Detection of the New Reactive Molecule Methyl(sulphido)boron, MeBS, by Microwave Spectroscopy

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Summary The new monomeric reactive molecule methyl(sulphido)boron, MeBS, has been detected in the products of a high temperature reaction between gaseous dimethyldisulphide, MeSSMe, and crystalline boron; the method promises to be readily extendable to the production of other substituted (sulphido)borons, RBS.

ALTHOUGH the reactive species (sulphido)boron, HBS, has now been studied by several techniques such as mass spectrometry[1] as well as microwave,[2] i.r.,[3] and photoelectron spectroscopy,[4,5] little is known about the substituted monomeric analogues RBS where R is an alkyl group or a halogen atom. This is because it is not immediately obvious how the method by which HBS was produced can readily be extended to produce these homologues. The method involves a very high temperature (1300 °C) reaction between H_2S and solid boron, conditions which are not favourable for the production of the more complex molecules.

Microwave and/or photoelectron techniques have recently been used to detect a wide range of similarly unstable and reactive species such as $H_2C{=}C{=}S$,[6] MeCH=Se,[7] $CH_2{=}PCl$,[8] MeC≡P,[9] and FC≡P.[10] The last two species are phospha-alkynes which contain the group –C≡P which is isoelectronic with the group –B=S. These techniques have now been extended to explore methods of producing new monomeric (sulphido)boron compounds (other than HBS) and characterising their molecular properties.

We report here on the development of a method for producing methyl(sulphido)boron, MeBS, by passing dimethyl disulphide, MeSSMe, over crystalline boron at high temperature. Broken boron chips (Koch-Light) are placed in a 20 cm section of a molybdenum lined (0·125 mm thick sheet) quartz reactor tube (8 mm i.d.) which is heated to *ca.* 850 °C in a furnace. The dimethyl disulphide (B.D.H.) is passed rapidly *via* the reactor directly into the cell of a microwave spectrometer at a pressure of *ca.* 10—20 μmHg. A Hewlett Packard 8460A spectrometer operating between 26·5 and 40 GHz was used. The cell was not cooled in dry ice as cooling appeared to reduce the lifetime of the species possibly by enhancing the rate of deposition on the cell walls.

Two groups of symmetric rotor lines lie within the range of the spectrometer; these are the $J = 3 \leftarrow 2$ and $J = 4 \leftarrow 3$ transitions. The lines show vibrational satellite and Stark structure typical of a symmetric rotor species.[11] The strongest lines can be assigned to the most abundant isotopic species $^{12}CH_3{}^{11}B^{32}S$ and a weaker set to the species

TABLE. Measured frequencies, derived parameters, and structural data for MeBS.

	$J = 4 \leftarrow 3, K = 0$[a]	$J = 3 \leftarrow 2, K = 0$[a]	B_0	D_J
$^{12}CH_3{}^{11}B^{32}S$	36 505·518	27 379·249	4 563·232 ± 0·003	0·0013 ± 0·0005 MHz
$^{12}CH_3{}^{10}B^{32}S$	36 578·269	27 433·863	4 572·345 ± 0·003	0·0019 ± 0·0005 MHz
$^{12}CH_3{}^{11}B^{34}S$	35 699·743	—	4 462·520 ± 0·003	0·0016[b] MHz

$r_s(B) = 0{\cdot}4640 \pm 0{\cdot}0026$;[c] $r_s(S) = 1{\cdot}1382 \pm 0{\cdot}0011$;[c] $r_s(B{=}S) = 1{\cdot}6022 \pm 0{\cdot}0036$ Å

[a] Measurement error ±0·01 MHz. [b] Assumed as average of D_J for the other two species. [c] This error determined from Costain's relation δr *ca.* $0{\cdot}0012/r$ (C. C. Costain, *Trans. Amer. Cryst. Assoc.*, 1966, **2**, 157).

$^{12}CH_3{}^{10}B^{32}S$. Boron quadrupole hyperfine splittings complicate the pattern causing the higher K lines to appear as multiplets. The positions of the $K = 0$ lines are however readily measured and these frequencies are given in the Table. A weak set of lines belonging to the species $^{12}CH_3$-$^{11}B^{34}S$ has also been detected and this has allowed a substitution determination[12] of the B=S bond length to be made. These data are also given in the Table.

The resulting bond length of 1·6022 Å for $r_s(B{=}S)$ is in very close agreement with that of 1·5995 Å observed in HBS and the slight tendency for the bond length to increase on substitution of H for Me parallels that in the cyanides where $r_s(C{\equiv}N) = 1{\cdot}15512$ Å in $HC{\equiv}N$[13] and 1·1571 Å in $CH_3C{\equiv}N$.[12]

It is interesting to consider the mechanism by which (sulphido)borons may be formed under these conditions. At first sight it is not obvious that this process should be particularly successful as a boron atom must somehow insert into the C–S bond of the parent MeSSMe. The mechanism probably involves an initial thermal scission of the weak S–S bond to form two very reactive MeS· radicals. These can attack the boron surface and form MeSB fragments which isomerise to the observed MeB=S species (Scheme). The final step is somewhat analogous to the isovalent cyanide–isocyanide rearrangement.

$$\text{MeSSMe} \xrightarrow{\text{Heat}} 2\text{MeS}\cdot \xrightarrow{\text{B}} [\text{MeSB}] \longrightarrow \text{MeBS}$$

SCHEME

Trapping experiments have been unsuccessful and experiments in which a static sample was held in the cell indicated a lifetime of *ca.* 2 s under our conditions.

This method in which the reaction is initiated by the easy cleavage of a weak disulphide bond to produce reactive XS· radicals would appear to be a more efficient route to (sulphido)borons than the previous technique which involves a sulphide.[1] It thus seems very likely that use of H_2S_2 rather than H_2S should produce better yields of HBS.

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Added in proof: Further work on this type of system has led to the identification of ClBS in the products of a reaction between Cl_2S_2 and boron at 1000 °C.

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