Reactions of Trimethylamine–Iodoborane (1/1) and Related Complexes in Liquid Ammonia

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The only trimethylamine–halogenoborane (1/1) in the series $NMe_3{\cdot}BH_yX_z$ ($y + z = 3$; X = Cl, Br, or I) to react with liquid ammonia is $NMe_3{\cdot}BH_2I$ which slowly gives diamminedihydroboron iodide $[BH_2(NH_3)_2]I$. The reaction rate is greatly increased in the presence of a range of halide salts. On reaction with Na[CN], $NMe_3{\cdot}BH_2I$ gives mainly $NH_3{\cdot}B(CN)H_2$ and with $Na[NH_2]$ mainly polymeric $[BH_2(NH_2)]_n$. The complexes $NMe_3{\cdot}BBr_2H$, $NMe_3{\cdot}BHI_2$, and $NMe_3{\cdot}BBr_3$, as well as $NMe_3{\cdot}BH_2I$, react with sodium in liquid ammonia; the products include $[BH_2(NH_2)]_n$ and (for $NMe_3{\cdot}BH_2I$) the borane complex $NMe_3{\cdot}BH_3$.

AMINE complexes of the boron halides, in contrast to the co-ordinatively unsaturated boron halides themselves, show considerable resistance to hydrolysis. In view of this it seemed possible that these complexes might be sufficiently stable to ammonolysis for their reactions to be studied in liquid ammonia. We report here treatment of the trimethylamine complexes $NMe_3{\cdot}BH_yX_z$ [1] ($y + z = 3$; X = Cl, Br, or I) (with the exception of $NMe_3{\cdot}BI_3$ which was not studied) with liquid ammonia, with ammoniacal solutions of halide and of other salts, and with ammoniacal solutions of sodium metal.

RESULTS AND DISCUSSION

The only complex found to react with liquid ammonia at −44 °C was $NMe_3{\cdot}BH_2I$. The other complexes of the series $NMe_3{\cdot}BH_yX_z$ were recovered unchanged after being treated with ammonia for many hours. The reaction with $NMe_3{\cdot}BH_2I$, which was very slow and took 40 h to proceed to completion, was an ammoniation rather than an ammonolysis and gave diamminedihydroboron iodide quantitatively. We have previously published [2] a vibrational spectral analysis of this

$$\mathrm{NMe_3{\cdot}BH_2I \xrightarrow{NH_3} [BH_2(NH_3)_2]I} \qquad (1)$$

compound and the corresponding chloride and bromide are known.[3]

The complexes $NMe_3{\cdot}BH_yX_z$ were treated with ammoniacal solutions of various metal and ammonium halide salts in order to investigate whether halide exchange, such as that demonstrated by us and other workers for $NMe_3{\cdot}BH_2I$ in organic solvents,[1,4] occurred. Once more, $NMe_3{\cdot}BH_2I$ was the only complex to react and the only products were the diamminedihydroboron salts, $[BH_2(NH_3)_2]X$. However, reaction of $NMe_3{\cdot}BH_2I$ in the presence of halide salts was much faster than in

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pure ammonia solution. For a mole ratio $NMe_3\cdot BH_2I$: MX (MX = NaCl or NaBr, for example) of 1 : 1, the time for complete reaction was 35—40 min. By varying the mole ratios from 1 : 0.1 to 1 : 5, the time for complete reaction varied between 60 and 20 min. A greater mole ratio than 1 : 5 produced no apparent further increase in reaction rate.

It seems clear that this effect of MX on the reaction rate is an example of the primary salt effect,[5] the increase in the ionic strength of the medium accelerating, in this case, the dissociation of the boron–iodine bond. Thus it seems likely that $[NMe_3\cdot BH_2]I$ is an intermediate and that the reaction scheme is as in (2).

$$NMe_3\cdot BH_2I \overset{\text{slow}}{\rightleftharpoons} [NMe_3\cdot BH_2]I \xrightarrow{\text{fast}} [BH_2(NMe_3)(NH_3)]I \xrightarrow{\text{fast}} [BH_2(NH_3)_2]I \quad (2)$$

The product $[BH_2(NH_3)_2]I$ did not react when heated under reflux with excess of trimethylamine and this gives credence to the irreversibility of the final step.

A number of mechanisms involving preionization of boron–halogen bonds in preference to breaking of boron–nitrogen-donor bonds for various reactions of amine–halogenoboranes have been postulated recently, for example the reaction [6] between BCl_3 and $NMe_3\cdot BBr_3$ and the hydrolysis [7] of trimethylamine–halogenoboranes. The lack of reactivity of $NMe_3\cdot BHI_2$ may be explained by an analogy with similar organic di-iodo-compounds.[8] In the case of $NMe_3\cdot BH_2I$, the single iodine atom will obtain a large partial negative charge by the σ-inductive effect, thus creating a polar B–I bond, favouring ionization. However, in $NMe_3\cdot BHI_2$, both of the iodine atoms will be competing for the available electron density, thus effectively reducing the polarity of each B–I bond. The lower reactivity of $NMe_3\cdot BHI_2$, as compared with $NMe_3\cdot BH_2I$, has also been observed in their hydrolysis reactions [7] which also go through a boron(1+) intermediate.

The monoiodo-derivative $NMe_3\cdot BH_2I$ was also the only complex of those examined (see Experimental section) to react with sodium cyanide. In this case a different reaction product, the cyano-derivative $NH_3\cdot B(CN)H_2$, was obtained together with a trace amount of $NMe_3\cdot B(CN)H_2$.[1,9] However, the latter complex was not an intermediate in the formation of $NH_3\cdot B(CN)H_2$ since treatment of a sample of $NMe_3\cdot B(CN)H_2$ with liquid ammonia, with or without the addition of Na[CN], had no effect. Conversely, $NH_3\cdot B(CN)H_2$ did not react with refluxing NMe_3. A probable intermediate in the formation of $NH_3\cdot B(CN)H_2$ is the boron(1+) ion $[BH_2(NH_3)_2]^+$ since when $[BH_2(NH_3)_2]I$ was prepared *in situ* from $NMe_3\cdot BH_2I$ and NaI, and then treated with Na[CN], the only product was $NH_3\cdot B(CN)H_2$. It is interesting that cyanide but not halide ion is able to displace ammonia from $[BH_2(NH_3)_2]^+$ even in the presence of a large excess of NH_3. We conclude that with Na[CN], two competing reactions, (3) and (4) occur.

$$\begin{tikzcd} & {[BH_2(NH_3)_2]^+} \arrow[r] & NH_3\cdot B(CN)H_2 \\ NMe_3\cdot BH_2I \arrow[ur, "(3)"] \arrow[dr, "(4)"'] \arrow[r, phantom, "\mathrm{NaCN{-}NH_3}"] & & \\ & NMe_3\cdot B(CN)H_2 & \end{tikzcd}$$

When the series of halogenoborane complexes were treated with sodium in liquid ammonia at −44 °C, the following complexes reacted: $NMe_3\cdot BH_2I$; $NMe_3\cdot BHI_2$; $NMe_3\cdot BBr_2H$; and $NMe_3\cdot BBr_3$. When an excess of sodium was used, z moles reacted for one of $NMe_3\cdot BH_yX_z$. In all these reactions new B–H bonds were formed. The complex $NMe_3\cdot BH_2I$ was the only one to give a volatile boron-containing product, *viz.* $NMe_3\cdot BH_3$, although some boron was in the form of an involatile residue (mixed with the sodium iodide formed in the reaction). The active H : B ratio of this residue was less than that required for $[BH_2(NH_2)]_n$ and possibly it was a mixture of $[BH_2(NH_2)]_n$ and $BH(NH_2)_2$. The other complexes which reacted gave only polymeric aminoborane $[BH_2(NH_2)]_n$.

$$NMe_3\cdot BH_2I \xrightarrow{\text{Na–NH}_3} NMe_3\cdot BH_3\ (64\%) + [BH_2(NH_2)]_n + [BH(NH_2)_2]\ (?) \quad (5)$$

$$NMe_3\cdot BHX_2\ (X = Br\ \text{or}\ I)\ \text{and}\ NMe_3\cdot BBr_3 \xrightarrow{\text{Na–NH}_3} [BH_2(NH_2)]_n \quad (6)$$

Diamminedihydroboron iodide, the product of ammoniation of $NMe_3\cdot BH_2I$, also reacted with sodium in a 1 : 1 mole ratio. Hydrogen was evolved and $[BH_2(NH_2)]_n$ was the only product. This reaction resembles that of related boron(1+) salts.[3,10]

$$[BH_2(NH_3)_2]I + Na \longrightarrow NaI + NH_3 + \tfrac{1}{n}[BH_2(NH_2)]_n + \tfrac{1}{2}H_2 \quad (7)$$

That the chloro-complexes $NMe_3\cdot BCl_zH_y$ (z = 1—3) and the bromo-complex $NMe_3\cdot BBrH_2$ did not react in homogeneous solution with sodium was surprising and shows how stable some of these four-co-ordinate boron complexes are. The stability towards ammonolysis of the four complexes which reacted with sodium was further tested by treating them with $Na[NH_2]$ solution. Only $NMe_3\cdot BH_2I$ reacted and gave mainly $[BH_2(NH_2)]_n$

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together with a trace amount of $NMe_3{\cdot}BH_3$. The complexes $NMe_3{\cdot}BHI_2$, $NMe_3{\cdot}BBr_2H$, and $NMe_3{\cdot}BBr_3$ were recovered in quantitative yield.

Finally, pyrolysis of $[BH_2(NH_3)_2]I$ proceeded in a different manner to that of $[BH_2(NMe_3)_2]X$ [11] and gave a mixture of aminoborane $[BH_2(NH_2)]_n$ and borazine $[BH(NH)]_3$. The aminoborane was probably formed as

$$[BH_2(NH_3)_2]I \longrightarrow [NH_4]I + BH_2(NH_2) \qquad (8)$$

$$3BH_2(NH_2) \longrightarrow [BH(NH)]_3 + 3H_2 \qquad (9)$$

a monomer [12] since it was apparently produced as a vapour and was collected in a trap at −196 °C. On warming, the $[BH_2(NH_2)]_n$ content of the trap was, however, completely involatile and was presumably polymeric.

EXPERIMENTAL

Starting Materials.—Trimethylamine–borane, m.p. 94 °C, was recrystallized. The complexes $NMe_3{\cdot}BH_2X$ and $NMe_3{\cdot}BHX_2$ (X = Cl, Br, or I) were prepared as described previously [13] and were freshly sublimed before use. Dihydrobis(trimethylamine)boron iodide [14] was prepared by the action of NMe_3 on $NMe_3{\cdot}BH_2I$ in benzene and recrystallized from EtOH–OEt_2, m.p. 213 °C. The adducts $NMe_3{\cdot}BX_3$ (X = F, Cl, or Br) were prepared by standard literature methods and had m.p.s in good agreement with the literature values.[15] Liquid ammonia was dried over sodium and distilled prior to use. Organic solvents were dried by conventional methods. All manipulations with liquid ammonia were *in vacuo*. All other manipulations were made under a dry-nitrogen atmosphere unless otherwise stated.

Instrumental and Analytical Methods.—I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer. Analyses for C, H, and N were by the Department of Organic Chemistry, University of Liverpool. Boron was estimated by titration as the boric acid–mannitol complex, and halogens were determined gravimetrically as silver(I) halide.

Reaction of Trimethylamine–Monoiodoborane (1/1) *with Liquid Ammonia.*—Trimethylamine-monoiodoborane (1/1) (4.96 g) was added to liquid ammonia (35 cm³) at −44 °C and was stirred at this temperature for 40 h. The ammonia was then removed *in vacuo*, leaving a white solid which was heated to 120 °C *in vacuo* to remove any trace of unchanged $NMe_3{\cdot}BH_2I$ from the involatile *diamminedihydroboron iodide*, m.p. 175 °C (decomp.) {Found: C, 0.0; H, 4.75; B, 6.35; I, 72.5; N, 15.4. $[BH_2(NH_3)_2]I$ requires C, 0.0; H, 4.65; B, 6.20; I, 73.0; N, 16.1%}. The i.r. spectrum has been reported elsewhere.[2] On alkaline hydrolysis, the compound evolved only ammonia.

Attempted Reaction of $[BH_2(NH_3)_2]I$ *with* NMe_3.—Trimethylamine (20 cm³) was added to $[BH_2(NH_3)_2]I$ (*ca.* 1 g) and was stirred at room temperature for 8 h. On evaporation of NMe_3, the starting material was recovered unchanged.

Reaction of $NMe_3{\cdot}BH_2I$ *with Liquid Ammonia in the Presence of Halide Salts.*—In a typical reaction, $NMe_3{\cdot}BH_2I$ (1.25 g, 6.3 mmol) and NaBr (0.88 g, 8.6 mmol) were mixed with liquid ammonia (25 cm³) at −44 °C, and stirred at this temperature for 1 h. Ammonia was then removed *in vacuo* and the residue was heated to 80 °C *in vacuo* for 2 h. There was no sublimation from the residue, showing the absence of $NMe_3{\cdot}BH_2I$ and $NMe_3{\cdot}BBrH_2$. The i.r. spectrum of the residue showed only bands attributable to $[BH_2(NH_3)_2]^+$. The same reaction occurred in the presence of NaX (X = F, Cl, Br, or I), AgX (X = Cl, Br, or I), $[NH_4]X$ (X = F, Cl, Br, or I), KX (X = Cl or Br), and $[BH_2(NH_3)_2]I$. In all cases, the reaction resulted in formation of only the $[BH_2(NH_3)_2]^+$ cation and in all cases the reaction was complete in 1 h or less.

Treatment of Other Trimethylamine–Borane Complexes with Liquid Ammonia and with Ammoniacal Solutions of Halide Salts.—The complexes $NMe_3{\cdot}BH_3$, $NMe_3{\cdot}BH_yX_z$ (X = Cl or Br), and $NMe_3{\cdot}BHI_2$ were recovered in virtually quantitative yield by sublimation after treatment for several hours with either liquid NH_3 or ammoniacal solutions of varied sodium, potassium, ammonium, and silver(I) halides.

Reaction of $NMe_3{\cdot}BH_2I$ *with Sodium Cyanide.*—Trimethylamine–monoiodoborane (1/1) (5.1 g, 25.6 mmol) and Na[CN] (1.27 g, 25.9 mmol) were mixed with liquid NH_3 (30 cm³) at −44 °C and stirred at this temperature for 4 h. Ammonia was removed *in vacuo* to leave an oily residue. To this, benzene (25 cm³) was added, and after 20 min the benzene solution was filtered and the filtrate was evaporated to dryness. The solid obtained was purified by sublimation *in vacuo* at 50 °C to yield $NMe_3{\cdot}B(CN)H_2$ (0.02 g, 0.2 mmol) which was identified by comparison of its m.p. (64 °C), mass spectrum (molecular ion at *m/e* 98), and i.r. spectrum with the literature.[1,9] The fraction which was not soluble in benzene was extracted with OEt_2, and n-hexane was added. The resulting white precipitate (0.48 g) was collected by filtration and dried *in vacuo* to give *ammonia–cyanoborane*, m.p. 89 °C (Found: C, 21.1; H, 9.10; B, 19.5; N, 48.9. $NH_3{\cdot}B(CN)H_2$ requires C, 21.5; H, 9.00; B, 19.35; N, 50.1%). The i.r. spectrum showed $\nu(BH_2)_{asym}$ at 2 430 and 2 410, $\nu(BH_2)_{sym}$ at 2 360, $\nu(CN)$ at 2 202, and $\nu(BN)$ at 714 cm^{-1}. Attempts to sublime $NH_3{\cdot}B(CN)H_2$ at 65 °C *in vacuo* led to considerable decomposition into hydrogen, ammonia, and hydrogen cyanide.

The compounds $NMe_3{\cdot}BH_3$, $NMe_3{\cdot}BHI_2$, and $NMe_3{\cdot}BBr_zH_y$ (z = 1—3) did not react with Na[CN] under similar conditions.

Reaction of $NMe_3{\cdot}BH_2I$ *with Sodium.*—Trimethylamine–monoiodoborane (1/1) (3.1 g, 15.6 mmol) was dissolved in liquid NH_3 (30 cm³) at −78 °C and sodium (0.368 g, 16.0 mmol) was added. The blue colour quickly faded (1—2 min). The liquid NH_3 was then removed *in vacuo via* a U trap held at −44 °C, leaving a white involatile residue in the reaction vessel. The contents of the trap were allowed to warm to room temperature and were purified by fractional distillation *in vacuo*. A white solid was formed and was identified as $NMe_3{\cdot}BH_3$ (0.723 g, 9.91 mmol) by comparison of its m.p. (94 °C) and i.r. spectrum with those in the literature.[13,16] The involatile residue was heated to 160 °C

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in vacuo but no sublimate was obtained. The mole ratio of active H : B of this residue was 1.403 : 1 suggesting that it was possibly a mixture of $\frac{1}{n}[BH_2(NH_2)]_n$ and $BH(NH_2)_2$ in the mole ratio of 1.0 : 1.5.

Reaction of Other Trimethylamine–Halogenoboranes with Sodium.—Sodium reacted with $NMe_3{\cdot}BBr_3$, $NMe_3{\cdot}BBr_2H$, and $NMe_3{\cdot}BHI_2$ in mole ratios 3 : 1, 2 : 1, and 2 : 1 respectively. In the case of the bromo-complexes, 5—10 min were required for complete reaction. When less sodium than that specified above was used unchanged starting materials were recovered, and when more sodium was used the solution remained permanently blue. The only volatile materials from these reactions were NH_3 and NMe_3 (only partially separated by vacuum fractionation). The only identifiable boron compound formed was $[BH_2(NH_2)]_n$ isolated by extraction with OEt_2 and evaporation of the filtrate *in vacuo*. Only in the case of $NMe_3{\cdot}BBr_2H$ was the yield of $[BH_2(NH_2)]_n$ determined. Thus $NMe_3{\cdot}BBr_2H$ (1.049 g, 4.6 mmol) and sodium (0.215 g, 9.3 mmol) gave $[BH_2(NH_2)]_n$ (0.130 g, 4.5 mmol) [Found: H, 13.6; B, 37.9; N, 47.9. Calc. for $BH_2(NH_2)$: H, 13.8; B, 37.95; N, 48.3%]. Products from the other reactions had similar analyses.

The fact that the bromo-complex $NMe_3{\cdot}BBrH_2$ and the chloro-complexes $NMe_3{\cdot}BCl_zH_y$ (z = 1—3) did not react with sodium under similar conditions was evident from the observation that the solutions remained permanently blue.

Reaction of $NMe_3{\cdot}BH_2I$ *with Sodium Amide.*—A solution of $Na[NH_2]$ was produced *in situ* by adding sodium (0.258 g, 11.2 mmol) to liquid NH_3 (25 cm^3) in the presence of an iron catalyst (removed by filtration). Trimethylamine–monoiodoborane (1/1) (2.237 g, 11.3 mmol) was added to the solution at −44 °C and was stirred at this temperature for 4 h. Ammonia was then removed *in vacuo*. The residue was heated to 80 °C and a small amount of $NMe_3{\cdot}BH_3$ (0.036 g, 0.5 mmol), identified by its m.p. (93 °C) and i.r. spectrum, was obtained in a trap at −196 °C. The white involatile material was extracted with OEt_2 and the solution evaporated to dryness leaving $[BH_2(NH_2)]_n$ (Found: H, 13.6; B, 37.8; N, 48.0%) as a white solid.

Reaction of $[BH_2(NH_3)_2]I$ *with Sodium.*—Diamminedihydroboron iodide (1.48 g, 8.5 mmol) and sodium (0.194 g, 8.4 mmol) were added to liquid NH_3 (20 cm^3) at −78 °C. The blue colour was dissipated within 1 min and a permanent gas was evolved. After 10 min, ammonia was removed *in vacuo* and the residue was heated to 100 °C *in vacuo*. No sublimate was observed. Extraction of the solid residue with OEt_2 gave $[BH_2(NH_2)]_n$ (Found: H, 13.7; B, 37.7; N, 47.9%) as a white solid.

Pyrolysis of $[BH_2(NH_3)_2]I$.—The compound (0.327 g, 1.9 mmol) was heated at 170 °C *in vacuo* for 3 h. A sublimate of ammonium iodide (0.26 g, 1.8 mmol) was formed on the cool part of the apparatus. A distillate was collected at −196 °C and was later allowed to warm to room temperature when it gave a gas and a solid. The gas was identified by its i.r. and mass spectrum as borazine $[BH(NH)]_3$. The solid, which was no longer volatile even at 180 °C *in vacuo*, was identified by elemental analysis and its i.r. spectrum as $[BH_2(NH_2)]_n$ (Found: H, 13.7; B, 37.8; N, 47.8%).

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