Aromatic Sulphonation. Part 53.[1] Kinetics and Mechanism of Sulphonation of ω-Phenylalkane-1-sulphonic Acids in Sulphuric Acid. Comparison of the Side-chain SO_3H and OSO_3H Substituent Effects

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The sulphonation of a series of sulphonic acids of the general structure $Ph[CH_2]_nSO_3H$ (n = 1,2,3—6) in concentrated aqueous sulphuric acid at 25 °C has been studied, and partial rate factors are reported. With benzenesulphonic acid the SO_3H substituent exhibits a $-M$ effect in addition to the combined inductive and direct field effect. The results of the ω-phenylalkane-1-sulphonic acids are explained in terms of the competing deactivating effect of the SO_3H group (a combined relayed inductive and direct field effect) and the activating hyperconjugative electron release of the benzylic CH_2 group. The former effect decreases with increasing n, whereas the latter effect only slightly increases upon increasing n from 1 to 2.

As judged from a comparison with the f_p of the sulphates of the general structure $Ph[CH_2]_nOSO_3H$ ($n \geqslant 2$) the electronic effects of the $[CH_2]_nOSO_3H$ and the $[CH_2]_nSO_3H$ groups are about the same.

INFORMATION concerning the substituent effect of the SO_3H group is rather limited, as was concluded in a recent review.[2] With the aim of obtaining information on the substituent effect of the SO_3H group, a study on 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 4-phenylbutane-1-, 5-phenylpentane-1-, and 6-phenylhexane-1-sulphonic acid.

In order to ascertain the steric requirements of the

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[1] Part 52, A. Koeberg-Telder and H. Cerfontain, *J.C.S. Perkin II*, preceding paper.

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

$[CH_2]_nSO_3H$ substituents, a comparison of the partial rate factors for this type of substituents has been made with those of the $[CH_2]_nBu^t$ group,[3] the steric requirements of the SO_3H group being considered comparable with those of the Bu^t group.

TABLE 1

Sulphonation of $Ph[CH_2]_nSO_3H$ at 25 °C

n	H_2SO_4 (wt. %)	$10^4{}_{ps}k_1/s^{-1}$	Degree of *ortho*-substitution (%)	Ref.
0	101.2		$\leqslant 1$	*a*
1	90.2	0.002 4 [b]	4 ± 1 (96.5% H_2SO_4)	*c*
2	81.8	0.022 [d]		
	83.8	0.045 [d]		
	90.2	3.16	7 ± 2	*e*
3	90.2	28.8	7 ± 3 (95.2% H_2SO_4)	*f*
4	90.2	116 [g]	18 ± 2	
5	90.2	167 [g]	26 ± 3	
6	90.2	215 [g]	23 ± 2	

[a] A. J. Prinsen, A. Koeberg-Telder, and H. Cerfontain, *Tetrahedron Letters*, 1970, **26**, 1953. [b] Extrapolated value based on the assumption that the sulphonation rate ratio of phenylmethanesulphonic acid to 2-phenylethane-1-sulphonic acid is the same for 90.2 and 98.4% H_2SO_4. [c] Z. R. H. Nienhuis, W. J. Spillane, and H. Cerfontain, *Canad. J. Chem.*, 1972 **50**, 1591. [d] Measured u.v. spectroscopically at λ 267 nm. [e] A. Koeberg-Telder, Z. R. H. Schaasberg-Nienhuis, and H. Cerfontain, *Canad. J. Chem.*, 1973, **51**, 462. [f] H. Cerfontain and Z. R. H. Schaasberg-Nienhuis, *J.C.S. Perkin II*, 1974, 536. [g] Measured u.v. spectroscopically at λ 265 nm.

Our recent studies on the sulphuric acid sulphation and sulphonation of ω-phenylalkan-1-ols [1] allowed us to make a comparison between the $[CH_2]_nSO_3H$ and $[CH_2]_nOSO_3H$ substituents.

TABLE 2

Partial rate factors for sulphonation of $Ph[CH_2]_nX$ by the $H_2S_2O_7$ mechanism at 25 °C

	f_p				f_o				f_m			f_o/f_p			σ_p^+	σ_m^+
n	X = SO_3H [a]	OSO_3H [b]	Bu^t	Me	X = SO_3H [a]	OSO_3H [b]	Bu^t	Me	X = SO_3H [a]	Bu^t	Me	X = SO_3H [a]	Bu^t	Me	X = SO_3H [a]	
0	(0.2 ±0.1).10^{-8} [c]		18 ±2 [d]	84 ±6 [e]	<0.04 ×10^{-8} [c]		<0.1 [d]	47 ±4 [e]	(4 ±3).10^{-8} [c]	1.5 ±0.3 [d]	4 ±1 [d,e]	<0.02	<0.05	0.56 ±0.01		
1	(4.6 ±1.0).10^{-4} [f,g]		82 ±12 [h]	73 ±6 [e]	(0.19 ±0.05).10^{-4} [g]		1.9 ±0.6 [h]	26 ±3 [e]	(2.3 ±0.5).10^{-4} [f,g]	5.7 ±1.4 [h]		0.4 ±0.01	0.025 ±0.008	0.36 ±0.03	0.59 ±0.05	0.64 ±0.05
2	1.9 ±0.2 [i]	3.5 ±0.4	80 ±8 [j]	80 ±8 [j]	0.07 ±0.03 [i]	<0.1	24 ±3 [k]	21 ±3 [e]	0.03 ±0.01 [h]			0.04 ±0.02	0.30 ±0.03	0.26 ±0.02	−0.05 ±0.01	0.28 ±0.05
3	15.0 ±1.5 [l]	21 ±3	80 ±8 [j]		0.6 ±0.3 [l]	1.5 ±0.4	23 ±3 [k]		0.32 ±0.16 [k]			0.04 ±0.02	0.29 ±0.03		−0.21 ±0.02	0.09 ±0.05
4	49 ±8 (54) [m]	46 ±6			6.0 ±1.2	4.3 ±1.5						0.12 ±0.02			−0.30 ±0.03	
5	64 ±12 (71) [m]	75 ±8			12.3 ±2.4	12 ±3						0.19 ±0.03			−0.32 ±0.03	
6	86 ±16 (95) [m]	93 ±10			14.1 ±2.8	12 ±4						0.16 ±0.03			−0.34 ±0.03	
7				80 ±8 [j]				23 ±3 [k]						0.29 ±0.03		
10		130 ±13				24 ±6										

[a] Only with benzenesulphonic acid ($n = 0$) the reacting substrate species is the sulphonate anion (see text). [b] A. Koeberg-Telder and H. Cerfontain, *J.C.S. Perkin II*, submitted for publication. [c] Calculated from the benzenesulphonic acid sulphonation isomer ratio (A. J. Prinsen, A. Koeberg-Telder, and H. Cerfontain, *Tetrahedron*, 1970, **26**, 1953) and the estimated benzenesulphonic acid to benzene rate ratio (H. Cerfontain, 'Mechanistic Aspects in Aromatic Sulphonation and Desulphonation,' Interscience, New York, 1968, p. 130). [d] H. de Vries and H. Cerfontain, *Rec. Trav. chim.*, 1967, **86**, 873. [e] H. Cerfontain and Z. R. H. Schaasberg-Nienhuis, *J.C.S. Perkin II*, 1974, 536. [f] Originally reported erroneously to be 10 times too high.[g] [g] Z. R. H. Nienhuis, W. J. Spillane, and H. Cerfontain, *Canad. J. Chem.*, 1972, **50**, 1591. [h] C. Ris, Z. R. H. Schaasberg-Nienhuis, and H. Cerfontain, *Tetrahedron*, 1973, **29**, 3165. [i] A. Koeberg-Telder, Z. R. H. Nienhuis, and H. Cerfontain, *Canad. J. Chem.*, 1973, **51**, 462. [j] Average of the available f_p values for primary alkylbenzenes which are all equal within experimental error.[e] [k] Calculated from f_p[j] and the reported [e] f_o/f_p ratio. [l] H. Cerfontain and Z. R. H. Schaasberg-Nienhuis, *J.C.S. Perkin II*, 1973, 1413. [m] Data calculated with an assumed *meta*- to *para*-substitution ratio of 0.10 ± 0.04.[e,i,l] The data in parentheses refer to calculations in which the degree of *meta*-substitution was taken to be zero.

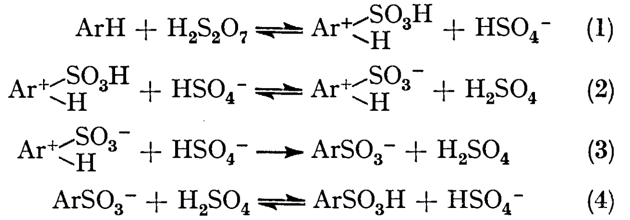
RESULTS

The pseudo-first-order rate constants for sulphonation of the ω-phenylalkane-1-sulphonic acids in a large excess of 90.2% H_2SO_4 (${}_{ps}k_1$) are given in Table 1. These overall rate constants increase with increasing length of the side-chain to level off to a limiting value of 250×10^{-4} s^{-1}.

The degree of *ortho*-substitution of the three ω-phenylalkane-1-sulphonic acids on sulphonation in 90.2% H_2SO_4 was estimated from the ^1H n.m.r. spectra of the reaction mixtures as such. The data are also given in Table 1. The derived partial rate factors are given in Table 2, together with other ones for comparison.

DISCUSSION

The sulphonation of aromatic substrates in 90—98% H_2SO_4 proceeds by the sequence (1)—(4).[4]



$$ArH + H_2S_2O_7 \rightleftharpoons Ar^{+}\!\begin{smallmatrix}\diagup SO_3H\\ \diagdown H\end{smallmatrix} + HSO_4^- \qquad (1)$$

$$Ar^{+}\!\begin{smallmatrix}\diagup SO_3H\\ \diagdown H\end{smallmatrix} + HSO_4^- \rightleftharpoons Ar^{+}\!\begin{smallmatrix}\diagup SO_3^-\\ \diagdown H\end{smallmatrix} + H_2SO_4 \qquad (2)$$

$$Ar^{+}\!\begin{smallmatrix}\diagup SO_3^-\\ \diagdown H\end{smallmatrix} + HSO_4^- \longrightarrow ArSO_3^- + H_2SO_4 \qquad (3)$$

$$ArSO_3^- + H_2SO_4 \rightleftharpoons ArSO_3H + HSO_4^- \qquad (4)$$

For the sulphonation at positions which do not exhibit steric restrictions step (3) becomes rate limiting only at acid concentrations >95% H_2SO_4.[5]

In the acid range of 90—98% H_2SO_4 the ω-phenylalkane-1-sulphonic acids are present predominantly in the un-ionized form, the half-deprotonation of, for example, phenylmethanesulphonic acid being at 82.6% H_2SO_4.[6]

The problem of whether the sulphonic acid or the sulphonate anion is the reacting species will be discussed on the basis of the rate profiles shown in Figure 1. For 3-phenylpropane-1-sulphonic acid at acid concentrations >88% H_2SO_4 and for 2-phenylethane-1-sulphonic acid in the range of 90—95% H_2SO_4 the correlation of log k with log $a_{H_2S_2O_7}$ are linear both with a slope of 0.82.

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[3] H. Cerfontain and Z. R. H. Schaasberg-Nienhuis, *J.C.S. Perkin II*, 1974, 536.

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

[5] C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, 1967, **88**, 865.

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

For toluene and benzene over the respective acid ranges of 87—91 and 82—96% H_2SO_4 linear correlations are observed with slopes of 0.87 and 0.89 respectively. The similarity in slope for the sulphonic acids and the hydrocarbons indicates that the sulphonating entity for the sulphonic acids is the same as for the hydrocarbons at high sulphuric acid, *viz.* $H_2S_2O_7$.[4] The upward curvature observed with the two sulphonic acids at lower sulphuric acid concentrations 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,[6-8] and half-deprotonation of, for example, phenylmethanesulphonic acid occurs at 82.6% H_2SO_4.[6]

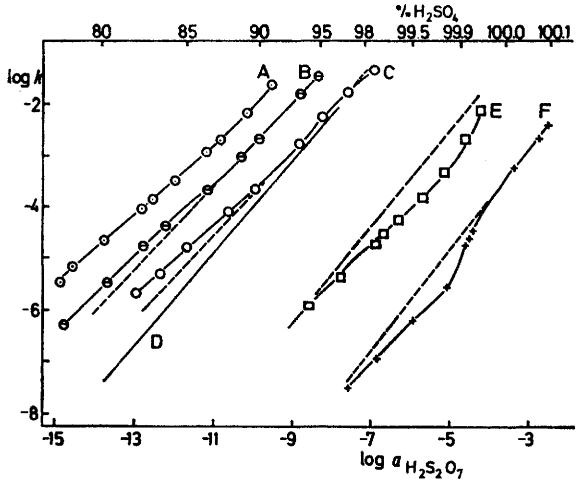

FIGURE 1 Rate profiles for sulphonation with concentrated aqueous sulphuric acid: A, *para*-position of toluene, slope >88% H_2SO_4 0.87 and <86% H_2SO_4 0.66; B, *para*-position of 3-phenylpropane-1-sulphonic acid, slope 0.82; C, *para*-position of 2-phenylethane-1-sulphonic acid, slope 0.82; D, one position of benzene (line), slope 0.89; E, *para*-position of phenylmethanesulphonic acid, slope broken line 0.94; F, one position in *p*-difluorobenzene, slope broken line 0.97

The occurrence of an inflection point in the graph of 3-phenylpropane-1-sulphonic acid seems to indicate[9] that this explanation applies at any rate.

A second explanation of the upward curvature at lower acid concentrations may be additional sulphonation by, for example, $H_3SO_4^+$.[10] 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.[4] For the sulphonation of benzene and the 3- and 4-position of toluene, the sulphuric acid concentrations of equal rate contributions are 79, 80, and 85.7% H_2SO_4 respectively.[4] For the *para*-positions of 3-phenylpropane-1- and 2-phenylethane-1-sulphonic acid, the reactivities are in between those of the 3- and 4-position of toluene, and those of the 3-position of toluene and 1-position of benzene respectively (Table 2), and the sulphuric acid concentrations of equal rate contributions by $H_2S_2O_7$ and $H_3SO_4^+$ would accordingly be at 81—82 and 79—80% H_2SO_4 respectively. However, with 2-phenylethane-1-sulphonic acid the upward curvature at low sulphuric acid concentrations occurs in fact at a much higher sulphuric acid concentration (Figure 1), indicating that with this substrate the upward curvature is also due to the sulphonic acid ionization. In electrophilic sulphonation, the sulphonate anion will be more reactive than the corresponding un-ionized sulphonic acid. This difference in rate will be maximal with benzenesulphonic acid, and will decrease with increasing length of the polymethylene side-chain. Support for this view comes from a comparison of the rate profiles of 3-phenylpropane-1- and 2-phenylethane-1-sulphonic acid (Figure 1), since the difference between the observed rate at low acid concentration and the linearly extrapolated rate from the high sulphuric acid concentration region is smaller with the propane- than ethane-sulphonic acid. The rate profiles of phenylmethanesulphonic acid and *p*-difluorobenzene are similar in shape (Figure 1). In 100% H_2SO_4 benzenesulphonic acid will be protonated in part with formation of $PhSO_3H_2^+$,[11] whereas *p*-difluorobenzene is not protonated.[12] The similarity in the shape of the rate profiles may indicate that only one phenylmethanesulphonic acid species is sulphonated over the whole acid range which is then thought to be the un-ionized sulphonic acid. As to benzenesulphonic acid the $[PhSO_3^-]/[PhSO_3H]$ ratio in 90 and 95% H_2SO_4 will be 0.12 and 0.03 respectively.* Because of the now direct connection between the sulpho and phenyl group the difference in rate of the uncharged benzenesulphonic acid and the negatively charged benzenesulphonate anion is thought to be at least a factor of 10^2. Accordingly with benzenesulphonic acid it is mainly the sulphonate anion which is undergoing sulphonation. In fact, the nitration of benzenesulphonic acid with mixed acid with a sulphuric acid concentration up to 98% H_2SO_4 is also considered to proceed through the sulphonate anion as the reacting substrate species.[14] It was, however, further suggested[14] that the ω-phenylalkane-1-sulphonic acids also reacted *via* the sulphonate anion.

The dependence of the logarithm of the partial rate factors on the length of the ω-phenylalkane-1-sulphonic acids is shown in Figure 2. For low values of *n* the three

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* The ionization ratios of benzenesulphonic acid were calculated according to $\log [PhSO_3^-]/[PhSO_3H] = m.H_0^a - pK_a$, using (extrapolated) H_0^a values[13] and the reported[7] pK_a and *m* values.

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

[8] H. Cerfontain, A. Koeberg-Telder, and C. Kruk, *Tetrahedron Letters*, 1975, 3639.

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

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

[11] R. J. Gillespie, *Rev. Pure Applied. Chem.*, 1959, **9**, 1.

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

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

[14] R. B. Moodie, K. Schofield, and T. Yoshida, *J.C.S. Perkin II*, 1975, 788.

types of substitution all increase strongly with increasing n to reach eventually limiting values which are equal to those of the corresponding 1-phenylalkanes. Thus for $n > 5$ there is no specific effect of the side-chain sulphonic acid group on the ring substitution. This renders the existence of an intramolecular sulphonic acid–phenyl (charge transfer) interaction for those substrates unlikely.

A further study of Figure 2 reveals that the curve of $\log f_m$ crosses those of $\log f_p$ and $\log f_o$. This observation will be discussed in terms of variations in the rate of formation of the various 1-arenium-1-sulphonic acid σ-complexes [step (1)].

With benzenesulphonic acid, the partial rate factors are very small (in the order of 10^{-8}). Considering that with this substrate it is the sulphonate anion which is the reacting substrate species, this may be explained in terms of the $-I$ effect relayed through the σ-bonds, the direct field effect and the $-M$ effect of the SO_3^- substituent. The combined inductive and direct field effect do not lead to marked discrimination between *meta-* and *para*-substitution,[15] as was concluded by Ridd from nitration studies of the anilinium and phenyltrimethylammonium ions. In fact, for sulphonation the f_m/f_p ratios for these two ions are in the order of unity, *viz.* 0.8 ± 0.1 [16] and 2.8 ± 0.2 [17] respectively, whereas it is as large as 33 for nitrobenzene.[18] The higher f_m/f_p ratio for nitrobenzene as compared with the anilinium ions has been ascribed to the $-M$ effect which operates with nitrobenzene but is absent with the anilinium ions.[15] For benzenesulphonic acid $f_m/f_p = 20$. This value then suggests that the SO_3^- substituent also exhibits a significant $-M$ effect in addition to the combined inductive and direct field effects.

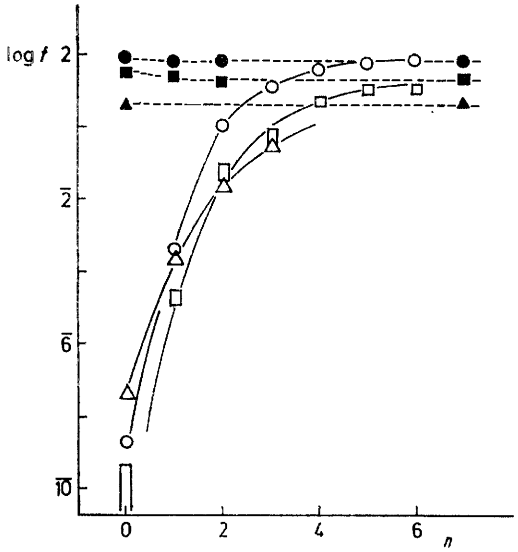
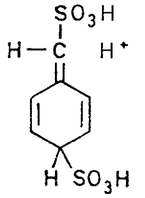


FIGURE 2 Partial rate factors for sulphonation of $Ph[CH_2]_nX$

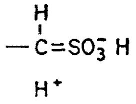
X	*para*	*meta*	*ortho*
SO_3H [a]	○	△	□
Me	●	▲	■

[a] See subscript *a* of Table 2.

With phenylmethanesulphonic acid the order of the f_m and f_p is just reversed from that of the benzenesulphonate anion (see before). This may be explained in terms of CH hyperconjugative stabilization of the transition state of step (1) for *para*-substitution. The partial rate factors are still significantly smaller than unity, indicating that the deactivation by the SO_3H group through a relayed inductive and direct field effect is dominant. With phenylmethanesulphonic acid in contrast to the higher homologues, the hyperconjugative electron release to the reaction centre for *para*-substitution (A) will be only weak, because of (competitive) hyperconjugative interaction between the sulphonic acid and methylene group (B).

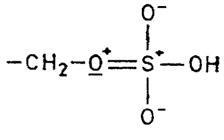


(A)



$$\overset{H}{-C}=SO_3^-\,H \quad H^+$$

(B)



$$-CH_2-\overset{+}{O}=\overset{+}{S}(O^-)_2-OH$$

(C)

With 2-phenylethanesulphonic acid $f_p = 1.3 \pm 0.1$. Apparently the combined inductive and direct field effect is further reduced and the benzylic CH hyperconjugative electron release enhanced (*vide supra*). With increasing length of the polymethylene side-chain the f_p increases to reach the limiting value of the linear alkyl side-chain as a result of a further decrease in the inductive and field effect of the sulphonic acid group.

As to the problem of the steric requirements for sulphonation *ortho* to the polymethylenesulphonic acid side-chain, the f_o/f_p ratios may be compared with those of the $C_6H_5[CH_2]_nBu^t$ series, since the Bu^t and SO_3H groups are comparable in size (Table 2). For $n = 2$ and 3 the f_o/f_p ratio is much smaller for the $[CH_2]_nSO_3H$ than for the $[CH_2]_nBu^t$ substituent (which are already equal to those of the $[CH_2]_nMe$ substituent). This is ascribed to the combined inductive and direct field effect of the side-chain SO_3H substituent and not due to steric hindrance.

The Hammett–Brown reaction constant ρ^+ for sulphonation in sulphuric acid by the mechanism shown in equations (1)—(4) is -5.7 ± 0.3.[4] The substituent constants σ^+ of the $[CH_2]_nSO_3H$ calculated from the partial rate factors with this value are given in Table 2.

For a given value of n ($n \geqslant 2$) the f_o and f_p of the $[CH_2]_nOSO_3H$ and $[CH_2]_nSO_3H$ substituent are about the same (Table 2). The similarity of the f_p values infers that the overall electronic effect of the OSO_3H and SO_3H groups are about the same. This seems to indicate that the carbon bonded sulphate oxygen carries a partial positive charge as indicated by mesomeric structure (C).

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[15] M. Brickman, J. H. P. Utley, and J. H. Ridd, *J. Chem. Soc.*, 1965, 6851.

[16] P. K. Maarsen and H. Cerfontain, unpublished results.

[17] J. C. D. Brandt and A. Rutherford, *J. Chem. Soc.*, 1952, 3927.

[18] H. Cerfontain, *Internat. J. Sulfur Chem.* (*A*), 1973, **2**, 297.

TABLE 3

^1H N.m.r. data of sodium ω-phenylalkane-1-sulphonates and sulphonation products

	Ar$[CH_2]_n$X			δ [a]					
				Arom.			Aliph.		
n	X	Ar	Solvent	2'-H [b]	3'-H [b]	5 H	Cω H_2	C^1H_2	$[CH_2]_{n-2}$
1	SO_3^-	Ph	D_2O			7.92 (s)	4.66 (s)		
2	SO_3^-	Ph	D_2O			7.77 (br, s)	3.56 (m)	3.56 (m)	
3	SO_3^-	Ph	D_2O (+CF_3CO_2H)			7.72 (br, s)	3.16 (br, t)	3.35 (br, t)	2.52 (br, q)
4	SO_3^-	Ph	D_2O (+CF_3CO_2H)			7.72 (br, s)	3.07 (br, t)	3.35 (br, t)	2.0—2.3 (m)
5	SO_3^-	Ph	D_2O			7.62 (br, s)	3.00 (br, t)	3.30 (br, t)	1.5—2.4 (m)
6	SO_3^-	Ph	D_2O			7.61 (br, s)	2.96 (br, t)	3.26 (br, t)	1.5—2.3 (m)
1	SO_3H	4'-$HO_3SC_6H_4$	96.5% H_2SO_4	8.19	8.52		5.18 (s)		
2	SO_3H	4'-$HO_3SC_6H_4$	90.0% H_2SO_4	8.08	8.49		3.87 (br, m)	4.21 (u)	
3	SO_3H	4'-$HO_3SC_6H_4$	93.4% H_2SO_4	7.88	8.32		3.30 (u)	3.75 (u)	2.66 (u)
4	SO_3H	4'-$HO_3SC_6H_4$	90.2% H_2SO_4	7.98	8.39		3.30 (u)	3.93 (u)	2.42 (u)
5	SO_3H	4'-$HO_3SC_6H_4$	90.2% H_2SO_4	7.99	8.39		3.29 (u)	3.92 (u)	1.9—2.9 (um)
6	SO_3H	4'-$HO_3SC_6H_4$	90.2% H_2SO_4	7.94	8.35		3.21 (u)	3.86 (u)	1.8—2.6 (um)
1	SO_3H	2'-$HO_3SC_6H_4$	96.5% H_2SO_4				5.60		
2	SO_3H	2'-$HO_3SC_6H_4$	90.0% H_2SO_4				4.16		
3	SO_3H	2'-$HO_3SC_6H_4$	93.4% H_2SO_4				3.53		
4	SO_3H	2'-$HO_3SC_6H_4$	90.2% H_2SO_4				3.58		
5	SO_3H	2'-$HO_3SC_6H_4$	90.2% H_2SO_4				3.54		
6	SO_3H	2'-$HO_3SC_6H_4$	90.2% H_2SO_4				3.48		

[a] The data in parentheses refer to the observed multiplicity of the signal; br, m, and u stand for broadened, multiplet, and unresolved, respectively. [b] AB system with *J ca.* 8 Hz.

EXPERIMENTAL

The three sodium ω-phenylalkane-1-sulphonates (Ph$[CH_2]_nSO_3Na$, n = 4—6) were obtained by reaction of the corresponding chlorides with aqueous sodium sulphite at 200 °C in an autoclave.[19]

The experimental procedures and the spectrometers employed have been described.[2,3] For ^1H n.m.r. spectroscopy tetramethylsilane (sealed capillary) was used as an external reference. Information concerning the products formed in the sulphuric acid sulphonation was obtained from ^1H n.m.r. spectroscopy (Table 3). In D_2O as solvent the spectra of $Ph[CH_2]_nSO_3Na$ (n = 4—6) consist of a pseudo singlet aromatic hydrogen absorption at δ 7.7 (5 H) and three complex aliphatic hydrogen absorptions at δ 3.3 (2 H), 3.0 (2 H), and 1.5—2.4 [2(n − 2)H]. After the spectra had been compared with that of $C_6H_5[CH_2]_3SO_3Na$,[3] the three aliphatic 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 $[CH_2]_{n-2}$ chain respectively. In the sulphuric acid sulphonation mixtures the presence of the ω-(*p*-sulphophenyl)alkane-1-sulphonic acids is apparent from the aromatic AB absorption patterns, that of the *o*-sulphophenyl derivatives from the low intensity absorptions ~ 0.25 p.p.m. to low field of the benzylic absorptions of the *p*-sulphophenyl isomers. The degree of *ortho*-substitution was calculated from the ratio of the area of the low field and the total benzylic absorptions.

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[19] R. M. Reed and H. V. Tartar, *J. Amer. Chem. Soc.*, 1935, **57**, 570.