Electrophilic Aromatic Substitution. Part XIV.[1] Kinetics of Nitration of Some Aromatic Sulphonic Acids in Sulphuric Acid

By **Roy B. Moodie, Kenneth Schofield,** and **Tadao Yoshida,*** Department of Chemistry, The University, Exeter EX4 4QD, and Department of Reaction Chemistry, Faculty of Engineering, Tokyo University, Hongo, Tokyo, Japan

Rates of nitration in sulphuric acid of the acids $Ph[CH_2]_n{\cdot}SO_3H$ (n = 0—3) have been measured. The acids react as their anions. Even in the case n = 3, the sulphonate group exerts a deactivating influence. The proportions of isomers formed from benzenesulphonic acid vary with acidity, and at high acidities a small proportion of the nitration may involve the un-ionised acid. Methyl phenyl sulphone is nitrated as the free base, but at high acidities both the rate of reaction and the change in isomer proportions suggest that hydrogen bonding may be occurring.

THE nitration of aromatic sulphonic acids attracted our interest for several reasons. First, it has never been demonstrated for compounds of this class whether nitration in aqueous sulphuric acid involves the neutral molecule or its anion; for benzenesulphonic acid in 82—100% sulphuric acid the involvement of the neutral molecule was assumed.[2] The degree of *meta*-nitration of phenylmethanesulphonic acid in nitric acid was thought to indicate reaction of the anion,[3] and for this case and that of β-phenylethanesulphonic acid from kinetic results for nitration in aqueous nitric acid 'it is made plausible that the sulphonic acids are nitrated through their anions.'[4] Secondly, little quantitative information is available about the characters of the substituents SO_3^- and SO_3H. Various σ values have been reported,[5] and for SO_3^- there are also σ^+ values[6] (see ref. 7*b*). Recently quantitative studies of the rates and products of sulphonation of benzene-,[7] phenylmethane-,[8] β-phenylethane-,[9] and γ-phenylpropanesulphonic acid[10] were reported, the results referring to the neutral molecules. Thirdly, it was of interest to examine how the negative charge on a sulphonic acid anion, in circumstances where this group was attached to a strongly activated aromatic ring and where the anion was the entity being nitrated, might influence the encounter rate of nitration.[11]

This paper describes an initial study of some of these problems.

EXPERIMENTAL

Materials.—AnalaR sulphuric acid was used. Pure nitric acid was prepared by vacuum distillation of fuming nitric acid from an equal volume of concentrated sulphuric acid and stored at −10°. The compositions of aqueous sulphuric acid solutions were determined either by measurement of their densities (<90% sulphuric acid) or by titration against a standard solution of sodium hydroxide.

Commercial benzenesulphonic acid, sodium benzenesulphonate, *p*-nitrobenzenesulphonic acid, *m*-nitrobenzenesulphonic acid, ethylbenzene, n-propylbenzene, mesitylenesulphonic acid, and methyl phenyl sulphone were used. Sodium phenylmethanesulphonate and sodium *o*-nitrobenzenesulphonate were prepared from the corresponding sulphonyl bromides by boiling with 95% v/v aqueous ethanol containing an equivalent amount of sodium hydroxide, and purified by recrystallisation from aqueous ethanol. Sodium salts of *o*-, *m*-, and *p*-nitrophenylmethanesulphonic, β-phenylethanesulphonic, and γ-phenyl-

---

[1] Part XIII, J. W. Barnett, R. B. Moodie, K. Schofield, and J. B. Weston, *J.C.S. Perkin II*, 1975, 648.

[2] B. Surfleet and P. A. H. Wyatt, *J. Chem. Soc.*, 1965, 6524.

[3] C. K. Ingold, E. H. Ingold, and F. R. Shaw, *J. Chem. Soc.*, 1927, 813.

[4] E. S. Halberstadt, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1950, 2441.

[5] H. Zollinger, *Nature*, 1953, **172**, 256; H. Zollinger, W. Buckler, and C. Wittmer, *Helv. Chim. Acta*, 1953, **36**, 1711; H. Zollinger and C. Wittmer, *ibid.*, 1956, **39**, 374; A. C. Hopkinson and P. A. H. Wyatt, *J. Chem. Soc.* (*B*), 1970, 530.

[6] C. Eaborn and P. M. Jackson, *J. Chem. Soc.* (*B*), 1969, 21.

[7] (*a*) A. J. Primsen, A. Koeberg-Telder, and H. Cerfontain, *Tetrahedron*, 1970, **26**, 1953; (*b*) H. Cerfontain, *Internat. J. Sulfur Chem.*, 1972, **2**, 297.

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

[9] A. Koeberg-Telder, Z. R. H. Nienhuis, and H. Cerfontain, *Canad. J. Chem.*, 1973, **51**, 462.

[10] H. Cerfontain and Z. R. H. Schaasberg-Nienhuis, *J.C.S. Perkin II*, 1973, 1413.

[11] R. G. Coombes, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1968, 800.

propanesulphonic acids were prepared from the corresponding bromides.[12]

Methyl *m*-nitrophenyl sulphone was obtained by nitrating methyl phenyl sulphone in 98% sulphuric acid.[13]

Kinetic Measurements.—Changes of the absorbance with time of the reacting solutions were observed in Unicam SP 800 or 1800 spectrophotometers fitted with thermostatted cell holders (25·0 ± 0·1°), as described earlier.[11] Rate constants were obtained either from plots of $\log (A_\infty - A_t)$ against time, or by the Guggenheim method.[14]

Isomer Proportions for the Nitration of Methyl Phenyl Sulphone.—Solutions of the sulphone (1·12 g) and nitric acid (1·61 g) each in 98·5% sulphuric acid (100 ml) were equilibrated at 25° in a two-legged tube. After mixing the reaction solution was kept for 1 h at the same temperature. The solution was quenched in water (800 ml), with cooling. Extraction with methylene chloride, drying ($MgSO_4$), and removal of the solvent gave a practically quantitative yield of mononitro-compounds. Similar experiments were carried out using 81·4 and 90·2% sulphuric acid. N.m.r. spectra of the products dissolved in $CDCl_3$ were recorded (JEOL; 100 MHz), with tetramethylsilane as the internal standard. The *o*-nitro-compound could be determined relatively accurately from its methyl proton signal. The spectrum of methyl *m*-nitrophenyl sulphone is very similar to that of *m*-nitrobenzenesulphonic acid, and analyses for methyl *m*- and *p*-nitrophenyl sulphone were performed using the method described for the benzenesulphonic acids (see later).

TABLE 1

N.m.r. data for reference nitro-compounds

Compound	Position of nitro-group	Chemical shifts (p.p.m. from standard [a]) H-2	H-3	H-4	H-5	H-6	H-α
$O_2NC_6H_4SO_3H$ in 20% H_2SO_4–H_2O [a,b]	2		8·09	multiplet 7·69—8·02			
	3	8·64		8·44	7·80	8·24	
	4	8·04	8·40		8·40	8·04	
$O_2NC_6H_4SO_2Me$ in $CDCl_3$ [a]	3	8·81		8·56	7·84	8·33	
$O_2NC_6H_4CH_2SO_3H$ in 20% H_2SO_4–D_2O [a]	2		8·02	multiplet 7·40—7·85			4·74
	3	8·29		8·23	7·65	7·84	4·33
	4	8·65	8·26		8·26	8·65	4·39

[a] Internal standard. [b] See ref. 7*b*.

Yields of methyl nitrophenyl sulphones were determined by nitrating methyl phenyl sulphone (*ca.* 1 g) for 10 half-lives, pouring the nitration solution onto ice, and extracting with chloroform. After being washed with sodium carbonate solution and then with water, and dried ($MgSO_4$), the chloroform was removed from the extract and the residue was weighed. Using 85·2, 90·4, and 98·4% sulphuric acid, the yields were 94, 96, and 96%.

Isomer Proportions for the Nitration of Benzenesulphonic Acid.—Solutions of benzenesulphonic acid (0·549 g) and nitric acid (0·531 g), each in 83·9% sulphuric acid were treated as above, except that the reaction time was 20 min. The reaction solution was poured into water (200 ml), and the resultant solution was poured into an aqueous solution (300 ml) of barium chloride heptahydrate (180 g). The precipitate was removed by centrifugation, and the solution was evaporated. The residue (2·48 g) was dissolved in a small volume of water and mixed with 20% sulphuric acid (4·0 ml). Further centrifugation and evaporation of the solution gave a residue (0·48 g) which was dissolved in water. The n.m.r. spectrum and integration curve was recorded. Spectra and integration curves for *o*-, *m*-, and *p*-nitrobenzenesulphonic acid in 20% sulphuric acid were also recorded (Table 1). For the three areas of the spectra of the mixtures bounded by the lines 8·84, 8·54, 7·76, and 7·40 p.p.m. from the peak for sodium 4,4-dimethyl-4-silapentane-1-sulphonate, the following experimental relations were obtained: $S_1 = 0{\cdot}246y$; $S_2 = 0{\cdot}282x + 0{\cdot}517y + 1{\cdot}00z$; $S_3 = 0{\cdot}718x + 0{\cdot}235y$, where S_1, S_2, and S_3 are the fractions of the total area represented by each division, and x, y, and z are the fractions of *o*-, *m*-, and *p*-nitrobenzenesulphonate anions present in a mixture.

Using the measured isomer proportions and the known u.v. extinction curves for solutions of *o*-, *m*-, and *p*-nitrobenzenesulphonic acid in sulphuric acid, the extinction curves for kinetic runs gave the following yields: 105, 104, and 92% in 98·4, 98·4, and 85·2% sulphuric acid.

Isomer Proportions for the Nitration of Phenylmethanesulphonic Acid.—Products formed from the nitration of phenylmethanesulphonic acid in 69·7% sulphuric acid were analysed by the method described above. To achieve good separations of the aromatic and methylene proton signals from a solvent signal, n.m.r. spectra were run using solutions in 25% sulphuric acid in deuterium oxide. The proportion of *o*-isomer was relatively accurately obtained from the methylene proton signal. The proportions of *m*- and *p*-isomers were determined using the following experimental relationships: $S_1 = 0{\cdot}017x + 0{\cdot}358y + 0{\cdot}259z$; $S_2 = 0{\cdot}016x + 0{\cdot}112y + 0{\cdot}234z$ (divisions were made 8·66, 8·24, 8·12, and 7·40 p.p.m. from the standard peak) where the symbols have the same meaning as before.

RESULTS

Rates.—Second-order rate constants for the nitration at 25° of the substrates in this work are given in Table 2.

Surfleet and Wyatt [2] measured rates of the nitration of benzenesulphonic acid in aqueous sulphuric acid using thermal analysis. Some of their results may be compared with ours (Figure 1). Some differences are observed but, considering that their results were obtained using high concentrations of benzenesulphonic acid, they are not great.

Relative rates for the nitration at 0° in aqueous nitric acid of phenylmethanesulphonic acid and β-phenylethanesulphonic acid with respect to the rate of exchange of isotopic oxygen for water were given by Bunton and Halevi [15] as 25—45 and 100—250, respectively. These

---

[12] E. B. Evans, E. E. Mabbott, and E. E. Turner, *J. Chem. Soc.*, 1927, 1159.

[13] C. A. Bunton and E. A. Halevi, *J. Chem. Soc.*, 1952, 4541.

[14] M. Ahmad and J. Hamer, *J. Chem. Educ.*, 1964, **41**, 249.

[15] C. A. Bunton and E. A. Halevi, *J. Chem. Soc.*, 1952, 4917.

TABLE 2

Second-order rate constants for nitration in aqueous sulphuric acid at 25·0 ± 0·1°

H_2SO_4 (%) [a]	$[HNO_3]$/mol dm^{-3}	k_2/dm^3 mol^{-1} s^{-1} (±5%)
	Benzenesulphonic acid [b]	
76·9	0·15, 0·14	$9·5 \times 10^{-4}$
81·4	0·11, 0·061	$3·7 \times 10^{-2}$
83·1	0·043, 0·064	$1·33 \times 10^{-1}$
85·2	0·0052, 0·0052	$5·9 \times 10^{-1}$
86·2	0·0031, 0·0026	1·35
88·4	0·0026, 0·0024	3·8
90·2	0·0015, 0·0013	5·0
92·5	0·0038, 0·0023	2·4
94·8	0·011, 0·012	1·13
97·1	0·013, 0·010	$2·7 \times 10^{-1}$
98·7	0·018, 0·019	$1·18 \times 10^{-1}$
	Methyl phenyl sulphone [b]	
83·1	0·15, 0·15	$1·35 \times 10^{-3}$
85·2	0·10, 0·099	$7·6 \times 10^{-3}$
86·2	0·059, 0·047	$1·55 \times 10^{-2}$
88·4	0·10, 0·069	$6·4 \times 10^{-2}$
90·2	0·052, 0·020	$9·0 \times 10^{-2}$
92·5	0·071, 0·12	$7·4 \times 10^{-2}$
94·8	0·15, 0·12	$4·4 \times 10^{-2}$
97·1	0·10, 0·21	$2·4 \times 10^{-2}$
98·7	0·10, 0·089	$1·53 \times 10^{-2}$
	Phenylmethanesulphonic acid [b]	
68·7	0·13, 0·12	$3·8 \times 10^{-3}$
69·6	0·16, 0·15	$9·5 \times 10^{-3}$
71·5	0·16, 0·13	$3·2 \times 10^{-2}$
74·1	0·037, 0·039	$3·2 \times 10^{-1}$
77·1	0·0053, 0·0090	4·6
80·0	0·00046, 0·00042	$4·9 \times 10^{-1}$
	β-Phenylethanesulphonic acid [b]	
63·4	0·18, 0·17	$1·86 \times 10^{-3}$
64·4	0·19, 0·16	$3·6 \times 10^{-3}$
64·6	0·20, 0·24	$4·3 \times 10^{-3}$
67·4	0·12, 0·11	$2·8 \times 10^{-2}$
69·8	0·15	$1·98 \times 10^{-1}$
71·8	0·0098, 0·012	1·09
74·1	0·00070, 0·00095	$1·34 \times 10^{-1}$
76·0	0·00062, 0·00084	$4·3 \times 10^{-1}$
	γ-Phenylpropanesulphonic acid [b]	
63·4	0·10, 0·11	$5·9 \times 10^{-3}$
64·6	0·12, 0·12	$1·27 \times 10^{-2}$
67·2	0·074, 0·078	$9·0 \times 10^{-2}$
69·7	0·022, 0·012	$5·2 \times 10^{-1}$
71·9	0·0018, 0·0040	3·2
	Mesitylenesulphonic acid [b]	
64·8	0·16, 0·19	$4·2 \times 10^{-3}$
67·3	0·20, 0·18	$2·1 \times 10^{-2}$
68·1	0·14, 0·14	$3·7 \times 10^{-2}$
69·9	0·045, 0·044	$1·16 \times 10^{-1}$
71·9	0·0031, 0·011	$5·9 \times 10^{-1}$
	Ethylbenzene [b]	
59·7	0·11, 0·14	$1·73 \times 10^{-3}$
63·4	0·11, 0·18	$2·2 \times 10^{-2}$
64·6	0·075, 0·11	$5·2 \times 10^{-2}$
67·2	0·081, 0·071	$3·2 \times 10^{-1}$
69·7	0·0058, 0·0056	2·2
	n-Propylbenzene [b]	
60·8	0·15, 0·16	$3·8 \times 10^{-3}$
63·4	0·080, 0·078	$1·94 \times 10^{-3}$
64·4	0·17	$4·6 \times 10^{-2}$
67·2	0·074, 0·068	$2·9 \times 10^{-1}$
69·5	0·0039	1·48
72·1	0·0019	$1·14 \times 10$

[a] ±0·1%. [b] [Aromatic] = 10^{-4}—10^{-5} mol dm^{-3}.

values give a rate ratio for the two acids different from, but of the same order as our value of 20. From nitrations in acidified aqueous nitric acid at 30° a value of 11—12 was obtained.[4]

Isomer Proportions.—The results for the nitration at 25° of methyl phenyl sulphone, benzenesulphonic acid, phenylmethanesulphonic acid, ethylbenzene, and n-propylbenzene are given in Table 3. Though not very accurate, our results for methyl phenyl sulphone and benzenesulphonic acid (see Experimental section) suggest that the yields of nitro-compounds were quantitative.

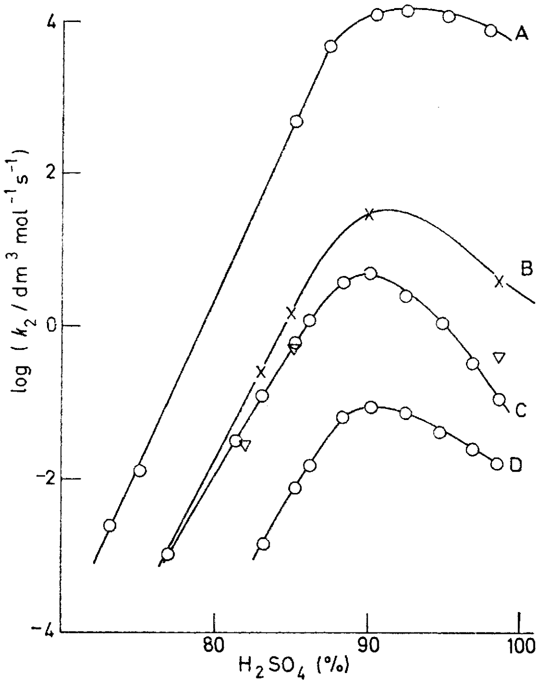

FIGURE 1 Rate profiles for nitration in aqueous sulphuric acid: A, *p*-dichlorobenzene (ref. 19); B, a calculated profile for benzenesulphonate anion; C, benzenesulphonic acid (this work, ○; ref. 2, ▽); D, methyl phenyl sulphone

TABLE 3

Isomer proportions for the nitration of some compounds at 25°

Compound	H_2SO_4 (%)	Proportions of isomers (%) *ortho*	*meta*	*para*
Methyl phenyl sulphone [a]	81·4	6·0 [c]	93 [d]	<2
	90·2	5·1 [e]	94 [d]	<2
	98·5	1·5 [f]	96 [d]	<2
Benzenesulphonic acid [a]	83·9	35 [g]	56 [g]	9 [g]
	90·2	31 [g]	61 [g]	8 [g]
	98·5	21 [g]	73 [g]	6 [g]
Phenylmethanesulphonic acid [a]	69·7	32 [h]	20 [d]	49 [d]
Ethylbenzene [b]	67·2	51 [g]	4·6 [e]	44 [g]
n-Propylbenzene [b]	63·4	46 [h]	4·6	50 [h]

[a] Measured by n.m.r. [b] Measured by g.l.c. [c] ±0·6%. [d] ±4%. [e] ±0·2%. [f] ±0·1%. [g] ±2%. [h] ±1%.

As regards methyl phenyl sulphone, earlier workers obtained 96—98% yields using a solution of potassium nitrate in sulphuric acid at 90°, and the *m*-nitro-compound was the major product.[16] By nitrating ethyl phenyl sulphone in acetic anhydride, the *o*-, *m*-, and *p*-nitro-compounds were obtained in 8·1, 88·6, and 3·3% yields, respectively.[17]

[16] R. F. Twist and S. Smiles, *J. Chem. Soc.*, 1925, **127**, 1248.
[17] E. L. Riley and E. Rothstein, *J. Chem. Soc.*, 1964, 3860.

By nitrating benzenesulphonic acid in mixed acid at 20—30° Obermiller [18] obtained the isomer proportions of 21 (*o*), 72·4 (*m*), and 6·5 (*p*), a result very similar to one of ours.

The nitration of phenylmethanesulphonate anion in aqueous nitric acid at −10 to −5° gave the proportions 33·5 (*o*), 13·7 (*m*), and 52·8 (*p*).[3] These are roughly similar to our results.

DISCUSSION

The Species undergoing Nitration.—Methyl phenyl sulphone. The rate profile for the nitration of methyl phenyl sulphone is given in Figure 1. Also depicted is the rate profile for *p*-dichlorobenzene which is parallel to that for benzene.[19] A comparison of the rate profiles for methyl phenyl sulphone and *p*-dichlorobenzene is made in Table 4. It is seen that the relative rate of nitration of these compounds varies with the concentration of sulphuric acid. The rate profile for methyl phenyl sulphone is rather similar to those for nitrobenzene [20] and the chloronitrobenzenes.[21] For chloronitrobenzene and *p*-nitrotoluene the change of rate of nitration at high acidities was ascribed to the change in the activity coefficients of the aromatic compounds, thought to be caused by hydrogen bonding of the nitro-group.[21a]

TABLE 4

Rates of the nitration of methyl phenyl sulphone and *p*-dichlorobenzene in aqueous sulphuric acid at 25°

	$3 + \log_{10}(k_2/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$		
H_2SO_4 (%)	Methyl phenyl sulphone	*p*-Dichlorobenzene [a]	Difference
83·1	0·13	4·72	4·59
85·2	0·88	5·70	4·82
86·2	1·19	6·10	4·91
88·4	1·81	6·90	5·09
90·2	1·95	7·10	5·15
92·5	1·87	7·16	5·29
94·8	1·64	7·10	5·46
97·1	1·38	6·98	5·60
98·7	1·19	6·84	5·65

[a] Expected values from ref. 19.

No information is available concerning the protonation of methyl phenyl sulphone. However, dimethyl sulphone is 20—30% protonated and diphenyl sulphone is not protonated in 100% sulphuric acid.[22] Clearly, under our experimental conditions the proportion of methyl phenyl sulphone protonated would be much less than 20% and it is unlikely that the marked change of isomer proportions is due to nitration of the conjugate acid, the more so since the latter would be much less reactive than the free base.

The slope of the rate profile at lower acidities shows the majority species, the free base, to be reacting, and we regard the change in relative rate and in isomer proportions at high acidities as being due to hydrogen bonding.

Benzenesulphonic acid. For benzenesulphonic acid in aqueous sulphuric acid, Cerfontain and Schnitger [23] gave the relationship $\log\ [PhSO_3H]/[PhSO_3^-] = -mH_0^a + pK_a$, where $m = 1{\cdot}04$, H_0^a is the benzophenone acidity function, and $pK_a = -6{\cdot}65$. Using the approximate value $m = 1{\cdot}00$, Bonner and Phillips' data [24] then give $\log\ [PhSO_3H]/[PhSO_3^-] = 0{\cdot}0971x - 8{\cdot}06$ where x is the weight % sulphuric acid, between 65 and 90% sulphuric acid. Our kinetic results and this relationship allow us to convert the experimental rate profile for benzenesulphonic acid (Figure 1, curve C) into that (Figure 1, curve B) appropriate for the benzenesulphonate anion. A comparison of the rate constants for the anion with those for methyl phenyl sulphone is given in Table 5; within experimental error the rate profiles are parallel. Clearly the benzenesulphonate anion is the major species reacting in the nitration of benzenesulphonic acid below 98% sulphuric acid. Nevertheless, the change in isomer proportions with acidity suggests that at higher acidities nitration of the neutral molecule may not be insignificant.

TABLE 5

Comparison of the rate constants for the nitration of benzenesulphonate anion and methyl phenyl sulphone in aqueous sulphuric acid at 25°

		$3 + \log_{10}(k_2/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$			
H_2SO_4 (%)	$\log I$ [a]	$PhSO_3H$ (obs.)	$PhSO_3^-$ (calc.)	$PhSO_2Me$	Δ [b]
83·1	0·00	2·13	2·43	0·13	2·30
85·2	0·08	2·78	3·12	0·88	2·24
86·2	0·32	3·13	3·62	1·17	2·45
88·4	0·51	3·59	4·22	1·81	2·41
90·2	0·69	3·70	4·47	1·95	2·52
92·5	0·92	3·38	4·35	1·87	2·48
94·8	1·14	3·05	4·22	1·64	2·58
97·1	1·37	2·44	3·83	1·38	2·45
98·7	1·52	2·08	3·61	1·19	2·42

[a] $I = [PhSO_3H]/[PhSO_3^-]$. [b] $\Delta = \log k_2(PhSO_3^-{}_{\text{calc.}}) - \log k_2(PhSO_2Me_{\text{obs.}})$.

Partial Rate Factors (p.r.f.) for the Nitration of Methyl Phenyl Sulphone and Benzenesulphonate Anion.—Using *p*-dichlorobenzene as reference standard [19] the p.r.f.s given in Table 6 were calculated. Also included are values for nitrobenzene, and values calculated from the Hammett relationship [19] with ρ −8·4 (the σ value for SO_3^- was estimated from the work of Eaborn and Jackson [6] on the assumption that the anion was reacting and independent of hydrogen bonding in their work). Clearly the observed p.r.f.s decrease with acidity and are lower than expected. Tillett's value for f_m for

---

[18] J. Obermiller, *J. prakt. Chem.*, 1924, **69**, 70.

[19] R. G. Coombes, D. H. G. Crout, J. G. Hoggett, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1970, 347.

[20] F. H. Westheimer and M. S. Kharasch, *J. Amer. Chem. Soc.*, 1946, **68**, 1871.

[21] (*a*) M. I. Vinnik, Th. E. Grabovskaya, and L. N. Argamaskova, *Russ. J. Phys. Chem.*, 1967, **41**, 580; (*b*) Th. E. Grabovskaya and M. I. Vinnik, *ibid.*, 1966, **40**, 1221.

[22] S. K. Hall and E. A. Robinson, *Canad. J. Chem.*, 1964, **42**, 1113.

[23] H. Cerfontain and B. W. Schnitger, *Rec. Trav. chim.*, 1972, **91**, 199.

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

nitrobenzene[25] lies between the two other values, presumably because it was calculated by using the rate profile for *m*-nitrotoluene, which would not be parallel to that for benzene, as the reference standard. Again, we suppose the changes in p.r.f.s with acidity to be due to hydrogen bonding, or, in the case of the acid, of protonation. The results underline the difficulty of attaching clear significance to these quantities as means of comparing substituent effects.

TABLE 6

Apparent partial rate factors for the nitration of methyl phenyl sulphone, benzenesulphonic acid, and nitrobenzene in aqueous sulphuric acid[a]

H_2SO_4 (%)	$PhSO_2Me$		$PhSO_3^-$			$PhNO_2$[b,c]
	o	*m*	*o*	*m*	*p*	*m*
83·9	$2{\cdot}0 \times 10^{-9}$	$3{\cdot}2 \times 10^{-8}$	$2{\cdot}3 \times 10^{-6}$	$3{\cdot}8 \times 10^{-6}$	$1{\cdot}3 \times 10^{-6}$	$2{\cdot}3 \times 10^{-8}$
90·2	$6{\cdot}9 \times 10^{-10}$	$1{\cdot}3 \times 10^{-8}$	$1{\cdot}5 \times 10^{-6}$	$2{\cdot}9 \times 10^{-6}$	$7{\cdot}6 \times 10^{-7}$	$9{\cdot}2 \times 10^{-9}$
98·5	$5{\cdot}9 \times 10^{-11}$	$3{\cdot}8 \times 10^{-9}$	$4{\cdot}3 \times 10^{-7}$	$1{\cdot}5 \times 10^{-6}$	$2{\cdot}3 \times 10^{-7}$	$4{\cdot}8 \times 10^{-9}$
		$(4{\cdot}2 \times 10^{-6})$[d]		$(1{\cdot}7 \times 10^{-5})$[d]	$(7{\cdot}4 \times 10^{-6})$[d]	$(1{\cdot}1 \times 10^{-6})$[d]
						$(1{\cdot}6 \times 10^{-7})$[e]

[a] Calculated using the rate profile for *p*-dichlorobenzene[19] as a reference. [b] *meta*-Isomer proportion of 92% was assumed.[23] [c] Rate constants were estimated from Westheimer and Kharasch.[20] [d] Estimated value from the Hammett relationship using $\rho - 8{\cdot}4$,[19] $\sigma_m(SO_3^-) = 0{\cdot}57$,[6] and $\sigma_p(SO_3^-) = 0{\cdot}61$.[6] [e] See ref. 23.

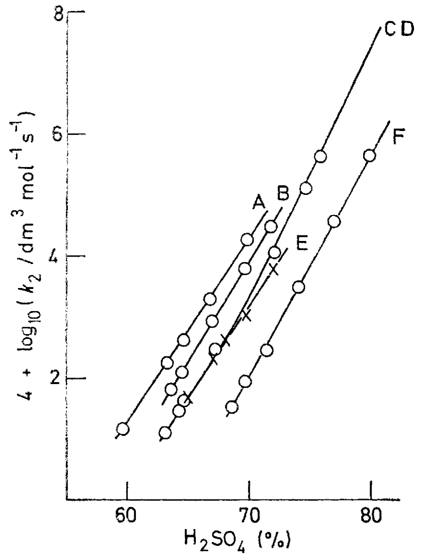

FIGURE 2 Rate profiles for nitration in aqueous sulphuric acid: A, ethylbenzene and n-propylbenzene; B, γ-phenylpropanesulphonic acid; C, benzene[11] (line only); D, β-phenylethanesulphonic acid (circles only); E, mesitylenesulphonic acid; F, phenylmethanesulphonic acid

The Sulphonate Anion as a Substituent.—The interesting feature of the group SO_3^- in its effect as a substituent influencing electrophilic substitution is that whilst carrying a negative charge it is nevertheless deactivating. Like the dominant *meta*-orientation imposed by the group[26] this might be ascribed to the formal positive charge on the sulphur atom. The diminished effectiveness of SO_3^- as compared with SO_2Me in both imposing *meta*-orientation and deactivating the nucleus could be ascribed to the increased number of negatively charged oxygen atoms in the former.

Separation of the sulphonate group from the nucleus by the interposition of even three methylene groups fails to suppress the deactivating influence. This can be seen from Figure 2 by comparison of the rate profiles for ethyl- and propyl-benzene with those for β-phenylethane- and γ-phenylpropane-sulphonic acid (the rate profiles for the latter two compounds leave no reason to doubt that in these cases the anions are reacting). Further analysis of these substituent effects must await the determination of isomer proportions, but it is interesting to note that the effects of the groups $[CH_2]_n{\cdot}SO_3^-$ on reactivity in nitration are analogous to their effects upon ionisation constants and some other kinetic phenomena.[27]

Mesitylenesulphonic Acid.—The low solubility of this compound, especially at lower acidities, limited the range of measurements which we could make (isodurenesulphonic acid was so insoluble that we could not measure rates in either sulphuric or perchloric acid).

[4/1980 *Received*, 26*th September*, 1974]

---

[25] J. G. Tillett, *J. Chem. Soc.*, 1962, 5142.

[26] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' London, 1969, 2nd edn., p. 279.

[27] R. P. Bell, 'The Proton in Chemistry,' London, 1973, 2nd edn., pp. 98 *et seq.*