Aromatic Sulphonation. Part 61.[1] Sulphonylation in the Reaction of Aromatic Compounds with Chlorosulphuric Acid in Nitromethane and in Dichloromethane

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Sulphonylation in the reactions of benzene, chlorobenzene, and toluene with chlorosulphuric acid in nitromethane and in dichloromethane has been studied. From the kinetic results it was concluded that the reactive electrophile in the sulphonylation in nitromethane is $ArS_2O_6H_2^+$. It is proposed that this entity also leads to secondary sulphonation. For dichloromethane as solvent the observed kinetics may be explained in terms of $ArS_2O_6H,ClSO_3H$ as the reactive sulphonylating entity.

THE primary and main products in the reaction of aromatic compounds with a deficiency of chlorosulphuric acid are arenesulphonic acids.[1] Under these conditions only small amounts of arenesulphonyl chlorides and diaryl sulphones, which are secondary products, are formed.[2] The mechanism of the sulphonation has been discussed.[1] The present paper deals with the kinetics and mechanism of the sulphonylation. Some time ago we reported that the sulphonylation in the reaction of benzene with chlorosulphuric acid proceeds without a substrate kinetic hydrogen isotope effect, k_H/k_D being 1.1 ± 0.1 (25 °C) for nitromethane and 1.3 ± 0.2 (0 °C) for dichloromethane as solvent.[3]

RESULTS AND DISCUSSION

Product formation in reactions of benzene, toluene, and chlorobenzene with chlorosulphuric acid in both nitromethane and dichloromethane has been studied. Details of all kinetic runs have been reported.[1,4] For both solvent systems the main and initial product is the arenesulphonic acid. With a deficiency of chlorosulphuric acid, the amounts of arenesulphonyl chloride are very small; $[ArSO_2Cl]/[ArSO_3H]$ increases with increasing $[ClSO_3H]_0/[ArH]_0$. The amounts of diaryl sulphone are also very small; with the exception of the reaction of benzene in CH_2Cl_2, $[Ar_2SO_2]/[ArSO_3H]$ increases with increasing reaction time and increasing $[ClSO_3H]_0$. Apparently both the sulphonyl chloride and the sulphone are secondary products.

With toluene in nitromethane no detectable amounts of ditolyl sulphone are formed.

Sulphonylation in Nitromethane.—The available data on sulphone formation in nitromethane show that for relatively low conversions the total amount of sulphone is proportional to the square of the total amount of sulphonic acid, and that $[Ar_2SO_2]/[ArSO_3H]^2$ is independent of the initial chlorosulphuric acid concentration (Figure 1). At higher conversions a downward curvature is observed. Accordingly, for the initial stages of the reaction we have equations (1)—(4), in

$$[Ar_2SO_2] = r[ArSO_3H]^2 \qquad (1)$$

$$d[Ar_2SO_2]/d[ArSO_3H] = 2r[ArSO_3H] \qquad (2)$$

$$d[Ar_2SO_2]/dt = 2rk[ArH][ClSO_3H]^{2.5} = {}^{sy}k[ArH][ClSO_3H]^{2.5} \qquad (3)$$

$$d[Ar_2SO_2]/dt = {}^{sy}k[ArH]_0[ClSO_3H]_0^{2.5}\,(1 - x/a)(1 - x)^{2.5} \qquad (4)$$

which r is a constant. Differentiation of (1) yields (2) which, on combination with equations (7) and (8) from ref. 1 yields (3), in which $2rk = {}^{sy}k$ (the observed sulphonylation rate constant).

Combination of equation (3) with equations (12) and (13) from ref. 1 yields (4).

The sulphonylation in the reaction of benzene with chlorosulphuric acid in nitromethane proceeds without a primary substrate kinetic isotope effect (at 25 °C, ${}^{sy}k_H/{}^{sy}k_D = 1.1 \pm 0.1$ [3]) and accordingly the rate

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[1] Part 60, M. P. van Albada and H. Cerfontain, *J.C.S. Perkin II*, preceding paper.

[2] B. Y. Yasnitskii, *Zhur. obshchei Khim.*, 1953, **23**, 107; V. O. Lukashevich, *Doklady Akad. Nauk S.S.S.R.*, 1954, **99**, 995.

[3] M. P. van Albada and H. Cerfontain, *Rec. Trav. chim.*, 1972, **91**, 499.

[4] M. P. van Albada, Thesis (in English), University of Amsterdam, 1975, Appendix.

equation (4) is that for the formation of the σ-complex intermediate. The corresponding transition state must contain a potential arenesulphonyl cation, which can only be formed from the sulphonic acid.

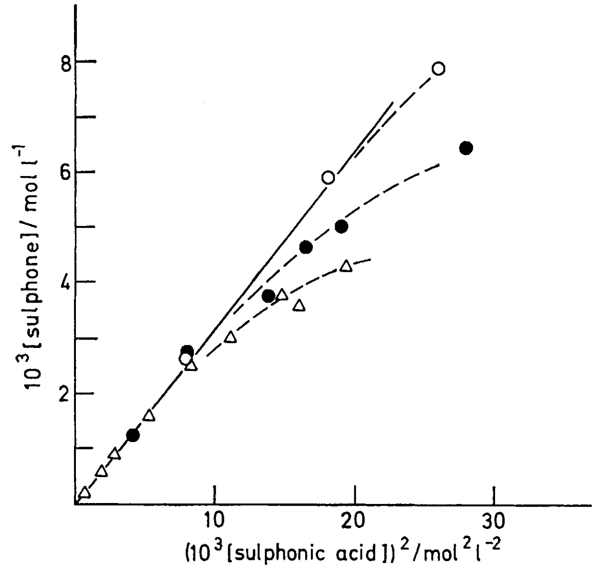


FIGURE 1 Reaction of benzene with $ClSO_3H$ in nitromethane at 25.0 °C; sulphone *vs.* sulphonic acid formation; $[C_6H_6]_0$ = 1.07 mol l^{-1}; $[ClSO_3H]_0$ = 0.283 (△), 0.566 (●), or 1.09 (○) mol l^{-1}

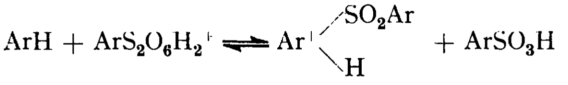
Combination of equation (4) with (7) from ref. 1 yields (5), which, on

$$d[Ar_2SO_2]/dt = {}^{sy}k[ArH]_0[ClSO_3H]_0^{1.5}[ArSO_3H] (1 - x/a)(1 - x)^{2.5}/x \quad (5)$$

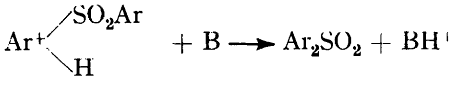
combination with (14) from ref. 1, yields (6). The

$$d[Ar_2SO_2]/d[ArSO_3H] = ({}^{sy}k/k)[ArSO_3H] \quad (6)$$

difference in composition of the σ-complexes for sulphonylation and sulphonation is thus a molecule of arenesulphonic acid. The sulphonating entity for the sulphonation with $ClSO_3H$ in $MeNO_2$ is $MeNO_2,SO_3H^+$.[1] Accordingly, the sulphonylating entity is $ArS_2O_6H_2^+$,-$MeNO_2$ or $ArS_2O_6H_2^+$,* and the sulphonylation may proceed by the route (7),(8) in which B stands for



$$ArH + ArS_2O_6H_2^+ \rightleftharpoons Ar^+\langle^{SO_2Ar}_{H} + ArSO_3H \quad (7)$$



$$Ar^+\langle^{SO_2Ar}_{H} + B \longrightarrow Ar_2SO_2 + BH^+ \quad (8)$$

$ArSO_3H$ and/or $MeNO_2$. In principle $ArS_2O_6H_2$ ($\equiv ArSO_3H,SO_3H^+$) may also act as a sulphonating entity. However, the kinetics of the sulphonation show that the major route for (initial) sulphonic acid formation is by reaction of $MeNO_2,SO_3H^+$ and not of $ArS_2O_6H_2^+$.[1,†]

No sulphone is formed in the reaction of toluene with chlorosulphuric acid. This may be explained as follows. The sulphonation is much faster for toluene than benzene. The rate of arenesulphonic sulphuric anhydride formation (9) will, however, not be greatly affected by the nature of the aryl group. Accordingly, if the rate of this reaction is of the same order of magnitude as the rate of sulphonation of benzene (and thus

$$ArSO_3H + ClSO_3H \rightleftharpoons ArS_2O_6H + HCl \quad (9)$$

much smaller than the rate of sulphonation of toluene) the sulphonic anhydride built up with toluene will be unimportant, and no detectable amount of ditolyl sulphone will be formed.

Sulphonylation in Dichloromethane.—The variation of the amount of sulphone with the amount of sulphonic acid formed in the reaction of benzene with chlorosulphuric acid in dichloromethane is shown in Figure 2. After the end of the induction period (*cf.* Figure 8 of ref. 1) the rate of sulphonylation becomes proportional to the rate of sulphonation. The rate of sulphonation of benzene after the end of the induction period is satisfactorily described by equation (10) [≡ (26) in ref. 1]

$$d[ArSO_3H]/dt = k'[ArH][ClSO_3H] \quad (10)$$

and accordingly the rate of sulphonylation by (11), in

$$d[Ar_2SO_2]/dt = {}^{sy}k'[ArH][ClSO_3H] \quad (11)$$

which k' and ${}^{sy}k'$ are the respective rate constants of sulphonation and sulphonylation.

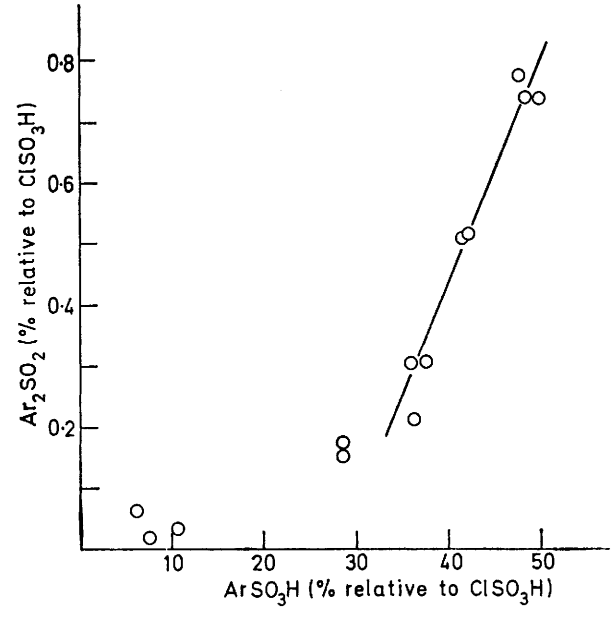


FIGURE 2 Reaction of benzene with $ClSO_3H$ in dichloromethane at −25.0 °C; sulphone *vs.* sulphonic acid formation; $[C_6H_6]_0$ = 1.08 mol l^{-1}; $[ClSO_3H]_0$ = 0.59 mol l^{-1}

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* Complex formation with the solvent nitromethane molecules will be less for $ArS_2O_6H_2^+$ than for SO_3H^+.

† There is an indication that in nitromethane sulphonation by $ArS_2O_6H_2^+$ may play a role after an appreciable amount of sulphonic acid has been built up: $[Ar_2SO_2]/[ArSO_3H]^2$, which is constant at low substrate conversion, tends to decrease at higher conversions (see Figure 1), as is to be expected if additional sulphonation occurs by an entity other than $MeNO_2,SO_3H^+$.

If the sulphonylation of chlorobenzene can also be described by equation (11), then, by combination with equation (28) from ref. 1, equations (12) and (13) follow.

$$d[Ar_2SO_2]/d[ArSO_3H] = (^{sy}k'/k')[HCl]/[ClSO_3H] \quad (12)$$

$$[Ar_2SO_2]/[ClSO_3H]_0 = 0.25(^{sy}k'/k')[-\log(1 - 2x) - 2x] \quad (13)$$

A test of equation (12) in its integrated form (13) is shown in Figure 3. From the slope of the linear graph it follows that $^{s}k'/k' = 0.013$; at 0.0 °C $k' = (6 \pm 1) \times 10^{-3}$ and accordingly $^{sy}k' = (8 \pm 2) \times 10^{-5}$ l mol^{-1} s^{-1}.

Figure 3 illustrates that the sulphonylation of chlorobenzene can be described by expression (11). The sulphonylation of benzene in dichloromethane proceeds without a primary substrate kinetic isotope effect [at 0 °C $^{sy}k_H'/^{sy}k_D' = 1.3 \pm 0.2$ (ref. 3)] and the rate equation (11) is that for the formation of the σ-complex intermediate.

The transition state leading to the sulphonylation σ-complex must contain a potential arenesulphonyl cation. Further the arenesulphonic sulphuric anhydride concentration in the reaction of chlorobenzene with $ClSO_3H$ in dichloromethane is low, and to a first approximation constant.[1] The rate equation for sulphone formation with chlorobenzene in dichloromethane (11) therefore complies with a transition state leading to the σ-complex which contains a molecule of the aromatic substrate, one of the arenesulphonic sulphuric anhydride, and one of chlorosulphuric acid. Accordingly, the sulphonylating entity is $ArS_2O_6H,ClSO_3H$ and, since the low polarity of the solvent renders ionic intermediates unlikely, the sulphonylation may proceed by the route (14),(15).

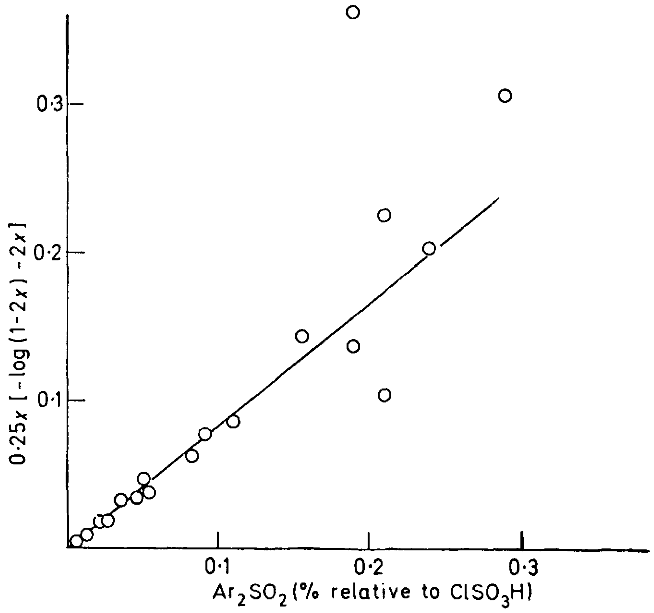
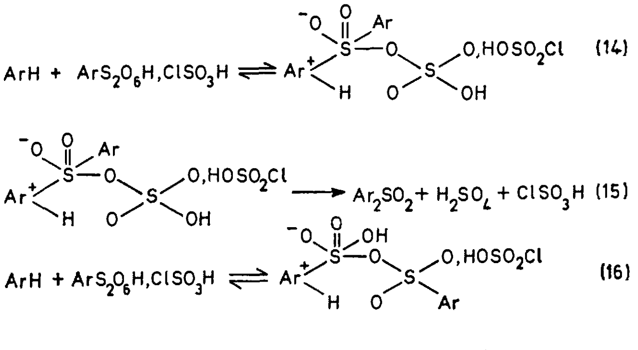


FIGURE 3 Sulphonylation of chlorobenzene with $ClSO_3H$ in dichloromethane at 0.0 °C; test of equation (11); $[PhCl]_0$ = 1.08 mol l^{-1}; $[ClSO_3H]_0$ = 0.287 mol l^{-1}



It was proposed that the sulphonation of benzene with $ClSO_3H$ in dichloromethane after the end of the induction period proceeds *via* process (16) [≡ (36) in ref. 1] as the σ-complex-forming step.[1] After the end of the induction period $d[Ar_2SO_2]/d[ArSO_3H]$ is constant (Figure 2). The total compositions of the transition states leading to the σ-complexes for the sulphonation and sulphonylation of benzene in dichloromethane are the same. Accordingly, a constant ratio for the rates of sulphonation and sulphonylation is to be expected as soon as the sulphonation proceeds mainly *via* process (16), *i.e.* after the end of the induction period, as is in fact observed.

Comparison with Other Sulphonylation Studies.—Diaryl sulphones are also formed as by-products in the sulphonation of aromatic compounds with sulphur trioxide.[5] It was proposed previously that the effective sulphonylating entity in both nitromethane and trichlorofluoromethane as solvent is the entity ArS_3O_9H,[6] and that the rate-limiting step is the formation of the σ-complex intermediate,[7] the sulphonylation substrate kinetic isotope effect for benzene (k_H/k_D) being 0.9 ± 0.1 for $MeNO_2$ (25 °C)[7a] and 1.1 ± 0.1 for CCl_3F (−35 °C).[7b]

These results and the present ones clearly show that the sulphonic sulphuric anhydride as such is not the reactive sulphonylating entity, as proposed previously by Lukashevich and by Christensen.[8] Apparently, with both SO_3 and $ClSO_3H$ as reagents the transition states leading to the sulphonylation σ-complexes require an additional reagent molecule for stabilization.

EXPERIMENTAL

The materials, sulphonation procedures, and methods of analysis were as described previously.[1]

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[5] For a current review, see H. Cerfontain, 'Mechanistic Aspects in Aromatic Sulphonation and Desulphonation,' Interscience, New York, 1968, pp. 13—20.

[6] J. K. Bosscher and H. Cerfontain, *Rec. Trav. chim.*, 1968, **87**, 873; *Tetrahedron*, 1968, **24**, 6543.

[7] (*a*) H. Cerfontain and A. Telder, *Rec. Trav. chim.*, 1965, **84**, 1613; (*b*) J. K. Bosscher and H. Cerfontain, *J. Chem. Soc.*, 1968, 1524.

[8] V. O. Lukashevich, *Proc. Acad. Sci. U.S.S.R.*, 1957, **112**, 113; N. H. Christensen, *Acta Chem. Scand.*, 1964, **18**, 954.