AN INVESTIGATION OF SOME REACTIONS OF ALUMINIUM HYDROBORATE

A thesis submitted for the degree of Doctor
of Philosophy

by

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CONTENTS

Contents (continued)

Contents (continued)

Contents (continued)

Contents (continued)

LIST OF TABLES

LIST OF FIGURES

List of Figures (continued)

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SUMMARY

The reaction of aluminium hydroborate with alcohols and thiols is discussed, and this is extended to cover possible mechanisms for aluminium hydroborate hydrolysis. The course of the reaction was found to be dependent on the structural type of alcohol or thiol used. Substitution of a thio alkyl group for hydroborate led to preparation of the type of compound $RSAl(BH_4)_2$ (where R = methyl, ethyl, benzyl) and properties of these compounds are discussed. Using an exchange reaction of aluminium hydroborate with alkyl borates, corresponding compounds of the type $ROAl(BH_4)_2$ (R = methyl, ethyl) were prepared, and their properties ascertained.

The behaviour of aluminium hydroborate with triethyl and trimethyl borane is considered. This work suggests that there is an exchange between the terminal hydrogens of the hydroborate groups and the borane alkyl groups, resulting in B-alkylated aluminium hydroborates. B-alkylated hydroborates are also believed to be formed from a novel reaction between triethylalane and tetraethyl diborane.

Some chemistry of the octahydrotriborate group linked to aluminium is also discussed. Starting from dimethyl aluminium octahydrotriborate an exchange reaction with excess aluminium hydroborate yields aluminium octahydrotriborate bis hydroborate. The properties of both compounds are discussed, and the relevance of the latter to aluminium hydroborate decomposition is noted.

The practical work involved extensive use of vacuum line and inert atmosphere techniques, and infra-red and n.m.r. spectral details were very useful.

CHAPTER 1

Introduction

Nomenclature

In this work boron hydrides will be described by adding the suffix 'borane' to the prefix, signifying the number of boron atoms in the molecule (1, 2). The number of hydrogen atoms is then indicated by enclosing the corresponding Arabic numeral in parentheses after the name. It is permissible in those cases where no ambiguity arises to leave out the numeral designation, e.g.

	BH_3	borane
	B_2H_6	diborane
but	B_5H_9	pentaborane (9)
and	B_5H_{11}	pentaborane (11).

In order to differentiate between bridging atoms, usually hydrogen, and terminal atoms, the prefix 'μ' will refer to a bridging atom and 'τ' to a terminal atom.

Derivatives of borane will be named by putting the names of the groups attached to the boron atom before the borane suffix, e.g. trimethyl borane, except in special cases, e.g. boron trifluoride. Derivatives of alane will be similarly described, e.g. chloro dimethyl alane.

Boron anions are borates and boron hydride anions hydroborates. The number of boron atoms is indicated by the prefix immediately prior to the 'borate' suffix and the number of hydrogen atoms by the prefix immediately prior to the 'hydro'. The charge on the ion is added in parentheses, e.g.

$LiBH_4$	Lithium tetrahydroborate (1-)
NaB_3H_8	Sodium octahydrotriborate (1-)

Where no ambiguity arises, the number of hydrogens and the charge may be absent. In this work the term 'hydroborate' will be used in all references to the BH_4^- entity (even in the title) and the term octahydrotriborate for the $B_3H_8^-$ entity. For ease of understanding, the compound $(CH_3)_2AlB_3H_8$ will be referred to as dimethyl aluminium octahydrotriborate and, not basing the nomenclature on the B_4H_{10} skeleton on which it could also be named as 2, 2-dimethyl-2-aluminate tetraborane (10). The words bis and tris will be used for emphasis on stoichiometry where necessary.

Units

The units used in the work are predominantly those recommended by the International Organisation for Standardisation (ISO) and designated SI. For some parameters where convention uses units not strictly SI but closely related to it, these units will be used. As such temperatures for cold baths are more easily quoted as negative values °C, infra-red frequencies as cm^{-1} and pressures as mm Hg.

The sign convention for ^{11}B n.m.r. will be that which keeps it in line with conventions with other nuclei in that signals upfield from the reference are quoted as negative and those downfield from the reference as positive. The reference in all ^{11}B n.m.r. being boron trifluoride diethyl etherate. The Bruker WH 90 machine uses this sign convention automatically and is in line with the suggestion put forward at the 3rd IME Boron conference in 1976.

Hydroborates - Historical

Probably the first observation of a compound of boron and hydrogen was by Sir Humphrey Davy who found that hydrogen produced by acidifying boric oxide and potassium had a disagreeable odour and burnt with a blue flame tinged with green (3a, 3b). It was not until the development of vacuum technique by Alfred Stock in the early 1900's that boron hydrides were prepared and characterised. Stock reviewed his own work in 1933 (4). Hydroborates were first prepared when Schlesinger and his co-workers, in attempting to prepare a compound with a borane group and a trimethyl alane unit isolated aluminium hydroborate (5, 6). This was the most volatile compound of the element known (b.pt. 44° C), and its discovery was closely followed by the isolation of beryllium hydroborate, again volatile, and lithium hydroborate, which was involatile and salt-like (7, 8). The consideration that the hydroborates of aluminium and beryllium were the most volatile derivatives of those elements prompted the search for a volatile derivative of uranium for use in isotope separation of ^{235}U from ^{238}U. This was accomplished when uranium hydroborate was prepared from uranium tetrafluoride and aluminium hydroborate (9). The work at this time also produced new methods of preparing lithium, sodium and potassium hydroborates and recognising their reaction with water being useful for reducing purposes.

Many elements in all parts of the periodic table are now known to form hydroborates, and they are tabulated in Table 1.1.

Hydroborates - Properties

A detailed discussion of the properties of all hydroborates is out of place here. A fairly recent, exhaustive review of metal hydroborates exists (10a) as does one on covalent hydroborates (10b) and several on the properties and preparation of diborane and of the interconversion of the boranes (11, 12, 13). The discussion in this introduction, therefore, will deal primarily with aluminium hydroborate, but will include details of other compounds where they are relevant to general trends in structure, spectroscopy or chemical reaction.

The physical properties of the metal hydroborates vary across the spectrum from typically ionic and salt-like to highly covalent, and particularly the covalent compounds can present handling difficulties either due to extreme moisture and oxygen sensitivity or to toxicity.

The properties of some selected hydroborates are tabulated in Table 1.2.

The chemical properties of the hydroborates have not been extensively studied except for the alkali metal hydroborates, in particular in relation to their reduction reactions with organic functional groups. Diborane, too, has found many uses with the now well-known technique of hydroboration.

The chemical reactions that seem to be common to all the hydroborates are reactions with oxygen and water.

The covalent hydroborates may react explosively with oxygen, but the ionic hydroborates need to be heated, e.g.

TABLE 1.1

Elements known to form simple hydroborates

$\underline{\mathrm{Li}}$	$\underline{\mathrm{Be}}$											$\underline{\mathrm{B}}$		N	
$\underline{\mathrm{Na}}$	$\underline{\mathrm{Mg}}$											$\underline{\mathrm{Al}}$			S
$\underline{\mathrm{K}}$	$\underline{\mathrm{Ca}}$		$\underline{\mathrm{Ti}}$		Cr	[Mn]	[Fe]	[Co]	Ni	Cu	$\underline{\mathrm{Zn}}$	[Ga]		As	
$\underline{\mathrm{Rb}}$	$\underline{\mathrm{Sr}}$	Y	$\underline{\mathrm{Zr}}$	Nb	Mo		Bu	Rh	Pd	Ag	[Cd]	[In]	[Sn]		
$\underline{\mathrm{Cs}}$	$\underline{\mathrm{Ba}}$	La	$\underline{\mathrm{Hf}}$		W			Ir	[Pt]	[Au]		Tl	Pb		
		Ce				Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
		$\underline{\mathrm{Th}}$		$\underline{\mathrm{U}}$	$\underline{\mathrm{Np}}$	$\underline{\mathrm{Pu}}$									

Elements underlined:form simple hydroborates.

Elements in brackets:form unstable hydroborates some of which may be isolated below room temperature.

Other elements: hydroborates isolated contain other groups.

TABLE 1.2

Physical properties of selected hydroborates

Compound	Melting point/^{o}C	Boiling point/^{o}C	Decomposition temperature/^{o}C	Reaction in air	Physical state at 25^{o} C
$LiBH_4$	268	-	380	Slowly hydrolysed	Involatile solid
$Be(BH_4)_2$	-	-	123	Explodes	Slightly volatile solid, 8 mm Hg 25^{o}C
B_2H_6	-165.5	-92.5	30	Inflames	Gas
$Al(BH_4)_3$	-64.5	44.5 extrapolated	30	Explodes	Volatile liquid
$U(BH_4)_4$	-	-	70	Slowly hydrolysed	Slightly volatile solid, 1 mm Hg 45^{o}C

$$NaBH_4 + O_2 \xrightarrow{400^{\circ}C} NaBO_2 + 2H_2$$

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$

The ionic hydroborates are stable in alkaline aqueous solution but react under acidic conditions. Other hydroborates react rapidly, liberating hydrogen immediately, e.g.

$$2BH_4^- + H_2O \xrightarrow{2H^+} B_2H_6 + 2H_2 \xrightarrow{H_2O} 2B(OH)_3 + 3H_2$$

$$Al(BH_4)_3 + 12H_2O \longrightarrow Al(OH)_3 + 3B(OH)_3 + 12H_2$$

i.e. complete hydrolysis with each B-H bond releasing 1 mole of hydrogen. This property is frequently utilised for analysis of aluminium hydroborate compounds.

The more commonly available hydroborates have been used to prepare the hydroborates of less readily available elements. The alkali metal hydroborates have been most commonly used, but aluminium hydroborate has also been useful, e.g.

$$Na(BH_4) + RbOH \longrightarrow RbBH_4 + NaOH$$

$$3UF_4 + 4Al(BH_4)_3 \longrightarrow 3U(BH_4)_4 + 4AlF_3$$

The hydroborates undergo exchange reactions of various sorts.

(i) Deuterium exchange

e.g. $NaBH_4 + D_2 \longrightarrow NaBH_3D + HD$

(ii) Exchange of terminal hydrogen for alkyl groups (see later), e.g. the preparation of alkyl diboranes

$$B_2H_6 + BEt_3 \longrightarrow Et_4B_2H_2$$

(iii) Exchange of intact hydroborate groups with alkyl groups, e.g. the alkyl aluminium hydroborates (see later).

$$Al(BH_4)_3 + Al_2Et_6 \longrightarrow 3Et_2AlBH_4$$

Those hydroborates whose metal has available empty bonding orbitals can also add various ligand molecules or ions. The formation of adducts with

Lewis bases is well known especially for borane and aluminium hydroborate with molecules like trimethylamine. Beryllium and aluminium hydroborates can add certain anionic species to form complex ions, e.g.

$$Be(BH_4)_2 + X^- \longrightarrow [X\,Be(BH_4)_2]^- \quad (X = Cl,\ Br,\ BH_4,\ H)$$

The existence of the hydroborate ion is an analagous reaction to that of borane with hydride.

$$BH_3 + H^- \longrightarrow BH_4^-$$

These reactions and the chemistry of hydroborates are discussed extensively by James and Wallbridge (10a) and that of diborane by Long (11).

Hydroborates - Structures

The hydroborates show an interesting diversity in their structures. Evidence for the present accepted structures has come from several physical techniques although direct structural evidence from diffraction methods is only available for a few hydroborates.

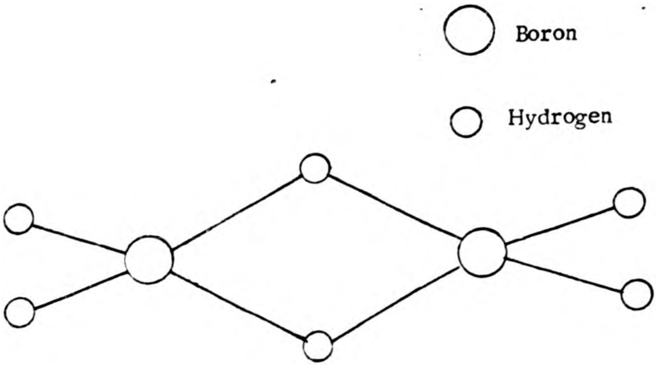
The simplest hydroborate, the BH_4^- ion, has been studied by neutron diffraction of potassium hydroborate (14) at 25° C and shows the expected tetrahedral arrangement of the hydrogen atoms round the boron atom with a boron-hydrogen distance of 126.0 pm.

Diborane has been examined by gas phase electron diffraction (15, 16) and crystal X-ray diffraction (17), and all these studies agree on a molecule with D_{2h} symmetry with two hydrogens bridging between the two boron atoms. The information obtained (16) showed B-B, 177.5 pm; B-H_T, 120 pm; B-H_μ, 134 pm; $\angle$ BBH_T, 120°; $\angle$ $H_\mu BH_\mu$, 97°.

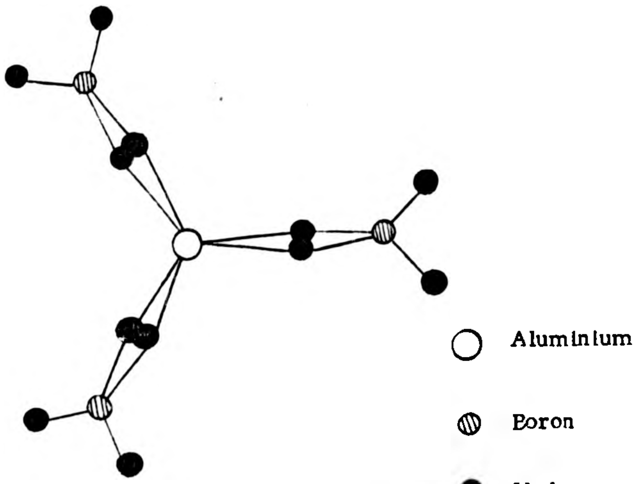
The structure of aluminium hydroborate has been assigned on the basis of electron diffraction data (18). This shows a planar aluminium boron skeleton AlB_3, with each boron surrounded by four hydrogen atoms. The boron is bound to the aluminium by a double hydrogen bridge, (Fig. 1.1), the exact symmetry of the bridge still being undetermined. If the plane of the bridge is such that a prismatic arrangement of the bridge hydrogens is formed, then the symmetry D_{3h} is obtained. However, the bridge planes may be somewhat twisted to produce an overall D_3 symmetry to the molecule.

Fig. 1.1

Structure of diborane



Structure of aluminium hydroborate



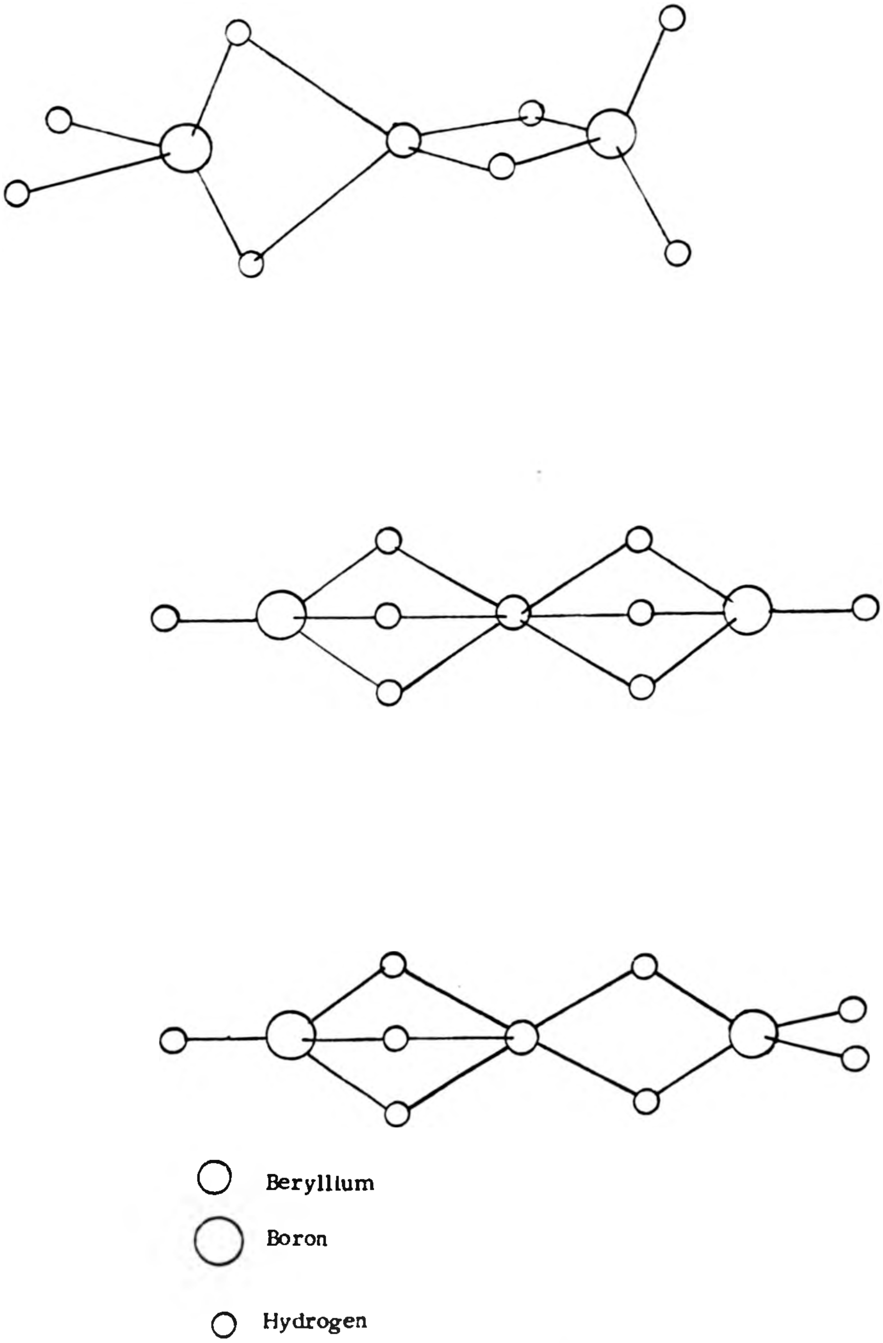
The distance and angle parameters obtained were: Al-B, 214.3 pm; Al-H_μ, 180 pm; B-H_μ, 128 pm; B-H_T, 120 pm; $\angle H_\mu AlH_\mu$, 73°; $\angle H_\mu BH_\mu$, 114°; $\angle H_T BH_T$, 116°.

The gas phase structure of beryllium hydroborate has produced much discussion (see ref. 19a and other references therein, 19b, 196). The conclusion reached by Lipscomb (19a), using S.C.F. calculations, rejected all structures based on a triangular BeBB framework and suggested that the vapour phase might contain a mixture of lower structures containing double and triple hydrogen bridges. The most recent information on the subject (196) establishes that, in the gas phase, beryllium hydroborate contains magnetically equivalent BH_4 groups in which there is rapid hydrogen exchange. A linear B-Be-B framework is the only explanation for the recorded ^{11}B and ^{1}H n.m.r. spectra, although whether double or triple bridged hydroborate groups are favoured is not clear. The solid phase crystal structure (20), however, shows only doubly bridged hydroborate groups in a helical polymeric structure. The hydrogens form an approximately trigonal prismatic arrangement round the beryllium.

In contrast the crystal structure of uranium hydroborate, $U(BH_4)_4$, shows interlocking helical chains, and, instead of three hydroborate groups, in the case of beryllium hydroborate there are six hydroborate groups associated with the central atom. There are two terminal groups bridged via a triple hydrogen bridge, and four further groups bridging uranium atoms with two pairs of hydrogen bridges (21, 22). A triply bridged structure in the gas phase is inferred from an infra-red study (23). The general structure trend in the covalent hydroborates would seem to be, then, that they are bonded by double and triple hydrogen bridged structures from boron to the central atom. To do this, the distance of the bridge hydrogen to the boron atom, B-H_μ, becomes longer than the boron hydrogen distance in the hydroborate ion and at the same time the boron to terminal hydrogen, B-H_T, becomes correspondingly shorter.

Fig. 1.2

Structures of beryllium hydroborate



Hydroborates - Bonding

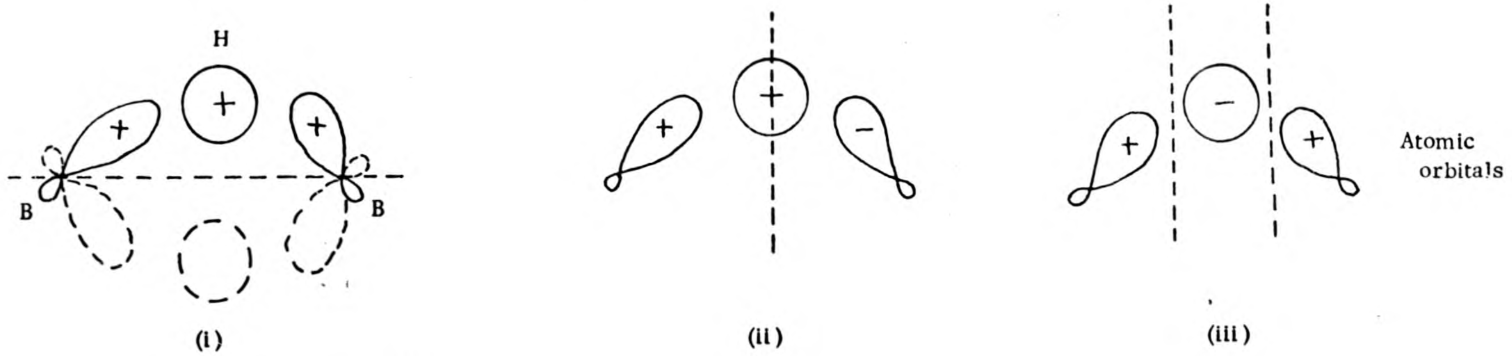
Before considering the infra-red spectra of several hydroborates which will involve such terms as 'bridge bond stretching', it would seem to be appropriate to consider in general terms the bonding involved in the boron-hydrogen bonds.

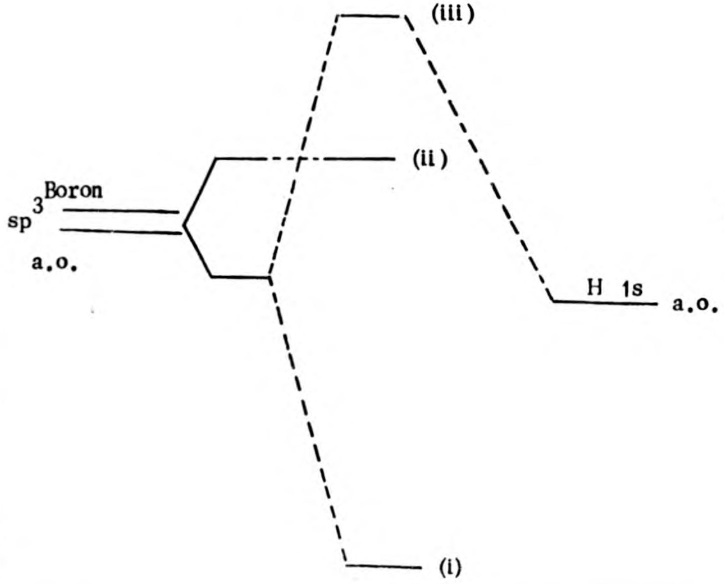
The realisation that the structure of diborane contained a bridge structure, which was suggested by symmetry considerations in the infra-red spectrum (discussed later) and confirmed by diffraction methods, required a new concept of bonding to explain its stability. On original bonding theories, each link between any two adjacent atoms was considered to contain 2 electrons. Diborane on this basis has 8 such links and would therefore need 16 bonding electrons. The constituents of diborane, i.e. 2 boron atoms and 6 hydrogen atoms, can only supply 14 bonding electrons and this has led to the misleading (as it implies instability) title of electron deficient. The accepted theory of the structure of the bridge bond is that an orbital from each of the boron atoms and the orbital of the hydrogen atom are combined to form an 3-centre molecular orbital. 2 electrons in the bonding molecular orbital are sufficient to form the bond.

There are two ways in the old fashioned valence theory in which the orbitals involved may be considered without too detailed an approach. The boron atoms may be considered to be sp^3 hybridised with 2 conventional covalent bonds to the terminal hydrogens. The remaining orbitals then interact with the orbitals of the hydrogen to produce the bridge system. Alternatively, the boron atoms can be considered as sp^2 hybridised again with two conventional covalent bonds to the terminal atoms, the remaining sp^2 orbital pointing towards the other boron atom. This then also leaves the boron p_z orbital available for the bridge system.

A description of molecular orbital theory and bonding schemes, using multi-centred bonds, can also be developed for the metal hydroborates. Detailed treatments are described elsewhere (33, 34).

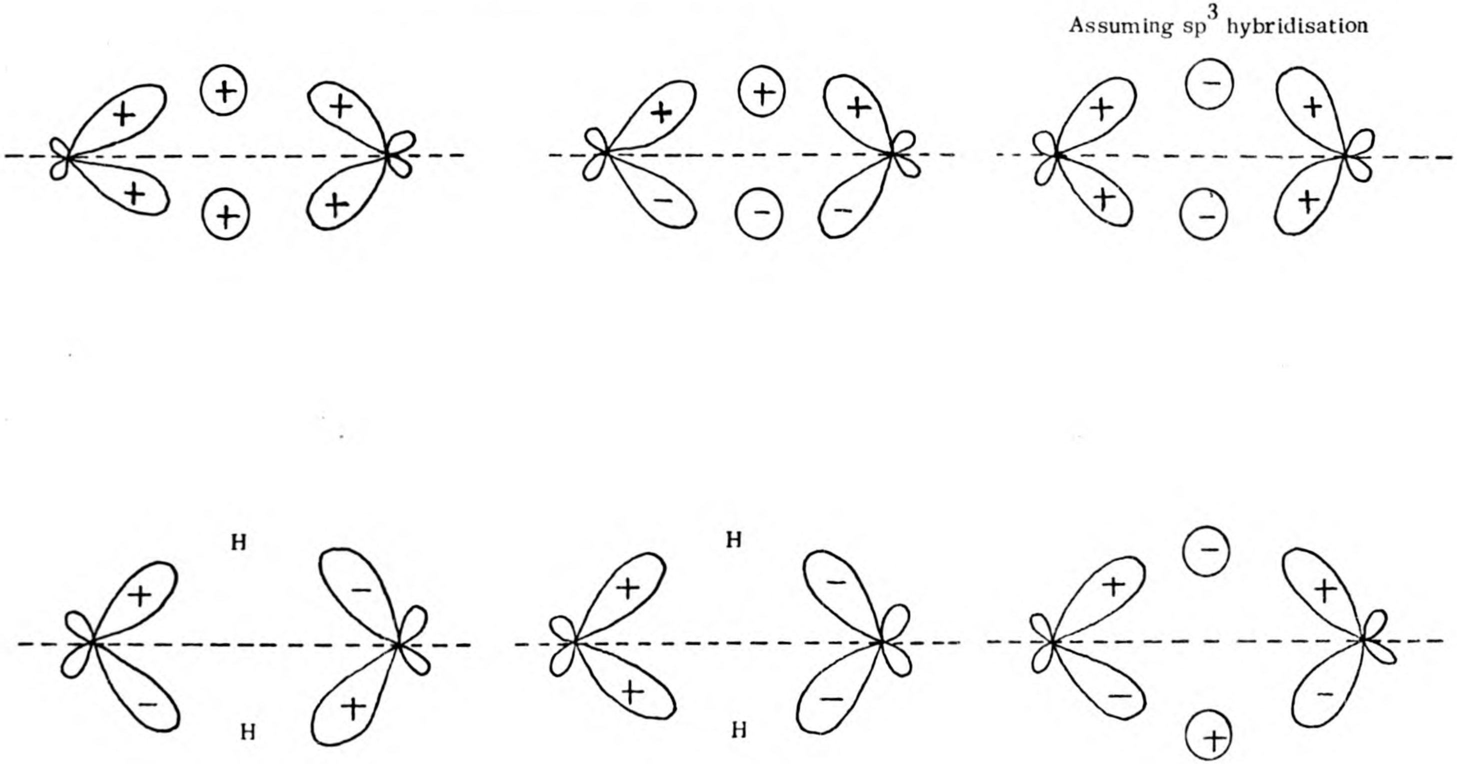
Fig. 1.3 Simple view of bonding in a B-H-B bridge





Orbital correlation diagram for a B-H-B bridge

Fig. 1.4 Simple view of bonding in the diborane bridge system.



Assuming sp^3 hybridisation

Hydroborates - Vibrational Spectroscopy

The information that can be inferred from the study of the vibration of spectra of hydroborates must first come from a knowledge of the vibrations produced by an entity of known symmetry. The tetrahydroborate ion has nine normal vibrations and has full Td symmetry. The vibrations transform so that two bands only turn out to be infra-red active, and four Raman active. The infra-red active bands are the anti-symmetric B-H stretch, and the anti-symmetric stretch BH_2 deformation and these have been observed near 2300 cm^{-1} and 1100 cm^{-1} respectively (24) and have been shown to be slightly solvent and cationic dependent (see ref. 25 and references therein). The four Raman active bands are the two above plus the symmetric B-H stretch, and the symmetric BH_2 deformation.

Diborane, being an eight atom molecule, has therefore a possible eighteen normal vibrations. The vibrations, interpreted in terms of the bridge D_{2d} structure, predict a spectrum with eight infra-red active modes, nine Raman active modes, and a uniquely inactive band as there are no coincidences. Bands with frequencies near 2500 cm^{-1} are again assigned to stretching modes, and those around 1100 cm^{-1} to BH_2 deformation. In addition, some new areas are defined. The regions around 1850 cm^{-1} and 1600 cm^{-1} show bands which are assigned to vibrations of the BH_2B bridge (26, 27).

As was suggested by the direct structural evidence that in forming a covalent B-H entity compared to BH_4^- the new terminal B-H bonds became shorter, and thus stronger than in BH_4^-, and the bands due to B-H stretching move to higher wavenumbers. Two B-H_T bands are observed at 2614 cm^{-1} and 2525 cm^{-1} corresponding to the antisymmetric and symmetric stretching modes respectively. The BH_2 deformation also moves to higher wavenumber at 1175 cm^{-1}. The stretching mode of the BH_2B bridge (tending towards formation of a linear BH_2^+ and tetrahedral BH_4^-) is the strongest band in the spectrum at 1602 cm^{-1}. The other stretching modes of the bridging BH_2 units occur at 1882 cm^{-1} and 1860 cm^{-1}.

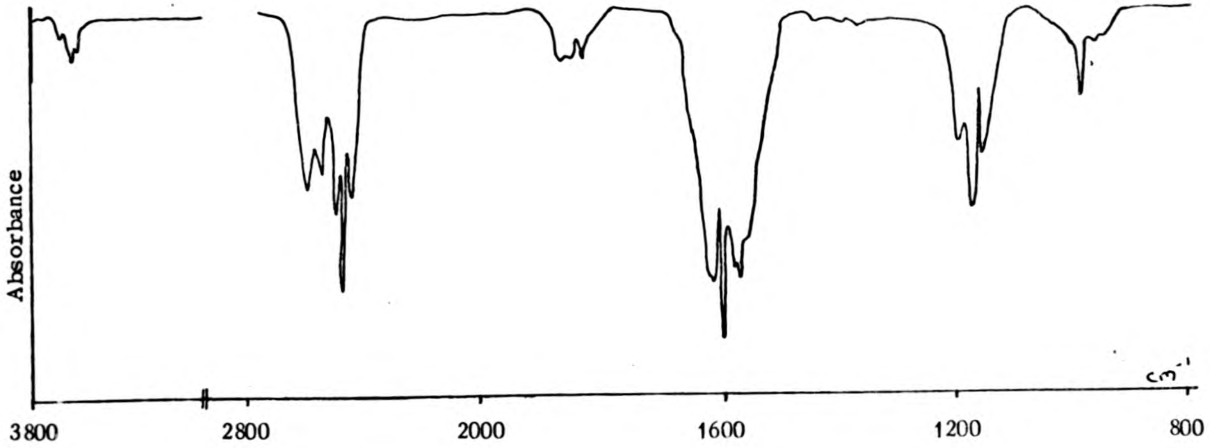


Fig. 1.5 Infra-red spectrum of diborane

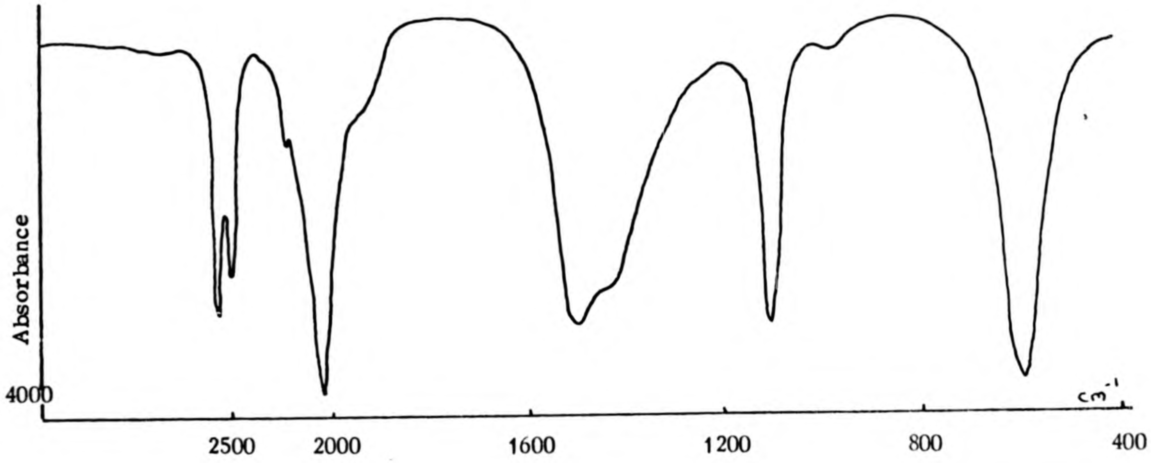


Fig. 1.6 Infra-red spectrum of aluminium hydroborate

These two spectral assignments are at opposite ends of the hydroborate scale. The hydroborate ion is at one side and the entirely covalent diborane at the other. Metal tetrahydroborates would be expected to lie somewhere between these extremes, and band positions can be used as an inference to the degree of covalency in the particular molecule.

The spectrum of aluminium hydroborate first reported by Price (24) will be discussed in detail later and is therefore only described in general terms here. The B-H$_T$ bands are observed at 2556 cm^{-1} and 2490 cm^{-1}, and those from the bridging BH$_2$ at 2032 cm^{-1} and 1940 cm^{-1}. This implies an increase in ionic character of the bonding over that in diborane as the bonds for terminal and bridging stretches have come closer together. Obviously in the case of the hydroborate ion they coincide. In addition, the AlH$_2$B bridge modes are at 1501 cm^{-1} and 1440 cm^{-1}. The deformation mode is observed at 1113 cm^{-1}.

The spectra of hydroborates containing a triple hydrogen bridge are obviously going to be slightly different. The B-H$_T$ stretch region of the infra-red spectrum of zirconium hydroborates which has an established triply hydrogen bridged gas phase structure (28) shows only one B-H$_T$ stretch and no band in the BH$_2$ deformation region (23, 29), and as uranium hydroborate has a very similar spectrum, it too is assigned a triply bridged structure in the gas phase (23, 30).

The infra-red spectrum of beryllium hydroborate (31), using the above criteria, can then be interpreted as a mixture where the boron is attached to beryllium by both double and triple hydrogen bridges, as it shows bonds in the positions expected for both structural types.

Some general rules for predicting structure types are presented in Fig. 1.7. Also see ref. 32.

Hydroborates - Nuclear Magnetic Resonance Spectral Properties

Boron has two naturally occurring isotopes, both of which have nuclear spin: ^{11}B (81.2% abundance), I = 3/2 and ^{10}B (18.8% abundance), I = 3. Aluminium has the one isotope ^{27}Al (100% abundance), I = 5/2.

I	II	III	IV
B-H stretch 2270 cm^{-1}	B-Hτ stretch 2560 2500 doublet	B-Hτ stretch 2560 sharp	B-Hτ 2 bands
	B-Hμ 2000 2 bands generally overlapping	B-Hμ 2100 2 bands	B-Hμ 1 band
BH_2 deformation 1090 cm^{-1}	Bridge stretch 1400-1500 cm^{-1}	Hμ-B-Hτ 1200 strong	Deformation 1000-1150 2 bands
	BH_2 deformation 1100-1150 cm^{-1}		

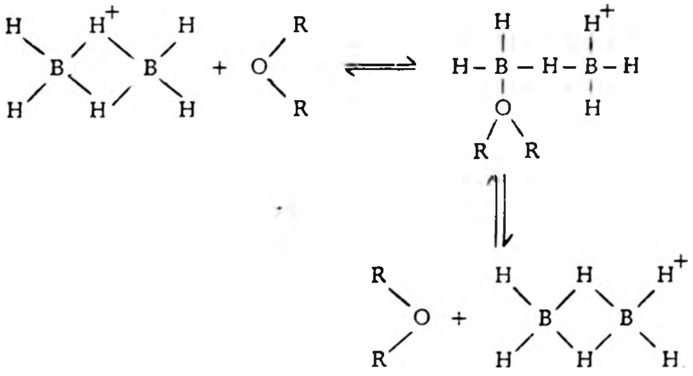
Fig. 1.7 General rules for predicting structure types in hydroborate groups

The magnetic resonance spectrum of the tetrahedral BH_4^- ion shows the equivalence of the four protons. The ^1H n.m.r. spectrum is a 1:1:1:1 quartet, due to coupling to the ^{11}B nucleus, and this is superimposed on a weaker 1:1:1:1:1:1:1 septet due to coupling to the ^{10}B nucleus. The coupling constant ($J_{^{11}B-H}$) was 82 Hz. The ^{11}B n.m.r. is a 1:4:6:4:1 quintet ($J_{^{11}B-H}$, 82 Hz) obtained by the coupling to the four equivalent hydrogens. Sharp lines indicate the high symmetry of the field around the boron atom (35).

Examination of the spectrum of diborane has been undertaken by several workers (35, 36a-e). The ^{11}B n.m.r. spectrum consists primarily of a triplet of triplets formed by splitting of the original signal into three by the nearest two terminal protons and into three again by the two bridge protons which have a smaller coupling constant ($J_{^{11}B-H_T}$, 133 Hz, $J_{^{11}B-H_\mu}$, 46 Hz). The ^1H n.m.r. spectrum shows, when the boron is not decoupled, a quartet for the terminal protons due to coupling to one boron atom and a septet for the bridge protons due to coupling with two boron atoms. When the boron decoupled spectrum is taken, the fine structure disappears to leave two resonances ratio 2:1 corresponding to the four terminal protons and the two bridging. The terminal protons are at lower field.

If, however, the spectrum is taken in ethers, a marked temperature dependence is observed (37). In diethyl ether at 30° C, the spectrum was a broad non-Lorentzian signal which, on warming to 84°C became a seven-line multiplet consistent with complete scrambling of all the protons to render them equivalent. On cooling below -36° C, the triplet of triplets observed for the neat sample was restored. The seven line multiplet is observed also if the spectrum is taken in an ethylene glycol dimethyl ether solution at room temperature. Ethers would therefore seem to catalyse the intramolecular scrambling, and the more basic the ether, the more effective the scrambling.

A possible equation would be



The n.m.r. spectra of aluminium hydroborates will be discussed later, but the general features will be pointed out here as they differ slightly from those observed for diborane. The ^{1}H n.m.r. consists of a broad structureless hump at room temperature caused by coupling to both aluminium and boron nuclei (38). The aluminium can be made to decouple by irradiation at the aluminium frequency to produce a 1:1:1:1 quartet due to the remaining boron coupling. The spectrum is temperature dependent in solution (see later). The ^{11}B n.m.r. spectrum consists of a 1:4:6:4:1 quintet, showing that a mechanism is in operation to produce equivalence of the protons. At no temperature can any distinction be found between bridging and terminal protons indicated by the previously mentioned diffraction work. This is a feature common to all the covalent tetrahydroborates. Intermolecular mechanisms would seem to be ruled out since exchange of either BH_3 groups or BH_4 groups would result in loss of coupling to the boron and aluminium nuclei respectively, and this is not observed.

Intramolecular processes that might be considered involve formation of an extra bridge bond followed by breaking of a different one, *i.e.*

Aluminium Hydroborate

Preparation

Schlesinger et al. first prepared aluminium hydroborate in yields of up to 70%, from the reaction of trimethyl alane with diborane (5, 6).

$$Al_2(CH_3)_6 + 4B_2H_6 \longrightarrow 2Al(BH_4)_3 + 2BMe_3$$

The reaction is inconvenient preparatively since it is slow, with the formation of intermediate products which are difficult to separate. The best yield was obtained by adding diborane in small quantities, and frequently removing the trimethyl borane produced.

Several methods using co-ordinating solvents have also been tried, but these two suffer from the drawback of the difficulty of product purification at the end of the reaction. An 88% yield was found when an ether solution of alane (aluminium hydride, AlH_3) was reacted with boron trichloride. The aluminium hydroborate formed as an etherate was freed of the ether by treatment with aluminium chloride (40, 41, 42).

$$4AlH_3.OEt_2 + 3BCl_3 \longrightarrow Al(BH_4)_3.OEt_2 + 3AlCl_3.OEt_2$$

Several other methods using aluminium hydride species have been used with or without a co-ordinating solvent (usually ether) (40, 41),

e.g. $LiAlH_4 + 2B_2H_6 \longrightarrow Al(BH_4)_3 + LiBH_4$

$$3LiAlH_4 + 3BCl_3 \xrightarrow{ether} Al(BH_4)_3 + 2AlCl_3 + 3LiCl$$

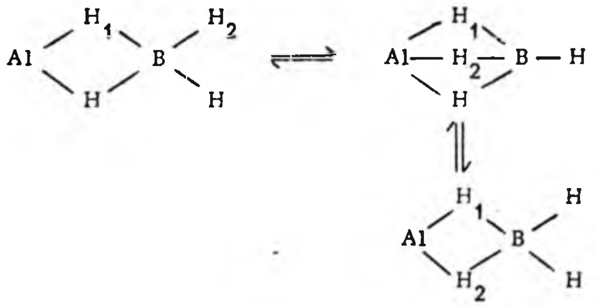
$$3LiAlH_4 + 3BF_3 \xrightarrow{ether} Al(BH_4)_3 + 2AlF_3 + 3LiF$$

These reactions also suffer from being low yielding and slow, and also wasteful as not all the boron and aluminium contents of the starting materials are transferred to the product.

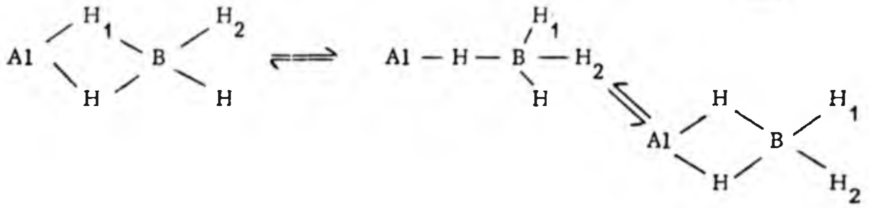
Again it was Schlesinger et al. who first used the double decomposition reaction of the aluminium chloride with alkali metal tetrahydroborates (43).

$$AlCl_3 + 3MBH_4 \longrightarrow Al(BH_4)_3 + 3MCl$$

The reactions take place in the solid phase and the yield of the product depends on the ratio of the reactants, and the nature of the cation M.



or breaking of a bridge bond followed by rotation and reforming, i.e.



or quantum mechanical tunnelling (38).

Although the last method cannot be ruled out, the mechanism that suggests the presence of a triple hydrogen bridge seems very plausible since there are hydroborates in which it exists preferentially, e.g. $U(BH_4)_4$ and one beryllium hydroborate which may have both a doubly bridged and a triply bridged hydrobrate group simultaneously.

The n.m.r. spectr~~a~~um of beryllium hydroborate proved difficult to obtain due to its low solubility in non-co-ordinating solvents. As was mentioned earlier, this has now been overcome and the ^{11}B and ^{1}H n.m.r. spectra have been recorded. The ^{11}B spectrum shows a quintet and the ^{1}H spectrum a 1:1:1:1 quartet, showing the equivalence of the protons by exchange processes. These spectra also establish a linear B-Be-B framework. The ^{1}H n.m.r. spectrum of methyl beryllium hydroborate in benzene/toluene solution at room temperature, however, again shows that there is a mechanism for equivalence of the hydroborate protons as a 1:1:1:1 quartet ($J11_{B-H}$. 86 Hz) is observed (39).

Aluminium Hydroborate

Preparation

Schlesinger et al. first prepared aluminium hydroborate in yields of up to 70%, from the reaction of trimethyl alane with diborane (5, 6).

$$Al_2(CH_3)_6 + 4B_2H_6 \longrightarrow 2Al(BH_4)_3 + 2BMe_3$$

The reaction is inconvenient preparatively since it is slow, with the formation of intermediate products which are difficult to separate. The best yield was obtained by adding diborane in small quantities, and frequently removing the trimethyl borane produced.

Several methods using co-ordinating solvents have also been tried, but these two suffer from the drawback of the difficulty of product purification at the end of the reaction. An 88% yield was found when an ether solution of alane (aluminium hydride, AlH_3) was reacted with boron trichloride. The aluminium hydroborate formed as an etherate was freed of the ether by treatment with aluminium chloride (40, 41, 42).

$$4AlH_3.OEt_2 + 3BCl_3 \longrightarrow Al(BH_4)_3.OEt_2 + 3AlCl_3.OEt_2$$

Several other methods using aluminium hydride species have been used with or without a co-ordinating solvent (usually ether) (40, 41),

e.g. $LiAlH_4 + 2B_2H_6 \longrightarrow Al(BH_4)_3 + LiBH_4$

$$3LiAlH_4 + 3BCl_3 \xrightarrow{ether} Al(BH_4)_3 + 2AlCl_3 + 3LiCl$$

$$3LiAlH_4 + 3BF_3 \xrightarrow{ether} Al(BH_4)_3 + 2AlF_3 + 3LiF$$

These reactions also suffer from being low yielding and slow, and also wasteful as not all the boron and aluminium contents of the starting materials are transferred to the product.

Again it was Schlesinger et al. who first used the double decomposition reaction of the aluminium chloride with alkali metal tetrahydroborates (43).

$$AlCl_3 + 3MBH_4 \longrightarrow Al(BH_4)_3 + 3MCl$$

The reactions take place in the solid phase and the yield of the product depends on the ratio of the reactants, and the nature of the cation M.

The greatest yield (in excess of 90%) occurs when aluminium chloride reacts with lithium tetrahydroborate in ratios close to stoichiometric. The reaction proceeds at room temperature if the aluminium hydroborate is continually removed and completion can be afforded by warming to 100° C. The aluminium hydroborate is easily purified by distilling in vacuo. When sodium tetrahydroborate is used, the yield is considerably less, but the yield can be increased by adding excess aluminium chloride and heating to 120° C. With potassium hydroborate alone the yield of aluminium hydroborate is essentially zero but can be put up to 40-60% by adding lithium chloride or lithium hydroborate respectively (44).

The course of the reaction is believed to go through intermediate chloroaluminium hydroborates which are formed in sequence. They are not stable in isolation, disproportionating to aluminium chloride and aluminium hydroborate (45, 46).

e.g. $LiBH_4 + AlCl_3 \longrightarrow Cl_2AlBH_4 + LiCl$

$$LiBH_4 + Cl_2AlBH_4 \longrightarrow ClAl(BH_4)_2 + LiCl$$

$$LiBH_4 + ClAl(BH_4)_2 \longrightarrow Al(BH_4)_3 + LiCl$$

$$3\ ClAl(BH_4)_2 \longrightarrow AlCl_3 + 2Al(BH_4)_3$$

Other methods, using alkali metal hydroborates, have used mineral oil or benzene as solvents, whilst an early method used calcium hydroborate in tetrahydrofuran solution (47).

Overall many methods have been published for aluminium hydroborate preparation. The main routes have been covered here, but small variations exist especially in the many patents taken out (48-58).

Synthetic Reactions using Aluminium Hydroborate - Uses

Aluminium hydroborate has been used to prepare other metal hydroborates, the first of which was uranium hydroborate by the reaction

$$UF_4 + 2Al(BH_4)_3 \longrightarrow U(BH_4)_4 + 2F_2AlBH_4$$

Similar reactions have been used to prepare the hafnium, zirconium, thorium, neptunium and plutonium hydroborates (59a, b, c).

$$NaMF_5 + 2Al(BH_4)_3 \longrightarrow M(BH_4)_4 + 2F_2AlBH_4 + NaF \quad (M = Hf, Zr)$$

$$MF_4 + 2Al(BH_4)_3 \longrightarrow M(BH_4)_4 + 2F_2AlBH_4 \quad (M = Th, Np, Pu)$$

Attempts have been made to prepare hydroborates of silicon, tin and lead using aluminium hydrobrate. The procedure was unsuccessful, the products isolated being shown below:-

$$6Me_3SiCl + 2Al(BH_4)_3 \longrightarrow Al_2Cl_6 + B_2H_6 + 6Me_3SiH \qquad (60)$$

$$MMe_4 + 2Al(BH_4)_3 \longrightarrow 2MeAl(BH_4)_2 + M + B_2H_4Me_2 + 2H_2 \qquad (61)$$

$$(M = Sn, Pb)$$

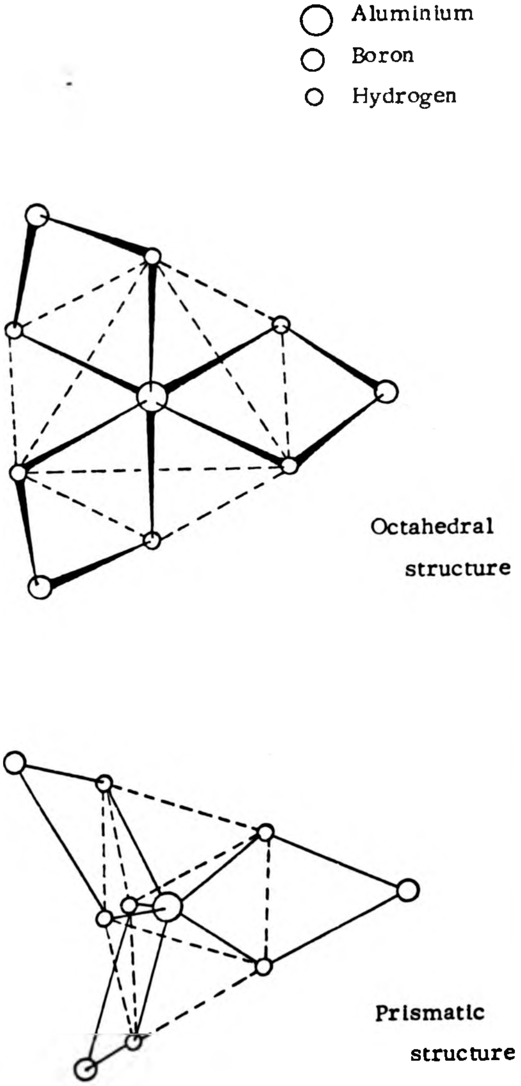
Aluminium hydroborate and its anionic derivatives have found the occasional use in organic reductions (e.g. 62) and could be an intermediate in reductions where sodium hydroborate is used in conjunction with aluminium choride (63, 64). Aluminium hydroborate has also been considered as a propellant for rocket and jet engines and as an ignition agent for jet engines (65-79).

Aluminium Hydroborate - Structure and Bonding

Soon after its discovery, aluminium hydroborate was being subjected to an electron diffraction study. The first results (80) indicated that the three boron atoms were arranged in a plane around the aluminium at angles of 120°. The boron was said to be near the centre of a trigonal bipyramid formed by the four hydrogens and the aluminium.

The exact positions of the hydrogen atoms is still not fully settled. In 1949 Price examined the infra-red spectrum of aluminium hydroborate (24) and concluded that the structure was a bridged one similar to diborane. Price adopted the suggestion put forward by Longuet-Higgins (81) that the hydrogen atoms round the aluminium atom could be arranged either in a prismatic manner (overall symmetry D_{3h}) where a line joining the bridge hydrogens is perpendicular to the $Al-B_3$ plane, or an antiprismatic (near octahedral, symmetry D_3) arrangement where the hydroborate group is rotated through 54°44' (half the tetrahedral angle). In addition an arrangement intermediate between the two could also be envisaged. This is also symmetry D_3 and termed aprismatic. Price concluded that the prismatic model was more likely.

Fig. 1.8 Structures of aluminium hydroborate



The early diffraction work was reanalysed and found to be consistent with the bridged structures (82, 83). More recently a more refined electron diffraction study (18) produced a result in favour of either the prismatic or a slightly aprismatic form. The molecular parameters were found to be Al-B, 214.3 pm, Al-H_μ, 180 pm, B-H_μ, 128 pm, B-H_T, 120 pm, $\angle H_\mu AlH_\mu$, 73°, $\angle H_\mu BH_\mu$, 114°, $\angle H_T BH_T$, 116°. Utilising these parameters, a theoretical calculation of the electronic structures of the prismatic and octahedral models of aluminium hydroborate was undertaken (84). Using the self-consistent molecular orbital method, it was concluded that the prismatic model was more stable by about 9 eV and thus argues that there ought not to be a labile equilibrium between the two forms. Inclusion of the 3d orbitals of aluminium slightly stabilised each structure. This paper also stated that it was the nuclear repulsion energy that decided the favoured geometry, being less for the prismatic form, and more than compensating for the greater electronic energy of the octahedral form. The electron densities were also stated as being 1.99 for aluminium, 3.12 for boron, 0.96 for H_T and 1.15 for H_μ. This shows that the aluminium charge has been partially removed into the hydrogen bridges and leaves the aluminium positively charged to the extent of about one unit. The calculations also showed that there was some direct Al-B bonding and that the aluminium and boron orbitals involved in the bridge bonds were predominantly the aluminium 3s and $3p_z$, and the favourably orientated $2p_z$ orbital of the boron.

A scheme showing the bonding molecular orbitals is attached. The e' and a_2'' molecular orbitals might be reversed. This utilises just the aluminium s and p orbitals as suggested by calculation, but an easier qualitative manner to describe the bonding might be to consider the system analagous to diborane as follows. The bridge system would then be considered to be made up an sp^2 and a p_z orbital from each boron, the bridging hydrogen s orbitals and alumium sp^3d^2 orbitals.

Fig. 1.9

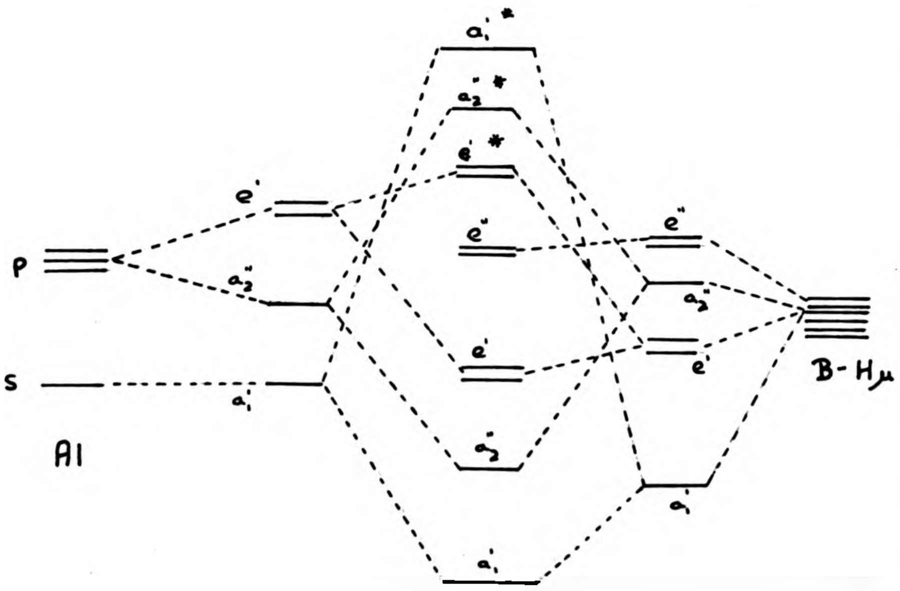
Molecular Energies of $Al(BH_4)_3$

Energies eV	Prismatic	Octahedral
Electronic	-1917.82	-1947.07
Nuclear	1524.70	1563.15
Total	-393.12	-383.92

Bond Orders (trigonal prismatic)

	Al-Hμ	B-Hμ	
3s	0.284	0.374	2s
3py	0.099	0.286	2py
3pz	0.213	0.682	2pz

Bonding molecular orbitals D3h Prismatic



Aluminium Hydroborate - Properties

Physical Properties

Aluminium hydroborate is the only metal hydroborate which is a liquid at room temperature. It is colourless and mobile in the liquid phase, volatile and unstable at room temperature, evolving hydrogen (see later). In the condensed phase there is very little interaction between the molecules, which may explain the low melting and boiling points (10b).

Selected Physical Properties

Property	Magnitude	Reference
Melting point /°C	-64.5	6
Boiling point/°C	+44.5 (extrapolated)	6
Vapour pressure/mm Hg	119.5 at 0° C	6
	$\log p = 9.56795 - 1799.1/T$	87
	$\log p = 7.808 - 1515/T$	6
Heat of formation/kJ mol^{-1}	-301	85 Ref. 85 also gives heat of combustion and heat of hydrolysis.
Density / g cm^{-3}	0.544	6
	$0.7866 - 0.000793/T$	86

Aluminium Hydroborate - Reactions

Probably the most noticeable properties of aluminium hydroborate are its extreme moisture and air sensitivity. Aluminium hydroborate explodes violently in air, but it has been reported not to explode in dry oxygen at 20° C over a pressure range of 1-300 mm. Explosions do occur at 110° (88). Further studies showed that it explodes in moist oxygen at 20° also igniting olefins (89). The oxide and hydroxide are formed

$$Al(BH_4)_3 + 12H_2O \longrightarrow Al(OH)_3 + 3B(OH)_3 + 12H_2$$

$$2Al(BH_4)_3 + 12\ O_2 \longrightarrow Al_2O_3 + 3B_2O_3 + 12H_2O$$

The hydrolysis is proposed to proceed in two steps (90), an initial formation of aluminium hydroxide and diborane followed by a slower hydrolysis of the latter.

$$Al(BH_4)_3 + 3H_2O \xrightarrow{\text{fast}} Al(OH)_3 + 3/2B_2H_6 + 3H_2$$

$$3/2B_2H_6 + 9H_2O \xrightarrow{\text{slower}} B(OH)_3 + 9H_2$$

The mechanism of the first step is interesting, bearing in mind the three observations below. Aluminium hydroborate is known to form adducts with oxygen donors (e.g. ethers); the formation of species of the type $MeOAl(BH_4)_2$ (see later) with methanol and the hydrate of diborane isolated by Jolly (91a, b). It is therefore tempting to suggest that the mechanism of the first step may be formation of a transient adduct, followed by replacement of the hydroborate groups on aluminium by OH, the hydroborate groups being liberated as BH_3 and H_2, e.g.

$$\begin{tikzcd} Al(BH_4)_3 + H_2O \arrow[r] & {[Al(BH_4)_3.OH_2]} \arrow[d, "\text{v. short lifetime}"'] \\ & HOAl(BH_4)_2 + BH_3 + H_2 \arrow[d, "\text{etc}"] \\ & (HO)_3Al + 3/2B_2H_6 + 3H_2 \end{tikzcd}$$

Unpublished work by McAvoy (92) shows that when reacting aluminium hydroborate with small amounts of water, diborane can be detected. With molar quantities of 1 $Al(BH_4)_3 : 3H_2O$, a flash reaction occurred; a large amount of hydrogen was measured (9 moles), diborane was detected and no aluminium hydroborate was recovered. A brown solid remained which was unidentified. This result would seem to agree with the above scheme, the excess hydrogen being explained in terms of an accelerated aluminium hydroborate decomposition in the flash zone. In postulating intermediate compounds of the type $(HO)_xAl(BH_4)_{3-x}$, it must be remembered, however, that hydrolysis of a diborane with limited quantitites of water always results in isolation of boric acid and unreacted diborane, presumably due to intermediate disproportionation (93), so the additional disproportionation reaction must also be considered in the aluminium hydroborate scheme.

$$2B_2H_6 + 6H_2O \longrightarrow 2B(OH)_3 + B_2H_6 + 3H_2$$

Postulate e.g. $3(HOBH_2)_2 \longrightarrow 2B_2H_6 + 2B(OH)_3$

$$3HOAl(BH_4)_2 \longrightarrow (HO)_3Al + 2Al(BH_4)_3$$

Exchange Reactions and Substituted Products

Both diborane and hydrogen exchange hydrogen with aluminium hydroborate whilst diborane also exchanges boron (94). The exchange between aluminium hydroborate and deutero diborane has been interpreted in terms of the following reaction scheme:-

$$\begin{aligned} Al(BH_4)_3 &\rightleftharpoons HAl(BH_4)_2 + BH_3 \\ B_2D_6 &\rightleftharpoons 2BD_3 \\ BH_3 + B_2D_6 &\rightleftharpoons BH_3BD_3 + BD_3 \\ BD_3 + HAl(BH_4)_2 &\longrightarrow Al(BD_3H)(BH_4)_2 \end{aligned}$$

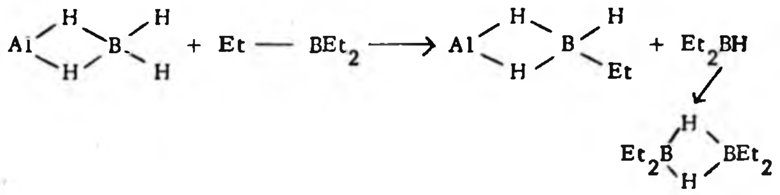
Boron exchange was shown by using ^{10}B in the diborane, and long reaction times showed that all twelve hydrogens exchanged.

The exchange with deuterium is believed to proceed via two mechanisms as either two or three of the hydrogen exchange more rapidly than the remainder. The predominant reaction has been suggested to be exchange of deuterium with borane fragments.

$$\begin{aligned} Al(BH_4)_3 &\rightleftharpoons Al(H)(BH_4)_2 + BH_3 \\ BH_3 + D_2 &\rightleftharpoons BH_2D + HD \end{aligned}$$

Initial dissociation producing a borane fragment would also be consistent with pyrolysis experiments which will be discussed later in conjunction with aluminium hydroborate decomposition and n.m.r. spectrum.

Aluminium hydroborate has been observed to exchange terminal hydrogens with boron alkyls (this work). As will be shown by n.m.r. spectra, the aluminium species becomes alkylated on the boron and the boron alkyl becomes an alkylated diborane, e.g.



Similar behaviour has been observed by Schlesinger et al. (95) for uranium hydroborate with trimethyl borane, the compounds $U(BH_4)_3(BH_3Me)$ and $U(BH_3Me)_4$ being isolated, and by Marks and Kolb for tris cyclo pentadienyl uranium hydroborate with triethyl borane (96).

Aluminium hydroborate is now known to undergo a general exchange/redistribution reaction with aluminium alkyls to produce alkyl aluminium hydroborates (97). The first alkyl aluminium hydroborates produced were the mono and dimethyl derivatives isolated by Schlesinger et al. (98), and they were also formed as by-products in the attempted preparation of tin and lead hydroborates by Holliday et al. (61). The next alkyl aluminium hydroborate to be isolated was the diethyl aluminium hydroborate of Davies and Wallbridge (99) who synthesised it by several methods including exchange between triethyl alane and aluminium hydroborate. These workers concluded that the diethyl derivative was more stable than the monoethyl which they were not able to isolate. This was in direct contrast to the known properties of the methyl derivatives, where the dimethyl derivative is unstable. Oddy repeated the preparations of the methyl and ethyl derivatives and showed that the preparative route, using redistribution reactions of aluminium alkyls with aluminium hydroborate in correct stoichiometric ratios, could be used for methyl, ethyl, n-propyl and isobutyl aluminium hydroborates (100, 101).

$$Al_2R_6 + 4Al(BH_4)_3 \longrightarrow 6RAl(BH_4)_2 \qquad R = Me,\ Et\ or\ Pr$$

$$Al_2R_6 + Al(BH_4)_3 \longrightarrow 3R_2AlBH_4 \qquad R = Me,\ Et$$

$$AlR_3 + 2Al(BH_4)_3 \longrightarrow 3RAl(BH_4)_2 \qquad R = isobutyl$$

Oddy concluded that the diethyl aluminium hydroborate reported by Davies had been wrongly assigned, due to diethyl aluminium hydroborate disproportionating to ethyl aluminium bis(hydroborate). A reinterpretation has very recently appeared (101). Other observations suggesting the existence of alkyl aluminium hydroborates have been by Brokaw and Pease in reactions of aluminium hydroborate with olefins (89, 102, 103), and by

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Brown and Subba Rao in the reaction of aluminium hydroborate with 1-octene in diethyl ether (63). The alkyl aluminium hydroborates are all volatile liquids and vaporise as the monomer in contrast to the lower aluminium alkyls. Like the parent compound, aluminium hydroborate, they have extreme air and moisture sensitivity and are also observed to form adducts with Lewis bases (100, 101). The dialkyl compounds are less stable than the monoalkyl species, and the stability of the monoalkyl species decreases as the size of the alkyl group increases, such that isobutyl aluminium bis hydroborate was extremely difficult to purify due to its ready disproportionation on distillation (101).

Oddy has also shown that the reaction of aluminium hydroborate with hydride dialkyl alanes can also lead to the substituted hydrido aluminium hydroborates. These are very unstable materials, disproportionating in the gas phase, but are of great interest in that any scheme to explain aluminium hydroborate decomposition, pyrolysis or exchange reaction uses aluminium hydroborate dissociation to a hydrido species and borane as an initial step.

$$Al(BH_4)_3 \longrightarrow HAl(BH_4)_2 + BH_3$$

$$(Et_2AlH)_3 + 6Al(BH_4)_3 \longrightarrow 3HAl(BH_4)_2 + 6EtAl(BH_4)_2$$

$$3HAl(BH_4)_2 \xrightarrow{\text{distillation}} AlH_3 \downarrow + 2Al(BH_4)_3$$

The hydrido aluminium hydroborate species can be stabilised by complexing with Lewis bases. The trimethyl amine adduct has been obtained in good yield by Ruff (104) by the reaction of lithium hydroborate with hydrido dichloro alane-trimethylamine in benzene solution.

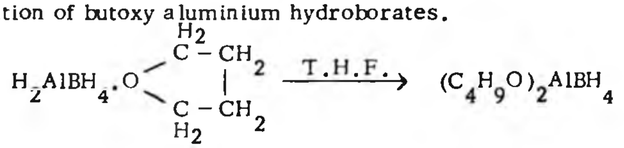
$$HAlCl_2.NMe_3 + 2LiBH_4 \longrightarrow HAl(BH_4)_2.NMe_3 + 2LiCl$$

Ether adducts have been prepared by two methods, both using diborane in ether solution either on lithium hydroaluminate or alane.

$$LiAlH_4 + 3/2B_2H_6 \xrightarrow{\text{ether}} HAl(BH_4)_2.OEt_2 + LiBH_4 \qquad (105)$$

$$AlH_3.OEt_2 + B_2H_6 \xrightarrow{\text{ether}} HAl(BH_4)_2.OEt_2 \qquad (106)$$

The related tetrahydrofuran adduct was also prepared (105), but in tetrahydrofuran solution this decomposes by ring cleavage leading to formation of butoxy aluminium hydroborates.



An adduct containing two moles of Lewis base has also been reported (107).

$$H_2AlBH_4.NMe_3 + NMe_3 \xrightarrow[\text{Oil}]{\text{Paraffin}} H_2AlBH_4.2NMe_3$$

A compound with the formula $H_2AlBH_4.C_6H_6$ has been isolated (45). Oddy has suggested that the uncomplexed form of hydrido aluminium bis hydroborate is monomeric based on the n.m.r. shift of the aluminium hydrogen, and on the same basis has suggested that bis hydrido aluminium hydroborate is dimeric. The hydrido aluminium hydroborate species are usually identified by an aluminium-hydrogen stretching frequency around 1850 cm^{-1} in the infra-red spectrum.

A recent report (174) mentions the preparation and properties of the hydrido gallium bis(hydroborate). This seems to be more stable than the aluminium species, although still unstable at room temperature. The compound is volatile (s.v.p. at -45° C, 10 mm Hg) and shown to be monomeric by estimation of the decomposition reaction

$$GaB_2H_9 \longrightarrow Ga + 3/2H_2 + B_2H_6$$

The structure is assigned a terminal Ga-H and two doubly bridged hydroborate groups on the basis of spectroscopic data. The compound also undergoes exchange with trimethyl gallium and forms an adduct with trimethyl amine.

This apparent stability of the gallium over the aluminium derivative is also seen for the dimethyl gallium derivative which is formed in preference to the tris(tetrahydroborate) on reaction of trimethyl gallium with diborane (175). This trend in stability is, of course, contrary to the scheme in aluminium chemistry where aluminium hydroborate is the more stable.

Alkoxy aluminium hydroborates have been observed in tetrahydrofuran cleavage reactions of hydrido aluminium hydroborate adducts (see above, 105), and have also been prepared previously by two other methods.

A compound formulated as $AlH_3(BH_3)_3.3Al(OC_3H_7)_3$ has been described as a colourless liquid, distillable *in vacuo*, obtained from the action of aluminium hydroborate on aluminium isopropoxide in tetrahydrofuran (108), and alkoxy aluminium hydroborates have also been formed from alkoxy hydrido alanes and diborane in ether solution (109).

$$B_2H_6 + ROAlH_2 \xrightarrow{\text{ether}} ROAl(BH_4)_2$$

This work will give details of preparation and some spectroscopic properties of alkoxy aluminium hydroborates, $ROAl(BH_4)_2$ (R = Me, Et) from the reaction of aluminium hydroborate with alkoxy boranes and of thioalkyl aluminium hydroborates, a class of compounds not reported previously, $RSAl(BH_4)_2$ (R = Me, Et, benzyl), prepared by the action of thiols on aluminium hydroborate.

The compounds are reported to be white associated solids (believed to be dimeric) and showing a much decreased sensitivity to moisture and air over the parent compound, aluminium hydroborate, and no observed tendency towards adduct formation with diethyl ether. The association is predicted to be *via* the alkoxy oxygen (109). An alkoxy beryllium hydroborate has recently been prepared and characterised. This is believed to be dimeric (182).

Siloxy species may be prepared by the reaction of lithium hydroborate with trimethyl siloxy aluminium dichloride (110).

$$4LiBH_4 + [R_3SiOAlCl_2]_2 \longrightarrow [R_3SiOAl(BH_4)_2]_2 + 4LiCl$$

The compound is dimeric with bridging oxygens, as are the corresponding hydrido and chloro derivatives $[R_3SiOAlXBH_4]_2$ (X = H, Cl). Reaction of these with amines or phosphines does not lead to adduct formation as in neat aluminium hydroborate chemistry, but directly to boron loss as a borane adduct.

Several dimethylamino derivatives of aluminium hydroborate now exist. The initial preparations made use of the reaction of lithium hydroborate on the corresponding amino chloro alane (104).

$$Cl_2AlNMe_2 + 2LiBH_4 \longrightarrow Me_2NAl(BH_4)_2 + 2LiCl$$

$$HAlClNMe_2 + LiBH_4 \longrightarrow HAlNMe_2BH_4 + LiCl$$

These were found to be associated in benzene solution to degrees between 2 and 3 by nitrogen bridging. A more recent method of preparing $Me_2NAl(BH_4)_2$ used the reaction of diborane on the related hydrido compound (110), and a similar compound has the dimethyl amino group bridging between the aluminium and the boron atoms as $H_2B(NMe_2)_2Al(BH_4)_2$ (111, 112). This compound can be prepared by the action of excess diborane on $HAl(NMe)_2$, $Al(NMe_2)_3$ or $[H_2B(NMe_2)_2]_2AlH$ in diethyl ether solution. The product is a colourless, slightly volatile solid which exhibits a triplet ($J_{^{11}B-H} = 115$ Hz) in its ^{11}B n.m.r. spectrum which is entirely consistent with the formulated terminal BH_2. Treatment of the compound with one mole of triphenyl phosphine removed a BH_3 as $BH_3.PPh_3$ leaving $H_2B(NMe_2)_2AlBH_4$, although this could not be separated from the staring material. An impure , oily compound formulated as $(Me_2NBH_3)_2AlBH_4$ results from the reaction of aluminium hydroborate with dimethyl amino borane (113). It exhibits similar chemical properties to the compound $H_2B(NMe_2)_2Al(BH_4)_2$.

A few chloro aluminium hydroborates have been reported. $ClAl(BH_4)_2$ itself appears to be an unstable liquid (melting around -10° C) and rapidly disproportionating to the dichloro compound and aluminium hydroborate. The dichloro compound is again unstable : it is solid and volatile and disporportionates below room temperature to aluminium hydroborate and aluminium chloride (114, 59a).

$$2ClAl(BH_4)_2 \longrightarrow Al_2AlBH_4 + Al(BH_4)_3$$

$$3Cl_2AlBH_4 \longrightarrow Al(BH_4)_3 + 2AlCl_3$$

The chloro aluminium hydroborates are compounds which again can be stabilised by complexing with diethyl ether (115, 116-120). The latter references by Russian workers also describe the spectroscopic properties of the adducts of the chloro aluminium hydroborates. The adducts are monomeric in the crystalline phase (117) and are liquids at room temperature (116). Assignments of vibrational frequencies were made

(118) and an increase in ionic character of the hydroborate group over that in aluminium hydroborate is suggested. Their n.m.r. spectra have been recorded (119).

The only other halo compound reported is the difluoro compound as a by-product of the reaction of aluminium hydroborate with heavy metal fluorides. Its isolation has not been reported (9, 59a).

Anionic Aluminium Hydroborate Compounds

Anionic aluminium hydroborate compounds were first suggested in the 1950's (121-126). Salts such as $\mathrm{LiAl(BH_4)_4}$ were believed to be formed when hydride species were reacted with either aluminium hydroborate or diborane in ethereal solutions.

$$\mathrm{LiH} + \mathrm{Al(BH_4)_3} \xrightleftharpoons{\text{ether}} \mathrm{LiAlH(BH_4)_3}$$

$$\mathrm{LiBH_4} + \mathrm{Al(BH_4)_3} \xrightleftharpoons{\text{ether}} \mathrm{LiAl(BH_4)_4}$$

$$\mathrm{LiAlH_4} + \mathrm{B_2H_6} \xrightleftharpoons{\text{ether}} \mathrm{LiAlH_2(BH_4)_2}$$

A possible structure for $[\mathrm{Al(BH_4)_4}]^-$ was suggested with two doubly bridged and two singly bridged bydroborate groups. Ashby et al. (105) concluded that some of the stable anionic hydroborates reported in tetrahydrofuran solution were the butoxy cleavage products, but agreed compounds of the type $\mathrm{LiAlH_3BH_4.nOEt_2}$ could exist although the preferred formulation was mixtures of adducts of $\mathrm{LiAlH_4}$ and $\mathrm{BH_3}$.

The $[\mathrm{Al(BH_4)_4}]^-$ ion has now been isolated by several workers; with the large cation $[\mathrm{C_8H_{17}NC_3H_7}]^+$ by Nöth et al. (127), with potassium (128, 129) and with tetra alkyl ammonium cations (130-132) by Russian workers. The tetra ethyl ammonium salt of $[\mathrm{Al(BH_4)_4}]^-$ was shown to contain four double hydrogen bridge bonds by infra-red and X-ray techniques and is stable to 150° C (130). The potassium salt is stable to 120° C (128) but the tetrabutyl slightly less so, decomposing at 90° C (132).

Several papers have dealt with the addition of lithium hydride or chloride or hydroborate to aluminium hydroborate. Spectra indicated the following equilibria with the ionic species predominant at room temperature and the equilibrium going to the right if the temperature was lowered or the solvent removed (45, 133-135).

$$LiX + Al(BH_4)_3 \xrightleftharpoons{ether} LiAlX(BH_4)_3 \xrightleftharpoons{ether} LiBH_4 + AlX(BH_4)_2$$

$X = BH_4$, Cl, Br, H

If lithium deuteride was used and the solvent removed, the product not only contained deuterium attached to aluminium but also in the hydroborate groups. The suggested mechanisms were intermolecular loss of BH_3 or an intramolecular rearrangement involving single hydrogen bridges to put the deuterium into the hydroborate groups.

There have been many short papers recently on the subject of mixed halo hydroborato anionic aluminium species by almost exclusively Russian workers (136-145).

An amine complex of tetrahydroborate trihydroaluminate has been reported (146) as being formed from trimethyl amine alane and tetrabutyl ammonium tetrahydroborate.

$$AlH_3NMe_3 \quad + \quad Bu_4N.BH_4 \longrightarrow Bu_4N^+[NMe_3AlH_3(BH_4)]^-$$

and is stated to have a single hydrogen bridge between boron and aluminium on the basis of infra-red evidence. Semenenko and his co-workers, however, working on the interaction of complexes $M[Al(BH_4)_4]$ with ammonia report that the reaction proceeds to produce MBH_4 and $[Al(NH_3)_6](BH_4)_3$ (144). An intermediate adduct was not reported, but this is not surprising as excess ammonia was used and the preferential reaction of aluminium hydroborate with ammonia is to absorb 2 or 6 moles (see later).

Adducts of Aluminium Hydroborates

The interaction of aluminium hydroborate with Lewis bases was first noted by Schlesinger et al. who obtained adducts of aluminium hydroborate with dimethyl ether and trimethylamine. This is an interesting reaction in that, although the orbitals of aluminium are involved in the hydrogen bridge bonding to boron, they are still capable of interacting with donors of this sort. The major site of electron deficiency in the aluminium hydroborate molecule is the aluminium atom, and it is not surprising that the donor molecule bonds preferentially at this site. With certain molecules, the donor can also attack at boron which results in breaking of a bridge bond and formation of a borane adduct.

Since the initial observation by Schlesinger et al., the major contribution to this field has been by Wallbridge with various co-workers (147-156, 30), other contributions having come from several other workers (157-169, 118, 119, 8, 48, 104).

Two major sorts of ligand species are formed where the stoichiometry is either of the type $Al(BH_4)_3.L$ or $Al(BH_4)_3.2L$, although reactions to form $Al(BH_4)_3.4L$ ($L = NH_3$ or N_2H_4) and $Al(BH_4)_3.6L$ ($L = NH_3$) are known. With ligands containing a donor atom from group VIB of the periodic table, only 1:1 adducts have been obtained, even at low temperature. These adducts are stable towards decomposition at room temperature under inert atmosphere and are soluble in excess of the ligand which is used in their preparation ; thus aluminium hydroborate is condensed on to the excess of ligand, stirring for several minutes at 0° C and then removing the excess at 0° C. Adducts have been prepared with dimethyl ether, diethyl ether, di-isopropyl ether, tetrahydrofuran, dimethyl sulphide and tetrahydrothiophene (this work). All are involatile liquids at room temperature, except for the di-isopropyl ether adduct which is a solid and possibly the tetrahydrothiophene adduct which was observed to deposit crystals on standing in which the tetrahydrothiophene ring was intact (by n.m.r.). In contrast the tetrahydrofuran adduct deposits a small number of crystals of butoxy aluminium bis hydroborate due to ring opening.

With compounds containing the donor atom from group VB, the situation is slightly different. More care must be taken in the preparation where excess aluminium hydroborate and a hydrocarbon solvent must be used. If this care is not taken, then cleavage of the hydroborate bridges can occur according to

$$R_3X + Al(BH_4)_3.XR_3 \longrightarrow HAl(BH_4)_2.XR_3 + BH_3XR_3$$

(X = N, P, As)

1:1 adducts have been formed with NMe_3, NMe_2H, NH_3, (possibly) NH_2Me, NEt_3, PMe_3, PPh_3 and $AsMe_3$ and hydrazine. 1:2 adducts have been formed with NMe_3, NH_2Me, NH_3 and PMe_3. A mixed adduct with PMe_3 and NMe_3 has also been prepared. All these compounds are solid with the exception of the dimethyl amine adduct, and are relatively stable at room temperature under nitrogen except for the triphenyl phosphine adduct. Information on the mono ammoniate is not available. The 1:2 adducts with trimethyl amine and trimethyl phosphine decompose slowly at room temperature, releasing the 1:1 species and cleavage products.

The strength of the bond between aluminium and the co-ordinating atom has been given a relative scale by displacement reactions to reveal the order

$$N \approx P > As \quad \text{and} \quad O > S$$

The existence of a bond between aluminium and the donor atom has been directly observed by X-ray diffraction. The most extensively studied compound is $Al(BH_4)_3.NMe_3$, which has been subjected to analysis at 25° C and -160° C (153-156), the study at the latter temperature determining the positions of the hydrogen atoms. At 25° C the arrangement of the three borons and the nitrogen is essentially tetrahedral around the aluminium whilst the three carbons and the aluminium around nitrogen is also tetrahedral. The two tetrahedra adopt a staggered configuration. The bond distances were Al-B 219 pm, Al-N 201 pm and C-N 158 pm. At -160° C the tetrahedral configuration around aluminium is distorted as one boron moves away from the nitrogen and the other two towards it ($\angle$ N-Al-B_1 122°; $\angle$ N-Al-$B_{2,3}$, 100°). The aluminium bridge hydrogens with the nitrogen ligand atom make up a distorted pentagonal bipyramid arrangement around aluminium. The apical positions are the nitrogen and a bridge hydrogen. Bond distances were Al-N 200 pm; Al-B 224 pm; Al-H_μ 188 pm; B-H_μ 143 pm; B-H_T 119 pm.

The X-ray data on the trimethyl arsine adduct (155) shows that the structure is similar to that of the low temperature form of the trimethylamine adduct. The data was considered by the workers to be of poor quality and further implications of the distortion were not pursued. Values that were given were $\angle$ As-Al-B_1 121°; $\angle$As-Al-$B_{2,3}$, 93°; AlB_1 247 pm; $AlB_{2,3}$ 218 pm; Al-As 255 pm.

The structure of the monoammoniate adduct has been reported (158, 159) as having two independent types of monomeric molecules, each having different interatomic distances and angles. The average values quoted were Al-B 223 pm, Al-N 197pm.

Cleavage reactions by excess amine or phosphine have been most extensively studied for the di- and trimethylamines. Addition of excess trimethyl amine resulted in an uptake of up to four moles and formation of a borane adduct,

e.g. $Al(BH_4)_3 + 4NMe_3 \longrightarrow AlH_3.NMe_3 + 3BH_3.NMe_3$

At an intermediate stage hydride aluminium bis(hydroborate) trimethyl amine could be isolated.

With dimethylamine in solution, up to six moles of amine are absorbed, and in the absence of a solvent a further one and a half.

$$Al(BH_4)_3 + 4NMe_2H \longrightarrow AlH_3.NMe_2H + 3BH_3.NMe_2H$$

$$AlH_3.NMe_2H + 2NMe_2H \longrightarrow Al(NMe_2)_3 + 3H_2$$

and

$$3BH_3NMe_2H \longrightarrow 3BH_2NMe_2 + 3H_2$$

$$3/2BH_2NMe_2 + 3/2NMe_2H \longrightarrow 3/2BH(NMe_2)_2 + 3/2H_2$$

Although the preferred reaction of aluminium hydroborate with ammonia is to form a 1:2 adduct (148), the reaction of excess of ammonia with aluminium hydroborate resulted in the formation of a white solid $Al(BH_4)_3.6NH_3$. It was insoluble in ether or hydrocarbon solvents (149, 163-166, 168, 160). Originally formulated as the ionic compound $[Al(NH_3)_6]^{3+} 3(BH_4^-)$ it was later amended to $[AlH_2(NH_3)_4]$-$[BH_2(NH_3)_2(BH_4)_2]$ by ^{11}B n.m.r. studies (168). Some later workers still prefer the ionic formulation (160).

Hydrazine behaves in a similar manner, forming a 1:1 adduct, and with excess a compound best formulated as $Al(N_2H_4)^{3+} (BH_4^-)_3$ (167).

Vibrational Spectra of Aluminium Hydroborate

In 1949 Price published the first infra-red spectrum of aluminium hydroborate (24) and concluded that the molecule contained double hydrogen bridges between the boron and the aluminium. In particular, agreement with the spectrum of diborane were bands at 2559 cm^{-1} and 2493 cm^{-1} in a region which had been designated as a B-Hᴛ stretching region. Two bands at 2031 cm^{-1} and 1500 cm^{-1} were considered analagous to bridge vibrations of diborane at 1860 cm^{-1} and 1602 cm^{-1}. Raman spectra have been reported, including a communication of results by Rice and Young which has not been fully published, by several workers (169,(also see 24), 170, 171). More recently a combined Raman and infra-red study, including the crystalline state of aluminium hydroborate, has been published by Semenenko et al. (172), but by far the most detailed studies are those of Marriott (23) and Nibler and Coe (173) which will be considered here. The assignments for $Al(^{11}BH_4)_3$ are given for both papers in Table 1.3. As can be seen from the table, the assignments given by these authors disagree in several places. In particular, the band at 2032 cm^{-1} is assigned by Marriott to the symmetric B-Hμ stretch with the antisymmetric B-Hμ stretch being the shoulder observed in the infra-red spectrum at 1940 cm^{-1}. Nibler, however, assigns the band at 2032 cm^{-1} to the antisymmetric B-Hμ and the symmetric B-Hμ to the band at 2059 cm^{-1}, which is a strong band in the solid state spectrum but not visible in the gas phase. In this instance this author prefers the assignment of Marriott because, as Oddy has shown (97, 100), that in the spectrum of the dimethyl aluminium hydroborate, the shoulder observed at 1940 cm^{-1} for aluminium hydroborate has become a very strong band, shifted slightly to 1960 cm^{-1}. The assignment of Nibler of the 1940 cm^{-1} band as a combination of the symmetric Al-B stretch and the symmetric bridge stretch would not seem to agree with this observation. The other major difference is near 1500 cm^{-1}. Whereas Marriott assigns the bridge stretch at 1501 cm^{-1} and the shear at 1440 cm^{-1}, Nibler suggests the shear at 1505 cm^{-1} and the bridge stretch at 1425 cm^{-1}.

Oddy found the spectra of the alkyl aluminium bis(hydroborate) series (alkyl = Me, Et, n-Pr, i-Bu) to resemble each other very closely in position of bands attributable to the hydroborate group. Thus all the B-Hᴛ bonds were near 2550 cm^{-1} and 2485 cm^{-1} and the bridge

Table 1.3a

Infra-red vibrations of aluminium hydroborate

Raman /cm^{-1}	I.r./cm^{-1}	Assignment (23)
dp 2551 ms	2556 s	ν_{15} as B-H_T stretch
	2490 s	ν_{16} s B-H_T stretch
p 2473 vs		ν_1 s B-H_T stretch
	2215 m	2 x ν_{19}
p 2079 vs		ν_2 s B-H_μ stretch
	2032 vs	ν_{17} s B-H_μ stretch
dp 2000 m		ν_{24} as B-H_μ stretch
	1940 sh	ν_{11} as B-H_μ stretch
p 1930 mw		?
	1501 vs	ν_{18} s bridge stretch
p 1501 s		ν_3 s bridge stretch
	1440 sh	ν_{12} bridge shear
dp 1385 mw		ν_{25} bridge shear
dp 1152 m		ν_{26} BH_2 twist
p 1122 m		ν_4 BH_2 deformation
dp 1113 mw	1113 vs	ν_{19} BH_2 deformation
dp 976 m	978 w	ν_{20} BH_2 rock in plane
	920 vw	ν_{13} ? BH_2 rock out of plane
dp 603 m	606 vs	ν_{21} as Al-B stretch
p 511 vs		ν_5 s Al-B stretch
	470 w	?
dp 323 m	325 w	ν_{22} Al-B deformation
	220 w	ν_{14} Al-B deformation

Table 1.3b

Infra-red vibrations of aluminium hydroborate

Raman/cm^{-1}	I.r./cm^{-1}	Assignment (173)
	2650 msh	$\nu_2 + \nu_{21}$
dp 2550 s	2555 vs	ν_{15} as B-H_T stretch
	2490 vs	ν_{16} as B-H_T stretch
p 2475 vs		ν_1 s B-H_T stretch
	2218 s	$\nu_4 + \nu_{19}$
p 2075 vs		ν_2 s B-H_μ stretch
	2030 vsb	ν_{11} as B-H_μ stretch
dp 2000 m		$\nu_{18} + \nu_{21}$
	1930 msh	$\nu_5 + \nu_{18}$
p 1925 m		$2\nu_{20}$
	1505 vs	ν_{12} bridge shear
p 1503 s		ν_3 s bridge stretch
dp 1386 msh	1425 ssh	ν_{18} s bridge stretch
dp 1155 m		ν_{26} BH_2 twist
p 1124 m		ν_4 BH_2 deformation
dp 1114 m	1112 vs	ν_{19} BH_2 deformation
dp 979 w	981 w	ν_{20} BH_2 rock in plane
	765 wsh	ν_{13} BH_2 rock out of plane
dp 601 m	605 vs	ν_{21} as Al-B stretch
p 512 s		ν_5 s Al-B stretch
dp 320 w	324 m	ν_{22} Al-B deformation
	222 m	ν_{14} Al-B deformation

stretching and BH_2 deformation modes centred around 2100 cm^{-1} and 1115 cm^{-1} respectively. This would indicate that the bonding in the hydroborate groups in these molecules is very similar, and that they are very little influenced by the alkyl group.

Across the series $Al(BH_4)_3$, $MeAl(BH_4)_2$, Me_2AlBH_4 the stretching vibrations, B-Hт, decrease in frequency by small amounts across the series, accompanied by a slight increase in the positions of the terminal BH_2 deformation and rocking modes. The most dramatic change is in the band attributed above to the asymmetric B-Hμ stretch which is a weak shoulder for aluminium hydroborate and becomes the strongest band in the region for the dimethyl compound. This dramatic change was not fully explained, but the other trends mentioned were explained on the basis of increasing charge density at the hydroborate group rendering it more ionic in nature and requiring movement towards coincidence of the B-Hμ and B-Hт modes and thus strengthening the bridge bonds at the expense of the terminal bonds.

A similar trend is observed when the aluminium hydroborates are complexed with ligands. Three sets of bands could be defined. Those bands which can be correlated with the free ligand, those bands which can be correlated with the original aluminium hydroborate framework and those bands which arise from the metal to donor atom bond.

The doublet arising from the vibrations of the B-Hт is moved approximately 60 cm^{-1} to lower frequency compared to the positions in the parent compound, and the bands from the bridging B-Hμ unit move approximately 120 cm^{-1} to higher frequency. As stated above, the convergence of the bands due to the terminal and bridge modes is seen as an increase in ionic character of the hydroborate groups. The B-Hμ stretching regions show one strong band and a shoulder for aluminium hydroborate ligand species and alkyl aluminium bis(hydroborate) ligand species, but for the dialkyl aluminium hydroborate ligand species this region again shows two bands but it is unclear which band is the symmetric and which the antisymmetric stretch (97). Only one band, which can be assigned to vibrational modes of the bridging AlH_2B grouping, appears in the adduct spectra around 1450 cm^{-1}, and is assigned to the stretching mode.

Comparison of the observed frequencies of the symmetric and antisymmetric C-O bands of etherates enabled predictions of the relative Lewis acidities of several aluminium species to be made.

The order was as follows:-

$Al(BH_4)_3 > RAl(BH_4)_2 > R_2AlBH_4 > R_3Al$

$MeAl(BH_4)_2 > EtAl(BH_4)_2 > \underline{i}BuAl(BH_4)_2$

This was applied more generally to

$AlX_3 > RAlX_2 > R_2AlX > R_3Al$ (X = Cl, Br, H, BH_4)

Aluminium chloride and aluminium hydroborate were found to be of the same order of Lewis acidity.

The range into which the C-O frequency fell also led to a method of prediction of the number of alkyl groups to aluminium thus:

$R_3Al.OEt_2$	1034 - 1044 cm^{-1}
$R_2AlX.OEt_2$	1021 - 1031 cm^{-1}
$RAlX_2.OEt$	1005 - 1018 cm^{-1}
$AlX_3.OEt_2$	990 - 1002 cm^{-1}

Bands attributable to the actual aluminium-ligand atom bond have not been identified because of the difficulty of assignment and the mixing of various modes at the wavenumbers required.

Nuclear Magnetic Resonance of Aluminium Hydroborates

The nuclear magnetic resonance spectrum of aluminium hydroborate has been the source of much controversy in explaining the changes that are observed when the sample is treated differently. Cooling the compound will be considered first, and warming it secondy, as this also has a bearing on aluminium hydroborate decomposition.

At 25°C the ^1H n.m.r. spectrum of pure aluminium hydroborate is a broad, essentially structureless resonance which is retained on cooling to the melting point (38, 97). Oddy gave the position of the centre as 0.7 ppm and the width at half height of about 325 Hz. Oddy then subjected a 12% solution of aluminium hydroborate in deuterated toluene to the same treatment. At 10° C the above signal is observed, but at -10° C a dip appeared in the top of the signal and between -15° C and -50° C a broadened quartet was reported. On further cooling this collapsed to an apparent doublet, and then further to a singlet at -70° C. This

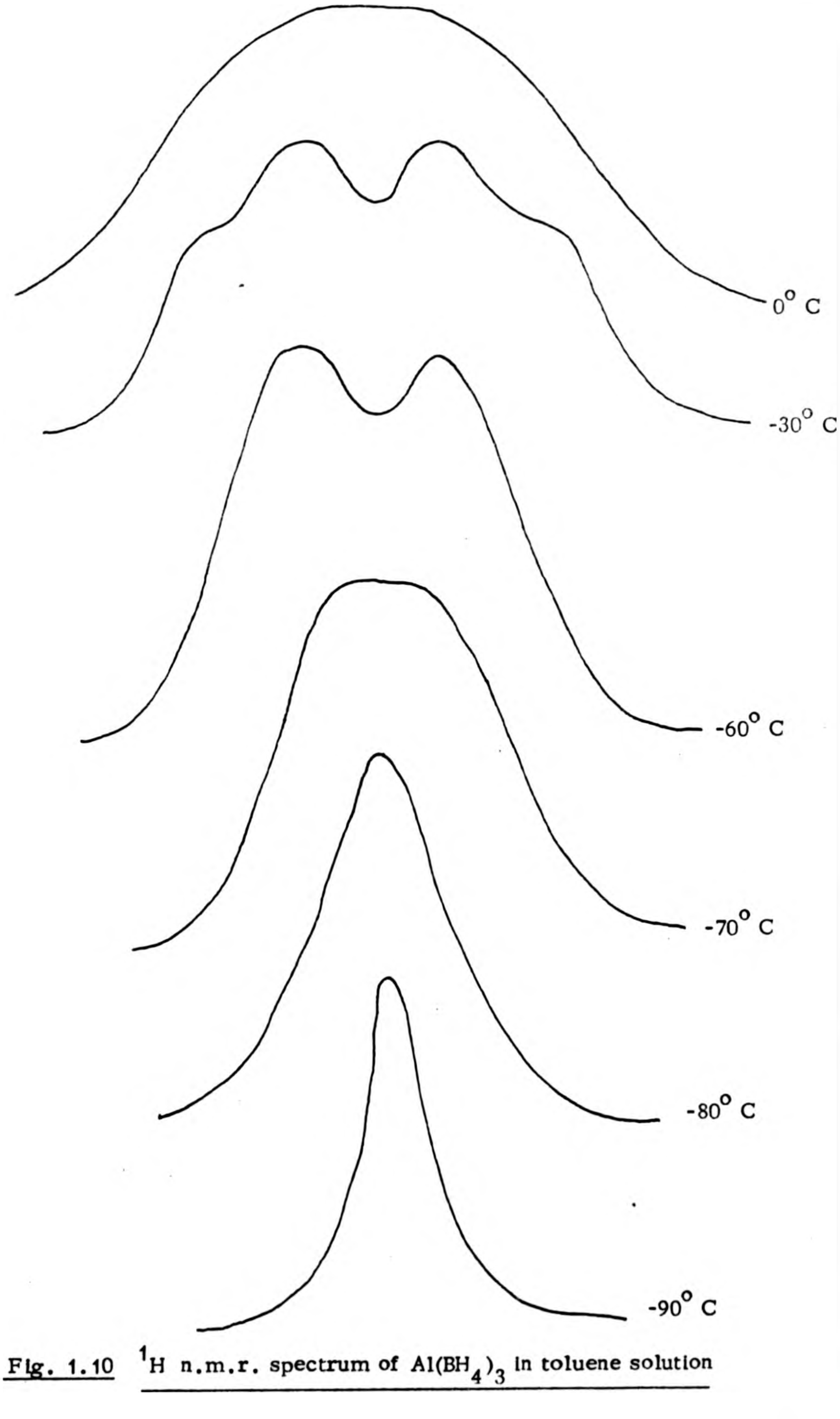


Fig. 1.10 ^1H n.m.r. spectrum of $Al(BH_4)_3$ in toluene solution

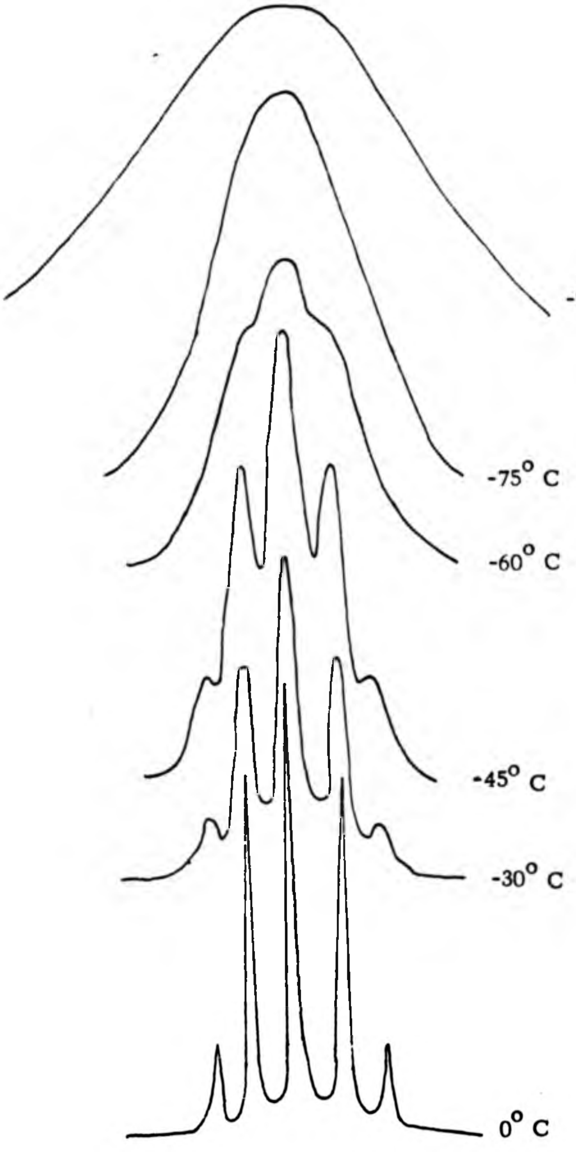


Fig. 1.11. ^{11}B n.m.r. spectrum of $Al(BH_4)_3$ in toluene solution

continued to sharpen as the temperature was lowered to -90° C. $W_{1/2}$ at this temperature was quoted as 52 Hz. This obviously shows that the bridging hydrogen, terminal hydrogen scrambling mechanism is still operating at this temperature or two separate resonances for them would be observed. These changes are ascribed to the increased rate of quadrupole relaxation caused by the decrease in temperature and consequent increased viscosity. This quadrupolar relaxation does not occur for the pure compound as it is less viscous than its toluene solution even at the melting point.

Similar effects are observed in the ^{11}B n.m.r. spectrum. The spectrum of the pure liquid remains invariant as a 1:4:6:4:1 quintet ($J_{^{11}B-H}$ 89 Hz) and a shift of -35.5 ppm down to the melting point. In toluene (or toluene/cyclopentane) solution, lowering the temperature broadened the signal such that at -60° C the signal resembled a broadened triplet, and this broadened further until a singlet with half width 710 Hz identical with the heteronuclear double resonance decoupled spectrum was obtained. This again indicated decoupling of boron from hydrogen by quadrupole relaxation. The spectra in the mixed solvent showed the same development, but at a lower temperature such that at -110° C complete decoupling was not observed. These conclusions on viscosity and quadrupolar relaxation were verified, using a plot of width at half height against viscosity over temperature as had been recently done for zirconium hydroborate (177).

The spectra of dimethyl aluminium hydroborate behaved in an analagous manner. The ^{1}H n.m.r. spectrum showed a quartet at room temperature indicating that coupling to ^{27}Al had already been lost due to the increased viscosity and a less symmetrical environment around aluminium. Cooling washed out other coupling at -30° C. All the alkyl aluminium hydroborates exhibited the quartet structure in their room temperature ^{1}H n.m.r. spectra and a quintet structure in their ^{11}B spectra. Further cooling experiments were not performed.

Heating aluminium nydroborate leads to complex changes, and these have now been discussed by five groups of workers (23, 38, 97, 173, 178).

Ogg and Ray (38) showed that on heating at 80° C and then rapidly cooling the sample, a quartet signal was formed in the ^{1}H n.m.r. spectrum which reverted back to the 'normal' broad signal over a period of days at room temperature. This was interpreted on the basis of the following equilibrium:-

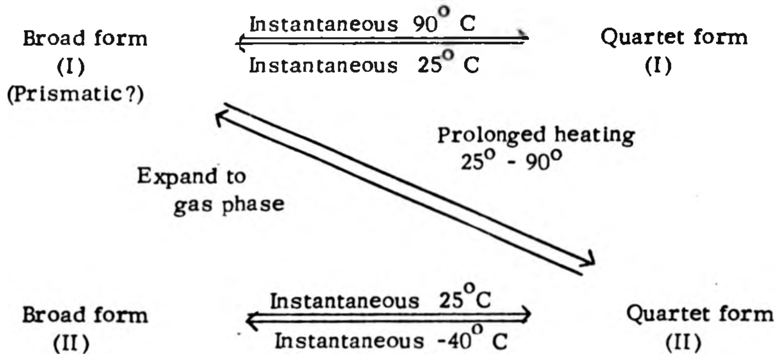
$$\underset{\text{broad signal}}{2Al(BH_4)_3} \rightleftharpoons \underset{\text{quartet signal}}{Al_2B_4H_{18}} + B_2H_6$$

With the dimeric species being dominant at the higher temperature, Maybury and Ahnell (178) re-examined the n.m.r. spectrum and in particular found no more than trace quantities of diborane. These workers explained their observations on the basis of there being two forms of aluminium hydroborate separating their results into two types.

(i) Temporary modification. Short heating time. Spectra reconvert to broad signal.

(ii) More permanent modification. Longer heating time. Spectra do not reconvert at room temperature.

The scheme was as below:-



Marriott (23) and Nibler and Coe (173) supplemented n.m.r. sampling with vibrational spectra. Both reports found similar behaviour in the n.m.r. to previous work, but there was no change in the vibrational spectrum except for the appearance of a weak bond around 800 cm^{-1} which could be the ν_4 of diborane. In addition, Nibler and Coe noticed some white solid of unknown composition formed above the level of the liquid in the n.m.r. tube.

The original explanations of Ogg and Ray and Maybury and Ahnell would seem to be eliminated by this later work as both methods would require a substantial change in the vibrational spectrum. The latter workers concluded that a better explanation would be an increased rate of exchange of hydroborate groups caused by a small amount of decomposition product as catalyst.

Oddy (97) agreed with the later workers and pointed out that quadrupolar relaxation could not be the method of decoupling as this occurred on cooling and not on heating, and that intermolecular exchange of hydroborate groups not borane groups must be responsible as the ^{11}B n.m.r. spectrum remains unaltered. He further suggested that the catalysts might be (i) $\mathrm{HAl(BH_4)_2}$ formed by dissociation of the aluminium hydroborate; (ii) $\mathrm{(B_2H_7)Al(BH_4)_2}$ formed by addition of diborane to the hydride, i.e. also explaining the almost total absence of diborane; (iii) $\mathrm{(B_3H_8)Al(BH_4)_2}$.

$$\mathrm{2Al(BH_4)_3 \rightleftharpoons 2HAl(BH_4)_2 + B_2H_6}$$

$$\mathrm{Al(BH_4)_3 + \tfrac{1}{2}B_2H_6 \longrightarrow (B_2H_7)Al(BH_4)_2}$$

$$\mathrm{HAl(BH_4)_2 + B_2H_6 \rightleftharpoons (B_2H_7)Al(BH_4)_2}$$

$$\mathrm{(B_2H_7)Al(BH_4)_2 + \tfrac{1}{2}B_2H_6 \longrightarrow (B_3H_8)Al(BH_4)_2 + H_2}$$

These three compounds needed only to be present in trace quantities to exchange hydroborate groups with aluminium hydroborate, thus causing decoupling from the aluminium nucleus. The extent of quartet formation could depend on two factors. Firstly, it would depend on the amounts of the decomposition products which would increase with longer heating times and higher reaction temperatures, and secondly on the temperature itself which would affect the exchange rate.

Applying these to the scheme of Maybury and Ahnell, Oddy suggested that the short heating time would only produce a trace amount of decomposition products and the extent of quartet formation would be dependent on the temperature, and on returning to room temperature a quartet would not be visible. Prolonged heating would produce more decomposition product and a quartet due to exchange would be visible at room temperature but not at -40° C. Volatising the heated sample would decompose any hydride species present and decrease the amounts of $B_2H_7Al(BH_4)_2$ and $B_3H_8Al(BH_4)_2$ which would be less volatile than $Al(BH_4)_3$ (179, and this work). Consequently, no quartet formation would be observed after this treatment.

Decomposition of Aluminium Hydroborate - Hydrido Aluminium Hydroborates

Heating aluminium hydroborate gives rise to several interesting changes, some of which have already been described previously. Further observations along a slightly different line will be presented here. Many of the results of research carried out to observe and explain the decomposition were obtained under American Office of Naval Research contracts, and are not available for scrutiny.

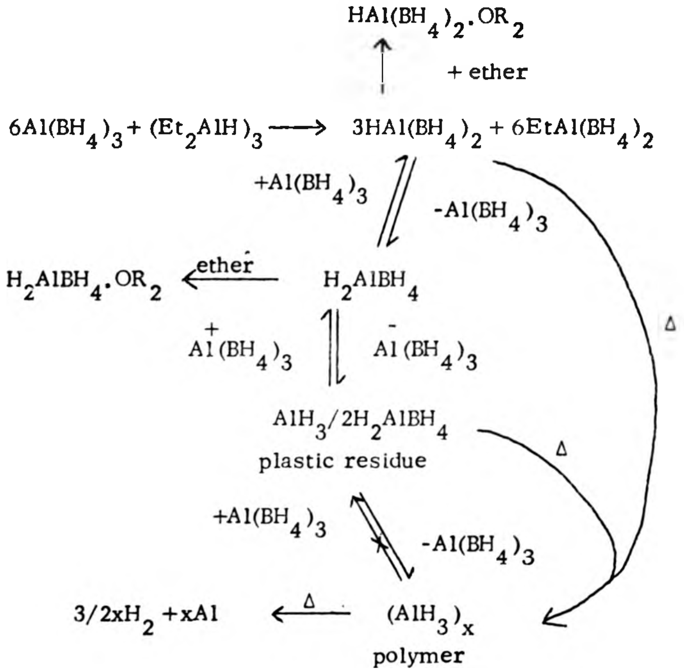
Aluminium hydroborate was observed by Schlesinger et al. to decompose from temperatures of room temperature upwards to evolve hydrogen, but no diborane. No explanation was put forward. The other products were found to be non-volatile compounds of aluminium, boron and hydrogen referred to as 'polymer'. The 'polymer' could behave in two ways: one, where it was soluble in aluminium hydroborate and was likely to detonate in air, and secondly where it was insoluble and having the approximate composition AlB_3H_9. A substance of metallic appearance was also observed.

At room temperature the decomposition occurred slowly and only in the liquid phase. The rate decreased with time and this was not due to hydrogen presence. Soluble 'polymer' only was produced. Heating aluminium hydroborate at 40° C for two days brought a marked retardation of the decomposition. If aluminium hydroborate was distilled off and replaced by fresh, the same retardation was evident, thus suggesting the soluble 'polymer' material was acting as a stabilising agent. Pumping of the soluble residue rendered it ineffective in this role.

Heating at a higher temperature did not produce these retardation effects. Much insoluble polymer was formed as was some metallic looking material. The decomposition of the vapour was one tenth the rate of the liquid decomposition. Addition of soluble polymer did not affect the rates.

Other evidence that has been put forward is the conclusion of Brokaw and Pease that, in the thermal decomposition of aluminium hydroborate at 150° C, a fragment with no more than three hydrogens is lost in the initial step. No dependence on hydrogen pressure was observed, so this would be consistent with an initial dissociation. These and further observations, which will be mentioned subsequently in Chapter 4, prompted Oddy to develop the following schemes for decomposition of aluminium hydroborate and the behaviour of hydrido aluminium hydroborates.

$$\begin{array}{rcll}
2Al(BH_4)_3 & \rightleftharpoons & 2HAl(BH_4)_2 + B_2H_6 & (1)\\
 & & \downarrow & \\
3HAl(BH_4)_2 & \rightleftharpoons & AlH_3 + 2Al(BH_4)_3 & (2)\\
2AlH_3 & \longrightarrow & 2Al + 3H_2 & (3)\\
2Al(BH_4)_3 + B_2H_6 & \rightleftharpoons & 2B_2H_7Al(BH_4)_2 & (4)\\
HAl(BH_4)_2 + B_2H_6 & \rightleftharpoons & B_2H_7Al(BH_4)_2 & (5)\\
2B_2H_7\,Al(BH_4)_2 + B_2H_6 & \longrightarrow & 2(B_3H_8)Al(BH_4)_2 + 2H_2 & (6)\\
2B_3H_8Al(BH_4)_2 + B_2H_6 & \longrightarrow & 2(B_4H_9)Al(BH_4)_2 + 2H_2 & (7)\\
2B_4H_9Al(BH_4)_2 + B_2H_6 & \longrightarrow & 2(B_5H_8)Al(BH_4)_2 + 4H_2 & (8)
\end{array}$$



Heating at 40^{o} C would produce retardation through reactions 1, 4, 5, 6, the hydrido aluminium hydroborates being stabilised by excess aluminium hydroborate. Above 40^{o} C, 2 and 3 would predominate.

Aluminium Hydride

Aluminium hydride is an interesting compound in that it has not been made in any quantity as pure aluminium hydride with only aluminium and hydrogen present and nothing else.

Pure aluminium hydride has been obtained by bombarding a very pure aluminium target with deuterons (183). The product was subjected to an X-ray diffraction and results similar to an earlier study were obtained.

Five crystalline modifications were found to exist in a sample prepared by an undisclosed method (184). In all the structures aluminium was found to be bonded to six hydrogen atoms. The most stable form had the hydrogens arranged octahedrally around the aluminium with each hydrogen involved in Al-H-Al 3-centre bonds. The Al-H distance was found to be 171.5 pm. The Al-Al distance of 324 pm indicated no metal-metal interactions. The resultant structure is a completely bridged 3-dimensional network of 3-centre 2 electron bonds.

Some evidence for monomeric and dimeric aluminium hydride has been indicated at high temperature and low pressure by mass spectrometry (185). Evaporation of aluminium into a stream of hydrogen in a flow system produced a peak at m/e 30, corresponding to AlH_3^+ at 1040° C. At 1170° C a peak corresponding to $Al_2H_6^+$ was also observed.

By chemical methods the first preparation of aluminium hydride was by Wiberg (48) who abstracted it as the trimethyl amine adduct from a reaction of trimethyl alane with hydrogen. He noted it to be an impure white solid which decomposed slowly. An alternative method originally presented by Schlesinger is to react lithium hydroaluminate with aluminium chloride in ether (42).

$$3LiAlH_4 + AlCl_3 \xrightarrow{ether} 4AlH_3 + 3LiCl$$

The product contained an Al-H ratio of 3:1 but prolonged pumping could only produce a 75 mole % of $(AlH_3)_x$ because of complex formation with the ether. It was reported that the polymer could be freed from ether if the aluminium hydride ether sooution was filtered into a large volume of non-co-ordinating solvent such as pentane where the fluffy solid that settled out was claimed to be free of ether after subsequent evaporation (186).

There has been a lot of controversy over the validity of claims for preparation of aluminium hydride greater than 80% mole pure, and the situation is still unclear (e.g. 187-190).

Aluminium Alkyls

These are highly reactive materials, the lower members being extremely sensitive to air and moisture. The early members are also associated, e.g. trimethyl alane and triethyl alane are dimeric. The order of the capacity of an alkyl group to bridge in these materials is

Me > Et > i Pr > t -Bu

which is in the reverse order expected from electron releasing properties. The dominant factor therefore is the bulk of the alkyl group such that $Al(\underline{t}\text{-}Bu)_3$ is monomeric.

The associated structure exists at low temperatures, and crystal data at -170° C on trimethyl alane show (191) a D_{2h} symmetry. This persists into the gas phase as shown by electron diffraction (192). In the liquid phase, the bridging and terminal methyl groups are exchanging and the ^{1}H n.m.r. shows only one sharp signal at room temperature. The spectrum at -50° C, however, shows two peaks, ratio 2:1 (193).

The reaction chemistry of alkyl alanes contains many features:

(i) they are useful alkylating and reducing agents and have been used commercially as such, and as catalysts in olefin polymerisation,

(ii) they react to form adducts with donor molecules similar in behaviour to diborane,

(iii) react with protic acid to release the hydrocarbon,

(iv) undergo exchange reactions, e.g. with other aluminium alkyls or aluminium halides (see, for example, 194).

Aluminium and Higher Hydroborate Derivatives - Octahydrotriborates

A few of these are known, but on the whole they are not well characterised.

A compound where an aluminium unit bridges a boron hydride cage is the trimethyl ammonium salt of $[H_2AlB_{10}H_{12}]$.n Et_2O. Here an AlH_2^+ unit internally bridges the 6, 9 positions of $B_{10}H_{12}$. The product is isolated as a white solid from the reaction of decaborane with alane trimethylamine in ether solution at room temperature.

$$B_{10}H_{14} + Me_3N.AlH_3 + nEt_2O \longrightarrow (Me_3NH^+)(H_2AlB_{10}H_{12}^-)nEt_2O + H_2$$

(198, 199).

Aluminium hydroborate has been claimed to react with decaborane in co-ordinating solvents to produce compounds of the type $(B_{10}H_{13})_xAl(BH_4)_{3-x}$ (where x = 2, 1) depending on the ratio of reactants used. This work also prepared the novel compound $AlB_{10}H_{13}$ from similar reactions. The compounds are claimed on the basis of stoichiometry of reaction and chemical analysis of the product, but none of these details nor any spectral details are available (179).

Similarly, compounds of the type $(B_3H_8)_xAl(BH_4)_{3-x}$ (x = 1, 2, 3) have been prepared from the reaction of aluminium hydroborate with tetraborane (10). These may be carried out in the absence of a solvent and the products have properties intermediate between the volatile aluminium hydroborate and the involatile glassy $Al(B_3H_8)_3$. Again no other properties or results are quoted (179).

The only octahydrotriborate compound of aluminium that has been anything like reported and characterised is the dimethyl aluminium octahydro triborate (200). This was prepared by the reaction of sodium octahydrotriborate with dimethyl chloroalane in vacuo to yield a volatile, reactive liquid, which was purified by distillation in vacuo.

$$Me_2AlCl + NaB_3H_8 \longrightarrow Me_2AlB_3H_8 + NaCl$$

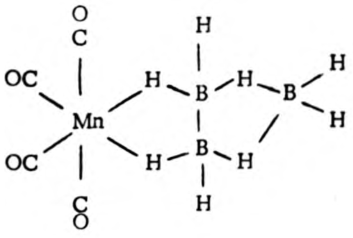
A recent addition to this field has been the preparation and characterisation of a beryllium bis(octahydrotriborate) (202). This was prepared from beryllium chloride and thallium octahydrotriborate in vacuo at temperatures slightly above room temperature. The product has conventional solid and liquid phases (cf. beryllium hydroborate) and a vapour pressure at 0^{o} C of 5-7 mm/Hg. Infra-red and n.m.r. data were recorded for the compound. Again, the molecule was found to be fluxional with the static structure again being where two borons in each group are hydrogen bridged to the beryllium, leaving a terminal BH_2 group.

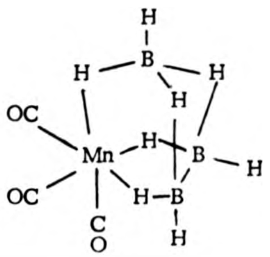
The octahydrotriborate species has been known for many years, being first reported as a product of the reaction of sodium with diborane (203). Salts of the octahydrotriborate species are white, non-volatile solids possessing varying degrees of stability depending on the cation and solvation. The free ion has each boron with two terminal hydrogens; two of the borons are joined by a boron-boron bond, and each of these is bonded to the unique boron by a hydrogen bridge. The infra-red spectrum contains B-H absorptions at 2450, 2400 cm^{-1} and 2120, 2080 cm^{-1}. The ^1H n.m.r. contains a ten line multiplet which shows that all three boron atoms become equivalent and ^{11}B n.m.r. shows a septet (expected nonet) due to coupling to eight protons that have also all become equivalent.

In recent years there has been a good deal of interest in octahydrotriborate ions being reacted with transition metal derivatives. This is partly due to the more ready synthesis of the species by methods that do not involve isolation and use of diborane under pressure. A recent example is the preparation of a manganese tetracarbonyl octahydro triborate from manganese tetracarbonyl bromide (204). This has a static structure which, in common with other metal B_3H_8 species, has the two borons that are directly bonded also bonded by hydrogen bridges to the metal. If this material is exposed to ultraviolet light, it loses one carbonyl group to produce a material where the B_3H_8 group shows only one absorption in the $B\text{-}H_T$ stretching region and a ^{11}B n.m.r. spectrum which shows all the borons to be equivalent. The proposed static structure in this case is for all three borons to be hydrogen bridge bonded to the metal.

$$Mn(CO)_4B_3H_8 \underset{CO}{\overset{u\text{-}v}{\rightleftharpoons}} Mn(CO)_3B_3H_8 + CO$$

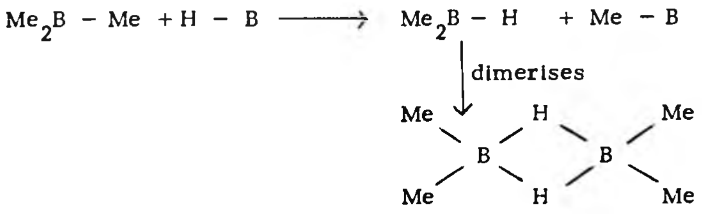
Bidentate CH_2Cl_2 Tridentate





Trialkyl Boranes. Alkyl Diboranes

Trimethyl and triethyl boranes have been known since 1862 (see 205) and are again air sensitive materials inflaming in dry air at room temperature. Trimethyl borane is a gas (b.p. -20° C) and triethyl borane a liquid. Both these compounds are monomeric. The important feature of their reaction chemistry that concerns this work is their exchange reactions with hydride species to form alkyl diboranes. Thus mixing of trialkyl borane with a stoichiometric amount of diborane forms the alkyl diborane. The alkyl diboranes are slightly less volatile than the corresponding trialkyl borane because of their associated nature.



The alkyl diboranes are still, however, extremely air and moisture sensitive. They may be identified by their n.m.r. spectra (see 206) and infra-red spectra (207 and references therein) by extrapolation from diborane.

A part of this work will show the exchange of alkyl groups for hydrogen by the trialkyl boranes.

CHAPTER 2

Reaction of Aluminium Hydroborate with Alcohols and Thiols and some Compounds containing Alkoxy Groups

The reaction of aluminium hydroborate with water and protic species has been known since the earliest preparation of the compound by Schlesinger and his co-workers. Very little information has been published on the exact nature of the hydrolysis reaction. The first workers merely stated that the reaction was rapid and complete with 12 moles of hydrogen being produced, i.e. one for each hydrogen atom present in the hydroborate. The reaction is quantitative and therefore used for analysis. The other products were boric acid and aluminium hydroxide.

$$Al(BH_4)_3 + 12H_2O \longrightarrow Al(OH)_3 + 3B(OH)_3 + 12\,H_2$$

As with all hydroborate hydrolyses the reaction proceeds better in acidic conditions.

A study in the 1950's indicated that the reaction with water occurred in two stages. There was an initial fast reaction which produced diborane and aluminium hydroxide, followed by a slower reaction involving the hydrolysis of diborane.

$$Al(BH_4)_3 + 3H_2O \xrightarrow{fast} Al(OH)_3 + 3/2B_2H_6 + 3H_2$$

$$3/2B_2H_6 + 9H_2O \xrightarrow{slow} 3B(OH)_3 + 9H_2$$

This, however, still does not give us any real clue to the very first step in the reaction.

It is very tempting to suggest that the initial step would be attaching of a water molecule to the aluminium hydroborate molecule paralleling with the behaviour of aluminium hydroborate with ethers. This is further suggested by the isolation of an apparent hydrate of diborane $B_2H_6.2H_2O$ although this is probably more correctly formulated as $[H_2B(OH_2)_2]BH_4$. This adduct may then be unstable and react further to form compounds of the type $[AlH_2(OH_2)_2]BH_4$ as in the reaction with ammonia or react in a stepwise substitution of OH for BH_4 forming intermediate compounds $(HO)_xAl(BH_4)_{3-x}$.

In the case of the nearest analagous compound diborane, except for the isolation of the hydrate mentioned above, the exact mechanism also remains undecided. Hydroxy derivatives of borane, except boric acid, seem incapable of isolation. Mass spectral evidence for the existence of $HOBH_2$ and $HB(OH)_2$ in the mass spectrum of a mixture of B_2H_6 and $B(OH)_3$ has been obtained, and their enthalpies of formation estimated from their equilibrium concentrations. The failure to isolate them is doubtless due to their thermodynamic and kinetic instability with respect to diborane and boric acid. No partially hydroxylated species have ever been isolated in the hydrolysis of diborane, even with small amounts of water and excess diborane. The products are always boric acid, hydrogen and unreacted diborane, indicating rapid disproportionation of possible partially hydroxylated species. Hydrolysis of diborane by ice at -80° C, however, does not go to completion, producing 4 moles of hydrogen instead of 6. The diborane-water reaction is 1st order with respect to water and 0.5 with respect to diborane.

Thus two mechanisms that might be proposed for the hydrolysis of aluminium hydroborate might be

$$\begin{array}{lll}
(1)\ 3Al(BH_4)_3 + 3H_2O & \longrightarrow & 3Al(BH_4)_3.H_2O \\
3Al(BH_4)_3.H_2O & \longrightarrow & 3HOAl(BH_4)_2 + 3/2B_2H_6 + 3H_2 \\
3HOAl(BH_4)_2 & \longrightarrow & Al(OH)_3 + 2Al(BH_4)_3
\end{array}$$

or continued reaction as above.

$$\begin{array}{lll}
\hline
Al(BH_4)_3 + 3H_2O & \longrightarrow & Al(OH)_3 + 3/2B_2H_6 + 3H_2 \\
\hline
(2)\ Al(BH_4)_3 + H_2O & \longrightarrow & Al(BH_4)_3.H_2O \\
Al(BH_4)_3.H_2O + H_2O & \longrightarrow & [AlH_2(H_2O)_2]BH_4 + B_2H_6 \\
[AlH_2(H_2O)_2]BH_4 + H_2O & \longrightarrow & Al(OH)_3 + BH_3 + 3H_2 \\
\hline
Al(BH_4)_3 + 3H_2O & \longrightarrow & Al(OH)_3 + 3/2B_2H_6 + 3H_2 \\
\hline
\end{array}$$

These schemes are based, as can be seen, on very small and extrapolated pieces of data. It was proposed by studying reactions that might proceed in an analagous manner that more relevant, although still extrapolated, information could be gathered.

Accordingly the reaction of aluminium hydroborate with alcohols and thiols which still have an active hydrogen were studied in some detail.

The reaction of diborane with methanol has many similarities to that with water with one or two important differences. An adduct has been isolated at low temperature and diborane undergoes methanolysis at normal temperatures with release of hydrogen. This release of hydrogen, however, is not violent as in the water reaction. By comparison, the reaction is sluggish in the later stages. The final products are trimethyl borate and hydrogen, but a stable intermediate $BH(OMe)_2$ can be isolated. It disproportionates slowly into trimethyl borate and diborane.

$$4MeOH + B_2H_6 \longrightarrow 2BH(OMe)_2 + 4H_2$$

$$2MeOH + 2BH(OMe)_2 \longrightarrow 2B(OMe)_3 + 2H_2$$

$$6BH(OMe)_2 \rightleftharpoons 4B(OMe)_3 + B_2H_6$$

White, apparently polymeric, methoxyborane $(BH_2OMe)_x$ has also been observed (11).

The known reactions of diborane with thiols are more complex. Methane thiol forms an adduct $MeSH.BH_3$ which readily loses hydrogen to give a white polymer $(MeSBH_2)_x$ which, on heating <u>in vacuo</u>, will undergo partial depolymerisation. With the ethyl analogue the most stable species seems to be the trimer, and the methyl trimer has also been reported. This decomposes at 140° C to give, among other things, $(MeS)_3B$. With n-propyl and n-butyl thiols, the compounds $[(RS)_2BH]_2$ have been reported, but their formulation as tetra-substituted diboranes has not been established.

Exchange of RS for hydrogen takes place with $B(SR)_3$ and B_2H_6 to give compounds such as $BH(SR)_2$. This is similar in behaviour to that with $B(OR)_3$.

The following section of this chapter deals with the reaction of aluminium hydroborate with alcohols, thiols and some alkoxide species.

Reaction of aluminium hydroborate with alcohols

1. With methanol

As might have been anticipated from the previous work in related fields, it was found that the reaction of aluminium hydroborate was very rapid indeed. The extent of the reaction could be judged by the amount of gas that was evolved when the two reactants met. The gas was found to consist of hydrogen and diborane with twice as much hydrogen as diborane present. The reaction had been approached in the expectation of the reaction being rapid, and the reaction conditions had been adjusted accordingly. The aluminium hydroborate was dissolved in a low melting point solvent, pentane and the methanol was added in small amounts to the cooled solution. Reaction, as witnessed by gas evolution, was observed to take place at least as low as the melting point of methanol (-98° C) and when the two reactants met there was no delay before gas evolution was witnessed.

This result suggests firstly that methoxy groups from the methanol were exchanging for the BH_4 of the aluminium

$$-BH_4 + MeOH \longrightarrow -OMe + H_2 + BH_3$$

and secondly that at -98° C there is no appreciable quantity of a stable aluminium hydroborate-methanol adduct, otherwise a delay in hydrogen evolution might be expected. If this adduct is formed, it will be decomposing over a period of a few minutes only to produce hydrogen and diborane.

$$\begin{tikzcd}
Al(BH_4)_3 + MeOH \arrow[r, "\text{possible}", "\text{formation}"'] \arrow[dr, "\text{or direct}"'] & Al(BH_4)_3.MeOH \arrow[d, "\text{rapid decomposition at } -98^{\circ}C"] \\
 & MeOAl(BH_4)_2 + H_2 + BH_3
\end{tikzcd}$$

The amounts of hydrogen and diborane that were recovered were measured by means of a Toepler pump. The figure for the amount of hydrogen was always consistent with the amount of methanol that had been added, thus each mole of methanol produced one mole of hydrogen. The diborane figure was always half the hydrogen figure. In a typical experiment, addition of 4.25 mmol of methanol produced 4.20 mmol of hydrogen and 2.09 mmol of diborane. These figures are therefore also in complete agreement with the equation

$$Al - BH_4 + MeOH \longrightarrow Al - OMe + H_2 + BH_3$$

The other product of the reaction is a white solid which was assumed to be polymeric to some degree as it was found to be insoluble in the hydrocarbon solvents which could safely be tried. The compound evidently contained methoxy groups and association through them was of course possible. Analysis of this compound showed that the compound was not pure $MeOAl(BH_4)_2$ as might have been anticipated from the amount of reactants used, nor was it aluminium methoxide caused by disproportionation of the above mentioned compound; the result was somewhere between and suggests a mixture of compounds.

Expected for	$MeOAl(BH_4)_2$	Active H 9.19%	Al 30.77%
	$Al(OMe)_3$	Active H 0%	Al 22.47%
Found		Active H 7.67%	Al 26.31%

This would seem to indicate that species of the type $MeO_xAl(BH_4)_{3-x}$ are formed and that they are stable to disproportionation, possibly due to association or being incorporated in a lattice with aluminium methoxide which is known to be polymeric, as are many other aluminium alkoxides. What the reaction would also seem to show is that the reaction is too fast to be specific: in other words, if the reaction proceeds through the following reaction series, as would seem likely,

$$Al(BH_4)_3 + MeOH \longrightarrow MeOAl(BH_4)_2 + BH_3 + H_2$$

$$MeOAl(BH_4)_2 + MeOH \longrightarrow (MeO)_2AlBH_4 + BH_3 + H_2$$

$$(MeO)_2AlBH_4 + MeOH \longrightarrow (MeO)_3Al + BH_3 + H_2$$

then the speeds of the second and third reactions must be of the same order of magnitude as the first. Methanol will then react with whichever aluminium species it comes into contact, regardless of the other groups on aluminium, and this will lead to a mixture of products.

2. With larger alcohols

As the reaction of aluminium hydroborate with methanol was found to be so rapid, it was thought that by increasing the size of the reacting alcohol molecule the rate of the reaction might be moderated and a particular alkoxy aluminium species might be isolated. This in fact proved to be the case. With cyclohexanol the reaction still proceeded at a moderate pace at -60° C and hydrogen and diborane were observed as gaseous products. A white solid product was observed which gave an analysis approaching that of mono-cyclohexanoxy aluminium bishydroborate, but still with a slightly low hydrogen analysis probably suggesting contamination with the bis cyclohexanoxy compound as had been noted for the product of the reaction between aluminium hydroborate and methanol.

With some other alcohols that were tried, a different reaction set in which for isolation of alkoxy aluminium hydroborates proved unsuccessful. The alcohols that were tried were large, sterically fairly bulky or else electron-rich and the reaction is these cases was reduction of the organic hydroxyl to organic alkane. Thus the reaction of aluminium hydroborate with 2-methyl propan-2-ol (t-butanol) produced 2-methyl propane (iso-butane) in approximately 50%(+) yield and similar reactions and corresponding products were noted when the reacting alcohol was p-methoxy benzyl alcohol (anisyl alcohol) or diphenyl methanol (benzhydrol).

The behaviour of the last three mentioned compounds is not altogether surprising, although to the author's knowledge has not been reported for pure aluminium hydroborate. It is known in the field of reduction of organic compounds by complex hydrides that certain alcohols can be reduced to alkenes or alkanes by the action of either lithium hydroaluminate and aluminium chloride or by sodium hydroborate and boron trifluoride. In these reactions carbonium ions seem to be intermediates which then combine with a hydride to become the hydrocarbon. The alcohols therefore, that fairly easily form carbonium ions, can then be reduced in this way. Aliphatic primary alcohols and unsubstituted benzyl alcohols are not reactive in any way, but secondary and tertiary aliphatic alcohols, activated benzylic alcohols and di- and tri-aryl carbinols may be deoxygenated. It is this behaviour which is being mirrored in the reaction of aluminium hydroborate.

It must be noted, however, that detailed investigation of the products of the reaction of aluminium hydroborate with these alcohols was not undertaken and that the conditions used were not the usual ones associated with organic solution reactions suitable for carbonium ion formation. So although the observations that were made would seem to correlate well with what has been previously reported, because of the above reasons a strict comparison may not be entirely valid.

The reaction of aluminium hydroborate with thiols

The reaction of aluminium hydroborate with thiols has been found to be basically similar to the behaviour of alumium hydroborate with alcohols. If excess aluminium hydroborate is reacted with methane thiol, even at low temperature gas evolution can be observed. If the two compounds are condensed together and allowed to stand at the melting point of methane thiol (-120° C), a slow evolution of hydrogen and diborane is involved. Again then, the conclusion may be drawn that if the first step in the reaction is a 1:1 adduct formation, then the adduct is not stable even at low temperatures and would be very difficult to isolate. The reactions of thiols are also similar to the reaction with alcohols in that full reaction of a mole of thiol to produce one mole of hydrogen and half a mole of diborane is observed.

In contrast the reaction of the thiol is somewhat moderated, and because of this by choosing excess aluminium hydroborate the reaction may be used to specifically prepare a monothioalkyl aluminium bis hydroborate. This assumes that of the reactions

$$\mathrm{Al(BH_4)_3 + RSH \longrightarrow RSAl(BH_4)_2 + H_2 + BH_3}$$

$$\mathrm{RSAl(BH_4)_2 + RSH \longrightarrow (RS)_2AlBH_4 + H_2 + BH_3}$$

$$\mathrm{(RS)_2AlBH_4 + RSH \longrightarrow (RS)_3Al + H_2 + BH_3}$$

the second and third are slower than the first, which therefore predominates.

In this way the compounds thiomethyl, thioethyl and thiobenzyl aluminium bis(hydroborates) have been prepared. Again these are white solids, probably associated to some degree. Discussion of these compounds will be covered later in this chapter. A thiobutyl compound could not be prepared from aluminium hydroborate tetrahydrothiophenate. The tetrahydrothiophene ring remained intact in contrast to observations for tetrahydrofuran (105).

The only other comparison that may be drawn between the thiols and alcohols reaction is with a tertiary compound. 2-methyl propane 2-thiol when reacted with alumium hydroborate produces 2-methyl propane as the major product. It would seem, therefore, that similar reducing properties and for similar reasons would be observed for the thiol series. From this author's limited experiments it would seem that primary aliphatic and unsubstituted benzyl thiols are not affected, but that tertiary aliphatic thiols have their sulphur removed and reduction to the alkane takes place. (There is much less information on reduction of a thiol group by hydride species available).

Preparation and attempted preparation of alkoxy and hydroxy aluminium hydroborate species using exchange reactions

Exchange reactions have been much used in aluminium chemistry, particularly for aluminium alkyl and halide chemistry. Oddy demonstrated particularly well the usefulness of these reactions in aluminium hydroborate chemistry. Aluminium hydroborate was found to exchange intact hydroborate groups.

Some exchange reactions using alkoxide groups have been attempted in this work. To directly mirror the exchange reactions used by Oddy, aluminium hydroborate was stirred with aluminium methoxide at room temperature. The reaction proved to be very slow indeed. For reaction to occur, the aluminium hydroborate would have to break down the polymeric network of aluminium oxygen bonds, and although the aluminium hydroborate is able to break up the dimeric forms of dimethyl aluminium and the trimeric forms of diethyl aluminium hydride in order to exchange with aluminium methoxide this is presumably too slow. Some reaction does occur as not all the aluminium hydroborate that is put into the reaction mixture can later be recovered.

An analagous reaction was attempted with aluminium hydroxide. No reaction was apparent, and all the aluminium hydroborate that was added could be recovered. The reasons for this may be two fold. Firstly is the possibility of aluminium being unable to break down the aluminium hydroxide structure as for the methoxide, or secondly that any reaction that might have taken place on the surface immediately being reversed by disproportionation.

This behaviour has already been discussed for possible hydroxy derivatives of diborane.

$$2Al(BH_4)_3 + Al(OH)_3 \rightleftharpoons 3Al(OH)(BH_4)_2$$

An exchange reaction involving alkoxide groups was observed for the reaction of aluminium hydroborate with alkoxyboranes. These are monomeric, relatively easy to handle liquids and thus do not suffer from the drawbacks experienced with the aluminium methoxide and hydroxide. Reaction of aluminium hydroborate with either trimethoxy or triethoxy borane resulted in transfer of an alkoxide group on to aluminium

$$\begin{tikzcd} 3Al(BH_4)_3 + B(OR)_3 \arrow[r] & 3ROAl(BH_4)_2 + [B(BH_4)_3]? \arrow[d] \\ & 2B_2H_6 \end{tikzcd}$$

The transfer of hydroborate groups might proceed as shown in the equation and indeed the only products that were isolated from the reaction were the excess aluminium hydroborate that had been used, diborane and the alkoxy species which was identified by analysis as a pure monoalkoxyaluminium hydroborate.

This has been the preferred route in this work to the preparation of these compounds, but the usefulness of the reaction is limited somewhat. Unless aluminium hydroborate is used in excess, all the components will not stay in solution and an incomplete reaction results. Attempts to prepare bis alkoxy aluminium hydroborate by this route have therefore not been undertaken. They have been prepared by another method. This route was not needed to prepare the mono thio alkyl bis hydroborate species, but reaction of aluminium hydroborate with the thiomethyl boranes should be equally successful.

One other experiment that might usefully be attampted would be the reaction of boric acid with aluminium hydroborate in an analagous reaction to try and produce hydroxy species.

Discussion of the mechanism of hydrolysis-type reactions

Having described the various reactions, it now seems appropriate to discuss the mechanism of hydrolysis type reactions in the light of the new information gained. It must be stressed again that experiments with water have not been carried out but that experiments with related molecules have been undertaken, and that conclusions to the hydrolysis reaction will be intuitive but at the same time reasonably valid. The only other recent work on aluminium hydroborate hydrolysis is some unpublished data by McAvoy (92). He has investigated the hydrolysis with limiting amounts of water and has noted the amount of hydrogen produced per mole of water added. At low concentrations of water a flash reaction was observed, and a molar amount of hydrogen above that of the water put in. This was explained on the basis of increased aluminium hydroborate decomposition in the flash zone. A solid deposit remained, but its composition was not determined.

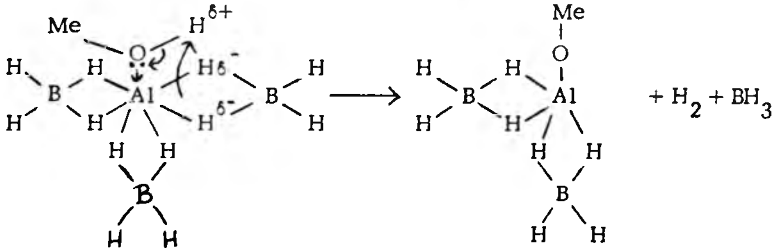
The very first step in a hydrolysis type reaction is almost certain to be thought of as an addition of the lone pair of an oxygen or a sulphur atom to the aluminium. This is of course well established for a series of related oxygen and sulphur containing ligands such as dimethyl ether, diethyl ether, tetrahydrofuran, dimethyl sulphide, which have been studied in detail. Bonding of the electronegative atom to the aluminium weakens the bonds to the adjacent atoms and thus, if diethyl ether is co-ordinated to aluminium hydroborate, the C-O stretching frequency of the ether is reduced.

Comparison of the C-O stretching positions of etherates of aluminium compounds

Compound	as C-O stretch/cm^{-1}	s C-O stretch/cm^{-1}
Ether	1116	934
$AlMe_3.OEt_2$	1041	904
$Al(BH_4)_3.OEt_2$	1000	878
$AlCl_3.OEt_2$	995	876

If a methanol molecule therefore were to bond to aluminium hydroborate in the same way, therefore a diminishing in the strength of the O-H bond would be expected. From polarisation considerations the hydrogen has some positive character and could therefore attack the hydrogen bridge system which, according to the analysis of Perkins (84) retains some slight negative character. The proximity of these two oppositely charged regions may therefore explain the instability of a methanol complex.

$$Al(BH_4)_3 + MeOH \longrightarrow Al(BH_4)_3.MeOH$$



A stepwise addition certainly of alcohol and thiol molecules is established in this work. The substance isolated from the careful reaction of aluminium hydroborate with methanol was clearly established as a mixture of alkoxy aluminium hydroborates by chemical analysis and later by comparision of infra-red spectra with that of an authentic sample of methoxy aluminium hydroborate. The stepwise reaction is demonstrated even better by the thiol reaction which can be controlled to halt after addition of one molecule.

The reason for this would not seem to be based on the acidity of the thiol or alcohol as thiols are more acidic than the corresponding alcohol and might be expected to react faster. Rather the reason would seem to be caused by the greater electronegativity of the oxygen atoms and the strength of the bonds being formed to the aluminium atom. It has been demonstrated that adducts of aluminium hydroborate with ethers have a stronger metal-oxygen bond than the metal sulphur bond in aluminium hydroborate adducts with sulphides.

Thus we have

$$Al(BH_4)_3.SMe_2 + OMe_2 \longrightarrow Al(BH_4)_3.OMe_2 + SMe_2$$

$$Al(BH_4)_3.OMe_2 + SMe_2 \not\longrightarrow Al(BH_4)_3.SMe_2 + OMe_2$$

but also

	pK_a		pK_a
H_2O	15.7	H_2S	6.97
CH_3OH	15.5		
C_2H_5OH	15.9	C_2H_5SH	10.5
$(CH_3)_3COH$	$\simeq$18.0		
		$C_6H_5CH_2SH$	9.43

and bond energy	O-H (in methanol)	428kJ mol^{-1}
	S-H	349 kJ mol^{-1}

Properties of alkoxy and thioalkyl aluminium hydroborate

The compounds isolated were found to be white solids, except for the thioethyl derivative , were stable under dry nitrogen but hydrolysed in the air. They were not pyrophoric in air, but reacted vigorously, sometimes inflaming if water was added to them. They were rapidly hydrolysed also by dilute acid, and this reaction was used for their analysis.

As isolated, the compounds were reluctant to dissolve in the hydrocarbon solvents that could be safely tried, although they were all soluble in benzene and toluene to some extent. On warming, one or two of the compounds produced a small amount of sublimate at low pressure and this showed very similar properties to the original solid except for an increased solubility. This it was believed was evidence for association with possibly more than one degree of polymerisation species present. This had also been suggested previously for some bis alkoxy aluminium hydroborates which had been suggested to have a degree of association between 2 and 3, or to be a mixture of dimers and trimer (109). A molecular weight determination was performed on ethoxy aluminium bis hydroborate, without it being sublimed, by cryoscopy in benzene solution, and this gave a molecular weight close to the value for a dimeric form. This would seem to suggest that the small amounts to sublime out might be a monomeric form, but this on the basis of other aluminium, oxygen and sulphur chemistry seems to be a little unlikely.

A more likely explanation would be for the molecular weight to be between 2 and 3 times the monomer weight with the sublimate being the dimer. The residue from the sublimation seemed to be stable to 200° C without reaction. The compounds did not melt below 200° C.

The anomalous nature of the thioethyl derivative should also be discussed here. Unlike the other compounds which were white solids, this was a colourless, involatile (at least at normal temperatures and vacuum line pressure) liquid. It exhibited all the properties of the other compounds except for its physical state. As it was made, it seemed to melt at about 17° C but subsequent cooling failed to properly solidify it. Spectroscopic analysis of some samples prepared also showed evidence of two compounds with very similar values and this could indicate a mixture of say dimers and trimers again. The exact reason for this apparently anomalous behaviour unfortunately remains unclear.

The compounds were found not to undergo adduct formation with ether. Two possible reasons might be postulated for this. With an alkoxy or a thioalkyl group attached to aluminium, the aluminium might be unwilling to accept another electronegative atom or this may make the compound unstable, or that the ether is unable to break down the dimeric or trimeric lattice of the hydroborate in order to form the adduct. Ether is known to be able to cleave trimeric aluminium compounds when the linking is done by hydrogen, but bridging by presumably stronger oxygen bridges would then be more difficult to break.

Spectroscopic properties

The infra-red spectra of the monoalkoxy and monothioalkyl aluminium hydroborates were obtained as Nujol mulls.

As in discussion of other aluminium hydroborates, the interest is in the position of the B-H_t bands near 2500 cm^{-1}, the B-H_μ band near 2000 cm^{-1} and the deformation near 1100 cm^{-1}.

For all the monoalkoxy and monothioalkyl species, the values for the B-H_t stretches have decreased from the values observed for aluminium hydroborate itself.

As can be seen from the tabled values, the B-H_t bands occur at 2520 and 2460 cm^{-1} which is approaching the values observed for aluminium hydroborate-ligand species.

Table 2.1

Selected spectral properties of RO and RS $Al(BH_4)_2$ compounds

	MeS	EtS	Benzyl S	MeO	EtO	
cm^{-1}	2520 s	2520 s	2520 s	2510 s	2520 s	
	2460 s	2460 s	2450 s	2450 s	2455 s	
	2120 s	2110 s	2100 s	2120 s	2102 s	
		1275 1265 m				
	1115 s	1130 s	1110 s	1120-1140 br	1112 s	
				1060 s	1065 s	
	975 m	970 m		980 sh	990 sh	
				920 m	890 s	
	780 m		760 m			
	690 m		695 m-s	630 m	650 m	
	500 m-s	500 m				
ppm	1.48	0.97	3.68	1.40	0.73	^{1}H nmr
		2.47	6.95		3.3	
	-34.9	-35.1	-34.8	-36.5		^{11}B nmr
				69.8		^{27}Al nmr

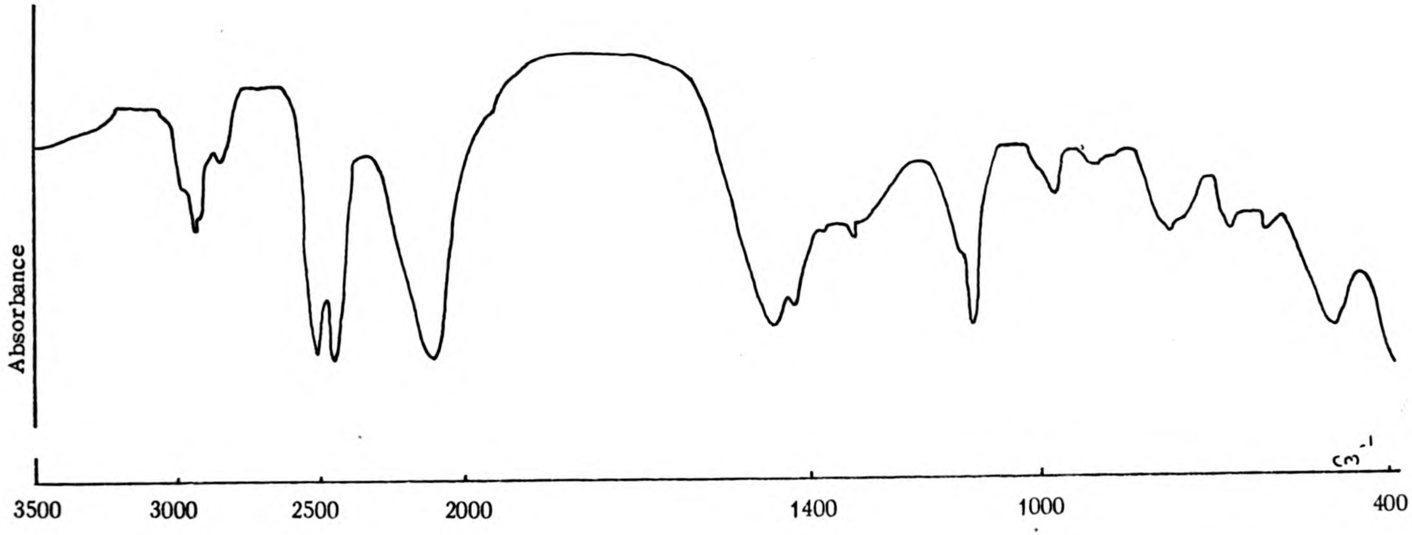


Fig. 2.1 Infra-red spectrum of $MeSAl(BH_4)_2$

Accompanying this trend, the B-H$_\mu$ band has increased in value from that associated with pure aluminium hydroborate. Thus the value is around 2110 cm^{-1} an increase of almost 80 cm^{-1} from the 2032 cm^{-1} for Al(BH$_4$)$_3$ and again approaching that for a ligand species.

In the case of an aluminium hydroborate-ligand species, this was explained on the basis that a convergence of the two sets of boron -hydrogen bands indicates a tendency towards more ionic nature in the hydroborate group. This is not unreasonable in the alkoxy and thio alkyl case. The presence of the electron-rich alkoxy or thio alkyl group will mean a greater electron density at aluminium which can be put into the Al-H-B bridge, thus strengthening it and leading to an increase in frequency. At the same time, this bridge strengthening could produce a slight decrease in frequency of the B-H$_t$ vibrations.

As for other vibrations, the deformation mode which occurs at 1113 cm^{-1} in Al(BH$_4$)$_3$ has moved slighly to around 1130 cm^{-1} in the EtS compound, but for some of the others it is almost unchanged. The rocking mode also hardly alters, being at 978 cm^{-1} in Al(BH$_4$)$_3$ and 970 cm^{-1} in the EtS compound. The bridge band region around 1500 cm^{-1} is more difficult to compare. There is still a little doubt as to the assignment of the bands in this region in aluminium hydroborate itself, the band at 1501 cm^{-1} in Al(BH$_3$) being assigned to the bridge stretch. In the alkoxy and thio alkyl compound this is further complicated by the presence in the same region of C-H bands, and if the highest intensity band at 1475 cm^{-1} in the EtS compound is the bridge stretch then this would mean that the bridge had weakened slightly compared to aluminium hydroborate, a conclusion opposite to the one proposed for the observed trend in the B-H$_t$ and B-H$_\mu$ region above 2000 cm^{-1}.

For the solid compounds this is not possible due to an obscuring by Nujol bands. These results are in good agreement with values published for one or two other alkoxy aluminium hydroborates. The mono butoxy aluminium bis hydroborates studied showed B-H$_t$ bands at 2525 and 2457 cm^{-1} and 2513 and 2445 cm^{-1} for the ^{t}BuO and BuO respectively. The B-H$_\mu$ bands were at 2146 and 2119 cm^{-1} respectively. Deformations were at 1116 and 1114 cm^{-1}. For their bis alkoxy aluminium hydroborates the frequencies for the B-H$_t$ decrease still further, e.g. to 2488 and 2427 for the (MeO)$_2$AlBH$_4$ and the B-H$_\mu$ increases to e.g. 2164 cm^{-1} thus reinforcing the view already expressed. (109)

Nuclear magnetic resonance spectra

Most of the compounds prepared have been subjected to ^{1}H n.m.r. and ^{11}B n.m.r. and one to ^{27}Al n.m.r. The proton spectra all have a similar form. There is a signal present due to the protons in the alkyl side chain and this is usually superimposed on a broad signal which is due to the hydroborate protons. A broad signal for hydroborate protons is common in aluminium hydroborate chemistry, and it is believed that this is due to there being an exchange by the bridge and terminal protons yet retaining coupling to the ^{11}B and ^{10}B nuclei and the ^{27}Al nucleus. Coupling to ^{27}Al is retained because of the high symmetry maintained around the aluminium atom. If this symmetry is perturbed, as it is for example in the case of the monomeric alkyl aluminium hydroborates, then the coupling to ^{27}Al is lost and the signal for the hydroborate protons becomes a 1:1:1:1 quartet due to coupling to ^{11}B. That the coupling to ^{27}Al is retained, therefore, in the case of the alkoxy and thio alkyl hydroborates would suggest that the compound is not monomeric which would produce an asymmetry at aluminium and that the molecule is associated which would produce a more symmetrical environment and thus retain coupling.

A variable temperature ^{1}H n.m.r. was taken for the thio ethylaluminium bis hydroborate, this being the most soluble of the compounds prepared. The solvent was d^{8} toluene. When this experiment was carried out by Oddy for aluminium hydroborate in the same solvent, this produced decoupling effects which he concluded were due to viscosity effects. This ethyl aluminium bis hydroborate at room temperature showed a broad signal for its hydroborate protons with the protons on the ethyl group centred at 0.97 ppm for the CH_3 and 2.47 ppm for the CH_2. On cooling, however, it was not the hydroborate resonance that altered but the signals for the ethyl group. At 238 K two signals for ethylgroups were becoming visible. For the high field CH_3 resonance the original had moved to 0.92 ppm and another was appearing at 1.03 ppm. At 223 K this was slightly more prominent. This may indeed mean that there is an equilibrium set up in solution between molecules of different degrees of association. The obvious choice, bearing in mind previous information, would be a dimer-trimer equilibrium where the chemical shifts of the alkyl group in the two forms are slightly different.

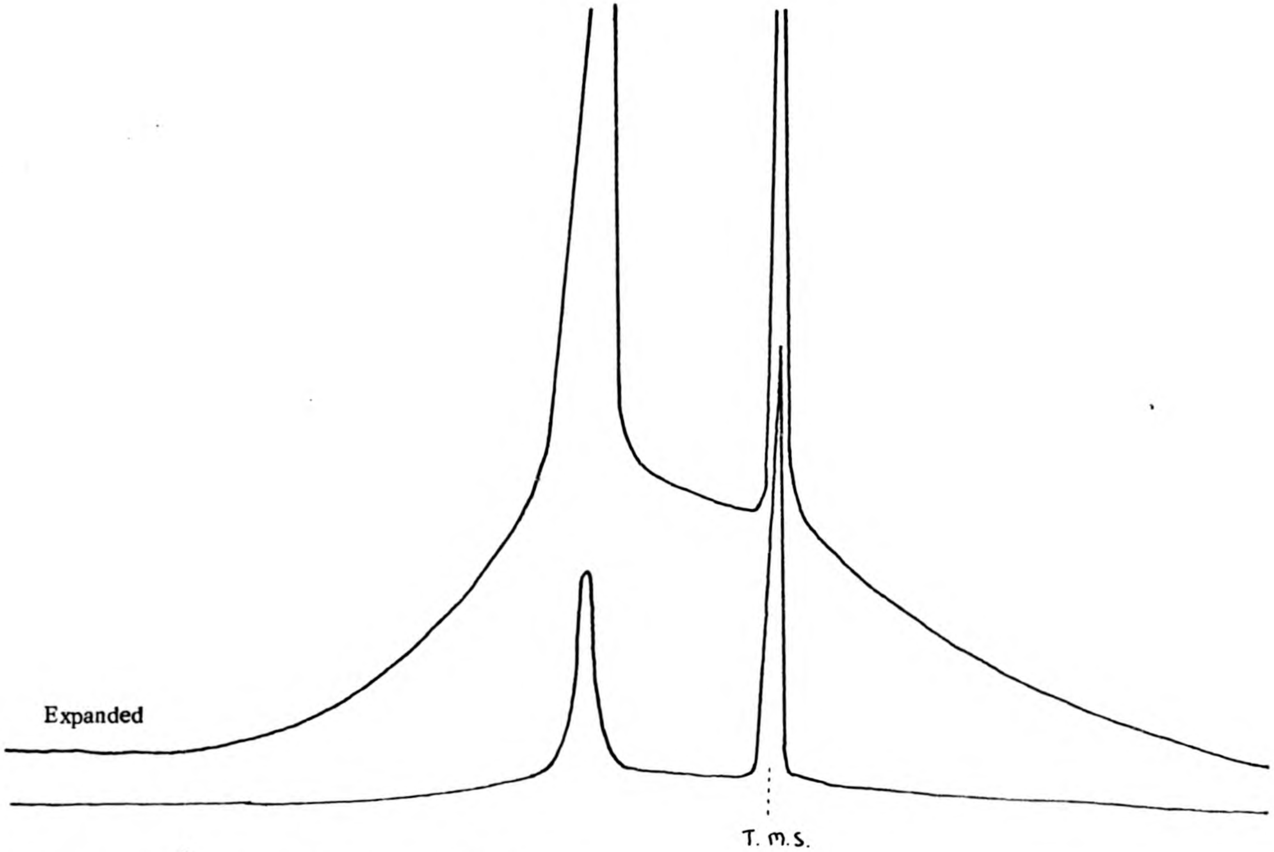


Fig. 2.2 ^{1}H n.m.r. spectrum of MeSAl$(BH_4)_2$

$$3[EtSAl(BH_4)_2]_2 \rightleftharpoons 2[EtSAl(BH_4)_2]_3$$

If the solution is warmed only to 343 K, one sharp set of signals can be seen but these are centred at 1.16 ppm for the CH_3 and 2.74 for the CH_2.

All the compounds show 1:4:6:4:1 quintets in their ^{11}B spectrum. This shows that all the protons in the hydroborate group are being made equivalent by exchange processes. The chemical shift of the ^{11}B signal seems to be dependent upon the electronegativity of the atom to which the aluminium is bonded. Thus the thio alkyl compounds all have shifts similar to or slightly lower field than the ^{11}B resonance for aluminium hydroborate. The alkoxy compounds resonate to slightly higher field than the parent hydroborate. This was also observed for the alkoxy species prepared by Nöth and Suchy (109).

CHAPTER 3

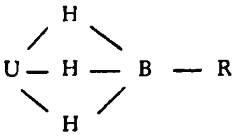
Exchange reactions of Aluminium Hydroborate with Trialkylboranes

Introduction

When aluminium hydroborate is reacted with species capable of exchanging alkyl groups, two centres of reaction are possible, namely the aluminium and boron atoms. The process of alkylation at a boron atom as opposed to the alkylation at aluminium which has been shown by Oddy to be a general reaction when aluminium alkyls are mixed with aluminium hydroborate, was first observed by Schlesinger et al. for uranium hydroborate, $U(BH_4)_4$. Treatment of uranium hydroborate with trimethylborane resulted in the isolation of a monomethyl and a tetramethyl derivative. The compounds were a green solid and a lavender solid respectively. Both the compounds were volatile and Schlesinger assigned them the formulae $U(BH_4)_3BH_3CH_3$ and $U(BH_3CH_3)_4$, the monomethyl derivative being more volatile than uranium hydroborate itself. Intermediate compounds were probably also present but were not isolated. Equally uranium hydroborate was found to react with triethyl borane and higher alkyl boranes, but pure products could not be isolated in these cases.

More recently other boron alkylated species have been prepared by Marks et al. They reported the preparation and spectral properties of $(C_5H_5)_3UBH_3Et$ and $(C_5H_5)_3UBH_3C_6H_5$, which are both brown solids.

The structure of uranium hydroborate is known to contain hydroborate groups attached by a triple hydrogen bridge to the metal. These formulations are therefore not surprising, and contain the structural unit



(where R = methyl, ethyl or phenyl).

The infra-red spectra recorded by Marks confirm this, since no trace of a B-H terminal band was observed. The ^1H n.m.r. shows a quartet for the BH_3 protons which collapses to a sharp singlet when ^{11}B decoupling is applied. Marks also argues that the collapse of the B-H signal at low temperature for $(C_5H_5)_3UBH_4$ is the first observation of the slowing of the bridge-terminal hydrogen exchange processes.

Although the bonding of the hydroborate group is different in aluminium hydroborate to that in uranium hydroborate, there being a double rather than a triple bridge to the metal, there seemed no reason why exchange of the terminal hydrogens should not take place with alkyl groups. In the aluminium case there is of course the possibility of the hydroborate group having one or two terminal hydrogens substituted by alkyl groups.

Reactions of aluminium hydroborate with trimethyl and triethyl borane were attempted at various concentrations. The vapour pressures of the mixtures were followed and the mixtures subjected to ^{11}B n.m.r. investigation. Later, separation and identification of the reaction products by infra-red spectroscopy was attempted, as was an alternative preparation of the alkylated compounds by a novel method involving neither aluminium hydroborate nor triethyl borane.

Nuclear magnetic resonance properties of aluminium hydroborate-triethyl borane mixtures

Triethyl borane - aluminium hydroborate (1:1 molar ratio)

In the ^{11}B n.m.r. spectrum of a sample that had been stirred at room temperature, and on which no attempt was made at separation, a quintet (1:4:6:4:1) at -35.8 ppm was observed along with a very small peak at +28 ppm. This sample was stored and the spectrum retaken after a period of three weeks. A quintet was still visible at -36.3 ppm but a quartet (1:3:3:1) also appeared at -21 ppm (J_{B-H} = 70 Hz). Small peaks around 28 ppm were also present. The ^{27}Al spectrum showed a single peak at 94.4 ppm.

A sample which had been distilled at 0^{o} C had an altered ^{11}B n.m.r. spectrum in which a very weak quintet at -35.6 ppm, a quartet at -20.6 ppm (J 71 Hz) and a small broad hump at -6.2 ppm were apparent, together with a large signal at +28.6 ppm. The ^{13}C n.m.r. showed peaks at -0.91, +0.84, +7.2 and +10.14 ppm.

Triethyl borane-aluminium hydroborate (5:1 molar ratio)

The ^{11}B n.m.r. spectrum of an untreated mixture showed a quintet at-35.0 ppm and a quartet (J_{B-H} = 73 Hz) at-19.9 ppm. There was a broad hump at-3.5 ppm and a large peak at +28 ppm. After a period of 2 weeks the spectrum had changed in that there had been an increase of the quartet and the hump with respect to the quintet, and there had been an increase in the size of the signal at +28 ppm in relation to the signal due to residual triethyl borane. This trend continued as the sample was left for a further 3 months.

On attempting to separate the mixture at 0° C, a volatile portion showed a quintet at-33.7 ppm with some triethyl borane, whilst the involatile portion showed an indistinct signal at-21 ppm, a hump at-6 ppm and a signal at +28 ppm.

Triethylborane-aluminium hydroborate (12:1 molar ratio)

The liquid mixture of this composition showed a signal in the ^{11}B n.m.r. spectrum which, when proton decoupling was applied, was found to be due to two signals at-33.9 ppm and-36.6 ppm. The spectrum also showed a broad hump, some residual triethyl borane, and a signal at +28 ppm. After 5 days the quintet had virtually disappeared, and the broad hump had increased in size and was centred at-3.5 ppm. The triethyl borane signal had decreased and the signal at +28 ppm increased.

Triethyl borane- aluminium hydroborate (25:1 molar ratio)

This mixture produced very similar results to the 12:1 mixture with initially two quintets centred at-36.5 and-33.7 ppm, followed by their disappearance on standing and increase of a broad hump signal at-4.2 ppm. Residual triethyl borane and a signal at +28 ppm were present.

Trimethylborane-aluminium hydroborate (5:1 molar ratio)

The products of this reaction were investigated after 18 hours at room temperature and an approximate total pressure of 6 atmospheres. The products were condensed in traps at -80° C and -110° C. The -80° C trap contained a small amount of residue which gave a braod structureless

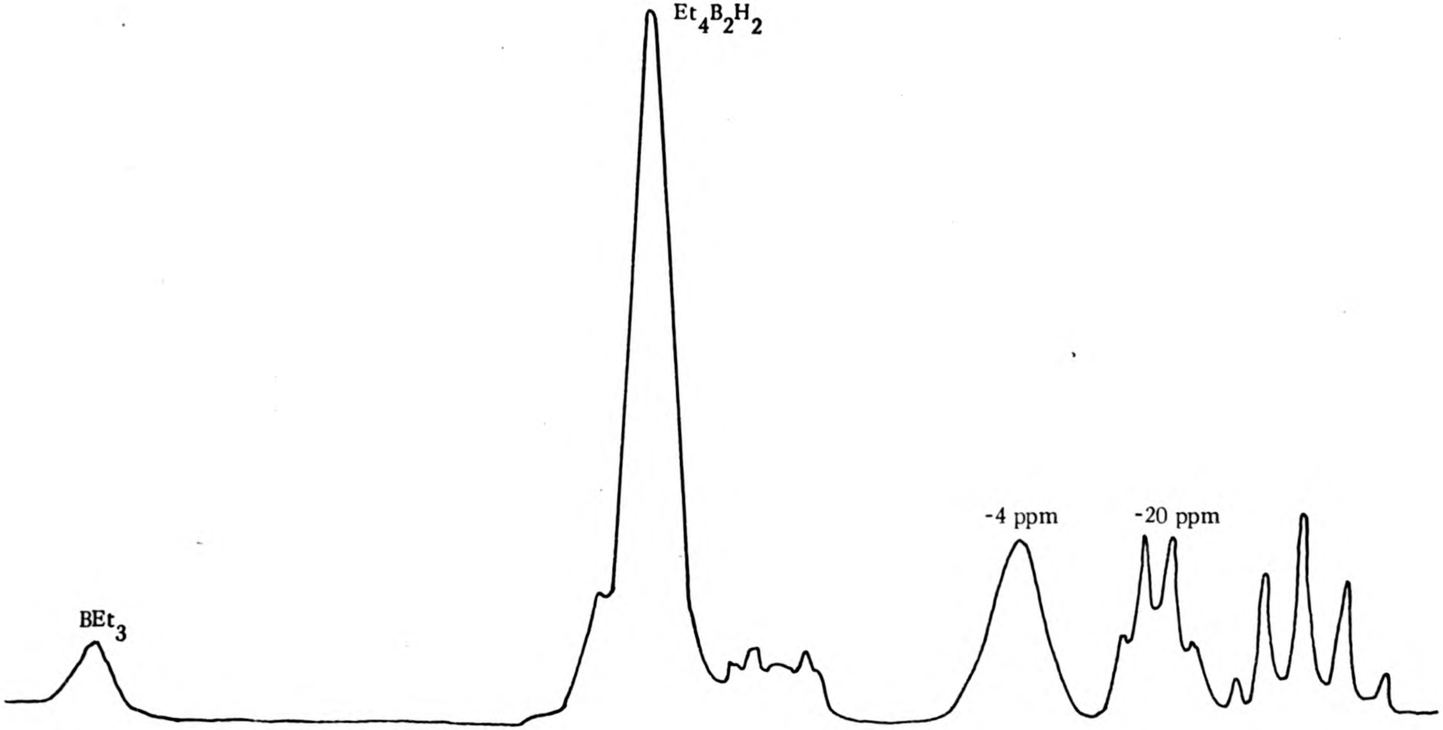


Fig. 3.1 Typical ^{11}B n.m.r. spectrum obtained by exchange between $Al(BH_4)_3$ and BEt_3

signal (^{11}B n.m.r. spectrum) centred at -36.2 ppm. The -110° C trap, when subjected to ^{11}B n.m.r., showed a quintet at -33.8 ppm, a quartet at -21 ppm (J_{B-H} = 72 Hz), and a trace of a signal at -5 ppm. A signal at +25 ppm was also present.

The reaction was repeated at 70° C with a reaction time of 6 hours. The total pressure was estimated to be 7 atmospheres. The fractionation temperatures were altered slightly to -95° C and -120° C. The ^{11}B n.m.r. spectrum of the -95° C fraction showed a quintet at -33 ppm and an ill-defined quartet at -20 ppm, as well as signals at +29, +25 and +14 ppm. In the -120° C fraction, the low field signals were also present but the high field signals showed a quintet at -33.8 ppm and a quartet (J_{B-H} = 72 Hz) at -21.0 ppm. On standing, this sample showed a decrease in the size of the quintet and an increase in the size of the quartet.

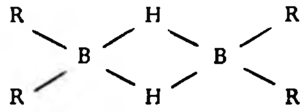
Trimethyl borane - dimethyl aluminium hydroborate (5:1 molar ratio)

As trimethyl borane boils at -20° C and dimethyl aluminium hydroborate tends to decompose at room temperature, this mixture was kept cold and showed no apparent reaction after a substantial time period.

Discussion

All these results are consistent with the formation of exchange products between the species involved.

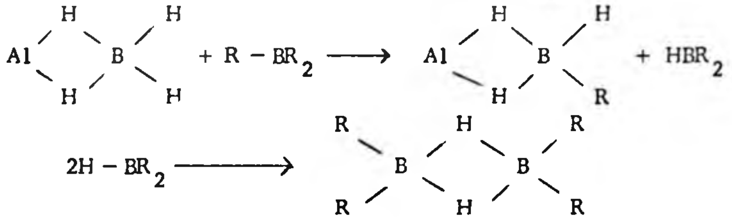
The commonly observed low field peaks of +28 ppm and +25 ppm in the ^{11}B n.m.r. spectrum were identified as being due to tetraethyl and tetramethyl diboranes respectively by comparison with published values (206). On some occasions the spectra showed these signals to have shoulders on them to indicate the expected triplet structure. In these two compounds the only hydrogens present are in bridge positions, and the ^{11}B-^{1}H coupling constant would be approximately 40 Hz.



These compounds are not entirely stable and have a tendency to disproportionate. The signals observed at +29 and +14 ppm in the ^{11}B n.m.r. spectra of the heated trimethyl borane-aluminium hydroborate reaction are due to trimethyl diborane formed by disproportionation of tetramethyl diborane according to

$$3Me_4B_2H_2 \longrightarrow 2Me_3B_2H_3 + 2BMe_3$$

In the exchange reactions with aluminium hydroborate, these compounds would probably be formed by the following scheme:-

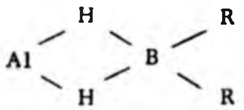


This leads to the aluminium containing species, and as shown in this equation the aluminium species formed would be expected to show a quartet in its ^{11}B n.m.r. spectrum, providing the presence of an alkyl group does not prevent bridge-terminal hydrogen exchange. This was not found to be the case, and a quartet was observed in most cases. The coupling constant ^{11}B-^{1}H was found to be consistent with an average of the value for the presence of one terminal and two bridging hydrogens.

$$(1\ B\text{-}H_t \text{ at } 120\,Hz + 2\,B\text{-}H_\mu \text{ at } 40\,Hz) \div 3 = 67\,Hz$$

The quintet signals observed are obviously from unreacted hydroborate groups, and it seems reasonable to assign quintets that resonate at values slightly lower than the aluminium hydroborate position, to hydroborate groups that are in a molecule with some degree of alkylation on other borons.

More than one terminal hydrogen per hydroborate group may be substituted. In this case the boron resonance would be expected to be a triplet. On no occasion was a triplet observed. However, the broad hump which was observed at positions around -4 ppm is assigned to this doubly substituted group.



The appearance observed for the resonance may be due to one of two causes. There is the possibility of viscosity of the liquid having an effect on the coupling, but in this case this would seem unlikely. More likely, possibly, in view of the fact that a doubly terminally alkylated hydroborate group is probably a rigid, non-intramolecularly exchanging group, then the ^{27}Al atom may be involved in the coupling to ^{11}B.

It should be noted in these reactions that the rate of reaction is slow and incomplete. To fully alkylate an aluminium hydroborate molecule will obviously require six alkyl groups in terminal positions. Thus, even if each triethyl borane molecule can only supply one alkyl group, and the other two are lost to exchange reactions as tetraethyl diborane, then any ratio greater than $6BEt_3 : 1Al(BH_4)_3$ has the amount necessary to go to completion. This is only observed for the mixtures with very large amounts of triethyl borane where the broad hump assigned to the doubly alkylated groups is found to dominate other Al-B signals. Below these ratios the broad hump is not present in substantial amounts. Even at a 5:1 ratio where two borons could be doubly alkylated, evidence of incomplete alkylation as witnessed by the presence of the quartet due to BH_3Et was always present. In this work, heating the triethyl borane mixtures was not attempted in view of the unstable nature of the starting compound, $Al(BH_4)_3$, possibly leading to even more complex products. Further work could involve heating of these mixtures to try and drive the reactions to completion. The reaction of dimethyl aluminium hydroborate and trimethyl borane in fact showed no reaction even after several weeks, but again this was kept cold to avoid complicating the system. Dimethyl aluminium hydroborate would tend to disproportionate at higher temperature.

The n.m.r. evidence is entirely consistent with these formulations. The increase in the amount of trialkyl borane available leads to a greater proportion of the broad hump, or quartet over quintet or broad hump over quartet. Increased reaction time also produces these effects. Accompanying this is an increase in the amount of tetraethyl diborane in relation to trialkyl borane. The evidence, however, is only circumstantial because, as was stated above, there is incomplete reaction and a mixture formed and the postulated compounds were not available for confirmatory analysis.

Attempts were made to separate the mixtures in vacuo and take gas phase infra-red spectra, but it seems appropriate to first present some data on the vapour pressures of the mixtures.

The mixtures containing triethyl borane produced vapour pressures well below that of aluminium hydroborate as expected.

By Raoult's Law the vapour pressures at 0° for the various mixtures would be expected to be

$Al(BH_4)_3 : BEt_3 = 1 : 1$ (119.5 x 0.5) + (10 x 0.5) = 65 mm Hg

$Al(BH_4)_3 : BEt = 1 : 5$ (119.5 x 0.167) + (10 x 0.833) = 28 mm Hg

The 1 : 1 mixture was found to have a vapour pressure of 62 mm Hg at 0° and the 1 : 5 mixture a vapour pressure of 14 mm Hg, and this may be explained by the chemical interaction taking place.

The data for an aluminium hydroborate : trimethyl borane = 1 : 5 mixture are presented in Table 3.1, along with a comparison for pure trimethyl borane. When the system had ceased to show a change in vapour pressure, excess trimethyl borane, 90% of the original amount used, was removed and the vapour pressure of the subsequent mixture was found to be

	-61° C	8 mm Hg
	-45° C	15 mm Hg
	-35° C	32 mm Hg
	-23° C	57 mm Hg
	0°C	148 mm Hg
Room temp.	19.4° C	257 mm Hg

By reducing the amount of trimethyl borane used initially, a mixture with a vapour pressure below an atmosphere at room temperature could be prepared without the need for any removal of volatile components.

Table 3.1

Comparison of the Vapour Pressure of Aluminium Hydroborate: Trimethyl Borane 1:5 with Trimethyl Borane

T/ °C	Observed vapour pressure	Literature for BMe_3/mm Hg (208)
-61	66	100
-52.7	100	
-45	146	245
-35	229	400
-33.4	245	
-23	374	683
-21.0	400	
-20.1	418	Atmosphere
-5.7	683	

Table 3.2 Measurements of Vapour Pressure and Hydrogen Evolution of an $Al(BH_4)_3:BEt_3 = 5:1$ molar mixture

Readings at 48 hourly intervals

(a) Accumulated hydrogen retained

Temp/°C	Total vapour pressure/mm Hg	Hydrogen pressure/mm Hg
21.2	234	4
20.5	222	9
20.5	228	13
22.7	246	13
18.9	219	14
18.9	230	19
21.8	249	24
20.4	237	22

(b) Accumulated hydrogen removed

Temp/°C	Total vapour pressure/mm Hg	Hydrogen pressure/mm Hg
22.6	235	5
23.1	240	2
20.3	214	4
17.6	200	7
18.0	200	9
18.4	215	14
21.6	223	3
20.5	211	3
21.4	217	5
22.8	223	3
22.1	221	9
20.4	212	7

For the aluminium hydroborate, triethyl borane = 5:1 mixture (Table 3.2) the vapour pressure was found to stabilise at 200-220 mm Hg at room temperature. The mixture continued to evolve hydrogen as would be expected for pure aluminium hydroborate. The triethyl borane did not seem to prevent decomposition, and the effect was not altered regardless of whether the hydrogen was retained or pumped away.

Infra-red spectral data on aluminium hydroborate, trialkyl borane exchange reactions

The study of the ^{11}B n.m.r. spectra of these exchange reactions and measurement of their vapour pressure gave an indication as to which species were present and their volatility. Accordingly, procedures were sought for separating the components by distillation in vacuo, and further characterisation by infra-red spectroscopy. There were several difficulties. As has already been stated, in no case had the reactions seemed to have reached completion, and the compounds formed were likely to have similar spectral properties to the initial compounds. Further, the alkyl diboranes and suggested B-alkylated hydroborates might also appear similar. This indeed appeared to be the case. Most of the spectral details observed could be assigned to the known compounds, aluminium hydroborate, trialkyl boranes and alkyl diboranes.

Table 3.3a

Infra-red spectral details of exchange reactions between $Al(BH_4)_3$ and BR_3

Compound or Mixture	Procedure	Infra-red frequencies/cm^{-1}
BEt_3		1460 1325 1110 920
$Et_4B_2H_2$		1582 1466 1400 1290 1109 1047 814
$Et_3B_2H_3$		2500 1582 1470 1435 1289 1114 1072 1024 838
$Me_4B_2H_2$		1605 1437 1324 - 1312 1147 1111 1055 1017 935 772
$Me_3B_2H_3$		2506
BMe_3		1300 - 1311 1163 1150 970 860
$Al(BH_4)_3$:BEt_3 1 : 5	Separation 0°	2500 small. Dominated by $Et_4B_2H_2$. Extra peaks in 1300 region.
	-78°	Dominated by BEt_3. 1540 cm^{-1}. Small peaks, 650 600
	-196°	Dominated by $Al(BH_4)_3$. No peak at 650
$Al(BH_4)_3$: BEt_3 1 : 12	Separation -35°	1580 cm^{-1}. Some BEt_3 peaks. No Al-H-B bands
	-60°	2540 2480 BEt_3 peaks. 650 600 (650 more intense) redistil -55° BEt_3 pure + 2545 2480 650 600 (600 more intense)
	-196°	Trace $Al(BH_4)_3$

Table 3.3b

Infra-red spectral details of exchange reactions between $Al(BH_4)_3$ and BR_3

Mixture	Procedure		Infra-red frequencies/cm^{-1}
$Al(BH_4)_3$: BMe_3 1 : 5	Separation	-80°	2540 2480 1600 1500 1300 1110 685 575
Room temp.		-110°	2550 2500 1600 1310 1150 1110 690 600
		-196°	BMe_3 73% recovery. 1600
$Al(BH_4)_3$: BMe_3 1 : 5	Separation	-95°	2515 2500 sharp superimposed on less intense signal. 1600 very strong.
70°			1310 Several bands 1200-1000 930 800 680 small
		-120°	Similar. No band 690
		-196	BMe_3

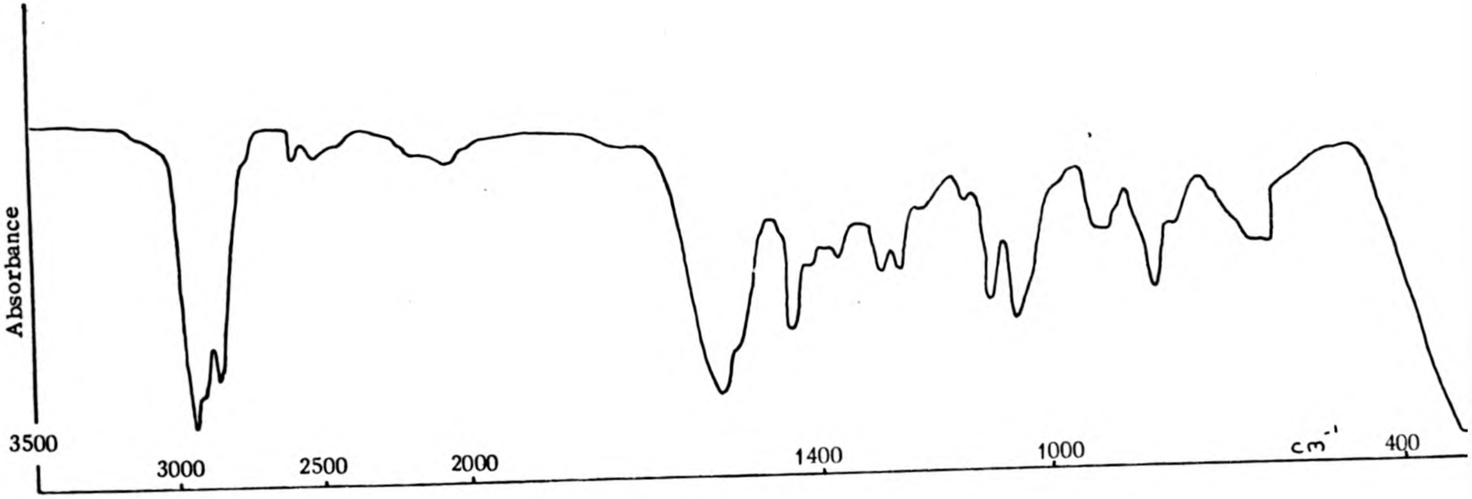


Fig. 3.2 Infra-red spectrum obtained from mixing of $AlEt_3$ and $Et_4B_2H_2$

The information obtained and the procedures used are summarised in Table 3.3.

The conclusion must therefore be that the spectra of the compounds formed in the exchange reactions are insufficiently different from the starting compounds to be positively identified by infra-red spectra of the mixtures.

Attempted preparation of B-alkylated aluminium hydroborates by a novel reaction

This was suggested by an analogous reaction from beryllium chemistry described in a U.S. patent (195). In this work tetraethyl diborane was reacted with diethyl beryllium at 0° C. Beryllium bis (diethyl borohydride) was stated to be formed.

$$2Et_4B_2H_2 + [Et_2Be] \longrightarrow Be(BEt_2H_2)_2 + 2BEt_3$$

On heating to 180° C under reduced pressure for 4-6 hours this gave a 71% yield of pure beryllium hydride.

By analogy a reaction was set up according to the equation

$$6Et_4B_2H_2 + (Et_3Al)_2 \longrightarrow 2Al(BEt_2H_2)_3 + 6BEt_3$$

Spectral analysis of the reaction products by ^{11}B n.m.r. spectroscopy showed the same broad signal at-4 ppm as had been observed in the exchange reactions of aluminium hydroborate. Triethyl borane was also observed to be formed. Study of the infra-red spectrum of the mixture which had been distilled to remove BEt_3 surprisingly did not show any strong band close to 2000 cm^{-1} which would indicate the presence of an Al-H-B bridge unit. There was only a very broad band spanning 2000 cm^{-1}. Bands due to C-H bonds were observed close to 3000 cm^{-1} and 1470 cm^{-1}. There were some bands around 1000 cm^{-1} which could not be assigned. No definite conclusion can therefore be drawn at this stage, and it appears as though a mixture of products is again obtained.

Conclusion

Much evidence has been accumulated pointing towards the formation of a new class of compounds, B-alkylated aluminium hydroborates, by two different routes. Completely definitive proof in the form of total separation and chemical analysis was not obtained.

CHAPTER 4

Reactions of Aluminium Hydroborate with some Octahydro Triborate and Hydride Species, and their Relevance to Aluminium Hydroborate Decomposition

Introduction

As was mentioned in Chapter 1, the observed decomposition of aluminium hydroborate has presented many problems. From the earlier work of Schlesinger and his co-workers, Brokaw and Pease, and some recent unpublished work by McAvoy, whose observation that heating diborane with aluminium hydroborate at 80° C produced a five-fold increase in hydrogen evolution and no diborane recovery, Oddy developed the reaction scheme below.

$$2Al(BH_4)_3 \rightleftharpoons 2HAl(BH_4)_2 + B_2H_6 \tag{1}$$

$$3HAl(BH_4)_2 \longrightarrow AlH_3\downarrow + 2Al(BH_4)_3 \tag{2}$$

$$2AlH_3 \longrightarrow 2Al + 3H_2 \tag{3}$$

$$2Al(BH_4)_3 + B_2H_6 \rightleftharpoons 2B_2H_7Al(BH_4)_2 \tag{4}$$

$$HAl(BH_4)_2 + B_2H_6 \rightleftharpoons B_2H_7Al(BH_4)_2 \tag{5}$$

$$2B_2H_7Al(BH_4)_2 + B_2H_6 \longrightarrow 2(B_3H_8)Al(BH_4)_2 + 2H_2 \tag{6}$$

$$2B_3H_8Al(BH_4)_2 + B_2H_6 \longrightarrow 2(B_4H_9)Al(BH_4)_2 + 2H_2 \tag{7}$$

$$2(B_4H_9)Al(BH_4)_2 + B_2H_6 \longrightarrow 2(B_5H_8)Al(BH_4)_2 + 4H_2 \tag{8}$$

These reactions could also be supplemented by further reactions to give hydroborates of higher percentage boron content and more than one hydroborate group per molecule could be involved in the reaction.

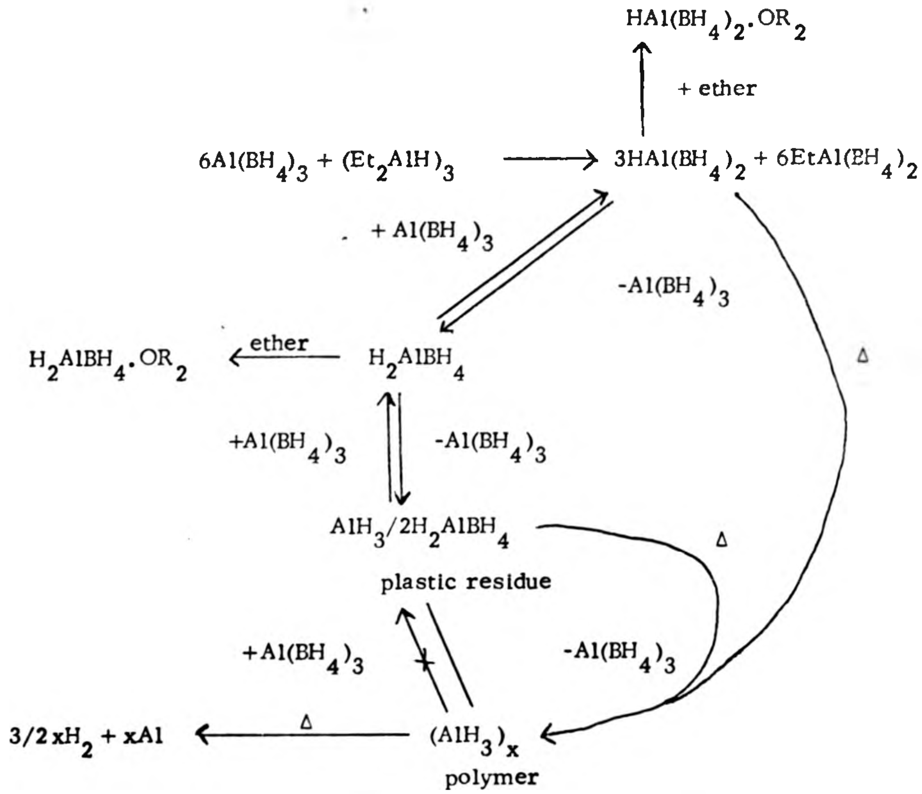
The build-up of higher hydroborate groups is consistent with the changes reviewed by Long for diborane decomposition where only B_4H_{10}, B_5H_{11}, B_5H_9, $B_{10}H_{14}$ and hydrogen are readily isolable (13).

Consideration of the reaction scheme laid out by Oddy predicts that no diborane will be obtained, and shows the likely behaviour when diborane is added as in the McAvoy experiment (1, 4, 5, 6, 7, 8). The scheme also predicts hydrogen as a decomposition product (3, 6, 7, 8).

However, it should be pointed out that as yet there is no direct experimental evidence for such a scheme as that above, and although Oddy investigated the $H_xAl(BH_4)_{3-x}$ (x = 1 or 2) compounds, there are no results which are relevant to the alumino-higher borane species. The purpose of this Chapter is to comment upon such species and their likely properties.

The earlier work of Oddy is relevant to this discussion and will therefore be presented briefly. Oddy mixed excess aluminium hydroborate with diethyl aluminium hydride and distilled off volatile products before redistilling aluminium hydroborate back into the reaction mixture and repeating. By this method it was possible to form an involatile fluffy white solid, insoluble in further aluminium hydroborate, which formed after a rapid polymerisation. This solid slowly darkened at room temperature. Chemical analysis of the solid showed it to be about 80 mole % aluminium hydride incorporated with alkyl and hydroborate groups, but contrary to many experiments in the past no co-ordinating solvent.

Mixing the reactants by stirring at 0° C for one hour in a closed system produced a clear colourless liquid. On removing the volatile components by distillation, the remainder became more viscous until it looked like a plastic residue. Up to this stage the residue could be redissolved in aluminium hydroborate to give a mobile liquid again. The liquid or plastic residue had to contain more Al-H units than the initial mixture as ethyl aluminium bis(hydroborate) was observed as a volatile product. The conclusions that Oddy reached are summarised in the following diagram, and this dovetails in nicely with the scheme proposed for aluminium hydroborate decomposition and the observations of Schlesinger.



The decomposition at 40° C would involve reactions 1, 4, 5, 6 with hydrido aluminium hydroborates being stabilised by the excess aluminium hydroborate. The hydrido aluminium hydroborate can then remove any diborane which might react as in 6, 7 or 8 to produce hydrogen by the reverse of reaction 1 or by 5. Addition of soluble 'polymer' which was identified as the soluble plastic residue prior to polymerisation to (predominantly) aluminium hydride should increase the aluminium hydroborate stability.

At temperatures above 40° C the stabilisation by hydrido aluminium hydroborate species was not possible as reactions 2 and 3 took over. Insoluble polymeric aluminium hydride and aluminium metal could be produced. The polymeric lattice was shown by Oddy to form with the composition $AlH_3 \mid 2X\ AlH_2$ where X was a hydroborate group. Since the hydroborate group in this case could be larger (say B_3H_8 or higher), the composition of the polymer could approach the observed AlB_3H_9.

Oddy has also shown that the hydrido aluminium hydroborates are extremely sensitive towards disproportionation. In anything but a closed system in vacuo they immediately deposit polymeric aluminium hydride according to

$$3HAl(BH_4)_2 \longrightarrow (AlH_3)_x \downarrow + 2Al(BH_4)_3 \uparrow$$

$$3H_2AlBH_4 \longrightarrow 2(AlH_3)_x \downarrow + Al(BH_4)_3 \uparrow$$

Consequently the hydrido aluminium hydroborates have not been found to exist in the gas phase and this has presumably prevented their isolation and characterisation as unco-ordinated compounds. The addition of ether to co-ordinate to the aluminium, however, stabilises the species, and spectra of the co-ordinated species can be observed.

The infra-red spectrum shows bands of the BH_4 group at 2495 cm^{-1}, 2435 cm^{-1}, 2150 cm^{-1} showing it is similar in structure to the aluminium hydroborate adducts. In addition, the spectrum shows an $Al\text{-}H_t$ stretching vibration at 1885 cm^{-1}.

The n.m.r. spectra also show some interesting features. The ^{11}B n.m.r. shows quintets indicating equivalence of the hydrogen atoms in the hydroborate group. The ^{27}Al n.m.r. shows the aluminium resonance to be a slightly higher shift for the hydrido alumium hydroborate adducts (82 ppm) than for the aluminium hydroborate adducts (65 ppm). The ^{1}H n.m.r. shift for the aluminium hydride in the adduct species was determined in a few cases. This was found to occur at approximately 3.7 ppm and was taken as evidence for a terminal hydride by comparison with the resonance position for the terminal hydride in $[HAl(Cl)OS{:}Me_3]_2$ (180). Bridging hydrides tend to come at a lower shift, e.g. in the dimethyl aluminium hydride trimer it is at 2.8 ppm (181).

For the uncomplexed hydrido aluminium hydroborates the hydride resonance was found to vary in position. For hydrido aluminium bis hydroborate in excess ethyl aluminium bis hydroborate, the hydride resonance was at 3.69 ppm, suggesting a terminal position. However, if the percentage of alkyl hydroborate is allowed to decrease or the aluminium hydroborate tends towards a bis hydrido species, then the shift of the hydride moves down to 3.2 to 3.3 ppm. Thus the structure is tending towards an associated species, and of course this is parallel to the observed bulk behaviour that the bis hydrido aluminium hydroborate species, with little alkyl aluminium hydroborate to stabilise it, tends to polymerise easily. Dimerisation must obviously be a first step in aluminium atoms associating through bridging hydrogens to form the polymeric aluminium hydride.

This work, however, did not attempt to isolate any compounds with higher hydroborate groups attached to aluminium. Some compounds of this type that have been isolated previously were mentioned in Chapter 1.

Although aluminium is the next atom to boron in Group III of the periodic table, it has not proved possible to incorporate an aluminium atom into a polyhedral boron cage. Compounds where it is associated with a carborane anion, e.g. in $EtAlB_9C_2H_{11}$ (209), however are known. A recent report suggests a possible route to aluminium insertion into a pentaborane cage. 2-Tetrahydroborato-2-beryllia-nido-hexaborane (11) prepared (197) from 1-chloro-pentaborane(9) and beryllium hydroborate, resulted from a cage opening reaction with subsequent incorporation of Be into the larger cage.

This chapter will discuss primarily the chemistry of some aluminium octahydrotriborate compounds and relate them to the aluminium hydroborate decomposition scheme.

Dimethyl Aluminium Octahydrotriborate

The brief report on this compound gave a method of preparation that was used in the present work, and a few spectroscopic properties. The (200) vapour pressure was also quoted but not thought to be a proper test of purity. In the present work, good agreement was found with the published data, but the compound was found to undergo decomposition only very slowly at room temperature and the vapour pressure of the compound is therefore a more useful and reliable property than had been hitherto reported. Other properties and data not fully reported previously have also been recorded. Thus the compound has been satisfactorily analysed,

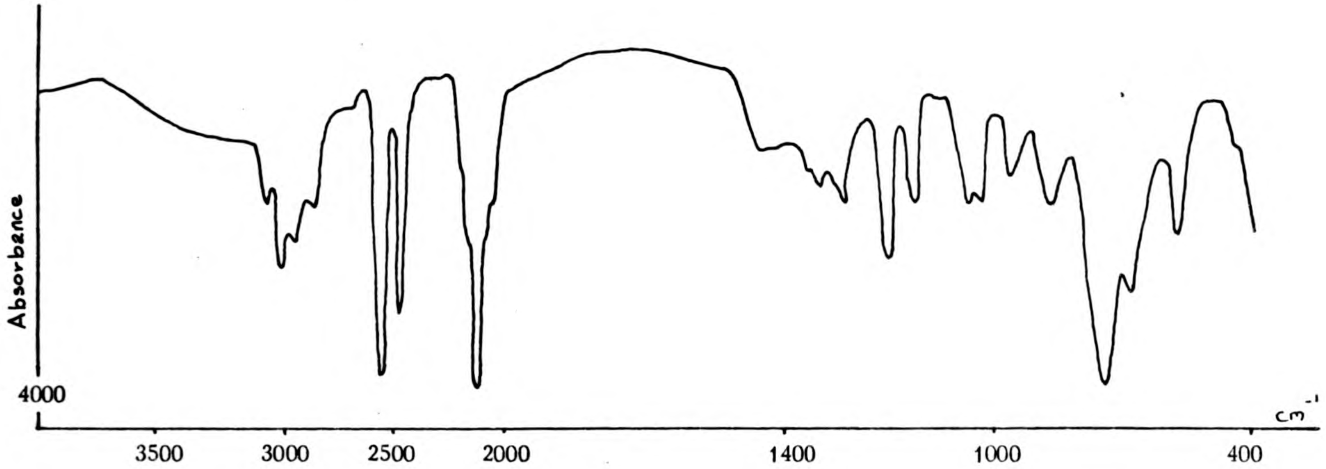


Fig. 4.1 Infra-red spectrum of $Me_2AlB_3H_8$

since this was not reported in the original note, for hydrolysable methyl and hydrogen (as CH_4 and H_2 respectively) and for aluminium (by EDTA titration). The infra-red spectrum (gas-phase) was confirmed as having $B\text{-}H_t$ bands at 2550 cm^{-1} and 2490 cm^{-1}, and a very strong $Al\text{-}H_b\text{-}B$ band at 2170 cm^{-1}. This latter absorption subsequently proved to be a very valuable identification band as did the presence (or absence) of the strong band at 715 cm^{-1} [$\nu(Al\text{-}C)$].

A fairly detailed examination of the nuclear magnetic resonance spectrum of the compound was undertaken, some agreement with the previous work being obtained. As stated in the original work, the ^{11}B n.m.r. is temperature dependent, but it is also solvent dependent. (201)

If the pure liquid is cooled, then at 0° C fine structure due to proton coupling is observed. Two boron signals, one a low field triplet J 120 Hz, and the other a quartet J 74, 79, 73 Hz are observed, this being in good agreement with the published spectrum. The low field resonance is assigned to the unique boron and the coupling pattern and coupling constant would seem to indicate that it is only coupling to its two terminal hydrogens. The high field resonance is assigned to the two equivalent borons. The coupling pattern and coupling constant here would seem to indicate that these borons are coupling with the terminal and bridging hydrogens of which there are one and two respectively associated with each boron. The coupling constant is a reflection of this ratio.

Below this temperature, several changes are observed in the ^{11}B n.m.r. At -33° C the resonances of the quartet are beginning to merge and at -38° have become a single resonance with two shoulders. The low field triplet at this temperature is beginning to broaden. At -43° C the high field signal appears to have two sets of shoulders, and at -57° has three sharp peaks at its apex with a spacing of 65 Hz. At temperatures between -57° and -73° a gradual change is observed so that at -83° virtually all the fine structure has disappeared, and at -93° no evidence of fine structure remains.

Table 4.1

Some n.m.r. parameters for $Me_2AlB_3H_8$

^{11}B Pure liquid

Temp.	Shift/ppm	Form of signal
22° C	-17.7	Broad singlet
	-40.2	Broad singlet
0° C	-14.0	Triplet J = 119.6 Hz
	-41.3	Quartet J = 72 Hz
-23° C	-14.0	Triplet J = 125 Hz
	-41.4	Quartet J = 79 Hz
-33° C	-14.0	Triplet J = 122 Hz
	-41.3	Ill defined quartet J outer 84 Hz inner 46 Hz
-38° C	-14.0	Triplet J = 122 Hz
	-41.4	Ill defined triplet J = 102 Hz
-43° C	-14.0	Broadening triplet J = 119 Hz
	-41.3	Singlet. Ill defined fine structure
-57° C	-13.9	Broadened triplet. Broad decoupled signal
	-39.0	Three sharp peaks at apex. Spacing 65 Hz. Sharp decoupled signal
	-41.3	
	-43.6	
-83° C	-14.2	Broad hump
	-41.2	Singlet. Ill defined fine structure
-93° C	-14.7	Very broad
	-41.2	Broad singlet

^{11}B Toluene solution

Temp.	Shift/ppm	Form of signal
20° C	-32.9	Singlet
-23° C	-34.2	Broadened singlet. Broad shoulder to low field side
-43° C	-38.2	Broadened singlet, Broad shoulder 11 to 15 ppm
-63° C	-18.5 (?)	Very broad singlet. Shift figure difficult to determine
	-40.9	Singlet

^{1}H Toluene solution

Singlet for methyls at all temperatures.
Width of signal varies.

^{27}Al Pure liquid

Temp.	Shift/ppm	Form of signal
23° C	189	Singlet

Fig. 4.2a ^{11}B n.m.r. spectrum of pure liquid $Me_2AlB_3H_8$

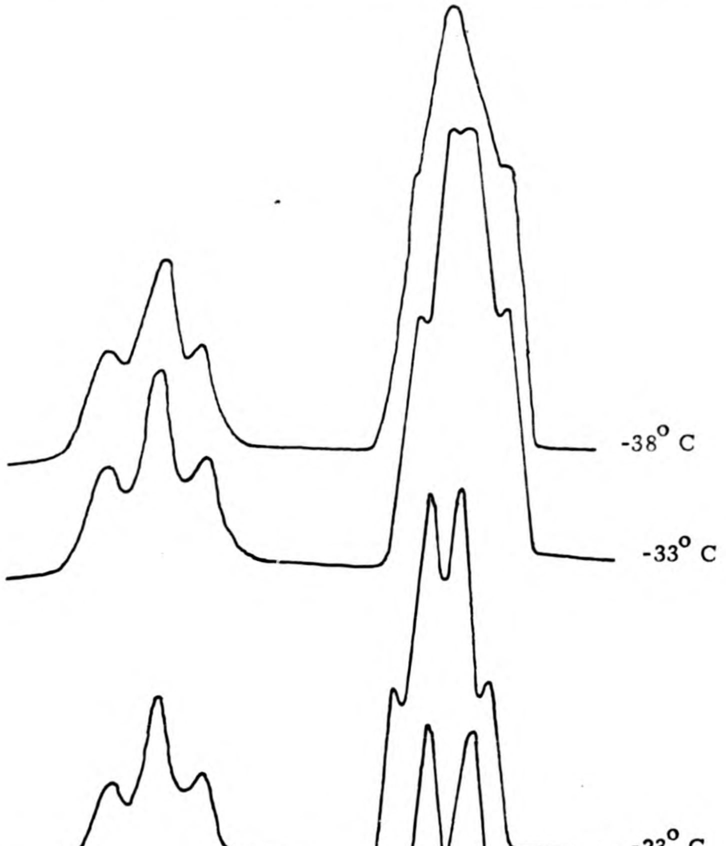
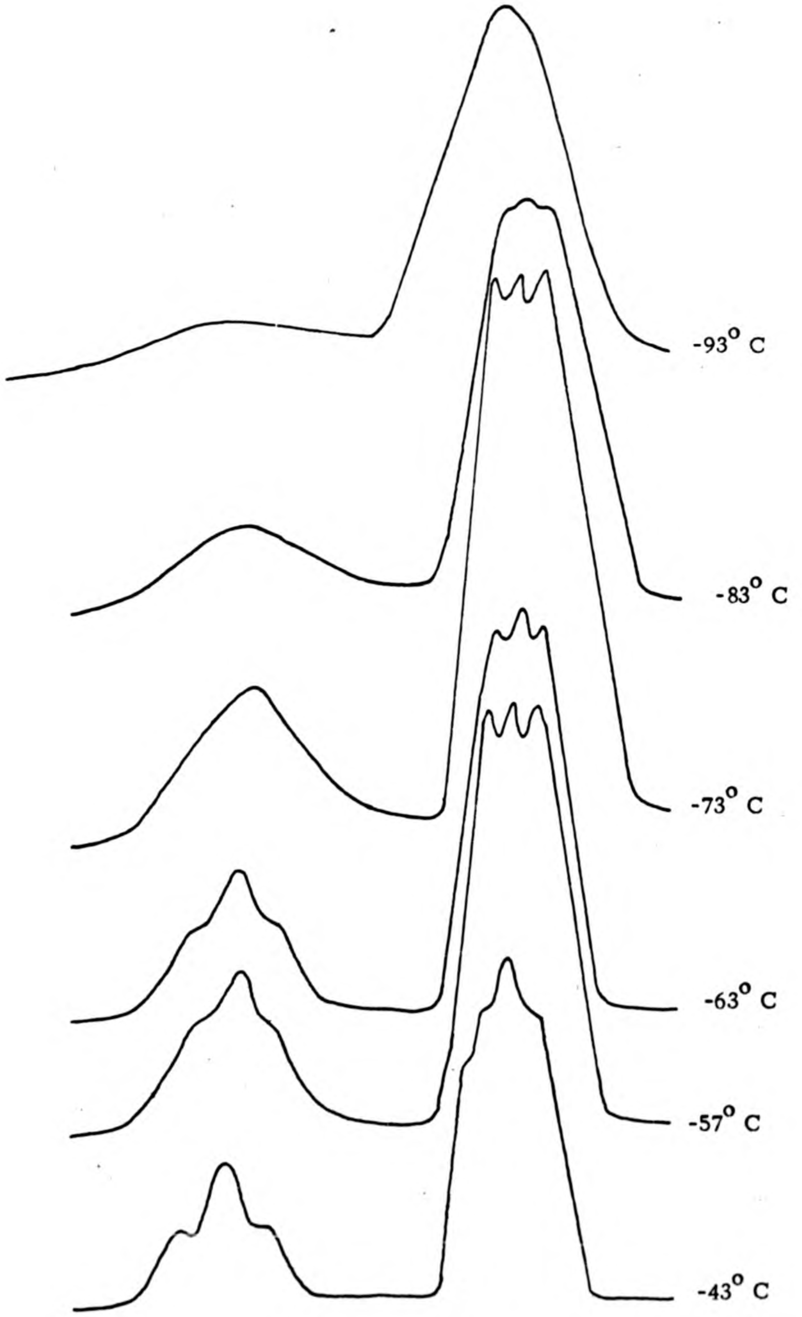


Fig. 4.2b ^{11}B n.m.r. spectra of pure liquid $Me_2AlB_3H_8$



An n.m.r. investigation was undertaken at various temperatures with a solution of dimethyl aluminium octahydrotriborate in toluene solution. The ^{11}B n.m.r. showed significant differences from that obtained from the pure liquid. At room temperature, just one signal at-32.9 ppm was observed, the chemical shift being in good agreement with the position obtained by Gaines for $Me_2AlB_3H_8$ at 50° C (-33.3 ppm). It corresponds fairly well to a time averaged position of two borons at a shift of-41.3 ppm and one boron at a shift of-14 ppm (2 x 41.3 + 14 ÷ 3 = -32.2 ppm). At -23° C the signal has shifted slightly to-34.2, has broadened, and has a very broad shoulder to the low field side. This trend continues as the temperature is lowered further, and only at -63° C are the two signals really separate.

In the ^{1}H n.m.r., necessarily carried out in toluene solution, the only feature that can be clearly distinguished is the methyl signal. This signal remains substantially unchanged as the temperature is reduced although it broadens below -80° C. It was not observed to split into two as reported by Gaines. In this investigation the hydrogen attached to boron remained too broad for any information to be gained.

The ^{27}Al n.m.r. showed a singlet and was at a shift of 189 ppm (downfield w.r.t. $Al(H_2O)_6^{3+} = 0$). The chemical shift of an aluminium signal reflects the stereochemistry and co-ordination number around that aluminium atom. Thus crowded aluminium atoms, as in aluminium hydroborate, have a resonance around 100 ppm, the dimeric aluminium alkyls with a 4 co-ordination around aluminium resonate around 150 ppm, and the monomeric trigonal aluminium alkyls, 3-co-ordination, resonate below 200 ppm. Dimethyl aluminium octahydrotriborate comes in between these latter two.

This confirms that dimethyl aluminium octahydrotriborate is monomeric and suggests that the bonding at aluminium is somewhere between the sp^2 needed for the trigonal arrangement in, say, $Al(i\text{-}Bu)_3$ and the near sp^3 in, say, Al_2Me_6.

Fig. 4.3 ^{11}B n.m.r. spectra of $Me_2AlB_3H_8$ in toluene d 8

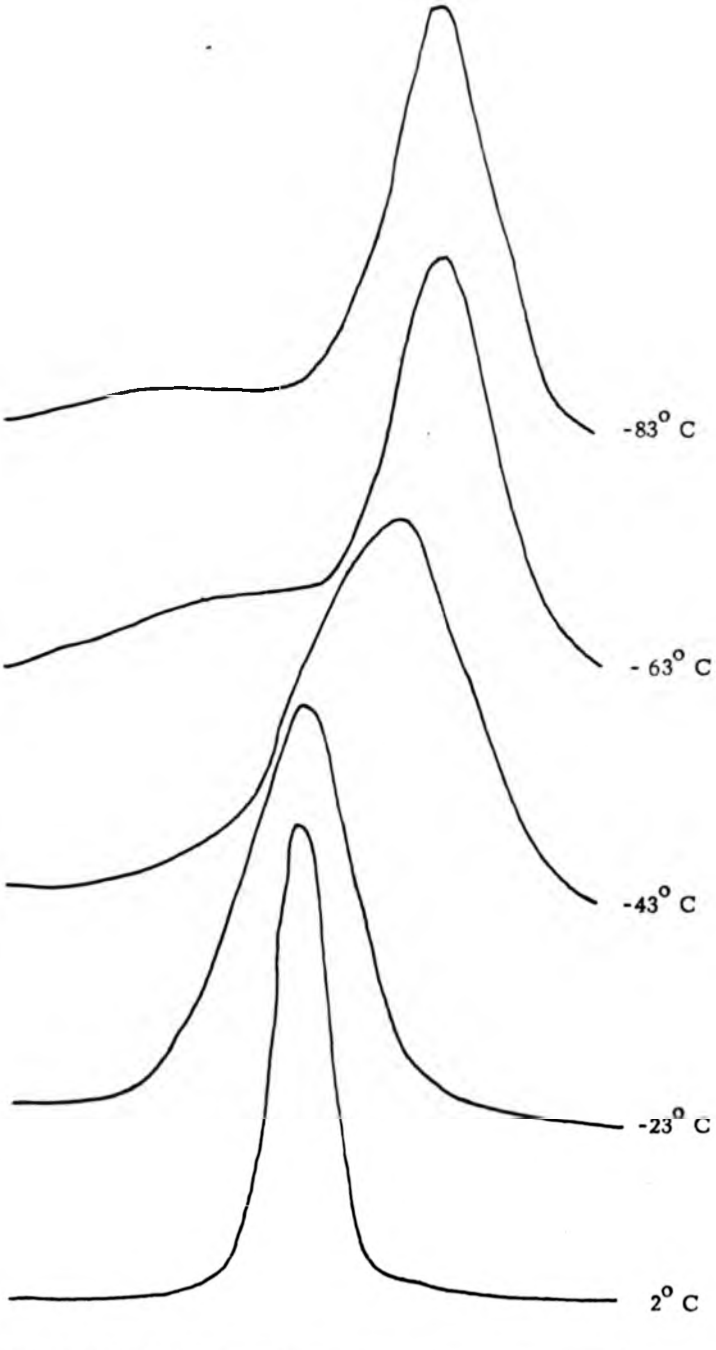
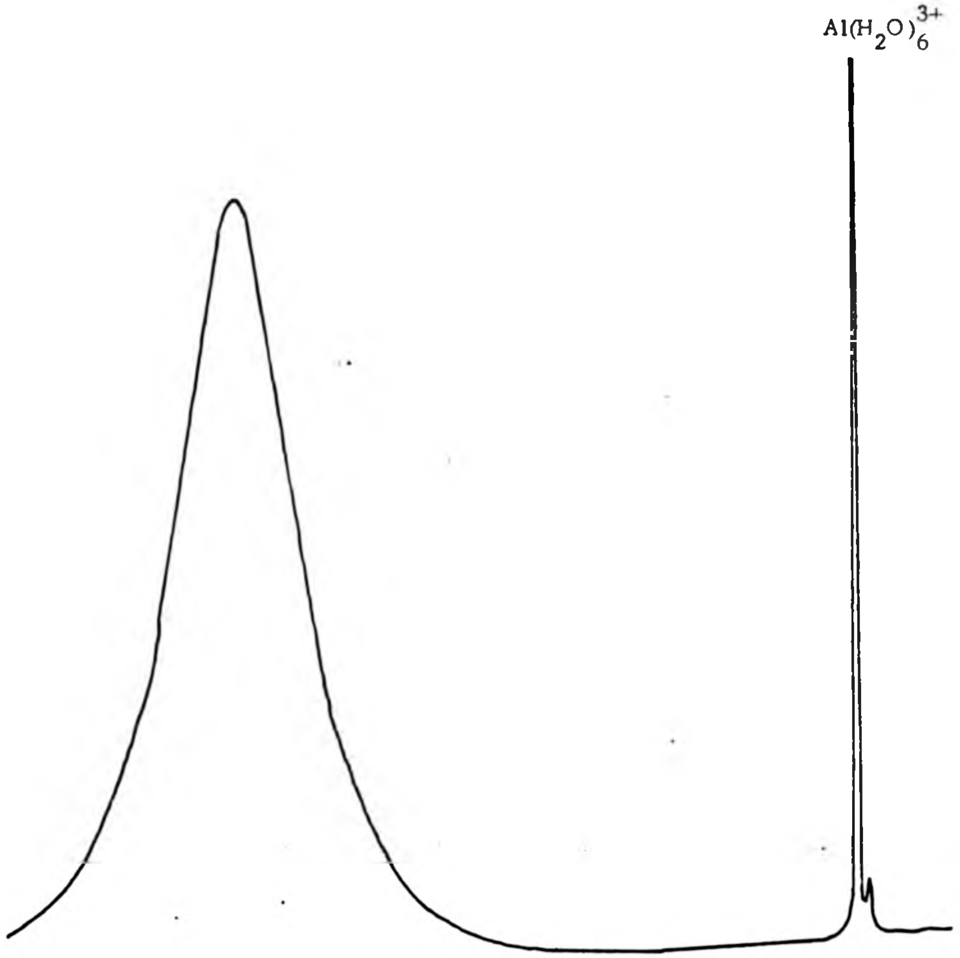


Fig. 4.4 ^{27}Al n.m.r. spectrum of pure $Me_2AlB_3H_8$ at +23° C



The molecule is obviously fluxional and the spectral changes observed in this work require a mechanism whereby the methyl groups are always equilibrating. If the structure was immobile, then the two methyls are not equivalent. The scheme proposed by Gaines (200) where one hydrogen bridge, Al-B, is broken and rotation of the Me_2Al group occurs seems quite satisfactory, as do the other intermediates to provide hydrogen exchange. The complex fine structure then observed on the high field signal would then be due to the temperature effect on the various equilibria and consequent slowing of the different exchanges at different rates.

The effect of the solvent is to alter the temperature at which the boron nuclei cease to fully exchange and also to effect the proton coupling to the boron nuclei. This is quite likely to be a quadrupolar effect brought about by the viscosity of the solution. The splitting out of the borons into their two environments will be encountered again with aluminium octahydrotriborate bis hydroborate.

Unlike the aluminium hydroborate series of compounds where complexing with ligands is well established, the dimethyl aluminium octahydrotriborate showed a complete contrast. With diethyl ether, which complexes readily with aluminium hydroborate compounds, showing no tendency to split off borane groups even when in excess, no simple adduct could be isolated. Indeed the reaction products proved to be quite varied. A trimethyl borane fragment as well as an aluminium hydroborate etherate fraction were identified, as well as at least one other borane fragment which was not identified. The product was a colourless oil, and an analysis for hydrolysable methane and hydrogen produced a figure which was close to that expected for $Me_2AlBH_4.OEt_2$. A disruptive reaction has obviously occurred, and it was thus not surprising that a reaction with trimethyl amine, which has a tendency to attack boron in aluminium hydroborate chemistry if at all in excess, was found to produce complex products.

This may, in fact, mean that it is the B_3H_8 group rather than the aluminium which is the first site for attack by the Lewis base, but suffice it to say that the Al-B_3H_8 entity possesses different properties from the Al-BH_4 and this will also become apparent when aluminium octahydro triborate bis hydroborate is considered.

Dimethyl aluminium octahydrotriborate was used as a precursor in the preparation of aluminium octahydrotriborate bis hydroborate. Two possible methods suggested themselves from past work. In the original preparation of aluminium hydroborate, Schlesinger and his co-workers used the reaction of trimethylalane with diborane, i.e. replacing methyl groups on aluminium with hydroborate groups, and transferring the methyls to boron.

$$2(AlMe_3)_2 + 5B_2H_6 \longrightarrow 2Al(BH_4)_3 + 4BMe_3 + 3H_2$$

Accordingly, since replacement of methyl by hydroborate was required, a preparation based on the equation below was set up.

$$3Me_2AlB_3H_8 + 4B_2H_6 \longrightarrow 3(BH_4)_2AlB_3H_8 + 2BMe_3$$

This was not successful. The only aluminium containing species that could be isolated was aluminium hydroborate. An exchange reaction of some sort had occurred however, as methyl diboranes, notably 1,1-dimethyldiborane, were identified by infra-red spectroscopy.

The second method was a redistribution reaction using aluminium hydroborate similar to the method used by Oddy in the preparation of hydrido aluminium hydroborate species.

$$Me_2AlB_3H_8 + 2Al(BH_4)_3 \longrightarrow (BH_4)_2AlB_3H_8 + 2MeAl(BH_4)_2$$

By using excess aluminium hydroborate, purifying and removing methyl aluminium hydroborates and then adding fresh aluminium hydroborate and repeating, the desired product could be achieved.

The progress of the reaction could be followed by gas phase infra-red spectra of the spectra. The strong methyl band above 700 cm^{-1} in dimethyl aluminium octahydrotriborate gradually diminished. When this band disappeared, the purity of the product was ascertained by chemical analysis, the number of moles of non-condensible gas that were evolved being indicative of the product purity. Complete conversion to aluminium octahydrotriborate bis hydroborate resulted in 16 moles of gas (hydrogen) being evolved, but for less pure products a smaller number as methyl groups still present would report as one mole as opposed to four for a hydroborate. The evolved gas would also contain some methane and this was confirmed by a mass spectrum.

The product obtained from this reaction was a colourless liquid which gave satisfactory analysis results.

Expected hydrolysable hydrogens for $(BH_4)_2AlB_3H_8$	16.0
Found " " " "	15.94

The analysis figure for aluminium was not recorded as it would be the same whatever compound or mixture of $Me_2AlB_3H_8$, $BH_4(Me)AlB_3H_8$ or $(BH_4)_2AlB_3H_8$ was present as the molecular weight of methyl and hydroborate groups are so similar.

The vapour pressure of the liquid, which was of course made use of in its preparation and separation through cold traps, was found to be 4 mm Hg at 0° C and 11 mmHg at room temperature, and it was entirely condensed by a trap of -75° C at a line pressure of 10^{-3} mm Hg. The compound formed a glass and so a melting point was not obtained. If the vapour pressures of the compounds $Me_2AlB_3H_8$ and $(BH_4)_2AlB_3H_8$ are compared with the series Me_2AlBH_4 to $Al(BH_4)_3$, then the trend observed for the octahydrotriborates is reversed, with $Me_2AlB_3H_8$ being the most volatile and the compound without methyl groups the least volatile. This may be a result of some intermolecular associations, since it will be shown later that the B_3H_8 group is not particularly stable in this compound, and it may be that association takes place through these groups which might rearrange to a larger hydroborate grouping. This may be favoured over a species where two rigid octahydrotriborate groups are maintained. The octahydrotriborate group would thus seem to impart slightly different properties to the aluminium boron or aluminium carbon nucleus than does the hydroborate groups, as was observed previously. While the above trends in vapour pressure appear anomalous, other properties of the compound were entirely consistent with its formulation and name. The aluminium octahydrotriborate bishydroborate was found to be unstable at room temperature as is aluminium hydroborate, but the course of the decomposition reaction is somewhat different. In the case of the octahydrotriborate compound, diborane was an identified decomposition product whereas only a trace has ever been observed in aluminium hydroborate decomposition. Aluminium hydroborate was the other major compound identified in the decomposition of the octahydrotriborate which seemed to occur in both liquid and gas phases. Hydrogen was also produced. Some unidentified solid residue was also produced. However, no simple equation can be deduced for the overall decomposition which appears to be a complex reaction. One possibility might be

$$2Al(BH_4)_2B_3H_8 \longrightarrow Al(BH_4)_3 + AlB_5H_{10} + B_2H_6 + 2H_2$$

if the aluminium took the place of boron in the B_6H_{10} framework. This is, of course, at best speculative and might better represented as producing a complex Al-H-B polymer as the residue.

The decomposition was fairly rapid, decomposition products being visible in, say, one hour, but the compound could, with care, be distilled intact and allow other properties of the compound to be determined.

The infra-red spectrum of the octahydrotriborate species was used as a guide in the preparation of the compounds with the disappearance of the 715 cm^{-1} Al-Me band in $Me_2AlB_3H_8$ as the key.

Aluminium octahydrotriborate bis hydroborate was found to have the infra-red spectral details as in the following table:-

cm^{-1}

$(BH_4)_2AlB_3H_8$	$Al(BH_4)_3$	$Me_2AlB_3H_8$
2565 vs	2556 s	2960 m
2495 s	2490 s	2550 vs
2210 s		2490 s
2040 vs	2032 vs	2170 vs
1500 s	1501 vs	
1215 m		1200 m
1120 s	1113 vs	
1000 m		
690 s	606 vs	715 vs
600 m		670 m
550 m		570 m

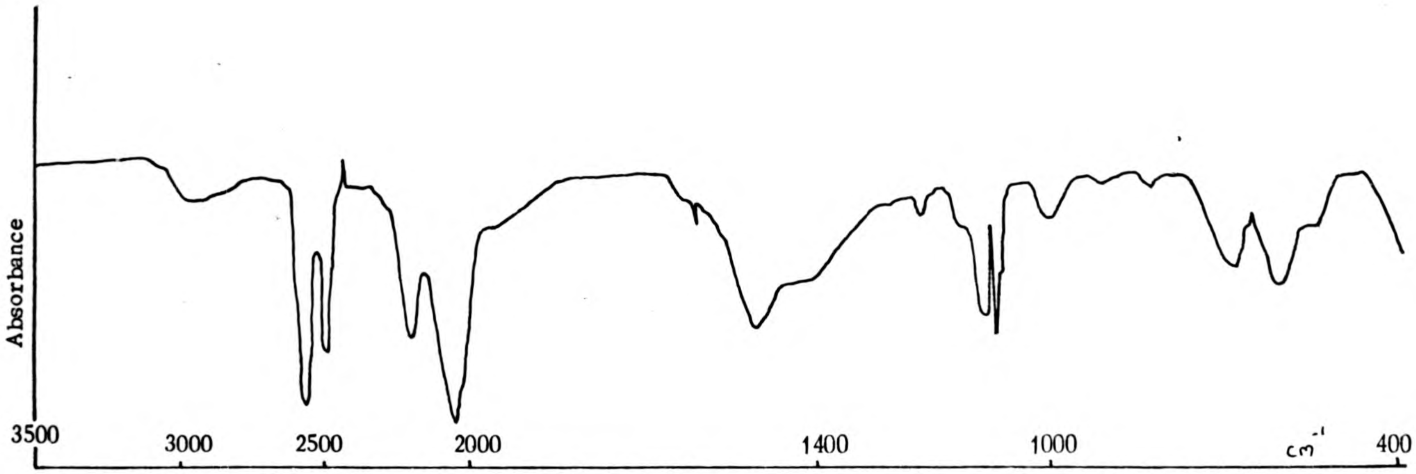


Fig. 4.5 Infra-red spectrum of $(BH_4)_2AlB_3H_8$

The values for the B-H_t bands are very close to those observed for both aluminium hydroborate and dimethyl aluminium octahydrotriborate. This indicates that the different atom arrangements do not alter the bonding to the terminal B-H bonds substantially. The value for the Al-H_b-B band hardly varies for the hydroborate groups in aluminium octahydrotriborate bis hydroborate, and aluminium hydroborate, but substitution of methyl for hydroborate groups alters the Al-H_b-B band in the octahydrotriborate groups in that the absorption shifts to higher wavenumber in the aluminium octahydrotriborate bishydroborate. In aluminium octahydrotriborate bis hydroborate, therefore, there would seem to be some strengthening of the Al-H-B bridges, but this does not seem to be at the expense of the B-H_t bonds. The symmetrical bridge mode occurs at a similar position to aluminium hydroborate, and the band at 690 cm^{-1} probably corresponds to the 670 cm^{-1} band in dimethyl aluminium octahydrotriborate and is probably a skeletal Al-B vibration with the 600 cm^{-1} vibration corresponding to the 606 cm^{-1} vibration in aluminium hydroborate.

The nuclear magnetic spectrum was taken of the compound for the ^{1}H and ^{11}B nuclei. Amount and difficulty of transfer of the compound meant that this was not as extensive as might be wished. In particular, a ^{27}Al spectrum was not taken, and the chemical shift of the resonance might have shed some light about the bonding around aluminium as was explained for dimethyl octahydrotriborate. Information on any association present in the liquid might help in explaining the vapour pressure in particular.

The ^{1}H n.m.r. at room temperature was a broad structureless signal which, in view of similar compounds, was as expected. The width of the signal was approximately 240 Hz, in which it is slightly narrower than the corresponding aluminium hydroborate and had a chemical shift at its centre of approximately 0.5 ppm downfield from TMS.

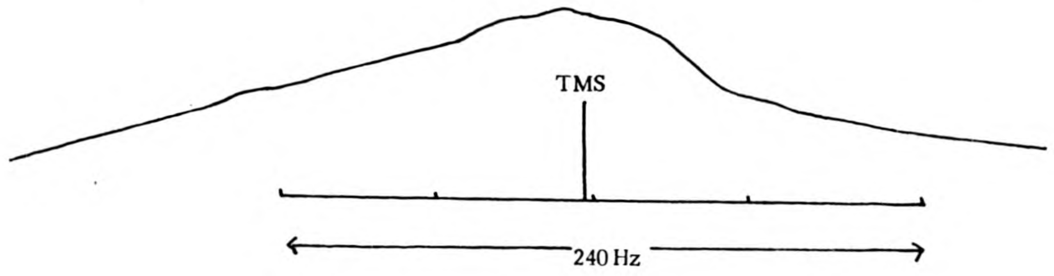


Fig. 4.6 ^{1}H n.m.r. spectrum of $(BH_4)_2AlB_3H_8$ at +30° C

Fig. 4.7a ^{11}B n.m.r. spectrum of $(BH_4)_2AlB_3H_8$ at + 10° C

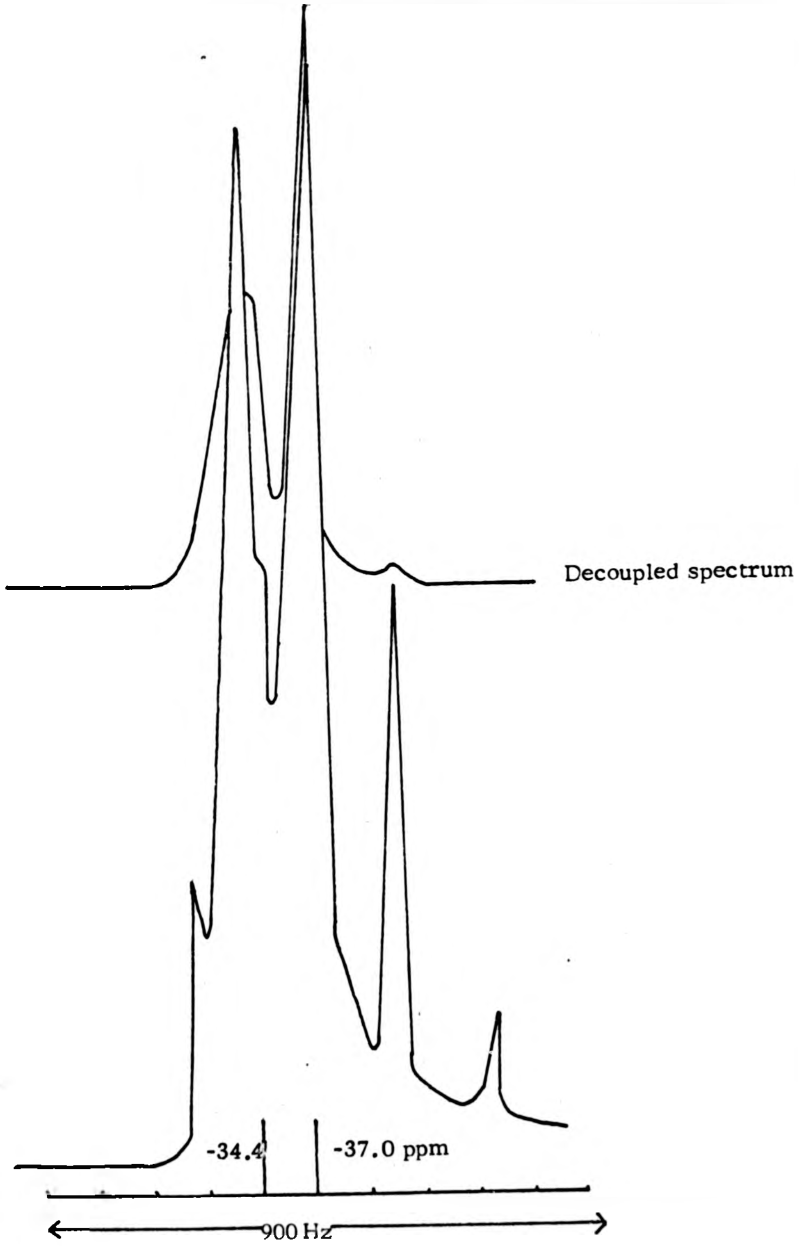


Fig. 4.7b ^{11}B n.m.r. spectrum of $(BH_4)_2AlB_3H_8$ at -13° C

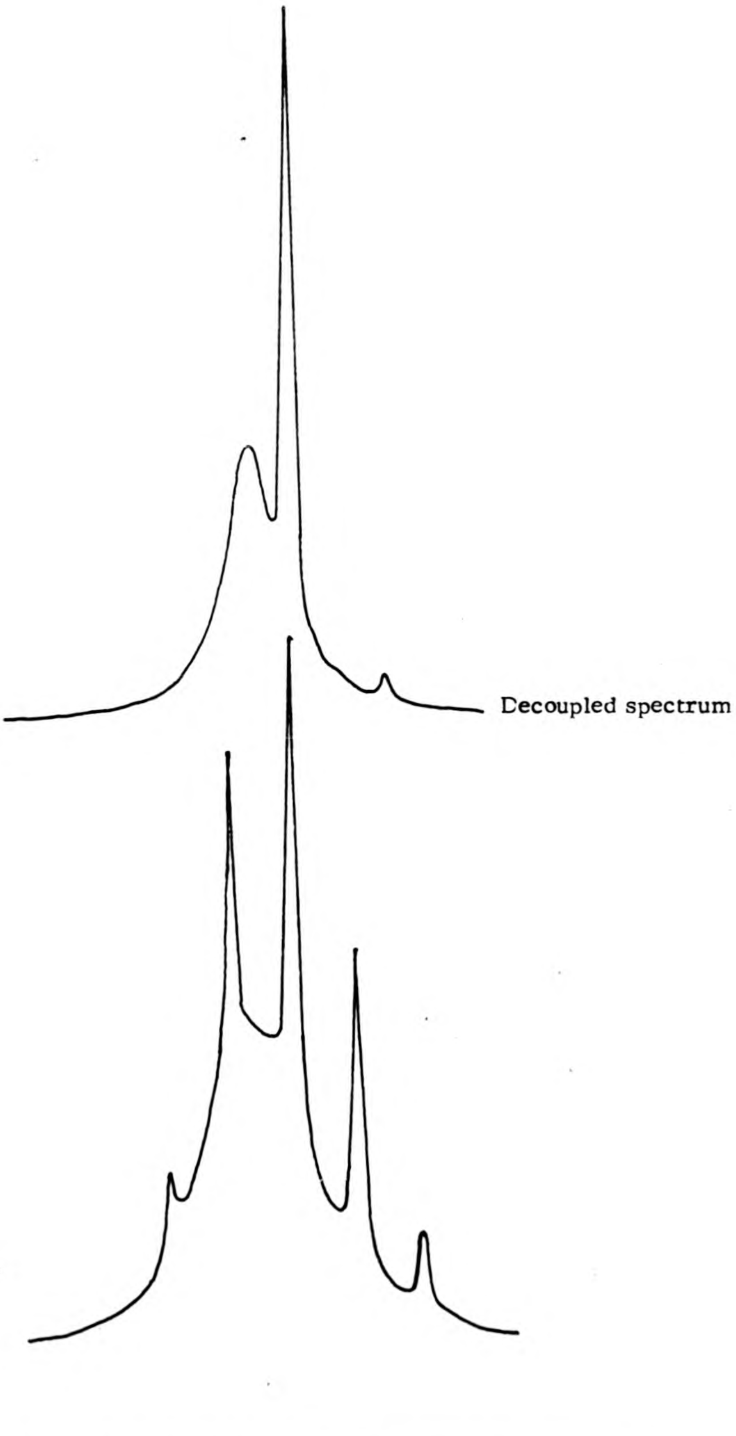


Fig. 4.7c ^{11}Bn.m.r. spectrum of $(BH_4)_2AlB_3H_8$ at -33° C

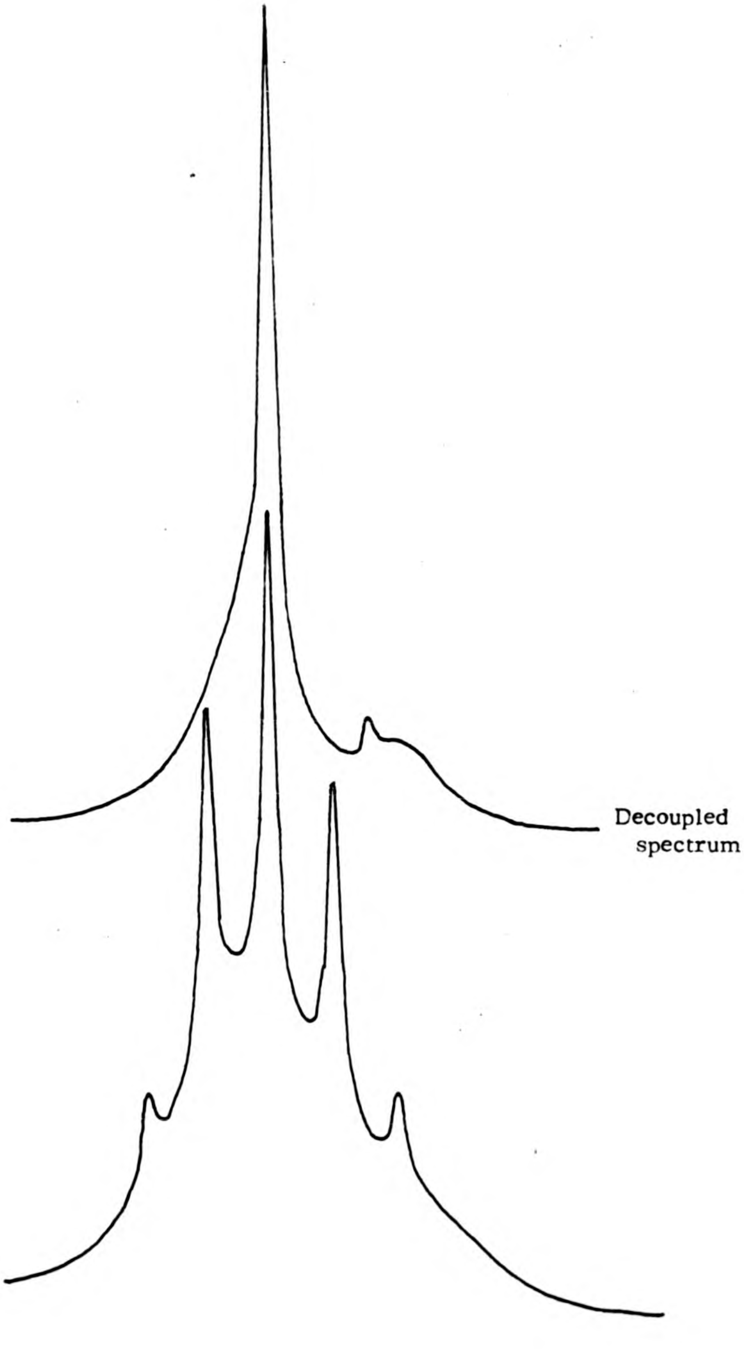
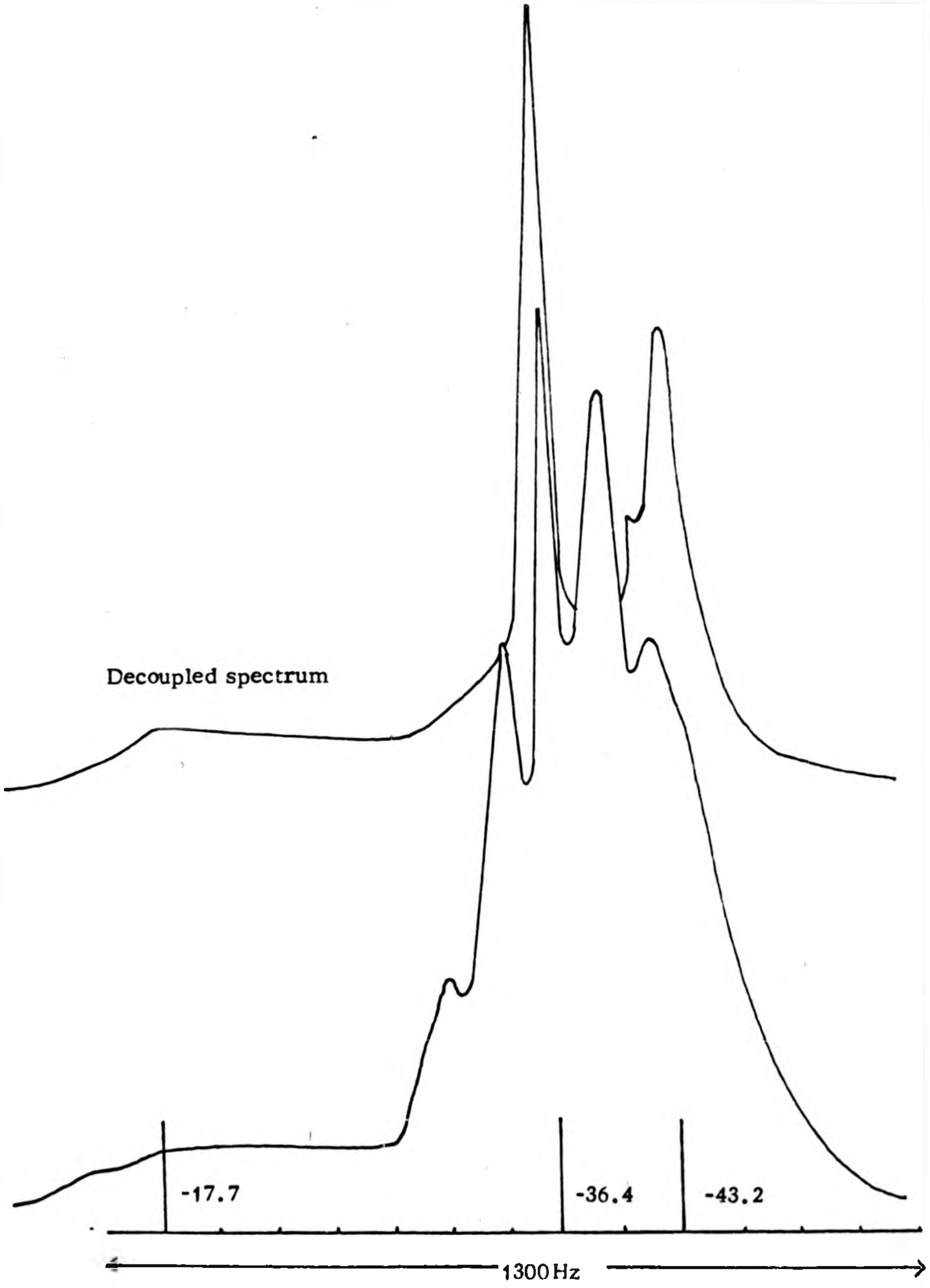


Fig. 4.7d ^{11}B n.m.r. spectrum of $(BH_4)_2AlB_3H_8$ at -50° C



The ^{11}B spectrum of the pure liquid was taken, and this was also subjected to a variable temperature study. At +10° the spectrum shows a sharp quintet superimposed on another broader signal. On proton decoupling these are separated as a 3:2 ratio with the broad signal centred at-34.4 ppm, ratio 3 and the quintet centred at-37.0 ppm, ratio 2. These shifts are in good agreement with the formulation of the compound as $(BH_4)_2AlB_3H_8$, and the chemical shifts are similar to those observed in $Me_2AlB_3H_8$ for the B_3H_8 resonance and in aluminium hydroborate for the BH_4 resonance. The shifts of the hydroborate borons are slightly increased and this is usually correlated with them taking an increased amount of electron density.

At this temperature there is obviously fluxional behaviour with the three boron atoms of the B_3H_8 group becoming equivalent. Equally there is complete coupling of the protons to the boron in the hydroborate groups.

On cooling the sample, the quintet due to the hydroborate groups broadens slightly and also moves slightly downfield, the signal being centred at δ =-36.4 ppm. The signal from the B_3H_8 borons gradually broadens until at -50° C two distinct separate signals may be observed for the two different boron environments. There was a broad low field signal centred at-17.7 ppm which sharpened somewhat on applying proton decoupling, and a less broad high field signal at-43.2 ppm. This was obscured under the hydroborate quintet until proton decoupling was applied.

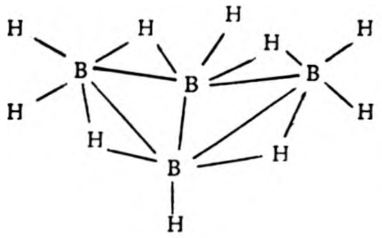
These values are in the same sort of shift region as was observed for dimethyl aluminium octahydrotriborate, but the slight difference must reflect the different bonding and properties of the B_3H_8 entity in the two compounds. The shift value obtained for the borons at +10° C is in good agreement with an average of the shift values for the individual environments. $(2 \times 43.2 + 17.7 \div 3 = -34.7)$. All these values are, in fact, higher field values than were observed for dimethyl aluminium octahydrotriborate. As stated above, this is usually correlated with an increase in electron density at the boron centre which combined with the observation on the hydroborate groups seems to indicate an electron deficient aluminium. The vapour pressure and viscosity then may be high due to possible association in an attempt to lessen the electron deficiency at the aluminium atom. The aluminium atom should be very susceptible to attack by Lewis bases. This is, of course, in contrast to dimethyl aluminium octahydrotriborate.

Thus the situation is

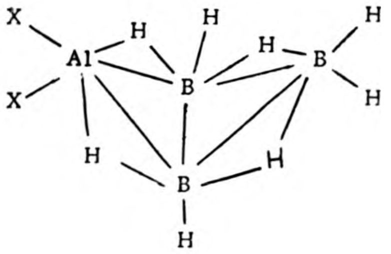
$(BH_4)_2AlB_3H_8$ $\longrightarrow$	$Me_2AlB_3H_8$
Electron density on boron.	Less electron density on boron.
Electron deficient aluminium.	Possible electron deficient boron.
Possible association.	No association.

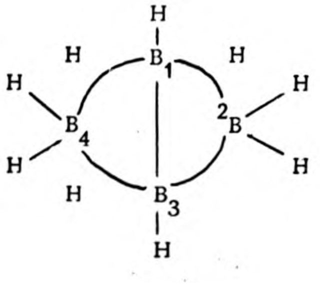
The spectra of aluminium octahydrotriborate bis hydroborate again show no coupling of boron to its attached hydrogens within the B_3H_8 group.

It is interesting at this point to draw a brief comparison with the known chemistry of tetraborane (10). Both dimethyl aluminium octahydrotriborate and aluminium octahydrotriborate bis hydroborate can be regarded as derivatives of tetraborane with boron 4 replaced by the aluminium grouping, as the diagrams show.



and





Tetraborane is volatile but has a tendency to decomposition. The reaction of tetraborane with ether involves attack at the electron poor B_4-H_μ bridge, and this leads to formation of the triborane 7 adduct.

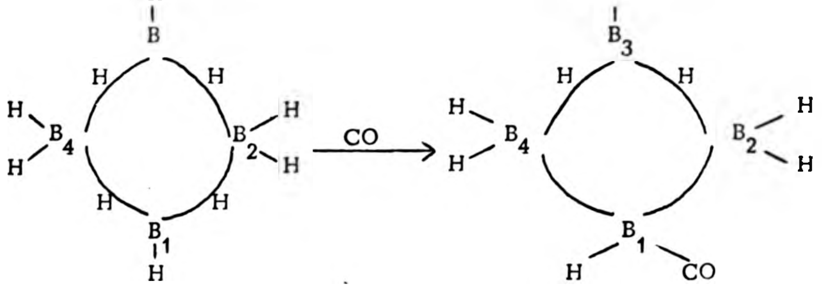
$$B_4H_{10} + 2Et_2O \longrightarrow B_3H_7Et_2O + BH_3.Et_2O$$

$$H_3B.B_3H_7 + 2Et_2O \longrightarrow B_3H_7Et_2O + BH_3Et_2O$$

A similar reaction occurs with trimethylamine.

The reaction observed for dimethyl octahydrotriborate with Lewis bases is thus likely to be initiated by a similar step. In aluminium octahydrotriborate bis hydroborate, the strengthening of the Al-H_μ-B bridge may prevent this.

Tetraborane is known to react with carbon monoxide to form carbon monoxide tetraborane 8 where the carbon monoxide attaches to the 1 position and the four boron atoms are retained.



This may prove to be a possible and interesting adduct for the aluminium compounds.

As mentioned above, the purpose of this section of the work is to prepare compounds of aluminium with higher borane anions as they had been postulated as intermediates in aluminium hydroborate decomposition. To the author's knowledge, this is the first such compound of which numerical details are available. A patent by Hough claims the synthesis of these compounds, but only details of preparation are available.

There has always been speculation on the decomposition of aluminium hydroborate, especially with regard to the so-called stabilisation of the decomposition observed by the early work of Schlesinger. Preliminary experiments performed in connection with the Department of Molecular Sciences disagree with this finding, and do not regard the decrease in rate to be as large as that reported by Schlesinger.

The search for a species which stabilises aluminium hydroborate may therefore be fruitless. Nevertheless it would seem that if such a species exists, then it is not aluminium octahydro triborate bis hydroborate as this is even more unstable than the parent aluminium hydroborate. Spectral analysis of some partially decomposed aluminium hydroborate failed to detect any of the higher hydroborate compound. Unless it is stabilised when dissolved in excess aluminium hydroborate and decomposed if this is removed (as some necessarily was to avoid swamping the spectrum), then it would seem not to be present. The spectral features observed in this experiment have yet to be identified, but the only signal visible, other than a hydroborate quintet, was a structured hump, possible a triplet, at-53 ppm.

This work therefore, not surprisingly, failed to positively identify aluminium species containing higher borane fragments in the complex mixture arising from decomposing aluminium hydroborate, but did show that such compounds could be prepared by exchange reactions.

Further exchange reactions

In his discussion of the spectral properties of aluminium hydroborate adducts and their possible chemical exchange, Oddy proposed the order of exchange

Two uncomplexed species > One complexed + one adduct > Two adducts

It was proposed to try and make use of these possible exchanges and in particular as a novel method of preparing hydrido aluminium hydroborate species, e.g.

$$2Al(BH_4)_3 + AlH_3.NMe_3 \longrightarrow HAl(BH_4)_2.NMe_3 + 2HAl(BH_4)_2$$

Accordingly, excess aluminium hydroborate was condensed on to alane trimethylamine (prepared from $LiAlH_4$ and $NMe_3.HCl$) and stirred at 0^o C. A redistribution reaction of some sort took place, as there was precipitation of a white solid which showed Al-H bands in its infra-red spectrum, but the only compound which could be conclusively identified was aluminium hydroborate trimethyl amine. Thus although an exchange reaction has occurred, it may only be transfer of trimethyl amine to aluminium hydroborate. If this is the case, then the compounds predicted by the above equation may not even be present in the reaction mixture and, if they were, extraction might be difficult. If transfer of trimethyl amine is the only reaction, then this could be another method of obtaining aluminium hydride. In view of the behaviour of aluminium hydroborate/hydride mixtures observed by Oddy and initially by Schlesinger et al., it is unlikely to be a method for preparation of pure aluminium hydride, also bearing in mind that the purification technique is likely to involve subliming out a not entirely stable impurity.

In spite of exchange of two adduct species being at the lower end of the proposed exchange rate sequence, it was found that exchange occurred quite readily between etherates of aluminium hydroborate and trimethyl alane. If these two compounds were mixed in the stoichiometric ratios required to produce methyl or dimethyl aluminium hydroborate, then the methyl and ether resonances of the trimethyl alane etherate was shifted to the value expected for the alkyl aluminium hydroborate etherates. Subsequent additions of aluminium hydroborate or trimethyl alane etherates would cause the signals to move in the appropriate directions.

CHAPTER 5

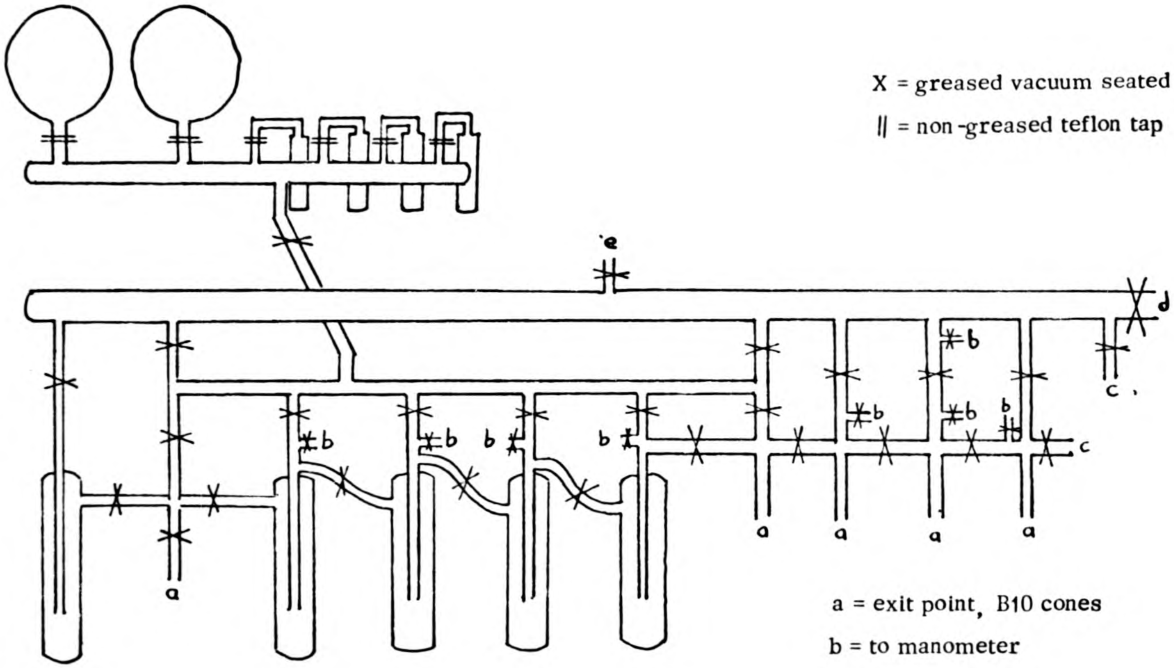
Experimental Details

> "It reacts readily with air, ... it inflames spontaneously, giving a blue white flash of unusual brilliance"
>
> H.I. Schlesinger

General techniques

Aluminium hydroborate, as first reported above, and its derivatives are extremely sensitive to oxidation and hydrolysis in the air. Consequently volatile compounds were manipulated in a conventional high vacuum line which was evacuated using either an Edwards ED 100 rotary oil pump or the rotary pump in conjunction with a mercury diffusion pump, this system being capable of maintaining a pressure of *ca.* 10^{-4} mm Hg. Pressure was measured with a Genevac Penning gauge. The line was fitted with ground glass vacuum seated stopcocks lubricated with "Apiezon N" grease. Manipulations of the less volatile compounds were performed in a glove box filled with nitrogen. The nitrogen, from the boil off of a nitrogen liquefaction plant, was maintained oxygen free by passing through a column containing BASF R3-11 catalyst and moisture free by passing through columns of silica gel. In addition dishes of phosphorus pentoxide inside the glove box absorbed moisture and occasionally solvent vapours.

All apparatus was dried prior to use by heating to 100° C. Solvents were dried and deoxygenated before use by treating them with lithium hydroaluminate or metallic sodium and distilling them in an atmosphere of nitrogen. They were stored in evacuated bulbs fitted with Young's greaseless stopcocks which were directly attached to the vacuum line. The waste materials collected in the line's 'muck' traps were treated with diethyl ether before being removed for subsequent cautious hydrolysis with isopropanol. Other hydroborate residues were treated first with ether and then, after lengthy standing, cautiously treated with isopropanol. Lithium hydroaluminate residues were destroyed by treatment with ethyl acetate diluted with hydrocarbon. A residue possibly containing diborane was treated with trimethyl amine before adopting the above procedures.



X = greased vacuum seated tap

|| = non-greased teflon tap

a = exit point, B10 cones

b = to manometer

c = to Töepler pump

d = to main and diffusion pumps

e = to vacuum gauge

Fig. 5.1 Vacuum line

Analytical techniques

Samples are hydrolysed to determine the quantity of gas, non-condensible at -196° C, followed by a metal analysis to determine the quantity of aluminium.

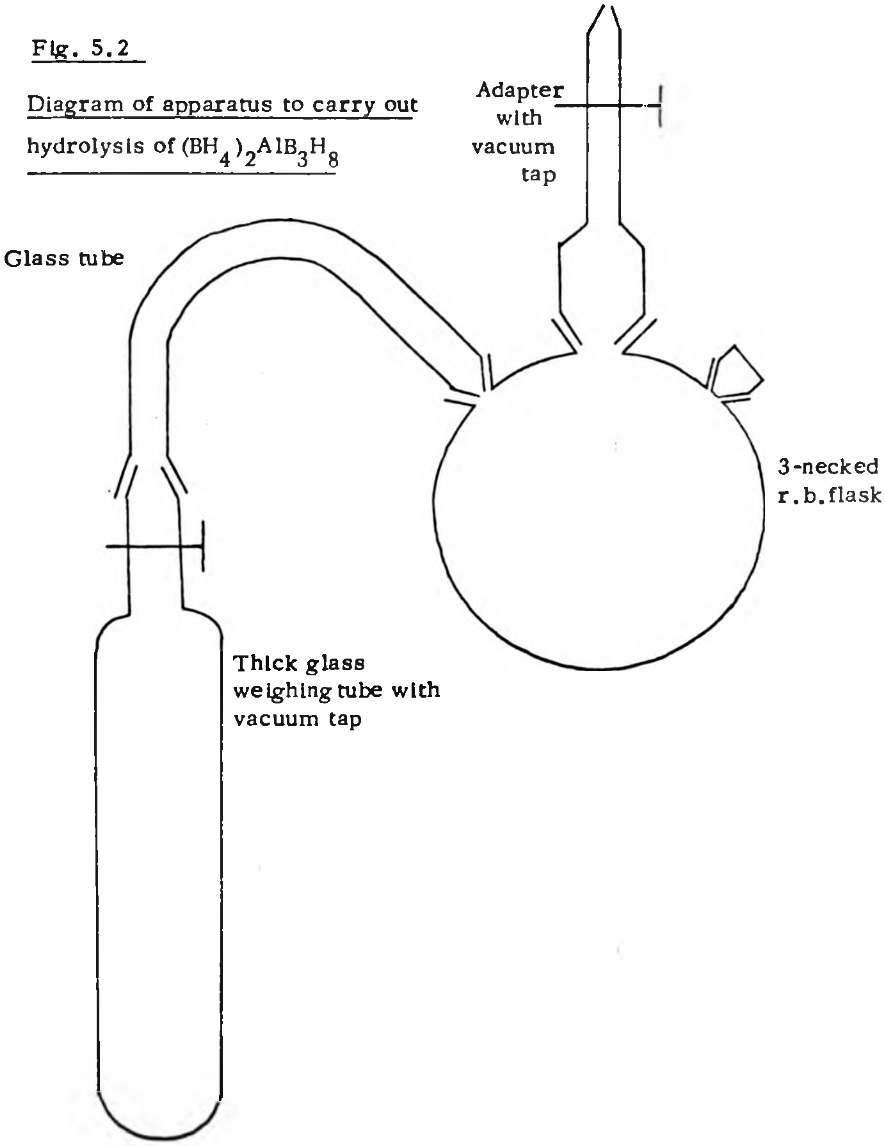
For most samples the hydrolysis was accomplished by weighing the sample in a small vial, transferring this to the bottom of a 500 cm^3 flask fitted with a tap adapter to the vacuum line and evacuating. About 15 cm^3 of degassed (by several thaw, freeze, pump cycles) dilute hydrochloric acid was condensed on to the sample at -196° C and the contents allowed to warm. Melting of the acid produced a vigorous reaction but the flask was left at room temperature for about 24 hours before cooling to -196° C and passing the non-condensible gases through a trap at -196° C and measuring with a Toepler pump. For most volatile samples the weighed amount was simply distilled on to the previously degassed acid.

The system for hydrogen analysis of aluminiumoctahydrotriborate bis hydroborate was slightly different. A three necked flask was used. The flask was charged with dilute acid and fitted with an adapter to the vacuum line and a stopper for two of the necks. In the third was a bent tube on the bottom of which was a ground glass cone to which a weighing tube sealed with a tap could be attached. The flask was then evacuated, the acid degassed and the flask isolated from the vacuum line. The acid was then distilled on to the sample in the weighing tube. This method eliminated losses of the compound by interaction with grease and decomposition on distillation after weighing.

The analysis for aluminium was carried out on the products of the hydrolysis reactions described above, the method being valid for aluminium concentrations up to 100 mg of aluminium in 100 cm^3 of water. The pH of the solution was adjusted to between two and three by adding sodium hydroxide pellets, and a known amount of 0.1 M EDTA (Fisons' volumetric solution) was added. This amount had to represent an excess. The resulting solution was boiled for 15 minutes to fully complex the EDTA and then cooled, and its pH adjusted to pH 6.5 with Analar sodium acetate (Fisons) before adding the indicator. The indicator used was

Fig. 5.2

Diagram of apparatus to carry out hydrolysis of $(BH_4)_2AlB_3H_8$



Xylenol orange; one microspatula full of a mixture obtained by grinding together 0.1 g of Xylenol orange with 10g of potassium nitrate. The indicator turned the solution yellow and this was titrated with previously standardised zinc sulphate (B.D.H., ca. 0.1 molar) to a distinctive red end point. The titration figure allowed the amount of the excess EDTA in the original solution and hence the aluminium content to be calculated.

Spectroscopic techniques

Infra red spectra were recorded on a Perkin Elmer 457 grating spectrometer or occasionally a PE 621 over the range 4000-250 cm^{-1} using either KBr plates or an 8 cm gas cell with KBr windows, depending on the nature of the sample to be investigated. Mulls were made with sodium dried, nitrogen purged Nujol in the glove box.

N.m.r. spectra were obtained on either of two machines. Routine proton spectra were run on a Perkin Elmer R12 and other proton, boron, aluminium and carbon spectra were run on the department's Bruker WH90 F.T.n.m.r. The samples were either sealed off under vacuum for the more reactive compounds, or made up under nitrogen for the less reactive compounds, the tight fitting plastic caps being found adequate protection against the air for the short time required.

Preparation of Precursors

Aluminium hydroborate

$$(AlCl_3)_2 + 6LiBH_4 \longrightarrow 2Al(BH_4)_3 + 6LiCl$$

This method is adapted from the methods of Schlesinger et al.(43).In the glovebox, finely ground, resublimed aluminium chloride (11 g, 83 mmol) was placed in the side arm of a 250 cm^3 flask. In the bottom of the flask was placed finely ground lithium hydroborate (5.3g, 240 mmol) and a magnetic follower. The flask was attached to the vacuum line with the usual stopcock adapter and the flask evacuated. The flask was opened to traps at -80° and -196° C and after mixing and stirring the reactants with the magnet, pumping through the traps was continued for approximately four hours. The flask was then heated with an oil bath up to 100° C for two hours, when the reaction was essentially complete. The flask was then removed from the vacuum line and treated for disposal as previously mentioned in the glove box.

The volatile components were purified in the following manner. The -80° C trap was allowed to warm up since this contained mainly chloro aluminium hydroborates which disproportionated into aluminium hydroborate and aluminium chloride on warming. The aluminium hydroborate was allowed to pass into the -196° trap, the residue of the -80° trap then being discarded. The contents of the -196 trap were then fractionated through traps at -80° and -120° C to collect aluminium hydroborate but not diborane, and -196° C trapping diborane. All but the contents of the -120° trap were then destroyed and the contents of the -120° trap redistilled until the vapour pressure of the product was 119 mm Hg at 0° C.

Trialkyl boranes

The method adopted was chosen simply because of the ease of the availability of starting materials and not because of any chemical advantage of preparation, say from Grignard.

Trimethyl borane

$$(AlMe_3)_2 + 2B(OMe)_3 \longrightarrow 2Al(OMe)_3 + 2BMe_3$$

$B(OMe)_3$, 4.8 g, was allowed to drip slowly from a pressure equalised dropping funnel on to $(AlMe_3)_2$, 3.3 g, cooled by a bath at -30° under a partial nitrogen pressure of ca. 100mm Hg. The reaction flask was opened to traps at -90° and -196° C which partially purified the reaction products as the initially vigorous reaction proceeded. The -30° C bath could be removed as the reaction moderated. The contents of the -90° C trap, intermediate methoxy alkyl boranes, were periodically returned to the reaction flask. On completion of the reaction, the contents of the -196° C trap, mainly trimethyl borane, were distilled through a trap at -120° C collecting at -196° C. The trimethyl borane was identified by its infra-red spectrum.

Triethyl borane

$$(AlEt_3)_2 + 2B(OEt)_3 \longrightarrow 2BEt_3 + 2Al(OEt)_3$$

$B(OEt)_3$, 8.5 g, was allowed to drip slowly from a pressure equalising dropping funnel on to $(AlEt_3)_2$, 8.3 g, under nitrogen. The reaction was exothermic and when the flask had cooled the funnel was replaced quickly by a stopper and the mixture warmed. The product was collected by passing it through a short Vigreux column and condensing with a water cooled condenser. On transfer to the vacuum line the product was found to have a vapour pressure of 10.5 mm Hg at 0° C and was used after one distillation at -30° C.

The preparation of trimethyl borane produced alumium methoxide as the other product which was used in the exchange reaction with aluminium hydroborate described in Chapter 2.

Octahydrotriborate Species

$NaB_3H_8(C_4H_8O_2)_3$

The octahydrotriborate species was prepared as sodium octahydrotriborate dioxanate following closely the procedure in Inorganic Syntheses, Volume XV.

Sodium hydroborate (10 g) was dissolved in 500 cm^3 of previously dried bis-(2-methoxyethyl)ether, known as diglyme, at ca. 40° C. The drying had been accomplished by refluxing for 4 hours with metallic sodium and distilling at atmospheric pressure (b.p. 158-162° C), followed by treatment with lithiumhydroaluminate and distilling under reduced pressure. The diglyme solution was in a 1000 cm^3 3-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a pressure-equalised dropping funnel which dipped below the level of the solution, containing distilled trifluoroborane diethyl etherate, 16 cm^3, dissolved in 50 cm^3 of diglyme. The effluent gases were bubbled through a wash bottle containing acetone to destroy any diborane or higher boron hydrides. The nitrogen inlet was clamped and the solution in the dropping funnel was added dropwise over a period of approximately 30 minutes. The solution was then heated to 100° C for approximately 2 hours. The reactions taking place were:-

$$7NaBH_4 + 4BF_3.(OEt_2) \xrightarrow{\text{room temp.}} 3NaBF_4 + 4NaB_2H_7 + (Et_2O)$$

$$4NaB_2H_7 \xrightarrow{100^{\circ}\text{ C}} 2NaB_3H_8 + 2NaBH_4 + 2H_2$$

$$5NaBH_4 + 4BF_3.(OEt_2) \longrightarrow 3NaBF_4 + 2NaB_3H_8 + 2H_2 + (Et_2O)$$

The reaction mixture was then allowed to cool to room temperature, the nitrogen flow being allowed to pass through the system to prevent sucking back of the acetone scrubbing solution. The mixture was filtered at the pump to remove the sodium tetrafluoroborate and the diglyme was then removed at ca. 60° C under vacuum (ca. 6-8 hours). The sodium octahydrotriborate was separated from the crude product by shaking with 150 cm^3 portions of sodium dried ether filtering, and the dioxanate adduct was precipitated by adding excess sodium dried dioxan to the ether solution. The extraction was stopped when no further precipitate appeared, and the product was filtered at the pump and dried in vacuo. The yield was variable, 6-11 g, dependent on several things, particularly dryness of the diglyme and dioxan.

$NMe_4B_3H_8$

Tetramethyl ammonium octahydrotriborate was prepared by adding, in a typical case, 3 g of the dioxanate to 1.4 g of tetramethyl ammonium bromide in 10 cm^3 of water, slowly and with stirring. On completion of the addition, a further 10 cm^3 of water were added, and the mixture cooled in an ice bath for several minutes. The precipitated product was filtered at the pump and dried in vacuo, and used without further purification. Yield: ca. 60%.

$Me_2AlB_3H_8$

The method used was similar to that published in the note by Gaines.

$$(Me_2AlCl)_2 + 2NMe_4B_3H_8 \longrightarrow 2Me_2AlB_3H_8 + 2NMe_4Cl$$

Excess tetramethyl ammonium octahydrotriborate, 1.63 g, was placed in the side arm of a 100 cm^3 round bottomed, two necked flask. The flask was evacuated on the vacuum line and chlorodimethyl alane, 1.3 g, was condensed into the flask. The flask was isolated and the solid added slowly from the side arm to the stirred chlorodimethyl alane. The reaction mixture became more and more viscous as the addition proceeded over a period of about 15 minutes. Stirring was continued for a further 5 minutes and all volatile materials were then condensed into a -196° C trap and the dimethyl aluminium octahydrotriborate was easily purified in vacuo by distilling at -45° C through a trap at -78° C where it condensed. It was identified by its infra-red spectrum and vapour pressure measurements which, contrary to the report of Gaines, were found very useful. The compound was analysed for CH_3, active hydrogen and aluminium. Analysis figures were not reported by Gaines.

Found: CH_3, H, 39.9%. Al, 27.2%

Expected for $Me_2AlB_3H_8$: CH_3, H, 39.1% Al, 27.7%

Other Precursors

Alanetrimethyl amine

This was prepared by using the following reaction:-

$$LiAlH_4 + Me_3N.HCl \longrightarrow H_3Al.NMe_3 + LiCl + H_2$$

Trimethyl amine hydrochloride was placed in the side arm of a three-necked 100 cm^3 round bottomed flask, the flask containing lithium hydroaluminate, 2.2g and 30 cm^3 of sodium-dried diethyl ether. The flask was equipped with a nitrogen supply and a water cooled condenser, and exhausted through a wash bottle of paraffin oil. The trimethylamine was added slowly to the stirred ether, and after complete addition the mixture was stirred for a further 15 minutes. The ether was then removed under vacuum and the alane trimethylamine was extracted from the crude product by sublimation in vacuo (ca. 40°, 10^{-3} mm Hg).

Dimethyl aluminium hydroborate

Dimethyl aluminium hydroborate was prepared by the method described by Oddy:-

$$(AlMe_3)_2 + Al(BH_4)_3 \longrightarrow 3Me_2AlBH_4$$

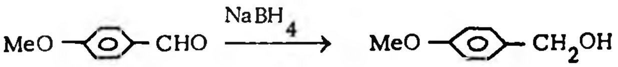
Slight excess of trimethyl alane (0.65 g) and aluminium hydroborate (0.3g) were stirred for 30 minutes at 0° C in a small flask on the vacuum line. The mixture was then passed through traps at -50° C, -75° C and -196° C. The contents of the -75° C trap were redistilled and found to be reasonably pure dimethyl aluminium hydroborate as shown by the infra-red spectrum.

Tetra ethyl diborane

$$4BEt_3 + B_2H_6 \longrightarrow 3Et_4B_2H_2$$

Triethyl borane (0.55 g, 5.6 mmol) was condensed with diborane (1.4 mmol measured by volume) into a 100 ml round bottomed flask and, left open to a manometer, was allowed to warm to room temperature. The extent of the reaction could be judged by the drop in vapour pressure of the mixture. When the vapour pressure at 0° C had dropped to below 10 mm Hg (several hours), the mixture was pumped at -20° C to remove less alkylated diboranes and the remaining tetraethyl diborane was identified by its infra red spectrum.

4-Methoxybenzyl alcohol (Anisyl alcohol)



5 g of the aldehyde in water were treated with sodium hydroborate in water (1.5g). The reaction was left overnight. More water was added, and the solution was extracted with ether. The ether was dried with anhydrous magnesium sulphate and then removed under reduced pressure. A crystalline solid was obtained which melted just above room temperature (Lit. m.p. 24-5° C). Absence of a carbonyl band in the infra-red spectrum indicated the compound to be of sufficient purity.

Reactions for Chapter 2

Reaction of aluminium hydroborate with methanol

Aluminium hydroborate (0.48 g, 6.71 mmol) was dissolved in ca. 5 cm^3 of pentane. Methanol (0.034 g, 1.10 mmol) was condensed on at -196° C and the mixture allowed to warm to -95° C (m.p. MeOH -97.7° C). After 30 minutes the mixture was frozen down to -196° C and the accumulated non-condensible gas measured at the Toepler pump and removed, and a further 2.10 mmol of methanol were condensed on. This was reacted for 1 hour at -78° C before meauring the non-condensible gas as before. A final 1.05 mmol methanol were reacted in a similar manner and the reaction mixture was warmed to room temperature before the final quantity of non-condensible gas was taken. The other volatile components were removed at -20° C, separated at -120° C and the quantity of diborane identified by its infra-red spectrum, was measured in a similar manner to the non-condensible gas. The non-condensible gas was assumed to be hydrogen as no C-H frequency for methane could be seen in the infra-red spectrum of a sample.

$Al(BH_4)_3$	6.71 mmol		
MeOH	4.25 mmol	H_2	4.20 mmol
		B_2H_6	2.09 mmol

Analysis of residual white solid:-

Active H H_2 Found 7.67% Al Found 26.31%

Calculated for $MeOAl(BH_4)_2$ 30.77% Al

9.19% active H_2

<u>Reaction of aluminium hydroborate with aluminium methoxide</u>

$$Al(OMe)_3 + 2Al(BH_4)_3 \longrightarrow 3MeOAl(BH_4)_2$$

Aluminium methoxide (0.65 g) and aluminium hydroborate (1.013 g, 28% excess for the above reaction) were stirred for 1 week at room temperature. After this time the aluminium hydroborate was distilled off and weighed.

Recovered: 0.633g $Al(BH_4)_3$ ∴ 0.38 g reacted ≡ 49%

This reaction was not pursued further.

A further reaction, using 0.39 g of aluminium methoxide and 1.015 g of aluminium hydroborate was observed to be incomplete even after several weeks.

Reaction of aluminium hydroborate with aluminium hydroxide

$$Al(OH)_3 + Al(BH_4)_3 \longrightarrow 3HOAl(BH_4)_2$$

Aluminium hydroxide (0.14g) and aluminium hydroborate (0.67 g) were stirred for several days at room temperature.

Amount $Al(BH_4)_3$ recovered: 0.64 g

Preparation of thiomethyl aluminium bis hydroborate

$$2Al(BH_4)_3 + 2MeSH \longrightarrow 2MeSAl(BH_4)_2 + B_2H_6 + 2H_2$$

Aluminium hydroborate (0.93g, 13 mmol) was condensed into a 100 cm^3 round bottomed flask and 0.34g,(7.1 mmol)of methane thiol was condensed on in three portions, each portion being stirred with the hydroborate at -50° C, so that both reactants were liquid, before the accumulated hydrogen was removed. When hydrogen evolution from the third portion slowed, the mixture was carefully warmed to room temperature and stirred for 15 minutes to complete the reaction. The hydrogen was measured and removed, and the other volatile materials, excess aluminium hydroborate and diborane, were distilled off, separated at -120° C and weighed and estimated by volume respectively. The product was a white solid.

Theoretical recovery		$Al(BH_4)_3$	0.43 g
Actual recovery		$Al(BH_4)_3$	0.42 g
Analysis:	Found.	Active H	7.62%
		Al	26.1%
Expected for $MeSAl(BH_4)_2$		Active H	7.77%
		Al	26.0%

Preparation of thio ethyl aluminium bis(hydroborate)

$$2Al(BH_4)_3 + 2C_2H_5SH \longrightarrow 2C_2H_5SAl(BH_4)_2 + B_2H_6 + 2H_2$$

Aluminium hydroborate (0.51 g, 7.1 mmol) was condensed at the bottom of a 100 cm^3 round bottom flask and ethane thiol (0.23 g, 3.7 mmol) was condensed at -196° C above the aluminium hydroborate. The flask was warmed to -60° C at which temperature the ethane thiol (m.p. -121° C) ran down on to the just liquid aluminium hydroborate (m.p. -64° C). Hydrogen evolution was observed and when this ceased, after two hours, the reaction flask was warmed to room temperature to ensure full reaction, then frozen to remove hydrogen and then warmed to distil off aluminium hydroborate and diborane as previously described.

The product was a virtually colourless oil.

Analysis: Found Active H 6.68% Al 23.0%

Expected for $C_2H_5SAl(BH_4)_2$: Active H 6.81% Al 22.90%

Preparation of thiobenzyl aluminium bis (hydroborate)

$$2Al(BH_4)_3 + 2C_6H_5CH_2SH \longrightarrow 2C_6H_5CH_2SAl(BH_4)_2 + 2H_2 + B_2H_6$$

0.5 ml, i.e. 0.53g, 4.3 mmol, of toluene - α - thiol was placed at the bottom of a 100 cm^3 round bottom flask in the glove box. Aluminium hydroborate, 0.6 g, 8.4 mmol, was condensed on at -196° C. The liquid nitrogen was removed and replaced by a bath at -60° C. The initial reaction was rapid, but as this slowed the mixture was allowed to warm to room temperature. On removing all the volatile products by pumping, a white solid remained.

Found: Active H 4.48% Al 15.0%

Expected for $C_6H_5CH_2SAl(BH_4)_2$ Active H 4.51% Al 15.0%

Reaction of aluminium hydroborate with 2-methyl propane-2-thiol

Possible reaction:-

$$2Al(BH_4)_3 + 2\,{}^tBuSH \longrightarrow 2\,{}^tBuSAl(BH_4)_2 + 2H_2 + B_2H_6$$

2-methyl propane-2-thiol, (0.353 g, 3.92 mmol), was condensed into a 100 cm^3 round bottom flask, and aluminium hydroborate, (0.488 g, 6.82 mmol), was condensed above it at -196° C. The components were allowed to react at -60° C initially, and the gases liberated were analysed.

Less than the theoretical quantity of hydrogen predicted by the above equation was found, along with some diborane and isobutane (ca. 2 mmol) identified by its vapour pressure and infra-red spectrum, which were compared with an authentic sample. A white solid residue remained.

Analysis: Active H 5.43% Al 37.7%

Expected for $C_4H_9SAl(BH_4)_2$ Active H 5.55% Al 18.5%

Reaction between aluminium hydroborate and tetrahydrothiophene

Aluminium hydroborate (0.52 g, 7.3 mmol) was condensed with a slight excess of tetrahydrothiophene (0.695 g, 7.9 mmol) at -196° C. The components were allowed to warm to room temperature for 15 minutes and then excess volatile material was pumped away. The product was an involatile oil and the similarity of the infra-red spectrum of the oil to that of other 1:1 adducts of aluminium hydroborate with Lewis bases would indicate this being a 1:1 adduct.

I.r. of oil	2470	2420	2130 cm^{-1}
I.r. of $Al(BH_4)_3.SMe_2$	2460	2410	2115 cm^{-1}

Reaction of aluminium hydroborate with cyclohexanol

This was carried out in a similar manner to above, using cyclohexanol (0.45 g dried over $MgSO_4$ and distilled) with excess aluminium hydroborate (0.44 g). Hydrogen and diborane only were observed as the gaseous products. The residue was a white solid.

Analysis	Active H	5.03%	Al	18.2%
Expected for $C_6H_{11}OAl(BH_4)_2$	Active H	5.18%	Al	17.3%

Reaction of aluminium tetrahydroborate with Anisyl alcohol (p-methoxy benzyl alcohol), benzhydrol (diphenyl methanol) and t-butanol (2-methyl propan-2-ol)

These were more quantitative reactions which were carried out in the already described manner on approximately the same scale, using excess aluminium hydroborate in each case.

In the first two cases, shaking the solid residue with deuterated benzene and taking a proton n.m.r. spectrum showed the formation of p-methoxy toluene and diphenyl methane, identified respectively by the position of the toluene methyl and comparison with the spectrum of authentic diphenyl methane. As for the reaction with 2-methyl-propane-2-thiol, the product with t-butanol was identified in the gaseous phase as isobutane.

The yield of these products was estimated to be about 50%.

Preparation of methoxy aluminium bis (hydroborate)

$$(MeO)_3B + 3Al(BH_4)_3 \longrightarrow 3MeOAl(BH_4)_2 + 2B_2H_6$$

Trimethoxyborane (0.2 g, 1.92 mmol measured by volume) and aluminium hydroborate (0.8g, 11.2 mmol) were condensed together at -196° C. The reactants were stirred at room temperature for several hours until the pressure due to diborane formation was observed to cease. Excess aluminium hydroborate and diborane were removed by pumping to leave a white solid residue.

Analysis	Active H	8.96%	Al 30.2%
Expected for $CH_3OAl(BH_4)_2$	H	9.19%	Al 30.8%

Preparation of ethoxy aluminium bis (hydroborate)

Aluminium hydroborate (0.67 g, 9.30 mmol) and triethoxyborane (0.23 g, 1.55 mmol) were condensed together at -196° C. As above, the reactants were stirred at room temperature for 36 hours. Volatile products and excess aluminium hydroborate were then removed by pumping at 0° C and a white solid which had been completely soluble in the excess aluminium hydroborate was obtained.

Analysis	Active H	7.77%	Al	26.1%
Expected for $C_2H_5OAl(BH_4)_2$	Active H	7.93%	Al	26.5%

Molecular weight determination of ethoxy aluminium bis (hydroborate) by a freezing point depression method

The molecular weight was carried out under a blanket of nitrogen, using the apparatus shown. The solvent used was benzene which had been twice refluxed and distilled from lithium hydroaluminate. The apparatus was calibrated using a solution of naphthalene in benzene prior to use. (Fig. 5.3a)

Naphthalene	0.1198 g in 43.95 g (50 cm^3) of benzene
	ΔT 0.110°
$EtOAl(BH_4)_2$	0.02684 g in 21.975 g (25 cm^3) of benzene
	ΔT 0.031°
	Mol. Wt. 206

Fig. 5.3a Beckmann freezing point apparatus

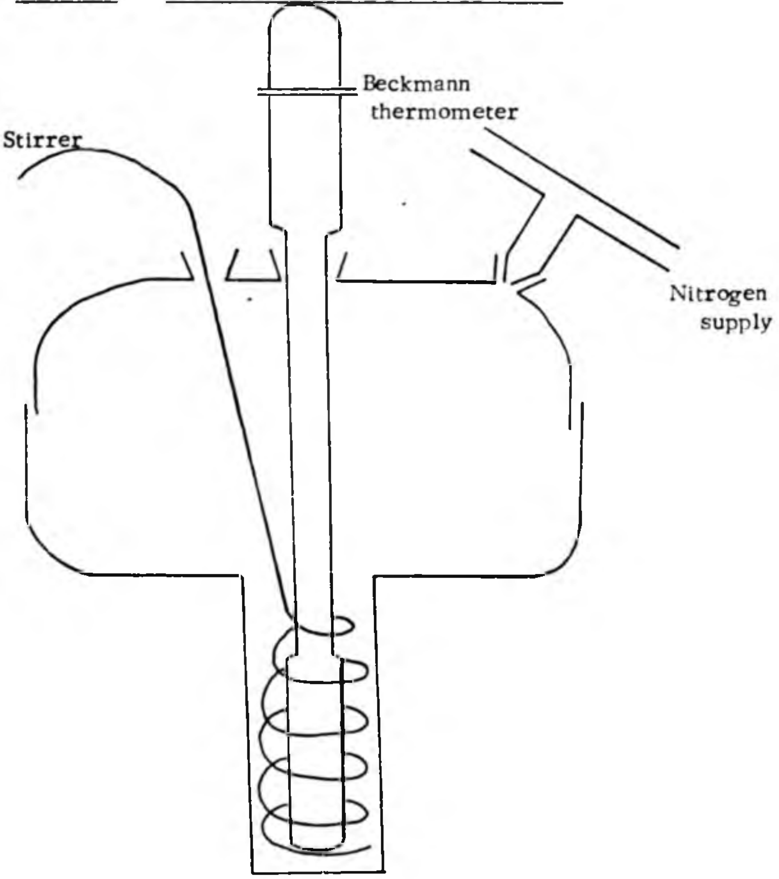
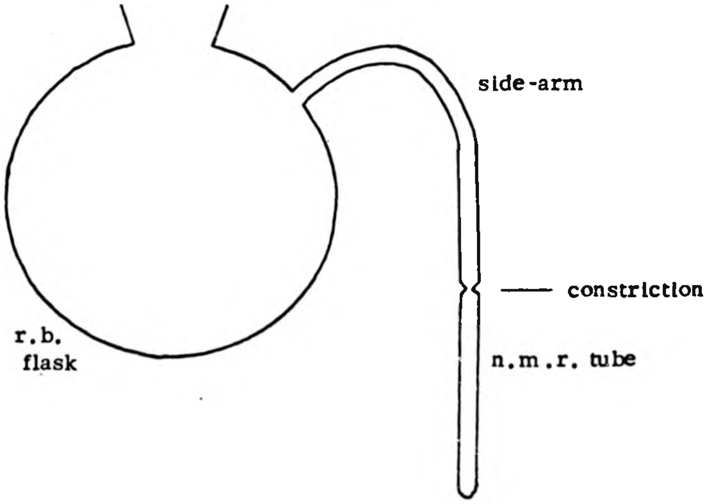


Fig. 5.3b Flask with n.m.r. tube side-arm



Reactions for Chapter 3

General

Most of these reactions were carried out on the vacuum line measuring relative molar amounts by their pressure in a bulb of known volume, i.e. a 2:1 mixture was prepared by mixing the amount of one component that produced a pressure of, say, 100 mm with the amount that produced a pressure of 200 mm of the other component.

A commonly used apparatus in these reactions was a flask with an n.m.r. tube attached to a side arm, such that the mixture could be poured into the tube without the need for distillation which might upset the liquid equilibria. See diagram (Fig. 5.3b)

Reaction of tetraethyl diborane with triethyl alane

Tetraethyl diborane made from the action of triethyl borane, (1.1g, 8.04 mmol), on diborane, (2.6 mmol), was reacted with triethyl alane (0.33 g, 2.9 mmol) at room temperature for four days. The mixture was distilled at 0° C.

The volatile products identified by their gas phase infra-red spectra were primarily triethyl borane (which had not been present when the triethyl alane was added), and traces of ethyl aluminium bis (hydroborate) and diborane.

The non-volatile products identified by the infra-red spectroscopy of the liquid phase showed some excess triethyl alane (bands at 660 cm^{-1} and 620 cm^{-1}) and bands which have been assigned to the compound also giving the peak at-6 ppm in the ^{11}B n.m.r.

Suggested reaction:-

$$3Et_4B_2H_2 + Et_3Al \longrightarrow Al(BH_2Et_2)_3 + 3BEt_3$$

Reactions for Chapter 4

Preparation of aluminium octahydrotriborate bis (hydroborate)

This method is similar to the redistribution reactions that Oddy showed were applicable to the preparation of alkyl aluminium hydroborates.

$$2Al(BH_4)_3 + Me_2AlB_3H_8 \longrightarrow (BH_4)_2AlB_3H_8 + 2MeAl(BH_4)_2$$

Dimethyl aluminium octahydrotriborate, (0.33 g, 3.36 mmol), was condensed with aluminium hydroborate (1.04 g, 14.6 mmol) at -196° C. The components were allowed to warm to 0° C and to stand at 0° C for 30 minutes. A large excess of aluminium hydroborate was used as this would then maximise the chance of the reaction proceeding in the direction of the arrow shown and not reversing or stopping at an intermediate methyl aluminium hydroborate octahydroborate $MeAl(BH_4)(B_3H_8)$ stage. The mixture was then distilled at 0° C through traps at -75° C, -95° C which is low enough to trap methyl aluminium bis (hydroborate) but not aluminium hydroborate and finally -196° C. The contents of the -75° C trap were retreated with fresh aluminium hydroborate (0.67 g) and treated similarly, as above, before a third treatment with a further portion of aluminium hydroborate (0.63 g). After a final distillation the product was found to have a vapour pressure at 0° C of 4 mm Hg.

Analysis	Active H	16.54%	
For $(BH_4)_2AlB_3H_8$		16.60%	Sample equivalent 15.94 Hydrolysable hydrogens

No methane was detected in the collected hydrogen. The aluminium analysis would not be helpful in this case as the difference between the figures for $Me_2AlB_3H_8$, $MeAl(BH_4)(B_3H_8)$ and $(BH_4)_2AlB_3H_8$ would be too close to the experimental error of the method. The aluminium figure was not determined.

Reaction of dimethyl aluminium octahydrotriborate with diborane

Possible reaction:-

$$3Me_2AlB_3H_8 + 4B_2H_6 \longrightarrow 3(BH_4)_2AlB_3H_8 + 2BMe_3$$

Dimethyl aluminium octahydrotriborate (0.184 g, 1.88 mmol) was reacted with the corresponding amount of diborane, according to the equation, for 8 hours at room temperature. The mixture was distilled at -78° C through traps at -130° C and -196° C. 1, 1-dimethyl diborane collected in the -130° C trap (identified by its infra-red spectrum). Fresh diborane was condensed into the material retained at -78° C and reacted for a further period at room temperature. The only products that could be isolated from the mixture were methyl diboranes, diborane and aluminium hydroborate. A small amount of solid residue was not identified.

Reaction of dimethyl aluminium octahydrotriborate with diethyl ether

Dimethyl aluminium octahydrotriborate (0.12 g, 1.2 mmol) was condensed with excess diethyl ether and the mixture allowed to warm to room temperature for 15 minutes. The excess ether was pumped away to leave an oil.

Analysis: Active H/CH_4 3.37%

Expected for $(CH_3)_2AlB_3H_8[O(C_2H_5)_2]$ Active H/CH_4 5.87%

Reaction of dimethyl aluminium octahydrotriborate with trimethyl amine

Dimethyl aluminium octahydrotriborate (0.19 g, 1.94 mmol) was dissolved in 10 cm^3 of pentane. Trimethyl amine (0.10 g, 1.7 mmol) was then condensed on at -196° C. The mixture was allowed to warm to -20° C over a period of 30 minutes with continuous stirring. The mixture was then recooled to -50° C and the volatile components pumped away. There was an oily residue which could not be identified.

Reaction of aluminium hydroborate with alane trimethyl amine

Excess aluminium hydroborate (0.93 g, 13.0 mmol) was condensed on to alane trimethyl amine (0.4 g, 4.49 mmol) and the mixture was stirred at 0° C. A white solid was precipitated which was subjected to an infra-red spectrum, after removal of excess aluminium hydroborate. This was then carefully sublimed whence a white sublimate, identified as aluminium hydroborate trimethyl amine by its infra-red spectrum, was obtained.

Preparation of aluminium hydroborate and trimethyl alane etherates

These were prepared by adding excess diethyl ether to the corresponding aluminium compound, stirring at 0° C for 15 minutes, and then removing the excess ether. The compounds, identified spectroscopically, were used without additional purification.

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