Studies on the Sulphonation of Anthracene. Part 1. Sulphonation in Neutral or Basic Solvents

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The reaction of anthracene with chlorosulphuric acid produces anthracene-1-, -2-, and -9-sulphonic acids, a mixture of anthracenedisulphonic acids, 9-chloroanthracene, 9,9′-bianthryl, and anthracene polymers, but the yield and formation of each depends on the experimental conditions and on whether chloroform, dioxan, or a mixture of pyridine and isoparaffin is used as solvent. Sulphonation also occurs with the pyridine–sulphur trioxide complex in isoparaffin. In basic systems, reversible suphonation at the 9-position is accompanied by irreversible sulphonation at the 1- and 2-positions. The formation of dimeric and polymeric species in some of these reactions is believed to occur *via* the anthracene proton complex.

THE sulphonation of anthracene has received considerable attention over the past century but much confusion still exists over the nature of the products obtained under specific experimental conditions. Sulphonation with concentrated sulphuric acid at 20 °C is claimed to give mainly anthracene-1,5- and -1,8-disulphonic acids [1] but 67% sulphuric acid at 130 °C gives the 2,6- and 2,7-isomers along with the 2-sulphonic acid.[2] Whereas sulphonation with chlorosulphuric acid in either acetic acid [3,4] or dioxan [5] at 100 °C gives a mixture of anthracene-1- and -2-sulphonic acids in approximately equal yields, a related reaction in a mixture of pyridine and paraffin at 170 °C is claimed to give a 90% yield of the 1-isomer.[4] No reaction apparently occurs with sulphur trioxide in pyridine,[6] though there is no doubt that the 9-sulphonic acid is the main product in dioxan.[7,8]

A reinvestigation of some of the chlorosulphuric acid reactions under conditions similar to those originally reported has cast doubt on some of the earlier results. The strongly exothermic reaction between anthracene and chlorosulphuric acid, which produces only small amounts of anthracenesulphonic acids and their 9-chloro-derivatives, is moderated by the presence of a neutral diluent such as chloroform, which is an appropriate solvent because it dissolves the substrate and is miscible with the mineral acid. The reaction of anthracene with 2 mol. equiv. of chlorosulphuric acid in an excess of chloroform at 10—20 °C during 80 min produces a pale green solid which is insoluble in water. An extraction with chloroform removes unchanged anthracene (20.7%), 9-chloroanthracene (28.0%), and smaller amounts of 9,9′-bianthryl, a trianthryl, a tetra-anthryl, and their monochloro-derivatives. The residue, of empirical formula $C_{49}H_{31}ClSO_x$, which remains after extraction (45% by weight), shows i.r. absorptions characteristic of an aromatic sulphonyl function, but the presence of a sulphonyl chloride group is ruled out by the absence of hydrolysis on prolonged boiling with aqueous sodium hydroxide. It is inferred that the product is probably a mixture of anthracene polymers or polyanthryls, which are partially chlorinated and contain a sulphone link. The products obtained from similar reactions in the absence of a diluent are much more complex, however, and are almost certainly related to those described above with the exception, and further complication, that sulphonation has occurred.

A reinvestigation of sulphonation in a basic solvent mixture of pyridine and isoparaffin has revealed that the product composition is far more complex than that described previously.[4] Thus, the reaction of anthracene with 1.8 mol. equiv. of chlorosulphuric acid and 4.0 mol. equiv. of pyridine in an excess of isoparaffin at 165 °C for 4 h gives a 39% conversion into anthracene-1-sulphonic acid (38.9%), the 2-isomer (14.0%), the 9-isomer (3%), 9-chloroanthracene (2.5%), anthracene-1,5-disulphonic acid (7.4%), a mixture of the 1,6- and 1,7-isomers (9.6%), the 1,8-isomer (7.1%), and traces of the 2,6- and 2,7-isomers. Furthermore, the claim that anthracene does not react with the pyridine–sulphur trioxide complex at high temperatures [6] has not been substantiated. Treatment of anthracene with 2.3 mol. equiv. of pyridine–sulphur trioxide complex in an excess of isoparaffin at 165 °C for 4 h gives an 83% conversion into anthracene-1-sulphonic acid (17.0%), the 2-isomer (15.5%), anthracene-1,5-disulphonic acid (11.1%), a mixture of the 1,6- and 1,7-isomers (13.1%), the 1,8-isomer (12.1%), and a mixture of the 2,6- and 2,7-isomers (6.3%).

A corresponding reaction between anthracene and 1.25 mol. equiv. of chlorosulphuric acid in an excess of dioxan proceeds readily to give 9-chloroanthracene, 9,9′-bianthryl, and anthracenemonosulphonic acids only. The sulphonic acid produced, however, depends on the reaction time and temperature. For example, the 9-sulphonic acid is formed initially at 40 °C but it isomerises and reverts on further reaction into the 1-sulphonic acid and 9-chloroanthracene (Figure 1). After 16 h reaction, the 1- and 9-sulphonic acids are present in approximately equal proportions, but after 28½ h, the former exceeds the latter. The proportion of 2-sulphonic acid formed at 40 °C is very small and only 2.7% can be detected

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[1] C. Graebe and C. Liebermann, *Ber.*, 1868, **1**, 186; E. Lincke, *J. prakt. Chem.*, 1875, **11**, 222; C. Liebermann, *Ber.*, 1875, **8**, 246.

[2] G.P. 72226; 73961; 76280/1893.

[3] G.P. 251695/1911; U.S.S.R. Pat. 187,805/1966.

[4] M. Battegay and P. Brandt, *Bull. Soc. chim. France*, 1923, **3**, 1667.

[5] E. P. Goodings and A. H. Mawby, personal communication.

[6] A. P. Terentev and A. V. Dombrovskii, *J. Gen. Chem.* (*U.S.S.R.*), 1949, **19**, 1467.

[7] H. Zorn, O. Hinterhofer, and H. Schindbauer, *Monatsh.*, 1967, **98**, 2406.

[8] A. Koeberg-Telder and H. Cerfontain, *Rec. Trav. chim.*, 1972, **91**, 22.

after 173 h. The 9-sulphonic acid is absent when a similar reaction is carried out at 70 °C for 48 h and the 1- and 2-isomers are produced in yields of 25.4 and 5.5%, respectively, based on the anthracene consumed, along with 9-chloroanthracene (47.8%) and 9,9′-bianthryl (19.7%). At 100 °C during the same reaction time, the isomer ratio changes and the 1- and 2-sulphonic acids are now produced in yields of 23.7 and 11.7%, respectively, along with the chloro-compound (40.5%) and the bianthryl (13.3%). A further reaction carried out at 70 °C for 24 h and then 100 °C for 24 h gives results almost identical with those obtained from the former reaction at 70 °C for 38 h. The yields and conversions obtained from this series of experiments are shown in the Table.

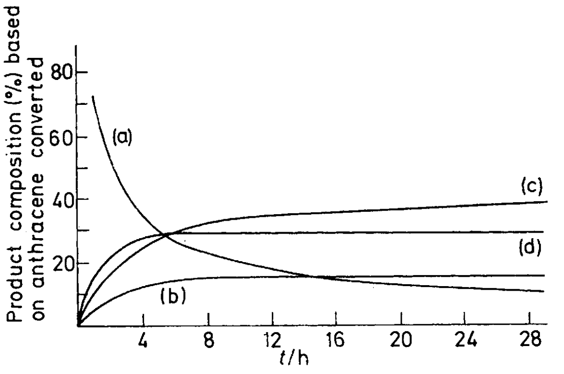

FIGURE 1 Variation in product composition with time during the reaction of anthracene with chlorosulphuric acid in dioxan at 40 °C: (a) anthracene-9-sulphonic acid; (b) anthracene-1-sulphonic acid; (c) 9-chloroanthracene; (d) 9,9′-bianthryl

Products from the reaction of anthracene with chlorosulphuric acid in dioxan

Product composition	Reaction temp. (time)							
	40 °C (½ h)	40 °C (4 h)	40 °C (17 h)	40 °C (28½ h)	40 °C (173 h)	70 °C (48 h)	100 °C (48 h)	70 °C (24 h) 100 °C (24 h)
Anthracene-1-sulphonic acid	Trace	15.6 g, 7.5%	20.6 g, 10.0%	23.0 g, 11.1%	27.5 g, 13.3%	36.1 g, 17.5%	36.4 g, 17.6%	36.2 g, 17.5%
Anthracene-2-sulphonic acid				Trace	3.9 g, 1.9%	7.9 g, 3.8%	17.9 g, 8.7%	8.5 g, 4.1%
Anthracene-9-sulphonic acid	76.4 g, 37.1%	41.2 g, 20.0%	20.6 g, 10.0%	16.8 g, 8.1%	2.2 g, 1.1%			
9-Chloroanthracene	9.0 g, 5.3%	24.4 g, 14.3%	38.6 g, 22.7%	46.4 g, 27.3%	46.2 g, 27.1%	56.1 g, 33.0%	51.3 g, 30.1%	53.7 g, 31.6%
9,9′-Bianthryl	12.4 g, 8.7%	22.7 g, 16.0%	28.2 g, 19.9%	29.3 g, 20.6%	30.8 g, 21.7%	19.3 g, 13.6%	14.0 g, 9.9%	16.0 g, 11.3%
Unchanged anthracene	67.1 g, 47.1%	60.1 g, 42.1%	50.2 g, 35.2%	43.1 g, 30.6%	42.0 g, 29.5%	44.3 g, 31.0%	36.7 g, 25.7%	40.8 g, 28.6%

DISCUSSION

Two main reactions occur when anthracene (A) is treated with strong acids, *viz.* protonation and oxidation. In sulphuric acid, reactions (1)—(3) are believed to occur [9] since the u.v.–visible spectrum of the green solution shows the presence of both the proton complex (AH^+) and the cation radical ($\dot{A}^+$).[10-12] The corresponding spectrum in hydrofluoric acid in the absence of oxygen shows only the proton complex,[13] but both species are found in its presence.[11] The cation radical has also been detected by u.v.–visible spectroscopy in solutions of boron trifluoride with either acetic acid or 1,2-dichloroethane,[11] in fluorosulphuric acid,[14] and by e.s.r. studies in a solution of antimony pentachloride in dichloromethane.[15]

$$A + H_2SO_4 \rightleftharpoons AH^+ + HSO_4^- \qquad (1)$$

$$A + AH^+ \rightleftharpoons \dot{A}H + \dot{A}^+ \qquad (2)$$

$$\dot{A}H + 2H_2SO_4 \rightleftharpoons \dot{A}^+ + 2H_2O + SO_2 + HSO_4^- \qquad (3)$$

When anthracene is dissolved in chlorosulphuric acid a transient yellow solution results which rapidly turns green. The spectrum of a freshly prepared solution [Figure 2(A)] shows the absorptions characteristic of the proton complex at 440 nm and the cation radical at 680 nm. After 2 h in the acid system, the concentration of the proton complex has diminished and a broader absorption has appeared [Figure 2(B)]. The close similarity of the first spectrum to those recorded in (i) a solution of 100% sulphuric acid which has been set aside for 1 h [Figure 2(C)] and (ii) a solution of antimony pentachloride in dichloromethane [Figure 2(D)] shows that the initial reaction involves protonation (or complex formation in the second case), then oxidation, and is followed by sulphonation/polymerisation. However, although the cation radical is rapidly formed in chlorosulphuric acid, the related reaction in sulphuric acid is considerably slower and its formation is accompanied by a decrease in the concentration of the initially formed proton complex. The spectrum of anthracene in a 0.025M-solution of antimony pentachloride in dichloromethane [Figure 2(D)] shows a strong absorption at 445 nm in addition to those absorptions which have been assigned to the cation radical and is probably due to the

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[9] A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 1959, 947.

[10] V. Gold and F. L. Tye, *J. Chem. Soc.*, 1952, 2172.

[11] W. Ij. Aalbersberg, G. T. Hoijtink, E. L. Mackor, and W. P. Weijland, *J. Chem. Soc.*, 1959; 3049; 3055.

[12] H. Kon and M. S. Blois, *J. Chem. Phys.*, 1958, **25**, 743.

[13] E. L. Mackor, A. Hofstra, and J. H. Van der Waals, *Trans. Faraday Soc.*, 1958, **54**, 66.

[14] Von D. Distler and G. Hohlneicher, *Ber. Bunsengesellschaft Phys. Chem.*, 1970, 960.

[15] I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, 1965, **43** (8), 2712.

formation of a σ-complex between the reagents. A similar complex is formed when anthracene is treated with boron trifluoride in 1,2-dichloroethane.[11]

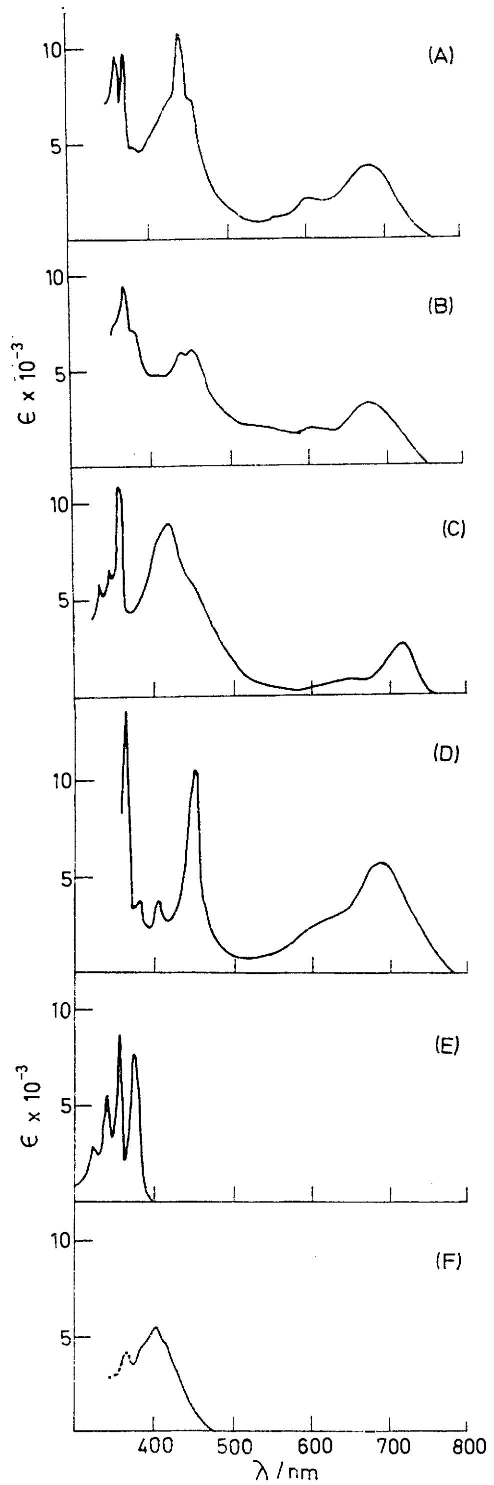
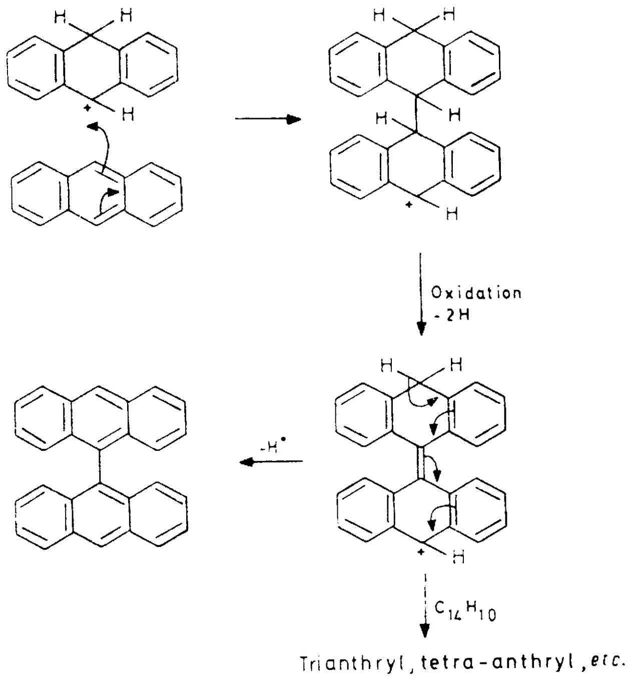


FIGURE 2 U.v.-visible spectra of anthracene: (A) in chlorosulphuric acid (freshly prepared solution); (B) in chlorosulphuric acid set aside for 2 h; (C) in 100 % sulphuric acid (after 1 h); (D) in 0.025M-antimony pentachloride in dichloromethane; (E) in dioxan; (F) in dioxan–chlorosulphuric acid (mol ratio 4 : 1)

The u.v.-visible spectrum of anthracene in dioxan shows four characteristic absorptions between 300 and 400 nm [Figure 2(E)]. However, the corresponding spectrum in a solution of chlorosulphuric acid in dioxan (mol. ratio 1 : 4) is different, showing a strong visible absorption at 410 nm [Figure 2(F)] almost certainly due to the proton complex although (i) a considerable hypsochromic shift has occurred from its relative position in sulphuric acid at 420 nm and in chlorosulphuric acid at 440 nm, and (ii) a small bathochromic shift has occurred from its position in anhydrous hydrofluoric acid at 408 nm.[11,13] Furthermore, the extinction coefficient observed (5 700) is between one-half and one-quarter of that observed in either sulphuric acid [10] or hydrofluoric acid,[13] which implies that only part of the anthracene is protonated under these conditions. The absence of an absorption in the 650—750 nm region rules out the presence of the cation radical in this system.

The formation of polynuclear species such as 9,9′-bianthryl in the sulphonating systems described here, therefore, does not occur *via* the cation radical. It is suggested that such species are produced by the reaction of the proton complex with anthracene itself as shown in Scheme 1. A similar Scheme has been proposed for the formation of polyphenyls from the reaction of benzene with Lewis acids such as aluminium chloride and molybdenum pentachloride.[16] The result of charge density calculations on the proton complex of anthracene



SCHEME 1 One pathway to 9,9′-bianthryl *via* the proton complex of anthracene

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[16] P. Kovacic and R. M. Lange, *J. Org. Chem.*, 1963, **28**, 968; P. Kovacic and J. Oxiomek, *ibid.*, 1964, **29**, 100; P. Kovacic and F. W. Koch, *ibid.*, 1963, **28**, 1864; P. Kovacic and A. Kyriakas, *J. Amer. Chem. Soc.*, 1963, **85**, 454.

by the semi-empirical CNDO/2 method [17] (Program 141 of QCPE; [18] 10 iterations) with the geometry shown in Figure 3, which is derived from selected *X*-ray crystallographic data for both anthracene [19] and 9,10-dihydroanthracene,[20] is illustrated in Figure 4. The greatest positive charge is located at the *meso*-sp^2-carbon atom; it follows that electrophilic attack by the proton complex on a further molecule of anthracene would be expected to result in a dimeric system linked at the *meso*-positions in the way shown (Scheme 1) since anthracene itself is most susceptible to attack at these positions.[21]

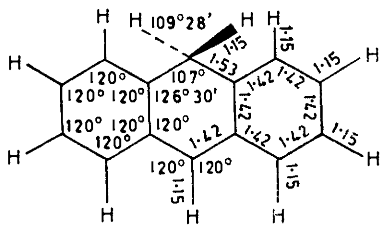


FIGURE 3 Geometry adopted for the anthracene proton complex

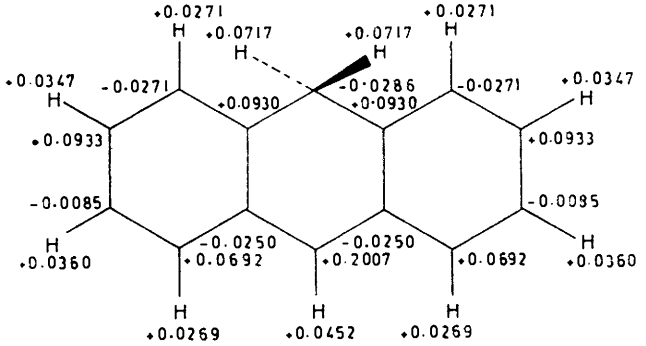


FIGURE 4 Total charge distribution in the anthracene proton complex calculated by the CNDO/2 method

Solutions of anthracene in mixtures of chlorosulphuric acid with pyridine and isoparaffin probably contain the free hydrocarbon only, since the excess of base present effectively absorbs the protons of the mineral acid. No bianthryls or polyanthryls would be expected to be formed in the absence of the proton complex, and, indeed, only traces of 9,9′-bianthryl can be detected. The mechanism is further supported by the absence of the polynuclear species in the related reaction of anthracene with either the pyridine–sulphur trioxide complex or the dioxan–sulphur trioxide complex.[8]

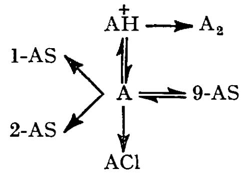
There seems little doubt that the protonation, sulphonation, and chlorination observed either in chloroform or in the absence of a solvent is due to the direct reaction of chlorosulphuric acid itself with the substrate. Different species, however, are involved when either dioxan or pyridine is present. Chlorosulphuric acid is believed to react with dioxan (D) to form the oxonium chlorosulphonate,[22] though the evidence for its formation is inconclusive. However, the exothermicity observed on addition of the acid to the ether does suggest that a neutralisation reaction is occurring on one or perhaps both oxygen atoms [equation (4)]. There is evidently

$$\mathrm{D} + \mathrm{ClSO_3H} \rightleftharpoons \overset{+}{\mathrm{D}}\mathrm{H} + \mathrm{ClSO_3}^- \qquad (4)$$

competition between dioxan and anthracene for the available protons since the latter is partly protonated in solution.

The aprotic sulphonation of anthracene with sulphur trioxide in dioxan leads to anthracene-9-sulphonic acid along with smaller amounts of the 1- and 2-isomers.[7,8] The sulphonic acid group in the 9-isomer is very labile because of its steric interaction with the two adjacent hydrogen atoms at positions 1 and 8. The transfer of the sp^3-carbon-bonded proton is expected to be rate-limiting in this compound, and, indeed, it has been found that the formation of the 9-isomer at 40 °C proceeds with a substrate kinetic isotope effect,[8] k_H/k_D, of *ca.* 7.

The corresponding protic sulphonation of anthracene with chlorosulphuric acid in dioxan also proceeds readily to give anthracenemonosulphonates but the reaction is complicated by the presence of substantial amounts of 9-chloroanthracene and 9,9′-bianthryl. The formation of the 9-sulphonic acid in this system is kinetically controlled since it isomerises into a mixture of the 1- and 2-isomers (see Figure 1). At higher temperatures, the isomerisation is more rapid and the ratio of the 1- to the 2-isomer formed decreases from 4.6 at 70 to 2.0 at 100 °C. However, since the ratio of products formed during 24 h at 70 °C does not change on a further 24 h reaction at 100 °C, it is concluded that both the 1- and 2-sulphonic acids are primary products and that reversible sulphonation at the 9-position is accompanied by irreversible sulphonation at the 1- and 2-positions. The reaction sequences, therefore, may be represented as in Scheme 2, where AS is the appropriate anthracenesulphonic acid, ACl is 9-chloroanthracene, and A_2 is 9,9′-bianthryl.



SCHEME 2

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[17] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, S129; J. A. Pople and G. A. Segal, *ibid.*, 1965, **43**, S136; 1966, **44**, 3289.

[18] P. A. Dobosh, CNINDO, Program 141, Quantum Chemistry Program Exchange, Indiana University.

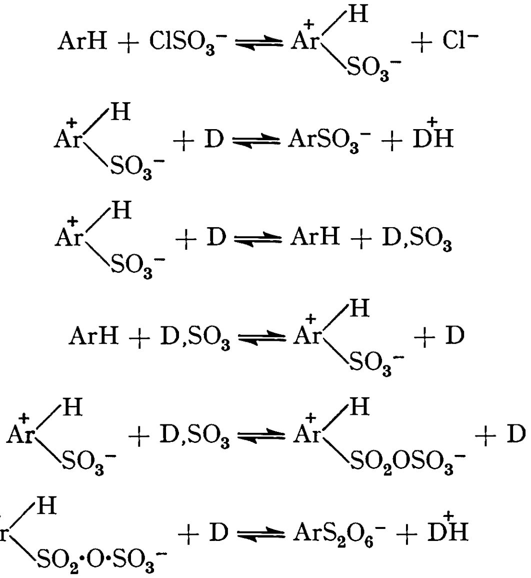
[19] R. Mason, *Acta Cryst.*, 1964, **17**, 547.

[20] M. C. Malmstrom, Ph.D. Thesis, University of Arkansas, 1972.

[21] G. Dallinga, A. A. Verrijn Stuart, P. J. Smit, and E. L. Mackor, *Z. Electrochem.*, 1957, **61**, 1019.

[22] C. M. Suter and J. D. Malkemus, *J. Amer. Chem. Soc.*, 1941, **63**, 978.

Although the mechanism of the sulphonation has not been resolved the initial reaction between anthracene and either the chlorosulphonate anion or the chlorosulphuric acid–dioxan complex probably results in the displacement of the chloride anion to give a σ-complex at the 9-position. The formation of the 9-sulphonic acid by subsequent proton transfer may be the rate controlling step as in the related aprotic sulphonation,[8,23] although alternative mechanisms cannot be ruled out. The formation of the 1- and 2-sulphonic acids, however, may occur in a different way since desulphonation of the 9-isomer would be expected to produce the dioxan–sulphur trioxide complex, which sulphonates by a different mechanism.[23] The sulphonation sequence, therefore, may be represented by equations (5)—(10),



$$\mathrm{ArH} + \mathrm{ClSO_3^-} \rightleftharpoons \overset{+}{\mathrm{Ar}}\left\langle\begin{matrix}\mathrm{H}\\ \mathrm{SO_3^-}\end{matrix}\right. + \mathrm{Cl^-} \quad (5)$$

$$\overset{+}{\mathrm{Ar}}\left\langle\begin{matrix}\mathrm{H}\\ \mathrm{SO_3^-}\end{matrix}\right. + \mathrm{D} \rightleftharpoons \mathrm{ArSO_3^-} + \mathrm{D\overset{+}{H}} \quad (6)$$

$$\overset{+}{\mathrm{Ar}}\left\langle\begin{matrix}\mathrm{H}\\ \mathrm{SO_3^-}\end{matrix}\right. + \mathrm{D} \rightleftharpoons \mathrm{ArH} + \mathrm{D,SO_3} \quad (7)$$

$$\mathrm{ArH} + \mathrm{D,SO_3} \rightleftharpoons \overset{+}{\mathrm{Ar}}\left\langle\begin{matrix}\mathrm{H}\\ \mathrm{SO_3^-}\end{matrix}\right. + \mathrm{D} \quad (8)$$

$$\overset{+}{\mathrm{Ar}}\left\langle\begin{matrix}\mathrm{H}\\ \mathrm{SO_3^-}\end{matrix}\right. + \mathrm{D,SO_3} \rightleftharpoons \overset{+}{\mathrm{Ar}}\left\langle\begin{matrix}\mathrm{H}\\ \mathrm{SO_2OSO_3^-}\end{matrix}\right. + \mathrm{D} \quad (9)$$

$$\overset{+}{\mathrm{Ar}}\left\langle\begin{matrix}\mathrm{H}\\ \mathrm{SO_2{\cdot}O{\cdot}SO_3^-}\end{matrix}\right. + \mathrm{D} \rightleftharpoons \mathrm{ArS_2O_6^-} + \mathrm{D\overset{+}{H}} \quad (10)\ *$$

where ArH is anthracene. The presence of 9-chloroanthracene and the virtual absence of any 9,10-dichloroanthracene in the products of these reactions indicates that a highly specific chlorination is occurring. The mechanism of this reaction is not known but the high specificity may be a consequence of transannular addition of the poorly solvated chloride anion formed in equation (5) to the 10-position of the σ-complex followed by elimination of the hydrogen sulphite anion across the centre ring.

In the related sulphonation of anthracene with chlorosulphuric acid and pyridine in an excess of isoparaffin, there is little doubt that the reacting species are pyridine hydrochloride and the pyridine–sulphur trioxide complex in view of the reaction (11).[24,25] Under the con-

$$\mathrm{ClSO_3} + \mathrm{C_5H_5N} \rightleftharpoons \mathrm{C_5H_5N,HCl} + \mathrm{C_5H_5N,SO_3} \quad (11)$$

ditions specified here, 39% of the anthracene is consumed when 1.8 mol. equiv. of each species is present. However, a similar heterogeneous reaction with 2.3 mol. equiv. of the pyridine–sulphur trioxide complex alone results in an 83% conversion into sulphonated products despite a previous claim[6] that the complex does not react with anthracene at 150 °C. The high conversion observed, the large proportion of disulphonic acids produced (57% of the total), and the almost equal ratio of the 1- and 2-sulphonic acids found in the products of the latter reaction show that a rapid but very unselective sulphonation is occurring, probably because the rate of reaction between the substrate, which is dissolved in the top isoparaffin layer, and the molten reagent, which forms the bottom layer of the heterogeneous system, is diffusion controlled. Conversely, the low conversion observed in the former reaction and the large proportion of monosulphonic acids produced (70% of the total) together with the relatively high ratio (2.8 : 1) of the 1- to the 2-isomers demonstrate that the reaction is slower and proceeds with greater selectivity than the reaction in the absence of pyridine hydrochloride. The hydrochloride, therefore, modifies the reactivity of the pyridine–sulphur trioxide complex possibly by hydrogen bonding since both species are molten at the reaction temperature and are miscible with each other but immiscible with the isoparaffin mixture.

EXPERIMENTAL

General purpose reagents were used throughout. Chloroform was washed free of ethanol with water and dried with molecular sieves (4 Å). The isoparaffin mixture, b.p. 162—174° (Esso, 'Isopar G'), was washed twice with concentrated sulphuric acid to remove residual aromatic material, then washed with water, and dried over calcium chloride. Both pyridine and dioxan were dried over molecular sieves (4 Å). Chlorosulphuric acid was used as received. I.r. spectra (potassium bromide discs) and u.v. spectra were recorded with Perkin-Elmer 457 and 124 spectrophotometers, respectively. N.m.r. spectra were recorded with a Perkin-Elmer R32 instrument operating at 90 MHz, and mass spectra with an A.E.I. MS9 instrument. Authentic samples of anthracene-mono- and -di-sulphonic acids, 9-chloroanthracene, and 9,9′-bianthryl were provided by I.C.I. Ltd.

Products insoluble in water were analysed by t.l.c. (Merck precoated Silica Gel 60 F_{254} aluminium plates with cyclohexane as eluant). Anthracene, 9-chloroanthracene, and 9,9′-bianthryl were observed at R_F 0.41, 0.53, and 0.22, respectively. The same products were identified also by ^{1}H n.m.r. spectroscopy in [^{2}H]chloroform and their amounts estimated from the peak heights of the sharp singlet absorptions of the 10- and 10′-protons of 9,9′-bianthryl, the 10-proton of 9-chloroanthracene, and the 9- and 10-protons of anthracene itself (δ 8.60, 8.30, and

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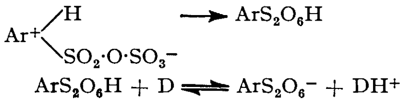
* A referee has suggested that intramolecular proton removal from the anthracen-9-ium-9-(disulphonate) intermediate is probably faster than the intermolecular proton removal by dioxan for entropic reasons. The reaction possibly proceeds as follows:



$$\mathrm{Ar}^{+}\left\langle\begin{matrix}\mathrm{H}\\ \mathrm{SO_2{\cdot}O{\cdot}SO_3^-}\end{matrix}\right. \longrightarrow \mathrm{ArS_2O_6H}$$

$$\mathrm{ArS_2O_6H} + \mathrm{D} \rightleftharpoons \mathrm{ArS_2O_6^-} + \mathrm{DH^+}$$

[23] H. Cerfontain, A. Koeberg-Telder, C. Ris, and C. Shenk, *J.C.S. Perkin II*, 1975, 966.

[24] P. Baumgarten, *Ber.*, 1926, **59**, 1166.

[25] H. H. Sisler and L. F. Audrieth, *Inorg. Synth.*, 1946, **2**, 173.

8.35, respectively). The proportion of 9-chloroanthracene present in a given mixture was assessed also by elemental analysis.

Mixtures of anthracenesulphonic acids were analysed by a combination of t.l.c. and n.m.r. spectroscopy. Either glass plates coated with 0.5 mm Cellulose F_{254} (Merck) and water as eluant or precoated Cellulose F_{254} aluminium plates (Merck) and dioxan–butan-1-ol–ammonia–water (4 : 2 : 1 : 1) as eluant were used for t.l.c. analysis. The first method gave the best overall resolution: the 2-sulphonic acid was observed at R_F 0.23; the 1-isomer at 0.42; the 9-isomer at 0.48; the 2,6- and 2,7-disulphonic acids at 0.56; the 1,6- and 1,7-isomers at 0.76; and the 1,5- and 1,8-isomers at 0.85. The second method showed the 1,5-, 1,6-, 1,7-, 2,6-, and 2,7-isomers unresolved at R_F 0.29, the 1,8-isomer separate at 0.48, and all the monosulphonates unresolved at 0.76. Because of the insolubility of the 2-sulphonic acid and its sodium salt, care was taken to ensure that the products were in solution prior to analysis. Thus, acidic samples were made alkaline with ammonia and diluted with a large quantity of water; the mixture was boiled to give a clear solution and then placed on the appropriate t.l.c. plates. Precipitates of either unchanged anthracene, or admixtures with 9-chloroanthracene and 9,9′-bianthryl, obtained from diluted sulphonation mixtures, were washed thoroughly with boiling water to remove the 2-sulphonic acid. ^{1}H N.m.r. spectroscopic analyses were carried out on the free sulphonic acids at 95 °C. Samples were prepared by evaporation of the sulphonic acid filtrates and washings, and treatment of the residues with 50% aqueous dioxan followed by addition of 20% by weight of a cation-exchange resin [Dowex 50W-X8(H^+)]. The mixture was boiled for a few minutes to dissolve the free acid, filtered rapidly, and analysed. Satisfactory analyses of the sodium salts in water, aqueous dioxan, or [$^2H_6$]dimethyl sulphoxide could not be obtained because of the low solubility of the 2-sulphonate. Products were analysed by measurement of the absorptions of the 9-proton of the 1,8-disulphonic acid at δ 10.10 (s); the 9- and 10-protons of the 1,5-isomer at δ 9.40 (s); the 10-protons of the 1,6- and 1,7-isomers at δ 8.60 (s); the 9-protons of the 2,6- and 2,7-isomers at δ 8.50 (s); the 9-proton of the 1-sulphonic acid at δ 9.30 (s); the 9-proton of the 2-isomer at δ 8.55 (s); and the 1- and 8-protons of the 9-isomer at δ 9.35 (d).

Reactions of Anthracene with Chlorosulphuric Acid.—(a) *In pyridine–isoparaffin.* Chlorosulphuric acid (60.0 g, 0.52 mol) was slowly added to a solution of dry pyridine (90.0 g, 1.14 mol) in isoparaffin (250 ml) which was maintained below 10 °C during the addition (ice-bath). Anthracene (50.0 g, 0.27 mol) was added to the white suspension and the mixture heated rapidly to 160—165 °C and kept there for 4 h. The mixture was cooled to 90 °C, added to water, and neutralised with aqueous sodium hydroxide; the pyridine and isoparaffin were then removed by steam distillation and the precipitate was filtered off, washed thoroughly with hot water, and dried at 70 °C to give anthracene (30.4 g, 60.8 recovery) and 9-chloroanthracene (0.56 g, 2.5%). The filtrates and washings were combined and found to contain anthracene-1-sulphonic acid (11.1 g, 38.9%), the 2-isomer (4.0 g, 14%), the 9-isomer (0.85 g, 3%), anthracene-1,5-disulphonic acid (2.75 g, 7.4%), a mixture of the 1,6- and 1,7-isomers (3.57 g, 9.6%), the 1,8-isomer (2.64 g, 7.1%), traces of the 2,6- and 2,7-isomers, and a further unidentified component, R_F 0.71 in the Cellulose F–water t.l.c. system.†

(b) *In chloroform.* A solution of chlorosulphuric acid (46.4 g, 0.4 mol) in chloroform (90 ml) was added slowly over 40 min to a suspension of anthracene (35.6 g, 0.2 mol) in chloroform (700 ml) maintained at an internal temperature of 5—10 °C during the addition (ice-bath). The mixture was stirred for a further 40 min at 20 °C and added carefully to cold water (500 ml), and the chloroform was removed by steam distillation. The product was filtered off, washed with hot water, and dried at 100 °C to give a pale green solid (35.1 g) which was extracted with chloroform (Soxhlet) until the extracts became colourless (*ca.* 4 h). Evaporation left a dark solid which was identified as unchanged anthracene (7.4 g, 20.7% recovery) and 9-chloroanthracene (11.9 g, 28.0%) along with small amounts of bianthryl, trianthryl, tetra-anthryl, and their monochloro-derivatives. The chloroform-insoluble product (15.8 g) of empirical formula $C_{49}H_{31}ClSO_x$ (Found: C, 76.9; H, 4.0; Cl, 4.6; S, 4.2%) defied characterisation but showed $\nu_{max.}$ 1 620m, 1 400s, 1 165s, 1 030s, 880m, 730s, and 600m cm^{-1}, characteristic of an aromatic sulphone. No chloride ion was detected on prolonged boiling with aqueous sodium hydroxide, which ruled out the presence of a sulphonyl chloride.

(c) *In dioxan.* Chlorosulphuric acid (116.5 g, 1 mol) was slowly added to dioxan (440.5 g, 5.0 mol) maintained below 25 °C during the addition (ice-bath). Anthracene (142.6 g, 0.8 mol) was added with shaking and the mixture was heated under the specified conditions (Table) and added to an equal volume of cold water; the precipitate was filtered off, washed free of acid with water, and dried at 70 °C. The analyses of products are shown in the Table.

Reaction of Anthracene with the Pyridine–Sulphur Trioxide Complex in Isoparaffin.—The reagent was prepared from pyridine and chlorosulphuric acid in chloroform and isolated by filtration; the residual pyridine hydrochloride was removed by washing with chloroform.[25] Elemental analysis showed that the dried product contained 0.1% of chlorine only. A mixture of anthracene (50.0 g, 0.27 mol), pyridine–sulphur trioxide complex (99.0 g, 0.62 mol), and isoparaffin (250 ml) was heated at 165—170 °C with shaking for 4 h, cooled to 90 °C, added to water, and neutralised with aqueous sodium hydroxide. The pyridine and isoparaffin were removed by steam distillation and the precipitate was filtered off, washed thoroughly with hot water, and dried at 70 °C to give unchanged anthracene (8.5 g, 17% recovery). The filtrates and washings were combined and found to contain anthracene-1-sulphonic acid (10.2 g, 17%), the 2-isomer (9.3 g, 15.5%), anthracene-1,5-disulphonic acid (8.75 g, 11.1%), a mixture of the 1,6- and 1,7-isomers (10.3 g, 13.1%), the 1,8-isomer (9.5 g, 12.1%), the 2,6- and 2,7-isomers (5.0 g, 6.3%), and two unidentified components, R_F 0.67 and 0.94, respectively, in the Cellulose F–water t.l.c. system.† The high R_F value of the last band coupled with the appearance of two pairs of equal absorptions at δ 9.50 and 9.60 and δ 10.15 and 10.25 in the ^{1}H n.m.r. spectrum of the sulphonation products suggested, on the basis of chemical shift data, that the 1,3,5- and 1,3,8-isomers of anthracene trisulphonic acid were present in *ca.* 6% yield.

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† There was no evidence to suggest that desulphonation of the 9-sulphonic acid had occurred during dilution with water since similar t.l.c. results were obtained with cold samples of the neat reaction mixture prior to dilution.