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REVIEW

MASS SPECTRA OF BORON COMPOUNDS

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CONTENTS

I. INTRODUCTION

The use of mass spectrometry in boron chemistry has expanded rapidly over the last ten years. A review covering the topic up to 1964 [24] quoted only 46 references and a recent book [233] quoted 267 references for the main Group III elements as a whole, whilst this present review, comprehensive up to the beginning of 1973, contains over 400. Mass spectra of boron compounds are simplified by the $^{11}B/^{10}B$ isotope ratio which facilitates the ready identification of boron-containing fragments and enables the number of boron atoms in a particular fragment to be calculated. Mass spectrometry has been used in boron chemistry not only for characterisation of compounds or for the determination of molecular weights by precise mass measurement of molecular ions, but also, in conjunction with gas chromatography, for the separation and identification of small amounts of material contained in mixtures. Computers have been used to produce the spectrum of one component from a mixture. The isotope ratio has itself been determined from the abundance of each isotope in a particular fragment ion, and vapour phase studies have produced enthalpies and bond dissociation energies from appearance potentials obtained for boron-containing ions.

Although the mass spectra of boron compounds have appeared throughout the literature they have been reviewed only twice, covering the period until 1964 [24], and the period June 1966 to June 1970 [49]; neither dealt with the topic in detail. This review endeavours to give a comprehensive account of boron mass spectrometry. The review has been divided into sections covering each of the major elements found bonded to boron in turn.

The text covers papers where detailed mass spectral information can be found. References to papers in which mass spectra are used only for identification of the compound can be found in the table after each section. These tables contain all the references appropriate to the section and comment on the content.

II. BORON

Boron has two naturally occurring isotopes ^{11}B and ^{10}B. The approximate 4/1 ratio of consecutive peaks facilitates the location of boron-containing fragments and by statistical evaluation the number of boron atoms contained in a particular fragment can be calculated.

Mass spectrometry was first used to determine the $^{11}B/^{10}B$ isotope ratio by Ingram [184], who recorded the positive ion spectrum of boron trifluoride and calculated a ratio of 4.59/1 [73] for $^{11}B/^{10}B$ of the BF_2^+ ion. Thode [374, 375] compared the isotopic content of various boron mineral deposits and found that after they had been converted to boron trifluoride they gave ratios which varied between 4.27 and 4.42 depending upon the source of the boron. Similar results have also been obtained for boron trifluoride [392, 315] and borax [291]. Lehman [230] found that ions produced from boron hydrides have a lower ratio of 4.00 and later [229] suggested that formation of the BF_2^+ ion from boron trifluoride was isotope-dependent as it was produced when the "elastic limit" is exceeded during asymmetric vibration leading to a heavy isotope weight value for the ratio. A study of the $Na_2BO_2^+$ peaks of borax [263] established the currently IUPAC-accepted value of 3.95–4.10 for the $^{11}B/^{10}B$ isotope ratio. Isotope ratio studies have also been made on BF_3 [204, 273], Me_3B [190], $(MeO)_3B$ [309], and various non-volatile boron compounds [26, 239], and the results are summarised [106], see also Table 1.

The boron content of waters has been determined using isotopic dilution [2] with irradiated ^{11}B and the boron content of various materials [394] has been determined from the number of helium atoms produced by the thermal and epithermal $^{10}B(n, \alpha)$ reaction. Studies of the dissociation energy of the homonuclear diatomic molecule B_2 showed boron to be essentially monoatomic in the gaseous phase [55, 62, 386].

III. METAL BORIDES

Mass spectral investigation of vapour produced in a Knudsen effusion cell produced ions for a zirconium–boron [382] system, and the heat of formation of zirconium diboride was calculated from the appearance potentials found for the ions. The hexaborides of lanthanum [380], calcium, barium and cerium [381] have been studied, but later work [144, 145] could not confirm the results. The dissociation energy of gold boride [139] and heats of atomisation for uranium boride, cerium boride and uranium diboride [140] have also been determined by mass spectral investigation of their vapours (Table 2).

IV. BORON–HYDROGEN COMPOUNDS

The mass spectra of boron hydrides were reviewed in 1961 [351], and briefly in 1968 [95]. References to individual boranes are tabulated (Table 3) at the end of this section.

The spectrum of the parent region of pentaborane(9) is shown in Fig. 1.

TABLE 1

BORON ISOTOPE RATIO INVESTIGATIONS

Compound	Comment	Reference
BF_3	$^{11}B/^{10}B$ ratios produced were generally high	184, 204, 229, 315 374, 375, 392
B_nH_n	$^{11}B/^{10}B$ ratio 4.00	230
Na_2BO_2	$^{11}B/^{10}B$ ratio 3.95–4.10	239, 263, 291
$(CH_3)_3B$	Ratio high	190
$(CH_3O)_3B$	$^{11}B/^{10}B$ ratio 4.15	309
$(CH_3BO)_3$	$^{11}B/^{10}B$ ratio 4.00	230

TABLE 2
METAL BORIDE DATA

Compound	Comment	Reference
ZrB_2	Heat of formation 72.1 kcal · $mole^{-1}$	382
LaB_6	Disoc. energy 5.7 eV	380
CeB	Disoc. energy 4.3 eV	381
	Heat of atomisation 72 ± 5 kcal · $mole^{-1}$	140
AuB	Disoc. energy 85.2 ± 5.0 kcal · $mole^{-1}$	139
UB	Heat of atomisation 76 ± 8 kcal · $mole^{-1}$	140
UB_2	Heat of atomisation 227 ± 10 kcal · $mole^{-1}$	140

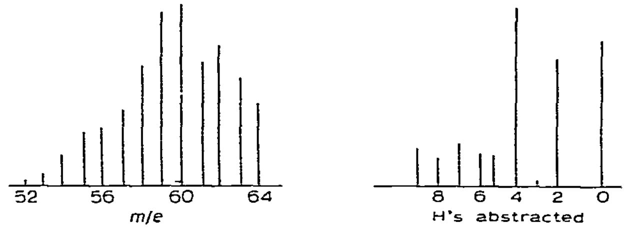


Fig. 1. B_5H_9. (a) Polyisotopic. (b) Monoisotopic

It can be seen from the monoisotopic spectrum, that the spectrum represents successive hydrogen loss superimposed on the B_5 isotopic pattern. This is typical of all boron hydride spectra; there is usually an intense parent region followed by peak groups at each lower B_n falling off in intensity as $n \rightarrow 1$. Thus the main features of boron hydride spectra are successive loss of hydrogen coupled with, to a smaller extent, successive boron loss. Polyisotopic spectra have been used mainly for the identification of the molecular ion and hence the formula of the compound. Before detailed examination of the fragmentation processes could be made, it was necessary to reduce the spectrum to a monoisotopic form. This was achieved physically by ^{10}B isotope enrichment studies or mathematically by a study of the contribution of each isotope to each fragment peak. Recently the latter has been studied by computer analysis [260, 261]. A least squares technique was applied to each B_n peak region in turn, in order to generate the best monoisotopic fit for the polyisotopic data supplied. The generated spectra were found to be in good agreement with the monoisotopic spectra which had been previously reported. Incorporation of a further parameter enabled the program to be applied to boranes containing one or two heteroatoms. Deuteriated boron hydrides have been widely used to determine which of the various possible fragmentations is responsible for a particular peak in the spectrum. The doubly charged ions of the boron hydrides [7] have been examined and the conclusion that twin cage boron hydrides have the largest double charges has been proposed.

A. Stable boranes

Diborane. A review of diborane [235] which included a short section on mass spectra has appeared recently. Deuteriated diborane [91] studies revealed that the fragmentation was only slightly affected by the substitution of D for H. The spectra of partially deuteriated diboranes [96] were found to be unresolvable. Negative ions [285, 286] are primarily formed by a pair ionisation, and the spectra are similar in form to the positive ion spectra. The chemical ionisation of diborane [357] in methane showed it to be ionised by dissociative proton transfer and hydride abstraction from the $(P-1)^+$ ion, and the relative proton affinity of the diborane was also determined. Molecular beam studies [364] produced fragments of higher intensity than had been previously observed.

Tetraborane. Tetraborane has been the subject of a detailed deuteriation study [118] with the aid of metastable transitions. However, only one metastable transition, which involved loss of a boron atom, was noted:

$$B_4D_2^{+\cdot} \rightarrow B_3D_2^+ + .\dot{B}.$$

but it was not detected in the unlabelled compound. Many more metastables were observed for the deuterium labelled compounds, and some losses of 3X where X = H or D were observed. Specific labelling of one boron atom [299] showed that the fragments $B_3H_x^+$, $B_2H_x^+$, $B_1H_x^+$ were formed in part by a non-random dissociation process of the $B_4H_x^+$ framework. The chemical ionisation spectrum [357] produced ions by dissociative proton transfer and hydride abstraction from the $(P-1)^+$ ion.

Pentaborane. Pentaborane(9) [92] showed a marked tendency for loss of 2 or 4 hydrogen atoms from the parent, pointing to a five-membered ring structure. The rapid loss of hydrogen from pentaborane during mass spectral analysis [383] was found to be inhibited by traces of ammonia. Bond dissociation energies [287] have been calculated for the 1 and 2 isomers by an extended Hückel method, leading to the observation that the 2 isomer has a larger B–X bond dissociation energy and hence is the more stable species thermodynamically. The chemical ionisation spectrum of B_5H_9 showed ions of the form $(P+1)^+$ and higher P complexes formed by reaction with hydrocarbon ions, whilst that of B_5H_{11} showed only dissociative proton transfer and proton abstraction from the $(P-1)^+$ ions.

Hexaborane. Hexaborane(10) [207] was identified as a product of silent discharge of diborane. It was found to have no B_5H_{11} and B_5H_{10} ion species [135] in its mass spectrum, as was B_6H_{12} [134]. The chemical ionisation spectrum of hexaborane(10) showed that the parent reacted with a number of hydrocarbon ions to form $(P+1)^+$ species and higher P complexes. The molecular beam spectrum of hexaborane(12) [369] has been reported.

Octaborane. Octaboranes [347, 113] have been found to be stable and their molecular beam spectra reported [368, 369].

Nonaborane, decaborane and duodecaborane. Nonaborane(15) has been characterised [99, 338] as was decaborane(14) [193] and duodecarborane(16) [162]. Attempts to calculate the monoisotopic spectrum of $B_{10}H_{14}$ [161] proved difficult as no one $^{11}B/^{10}B$ isotope ratio could be found which would reduce all the peak groups. As a result of mass spectral studies, duodecaborane(16) has been proposed [280].

B. Unstable boranes

These boranes are not found to exist independently, but are found as intermediates in borane reactions and can be characterised by mass spectrometry. Borane produced from boranecarbonyl will be dealt with later.

Borane. Borane has been obtained from the pyrolysis of diborane [121] and appearance potential, ionisation potential and spectral data presented. Differences in reactivity were used to distinguish between BH_x^+ produced by BH_3 and B_2H_6 fragmentation [17] and the bond dissociation energy $D(H_3B{-}BH_3)$ has been calculated [397].

Triborane. Triboranes (B_3H_7, B_3H_9) have been observed as unstable intermediates in the spectra of boron hydrides [337, 364]. A triborane [128, 129], prepared by the reaction of BH_3 and B_2H_6 has recently been identified by mass spectrometry and reported as the first evidence for the existence of a borohydride containing three boron atoms.

Heptaborane. Evidence for heptaborane(13) or -(15) was found in an impure sample of tetraborane [339]. Heptaborane(17) [97] has been proposed as an unstable heptaborane. Computer analysis [262] of the spectra of B_7H_{11}, B_7H_{12}, B_7H_{13} confirmed only the existence of B_7H_{11} as a separate compound; the others could not be identified as independent fragment groups.

Tetraborane(8). Tetraborane(8) [15, 364] was observed as a major intermediate in the pyrolysis of tetraborane(10), tetraborane(8) carbonyl [179] and pentaborane(11), but not in pentaborane(9).

Ion cyclotron studies of several boron hydrides [108] in which both positive and negative ion spectra were obtained, supported previous results and ion-molecule condensation reactions were also observed.

C. Borane complexes

Borane carbonyl complexes. The dissociation of borane carbonyl into carbon monoxide and monoborane has been the subject of considerable interest (see Table 3). The complete spectrum, the monoborane spectrum, appearance potentials of borane fragments and bond dissociation energies for $H_3B{-}CO$ and $H_3B{-}BH_3$ have been determined. ^{10}B isotope enrichment studies have also been used. Tetraborane carbonyl [179, 365] has been studied similarly.

Nitric oxide has been found to form a complex with borane carbonyl [177, 178]. Mass spectrometry was used to show that complexes of different $BH_3CO{:}NO$ ratios can be formed which depend on the original ratio of the reactants.

Borane–amine complexes. The trimethylamine adduct of borane has been examined in conjunction with a study of trimethylamine adducts of the boron halides [215].

The spectra of dimethylamine and trimethylamine borane [243] both showed low abundance parent ions, but large peaks for the $(P\text{–}H)^+$ and $(P\text{–}3H)^+$ ions. The loss of even number of hydrogen atoms was less probable in marked contrast to the boron hydrides where even numbers of hydrogen atoms are lost most readily.

Borane–phosphine complexes. Trihalophosphines and dimethylaminedihalophosphines have been used to stabilise intermediate boranes, BH_3 [311, 313], B_3H_7 [312, 314] B_4H_8 [313] and their mass spectra were characterised.

D. Substituted boranes

Boranes substituted with alkyl, amine, alkoxy, halogeno and mercapto groups will be discussed under the relevant boron–element heading. The structure of beryllium borohydride [64] was elucidated with the help of deuteriation studies, and metastables were noted for the loss of D_2 from BeB_2D_8. The mass spectrum of $B_{10}H_8(N_2)_2$ [277] was compared with that of $B_{10}H_{14}$. The compound showed less fragmentation than the borane; its most predominant ions were $B_{10}H_8N_4^+$ and $B_{10}H_8N_2^+$ and there was no evidence for similar ions with fewer than eight hydrogen atoms. Appearance potentials and metastable ions were recorded for successive N_2 loss.

The tetrahydrofuran derivative of a scandium tris(tetrahydroborate), $Sc(BH_4)_3 \cdot THF$ [283], showed peaks of the greatest intensity in the parent region, but there was also some contribution from hydrogen abstraction. Successive loss of BH_4 as a neutral species produced the major fragment groups,

$$[Sc(BH_4)_3 \cdot THF]^+ \rightarrow [Sc(BH_4)_2 \cdot THF]^+ \rightarrow [ScBH_4 \cdot THF]^+$$

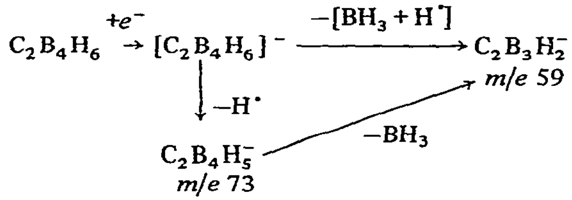
Zirconium borohydride ($Zr(BH_4)_4$) [198] fragmented similarly. Hydrogen abstraction from the parent was observed, and the base peak $Zr(BH_4)_2^+$ was formed by successive loss of BH_4.

E. Carboranes

Carboranes can be classified under two headings, *closo*-carboranes and *nido*-carboranes. *closo*-Carboranes have a closed cage structure and are significantly more stable under electron impact, whilst *nido*-carboranes have an open cage structure and a stability under electron impact similar to that of the boron hydrides.

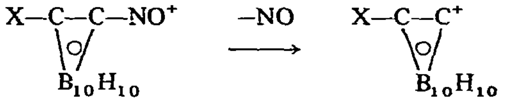
One review of carborane mass spectra has appeared [95].

closo-Carboranes. closo-Carboranes are stable under electron impact. There is a small degree of hydrogen abstraction, but the parent is usually of considerably greater intensity than the fragments. The fragments observed are mainly due to hydrogen abstraction whilst the boron–carbon skeleton remains intact. The stability can be attributed to resonance. Alkyl derivatives of carboranes [151] fragment in almost the same manner as their non-alkylated precursors, and the alkyl side chain hydrogens have the same resistance to abstraction as do those from the carborane skeleton. Peaks are observed for losses typical of the alkyl side chain. Negative ion spectra of *closo*-carboranes [307] showed stable parent regions. The $(P-1)^-$peak was more intense than the molecular ion, indicating that conjugate base anions of the cage were formed. Negative ions were more difficult to form, reflecting the lack of bridge hydrogens in these carboranes; an unusual fragmentation via BH_3 loss to produce the base peak was recorded in the spectrum of 1,2-$C_2B_4H_6$.



nido-Carboranes. nido-Carboranes contain bridged hydrogens and their spectra are very closely similar to those of the boranes. Thus they are considerably less stable than the *closo*-carboranes in that the parent accounts for less of the overall intensity and hydrogen abstraction is more predominant. Negative ion spectra of *nido*-carboranes [44, 45] showed that negative ion formation occurred predominantly via resonance capture and dissociative resonance capture mechanisms. Deuteriation studies showed that a $(P-1)^-$anion, which was specific for the loss of a bridged hydrogen was present.

Substituted carboranes. Chlorocarboranes [305] have been characterised by mass spectra, as was a phosphate carborane heterocycle [150]. Nitrosocarboranes [195] gave a base peak due to the loss of NO, (X = H, Me).



Carboranes were produced by carbon atom insertion into decaborane(14) with alkylisocyanates [182, 183]. Mass spectral evidence from the normal and deuteriated compounds was used in the prediction of a Zwitterionic structure:

$R^+NR'_2[CB_{10}H_{12}]^-$

A tricarbahexaboranyl manganese tricarbonyl π complex [180, 181] $(\pi\text{-}2CH_3C_3B_3H_5)$-$Mn(CO)_3$ showed the presence of three boron atoms, and primary fragmentation was by successive carbonyl loss.

V. BORON–CARBON COMPOUNDS

A. Small boron–carbon species

Mass spectral studies of gaseous boron–carbon [387] species in vapour from a Knudsen cell showed several boron–carbon ions, BC^+, B_2C^+, BC_2^+. Addition of hexagonal silicon

(Continued on p. 172)

TABLE 3
BORON–HYDROGEN COMPOUNDS

Compound	Comment	Reference
A. Stable boranes		
B_2H_6	^{10}B enriched spectrum	17
	Normal spectrum	176
	Enriched spectrum	300
	m/e 32 doublet due to O_2 impurity	301
	B_2D_6 and B_2D_5H	91
	Normal spectrum	29
	Spectrum and appearance potentials	245
	Appearance potentials for B_2H_6, $^{10}B_2H_6$, B_2D_6, $^{10}B_2D_6$	206
	Spectrum and fragmentation	327
	B_2D_6 and 5 partially deuteriated spectra	96
	Pyrolysis	121, 282, 354
	Appearance potentials	397
	Chemical ionisation in methane	357
	Negative ion spectrum	114, 285, 286
	Determination of impurities	401
	Normal spectrum	83
	Molecular beam of pyrolysis	364
	Normal spectrum	337
	Metastable transitions	119
	Normal and calculated monoisotopic spectrum	88
	Positive + negative molecular ion by ion cyclotron resonance	107
B_4H_{10}	Normal spectrum	29
	Negative ion spectrum	285, 286
	^{10}B enriched with 4 position ^{11}B labelled	340
	B_4D_{10}, $B_4H_8D_2$ and normal	118
	$B_4H_8D_2$, $B_4D_8H_2$	298
	$^{10}B_4H_{10}$, $^{10}B_4D_{10}$ and specifically labelled $^{10}B^{11}B_3H_{10}$	299
	Appearance potentials	193
	Chemical ionisation spectrum	357
B_5H_9	Normal spectrum	29
	Negative ion spectrum	114, 285, 286, 328, 179A
	Bond dissociation energies of 1 and 2 isomers	287
	Normal spectrum and fragmentation	327
	Metastable transitions	119
	Ion molecule reactions	169
	Normal spectrum	92, 383
	Normal and B_5D_9 spectra	194
	B_5D_9 and B_5HD_8 spectra	345

(Continued)

TABLE 3 (continued)

Compound	Comment	Reference
	Partially deuteriated spectra	192
	Chemical ionisation spectrum	357, 168
B_5H_{11}	Normal spectrum	29
	Normal and B_5D_{11} spectra	119
	Deuterium labelled	298
	Chemical ionisation spectrum	357
B_6H_{10}	Metastable transitions and spectrum	119
	Partial spectrum	207
	Normal spectrum	135
	Spectrum	20
	Spectrum	237
	Chemical ionisation spectrum	357
B_6H_{12}	Spectrum	237, 130
	Spectrum	128, 129
	Molecular beam spectrum	369
	Spectrum and comparison with B_6H_{10}	134
B_8H_{12}	Molecular beam spectrum	369
	Normal spectrum	347, 99, 113
B_8H_{18}	Molecular beam spectrum	313
B_9H_{15}	Normal spectrum	54, 97, 99, 338, 100, 101, 350
$B_{10}H_{14}$	Spectrum and fragmentation pattern	327, 251
	Tentative normal spectrum	302
	Normal spectrum	114, 193, 161
$B_{10}H_{16}$	Spectrum	160
$B_{16}H_{20}$ $B_{18}H_{22}$	Partial spectra	320
$B_{20}H_{16}$	Spectrum	280
General	Appearance potentials for most borane ions	127, 186
	Various B hydride spectra	243
B. Unstable boranes		
BH_3	Mass spectrum used for analysis only	117
	Spectrum, produced from pyrolysis of B_2H_6	17, 121
	Appearance potentials	397
	Decomposition product of pyrolysis B_5H_{11}	179
	Molecular beam spectrum	364
B_3H_7	Spectrum	16, 314, 364, 337
B_3H_9	Spectrum of possibly stable species	128, 129, 364
B_4H_8	Spectrum, produced of pyrolysis B_4H_{10}	15, 16
	Spectrum	365, 337
	Spectrum confirmed classification as a stable borane	179
B_7H_{11}	Molecular beam spectrum confirmed existence. Spectrum	364

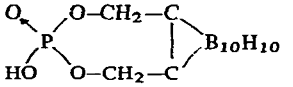
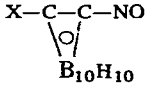
(Continued)

TABLE 3 (continued)

Compound	Comment	Reference
B_7H_{13}	Spectrum	227, 339, 120
B_7H_{17}	Spectrum	97
B_9H_{13}	Tentative spectrum	302, 94
C. Borane complexes		
BH_3CO	Spectrum and D value for $H_3B{-}BH_3$	121, 122, 123
	Appearance potentials	131
	^{10}B enriched spectrum	167
B_4H_8CO	Mass spectrum used for analysis spectra	244, 179, 298, 365
$PH_3CO{=}NO$	Spectra and discussion	177, 178
Me_2NHBH_3	Spectrum	243
$Me_3N{=}BH_3$	Spectra and discussion	243, 215
$Et_3N{=}BH_3$	Spectrum used to check purity	80
$(RNCX{=}BH_3)_3$ (R = Me, Ph, Me; X = O, O, S)	Precise mass identification of parents	281
$F_4P_2 \cdot BH_3$	Identification	311
$HF_2P \cdot BH_3$	Spectrum and formula assignment characterised	334
$F_3P \cdot B_3H_7$	Spectrum	312, 314
$(F_3P)_2 \cdot B_2H_4$	Spectrum	81
$F_2XP \cdot BH_3$ (X = Cl, Br, I)	Spectrum	313
$F_2ClP \cdot B_4H_8$	Spectrum	313
$Me_2NF_2PB_3H_7$	Spectra and appearance potentials	314
$Me_2N_2 \cdot BH_3$	Characterised	189
D. Substituted Boranes		
BeB_2H_8	Spectra including deuteriated, discussion	64
$B_{10}H_8(N_2)_2$	Spectra and discussion	277
$Sc(BH_4)_3 \cdot THF$	Spectra and discussion	283
$Zr(BH_4)_4$	Spectra and discussion	198
E. Carboranes		
$C_2B_3H_5$	Spectrum and deuteriated spectra	346
$(CH_3)_2C_2B_3H_3$	Characterized	151, 344
$C_2B_4H_6$	Spectrum and deuteriated spectra	348
$C_2B_{10}H_{12}$	Characterised	316, 317
$CH_3C_2B_{10}H_{12}$	Characterised	147
$CH_3CB_5H_8$	Spectra and discussion	304
Carboranes (general)	Spectra of a series of small carboranes	152
	Carborane-2,5 characterised	306
	Negative ion spectra *nido*-carboranes	44, 45
	Negative ion spectra *closo*-carboranes	307

(Continued)

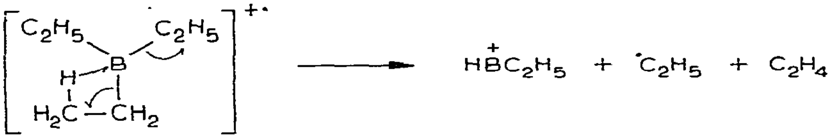
TABLE 3 (continued)

Compound	Comment	Reference
	Review of spectra of carboranes	95
CB_5H_7, $C_3B_5H_{13}$	Characterised	308
$CH_3GaC_2B_4H_6$	Characterised	153
$4ClC_2B_5H_6$	Characterised	305
	Characterised	195
	X = H, Me	
$R^+NR_2(CB_{10}H_{12})^-$	Spectra including deuteriated compounds	182, 183
$(\pi\text{-}2CH_3C_3B_3H_5)Mn(CO)_3$	Characterised	180, 181

carbide produced some boron—silicon ions, BSi^+, $BCSi^+$, BSi_2^+. The heats of atomisation of BCN [138] and OBCN [141] have been measured using a mass spectrometer and OBCN was suggested as a possible formula because the heats of atomisation of BCN and OBCN differ approximately by the dissociation energy of BO.

B. Alkyl-substituted boranes

Trialkylboranes. The primary fragmentation process of both methyl and ethyl substituted trialkylboranes, with the exception of Et_2BMe, produced a peak at *m/e* 41 due largely to the $^{11}BC_2H_6^+$ ion. The di- and trimethyl compounds produced the peak by B—C cleavage, whilst the ethyl compounds achieved the ion by a rearrangement process involving multiple fragmentation followed by hydrogen transfer. It has been suggested [259] that in the case of triethylborane, Et_3B, the rearrangement could involve a four-membered cyclic transition state.



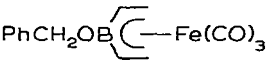
The parent was prominent in most compounds investigated. Loss of the alkyl side chain was the most probable fragmentation process and peaks formed in that manner can be used to determine the structure. The fragment R_2B^+ was noted throughout and can be explained by assuming that the unpaired $2p$ electron from boron is lost in the ionisation process.

Trialkylboranes were briefly reviewed in 1961 [351] and numerous spectra have been reported (see Table 4). These include appearance potential and deuteriation studies. Ionisation potentials of the products of redistribution reactions between BEt_3 and BCl_3 have been obtained [223]. Mixed trialkylborane spectra have been studied [163] with particular reference to the formation of the BR_2^+ ion. Mixtures of alkylboranes and their pyrolysis products have been identified by mass spectrometry after their gas chromatographic separation [202, 343]. Trialkylborane spectra have also been used for examination of $^{11}B/^{10}B$ isotopic abundances [231, 351]; the results varied between different groups of peaks, depending upon whether the fragmentation producing the groups had been isotope-dependent. The trimethylborane molecule behaved similarly to the boron trifluoride [229] molecule in that the Me_2B^+ ion is produced by an isotope-dependent asymmetric vibration. No intermolecular methyl migration was observed in the spectrum of ^{13}C labelled Me_3B over a wide range of conditions [379].

Spectra have been reported for methylvinylboranes [143], including some partial monoisotopic spectra. Lithium tetramethylborate [158] has been characterised by mass spectrometry.

C. Cyclic boron–carbon systems

Some transition metal complexes containing boron–carbon systems have been reported:



(ref. 165)

$Co(C_5H_5)(C_5H_5BR)$
$Co(C_5H_5BR)_2$ R = Me, Ph (ref. 164)

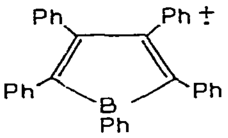
$(HBPz_3)Ru(CO)_2X$ X = Cl, Br, I; Pz = pyrazolyl (ref. 50)

The carbonyl compounds are seen to fragment via successive loss of CO, whilst the cobalt tended to lose the substituent R, followed by ring fragmentation. Of particular interest were two fragmentations which involved breaking of the π bond.

$CoC_5H_5B^+ \rightarrow Co^+ + C_5H_5B$ (*meta* 25.7)

$CoC_9H_7B^+ \rightarrow C_9H_7B^+ + Co$ (*meta* 85.9)

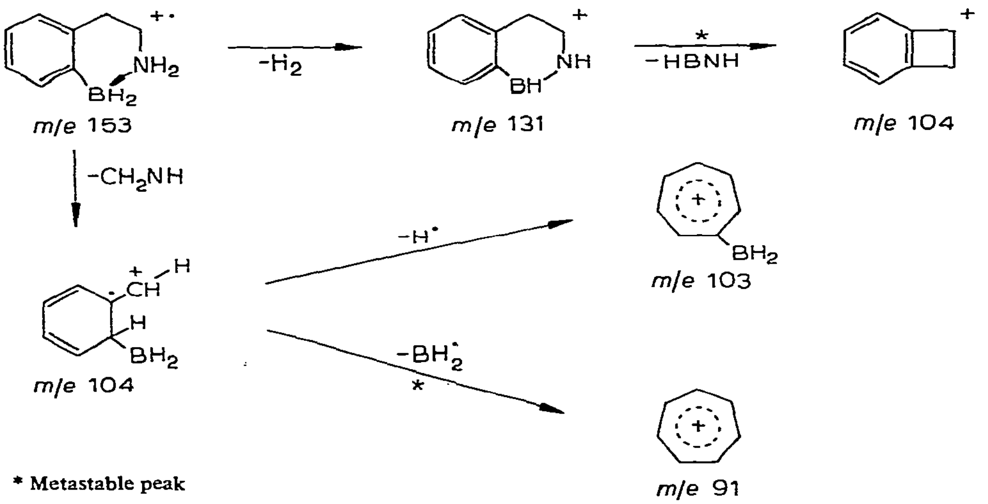
Pentaphenylborole [111] was studied as a complex with pyridine; the base peak at *m/e* 444 was for loss of the pyridine leaving the borole (I) intact, and prominent low mass peaks were observed for pyridine and its fragments.



m/e 444

(I)

The spectra of three cyclic amine boranes [58] have been reported. Loss of one, two or three hydrogens from the parent ion was observed, and the base peak was the $(P{-}2H)^+$ ion, 1,2 borazatetralin, *m/e* 131.

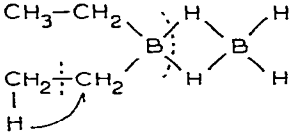


* Metastable peak

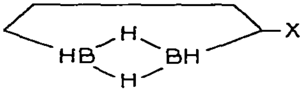
Further fragmentation produced ions at *m/e* 104, 103 and 91. These were assigned either to the formation of a cyclic phenethyl ion (*m/e* 104) or to loss of ethyleneimine resulting by loss of either H$^{\cdot}$or BH$_2^{\cdot}$ in the formation of either a tropylium or a borane-tropylium ion. *N*-Substituted amine boranes were observed to lose tropylium from the $(P{-}2)^+$ ion.

D. Substituted higher boranes

The mass spectra of alkyldiboranes were reviewed in 1961 [351]. A number of ions are observed that can be explained, as were similar ions in boron trialkyls, by assuming that the unpaired 2*p* electron from boron is lost in the ionisation process. If the positive charge is then located on boron, the ions in the spectrum of the diethyl compound can be interpreted as Et$\overset{+}{\text{B}}$Et (A), Et$\overset{+}{\text{B}}$H (B), and Et$\overset{+}{\text{B}}$CH$_3$ (C). This last ion can be explained by the following fragmentation mode:



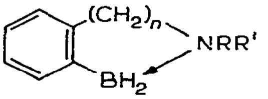
The methyl and dimethyl derivatives of tetraborane [82, 238] and pentaborane [238] have been determined by mass spectrometry and bis(1,2-tetramethylene) diborane [399] has been characterised. The cyclic organodiboranes [393] where X = H, Me, were characterised with the use of ^{10}B isotope enrichment and deuteriation studies:



A series of cyanoboranes $(BH_2CN)_n$ ($n = 4-9$) [359] were identified by mass spectometry.

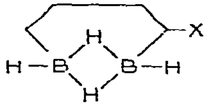
TABLE 4

BORON–CARBON COMPOUNDS

Compound	Comment	Reference
BC, B_2C, BC_2	Ions identified, tentative atomisation	387
BH, HBC_2	Gaseous molecules identified from H_2–BC system	367
BSi, BCSi, BSi_2	Energies	388
BCN	Heat atomisation	136
OBCN	Heat atomisation	141
$B(CH_3)_3$	Spectrum	143, 226, 243
	^{10}B enrichment and deuteriation studies	89, 90, 256
	Spectrum and appearance potentials	142, 231
	^{13}C study of CH_3 migration	379
	^{12}C, ^{13}C studies	21, 335, 336, 370
$B(CH_2CH_3)_3$	Spectrum	143, 223, 243
	Discussion of fragmentation	259
	Redistribution reactions with BCl_3	223
	Spectrum and appearance potentials	190
BR_3(R = Pr, Bu)	Identification after GC separation	343
BRR′R″ (R, R′, R″ = Me, Et, Pr, Pr-i)	Characterisation by GC separation and mass spectrum	163
	Identification of pyrolysis products from trialkylboranes	202
Me_2BCH_2X (X = Cl, N_3, NH_2, OH)	Characterised, discussion of fragmentation	341
Methylvinylboranes	Spectra	143
$LiB(CH_3)_4$	Characterised	158
Ph_5C_4B	Characterised	111
	Spectra and discussion	58

(Continued)

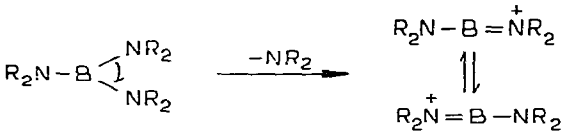
TABLE 4 (continued)

Compound	Comment	Reference
$R_2B_2H_4$ (R = Me, Et)	Spectra and deuteriation studies	398, 351
	Spectrum	238
$B_5H_{10}Me$, $B_5H_9Me_2$	Spectrum	238
B_4H_9Me, $B_4H_8Me_2$	Spectrum	82, 238
$B_{10}H_{13}Et$	Spectrum and fragmentation pattern	327
1,2-Tetramethylenediborane(6)	Characterised	399
 (X = H, Me)	Spectra and ^{10}B studies enriched, deuteriation studies	393
$(BH_2CN)_n$ (n = 4–9)	Identified	359

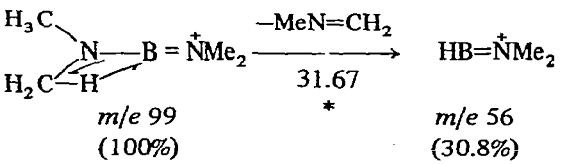
VI. BORON–NITROGEN COMPOUNDS

A. *Aminoboranes*

Tris(dialkylamino)boranes [77] showed intense parent regions. Primary fragmentation to the base ion was via loss of a dialkylamino group.

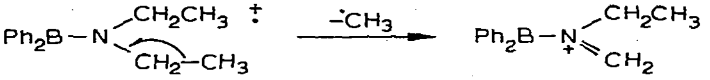


This fragment is probably resonance stabilised and was produced by a β-cleavage, at boron, with respect to a nitrogen atom. Further fragmentation involved loss of alkyl species from one of the amine side chains. The ion $HB{=}\overset{+}{N}R_2$ was formed by hydrogen rearrangement during loss of one amine grouping. This rearrangement can be explained for tris(dimethylamino)borane as follows:



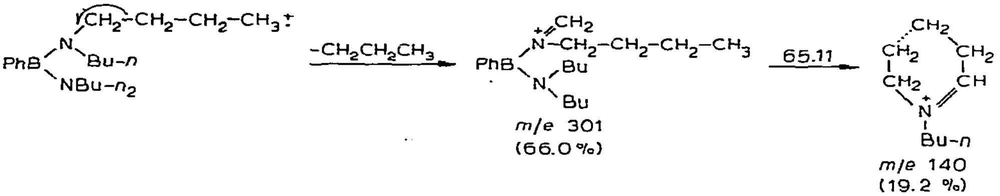
Some fragmentation of charged amine species was observed.

Bis(dialkyl)aminophenylboranes also lost an alkylamino group to form their base peak, and ions produced by hydrocarbon rearrangement from the aminoalkyl side chain to the phenyl group with subsequent loss of a neutral boron amine species were identified. Diethylaminodiethylborane [243] lost an ethyl group to give the base peak, however dialkylaminodiphenylboranes [77] did not lose a phenyl group, but instead lost alkyl fragments from the amine group.



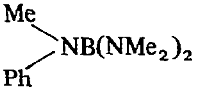
Thus alkylaminoborane fragmentation can be summarised in terms of primary β-cleavage with respect to the amine-nitrogen atom.

An unusual rearrangement occurred in the spectrum of bis(di-n-butylamino)phenylborane [77]. It involved both amine groups and formed a cyclic amino ion checked by precise mass measurement.



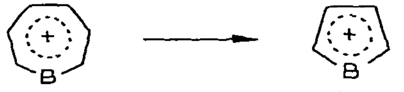
Organoboron-amino derivatives have been noted for their high, doubly charged ions [86], and it was argued that since only aromatic organic systems appear to give such ions, then these compounds may be partially aromatic.

Phenyl-substituted dialkylaminoboranes have been observed to form tropylium ions by intramolecular rearrangement [63, 77]. The mechanism for the rearrangement will be discussed as a part of the boron–oxygen section dealing with 2-phenyl-1,3,2-dioxaboracycloalkanes. No tropylium rearrangement was observed for bis(dimethylamino)methyl(phenyl)aminoborane [63].



$(Me)(Ph)NB(NMe_2)_2$

The boratropylium ion (II) and its fragmentation to the boracyclopentadienyl ion (III) has been observed for phenyldialkylaminoboranes [63, 72] and the mechanism will be



m/e 89 m/e 63

(II) (III)

discussed in the boracycloalkane subsection. In all recorded spectra, substitution of boron by a phenyl group stabilised the molecular ion of the compound.

The appearance potentials of a series of chlorinated dimethylaminoboranes have been reported [223] and the results were discussed in terms of simple Hückel molecular orbital theory [10] and by a new empirical molecular orbital method [217]. The compound H_2BNH_2 [365] has been identified as a reaction intermediate in the pyrolysis of H_3BNH_3

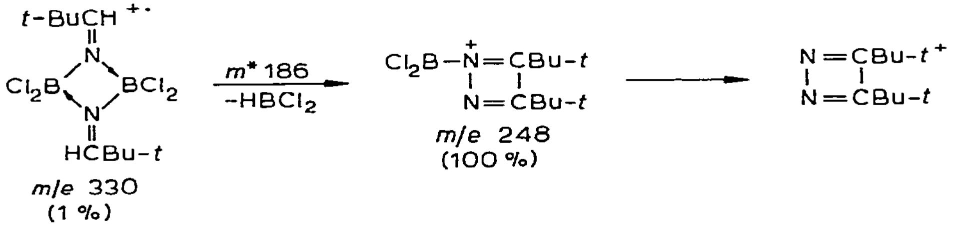
and was characterised. Aminoborane, mono- and dichloroaminoborane were observed in a sample of borazine subjected to radiofrequency discharge [212, 213], and diborane, hydrazine, borazanaphthalene and diborzinyl were alse detected. The dimethylaminopolyboranes $B_3(NMe_2)_5$, and $B_4(NMe_2)_6$ [166] were characterised by mass spectrometry, and were found to be monomeric, the boron atoms forming chains. Both compounds gave parent peaks of about 40% the intensity of the base peak, which was assigned as the $B(NMe_2)_2^+$ ion.

The spectrum of the substituted diborane [48] $(Me_2N)_2B{-}B(NMe_2)_2$ showed a large peak for the $B(NMe_2)_2^+$ ion produced B—B fission which suggests an amine β-cleavage mechanism.

Iminoboranes. The parent peak of iminoboranes is often of low intensity, or cannot be detected, particularly in the spectra of halogenated iminoboranes. In the spectra of the latter, fragments formed by the loss of halogen atoms give strong peaks. Dimeric iminoboranes often give monomers in the vapour phase and thus do not exhibit peaks at higher *m/e* than the monomer parent ion. Group transfer from carbon to boron has been observed [371]. A list of iminoboranes on which mass spectral details have been published was incorporated in a review of iminoboranes [266]. A complete listing can be found in Table 5.

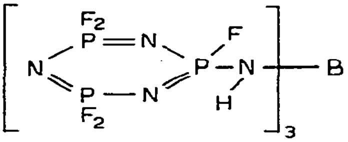
Diphenylketimino dihaloboranes ($Ph_2C{=}NBX_2$, X = F, Cl, Br) have been studied [186]. The mass spectra of the chlorinated and brominated derivatives showed peaks which could be attributed to fragmentation from the dimer by loss of phenyl or halo neutral species, but the dimer parent was not seen. The fluorinated derivative showed no peaks at higher *m/e* than the monomer parent ion and a peak corresponding to a $Ph_2CNBNCPh_2$ ion was seen in the spectra of all three compounds. The spectra of some mesityl and phenyl substituted diphenylketiminoboranes [371] were discussed briefly. The B—N bond proved to be strong as few fragments of its scission were observed. The Ph_2B^+ ion was also observed suggesting phenyl group transfer from carbon to boron. In particular the spectrum of $(Ph_2CNBO_2C_6H_4)_2$ had Ph_2CN^+ and Ph^+ ions as the most abundant species, presumably due to the stabilising effect of the aromatic ring weakening the B—N bond. Conversely $Ph_2BN{=}C(CF_3)_2$ [294] gave a base peak at $(P{-}1)^+$ and fragmented both by loss of phenyl and by scission at the B—N bond to form Ph_2B^+ and $(CF_3)_2CN^+$ ions in high abundance.

The t-butylaldiminodichloroborane [105] primary fragmentation route was via loss of $HBCl_2$ to give a base peak at *m/e* 248. This ion rearranged to a cyclic structure and fragmented further by successive loss of t-Bu—H.



Minor fragmentations from the parent included loss of t-BuCl and formation of the monomer ion.

N-Substituted aminoboranes. The base peak in the spectrum of $(Me_3Si)_2NBClNHSiMe_3$ [396] was formed by loss of a methyl radical. A methyl radical was also lost by $(Me_3Si)_2NBCl_2$, but the base peak was for the $MeSi^+$ ion. The tris-aminoborane (IV) [331]



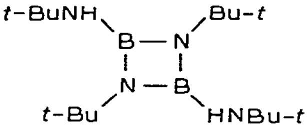
(IV)

lost one complete amino group to form the base peak; all other major ions contained one intact amine ring in contrast to $(S{=}PF_2NH)_3B$ which was stable and fragmented by complete loss of amine group, whilst $PhB(NHPF_2{=}S)_2$ lost either sulphur or benzene in primary fragmentation from the parent ion.

B. Boron–nitrogen cyclic compounds

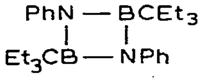
Four-membered B–N rings.

1,3-Di-t-butyl-2,4-t-butylamino-1,3-diaza-2,4-boretane (V) [220,221] was characterised by mass spectrometry and the parent peak was shown to be the base peak. Fragmentation was by successive loss of t-butyl groups followed by rearrangement of a single hydrogen atom.



(V)

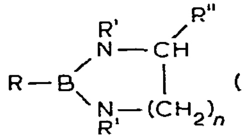
Fragmentation steps were confirmed by metastable ions. Ring stability was shown to persist through fragmentation.



(VI)

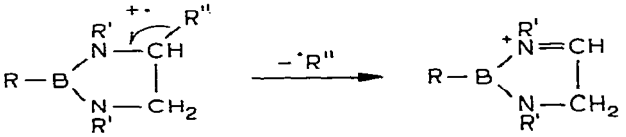
The spectrum of the diazaboretane (VI) [57] had no parent peak but ions for the loss Et, CEt_3 and CEt_3 + 2Et were observed, again the ring remained intact throughout fragmentation.

Five-membered B–N rings. 1,3,2-Diazaboracycloalkanes

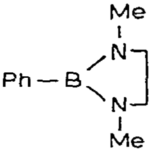


(R=Me,Ph; R'=H,Me,Et; R''=H,Me; n=1,2,3)

The molecular ions of 1,3,2-diazaboracycloakanes [77, 295] were stable. The primary fragmentation was by loss of the annular substituent β to one of the nitrogen atoms (R'') by the normal β-amine mechanism. Fragmentation proceeded via boron-containing ion



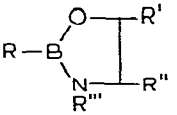
species to produce ions containing two boron–nitrogen bonds of the type $(RBN_2H_2)^+$ or one boron–nitrogen bond of the type $(RBNCH_2^+)$. A few cyclic amine fragment ions were also observed. Although the annular exocyclic substituents were lost with relative ease, the boron substituent was not lost when fragmentation involved scission of a boron–carbon bond. The nitrogen substituents were not lost.



(VII)

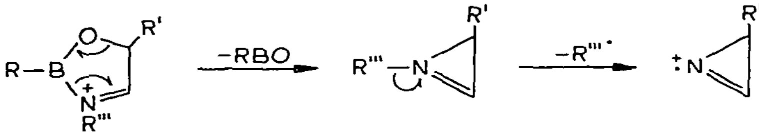
1,3-Dimethyl-2-phenyl-1,3,2-diazaborolane (VII) [186] was observed to give a strong doubly charged molecular ion.

1,3,2-Oxazaboracycloalkanes

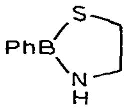


(R=Me,n-Bu,Ph; R'=H,Me,Ph; R''=H,Me,Ph; R'''=H,Me,CH$_2$Ph)

The spectra of 1,3,2-oxazaborolanes [40, 77] and borinanes [77] have been studied by mass spectrometry, and were found to fragment in a similar manner to the diazaboracycloalkanes. The primary fragmentation involved loss of the annular substituent R'' by an amine β-cleavage mechanism. Further fragmentation produced ions of the type $(RBNCH_2^+)$ and, to a smaller extent, $(RBOCH_2^+)$. The further fragmentation of the latter ion when R = Ph will be discussed in the boron–oxygen section dealing with 2-phenyl-1,3,2-dioxaboracycloalkanes. The *N*-substituent was not observed to be lost, although it did lose alkyl side chain components as did the boron substituent. Cyclic amine species were generated by loss of RBO, and were observed further to lose R″.



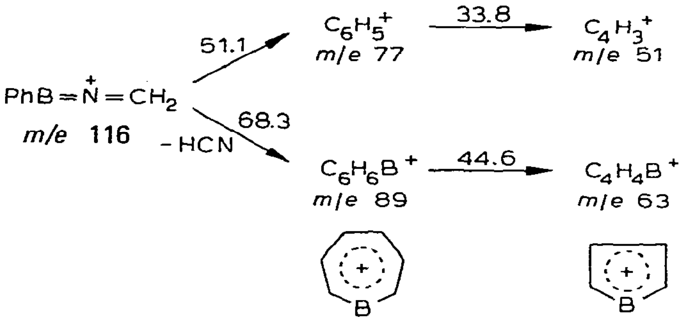
2-Phenyl-1,3,2-azathiaborolane



2-Phenyl-1,3,2-azathiaborolane [76] showed a similar mode of fragmentation to the diaza and oxaza compounds. The primary route was by loss of an annular hydrogen and further fragmentation proceeded through ions of the type $PhBNCH_2^+$. Very few sulphur-containing ions were observed, presumably because the boron-sulphur bond was the weakest bond in the ring and it was in a position to be β-cleaved by the nitrogen atom.

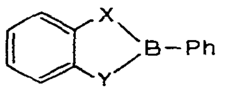
The tropylium ion rearrangement was observed for all three types of boracycloalkane (where R = Ph); the mechanism will be discussed in the boron—oxygen section.

The $RBNCH_2^+$ ion (where R = Ph) was observed to fragment by two specific routes:



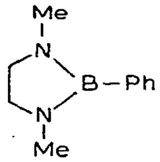
either to the phenyl ion, or by loss of HCN to a boratropylium ion which was observed to further fragment to a boracyclopentadienyl ion [72, 76, 77]. All processes were checked by precise mass measurement. The boratropylium ion was also formed from the $PhB{=}\overset{+}{N}H_2$ ion, and has been reported for similar systems [40, 63].

When the substituent group R was a phenyl radical, the molecular ion was found to be stabilised. No fragment ion species corresponding to loss of the phenyl radical or fragmentation within the phenyl ring were observed even in compounds with particularly stable rings [209], e.g. (VIII) and (IX).



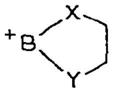
(VIII)

(X,Y = O, NH, NMe or S)

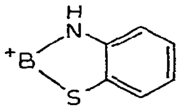


(IX)

Charged phenyl ions were observed. Thus B–Ph substituted compounds do not produce cyclic borenium ions (X) or (XI) as an abundant species in their mass spectra.



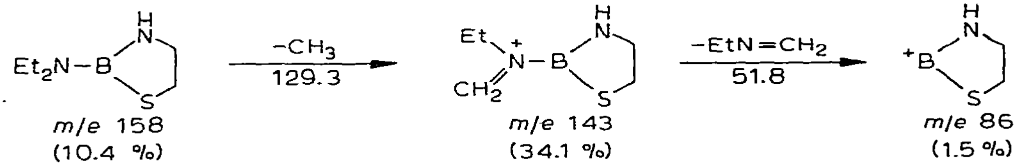
(X)



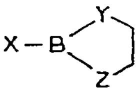
(XI)

(X,Y = O, NH, NMe or S)

However if the exocyclic boron substituent is NR_2 or SR [70] (R = Me, Et, n-Pr) then cyclic borenium ions are formed [76, 77]. 2-Diethylamino-1,3,2-azathiaborolane [76] was observed to fragment primarily by loss of a methyl radical by an amine β-cleavage in the amine side chain. This ion further fragmented by loss of the remainder of the exocyclic amine group.



This second fragmentation can be interpreted as an amine β-cleavage of the cyclic nitrogen atom. Although the cyclic borenium ion was most abundant in compounds containing a cyclic nitrogen atom, it was also found in compounds with oxygen and/or sulphur in the cycle. Compounds with unsymmetrical ring 1,3-substituents were found to give larger cyclic borenium ions than those where the substituents were identical. Cyclic borenium ion formation has also been reported for a compound where X = Me [40]

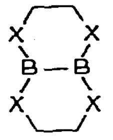


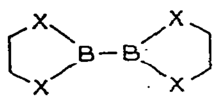
(Y, Z = O, NH, NMe)

but was not observed when X = Cl, Et, OH [209].

From the available data it would appear that cyclic borenium ions may be formed when X = alkyl, NR_2, or SR but not when X = halide, aryl or OR.

Lack of the presence of fragments attributable to cyclic borenium ions was used to explain the structure of some diborane bicycles [48].

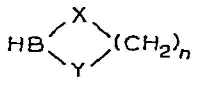

(XII)


(XIII)

(X=O, S, NMe$_2$)

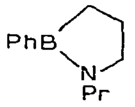
If bond strength can be used as a method for predicting probable cyclic borenium ion formation, then borenium ion formation is more likely to occur in (XII) than in (XIII) where three bonds must be broken. Thus structure (XII) was preferred to structure (XIII).

2-Halo-1,3,2-diazaboracycloalkanes [391] were found to fragment primarily by loss of an annular hydrogen to give the base peak. 2-Hydridoboracycloalkanes (XIV) [293, 332] have been characterised by mass spectrometry.


(X,Y = O,S,NR; n = 2,3)

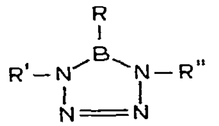
(XIV)

The base peak in the spectrum of 1-n-propyl-2-phenyl-1,2-azaborolane [53] (XV)

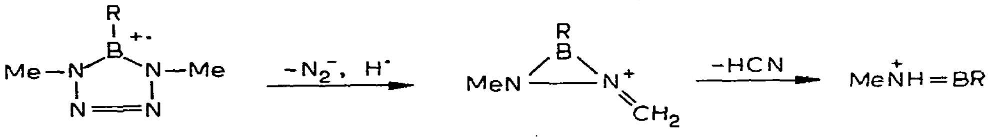

(XV)

correspond to ethyl loss from the parent, consistent with a mechanism involving rupture of the C—C bond β to nitrogen. A rupture of the ring between C_4 and C_5 produced an ion $(C_6H_5BC_2H_4)^+$. A peak at m/e 89 was observed, presumably due to the boratropylium ion, and a peak at m/e 63 was also observed.

Tetrazaborolanes

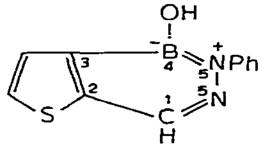

(R = H, D, Et, CH=CH$_2$, Cl, Br;
R' = Me, Et, Ph;
R" = Me, Et, Ph, C$_6$H$_4$Cl)

Substituted tetrazaborolanes [33, 34, 35, 227] were found to have strong molecular ion peaks. Major fragmentation was either by loss of N_2 or by loss of N_2 and H. B-Substitution studies showed that H$^\cdot$ loss occurred from the amine-alkyl side chain and not from the boron substituent to form an ion which further fragmented by loss of HCN.

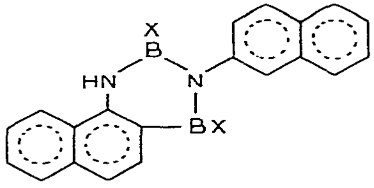


Other fragmentation included loss of R′ and R″ substituents. The compound where $R = H, R' = R'' = C_6H_4Cl$ [227], fragmented to give the base peak by loss of N_2. A minor fragmentation route was by successive loss of Cl.

Six-membered B–N cycles. 4-Hydroxy-5-phenyl-4,5,6-borazarothien-2,3-*c*-pyridine (XVI) [154] was one of a series of similar boron heterocycles reported showing a parent peak, and at higher mass, a peak region assigned to an ethereal form derived from two molecules by abstraction of water. 3,2-Borazaropyridines have been characterised [156], as have the diboradiazano compounds (XVII) [78].



(XVI)

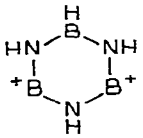


(XVII) (X = Cl, Me)

In both cases the main fragmentation was reported as successive loss of substituent X from the compound. Some halogeno-2,5-diboradihydropyrazines [267] have been reported.

C. Borazines

The mass spectra of borazine, *B*-trimethyl- and *B*-trichloro-borazine were published by Loughran et al. [236], and were compared with their isoelectronic analogues. The fragmentation of the borazines was much greater than that of the analogues, which lead to the conclusion that they were less aromatic. The borazine molecular ion did not produce a doubly charged ion, but the species $B_3N_3H_4$ (XVIII) was found to be doubly charged.



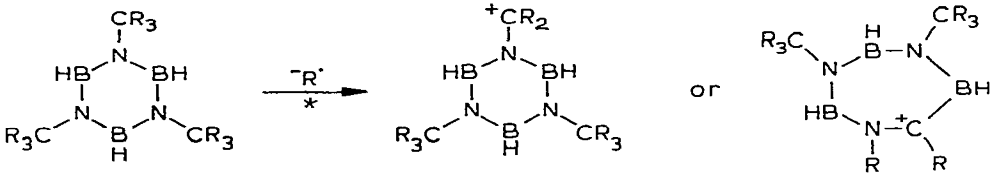
(XVIII)

Ions that were formed by the removal of 2 ring atoms were most abundant, as in the case of benzene, presumably due to the stability of the departing neutral fragments. The proton affinity of borazine has been studied using various mixtures of proton donors

[23, 357] including various hydrocarbons (some of which were deuteriated), ammonia and phosphine. It was concluded that an affinity of 203 ± 7 kcal · mole^{-1} was the best value for borazine. Thus it has a greater proton affinity than most hydrocarbons and phosphine, but less than that of ammonia.

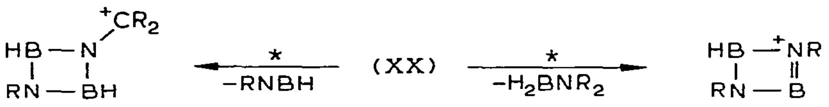
The natural boron isotopic abundances for various ions found in borazine spectra have been calculated [250]. The base peak in the spectrum of tri-*N*-t-butylborazine [272] was the $(P-\text{Me})^+$ ion in which the ring remained intact.

The mass spectra of tri-*N*-alkylborazines (XIX) [325], where the alkyl group is Et, n-Pr, i-Pr, n-Bu, s-Bu, i-Bu or t-Bu, have been reported. The main feature of the spectra was a group of ions which arose by an amine *β*-cleavage in the amine alkyl side chain.



(XIX) (XX)

These fragment species are isoelectronic with the benzyl or tropylium ions observed in the mass spectra of alkylbenzenes. Thus the ion structure could be represented as a tropylium analogue (XX). Deuterium studies were used in the elucidation of the structure but no conclusion as to the structure was reached. Further fragmentation was to a four-membered cyclic structure, either by loss of RNBH or by hydrogen transfer and loss of H_2BNR_2.



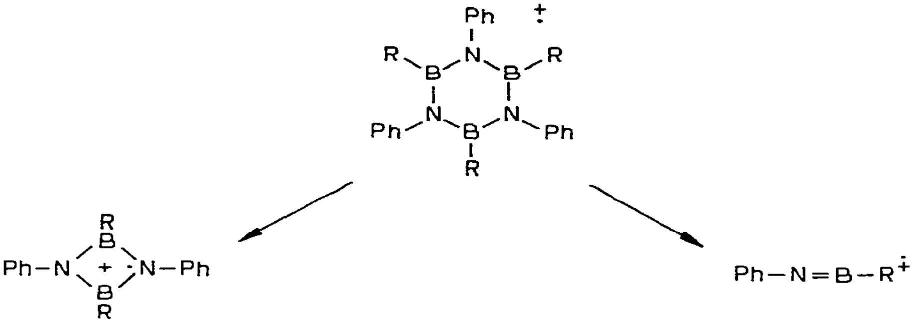
(XXI)

Presumably species (XX) could be represented as an analogue of the cyclopentadienyl ion by which the tropylium ion is seen to fragment. The spectrum of tris(diphenylmethyl)-borazine $(Ph_2CHNBH)_3$ [319] confirmed its structure, as no tetramer peak was present. Fragmentation was by amine *β*-cleavage. the loss of hydrogen from boron, or phenyl from the amine side chain, leaving the ring intact. The hydrocarbon fragments Ph_2C^+, Ph_2CH^+, $Ph_2CH_2^+$ were observed, but Ph_2CN^+ was not.

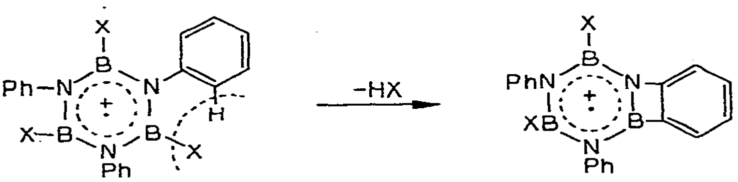
A series of *B*-monosubstituted borazines [19] has been reported where the monosubstituent was MeO, F, Br, and the major ions were tabulated. No trend could be found to join either species or substituent. The photolysis of borazine [303] with various halogenated alkanes produced the corresponding *B*-monohalogenated borazines; when alcohols were used, *B*-monoalkoxyborazines [289] were produced. Their spectra were similar to that of borazine except that there was a general shift to higher mass number caused by the replacement of hydrogen by a heavier substituent; fragmentation of the alcohol side chain produced some new ions in the spectra of the monoalkoxyborazines. Mass spectrometry has been used for the characterisation of *B*-trifluro- and *B*-trichloroborazines [225]. The major fragmentation in trifluoroborazine was due to loss of NH and H to give $F_3B_3N_2H^+$. The observations were consistent with boron—fluorine bonds having a higher stability than the boron—nitrogen cyclic bonds. *B*-Triferrocenylborazine [208] showed no fragmentation, and only the parent and doubly charged parent species were observed.

In the spectrum of 1-methylborazine [18], the base peak was due to the $(P\text{–}H)^+$ ion, whilst in 2-methylborazine it was due to loss of Me, thus the primary fragmentation of both was by an amine β-cleavage where boron was the β atom. These differences were also seen in the dimethylborazines.

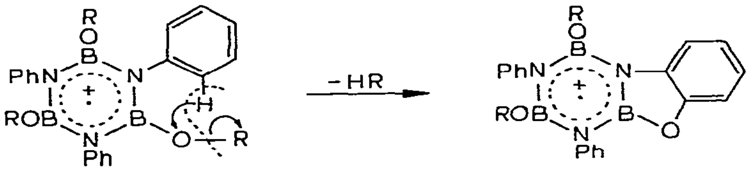
Tri-*N*-phenyl-tri-*B*-alkyl- and -tri-*B*-alkoxyborazines [356] produced a large parent peak which was normally also the base peak, except in cases where alkyl fragmentation was the primary route. The *B*-phenylborazines lost the complete group rather than fragment the phenyl ring. In the alkoxy compounds, the C—O rather than the B—O linkage was cleaved. The *N*-phenyl group was not lost even after ring cleavage and high abundances of PhN^+ and $PhNH_2^+$ were seen. The fragmentation of the nucleus resulted in two main types of ion formed by loss of either one B—N or two B—N units.



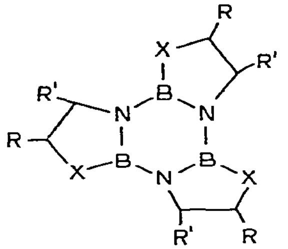
Various rearrangement ions were observed in the spectrum of tri-*N*-phenyltri-*B*-chloroborazine. Loss of two successive HCl fragments was noted, and the species produced had a large doubly-charged ion portion. The loss of HX, where X was the boron substituent, was observed in most of the spectra. The following mechanism was proposed:



When X was an alkoxy substituent the mechanism was similar and the oxygen atoms was retained in the new heterocycle.

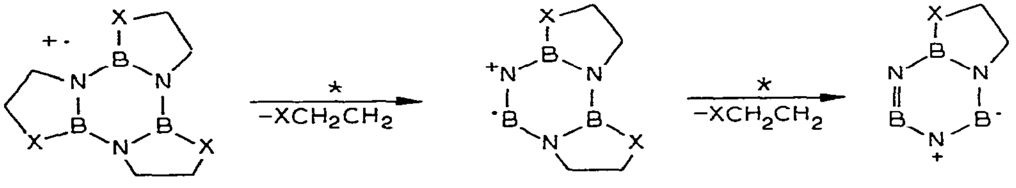


Successively chlorinated tri-*B*-methylborazines have been characterised [227].

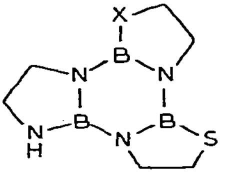


(X = O, S, NH, NMe, NEt;
OCH_2, $N(H)CH_2$, $N(Me)CH_2$, $N(Et)CH_2$;
R = H, Me, Ph; R' = H, Me)

The primary fragmentation of polycyclic borazines [75, 76, 77] was loss of one R′ substituent by an amine β-cleavage mechanism. The major fragmentation was by successive loss of two of the exocyclic rings leaving the nucleus intact.



No ions formed by the loss of 1/3 or 2/3 of the molecules were observed due, presumably, to the high stability of the compounds. A mixed polycyclic borazine (XXII) has also been studied. The loss of either exocyclic substituent was equally probable.

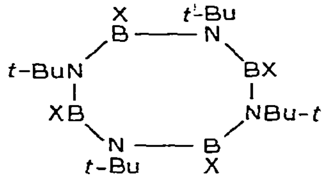


(XXII)

Decomposition of borazine has produced various more complex borazine structures such as $B_6N_6H_{10}$ (an analogue of biphenyl), $B_5N_8H_{11}$ (a triamine analogue of naphthalene) as well as diaminoborazines [224, 242], and diborazinylamine [59] ($B_6H_{11}N_7$) was also identified by mass spectrometry.

Eight-membered B–N rings and bicycles

Borazyne [77, 384] compounds containing an 8-membered boron–nitrogen ring have been studied and details of the fragmentation of the compounds (XXIII) where boron was substituted by chlorine and thiocyanate were



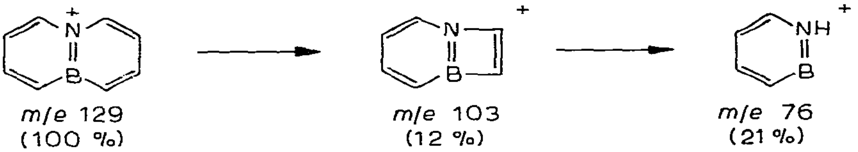
(XXIII)

(X=Cl,NCS)

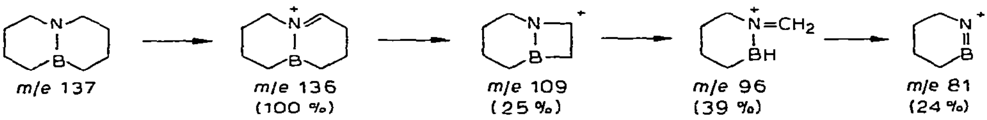
given. The primary fragmentation by loss of a methyl radical left the ring intact. Further fragmentation involved loss of ring atoms. The parent molecular ion of some of the borazynes was not observed [384] but high resolution mass spectra [77] facilitated their identification.

10,9-Borazarophenanthrene, 2,1-borazaronaphthalene and 4,3-borazaroisoquinoline have been studied by mass spectrometry [104]. The spectra of these heteroaromatic boron compounds were interpreted by analogy with related hydrocarbons, and similarities between C=C and $B^-{=}N^+$ units were observed. Fragmentation involving the elimination of one heteroatom usually resulted in the boron remaining with the charged ion, because of the stability of $[R_2B]^+$ ions. α-Cleavage reactions are more important in groups attached to the heteroatoms than with the hydrocarbons, and large differences in β-cleavage reactions in *B*- or *N*-alkyl groups were qualitatively explained using the P.M.O. method.

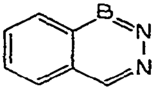
Borazarophenanthrene showed similarities to phenanthrene and diphenylacetylene, although fewer doubly-charged ions were observed. Ions readily lost H_2 or C_2H_2 followed by loss of HCN, and boron substituents were readily eliminated. The naphthalene analogues, also studied by Dewar [79], showed greater fragmentation than the parent hydrocarbon. The fragmentation proceeded by ring cleavage of one benzenoid ring.



The borazarodecalin showed a $(P{-}H)^+$ base peak, formulated as a methylene ammonium ion.



The spectrum of the heterocycle (XXIV) was found to be qualitatively similar to that of the hydrocarbon, without N_2 elimination as found with other diazines. The major differences were suppression of β-cleavage, the low intensity of $(P\text{–}H_2CN)^+$, and the higher intensities of $(P\text{–}Me)^+$ and $(P\text{–}HCN)^+$.



(XXIV)

Boron–nitrogen compounds which have been identified using mass spectroscopy are listed in Table 5.

VII. BORON–OXYGEN COMPOUNDS

A. *Boric oxide and metal borates*

Mass spectrometry has been used to calculate the heat of evaporation of B_2O_3 [296], and the positive ion spectrum of B_2O_3 has been reported. The thermodynamic properties of the negative ions of the lower boron oxides BO and BO_2 have been studied and the heats of formation of the ions calculated [361]. Vapour studies have been carried out on the $B\text{–}B_2O_3$ [185] and $Al_2O_3\text{–}B_2O_3$ [27] systems.

Vapour studies of the $MgF_2\text{–}B_2O_3$ [171, 174] and the $BF_3\text{–}B_2O_3$ [175] systems have shown that the two speices BOF and $(BOF)_3$ exists as their vapours, and their heats of formation have been calculated. Further studies [25, 31] showed that the species B_2OF_4 was also present and its heat of formation was calculated, and BO_2 and BOF_2 [385] were also identified.

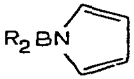
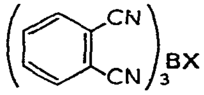
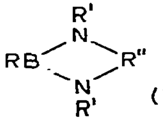
(Continued on p. 193)

TABLE 5
BORON–NITROGEN COMPOUNDS

Compound	Comment	Reference
A. Aminoboranes and iminoboranes		
H_2BNH_2	Reaction intermediate in pyrolysis of $H_3B\cdot NH_3$	365
	Reaction intermediate in pyrolysis of borazine	213
	Spectrum and also $ClHBNH_2$, Cl_2BNH_2	212
$B(NMe_2)_3$	Doubly charged ions	86
	Appearance potentials of halogenated compounds and molecular orbital calculations	10, 217, 218, 223
$Me(Ph)NB(NMe_2)_2$	No tropylium ion observed	63
$PhB(NR_2)_2$, Ph_2BNR_2	Doubly charged ions	86
	Tropylium ions	63
	Boratropylium, boracyclopentadienyl ions	72

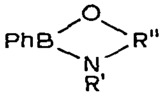
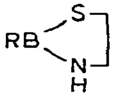
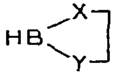
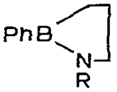
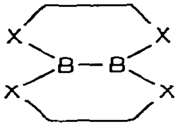
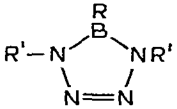
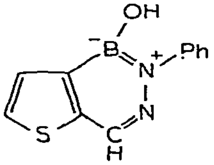
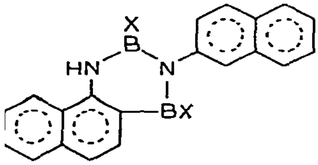
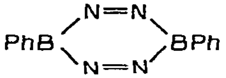
(Continued)

TABLE 5 (continued)

Compound	Comment	Reference
	Borenium ions	209
	Mol. wt. determination, and spectrum	22
$B_3(NMe_2)_5$, $B_4(NMe_2)_6$	Spectra	166
$(Me_2N)_2B-B(NMe_2)_2$	Formation of borenium ion	48
μ-$Et_2NB_2H_5$	Spectrum	188
Iminoboranes	Review	266
$Ph_2C{=}NBX_2$ (X = F, Cl, Br)	Spectra	186
$Ph_2C{=}NB(mesityl)_2$ $PhCH{=}NB(mesityl)_2$	Spectra	371
$Ph_2C{=}NBO_2C_6H_4$	Spectra and discussion	371
$Ph_2BN{=}C(CF_3)_2$	Spectra	294
$X_2BN{=}C(CF_3)_2$	Spectra	237
$Ph_2C{=}NBMe_2$	No parent seen	318
$[Ph(MeS)C{=}NBCl_2]_2$	No parent seen	270
$[Cl_2C{=}NBCl_2]_2$	No parent seen	268
Haloiminoborane	B and halogen recognised by their fragments	162
$(Me_3CCH{=}NBCl_2)_2$	Weak parent	56
$(BuCH{=}NBCl_2)_2$	Spectrum and discussion	105
$(Me_3Si)_2NB(NH)_2NHSiMe_3$	Characterisation	395
$(Me_3Si)_2NBCl_2$	Spectrum	396
$(F_5P_3N_3NH)_3B$, $(S{=}PF_2NH)_3B$, $(S{=}PF_2NH)_2BPh$	Characterisation	331
$(Et_3SiNH)_2B-B(HNSiEt_3)_2$	Characterisation	3
Hydrazinoboranes	Also pyrolysis products (diborazanes)	265
 (X = Cl, F)	Phthalocyanoboron complexes, spectra	271
$PhCX_2N[B(NMe_2)_2]_2PdX$ (X = I)	Characterisation	342
B. Cyclic boron–nitrogen compounds		
$(t\text{-}BuNHBNBu\text{-}t)_2$	Discussion	220, 221
$(Et_3CB{-}NPh)_2$	Discussion	57
	Doubly charged ions	86
	Tropylium ions	63
	Boratropylium, boracyclopentadienyl ions	72
(R = Ph)	Discussion	295
(R = halogen)	Discussion	391

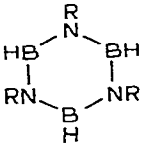
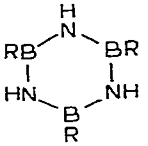
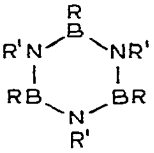
(Continued)

TABLE 5 (continued)

Compound	Comments	Reference
(R=H)	Discussion	293, 332
	Borenium ions	209
	Borenium ions	209
	Detailed fragmentation	5, 40, 6
	Boratropylin, Boracyclopentadienyl ions	72
	Detailed fragmentation	76
 (X,Y = O,S,NR)	Characterisation	293
	Discussion	53
 (X = O, S, NMe$_2$)	Borenium ion formation, discussion	48
	Spectra and discussion	33, 34, 35, 227, 124
	Discussion	154
3,2-Borazaropyridines	Characterisation	156
	Discussion	78
Halo-2,5-diboradihydropyrazines	Characterisation	267
	Acetylated identification	279

(Continued)

TABLE 5 (continued)

Compound		Comment	Reference
Borazine		Spectrum	4
		Spectrum also tri-*B*-methylated tri-*B*-chlorinated and hydrocarbon analogues	236
		Chemical ionisation spectra with various hydrocarbons	23, 324, 357
		Calculations of borazine isotopic abundances	250
		Ionisation potential	211
	(R = Me)	Ionisation potential	211
	(R = t-butyl)	Discussion	272
	(R = Et, n-Pr, i-Pr, n-Bu, s-Bu, i-Bu, t-Bu)	Discussion	325
	(R = Ph_2CH)	Discussion	319
	(R = MeO, F, Br)	Monosubstituted characterisation	19
	(R = Cl, Br)	Monosubstituted characterisation	303
	(R = MeO, EtO)	Monosubstituted characterisation	289
	(R = F, Cl)	Discussion	225
	(R = F)	Identifucation	333
	(R = ferrocene)	Identification	208
	(R = amino)	Characterisation	228
	(R = chloromethyl)	Characterisation	228
	(R = pentamethyl vinyl)	Characterisation	201
	(R = Me)	Spectrum	243
		Ionisation potential	211
	(R or R′ = H or Me)	Monosubstituted characterisation	18
	(R′ = Ph, R = Me, Et, Bu, Ph, Cl, MeO, i-PrO)	Discussion and spectra	356
	(R′ = alkyl, R = Ph)	Identification	8
	(R′ = Me, R = Cp)	Identification characterisation	373
Polycyclic Borazines		Discussion	68, 76
$B_5N_5H_8$, $B_6N_6H_{10}$		Pyrolysis products of borazine	224, 242
Diborazinylamine $B_6H_{11}N_7$		Characterisation	59
Cyclotriborazanes		Discussion	46, 47

(Continued)

TABLE 5 (continued)

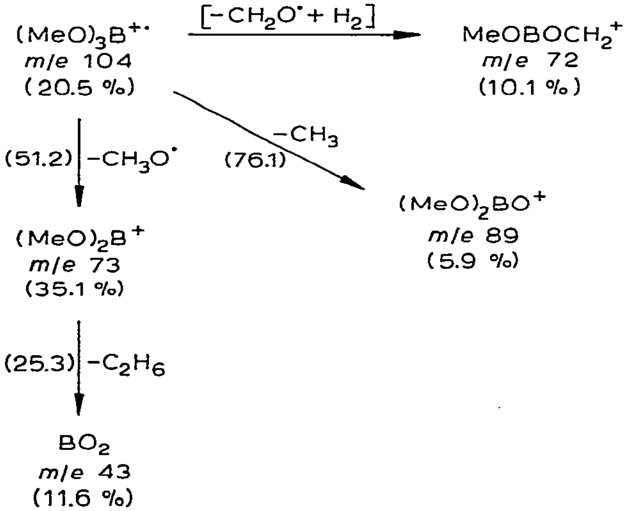
Compound	Comment	Reference
Borazynes: $(XBNBu\text{-}t)_4$ ($X = Cl, NCS$)	Discussion	384
10,9-Borazarophenanthrene	Discussion and comparison with analogous hydrocarbons	104
2,1-Borazaronaphthalene		79, 104
4,3-Borazaroisoquinoline		104
10,9-Borazadecalin	Discussion	79

Metal borate vapours have been studied, their mass spectra characterised and heats of formation found for the following metals: Li, Na, Be, Mg, K, Rb, Cs, Nd, (for references see Table 6). Studies to determine the $^{11}B/^{10}B$ isotope ratio have been carried out on samples of borax [329] (see also Section II).

B. Acyclic borates

The spectrum of trimethylborate [226, 389] has been reported and the heats of formation for the principal ions calculated. Higher trialkylborates [115] $B(OR)_3$ (where $R = Et$, n-Pr, n-Bu) were studied and a fragmentation pattern for $(MeO)_3B$ presented, which has since been further defined [73].

The primary fragmentation of trimethylborate, to produce the base ion was loss of one methoxy group, further fragmentation was to the BO_2^+ ion. Other fragmentation routes of the parent were by loss of methyl and via loss of $CH_2O^{\bullet}$ and hydrogen, though the latter could not be verified by a metastable ion.



The fragmentation of the higher trialkylborates was similar to that of trimethylborate. Alkyl side chain loss was observed and a rearrangement process involving hydrogen transfer and alkene elimination was studied.

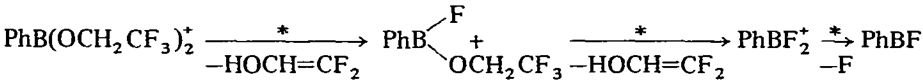
$$RCH_2CH_2OB\langle^{+\cdot} \xrightarrow{-RCHCH_2} HOB\langle^{+\cdot} \qquad (R = H, CH_3, CH_3CH_2)$$

Thus the most prominent peaks in the spectra were due to the parent P^+,$(P–R)^+$ and $(P–OR)^+$. Rearrangement ions of the type ROBOH were prominent giving rise to the highest peak in isopropylborate. The parent ions of alkylalkoxyboranes were of markedly lower abundance than those of trialkylborates.

Mass spectrometry has been used to show that exchange reactions occur between mixtures of trialkylborates [116, 170]. The two precursors were first independently run, then the mixture. Peaks in the mixture which showed greater relative intensity than those in the summed component spectra were tentatively assigned to mixed ester ions. The mixed ions $B(OMe)_2OEt$ and $BOMe(OEt)_2$ were observed in the spectrum of a mixture of trimethyl- and triethylborates. Primary fragmentation via loss of an ester group was identified by metastable analysis and also the alkene elimination via hydrogen rearrangement. Assignments were limited in that they could only be qualitative owing to difficulty in assigning sensitivities. The ionisation potentials of molecular ions BX_2Y^+ and $BXYZ^+$ (where X, Y, Z = F, Cl, Br, I, NMe_2, OMe, OEt, OPr, SMe, Et) [217, 218] have been obtained by redistribution reactions and characterised mass spectrometrically. Molecular orbital calculations were carried out to estimate the lone pair orbital interaction of adjacent atoms from the ionisation potential data.

The spectrum of $HB(OMe)_2$ [226] has been reported. The fragmentation patterns of $B(OR)_3$, F_2BOR [400] (where R = Me, Et) have been tabulated and correlations made between the spectra. Me_2BOBMe_2 [214] showed a weak parent P^+ with base peak $[CH_3BOH]^+$. Rearrangement ions were formed, but the only metastable-supported transition was for loss of MeBO from the $[P–Me]^+$ ion. The removal of two electrons was facilitated by the site of π-electron density, and $(MeBOBMe)^{2+}$ was found.

The fragmentation of $PhB(OH)_2$ [74] has been assigned. The primary route was rearrangement to lose BO_2H leaving benzene as the positive ion; the ion $B(OH)^+$ was also identified. Phenyl and diphenyl alkoxyboranes ($PhB(OR)_2$, Ph_2BOR) [63, 77] have been observed to form tropylium ions. Fluorination of the alkyl side chain [77] produced fluorinated rearrangement species. Rearrangement of fluorine to the boron atom was also observed.

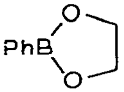


$$PhB(OCH_2CF_3)_2^{+\cdot} \xrightarrow[-HOCH=CF_2]{*} PhB\begin{smallmatrix}F\\ \\OCH_2CF_3\end{smallmatrix}{}^{+} \xrightarrow[-HOCH=CF_2]{*} PhBF_2^{+\cdot} \xrightarrow[-F]{*} PhBF^{+}$$

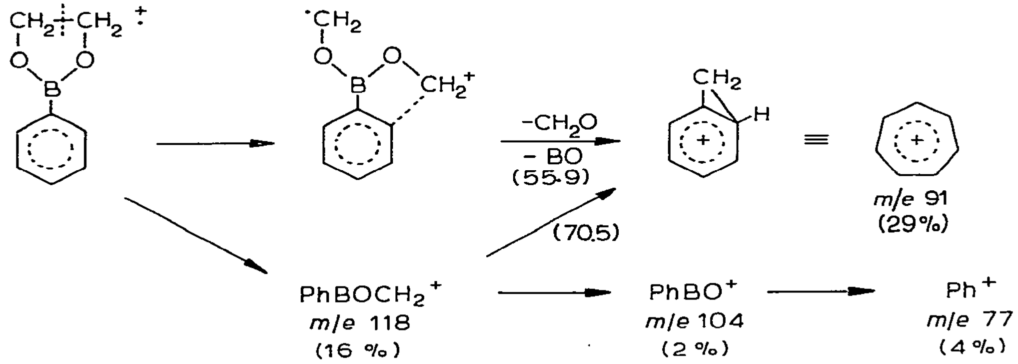
$Me_2C{=}NOBMe_2$ has been fully reported. The base peak was produced by N–O scission leaving Me_2CN as the charged particle, and Me_2BO^+ was also observed [187]. 2,4,6-t-$Bu_3C_6H_2B(X)OBu$ [362] (X = substituted phenyl) and related compounds have been characterised and their fragmentations compared in terms of steric hindrance. Tetramethoxydiborane fragmented to $B(OMe)_2^+$ (the base peak) by B—B bond scission [48]. The molecular ion was the base peak in the structure of ethoxydecaborane $C_2H_5OB_{10}H_{13}$ [297].

C. Cyclic boron–oxygen compounds

The spectrum of 2-phenyl-1,3,2-dioxaborolane [67, 71] showed a prominent peak at *m/e* 91, which was assigned as a tropylium ion. The fragmentation pattern of 2-phenyl-1,3,2-dioxaborolane [68] indicated an unexpectedly high stability of the parent ion.

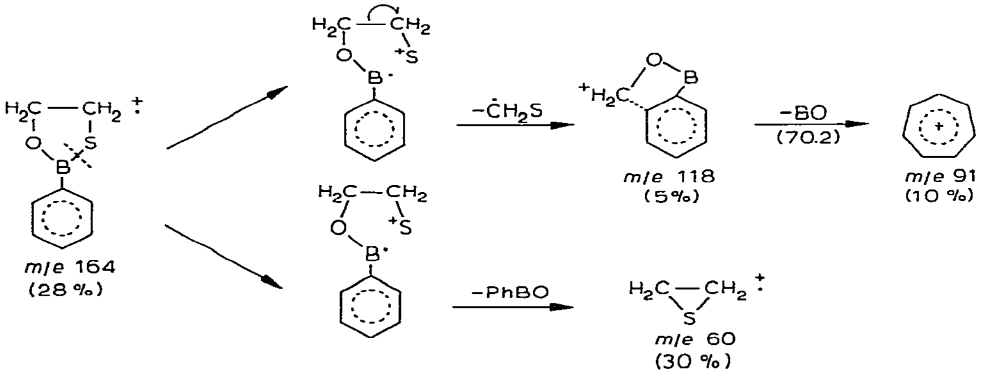


Primary fragmentation was by C_4-C_5 bond fission, which produced either the tropylium ion by hydrocarbon rearrangement and loss of $CH_2O + BO$, or a $PhBOCH_2^+$ ion which further fragmented to $PhBO^+$ and Ph^+.

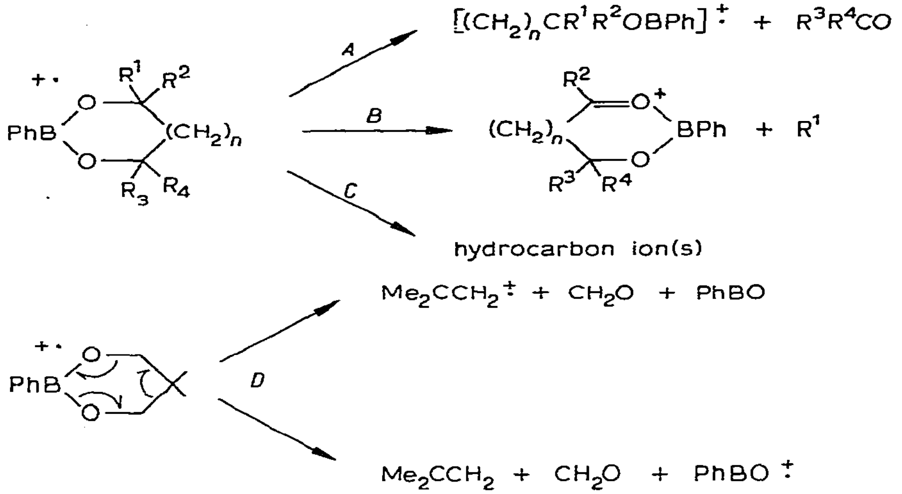


A study of 2-phenyl-1,3,2-oxathia- and dithia-borolanes [67, 68] showed that these compounds also exhibited tropylium ions, although in the latter compound only in low intensity, and that the intensity of the ions could be directly related to the bond energies of the various atoms in the borolane ring.

2-Phenyl-1,3,2-oxathiaborolane [68] was observed to fragment by B—S fission. The fragmentation produced either a $PhBOCH_2^+$ ion and thence the tropylium ion, or led to a cyclic disulphide ion.

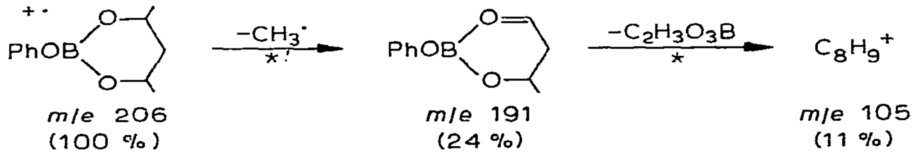


The tropylium rearrangement was observed to be a general property of phenylboronates [257]. A series of cyclic boronates gave rise to rearrangements to tropylium and higher hydrocarbon ions. There were found to be four major fragmentation modes [258] (*A*–*D*):



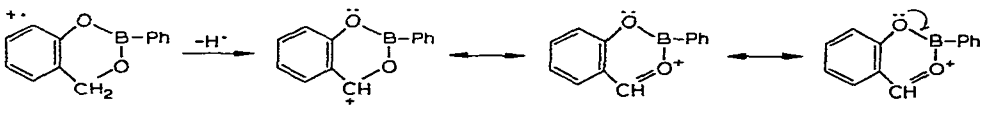
A, elimination of an oxo compound; *B*, fission of an exocyclic C—C bond; *C*, skeletal rearrangement to hydrocarbon ions; *D*, a mode exclusive to six membered compounds; double elimination of neutral molecules giving rise to either an hydrocarbon ion or a $PhBO^+$ ion.

Deuteriation studies of 2-phenoxydioxaborolane and borinanes produced further evidence for the tropylium rearrangement [28] and 4,6-dimethyl-2-phenoxy-1,3,2-dioxaborinane [32] was found to give a hydrocarbon rearrangement.



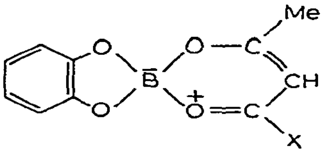
The ion $PhOH^+$ was also observed and was presumably due to hydrolysis.

2-Phenyl-1,3,2-dioxabenzo[*d*]borinane [69] was the first example of a compound containing a CH_2O-group attached to boron which did not rearrange to form a tropylium ion to a significant extent. The spectrum also contained a large doubly charged $(P{-}1)^{2+}$ ion which can be said to have pseudo-aromatic character.



1,2- And 1,3-diols [42] were characterised by gas chromatographic separation followed by mass spectral identification of their cyclic boron esters. The phenyl- and n-butyl-boron esters of eight diols were prepared and their mass spectra showed certain characteristic fragments. The technique [352] has been used to examine the n-butyl boronate derivatives of humulone, cohumulone and colupulone found as hop resin constituents, and for characterisation of steroidal diols [43]. More recently corticosteroid boronates [41] of various classes of steroid have been reported and discussed in detail, each gave rise to characteristic fragmentation modes.

β-Ketoenolate compounds (XXV) have been examined [216]. The fragmentation of the β-ketoenolate ring when X = Me occurred by a stepwise mechanism after initial methyl loss, whilst the spectra of the compounds where X = NEt_2, $NPr\text{-}i_2$, OEt all showed

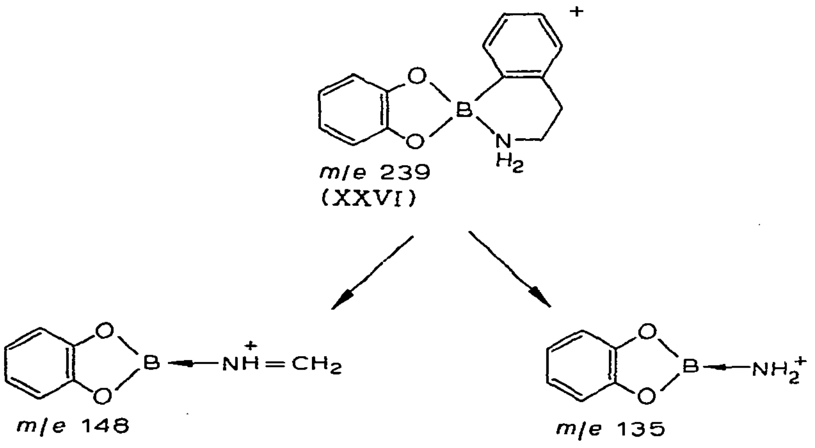


(XXV)

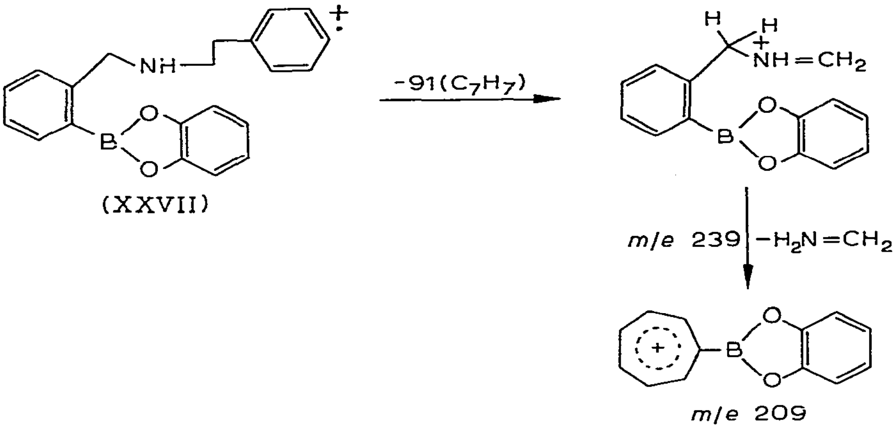
(X = Me, NEt_2, $NPr\text{-}i_2$, OEt)

three identical fragments: $(o\text{-}C_6H_4BOCMeCHCO)^+$, $(o\text{-}C_6H_4O_2BOH)^+$, and $(o\text{-}C_6H_4O_2B)^+$. No peaks for an ion of type $(BOCMeCHCOX)^+$ were found, except when X = Me, thus fragmentation occurred in the β-ketoenolate ring rather than the benzodioxolane ring.

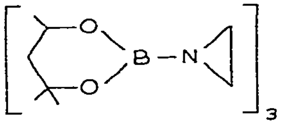
The spectra of the catechol derivatives of 1,2-borazatetraline (XXVI) and 2-(2′-phenylethyl)-3,2-borazindane (XXVII) [58] have been recorded. The spectrum of the former showed peaks at both *m/e* 91 ($C_7H_7^+$) and *m/e* 104 ($C_8H_8^+$) and corresponding ions which had lost 91 and 104 mass units respectively.



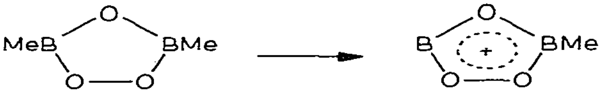
The spectrum of the latter (XXVII) showed an unusual rearrangement to produce a tropylium ion bonded to a 1,3,2-dioxaborone cyclic system.


(XXVII)

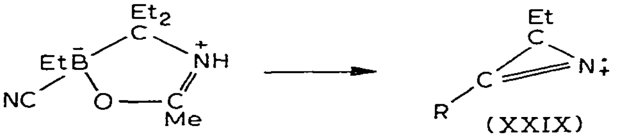
2-Azividinyl-4,4,6-trimethyl-1,3,2-dioxaborinane [355] was found to be a trimer, (XXVIII), a weak parent lost $N(CH_2)_2$, the monomer parent was relatively intense, and


(XXVIII)

a peak was observed at m/e 43 for either $HN(CH_2)_2$ or BO_2. Borenium ions were not produced by a series of oxygen-containing boron heterocycles [48, 209]; for details see the boron–nitrogen section. 3,5-Dimethyl-1,2,4-trioxa-3,5-diborolane [11] has been prepared. The fragmentation gave rise to a stable cyclic borenium ion, and it was suggested that this was due to the partial aromatic character of the system.



Triethylcyanoborate [30], and seven similar compounds have been characterised.


(XXIX)

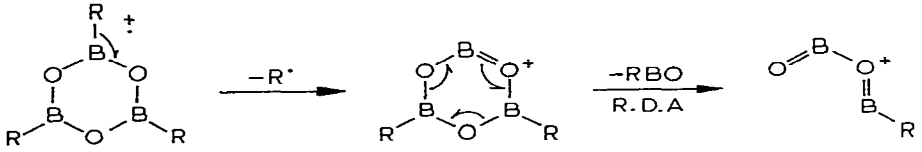
The fragmentation of all seven compounds proceeded via a cyclic species (XXIX).

D. Boroxines

Mass spectral studies of an H_2O–B_2O_3 vapour system [276] showed the presence of various species including boroxine ($H_3B_3O_3$). Further studies showed that both hydroboroxine ($H_3B_3O_4$) and $H_2B_2O_3$ were present as intermediate species [12, 323, 353] and heats of formation were calculated. $H_4B_4O_4$ and $H_4B_6O_7$ have also been identified in the system [159]. Partial oxidation of B_5H_9 produced $B_2H_2O_3$ which was characterised by mass spectral deuteriation studies. It also produced boroxine [13], but B_4H_{10}, and BH_3CO produced $B_2H_2O_3$ as their only oxidation product. The precursors HBO and H_2BOH have been observed for B_5H_9, but only H_3BO_2 was produced by the other two compounds. Oxidation of diborane produced both $B_2H_2O_2$ and $B_3O_3H_3$ [322].

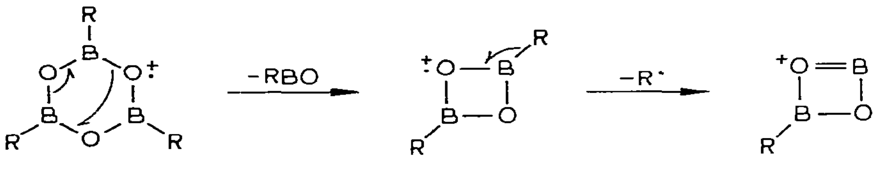
Trimethylboroxine [232] and triethylboroxine [243], like borazines, showed low parent ion abundances. The base peak was for the $(P–R)^+$ ion R = Me, Et. Ions corresponding to both 1/3 and 2/3 of the molecular formula BOR and $(BOR)_2$ were observed, and in addition, $(1/3P–1)^+$, $(2/3P–1)^+$, $(1/3P–R)^+$ ions were recorded. It was observed that ring cleavage ions were much less abundant than in borazines, and there was a lack of intense fragment peaks. Comparison of trimethylboroxine with its benzene analogue showed that it had considerable aromatic character.

The spectra of tri-n-butyl-, tri-t-butyl-, tricyclohexyl- and triphenyl-boroxine have been reported [38]. The intensities of the molecular ions reflected the stability of the boron substituents to fragmentation and this ion was the base peak in the triphenyl derivative. Major fragmentation in the compounds followed four routes:

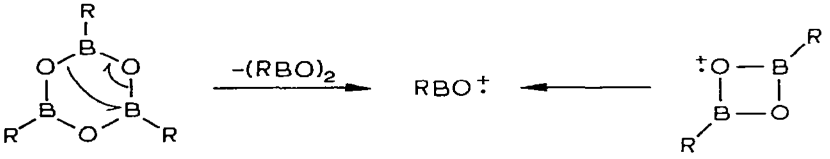


Loss of a boron substituent was followed by a retro–Diels–Alder (R.D.A.) fragmentation to give an acyclic ion.

Skeletal rearrangement of the molecular ion, with elimination of an RBO group to form a four-membered ring may be followed by loss of a boron substituent. The radical



ion $RBO^{+\bullet}$ was formed from both the molecular ion and the four membered ring.

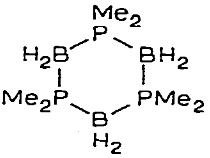


The fragmentation pattern of triphenylboroxine has been further refined [74] and peaks formed by rearrangements not previously identified were explained.

VIII. BORON–PHOSPHORUS COMPOUNDS

Very few mass spectra of boron–phosphorus compounds have been reported and thus no general conclusion about their behaviour under electron impact can be made.

A trimer of dimethylphosphinoborane [125] has been studied at various ionising voltages.



(Continued on p. 202)

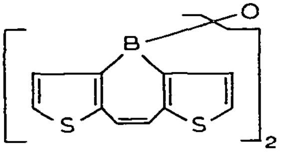
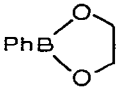
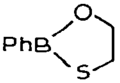
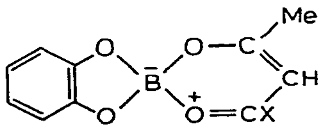
TABLE 6

BORON–OXYGEN COMPOUNDS

Compound	Comment	Reference
A. Boric oxide and metal borates		
B_2O_3	Spectrum	296
B_2O_2	BO^- and BO_2^- heats of formation	27, 185, 305
BOF, $(BOF)_3$	Spectra	171, 174, 175
B_2OF_4	Spectrum and heat of formation	25, 32
BOF_2	Spectrum and heat of formation	385
$LiBO_2$, $Li_2(BO_2)_2$, $Li_3(BO_2)_3$	Spectra	1, 51, 52, 146, 241
$NaBO_2$, $Na_2(BO_2)_2$, $Na_3(BO_2)_3$	Spectra	1, 51, 52, 146, 241, 329
$Be(BO_2)_2$	Spectra	52
$Mg(BO_2)_2$	Spectra	52
KBO_2	Spectra	146, 241
$RbBO_2$	Spectra	146, 241
$CsBO_2$	Spectra	146, 241
NdBO, $NdBO_2$	Spectra	326, 329
B. Acyclic borates		
$B(OMe)_3$	Spectrum appearance potentials, heats of formation	389
	Spectrum, also $HB(OMe)_2$	226
	Fragmentation pattern	73
$B(OR)_3$	Spectra	115, 243
(R = Me, Et, n-Pr, n-Bu)	Spectra	115, 243

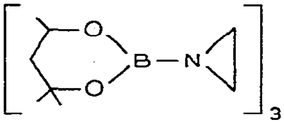
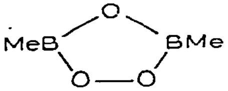
(Continued)

TABLE 6 (continued)

Compound	Comment	Reference
	Redistribution reactions, mixture spectra	116, 170
	Appearance potentials, MO calculations	217, 218
$B(OR)_3$, F_2BOR (R = Me, Et)	Spectra	400
Me_2BOBMe_2	Spectrum	214
$PhB(OH)_2$	Discussion	74
$PhB(OR)_2$ (R = Et, Me)	Tropylium ion observation	63
$Me_2BONCMe_2$	Discussion	187
t-$Bu_3C_6H_2B(X)OBu$ (X = substituted phenyl)	Discussion	362
 Bis(dithienoborepinyl) ether	Discussion	155
$B_{10}H_{13}OC_2H_5$	Characterisation	297
$(MeO)_2B{-}B(OMe)_2$	Borenium ion discussion	48
C. Cyclic boron–oxygen compounds		
	Tropylium ion formation	71
	Tropylium ion formation	67
	Complete fragmentation of both above compounds	68
Phenyl boronates	Discussion of hydrocarbon rearrangement ion formation (and other fragmentation processes)	257, 258
	Deuteriation studies for tropylium ions	28
Phenoxy boronates	Hydrocarbon rearrangement ions	32
Substituted boronates	Cyclic borenium ion formation	48, 209
Phenyl boronates	Complex 1,2- and 1.3-diols	39, 42
	of humulone, cohumulone, colupulone	352
	of corticosteroid diols	9, 36, 37, 41, 43
β-Keto-enolates	Various chelating agents, identification	203
 (X = Me, NEt_2, N-*i*-Pr_2, OEt)	Discussion	216

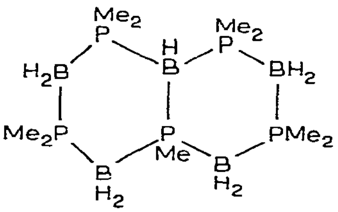
(Continued)

TABLE 6 (continued)

Compound	Comment	Reference
Catechol derivatives of borazatetraline	Discussion	58
Borazindane 	Characterisation	355
Triborylamine	Identification	224
	Discussion	11
Cyanoborates	Discussion	30
D. Boroxines		
$(HBO)_3$	Spectrum, heat of formation	276, 322
$(HBO)_3$, $H_2B_2O_3$	Spectrum, heat of formation	12, 14, 323, 353
HBO, H_2BOH, H_3BO_2	Spectrum, heat of formation	98, 13
$(HBO)_4$, $H_4B_6O_7$	Identified from spectra	159
$(MeBO)_3$	Spectrum, discussion	232
$(EtBO)_3$	Spectrum	243
$(RBO)_3$ (R = n-Bu, t-Bu, cyclohexyl, Ph)	Spectra, discussion	38
$(PhBO)_3$	Discussion of fragmentation	74

The spectrum was complex, but the most abundant ion due to BMe_2^+ exhibits a very unusual type of rearrangement involving the migration of two methyl groups; the appearance potential (over 20 eV) was also high.

The pentameric form of dimethylphosphinoborine [390] was similar to the trimer, although the relative abundances of many of the ions were different. The ion BMe_2^+ was again seen but was not as abundant. Hydrogen ions were readily lost in the ionising pro-



cess which disguised the structure of the resulting ions, but it could be deduced that the hydrogen atoms were lost in pairs, as in the boron hydrides.

In the spectrum of the trimer, tetramethylphosphinoborine, the major peaks observed were produced by the breaking of the carbon–boron, phosphorus–boron and carbon–phosphorus bonds, rather than the loss of hydrogen atoms.

IX. BORON–SULPHUR COMPOUNDS

A. Boron sulphides and selenides

A mass spectrum of the vapour produced by a mixture of zinc sulphide and boron at high temperature showed four ions containing boron and sulphur namely; BS^+, BS_2^+, $B_2S_2^+$, and $B_2S_3^+$. There were no ions of higher molecular weight [358]. A mass-spectral study on sulphur-rich samples resulted in the observation of ions of various combinations of boron and sulphur up to $B_{10}S_{17}$, which it was suggested contained ring structures [148]. Further studies showed that the parent molecules were BS_2 polymers from B_6S_{12} to $B_{10}S_{20}$ [149]. Ions containing B–S–Si and B–S–O were also produced and identified as coming from contaminants within the system. In a Cr_2S_3–B system [248], the ions BS^+ and B_2S^+ were suggested as parents. A study of stoichiometric sulphides and sulphur-enriched sulphides concluded that polysulphide bonds were the reason for the incongruent vaporisation of the sulphur-rich boron sulphides [60].

Boron selenide [274, 275] produced two gaseous parent species $BSe_2(g)$ and $B_2Se_3(g)$. Various products from the hydrolysis reaction with the condensed B_2Se phase were observed, including $HSeB^+$, $H_2BSe_2^+$ and $H_2B_2Se_3^+$. Boron selenide showed similar vaporisation behaviour to boron sulphide except that there was an absence of polymer formation.

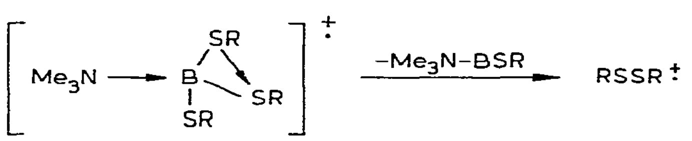
A further study of boron sulphide $B_2S_3(g)$ and the dimeric form $B_4S_6(g)$ [61] suggested that the polymerisation of boron sulphide proceeded via a four-membered ring form, linking two B_2S_3 units. The absence of polymers in boric oxide was explained by the interaction of a boron atom with a fourth sulphur atom in solid boron sulphide.

B. Acyclic thioboranes

A detailed account of the fragmentation of trimethylthioborate has appeared [73]. Two primary fragmentation modes were reported for the parent ion, the first to produce a $(MeS)_2B^+$ ion and the second a $(MeS)_2BS^+$ ion, both of which are analogues of species observed in the spectrum of trimethylborate. Further decomposition from the ions was by routes different to those observed in the oxygen compound. A small amount of dimethyldisulphide was produced from the parent.

$$\begin{tikzcd}
\begin{array}{c}\mathrm{MeSSMe}^{+\cdot}\\ m/e\ 94\\ (1.1\%)\end{array} & \begin{array}{c}\mathrm{(MeS)_3B}^{+\cdot}\\ m/e\ 152\\ (19.8\%)\end{array} \arrow[l, "-\mathrm{CH_3SB}" above, "58.2" below] \arrow[r, "-\mathrm{CH_3}^{\cdot}" above, "123.5" below] \arrow[d, "72.5" left, "-\mathrm{CH_2S}^{\cdot}" right] & \begin{array}{c}\mathrm{(MeS)_2BS}^{+}\\ m/e\ 137\\ (11.2\%)\end{array} \\
 & \begin{array}{c}\mathrm{(MeS)_2B}^{+}\\ m/e\ 105\\ (13.0\%)\end{array} &
\end{tikzcd}$$

The molecular ion of the higher alkylthioborates [66] was generally stable. The primary fragmentation was loss of an alkylthio group, although when the alkyl group was increased above propyl, the spectra became more complex. The formation of the disulphide ion gave increasingly larger abundances as the alkyl side chain lengthened. Complexes of trialkylthioboranes with pyridine showed no ions produced by the complexed form; instead pyridine and the thioborate were observed as independent species [77]. In contrast complexes with trimethylamine showed some additive species. Of particular interest was the increased abundance of the disulphide ion, the elimination became more sterically favoured in the four-membered system,



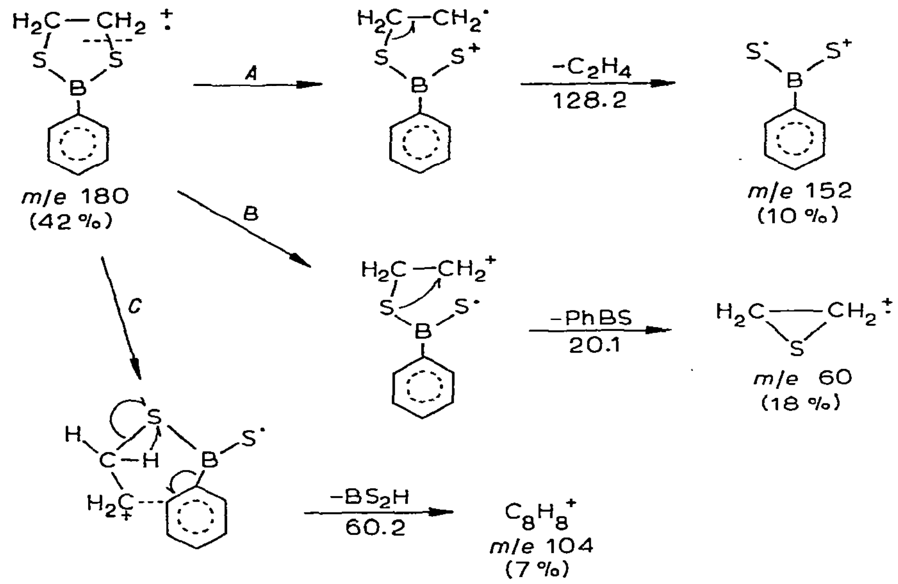
Mass-spectral analysis of the products of redistribution reactions between trialkyl thioborates showed mixed ions [77]. The appearance potentials of various methylthio-containing mixed boranes have been recorded [217, 218].

Phenyl- and diphenyl-substituted thioborates underwent electron impact induced rearrangement to form a tropylium ion [66]. Negative ion spectra of the ethylthiophenyl-, and diphenyl-borates produced few ions. The only abundant ions seen were for ethyl loss from the molecular ions [77].

Both μ-mercaptodiborane (B_2H_5SH) [197] and tetraethylammonium thiotrihydroborate ($(Et_4N)(HSBH_3)$) [196] have been characterised by mass spectrometry, the former with the aid of ^{10}B enrichment and deuteriation studies. Tetramethylthiodiborane $(MeS)_2BB(SMe)_2$ has been shown to produce a base peak for a linear borenium ion $B(SMe)_2^+$ [48].

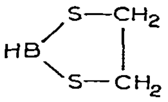
C. Cyclic boron–sulphur compounds

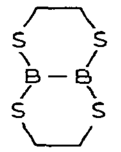
2-Phenyl-1,3,2-dithiaborolane has been fully investigated by mass spectrometry [67, 68]. It was shown to undergo the tropylium rearrangement, but in poor yield. The parent ion was stable and primary fragmentation followed C—S scission by three competitive routes:



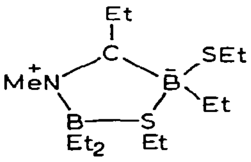
A, loss of ethylene leaving a phenyl–boron–disulphide fragment; *B*, formation of a cyclic sulphide ion; *C*, rearrangement to form an hydrocarbon ion.

Introduction of methyl at the C_4 position [65] did not alter the basic mode of fragmentation of the borolane ring, although loss of methyl was a major fragmentation. Introduction of a dialkyl or alkylamino group at boron produced a fragmentation mechansim which centered on the amino side chain. The spectrum of 1,3,2-dithiaborolane (XXX) [112] has been recorded and shown to be a monomer in the vapour phase.


(XXX)

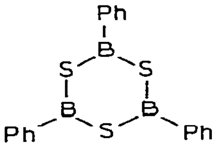

(XXXI)

The diborane heterocycle (XXXI) did not produce cyclic borenium ions as a major fragmentation process [48]. The mass spectrum of a 5-membered dibora-heterocycle (XXXII)


(XXXII)

[157] has been reported. The major primary fragmentations were loss of C_2H_5 leading to the base peak and loss of SEt, further fragmentation involved rearrangement and ring scission.

Triphenylborthiin (XXXIII) [77] has a stable molecular ion, and fragments corre-



(XXXIII)

sponding to $(P-1/3)^+$ and $(P-2/3)^+$ ions were not observed in the spectrum. Loss of phenyl occurred to a small extent, fragmentation occurred to a lesser extent than in the corresponding borazine and was similar in amount to that in triphenylboroxine. Comparison with the benzene analogue showed that the system had considerable aromatic character. Tribromoborthiin had a less intense molecular ion and $(P-1/3)^+$, $(P-2/3)^+$ ions were observed.

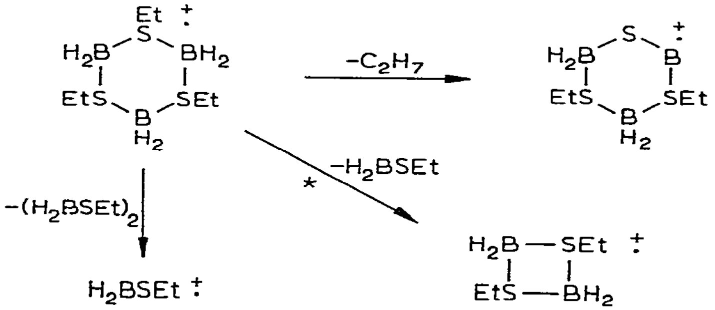
The decomposition of metathioboric acid [109, 110] by vaporisation produced the gaseous trimer $(HBS_2)_3(g)$. The spectrum of a ^{10}B enriched sample showed that the trimer fragmented by two major routes, established in both cases by metastable ion formation.

$$(HBS_2)_3^{+\cdot} \xrightarrow[*]{-HBS_2} (HBS_2)_2^{+\cdot}$$

$$(HBS_2)_2^{+\cdot} \xrightarrow[*]{-BS_2} (H_2BS_2)^+$$

Thermal decomposition [137] has been used for the formation of various BS_2 polymer ions, the most prominent of which was $B_8S_{16}^{+\cdot}$. Its low appearance potential and metastable decomposition to $B_8S_{14}^{+\cdot}$ suggested the existence of $B_8S_{16}(g)$ as a neutral molecule.

Ethylthioborane [136] has been examined by mass spectrometry and found to be a trimer. The main fragmentation was via loss of one unit of the trimer, but both loss of two parts and loss of C_2H_7 were observed.



Boron–sulphur compounds which have been identified using mass spectroscopy are listed in Table 7.

X. BORON–HALOGEN COMPOUNDS

Trihaloboranes fragmented by loss of successive halogen units, and the BX_2^+ ion was strong. In more complex haloboranes, the BX_2 unit remained intact throughout most fragmentations. The BX_2 units was most stable when X = F, and the relative stability decreased as X increased in weight. Loss of a neutral halide species became more frequent in the higher halides (cf. the boron hydrides).

A. Boron–fluorine

Boron trifluoride has been the subject of a series of mass-spectrometric investigations to discover the appearance potentials of its positive ions [226, 310, 372], ionisation potentials [210, 172, 173] and the mass spectrometric reactions of the ions [249]. The enthalpy of the BF_2^+ ion has been calculated [247]. Its photoionisation spectrum and photo-

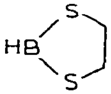
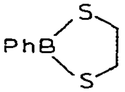
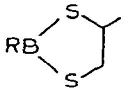
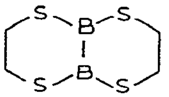
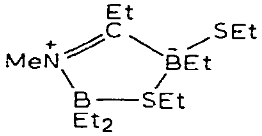
TABLE 7

BORON-SULPHUR COMPOUNDS

Compound	Comment	Reference
A. Boron sulphides and selenides		
B_2S_3	Spectrum	358
$B_{10}S_{17}$	Sulphur enriched sample	148
$B_{10}S_{20}$	Sulphur enriched sample	149
BS^+, B_2S^+	Cr_2S_3–B system	248
B_2S_3	Comparison stoichiometric and enriched samples	60
BSe_2, B_2Se_3	Spectra	274, 275
B_4S_6	Polymerisation by 4-membered units	61
B. Acyclic thioboranes		
$B(SMe)_3$	Discussion of fragmentation	73
$B(SR)_3$ (R = Et, Pr, Bu)	Discussion	66
$PhB(SR)_2$, $Ph_2B(SR)$	Discussion, tropylium ion formation	66
$B(SMe)X_2$	Appearance potentials and MO calculations	217, 218
B_2H_5SH	^{10}B enriched deuteriated spectra	197
$(Et_4N)(HSBH_3)$	Characterisation	196
$(MeS)_2B–B(SMe)_2$	Borenium ion formation	48

(Continued)

TABLE 7 (continued)

Compound	Comment	Reference
C. Cyclic boron–sulphur compounds		
	Spectrum	112
	Discussion of fragmentation Tropylium ion formation	68 67
 (R = Ph, Et_2N, BuHN)	Discussion of fragmentation	65
	Cyclic borenium ion formation	48
	Discussion and fragmentation	157
$(HBS_2)_3$	Discussion	109, 110
	Higher sulphides produced from	137
$(H_2BSEt)_3$	Discussion	136

ionisation yield curves for various ions [87] have been reported. Negative ion mass spectra produced the heat of formation of the BF_4^- ion [264].

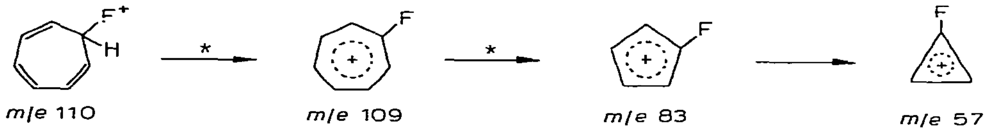
Reactions of boron trifluoride with $BCl_3(g)$, $B(OH)_3(g)$ and $B_2O_3(l)$ have been studied, and heats of formation for the reactions calculated [321].

The B–Cl–F system has been studied [360]. The ionisation potentials of the molecular ions, BX_3^+, BX_2Y^+ and $BXYZ^+$ (X, Y, Z = F, Cl, Br, I, NMe_2, OMe, OEt, O-n-Pr, SMe, Et) [217, 218, 219, 223] have been obtained by redistribution reactions and characterised by mass spectrometry. Molecular-orbital calculations were carried out to estimate the lone-pair orbital interaction of adjacent atoms from the ionisation potential data.

The spectrum of diboron tetrafluoride has been reported [87, 133] and also that of octaborane (F-12) [199]. A loss of BF_3 as a neutral molecule is usually the most ready process in boron–fluorine chemistry and the compound B_8F_{12} exhibited its lowest appearance potential for loss of a neutral BF_3 unit from the parent, loss of BF_3 has been observed in the spectrum of B_3F_5 [373].

The dissociation energy of $BF_3 \cdot Et_2O$ was calculated mass spectrometrically [288] and the spectra of $(BF_2)_3BCO$ and $(BF_2)_3BPF_3$ [199] were used to identify the compounds. The spectrum of $Si_2B_2PFSCl_6$ was identified by use of precise mass measurement.

The spectrum of tropylium fluoroborate [131] showed, superimposed on the normal tropylium fragmentation, fluorine loss from the fluoroborate to the tropylium ion, followed by fluorotropylium fragmentation.



Tricarbonyl(cycloheptatriene)manganese tetrafluoroborate was identified by mass spectrometry [278].

The organoboron difluorides [366] RBF_2 where R = H, Me, Et, $CH_2{=}CH$, Me_2CH have been studied, and appearance potential and dissociation energy data reported. The main features of the spectra were loss of F or HF from the parents as neutral molecules leaving RBF^+ ions. The BF_2^+ ion was usually present in the spectra in high abundance.

B. Boron–chlorine

Boron trichloride has been studied in conjunction with other Group III and IV elemental chlorides [84] and certain characteristics of the fragmentation were seen to have a periodic significance. The photoionisation of BCl_3 and B_2Cl_4 [93] has afforded information on heats of formation and dissociation energies for the B–Cl bonds. B_4Cl_4, an electron deficient subchloride, showed no peaks for parent doubly charged ions, but various higher species including $B_{11}Cl_{11}^+$, $B_{12}Cl_{12}^+$ and $B_9Cl_9^+$ were tentatively identified by mass spectrometry [253, 254]. The mass spectrum of B_9Cl_8H [126] was reported as having all possible $B_xCl_y^+$ fragments represented up to $B_{10}Cl_{10}$ with a base peak at *m/e* 298 ($B_8Cl_6^+$ or possibly $B_5Cl_7^+$) and there was some evidence for recombination.

Tetrakis(dichloroboryl)methane $C(BCl_2)_4$ showed intense peaks for the loss of Cl_2, and BCl_3 and a base peak produced by the BCl_2^+ ion [102, 103]. Part of the spectrum of Cl_2BSiCl_3 [252] showed stepwise single chlorine atom loss.

C. Boron–bromine and boron–iodine

The study of bromo- and iodo-pentaboranes [160, 349] has shown that substitution of these atoms produced very different effects. The iodopentaborane lost iodine easily leaving the rest of the molecule intact whilst loss of bromine caused boron skeleton cleavage and loss of HBr. Hydrogen atoms were lost in pairs from both compounds as they were in pentaborane itself.

D. Boron–halogen group

Various studies have been made of the boron trihalides as a group [191, 205, 226, 249], one including pseudohalides [363].

The trihaloborane BX_3 ($X = F, Cl, Br$) complexes with $(CF_3)_2CNH$ [292] were reported. The parent ions of $X = Cl, Br$ were observed, but for BF_3 the spectrum showed only the superimposed spectra of the two components, no products of combination were observed. The trimethylamine adducts of the boron halides [215] and some mixed trihalides have been reported. Trends in ion abundance became evident when the atomic weight of the halide was increased. Detailed analysis in terms of boron–nitrogen and boron–halogen bond strengths were discussed.

Ethynylboron halides [332] HC_2BX_2 ($X = Cl, F$) were found to be monomers, and hydrogen loss was the only reported fragmentation.

Phenylboron dichloride [235], ($PhBCl_2$), fragmented by both B–Cl and B–C fission, one B–Cl fission produced the base peak. Minor amounts of BCl_2^+ and PhB^+ ions were seen. Phenylboron difluoride [289] ($PhBF_2$) showed a base peak for the $(P-1)^+$ ion. The boron–carbon bond was easily cleaved, but the BF_2 unit remained intact. Both the dichloro- and dibromophenylboranes ($PhBCl_2$, $PhBBr_2$) fragmented by the loss of HCl and HBr respectively to form their base peaks. The phenylboron dichloride base peak prediction was a direct contradiction of the earlier published result [235].

Boron–halogen compounds which have been identified using mass spectroscopy are listed in Table 8.

TABLE 8

BORON–HALOGEN COMPOUNDS

Compound	Commment	Reference
BF_3	Appearance potentials	310, 226, 372
	Ionisation potentials	172, 173, 210
	Fragmentation detail	249
	Enthalpy of BF_2^+ ion	247
	Photoionisation spectrum	87
	Negative ion spectrum ΔH_f BH_4	264, 240
	Reactions with BCl_3, $B(OH)_3$, B_2O_3	321
	BF_2Cl, $BFCl_2$ ΔH_f data	360
	Resdistribution appearance potential data	217, 218, 219
	MO calculations	223
	Doubly charged ions	85
F_2B-BF_2	Spectra	87, 133
B_8F_{12}	Spectrum	199
B_3F_5	Spectrum	373
BF_3Et_2O	Dissociation energy	288

(Continued)

TABLE 8 (continued)

Compound	Comment	Reference
$(BF_2)_2SiF_2(BF_2)_3SiF$, $(BF_2)_3BCO$, $(BF_2)_3BPF_3$, $Si_2B_2PF_5Cl_5$	Identification	199
Si_2BF_7	Identification	255
$C_7H_7^+BF_4^-$	Discussion	131
$C_7H_8Mn(CO)_3BF_4$	Identification	278
RBF_2 ($R = H$, Me, Et, $CH_2{=}CH$, Me_2CH)	Discussion	366
BCl_3	Appearance potentials fragmentation	226, 310, 249
	Part of elemental chloride study	84
BCl_3, B_2Cl_4	Photoionisation study	93
B_nCl_n ($n = 9, 11, 12$)	Identification	253, 254
B_9Cl_8H	Discussion	126
$C(BCl_2)_4$	Discussion	102, 103
Cl_2BSiCl_3	Characterisation	252, 377
$(MeBCl)_2$	Identification	378
B_5H_8X ($X = Br, I$)	Discussion	160, 349, 246
BX_3 ($X = F, Cl, Br, I$)	Discussion	191, 226, 249
(X = pseudohalide, Cl, F)	Discussion	306, 363
($X = Cl, Br, I$)	Appearance potentials	205
($X = F, Cl, Br$)	Complexes with $(CF_3)_2CNH$	292
($X = F, Cl, Br, I$)	Complexes with Me_3N	215
HC_2BX_2 ($X = F, Cl$)	Characterisation	330
$PhBX_2$ ($X = Cl, Br$)	Spectrum and discussion	235
($X = F, Cl, Br$)	Spectrum and discussion	289

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