Aromatic Sulphonation. Part 76.[1] Sulphonation in Sulphuric Acid of ω-Phenylalkanes containing the NH_3^+, NMe_3^+, or NO_2 Substituent at Position 1. Comparison of the Side-chain NH_3^+, NMe_3^+, NO_2, SO_3H, and OSO_3H Substituent Effects

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The sulphonation of a series of ω-phenylalkanes containing at position 1 the NH_3^+, NMe_3^+, and NO_2 substituent in concentrated sulphuric acid at 25 °C has been studied, and partial rate factors for the mechanism with $H_2S_2O_7$ as sulphonating entity are reported. The limiting values of the partial rate factors for *para*- and *meta*-substitution are equal to those of the corresponding 1-phenylalkanes, but the limiting value for *ortho*-substitution is smaller. The variation of the degree of *ortho*-substitution with the nature of the substituent (NMe_3^+, NH_3^+, NO_2, OSO_3H, SO_3H, and Me) is taken to indicate the operation of an inductive effect in addition to the now generally accepted field effect.

THE effect on the reactivity of benzene of a positively charged substituent at the end of an alkyl side-chain, or directly attached to the phenyl group, has been extensively studied only in aromatic nitration, mainly by Ridd,[2] but also by others.[3] It was therefore thought of interest to study the sulphonation of this type of substrate, especially in relation to our recent results on the sulphonation of ω-phenylalkane-1-sulphonic acids [4] and ω-phenylalkan-1-ols (as their sulphates).[5] We now report the sulphonation in sulphuric acid of a series of ω-phenylalkane-1-ammonium ions, the corresponding trimethylammonium ions, and two ω-phenyl-1-nitroalkanes. A theoretical approach to the effects of positively charged substituents on isomer distribution in electrophilic substitution relevant to our work was published recently.[6]

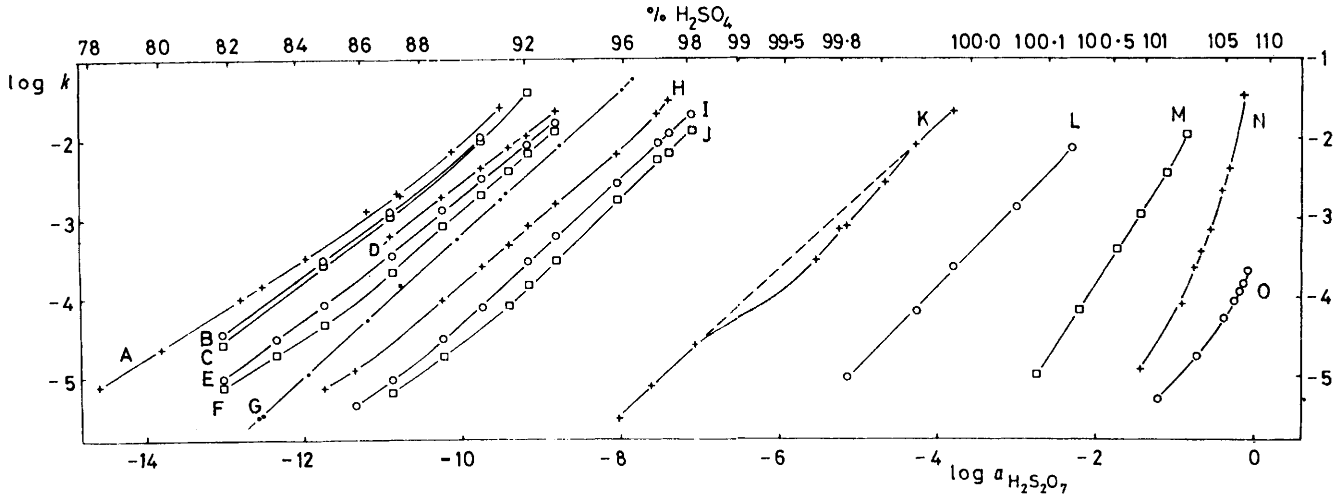

FIGURE 1 Rate profiles for sulphonation in sulphuric acid: A, toluene,[a] slope 0.69—1.23; B, $Ph(CH_2)_4NH_3^+$, slope 0.72—1.20; C, $Ph(CH_2)_4NMe_3^+$, slope 0.73—1.03; D, $Ph(CH_2)_3NO_2$, slope 0.75; E, $Ph(CH_2)_3NH_3^+$, slope 0.69—0.74; F, $Ph(CH_2)_3NMe_3^+$, slope 0.62—0.84; G, benzene,[b] slope 0.90; H, $Ph(CH_2)_2NO_2$, slope for 87—97% H_2SO_4, 0.84; I, $Ph(CH_2)_2NH_3^+$, slope for >89% H_2SO_4, 0.91; J, $Ph(CH_2)_2NMe_3^+$, slope for >92% H_2SO_4, 0.98; K, $PhCH_2NH_3^+$, slope of dotted line 0.91; L, $PhCH_2NMe_3^+$, slope for <100.18% H_2SO_4, 1.01; M, $PhNH_3^+$,[c] slope 1.54; N, $PhNMe_3^+$,[d] slope 1.5—4.8; O, $PhNO_2$,[e] slope 1.1—2.3. The activities of $H_2S_2O_7$ were taken from ref. *f* and for acid concentrations below 97% H_2SO_4 calculated from the activity data of H_2SO_4 and H_2O given in ref. *g*

[a] A. W. Kaandorp, H. Cerfontain, and F. L. J. Sixma, *Rec. Trav. chim.*, 1963, **82**, 113. [b] A. W. Kaandorp. H. Cerfontain, and F. L. J. Sixma, *Rec. Trav. chim.*, 1962, **81**, 969. [c] P. K. Maarsen and H. Cerfontain, *J.C.S. Perkin II*, 1977, 1008. [d] J. C. D. Brand, *J. Chem. Soc.*, 1950, 1004. [e] J. C. D. Brand and W. C. Horning, *J. Chem. Soc.*, 1952, 3922. [f] C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, 1969, **88**, 1298. [g] *Idem, ibid.*, 1968, **87**, 24.

RESULTS

The first-order rate constants for sulphonation of $Ph(CH_2)_nX$ [X = NH_3^+, NMe_3^+, and NO_2] in a large excess of sulphuric acid ($_{ps}k_1$) are collected in Table 1.† For a given sulphuric acid concentration and a given substituent X the overall rate constant increases with increasing length of the side-chain to level off to a limiting value which is significantly greater than the rate constant of benzene,[7] but somewhat smaller than that of toluene.[8] The rate profiles of the

† Phenylnitromethane in both concentrated aqueous and fuming sulphuric acid was found to decompose.

TABLE 1

First-order sulphonation rate constants at 25.0 ± 0.5 °C

		10^4k_1(s^{-1}, ±3%)									
		$Ph(CH_2)_nNH_3^+$				$Ph(CH_2)_nNMe_3^+$				$Ph(CH_2)_nNO_2$	
H_2SO_4 (wt %)	$-\log a_{H_2S_2O_7}$ * (±0.04)	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 2$	$n = 3$
		λ† : 268.0	267.0	266.5	266.0	275.0	267.0	266.0	265.0	267.0	274.0
81.8 ± 0.1	13.02			0.095	0.36			0.075	0.27		
83.3	12.35			0.32				0.19			
84.8	11.74			0.83	3.0			0.47	2.8	0.072	
85.5	11.35		0.043							0.124	
87.0	10.88		0.091	3.4	12.2		0.064	2.1	10.8		6.1
88.8	10.23		0.30	12.6			0.184	8.2		0.97	19.1
90.3	9.73		0.76	34	99			20	96	2.5	43
91.3	9.39			56			0.80	37		4.8	79
92.1	9.16		2.9	84			1.46	68	390	8.2	110
93.3	8.80		6.0	157			2.9	130		15.5	230
95.8	8.03	0.029	27				17.0			63	
96.9	7.62	0.075	38								
97.2	7.52		87				53			210	
97.5	7.38		114				64			300	
98.1	7.09		194				122				
98.2	7.05	0.25									
99.70 ± 0.01	5.53	2.9									
99.82	5.14	7.8				0.096					
99.91	4.65	27									
99.96	4.27	81				0.64					
99.99	3.80	210				2.4					
100.04	2.99					13.5					
100.17	2.30					74					

* C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, 1969, **88**, 1298. † Wavelength in nm at which the rate measurement was made.

TABLE 2

Isomer distribution in the sulphonation in sulphuric acid at 25.0 ± 0.5 °C

		Isomer distribution			
Substrate	H_2SO_4 (wt %)	*ortho*	*meta*	*para*	Ref.
$PhCH_2NH_3^+$	98; 102	5 ± 1	56 ± 5	39 ± 5	
$Ph(CH_2)_2NH_3^+$	92; 98	7 ± 2	11 ± 2	80 ± 5	
$Ph(CH_2)_3NH_3^+$	92; 98	8 ± 2	6 ± 2	85 ± 5	
$Ph(CH_2)_4NH_3^+$	90	7 ± 2	5 ± 2	88 ± 5	
$(PhCH_2)_2NH_2^+$	102	7 ± 3	43 ± 5	50 ± 5	
$(PhCH_2)_3NH^+$	102	3 ± 2			
$PhCH_2NMe_3^+$	102	4 ± 1	78 ± 3	18 ± 2	
$Ph(CH_2)_2NMe_3^+$	92; 98	(4 ± 4 [a])	16 ± 5	80 ± 5	
$Ph(CH_2)_3NMe_3^+$	92; 98	(2 ± 4 [a])	13 ± 5	85 ± 5	
$Ph(CH_2)_4NMe_3^+$	92; 98	(2 ± 4 [a])	10 ± 5	88 ± 5	
$Ph(CH_2)_2NO_2$	98	4 ± 2	10 ± 2	80 ± 5	
$Ph(CH_2)_3NO_2$	92; 98	6 ± 2	7 ± 2	85 ± 5	
$Ph(CH_2)_7Cl$	98	33 ± 4			
PhMe	91.0	48 [b]	4 [b]	48 [b]	*c, d*
PhMe	95.8	50.2	4.9	44.9	*d*
PhMe	98.8	49.3	5.2	45.5	*d*
$Ph(CH_2)_7Me$	95	34 ± 2			*e*

[a] % *ortho* = 100 − % *meta* − % *para*. [b] Graphically interpolated value. [c] L. Vollbracht, Thesis (in English), University of Amsterdam, 1962, p. 65. [d] H. Cerfontain, F. L. J. Sixma, and L. Vollbracht, *Rec. Trav. chim.*, 1963, **82**, 659. [e] H. Cerfontain and Z. R. H. Schaasberg-Nienhuis, *J.C.S. Perkin II*, 1974, 536.

various substrates and of some other relevant substrates are shown in Figure 1. The profiles show that the reactivity order for a given chain length is $NO_2 > NH_3^+ > NMe_3^+$, and that the reactivity for a given substituent X increases with increasing length of the polymethylene chain. The sulphonation isomer distributions for the three types of substrates are given in Table 2. The partial rate factors for the three types of substrates, derived from the data of the Tables 1 and 2, are compiled in Table 3. Those of $Ph(CH_2)_nX$ [$X = NH_3^+$, $n = 0, 1$; $X = NMe_3^+$, $n = 0, 1$; $X = NO_2$, $n = 0$] were calculated from the reported sulphonation isomer distributions (ref. 9 and Table 2 *) and the estimated rate constants for these substrates (ref. 9, 12, 13 and Table 1) relative to that for benzene.[7] The k_{PhY}/k_{PhH} ratios ($Y = NO_2$, NMe_3^+, NH_3^+, $CH_2NH_3^+$) were estimated by a stepwise comparison by using the kinetic results of *p*-difluorobenzene,[14] the reactivity of which is between those of PhX and benzene, as described [15,16] elsewhere.† The partial rate factors for the SO_3^-, $(CH_2)_nSO_3H$,[4] (CH_2)–OSO_3H [5] and $(CH_2)_nMe$ [17] substituents have been published previously.

The isomer distributions for the sulphonation of $(PhCH_2)_pNH_{4-p}^+$ [$p = 2, 3$] have also been determined (Table 2). The degree of *ortho*-substitution decreases with increasing *p*. The sulphonation of $(PhCH_2)_3NH^+$ is much

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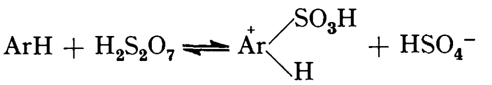
* For $PhNMe_3^+$ the amount of *ortho*-substitution was taken to be <2%, *i.e.* the upper limit of *ortho*-sulphonation of t-butylbenzene,[10] and the *meta* : *para* ratio the value reported by Brand.[11]

† The rate constants for the substrates relative to that for benzene (k_{PhY}/k_{PhH}) thus determined are: $PhNO_2$, 2.9 × 10^{-11}; $PhNH_3^+$, 1.6 × 10^{-9}; $PhNMe_3^+$, 6.8 × 10^{-11}; $PhCH_2NMe_3^+$, 4.3 × 10^{-7}.

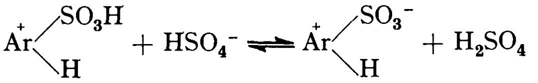
slower than that of $(PhCH_2)_2NH_2^+$,* the rate constant for which is about the same as that for $PhCH_2NH_2^+$.

DISCUSSION

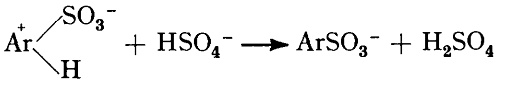
The sulphonation of aromatic substrates in 90—99% H_2SO_4 proceeds by the sequence (1)—(4).[18] For the sulphonation at positions which do not exhibit steric restrictions step (3) becomes rate limiting only at acid concentrations >95% H_2SO_4.[19] The rate-limiting character of step (3) is enhanced for sulphonation at positions which do encounter steric restrictions.[20]



$$ArH + H_2S_2O_7 \rightleftharpoons \overset{+}{Ar}(SO_3H)(H) + HSO_4^- \qquad (1)$$



$$\overset{+}{Ar}(SO_3H)(H) + HSO_4^- \rightleftharpoons \overset{+}{Ar}(SO_3^-)(H) + H_2SO_4 \qquad (2)$$



$$\overset{+}{Ar}(SO_3^-)(H) + HSO_4^- \longrightarrow ArSO_3^- + H_2SO_4 \qquad (3)$$

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

The dependence of the logarithm of the partial rate factors on the length of the side-chain for the three types of compounds are shown in Figure 2 in which they are further compared with that of the SO_3H substituent (which was found to exhibit about the same overall electronic effect as the OSO_3H substituent [4]). For low values of n, the rate constants all increase strongly with increasing n to reach eventually limiting values which for *meta*- and *para*-substitution are equal to those for the corresponding 1-phenylalkanes (Figure 2A, B), as observed with the ω-phenylalkane-1-sulphonic acids [4] and the ω-phenyl-1-alkyl hydrogen sulphates.[5] On the other hand, the limiting f_o values for high values of n appear to be lower than those for the corresponding 1-phenylalkanes and the ω-phenylalkane-1-sulphonic acids (Figure 2C). Also the degree of *ortho*-substitution is smaller for the nitration and bromination of $Ph(CH_2)_n$-X [X = NH_3^+, NMe_3^+, SMe_2^+; n = 1, 2],[21] than for the nitration [22] and bromination [21] of the corresponding 1-phenylalkanes.

For a given side-chain length with $n \geqslant 2$, the degree of *ortho*-sulphonation increases with variation of the substituent in the order $NMe_3^+ < NH_3^+ = NO_2 < SO_3H \leqslant OSO_3H < Me$ (*cf.* Table 2 and refs. 4, 5) which is the order of decreasing positive charge of the atom of the substituent attached to the polymethylene chain with the exception of NO_2.†

The equality of the limiting partial rate factor values, *i.e.* for $n \geqslant 4$, for *para*-substitution of the ammonium type of substrates and the 1-phenylalkanes seems to render the existence of an intramolecular close-contact ammonium-phenyl (charge transfer) interaction for the ammonium type of substrates unlikely.

According to Rees, Ridd, and Ricci the variation in the partial rate factors for *meta*-substitution (which are a measure of non-conjugative interaction) of $Ph(CH_2)_n$-NMe_3^+ with the side-chain length is more consistent with the operation of a field effect than with that of an inductive effect,[2a] although other work by Rees and Ridd

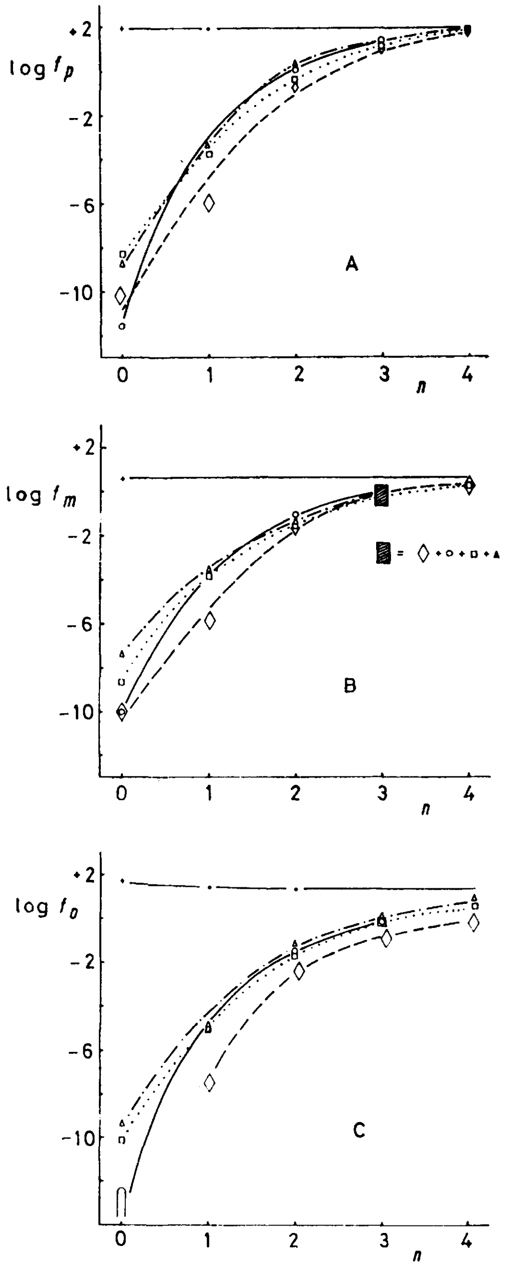


FIGURE 2 Partial rate factors for *para*-(A), *meta*-(B), and *ortho*-(C) sulphonation of $Ph(CH_2)_nX$

X	
NO_2	○ ——— ○
N^+H_3	□ ········ □
N^+Me_3	◊ – – – – – – ◊
SO_3H	△ —·—·— △
Me	+ ——— +

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* $(PhCH_2)_2NH_2^+$ and $(PhCH_2)_3NH^+$ in 100.0% H_2SO_4 at 25 °C for one week are sulphonated to the extent of 100% and 50% per phenyl ring, respectively.

† The effective positive charge at nitrogen of *e.g.* the $PhNH_3^+$ ion in sulphuric acid is substantially less than that of the $PhNMe_3^+$ ion as result of dispersion of the positive charge by solvation,[6] *i.e.* by hydrogen bonding of the ammonium hydrogens of $PhNH_3^+$ with the solvent bisulphate ions.

on the hydrogen exchange in a bridged anthracene derivative carrying a NH_3^+ substituent[23] does not seem in line with this view. The present results for the *ortho*-substitution with the neutral but multipolar substituents like NO_2, SO_3H, and OSO_3H in relation to those of the ammonium substituents cannot be easily reconciled with the presently favoured view of the selective importance of the through space (field) effect, and may indicate the additional operation of an inductive effect *via* the σ-bonds of the methylene chain.

As pointed out by Ridd,[24] the degree of *ortho*-substitution of the ions $Ph(CH_2)_nNH_3^+$ and $Ph(CH_2)_nNMe_3^+$ for a given value of n decreases in the order bromination[21] > nitration[22] > sulphonation (Table 2). This order seems to indicate that the disturbing factor for the *ortho*-substitution is steric rather than polar in origin. This interpretation of course infers that the conformation of the carbon chain is not restricted to that giving the greatest separation of the pole from the phenyl ring.[24] The Hammett-Brown reaction constant ρ^+ for sulphonation in sulphuric acid by the mechanism shown in equations (1)—(4) is -5.7 ± 0.3.[18] The substituent constants σ^+ of $(CH_2)_nX$ ($X = NH_3^+$, NMe_3^+, and NO_2) calculated from the partial rate factors with this value are given in Table 3.

TABLE 3

Partial rate factors and substituent constants for the sulphonation of some monosubstituted benzenes by the $H_2S_2O_7$ mechanism at 25 °C

Substituent	f_o [a]	f_m [a]	f_p [a]	f_o/f_p	f_m/f_p	σ^+_m	σ^+_p
NH_3^+	7×10^{-11}	2×10^{-9}	4×10^{-9}	0.02	0.55	1.5	1.5
$CH_2NH_3^+$	1.2×10^{-5}	1.3×10^{-4}	1.8×10^{-4}	0.13	0.7	0.68	0.66
$(CH_2)_2NH_3^+$	0.017	0.027	0.39	0.04	0.07	0.28	0.07
$(CH_2)_3NH_3^+$	0.6	0.5	13.4	0.05	0.04	0.06	−0.20
$(CH_2)_4NH_3^+$	2.4	1.8	62	0.04	0.03	−0.04	−0.31
NMe_3^+	$<4 \times 10^{-12}$	16×10^{-11}	6×10^{-11}	<0.07	2.8	1.7	1.8
$CH_2NMe_3^+$	5×10^{-8}	10×10^{-7}	4×10^{-7}	0.11	2.2	1.05	1.12
$(CH_2)_2NMe_3^+$	$(1—8) \times 10^{-3}$	0.018	0.18	*ca.* 0.02	0.10	0.31	0.13
$(CH_2)_3NMe_3^+$	0.04—0.3	0.7	8.9	*ca.* 0.01	0.08	0.03	−0.17
$(CH_2)_4NMe_3^+$	0.1—1.1	1.8	52	*ca.* 0.01	0.04	−0.05	−0.30
NO_2	$\leqslant 4 \times 10^{-13}$	9×10^{-11}	3×10^{-12}	⩽0.17	33.0	1.8	2.0
$(CH_2)_2NO_2$	0.03	0.07	1.0	0.02	0.06	0.21	−0.007
$(CH_2)_3NO_2$	0.7	0.8	20	0.04	0.04	0.02	−0.22

[a] The precision of the partial rate factors follows from the precision of the data in the Tables 1 and 2.

In the acid range of 90—98% H_2SO_4 the graphs of log k *vs.* log $a_{H_2S_2O_7}$ are linear, as observed for chlorobenzene,[19] and with a similar slope. It is therefore suggested by analogy that the sulphonation in that acid range of the substrates presently studied proceeds by the mechanism proposed for chlorobenzene,[19] *viz.* by the sequence (1)—(4) with (3) as rate-limiting step.

The variation of log k with log $a_{H_2S_2O_7}$ of $PhCH_2NH_3^+$ (Figure 1) is very similar to that of the sulphonation of *p*-difluorobenzene,[14] phenylmethanesulphonic acid,[25] and phenylsulphamic acid[26] and may therefore be explained in terms of the mechanism proposed for those substrates.[14]

With the $PhNH_3^+$ and $PhNMe_3^+$ ions, the partial rate factors are very small (in the order of 10^{-9} and 10^{-10}, respectively). This may be explained in terms of the combined inductive and direct-field effect. The higher values for the $PhNH_3^+$ ion are ascribed to a higher degree of solvation of this ion, as compared with the $PhNMe_3^+$ ion, due to hydrogen bonding (see before) which reduces the effective positive charge at nitrogen. This difference between the two types of ammonium ions is still apparent for the ions with $n = 1$ and 2.

EXPERIMENTAL

Materials.—The ω-phenyl-1-aminoalkanes, 1-phenyl-7-chloroheptane, and phenylnitromethane were commercial products. The salts $Ph(CH_2)_nNMe_3^+Br^-$ ($n = 1, 2, 3$) were prepared by the introduction of trimethylamine vapour into an ethereal solution of the corresponding bromide, and recrystallization of the precipitate from ethanol.[27] $Ph(CH_2)_4NMe_3^+I^-$ was prepared by refluxing the corresponding amine (8.6 g), methyl iodide (30 g), and sodium carbonate (5.6 g) in a mixture of water (100 ml) and ethanol (50 ml) for 3 h,[28] subsequent removal of the solvent, and recrystallization of the residue from ethanol. The two ω-phenyl-1-nitroalkanes were prepared from the corresponding bromides.[29] The crude product was purified by preparative g.l.c. (2 m copper column, 20% Apiezon M on Kieselguhr, 42—60 mesh, 158 °C, 85—90 ml He/min). Satisfactory elemental microanalysis were obtained for all compounds with the exception of $Ph(CH_2)_3NO_2$ which, according to ^1H n.m.r., contained *ca.* 15% of an impurity.* The concentrations of the sulphuric acid solutions employed were determined by measuring the rate constants of sulphonation of substrates for which the rate constants had been determined with high precision previously, *viz.* $Ph(CH_2)_3SO_3K$,[4] potassium biphenyl-3- and -4-sulphonate,[30] bromobenzene,[31] *p*-difluorobenzene, and 1,2,3,4-tetrafluorobenzene.[14]

Sulphonation Procedures and Spectrometers.—The experimental procedures and ^1H n.m.r. spectrometers employed have been described previously,[4,17] except for the Bruker HX-360 instrument used for the analysis of the monosulphonic acid mixtures obtained with both $PhCH_2NH_3^+$ and $PhCH_2NMe_3^+$.

In order to improve the resolution of the ^1H n.m.r. spectra, the fuming sulphuric acid reaction mixtures were usually diluted to *ca.* 80% H_2SO_4 by bubbling nitrogen through the solution (to remove SO_3) and subsequently adding ice.

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* The reaction of the impurity in a given sulphuric acid concentration was found to be very slow relative to the sulphonation of $Ph(CH_2)_3NO_2$.

TABLE 4

^{1}H N.m.r. data of $Ph(CH_2)_nX$ [X = NO_2, NH_3^+, and NMe_3^+] and sulphonation products

$Ar(CH_2)_nX$				Arom.					Aliph.					
n	X	Ar	Solvent	2′-H	3′-H	4′-H	5′-H	6′-H	C^1H_2	C^3H_2	C^3H_2	C^4H_2	NH_3^+	NMe_3^+
2	NO_2	Ph	CCl_4	←		7.40—7.75^h		→	3.60^a	4.84^a				
2	NO_2	$4'$-$C_6H_4SO_3H$	98% H_2SO_4	7.98^b	8.40^b				3.93^a	5.35^a				
2	NO_2	$2'$-$C_6H_4SO_3H$	98% H_2SO_4	8.54					4.4					
2	NO_2	$2',4'$-$C_6H_3(SO_3H)_2$	103% H_2SO_4		9.13^e		8.82^b	8.37^b	4.40^d	5.51^d				
2	NO_2	$3',5'$-$C_6H_3(SO_3H)_2$	103% H_2SO_4	8.98		9.22			4.03^d	5.46^d				
3	NO_2	Ph	CCl_4	←		7.45—7.80^h		→	3.13^a	2.71^f	4.69^a			
3	NO_2	$4'$-$C_6H_4SO_3H$	92% H_2SO_4	7.91^b	8.34^b				3.29^a	2.82^f	5.02^a			
3	NO_2	$2',4'$-$C_6H_3(SO_3^-)_2$	D_2O		8.70^e		8.33^b	7.98^b	3.03^a	1.60^f	3.78^a			
3	NO_2	$2',4'$-$C_6H_3(SO_3H)_2$	107% H_2SO_4		9.21		8.93^b	8.43^b	3.81^d	3.10^d	5.61^d			
3	NO_2	$3',5'$-$C_6H_3(SO_3H)_2$	107% H_2SO_4	9.07		9.27								
1	NH_3^+	$4'$-$C_6H_4SO_3H$	98% H_2SO_4	8.25^b	8.58^b				4.99^g				6.8	
1	NH_3^+	$2'$-$C_6H_4SO_3H$	98% H_2SO_4						5.21^g					
1	NH_3^+	$3'$-$C_6H_4SO_3H$	98% H_2SO_4	8.60					4.99^g				6.8	
1	NH_3^+	$2',4'$-$C_6H_3(SO_3H)_2$	99% H_2SO_4		9.26		9.05^b	8.61^b	5.26^d				6.8	
1	NH_3^+	$3',5'$-$C_6H_3(SO_3H)_2$	99% H_2SO_4	9.06		9.25			5.15^d				6.8	
2	NH_3^+	$4'$-$C_6H_4SO_3H$	98% H_2SO_4	8.00^b	8.41^b				3.65^a	3.94^a			6.55	
2	NH_3^+	$2',4'$-$C_6H_3(SO_3H)_2$	107% H_2SO_4		9.28^e		9.01^b	8.47^b	← 4.13^d →				6.42	
3	NH_2	Ph	CCl_4	←		7.40—7.70^h		→	3.02^a	2.08^f	3.04^a		1.58 (NH_2)	
3	NH_3^+	$4'$-$C_6H_4SO_3H$	98% H_2SO_4	7.93^b	8.35^b				3.32^a	2.56^f	3.65^a		6.49	
3	NH_3^+	$2',4'$-$C_6H_3(SO_3H)_2$	103% H_2SO_4		9.20^e		8.92^b	8.44^b	3.83^d	2.72^d	3.83^d		6.28	
4	NH_2	Ph	CCl_4	←		7.00—7.20^h		→	2.58^a	1.50^f	1.55^f	2.62^a	0.97 (NH_2)	
4	NH_3^+	$4'$-$C_6H_4SO_3H$	90% H_2SO_4	7.84^b	8.28^b				3.18^d	2.15^d	2.18^d	3.67^d	6.59	
4	NH_3^+	$2',4'$-$C_6H_3(SO_3H)_2$	106% H_2SO_4		9.18^e		8.89^b	8.42^b	3.75^d	2.38^d	2.38^d	3.75^d	6.16	
1	NMe_3^+	Ph	D_2O	←		7.85—8.15^h		→	4.42					3.52
1	NMe_3^+	Ph	98% H_2SO_4	←		7.70—8.20^h		→	4.74					3.45
1	NMe_3^+	4-$C_6H_4SO_3H$	99.5% H_2SO_4		8.25^b				4.93					3.57
1	NMe_3^+	$3'$-$C_6H_4SO_3H$	99.5% H_2SO_4	←		8.20—8.80^h		→	4.95					3.57
1	NMe_3^+	$2'$-$C_6H_4SO_3H$	99.5% H_2SO_4						5.12					
1	NMe_3^+	$2',4'$-$C_6H_3(SO_3H)_2$	102% H_2SO_4		9.33		8.56	8.56	5.05					3.59
1	NMe_3^+	$3',5'$-$C_6H_3(SO_3H)_2$	102% H_2SO_4	9.03		8.85			4.90					3.53
2	NMe_3^+	Ph	D_2O	←		7.60—7.90^h		→	3.48^a	3.93^h				3.56
2	NMe_3^+	$4'$-$C_6H_4SO_3H$	98% H_2SO_4	8.03^b	8.43^b				3.73^d	3.93^d				3.64
2	NMe_3^+	$2',4'$-$C_6H_3(SO_3H)_2$	102% H_2SO_4		9.20^e		8.91^b	8.44^b	4.04^d	3.89^d				3.67
2	NMe_3^+	$3',5'$-$C_6H_3(SO_3H)_2$	102% H_2SO_4	8.97		9.08^e								
3	NMe_3^+	Ph	D_2O	←		7.60—7.90^h		→	3.12^a	2.48^f	3.69^h			3.45
3	NMe_3^+	$4'$-$C_6H_4SO_3H$	98% H_2SO_4	7.98^b	8.39^b				3.32^d	2.63^d	3.76^d			3.54
3	NMe_3^+	$2',4'$-$C_6H_3(SO_3H)_2$	98% H_2SO_4		9.03^e		8.72^b	8.31^b	3.62^d	2.70^d	3.78^d			3.57
3	NMe_3^+	$3',5'$-$C_6H_3(SO_3H)_2$	98% H_2SO_4			8.86								
4	NMe_3^+	Ph	$(CD_3)_2SO$	←		7.15—7.40^h		→	2.67^a	1.65^f	1.72^f	3.47^a		3.11
4	NMe_3^+	$4'$-$C_6H_4SO_3H$	90% H_2SO_4	7.96^b	8.37^b				3.32^d	← 2.26^d →		3.74^d		3.57
4	NMe_3^+	$2',4'$-$C_6H_3(SO_3H)_2$	99.5% H_2SO_4		9.01^e		8.69^b	8.25^b	3.50^d	← 2.18^d →		3.50^d		3.4

^{a} Triplet $J = 7$ Hz. ^{b} Doublet $J = 8$ Hz. ^{d} Broadened signal. ^{c} Doublet $J = 1.5$ Hz. ^{f} Quintet $J = 7$ Hz. ^{g} Quartet $J = 5$ Hz. ^{h} Multiplet.

Sulphonic Acid Analysis.—The isomer distributions of the monosulphonic acid mixtures were determined by multicomponent ^{1}H n.m.r. analysis [32] of the sulphuric acid reaction mixtures directly (*cf.* ref. 17), and of the mixtures obtained after further sulphonation upon addition of sulphur trioxide (and if required heating to 100 °C) to yield a mixture of disulphonic acids. The *o*- and the *p*-sulphonic acid then yield solely the 2′,4′-disulphonic acid; [33–35] it was further assumed that the *m*-sulphonic acid in strongly fuming sulphuric acid yields predominantly the 3′,5′-disulphonic acid.[34,35]

The ^{1}H n.m.r. data of the various assigned mono- and di-sulphonic acids are listed in Tables 4 and 5.

For the three types of substrates the isomer distributions

TABLE 5

^{1}H N.m.r. data for $(PhCH_2)_nNH_{3-n}$ and sulphonation products

				δ						
$(ArCH_2)_nX$			Solvent	Arom.						
n	X	Ar		2′-H	3′-H	4′-H	5′-H	6′-H	CH_2	NH_{4-n}^+
2	NH	Ph	CCl_4	←		7.63^a		→	4.11	1.76 (NH)
2	NH_2^+	Ph	98% H_2SO_4	←		7.80^a		→	4.59	6.76
2	NH_2^+	$4'$-$C_6H_4SO_3H$	102% H_2SO_4	8.23^b	8.55^b				4.99	7.23
2	NH_2^+	$3'$-$C_6H_4SO_3H$	102% H_2SO_4	8.59		8.55	8.37	8.29	4.99	7.23
2	NH_2^+	$2'$-$C_6H_4SO_3H$	102% H_2SO_4						5.2	
2	NH_2^+	$2',4'$-$C_6H_3(SO_3H)_2$	108% H_2SO_4		9.35		9.05	8.72		7.18
2	NH_2^+	$3',5'$-$C_6H_3(SO_3H)_2$	108% H_2SO_4	9.12		9.35			5.20	7.18
3	N	Ph	CCl_4	←		7.45—7.85		→	3.91	
3	NH^+	Ph	98% H_2SO_4	←		7.45—8.10^c		→	4.59	6.9
3	NH^+	$4'$-$C_6H_4SO_3H$	102% H_2SO_4	8.15^b	8.56^b				5.06	7.61
3	NH^+	$3'$-$C_6H_4SO_3H$	102% H_2SO_4	8.60		8.50	8.27	8.29	5.06	7.61
3	NH^+	$2'$-$C_6H_4SO_3H$	102% H_2SO_4						5.2^5	
3	NH^+	$3',5'$-$C_6H_3(SO_3H)_2$	108% H_2SO_4	9.00		9.35				

^{a} Singlet. ^{b} Doublet $J = 6$ Hz. ^{c}Two multiplets in an area ratio of 3 : 2.

were determined as follows. For $Ph(CH_2)_2NO_2$ the degree of *ortho*-substitution was determined from the area ratio of the low field benzylic hydrogen absorption to the total benzylic hydrogen absorption. For $Ph(CH_2)_3NO_2$ it was calculated from the ratio of the difference in area of the low field methylene absorption [which comprises the benzylic (= α-methylene) hydrogens of the *o*-sulphonic acid and the γ-methylene ones of the three sulphonic acids] and the area of the benzylic hydrogens of the *p*- and *m*-sulphonic acid centred at δ 3.3. The degree of *meta*-substitution for the two nitro-compounds was estimated from the disulphonic acid spectra, *viz.* from the ratio of the singlet absorptions of the 4′-H of the 3′,5′-disulphonic acid and the 3′-H of the 2′,4′-isomer, and for $Ph(CH_2)_2NO_2$ also from the ratio of the benzylic hydrogens of these two disulphonic acids.

The degree of *ortho*-substitution obtained with $(PhCH_2)_nNH_{4-n}^+$ (n = 1, 2, 3) was determined from the contribution of the low field benzylic absorptions at *ca.* δ 5.2 to the total benzylic absorption. For the homologues of $PhCH_2NH_3^+$, it was estimated as described for $Ph(CH_2)_2NO_2$. The degree of *meta*-substitution was estimated for the disulphonic acid mixture from the ratio of the difference of the high-field absorption at *ca.* δ 8.4 (which comprises only the 6′-H of the 2′,4′-disulphonic acid) and the absorption area between this signal and the low-field doublet with J = 1.5 Hz (which comprises the 5′-H of the 2′,4′-disulphonic acid and the three aromatic hydrogens of the 3′,5′-disulphonic acid) to the total aromatic absorption.

As to the $Ph(CH_2)_nNMe_3^+$ ions, the degree of *ortho*-substitution of $PhCH_2NMe_3^+$ was determined from the ratio of the low-field benzylic to the total benzylic absorption and that of the higher homologues obtained by subtraction of the percentages of *para*- and *meta*-substitution from 100. For $Ph(CH_2)_nNMe_3^+$ (n = 2—4) the content of the *p*-sulphonic acid was estimated from the contribution of high-field part of its AB pattern (which in the 360 MHz spectrum is at 42 Hz higher field than the main absorption of the *meta*-isomer) to the total aromatic absorption. The degree of *meta*-substitution of all the trimethylammonium ions was obtained from the disulphonic acid mixture and calculated (i) for $PhCH_2NMe_3^+$ from the contribution of the specific aromatic singlet absorptions of the 3′,5′-disulphonic acid to the total aromatic absorption, (ii) in general from the estimated ratio of the partly overlapping singlets of the 4′-H of the 3′,5′-disulphonic acid and the 3′-H of the 2′,4′-disulphonic acid.

For all substrates, with the exception of $Ph(CH_2)_nNMe_3^+$ (n = 2, 3, 4) (see earlier), the degree of *para*-substitution was taken to be the difference between the contents of the 2′,4′-isomer in the disulphonic acid mixture and the *ortho*-isomer in the monosulphonic acid mixture.

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