Aromatic Sulphonation. Part 57.[1] Phenylsulphamic Acid in Sulphuric Acid: Solvolysis *versus* Sulphonation

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Phenylsulphamic acid in a large excess of 86.8% H_2SO_4 at room temperature yields both the anilinium ion and a mixture of aniliniumsulphonic acids by solvolysis and sulphonation (followed by solvolysis) respectively. Both the higher *ortho* : *para* sulphonation ratio as compared with that for >96% H_2SO_4 and the deviation of the sulphonation rate constant from the one estimated by extrapolation of the kinetics observed in >97% H_2SO_4, are discussed in terms of medium effects, and a change in the reacting substrate species and the sulphonating entity. The solvolysis and sulphonation reactions of the *o*- and *p*-sulphophenylsulphamic acids in a large excess of weakly fuming sulphuric acid at 25° are controlled by the electronic and steric effects of the aromatic sulpho-group. Phenylsulphamic acid in 99.9% H_2SO_4 at 100° under heterogeneous conditions undergoes both sulphonation and solvolysis, whereas under homogeneous conditions, only sulphonation is observed.

PHENYLSULPHAMIC ACID in aqueous sulphuric acid up to *ca.* 70% H_2SO_4 at 25° is only solvolysed (with formation of the anilinium ion) while in >96% H_2SO_4 only sulphonation takes place. The resulting *o*- and *p*-sulphophenylsulphamic acids in >96% H_2SO_4 are subsequently solvolysed with formation of the *o*- and *p*-aniliniumsulphonic acids † respectively. In 99.9—100.2% H_2SO_4 in addition some anilinium-2,4-di- and even small amounts of anilinium-2,4,6-tri-sulphonic acid are formed.[1]

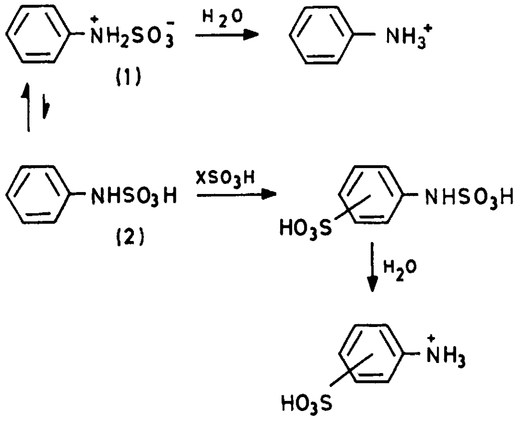
These results prompted us to study the formation of the di- and tri-sulphonic acid from phenylsulphamic acid in weakly fuming sulphuric acid in more detail. The anilinium-monosulphonic acids themselves in weakly fuming sulphuric acid at 25° are not sulphonated.[1] The behaviour of phenylsulphamic acid in 86.8% H_2SO_4, *i.e.* an acid concentration where solvolysis competes with sulphonation, was also studied.

RESULTS AND DISCUSSION

Solvolysis and Sulphonation in 86.8% H_2SO_4.—Reaction of potassium phenylsulphamate in 86.8% H_2SO_4 at 25° for 504 days yielded 51.4 ± 0.2% anilinium ion, 16.9 ± 0.5% orthanilic acid, <1% metanilic acid, and 31.7 ± 1.4% sulphanilic acid. The pseudo-first-order rate constants for solvolysis and sulphonation were calculated from this product composition and the observed overall rate constant ($_{ps}k_1$ 1.22×10^{-7} s^{-1}) to be log $_{ps}k_1^{solv}$ −7.20 and log $_{ps}k_1^{sulph}$ −7.23 respectively. The rate constant of solvolysis in 86.8% H_2SO_4 fits the linear graph of log $_{ps}k_1^{solv}$ (BH) *versus* loga_{H_2O}, found for the solvolysis of the zwitterion ($BH = Ph\overset{+}{N}H_2SO_3^-$) in the range 38—70% H_2SO_4.[1] The graph of log $_{ps}k_1^{solv}$ (BH) *versus* log a_{H_2O} over the total acid range 38.0—86.8% H_2SO_4 is linear with a slope of 1.14 ± 0.01 (*r* 0.980). Accordingly, in this acid concentration H_2O and not HSO_4^- (*cf.* ref. 2) is the major nucleophile involved in solvolysis.

The rate of sulphonation in 86.8% H_2SO_4 is *ca.* 20 times higher than expected on the basis of an extrapolation of the graph of log $_{ps}k_1^{sulph}$ *versus* log $a_{H_2S_2O_7}$ for the range 100—97% H_2SO_4.[1] The content of orthanilic acid in the sulphonated product is 35 ± 1%.

The solvolysis and sulphonation of phenylsulphamic acid in 86.8% H_2SO_4 may be explained in terms of Scheme 1. Extensive studies on the solvolysis of phenylsulphamic acid in moderate acidic media[1,3,4] revealed that the substrate reacts in its zwitterion form (1) with a molecule of water. Sulphonation in 97—100% H_2SO_4 occurs by reaction of the entity $H_2S_2O_7$ (*i.e.* X = HSO_4) with the minor uncharged species (2).[1] Based on an extrapolation of both the solvolysis and sulphonation kinetics to 86.8% H_2SO_4, it follows that sulphonation of the *N*-unprotonated species (2) by $H_2S_2O_7$ will compete with nucleophilic attack by water on the major species, *i.e.* the zwitterion (1). A similar type of competition between sulphonation and solvolysis was observed for acetanilide in *ca.* 70% H_2SO_4 at 80°.[5]



SCHEME 1

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† In systematic nomenclature, *o*- and *p*-sulphoanilinium ions.

[1] Part 56, P. K. Maarsen and H. Cerfontain, *J.C.S. Perkin II*, preceding paper.

[2] R. A. Cox, *J. Amer. Chem. Soc.*, 1974, **96**, 1059.

[3] (*a*) W. J. Spillane, C. B. Goggin, N. Regan, and F. L. Scott, *Internat. J. Sulfur Chem.*, 1976, **8**, 565; (*b*) F. L. Scott and W. J. Spillane, *Chem. and Ind.*, 1967, 1999.

[4] (*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*) Yu. Belyaev, L. I. Kotlyar, and L. M. Timokhina, *ibid.*, 1970, **7**, 294 (*Chem. Abs.*, 1970, **73**, 130 383).

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

In 86.8% H_2SO_4 the observed rate of sulphonation is *ca.* 20 times that estimated by extrapolation from the very concentrated sulphuric acid region (see earlier). Three possible explanations for this rate difference may be advanced. (i) Sulphonation occurs at least in part by $H_3SO_4^+$ (*i.e.* $X = H_2O$) instead of $H_2S_2O_7$ ($X = HSO_4$) as the sulphonating entity. The point of equal sulphonation rate contributions by the two species depends on the reactivity of the individual positions of the substrate.[6] Although the overall reactivity of phenylsulphamic acid relative to that of benzene is small (*e.g.* 3×10^{-5} for 97% H_2SO_4[1]), the reactivity of the uncharged species (*i.e.* $PhNHSO_3H$) will be at least equal to that of unprotonated methanesulphonanilide,* for which the acid concentration of equal rate contributions by the two mechanisms is at 87.5 ± 2% H_2SO_4.[8] (ii) The sulphamate anion, $PhNHSO_3^-$, also undergoes sulphonation. In 86.8% H_2SO_4, the amount of the anion is probably slightly smaller than that of its conjugated acid $PhNHSO_3H$.† Its reactivity will, however, be greater than that of neutral sulphamic acid.* It must be stressed that the more reactive anion may very well be sulphonated by the less reactive $H_3SO_4^+$ species. (iii) There is a distinct change in the ratio of the activity coefficients of the two partners of the tautomeric equilibrium $Ph\overset{+}{N}H_2SO_3^- \rightleftharpoons PhNHSO_3H$ on going from 97 to 86.8% H_2SO_4,† in such a way that the equilibrium shifts to the right hand side and enhances the effective reactivity of phenylsulphamic acid. In the range 100—97% H_2SO_4 the medium consists mainly of undissociated neutral H_2SO_4 molecules. In 86.8% H_2SO_4, the medium is significantly different, consisting mainly of the ionic species H_3O^+ and HSO_4^-.[6b]

The *o* : *p* ratio for the sulphonation of phenylsulphamic acid in 86.8% H_2SO_4 is significantly higher than in 97% H_2SO_4 (35 *versus* 28%[1] respectively). Such a decrease in the *o* : *p* ratio with increasing acid concentration has also been observed for the sulphonation of methanesulphonanilide[8] and the nitration of several anilides[11] in the range 80—98% H_2SO_4. It is opposite to the change in the *o* : *p* ratio observed for the sulphonation of *e.g.* toluene which was ascribed to the changeover from the $H_3SO_4^+$ to the $H_2S_2O_7$ mechanism.[6,12] As to the nitration of the anilides in mixed acid, Schofield[11] attributed the decrease of the *o* : *p* ratio with increasing sulphuric acid concentration to a change in solvation, *e.g.* to an increase in hydrogen bonding of the substituent. The presently observed decrease in the amount of orthanilic acid with increasing sulphuric acid concentration indicates that the effect of the variation of the substrate solvation dominates over any opposing effect due to the changeover from the $H_3SO_4^+$ to the $H_2S_2O_7$ mechanism.

As an alternative, the change in *ortho* content may be explained in terms of the sulphamate anion being the reacting substrate species in 86.8% H_2SO_4. The $NHSO_3^-$ substituent will have a smaller $-I$ effect than the $NHSO_3H$ group. Accordingly, the sulphamate anion will give rise to a higher *o* : *p* ratio than $PhNHSO_3H$. The change in the *o* : *p* sulphonation ratio of phenylsulphamic acid with increasing sulphuric acid concentration is similar to that of *e.g.* methanesulphonanilide, which compound reacts as the free base over the total acid region studied.[8] This seems to render this explanation unlikely.

TABLE 1

Products of potassium phenylsulphamate[a] in 100.04% H_2SO_4 at 25°, after dilution of the samples to 38.0% H_2SO_4

	Aniliniumsulphonates (%)[b]			
t/ks	*ortho*	*para*	2,4-di	$10^3 \times \hat{s}$[c]
0.00	25.5 ± 1[e]	74.5 ± 1[e]		
0.08[d]	23.8 ± 1.2	74.1 ± 1.0	2.1 ± 0.2	0.7
0.165[d]	21.2 ± 1.1	74.8 ± 1.0	4.0 ± 0.1	0.8
0.26	20.0 ± 0.8	73.7 ± 0.8	6.3 ± 0.1	0.6
0.39	17.0 ± 1.1	74.7 ± 1.0	8.3 ± 0.2	0.8
0.72	14.6 ± 1.3	73.2 ± 1.2	12.2 ± 0.2	1.1
3.6	11.2 ± 1.4	71.1 ± 1.2	17.7 ± 0.1	1.4
259	10.6 ± 1.3	65.0 ± 1.3	24.4 ± 0.1	0.9
950	10.0 ± 1.7	66.2 ± 1.6	23.8 ± 0.1	1.7

[a] The substrate contained 2% anilinium sulphate. All product data are corrected for this contamination. [b] The amount of metanilic acid was <2%. The u.v. analyses were made in duplicate. [c] Mean standard deviation in the extinction. [d] The quenching products of the first and second sample in fact also contained 9.2 and 1.8% of the anilinium ion respectively, illustrating that sulphonation of the starting compound was not complete. [e] Data calculated by zero time extrapolation.

Reactions in Weakly Fuming Sulphuric Acid.—The conversion of phenylsulphamic acid and its *C*-sulpho-derivatives in *ca.* 100% H_2SO_4 was followed by taking samples of the reaction mixture. These were poured into a large excess of dilute aqueous sulphuric acid (35—45% H_2SO_4), thus both quenching the sulphonation and solvolysing the sulphamic acid group to yield an ammonium group.[1] Accordingly, in the resulting dilute aqueous sulphuric acid solution, the amount of anilinium ion is equal to the amount of unchanged phenylsulphamic acid, the amount of *o*-aniliniumsulphonate equal to the sum of the amounts of *o*-sulphophenylsulphamic acid

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[*] According to Zollinger[7] the electron withdrawing effect increases in the order $SO_3^- < SO_3H < SO_2CH_3$.

[†] *N*- and *O*-protonation follow the H_0[9] and H_0^a[10] acidity function respectively. From the data obtained for the *N*-protonation of phenylsulphamate ion,[1] $\log[PhNHSO_3^-]/[Ph\overset{+}{N}H_2SO_3^-]$ for 86.8% H_2SO_4 was calculated to be −5.8. Applying the aforesaid assumptions regarding *O*-protonation of the sulphamate,[1] $\log[PhNHSO_3H]/[PhNHSO_3^-]$ for 86.8% H_2SO_4 was calculated to be *ca.* 0.4. Thus $\log[PhNHSO_3H]/[Ph\overset{+}{N}H_2SO_3^-]$ is *ca.* −5.4 for 86.8% H_2SO_4, whereas it was calculated before[1] to be *ca.* −6.2 for 97% H_2SO_4.

[6] C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, 1968, **87**, 24; (*b*) H. Cerfontain and C. W. F. Kort, *Internat. J. Sulfur Chem. C*, 1971, **6**, 123.

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

[8] P. K. Maarsen and H. Cerfontain, *J.C.S. Perkin II*, in the press.

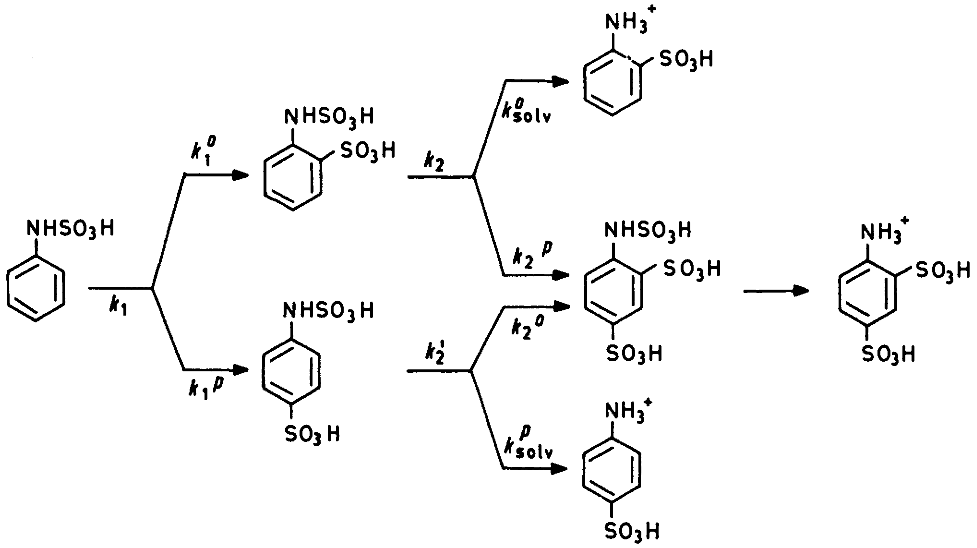
[9] C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, 1969, **91**, 6654.

[10] T. G. Bonner and J. Philips, *J. Chem. Soc.* (*B*), 1966, 650.

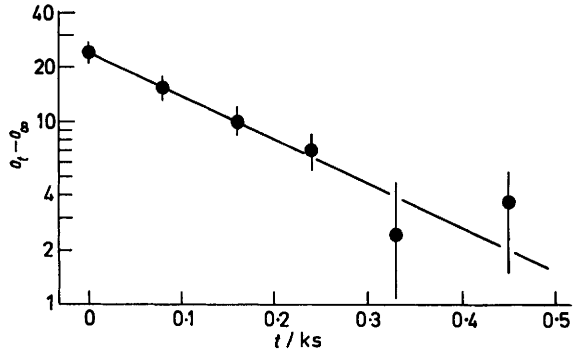
[11] S. R. Hartshorn, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1971, 2454.

[12] H. Cerfontain, F. L. J. Sixma, and L. Vollbracht, *Rec. Trav. chim.*, 1963, **82**, 659.

and *o*-aniliniumsulphonic acid, and the amount of *p*-aniliniumsulphonate equal to the sum of the amounts of *p*-sulphophenylsulphamic acid and *p*-aniliniumsulphonic acid. The composition of the samples in dilute aqueous sulphuric acid has been determined by multicomponent u.v. analysis.[13] The results for the reaction in 100.04% H_2SO_4 are given in Table 1. Similar results have been obtained for 100.14% and were reported previously for 99.97% H_2SO_4.[1] From these data and by analogy with the behaviour of phenylsulphamic acid in 86.8% H_2SO_4, it may be concluded that the intermediate *o*- and *p*-sulphophenylsulphamic acids in *ca.* 100% H_2SO_4 are in part solvolysed to yield the corresponding *o*- and *p*-aniliniumsulphonic acids respectively and in part sulphonated to yield after subsequent solvolysis the 2,4-disulphonic acid. This is illustrated in Scheme 2 in which, for the sake of simplicity, the sulphamic acids are written in their uncharged form. The pseudo-first-order overall rate constant for the conversion of *o*-sulphophenylsulphamic acid (k_2) was calculated from the slope of the linear graph, obtained by plotting log ($[ortho]_t - [ortho]_\infty$) *versus* time (see *e.g.* Figure), where $[ortho]_t$ is the amount of *o*-aniliniumsulphonate obtained after quenching in dilute aqueous sulphuric acid at time *t*. The initial amount of *o*-sulphophenylsulphamic acid (*A*, Table 2), which is equal to $[ortho]_o$, was taken directly from Table 1.* The ordinate of the graph, *i.e.* ($[ortho]_o - [ortho]_\infty$), is equal to the amount of the anilinium-2,4-disulphonic acid formed from the *o*-sulphophenylsulphamic acid at complete conversion. From the ratio of the amounts of the anilinium-mono-



SCHEME 2



Reactions of *o*- and *p*-sulphophenylsulphamic acid in 100.14% H_2SO_4 at 25.0°

TABLE 2

Reactions of *o*- and *p*-sulphophenylsulphamic acid in weakly fuming sulphuric acid at 25°

H_2SO_4 (%)	Substrate isomer	*A* [a] (%)	*B* [b] (%)	*C* [c] (%)	k_2^d/ks^{-1}	$k_{2'}^d$/ks^{-1}
100.04	*ortho*	25.5	10.5	15.0	1.9 ± 0.5	
	para	74.5	65.2	9.3	<0.1	
100.14	*ortho*	27.5	3.3	24.2	5.3 ± 1.3	
	para	72.5	52.7	19.8		0.07 ± 0.02

[a] The relative amount of the *o*- or *p*-sulphophenylsulphamic acid isomer (±1%) at zero time. [b] The amount of anilinium-monosulphonic acid (±1%) after complete conversion of the corresponding sulphophenylsulphamic acid (see *e.g.* Table 1). [c] The amount of the anilinium-2,4-disulphonic acid (±0.5%) at complete conversion, formed from the substrate isomer under consideration. [d] k_2 and $k_{2'}$ are the pseudo-first-order overall rate constants for the conversion of *o*- and *p*-sulphophenylsulphamic acid respectively (see Scheme 2).

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* This approach seems to be legitimate, as the amount of *p*-aniliniumsulphonate is virtually constant in the samples taken in the early stages of the reaction for both acid concentrations studied (*cf.* Figure). Accordingly in the very beginning of the reaction, all 2,4-disulphonic acid originates from *o*-sulphophenylsulphamic acid.

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

and -2,4-di-sulphonic acids formed from *o*-sulphophenylsulphamic acid (see Table 2, *B* and *C* respectively) and the overall rate constant for the conversion of *o*-sulphophenylsulphamic acid (k_2), the rates of solvolysis (k_{solv}^{o}) and sulphonation (k_2^{p}) of that compound were calculated (Table 3).

TABLE 3

Pseudo-first-order rate constants (ks^{-1})[a] for sulphonation and solvolysis of (sulpho)phenylsulphamic acids in weakly fuming sulphuric acid at 25°

	PhNHSO$_3$H		*o*- and *p*-HO$_3$SC$_6$H$_4$NHSO$_3$H			
H_2SO_4 (%)	Sulphonation		Sulphonation		Solvolysis	
100.04	k_1	34.7 ± 1.8 [b]				
	k_1^{o}	9.0 ± 0.5	k_2^{o}	<0.01	k_{solv}^{o}	0.8 ± 0.3
	k_1^{p}	25.7 ± 1.5	k_2^{p}	1.1 ± 0.4	k_{solv}^{p}	<0.1
	k_1^{o}/k_1^{p}	0.35 ± 0.02	k_2^{o}/k_2^{p}	<0.01	$k_{\mathrm{solv}}^{o}/k_{\mathrm{solv}}^{p}$	>5
100.14	k_1	115 ± 6 [b]				
	k_1^{o}	32 ± 5	k_2^{o}	0.02 ± 0.005	k_{solv}^{o}	0.6 ± 0.3
	k_1^{p}	83 ± 8	k_2^{p}	4.7 ± 1.5	k_{solv}^{p}	0.05 ± 0.02
	k_1^{o}/k_1^{p}	0.38 ± 0.02	k_2^{o}/k_2^{p}	0.004 ± 0.002	$k_{\mathrm{solv}}^{o}/k_{\mathrm{solv}}^{p}$	12 ± 8

[a] The rate constants are defined in Scheme 2. [b] Calculated by extrapolation of the graph log $_{\mathrm{ps}}k_1$ *versus* log $a_{H_2S_2O_7}$ over the range 97.1—100.03% H_2SO_4.[1]

The overall rate constant for the conversion of *p*-sulphophenylsulphamic acid (k_2'), its amount at zero time (*A*, Table 2) and the amounts of *p*-aniliniumsulphonic acid (*B*) and the anilinium-2,4-disulphonic acid (*C*) formed at complete conversion of the *p*-sulphophenylsulphamic acid, were obtained similarly. The rate constants for the solvolysis (k_{solv}^{p}) and sulphonation (k_2^{o}) of *p*-sulphophenylsulphamic acid are compiled in Table 3. The overall rate of sulphonation of *o*- and *p*-sulphophenylsulphamic acid ($k_2^{o} + k_2^{p}$) is only 25 times smaller than that of phenylsulphamic acid itself (k_1). This decrease in the rate of sulphonation upon introduction of a sulpho-group into the aromatic ring is very small as compared with that of *e.g.* toluene.[14] It may be explained in terms of a higher relative content of the reactive species, *i.e.* ArNHSO$_3$H in the case of the sulphophenylsulphamic acids as compared with the parent phenylsulphamic acid. The nitration of *p*-nitroaniline under certain conditions leads to the formation of 2,4,6-trinitroaniline, the yield of 2,4-dinitroaniline being very small.[15] Apparently, the nitro-group shows the same effect even stronger. This 'compensating' type of effect is also responsible for the large difference in sulphonation reactivity of *p*- and *o*-sulphophenylsulphamic acid, the $k^{o}:k^{p}$ ratio being 100 ± 50 times smaller than that for the sulphonation of phenylsulphamic acid itself.* Based on a comparison with the basicities of orthanilic and sulphanilic acid [16] it is to be expected that the relative amount of *N*-unprotonated substrate species will be much higher for *o*- than for *p*-sulphophenylsulphamic acid.

The rate of solvolysis of *o*-sulphophenylsulphamic acid is *ca.* 10 times that of the *para*-isomer. This may be explained in terms of both steric and electronic effects, since electron-withdrawing substituents are known to accelerate the solvolysis of phenylsulphamic acids in acidic media.[3,4]

The formation of *ca.* 7% anilinium-2,4,6-trisulphonic acid in 100.14% H_2SO_4 takes place apparently by sulphonation of the 2,4-disulphophenylsulphamic acid in its neutral form (ArNHSO$_3$H), which reaction competes with solvolysis of the latter compound in its zwitterion form ($Ar\overset{+}{N}H_2SO_3^-$), leading to anilinium-2,4-disulphonic acid.

Reactions under Heterogeneous Conditions in 99.9% H_2SO_4 *at* 100°.—There is an apparent contradiction between the phenylsulphamic acid 'rearrangement' in dioxan–sulphuric acid at 100°,[17,18] which involves a rapid *N*-desulphonation followed by a slow and incomplete *C*-sulphonation [17a] and that in neat concentrated sulphuric acid at 25° which involves *C*-sulphonation followed by *N*-desulphonation.[1] Spillane [17b] ascribed this phenomenon to the difference in conditions of the two experiments, the former being carried out under heterogeneous conditions and the latter in a large excess of sulphuric acid which ensures a homogeneous reaction. Supporting evidence for this view comes from some preparative experiments we performed with potassium phenylsulphamate in 99.9% H_2SO_4 at 100°, both under homogeneous and heterogeneous conditions. The homogeneous conditions were achieved either by adding the substrate slowly and with rapid stirring to the sulphuric acid at 100° (final substrate concentration 0.3M), or by heating a solution of the substrate (0.3M), prepared in 99.9% H_2SO_4 at 40°, rapidly to 100°. The reaction was stopped after 20 min by external water cooling. The products were found to be orthanilic and sulphanilic acid (Table 4), as observed before for reaction in 96.5—100.1% H_2SO_4 at 25° [1] and in 97% H_2SO_4 at 100°.[19]

The (partly) heterogeneous conditions were created by adding the phenylsulphamate quickly and without

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* This is in contrast with the sulphonation of toluene and its *o*- and *p*-sulphonic acids, where the k^{o}/k^{p} ratio for mono- and di-substitution is about the same.[14]

[14] H. Cerfontain, *Rec. Trav. chim.*, 1965, **84**, 551.

[15] S. R. Hartshorn and J. H. Ridd, *J. Chem. Soc.* (*B*), 1968, 1068.

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

[17] (*a*) W. J. Spillane and F. L. Scott, *J. Chem. Soc.* (*B*), 1968, 779; (*b*) W. J. Spillane, *Internat. J. Sulfur Chem.*, 1973, **8**, 469.

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

stirring to 99.9% H_2SO_4 at 100°, since the substrate then appears to dissolve slowly. After 20 min reaction apart from orthanilic and sulphanilic acid, the formation of *ca.* 40% aniline was observed (Table 4). Sulphonation of the anilinium ion in 99.9% H_2SO_4 is extremely slow.[19] Apparently, under these heterogeneous conditions, phenylsulphamic acid is, in part, hydrolysed as observed in the homogeneous reaction in acidic media of a lower sulphonating activity, *e.g.* in aqueous $\leqslant$ 86.8% H_2SO_4 or in aqueous $HClO_4$.[4]

TABLE 4

Reaction products of potassium phenylsulphamate (0.3M) in 99.9% H_2SO_4 at 100° [a]

Conditions	Anilinium ion (%)	Aniliniumsulphonic acids (%) *ortho*	*para*	2,4-di
Homogeneous		13.6 ± 2	82.9 ± 2	3.5 ± 1.5
Homogeneous [b]		17.2 ± 2	78.4 ± 2	4.4 ± 1.5
Heterogeneous	39.5 ± 4	11.5 ± 2	49 ± 4	

[a] Reaction mixtures were analysed by multicomponent n.m.r. analysis. [b] Temperature 40—100°.

EXPERIMENTAL

The synthesis and purification of all materials has been described before.[1]

Rate Measurements.—Reactions were carried out in a thermostatically controlled room, kept at 25.0 ± 0.5°. The u.v. measurements for the reaction of potassium phenylsulphamate in 86.8% H_2SO_4 were carried out using a Cary 14 spectrophotometer. The rate was determined from the dependence of the u.v. extinction at 263.5 and 270.0 nm on reaction time. Plots of log $(E_t - E_\infty)$ *versus* time were found to be linear for at least three half lives ($t_{\frac{1}{2}}$ 66 days).

The rates of reaction of the sulphophenylsulphamic acids in weakly fuming sulphuric acid were determined from the dependence on time of the composition of the samples as determined after dilution to *ca.* 40% H_2SO_4. The plots of log $(AS_t - AS_\infty)$ against time were found to be linear for at least 50% conversion, where AS_t represents the amount of *o*- or *p*-aniliniumsulphonate obtained by multicomponent u.v. analysis.

Isomer Distributions.—The composition of the product mixtures obtained on reaction of phenylsulphamic acid in both 86.8% H_2SO_4 and weakly fuming sulphuric acid at 25° were determined by multicomponent u.v. analysis.[13] Measurements were made over the combined regions 204—228 (increment 1 nm) and 248—275 nm (increment 2 nm) on a Zeiss PMQ 3 spectrophotometer. Absorbances of the reaction mixture in 86.8% H_2SO_4 were measured simultaneously with those of the freshy prepared reference solutions in the same acid concentration, containing potassium phenylsulphamate, anilinium sulphate, and the three aniliniumsulphonates. Samples of the reaction mixtures in 100.04 and 100.14% H_2SO_4 were poured into an excess of 27.8 and 29.6% H_2SO_4, respectively, to yield final acid concentrations of 38.0 and 40.2% H_2SO_4, respectively. Solutions of the references, *i.e.* anilinium sulphate, the three aniliniumsulphonates, and calcium aniline-2,4-disulphonate (4-aminobenzene-1,3-disulphonate) made up in 100.04% H_2SO_4, were similarly diluted to obtain 38.0 and 40.2% H_2SO_4 solutions. For the analysis of the reaction products formed in 100.14% H_2SO_4 and a reaction time of one year tripotassium aniline-2,4,6-trisulphonate was included as a reference compound. Because of the similarity of the u.v. spectra of the monosulphonic acids,[1] the *meta*- and *para*-isomers were slightly interchangeable (<1.5%) in 86.8% H_2SO_4, while the *ortho*- and *meta*-sulphonates were slightly interchangeable (< 1.5%) in *ca.* 40% H_2SO_4. When the aniline-2,4,6-trisulphonate was present in the reaction mixture in 40% H_2SO_4, nearly random interchange between the three anilinium-monosulphonates occurred, due to the relatively high extinction of the trisulphonate.*

Reaction mixtures of potassium phenylsulphamate (0.3M) in 99.9% H_2SO at 100° were cooled after 20 min of reaction and analysed by multicomponent n.m.r. analysis using a Varian HA 100 n.m.r. spectrometer. N.m.r. data of the anilinium sulphonic acids in 98.4% H_2SO_4 have been presented before.[1] The absorptions of the anilinium ion, δ 7.8—8.1 (ArH) and 8.2 (NH_3), are in the same region as the high field absorptions of orthanilic and sulphanilic acid. Accordingly, in the presence of the anilinium ion, the accuracy of the analysis is reduced (see Table 4).

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* Tripotassium aniline-2,4,6-trisulphonate in 39.4% H_2SO_4 exhibits the following absorption maxima (nm) and corresponding molar extinction coefficients (l mol^{-1} cm^{-1}): 207, 26 000; 213, 27 000; 260, 11 500; and 313, 2 850. The high values indicate a (partly) unprotonated amino-group.

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