Dimeric Cations from Alkanesulphenyl Chlorides. The Elusive Nature of Sulphenylium Ions

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Conductimetric and ^1H n.m.r. evidence on the formation of alkyl(alkylthio)(chloro)sulphonium ions [$R\overset{+}{S}(Cl)SR$] by reaction of methane and ethanesulphenyl chlorides in liquid sulphur dioxide with Lewis acids (SbF_5, BCl_3, $SbCl_5$, BF_3) is reported. In the presence of BCl_3 or BF_3 dynamic behaviour in the n.m.r. spectra leading to the equivalence of the two alkyl groups is observed. This is explained by attack of chloride ion on the sulphonium salts and their dissociation into sulphenyl chlorides. The n.m.r. and conductimetric behaviour of the sulphenyl chlorides suggests that partial ionization into alkyl(alkylthio)(chloro)sulphonium ions may occur even in the absence of added Lewis acids. Sulphonium ions are also formed in 98% sulphuric acid and fluorosulphuric acid. Under no conditions was an indication of the presence of sulphenylium ions (RS^+) found.

THE electrophilic properties of sulphenyl chlorides and sulphur dichloride are well known and unimolecular sulphur–chlorine bond fission to give the sulphenylium ion (RS^+) has been suggested as a possible reaction pathway in various electrophilic reactions.[1-3] Detailed

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[1] C. R. Russ and I. B. Douglass, in ' Sulphur in Organic and Inorganic Chemistry,' ed. A. Senning, Dekker, New York, 1971, vol. 1, ch. 8, pp. 239—259.

[2] N. Kharasch in ' Organic Sulfur Compounds,' ed. N. Kharasch, Pergamon, New York, 1961, vol. 1, ch. 32, pp. 375—398.

[3] R. E. Benesch and R. Benesch, *J. Amer. Chem. Soc.*, 1958, **80**, 1666.

kinetic analyses[4-7] failed, however, to support such a mechanism. Rather, they suggest that the undissociated sulphenyl chloride is the electrophilic reagent. The strongest evidence supporting the existence of sulphenylium ions so far available is the ionic behaviour of sulphenyl chloride–Lewis acids adducts[8] and results from conductivity, spectroscopic, and cryoscopic studies of 2,4-dinitrobenzenesulphenyl chloride in sulphuric acid solutions.[9] For these results, however, alternative explanations have been offered.[10-12]

$$\begin{array}{ll} \text{RSCl} & \text{a; R} = \text{Me} \\ \text{(I)} & \text{b; R} = \text{Et} \end{array}$$

Although the characterisation of free sulphenylium ions is difficult[7,13] we undertook further attempts in this direction because of the potential interest of these species both on theoretical and preparative grounds. We report in this paper the ^{1}H n.m.r. and conductimetric behaviour of methane- and ethane-sulphenyl chloride in liquid sulphur dioxide in the presence of Lewis acids.[14]

RESULTS

The n.m.r. and conductimetric experiments were carried out on freshly distilled[15] methane- (Ia) and ethane-sulphenyl chloride (Ib).

N.m.r. Spectra.—0·6M-Methanesulphenyl chloride (Ia) in liquid SO_2 presents a single sharp absorption in the temperature range investigated (−10 to −80°) but at the lower temperature, where some broadening is observed the chemical shift (δ 3·55 at −80° and 2·84 at −10°) is more temperature dependent than usually reported.[16]

Addition of BF_3 in molar ratios from 1·1 to 5·4 to the above solutions gives rise at low temperatures to a two-line (δ 4·06 and 3·24) spectrum which eventually collapses to a single line with increasing temperature. The collapsed spectrum moves with increasing temperature to higher fields in a fashion similar to that observed for methanesulphenyl chloride spectrum in the absence of BF_3. In contrast the two-line spectrum observed at the lower temperatures shows only the normal small temperature dependence.[16]

The intensity ratio of the two lines in the spectrum is 1 : 1 whatever the BF_3 concentration. The line separation is field dependent (74 Hz at 90 MHz and 49 Hz at 60 MHz) and they therefore correspond to protons with different magnetic environments. The n.m.r. spectrum can be explained on the basis of the formation of chloro(methyl)methylthiosulphonium ion (IIa) [equation (1)]. This point will be discussed further in the appropriate section.

$$2\text{RSCl} + \text{E} \rightleftharpoons \text{R}\overset{+}{\text{S}}\text{(Cl)–SR} + \text{ClE}^- \qquad (1)$$

$$\text{(II)}$$

$$\text{E} = \text{Lewis acid}$$

The n.m.r. spectrum of ethanesulphenyl chloride (Ib) under similar experimental conditions (+20 to −60°; sulphur dioxide solution) consists of a triplet ($\delta_{+20°}$ 1·38; $\delta_{-60°}$ 1·65) and a quartet ($\delta_{+20°}$ 3·04; $\delta_{-60°}$ 3·69). On decreasing the temperature further the triplet is not significantly modified whereas the quartet merges into a broad band centred at δ 3·94 at −80°. The spectrum of 0·5M-ethanesulphenyl chloride is affected by addition of 2·15M-boron trifluoride in a fashion similar to that observed with methanesulphenyl chloride (Figure 1). At high temperature (+35°) the spectrum still comprises a triplet (δ 1·74) and a quartet [δ 3·84 (J 7·3 Hz)], but with lowering of the temperature the absorption systems first broaden and then split to give four absorptions. At −80° the spectrum consists of two overlapping triplets, one quartet, and a higher order absorption appearing as an overlapping double quartet. The spectrum was analysed by double resonance and is consistent with an A_2X_3 and an ABX_3 pattern [δ_A 4·30; δ_X 1·87 ($J_{A\text{-}X}$ 7·2 Hz); δ_A 3·78; δ_B 3·66; δ_X 1·70 ($J_{A\text{-}B}$ 14·3, $J_{A\text{-}X} = J_{B\text{-}X} =$ 7·4 Hz)]. This spectrum would agree with that expected for chloro(ethyl)ethylthiosulphonium ion (IIb) [see equation (1)] with two different ethyl groups one of which has a diastereotopic methylene because it is linked to a trico-ordinate sulphur.[17]

Boron trichloride interacts with methane- (Ia) and ethane-sulphenyl chloride (Ib) solutions in sulphur dioxide to give, basically, the same dynamic n.m.r. pattern as observed with boron trifluoride.*

This is particularly true for low concentrations of boron trichloride (*e.g.* MeSCl : BCl_3 = 1 : 0·6). At higher concentration of the Lewis acid a second dynamic process involving only the absorption at lower fields was observed.

In a typical experiment (0·6M-MeSCl; 1·06M-BCl_3) it was observed that the sharp line at lower fields (δ 4·12) broadens with increasing temperature from −60 to −20° to become sharp again with further increase of temperature. Subsequently the collapse process, as described above in detail for boron trifluoride, takes place. The same phenomenon was observed with other boron trichloride concentrations and also in the case of ethanesulphenyl chloride (Ib).

The chemical shifts, the band width, and the multiplicity (in the case of ethanesulphenyl chloride) are not affected to any significant extent by the process.

Further experiments were carried out with antimony pentafluoride as Lewis acid as well as with $AgBF_4$. In these cases the n.m.r. spectrum of methanesulphenyl chloride appears as two sharp singlets at every temperature investigated up to +37° when the ratio Lewis acid : sulphenyl chloride is >2. At lower ratios a single line spectrum was observed even at the lower temperatures (−80°).

The n.m.r. parameters of (Ia) in sulphur dioxide as function of Lewis acid added and of the temperature are summarized in Table 1.

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* In the preliminary communication[14] it was erroneously reported that boron trichloride did not cause any splitting of the absorption of (Ia).

[4] G. Modena and G. Scorrano, *Mechanisms of Reactions of Sulfur Compounds*, 1968, **3**, 115.

[5] E. Ciuffarin and A. Fava, *Progr. Phys. Org. Chem.*, 1968, **6**, 81.

[6] W. H. Mueller, *Angew. Chem. Internat. Edn.*, 1969, **8**, 482.

[7] J. L. Kice, *Progr. Inorg. Chem.*, 1972, **17**, 147.

[8] S. N. Nabi and M. A. Khaleque, *J. Chem. Soc.*, 1965, 3626.

[9] N. K. Kharasch, C. M. Buess, and W. King, *J. Amer. Chem. Soc.*, 1953, **75**, 6035.

[10] E. A. Robinson and S. A. A. Zaidi, *Canad. J. Chem.*, 1968, **46**, 3927.

[11] K. C. Malhotra and J. K. Puri, *Indian J. Chem.*, 1971, **9**, 1409.

[12] M. E. Peach, *Canad. J. Chem.*, 1969, 1676.

[13] G. K. Helmkamp, D. C. Owsley, W. M. Barnes, and H. N. Cassey, *J. Amer. Chem. Soc.*, 1968, **90**, 1635.

[14] Preliminary report; G. Capozzi, V. Lucchini, and G. Modena, *Chimica e Industria*, 1972, **54**, 41.

[15] J. B. Douglass, R. V. Norton, R. L. Weichman, and R. B. Clarkson, *J. Org. Chem.*, 1969, **34**, 1803.

[16] S. A. Pople, W. G. Schneider, and H. S. Berstein, 'High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959, p. 98.

[17] K. Mislow and M. Raban, *Topics Stereochem.*, 1967, **1**, 1.

Finally we observed for solutions of (Ia and b) in either 98% sulphuric acid or fluorosulphuric acid at +37° the same system of absorptions characteristic of sulphur dioxide solutions at low temperatures in the presence of excess of Lewis acid.

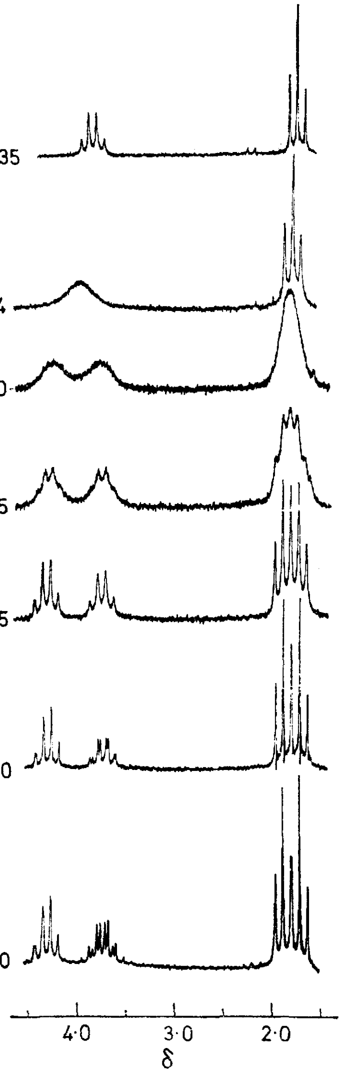

FIGURE 1 N.m.r. spectra (90 MHz) of ethanesulphenyl chloride (0·5M) in SO_2 in the presence of BF_3 (2·15 M) at different temperatures

TABLE 1

N.m.r. data for 0·6M-methanesulphenyl chloride in SO_2 with Lewis acids

[Lewis acid]/M	Chemical shifts δ (t/°C)
None	3·55 (−80); 2·84 (−10)
BF_3, 0·30	3·60 [a] (−81); 3·18 (+15)
BF_3, 0·65	4·07 and 3·24 (−54); 3·57 (−7); 3·43 (+13)
BF_3, 3·25	4·06 and 3·24 (−12); 3·61 (+13)
BCl_3, 0·40	4·12 and 3·27 (−60); 3·59 (+30)
BCl_3, 2·35	4·11 and 3·27 (−50) [b]
SbF_5, 0·27	3·55 [a] (−80); 3·16 (0)
SbF_5, 0·58	4·05 and 3·23 (−80); 4·09 and 3·27 (0)
$AgBF_4$, 2·4	4·02 and 3·20 (+37)

[a] Broad signal. [b] Coalescence temperature > 25°.

Kinetics.—The factors which affect the rates of the dynamic process observed in the n.m.r. spectra of SO_2 solutions of (Ia and b) in the presence of BF_3 and BCl_3 with change of temperature were studied in some detail. The system may be dealt with as a pseudo-first-order process which exchanges the magnetic environment of the two non-equivalent alkyl groups. The exchange rates were evaluated by full line-shape analysis.[18]

A first set of experiments were carried out at constant methanesulphenyl chloride concentration (0·6M) and variable BF_3 concentration. In Figure 2 the experimental and calculated spectra at −12° are reported together with the rate coefficients calculated for a pseudo-first-order process [18] at the same temperature. Addition of chloride ion as *N*-methylpyridinium chloride to the sulphur dioxide–boron trifluoride solution of methanesulphenyl chloride causes a quite significant acceleration of the process. At constant (Ia) (0·6M) and boron trifluoride (3·0M) concentration $k_{-12^{\circ}}$ is $0·32 \times 10^2$, and $0·50 \times 10^2$ s^{-1} for 0·28 and 0·47M-*N*-methylpyridinium respectively.

The experiments with boron trichloride present a similar trend. The exchange rates at −12°, extrapolated from data at temperatures varying from 0 to 30°, are 8·0 and 1·5 s^{-1} for boron trichloride concentration of 0·40 and 2·35M at constant methanesulphenyl chloride (0·6M).

Conductimetry.—Experiments were carried out by adding successive amounts of methanesulphenyl chloride to weighed $SbCl_5$ and $AgBF_4$ dissolved or suspended ($AgBF_4$) in liquid sulphur dioxide at −63°. The conductivity, measured after each addition, increased regularly up to an inflection point. Further additions of methanesulphenyl chloride increased

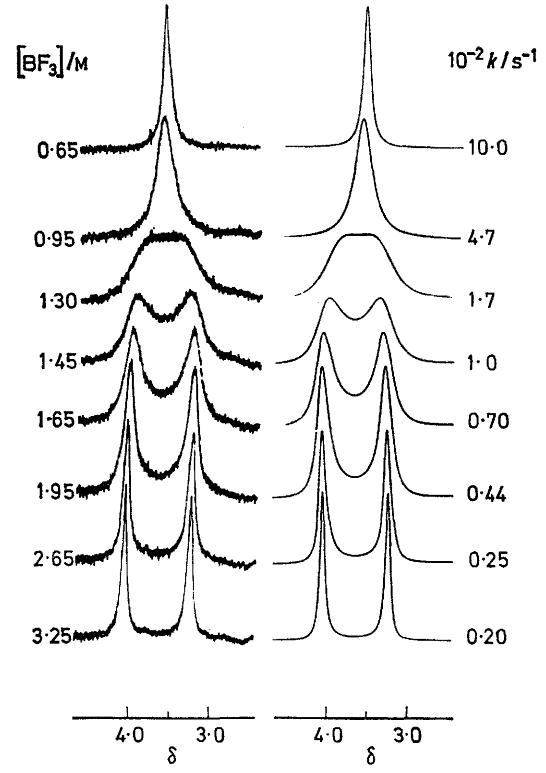

FIGURE 2 Experimental (90 MHz) and calculated spectra for methanesulphenyl chloride (0·6M) in SO_2 at −12° in the presence of BF_3

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[18] H. M McConnel, *J. Chem. Phys.*, 1958, **28**, 430.

the conductivity but with a different slope. The inflection point occurs at a molar ratio sulphenyl chloride : Lewis acid of 1·9 : 1 for $AgBF_4$ and 1·7 : 1 for $SbCl_5$ experiments (see Figure 3). When methanesulphenyl chloride was added to liquid sulphur dioxide at −63° the conductivity of the solution gradually increased in an almost linear fashion (see Figure 3).

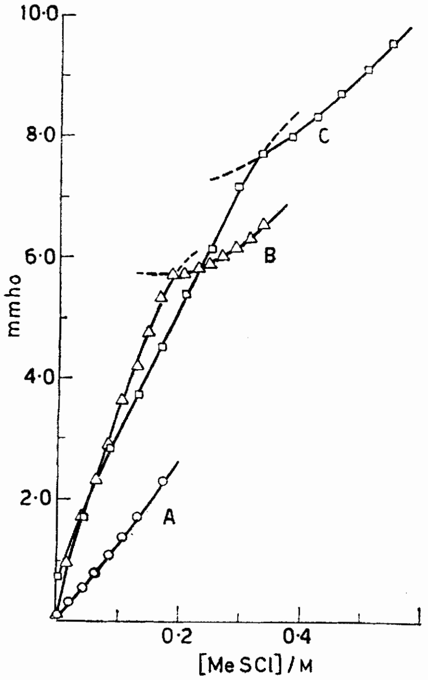

FIGURE 3 Conductance of A, MeSCl in SO_2 at −63°; and B, 0·11M-$SbCl_5$ and C, 0·17M-$AgBF_4$ in SO_2 at −63° as a function of added methanesulphenyl chloride. $AgBF_4$, inflection point at 0·33M-MeSCl; $SbCl_5$, inflection point at 0·19M-MeSCl

To obtain more detailed information, the equivalent conductivities were evaluated by the measured conductance of 0·04M-methanesulphenyl chloride in liquid sulphur dioxide in the absence and in the presence of excess of the two strong Lewis acids. The results are reported in Table 2 as equivalent conductivities of the dimeric salt. Under the same experimental conditions the equivalent conductivities of tetra-n-butylammonium chloride, tetrafluoroborate, and hexachloroantimonate were also evaluated by measurements at 0·02M.

TABLE 2

Equivalent conductances (ohm^{-1} cm^2 mol^{-1}) of [(2 MeSCl)–Lewis acid] [a] and tetra-n-butylammonium salts in liquid sulphur dioxide at −63°

Conductance			
[(2 MeSCl),SO_2]	11	$Bu^nN^+Cl^-$	53
[(2 MeSCl),$AgBF_4$]	28	$Bu^nN^+BF_4^-$	47
[(2 MeSCl),$SbCl_5$]	39	$Bu^nN^+SbCl^-$	32

[a] In the presence of excess of Lewis acid.

DISCUSSION

The n.m.r. spectra of methane- and ethane-sulphenyl chloride in liquid sulphur dioxide in the presence of a strong Lewis acid at low temperatures as well as those in sulphuric or fluorosulphuric acids indicate the formation of species with two alkyl groups in different magnetic environments. The hypothesis of a simple association between sulphenyl chloride and Lewis acid [see equation (2)] has to be ruled out because the intensity ratio of the

$$RCl + BF_3 \rightleftharpoons RSCl{\rightarrow}BF_3 \qquad (2)$$

two signals is always 1 : 1 and does not depend on the Lewis acid concentration or strength. Also the possibility of sulphenyl fluoride formation *via* halogen exchange [in the case of fluoro-Lewis acid reactions; equation (3)], and hence splitting due to coupling of the

$$RSCl + BF_3 \rightleftharpoons RSF + BF_2Cl \qquad (3)$$

protons with fluorine is untenable on, at least, two grounds: first the same phenomenon is observed with fluoro- and non-fluoro-Lewis acids and secondly the splitting is field dependent and, in any case, too large to be associated with a coupling process.[19] A rationale for the experimental results obtained can be found on the basis of the formation of a dimeric cationic species [equation (1)].

A species such as (II) should have the two R groups non-equivalent, as observed, and one of the two linked to a chiral trico-ordinate sulphur.[17] The splitting of one of the two methylene quartets of (IIb) into an ABX_3 system is therefore fully consistent with the above hypothesis. Indeed the observation of the methylene anisochronism has to be considered clear-cut evidence in favour of structure (II).

It might be expected that the diastereotopic methylene signals would occur at lower fields than those of the non-diastereotopic methylene group because of the location of the formal charge. However, the assignment of chemical shifts by this very simple criterion quite often fails because the charge density is only one of the various factors on which the chemical shifts depend.[16,19] Moreover one could write resonance structures with the charge delocalised between the two sulphur atoms. We have not investigated this point further.

Equation (1) also requires that the sulphenyl chloride solutions in the presence of Lewis acids behave as electrolytes and that, under appropriate conditions, the two alkyl groups become equivalent giving rise to simpler n.m.r. spectra. Both these requirements are fulfilled (see Results section).

The simplest hypothesis which explains the n.m.r. spectroscopic behaviour of the sulphenyl chloride solutions in the presence of the various Lewis acids is to consider equation (1) as an equilibrium. The position of the equilibrium must depend on the strength and concentration of the Lewis acids, because of their ability to complex chloride ion. The rate of the reverse reaction must also depend on these factors.

The observation of spectra with extra splitting only with the strongest Lewis acids (SbF_5, $AgBF_4$, $SbCl_5$) indicates that the equilibrium is virtually completely shifted to the right in these cases. On the other hand the

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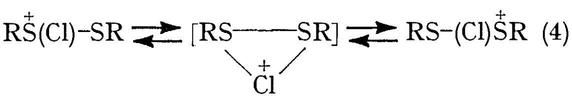
[19] L. M. Jackmann and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 1969, p. 349.

results with boron trifluoride and trichloride, weaker Lewis acids, suggest that the equilibria are still shifted to the right but that in these cases the reverse reaction may be fast on the n.m.r. time scale at appropriate temperatures. Moreover the results show a dependence of the exchange rate with the concentration of these Lewis acids.

The reaction with BF_3 was investigated in greater detail with the aim to define its dependence on Lewis acid concentration. However conventional plots of log k against log $[BF_3]$ failed to give an unambiguous answer although the general trend suggests that the rates decrease more than required by a dependence on $[BF_3]^{-1}$. Possibibly species like $[(BF_3)_2Cl]^-$ and, perhaps, higher homologues play a role. Furthermore halogen exchange processes to form mixed boron trihalides, such as BF_2Cl, may complicate the kinetics. All this is not unexpected since the ability of Lewis acids to give complexes with halide ions of order greater than one as well as halogen interchange among boron halides are well documented.[20]

The role of chloride ion, free or complexed, in carrying on the exchange process is further confirmed by the observation that addition of chloride ion (as *N*-methylpyridinium chloride) at constant boron trifluoride concentration increases the reaction rate significantly.

In principle, one might expect that as an alternative to bimolecular exchange, the two alkyl groups become equivalent by a 1,2-sulphur shift of chlorine [equation (4)]. Evidence in favour of this mechanism has not been found in the range of temperature considered. Indeed the absence of exchange with the strongest Lewis acids does, by itself, exclude this unimolecular mechanism as well as the other hypothetical ones based on formation of a sulphenylium cation [equation (5)].



$$R\overset{+}{S}(Cl)\text{-}SR \rightleftharpoons \left[\underset{\overset{+}{Cl}}{RS\text{——}SR}\right] \rightleftharpoons RS\text{-}(Cl)\overset{+}{S}R \quad (4)$$

$$RS\text{-}\overset{+}{S}(Cl)R \rightleftharpoons RSCl + RS^+ \rightleftharpoons RS^+ + RSCl \rightleftharpoons RS\text{-}(Cl)\overset{+}{S}R \quad (5)$$

The conductimetric study gives further insight to the problem. The experiments indicate a 2 : 1 irreversible reaction between the sulphenyl halides and strong Lewis acids. The fact that the inflection point occurs at ratios smaller than two can be probably attributed to impurity in the solvent and/or in the Lewis acid. Indeed the larger deviation in respect to the theoretical ratio is observed with $SbCl_5$, a quite hygroscopic compound.

The equivalent conductivities measured with a slight excess of Lewis acid to ensure complete reaction are of the same order of magnitude as those of the corresponding tetra-n-butylammonium salts. This is particularly true for hexachloroantimonates, less so for fluoroborates. Ion pairing phenomena, known to be quite important in liquid sulphur dioxide,[21] and probably more important for BF_4^- than for $SbCl_6^-$, could be responsible for the observations.

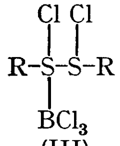
A further point is the high conductivity shown by methanesulphenyl chloride in the absence of any added Lewis acid. This cannot be due to an impurity in the reagent or the solvent and has to be attributed to self-dissociation. This is not unexpected because sulphur dioxide itself is a Lewis acid and its ability to co-ordinate halide ions is well known.

The dissociation of sulphenyl chloride in sulphur dioxide solutions could be also responsible for the observed temperature dependence of the chemical shifts in the n.m.r. spectra of alkanesulphenyl chlorides. Indeed in other solvents no shifts of this kind were observed.

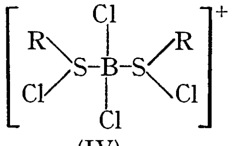
A further piece of evidence in favour of some dissociation following equation (1) of (Ia and b) in liquid sulphur dioxide is offered by the broadening of the n.m.r. spectra of (Ia) and particularly (Ib) at the lower temperatures.

The process responsible for the broadening of the signals in the spectra of (Ia and b) in the presence of boron trichloride in the temperature range −60 to −20° which occurs before the collapse of the bands (see Results section) has not been investigated in detail. Possibly such a phenomenon is linked to a tight association of boron tetrachloride ion with the cation or further complexation with excess of boron trichloride.

We think that the recently proposed [22] structures (III) and (IV) are not valid alternatives to (II). Indeed both R groups are diastereotopic in (IIIb) and (IVb), whereas we found that only one of the methylenes in ethanesulphenyl chloride is anisochronous. Furthermore (III) is not ionic and (IV) requires the two R groups to be equivalent. Nevertheless, we prefer to leave open this problem which, however, we consider secondary in respect to the overall picture that stems from all the other results.



(III)



(IV)

a; R = Me
b; R = Et

As discussed above our n.m.r. and conductimetric results put on a firm basis the hypothesis already advanced by several authors [5,7] of the intermediacy of cations such as (II) in the reactions of sulphenyl halides and disulphides.

It is noteworthy that alkyl(alkylthio)chlorosulphonium chlorides (II) are already present in significant amount in liquid sulphur dioxide in the absence of any other added

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[20] (*a*) P. A. W. Dean and R. J. Gillespie, *J. Amer. Chem. Soc.*, 1969, **91**, 7260, 7264; (*b*) J. Bacon, P. A. W. Dean, and R. J. Gillespie, *Canad. J. Chem.*, 1969, **47**, 1655; (*c*) H. Noth, *Progr. Boron Chem.*, 1970, **3**, 211; (*d*) D. T. Coyle and F. G. A. Stone, *ibid.*, 1964, **1**, 83.

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[22] H. Noth and G. Mikulaschek, *Chem. Ber.*, 1964, **97**, 709.

Lewis acid and that species such as (II) are also formed in media like sulphuric and fluorosulphuric acids. On the other hand our results confirm the general reluctance of sulphenyl compounds to release free sulphenylium ions.

EXPERIMENTAL

Materials.—Methane-[23] and ethane-sulphenyl chloride,[24] *N*-methylpyridinium chloride,[25] and tetra-n-butylammonium tetrafluoroborate[26] were prepared by literature methods. *Tetra-n-butylammonium hexachloroantimonate* was prepared by addition of $SbCl_5$ dissolved in anhydrous dichloromethane to a solution of tetra-n-butylammonium chloride in the same solvent (Found: C, 33·1; H, 6·2; N, 2·4. $C_{16}H_{36}Cl_6NSb$ requires C, 33·3; H, 6·3; N, 2·45%). High purity commercial solvents and gases were used without further purification.

N.m.r. Spectra.—N.m.r. spectra were recorded on Bruker HFX-10 (90 MHz) or Varian A-60 (60 MHz) instruments equipped with variable temperature units. Spectra at +37° were recorded in some instances with a Perkin-Elmer R-12 instrument.

Tetramethylsilane (TMS) was used as internal standard for the n.m.r. spectra except for samples containing antimony pentafluoride. In this case dichlorofluoromethane [δ_{TMS} (in SO_2) 7·63 (J_{H-F} 53 Hz)] was employed. Trichlorofluoromethane was chosen as internal reference for the ^{19}F n.m.r. spectra.

Sulphur dioxide and the gaseous reagents were transferred through a manometrically controlled line to a 5 mm n.m.r. tube attached to a vacuum line and sealed under vacuum. The boron trifluoride concentrations were determined by integration of the ^{19}F n.m.r. signals. Volumetrically controlled amounts of hexafluorobenzene supplied the internal calibration.

The temperature was checked by the methanol chemical shift method making reference to appropriate calibration equations.[27]

Line-shape analysis was performed with a CDC-6600 computer using the DNMR program developed by Binsch.[28] The rate-dependent methyl resonances of (IIa) were simulated for the chlorine atom exchanging between two sites. Iterative fitting to digitized spectra[29] was employed in the case of the (Ia)–boron trifluoride system. The scale employed for both the experimental and computer-simulated spectra was 10 Hz cm^{-1}.

Conductance Titrations.—Conductances were measured by means of a Radiometer CDM-3 bridge equipped with automatic compensation for cable and cell capacities.

Conductance titrations were carried out by placing a sulphur dioxide solution (7 ml) of the Lewis acid or suspension of silver tetrafluoroborate in a conductance cell at −63°. Volumetrically controlled amounts of (Ia) were added stepwise and the conductances were measured after each addition. The conductance of the solution did not change with time. The cell constant was found to be 0·565 cm^{-1} from measurements of a 0·01M aqueous solution of KCl at 25°.

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[23] H. Britzinger, H. Koddesbuch, K. H. Kling, and G. Jung, *Chem. Ber.*, 1952, **85**, 455.

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