538. *The Reaction of Ammonia–Trimethylboron with Potassium in Liquid Ammonia, and Some Properties of Potassium Aminotrimethylborate.*

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Potassium and trimethylboron in liquid ammonia react to form potassium aminotrimethylborate $K[H_2N{\cdot}BMe_3]$. When heated, this readily loses two mols. of methane, giving a polyanionic salt which yields hydrogen and methane on hydrolysis. Trimethylboron and diborane do not react with the solid aminotrimethylborate; in ether, diborane reacts to give a solid $K[H_2N,B_2H_6]$ which is shown to be an equimolar mixture of potassium borohydride and polymeric aminoborine. It is suggested that this reaction is an example of the unsymmetrical fission of diborane.

Reaction with an alkali metal in liquid ammonia can effect fission of an alkyl group (*e.g.*, from R_4Pb[1]) or of hydrogen (*e.g.*, from ammonia); or reduction may occur, *e.g.*, tetramethyldiborane $(Me_2BH)_2$ forms [2] the anion $[Me_2BH]^{2-}$. Monomeric boron compounds BX_3, however, co-ordinate with solvent molecules to give H_3N,BX_3, and here fission of H or X, or reduction, may occur. Thus with boron trifluoride, McDowell and Keenan [3] found in general that hydrogen and fluoride ions were formed:

$$H_3N,BF_3 + e^- \longrightarrow H_2N{\cdot}BF_2 + F^- + \tfrac{1}{2}H_2$$

Kraus and Smith found only hydrogen from trimethylboron,[4] *i.e.*,

$$H_3N,BMe_3 + e^- \longrightarrow [H_2N{\cdot}BMe_3]^- + \tfrac{1}{2}H_2$$

We have confirmed this observation quantitatively, using potassium, which gives potassium aminotrimethylborate in liquid ammonia solution; slight decomposition of this produces a trace of methane (see below). Potassium amide is also produced, but extraction with ether after removal of ammonia separates the aminotrimethylborate from the insoluble amide. Some properties of this white solid salt, $K[H_2N{\cdot}BMe_3]$, will now be described.

Thermal Decomposition and Hydrolysis.—Heating at 140° for several hours caused the loss of two mols. of methane; more prolonged heating produced only a little more methane. There was a slow loss of methane at room temperature, and the appearance of a trace in the preparation has been noted. Ammonia–trimethylboron loses methane on heating,[5] and the loss from the aminotrimethylborate probably occurs similarly:

$$\begin{aligned} H_3N,BMe_3 &\longrightarrow H_2N{\cdot}BMe_2 + MeH \\ [H_2N{\cdot}BMe_3]^- &\longrightarrow [HN{:}BMe_2]^- + MeH \\ [HN{:}BMe_2]^- &\longrightarrow [NBCH_3]^- + MeH \end{aligned}$$

Aminodimethylborine, $H_2N{\cdot}BMe_2$, is known to be polymeric when prepared in this way, and the change in appearance of the potassium aminotrimethylborate on heating from a crystalline to a sticky amorphous solid suggests the formation of polyanions. Further evidence relating to the anion given above as $[NBCH_3]^-$ is considered below; here, it may be noted that in the series BMe_3, $H_3N{\cdot}BMe_3$, $[H_2N{\cdot}BMe_3]^-$ the thermal stability decreases steadily; trimethylboron does not decompose appreciably below 400° and ammonia–trimethylboron loses only one molecule of methane at 220°. This change may be due to weakening of the B–C bonds by the increasing electron density on the boron atom, by co-ordination in $H_3N{\cdot}BMe_3$, and also by presence of the negative charge in $[H_2N{\cdot}BMe_3]^-$.

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[1] Holliday and Pass, *J.*, 1958, **3485**.
[2] Campbell, *J. Amer. Chem. Soc.*, 1957, **79**, 4023.
[3] McDowell and Keenan, *J. Amer. Chem. Soc.*, 1956, **78**, 2065.
[4] Kraus and Smith, *J. Amer. Chem. Soc.*, 1951, **73**, 2751.
[5] Wiberg, *Naturwiss.*, 1948, **35**, 185.

Acid-hydrolysis of potassium aminotrimethylborate at room temperature was quantitative in accordance with the reaction

$$[H_2N{\cdot}BMe_3]^- + 2HCl \longrightarrow NH_4^+ + 2Cl^- + BMe_3$$

and confirmed the formula. Aqueous hydrolysis of the pyrolysis product $K[NBCH_3]$ was vigorous at ordinary temperature and produced ammonia, hydrogen, methane, a trace of carbon monoxide, and boric acid; only the last was recovered quantitatively and some residual carbon remained. These results are certainly not typical for the hydrolysis of compounds containing alkyl–boron bonds, where hydrolysis is usually difficult and produces alkylboric acids and not boric acid. They suggest the formation of B–H bonds in the pyrolysis product, which might therefore be tentatively formulated as $K_n[({\cdot}N{:}BH{\cdot}CH_2{\cdot})_n]$.

Reactions with Acceptor Molecules.—There are several well-established examples of the formation of a bond to boron by a nitrogen atom already bound to boron, *e.g.*, the compound $Me_2N{\cdot}B_2H_5$ has been shown to contain the $B–NMe_2–B$ bridge; [6,7] B–N–B linkages also occur in borazole and polymeric $R_2N{\cdot}BR_2$ molecules, but not in the " diammoniate of diborane," which has the structure $[BH_2(NH_3)_2]BH_4$ and not $NH_4[H_3B{\cdot}NH_2{\cdot}BH_3]$.[8] There seems no reason why a nitrogen atom in an anion of type $[H_2N{\cdot}BR_3]^-$ should not co-ordinate to a second boron atom, and the absence of any boron–nitrogen double bonding in this anion might well enhance the donor character of the nitrogen. The reactions of potassium aminotrimethylborate with trimethylboron, boron trifluoride, and diborane have therefore been studied.

With trimethylboron (the weakest acceptor) there was no reaction in absence or presence of ether as solvent. Boron trifluoride reacted in absence of solvent, but non-integral reaction ratios precluded a clear interpretation; better results have been obtained by using the dimethylaminotrimethylborate $K[Me_2N{\cdot}BMe_3]$ and these will be reported later. Diborane did not react with solid potassium aminotrimethylborate but reacted slowly with an ethereal solution at —78° giving a white precipitate. Analysis of the latter gave a K : B ratio of 1 : 2, indicating uptake of a BH_3 group. A complete separation of the volatile products from unchanged diborane and ether was impracticable; the infrared spectrum of the partially separated products suggested the presence of methylated diboranes. The mixture of products, diborane, and ether was therefore treated with trimethylamine and the mixture of adducts so obtained hydrolysed to determine [9] the overall composition $B_2H_{6-x}Me_x$. The results indicated almost complete replacement of the methyl groups of the anion by hydrogen, *i.e.*, the reaction with diborane involved both addition and replacement:

$$2[H_2N{\cdot}BMe_3]^- + 3B_2H_6 \longrightarrow 2[H_2N,B_2H_6]^- + 2B_2H_3Me_3$$

the mixed methylated diboranes being represented by the mean composition $B_2H_3Me_3$. Acid-hydrolysis of the white solid product gave hydrogen in amount slightly less than expected from complete hydrolysis of $K[H_2N,B_2H_6]$ and a little methane; the titratable boron in the hydrolysate was also low. These facts suggest incomplete replacement of methyl groups by hydrogen, and consequent incomplete hydrolysis, since any $B–CH_3$ groups remaining would tend to resist hydrolysis and give only a little methane, the unhydrolysed part appearing as non-titratable methylboric acids. In many experiments, using repeated or prolonged treatment with diborane, complete replacement of methyl groups was rarely effected.

Although acid-hydrolysis of the product $K[H_2N,B_2H_6]$ was fairly rapid, alkaline hydrolysis was slow and incomplete. The solid salt slowly evolved hydrogen at 150°, but

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[6] Schlesinger, Ritter, and Burg, *J. Amer. Chem. Soc.*, 1938, **60**, 2297; Burg and Good, *J. Inorg. Nuclear Chem.*, 1956, **2**, 237.

[7] Hedberg and Stosick, *J. Amer. Chem. Soc.*, 1952, **74**, 954.

[8] Schultz and Parry, *J. Amer. Chem. Soc.*, 1958, **80**, 4.

[9] Holliday and Jeffers, *J. Inorg. Nuclear Chem.*, 1958, **6**, 134.

no diborane or borazole. Trimethylamine reacted very slowly and incompletely. These facts do not support a formula $K[H_3B{\cdot}NH_2{\cdot}BH_3]$ for the salt, from which diborane or borazole would be expected as pyrolysis products, from which trimethylamine might readily remove a borane group as $Me_3N{\cdot}BH_3$, and which would be hydrolysed readily in acid or alkaline solution. The rapid acid and slow alkaline hydrolysis observed are however characteristic of an alkali-metal borohydride; this would not react readily with trimethylamine and would not decompose easily when heated. If the apparent $K[H_2N,B_2H_6]$ does contain the borohydride KBH_4, then the other constituent is probably polymerised aminoborine, $H_2N{\cdot}BH_2$, and this also would not react with trimethylamine and would slowly yield hydrogen on being heated. The difficulty of completely replacing the methyl groups could then be explained if these were present in the polymeric aminoborine; their presence in the borohydride anion is much less probable.

Potassium borohydride is soluble in liquid ammonia without reaction; aminoborine is slowly ammonolysed:[10]

$$H_2N{\cdot}BH_2 + xNH_3 \longrightarrow (H_2N)_{1-x}BH_{2-x} + xH_2$$

The solid $K[H_2N,B_2H_6]$ in liquid ammonia only evolved hydrogen very slowly even above 33°, but addition of ammonium chloride produced rapid evolution at low temperature. After warming to destroy the ammonium borohydride also formed (see below) and to remove solvent ammonia, addition of more ammonia produced more hydrogen containing a trace of methane, and an equivalent amount of ammonia was taken up. This suggests that ammonolysis of the aminoborane was occurring, presumably catalysed by the ammonium ions present. In another experiment, ammonia and ammonium chloride were added and the ammonia was immediately removed at low temperature to minimise ammonolysis of the aminoborine. The solid then remaining was assumed to contain the latter and an equal amount of ammonium borohydride formed by the metathetic reaction

$$NH_4Cl + KBH_4 \longrightarrow NH_4BH_4 + KCl$$

At room temperature, the solid gradually lost hydrogen in an amount required by the reaction $NH_4BH_4 \longrightarrow H_3N,BH_3 + H_2$ which should occur at room temperature.[11] At 90° rather less hydrogen was produced than required by the reaction

$$H_3N,BH_3 \longrightarrow H_2N{\cdot}BH_2 + H_2$$

but the temperature at which this reaction is complete is ill-defined.[12,13] Finally, heating at 200° produced more hydrogen than required by the reaction [13]

$$2H_2N{\cdot}BH_2 \longrightarrow 2HN{:}BH + 2H_2$$

(two mols. of aminoborine, one originally present and one formed as just described). The overall loss of hydrogen was that expected for the decomposition of an equimolar mixture of aminoborine and ammonium borohydride to give the iminoborine $HN{:}BH$; the only other volatile product was a trace of substance tentatively identified as borazole, again a product to be expected here.[13] These considerations support the other evidence that " $K[H_2N,B_2H_6]$ " is a mixture of KBH_4 and $H_2N{\cdot}BH_2$ polymer.

The reactions by which this mixture was produced must now be considered. A scheme such as

$$[H_2N{\cdot}BMe_3]^- \longrightarrow [H_3B{\cdot}NH_2{\cdot}BMe_3]^- \longrightarrow [H_3B{\cdot}NH_2{\cdot}BH_3]^-$$

does not explain the need for a solvent, and there is no apparent reason why replacement of methyl groups should be so difficult. There is now no other evidence for an anion $[H_3B{\cdot}NH_2{\cdot}BH_3]^-$, and if it was formed here decomposition with loss of a borine group seems more likely than that suggested above.

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[10] Schaeffer, Adams, and Koenig, *J. Amer. Chem. Soc.*, 1956, **78**, 725.
[11] Parry, Schultz, and Girardot, *J. Amer. Chem. Soc.*, 1958, **80**, 1.
[12] Thorpe, Ph.D. Thesis, Liverpool, 1959.
[13] Wiberg and Bolz, *Ber.*, 1940, **73**, 209.

Parry and Edwards [14] have pointed out that most donor molecules or ions, D, produce symmetrical fission of diborane to give D,BH_3, but two—ammonia and the amide ion—produce unsymmetrical fission to give a borohydride ion. Hence lithium amide in ether reacts with diborane thus: [15]

$$LiNH_2 + B_2H_6 \longrightarrow LiBH_4 + H_2B{\cdot}NH_2$$

and there is no reaction in absence of solvent. The corresponding reaction here would be

$$[H_2N{\cdot}BMe_3]^- + B_2H_6 \longrightarrow H_2B{\cdot}NH_2{\cdot}BMe_3 + BH_4^-$$

followed by loss of trimethylboron, the latter then forming methylated diboranes by interaction with excess of diborane. The solvent might assist reaction, not only by dissolving the potassium aminotrimethylborate and diborane, but also by causing precipitation of the potassium borohydride and forming an ether complex with the trimethylboron. The tenacious retention of methyl groups could be due to a rearrangement such as

$$H_2B{\cdot}NH_2{\cdot}BMe_3 \longrightarrow HMeB{\cdot}NH_2{\cdot}BMe_2H$$

followed by loss of $BHMe_2$ (appearing as tetramethyldiborane), leaving finally polymeric $HMeB{\cdot}NH_2$ in which replacement of methyl groups might be difficult. An experiment showed that solid aminodimethylborine $H_2N{\cdot}BMe_2$ (prepared by heating ammonia–trimethylboron) reacted readily with diborane in absence of any solvent to give methylated diboranes with complete replacement of the methyl groups in the solid. It seems likely that the aminoborine formed from the aminotrimethylborate is more highly polymerised than that formed in other ways, since it does not readily undergo ammonolysis or substitution.

EXPERIMENTAL

(Unless otherwise stated, all quantities recorded here are in terms of mmoles or mg.-atoms.)

Reductions and manipulations in liquid ammonia solution were carried out in a high-vacuum apparatus by methods previously described.[1,16] Diborane was prepared by heating a mixture of anhydrous stannous chloride and potassium borohydride at 200°, and purified by fractionation.[17] Other starting materials were prepared by conventional methods; crude trimethylboron was converted into the ammonia addition compound, the latter sublimed *in vacuo*, and trimethylboron obtained by addition of hydrochloric acid, and stored over sodium hydroxide.

Typical experiments were as follows:

Preparation and Hydrolysis of Potassium Aminotrimethylborate.—Trimethylboron (0·55) and excess of ammonia were mixed and potassium (0·92) was added at −78°; the blue solution was left until colourless, hydrogen (0·45) and methane (0·01) being formed. After removal of solvent, dry ether was added, the mixture refluxed and filtered, and the ether removed. The solid product on hydrolysis with hydrochloric acid gave trimethylboron (0·50) as the only volatile product and the residue evolved ammonia (0·42) on treatment with alkali and contained potassium (0·49).

Pyrolysis.—The aminotrimethylborate (0·95) was heated for 45 hr. at 140°; methane (2·13) was produced. Water was condensed on to the brown product, and after the violent reaction at room temperature the mixture was heated at 100°; hydrogen (0·25), methane (0·10), and a trace of carbon monoxide were evolved; the remaining liquid was distilled into standard acid and ammonia (0·42) was found. Titration of the residue gave boric acid (0·89) and a black solid identified as carbon.

Reaction with Diborane.—The aminotrimethylborate (1·35), prepared in ether solution as described above, was shaken for 7 days with excess (5·01) of diborane at −78°. A trace of hydrogen was formed; other volatile products were removed with the ether; the solid residue gave potassium (1·34) and, after fusion with sodium peroxide, boron (2·48). In another experiment with aminotrimethylborate (1·2), trimethylamine was added to the mixture of

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[14] Parry and Edwards, *J. Amer. Chem. Soc.*, 1959, **81**, 3554.

[15] Schaeffer and Basile, *J. Amer. Chem. Soc.*, 1955, **77**, 331.

[16] Hazlehurst, Holliday, and Pass, *J.*, 1956, 4653.

[17] Jeffers, unpublished work.

excess of diborane and volatile reaction products, to give a solid adduct (10·3). Hydrolysis of this gave hydrogen (27·7) ($Me_3N{\cdot}BH_3$ requires 30·9); hence a fraction 3·20/3·60 of the methyl groups of the salt was replaced by hydrogen. The following reactions were carried out on the solid product of the above reaction:

Hydrolysis. Hydrolysis of 1·22 mmoles with constant-boiling hydrochloric acid for 24 hr. at 100° gave hydrogen (5·79) and methane (0·20) and a residue containing boron (1·92) in titratable form. Hydrolysis of the solid (1·0) with sodium hydroxide solution for 7 days at room temperature gave only hydrogen (0·26).

Pyrolysis. 1·22 mmoles heated for 18 hr. at 150° gave hydrogen (0·33).

Reaction with Trimethylamine.—The aminotrimethylborate (1·13) was treated with excess of trimethylamine for 14 days at room temperature; hydrogen (0·20) was formed and trimethylamine (0·11) absorbed.

Reaction with Ammonia and Ammonium Chloride.—The potassium salt (1·05) with excess of ammonia at room temperature for 72 hr. gave hydrogen (0·05). Ammonium chloride was then added, and ammonia removed at $-23°$; on storage for 20 hr. at 20°, hydrogen (1·05) was formed; 30 hr. at 90° gave a further 0·73 mmole, and at 200° another 2·68 mmoles were evolved. In another experiment with solid (0·65), very slow removal of solvent ammonia after addition of ammonium chloride gave hydrogen (0·24); after warming to room temperature to convert ammonium borohydride into ammonia–borine, addition of more ammonia and reaction at 20° for 24 hr. gave hydrogen (0·20) and methane (0·01) with loss of ammonia (0·21). Subsequent removal of ammonia and further heating gave more hydrogen and a trace of condensable substance, v. p. 90 mm. at 0° (v. p. of borazole, 85 mm. at 0°).

Reaction of Aminodimethylborane with Diborane.—1·15 Mmoles, prepared by heating ammonia–trimethylboron, were treated with diborane (2·01) for 7 days at $-78°$. Volatile material (2·04 assumed to be methylated diboranes) was recovered and gave on hydrolysis hydrogen (9·91) and a trace of methane (required for diborane: hydrogen, 12·04); hence hydrogen (1·06) was lost from the diborane. Reaction of the residue with constant-boiling hydrochloric acid gave hydrogen (0·39).

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