

## The Formation of Sulphonic Anhydride and Sulphone in Aromatic Sulphonation

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The mechanisms of the formation of iodobenzene sulphonic anhydride, the corresponding sulphone and the sulphonic acid in the sulphonation of iodobenzene with sulphur trioxide in nitromethane have been investigated. It has been shown that the sulphonic anhydride can be prepared by reaction between sulphonic acid and sulphur trioxide, and that the sulphone can be formed by reaction between sulphonic anhydride and iodobenzene, catalysed by sulphur trioxide. Furthermore, solubility measurements and other experiments indicate the existence of a soluble complex between sulphonic anhydride and sulphuric acid. Preparative and kinetic data suggest that this complex reacts with iodobenzene forming the sulphonic acid.

The experimental data are found to give evidence for mechanisms involving pyrosulphonic acid ( $\text{RSO}_3\text{SO}_3\text{H}$ ).

The mechanisms underlying the reactions in aromatic sulphonation have remained little understood in comparison with other electrophilic substitution mechanisms. However, it now appears to be widely accepted that the monomer,  $\text{SO}_3$ , is the only sulphonating species in aprotic solvents for sulphur trioxide as well as in protic agents, *e.g.* fuming sulphuric acid.<sup>1-4</sup> According to the present theories a sulphonic acid,  $\text{RSO}_3\text{H}$ , is formed in a protic medium and a pyrosulphonic acid,  $\text{RSO}_3\text{SO}_3\text{H}$ , in an aprotic medium. The final reaction products obtained, from both types of solvents, are sulphonic acids, sulphones,  $\text{R}_2\text{SO}_2$ , and sulphonic anhydrides,  $(\text{RSO}_2)_2\text{O}$ . The variety of reaction products demonstrates the existence of other reactions than the sulphonation steps. These *secondary reactions* of the sulphonation constitute the main object of the present study.

Since sulphonation of iodobenzene yields sulphonic anhydride as well as sulphone,<sup>5</sup> this system was considered suitable for studying the secondary reactions. The effect on the reaction products of varying the mole ratio  $[\text{SO}_3]/[\text{C}_6\text{H}_5\text{I}]$  was studied at 0° and 40°. Furthermore reactions between various reaction products and reactants were investigated, and the solubility of iodobenzene sulphonic anhydride was measured. Finally, previously reported

rate-data were analysed in the light of information furnished by the preparative experiments.

### EXPERIMENTAL

*Materials.* Iodobenzene, sulphur trioxide and nitromethane were purified as reported previously.<sup>6</sup>

Samples of labeled *p*-iodobenzene sulphonic anhydride with a specific activity of the order of 1  $\mu$ C/mg, were obtained from the Isotope Laboratory, Risø. They were recrystallised from nitromethane and had m.p. higher than 215°. <sup>35</sup>S- as well as <sup>131</sup>I-labeled substances were used.

Pure samples of *p*-iodobenzene sulphonic anhydride for solubility measurements and other purposes were prepared by sulphonation of iodobenzene in nitromethane. The melting points were 218–221° after recrystallisation from nitromethane. The substance is insoluble in ether and pentane, readily hydrolysed in hot 1 N NaOH or in steam, but slowly hydrolysed in boiling water. For further characterisation of the substance cf. Ref.<sup>7</sup>

*p*-Iodobenzene sulphonic acid (monohydrate or anhydrous) was prepared by steam hydrolysis of the sulphonic anhydride and subsequent drying, finally *in vacuo*. The substance is readily soluble in nitromethane and water.

Two samples of pure di-(iodophenyl) sulphone were prepared. Sample A was prepared according to Huntress and Carten<sup>8</sup> by treating iodobenzene with chlorosulphuric acid at 50°. After recrystallisation from acetic acid the substance had m.p. 210°, iodine found: 53.6 %, calc.: 54.0 %. Sample B was pooled crude samples isolated from the reaction products of the sulphonation experiments (cf. below.) It had m.p. 206°, iodine content 53.5 %. Both samples were stable towards hot 1 N NaOH, and both were soluble in nitromethane and ether. The m.p. of purified di-(iodophenyl) sulphone has been reported to be 213°.<sup>9</sup>

The sulphonation of the mono-halobenzenes yields almost exclusively the *p*-isomers (Holleman,<sup>10</sup> Lauer<sup>11</sup>).

*Preparative studies.* These experiments were carried out in bifurcated vessels of 10 ml capacity using weighed amounts of the components dissolved in nitromethane. The systems studied were:

*Series A:* iodobenzene + sulphur trioxide (or 100 % H<sub>2</sub>SO<sub>4</sub>).

*Series B:* *p*-iodobenzenesulphonic acid + sulphur trioxide (in one case using <sup>35</sup>S-labelled SO<sub>3</sub>),

*Series C:* sulphur trioxide and <sup>131</sup>I-labelled *p*-iodobenzene sulphonic anhydride + iodobenzene (or di-(iodophenyl) sulphone.)

In those experiments where the sulphonic anhydride was formed, this compound usually separated as a precipitate during the first 5–20 seconds of the reaction. The reaction mixtures were kept for 25 min at the given temperature. Reaction mixtures at 0° were immediately worked up, mixtures of higher temperature were first cooled for 5 min at 0°.

The precipitate was collected on a glass filter, washed with nitromethane and ether, dried and weighed as the sulphonic anhydride. The mother liquor was washed with water in order to extract sulphonic acid. The amount of sulphonic acid in the aqueous phase was determined photometrically (cf. Ref.<sup>6</sup>). The combined organic phases were evaporated and the residue was washed with hot 1 N NaOH, dried and weighed as the sulphone.

The above procedure was followed in series A and B, and the material balances were 91–95 % in the experiments with excess of SO<sub>3</sub>. In series C only the sulphone was isolated. <sup>131</sup>I-Activity was measured with scintillation equipment, <sup>35</sup>S-Activity with endwindow Geiger-Müller-tube.

*Solubility determination.* Samples of sulphonic anhydride were shaken in nitromethane to which various compounds had been added. The content of sulphonic anhydride in the clear supernatant was determined spectrophotometrically after evaporation of the organic solvent and hydrolysis of the residue.

*Rate-measurements of product formation.* The experimental procedure has previously been published.<sup>6</sup> It should be noted that the analytical procedure determines the sum

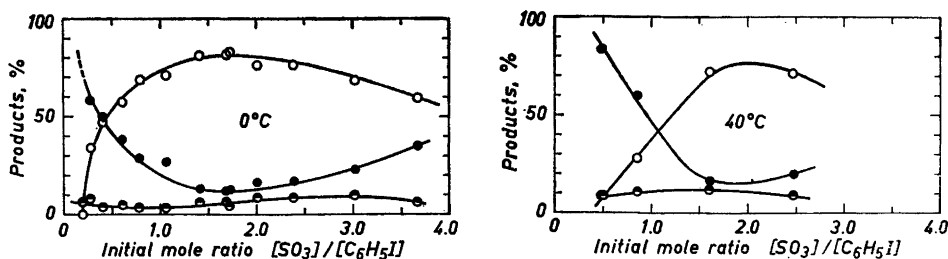


Fig. 1. Series A, sulphonation of iodobenzene with sulphur trioxide in nitromethane. The proportional distribution of iodophenyl groups on the three reaction products formed at 0° and at 40°: precipitated sulphonic anhydride (○), solvated product (●) and sulphone (◐).

of the equivalent concentrations of sulphonic acid and sulphonic anhydride in the mixture at a given time. The initial sulphur trioxide concentration is identified with the concentration of sulphonic acid at infinite time, as the small sulphone formation may be neglected in these experiments.

## RESULTS

*Iodobenzene — sulphur trioxide.* (Series A). In these experiments sulphonic anhydride, sulphone and sulphonic acid were isolated. Since none of these products were found in control experiments using 100 % sulphuric acid instead of sulphur trioxide, it is justifiable to apply the following stoichiometric equations:



The yields of the three products are presented in Fig. 1, the mole ratio and the temperature being the parameters varied. The sulphone yield is rather low, independent of mole ratio and temperature. The amount of sulphonic anhydride precipitated is fairly large through most of the range investigated. It is shown below that the sulphonic acid has passed through the anhydride stage. The tendency to anhydride formation is therefore more

Table 1. Series B, reaction between sulphonic acid and sulphur trioxide in 3–4 ml nitromethane at 40°

SO <sub>3</sub> added, mmole per mmole sulphonic acid	Yields in % of initial sulphonic acid	
	Sulphonic anhydride	Sulphonic acid (water-extracted)
0.95	69	not determined
1.2	73	22
4.0	43	52

pronounced than suggested by the quantities precipitated, and it will appear from the following that it even may be independent of the sulphonation conditions.

*Sulphonic anhydride.* (Series B). The results of the dehydration experiments have been given in Table 1. The sulphonic anhydride separates rapidly when mixing the sulphonic acid with sulphur trioxide, thereby demonstrating the existence of the reaction:



It should be pointed out that sulphone was not found in the reaction mixtures of these experiments.

In one of the experiments the sulphonic acid was labelled with  $^{35}\text{S}$ . The dehydration had no effect on the specific activity, *i.e.* there is no exchange of sulphur. This observation indicates that reaction (4) is similar to previously reported instances of formation of sulphonic anhydrides from sulphonic acids by reaction with inorganic acid anhydrides and halides.<sup>12-14</sup>

*Solubility of sulphonic anhydride.* The data given in Table 2 show a very low solubility in pure nitromethane, but a moderate solubility in nitromethane containing 0.3–0.6 m sulphuric acid. The experiments have further demonstrated a very low dissolution rate at 0°.

A likely explanation for the increased solubility is formation of complexes between  $\text{H}_2\text{SO}_4$  and  $(\text{RSO}_2)_2\text{O}$ . Carboxylic anhydrides are known to form complexes with sulphuric acid.<sup>15</sup> Moreover, evidence for the existence of solvated complexes between sulphonic anhydrides and sulphuric acid may be deduced from certain observations on sulphonation reported by Lukashevich.<sup>5</sup> In these experiments fuming sulphuric acid in excess was the sulphonating agent, and precipitation of the sulphonic anhydride in the reaction mixture occurred only rarely. However, the sulphonic anhydrides were often precipitated in good yields when the reaction mixtures were poured on ice.

Sulphuric acid is present in the sulphonation mixtures, *cf. eqns.* (2) and (3). The concentration of  $\text{H}_2\text{SO}_4$  has been calculated for each of the experiments with iodobenzene—sulphur trioxide, and the results are shown in Fig. 2 (broken line). It will be seen that the concentration of sulphuric acid has been 0.3–0.5 m over most of the range investigated; the concentration

Table 2. Solubility of *p*-iodobenzene sulphonic anhydride in nitromethane solvents at 0°. Method 1 employs constant temperature; method 2, cooling from a warm solution.

Solvent	Method 1	Method 2
Pure nitromethane	1.2 mg/g	2.1 mg/g
0.3 m $\text{H}_2\text{SO}_4$ (101 %)		26 —
0.6 — — —		35 —
1.8 — — —	17 (4 h) mg/g	
— — — —	4 (1—) —	
2.1 — — —	22 (4—) —	
— — — —	14 (1—) —	

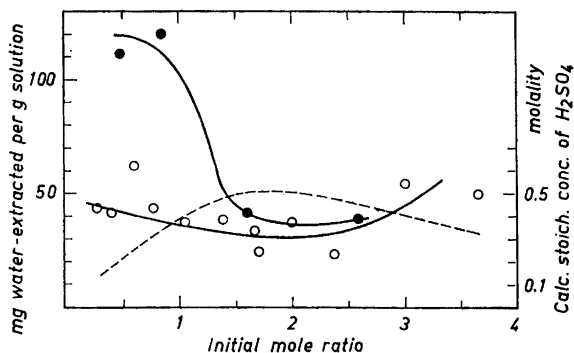


Fig. 2. Series A, water-extracted products, concentration in reaction mixtures cooled to 0°, *cf.* Fig. 1. Sulphonation of iodobenzene at 0°: ○, and at 40°: ●. The broken line indicates calculated concentration of sulphuric acid in the reaction mixtures, individual points not being shown.

of “solvated product” in the reaction mixtures should therefore be of the order of 25–35 mg/g.

The concentrations of water-extractable product in the nitromethane-phase (experimental series A) are shown in Fig. 2 (full line). Most values are seen to lie in or near the expected range (25–35) mg/g suggesting that a complex-formation between sulphonic anhydride and sulphuric acid is the primary cause for the existence of the sulphonic acid in the aqueous extract. However, several values are significantly higher, showing that other reactions must be at work. It will be shown below how the discrepancies found with mole ratios less than 1.5 may be accounted for.

*Reactivity of sulphonic anhydride.* In sulphonation mixtures with excess of iodobenzene the sulphonic anhydride is an intermediate for the formation of sulphonic acid, as demonstrated by the following experiment.

After sulphonation at 0° at  $[\text{SO}_3]/[\text{RH}] = 0.33$  the first formed precipitate was dissolved by heating the mixture to 70° for 3 min. By cooling to 0° it was evident that the yield of precipitate had been reduced. After repetition of this operation three times, no precipitate was formed by cooling the mixture, not even by seeding with crystals of sulphonic anhydride.

This observation is consistent with the low yields of sulphonic anhydride found in sulphonation experiments with mole ratios less than 1.5 made at 40°, as compared to the results at 0°, *cf.* Fig. 1. Since the acid is found in high yields under the same circumstances, *cf.* Figs. 1 and 2, the existence of the following reaction is indicated.

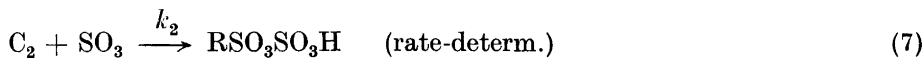
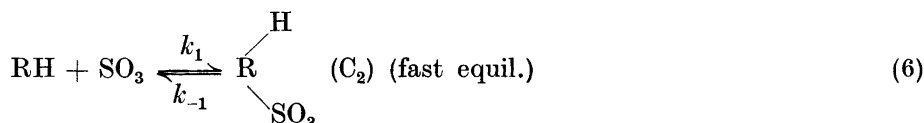


According to the above the sulphonic anhydride, which is always formed, may precipitate or form a soluble complex with the simultaneously formed sulphuric acid. The complex will react with the aromatic substrate, but reaction (5) is slow compared to the rate of crystallisation, and the anhydride may

therefore be isolated even when the aromatic substrate is in excess, provided neither the temperature nor the excess is too high.

*Rate-measurements.* One of the most characteristic features in the kinetic picture of aprotic sulphonation with the aromatic substrate in excess is the retardation of the product formation.<sup>6,16-18</sup> The fact that sulphonic anhydride may appear as a major product under some conditions, and the evidence that it is formed as an intermediate under others, suggest an explanation of the retardation; a quantitative interpretation will be attempted below.

The usual mechanism for aprotic sulphonation is accepted.



In order to explain a predominant concentration of sulphonic anhydride, the following fast reaction is postulated:



The concentration of pyrosulphonic acid is accordingly negligible during the reaction. It is furthermore assumed that the reaction (5) is sufficiently slow to enable the sulphonic anhydride to appear as a long-lived intermediate. Reaction (5), consequently, predominates only during the last period of a run. During the first part, step (5) is negligible and reaction (7) is rate-determining. Let  $[\text{RSO}_3\text{H}]$  denote the concentrations of total product in terms of equivalent acid. For the first period the following expression can be derived:

$$d[\text{RSO}_3\text{H}]/dt = k_1 \times k_2/k_{-1} \times [\text{RH}] [\text{SO}_3]^2 \quad (9)$$

As long as the sulphonic anhydride predominates, the following equation is valid

$$[\text{SO}_3]_0 = [\text{SO}_3] + 3/2 [\text{RSO}_3\text{H}] \quad (10)$$

where index zero indicates the initial concentration.

Insertion of (10) into (9), introduction of  $\alpha = [\text{RSO}_3\text{H}]/[\text{SO}_3]_0$  and integration give:

$$\frac{1}{1 - 3/2 \times \alpha} = \frac{3 k_1}{2 k_{-1} k_2} [\text{RH}]_0 [\text{SO}_3]_0 t + 1 \quad (11)$$

treating  $[\text{RH}]$  as constant.

From the diagrams presented in Figs. 3 and 4 it will be seen that the experimental data obey eqn. (11) with respect to linearity with time as well as with respect to the second order constant being proportional to  $[\text{RH}]_0$  and  $[\text{SO}_3]_0$ .

The retardation in sulphonation rate was also observed by Hinshelwood and coworkers,<sup>16-18</sup> in their study on aromatic sulphonation, using nitrobenzene as solvent and sulphur trioxide as sulphonating agent. They ascribed the phenomenon to the formation of pyrosulphonic acid, but they did not

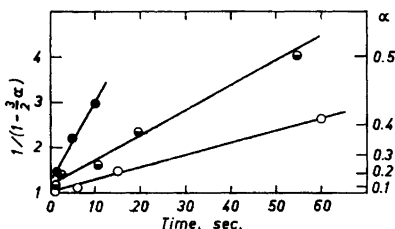


Fig. 3. Rate measurements of iodobenzene sulphonation at 0°.  $\alpha = [\text{RSO}_3\text{H}]/[\text{RSO}_3\text{H}]_\infty$ . Runs with initial concentrations (stoich):  $\text{SO}_3$  g-mole/kg  $\text{C}_6\text{H}_5\text{I}$  g-mole/kg

○	0.027	0.46
◐	0.100	0.45
●	0.097	1.18

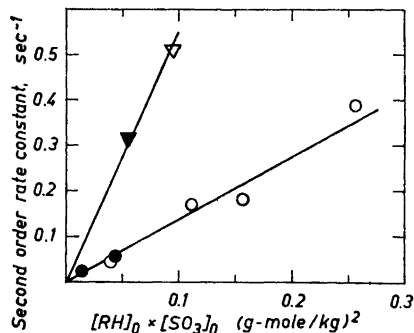


Fig. 4. Sulphonation of iodobenzene. Second order rate constants.

0°	40°	
●	▼	Initial iodobenzene conc. 0.5 m
○	▽	Initial iodobenzene conc. 1.2 m

consider the possibility that sulphonic anhydride was formed as an intermediate. Their kinetic picture was found using a number of different aromatics, but the only instance, where the published data are detailed enough to permit a reevaluation, is the sulphonation of nitrobenzene itself.<sup>16</sup>

Corresponding values of  $\alpha$  and time for three runs with different initial sulphur trioxide concentrations have been taken from the rate-data presented p. 1374, Ref.<sup>16</sup> These values have been recalculated, and the results are shown in Fig. 5. It will be seen that linearity is obtained with good accuracy for a long period during each run. A discrepancy exists for the initial period of the run with high sulphur trioxide concentration; this could have been effected by the marked change taking place in the medium during that period. It is furthermore seen that the slopes of the lines are proportional to the initial sulphur trioxide concentration, as predicted by eqn. (11).

Hence it appears that the kinetic data on sulphonation of iodobenzene and nitrobenzene are consistent with the mechanism (6)–(7)–(8)–(5).

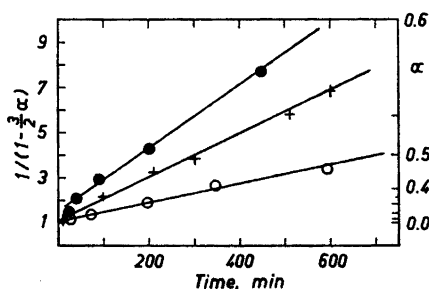


Fig. 5. Kinetics of sulphonation of nitrobenzene by sulphur trioxide. Recalculated data from Fig 2, *J. Chem. Soc.* 1939 1374. Runs with initial concentrations of sulphur trioxide, 0.974, 0.679 and 0.286 g-mole per litre. The ratios of the slopes to the initial conc. of  $\text{SO}_3$  are: 0.0144, 0.0142 and 0.0149 litre.min<sup>-1</sup> g-mole<sup>-1</sup>, respectively.

Table 3. Series C, sulphone formation in iodobenzene sulphonation using  $^{131}\text{I}$ -labelled sulphonic anhydride. Reaction period 25 min at  $50^\circ$ , 5 ml samples in nitromethane. The radioactivity recovered in the sulphone has been given in percent of the amount of radioactivity added as sulphonic anhydride.

Components added, mmole				Sulphone recovered	
$(\text{R}^*\text{SO}_2)_2\text{O}$	$\text{SO}_3$	RH	$\text{R}_2\text{SO}_2$	mmole	% activ.
0.078	2.8	2.25	—	0.088	5.9
0.052	2.8	2.25	—	0.078	6.4
0.237 <sup>a</sup>	2.8	2.25	—	0.133	5.0
0.132 <sup>a</sup>	2.8	2.25	—	0.054	2.6
0.024	2.8	—	0.113 (A)	0.102	<0.06
0.042	2.8	—	0.034 (A)	0.031	<0.02
0.158 <sup>a</sup>	2.8	—	0.163 (B)	0.150	<0.04

<sup>a</sup> not completely dissolved.

*Sulphone formation.* (Series C). The results of the tracer experiments have been given in Table 3. It will be seen that about 5 % of the radioactivity was recovered in the isolated sulphone, when free iodobenzene was present, but only insignificant labeling of sulphone occurred in the control experiments. Attempts to prepare sulphone from mixtures of sulphur trioxide and sulphonic anhydride, and from mixtures of iodobenzene and sulphonic anhydride, gave negative results. It must therefore be concluded that for the formation of the labelled sulphone in the tracer experiments all three components have been necessary. Thus these experiments have documented a reaction path for sulphone formation in sulphonation mixtures which has been assumed for a long time: reaction between an unsulphonated and a sulphonated component. The experiments have further demonstrated that the interaction of a third component, in this case  $\text{SO}_3$ , is necessary.

## DISCUSSION

*Formation and disappearance of pyrosulphonic acid.* The rate of sulphonation in aprotic medium has been found to depend upon the square of the sulphur trioxide concentration, and it seems difficult to account for these kinetics in other ways than by accepting the hypothesis of primary formation of the pyrosulphonic acid, *cf.* eqns. (6)—(7) and Refs.<sup>1,2,19</sup> On the other hand all experimental evidence given above indicates that the pyrosulphonic acid can only exist as a shortlived intermediate in the system investigated, and it would therefore appear that the pyrosulphonic acid is a very reactive compound.

Reaction (8) which appears to be the main reaction path when the substituent in  $\text{RSO}_3\text{SO}_3\text{H}$  is the *p*-iodophenyl group, is not likely to be sensitive to the nature of the organic substituent, since the attack is at the S-O-S groups. In this connection it is of interest to note that rate constant and energy of



activation for the hydrolysis of sulphonyl chlorides do not show great variations with various substituents.<sup>20</sup>

The postulated reactivity of the pyrosulphonic acid, especially with regard to reaction (8), should therefore relate to pyrosulphonic acids in general. The hypothesis is therefore in conflict with the statements of Hinshelwood<sup>16-18</sup> and of Sandeman<sup>21</sup>, that their experimental data give evidence for the existence of metastable or even stable pyrosulphonic acids.

However, it has been shown above that the data published by Vicary and Hinshelwood<sup>16</sup> do not exclude the fast formation of sulphonic anhydride in the sulphonation of nitrobenzene. Since the same kinetic picture was observed using a number of aromatics, among which were chloro- and bromobenzene<sup>17,18</sup>, another argument may be presented in support of the formation of sulphonic anhydrides in these systems, namely that chlorobenzene and especially bromobenzene are known to yield sulphonic anhydrides at experimental conditions only differing slightly from those of Hinshelwood, *cf.* Ref.<sup>7</sup>

Finally, the spectroscopic and cryoscopic evidence for the existence of the methanepyrosulphonic acid in mixtures of sulphur trioxide and methanesulphonic acid obtained by Sandeman<sup>21</sup> calls for attention. As to the Raman-lines, which were assigned by Sandeman to the pyrosulphonic acid, many of these appear to be identical with lines observed in a later spectroscopic study on methanesulphonic anhydride by Simon and Kriegsman.<sup>22</sup> Furthermore, in Sandeman's cryoscopic investigation a melting point peak was found for a mixture containing 21 wt. % of SO<sub>3</sub>, but no peak was found to correspond with the composition of CH<sub>3</sub>SO<sub>3</sub>SO<sub>3</sub>H (45 % SO<sub>3</sub>).

The existence of the methanesulphonic anhydride in these mixtures is actually indicated by Sandeman's own observation that the sulphonic anhydride is formed as insoluble precipitate, when the mixture is poured into water. Sandeman ascribed, however, the observation to the reaction:



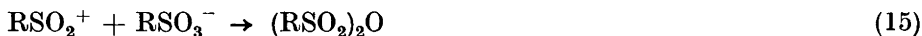
In view of the analogy between RSO<sub>3</sub>SO<sub>3</sub>H and H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, especially pointed out by Sandeman himself mechanism (12) appears to be unlikely. A more likely explanation is that the mixtures of CH<sub>3</sub>SO<sub>3</sub>H and SO<sub>3</sub> contained sulphonic anhydride, quite possible as complexes with H<sub>2</sub>SO<sub>4</sub> or CH<sub>3</sub>SO<sub>3</sub>H.

It will appear from the above considerations that neither Hinshelwood's nor Sandeman's data present any obstacle to the hypothesis of the fast reaction (8).

As regards the detailed mechanism of the reactions of the pyrosulphonic acid, the fission suggested by Joly *et al.*<sup>23</sup>

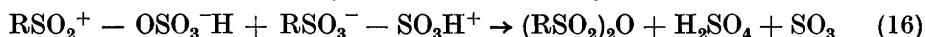


furnishing free sulphonyl cations, would appear attractive, since the sulphonyl cation is one of the most powerful electrophilic components known,<sup>24</sup> and evidence for the reactions



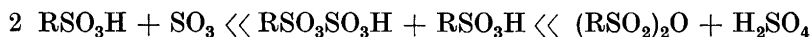
has been obtained previously.<sup>25,26</sup>

On the other hand it is likely that the polarised molecules are so reactive, that the mechanism for anhydride formation may be:



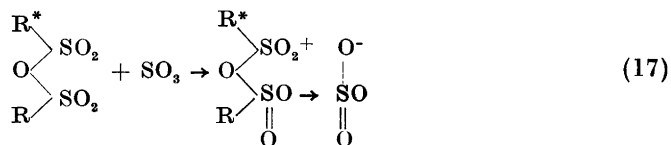
where it should be understood that  $\text{SO}_3$  may enter into further reactions. Scheme (16) is essentially the same as that suggested by Lukashevich.<sup>27</sup>

These observations would be explained, in short, by increasing stability through the stages:



reflecting the strong tendency in the sulphur trioxide to form the sulphate group.

*Sulphone formation.* The mechanism for the formation of the *labelled* sulphone in the tracer experiments (series C) is thought to be:



where the pyrosulphonic acid will enter into further reactions.

According to this scheme the reaction is a sulphonylation catalysed by sulphur trioxide. The complex of eqn. (17),  $(\text{RSO}_2)_2\text{O}, \text{SO}_3$ , is similar to such compounds, *e.g.*  $\text{RSO}_2^+ - \text{AlCl}_4^-$ , which are believed to be the active components in Friedel-Crafts sulphonylation.<sup>25</sup> It is a further support for this scheme that Field<sup>13</sup> has recorded excellent yields of diphenylsulphone formed from benzenesulphonic anhydride, benzene and aluminium chloride. Sulphur trioxide is probably a stronger Lewis acid (electrophilic reagent) than aluminium chloride, but its effect as a Lewis acid is usually not detectable because of the more drastic effect of its sulphonating property. However, if scheme (17)–(18) were the only mechanism also for formation of the *unlabelled* sulphone, the formation of labeled sulphone should be greatly favoured in these experiments, and the activity recovered in the sulphone should be about 50% *i.e.* ten times higher than observed, *cf.* Table 3, because the labeled complex  $(\text{R}^*\text{SO}_2)_2\text{O}, \text{SO}_3$  has been present from the moment of mixing with the iodobenzene, while the unlabeled complex first has to be formed through a number of steps. It must therefore be concluded that at least one species more than  $(\text{RSO}_2)_2\text{O}, \text{SO}_3$  has sulphonylated the iodobenzene. It is a further consequence that the species should be formed faster than the complex  $(\text{RSO}_2)_2\text{O}, \text{SO}_3$ . Since the sulphonic anhydride itself has no detectable sulphonylating property, the pyrosulphonic acid will come into consideration. Thus the tracer experiments have provided indirect evidence for the mechanism

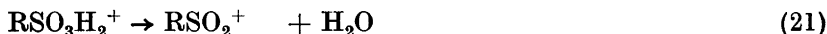


which often has been suggested in the literature.<sup>23,27–29</sup>

The fairly constant yield of the sulphone found in the sulphonation experiments, Fig. 1, may reflect that more than one sulphonylating mechanism is available. With lower mole ratios the pyrosulphonic acid may be the only sulphonylating species likely to be formed; with higher mole ratios complexes such as  $(\text{RSO}_2)_2\text{O}\cdot\text{SO}_3$  and perhaps polysulphonic acids, *e.g.*  $\text{RSO}_3\text{SO}_3\text{SO}_3\text{H}$ , may also contribute, but the rate of the competitive main-reaction, the sulphonation, will also increase with increasing mole ratios, thereby counterbalancing the sulphonylation.

*Amphiprotic media.* The usual sulphonating media, fuming or strong sulphuric acid, have higher dielectric constants and much higher proton activities than the medium used in the present investigation. Furthermore sulphur trioxide is not free, but complex-bound as  $\text{H}_2\text{S}_2\text{O}_7$ . Kinetics on sulphonation in such media are consistent with the primary formation of the sulphonic acid. It is therefore not likely that pyrosulphonic acids play the dominant role for the secondary reactions in protic media as they do in aprotic media, not withstanding the fact that some of the hypotheses involving pyrosulphonic acid were originally advanced for sulphonation in protic media.<sup>23,27</sup>

According to Lewis and Biegeleisen<sup>30</sup> it is often impossible to distinguish between the effects of the proton and the sulphur trioxide molecule in fuming sulphuric acid. It would therefore appear plausible that the proton, when present, may replace the sulphur trioxide molecules in the secondary reactions; thus the scheme, implicitly stated by Drews *et al.*<sup>31</sup> will be arrived at:



Since sulphonyl cations are capable of formation of sulphone as well as of sulphonic anhydride, *cf.* eqns. (14) and (15), the hypothetical scheme (20)–(21) would account for the secondary reactions occurring in protic sulphonation.

Evidence for the first part of the scheme, eqn. (20) has been obtained by cryoscopic measurements<sup>32</sup> and by certain solubility experiments.<sup>33</sup> The total scheme (20)–(21) bears relation to the formation of triphenylcarbonium-ion,<sup>34</sup> the nitronium ion<sup>35</sup> and the sulphonylium ion  $(\text{RSO}^+)$ <sup>36</sup> formed in strong acid milieu from triphenylcarbinol, nitric acid and sulphinic acid, respectively.

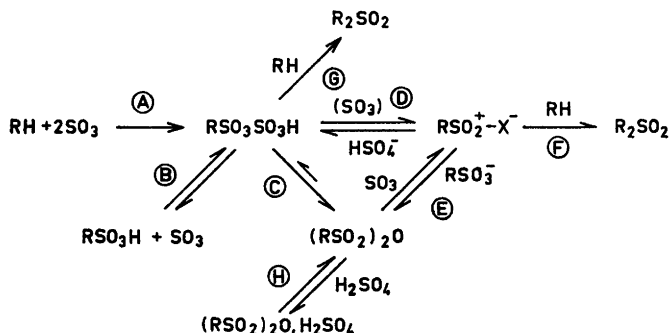


Fig. 6.

## CONCLUSION

The experimental results demonstrate the occurrence of a number of consecutive and simultaneous reactions in the system investigated (Fig. 6).

A is assumed on kinetic evidence in the present and in analogous systems. B is based on analogy with the pyrosulphuric acid equilibrium. B—C is established by dehydration of sulphonic acid by means of sulphur trioxide, and its reverse explains the formation of sulphonic acid as end-product in sulphonation with excess of aromatic substrate. D is mainly included in order to stress the influence of the Lewis acid, sulphur trioxide, on the sulphonylation property. E—F represents the sulphonylation observed in experiments using radioactive sulphonic anhydride. The branch G is included to indicate the possibility that the pyrosulphonic acid has a sulphonylating property in the undissociated state. The branch H accounts for the partial solvation of the anhydride in the reaction mixture. It is possible that it should be included in reaction C, letting the complex represent an intermediate stage between the pyrosulphonic acid and the anhydride.

The scheme does not take into consideration the very low solubility of the *p*-iodobenzene sulphonic anhydride, which is important for its appearance as product under conditions where it is thermodynamically unstable.

The scheme is believed to describe secondary sulphonation reactions occurring in aprotic sulphonation systems in general. However, the kinetics and product-distribution must be expected to depend upon the reactivity of the aromatic component and on solubility data for the sulphonic anhydride in question.

In sulphuric acid, oleum and chlorosulphuric acid the pyrosulphonic acid is thought to be of no importance. In these media the high proton activity is believed to be the main reason for the formation of sulphonyl groups or sulphonyl cations necessary for the secondary reactions.

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