Aromatic Sulphonation. Part 64.[1] Sulphonation of Biphenylmonosulphonic Acids and Some Other Biphenyls, containing a Deactivating Substituent, in Concentrated Sulphuric Acid

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The (homogeneous) sulphonation of a number of biphenyl derivatives containing a deactivating substituent, *viz.* the three biphenylsulphonic acids, the three nitrobiphenyls, and some other mainly 4-substituted biphenyls, in concentrated aqueous sulphuric acid at 25 °C has been studied, and rates and/or isomer distributions have been determined. The sulphonation is first-order with respect to the substrate and takes place in the unsubstituted ring, predominantly (>96%), with the exception of biphenyl-2-sulphonic acid, at the 4′-position. From the rate measurement it was concluded (i) that the substrate species undergoing sulphonation are mainly the biphenylsulphonate anions, and unprotonated 4-nitro- and 4-acetyl-biphenyl and biphenyl-4-carboxylic acid, and (ii) that the sulphonating entity is $H_2S_2O_7$. Partial rate factors for these sulphonations and the σ^+ value for the substituents C_6H_4X (X = 2-SO_3^-, 3-SO_3^-, 4-SO_3^-, 4-NO_2, 4-COMe, and 4-CO_2H) are reported. The very low partial rate factors for 2′-substitution are explained in terms of steric hindrance between the incoming sulpho-group and the adjacent hydrogen atom or group X at the 2-position of the C_6H_4X substituent to the formation of the σ-complex leading to the 2′-sulphonic acid. The $f_{4'}$ values of biphenyl-3- and -4-sulphonate anions are substantially greater than unity, indicating enhanced inter-ring mesomeric stabilization in the σ-complexes leading to 4′-substitution as compared with the substrates. The $f_{4'}$ value is appreciably smaller for 4-nitrobiphenyl than for biphenyl-4-sulphonate which is ascribed to the larger $-M$ effect of NO_2 as compared with the SO_3^- substituent.

The very low $f_{3'}$ values of the 3- and 4-substituted biphenyls are explained in terms of the absence of inter-ring mesomeric stabilization in the σ-complexes leading to 3′-substitution.

DATA regarding the rates of sulphonation of the three biphenylmonosulphonic acids and other biphenyls containing a deactivating substituent are scarce. Recently, Zaraiskii and Kachurin[2] reported rate constants for the sulphonation of the three biphenylmonosulphonic acids with sulphuric acid in nitrobenzene as solvent. The 3-sulphonic acid is the most and the 2-sulphonic acid the least reactive isomer. From synthetic procedures it appears that the sulphonation of biphenyl-4-sulphonic acid[3] and 4-nitrobiphenyl[4] proceeds mainly at the 4′-position.

TABLE 1

Pseudo-first-order rate constants for the homogeneous sulphonation of some monosubstituted biphenyls at 25.0 ± 0.1 °C

wt % H_2SO_4 (±0.1)	$10^6\ {}_{ps}k/s^{-1}$ (±5%)					
	2-SO_3K	3-SO_3K	4-SO_3K	4-NO_2 [a]	4-COMe [a]	4-CO_2H [a]
83.8		11.5	5.14			
86.8	4.23	67.2	42.4			
89.8	29.5	451	251			
89.9					6.10	
91.9				206		
92.7					45.2	
92.9				478		
93.2	171	3 000	1 650			
94.9	407	7 050	3 980			
95.0				2 320	123	1 250
96.8	1 320	25 100	12 500			
97.0					373	3 650
97.4	1 990		18 600			
97.9					657	6 030
98.4	3 660		35 000		1 220	19 500
98.8	8 180					
99.1	12 700					

[a] Reaction temperature 25.0 ± 0.5 °C.

RESULTS

The kinetics of the homogeneous (mono)sulphonation of the three biphenylmonosulphonic acids, 4-nitrobiphenyl, 4-acetylbiphenyl, and biphenyl-4-carboxylic acid have been studied in concentrated aqueous sulphuric acid at 25.0 °C. Sulphonation was carried out in a very large excess of sulphuric acid, thus excluding a significant decrease in acid concentration during the reaction. The reactions were found to follow first-order kinetics with respect to the aromatic substrate. The pseudo-first-order rate constants, ${}_{ps}k$, are collected in Table 1.

The isomer distributions of the biphenyldisulphonic acids, resulting from the homogeneous sulphonation of the biphenylmonosulphonic acids are given in Table 2. The isomer distributions obtained with some other biphenyls containing a deactivating substituent are also listed in Table 2.

TABLE 2

Sulphonic acid isomer distributions of some monosubstituted biphenyls at 25 ± 1 °C [a]

Substituent	wt % H_2SO_4 (±0.1)	Isomer distribution (%)		
		2′	3′	4′
2-SO_3H	86.8	0 ± 5	52 ± 5	48 ± 5
	96.8	0 ± 5	55 ± 5	45 ± 5
3-SO_3H	86.8	0.0 ± 0.0	0.5 ± 0.3	99.5 ± 0.1
	96.8	0.0 ± 0.0	1.0 ± 0.2	99.0 ± 0.2
4-SO_3H	86.8	0.0 ± 0.0	1.2 ± 0.2	98.8 ± 0.1
	96.8	0.6 ± 0.2	1.7 ± 0.2	97.4 ± 0.1
2-NO_2	93.2			>96
3-NO_2	93.2			>96
4-NO_2	98.4			>96
4-F	98.4			>96
4-Cl	98.4			>96
4-Br	98.4			>96
4-N^+H_3	98.4			>96 [b]
4-N^+Me_3 (I^-)	98.4			>96 [b]
4-COMe	93.2			>96
	102.3			>96
4-CO_2H	95.8			>96

[a] The sulphonation of the three biphenylsulphonic acids proceeded homogeneously, that of the other substrates heterogeneously. [b] From both ^1H n.m.r. and i.r.

Biphenyl-2-carboxylic acid upon reaction with 93.2 wt % H_2SO_4 is completely converted into 9-fluorenone (by

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[1] Part 63, P. K. Maarsen, R. Bregman, and H. Cerfontain, *J.C.S. Perkin II*, 1977, 1863.

[2] A. P. Zaraiskii and O. I. Kachurin, *J. Org. Chem. U.S.S.R.*, 1973, **9**, 991.

[3] J. Feldmann, *Helv. Chim. Acta*, 1931, **14**, 751; J. Rahm and F. Juracka, *Chem. Listy*, 1956, **50**, 837.

[4] C. Finzi and G. Leandri, *Ann. Chim.* (*Italy*), 1950, **40**, 334, (*Chem. Abs.* 1951, **45**, 9009).

comparison of the ^{1}H n.m.r. spectrum with that of an authentic sample of 9-fluorenone in 93.2 wt % H_2SO_4). Upon reaction of biphenyl-2-carboxylic acid with 102.3 wt % H_2SO_4 the initially formed 9-fluorenone is sulphonated to *yield* 9-oxofluorene-2,7-disulphonic acid.

DISCUSSION

Sulphonation of the substrates studied takes place in the unsubstituted phenyl ring, illustrating that this ring is much less deactivated by the electron-withdrawing substituent than the substituted ring itself. The reactivity of the sulphonic acids decreases in the order biphenyl-3- > biphenyl-4- > biphenyl-2-sulphonic acid.

The pseudo-first-order overall rate constants strongly increase with increasing sulphuric acid concentration. To obtain information as to the sulphonating entity a correlation has been sought between the observed rate constants and the activities of the two sulphonating entities reactive in concentrated aqueous sulphuric acid, *viz.* $H_3SO_4^+$ and $H_2S_2O_7$.[5] The graphs of log $_{\text{ps}}k$ against log $a_{\text{H}_3\text{SO}_4^+}$ are curved for the six biphenyl derivatives studied, thus rendering it unlikely that $H_3SO_4^+$ is the sulphonating entity. The graphs of log $_{\text{ps}}k$ against log $a_{\text{H}_2\text{S}_2\text{O}_7}$ are linear for the biphenyl derivatives under study (Figure 1). The slopes of the graphs as calculated by least squares treatment are 0.75 ± 0.01, 0.74 ± 0.01, 0.74 ± 0.01, 0.75 ± 0.03, 1.10 ± 0.01, and 0.82 ± 0.12 for biphenyl-2-, -3-, and -4-sulphonic acid, 4-acetylbiphenyl, 4-nitrobiphenyl, and biphenyl-4-carboxylic acid respectively. These correlations do apply to the major substitution which is at the 4'-position with the exception of biphenyl-2-sulphonic acid which is mainly substituted at the 3'- and 4'-position (see Table 2). The presently observed slopes (except that of 4-nitrobiphenyl) are somewhat smaller than those for the sulphonation of *e.g.* the halogenobenzenes[5,6] which are in between 0.88 and 0.93. The lower values observed with the biphenyl derivatives may be explained in terms of protonation of the substrate species at the higher sulphuric acid concentrations. In fact it was shown that arenesulphonate anions,[7] acetophenones,[8] benzoic acids,[9] and nitrobenzenes[10] are protonated in concentrated sulphuric acid. Because of the difference in charge the protonated species will be far less reactive for electrophilic substitution than the unprotonated ones.

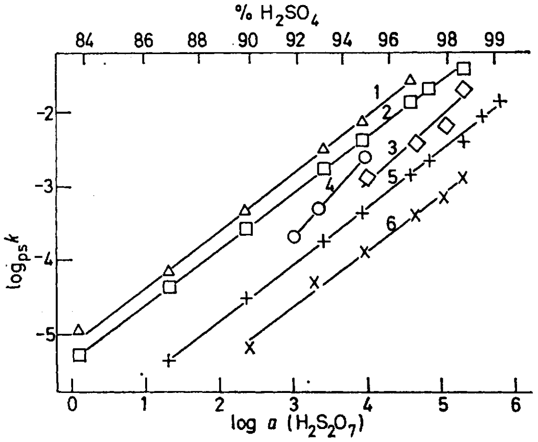

FIGURE 1 Plots of log $_{\text{ps}}k$ against % H_2SO_4 and log a ($H_2S_2O_7$) for: 1, biphenyl-3-sulphonic acid; 2, biphenyl-4-sulphonic acid; 3, biphenyl-4-carboxylic acid; 4, 4-nitrobiphenyl; 5, biphenyl-2-sulphonic acid; 6, 4-acetylbiphenyl

The ratios of protonated (BH^+) and unprotonated species ($B = ArSO_3^-$, $ArCOMe$, $ArCO_2H$, and $ArNO_2$) were calculated with equation (1),[11] in which

$$\log[BH^+]/[B] = pK_a - mH \qquad (1)$$

H stands for the appropriate acidity function and m for d(log[BH$^+$]/[B])/d(log H). The pK_a values of biphenyl-3- and -4-sulphonic acid have been calculated from the pK_a of benzenesulphonic acid (−6.65 ± 0.05), the reaction constant for the arenesulphonic acid ionization (ρ 0.7 ± 0.1 [7a]) and the substituent constants $\sigma_{m\text{-Ph}}$ 0.06 and $\sigma_{p\text{-Ph}}$ −0.01 [10]) to be −6.69 ± 0.05 and −6.64 ± 0.05 respectively. Considering that the phenyl substituent in biphenyl-2-sulphonic acid can only exert its $-I$ effect the pK_a of this acid was assumed to be −6.6. The pK_a values for the conjugate acids of 4-nitrobiphenyl, 4-acetylbiphenyl, and biphenyl-4-carboxylic acid were calculated similarly from literature data on the nitrobenzenes,[10] the acetophenones[11a,12] and the benzoic acids[13] to be −11.75, −8.61, and −7.53 respectively. For the calculation of the [BH$^+$]/[B] ratios m was taken to be 1.0.

The sulphonate anion protonation as well as the protonations of the other biphenyl derivatives studied, which all occur on oxygen, are governed by the benzophenone H_0^a acidity function.[14] This acidity function is only reported up to 90 wt % H_2SO_4.[14] Recently Maarsen has estimated the H_0^a function for 97 wt % H_2SO_4, using sulphanilic acid as indicator, to be −8.1 ± 0.1.[15] The [BH$^+$]/[B] ratios, calculated using the combined H_0^a scale,[14,15] are collected in Table 3. In the sulphuric acid range under study the majority species are the unionized sulphonic acids and protonated 4-acetylbiphenyl. 4-Nitrobiphenyl and biphenyl-4-carboxylic acid are only protonated to a small extent.

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

[6] C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, 1967, **86**, 865; 1969, **88**, 860.

[7] (*a*) P. K. Maarsen, R. Bregman, and H. Cerfontain, *Tetrahedron*, 1974, **30**, 1211; (*b*) H. Cerfontain and B. W. Schnitger, *Rec. Trav. chim.*, 1972, **91**, 199; A. Koeberg-Telder and H. Cerfontain, *J.C.S. Perkin II*, 1975, 226.

[8] R. J. Gillespie and J. A. Leisten, *Quart. Rev.*, 1954, **8**, 40; *J. Chem. Soc.*, 1954, 1, 7; S. J. Bass, R. J. Gillespie, and J. V. Oubridge, *ibid.*, 1960, 837; L. A. Flexser, L. P. Hammett, and A. Dingwall, *J. Amer. Chem. Soc.*, 1935, **57**, 2103.

[9] R. Stewart and K. Yates, *J. Amer. Chem. Soc.*, 1960, **82**, 4059; K. Yates and H. Wai, *Canad. J. Chem.*, 1965, **43**, 2131.

[10] M. Liler, *J. Chem. Soc.*, 1962, 4272.

[11] (*a*) C. C. Greig and C. D. Johnson, *J. Amer. Chem. Soc.*, 1968, **90**, 6453; (*b*) C. D. Johnson, A. R. Katritzky, B. J. Ridgewell, N. Shaker, and A. M. White, *Tetrahedron*, 1965, **21**, 1055; W. M. Schubert and H. K. Latourette, *J. Amer. Chem. Soc.*, 1952, **74**, 1829.

[12] R. Stewart and K. Yates, *J. Amer. Chem. Soc.*, 1958, **80**, 6355.

[13] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1968, **23**, 420.

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

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

Both the protonated and unprotonated species of a given substrate will be sulphonated, but the unprotonated ones much faster, because of their much higher nucleophilicity. Accordingly, the sulphonation reaction will proceed in effect mainly *via* the unprotonated species, especially at the lower sulphuric acid concentrations.

TABLE 3

$[BH^+]/[B]$ Ratios of monosubstituted biphenyls in aqueous sulphuric acid at 25 °C

wt % H_2SO_4 ($\pm$0.1)	[BH+]/[B] 2-SO_3^-	3-SO_3^-	4-SO_3^-	4-NO_2	4-COMe	4-CO_2H
83.8		1.1	1.2			
86.8	2.5	2.0	2.2			
89.8	5.0	3.5	3.9			
89.9					0.62	
91.9				0.000 059		
92.7					1.2	
92.9				0.000 072		
93.2	11	7.2	7.9			
94.9	16	10	11			
95.0				0.000 10	2.0	0.16
96.8	25	15	17			
97.0					3.1	0.26
97.4	29	17	19			
97.9					3.7	0.32
98.4	36	21	23		4.1	0.35

The pseudo-first-order (overall) rate constant, ${}_{\mathrm{ps}}k$, is defined by (2), where v is the rate of sulphonation and

$$v = {}_{\mathrm{ps}}k([B] + [BH^+])a_X \qquad (2)$$

X the effective sulphonating entity. Further equation (3) applies. For sulphuric acid concentrations where

$$v = ({}_{\mathrm{ps}}k_B[B] + {}_{\mathrm{ps}}k_{BH^+}[BH^+])a_X \qquad (3)$$

${}_{\mathrm{ps}}k_{BH^+}[BH^+] \ll {}_{\mathrm{ps}}k_B[B]$ equation (4) follows from (2) and (3). The first-order (overall) rate constants for the

$${}_{\mathrm{ps}}k_B = {}_{\mathrm{ps}}k([B] + [BH^+])/[B] \qquad (4)$$

unprotonated species, ${}_{\mathrm{ps}}k_B$, were calculated from the observed pseudo-first-order (overall) rate constants, ${}_{\mathrm{ps}}k$, according to (4). The data are listed in Table 4. The correlations of log ${}_{\mathrm{ps}}k_B$ with the log of the activities of $H_2S_2O_7$ are shown graphically in Figure 2. The graphs are linear with slopes of 1.00 $\pm$ 0.01 for the biphenyl-2-sulphonate anion, 0.94 $\pm$ 0.02 for the biphenyl-3-sulphonate anion, 0.95 $\pm$ 0.01 for the biphenyl-4-sulphonate anion, 1.10 $\pm$ 0.01 for the unprotonated 4-nitrobiphenyl species, 0.92 $\pm$ 0.02 for the unprotonated 4-acetylbiphenyl species, and 0.87 $\pm$ 0.12 for the unprotonated biphenyl-4-carboxylic acid species as calculated by least squares treatment. These values are similar to those of the halogenobenzenes,[5,6] with the exception of that of 4-nitrobiphenyl.* Accordingly, it is concluded that the sulphonating entity for the biphenyl derivatives under study is also $H_2S_2O_7$ and that the sulphonation proceeds by the same mechanism as for the halogenobenzenes, *viz.* the sequence (5)—(8).[5,6] At sulphuric acid concentrations below 96 wt % H_2SO_4 step (5) is rate limiting and the products are formed predominantly *via* (7), (8), and at most in part by (6). At higher acid concentrations (8) becomes partly rate limiting as a result of the decrease in the hydrogen sulphate ion concentration.[6]

TABLE 4

Pseudo-first-order rate constants for the homogeneous sulphonation of the biphenylsulphonate anions, and the unprotonated 4-nitrobiphenyl, 4-acetylbiphenyl, and biphenyl-4-carboxylic acid species in aqueous sulphuric acid at 25 °C

wt % H_2SO_4 ($\pm$0.1)	$10^6\ {}_{\mathrm{ps}}k_B/s^{-1}$ ($\pm$10%) 2-SO_3^-	3-SO_3^-	4-SO_3^-	4-NO_2	4-COMe	4-CO_2H
83.8		24.2	11.3			
86.8	14.8	202	136			
89.8	177	2 030	1 230			
89.9					9.88	
91.9				206		
92.7					99.4	
92.9				478		
93.2	2 050	24 600	14 700			
94.9	6 920	77 600	47 800			
95.0				2 320	369	1 450
96.8	34 300	402 000	225 000			
97.0					1 530	4 500
97.4	59 700		372 000			
97.9					3 090	7 960
98.4	135 000		840 000		6 220	26 300

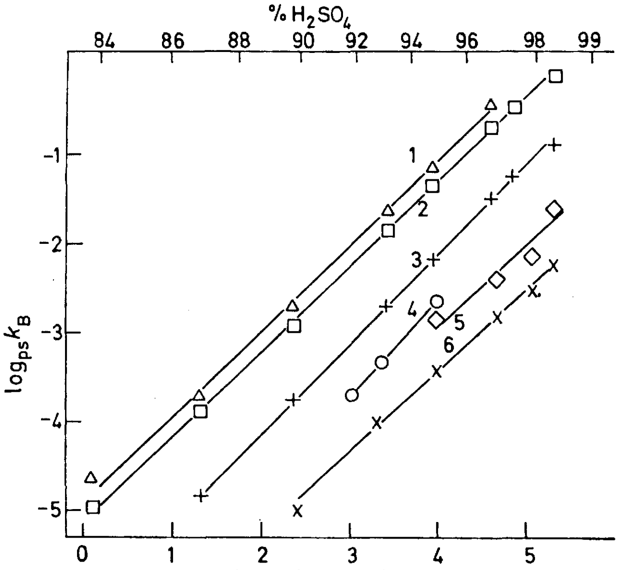

FIGURE 2 Plots of log ${}_{\mathrm{ps}}k_B$ against % H_2SO_4 and log a ($H_2S_2O_7$) for: 1, biphenyl-3-sulphonate; 2, biphenyl-4-sulphonate; 3, biphenyl-2-sulphonate; 4, 4-nitrobiphenyl; 5, biphenyl-4-carboxylic acid; 6, 4-acetylbiphenyl

From a comparison of Figures 1 and 2 it appears that the biphenyl-2-sulphonate anion is at least 50 times, biphenyl-3-sulphonate anion at least 25 times, and biphenyl-4-sulphonate anion at least 30 times as reactive as the corresponding biphenylsulphonic acid species.

The partial rate factors for sulphonation of the biphenylsulphonate anions and unprotonated 4-nitrobiphenyl, 4-acetylbiphenyl, and biphenyl-4-carboxylic

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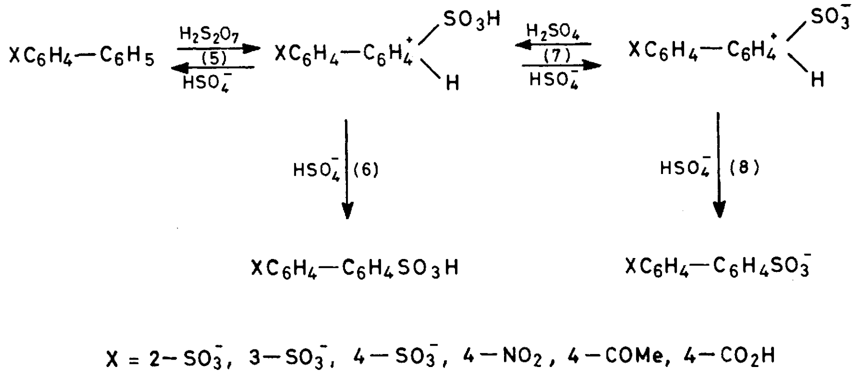
* The slope d(log ${}_{\mathrm{ps}}k$)/d log a (sulphonating entity) for the sulphonation of nitrobenzene in strongly fuming sulphuric acid is also different from those of other benzene derivatives, but now appreciably smaller (0.75), as against 1.03 for pentafluorobenzene and 0.97 for the phenyltrimethylammonium cation.[16]

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

acid have been calculated from the $_{ps}k_B$ values, the isomer distributions, and the $_{ps}k$ values of benzene.[17] The isomer distributions of the sulphobiphenyl derivatives in 86.8 wt % H_2SO_4 are mainly the result of sulphonation of the sulphonate anions, because the $[BH^+]/[B]$ ratios in that sulphuric acid concentration (see Table 3) are only *ca.* 2 and the sulphonate anions are at least 25 times as reactive as the corresponding sulphonic acid species (see before). Accordingly, the majority of the sulphonation (>90%) proceeds *via* the sulphonate anions. The partial rate factor data are collected in Table 5.



SCHEME

In 86.8 and 95.0 wt % H_2SO_4 the sulphonating entity is $H_2S_2O_7$ (see before). For this type of sulphonation ρ^+ is -5.7 ± 0.3.[5] The σ^+ values, calculated from the partial rate factors with the Hammett–Brown free energy relationship $\log k/k_H = \rho^+\sigma^+$, are collected in Table 6.

TABLE 5

Partial rate factors of some unprotonated monosubstituted biphenyl derivatives for sulphonation in concentrated aqueous sulphuric acid by the entity $H_2S_2O_7$ at 25 °C

Substituent	wt % H_2SO_4 (± 0.1)	$f_{2'}$	$f_{3'}$	$f_{4'}$
2-SO_3^- [a]	86.8 [b]	$\leqslant 0.025$	0.26 ± 0.04	0.48 ± 0.08
3-SO_3^-	86.8 [b]	<0.007	0.034 ± 0.004	13.5 ± 1.5
4-SO_3^-	86.8 [b]	<0.005	0.055 ± 0.006	9.1 ± 0.9
4-NO_2	95.0	<0.006	<0.006	0.6 ± 0.1
4-COMe	95.0	<0.001	<0.001	0.10 ± 0.05
4-COOH	95.0	<0.004	<0.004	0.38 ± 0.04

[a] Calculated with a $_pK_a$ value for biphenyl-2-sulphonic acid of -6.6 (see text). [b] In 86.8% H_2SO_4 the sulphonation proceeds for >90% *via* the sulphonate anion substrate species (see text).

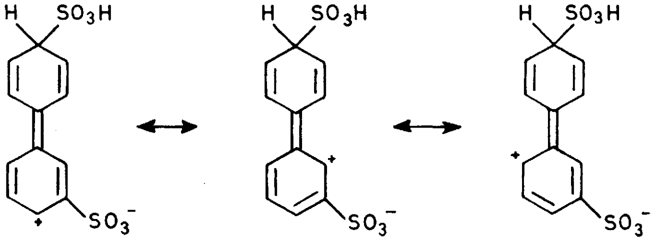
TABLE 6

Hammett–Brown σ^+ substituent constants at 25 °C

Substituent	σ_m^+	σ_p^+
o-$C_6H_4SO_3^-$	0.10 ± 0.01	0.06 ± 0.02
m-$C_6H_4SO_3^-$	0.26 ± 0.05	-0.20 ± 0.04
p-$C_6H_4SO_3^-$	0.22 ± 0.05	-0.17 ± 0.04
p-$C_6H_4NO_2$		0.04 ± 0.01
p-C_6H_4COMe		0.18 ± 0.05
p-$C_6H_4CO_2H$		0.07 ± 0.02

The partial rate factors for 4′-substitution of the biphenyl-3- and biphenyl-4-sulphonate anions are substantially greater than unity illustrating stabilization of the σ-complexes leading to 4′-substitution relative to that of benzene by mesomeric electron release from the sulphophenyl group, as illustrated for the biphenyl-3-sulphonate anion.

The $f_{3'}$ and $f_{4'}$ values of the biphenyl-2-sulphonate anion are somewhat smaller than unity. In both the substrate and the derived σ-complexes for 3′- and 4′-substitution, the two phenyl rings will be close to perpendicular as a result of steric repulsion between the sulpho-group at position 2 and the hydrogens at positions 2′ and 6′. The partial rate factors follow the order $f_{2'} \ll f_{3'} < f_{4'} < 1$ which may be explained in terms of the (small) $-I$ effect of the 2-$C_6H_4SO_3^-$ substituent and which is apparently more effective than any (rate enhancing) field effect of the SO_3^- group. The very low value of $f_{2'}$ is thought to be for the remaining part the result of steric hindrance between the incoming and the original sulpho-group.



2-Nitrobiphenyl undergoes, in contrast to biphenyl-2-sulphonate anion, >96% substitution at the 4′-position. This indicates conjugative stabilization by mesomeric electron release from the *o*-phenylene group in the σ-complex leading to 4′-substitution. Apparently in the σ-complex the two ring systems are not perpendicular,* possibly because the nitro-group has rotated on the C–N bond out of the plane of the phenylene group, to which it is attached.

The $f_{4'}$ value is substantially smaller for 4-nitro- and 4-acetyl-biphenyl and biphenyl-4-carboxylic acid than for the biphenyl-4-sulphonate anion (see Table 5).

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* The interplanar angle between the two phenyl groups in 2-nitrobiphenyl is reported to be 53°.[18]

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

[18] A. Unanue and P. Botherel, *Bull. Soc. chim. France*, 1966, 1640.

The present value of $f_{4'}$ (0.6 ± 0.1) for the $H_2S_2O_7$ sulphonation of 4-nitrophenyl (ρ^+ −5.7 ± 0.3[6]) compares with the value of 1.3 reported for its nitration with nitric acid in acetic anhydride[19] (ρ^+ −6.5[20]). The higher reactivity of biphenyl-4-sulphonate as compared with 4-nitrobiphenyl may be explained in two ways. The first is in terms of the weaker $-M$ effect of the SO_3^- as compared with the NO_2 substituent, leading to a greater conjugative stabilization of the σ-complex leading to 4′-substitution by mesomeric electron release from the *p*-phenylene group with the sulpho- as compared with the nitro-derivative. The second is in terms of the negative charge of biphenyl-4-sulphonate which would render this anion more ready than neutral 4-nitrobiphenyl to undergo electrophilic substitution. The latter explanation is rendered highly unlikely in view of the absence of any rate enhancement in the case of biphenyl-2-sulphonate anion, the partial rate factors of which are somewhat smaller than unity. Evidence in favour of the former explanation was recently obtained from the f_m/f_p ratio of benzenesulphonic acid (20[21]), which is in between that of nitrobenzene (33[22]), in which the substituent exerts a large $-M$ effect, and the anilinium (0.6[23]) and phenyltrimethylammonium (2.8[24]) cations, in which the substituent only exerts a $-I$ and no $-M$ effect.

The partial rate factors for 3′-substitution of the 3- and 4-substituted biphenyls are much smaller than unity (Table 5). With the σ-complex for 3′-substitution there will be no inter-ring mesomeric stabilization. Such a mesomeric stabilization does exist in the starting substrates. Accordingly the activation energies for the formation of these σ-complexes will be relatively high, *e.g.* higher than for the formation of the σ-complexes from biphenyl-2-sulphonate for which there is no mesomeric interaction between the phenyl groups because of their perpendicular orientation.

The very low partial rate factors for 2′-substitution observed with all biphenyls studied (see Table 5) are ascribed to steric hindrance between the incoming sulpho-group and the nearby *o*-hydrogen atom or group X of the C_6H_4X substituent to the formation of the σ-complex leading to the 2′-sulphonic acid.

EXPERIMENTAL

Apparatus and Materials.—^{1}H N.m.r. spectra were recorded on a Varian HA 100 spectrometer using (neat) tetramethylsilane, sealed capillary, as an external reference. The rate measurements have been carried out with a Zeiss PMQ II spectrophotometer in quartz cells with a path length of 10 mm. The multicomponent u.v. analysis was performed with a Zeiss PMQ 3 spectrophotometer, and an Electrologica X8 computer.

Sulphuric acid (AnalaR; *d* 1.84) was obtained from B.D.H. This acid was diluted with demineralized water to obtain the desired concentrations $<$98.4 wt % H_2SO_4, whereas sulphur trioxide was added to obtain the desired concentrations $>$98.4 wt % H_2SO_4. Sulphur trioxide was obtained from Hardman and Holden Ltd. Cyclohexane (Uvasol) was obtained from Merck. The synthesis of the potassium biphenylmono- and -di-sulphonates has been described previously.[25a] *NNN*-Trimethylbiphenyl-4-ylammonium iodide was prepared from the corresponding amino-compound and methyl iodide.[26] The other substrates and 9-fluorenone were obtained commercially.

Procedure.—The rate measurements were based on the difference between the u.v. absorption spectra of the starting compounds and those of their reaction products. The reaction rates were determined by measuring the u.v. extinction at a given wavelength as a function of time. The wavelengths, chosen so as to allow a maximum variation in the extinction, were 238 nm for biphenyl-2-sulphonic acid, 275 nm for biphenyl-3-sulphonic acid, 267 nm for biphenyl-4-sulphonic acid, 378 nm for 4-acetylbiphenyl, and 301 nm for biphenyl-4-carboxylic acid.

The rates of sulphonation of 4-nitrobiphenyl were determined by a different method.[17] The reactions were carried out in 250 ml flasks which contained sulphuric acid (100 ml) of the desired concentration and to which was added a known amount of 4-nitrobiphenyl (*ca.* 20 mg). The stoppered flasks were shaken periodically. After an appropriate time the reactions were stopped by extracting the unchanged 4-nitrobiphenyl with cyclohexane (3 × 10 ml). The amount of unconverted 4-nitrobiphenyl was determined spectrophotometrically by measuring the u.v. absorption of the cyclohexane extract at 322 nm.

The product composition of the sulphonation mixtures of the biphenylsulphonic acids in sulphuric acid was determined by multicomponent u.v. analysis.[27] Accurately known amounts of the potassium biphenylmonosulphonates were dissolved in 86.8 and 96.8 wt % H_2SO_4. At the same time accurately known amounts of the six dipotassium biphenyldisulphonates (the reference compounds) were dissolved in sulphuric acid of the same concentration. At the end of the sulphonation of the biphenylmonosulphonates the solutions were transferred into 10 mm quartz cells. The u.v. extinctions of the reaction mixtures and all the reference compounds were determined spectrophotometrically at every even wavelength between 210 and 304 nm. The spectra of the reaction mixtures were then resolved in terms of those of the reference components with the aid of an electronic computer.

The product composition of the reaction mixtures obtained with the other substituted biphenyls (*ca.* 100 mg per 1.0 ml of sulphuric acid of the desired concentration) at 25 ± 1 °C was determined after complete substrate conversion by ^{1}H n.m.r. spectroscopy. The ^{1}H n.m.r. data of the resulting products have been reported previously.[25b]

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