Aromatic Sulphonation. Part 58.[1] Protonation and Sulphonation of Methanesulphonanilide in Aqueous Sulphuric Acid

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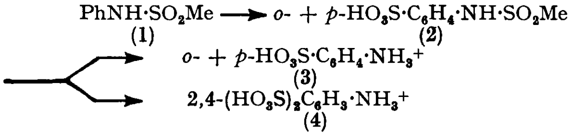
Kinetic and protonation studies in aqueous sulphuric acid at 25 °C show that sulphonation of methanesulphonanilide is preceded by a protonation equilibrium step. Half-protonation of the anilide occurs at 84% H_2SO_4. The substrate entity undergoing sulphonation is the unprotonated methanesulphonanilide. At relatively low sulphuric acid concentrations it is sulphonated by the entity $H_3SO_4^+$ and above 90% H_2SO_4 by the entity $H_2S_2O_7$. The decrease in the *ortho* : *para* sulphonation ratio with increasing sulphuric acid concentration in the region 80—99.8% H_2SO_4 is ascribed to a change in substrate solvation.

THE rate of sulphonation of phenylsulphamic acid in the concentration range 97—100% H_2SO_4 was found, to a first approximation, to be independent of the acidity of the medium. This was explained in terms of a tautomeric equilibrium between the non-reactive *N*-protonated majority species $Ph\overset{+}{N}H_2SO_3^-$, and the reactive *O*-protonated minority species $PhNHSO_3H$.[2] As reference compounds in which the latter tautomeric structure is immobilized by a fixed substituent, methanesulphonanilide ($PhNHSO_2Me$) and methyl phenylsulphamate ($PhNHSO_2OMe$) were considered. The former was preferred in view of the instability of an alkyl sulphate in acidic media.[3]

The nitration of methanesulphonanilide in sulphuric acid has been investigated previously. From studies of product formation [4,5] and nitration kinetics in 60—80% H_2SO_4 [5] it was concluded that the unprotonated substrate was the reacting species which yields the *o*- and *p*-nitro-products. In preliminary experiments we observed that the rate of sulphonation of methanesulphonanilide in >80% H_2SO_4 increases less rapidly with increasing acid concentration than the rates for other aromatic substrates which do not undergo protonation.[6] Protonation of methanesulphonanilide was reported [5] to occur in >50% H_2SO_4. The u.v. extinction coefficient of the protonated form was, however, not measured because of the interference of sulphonation in the region >90% H_2SO_4.[5] By combining protonation equilibrium and sulphonation rate studies we aimed to overcome this problem and to obtain information pertinent to the mechanism of sulphonation.

RESULTS

The reaction of methanesulphonanilide (1) in aqueous sulphuric acid was followed by ^1H n.m.r. (Table 1) and u.v. spectroscopy (Table 2). The n.m.r. spectra indicate that the substrate is converted into a mixture of *o*- and *p*-sulphomethanesulphonanilides (2), the *para*-isomer being the main product (Scheme). The sulphomethanesulphonanilides (2) are subsequently converted into anilinium-*o*- and -*p*-sulphonic acids (3) and anilinium-2,4-disulphonic acid (4) by solvolysis and by sulphonation followed by solvolysis, respectively. The conversion of the sulphomethanesulphonanilides (2) is slow relative to the preceding sulphonation, in both 86.8 and 99.7% H_2SO_4.



$$\underset{(1)}{PhNH\cdot SO_2Me} \longrightarrow o\text{-} + \underset{(2)}{p\text{-}HO_3S\cdot C_6H_4\cdot NH\cdot SO_2Me}$$

$$\longrightarrow o\text{-} + \underset{(3)}{p\text{-}HO_3S\cdot C_6H_4\cdot NH_3^+}$$

$$\longrightarrow \underset{(4)}{2,4\text{-}(HO_3S)_2C_6H_3\cdot NH_3^+}$$

SCHEME

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[1] Part 57, P. K. Maarsen and H. Cerfontain, *J.C.S. Perkin II*, 1977, 929.

[2] P. K. Maarsen and H. Cerfontain, *J.C.S. Perkin II*, 1977, 921.

[3] (*a*) B. D. Batts, *J. Chem. Soc.* (*B*), 1966, 551; (*b*) E. E. Gilbert, ' Sulfonation and Related Reactions,' Interscience, New York, 1965, ch. 6.

[4] R. L. Shriner, M. T. Goebel, and C. S. Marvel, *J. Amer. Chem. Soc.*, 1932, **54**, 2470.

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

[6] H. Cerfontain and C. W. F. Kort, *Internat. J. Sulfur Chem.*, 1971, **6**, 123.

Protonation.—The low solubility of the unprotonated methanesulphonanilide in aqueous sulphuric acid made it necessary to study its protonation by u.v. spectroscopy (instead of ^{1}H n.m.r. spectroscopy, which had been applied successfully to some aliphatic sulphonamides).[7] Because of the occurrence of sulphonation of the substrate in concentrated sulphuric acid we studied the protonation at a wavelength where the change in extinction as a result of sulphonation is almost negligible, *viz.* 221.4 nm, which is also near the wavelength of maximum absorbance of the unprotonated form in dilute aqueous sulphuric acid (Table 2). By plotting the molar extinctions against the acidity functions H_0,[8] H_A,[9] and H_0^{a},[10] sigmoid curves were obtained (*e.g.* Figure 1). There is no medium effect on the protonated form. The medium effect on the unprotonated form is substantial. Values of log ([BH$^+$]/[B]) were determined in the acid concentration range 76.3—88.2% H_2SO_4 and plotted against the three acidity functions. The slopes of the straight lines obtained and the H_x values at which half-protonation occurs are given in Table 3. On the basis of the unit slope criterion it follows that the protonation is governed by the H_0 acidity function. This indicates that protonation occurs on nitrogen.

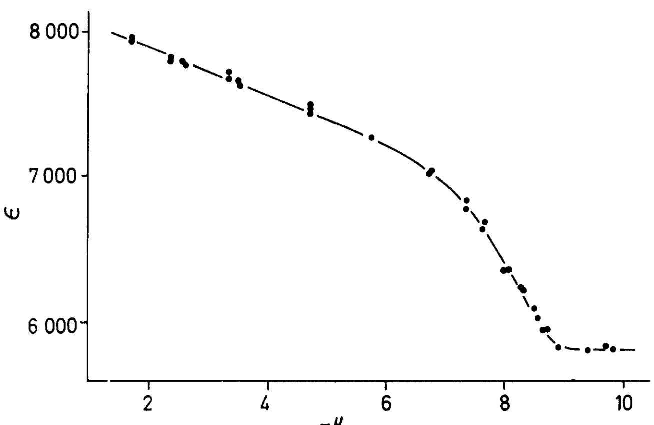

FIGURE 1 Correlation of the molar extinction coefficient of methanesulphonanilide at 221.4 nm with H_0

TABLE 2

U.v. data of methanesulphonanilide and its reaction products in 85.0% H_2SO_4

Compound	$\lambda_{max.}$/nm [a]
PhNH·SO$_2$Me [b]	218 (6 700), 267 (300)
HO$_3$S·C$_6$H$_4$·NHSO$_2$Me [c]	238 (11 900), 267sh
HO$_3$S·C$_6$H$_4$·NH$_3^+$ [c]	215 (8 600), 258sh, 264 (900), 270 (800)

[a] Molar extinctions in parentheses. [b] In 85% H_2SO_4 *ca.* 50% of the compound is protonated. In 29.6% H_2SO_4, *i.e.* for the free base, $\lambda_{max.}$ 221 nm (ε 8 100). [c] Mixture of *ortho*- and *para*-isomers in *ca.* 1 : 6 ratio.

TABLE 1

^{1}H N.m.r. data for methanesulphonanilide (0.5M) and its reaction products in 86.8% H_2SO_4 [a]

<table>
<tr><th rowspan="2">Compound</th><th colspan="7">δ [b]</th></tr>
<tr><th>2-H</th><th>3-H</th><th>4-H</th><th>5-H</th><th>6-H</th><th>NH</th><th>Me</th></tr>
<tr><td>PhNH·SO$_2$Me</td><td colspan="5">← 7.8—8.1 →</td><td>*c*</td><td>3.88</td></tr>
<tr><td>*o*-HO$_3$S·C$_6$H$_4$·NH·SO$_2$Me</td><td></td><td>8.5</td><td colspan="3">← 7.8—8.3 →</td><td>*c*</td><td>3.92</td></tr>
<tr><td>*p*-HO$_3$S·C$_6$H$_4$·NH·SO$_2$Me</td><td>7.94</td><td>8.50</td><td></td><td>8.50</td><td>7.94</td><td>*c*</td><td>3.88</td></tr>
<tr><td>*o*-HO$_3$S·C$_6$H$_4$·NH$_3^+$</td><td></td><td>8.65</td><td colspan="3">← 8.0—8.5 →</td><td>9.3 [d]</td><td></td></tr>
<tr><td>*p*-HO$_3$S·C$_6$H$_4$·NH$_3^+$</td><td>8.28</td><td>8.66</td><td></td><td>8.66</td><td>8.28</td><td>9.1 [d]</td><td></td></tr>
<tr><td>MeSO$_3$H</td><td></td><td></td><td></td><td></td><td></td><td></td><td>3.81</td></tr>
</table>

[a] More than 50% of the substrate is present in the protonated form (see text). [b] The absorptions of the aromatic protons of *o*-sulphomethanesulphonanilide and orthanilic acid are obscured (for the greater part) by those of the corresponding *para*-isomers. The data for anilinium-*o*-sulphonic acid were confirmed from spectra of an authentic sample, those for *o*-sulphomethanesulphonanilide were calculated by assuming additivity of substituent effects. For the *para*-isomers $J_{2.3} = J_{5.6} = 8.5$ Hz. ^{1}H N.m.r. data for the aniliniumsulphonic acids in 98—99% H_2SO_4 have been reported previously.[2] [c] Not observed because of fast exchange. [d] The relatively small peak area indicates proton exchange.

Kinetics.—The rate of sulphonation of methanesulphonanilide, *i.e.* its conversion into the isomeric sulphomethanesulphonanilides, was determined in a large excess of 76.5—99.61% H_2SO_4 at 25 °C. The observed first-order rate constants are given in Table 4. The graph of log $k_1^{obs.}$ *vs.* % H_2SO_4 shows a strong downward curvature with increasing acid concentration in comparison with the graphs of benzene and chlorobenzene [6] (Figure 2). The ionization ratios and first-order rate constants for the free base, k_1^{fb} (Table 4), were calculated according to equations (i) and (ii).[11] The graph of log k_1^{fb} against log $a(H_3SO_4^+)$ (Figure 3) is linear at acid concentrations <85% H_2SO_4 and that of log k_1^{fb} against log $a(H_2S_2O_7)$ (Figure 4) is linear

$$\log([BH^+]/[B]) = m(H_0^{\frac{1}{2}} - H_0) \qquad (i)$$

$$k_1^{fb} = k_1^{obs}[B]_{stoich}/[B] \qquad (ii)$$

in the range 90—97% H_2SO_4, both with a slope of 0.87 ± 0.02 (correlation coefficients 0.998, both based on five points). The point of equal contributions by the two sulphonating species $H_3SO_4^+$ and $H_2S_2O_7$ to the overall reaction rate was determined from the rate profiles [6,12] to be at 87.5 ± 2% H_2SO_4. The reactivities of unprotonated methanesulphonanilide relative to benzene were calculated for 77.8 and 96.1% H_2SO_4 to be 60 and 8, respectively. The first-order rate constants for sulphonation of benzene in 77.8% H_2SO_4 (by $H_3SO_4^+$) and 96.1% H_2SO_4 (by $H_2S_2O_7$) are $(3.55 \pm 1.0) \times 10^{-8}$ and (5.25 ±

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[7] (*a*) R. G. Laughlin, *J. Amer. Chem. Soc.*, 1967, **89**, 4268; (*b*) M. Liler, 'Reaction Mechanisms in Sulphuric Acid,' Academic Press, London, 1971, p. 110.

[8] (*a*) M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, 1963, **85**, 878; (*b*) R. J. Gillespie, T. E. Peel, and E. A. Robinson, *ibid.*, 1971, **93**, 5083.

[9] (*a*) K. Yates, J. B. Stevens, and A. R. Katritzky, *Canad. J. Chem.*, 1974, **42**, 1957; (*b*) C. D. Johnson, A. R. Katritzky, and N. Shakir, *J. Chem. Soc.* (*B*), 1971, 1235.

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

[11] J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, 'Nitration and Aromatic Reactivity,' Cambridge University Press, 1971, ch. 8.

0.2) × 10^{-2} s^{-1}, respectively.[12b, 13] The partial rate factors for sulphonation of methanesulphonanilide in 77.8% H_2SO_4 by $H_3SO_4^+$ were calculated from the former datum for benzene, the first-order rate constant for the free base of methanesulphonanilide (log $k_1^{fb} = -5.37 \pm 0.03$; Table 4), and the proportions of isomers ($o/p = 0.18 \pm 0.03$; Table 5) as follows: $f_o = 55 \pm 25$; $f_p = 610 \pm 200$.* The partial rate factors for sulphonation by $H_2S_2O_7$ in 96.1% H_2SO_4 were similarly calculated from the rate constants for benzene (see before) and methanesulphonanilide (log $k_1^{fb} = -0.40 \pm 0.12$; Table 4) and the proportions of isomers ($o/p = 0.12 \pm 0.02$; Table 5) as follows: $f_o = 2.5 \pm 1.2$; $f_p = 41 \pm 15$.*

TABLE 3

Protonation of methanesulphonanilide in aqueous sulphuric acid [a]

Acidity function	m [b]	$-H_x^{\frac{1}{2}}$ [c]	% H_2SO_4 (hp) [d]
H_A	1.61 ± 0.1	4.92 ± 0.1	84.1 ± 1
H_0 [a]	1.52 ± 0.1	6.67 ± 0.1	83.3 ± 1
H_0	0.95 ± 0.05	7.97 ± 0.1	84.0 ± 0.7

[a] U.v. measurements made at 221.4 nm. [b] Slope of the plot of log ([BH+]/[B]) *vs.* H_x (14 points; correlation coefficients 0.952, 0.971, and 0.987 for H_A, H_0^a, and H_0, respectively) (BH+ and B stand for protonated and unprotonated methanesulphonanilide respectively). [c] H_x Value at half-protonation. [d] Sulphuric acid concentration at which half-protonation occurs.

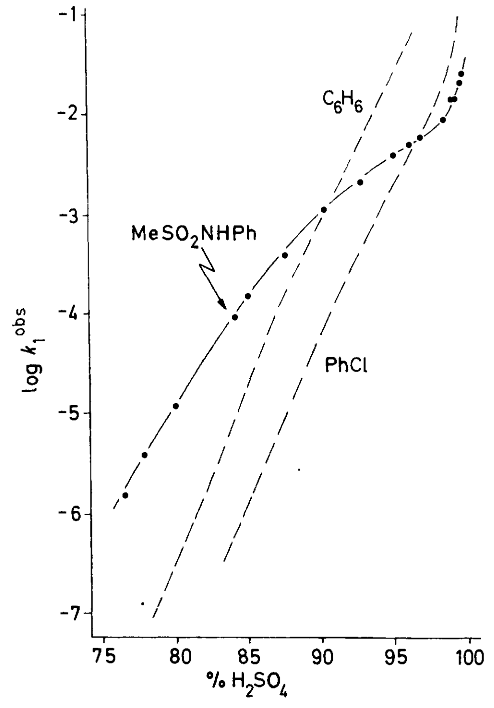

FIGURE 2 Observed first-order rate constants for sulphonation at 25.0 ± 0.5 °C

The Brown substituent constant (σ_p^+) for *p*-$NHSO_2Me$ was determined from partial rate factors in 77.8 and 96.1% H_2SO_4 and the corresponding reaction constants for the two types of sulphonation [$\rho^+(H_3SO_4^+) = -9.3 \pm 1$; $\rho^+(H_2S_2O_7) = -5.7 \pm 0.3$] [6] to be -0.30 and -0.28 ± 0.04, respectively. The σ_p^+ value calculated from the Swain and Lupton equation [$\sigma_p^+ = -0.84\sigma_m + 1.81\sigma_p - 0.07$],[14] by using $\sigma_m = 0.20$ and $\sigma_p = 0.03$ (taken from ionization studies on substituted benzoic acids in aqueous alcohols [15]), is -0.19 ± 0.1. Variations in empirical σ^+ values for *N*- and *O*-containing substituents originating

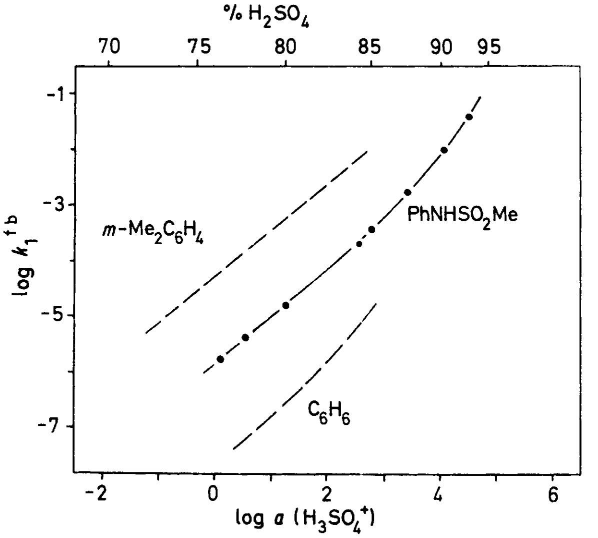

FIGURE 3 Correlation of first-order rate constants for sulphonation of unprotonated methanesulphonanilide, benzene,[6] and *m*-xylene [6] with the activity of $H_3SO_4^+$

TABLE 4

First-order rate constants (s^{-1}; ±5%) for sulphonation of methanesulphonanilide at 25.0 ± 0.5 °C

H_2SO_4 (%)	$-\log k_1^{obs.}$ [a]	log ([BH+]/[B]) [b]	log k_1^{fb} [c]
76.5	5.81	−1.11	−5.78
77.8	5.41	−0.97	−5.37
80.0	4.92	−0.60	−4.82
84.1	4.03	0.01	−3.72
85.0	3.82	0.18	−3.42
87.6	3.42	0.58	−2.74
90.2	2.97	0.93	−1.99
92.7	2.69	1.38	−1.38
95.0	2.43	1.79	−0.64
96.1	2.35	1.95	−0.40
96.8	2.26	2.10	−0.16
98.36	2.05	2.47	0.42
99.02	1.90	2.74	0.84
99.06	1.90	2.75	0.85
99.47	1.72	2.95	1.23
99.61	1.65	3.04	1.39

[a] U.v. measurements made at 240, 250, or 255 nm. [b] Ionization ratios were calculated from equation (i) with $m = 0.95$ and $H_0^{\frac{1}{2}} = -7.97$ (see Table 3); H_0 values taken from ref. 8. [c] First-order rate constants of the free base calculated according to equation (ii).

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* The contributions of sulphonation by $H_2S_2O_7$ and $H_3SO_4^+$ to the overall reaction rate in 77.8 and 96.1% H_2SO_4, respectively, were determined from the rate profiles to be less than 5%. The uncertainties in the partial rate factors at low and high sulphuric acid concentrations are mainly due to the uncertainty in the rate constant for sulphonation of benzene by $H_3SO_4^+$ [12b] and the protonation ratio of methanesulphonanilide, respectively.

[12] C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, (*a*) 1967, **86**, 865; (*b*) 1968, **87**, 24; (*c*) 1969, **88**, 1298.

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

[14] C. G. Swain and E. C. Lupton, *J. Amer. Chem. Soc.*, 1968, **90**, 4328.

[15] O. Exner and J. Lakomy, *Coll. Czech. Chem. Comm.*, 1970, **35**, 1371.

from solvent effects, *e.g.* hydrogen bonding,[16] are frequently observed.

Isomer Distribution.—The amounts of anilinium-*o*- and -*p*-sulphonic acid and anilinium-2,4-disulphonic acid eventually produced from reactions of methanesulphonanilide in concentrated aqueous sulphuric acid at 25 °C (Scheme) were determined by ^{1}H n.m.r. spectroscopy (Table 5). It was shown by multi-component u.v. analysis of the mixture from a reaction in 86.8% H_2SO_4 that the amount of anilinium-*m*-sulphonic acid was less than 1%. The amount of anilinium-2,4-disulphonic acid increases with increasing sulphuric acid concentration. The degree of *ortho*-substitution in the primary sulphonation was determined from the ^{1}H n.m.r. spectra of intermediate reaction mixtures. The relative area of the methyl absorption at δ 3.92 in the spectrum of the sulphomethanesulphonanilides (Table 1) is larger for reaction in 86.8 than in 99.7% H_2SO_4, indicating that the amount of *ortho*-isomer decreases with increasing sulphuric acid concentration. Quantitative n.m.r. analyses were carried out after heating the reaction mixtures, which were diluted to 80% H_2SO_4 after *ca.* 95% of primary sulphonation had taken place (see Experimental section). The starting material and the sulphomethanesulphonanilides in *ca.* 80% H_2SO_4 undergo solvolysis at elevated temperatures to yield the anilinium ion [17] and the corresponding aniliniumsulphonic acids, respectively. Heating both anilinium-*o*- and -*p*-sulphonate in 80% H_2SO_4 at 90 °C for 4 days did not lead to any isomerization. Further, the same relative amounts of *o*-aminobenzenesulphonic and sulphanilic acid are formed on carrying out the solvolysis at 85 and 150 °C, indicating that no isomerization of the initial *o*- and *p*-sulphomethanesulphonanilides occurs either.

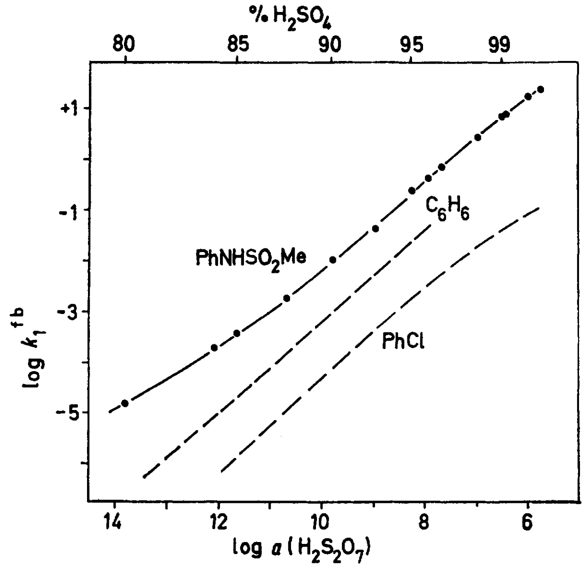

FIGURE 4 Correlation of the first-order rate constants for sulphonation of unprotonated methanesulphonanilide, benzene,[6] and chlorobenzene [6] with the activity of $H_2S_2O_7$

DISCUSSION

Protonation.—Methanesulphonanilide is the weakest base of a number of sulphonamides and sulphonanilides which all undergo protonation on nitrogen.[7,18,19] The *N*-methylsulphonyl- and *N*-arylsulphonyl-anilines are much less basic (ΔpK_a 5—6) than phenylsulphamate. This confirms earlier results that the electron-withdrawing effect of the sulphonyl group (SO_2R) is much stronger than that of the sulphonate group (SO_3^-); this difference is both inductive (for the most part) and mesomeric in origin.[7,20]

Sulphonation.—From the kinetic and product composition studies it follows that sulphonation of the unprotonated methanesulphonanilide [equation (iv)] is preceded by a protonation equilibrium step (iii). At relatively low acidities the free base (which is the

$$Ph\overset{+}{N}H_2SO_2Me \rightleftharpoons PhNHSO_2Me + H^+ \quad \text{(iii)}$$

$$PhNHSO_2Me + XSO_3H^+ \longrightarrow \text{sulphonation products} \quad \text{(iv)}$$

TABLE 5

Isomer distributions for the sulphonation of methanesulphonanilide (0.5M) in sulphuric acid at 25 °C [a]

H_2SO_4 (%)	Aniliniumsulphonic acids (%) *ortho*	*para*	2,4-di	Degree of *ortho*-substitution in primary sulphonation (%)
80.0	15 ± 2	85 ± 2	<2	15 ± 2 [c]
86.8	13.7 ± 1.2 [b]	81.8 ± 0.9 [b]	4.3 ± 0.2 [b]	
	14.4 ± 1.5	81.6 ± 2	4 ± 1.5	
90.2				15 ± 2 [c]
96.8	9.7 ± 1.5	76.9 ± 2	13.4 ± 1.5	10.6 ± 2 [c]
				10.1 ± 1.5 [d]
99.7	<2	73.5 ± 2	26.5 ± 5	
99.8				10.3 ± 2 [d]
				9.0 ± 1.5 [c]

[a] Multi-component ^{1}H n.m.r. analysis. The data for the *para*-isomer include <1% of anilinium-*m*-sulphonic acid (see footnote *b*). [b] Multi-component u.v. analysis. The amounts of anilinium ion and anilinium-*m*-sulphonic acid were determined to be both <0.4%. [c] After completion of the primary sulphonation (part of) the reaction mixture was diluted to 80% H_2SO_4 and heated at 150 °C for 2 h. [d] As in footnote *c*, but the diluted sample was heated at 85 °C for 2 days.

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[16] J. M. McKelvey, S. A. A. Streitwieser, J. L. M. Abboud, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1976, **98**, 244.

[17] A. I. Vogel, 'Practical Organic Chemistry,' Longman, London, 3rd edn., 1970, p. 1076.

[18] (*a*) P. O. I. Virtaanen and M. Maikula, *Tetrahedron Letters*, 1968, 4855; (*b*) P. O. I. Virtaanen and K. Heinamaki, *Suomen Kem.*, 1969, **42**, 142.

[19] E. Yu. Belyaev and L. I. Kotlyar, *Reakts. spos. org. Soedinenii*, 1973, **10**, 269.

[20] H. Zollinger and C. Wittwer, *Helv. Chim. Acta*, 1956, **39**, 347.

majority species up to *ca.* 84% H_2SO_4) is sulphonated by $H_3SO_4^+$ ($X = H_2O$), whereas the sulphonating entity attacking the unprotonated minority species $PhNHSO_2Me$ in >90% H_2SO_4 is $H_2S_2O_7$ ($X = HSO_4^-$). The kinetic sulphonation behaviour of unprotonated methanesulphonanilide is comparable with the behaviour of alkyl- and halogeno-benzenes,[6] which do not undergo protonation, and with that of phenylsulphamic acid in the range 97—100% H_2SO_4. The latter compound exists in a tautomeric equilibrium which is to a first approximation independent of the acidity of the medium.[2]

In view of the conclusions reached in a study on the nitration of several anilides in mixed acid,[5] the decrease of the *ortho* : *para* ratio in the primary sulphonation of methanesulphonanilide with increasing sulphuric acid concentration observed in the present work may be ascribed to a change in solvation of the substrate, *e.g.* to an increase in hydrogen bonding. This effect apparently dominates the opposite effect due to the change-over from the $H_3SO_4^+$ to the $H_2S_2O_7$ mechanism, as observed for, for example, toluene, for which the *ortho* : *para* sulphonation ratio increases with increasing acid concentration.[6,12b]

EXPERIMENTAL

Materials.—Methanesulphonanilide was prepared from aniline and methanesulphonyl chloride [21] and recrystallized from 95% ethanol (Found: C, 49.1; H, 5.2; N, 8.3; S, 18.6. Calc. for $C_7H_9NO_2S$: C, 49.1; H, 5.3; N, 8.2; S, 18.75%). The synthesis and purification of anilinium sulphate and the anilinesulphonic acids have been described before.[2,22] The preparation of absolute and constant-boiling sulphuric acid has been described previously.[23] All other sulphuric acid concentrations were obtained by mixing water, 98.4% H_2SO_4 (AnalaR), and constant-boiling and absolute sulphuric acid, as required. All manipulations of the concentrated sulphuric acid solutions were carried out in an atmosphere of nitrogen to prevent ingress of moisture.

Protonation Studies.—U.v. measurements were carried out with a Zeiss PMQ-II spectrophotometer kept at 25.0 ± 0.5 °C. A stock solution of the anilide in 61.9% H_2SO_4 was stored at 25 °C. For absorption measurements of acid solutions >85% H_2SO_4 the following procedure was applied. A weighed amount of the stock solution was mixed with a large excess of sulphuric acid of the desired concentration with external cooling as to obtain a temperature of the resulting solution of 25 ± 1 °C. After reweighing, a portion of the solution was transferred to the absorption cell and the extinction at 221.4 nm was followed. The extinction of the methanesulphonanilide was obtained by zero time extrapolation of the graph of log $(E_t - E_\infty)$ *vs.* time. At 221.4 nm the overall change of extinction due to sulphonation was very small $[(E_0 - E_\infty)/E_\infty < 0.02]$.

Rate Measurements.—The rates of sulphonation were determined at 25.0 ± 0.5 °C with a Cary 14 and a Zeiss PMQ-II spectrophotometer. For reactions in >99% H_2SO_4, *i.e.* with $t_{\frac{1}{2}} < 1$ min, the substrate was first dissolved in 90.2% H_2SO_4. Then an amount of the solution was transferred to the absorption cell and rapidly mixed with a large excess of sulphuric acid of the desired concentration. The reaction temperature, measured afterwards, remained almost constant in the time needed to perform the rate measurement, as was verified in control experiments.[12a] Plots of either log $(E_t - E_\infty)$ or log $(E_t - E_{t+\Delta t})$ against time were linear for at least three half-lives.

Isomer Distribution.—The reaction products from methanesulphonanilide (0.5M) in sulphuric acid at 25 °C were determined by multi-component ^1H n.m.r. analysis.[2] The spectra were recorded with a Varian HA 100 spectrometer, by using either neat liquid tetramethylsilane (sealed capillary) as an external standard or the sulphuric acid solvent itself as an internal standard.[24] The composition of the reaction mixture in 86.8% H_2SO_4 was also determined by multi-component u.v. analysis,[2] with anilinium sulphate, the aniliniumsulphonic acids, and calcium aniline-2,4-disulphonate as reference compounds, by measuring the extinctions in the wavelength regions 204—228 and 248—275 nm with a Zeiss PMQ-III spectrophotometer provided with a rotating cell holder.

The degree of *ortho*-substitution was determined after *ca.* 95% of the methanesulphonanilide had been sulphonated (4—5 half-lives) by dilution of the reaction mixture to 80% H_2SO_4, heating the resulting solution either for 2 h at 150 °C or for 2 days at 85 °C, and subsequent n.m.r. analysis. Up to a substrate conversion of *ca.* 95% no 2,4-disulphonic acid was found to be present within the limits of detection (2%). Under the conditions applied to effect solvolysis the unconverted substrate and the sulphomethanesulphonanilides were completely converted into the anilinium ion and its monosulphonic acids, respectively.

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[21] C. S. Marvel, *J. Amer. Chem. Soc.*, 1929, **57**, 1272.

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

[23] J. E. Kunzler, *Analyt. Chem.*, 1953, **25**, 93.

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