Aromatic Sulphonation. Part 60.[1] Sulphonation in the Reactions of Aromatic Compounds with Chlorosulphuric Acid in Nitromethane and in Dichloromethane

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Kinetic and product studies have been carried out on the reactions of benzene, toluene, and chlorobenzene with chlorosulphuric acid in nitromethane and in dichloromethane. The initial and main products are arenesulphonic acids. The arenesulphonyl chlorides and diaryl sulphones are secondary products; with an initial chlorosulphuric acid to aromatic substrate ratio of less than 1 : 1 they are formed only in small amounts On the basis of kinetic evidence it is proposed that the sulphonation in nitromethane in the initial stages proceeds by electrophilic attack of $MeNO_2,SO_3H^+$ on the aromatic substrate. From the substituent effect on the rate of substitution the reaction constant for this type of sulphonation was estimated ($\rho = -10 \pm 1$). In dichloromethane, the sulphonating species in the reaction of chlorobenzene is ClS_2O_6H. The sulphonation of benzene, in contrast to that of chlorobenzene, exhibits an induction period. The sulphonating entity for the main reaction of benzene is $ArS_2O_6H,ClSO_3H$, whereas that for the initial reaction is probably the same as for chlorobenzene, *viz.* ClS_2O_6H. The behaviour of chlorosulphuric acid in both nitromethane and dichloromethane was studied u.v.-spectroscopically with the aid of aromatic indicators (In). Evidence was obtained for ion pair formation in nitromethane according to the equation: $In + 2\,ClSO_3H \rightleftharpoons InH^+,ClSO_3(ClSO_3H)^-$. Apparently the chlorosulphate anion requires two molecules of acid for (self-conjugative) stabilization.

AROMATIC sulphonation has been studied extensively and has been reviewed.[2] Electrophilic sulphonation can be effected with a variety of reagents. They may be divided into two main groups, *viz.* (i) sulphur trioxide donors, like SO_3 itself and its complexes with aprotic Lewis bases, and (ii) compounds formed by reaction of SO_3 with a Brönsted acid, like water, halogen acids, and sulphonic acids. The reagents of the latter group are very strong acids and may thus also act as proton donors.

Mechanistic studies on electrophilic aromatic sulphonation have been less extensive. They have concentrated mainly on sulphonation with SO_3 in organic aprotic solvents, and with aqueous and fuming sulphuric acid. The mechanisms for these systems seem now to be clarified,[3] although there still exists some doubt on the nature of the reacting entity in sulphonation with SO_3.[3a]

Sulphonation with chlorosulphuric acid yields arenesulphonic acids, sulphonyl chlorides, and sulphones. The latter two types of compound are secondary products from the initially formed sulphonic acid.[4]

It was thought of interest to obtain information on the mechanism of aromatic sulphonation with chlorosulphuric acid. In view of the lack of information on the stoicheiometric composition of the chlorosulphuric acid system, and the activities of the entities present in it,[5] as well as the high reactivity of neat chlorosulphuric acid, it was decided to study the sulphonation in solution, *viz.* in nitromethane and in dichloromethane. No information is available on the behaviour of chlorosulphuric acid in these solvents. Accordingly a brief investigation of these systems was made by u.v.-spectroscopic and cryoscopic techniques.

Some time after we had started our study, Gnedin [6] reported on the mechanism of sulphonation with chlorosulphuric acid in dichloroethane and concluded that the aromatic substrate reacts successively with two molecules of chlorosulphuric acid to yield the arenesulphonic sulphuric anhydride. This conclusion differs from the one obtained in the present paper.

The formation of the secondary products in the reaction of chlorosulphuric acid with aromatic substrates will be dealt with in a subsequent paper.

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[1] Part 59, P. K. Maarsen and H. Cerfontain, *J.C.S. Perkin II*, 1977, 1008.

[2] E. E. Gilbert, 'Sulphonation and Related Reactions,' Interscience, New York, 1965; H. Cerfontain, 'Mechanistic Aspects in Sulphonation and Desulphonation,' Interscience, New York, 1968.

[3] (*a*) H. Cerfontain and C. W. F. Kort, *Internat. J. Sulfur. Chem.* (*C*), 1968, **5**, 23; (*b*) *ibid.*, 1971, **6**, 123; (*c*) J. K. Bosscher and H. Cerfontain *Rec. Trav. chim.*, 1968, **87**, 873; (*d*) *idem, Tetrahedron*, 1968, **24**, 6543; (*e*) J. K. Bosscher, Thesis (in English), University of Amsterdam, 1967; (*f*) C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, 1967, **86**, 857; (*g*) *idem, ibid.*, 1968, **87**, 24; (*h*) *idem, ibid.*, 1969, **88**, 860; (*i*) *idem, ibid.*, 1969, **88**, 1298; (*j*) C. W. F. Kort, Thesis (in English), University of Amsterdam, 1970.

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

[5] J. R. Donovan, 'Kirk Othmer Encyclopaedia of Chemical Technology,' 2nd edn., 1964, vol, 5, p. 357.

[6] B. G. Gnedin and N. I. Rudakova, *Izvest. Vyssh. Ucheb Zaved.*, 1972, **15**, 716.

RESULTS AND DISCUSSION

The Dichloromethane–Chlorosulphuric Acid System.—The variation of the u.v. absorption of the indicator (In) *p*-nitrotoluene in CH_2Cl_2 upon addition of $ClSO_2H$ is shown in Figure 1. The absorption maximum of the ^1L_a band of the free base form of the indicator is at 278 nm. Upon addition of small amounts of chlorosulphuric acid this band is replaced by a band with maximum at 310 nm (isosbestic point at 290 nm). Upon a further increase in acidity the 310 nm absorption is replaced by a new band centered at 380 nm (isosbestic point at 341 nm). The absorption bands at 380 and 310 nm are attributed to the monoprotonated indicator InH^+ [7] and a complex $InHOSO_2Cl$, respectively. The occurrence of two isosbestic points indicates two distinct equilibria rather than solvent effects alone.

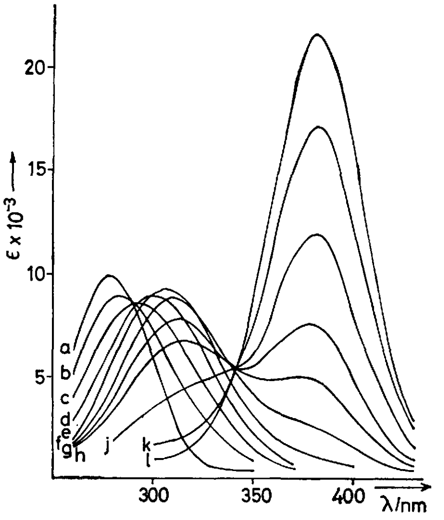

FIGURE 1 Spectra of *p*-nitrotoluene with various concentrations of chlorosulphuric acid (mmol l^{-1}) in dichloromethane. a, 0; b, 25.4; c, 60; d, 142; e, 285; f, 498; g, 748; h, 997; j, 1 440; k, 2 240; l, 4 930

The value of $[InH^+]/[InHOSO_2Cl]$ was calculated from the extinctions at 380 and 310 nm [assuming $\varepsilon_{380}(InHOSO_2Cl) = 0$]. It was estimated graphically that $\varepsilon_{380}(InH^+) = 23000$, $\varepsilon_{310}(InH^+) = 0$, and $\varepsilon_{310}(InHOSO_2Cl) = 9\,800$ l mol^{-1} cm^{-1}. The value of $[InHOSO_2Cl]/[In]$ was calculated from the extinctions at 310 nm of the set of spectra which belong to the isosbestic point at 290 nm with $\varepsilon_{310}(In) = 2\,590$ l mol^{-1} cm^{-1}. The graphs (Figure 2) of both $\log([InHOSO_2Cl]/[In])$ and $\log([InH^+]/[InHOSO_2Cl])$ *vs.* $\log[ClSO_3H]$ are linear with slopes 0.97 ± 0.05 and 2.05 ± 0.1, respectively.

These observations may be explained as follows. At $[ClSO_3H] < 100$ mmol l^{-1} the indicator is in equilibrium with the (probably hydrogen-bridged) complex $In \cdots HOSO_2Cl$ [equilibrium (1)], for which $d[\log([InHOSO_2Cl]/[In])]/d(\log(ClSO_3H])$ will be unity, as is in fact observed. At $[ClSO_3H] > 250$ mmol l^{-1} an equilibrium between $InHOSO_2Cl$ and InH^+ is set up, for which the indicator ratio is proportional to $[ClSO_3H]^2$. This may be explained in terms of ion pair formation by equilibrium (2).* The chlorosulphate anion in CH_2Cl_2 apparently requires stabilization by self-conjugation [8] with three molecules of acid.

$$In + ClSO_3H \rightleftharpoons InHOSO_2Cl \qquad (1)$$

$$InHOSO_2Cl + 2\,ClSO_3H \rightleftharpoons InH^+,ClSO_3(ClSO_3H)_2^- \qquad (2)$$

The Nitromethane–Chlorosulphuric Acid System.—The molecular weight of chlorosulphuric acid in nitromethane (0.0193—0.0365 mol $ClSO_3H$ per 100 g $MeNO_2$) was determined cryoscopically to be constant with a value of 121 ± 5.[9a] This value is equal within experimental error to that of the entity $ClSO_3H$ (116.5). Apparently the degree of dissociation according to equation (3) and of ionization is at most very small.

$$ClSO_3H \rightleftharpoons SO_3 + HCl \qquad (3)$$

The behaviour of the indicators anthraquinone and *p*-nitroaniline in nitromethane upon addition of chlorosulphuric acid was studied by u.v. spectroscopy (Table 1). The absorption of the free bases cannot be observed because of solvent absorption. Upon addition of chlorosulphuric acid an absorption band, attributed to InH^+, with $\lambda_{max.}$ 390 nm for anthraquinone and $\lambda_{max.}$ 420 nm for *p*-nitroanisole, is observed. It was estimated that ε_{390}(anthraquinone,H^+) was 1.12×10^4 (assuming the protonation to be complete for $[ClSO_3H] = 2.68$ mol l^{-1}; *cf.* Table 1) and ε_{420}(*p*-nitroanisole,H^+) was 2×10^4 l

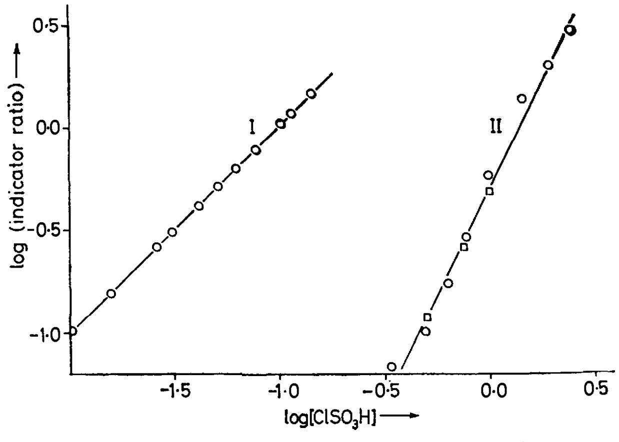

FIGURE 2 Correlation of the indicator ratio of *p*-nitrotoluene with the chlorosulphuric acid concentration; $[In]_{stoich} = 8.7 \times 10^{-5}$ (○) and 2.2×10^{-4} (□) mol l^{-1}; indicator ratio $[InHOSO_2Cl]/[In]$ (I) (slope 1.0 ± 0.1) or $[InH^+]/[InHOSO_2Cl]$ (II) (slope 2.0 ± 0.1)

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* No substantial dissociation of the ion pair is thought to occur in view of the low polarity of the solvent. Moreover, the graph of $\log([InH^+]/[InHOSO_2Cl])$ would then not be linear, in contrast to obervation (see Figure 2, II).

[7] J. C. D. Brand, W. C. Horning, and M. B. Thornley, *J. Chem. Soc.*, 1952, 1374.

[8] (*a*) H. van Looy and L. P. Hammett, *J. Amer. Chem. Soc.*, 1959, **81**, 3872; Y. Pocker, *J. Chem. Soc.*, 1958, 997; (*b*) J. F. Coetzee, *Progr. Phys. Org. Chem.*, 1967, **4**, 45.

[9] M. P. van Albada, Thesis (in English), University of Amsterdam, 1975, (*a*) ch. 2; (*b*) ch. 4; (*c*) ch. 3.

mol^{-1} cm^{-1}.* Further ε_{390}(anthraquinone) = 150 and ε_{420}(*p*-nitroanisole) = 0 l mol^{-1} cm^{-1}. The indicator ratios were calculated from the extinctions and these molar extinction co-efficients by a self-consistent method (Table 1). The graphs of log[InH$^+$]/[In] *vs.* log[ClSO$_3$H] are linear with slope *ca.* 2 for both indicators (Figure 3).

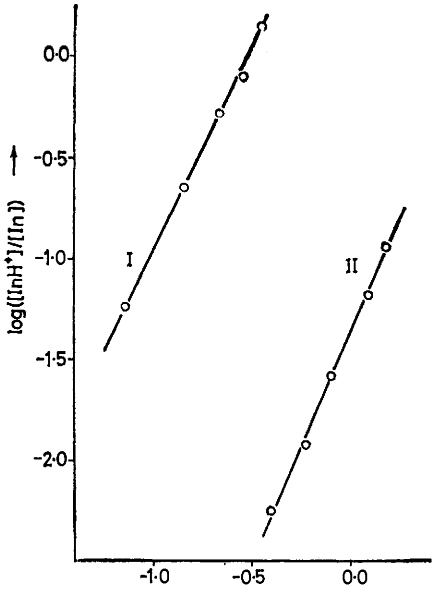

FIGURE 3 Correlation of [InH$^+$]/[In] with the chlorosulphuric acid concentration; anthraquinone (I), slope 2.0 ± 0.1, and *p*-nitroanisole (II), slope 2.3 ± 0.2

TABLE 1

Indicator ratios for nitromethane as solvent

Indicator	[In] mmol l^{-1}	[ClSO$_3$H] mmol l^{-1}	$E \times 10^{3\,a}$	log[InH$^+$]/[In]
Anthraquinone	0.254	0	38	
	0.131	73.3	96	−1.25
		146	279	−0.66
		220	501	−0.30
		278	648	−0.12
		366	852	+0.13
	0.065 8	2 680	729	
p-Nitroanisole	0.518	0	0	
		397	59	−2.26
		595	127	−1.93
		793	278	−1.59
		1 190	652	−1.19
		1 490	1 090	−0.95

^{a} Extinction at 390 and 420 nm for anthraquinone or *p*-nitroanisole, respectively, both corrected for ClSO$_3$H absorption.

The linearity and the observed slopes may be explained in terms of ion pair formation according to equilibrium (4). In this solvent, the formation of a complex which

$$\mathrm{In} + 2\,\mathrm{ClSO_3H} \rightleftharpoons \mathrm{InH^+,ClSO_3(HSO_3Cl)^-} \qquad (4)$$

precedes ion pair formation is less probable than with dichloromethane in view of the higher basicity of the solvent. In this solvent the self-conjugative stabilization is restricted to only two molecules of acid.

Sulphonation Products and Kinetic Runs.—The sulphonation of benzene, toluene, and chlorobenzene with chlorosulphuric acid was studied in nitromethane and in dichloromethane. Some typical results are in Table 2 (all kinetic runs are reported in the appendix of ref. 9). For both solvent systems the main and initial product is the arenesulphonic acid. With a deficiency of ClSO$_3$H the the relative amount of arenesulphonyl chloride is very small; [ArSO$_2$Cl]/[ArSO$_3$H] increases with increasing [ClSO$_3$H]$_0$/[ArH]$_0$. The amounts of diaryl sulphone are also very small; [Ar$_2$SO$_2$]/[ArSO$_3$H] increases with increasing reaction time and increasing [ClSO$_3$H]$_0$. Apparently both the sulphonyl chloride and the sulphone are secondary products.

Sulphonation in Nitromethane.—†The results of three series of sulphonations of a given chlorosulphuric acid concentration and different substrate concentrations are shown in Figure 4. The dotted and broken lines were calculated from the solid line on the assumption that the reaction time required to reach a given chlorosulphuric acid conversion is inversely proportional to the concentration of the aromatic substrate. The fit between the observed and calculated conversions is satisfactory and accordingly it is concluded that the order in the aromatic substrate is 1.

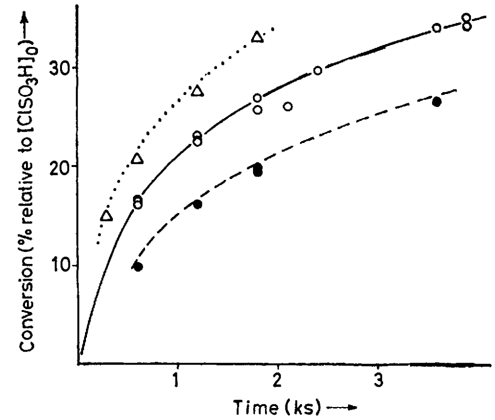

FIGURE 4 Sulphonation of C$_6$H$_6$ with ClSO$_3$H in nitromethane at 25.0 °C; dependence on substrate conversion; [ClSO$_3$H]$_0$ = 0.284 mol l^{-1}; [C$_6$H$_6$]$_0$ = 0.57 (●), 1.08 (○), or 1.96 (△) mol l^{-1}; broken lines calculated from the solid curve for an assumed substrate order of 1

A similar set of experiments but now with a given substrate concentration and different chlorosulphuric acid concentrations is shown in Figure 5. The dotted and broken lines were calculated from the solid line on the assumption that the rate of chlorosulphuric acid conversion is proportional to [ClSO$_3$H]$_0^{\frac{1}{2}}$, which implies that the rate of sulphonation is proportional to [ClSO$_3$-

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* For this mononitro compound $\varepsilon_{\text{max.}}$(InH$^+$) was taken to be twice $\varepsilon_{\text{max.}}$(In) [see *e.g.* ref. 7 and the data for *p*-nitrotoluene (see earlier)]. For *p*-nitroanisole $\lambda_{\text{max.}}$ = 306 nm with ε 1.04 × 10^4 l mol^{-1} cm^{-1}. The conclusions derived by use of this value are not seriously affected if ε_{420}(InH$^+$) differs from the assumed value by a factor of two, because of the low degree of protonation.

† Chlorosulphuric acid reacts yery slowly with nitromethane to yield hydroxyammonium chlorosulphate.[10] This reaction is, however, slow relative to the aromatic sulphonation.

[10] G. Bourjol, *Mém. Poudre*, 1952, **34**, 63 (*Chem. Abs.*, 1955, **49**, 9236).

TABLE 2

Reactions of aromatic compounds with chlorosulphuic acid

Solvent	Substrate	Temp. (t/°C) (±0.2)	$\frac{[\mathrm{ArH}]_0}{\mathrm{mol\ l^{-1}}}$	$\frac{[\mathrm{ClSO_3H}]_0}{\mathrm{mol\ l^{-1}}}$	Time (t/s)	$\frac{[\mathrm{ArSO_3H}]}{\mathrm{mmol\ l^{-1}}}$ (±5%)	$\frac{10^3[\mathrm{Ar_2SO_2}]}{[\mathrm{ArSO_3H}]}$ (±10%)	$\frac{10^3[\mathrm{ArSO_2Cl}]}{[\mathrm{ArSO_3H}]}$ (±20%)
$MeNO_2$	C_6H_6	0.0	1.14	0.261	1 800	21.6		
					9 000	44.5	1.0	7.4
					75 600	102	5.5	8.9
		25.0	1.08	0.144	60	5.9		
					420	19.4	3.0	
					4 200	50	10.7	
			1.07	0.283	65	15.3	5.5	
					360	40	14.0	
					3 610	102	30	
					10 800	478	32	
			0.100	1.00	122	26.0	29	2.5
					600	57	62	4.7
					1 830	73	75	7.8
					3 600	77	80	11.8
			0.95	0.188	61 200	132	52	6.5
				0.530	61 200	332	108	18.4
				0.88	61 200	502	131	30
			0.386	0.306	86 400	161	25	
			1.08	0.286	86 400	184	18	
			2.50	0.246	86 400	176	8.0	
	PhMe	25.0	1.09	0.144	45	83		
					123	103		
					360	115		
	PhCl	25.0	1.09	0.284	4 200	18.7	7.9	
					7 860	28.4	11.0	
					152 000	92	15.7	
CH_2Cl_2	C_6H_6	0.0	1.08	0.286	20	13.2		
					45	87	2.3	
					180	134	6.4	
	PhCl	0.0	1.08	0.288	60	7.8	0.9	
					240	16.5	1.6	
					2 520	32.9	6.4	

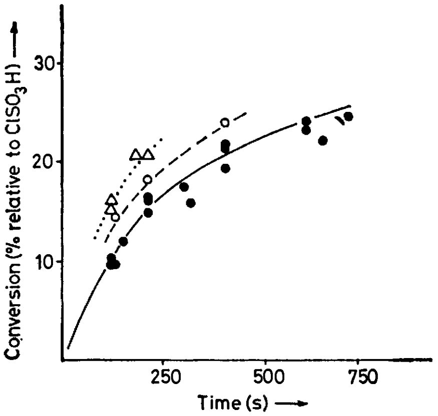

FIGURE 5 Sulphonation of PhMe with $ClSO_3H$ in nitromethane at 25.0 °C; dependence on $ClSO_3H$ concentration; $[\mathrm{PhMe}]_0$ = 1.14 mol l^{-1}; $[\mathrm{ClSO_3H}]_0$ = 0.150 (●), 0.300 (○), or 0.60 (△) mol l^{-1}; broken lines calculated from the solid curve for an assumed order in $ClSO_3H$ of 1.5

$\mathrm{H}]_0{}^{1.5}$. It appears that these rate orders, derived for the range 10—30% chlorosulphuric acid conversion do not account for the rapid decrease in rate observed at higher chlorosulphuric acid conversion. Accordingly, in order to test whether this rapid decrease is the result of the consumption of more than one molecule of chlorosulphuric acid per molecule of sulphonic acid formed, or due to the presence of a product, the influence of hydrogen chloride was studied. From a comparison of these experiments with those without initially added dry hydrogen chloride (gas) it appeared that the reaction is strongly retarded by hydrogen chloride.[9b] The stoicheiometry of the sulphonation is given by equation (5). In the absence of initially added HCl, the HCl concentration during the sulphonation is given by expression (6) * in which $x = [\mathrm{ArSO_3H}]/[\mathrm{ClSO_3H}]_0$, *i.e.* the degree of conversion relative to $ClSO_3H$. The apparent order with respect to chlorosulphuric acid was found to be

$$\mathrm{ArH} + \mathrm{ClSO_3H} \longrightarrow \mathrm{ArSO_3H} + \mathrm{HCl} \qquad (5)$$

$$[\mathrm{HCl}] = [\mathrm{ClSO_3H}]_0 x \qquad (6)$$

$$[\mathrm{ArSO_3H}] = [\mathrm{ClSO_3H}]_0 x \qquad (7)$$

1.5 (see earlier). If the order with respect to HCl is $-a$, it then follows from (6) that the order with respect to $ClSO_3H$ is $1.5 + a$. Assuming an order of -1 for HCl, equations (8) and (9) then follow. The rate equation

$$\mathrm{d}[\mathrm{ArSO_3H}]/\mathrm{d}t = k[\mathrm{ArH}][\mathrm{ClSO_3H}]^{2.5}[\mathrm{HCl}]^{-1} \qquad (8)$$

$$[\mathrm{ArH}]_0{}^{-1}[\mathrm{ClSO_3H}]_0{}^{-0.5}\int \frac{x\mathrm{d}x}{(1 - x/a)(1 - x)^{2.5}} = kt \qquad (9)$$

(8) was tested in its integrated form (9) for all the kinetic runs performed in nitromethane, applying an iterative procedure based on Simpson's rule using an electronic computer.[9b] This test proved satisfactory, as shown in

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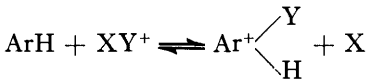
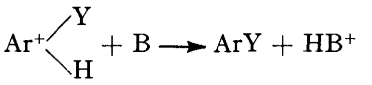
* The HCl concentration at the very beginning of the sulphonation is determined by equilibrium (3), and will thus be equal to $\{K_3[\mathrm{ClSO_3H}]_0\}^{\frac{1}{2}}$.

Figure 6. The rate constants calculated with equation (8) are collected in Table 3.

Mechanism of Sulphonation in Nitromethane.—The mechanism will be discussed in terms of the sequences (10) and (11). The kinetic isotope effect k_H/k_D for the sulphonation of benzene with $ClSO_3H$ in nitromethane at 25 °C is 1.7 ± 0.1.[11] It was concluded that step (11) is only at most partly rate-limiting for C_6D_6 and less so for C_6H_6. In the following reasoning it will be assumed that step (10) is rate-limiting.



$$ArH + XY^+ \rightleftharpoons Ar^+(Y)(H) + X \qquad (10)$$



$$Ar^+(Y)(H) + B \longrightarrow ArY + HB^+ \qquad (11)$$

The observed rate expression for the sulphonation in nitromethane is (8). From the stoicheiometry of the sulphonation (5) and the conclusion that the ionization and dissociation of $ClSO_3H$ are relatively unimportant (see earlier), equations (12) and (13) follow. Combination of equation (8) with (6), (7), (12), and (13) yields (14).

TABLE 3

Sulphonation in nitromethane

Substrate	HCl addendum (mmol l^{-1})	Temp. (t/°C) (±0.2)	$k \times 10^5$ l$^{1.5}$ mol$^{-1.5}$ s^{-1}
Benzene	0	0.0	0.5 ± 0.1
	0	25.0	6.6 ± 0.5
	880	25.0	5.8 ± 0.5
	0	50.0	40 ± 20
Toluene	0	−25.0	18 ± 2
	0	0.0	260 ± 30
	0	25.0	3 000 ± 300
	915	25.0	3 200 ± 300

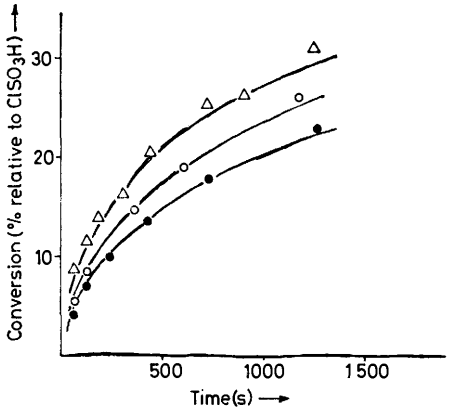


FIGURE 6 Sulphonation of benzene with $ClSO_3H$ in nitromethane at 25.0 °C; test of equation (8); curves calculated from (8) with $k = 6.6 \times 10^{-5}$ l$^{1.5}$ mol$^{-1.5}$ s^{-1}; $[ClSO_3H]_0 = 0.144$ (●), 0.283 (○), or 0.576 (△) mol l^{-1}

$$[ArH] = [ArH]_0(1 - x/a) \qquad (12)$$

$$[ClSO_3H] = [ClSO_3H]_0(1 - x) \qquad (13)$$

$$d[ArSO_3H]/dt = k\{[ArH]_0(1 - x/a)\}\text{-}\{[ClSO_3H]_0(1 - x)\}^{1.5}(1 - x)/x \qquad (14)$$

The SO_3 concentration is determined by equilibrium (3). With (6) and (13), equation (15) then follows.

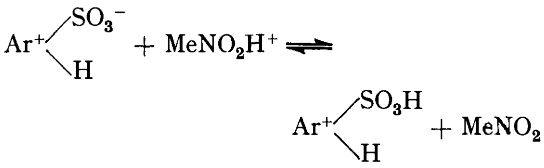
$$[SO_3] = K_3(1 - x)/x \qquad (15)$$

The transition state for the formation of the σ-complex intermediate contains at any rate the aromatic substrate and SO_3. Substitution of the concentration dependencies of these species [(12) and (15)] into equation (14) yields (16). The factor $[ClSO_3H]_0(1 - x)^{1.5}$ is proportional to the concentration of a solvated proton provided that it is formed in this system according to expression (17).* Evidence for the presumed self-conjugative stabilization of the $ClSO_3^-$ ion has been presented (see earlier). Accordingly the σ-complex for the sulphonation contains, in addition to ArH and SO_3, a proton, and has the structure $Ar^+H(SO_3H)$. Two different routes leading to its formation may be considered, *viz.* (19), (20), and (21), (22).† The latter sequence is more likely than the former in view of the expected higher electrophilicity of SO_3H^+, as compared with SO_3. Moreover,

$$d[ArSO_3H]/dt = k/K_3[ArH][SO_3]\{[ClSO_3H]_0(1 - x)\}^{1.5} \qquad (16)$$

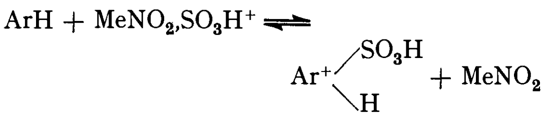
$$MeNO_2 + 3ClSO_3H \rightleftharpoons MeNO_2H^+ + ClSO_3(ClSO_3H)_2^- \qquad (17)$$

$$ArH + MeNO_2,SO_3 \rightleftharpoons Ar^+(SO_3^-)(H) + MeNO_2 \qquad (19)$$



$$Ar^+(SO_3^-)(H) + MeNO_2H^+ \rightleftharpoons Ar^+(SO_3H)(H) + MeNO_2 \qquad (20)$$

$$MeNO_2,SO_3 + MeNO_2H^+ \rightleftharpoons MeNO_2,SO_3H^+ + MeNO_2 \qquad (21)$$



$$ArH + MeNO_2,SO_3H^+ \rightleftharpoons Ar^+(SO_3H)(H) + MeNO_2 \qquad (22)$$

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* The indicator measurements in nitromethane indicate the formation of the ion pair $InH^+,ClSO_3(ClSO_3H)^-$ and not of the ions $InH^+ + ClSO_3(ClSO_3H)_2^-$. It thus appears that the chlorosulphate anion in the ion pair requires stabilization by two molecules of acid, *viz.* InH^+ and $ClSO_3H$. The dissociation of the ion pair thus will require an additional $ClSO_3H$ molecule (18). The ion pair will be a poorer proton donor than the ion InH^+.

$$InH^+,ClSO_3(ClSO_3H)^- + ClSO_3H \rightleftharpoons InH^+ + ClSO_3(ClSO_3H)_2^- \qquad (18)$$

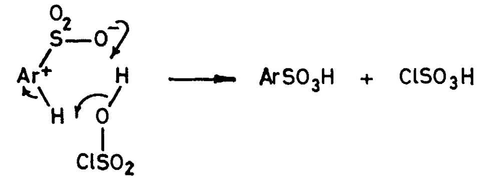
It is thought that only a small amount of the ion pair is dissociated according to expression (18).

† Sulphur trioxide in nitromethane as solvent is strongly complexed and thus (predominantly) present as $MeNO_2,SO_3$.[12] The stronger Lewis acid SO_3H^+ will be complexed even more strongly.

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

[12] H. Cerfontain and A. Koeberg-Telder, *Rec. Trav. chim.*, 1970, **89**, 569.

it is to be expected that the $Ar^+H(SO_3^-)$ intermediate would react according to equation (23). The sequence (19), (20), (23) is, however, not in agreement with the observed rate expression (14).



(23)

Isomer Distributions, Partial Rate Factors, and Activation Parameters in Nitromethane as Solvent.—The relative rates of sulphonation of some substrates with $ClSO_3H$ in nitromethane were determined competitively [9b] (Table 4). The results agree with those obtained from non-competitive experiments. The isomer distributions were found to be independent of the reagent-to-substrate ratio and of the substrate conversion. Disulphonic acids were absent within the limits of detection (*i.e.* 1%). The results are also in Table 4. Saturation of the nitromethane solvent with gaseous hydrogen chloride does not affect the isomer distribution. This is in accord with the proposed sulphonation mechanism, since the HCl concentration only affects the concentration of SO_3 and thus of the electrophilic reagent SO_3H^+.

TABLE 4

Sulphonation with $ClSO_3H$ in nitromethane

Substrate	Temp. (t/°C) (±0.2)	k/k_{PhH} [a]	k/k_{PhMe}	Isomer distribution (%)			Partial rate factors		
				2-	3-	4-	2-	3-	4-
PhMe	−25.0	560		6.8 ± 0.2	0.8 ± 0.2	92.0 ± 0.1	114 ± 10	13 ± 3	3 100 ± 200
	0.0	420		5.3 ± 0.2	0.9 ± 0.2	93.8 ± 0.1	68 ± 6	12 ± 3	2 400 ± 100
		(520 ±150)		5.4 ± 0.2 [b]	0.8 ± 0.2 [b]	93.8 ± 0.1 [b]			
	25.0	370		5.1 ± 0.2	1.0 ± 0.2	93.9 ± 0.1	57 ± 6	11 ± 3	2 100 ± 100
		(400 ±100)							
PhCl	−25.0	0.017				99			0.10 ± 0.01
	0.0	0.018				99			0.11 ± 0.01
	25.0	0.023		1.3 ± 0.3	0.0 ± 0.3	98.7 ± 2	(9 ± 2) × 10^{-4}		0.14 ± 0.01
1,2-$C_6H_4Me_2$	−25.0		9.4		4.8 ± 1	95.2 ± 2		760 ± 200	15 000 ± 1 000
	0.0		9.9		2.6 ± 0.5	97.4 ± 2		300 ± 80	12 500 ± 500
	25.0		10.8		1.9 ± 0.4	98.1 ± 2		230 ± 60	11 800 ± 500

[a] Data in parentheses were calculated from results of non-competitive experiments (*cf.* Table 3). [b] The nitromethane was saturated with dry HCl gas.

Partial rate factors were calculated from the relative rates and the isomer distribution (Table 4). The corresponding activation parameter differences were calculated according to the equation $\ln f = \Delta\Delta S^{\ddagger}/R - \Delta\Delta H^{\ddagger}/RT$ and are given in Table 5. The activation parameters for the sulphonation of the *para*-position in toluene were calculated with the aid of the absolute rate constants (Table 3) and the isomer distributions (Table 5) according to $\ln k = \ln (kT/h) + \Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R$ to be $\Delta H^{\ddagger} = 14.4 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -17 \pm 2$ cal mol^{-1} K^{-1}.

The plots of $\log f$ for a given temperature against the Hammett–Brown substituent constant σ^+ are linear, as shown for 25 °C in Figure 7. At that temperature the slope (ρ) is -10 ± 1. The differences in rate of sulphonation of benzene and the much more reactive *para*-position of toluene and the 4-position of *o*-xylene (Table 4) are mainly due to differences in $\Delta S^{\ddagger}$ (Table 5). This is unexpected, since for example toluene was found to obey the same rate law as benzene [*] and since the substituent is remote from the reaction centre for the substitutions under consideration. The predominance of the entropy factor may be explained as follows. The various $MeNO_2,SO_3H^+$ entities may be solvated by the solvent nitromethane molecules to a different degree. The electrophilicity will be less for the highly solvated entities as compared with the weakly or unsolvated ones. The less reactive benzene may be sulphonated to a higher degree

TABLE 5

Sulphonation with $ClSO_3H$ in nitromethane; activation parameters relative to those of benzene

Substrate	$\Delta\Delta H^{\ddagger}$/kcal mol^{-1}			$\Delta\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}		
	2-	3-	4-	2-	3-	4-
PhMe	−2.6 ±0.6	−0.6 ±0.2	−1.5 ±0.5	−1 ± 2	3 ± 6	10 ± 2
PhCl			1.3 ±0.8			0 ± 2
1,2-$C_6H_4Me_2$		−4.5 ±2	−1.0 ±0.5		−5 ± 7	16 ± 2

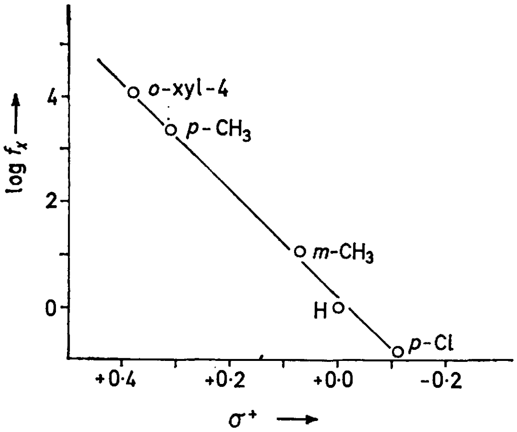


FIGURE 7 Correlation of f with σ^+ for sulphonation with $ClSO_3H$ in nitromethane at 25.0 °C; σ^+ (*o*-xylene-4) taken to be σ^+ (*m*-Me) + σ^+ (*p*-Me)

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[*] With *o*-xylene only competitive rate studies were made.

by the most reactive, *i.e.* the MNeO$_2$,SO$_3$H$^+$ entities; conversely the more reactive toluene and *o*-xylene may be sulphonated to a higher degree by the less reactive, *i.e.* the solvated entities. Provided that the degree of complex formation of the various σ-complexes with the solvent is the same, this would lead to a higher activation entropy for the sulphonation of the reactive positions of *o*-xylene and toluene than for those of benzene, as is in fact observed.

TABLE 6

Isomer distribution in sulphonations with chlorosulphuric acid

Substrate	Solvent	Temp. (t/°C, ±0.5)	Procedure [a]	Isomer distribution (%) [b]		
				o (±1.0)	*m* (±0.4)	*p* (±0.4)
PhMe	CH$_2$Cl$_2$	−25.0	A, homogeneous	9.8	0.5	89.7
		−25.0	B, heterogeneous	19.2	1.0	79.8
		0.0	A, homogeneous	7.6	0.6	91.8
		0.0	B, homogeneous	7.6 (8.0)	0.6	91.8
		25.0	B, homogeneous	7.0	0.7	92.3
	CHCl$_3$	−25.0	B, heterogeneous	20.5 (20.1)	0.9	78.6
		0.0	B, ?	10.2 (10.2)	1.1	88.7
	CCl$_4$	−25.0	B, heterogeneous	29.3	1.9	68.8
		0.0	B, heterogeneous	23.5 (22.2)	1.1	75.4
	PhMe	−25.0	B, heterogeneous	22.5	1.3	76.2
		0.0	B, ?	9.9	0.7	89.5
	ClSO$_3$H	−25.0	C, heterogeneous	50 ± 4	7 ± 3	43 ± 3
PhCl	CH$_2$Cl$_2$	0.0	A, homogeneous	0.2 ± 0.1	0.0	99.8

[a] Procedure A: to the ClSO$_3$H in the appropriate solvent was added in one portion a two- to ten-fold excess of the substrate. Mixing was effected by bubbling nitrogen through the solution for 10 s. Procedure B: to a stirred mixture of toluene (2 ml) and the solvent (10 ml) was added in 10 min from a capillary neat ClSO$_3$H (1 ml). Procedure C: toluene (0.025—1.0 ml) was added slowly (in 10 min) to a large excess of ClSO$_3$H (15 ml), with stirring. [b] Data obtained by multi-component u.v. analysis; data in parentheses obtained by ^{1}H n.m.r. analysis. Toluene-2,4-disulphonic acid was found to be absent within the limits of detection, *i.e.* 0.2% for both u.v. and ^{1}H n.m.r. analysis.

Sulphonation in Nitromethane; *Comparison with Other Sulphonating Reagents*.—The aromatic sulphonation with chlorosulphuric acid in nitromethane proceeds by a two-step mechanism in which the second step is only partly rate-limiting. The sulphonating entity is MeNO$_2$,SO$_3$H$^+$. On the basis of a study of the isomer distribution in the sulphonation of toluene with various protic sulphonating reagents (ClSO$_3$H, FSO$_3$H, fuming sulphuric acid, and methane- and benzene-sulphonic sulphuric anhydrides) in nitromethane, it was proposed that the sulphonating entity in all these systems was the same,[13] *viz.* MeNO$_2$,SO$_3$H$^+$. In this respect it is of interest that the sulphonating entities in aqueous sulphuric acid are H$_3$SO$_4$$^+$ (H$_2$O,SO$_3$H$^+$) and H$_2$S$_2$O$_7$ (HSO$_4$$^-$,SO$_3H^+$), and in weak fuming sulphuric acid H$_3$S$_2$O$_7$$^+$ (H$_2$SO$_4$,SO$_3$H$^+$).[3b] It thus may be concluded that in *protic* sulphonating systems the sulphonating entity is B,SO$_3$H$^+$ in which the structure of B depends on the solvent: in general it is a majority species of the solvent system involved.

Isomer Distribution in Dichloromethane.—The isomer distribution data for the sulphonation with chlorosulphuric acid in CH$_2$Cl$_2$ are collected in Table 6, together with those in related solvents and without solvent. For the homogeneous sulphonation the isomer distributions were found to be independent of the reagent-to-substrate ratio and of the substrate conversion. With toluene under homogeneous conditions there is a high degree of *para*- and a very low degree of *meta*-substitution. The temperature dependence on the *ortho*-to-*para* ratio is small and corresponds to $\Delta H_p^\ddagger - \Delta H_o^\ddagger = 1.0 \pm 0.3$ kcal mol^{-1} and $\Delta S_p^\ddagger - \Delta S_o^\ddagger = 10 \pm 1$ cal mol^{-1} K^{-1}, indicating steric hindrance for the *ortho*-substitution.

The relatively high degree of *ortho*-substitution observed with toluene at the lower temperatures is ascribed to the (in some cases visually observed) non-homogeneity of the reaction mixture, and hence to (additional) sulphonation in the chlorosulphuric acid phase, in view of the high value of 50 ± 4% observed at −25 °C using a large excess of neat chlorosulphuric acid. The value of 50 ± 4% fits in with those (55 and 51%) reported by Spryskov and Gnedin for −20 and −50 °C, respectively.[14]

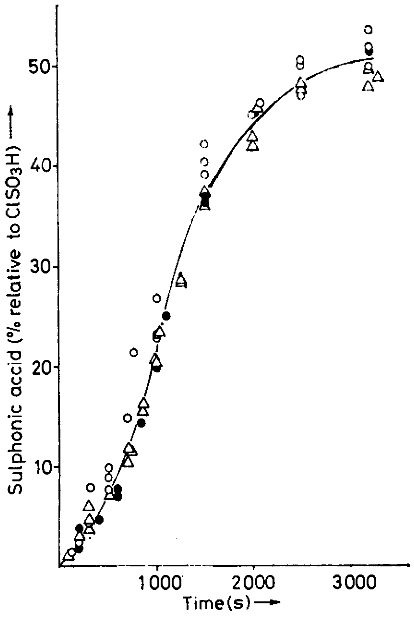

FIGURE 8 Formation of ArSO$_3$H in the reaction of benzene with ClSO$_3$H in CH$_2$Cl$_2$ at −25.0 °C; [C$_6$H$_6$]$_0$ = 1.09 mol l^{-1}; [ClSO$_3$H]$_0$ = 0.144 (●), 0.288 (○), or 0.576 (△) mol l^{-1}

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[13] M. P. van Albada, H. Cerfontain, and A. Koeberg-Telder. *Rec. Trav. chim.*, 1972, **91**, 33.

[14] A. A. Spryskov and B. G. Gnedin, *J. Gen. Chem.* (*U.S.S.R.*), 1963, **33**, 1069.

Sulphonation Kinetics in Dichloromethane.—In dichloromethane as solvent the sulphonation is faster than in nitromethane (Table 2). The variations of the conversion with reaction time for benzene and chlorobenzene are shown in Figures 8 and 9, respectively. The rate of sulphonation decreases strongly on reaching 50% chlorosulphuric acid conversion, indicating a consumption of 2 molecules of $\mathrm{ClSO_3H}$ per molecule of $\mathrm{ArSO_3H}$ produced. Accordingly we have equation (24). The sulphonation shows an induction period for benzene but not for chlorobenzene. The ratio of sulphonic acid formed to initial chlorosulphuric acid is independent of the initial chlorosulphuric acid concentration.

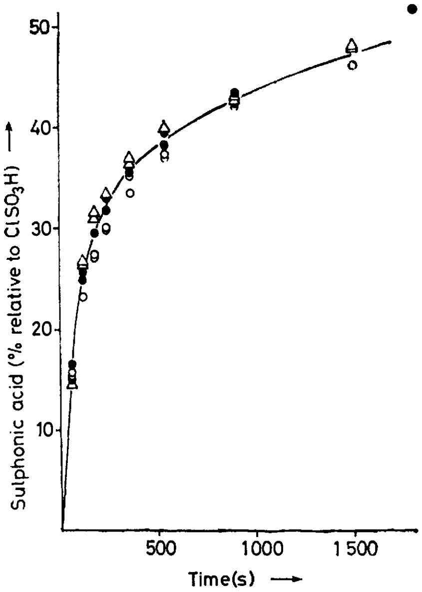


FIGURE 9 Formation of $\mathrm{ArSO_3H}$ in the reaction of chlorobenzene with $\mathrm{ClSO_3H}$ in $\mathrm{CH_2Cl_2}$ at 0.0 °C; $[\mathrm{PhCl}]_0 = 1.08$ mol $\mathrm{l^{-1}}$; $[\mathrm{ClSO_3H}]_0 = 0.128$ (○), 0.280 (●), or 0.560 (△) mol $\mathrm{l^{-1}}$

$$[\mathrm{ClSO_3H}] = [\mathrm{ClSO_3H}]_0 - 2[\mathrm{ArSO_3H}] = [\mathrm{ClSO_3H}]_0(1 - 2x) \quad (24)$$

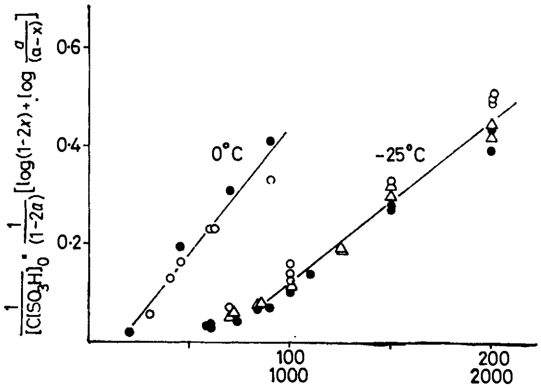


FIGURE 10 Sulphonation of benzene with $\mathrm{ClSO_3H}$ in $\mathrm{CH_2Cl_2}$; test of equation (25); concentrations of reactants as in Figure 8

It appeared that the sulphonation of benzene after the end of the induction period is described satisfactorily by equation (25) (*cf.* Figure 10), which is the integrated form of (26). The rate constants for benzene, k', were

$$[\log(1 - 2x) + \log a/(a - x)]/[\mathrm{ClSO_3H}]_0(1 - 2a) = k't \quad (25)$$

$$\mathrm{d}[\mathrm{ArSO_3H}]/\mathrm{d}t = k'[\mathrm{ArH}][\mathrm{ClSO_3H}] \quad (26)$$

calculated from the slope of the graphs of Figure 10 to be $(3.3 \pm 0.5) \times 10^{4}$ and $(5 \pm 1) \times 10^{3}$ l mol^{-1} s^{-1} for −25.0 and 0.0 °C respectively.

The sulphonation of chlorobenzene does not show an induction period. It can be described by equation (27) [and not by (25) (*cf.* Figure 11)], which is the integrated form of (28). The rate constant of chlorobenzene, k'',

$$\int\{x\mathrm{d}x/[(a - x)(1 - 2x)^2]\}/[\mathrm{ClSO_3H}]_0 = k''t \quad (27)$$

$$\mathrm{d}[\mathrm{ArSO_3H}]/\mathrm{d}t = k''[\mathrm{ArH}][\mathrm{ClSO_3H}]^2[\mathrm{HCl}]^{-1} = k''[\mathrm{ArH}]_0[\mathrm{ClSO_3H}]_0(1 - x/a)(1 - 2x)^2/x \quad (28)$$

was calculated from Figure 11 to be $(6 \pm 1) \times 10^{-3}$ l mol^{-1} s^{-1} at 0.0 °C.

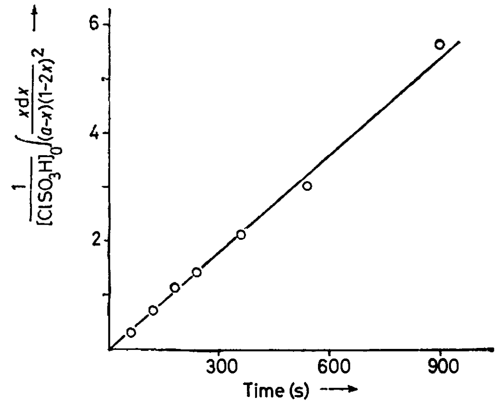


FIGURE 11 Sulphonation of chlorobenzene with $\mathrm{ClSO_3H}$ in $\mathrm{CH_2Cl_2}$ at 0.0 °C; test of equation (27); $[\mathrm{PhCl}]_0 = 1.08$ mol $\mathrm{l^{-1}}$; points are the average results for $[\mathrm{ClSO_3H}]_0 = 0.127$, 0.288, and 0.560 mol $\mathrm{l^{-1}}$

Mechanism of Sulphonation in Dichloromethane.—The consumption of two molecules of chlorosulphuric acid per molecule of sulphonic acid formed may be explained in terms of complex formation between the two acids. The chlorosulphuric acid, which is poorly solvated by dichloromethane, forms a hydrogen bond with the relatively basic oxygens of the sulphonic acid. The stoicheiometry of the sulphonation is then given by expression (29). The $\mathrm{SO_3}$ concentration is determined by equilibrium (3).

$$\mathrm{ArH} + 2\,\mathrm{ClSO_3H} \longrightarrow \mathrm{ArSO_3H{,}ClSO_3H} + \mathrm{HCl} \quad (29)$$

With (24), equation (30) then follows.

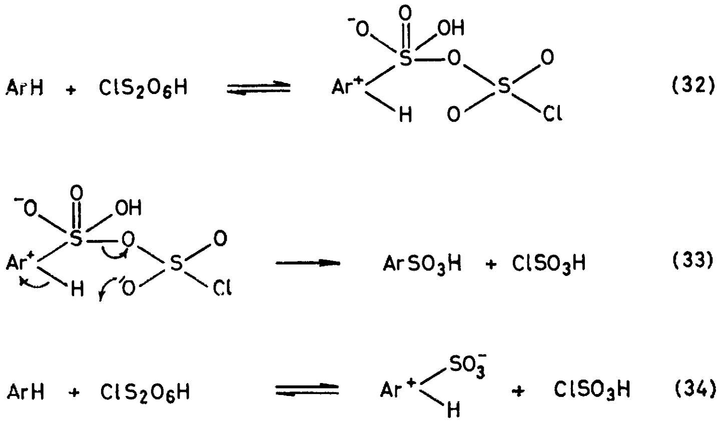
$$[\mathrm{SO_3}] = K_3(1 - 2x)/x \quad (30)$$

The substrate kinetic isotope effect for sulphonation in dichloromethane is small, *viz.* $k_\mathrm{H}/k_\mathrm{D} = 1.5 \pm 0.1$.[11] Accordingly, the formation of the σ-complex [step (10)] is considered to be the rate-limiting step of the sulphonation.

As to the sulphonation of chlorobenzene, the transition state for the formation of the σ-complex contains at any rate the substrate and SO_3. Substitution of the concentration dependencies of these species and of $ClSO_3H$ [(12), (30), and (24)] in expression (28) leads to (31).

$$d[ArSO_3H]_4/dt = (k''/K_3)[ArH][SO_3][ClSO_3H] \quad (31)$$

Accordingly the attacking electrophile in the sulphonation of chlorobenzene is thought to be $ClSO_2O_6H$.

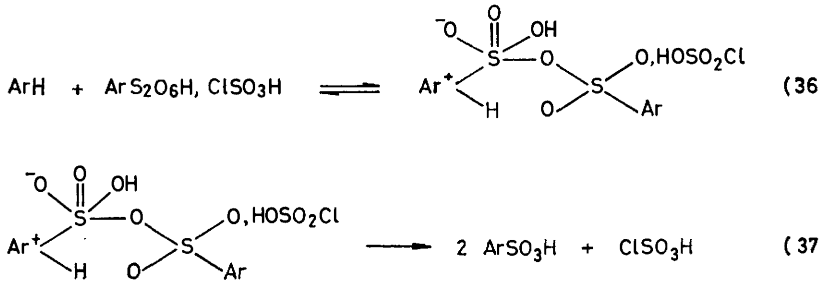


Thus, in view of the low polarity of the solvent, which excludes the intermediacy of ionic species, the reaction may proceed by the route (32), (33) or (34), (23), which both have the formation of the σ-complex as rate-limiting step. At present no preference can be expressed for one or other of these routes.

$$ArSO_3,HClSO_3H \rightleftharpoons ArS_2O_6H + HCl \quad (35)$$

The sulphonation of benzene with chlorosulphuric acid in CH_2Cl_2 shows an induction period. This suggests that an initial product is involved in the further sulphonation. After the induction period, the kinetic behaviour is described by expression (26). This rate law may be explained in terms of a transition state for the formation of the σ-complex which contains the aromatic substrate and one molecule of $ClSO_3H$. However, such an interpretation does not account for the induction period.

In the reaction mixture benzenesulphonic sulphuric anhydride may be present in small amounts formed according to expression (35). Considering that $[ArS_2O_6H] \ll [ArSO_3H,ClSO_3H]$, it follows from (29) that $[ArSO_3H,ClSO_3H] = [HCl]$, and from (35) that $[ArS_2O_6H] \simeq K_{35}$, *i.e.* the sulphonic sulphuric anhydride concentration is constant. Accordingly, a transition state leading to the σ-complex containing the aromatic substrate, chlorosulphuric acid and pyrosulphonic acid also accounts for the observed rate law (26). It is therefore proposed that the reactive electrophile is $ArS_2O_6H,ClSO_3H$. Accordingly, and in view of the low polarity of the solvent, the sulphonylaton may proceed by the route (36), (37) with (36) as rate-limiting step.



Further, from the observation of an induction period (Figure 8), it follows that the formation of ArS_2O_6H by step (35) is not fast relative to the sulphonation by $ArS_2O_6H,ClSO_3H$, and accordingly the equilibrium concentration of ArS_2O_6H is built up only slowly.

The initial sulphonation of benzene in CH_2Cl_2 probably proceeds by the same mechanism as proposed for chlorobenzene (see earlier).

EXPERIMENTAL

Materials.—The aromatic compounds were puriss. grade commercial products. Chlorosulphuric acid (B.D.H.) was distilled before use. Nitromethane was purified as described elsewhere.[8a]

Sulphonation Procedures.—Most of the kinetic runs were carried out in a reaction vessel the design of which as well as the starting and sampling procedure were described previously.[9b]

Analysis.—The samples of the reaction mixtures were quenched with a large excess of water (25 ml) and extracted three times with 10 ml of CH_2Cl_2. The remaining aqueous solution, containing the sulphonic acids, was submitted to steam distillation for 20 min to remove traces of $MeNO_2$ and CH_2Cl_2. The concentration(s) of the arenesulphonic acid(s) in the aqueous solution was (were) determined by single-component [9b] and multi-component [15] u.v. analysis.

To the combined CH_2Cl_2 extracts water was added, and the mixture likewise submitted to steam distillation in order to convert the sulphonyl chloride(s) into sulphonic acid(s) and to remove the organic solvents. After cooling, the sulphone was extracted from the aqueous solution with CH_2Cl_2. The sulphone concentration in the CH_2Cl_2 extract was determined by u.v. spectroscopy. The aqueous fraction, containing the sulphonic acid(s), was distilled with steam once more to remove traces of CH_2Cl_2. The resulting aqueous solution of arenesulphonic acid(s) was used for the u.v.-spectroscopic determination (see earlier) of the sulphonyl chloride(s).

The method of analysis proved satisfactory with test mixtures containing sodium benzenesulphonate and small amounts of benzenesulphonyl choride and diphenyl sulphone in nitromethane as solvent.[9b]

[6/1932 *Received*, 15*th October*, 1976]

[15] J. M. Arends, H. Cerfontain, I. S. Herschberg, A. J. Prinsen, and A. C. M. Wanders, *Analyt. Chem.*, 1963, **35**, 1005.