Aromatic Sulphonation. Part XLI.[1] Sulphonation of 3-Phenylpropane-1-sulphonic Acid in Sulphuric Acid

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The kinetics of sulphonation of 3-phenylpropane-1-sulphonic acid in 77·8—94·8% H_2SO_4 at 25° have been studied. The results are discussed in terms of sulphonation of the un-ionized sulphonic acid and its conjugate base, the sulphonate anion, by the entities $H_2S_2O_7$ and $H_3SO_4^+$. The partial rate factors for the $[CH_2]_3SO_3H$ substituent for sulphonation with $H_2S_2O_7$ are $f_p = 10·1 \pm 1·1$, $f_m = 0·22 \pm 0·13$, and $f_o = 0·39 \pm 0·14$.

INFORMATION concerning the substituent effect of the SO_3H group is rather limited. From a u.v.-spectroscopic study on phenolphthalein and phenolsulphonphthalein monopositive ions Hopkinson and Wyatt concluded that $\sigma_m(SO_3H) = 0·56$.[2] Zollinger has reported the σ_m and σ_p values for the SO_3^- group from a potentiometric and u.v.-spectroscopic study on the ionization of sulphobenzoic acids and anilino- and phenoxy-benzenesulphonic acids.[3]

σ^+ Values have been reported by Eaborn and Jackson from protiodesilylation studies.[4] However the suggested σ^+ data probably do not refer to the SO_3H substituent, as was presumed, but instead to the SO_3^- group, for the reactions were performed in acetic acid–aqueous sulphuric acid solutions in which the sulphonic acids are present mainly as sulphonate anions.[5] Recently

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[1] Part XL, A. Koeberg-Telder and H. Cerfontain, *J.C.S. Perkin II*, 1973, 633.

[2] A. C. Hopkinson and P. A. H. Wyatt, *J. Chem. Soc.* (*B*), 1970, 530.

[3] (*a*) H. Zollinger, *Nature*, 1953, **172**, 256; (*b*) H. Zollinger, W. Büchler, and C. Wittmer, *Helv. Chim. Acta*, 1953, **36**, 1711; (*c*) H. Zollinger and C. Wittmer, *ibid.*, 1956, **39**, 347.

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

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

Cerfontain has reported the order of sequence of the σ_m^+ and σ_p^+ values for the SO_3H, NO_2, and NMe_3^+ substituents.[6]

With the aim of obtaining more information on the substituent effect of the SO_3H and SO_3^- groups, a study of the reactivity towards sulphonation of various sulphonic acids of the general structure $Ph[CH_2]_nSO_3H$ ($n = 1, 2, 3,$ *etc.*) was carried out. We now report on the sulphonation of 3-phenylpropane-1-sulphonic acid in concentrated sulphuric acid.

In order to ascertain the steric requirements of the $[CH_2]_nSO_3H$ substituent, work is in progress to determine the partial rate factors for sulphonation of the corresponding hydrocarbons $Ph[CH_2]_nBu^t$, the steric requirements of the SO_3H group being considered comparable with those of the Bu^t group. A discussion of the partial rate factors of the $[CH_2]_nSO_3H$ and $[CH_2]_nBu^t$ substituents will be reported in due course.

RESULTS AND DISCUSSION

The pseudo-first-order rate constants for sulphonation of sodium 3-phenylpropane-1-sulphonate (PPSA) in a very large excess of sulphuric acid are given in Table 1.

TABLE 1

Pseudo-first-order rate constant for sulphonation of sodium 3-phenylpropane-1-sulphonate at 25·0 °C [a]

H_2SO_4 (%) (±0·1)	$10^4\,{}_{ps}k_1/s^{-1}$	$-\log a_{H_2S_2O_7}$ [b]
77·8	0·0060	14·76
80·3	0·038	13·66
82·3	0·21	12·79
83·7	0·50	12·19
86·3	2·42	11·14
88·6	10·8	10·29
90·0	25·6	9·84
93·4	189	8·76
94·8	391	8·32

[a] Measured at 266 nm. [b] $a_{H_2S_2O_7}$ is proportional to $a_{H_2SO_4}/a_{H_2O}$. Thus $\log a_{H_2S_2O_7} = 2 \log a_{H_2SO_4} - \log a_{H_2O} + C$. The constant C was taken to be −12·25. It is the (constant) difference between the $\log a_{H_2S_2O_7}$ data calculated for 114—97% H_2SO_4 [11] and for 78—100% H_2SO_4 [7] in the overlapping acid range. The present data refer to 110% H_2SO_4 as standard state.[11]

The isomer distribution was estimated from the n.m.r. spectrum of the sulphonation mixture of PPSA in 95·2% H_2SO_4 and that of the mixture obtained after further addition of fuming sulphuric acid to be 90 ± 4% *para*, 4 ± 2% *meta*, and 7 ± 2% *ortho*.

The correlation of the ${}_{ps}k_1$ with the activity of $H_2S_2O_7$ is shown in Figure 1. At high sulphuric acid concentration a linear correlation is observed with a slope $d(\log {}_{ps}k_1)/d(\log a_{H_2S_2O_7})$ of 0·82. For benzene over the acid range of 96—82% H_2SO_4 the slope is 0·89.[7] The similarity in slope for PPSA at high acid concentrations and for benzene indicates that the sulphonating entity for PPSA is the same as the one proposed for benzene at high acid concentration, *viz.* $H_2S_2O_7$.[7,8]

The upward curvature at acid concentrations below 88% H_2SO_4 may be explained in terms of ionization of the sulphonic acid with formation of the sulphonate anion which will be more susceptible to electrophilic sulphonation. In fact, alkylbenzene- and alkane-sulphonic acids ionize in concentrated aqueous sulphuric acid and half deprotonation occurs at 82—84% H_2SO_4.[5,9] The occurrence of an inflection point in the graph of Figure 1 seems to indicate [10] that this explanation applies at any rate.

A second explanation of the upward curvature may be additional sulphonation, by *e.g.* $H_3SO_4^+$.[7] The sulphuric acid concentration at which the contributions to the rate of sulphonation by the entities $H_2S_2O_7$ and $H_3SO_4^+$ are equal, increases with increasing reactivity of the substrate position to be sulphonated.[8] For the sulphonation of the 3- and 4-position of toluene, the sulphuric acid concentrations of equal rate contributions are 80 and 85·7% H_2SO_4 respectively.[11] For the 4-position of PPSA, the reactivity of which is in between that of the 3- and that of the 4-position of toluene, the sulphuric acid concentration of equal rate contributions by $H_2S_2O_7$ and $H_3SO_4^+$ would accordingly be at 81—82% H_2SO_4.

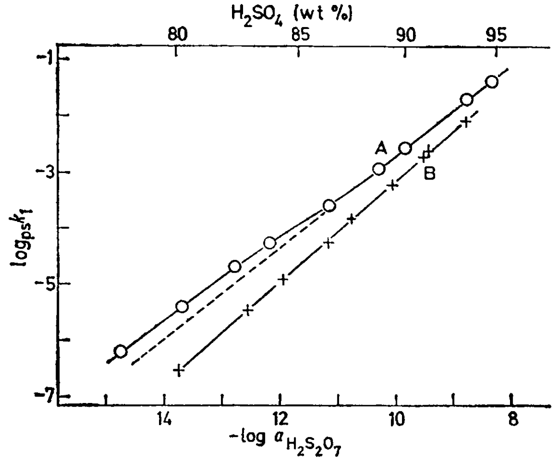

FIGURE 1 Correlation of rate of sulphonation with $a_{H_2S_2O_7}$ for A, PPSA, slope 0·82 (88—95% H_2SO_4); and B, benzene, slope 0·89

The complicating effects on the rate are minimal at 94·8% H_2SO_4. At that acid concentration the rate ratio of PPSA to benzene is 1·87 ± 0·14. The partial rate factors for sulphonation of the un-ionized sulphonic acid by the entity $H_2S_2O_7$ were calculated from the rate ratio and the isomer distribution to be $f_p = 10{\cdot}1 \pm 1{\cdot}1$, $f_m = 0{\cdot}22 \pm 0{\cdot}13$, and $f_o = 0{\cdot}39 \pm 0{\cdot}14$. Treatment of the monosulphonation mixture of PPSA (0·10 g) in 95·2% H_2SO_4 (1·0 ml) with 115% H_2SO_4 (1·0 ml) leads to further sulphonation with formation of almost exclusively (⩾95%) 2,4-disulpho-PPSA and (3·5 ± 1·5)% 3,5-di-

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[6] H. Cerfontain, *Internat. J. Sulfur Chem.*, in the press.

[7] C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, 1968, **87**, 24.

[8] H. Cerfontain and C. W. F. Kort, *Internat. J. Sulfur Chem.*, 1971, **6**, 23.

[9] A. Koeberg-Telder and H. Cerfontain, unpublished results.

[10] G. P. Bean, C. D. Johnson, A. R. Katritzky, B. J. Ridgewell, and A. M. White, *J. Chem. Soc.* (*B*), 1967, 1219.

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

sulpho-PPSA (Figure 2). The former isomer results from sulphonation of both 2- and 4-, the latter from 3-sulpho-PPSA. Other products which may be formed are 2,5- and 3,4-disulpho-PPSA. The formation of the former product is unlikely in view of the low $f_o:f_p$ ratio for the monosulphonation of PPSA. The relative amount of the latter will only be small, because of the preferred conformation of the propanesulphonic acid substituent.* The degree of *meta*-substitution will thus be somewhat greater than the relative amount of the 3,5-isomer in the disulpho-PPSA mixture and was taken to be 4 ± 2%.

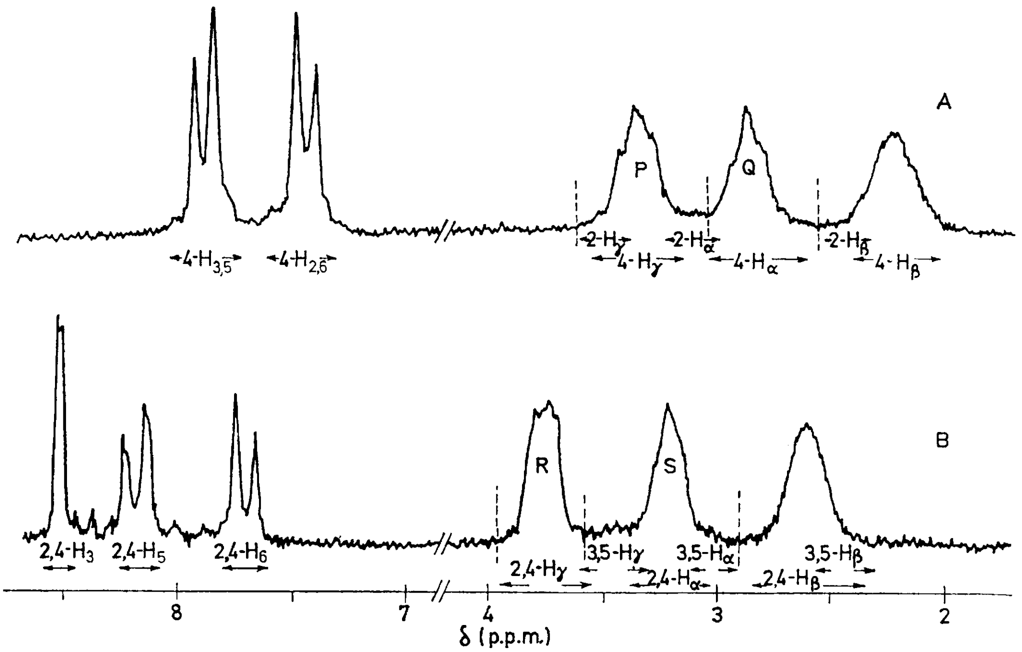

FIGURE 2 N.m.r. spectra of sulphonation mixtures of sodium 3-phenylpropane-1-sulphonate. The assignments of the methylene absorptions were based also on a comparison with those of sulphonation mixtures of 2-phenylethane-1-sulphonic acid:[14] A, sulphonation in an excess of 95·2% H_2SO_4; and B, sulphonation, first in an excess of 95·2% H_2SO_4, then with an equal volume of 115% H_2SO_4 (4-H$_\beta$ = signal for β-CH_2 of 4-sulpho-isomer, *etc.*)

TABLE 2

N.m.r. data [δ (p.p.m.)] of 3-phenylpropane-1-sulphonic acid (PPSA) and related compounds (70—100 mg ml^{-1})

		ArH							CH$_2$		
Compound	Solvent [a]	2-H	3-H	4-H	5-H	6-H	J_{ortho}/ Hz	J_{meta}/ Hz	Adjacent to sulpho-group (γ)	Benzylic (α)	Middle (β)
$Ph[CH_2]_3SO_3^-$	D_2O	⟵ 7·40—7·00 ⟶							3·02—2·77	2·77—2·45	2·26—1·84
$Ph[CH_2]_3SO_3^-$	61·9% H_2SO_4	⟵ 7·50—7·15 ⟶							3·20—2·88	2·88—2·54	2·30—1·88
$4\text{-}HO_3SC_6H_4[CH_2]_3SO_3H$	95·2 (93·4)% H_2SO_4	7·44	7·88		7·88	7·44	8·2		3·55—3·15	3·03—2·60	2·40—2·00
$2\text{-}HO_3SC_6H_4[CH_2]_3SO_3H$	95·2 (93·4)% H_2SO_4		8·0 [b]						3·6—3·4	3·2—3·0	2·5—2·3
$2,4\text{-}(HO_3S)_2C_6H_3[CH_2]_3\text{-}SO_3H$	104·3 (102·5)% H_2SO_4		8·51		8·18	7·71	8·5	1·7	3·95—3·56	3·38—3·05	2·84—2·35
$3,5\text{-}(HO_3S)_2C_6H_3[CH_2]_3\text{-}SO_3H$	104·3 (102·5)% H_2SO_4								3·6—3·3	3·2—2·9	2·6—2·3

[a] The data in parentheses refer to the acid concentration after sulphonation. [b] 3-H of toluene-*o*-sulphonic acid absorbs at slightly lower field than 3-H of toluene-*p*-sulphonic acid.[15]

EXPERIMENTAL

Sodium 3-phenylpropane-1-sulphonate (Found: C, 44·2; H, 5·4; S, 13·1; Na, 9·4. Calc. for $C_9H_{11}NaO_3S,1{\cdot}25H_2O$: C, 44·2; H, 5·4; S, 13·1; Na, 9·4%) was prepared by reaction of 1-bromo-3-phenylpropane (puriss. Schuchardt) with sodium sulphite.[13] The experimental procedures and the spectrometers employed have been described.[14] For

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* In the preferred conformation of n-propylbenzene, and accordingly of 3-sulpho-PPSA, one of the benzylic C–H bonds is in a position which is eclipsed by the benzene ring.[12] This C–H bond thus cannot exert any hyperconjugative electron release. The other benzylic C–H is in a situation which is less favourable for this type of electron release than those of the benzylic C–H bonds of the freely rotating methyl group in toluene [12] and thus in toluene-*m*-sulphonic acid. C–C Hyperconjugation is generally considered to be less than C–H hyperconjugation. Accordingly, the ratio of 4- to 5-substitution of 3-sulpho-PPSA will be much smaller than 0·28,[1] the value observed for toluene-*m*-sulphonic acid.

[12] J. M. A. Baas, Thesis, Technische Hogeschool, Delft, The Netherlands, 1970, p. 65; J. M. A. Baas and B. M. Wepster, *Rec. Trav. Chim.*, 1971, **90**, 1081.

[13] E. B. Evans, E. E. Mabbott, and E. E. Turner, *J. Chem. Soc.*, 1927, 1161.

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

[15] C. Ris, Thesis, University of Amsterdam, 1973, ch. 2.

n.m.r. spectroscopy 'TSP' (sodium 2,2,3,3-tetradeuterio-4,4-dimethyl-4-silapentanoate) was used as external reference.

Information concerning the products formed in the sulphonation was obtained from n.m.r. spectroscopy (Table 2). In D_2O as solvent, the spectrum of sodium 3-phenylpropane-1-sulphonate consists of an aromatic hydrogen absorption centred at δ 7·22 (5H), and three complex absorptions at δ 3·0—2·8 (2H), 2·8—2·5 (2H), and 2·3—1·8 (2H). After the spectrum had been compared with the spectra of ethylbenzene, ethanesulphonic acid, and 2-phenylethane-1-sulphonic acid in 80% H_2SO_4,[14] the three methylene absorptions from low to high field were assigned to the CH_2 adjacent to the sulphonate group, to the benzylic CH_2, and to the intermediate CH_2 respectively. This assignment was verified by decoupling experiments. Saturation of the high field CH_2 leads to two singlet absorptions for the other two methylene absorptions. On the other hand, saturation of the low field methylene reduces the high field CH_2 absorption pattern to a triplet.

The degree of *ortho*-substitution was calculated from the absorption areas of the methylene hydrogens P and Q (Figure 2A) by the equation: % *ortho* = $(P - Q)/(P + Q)$.

The relative amount of the 3,5-disulpho-isomer present in the oleum sulphonation mixture was calculated from the absorption areas of the methylene hydrogens R and S (Figure 2B) by the equation: % 3,5-isomer = $(S - R)/(R + S)$.

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