Mixed Boron Trihalide Adducts. A Nuclear Magnetic Resonance Study of Donor Site and Halogen Redistribution in Boron Trihalide Adducts of Methyl Acetate and its Sulphur Analogues

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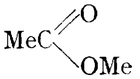
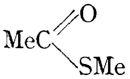
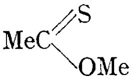
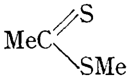
In methyl acetate and its mono- and di-thioanalogues, donation to the boron trihalides to form 1 : 1 complexes is from the carbonyl or thiocarbonyl group. Thus preference for the doubly bonded donor atom outweighs preferences previously noted between oxygen and sulphur as donor atoms. Complexes involving carbonyl and thiocarbonyl donation show contrasting behaviour which appears to be typical of oxygen and sulphur donation.

RECENT studies have demonstrated contrasting behaviour in the interactions of dimethyl ether and dimethyl sulphide with the boron trihalides.[1,2] In the 1 : 1 adducts rates and equilibria of halogen redistribution and rates of donor–acceptor bond breaking are very different. The present work was carried out to provide further information on any inherent differences between oxygen and sulphur as donor atoms. Adducts of the series of bases (I)—(IV) were chosen for study since the effects of stepwise replacement of oxygen by sulphur can be observed. In particular the Lewis base properties of the two isomeric monothioesters can be compared.


(I)
Methyl acetate


(II)
S-Methyl thioacetate


(III)
O-Methyl thioacetate


(IV)
Methyl dithioacetate

Carboxylic esters are well established to complex with the boron trihalides by donation from the carbonyl oxygen.[3] The interactions of thiocarboxylic esters with Lewis acids have not been extensively studied, and the preferred donor site is not obvious. The possibilities are: (i) the doubly bonded donor (carbonyl or thiocarbonyl) might remain consistently the better donor; (ii) either oxygen or sulphur might remain the preferred donor when both are present in the same molecule; or (iii) discontinuities in donor site might occur as *n* changes from 0 to 3 across series of BF_nCl_{3-n} and BF_nBr_{3-n} adducts, because of different relative affinities of the different Lewis acids for oxygen and sulphur.

EXPERIMENTAL

Methylene chloride, the boron trihalides, and the n.m.r. reference compounds were purified as described previously.[1] Methyl acetate was purified by fractional distillation and dried over molecular sieves before use.

Methyl thioacetate was prepared according to the method of Schleppnik and Zienty.[4] The product (b.p. 95—97 °C, lit.,[5] 95—96 °C; parent ion peak at *m/e* 90 in the mass spectrum) gave two ^1H n.m.r. (35 °C) peaks of equal intensity at δ 2·28 and 2·32, which shifted to δ 2·34 and 2·42, respectively, at −90°.

$[^2H_3]$*S*-Methyl thioacetate $[CD_3C(O)SCH_3]$ was prepared by a similar method. $[^2H_6]$Acetic anhydride (5 g) (Merck, Sharp, and Dohme) and triethylamine (4·7 g) were added by syringe to a nitrogen-filled reaction vessel which was then cooled to −196° and evacuated. An equimolar quantity of methanethiol was condensed in, and the mixture allowed to warm. The product was extracted into ether, washed several times, and fractionated. The clear colourless thioester (b.p. 96—98 °C, parent ion peak at *m/e* 93) gave a single ^1H n.m.r. (35 °C) peak at δ 2·27, which shifted to δ 2·33 at −90°. This confirms the previous assignment of the higher-field peak of (II) to the *S*-methyl group.[6]

O-Methyl thioacetate was prepared by a modification of a procedure for the synthesis of the ethyl ester.[7] Hydrogen sulphide was bubbled into a stirred mixture containing 1,1,1-trimethoxyethane (42 g) and ferric chloride (0·2 g) for 42 h. Fractionation gave a product which distilled at 60 °C, probably an azeotrope with the methanol formed in the reaction. This product was dissolved in ether, washed several times to remove the methanol, dried, and fractionated to give a product distilling at 82—85 °C (lit.,[5] 88—91 °C). Redistillation on the vacuum line gave a pale yellow liquid with a parent ion peak at *m/e* 90 and ^1H n.m.r. (35 °C) peaks of equal intensity at δ 2·57 and 4·06, which shifted to δ 2·66 and 4·13 at −90°. The higher field peak is assigned to the *C*-methyl by analogy with the ethyl ester.[7]

Methyl dithioacetate was prepared by the reaction of carbon disulphide (0·25 mol) with methyl magnesium iodide (0·33 mol) in dry ether at −10°, followed by warming to 25 °C for 0·5 h, then addition of methyl iodide (0·33 mol) under reflux, and finally gentle hydrolysis. The dark red oil which resulted was vacuum distilled twice yielding a bright red oil having a large peak at *m/e* 106 in the mass spectrum and small peaks at higher *m/e* values, including one at *m/e* 138. The ^1H n.m.r. (35 °C) spectrum contained two peaks of equal intensity at δ 2·62 and 2·86 and a third of slightly greater intensity at δ 2·76. Distillation at 160° (lit.,[5] 142 °C) gave a low yield of a yellow-orange oil which gave equal-intensity ^1H n.m.r. peaks at δ 2·63 and 2·87, and a small impurity peak at δ 2·76. At −90° these shifted to δ 2·68, 2·96, and 2·83, respectively. This material was used without further purification. The chief impurity is apparently $(MeS)_2CS$ which was the only product in an attempted synthesis of (IV) from methyl-lithium and carbon disulphide.

The n.m.r. instrumentation and the methods of preparation of n.m.r. samples have been described previously.[1]

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[1] M. J. Bula, D. E. Hamilton, and J. S. Hartman, *J.C.S. Dalton*, 1972, 1405.

[2] M. J. Bula and J. S. Hartman, *J.C.S. Dalton*, 1973, 1047.

[3] M. F. Lappert, *J. Chem. Soc.*, 1961, 817; 1962, 542.

[4] A. A. Schleppnik and F. B. Zienty, *J. Org. Chem.*, 1964, **29**, 1910.

[5] I. M. Heilbron and H. M. Bunbury, ' Dictionary of Organic Compounds,' Eyre and Spottiswood, London, 1965.

[6] R. L. Middaugh and R. S. Drago, *J. Amer. Chem. Soc.*, 1963, **85**, 2575.

[7] A. Ohno, T. Koizumi, and G. Tsuchihasi, *Tetrahedron Letters*, 1968, 2083.

Mass spectra were run on an A.E.I. MS30 double beam mass spectrometer with the reference perfluorokerosene in the second beam.

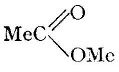
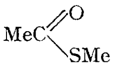
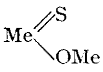
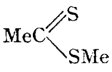
RESULTS

^1H and ^{19}F N.m.r. parameters of the adducts of methyl acetate and its sulphur analogues are given in Tables 1 and 2 respectively. In all systems, free base and adduct ^1H n.m.r. peaks were collapsed together at room temperature due to rapid chemical exchange. At −90° separate peaks could be observed for each adduct and for free base, with the exception of the BF_3 adducts of (III) and (IV) which remained coalesced with the free-base peak to temperatures below −100°. No splittings due to $^1H^{11}B$ coupling were observed. Splittings due to $^{11}B^{19}F$ coupling could be observed at room temperature in the ^{19}F spectra of some of the fluorine-containing adducts, but the 1 : 1 : 1 : 1 quartets collapsed to broad single peaks at lower temperatures. Fluorine-containing mixed boron trihalide adducts of (I) and (II), but not of (III) or (IV), were detected by both ^1H and ^{19}F n.m.r. It was not possible to resolve ^1H peaks arising from BCl_2Br or $BClBr_2$ adducts of any of the bases, apparently because differences in the ^1H chemical shifts of the adducts were too small. However the broad single ^1H peak observed in each ester–BCl_3–BBr_3 system indicated that these mixed adducts were present.

Adducts of Methyl Acetate.—Solutions of an excess of (I) with BF_3 and BCl_3 gave an initial −90° ^1H n.m.r. spectrum containing three pairs of peaks arising from methyl acetate and its BF_3 and BCl_3 adducts (Figure 1A). *C*-Methyl complexation shifts are larger than *O*-methyl complexation shifts. Warming to 25° for 1 min caused the appearance of two new pairs of −90° peaks of intermediate chemical shift (Figure 1B) which are assigned to the BF_2Cl and $BFCl_2$ adducts as in Table 1. The assignments were confirmed by varying the relative amounts of the halogens present and observing changes in relative areas of the mixed-adduct peaks. Little further change occurred in relative

TABLE 1

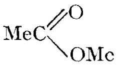
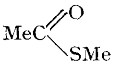
−90 °C Proton chemical shifts[a] of boron trihalide adducts of methyl acetate and its sulphur analogues

Adduct of:	 (I)	 (II)	 (III)	 (IV)
(i) *C*-Methyl chemical shifts				
b	2·13	2·42	2·66	2·96
BF_3	2·67	2·88	2·96	
BF_2Cl	2·80	3·01		
$BFCl_2$	2·90	3·13		
BCl_3	3·00	3·24	3·24	3·48
BF_2Br	2·88	3·06		
$BFBr_2$	3·02	3·18		
BBr_3	3·13	3·33	3·30	3·54
(ii) *O*- and *S*-Methyl chemical shifts				
b	3·75	2·34	4·13	2·68
BF_3	4·23	2·70	4·40	
BF_2Cl	4·28	2·75		
$BFCl_2$	4·33	2·79		
BCl_3	4·37	2·82	4·48	3·00
BF_2Br	4·37	2·78		
$BFBr_2$	4·42	2·82		
BBr_3	4·47	2·88	4·54	3·07

[a] Methylene chloride solution, p.p.m. to low field of tetramethylsilane. [b] Uncomplexed base.

TABLE 2

^{19}F N.m.r. parameters of boron trihalide adducts of methyl acetate and *S*-methyl thioacetate

				
Adduct of:	Chemical shift[a]	$J(^{11}B^{19}F)$/Hz[b]	Chemical shift[a]	$J(^{11}B^{19}F)$/Hz[b]
BF_3	149·4		148·0	
BF_2Cl	126·2	27·5	125·4	28·1
$BFCl_2$	112·0	58·2	110·0	59·3
BF_2Br	117·4		116·7	39·0
$BFBr_2$	99·6			

[a] P.p.m. to high field of $CFCl_3$. [b] Visible at room temperature only.

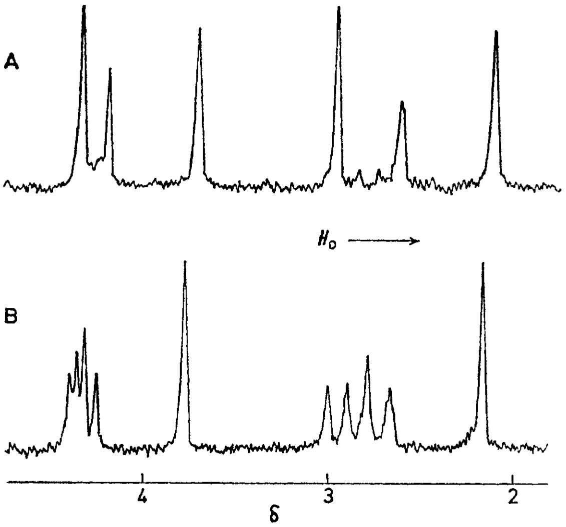


FIGURE 1 −90° ^1H N.m.r. spectra (p.p.m.) of a methylene chloride solution of methyl acetate, BF_3, and BCl_3 in a 3 : 1 : 1 molar ratio. A, initial spectrum; B, after equilibration at room temperature peak areas on further warming to 25 °C. Equilibrium constants K_1 and K_2 for the halogen redistribution were determined to be 1·27 ± 0·10 and 0·53 ± 0·10 respectively.

$$K_1 = \frac{[\text{donor},\text{BF}_2\text{Cl}][\text{donor},\text{BCl}_3]}{[\text{donor},\text{BFCl}_2]^2} \qquad (1)$$

$$K_2 = \frac{[\text{donor},\text{BF}_3][\text{donor},\text{BFCl}_2]}{[\text{donor},\text{BF}_2\text{Cl}]^2} \qquad (2)$$

C-Methyl ^{1}H resonances obtained at various temperatures are shown in Figure 2. The BF_3 adduct peak coalesces with the free-base peak at quite low temperatures, and the remaining three adduct peaks coalesce with the averaged peak in a much higher temperature range. A similar coalescence pattern occurs but at lower temperatures for the less well separated *O*-methyl resonances. Slow decomposition of the chlorine-containing adducts occurs at room temperature,[8] giving the small impurity peak which shows up at the higher temperatures (Figure 2).

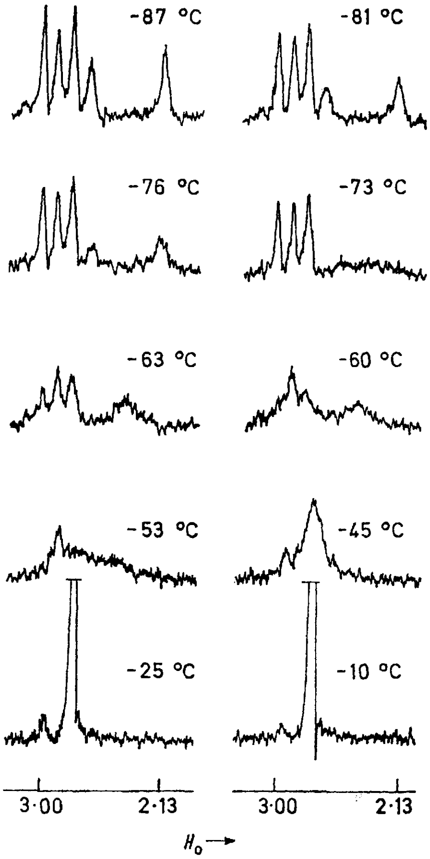


FIGURE 2 Temperature dependence of the *C*-methyl proton resonances (δ/p.p.m.) of the sample shown in Figure 1, after the attainment of equilibrium in the halogen redistribution reaction

Similar coalescence of ^{1}H n.m.r. peaks occurs when boron trihalide rather than methyl acetate is present in an excess (Figure 3). Coalescence temperatures are higher. Again the BF_3 adduct peak is the first to collapse, this time with the BF_2Cl adduct peak. As in the corresponding Me_2O adduct system,[1] halogen redistribution probably remains slower than donor–acceptor bond breaking under these conditions.

In the methyl acetate–BF_3–BBr_3 system decomposition of the bromine-containing adducts is competitive with halogen redistribution. Thus after warming such a sample containing an excess of base to 25 °C for 1 min the −90° ^{1}H n.m.r. spectrum contained large peaks at δ 2·88 (CH_3COBr) and δ 4·45 (CH_3OBBr_2). However large amounts of the BF_2Br and $BFBr_2$ adducts can be formed at low temperatures by reacting methyl acetate with an already equilibrated mixture of BF_3 and BBr_3; such a mixture contains large amounts of BF_2Br and $BFBr_2$.[9]

^{19}F Spectra confirm the existence of mixed boron trihalide adducts. Broadened 1 : 1 : 1 : 1 quartet fine structure due to ^{11}B^{19}F coupling appears at room temperature in the BF_2Cl and $BFCl_2$ adduct resonances, but collapses to give broad single peaks at lower temperatures. The BF_2Br and $BFBr_2$ adducts gave broad single peaks at low temperatures; room temperature spectra could not be obtained because of the high reactivity of the compounds.

Adducts of S-*Methyl Thioacetate*.—An unwarmed sample containing an excess of (II) with BF_3 and BCl_3 gave three pairs of −90° ^{1}H n.m.r. peaks, assigned to (II) and its BF_3 and BCl_3 adducts. Brief warming to 25 °C caused the appearance of peaks at intermediate positions, assigned to the mixed adducts (Figure 4A). *C*- and *S*-Methyl resonances were identified by comparison with spectra of the adducts of the deuteriated ester (Figure 4B).

Equilibrium in the halogen redistribution reaction was attained after a few minutes at 25 °C. However by this time small amounts of a solid, which was not further investigated, began to precipitate. Approximate K_1 and K_2 values for the halogen redistribution equilibrium are 0·92 ± 0·15 and 0·51 ± 0·15 respectively.

Bromine-containing adducts of (II) are much more stable than those of (I). Thus the BF_2Br and $BFBr_2$ adducts of (II) could be formed by allowing a solution of the BF_3 and BBr_3 adducts to warm to room temperature. Again small amounts of insoluble material began to precipitate as the halogen redistribution approached equilibrium.

^{19}F Spectra of the mixed-halogen adducts of (II) closely resemble the spectra of corresponding adducts of (I) in the appearance of the peaks and in their chemical shifts and coupling constants. The mixed adducts gave broad single peaks at low temperature and 1 : 1 : 1 : 1 quartet fine structure at room temperature.

Adducts of O-*Methyl Thioacetate*.—Solutions of BF_3 with an excess of (III) did not give separate ^{1}H n.m.r. signals for free and complexed base even at −100° but only averaged signals. Solutions of BCl_3 and BBr_3 with an excess of (III) did give separate −90° signals for free and complexed base. This pattern is reminiscent of Me_2S adducts.[2]

Solutions of (III) with any of the boron trihalides underwent rapid decomposition at room temperature with vigorous bubbling and darkening. The decomposing samples gave a number of ^{1}H n.m.r. peaks including 1 : 2 : 1 triplets with low-temperature ^{1}H n.m.r. chemical shifts of δ 1·46 (*J* 7·4 Hz) for the BF_3 adduct, δ 1·62 (*J* 7·0 Hz) for the BCl_3 adduct, and δ 1·68 (*J* 7·1 Hz) for the BBr_3 adduct. The products of decomposition were not further studied.

Unwarmed samples of (III), BF_3, and BCl_3 in the mole ratio 3 : 1 : 1 showed two pairs of −90° ^{1}H n.m.r. peaks arising from (i) the BCl_3 adduct and (ii) the averaged peak

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[8] W. Gerrard and M. A. Wheelans, *J. Chem. Soc.*, 1956, 4296; W. Gerrard and M. F. Lappert, *Chem. Rev.*, 1958, **58**, 1081.

[9] M. F. Lappert, M. R. Litzow, J. B. Pedley, T. R. Spalding, and H. Noth, *J. Chem. Soc.* (*A*), 1971, 383.

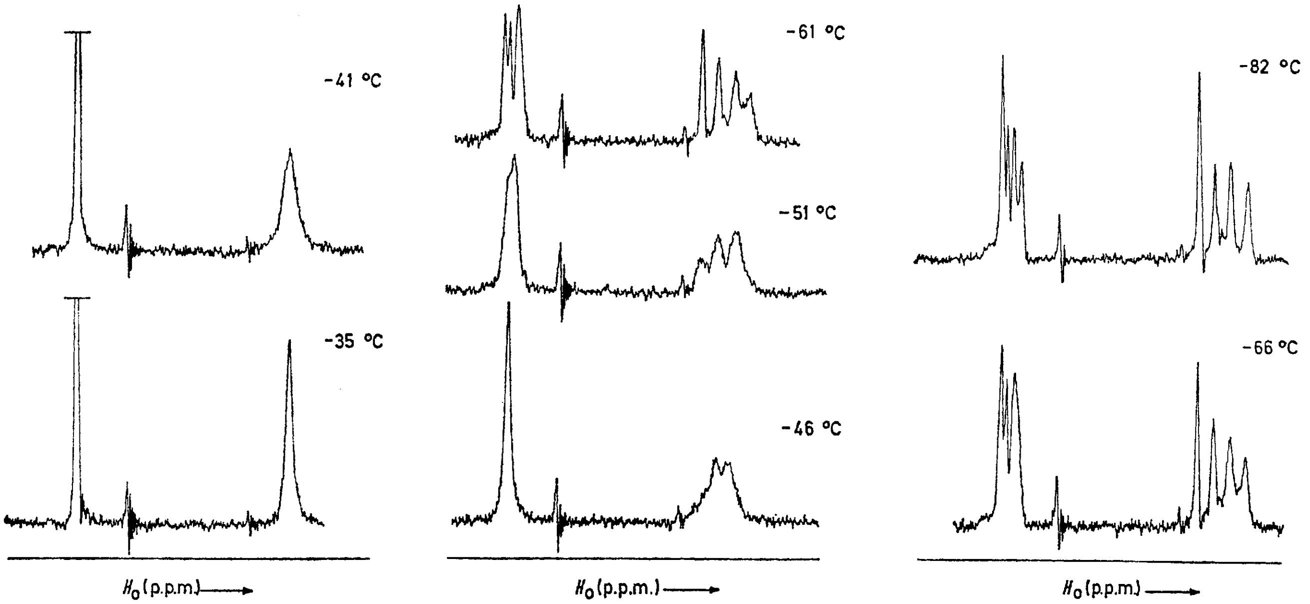

FIGURE 3 Temperature dependence of the ^1H spectrum of a methyl acetate–BF_3–BCl_3 solution containing an excess of Lewis acid

of the BF_3 adduct and free base. Brief warming to 25 °C caused decomposition and the appearance of numerous peaks to high field; no mixed-adduct peaks could be identified. Attempts to obtain the mixed adducts by condensing pre-equilibrated BF_3–BCl_3 and BF_3–BBr_3 mixtures onto methylene chloride solutions of (III) were not successful despite extreme care to prevent warming of the samples above −78°. The halogens seemed to ' unmix ' too rapidly to allow the detection of −90° n.m.r. signals of the mixed adducts. In one experiment there seemed to be an initial absorption in the region where mixed-adduct peaks were expected, but resolution was poor, the absorption rapidly disappeared, and it is not certain that it arose from mixed adducts.

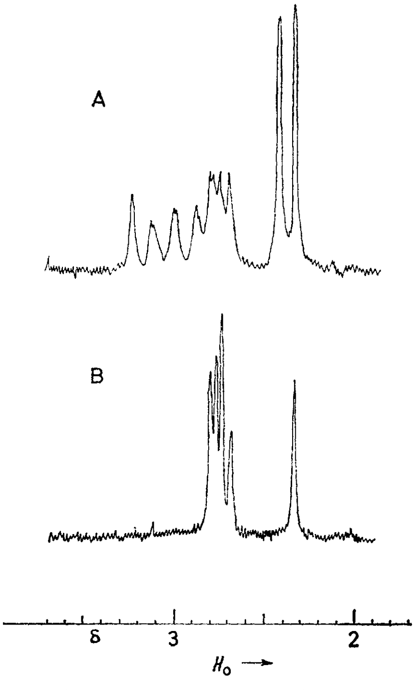

FIGURE 4 −90° ^1H N.m.r. spectra (p.p.m.) of methylene chloride solutions of *S*-methyl thioacetate, BF_3, and BCl_3 with an excess of base present, after the attainment of equilibrium in the halogen redistribution reaction; A, $CH_3C(O)SCH_3$; B, $CD_3C(O)SCH_3$

A solution of the BF_3 adduct of (III) gave rise to two low-temperature ^{19}F peaks at 148·9 and 153·2 p.p.m. Assignment of these is not certain. Since no additional peaks were observed when BCl_3 or BBr_3 was present in the solution in addition to BF_3, we can conclude that no appreciable amounts of fluorine-containing mixed adducts were present.

Adducts of Methyl Dithioacetate.—Solutions of BF_3 with an excess of (IV) did not give separate ^1H n.m.r. signals for free and complexed base even at −100°. Solutions of BCl_3 and of BBr_3 did give separate signals at −90°. All the boron trihalide adducts of (IV) are fairly stable in solution. After a day at room temperature small amounts of insoluble material had appeared, but there was little change in the proton spectra and little darkening of the originally orange-yellow solutions.

^1H N.m.r. spectra (−90 °C) of solutions containing (IV), BF_3, and BCl_3 gave no evidence of mixed boron trihalide adducts. This was also the case when an already equilibrated mixture of BF_3 and BCl_3 was reacted with an excess of (IV) at low temperatures. Warming to room temperature had no effect. Two pairs of low-temperature peaks, assigned to (i) the BCl_3 adduct and (ii) the exchange-averaged peak arising from the free base and the BF_3 adduct, were present. The (IV)–BF_3–BBr_3 system gave a similar result.

The tentative assignments of ^1H n.m.r. peaks of (IV) to *C*- and *S*-methyl (Table 1) are made by analogy with adducts of (I)—(III) in which the *C*-methyl resonance undergoes a larger complexation shift than the *O*- or *S*-methyl.

DISCUSSION

Effects of Sulphur Substitution: Oxygen vs. *Sulphur Donation*.—Adducts of (II) are so similar to the corresponding adducts of (I) in their ^{19}F n.m.r. parameters, in the halogen redistribution equilibrium, and in exchange rates, that the same donor site, carbonyl oxygen, is indicated with a high degree of certainty. Carbonyl donation in adducts of (II) is consistent with the few previous studies of donor site in *S*-alkyl thioesters.[10,11]

An abrupt change in adduct properties between adducts of (II) and (III) is to be expected since (III) has no carbonyl oxygen. The choice of donor site is between thiocarbonyl sulphur and alkyl oxygen. Low-temperature n.m.r. provides sufficient information to identify sulphur as the donor site. This choice is based on a pattern of differences between Me_2O and Me_2S adducts [1,2] which is repeated in the present series of adducts as an abrupt division between adducts of (I) and (II) on the one hand and adducts of (III) and (IV) on the other, and which appears to be characteristic of oxygen donation *vs.* sulphur donation. This pattern of differences consists of the following:

(i) Halogen redistribution equilibria are very different. Equilibrium constants K_1 and K_2 [equations (1) and (2)] are given in Table 3 for the various donors in the order of increasing deviation from the ideal random case. Compounds (I) and (II) give values not too different from the Me_2O values. The values for Me_2S are much larger and correspond to very small proportions of the mixed adducts at equilibrium. Since mixed adducts of (III) and (IV) could not be detected under the same conditions these bases are beyond Me_2S in the series. It is of interest that the increases in K_1 and K_2 correspond to greater polarizability of the donor atom, from ether oxygen to carbonyl oxygen to sulphide to thiocarbonyl sulphur.

TABLE 3

Halogen redistribution equilibrium constants [a]

Donor	K_1	K_2
Ideal random case	0·33	0·33
Dimethyl ether [b]	0·80	0·23
S-Methyl thioacetate (II)	0·92	0·51
Methyl acetate (I)	1·27	0·53
Dimethyl sulphide [c]	6·3	2·3
O-Methyl thioacetate (III)	Large [d]	Large [d]
Methyl dithioacetate (IV)	Large [d]	Large [d]

[a] Equations (1) and (2). [b] Ref. 1. [c] Ref. 2. [d] No mixed adducts detected.

(ii) The attainment of equilibrium can be monitored by low-temperature n.m.r. in the Me_2O, (I), and (II) adduct systems, but in the Me_2S, (III), and (IV) adduct systems the halogen redistribution is much too fast for this.

(iii) Rates of donor–acceptor bond breaking, reflected in ^{1}H n.m.r. peak coalescence patterns, show distinctive differences. The BF_3 adducts of Me_2S, (III), and (IV) undergo such rapid exchange with free base that separate free-base and BF_3 adduct peaks cannot be resolved even at the lowest temperatures attainable. This contrasts with Me_2O, (I), and (II) where the BF_3 adduct peak and the free-base peak coalesce well above −90°. The smaller complexation shifts of the BF_3 adducts of Me_2S, (III), and (IV) cannot alone account for these differences. There is also some difference in the appearance of the coalescence pattern of the mixed-adduct peaks of Me_2S on the one hand and Me_2O, (I), and (II) on the other. The BF_2Cl, $BFCl_2$, and BCl_3 adduct peaks of Me_2S coalesce one by one as the temperature is raised (Figure 4 of ref. 2), whereas in the other systems all three of these peaks coalesce in about the same temperature range (Figure 2, and Figure 1 of ref. 1).

(iv) Me_2S adduct ^{19}F n.m.r. parameters are very different from the corresponding Me_2O adduct parameters. This is a particular case of the pronounced dependence of these parameters on the donor atom, which we have discussed elsewhere.[12] Compounds (I) and (II) follow the oxygen-donor pattern, but (III) is ambiguous since BF_3-adduct solutions give rise to more than one ^{19}F n.m.r. peak.

All the above, taken together, is conclusive in establishing the donor site. ^{1}H Complexation shifts confirm that oxygen and sulphur are the donor atoms in (II) and (III) respectively. The *C*-methyl protons which are nearer to the donor site have larger complexation shifts than the *S*- and *O*-methyl protons.

Adduct decomposition follows a different pattern, being more dependent on the presence of the OMe group than on the presence of carbonyl as opposed to thiocarbonyl. Susceptibility to adduct decomposition varies in the order (III) > (I) > (II) ~ (IV). Ester adducts decompose according to: [8]

$$\mathrm{RC(O)OR',BX_3} \longrightarrow \mathrm{RC(O)X + R'OBX_2} \quad (\mathrm{X = Cl,Br}) \qquad (3)$$

Adducts of (III) as well as (I) undergo decomposition by this pathway while adducts of (II) and (IV) do not. The extreme ease of decomposition of all the boron trihalide adducts of (III) might arise from the presence of traces of the oxygen-donor isomer in equilibrium with the predominant sulphur-donor isomer. This isomer could break apart to give $MeOBX_2$ with little rearrangement required, in a fashion similar to the decomposition of protonated thiocarboxylic acids and esters which apparently involves a shift of the added proton.[11]

A problem remains with the BF_3 adduct of (III) which gives two ^{19}F peaks, both at higher field than expected for a sulphur-donor BF_3 adduct. This system merits further study to investigate possibilities such as (i) oxygen donation competing to a considerable extent with sulphur donation to BF_3; (ii) isomerization of (III) to (II) in the presence of BF_3, similar to the reported isomerization of $(RO)_3P{=}S$ to $(RO)_2(RS)P{=}O$ by BF_3.[13] A further possibility is that a broad resonance due to the sulphur-donor adduct could be missed and the small

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peaks observed might be due to the readily formed decomposition products.

N.m.r. Parameters.—The complexation shifts of corresponding adducts decrease markedly in the order (I) > (II) > (III) ~ (IV), suggesting a corresponding decrease in donor strength. The relative magnitudes of *C*- and *O*-methyl complexation shifts (Table 4) support carbonyl and thiocarbonyl donation in the adducts of (I)—(III) but not in the adducts of (IV) since the peak assignments are only tentative.

TABLE 4

^{1}H N.m.r. complexation shifts (p.p.m.) of *C*-methyl protons (α) and of *O*- and *S*-methyl protons (β) in methyl acetate and its sulphur analogues

Adduct of:	Methyl acetate			*S*-Methyl thioacetate		
	α	β	α/β	α	β	α/β
BF_3	0·54	0·48	1·12	0·46	0·36	1·28
BF_2Cl	0·67	0·53	1·26	0·59	0·41	1·44
$BFCl_2$	0·77	0·58	1·33	0·71	0·45	1·58
BCl_3	0·87	0·62	1·40	0·82	0·48	1·71
BF_2Br	0·73	0·62	1·21	0·64	0·44	1·45
$BFBr_2$	0·89	0·67	1·33	0·76	0·48	1·58
BBr_3	1·00	0·72	1·39	0·91	0·54	1·69

	O-Methyl thioacetate			Methyl dithioacetate		
	α	β	α/β	α	β	α/β
BF_3	0·30	0·27	1·11			
BCl_3	0·48	0·35	1·37	0·52	0·32	1·63
BBr_3	0·64	0·41	1·56	0·58	0·39	1·49

^{1}H Complexation shifts within a series of adducts of a given base are often approximately proportional to the heats of complexation[14] although exceptions exist.[2] From the complexation shifts of the mixed boron trihalide adducts of trimethylamine we have estimated the following relative acceptor powers:[15] $BBr_3 > BCl_3 > BFBr_2 > BFCl_2 > BF_2Br > BF_2Cl > BF_3$. The *C*-methyl complexation shifts of adducts of (II) are in agreement with this ordering, while those of (I) invert the positions of $BFBr_2$ and BCl_3 (Table 4). Interestingly the *O*- and *S*-methyls give rather different orderings of complexation shift than the corresponding *C*-methyls, confirming that the relationship between proton complexation shift and acceptor strength can only be approximate. The variations in the ratio of *C*- to *O*- and *S*-methyl complexation shifts in different adducts of the same base (α/β in Table 4) also confirms that proton complexation shifts do not arise solely from an inductive shift of electron density from the rest of the donor molecule toward the donor site. Chemical shifts are affected by long-range shielding.[16] In the adducts nearby heavier halogens can cause significant changes in chemical shifts and hence irregularities in series of complexation shifts.

Coupling to boron-11 is not apparent in the ^{1}H spectra of any of the adducts of (I)—(IV). The ^{19}F n.m.r. spectra of the mixed boron trihalide adducts of (I) and (II) do show coupling to boron-11 at room temperature. The collapse of the spin–spin splittings at lower temperatures is due to quadrupole relaxation of boron, and is more pronounced at any given temperature than in the corresponding Me_2O adducts.[1] Since the other factors affecting collapse of the splittings[2] are approximately constant between the ether and ester adducts, we can conclude that there is a somewhat greater electric-field gradient at boron in the ester adducts. Esters are weaker donors than ethers to BF_3,[17] and probably to the mixed boron trihalides as well. The lower symmetry about boron in the ester adducts can thus be attributed to a greater discrepancy between the three strong halogen ligands and the weaker oxygen ligand.

Summary.—It has been possible to use characteristic features of oxygen and sulphur donation in boron trihalide adducts to identify the donor site in adducts in which both oxygen and sulphur are potential donor atoms. Preliminary studies indicate that these differences in behaviour between oxygen- and sulphur-donor adducts are general properties which apply to a wide range of classes of Lewis bases, and should be of use in further studies of adducts.

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