Boron-Sulphur Compounds. Part III.[1] Fragmentation of Trimethyl Thioborate under Electron Impact

By **R. H. Cragg, J. F. J. Todd,*** and **A. F. Weston,** The Chemical Laboratory, University of Kent at Canterbury

The mass spectrum of trimethyl thioborate has been obtained and a mechanism of fragmentation has been postulated from the presence in the mass spectrum of relevant metastable peaks. Comparison is made both with the authors' and with the published data on trimethyl borate.

As part of a comprehensive study of the role of bond energetics in the mass spectra of compounds containing boron heteroatom linkages we have examined the fragmentation patterns of a number of phenylborolanes,[2] phenylboronic acid, and triphenylboroxine[3] and the alkyl esters and thioesters of phenyl and diphenylboronic acid.[4] A natural extension of this work is the examination of the fragmentation processes in alkyl borates and thioborates.

This study is further stimulated by the lack of publised data on thioborates, the closest investigations being those on boron sulphides,[5] metathioboric acid[6] and ethylthioborane.[7] Trimethyl borate has been more fully reported, both from an energetics standpoint[8,9] and in terms of postulated fragmentation mechanisms.[10] In this report we present a comparison between results obtained in this Laboratory for trimethyl thioborate and its oxygen analogue.

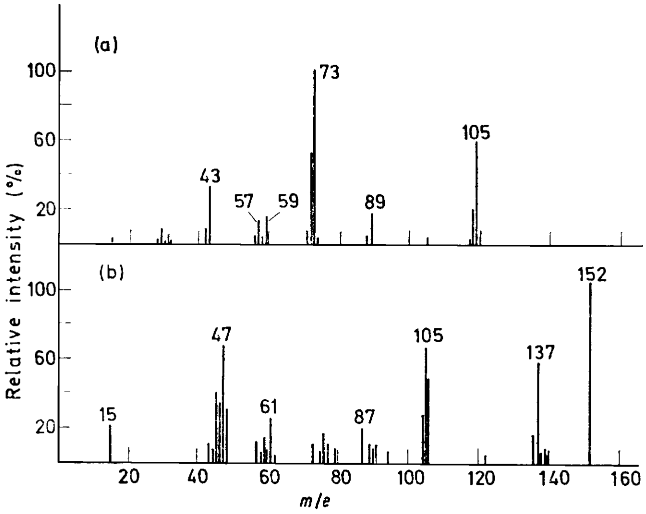

FIGURE 1 Bar diagrams showing the relative intensities (percentages) of the principal peaks in the mass spectra of (a) trimethyl borate (I), *M*, 104, and (b) trimethyl thioborate(II), *M*, 152

Mass Spectra.—The 70 eV mass spectra of trimethyl borate (I), $(MeO)_3B$, and trimethyl thioborate (II), $(MeS)_3B$, are presented as bar diagrams in Figure 1. A significant difference between the spectra of the two compounds is the apparent relative stability of the parent ion from (II), which forms the base peak of the spectrum, compared with (I) in which the loss of a methoxyl radical is the most dominant process. However, a more detailed comparison of the spectra is greatly facilitated by presenting them in a ' reduced ' form by removing those ions which contain the ^{10}B isotope and reducing the intensities of non-boron-containing ions by 20%, corresponding to that fraction being formed from ^{10}B precursors. The Table summarises these reduced spectra with the yields expressed as percentage total ionisation.

Reduced mass spectra[a]

(*a*) Trimethyl borate

m/e	% Total ionisation	Assignment
104	20·5	$(MeO)_3B$
103	1·8	$(MeO)_2BOCH_2$
89	5·9	$(MeO)_2BO$
73	35·1	$(MeO)_2B$
72	10·1	$MeOBOCH_2$
59	5·6	MeOBOH
57	4·7	$OBOCH_2$
43	11·6	BO_2
31	1·4	MeO
30	0·4	CH_2O
29	2·4	CHO
15	0·6	CH_3

(*b*) Trimethyl thioborate

m/e	% Total ionisation	Assignment
152	19·8	$(MeS)_3B$
137	11·2	$(MeS)_2BS$
105	13·0	$(MeS)_2B$
94	1·1	MeSSMe
91	1·8	MeSBSH
90	1·6	MeSBS
79	1·4	MeS_2
77	1·8	$B(SH)_2$
73	1·8	MeSBMe
62	0·5	Me_2S
61	4·8	$MeSCH_2$
59	2·7	MeSBH
58	1·1	MeSB
57	2·2	CH_2SB
48	4·8	MeSH
47	10·8	MeS
46	5·4	CH_2S
45	6·5	CHS
43	2·0	BS
15	2·8	CH_3

[a] Based on intensities of ^{11}B-containing ions only and 80% of intensities of non-boron-containing ions.

---

[1] R. H. Cragg, J. P. N. Husband, and P. R. Mitchell, *Org. Mag. Res.*, submitted for publication.

[2] R. H. Cragg, G. Lawson, and J. F. L. Todd, *J.C.S. Dalton*, 1972, 878.

[3] R. H. Cragg, J. F. J. Todd, and A. F. Weston, *Org. Mass. Spec.*, in press.

[4] R. H. Cragg, G. Lawson, and J. F. L. Todd, to be published.

[5] F. T. Greene and P. W. Gilles, *J. Amer. Chem. Soc.*, 1962, **84**, 3598.

[6] J. G. Edwards, H. Wiedemeir, and P. W. Gilles, *J. Amer. Chem. Soc.*, 1966, **88**, 2935.

[7] J. W. Gilje, *Internat. J. Mass. Spec. Ion Physics*, 1968, **1**, 500.

[8] R. W. Law and J. L. Margrave, *J. Chem. Phys.*, 1956, **25**, 1086.

[9] Y. Wada and R. W. Kiser, *J. Phys. Chem.*, 1964, **68**, 1588.

[10] P. J. Fallon, P. Kelly, and J. C. Lockhart, *Internat. J. Mass. Spec. Ion. Physics*, 1968, **1**, 133.

An interesting feature of the spectra presented in this form is that notwithstanding the contrast between the parent ion intensities made earlier, in each case the $P^{+\cdot}$ ion accounts for *ca.* 20% of the total ionisation. Very clear evidence for the strength of the boron–oxygen bond is to be seen from the fact that whereas 93% of all the ions from (I) contain at least two B–O bonds 38% of the ions from (II) contain no B–S bonds at all. This stability dominates the spectrum of $(MeO)_3B$ which fragments into relatively few ions: the eight largest peaks from this compound account for 96% of all the ions formed. In addition the thioborate appears to give rise to fairly high yields rearrangement ions such as $MeSCH_2^+$, $MeSH^{+\cdot}$, $MeSSMe^{+\cdot}$, *etc.* Analogous products from (I) are not observed to be significant.

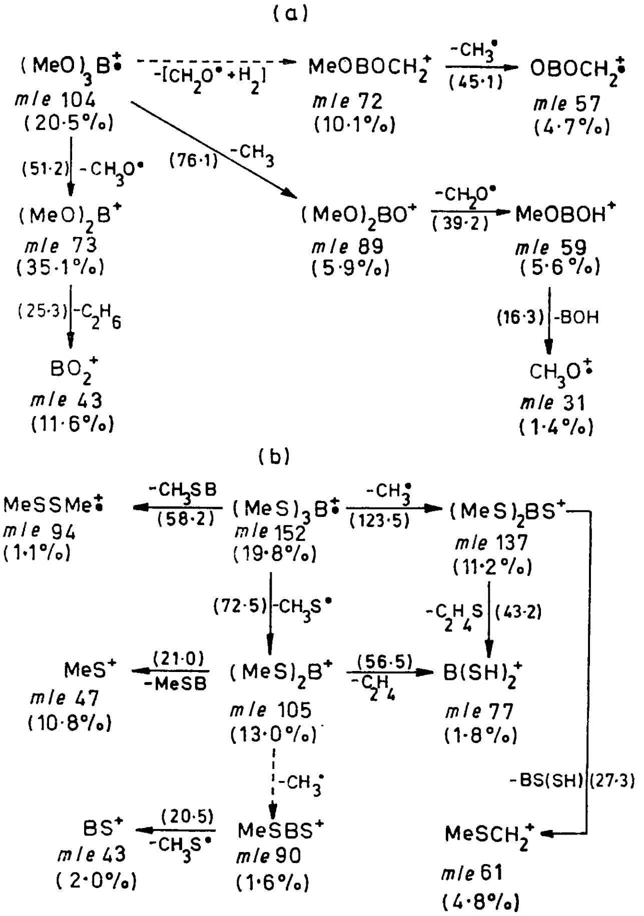

FIGURE 2 Postulated principal fragmentation paths (^{11}B species only). Heavy arrows indicate confirmation by observed metastable ions (in parentheses). The percentages are expressed in terms of total ionisation. (a) Trimethyl borate (I) and (b) trimethyl thioborate (II)

Fragmentation Paths.—The occurrence of metastable ions in the mass spectra of (I) and (II) has permitted the deduction of postulated fragmentation paths for the principal ions. These are shown in Figure 2 together with the total percentage yields for the ^{11}B-containing species only.

The scheme presented for trimethyl borate (I) is essentially the same as that deduced by Fallon *et al.*[10] although we would disagree with their assignment of the metastable ion at *m/e* 24·6 to the transition *m/e* 75 ⟶ 43, corresponding to the loss of methanol from the species $(MeO)BO(OH)^+$. An ion of this mass value does not appear to be significant in our spectrum, and, furthermore, the intensity of *m/e* 24·6 compared to that of the ion at *m/e* 25·3 leads us to suggest that the former arises from the decay *m/e* 72 ⟶ 42 for the ^{10}B isotopic analogue of the ion *m/e* 73. No metastable ion was observed for the formation of $MeOBOCH_2^+$ and the fragmentation route shown as a dotted arrow is postulated on the basis of the energetics for this transition as proposed by Wada and Kiser.[9]

As is expected from the more extensive fragmentation of trimethyl thioborate the decomposition map of this compound is more complex involving a greater degree of branching of the decay routes. The two primary decomposition modes of the parent ion to give $(MeS)_2B^+$ and $(MeS)_2BS^+$ are analogous to those observed from (I) but subsequent decompositions of these ' first generation ' daughter ions are to different ions in nearly every case. It is interesting that the proportion of the charge carried by ions which are postulated to result from the decomposition of ions of the type $(MeX)_2B^+$ compared to those from $(MeX)_2BX^+$ is very much greater for when X = O (3·6 : 1) than when X = S (1·7 : 1).

DISCUSSION

The results obtained in the present work support a a conclusion which is borne out by the information derived from other studies. This is that despite the strength of the B–O bond (*ca.* 120 kcal mol^{-1}),[11] arising from the back-donation of π-electron density from the oxygen to the boron atom, the presence of additional oxygen–boron bonds produces a mutual labilising effect so favouring fragmentation of the parent ions from such compounds.

For the compounds under investigation we see that the $(P - MeO)^+$ ion is formed in high yield and that the major decay route appears to take place *via* this ion. The mass spectra of the higher trialkyl borates have analogous ions as their base peaks.[10] A similar situation concerning the relative stabilities of the parent ions is observed [4] in the mass spectra of $PhB(OMe)_2$ (III) and $PhB(SMe)_2$ (IV) where the relative intenstities are 68 and 100% respectively. One might postulate that in the case of (III) the presence of π-interaction between the benzene ring and the boron atom is participating to some degree, as implied by our work on phenyl boronic acid.[3] Certainly in the mass spectrum [8] of the one compound of this type in which the π-interaction would be expected to be reduced, namely $HB(OMe)_2$, the $P^{+\cdot}$ ion is the base and the $(P - MeO)^+$ ion intensity is 65%.

Direct energetic data in support of our contention is fairly sparse but from the appearance potential data of

---

[11] T. L. Cotterell, ' The Strengths of Chemical Bonds,' Butterworths, London, 1958, 2nd edn.

Wada and Kiser[9] one concludes that $D[(MeO)_2B-OMe]^+$ is of the order 45 kcal mol^{-1}.

EXPERIMENTAL

Trimethyl thioborate was prepared by the established literature method[12] and was distilled several times, the middle fraction being used for the determination of the mass spectrum. A redistilled commercial sample of trimethyl borate was employed. The data were obtained using an A.E.I. MS902 mass spectrometer with an electron beam energy of 70 eV and source temperature of *ca.* 150 °C. In general only those peaks of relative intensity of greater than 5% were considered. The interpretation of the identities of the ion abundances came from isotopic patterns using the values of the naturally occurring isotopic mixtures of boron and sulphur (^{10}B, 20%, ^{11}B, 80%; ^{32}S, 95%, ^{33}S, 0·76%, and ^{34}S, 4·2%).

We thank the S.R.C. for grants in support of this work.

[1/2454 *Received, 22nd December*, 1971]

---

[12] R. H. Cragg, M. F. Lappert, and B. P. Tilley, *J. Chem. Soc.* (*A*), 1967, 947.