Aromatic Sulphonation. Part 59.[1] Sulphonation of Aniline in Concentrated Aqueous and Fuming Sulphuric Acid

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From kinetic and product studies it has been concluded that the sulphonation of anilinium sulphate in a large excess of 99.99—102.3% H_2SO_4 at 25 °C proceeds by direct electrophilic attack of the sulphonating entity $H_3S_2O_7^+$ on the aromatic ring of the anilinium cation. The main products are *m*-aminobenzenesulphonic and sulphanilic acid, the amount of *o*-aminobenzenesulphonic acid being <2%.

In an excess of concentrated aqueous sulphuric acid at elevated temperatures anilinium sulphate is converted into *o*-aminobenzenesulphonic and sulphanilic acid as the main products. Phenylsulphamic acid was previously thought to be an intermediate in the sulphonation of aniline in *ca.* 97% H_2SO_4 at ⩾100 °C. Phenylsulphamic acid itself does not yield any *m*-aminobenzenesulphonic acid. Accordingly, the formation of 5—15% of *m*-aminobenzenesulphonic acid from anilinium sulphate in 96.8—99.9% H_2SO_4 at 60—100 °C indicates that the reaction under the given conditions proceeds at least partially by direct ring sulphonation of the anilinium ion.

THE sulphonation of aniline has been studied under a variety of conditions. In aprotic media with *e.g.* chlorosulphuric acid or sulphur trioxide complexes at room temperature *N*-sulphonation is observed,[2a,3] whereas at elevated temperatures *o*-aminobenzenesulphonic and (mainly) sulphanilic acid are formed.[2b,3] Ring sulphonation can also be effected by the so-called ' baking ' process, *i.e.* by heating the dry hydrogen sulphate salt as such or in an inert solvent at a sufficiently high temperature.[2c,3]

In concentrated aqueous sulphuric acid at temperatures ⩾100 °C sulphonation of aniline or its (hydrogen) sulphate leads to *o*-aminobenzenesulphonic and sulphanilic acid. For this conversion phenylsulphamic acid, which yields a product mixture of the same composition, was thought to be an intermediate.[4,5b] This was substantiated by the difference in behaviour of aniline and its *NN*-dimethyl derivative. The latter, in contrast to the former, is not sulphonated in concentrated aqueous sulphuric acid; this was ascribed to its inability to form a sulphamic acid.[5] From the relative reactivities it was concluded that the conversion of the anilinium sulphate into phenylsulphamic acid is the rate-limiting step in the conversion of the anilinium ion in concentrated aqueous sulphuric acid at elevated temperatures [4,5] into the aniliniumsulphonic acids.

The reaction of aniline with fuming sulphuric acid at room temperature yields predominantly anilinium-*m*- and -*p*-sulphonic acids.[5a,6] The same type of orientation, *i.e.* a high *meta*- and a very low *ortho*-content, was found in the nitration of aniline in (a large excess of) sulphuric acid at room temperature. From kinetic and product studies of the nitration it was concluded that the anilinium cation is the reacting substrate species.[7] Because no such precise studies have been reported on the sulphonation of aniline, we have investigated the reaction of this compound in an excess of (fuming) sulphuric acid at 25 °C. We have further investigated the influence of the sulphuric acid and substrate concentrations on the product composition, at both low and high temperatures.

RESULTS

Sulphonation with Fuming Sulphuric Acid at Room Temperature.—The rate of sulphonation of anilinium sulphate in a large excess of 100.07—102.30% H_2SO_4 at 25.0° was determined. The first-order rate constants, k_1, are given in Table 1. The graph of log k_1 against log $a(H_2S_2O_7) - H_0$ is linear with a slope of 1.02 (Figure).

TABLE 1

First-order rate constants for sulphonation of anilinium sulphate at 25.0 ± 0.2 °C

H_2SO_4 (%)	$-\log k_1/s^{-1}$ [a]	$\log a(H_2S_2O_7) - H_0$ [b]
100.07 ± 0.01	4.98	9.32
100.21 ± 0.01	4.17	10.03
100.56 ± 0.02	3.40	10.78
100.92 ± 0.02	2.96	11.24
101.54 ± 0.03	2.44	11.77
102.30 ± 0.05	1.96	12.21

[a] U.v. measurements (in duplicate) were made at 271 nm. [b] Values of log $a(H_2S_2O_7)$ taken from ref. 12; those of H_0 from R. J. Gillespie, T. E. Peel, and E. A. Robinson, *J. Amer. Chem. Soc.*, 1971, **93**, 5083.

In 100.9% H_2SO_4 anilinium sulphate is 90 times more reactive than the phenyltrimethylammonium ion.[8]

The isomer distribution for the sulphonation of anilinium sulphate in 99.99—102.3% H_2SO_4 was determined by means of multi-component ^1H n.m.r.[9a] and u.v.[9b] analysis (Table 2). The main products are the anilinium-*m*- and -*p*-sulphonic acids; only a trace of the *ortho*-isomer is formed. The amount of *meta*-isomer increases with increasing oleum concentration. It decreases slightly with increasing substrate concentration; this is apparent from the data for 102.3% H_2SO_4.

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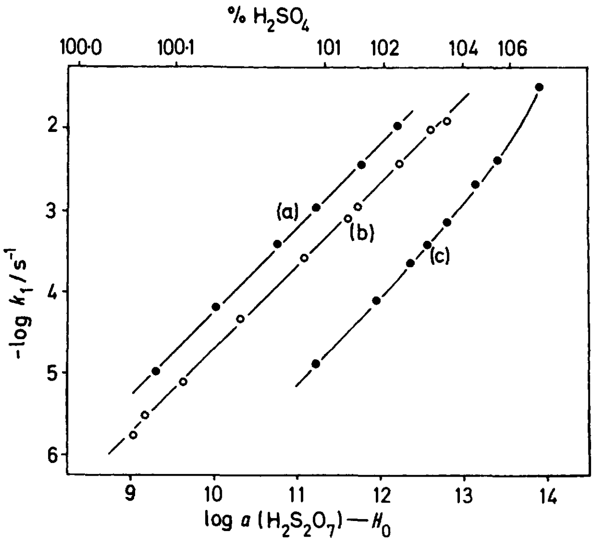
Sulphonation with Concentrated Aqueous Sulphuric Acid at Elevated Temperatures.—The mixtures obtained on sulphonation of anilinium sulphate (0.25—0.5 mol l^{-1}) in 96.8% H_2SO_4 at 100 °C and in 99.9% H_2SO_4 at 60—100 °C after complete substrate conversion were analysed by ^1H n.m.r. spectroscopy (Table 3). The products are anilinium-*o*-, -*m*-, and -*p*-sulphonic acids. The proportion of the *ortho*-isomer is substantial, whereas that of the *meta*-isomer is much lower than in fuming sulphuric acid at 25 °C. The amount of *meta*-isomer increases with (i) increasing sulphuric acid concentration, (ii) decreasing temperature, and (iii) decreasing substrate concentration. In 99.9% H_2SO_4 some 2,4-disulphonic acid was also found.



Correlation of log k_1 with log $a(H_2S_2O_7)$ — H_0 for the sulphonation of (a) anilinium sulphate, (b) 1,2,3,4-tetrafluorobenzene,[12] and (c) the phenyltrimethylammonium ion [8] in fuming sulphuric acid at 25 °C

o-Aminobenzenesulphonic acid in 99.9% H_2SO_4 at 100 °C for 2 days is not isomerized, *i.e.* it does not yield any anilinium-*m*- or -*p*-sulphonic acids, but only some anilinium-2,4-di- and -2,4,6-tri-sulphonic acids. This is in agreement with the observation that *o*-aminobenzenesulphonic acid in 97% H_2SO_4 at 100 °C is not isomerized.[4] At temperatures above 120 °C some isomerization to sulphanilic acid exclusively does take place.[10]

Potassium phenylsulphamate (0.3 mol l^{-1}) in concentrated aqueous sulphuric acid at both low and high temperatures is converted into anilinium-*o*- and -*p*-sulphonic acids; *m*-aminobenzenesulphonic acid is not formed to a measurable extent ($\not> 1.5\%$).[11]

DISCUSSION

Reaction in Fuming Sulphuric Acid at 25 °C.—The sulphonation rate dependence of anilinium sulphate in a large excess of fuming sulphuric acid at 25.0 °C on the acid concentration is similar to that of 1,2,3,4-tetrafluorobenzene.[12] Accordingly it is proposed that the sulphonating entity for the two substrates is the same, *viz.* $H_3S_2O_7^+$ (*cf.* ref. 12). The reactivity ratio for sulphonation of anilinium sulphate and the phenyltrimethylammonium ion * (*ca.* 90 : 1 in 100.9% H_2SO_4) is similar to that for nitration of the two cations in concentrated aqueous sulphuric acid (*ca.* 55).[13] The sulphonation product composition (Table 2) is almost the same as that for the nitration of the anilinium ion in concentrated aqueous sulphuric acid, which also yields predominantly the *meta*- and *para*-isomers.[7] These results show that under the applied conditions of sulphuric acid concentration (99.99—102.3% H_2SO_4) and temperature (25 °C) the sulphonation occurs by direct electrophilic attack of $H_3S_2O_7^+$ on the aromatic ring of the anilinium cation. The (small) effects of both the sulphuric acid and the substrate concentration on the *meta* : *para* ratio observed in the sulphonation as well as in the nitration [7] can be ascribed to changes in solvation. The efficiency with which the positive charge of the anilinium ion is dispersed by *e.g.* hydrogen

TABLE 2

Isomer distribution for the sulphonation of anilinium sulphate at 25 °C

H_2SO_4 (%)	Substrate concn. (mmol l^{-1})	Method of analysis	Aniliniumsulphonic acids (%)		
			ortho	*meta*	*para*
99.99	5.6	U.v.	1.5 ±0.3	51.7 ±1.6	46.8 ±1.2
100.07	1.4	U.v.	0.9 ±1.6	54.9 ±1.4	44.2 ±1.5
100.5	60	^1H N.m.r.	<2	49.0 ±1.5	51.0 ±1.5
100.9	1.0	U.v.	0.4 ±4.5	54.6 ±4.4	45.0 ±3.2 [a]
102.3	1.5	U.v.	*b*	62.5 ±3.0	37.5 ±3.4 [a]
	60	^1H N.m.r.	<2	56.5 ±1.5	43.5 ±1.5
	300	^1H N.m.r.	<2	50 ±2	50 ±2

[a] These figures include 1.9 and 3.9% anilinium-2,4-disulphonic acid for 100.9 and 102.3% H_2SO_4, respectively. [b] Not determined.

TABLE 3

Isomer distribution for the sulphonation of anilinium sulphate in concentrated aqueous sulphuric acid at elevated temperatures

H_2SO_4 (%) [a]	Substrate [b] concn. (mol l^{-1})	Temp. (°C) (±3)	Aniliniumsulphonic acids (%) [c]			
			ortho	*meta*	*para*	2,4-di
96.8	0.25	100	18 ± 3	9 ± 1	73 ± 3	
	0.5	100	20 ± 3	5 ± 2	75 ± 3	
97	0.45	100	14 [d]		86 [d]	
99.9	0.25	100	*e*	13 ± 2	*e*	
	0.3	100	10 ± 3	11 ± 1	71 ± 3	8 ± 1
	0.3	80	13 ± 3	15 ± 1	68 ± 3	4 ± 1
	0.3	60	9 ± 2	16 ± 2	69 ± 2	6 ± 2

[a] Initial concentration. [b] $(PhNH_2)_2,H_2SO_4$. [c] Analyses by ^1H n.m.r.; the ^1H n.m.r. data of the aniliniumsulphonic acids in 98.4% H_2SO_4 have been reported.[11] [d] Data from ref. 4. [e] Not determined.

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* The phenyltrimethylammonium ion is in part sulphonated by the stronger electrophile $H_2S_4O_{13}$.[12]

[10] W. J. Spillane and F. L. Scott, *Tetrahedron*, 1968, **24**, 5011.

[11] (*a*) Part 56 and (*b*) Part 57, P. K. Maarsen and H. Cerfontain, *J.C.S. Perkin II*, 1977, 921, 929.

[12] C. W. F. Kort, and H. Cerfontain, *Rec. Trav. chim.*, 1969, **88**, 1298.

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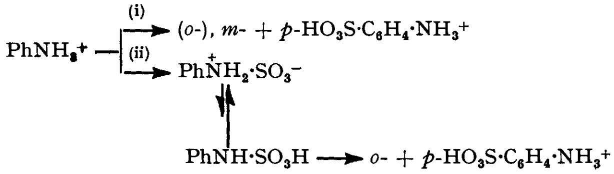
bonding with the solvent influences the isomer distribution.[13]

Reaction in Concentrated Aqueous Sulphuric Acid at $\geqslant$*60 °C.*—On the basis of kinetic and product studies it was previously proposed that the sulphonation of aniline at elevated temperatures, *e.g.* in an excess of 97% H_2SO_4 at 100 °C, proceeds *via* phenylsulphamic acid, which eventually gives *o*-aminobenzenesulphonic and sulphanilic acids.[4,5] We recently showed that phenylsulphamic acid yields *ortho*- and *para*-substituted products with virtually no *meta*-isomer.[11] The present results on anilinium sulphate (Table 3) show, however, that at 100 °C in both 96.8 and 99.9% H_2SO_4, besides *o*-aminobenzenesulphonic and sulphanilic acids, (some) *m*-aminobenzenesulphonic acid is formed. The formation of the *meta*-isomer acid by isomerization can be excluded (see earlier). Thus the sulphonation of anilinium sulphate under these conditions must occur at least partially by direct electrophilic attack on the aromatic ring of the anilinium ion.

For the sulphonation of anilinium sulphate in *ca.* 100% H_2SO_4 there are thus two competing routes (Scheme).



SCHEME

Route (ii) is favoured over route (i) with increasing temperature and decreasing sulphuric acid concentration. At room temperature in a large excess of fuming sulphuric acid (Table 2) the sulphonation takes place exclusively *via* route (i); at elevated temperatures with concentrated aqueous sulphuric acid and relatively high substrate concentrations (Table 3) the reaction predominantly proceeds *via* the indirect route (ii).*

EXPERIMENTAL

Materials.—The synthesis and purification of anilinium sulphate, the anilinesulphonic acids, calcium aniline-2,4-disulphonate and tripotassium aniline-2,4,6-trisulphonate have been described previously.[11a,15] The preparation of absolute sulphuric acid [12] and the preparation and purification of fuming sulphuric acid [16] have been reported elsewhere. All other sulphuric acid concentrations were obtained by mixing known amounts of water, 98.4% H_2SO_4 (B.D.H. AnalaR), and absolute and fuming sulphuric acid, as required. Liquid sulphur trioxide (Sulfan) was obtained from Hardman and Holden.

Rate Measurements.—The reactions in 100.07 and 100.21% H_2SO_4 were carried out by preparing a stock solution of anilinium sulphate (*ca.* 10^{-3}M) in acid of the desired concentration. Portions of the solution were transferred to cylindrical flasks placed in a thermostatted water-bath, kept at 25.0 ± 0.2 °C. The reactions with the acid at other concentrations were carried out directly in the absorption cells in the thermostatted (25.0 ± 0.1 °C) cell holder of a Zeiss PMQ-II spectrophotometer. For both methods the reaction was followed by monitoring the change in absorbance at 271 nm. At that wavelength the aniliniumsulphonic acids have an extinction maximum, whereas anilinium sulphate does not absorb.[11a] Plots of log $(E_t - E_\infty)$ *vs.* time were linear for at least three half-lives.

Isomer Distribution.—The compositions of the mixtures obtained from reactions at 25 °C were determined by multi-component u.v. and ^{1}H n.m.r. analyses.

For the u.v. analysis in 99.99% H_2SO_4 freshly prepared solutions of anilinium sulphate, the anilinesulphonic acids, and calcium aniline-2,4-disulphonate were used as references. The extinctions of the reaction mixture and the reference solutions in the wavelength regions 204—230 and 250—278 nm with an increment of 2 nm were measured simultaneously on a Zeiss PMQ-II spectrophotometer provided with a rotating cell holder. The u.v. analyses of the fuming sulphuric acid reaction mixtures were made similarly after removal of SO_3 by bubbling nitrogen through the solutions and subsequent dilution with water to 40% H_2SO_4. The reference solutions were prepared in acid of the same concentration.

The ^{1}H n.m.r. analyses were carried out as follows. At complete conversion the compositions of the mixtures from reactions of anilinium sulphate in both concentrated aqueous sulphuric acid at elevated temperatures and fuming sulphuric acid at 25 °C were analysed in terms of the relative amounts of anilinium-*o*-sulphonic acid, the 2,4-disulphonic acid, and the *m*- and *p*-sulphonic acids together. The amount of *meta*-isomer was determined by adding an equal volume of SO_3 to the mixture and heating the resulting *ca.* 110% H_2SO_4 solution for 4 h at 100—105 °C. Thus the *o*-, *p*-, and 2,4-di-sulphonic acids were converted completely into the 2,4,6-trisulphonic acid, whereas the *m*-isomer did not react, as verified by control experiments.[11a] The ^{1}H n.m.r. spectra were recorded with a Varian HA 100 spectrometer [neat liquid tetramethylsilane (sealed capillary) as an external standard].

The reactions in concentrated sulphuric acid at elevated temperatures were carried out in small cylindrical stoppered flasks immersed in an oil-bath. Either the substrate was dissolved in sulphuric acid and the solution heated by transferring the flask to the oil-bath, or the substrate was dissolved in sulphuric acid preheated to the desired temperature. The two procedures yielded the same isomer distribution because the reactions were relatively slow even at 100 °C (the half-lives were at least several hours).

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* The temperature dependence of the isomer distribution of route (i) may be substantial as a result of changes in solvation of the anilinium ion with increasing temperature and increasing substrate concentration and not only the result of a change in the reaction mechanism. Accordingly, a more precise quantization of the contributions by the two mechanisms to the overall reaction in *ca.* 100% H_2SO_4 at elevated temperatures is difficult. An example of the dramatic influence of temperature, acidity, and substrate concentration on the product composition for one and the same reaction mechanism has been reported for the nitration of 2-pyridones.[14]

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