Aromatic Sulphonation. Part 56.[1] The Rearrangement of Phenylsulphamic Acid to Aniliniumsulphonic Acids † in Concentrated Sulphuric Acid: Evidence for an Intermolecular Reaction Pathway

By **Paul K. Maarsen** and **Hans Cerfontain,*** Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, Amsterdam, The Netherlands

Phenylsulphamic acid in a large excess of 96—100% H_2SO_4 at 25° yields both orthanilic and sulphanilic acid *inter*molecularly by initial *C*-sulphonation and subsequent *N*-desulphonation. This conclusion is based on (i) the u.v. and n.m.r. observation in *ca.* 100% H_2SO_4 of *o*- and *p*-sulphophenylsulphamic acid as reaction intermediates and (ii) the dependence of both the rate of sulphonation of phenylsulphamic acid and of the isomer distribution of the aniliniumsulphonic acid products on the sulphuric acid concentration. The reacting and the major substrates were identified by kinetic, product, and protonation studies to be $PhNHSO_3H$ and $Ph\overset{+}{N}H_2SO_3^-$ respectively. The ionization $Ph\overset{+}{N}H_2SO_3^- \rightleftharpoons PhNHSO_3^- + H^+$ has an apparent pK_a value of −2.03, based on the H_0 acidity function.

PHENYLSULPHAMIC ACID has been postulated as an intermediate in the sulphonation of aniline at elevated temperatures, *e.g.* in excess of 97% H_2SO_4 at 100° [reaction (1)].[2] The rearrangement of phenylsulphamic

$$PhNH_3^+ \longrightarrow PhNHSO_3H \longrightarrow o\text{-} + p\text{-}HO_3SC_6H_4NH_3^+ \quad (1)$$

acid to sulphanilic acid was performed under a variety of reaction conditions [3,4] and was in general considered to be an *intra*molecular process.[5] Recently, Scott and Spillane [6] found that potassium phenylsulphamate in dioxan at 100° using an equimolar amount of sulphuric acid rearranges *inter*molecularly. The phenylsulphamate is first hydrolysed in a relatively fast step to yield anilinium sulphate which is in part resulphonated slowly to yield sulphanilic acid [reaction (2)]. At the same time

$$PhNHSO_3K \longrightarrow PhNH_3^+ \longrightarrow {}^-O_3SC_6H_4NH_3^+ \quad (2)$$

Vrba and Allan [2] studied the rearrangement of phenylsulphamic acid in an excess of concentrated sulphuric acid. From kinetic measurements at 40 °C they concluded the rate equation to be $v = k''h_0[Ph\overset{+}{N}H_2SO_3H]$ which infers that the rearrangement would be dependent only on the acidity of the reaction medium ($v \sim h_0^2$) and thus *e.g.* independent of the activity of any sulphonating entity. Accordingly they suggested the rearrangement to sulphanilic acid to be *intra*molecular. An attempt to prove this *intra*molecular mechanism by using labelled 98% $H_2{}^{35}SO_4$ failed because of a rapid exchange of the *N*-sulpho-group with the medium.[2b] In order to explain the *intra*molecular nature of the reaction, Allan postulated deformation of the six-membered ring in the transition state leading to *p*-aniliniumsulphonic acid.[2,7]

A related reaction is the *N*-nitroaniline rearrangement. However, there is an important difference in product formation, since the rearrangement of phenylsulphamic acid [2] leads mainly to the *para*-product, whereas the acid catalysed *N*-nitroaniline rearrangement,[8] which, by labelling experiments, was proved indeed to be *intra*molecular in concentrated aqueous sulphuric acid, leads mainly to the *ortho*-product. U.v. studies in our laboratories [9] under similar conditions (*ca.* 100% H_2SO_4; 25°) to those used by Allan, showed evidence for the occurrence of an intermediate in the conversion of phenylsulphamic acid to *o*- and *p*-aniliniumsulphonic acid. In order to gain a further insight into the nature of this conversion, an extensive study was made on the behaviour of phenylsulphamic acid in sulphuric acid.

RESULTS AND DISCUSSION

Evidence for an Intermediate.—Both u.v. and n.m.r. studies showed that phenylsulphamic acid in $< 99.6\%$ H_2SO_4 at room temperature is slowly converted into a mixture of *o*- and *p*-aniliniumsulphonic acids. However, in sulphuric acid in between 99.9 and 100.1% H_2SO_4, u.v. evidence (Table 1) was obtained for the rapid formation of an intermediate (or intermediates) which slowly yield(s) the aniliniumsulphonic acids. In $>100.1\%$ H_2SO_4 the subsequent conversion of the intermediate(s) into the sulpho-products becomes so fast as to render the observation of the intermediate(s) impossible.

Two possible types of structure for the intermediate(s) may be envisaged, *NN*-disulphoaniline (2) [6d] or *o*- and *p*-sulphophenylsulphamic acid (3). The *NN*-disulpho-compound (2) could then, upon rearrangement and subsequent solvolysis, yield orthanilic (4) and sulphanilic

---

† In systematic nomenclature, sulphoanilinium ions.

[1] Part 55, H. Cerfontain, A. Koeberg-Telder, and C. Ris, *J.C.S. Perkin II*, 1977, 720.

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

[3] E. R. Alexander, *J. Amer. Chem. Soc.*, 1948, **70**, 1274.

[4] G. Illuminati, *J. Amer. Chem. Soc.*, 1956, **78**, 2603.

[5] J. B. Hendrikson, D. J. Cram, and G. S. Hammond, 'Organic Chemistry,' McGraw-Hill, New York, 3rd edn., 1970, p. 730.

[6] (*a*) W. J. Spillane and F. L. Scott, *J. Chem. Soc.* (*B*), 1968, 779; (*b*) F. L. Scott and W. J. Spillane, *Internat. J. Sulfur Chem.*, 1968, **2**, 133; (*c*) W. J. Spillane and F. L. Scott, *ibid.*, 1970, **5**, 79; (*d*) W. J. Spillane, *ibid.*, 1973, **8**, 469.

[7] Z. J. Allan, *Tetrahedron Letters*, 1971, 4225.

[8] (*a*) S. Brownstein, C. A. Bunton, and E. D. Hughes, *J. Chem. Soc.*, 1958, 4354; (*b*) D. V. Banthorpe, E. D. Hughes, and D. L. H. Williams, *ibid.*, 1964, 5349.

[9] G. T. Berends and H. Cerfontain, unpublished results.

acid (5), while (3) upon solvolysis, would directly yield the same compounds (Scheme 1).*

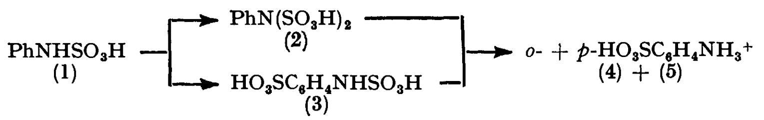
We failed to isolate the very unstable intermediate(s) from the sulphuric acid reaction mixture and attempts to synthesise and isolate (3) or one of its salts were unsuccessful (see Experimental section). Discrimination between the two possibilities can, however, be made from quenching experiments. Quenching of the reaction during the conversion of phenylsulphamic acid into the intermediate(s) by dilution of samples of the reaction mixture to *ca.* 40% H_2SO_4 would yield different products for the two types of intermediates. In dilute aqueous acid the intermediate (2) will, just as the starting material (1), be solvolysed (*N*-desulphonated) to yield the anilinium ion $PhNH_3^+$. The solvolysis of (2) will be faster than that of (1) as a result of the additional electron-withdrawing effect of the sulpho-group.[10,11] Solvolysis of the *o*- and *p*-sulphophenyl sulphamic acids (3) will on the other hand lead only to the formation of the *o*- and *p*-aniliniumsulphonates respectively, as *C*-desulphonation does not occur under these mild conditions.[10a,12] In fact, besides the anilinium ion, the aniliniumsulphonates were found as the quenching products (Table 2), thus illustrating the intermediacy of the isomeric sulphophenylsulphamic acids (3) in concentrated sulphuric acid.

TABLE 1

U.v. data for the reaction of phenylsulphamic acid in 100.0% H_2SO_4

Compound(s)	$\lambda_{max.}$/nm [a]			
Starting material [b]	207 (7 000)	255 (320)	260 (360)	266 (290)
Intermediate(s)	218 (11 000)	261sh (850)	267 (1 220)	274 (1 060)
Sulphonic acid products [c]	215 (7 200)	258sh (710)	264 (1 010)	271 (960)

[a] Extinction coefficients (l mol^{-1} cm^{-1}) in parentheses. [b] Because of the rapid substrate conversion in 100% H_2SO_4, the spectrum was recorded in 98.4% H_2SO_4. [c] Containing *ca.* 10% 2,4-disulphonic acid.



SCHEME 1

TABLE 2

Products of potassium phenylsulphamate [a] in 99.97% H_2SO_4 after dilution of the samples to 46% H_2SO_4

	Quenching products (%) [b]			
	Anilinium	Aniliniumsulphonates [c]		
t/ks	ion	*ortho*	*para*	2,4-di
0.18	35.7 ± 0.5	13.9 ± 1.3	50.4 ± 1.2	<0.5
0.45	12.8 ± 0.3	19.7 ± 0.7	66.6 ± 0.6	0.9 ± 0.1
0.69	6.7 ± 0.3	19.6 ± 0.6	72.0 ± 0.6	1.7 ± 0.1
3.0	1.9 ± 0.3	18.8 ± 0.7	75.0 ± 0.6	4.3 ± 0.1
68.4	2.2 ± 0.4	17.4 ± 0.8	72.7 ± 0.7	7.7 ± 0.2
432	<0.5	18.9 ± 0.6	72.7 ± 0.5	8.4 ± 0.1

[a] The starting material contained *ca.* 2% anilinium sulphate, which was slowly sulphonated to equal amounts of *m*- and *p*-aniliniumsulphonic acid. [b] The material balance was 96.5 ± 1%. [c] The amount of *meta*-isomer was <2%.

At high conversion, after quenching, some additional anilinium-2,4-disulphonate was found. As was shown in control experiments, anilinium-2,4-disulphonic acid is not formed at all from orthanilic or sulphanilic acid under the sulphonation conditions (not even in a year). The formation of the 2,4-disulphonic acid from the intermediate(s) is the subject of the following paper.[13a]

N.m.r. Evidence.—Supporting evidence for the intermediacy of (3) was obtained by following the progress of the reaction of phenylsulphamic acid in 100.0% H_2SO_4 by n.m.r. (Figure 1). In the first two spectra, recorded after 7 and 16 min respectively, the conversion of the starting material (1) into a mainly *para*-substituted intermediate (3), characterized by its AA'BB' absorption pattern, can be observed. The final spectrum, recorded after 20 h, is identical with that of a 1 : 3 mixture of *o*- and *p*-aniliniumsulphonic acid. As to the *para*-intermediate (3) the aromatic protons *ortho* to the ammonium

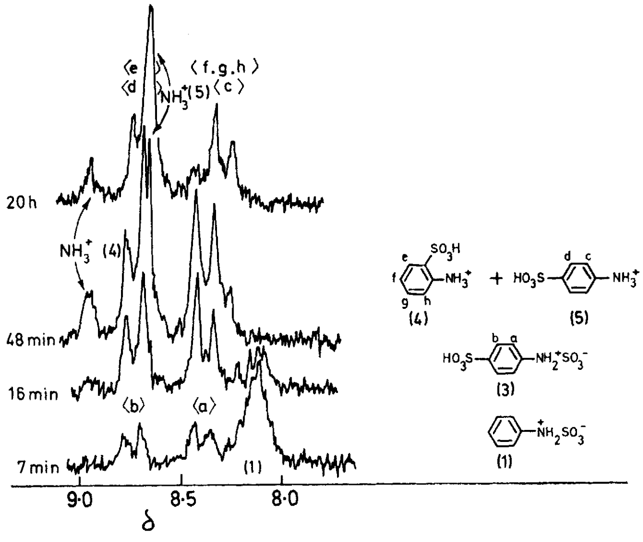


FIGURE 1 N.m.r. spectra for the reaction of $PhNHSO_3K$ (0.05M) in 100.0% H_2SO_4 at 31°

---

* For the sake of simplicity, the sulphamic acids are written in their neutral form.

[10] (*a*) E. Yu. Belyaev, L. I. Kotlyar, B. A. Porai-Koshits, and K. A. Serkova, *Reakts. spos org. Soedinenii*, 1968, **5**, 1033 (*Chem. Abs.*, 1969, **71**, 21 361); (*b*) E. Yu. Belyaev, L. I. Kotlyar, and L. M. Timokhina, *ibid.*, 1970, **7**, 294 (*Chem. Abs.*, 1970, **73**, 130 383).

[11] F. L. Scott and W. J. Spillane, *Chem. and Ind.*, 1967, 1999.

[12] A. C. M. Wanders, H. Cerfontain, and C. W. F. Kort, *Rec. Trav. chim.*, 1967, **86**, 301.

[13] P. K. Maarsen and H. Cerfontain, *J.C.S. Perkin II*, (*a*) following paper; (*b*) in the press.

substituent absorb at somewhat lower field (see *e.g.* the spectrum recorded after 48 min) than the corresponding protons of sulphanilic acid (5). The seeming absence of the absorption of the ammonium protons of the sulphamic acids (3) and (1) may be explained in terms of the much higher acidity of the $\overset{+}{N}H_2SO_3^-$ compared with the NH_3^+ group of the aniliniumsulphonic acids (4) and (5).[14]

A similar type of reaction route, *i.e.* ring sulphonation followed by removal of the side-chain substituent (Scheme 2) has been observed in the sulphonation of acetanilide (6; R = COMe) and of *N*-methylsulphonylaniline (6; R = SO_2Me) in concentrated sulphuric acid. In those cases the (*para*-)intermediates, *i.e.* *N*-acetylsulphanilic acid (7; R = COMe) and *N*-methylsulphonylsulphanilic acid (7; R = SO_2Me), were isolated from the reaction mixture[15] and identified unequivocally[13b] by u.v. and n.m.r. spectra of the sulphuric acid mixtures, respectively. In both cases the solvolysis of the intermediate is apparently slow relative to the substrate sulphonation.

$$\underset{(6)}{\mathrm{PhNHR}} \longrightarrow \underset{(7)}{\mathrm{HO_3SC_6H_4NHR}} \longrightarrow \underset{(5)}{p\text{-}\mathrm{HO_3SC_6H_4NH_3^+}}$$

SCHEME 2

TABLE 3

Pseudo-first-order rate constants for sulphonation of potassium phenylsulphamate at 25.0°

H_2SO_4 (%)	λ/nm[a]	$10^4\,{}_{ps}k_1/s^{-1}$ ($\pm$ 5%)	$-\log a_{H_2S_2O_7}$[b]
97.14 ± 0.05	261.5	0.028 8	7.52
99.15 ± 0.01	261.5	0.248	6.33
99.498 ± 0.005	261.5	0.566	5.94
99.758 ± 0.003	261.5	1.70	5.35
99.919 ± 0.003	262.0	9.47	4.56
99.959 ± 0.003	259.0, 261.5	26.0, 26.2	4.19
99.998 ± 0.003	270.0	59.8	3.79
99.993 ± 0.002	262.0, 270.0	75.7	3.69
99.988 ± 0.002	270.0, 274.0	95.6	3.59
100.007 ± 0.006	259.0	159	3.43
100.012 ± 0.006	270.0	152	3.34
100.033 ± 0.006	259.0	315	3.04

[a] Wavelengths at which the rate measurements were made.
[b] Taken from ref. 19*b*.

The same reaction path has in fact been proposed for the conversion of phenylsulphamic acid formed as an intermediate in the sulphonation of aniline in 96% H_2SO_4 at 140°.[16]

Kinetics.—The rate of sulphonation of potassium phenylsulphamate in a large excess of 97.14—100.03% H_2SO_4 at 25°, *i.e.* its conversion into the isomeric sulphophenylsulphamic acids, was determined by u.v. spectroscopy. In >99.96% H_2SO_4 the rate of formation of the intermediates is very much greater than the subsequent solvolysis into the aniliniumsulphonic acids. Since this condition, which leads to first-order kinetics with respect to the aromatic substrate, is no longer met below 99.96% H_2SO_4, the rate measurements were made at the wavelengths of the isosbestic points[17] of the isomeric intermediates and the anilinium-monosulphonic acid products (see Experimental section). Plots of log $(E_\infty - E_t)$ *versus* time were found to be linear for a substrate conversion up to at least 90%. The experimental pseudo-first-order rate constants ${}_{ps}k_1$ (Table 3) correlate satisfactorily with the activity of $H_2S_2O_7$, the curve approaching a straight line with a slope of 0.9 at both low and high acid concentrations (Figure 2). The correlation with h_0^2, suggested by Allan,[2] however, is less

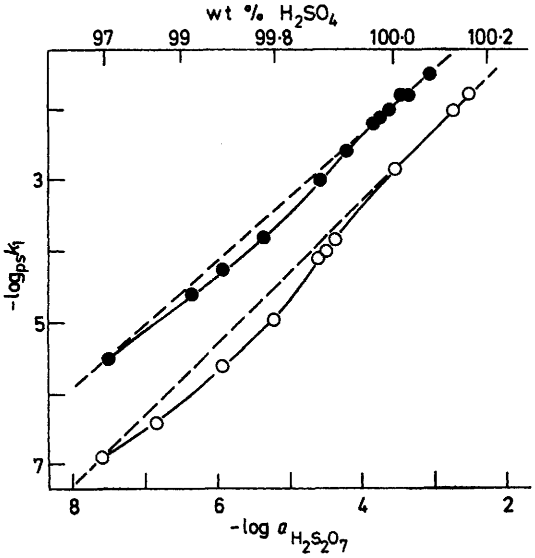


FIGURE 2 Correlation of log ${}_{ps}k_1$ with log $a_{H_2S_2O_7}$ for the reaction of phenylsulphamic acid (●) and *p*-difluorobenzene (○) in sulphuric acid at 25°

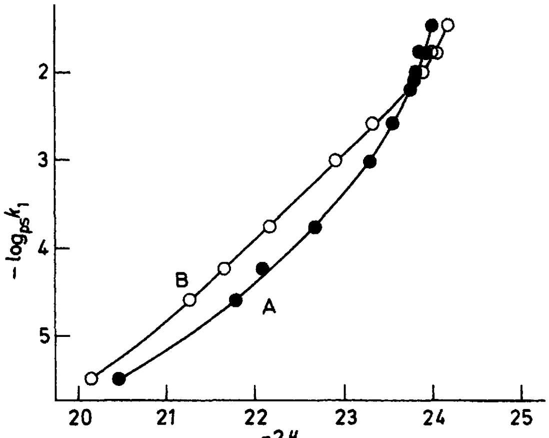


FIGURE 3 Correlation of log ${}_{ps}k_1$ with $2H_0$[18] for the reaction of phenylsulphamic acid in sulphuric acid at 25°. H_0 values according to refs. 18*a* (●, curve A) and 18*b* (○, curve B)

---

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

[15] J. W. Barnett and C. J. O'Connor, *Chem. and Ind.*, 1970, 1172.

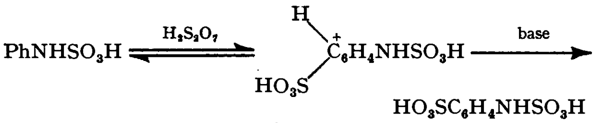
[16] E. R. Alexander, *J. Amer. Chem. Soc.*, 1947, **69**, 1599.

[17] H. Schlaefer and O. Kling, *Angew. Chem.*, 1956, **68**, 667.

[18] (*a*) R. J. Gillespie, T. E. Peel, and E. A. Robinson, *J. Amer. Chem. Soc.*, 1971, **93**, 5083; (*b*) M. I. Vinnik, *Russ. Chem. Rev.*, 1966, **35**, 802.

satisfactory, especially in the acid region close to 100% H_2SO_4 (Figure 3).

The kinetic behaviour of phenylsulphamic acid is very similar to that of the sulphonation of *p*-difluorobenzene [19a,b] and phenylmethanesulphonic acid [20] and may be explained by the mechanism advanced for those substrates, shown in Scheme 3. The overall reactivity of phenylsulphamic acid relative to benzene for 97.14% H_2SO_4 was calculated to be 3×10^{-5}, by use of the rate constant of benzene, obtained by extrapolation from the range 77.6—96.3% H_2SO_4.[21] The pseudo-first-order sulphonation rate constant of the anilinium ion in 100.033% H_2SO_4 at 25° was calculated by extrapolation of the data for the 100.067—102.3% H_2SO_4 range,[13b] to be 4.9×10^{-6} s^{-1}. Thus phenylsulphamic acid, which is sulphonated by $H_2S_2O_7$, is *ca.* 6 000 times as reactive as the anilinium ion, which undergoes sulphonation in weakly fuming sulphuric acid by the stronger electrophile $H_3S_2O_7^+$.[13b] According to Allan, phenylsulphamic acid in 98% H_2SO_4 at 40° reacts *ca.* 1 700 times faster than the anilinium ion.[2a]



SCHEME 3

TABLE 4

Isomer distribution for the sulphonation of phenylsulphamic acid [a] at 25°

H_2SO_4 (%)	Aniliniumsulphonic acids (%) *ortho*	*para*	2,4-di	Degree of *ortho*-substitution in primary sulphonation (%)
96.5 ± 1	28.3 ± 2 [b]	71.7 ± 2 [b]		
97.1 ± 0.1	28.6 ± 0.6	71.4 ± 1.2		
	28.9 ± 0.4	71.1 ± 0.8		
98.3 ± 0.2	25.6 ± 1.5 [b]	74.4 ± 1.5 [b]		
98.4 ± 0.1	26.2 ± 1.3	73.8 ± 2.0		
	26.4 ± 0.8	73.6 ± 1.3		
99.1 ± 0.1	25.2 ± 1.0	74.8 ± 2.0		
99.65 ± 0.1	22.8 ± 1.6	77.2 ± 2.3		
99.7 ± 0.1	21.5 ± 2 [b]	78.5 ± 2 [b]		
99.89 ± 0.01	18.6 ± 0.5	76.1 ± 1.0	5.3 ± 0.4	
99.9 ± 0.1	18.6 ± 2 [b]	77.4 ± 2 [b]	4.0 ± 1 [b]	
99.97 ± 0.01	18.9 ± 0.6	72.7 ± 0.5	8.4 ± 0.1	23.5 ± 1 [c]
99.99 ± 0.01	17.0 ± 1.2	73.9 ± 1.1	9.1 ± 0.3	
	16.3 ± 0.7	73.3 ± 0.9	10.4 ± 0.7	
100.04 ± 0.01	10.5 ± 1.4	65.2 ± 1.4	24.3 ± 0.2	25.5 ± 1 [c]
100.1 ± 0.1	7.5 ± 0.7	56.5 ± 1.0	36.0 ± 1.0	
100.14 ± 0.01	3.3 ± 1.2	52.7 ± 0.8	44.0 ± 0.2 [d]	27.5 ± 1 [c]

[a] See note *a* of Table 2. [b] These analyses were made by n.m.r. The substrate concentrations were *ca.* 0.02M, except for 96.5% H_2SO_4 (0.5M). The data for the *para*-acid include <2% metanilic acid. [c] Zero time extrapolated datum. [d] After long reaction times some 2,4,6-trisulphonic acid was formed (*ca.* 7%).

Isomer Distribution.—The composition of the mixtures of the products formed on reaction of phenylsulphamic acid in various concentrations of sulphuric acid at room temperature was determined by means of u.v.[22] and n.m.r.[23] multicomponent analyses. The results obtained with the two methods agree within experimental error (Table 4 and Figure 4). In ⩽99.7% H_2SO_4, the main products are orthanilic and sulphanilic acid, the amount of metanilic acid being <2%. The latter datum was independently substantiated by n.m.r. analysis after treatment of the reaction mixture with SO_3 at 100° (see Experimental section). In >99.7% H_2SO_4 anilinium-2,4-disulphonic acid is also formed. Its amount increases strongly with increasing sulphuric acid concentration. In 100.14% H_2SO_4 a small amount of the 2,4,6-trisulphonic acid was found.

In order to establish the ratio of the initially formed *ortho*- and *para*-intermediates in >99.7% H_2SO_4, the quenching technique was used again and the quantities of the three aniliniumsulphonates were determined by means of multicomponent u.v. analyses. The results (Table 4 and Figure 4) show that the relative amount of the *ortho*-isomer reaches a minimum value at 99.9% H_2SO_4.

The decrease of the $o : p$ ratio on varying the sulphuric acid concentration from 97 to 99.9% H_2SO_4 was also observed for the $f_o : f_p$ ratio of toluene and the $f_3 : f_4$ ratio of *o*-xylene.[19a] It may be explained in terms of steric hindrance for substitution *ortho* to the substituent, leading to a lowering of the degree of *ortho*-substitution when hydrogen abstraction from the intermediate σ-complex (Scheme 3) becomes (partly) rate limiting. According to the postulated sulphonation mechanism,[19a,b] the formation of the σ-complex becomes again rate limiting near 100% H_2SO_4. This is in fact reflected in an increase of the amount of *ortho*-isomer on going from 99.9% H_2SO_4 to higher sulphuric acid concentrations.

---

[19] (*a*) H. Cerfontain and C. W. F. Kort, *Internat. J. Sulfur Chem. C*, 1971, **6**, 123; C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, (*b*) 1969, **88**, 1298; (*c*) 1968, **87**, 24; (*d*) 1967, **86**, 865.

[20] Z. R. H. Nienhuis, W. J. Spillane, and H. Cerfontain, *Canad. J. Chem.*, 1972, **50**, 1591.

[21] A. W. Kaandorp, H. Cerfontain, and F. L. J. Sixma, *Rec. Trav. chim.*, 1962, **81**, 969.

[22] J. M. Arends, H. Cerfontain, I. S. Herschberg, A. J. Prinsen, and A. C. M. Wanders, *Analyt. Chem.*, 1964, **36**, 1802.

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

Protonation and Solvolysis.—In order to obtain information on the structure of the reacting and the major substrates in concentrated sulphuric acid, the protonation of the phenylsulphamate ion was studied over the whole aqueous sulphuric acid range. Because of solvolysis of phenylsulphamate in 1—70% H_2SO_4 into the anilinium ion, the kinetics of this reaction were also studied at 25°. The pseudo-first-order solvolysis rate constants show a maximum value at moderate sulphuric acid concentration (Table 5), as observed with aqueous perchloric [10] and hydrochloric [24] acid. This maximum was ascribed to the opposing effects of increasing protonation and decreasing water activity.[24]

TABLE 5

Pseudo-first-order rate constants for solvolysis of sodium phenylsulphamate at 25 ± 1°

H_2SO_4 (%)	$-\log_{ps}k_1^{obs}$/ s^{-1} [a]	$\log c_{H_3O^+}$ [b]	$-\log_{ps}k_1^{BH}$/ s^{-1} [c]	$-\log a_{H_2O}$ [d]
1.0	6.02	−0.92		
1.95	5.72	−0.63		
6.8	5.17	−0.06		
15.05	4.92	0.32		
22.75	4.60	0.53		
29.0	4.49	0.66		
34.6	4.26	0.75	3.95	0.172
38.0	4.07		3.86	0.219
41.3	4.05		3.91	0.270
44.8	4.04		3.96	0.334
49.8	4.18		4.15	0.448
61.9	4.55		4.55	0.86
69.9	5.10		5.10	1.34

[a] Measured at λ 275 and 280 nm. [b] The hydronium ion concentrations were taken from ref. 25*a*. These values differ only slightly from the ones calculated from the hydrogen sulphate and sulphate ion concentrations reported by Vinnik.[25b] [c] ${}_{ps}k_1^{BH} = {}_{ps}k_1^{obs}([BH] + [B^-])/[BH]$. The protonation ratios were calculated from the regression line: $\log([BH]/[B^-]) = m(H_0^{\frac{1}{2}} - H_0)$, where m and $H_0^{\frac{1}{2}}$ (see text) are mean values from measurements at 275 and 280 nm. [d] Taken from ref. 26.

The extinction of phenylsulphamic acid in a given sulphuric acid concentration was obtained by plotting log $(E_t - E_\infty)$ *versus* time for the conversion of the substrate into the anilinium ion and extrapolation to zero time.[27] By plotting the molar extinction coefficients at an appropriate wavelength *versus* the acidity functions [28] H_0, H_A, and H_0^a, sigmoidal curves were obtained from which the $[BH] : [B^-]$ ratios were calculated, where B^- and BH stand for the sulphamate anion and its protonated form respectively. At the wavelengths employed (275 and 280 nm) there is no medium effect on ε with either form. In aqueous sulphuric acid protonation follows the H_0 [28a] (or H_0^a,[28c] which are equal to each other up to 60% H_2SO_4), and not the H_A [28b] function, the slopes of log $[BH]/[B^-]$ *versus* H_0 and H_A being 0.89 ± 0.02 (*r* 0.999) and 1.28 ± 0.05 (*r* 0.996) respectively. Half-protonation occurs at H_0 −2.03 ± 0.05, a value close to that reported by Belyaev [10] for *p*-methoxyphenylsulphamic acid. The protonation occurs at the nitrogen atom.

For solvolysis in 1—29% H_2SO_4 a satisfactory linear correlation between $\log {}_{ps}k_1^{obs}$ and $\log c_{H_3O^+}$ (see Table 5) was observed, $d(\log_{ps}k_1^{obs})/d(\log c_{H_3O^+})$ being 0.95 ± 0.03 (*r* 0.995), whereas for 38—70% H_2SO_4 the logarithm of the calculated rate constant for the zwitterion, $\log {}_{ps}k_1^{BH}$, was found to be proportional to $\log a_{H_2O}$ (slope 1.11 ± 0.02; *r* 0.999). These results are consistent with the mechanisms advanced for the solvolysis of phenylsulphamic acid(s) in dilute and moderately concentrated aqueous mineral acids.[10, 24]

Structure of the Reacting and Major Species in Concentrated Sulphuric Acid.—Phenylsulphamic acid in 98—100% H_2SO_4 is sulphonated at least 10^3 times faster than the anilinium ion. The substrate yields mainly orthanilic and sulphanilic acid with at most a trace of metanilic acid. Accordingly the nitrogen atom of the reacting substrate must be unprotonated. Furthermore, it seems unlikely that species such as the zwitterion (9) or the *N*-protonated phenylsulphamic acid (11) would be so much more reactive than the anilinium ion. Besides, just as observed for the anilinium ion, we would then expect predominantly *meta-* and *para*-substitution.[*] This leaves the phenylsulphamate anion (8) or the neutral form of phenylsulphamic acid (10) as the possible reacting substrate.

The major species in concentrated sulphuric acid must, however, be an *N*-protonated one, *i.e.* (9) or (11), as is indicated by the following evidence. First, the u.v. spectral data of phenylsulphamic acid in concentrated sulphuric acid are very much like that of the anilinium ion, but differ strongly from the spectral data of unprotonated species, such as those of aniline in aqueous methanol and the phenylsulphamate anion (8) in 15%

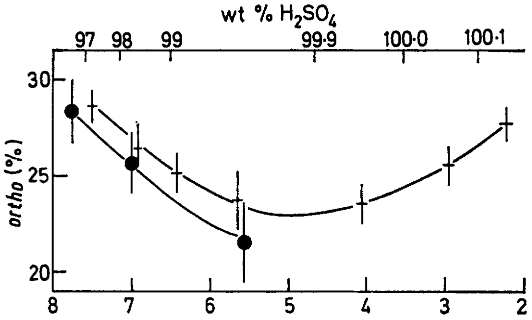


FIGURE 4 Degree of *ortho*-substitution in the primary sulphonation of phenylsulphamic acid at 25°, determined by u.v. (+) and n.m.r. (●) spectroscopy

---

[*] Nitration of the anilinium ion in 98% H_2SO_4 at 25° gave 62% *meta-*, 36.5% *para*, and 1.5% *ortho*-substitution [29] and sulphonation in 100.5% H_2SO_4 at 25° 49% *meta-*, 51% *para-*, and <2% *ortho*-substitution.[13b]

[24] W. J. Spillane, C. B. Goggin, N. Regan, and F. L. Scott, *Internat. J. Sulfur Chem.*, 1976, **8**, 565.

[25] (*a*) H. Chen and D. E. Irish, *J. Phys. Chem.*, 1971, **75**, 2672; (*b*) N. G. Zarakhani, N. B. Librovich, and M. I. Vinnik, *Russ. J. Phys. Chem.*, 1971, **45**, 981.

[26] W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, *J. Amer. Chem. Soc.*, 1960, **82**, 62.

[27] V. C. Armstrong and R. B. Moodie, *J. Chem. Soc.* (*B*), 1969, 934.

[28] (*a*) C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, 1969, **91**, 6654; (*b*) K. Yates, J. B. Stevens, and A. R. Katritzky, *Canad. J. Chem.*, 1964, **42**, 1957; (*c*) T. G. Bonner and J. Philips, *J. Chem. Soc.* (*B*), 1966, 650.

[29] S. R. Hartshorn and J. H. Ridd, *J. Chem. Soc.* (*B*), 1968, 1063.

H_2SO_4 (Table 6). Secondly, the reactivity of phenylsulphamic acid in *e.g.* 97% H_2SO_4 is *ca.* 10^{-5} times that of benzene. In concentrated sulphuric acid the unprotonated *N*-methylsulphonylaniline is 1.8 and 8 times more reactive than benzene in nitration [31] and in sulphonation by $H_2S_2O_7$ [13] respectively.

TABLE 6

U.v. spectra of aniline and phenylsulphamic acid

		K band		B band	
Substrate	Medium	$\lambda_{max.}$/nm	$\varepsilon_{max.}$	$\lambda_{max.}$/nm	$\varepsilon_{max.}$
$PhNH_2$	H_2O [a]	230	8 600	280	1 430
$PhNH_3^+$	15% H_2SO_4	203	8 500	254	160 [b]
	90% H_2SO_4	203	7 900	253	190 [b]
$PhNHSO_3^-$	15% H_2SO_4	227	8 350	273.5	690
$Ph\overset{+}{N}H_2SO_3^-$ [c]	98% H_2SO_4	207	7 000	260	360 [b]

[a] Containing a trace of methanol.[30] [b] The B band shows vibrational fine structure. [c] See text.

Now let us subsequently consider the following possible pairs of *N*-unprotonated reacting and *N*-protonated major species: (i) (9) and (8), (ii) (11) and (10), and (iii) (9) and (10). Equilibrium (3) which

$$\underset{(9)}{Ph\overset{+}{N}H_2SO_3^-} \rightleftharpoons \underset{(8)}{PhNHSO_3^-} + H^+ \qquad (3)$$

governs the ratio of (8) to (9) will be strongly dependent on the acidity of the medium. From the dependence of the ionization (3) on H_0 the ratio $[PhNHSO_3^-] : [Ph\overset{+}{N}H_2SO_3^-]$ was calculated for 97.0 and 100.0% H_2SO_4 to be $10^{-7.2}$ and $10^{-8.8}$ respectively. Accordingly, considering the sulphamate anion (8) as the reacting species, the rate increase on going from 97.0 to 100.0% H_2SO_4 would be 40 times less than predicted by the increase of $a_{H_2S_2O_7}$. As the observed rate dependence of phenylsulphamic acid on $a_{H_2S_2O_7}$ is the same as that of *p*-difluorobenzene, which substrate does not undergo protonation (Figure 2), this combination of major and reacting species can be ruled out.

The combination of (11) and (10) [equilibrium (4)] as the respective major and reacting species can be rejected

$$\underset{(11)}{Ph\overset{+}{N}H_2SO_3H} \rightleftharpoons \underset{(10)}{PhNHSO_3H} + H^+ \qquad (4)$$

by reasoning similar to that advanced to rule out combination (3). This leaves the third combination, *i.e.* phenylsulphamic acid is present as the zwitterion (9) and reacts *via* its neutral form (10). The position of equilibrium (5) is to a first approximation independent of the acidity.[*] The activity coefficients of both species (9) and (10) may, of course, vary in a different way with the medium, which in the concentration range under consideration largely consists of undissociated H_2SO_4.[19] In fact, *N*- and *O*-protonation are governed by different

$$(9) \rightleftharpoons (10) \qquad (5)$$

acidity functions, *viz.* H_0 and H_0^a.[14] The protonated phenylsulphamic acid (11) may be involved as a minor species in concentrated sulphuric acid, but, of course, the reactivity of this compound as well as that of (9) is negligibly small relative to that of (10). The position of the tautomeric equilibrium (5) can be calculated from physical and chemical data as follows.[33] The position of the equilibrium $BH \rightleftharpoons B^- + H^+$ is defined by log $([BH]/[B^-]) = m(H_x^{\frac{1}{2}} - H_x)$, where m is the slope of the graph obtained by plotting log $([BH]/[B^-])$ *versus* the appropriate acidity function H_x, and $H_x^{\frac{1}{2}}$ is the value of H_x at half-protonation. According to Scheme 4, the

$$\begin{tikzcd}
(9) \arrow[rr, rightleftharpoons] \arrow[dr, rightleftharpoons] & & (10) \arrow[dl, rightleftharpoons] \\
& (8) + H^+ &
\end{tikzcd}$$

SCHEME 4

position of equilibrium (5) is given by the equation log $([PhNHSO_3H]/[Ph\overset{+}{N}H_2SO_3^-]) = m_2[(H_0^a)^{\frac{1}{2}} - H_0^a] - m_1(H_0^{\frac{1}{2}} - H_0)$, where the two terms at the right hand side of the equation refer to the equilibria (10) $\rightleftharpoons$ (8) and (9) $\rightleftharpoons$ (8) respectively. The equilibrium (9) $\rightleftharpoons$ (8) is governed by H_0 with $H_0^{\frac{1}{2}} = -2.03$ and $m_1 = 0.89$. A rough estimate of the position of the equilibrium (10) $\rightleftharpoons$ (8) can be made by assuming that protonation on oxygen is governed by H_0^a and that half-protonation occurs at the same acidity as that of the phenylmethanesulphonate anion,[†] *i.e.* at $(H_0^a)^{\frac{1}{2}} = -6.5$ with $m = 0.7$.[34] The H_0^a value for 97% H_2SO_4 was estimated to be -8.1 ± 0.1 by extrapolation of the H_0^a scale which is known up to 90% H_2SO_4[28c] using the ionization ratios of several sulphonic acids over the range 80—98% H_2SO_4.[14] Thus, it was calculated that for 97% H_2SO_4 log $([PhNHSO_3H]/[Ph\overset{+}{N}H_2SO_3^-])$ is *ca.* −6.2.

The reactivity towards sulphonation of the species $PhNHSO_3H$ will be not much different from that of (unprotonated) $PhNHSO_2Me$.[‡] The ratio of the rates of the phenylsulphamic acid system and unprotonated methanesulphonanilide in 97—99.5% H_2SO_4 is *ca.*

---

[*] A similar tautomeric equilibrium in aqueous sulphuric acid between reacting and major species has been postulated for the acid catalysed hydrolysis of phosphinanilides.[32]

[†] Substituent effects on the protonation equilibria of sulphonates are small.[14]

[‡] The field and resonance effects of the $NHSO_2Me$ and $NHSO_2Ph$ substituents are almost equal.[35] The electron-withdrawing effect of the SO_2Me group is somewhat greater than that of the SO_3H group.[36] Accordingly $PhNHSO_3H$ is expected to be somewhat more reactive than $PhNHSO_2Me$.

[30] H. H. Jaffé and M. Orchin, 'Theory and Applications of Ultraviolet Spectroscopy,' Wiley, New York, 1962, ch. 12.

[31] S. R. Hartshorn, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1971, 2454.

[32] D. A. Tyssee, L. P. Bausher, and P. Haake, *J. Amer. Chem. Soc.*, 1973, **95**, 8066.

[33] (*a*) A. R. Katritzky, *Chimia*, 1970, **24**, 134; (*b*) A. Albert and E. P. Serjeant, 'The Determination of Ionization Constants,' Chapman and Hall, London, 1971, 2nd edn., p. 76.

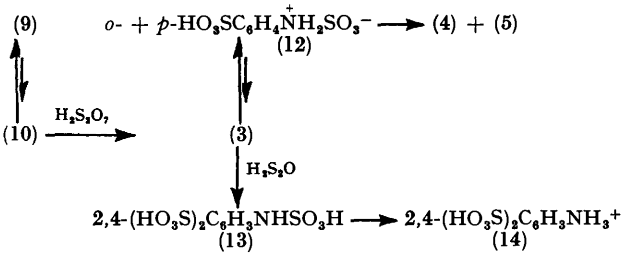
[34] A. Koeberg-Telder and H. Cerfontain, *J.C.S. Perkin II*, 1975, 226.

[35] C. Hansch, A. Leo, S. H. Unger, K. H. Kim, D. Nikaitani, and E. J. Lien, *J. Medicin. Chem.*, 1973, **16**, 1207.

[36] H. Zollinger and W. Wittwer, *Helv. Chim. Acta*, 1956, **39**, 347.

$10^{-5.5}$.[13] Thus, calculation on the basis of chemical data leads to log ([PhNHSO$_3$H]/[PhN$\overset{+}{H}_2$SO$_3^-$]) *ca.* −5.5 against the value of −6.2 derived from physical data.

Conclusions.—The sulphonation of phenylsulphamic acid in concentrated sulphuric acid may be described by Scheme 5. Phenylsulphamic acid, present predominantly as the zwitterion (9), reacts in the form of the minor species (10) with formation of *o*- and *p*-sulphophenylsulphamic acids. These compounds may either be solvolysed by reaction of the dipolar species (12) to yield the corresponding aniliniumsulphonic acids (4) and (5), or be sulphonated by reaction of species (3) to yield 2,4-disulphophenylsulphamic acid (13) which is readily solvolysed, probably also *via* its dipolar sulphamic acid, to yield anilinium-2,4-disulphonic acid (14).



Scheme 5

EXPERIMENTAL

Materials.—Potassium phenylsulphamate was prepared by the method of Boyland [37] but the reaction mixture was neutralized with a solution of potassium carbonate instead of hydroxide. The product was recrystallized from 96% ethanol and dried overnight over phosphorus pentaoxide (40° and 20 mmHg) (Found: C, 33.9; H, 2.9; K, 18.4; N, 6.6; O, 22.9; S, 15.0. Calc. for $C_6H_6KNO_3S$: C, 34.1; H, 2.85; K, 18.5; N, 6.65; O, 22.7; S, 15.2%). Sodium phenylsulphamate was synthesized by a different route [38] (Found: C, 36.8; H, 3.2; N, 7.15; Na, 11.8; S, 16.45. Calc. for $C_6H_6NNaO_3S$: C, 36.9; H, 3.1; N, 7.2; Na, 11.8; S, 16.45%). Anilinium hydrogen sulphate [39] was recrystallized four times from water to give the neutral salt (Found: C, 50.8; H, 5.75; N, 9.9; S, 11.15. Calc. for $C_{12}H_{16}N_2O_4S$: C, 50.7; H, 5.65; N, 9.85; S, 11.25%). The purification of the three anilinesulphonic acids has been described previously [14] (Found: C, 41.6—41.8; H, 4.0—4.2; N, 7.95—8.05; S, 18.3—18.4. Calc. for $C_6H_7NO_3S$: C, 41.6; H, 4.05; N, 8.1; S, 18.5%). Calcium aniline-2,4-disulphonate was made by heating sulphanilic acid in an excess of fuming sulphuric acid (20% 'free' SO$_3$) at 180° for 5 h.[40] The isolated calcium salt was recrystallized from 96% ethanol and dried over CaCl$_2$ (Found: C, 22.5; H, 2.6; Ca, 12.55. Calc. for $C_6H_5CaNO_6S_2,1.5H_2O$: C, 22.65; H, 2.55; Ca, 12.6%). Potassium aniline-2,4,6-trisulphonate was prepared by heating orthanilic acid with a large excess of fuming sulphuric acid (65% 'free' SO$_3$) for 3 h at 140°.[40] The mixture was poured onto ice, neutralized with KOH and evaporated to dryness. After several extractions with small amounts of aqueous ethanol, the pure trisulphonate, free from K$_2$SO$_4$, was obtained (Found: C, 15.3; H, 1.45; K, 24.5; N, 2.9; S, 20.2. Calc. for $C_6H_4K_3NO_9S_3,1.5H_2O$: C, 15.2; H, 1.5; K, 24.7; N, 2.95; S, 20.25%). All materials were kept in a desiccator in the presence of CaCl$_2$.

Attempts to synthesize *p*-sulphophenylsulphamate were unsuccessful. Both the reaction of SO$_3$ with sulphanilic acid, or its sodium salt, suspended in CCl$_4$,[9] and the reaction of the sodium salt with SO$_3$–pyridine in water,[41] yielded the starting material. Although Allan reported the synthesis of *p*-sulphophenylsulphamic acid *via* the Piria reaction,[42a] he was not able to isolate it because of rapid hydrolysis.[42b]

Sulphuric acid (98.4% H$_2$SO$_4$) was from B.D.H. (AnalaR grade). The purification of fuming sulphuric acid,[43] the preparation of absolute sulphuric acid, 100.00 ± 0.002%, and constant boiling sulphuric acid, 98.48 ± 0.01%, have been described.[19b] All other sulphuric acid concentrations were obtained by mixing known amounts of water, constant boiling, absolute, and fuming (102.51 ± 0.02% H$_2$SO$_4$ *) sulphuric acid (free of SO$_2$ [43]) as required.

Rate Measurements.—The reactions were carried out in a thermostatically controlled room, kept at 25.0 ± 0.5°. The u.v. measurements were made with Cary 14 and Zeiss PMQ II spectrophotometers, fitted with thermostatted (25.0 ± 0.1°) cell holders.

Rates of sulphonation of potassium and sodium phenylsulphamate in concentrated sulphuric acid were determined by u.v. spectroscopy. All plots of either log ($E_t - E_\infty$) or log ($E_t - E_{t+\Delta t}$) [44] against time were found to be linear for at least four half-lives. For reactions in $>100.00\%$ H$_2$SO$_4$, *i.e.* with $t_{\frac{1}{2}} < 1$ min, the substrate was first dissolved in 98.48% H$_2$SO$_4$. Then a known amount of the solution was transferred into the absorption cell and rapidly mixed with a large excess of sulphuric acid of the desired concentration.[19d] The temperature remained virtually constant (25.0 ± 0.5°). In H$_2$SO$_4$ $<99.96\%$ the substrate conversion was measured at the wavelengths of the isosbestic points of the intermediates and the monosulphonic acid products, *viz.* 259.0 and 261.5 nm. The u.v. spectrum of the mixture of phenylsulphamate in 100.00% H$_2$SO$_4$ after 10—15 min was taken to represent that of the intermediates.

The molar extinction coefficient of the 2,4-disulphonic acid, a minor product in $<99.96\%$ H$_2$SO$_4$, was found to deviate not more than 20% at 259.0 nm and 5% at 261.5 nm from the molar extinction coefficients of the intermediates and *o*- and *p*-aniliniumsulphonic acids.

The solvolysis of sodium phenylsulphamate in 1—69.9% H$_2$SO$_4$ at 25 ± 1° was studied by following the change of the u.v. spectrum of the reaction mixture with time. The eventual spectrum obtained was identical with that of the anilinium ion.[10, 14] The decrease of the extinction at 275.0 and 280.0 nm with time was used for the determination of the pseudo-first-order solvolysis rate constant. The molar

---

* The concentration of this acid was determined by titration from the relative amount of constant boiling sulphuric acid required to obtain absolute sulphuric acid, *i.e.* acid with a maximum freezing point.[19b]

[37] E. Boyland, D. Manson, and S. F. D. Orr, *Biochem. J.*, 1957, **65**, 417.

[38] W. Traube, *Ber.*, 1890, **23**, 1653.

[39] W. Huber, *Helv. Chim. Acta*, 1932, **15**, 1372.

[40] C. M. Suter, 'The Organic Chemistry of Sulfur,' Wiley, New York, 1944, p. 245.

[41] W. M. Lauer, M. M. Sprung, and C. M. Langkammerer, *J. Amer. Chem. Soc.*, 1936, **58**, 225.

[42] (*a*) Z. J. Allan and J. Podstata, *Coll. Czech. Chem. Comm.*, 1964, **29**, 752; (*b*) Z. J. Allan, personal communication.

[43] J. C. D. Brand, *J. Chem. Soc.*, 1950, 997.

[44] E. A. Guggenheim, *Phil. Mag.*, 1926, **2**, 538; M. Ahmad and J. Hamer, *J. Chem. Educ.*, 1964, **41**, 29.

extinction coefficient of the phenylsulphamate for a given wavelength and sulphuric acid concentration was obtained by extrapolation to zero time [27] of the linear plot of log E_t against time ($E_\infty = 0$). The error introduced is small since the time required for the dissolution of the substrate is small relative to the rate of solvolysis ($t_{\frac{1}{2}} > 2$ h).

TABLE 7

U.v. spectra of aniline and its sulphonic acids in 99.9% H_2SO_4

Substrate	$\lambda_{max.}$/nm [a]			
Anilinium ion	203 (7 900)	247.2 (150)	253.0 (190)	259.2 (140)
Orthanilic acid	217.5 (8 240)	259sh (780)	264.4 (1 050)	271.5 (930)
Metanilic acid	215 (8 110)	259sh (590)	264.3 (840)	271.2 (760)
Sulphanilic acid	214 (9 030)	259sh (800)	264.0 (1 140)	271.2 (1 060)
2,4-Disulphonic acid [b]	214.5 (9 080)	263sh (840)	268.8 (1 280)	276.3 (1 200)

[a] Extinction coefficients are in parentheses. [b] Protonation of the sulphonate groups is probably incomplete.[14]

Isomer Distribution.—For the multicomponent u.v. analyses, the absorbances of the reaction mixture and the solutions containing the components (all in sulphuric acid of the same concentration, free from SO_2 [43]) were measured simultaneously at a large number of equidistant wavelengths [preferably 208—230 nm with an increment of 1 nm because of the high degree of similarity of the spectra of metanilic and sulphanilic acid in the 245—280 nm region (Table 7), or 208—270 nm with an increment of 2 nm]. The absorbances were then subjected to a least squares treatment by an electronic computer. Satisfactory analyses with test mixtures were obtained.[45] The products of the reaction in 99.97—100.14% H_2SO_4 were analysed after pouring the reaction mixture and known amounts of reference solutions into a large excess of $\simeq$40% H_2SO_4. The absorbances of the resulting solutions were measured after the time required for complete hydrolysis of any of the sulphamic acids present. For the analysis of the products of reaction in 100.14% H_2SO_4 a solution of the potassium salt of aniline-2,4,6-trisulphonic acid in 40% H_2SO_4 was used as an additional reference.

The occurrence of *ca.* 2% anilinium sulphate in the starting material was established from the analysis of the reaction mixture of potassium phenylsulphamate in 98.4% H_2SO_4. In $H_2SO_4 > 99\%$ the amount of aniline was found to be lower because of the (slow) sulphonation of the anilinium ion which leads to about equal amounts of metanilic and sulphanilic acid.[13]

N.m.r. Analysis.—The spectra were recorded with a Varian HA 100 spectrometer using the Multi-scan averaging technique when the substrate concentration was $<1\%$ w/w. As external standards sodium 2,2,3,3-tetradeuterio-3-(trimethylsilyl)propionate (15% w/w) in D_2O or liquid tetramethylsilane in a sealed capillary were used, and as an internal standard the absorption peak of the sulphuric acid solvent itself.[34] The composition of the reaction mixture in a given sulphuric acid concentration was analysed in terms of the relative amounts of *o*-aniliniumsulphonic acid, the 2,4-disulphonic acid, and the sum of the *m*- and *p*-sulphonic acids by comparison of the resulting n.m.r. spectrum with those of the reference compounds (Table 8). The analysis of test mixtures of orthanilic and sulphanilic acid was satisfactory (99.8% H_2SO_4, orthanilic acid taken, 28.9%, and found, 30.5 ± 2%; 99.9% H_2SO_4, orthanilic acid taken, 20.6%, and found, 22 ± 2%).

Metanilic acid was not formed on reaction of potassium phenylsulphamate (0.35M) in 99.9% H_2SO_4, as was determined by adding an equivalent volume of SO_3 to the reaction mixture and heating the resulting *ca.* 110% H_2SO_4 solution for 4 h. From the absence of absorption below δ 9.0 (Table 8), it was concluded that the amount of metanilic acid is $<2\%$. The n.m.r. spectra of test mixtures of *o*- and *p*-, and of *m*- and *p*-aniliniumsulphonic acid after heating in 110% H_2SO_4 at 105° for 4 h showed that both the *o*- and *p*-isomer are converted completely into the 2,4,6-trisulphonic acid, δ 9.5 (s), but that the *m*-isomer had not reacted at all (taken, 20.1%, and found, 20.7 ± 1%).

TABLE 8

N.m.r. data of aniliniumsulphonic acids [a] in 98.4% H_2SO_4

Position SO_3H	δ [b]					
group(s)	H-2	H-3	H-4	H-5	H-6	NH_3 [c]
2		8.6	8.0—8.5			8.9
3	8.6		8.65	8.3—8.5		8.6
4	8.25	8.65		8.65	8.25	8.6
2,4		9.15		8.9	8.45	*d*

[a] 0.5M solutions. [b] Relative to external tetramethylsilane. For the 2-isomer, $J_{3.4}$ 7 and $J_{3.5}$ *ca.* 2 Hz; for the 3-isomer, $J_{2.4}$ *ca.* 2 Hz; for the 4-isomer, $J_{2.3}$ 8 Hz; for the 2,4-disulphonic acid, $J_{5.6}$ 8.5 and $J_{3.5}$ *ca.* 2 Hz. [c] The chemical shift varies with the sulphuric acid concentration. In H_2SO_4 $<98\%$ (slow) exchange of the ammonium protons occurs, resulting in a decrease of the NH_3 peak area. [d] Not observed, because of fast exchange.

We thank Dr. G. T. Berends and Mr. R. Bregman for synthetic assistance, Mr. H. Pieters for the elemental analyses, and Dr. C. W. F. Kort for stimulating discussions and for carrying out the calculations on the X 8 electronic computer of the Mathematical Centre, Amsterdam.

[6/065 *Received*, 9*th January*, 1976]

---

[45] P. K. Maarsen, Thesis (in English), University of Amsterdam, 1977.