Aromatic Sulphonation. Part 62.[1] Sulphonation of Biphenyl in Concentrated Aqueous Sulphuric Acid

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The homogeneous (mono)sulphonation of biphenyl in a large excess of aqueous sulphuric acid (81.5—96.8 wt. %) at 25 °C has been studied, and rates and isomer distributions have been determined. The sulphonation is first-order with respect to the substrate, and takes place predominantly (>90%) at the *para*-position. Up to an acid concentration of 86 wt. % H_2SO_4 the active sulphonating entity is $H_3SO_4^+$. For this type of sulphonation $^{Ph}f_p = 600 \pm 300$, from which it was calculated that $\rho^+(H_3SO_4^+) = -10.0 \pm 1.2$. The high degree of *para*-substitution indicates substantial conjugative stabilization of the corresponding σ-complex. The relatively low degree of *ortho*-substitution may be explained in terms of steric hindrance by the adjacent *ortho*-hydrogen atom of the phenyl substituent to the formation of the σ-complex leading to the *ortho*-sulphonic acid. The syntheses of the three biphenylmonosulphonic acids and the six biphenyldisulphonic acids containing one sulpho-group per phenyl ring, required as reference compounds for the multicomponent u.v. analysis, are reported.

DATA on the orientation and rate of sulphonation of biphenyl are scarce. Various reports are available on the synthesis of biphenyl-4-sulphonic acid [2] and biphenyl-4,4′-disulphonic acid.[3] From the reported yields it appears that the sulphonation of biphenyl takes place predominantly at the *para*-position(s). Recently Zaraiskii and Kachurin [4] have reported rate constants for the sulphonation of biphenyl with sulphuric acid in nitrobenzene.

RESULTS

The kinetics of the homogeneous (mono)sulphonation of biphenyl were studied in aqueous sulphuric acid (81.5—90.6 wt. % H_2SO_4) at 25 ± 1 °C. The reactions, which were carried out in a very large excess of sulphuric acid, followed first-order kinetics with respect to biphenyl. The first-order (overall) rate constants, *k*, are collected in Table 1. The isomer distributions of the three biphenylmonosulphonic acids formed initially and those of the six biphenyldisulphonic acids formed eventually are given in Table 2.

TABLE 1

First-order rate constants for the homogeneous sulphonation of biphenyl at 25 ± 1 °C

Wt. % H_2SO_4 (±0.1)	$10^6\ k/s^{-1}$ (±10%)
81.5	58.6
82.8	166
83.6	217
85.0	655
86.0	961
87.3	2 870
88.4	5 130
89.5	11 700
90.6	18 000

The isomer distribution for the monosulphonation of biphenyl was also calculated indirectly from the isomer distribution of the biphenyldisulphonic acids resulting from the sulphonation of biphenyl (Table 2) and the isomer distributions of the biphenyldisulphonic acids resulting from the sulphonation of each of the three biphenylmonosulphonic acids [5] as follows. Let us denote the fractions of initially formed biphenyl-2-, -3-, and -4-sulphonic acid by a_o, a_m, and a_p, respectively, and the fractions of the biphenyldisulphonic acids resulting from a given biphenylmonosulphonic acid ${}_xb_{o'}$, ${}_xb_{m'}$ and ${}_xb_{p'}$, where the *x* indicates the position (*o*, *m*, or *p*) of the sulphonic acid group present in the starting monosulphonic acid. Then the fractions of the biphenyl-2,2′-, -2,3′-, -2,4′-, -3,3′-, -3,4′-, and -4,4′-disulphonic acids formed eventually upon sulphonation of biphenyl, will be $a_o \cdot {}_ob_{o'}$, $(a_o \cdot {}_ob_{m'} + a_m \cdot {}_mb_{o'})$, $(a_o \cdot {}_ob_{p'} + a_p \cdot {}_pb_{o'})$, $a_m \cdot {}_mb_{m'}$, $(a_m \cdot {}_mb_{p'} + a_p \cdot {}_pb_{m'})$, and $a_p \cdot {}_pb_{p'}$, respectively. By setting these fractions equal to the values of the corresponding isomeric fractions of the disulphonic acids (*cf.* Table 2), the isomer distribution for the (mono)-sulphonation of biphenyl was calculated. The data are given in Table 2 in parentheses.

DISCUSSION

In order to obtain information as to the reactive electrophilic entity in the sulphonation of biphenyl in concentrated aqueous sulphuric acid a correlation was sought between the first-order rate constant and the activities of the two possible sulphonating entities of the aqueous sulphuric acid system, *viz.* $H_2S_2O_7$ and $H_3SO_4^+$.[6] The graph of log *k vs.* log $a(H_2S_2O_7)$ is linear in the acid regions up to and above 86 wt. % H_2SO_4 with slopes (as calculated by least squares treatment) of 0.65 ± 0.03 (5 data points) and 0.72 ± 0.04 (4 data points) respectively (Figure 1).† The graph of log *k vs.* log $a(H_3SO_4^+)$ is linear up to a sulphuric acid concentration of 86 wt. % with a slope of 0.95 ± 0.04 (5 data points, as calculated by least squares treatment), whereas at higher acid concentrations the linear plot has a slope of 1.12 ± 0.06 (4 data points). Similar slopes and differences in slope

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† Least squares treatment of the nine data points of Figure 1 leads to a slope of 0.71 ± 0.02. The preferred division of the plot of Figure 1 into two linear graphs is indicated by the more pronounced difference in slopes observed for the two sulphuric acid regions in Figure 2.

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

[5] T. A. Kortekaas and H. Cerfontain, in preparation.

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

between the two types of graph were observed for toluene,[6,7] isopropylbenzene,[6,7] and the three xylenes.[6,7] Considering the presently observed slopes and the interpretation of the results for the alkylbenzenes, we propose, on the basis of the unit slope criterion * that the main sulphonation of biphenyl, *i.e.* the *para*-substitution, in acid concentrations up to 86 wt. % H_2SO_4, is due to the entity $H_3SO_4^+$, and follows the same mechanism as proposed for the alkylbenzenes, *viz.* the sequence (**1**)—(**3**).

TABLE 2

Isomer distributions of the biphenylmono- and biphenyldi-sulphonic acids obtained in the homogeneous sulphonation of biphenyl with sulphuric acid at 25.0 ± 0.5 °C

Monosulphonic acid	Disulphonic acid	Content (% [a]) 86.8% H_2SO_4		96.8% H_2SO_4	
2-		3.2 ± 0.2 (3.2)		6.3 ± 0.2 (6.4)	
3-		0.5 ± 0.2 (1.3)		2.4 ± 0.2 (3.0)	
4-		96.4 ± 0.1 (96.5)		91.4 ± 0.1 (91.5)	
	2,2′-		0.0 ± 0.0		0.0 ± 0.0
	2,3′-		1.6 ± 0.1		3.6 ± 0.2
	2,4′-		1.5 ± 0.2		3.4 ± 0.4
	3,3′-		0.0 ± 0.0		0.0 ± 0.0
	3,4′-		1.8 ± 0.2		3.9 ± 0.3
	4,4′-		95.4 ± 0.1		89.1 ± 0.1

[a] Data in parentheses calculated indirectly from the disulphonic acid composition; see text.

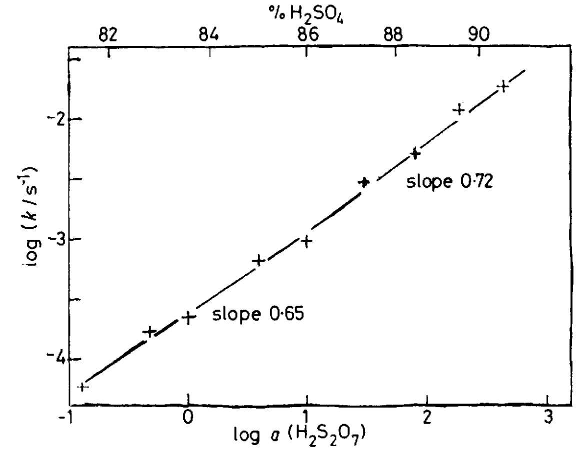
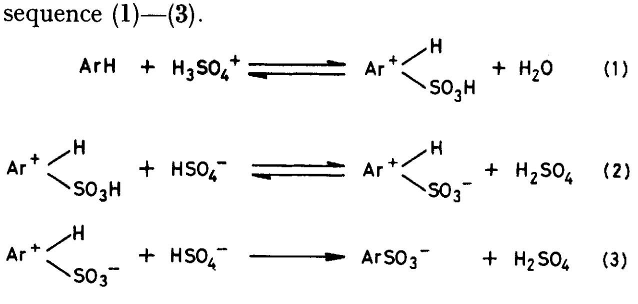


FIGURE 1 Correlation of log k with log $a(H_2S_2O_7)$ for the sulphonation of biphenyl



$$\mathrm{ArH} + \mathrm{H_3SO_4^+} \rightleftharpoons \mathrm{Ar^+}\!<^{\mathrm{H}}_{\mathrm{SO_3H}} + \mathrm{H_2O} \qquad (1)$$

$$\mathrm{Ar^+}\!<^{\mathrm{H}}_{\mathrm{SO_3H}} + \mathrm{HSO_4^-} \rightleftharpoons \mathrm{Ar^+}\!<^{\mathrm{H}}_{\mathrm{SO_3^-}} + \mathrm{H_2SO_4} \qquad (2)$$

$$\mathrm{Ar^+}\!<^{\mathrm{H}}_{\mathrm{SO_3^-}} + \mathrm{HSO_4^-} \longrightarrow \mathrm{ArSO_3^-} + \mathrm{H_2SO_4} \qquad (3)$$

The *ortho* : *para* and *meta* : *para* ratios for the sulphonation of biphenyl are both small (*cf.* Table 2). The low degree of *ortho*-substitution can be explained by steric hindrance caused mainly by the *ortho*-hydrogen atom of the phenyl substituent adjacent to the reaction centre. Molecular models reveal that the formation of the σ-complex for *ortho*-substitution is very difficult. The low *meta* : *para* ratio illustrates the absence of conjugative stabilization of the transition state leading to the *meta*-σ-complex and the presence of a relatively strong conjugative stabilization of the transition state leading to the *para*-σ-complex intermediate.

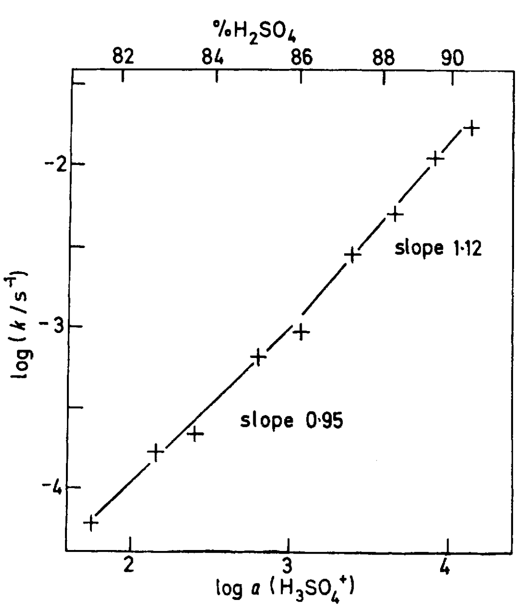


FIGURE 2 Correlation of log k with log $a(H_3SO_4^+)$ for the sulphonation of biphenyl

The partial rate factor for the *para*-position † of

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* From the relationship $k = k_2a_X$, where X is the sulphonating entity, it follows that log k = log a_X + log k_2, and accordingly that a graph of log k *vs.* log a_X should be linear with unit slope.

† Only partial rate factors derived from rate constants for biphenyl and benzene for the same type of reaction mechanism, and thus for the same sulphonating entity, are relevant. For the *para*-substitution of biphenyl this is the $H_3SO_4^+$ mechanism, whereas it is more likely to be the $H_2S_2O_7$ mechanism for the *ortho*- and the *meta*-substitution in view of their much lower reactivity.[6] For the calculation of the partial rate factors of the latter two positions the relative rate of sulphonation by the $H_2S_2O_7$ mechanism is required. Unfortunately, in the sulphuric acid region where the $H_2S_2O_7$ mechanism will predominate for all three substitutions, no measurements could be made as the rates are too high.

[7] A. W. Kaandorp, H. Cerfontain, and F. L. J. Sixma, *Rec. Trav. chim.*, 1963, **82**, 113; A. W. Kaandorp and H. Cerfontain, *Rec. Trav. chim.*, 1969, **88**, 725; A. J. Prinsen and H. Cerfontain, *ibid.*, p. 833.

biphenyl (${}^{\text{Ph}}f_p$) in 86.8 wt. % H_2SO_4 was calculated from the rate constant and the isomer distribution for biphenyl and the rate constant for benzene * to be 600 ± 300. The Hammett–Brown reaction constant for the sulphonation by the $H_3SO_4^+$ mechanism could then be calculated. A complicating factor was the observed linear variation of σ^+ for the *para*-phenyl substituent with the reaction constant ρ^+ from −0.29 for bromination ($\rho^+ = -12.1$) to −0.15 for ethylation ($\rho^+ = -2.4$).[9] The origin of the dependence of $\sigma^+_{p\text{-Ph}}$ on ρ^+ is the energy barrier for achievement of coplanarity between the two phenyl rings in the transition state for the formation of the *para*-σ-complex, leading to a variation in the resonance interaction as a function of the electron demand. By using an initial σ^+ value of -0.26 ± 0.02 for the *para*-phenyl substituent, obtained by interpolation in the linear graph given in ref. 9 taking $\rho^+(H_3SO_4^+)$ as -9.3 ± 1.0 [6] and a subsequent iterative procedure, the reaction constant $\rho^+(H_3SO_4^+)$, calculated from the present ${}^{\text{Ph}}f_p$ value, was -10.0 ± 1.2. This value agrees with the previous estimate of -9.3 ± 1.0, based on ${}^{\text{Me}}f_p$.[6]

TABLE 3

^{1}H N.m.r. data of the potassium biphenylsulphonates [a]

		Chemical shift (p.p.m.) [b]									
Substituent(s)	Solvent	2-H	3-H	4-H	5-H	6-H	2′-H	3′-H	4′-H	5′-H	6′-H
2-SO_3K	D_2O		8.08—7.95 (m)	← 7.62—7.25 (m) →							
3-SO_3K	D_2O	8.41 (s)		8.19 (d)	← 8.00—7.75 (m) →						
4-SO_3K	D_2O	8.14 (d)	8.30 (d)		8.30 (d)	8.14 (d)	← 8.17—7.84 (m) →				
2,2′-$(SO_3K)_2$	80% H_2SO_4		8.32 (d)	7.93 (t)	7.93 (t)	7.62 (d)		8.32 (d)	7.93 (t)	7.93 (t)	7.62 (d)
2,3′-$(SO_3K)_2$	80% H_2SO_4		8.35—8.07 (m)	← 7.86—7.51 (d) →			8.35—8.07 (m)		8.35—8.07 (m)	← 8.35—7.51 (d) →	
2,4′-$(SO_3K)_2$	80% H_2SO_4		8.13 (m)	← 7.97—7.42 (m) →				8.13 (m)		8.13 (m)	7.97—7.42 (m)
3,3′-$(SO_3K)_2$	D_2O	8.50 (s)		8.32—8.18 (m)	8.02 (t)	8.32—8.18 (m)	8.50 (s)		8.32—8.18 (m)	8.02 (t)	8.32—8.18 (m)
3,4′-$(SO_3K)_2$	80% H_2SO_4	8.01 (d)		8.01 (d)	7.70 (d)	7.70 (d)	7.70 (d)	8.01 (d)		8.01 (d)	7.70 (d)
4,4′-$(SO_3K)_2$	80% H_2SO_4	7.93 (d)	8.15 (d)		8.15 (d)	7.93 (d)	7.93 (d)	8.15 (d)		8.15 (d)	7.93 (d)

[a] J_{ortho} 8—9, J_{meta} 1—2 Hz. [b] Measured on a Varian HA 100 spectrometer [neat tetramethylsilane (sealed capillary) as external standard].

EXPERIMENTAL

Materials.—Dipotassium biphenyl-3,3′-disulphonate was obtained by deamination of dipotassium 4,4′-diaminobiphenyl-3,3′-disulphonate,[10] which was prepared by sulphonation of 4,4′-diaminobiphenyl in a baking process.[11]

The potassium salts of the other biphenylmono- and -disulphonic acids were obtained by hydrolysis of the corresponding biphenylmono- and -di-sulphonyl chlorides, with 2 equiv. of potassium hydroxide in ethanol. The sulphonyl chlorides were prepared from the corresponding amino-compounds by the modified Sandmeyer procedure, first described by Meerwein,[12,13a] with the exception of the commercially available biphenyl-4,4′-disulphonyl chloride. The required (di)aminobiphenyls, if not commercially available, were prepared by reduction of the corresponding (di)nitrobiphenyls.[13a,14] These nitrobiphenyls are commercially available, except 2,3′- and 3,4′-dinitrobiphenyl which were obtained by nitration of 3-nitrobiphenyl with concentrated nitric acid.[13a,15]

The potassium biphenylsulphonates were purified by repeated recrystallization from aqueous ethanol. The i.r. spectra (KBr) of the potassium biphenylsulphonates all showed an aromatic C–H stretching absorption in the region 3 050—3 030 cm^{-1} and an SO_3^- absorption at 1 220—1 180 cm^{-1}. The ^{1}H n.m.r. data are given in Table 3 and the elemental analyses in Table 4.

TABLE 4

Elemental analyses of the potassium biphenylsulphonates (%)

Compound	C	H	S	K
$C_{12}H_9$-2-SO_3K	52.9	3.4	11.9	14.2
$C_{12}H_9$-3-SO_3K	52.9	3.4	11.7	14.6
$C_{12}H_9$-4-SO_3K	52.9	3.4	12.0	14.3
Calc. for $C_{12}H_9SO_3K$	52.92	3.33	11.77	14.35
$C_{12}H_8$-2,2′-$(SO_3K)_2$	36.7	2.2	16.4	20.2
$C_{12}H_8$-2,3′-$(SO_3K)_2$	36.7	2.2	16.3	20.0
$C_{12}H_8$-2,4′-$(SO_3K)_2$	36.8	2.0	16.3	19.9
$C_{12}H_8$-3,3′$(SO_3K)_2,H_2O$	34.7	2.5	15.2	18.8
$C_{12}H_8$-3,4′-$(SO_3K)_2$	36.7	2.2	16.3	19.8
$C_{12}H_8$-4,4′-$(SO_3K)_2$	36.9	2.1	16.5	20.0
Calc. for $C_{12}H_8(SO_3K)_2$	36.91	2.05	16.42	20.05
Calc. for $C_{12}H_8(SO_3K)_2,H_2O$	35.28	2.5	15.70	19.15

Sulphuric acid (d 1.84) (B.D.H. AnalaR) was diluted with demineralized water to the desired concentrations. Biphenyl was a zone-refined sample from Aldrich, m.p. 68.95 °C. 2-Aminobiphenyl (purum), 4-aminobiphenyl (purum), 2,4′-dinitrobiphenyl (tech.), and benzidine (tech.) were obtained from Fluka, and 3-nitrobiphenyl (tech.), 2,2′-dinitrobiphenyl (tech.), and biphenyl-4,4′-disulphonyl chloride (tech.) from Aldrich.

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* The rate constant for the sulphonation of benzene in 86.8 wt. % H_2SO_4 at 25 °C by the $H_3SO_4^+$ mechanism was obtained by extrapolation of the linear graph for 77.6—84.3% H_2SO_4 to be 7.9×10^{-6} s^{-1}.[8]

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

[9] L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35.

[10] N. Kornblum, *Org. Synth.*, Coll. Vol. III, 1955, p. 295; C. C. Barker and F. D. Casson, *J. Chem. Soc.*, 1953, 4184.

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[12] H. Meerwein, G. Dittmar, R. Göllner, K. Hafner, F. Mensch, and O. Steinfort, *Chem. Ber.*, 1957, **90**, 841; A. J. Prinsen and H. Cerfontain, *Rec. Trav. chim.*, 1965, **84**, 24.

[13] T. A. Kortekaas, Thesis (in English), University of Amsterdam, 1976, (*a*) ch. 2; (*b*) p. 40.

[14] P. M. G. Bavin, *Org. Synth.*, 1960, **40**, 5.

[15] F. H. Case and A. Idelson, *J. Org. Chem.*, 1962, **27**, 4651.

Rate Measurements.—The rate constants for the homogeneous sulphonation of biphenyl were determined u.v. spectrophotometrically with a Zeiss PMQ II spectrophotometer in a thermostatically controlled room, kept at 25 ± 1 °C. First a saturated * solution of biphenyl in 70.3% sulphuric acid, in which no sulphonation takes place, was prepared. Then to a known amount of this biphenyl solution contained in a quartz cell (path length 50.0 mm) was added an amount of cooled aqueous sulphuric acid of a higher acid concentration The temperature of the cold added sulphuric acid was chosen so as to obtain a temperature in the resulting sulphuric acid solution of 25 ± 1 °C. The concentration of the resulting sulphuric acid solution was calculated after the u.v. rate measurement had been made by weighing the quartz cell and thus determining the weight of added sulphuric acid.

The rate measurements were based on the differences in u.v. absorption of biphenyl and its reaction products. The rate constants were determined by measuring the u.v. absorption at 284 nm as a function of time. That wavelength was chosen because the variaton in absorption upon monosulphonation is very large relative to that for the subsequent sulphonation to the disulphonic acids.[13b] The first-order overall rate constants, k, were derived from plots of $\log|E_\infty - E_t|$ *vs.* time, where E_∞ and E_t refer to the extinction of the reaction mixture at infinite time (final products), and time t, respectively.

Isomer Distributions.—For the determination of the isomer distributions a known amount of biphenyl was dissolved in either 86.8 or 96.8% sulphuric acid at 25.0 ± 0.5 °C. At the same time accurately known amounts of the three biphenylmono- and the six biphenyldi-sulphonic acids were dissolved in sulphuric acid of the same concentration. At the end of the sulphonations of both biphenyl and the three monosulphonic acids, all the appropriately diluted solutions of the reaction mixtures and the solutions of the biphenylmono- and the biphenyldi-sulphonic acids were transferred to 10.0 mm quartz cells. The u.v. extinctions of all compounds and mixtures were determined at every even-number wavelength in the region 210—304 nm, by using a Zeiss PMQ II or a Zeiss PMQ 3 spectrophotometer, equipped with a rotating cell holder [16] which could accommodate 24 quartz cells of 10.0 mm path length. The spectra of the mixtures were then resolved in terms of those of their components with the aid of an Electrologica X 8 electronic computer.

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* It was checked, on the basis of the applicability of Beer's law, that the solution was homogeneous.

[16] H. Cerfontain and J. Groot, *Appl. Optics*, 1964, **3**, 782.