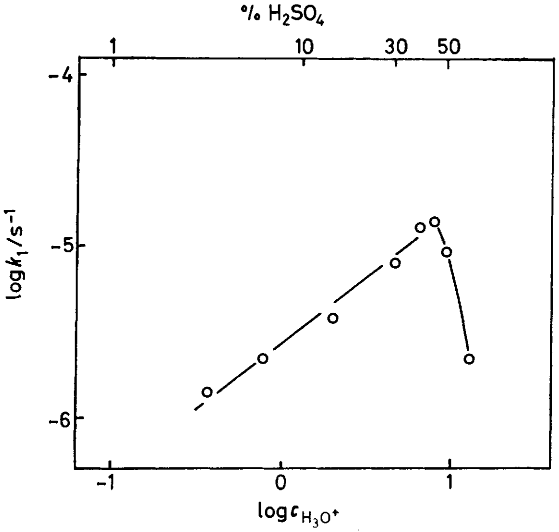


FIGURE 1 Correlation of $\log k_1$ with $\log c_{H_3O^+}$ for desulphonation of dicalcium aniline-2,3,4,6-tetrasulphonate in aqueous sulphuric acid at 25 °C

has an absorption maximum, whereas the protonated form (BH^+) does not absorb. The curve of ε_{345} against H_0 is sigmoid (Figure 3); no medium effects are observed. The plot of log ([B]/[BH^+]) *versus* H_0 in 29.8—50.7% H_2SO_4 is linear with a slope of 1.03 ± 0.03 (*r* 0.992, 7 points). This indicates that protonation occurs on the nitrogen atom. The substrate is half-protonated at 39.8 ± 0.7% H_2SO_4 and has a pK_a value of −2.40 ± 0.05.

In 98.4 and 99.8% H_2SO_4 at 25 °C the u.v. spectrum of aniline-2,3,4,6-tetrasulphonic acid changes slowly ($t_{\frac{1}{2}}$ *ca.* 1 week) into that of a product identified as an (intramolecular) anhydride on the basis of (i) the observation that the ^1H n.m.r. spectrum does not change over the same period of time [δ 9.5 (s)] and (ii) intramolecular anhydride formation

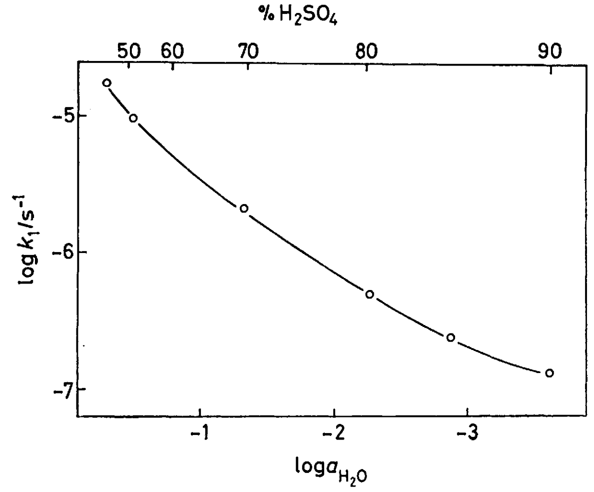


FIGURE 2 Correlation of $\log k_1$ with $\log a_{H_2O}$ for desulphonation of dicalcium aniline-2,3,4,6-tetrasulphonate in aqueous sulphuric acid at 25 °C

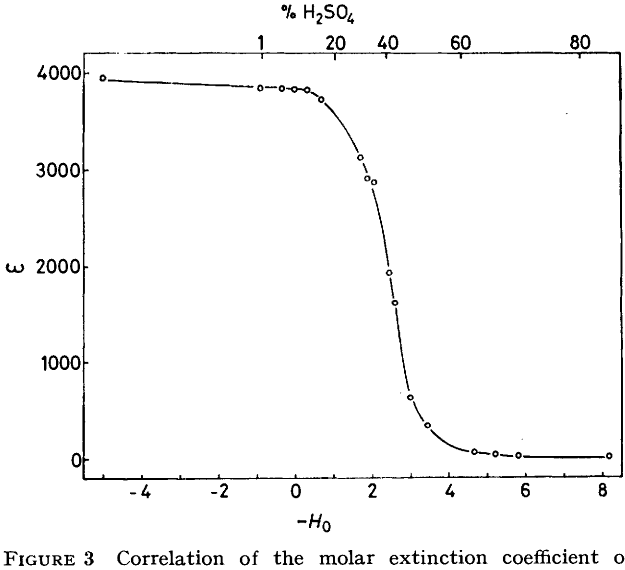
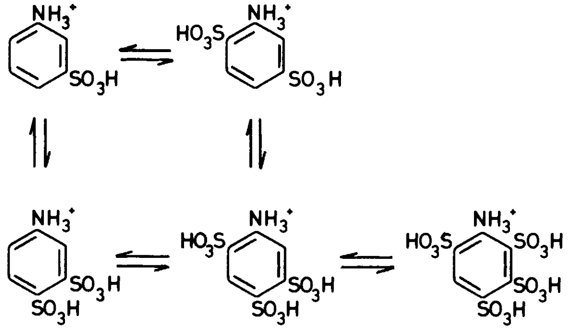


FIGURE 3 Correlation of the molar extinction coefficient of dicalcium aniline-2,3,4,6-tetrasulphonate at 345 nm with H_0

is generally observed with arene-1,2-disulphonic acids in $>100\%$ H_2SO_4[2] and with the overcrowded 3,4,5,6-tetramethylbenzene-1,2-disulphonic acid even in $\geqslant 97\%$ H_2SO_4.[2,7]

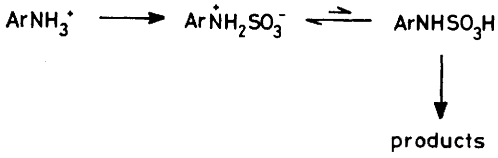
DISCUSSION

Sulphonation of m-*Aminobenzenesulphonic Acid in Fuming Sulphuric Acid.*—*m*-Aminobenzenesulphonic acid is present in dilute aqueous sulphuric acid as *m*-ammoniobenzenesulphonate and in $>96\%$ H_2SO_4 mainly as *m*-ammoniobenzenesulphonic acid.[8] The sulphonation of this *m*-ammoniobenzenesulphonic acid at elevated temperatures occurs only *ortho* and *para* to the ammonio-group (Scheme 1); no substitution *meta* to that group was found. The possibility that the *ortho*- and *para*-products are formed *via* initial *meta*-substitution and subsequent isomerization can be excluded, as authentic anilinium-3,5-disulphonic acid does not isomerize under the applied conditions. The same type of orientation, *i.e. ortho*- and *para*- without *meta*-substitution, was observed in the sulphonation of 6-methylanilinium-3- and -4-sulphonic acids in fuming sulphuric acid at 140—150 °C.[9]



SCHEME 1

These findings suggest that sulphonation of *m*-ammoniobenzenesulphonic acid occurs *via* a species in which the nitrogen atom is unprotonated. This is supported by the observation that *m*-trimethylammoniobenzenesulphonic acid under the same conditions is not sulphonated at all. Reaction in fuming sulphuric acid ($H_0 < -12$) of a species with an unprotonated amino-group can be excluded on the basis of the relatively



$$ArNH_3^+ \longrightarrow Ar\overset{+}{N}H_2SO_3^- \rightleftharpoons ArNHSO_3H \xrightarrow{\quad} \text{products}$$

SCHEME 2

strong basicity of the *m*-ammoniobenzenesulphonate species (pK_a 3.74 for *N*-deprotonation).[10] By analogy with the sulphonation of anilinium sulphate in *ca.* 100% H_2SO_4 at elevated temperatures[11,12] the reaction is considered to proceed *via* the sulphamic acid species (Scheme 2). The conversion of *m*-ammoniobenzenesulphonic acid into the corresponding sulphamic acid appears to be rate-limiting in the series of subsequent sulphonations, as the ratio of the three sulphonic acid products is independent of the substrate conversion (see Table 3).

TABLE 3

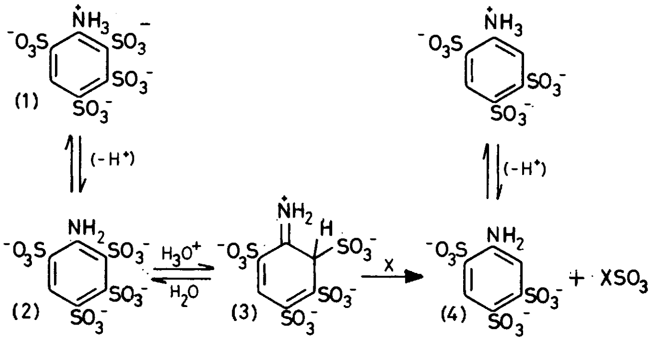
Sulphonation of *m*-aminobenzenesulphonic acid in 102.3% H_2SO_4 at 140 °C

	Aniliniumsulphonic acids (%)[a]			
t/h	*meta*	2,5-di-	2,4,5-tri-	2,3,4,6-tetra-
0.5	70	7	22	1
1	53	9	36	2
2	22	16	59	3
4	9	22	67	2

[a] The amount of the 3,4-disulphonic acid is less than 2%.

Desulphonation of Dicalcium Aniline-2,3,4,6-*tetrasulphonate.*—In aqueous sulphuric acid the tetrasulphonate is easily desulphonated to yield the 2,4,5-trisulphonate. The orientation in the desulphonation indicates that the reactive substrate species has an unprotonated nitrogen atom (*cf.* ref. 13). The driving force for this reaction is the relief of steric strain as a result of the replacement of the 2-sulphonate group, *i.e.* that *ortho* to the *N*-containing substituent, by a hydrogen atom.

The desulphonation mechanism will be discussed in terms of Scheme 3. In the acid concentration range



SCHEME 3

3.0—45.3% H_2SO_4 the rate of desulphonation increases linearly with increasing hydronium ion concentration. This indicates that the formation of the σ-complex (3) from the *N*-unprotonated compound (2) is rate-limiting. The deviation of the slope of the graph log k_1 *versus* log $c_{H_3O^+}$ from unity may be ascribed to medium effects of the substrate, which in fact contains four (negatively) charged sulphonate substituents. At $>50\%$ H_2SO_4 the tetrasulphonate is more than 90% protonated on nitrogen (1). The rate of desulphonation no longer

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[7] A. Koeberg-Telder and H. Cerfontain, unpublished results.

[8] P. K. Maarsen, R. Bregman, and H. Cerfontain, *Tetrahedron*, 1974, **30**, 1211.

[9] A. Courtin and K. Brenneisen, *Chimia* (*Switz.*), 1972, **26**, 307.

[10] J. J. Christensen and L. D. Hansen, *J. Chem. Soc.* (*A*), 1969, 1212.

[11] Z. Vrba and Z. J. Allan, (*a*) *Coll. Czech. Chem. Comm.*, 1968, **33**, 2502; (*b*) *Tetrahedron Letters*, 1968, 4507.

[12] E. R. Alexander, *J. Amer. Chem. Soc.*, 1947, **69**, 1599.

[13] B. I. Karavaev and V. S. Vorotilova, *Izvest. Vyssh. Ucheb. Zaved. Khim. i khim. Tekhnol.*, 1971, **14**, 1358 (*Chem. Abs.*, 1971, **76**, 13,408).

increases with H_3O^+ concentration, but decreases along with the water activity. Two explanations can be advanced: either (i) the conversion of (1) into (3) is rate-limiting, or (ii) that of (3) into (4) is rate-limiting. Changes in solvation of the substrate, *e.g.* an increase in hydrogen bonding with the sulphonate groups, and at the acid concentrations $>80\%$ H_2SO_4 even in protonation of one (or several) of the sulphonate groups,[8] might be responsible for the observation that the rate constant decreases less sharply than the water activity.

At the highest sulphuric acid concentrations the anilinium-2,3,4,6-tetrasulphonic acid is considered to form an intramolecular anhydride to reduce steric compression.

EXPERIMENTAL

Materials.—*m*-Aminobenzenesulphonic acid (Fluka) was treated with charcoal and recrystallized from aqueous ethanol (Found: C, 41.6; H, 4.0; N, 8.0; S, 18.4. Calc. for $C_6H_7NO_3S$: C, 41.6; H, 4.05; N, 8.1; S, 18.5%), δ* (D_2O–NaOH) 6.39 (m, H-6), 7.62 (m, H-2), 7.64 (m, H-4), and 7.77 (m, H-5).

Calcium aniline-2,5-disulphonate was prepared by heating *m*-aminobenzenesulphonic acid in an excess of weakly fuming sulphuric acid at 180 °C for 5 h. The mixture was neutralized with $CaCO_3$. After removal of the solid $CaSO_4$ the filtrate was treated with charcoal. The calcium disulphonate was then precipitated by addition of ethanol and recrystallized several times from aqueous ethanol[14] (Found: C, 24.9; H, 1.8; Ca, 13.7. Calc. for $C_6H_5CaNO_6S_2$: C, 24.8; H, 1.75; Ca, 13.8%), δ (D_2O–NaOH) 7.66 (m, H-4), 7.80 (d, H-6), and 8.26 (d, H-3) ($J_{3,4}$ 8.5, $J_{4,6}$ 2 Hz).

Dipotassium 1-*nitrobenzene*-3,4-*disulphonate.* Dipotassium *o*-benzenedisulphonate (3.5 g) was dissolved in 104% H_2SO_4 (20 ml), then 95% HNO_3 (1.5 ml) was added, and the mixture was heated at 100 °C for 3 h. After cooling, the precipitated potassium salts were filtered off and the filtrate neutralized (KOH). After removal of solid, an excess of aqueous ethanol was added in order to precipitate the remaining K_2SO_4, which was filtered off. The filtrate was evaporated. The residue was dissolved in a minimal amount of water and precipitated by slow addition of ethanol; yield 2 g of yellow material, δ (D_2O) 8.16 (d, H-5), 8.17 (d, H-2), and 8.75 (m, H-6) ($J_{2,6}$ 3.5, $J_{5,6}$ 6 Hz). The product was contaminated with some 2,3-disulpho-isomer (see below).

Dipotassium aniline-3,4-*disulphonate.* The nitrobenzene-3,4-disulphonate was reduced with Fe–HCl.[15] After filtration, neutralization was carried out with aqueous KOH. The iron oxides were removed by centrifugation. The product was precipitated with ethanol, recrystallized several times by water–ethanol treatment and dried (Found: C, 20.8; H, 2.1; K, 22.7. Calc. for $C_6H_5K_2NO_6S_2,H_2O$: C, 20.7; H, 2.05; K, 22.5%), δ (D_2O–NaOH) 7.33 (m, H-6), 7.89 (d, H-2), and 8.31 (d, H-5) ($J_{2,6}$ 2.5, $J_{5,6}$ 8.5 Hz). The ^1H n.m.r. spectrum indicated contamination with *ca.* 20% of the 2,3-disulpho-isomer: δ 7.49 (m, H-6), 7.75 (m, H-5), and 7.99 (m, H-4) ($J_{4,5} = J_{5,6} = 8$, $J_{4,6}$ *ca.* 2 Hz). No attempt at further purification was made.

Dipotassium 1-*nitrobenzene*-3,5-*disulphonate.* This was prepared by nitration of benzene-3,5-disulphonic acid, formed *in situ* from benzene and fuming sulphuric acid.[16] The mixture was poured on ice, the resulting solution neutralized with aqueous KOH, and the precipitated dipotassium salt filtered off and recrystallized from aqueous ethanol; δ (D_2O) 8.88 (m, H-4) and 8.97 (d, H-2 and -6) ($J_{2,4} = J_{4,6} =$ *ca.* 1.5 Hz).

Dipotassium aniline-3,5-*disulphonate.* This was obtained from the 1-nitrobenzene-3,5-disulphonate by reduction, as for the 3,4-disulpho-isomer; δ (D_2O–NaOH) 7.79 (d, H-2 and -6) and 8.00 (m, H-4) ($J_{2,4} = J_{4,6} = 1.5$ Hz).

2-*Sulphoanilinium*-4,5-*disulphonic anhydride.* This was obtained by heating *m*-aminobenzenesulphonic acid (1 g) in 105% H_2SO_4 (10 ml) at 100 °C for 1 week. After cooling a precipitate was formed, SO_3 was removed with a stream of nitrogen, and filtration yielded the product (250 mg), δ (D_2O) 2.80 (s, H-6) and 3.35 (s, H-3), relative to HDO (these data apply to the aniline-2,4,5-trisulphonate).

Barium salt of aniline-2,4,5-*trisulphonic acid.* *m*-Aminobenzenesulphonic acid was heated in a large excess of 105.5% H_2SO_4 at 140 °C for 2 h. The mixture was poured on ice and neutralized [$Ba(OH)_2$]. The isolated barium salt was recrystallized from aqueous ethanol (Found: C, 12.5; H, 1.4; Ba, 36.2; N, 2.5. Calc. for $C_6H_4Ba_{1.5}NO_9S_3,2H_2O$: C, 12.6; H, 1.4; Ba, 36.0; N, 2.45%), δ (D_2O) 8.05 (s, H-6) and 8.80 (s, H-3). The calcium salt was obtained in a similar way by neutralization with $CaCO_3$.

Dicalcium salt of aniline-2,3,4,6-*tetrasulphonic acid.* *m*-Aminobenzenesulphonic acid (5 g) was heated in 105.5% H_2SO_4 (40 ml) at 140 °C for 2 h. After cooling, SO_3 (10 ml) was added and the mixture heated again at 140 °C for 2 h. The cooled mixture was poured onto ice and neutralized ($CaCO_3$). After removal of solid $CaSO_4$, the aqueous solution was evaporated. The residue was dissolved in water, treated with charcoal and, after filtration, precipitated with ethanol; yield 5 g of a mixture of 2,4,5-tri- and 2,3,4,6-tetra-sulphonates (2 : 1 by ^1H n.m.r.). The materials were separated by repeated water–methanol treatment (the tetrasulphonate being slightly less soluble than the trisulphonate). The eventually obtained dicalcium tetrasulphonate (0.6 g) still contained *ca.* 7 mole % of the trisulphonate (Found: C, 11.7; H, 2.55; Ca, 13.2; N, 2.55. Calc. for $C_6H_3Ca_2NO_{12}S_4,6H_2O$: C, 12.05; H, 2.55; Ca, 13.4; N, 2.35%), δ (D_2O) 8.85 (s, H-5). In the ^1H n.m.r. spectrum of one of the crystallization fractions the presence of an unknown compound was observed [δ 7.50 and 8.32 (*J* 9 Hz)] which was considered to be the aniline-2,3,6-trisulphonate.

m-Trimethylammoniobenzenesulphonate was prepared as described before.[8]

All materials were kept in a desiccator over $CaCl_2$.

Spectra.—The i.r. spectra (KBr pellets) of *m*-aminobenzenesulphonic acid and the metal salts of the anilinepolysulphonic acids all showed strong absorption bands in the 1 020—1 240 cm^{-1} region due to SO_3^-. *m*-Aminobenzenesulphonic acid has NH_3^+ absorptions at 2 600m and 3 050s cm^{-1}. Calcium aniline-2,5-disulphonate has typical absorptions at 3 390m and 3 490m cm^{-1}, due to NH_2. In the spectra of the salts of the other polysulphonic acids the NH_2 absorptions are obscured by

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* All δ values are relative to external tetramethylsilane (sealed capillary).

[14] G. T. Berends, University of Amsterdam, unpublished results.

[15] A. I. Vogel, 'Practical Organic Chemistry,' Longman, London, 3rd edn., 1970, p. 589.

[16] G. M. Bennett and G. H. Willis, *J. Chem. Soc.*, 1929, 256.

TABLE 4

^{1}H N.m.r. data of aniliniumsulphonic acids in sulphuric acid [a]

Position of sulpho-group(s)	H_2SO_4 (%)	δ [b] H-2	H-3	H-4	H-5	H-6	NH_3
3	81.5	8.55		8.6	← ca. 8.4 →		9.1 [c]
	98.4	8.6		8.65	← ca. 8.4 →		8.6
	102.3	8.65		8.7	← ca. 8.4 →		8.45
	107	8.64		8.84	8.44	8.49	8.15
2,5	82.4		8.81	8.81		8.76	9.5 [c]
	98		8.87	8.87		8.78	9.2 [c]
	102		8.92	8.92		8.81	9.15
	104.5		8.98	8.98		8.82	9.15
3,4	98	8.9			9.0	8.55	8.9
	105	8.8			← 8.6—9.0 →		
2,4,5	82.4		9.32			9.10	
	98.4		9.36			9.08	
	102		9.42			9.00	
	106.5		9.42			8.98	
2,3,4,6	85				9.49		
	99.5				9.50		
	102				9.63		
	106.5				9.63		
3,5	85	8.88		9.10		8.88	9.2 [c]
	98	8.95		9.15		8.95	8.9 [c]
	102	8.97		9.24		8.97	8.75
	105.5	9.05		9.35		9.05	8.65

[a] Substrate concentration 0.2—0.4M. [b] Relative to external tetramethylsilane (sealed capillary). For the 3,4-disulphonic acid $J_{5,6}$ ca. 8 Hz. With the 2,4,5-tri- and 2,3,4,6-tetra-sulphonic acids the NH_3^+ signals are not observed because of fast exchange with the solvent protons. [c] Broadened and reduced in peak area because of (slow) exchange of the ammonium protons.

absorptions due to water of crystallization. The absence of an absorption in the 2 000—2 800 cm^{-1} region indicates the absence of NH_3^+ in these salts.

The u.v. spectra of the aniliniumsulphonic acids in 98.4% H_2SO_4 show, apart from a bathochromic shift for the B-band, an increase in molar extinction on going from the *meta- via* the 2,5-di- to the 2,4,5-tri-sulphonic acid. The molar extinction coefficients of the overcrowded 2,3,4,6-tetrasulphonic acid are much smaller than that of the 2,4,5-trisulphonic acid. The wavelengths of maximum absorption and molar extinctions for the four compounds are, respectively, 264 (840), 272 (1 340), 276 (2 990), and 285 nm (1 050 l mol^{-1} cm^{-1}). This phenomenon was recently reported for a series of benzene(poly)sulphonic acids in water.[17]

Sulphuric acid of appropriate concentration was obtained by mixing known amounts of water, 98.4% H_2SO_4 (B.D.H. AnalaR), and fuming sulphuric acid (65% 'free' SO_3), as required. Liquid sulphur trioxide (Sulfan) was obtained from Hardman and Holden (Manchester).

Sulphonation of m-*Aminobenzenesulphonic Acid*.—The reactions were carried out in a flask provided with two condensers in series which were cooled with water kept at 30 °C in order to prevent solidification of SO_3 in the cooling system. The top condenser was provided with a calcium chloride tube. The product distribution was determined by ^{1}H n.m.r. spectroscopy (comparison of the spectrum of the reaction mixture with the spectra of the reference compounds in sulphuric acid of the same concentration) (Table 4). Further, as the absorption peaks of the ammonium protons of the mono- and di-sulphonic acids appeared in the aromatic region, the reaction mixtures were diluted to ca. 80% H_2SO_4 and the spectra again analysed by comparison with the references, for which at this acid concentration the NH_3^+ absorptions had (almost) disappeared because of proton exchange with the solvent (Figure 4). The aromatic proton signals shifted to lower field with increasing aqueous H_2SO_4 concentration as a result of protonation of the sulphonate substituent(s) and

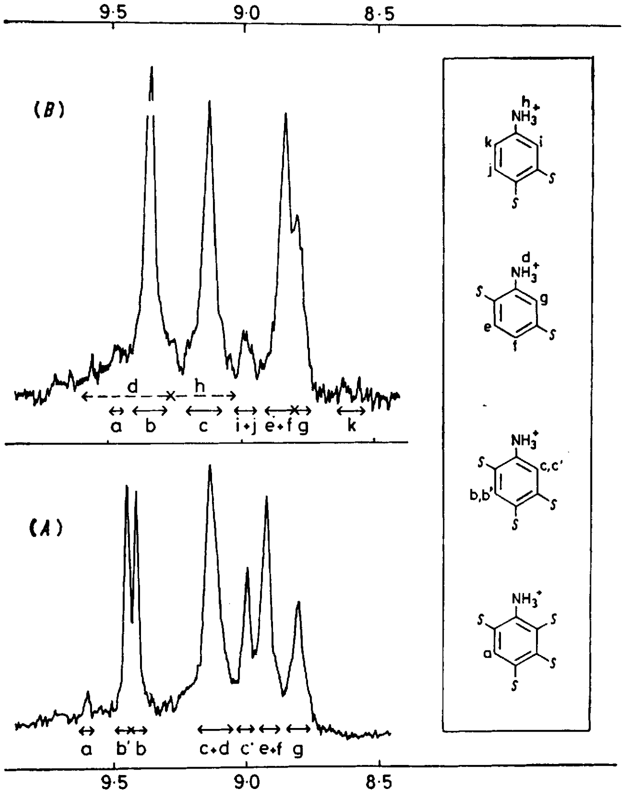

FIGURE 4 ^{1}H N.m.r. spectra of a sulphonation mixture of *m*-aminobenzenesulphonic acid in 104% H_2SO_4 (*A*) and, after dilution, in 84% H_2SO_4 (*B*); *S* stands for SO_3H or SO_3^-, depending on the sulphuric acid concentration; b, c and b′, c′ refer to the aromatic protons of the anilinium-2,4,5-trisulphonic acid and its anhydride, respectively. For both disulphonic acids in 84% H_2SO_4 the NH_3^+ absorptions d and h are broadened and greatly reduced in area

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[17] N. S. Dokunikhin and G. A. Mezentseva, *Russ. J. Org. Chem.*, 1976, **12**, 613.

in $>100\%$ H_2SO_4 also in some cases as a result of formation of an (intra)molecular sulphonic anhydride.[18]

The formation of anhydrides is indicated by the occasional (slow) precipitation of material from solutions containing >50 mg ml^{-1} of the 3,4-di-, 2,4,5-tri-, and 2,3,4,6-tetrasulphonic acids in *ca.* 100% H_2SO_4 at room temperature. For the 2,4,5-trisulphonic acid the absorptions of the trisulphonic acid and the 2-sulpho-4,5-disulphonic anhydride were sometimes observed simultaneously in the ^1H n.m.r. spectrum (Figure 4).

Because the sulphuric acid concentration decreased somewhat during the high temperature reactions as a result of loss of SO_3 and/or ingress of moisture, the concentration of the sulphuric acid was determined afterwards from the position of the solvent peak. A calibration curve (*cf.* ref. 19) was set up in the 75—110% H_2SO_4 range for solutions containing *ca.* 0.3M-aniliniumsulphonic acid.

The ^1H n.m.r. spectra were recorded with a Varian HA 100 spectrometer with, unless otherwise stated, neat liquid tetramethylsilane (sealed capillary) as an external standard.

*Protonation and Desulphonation of the Dicalcium Salt of Aniline-*2,3,4,6-*tetrasulphonic Acid*.—Sulphuric acid solutions of the substrate (*ca.* 10^{-4}M) were stored at 25 ± 1 °C. For u.v. measurements a portion of the solution was transferred into the absorption cell of a Cary 14 spectrophotometer.

The protonation of the tetrasulphonate was studied in 0—85% H_2SO_4 at 345 nm (wavelength of maximum absorption of the unprotonated form).

The rate of desulphonation in 3—90% H_2SO_4 was measured by following the change of the u.v. spectrum with time. In $<40\%$ H_2SO_4 the decrease at 345 nm and at higher acid concentrations the change of absorption at two wavelengths in the 265—310 nm region was measured. The eventual u.v. spectrum was identical with that of authentic aniline-2,4,5-trisulphonate. In 90% H_2SO_4, however, a deviation of *ca.* 20% in absorbance was found, probably due to the formation of an anhydride (see Results section). The plots of log $(A_t - A_\infty)$ against time were linear for at least three half-lives.

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[7/382 *Received*, 3rd *March*, 1977]

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[18] H. Cerfontain, A. Koeberg-Telder, C. Kruk, and C. Ris, *Analyt. Chem.*, 1974, **46**, 72.

[19] A. Koeberg-Telder and H. Cerfontain, *J.C.S. Perkin II*, 1975, 226.