TABLE IV

THERMODYNAMIC DATA FOR HOMOGENEOUS GAS PHASE ASSOCIATIONS[a]

ΔS^0 in e.u. at 300° and one atmosphere (ideal gas state); ΔH^0 in kcal./mole.

		$\Delta S^0_{\text{comp.}}$	$\Delta S^0_{\text{meas.}}$	ΔH^0	Ref.
(3)	$BH_3 + BH_3 = B_2H_6$	−34.22		−28.5	*b*
	$BHMe_2 + BHMe_2 = B_2H_2Me_4$			−25.0	*b*
(4)	$CO + BH_3 = OC{:}BH_3$	−33.17		−18.8	*b*
(5)	$BF_3 + CO = OC{:}BF_3$	−36.0		(−14)[a]	16
(6)	$CO + {}^1/_2B_2H_6 = OC{:}BH_3$	−16.05		− 4.57	25
(7)	$Me_3N + BH_3 = Me_3N{:}BH_3$	−37.80		−31.5	*b*
(8)	$Me_3N + {}^1/_2B_2H_6 = Me_3N{:}BH_3$	−20.69		−17.3	*b*
	$Me_3N + BHMe_2 = Me_3N{:}BHMe_2$	(−44)[c]		−23.4	*b*
	$Me_3N + {}^1/_2B_2H_2Me_4 = Me_3N{:}BHMe_2$			−11.0	*b*
	$Me_3N + BMe_3 = Me_3N{:}BMe_3$		−45.7	−17.6	8
	$Me_3N + BMe_2F = Me_3N{:}BMe_2F$		−47.2	∼−20.5	26
	$Me_3N + BMeF_2 = Me_3N{:}BMeF_2$		−47.2	−23.1	26
(9)	$Me_3N + BF_3 = Me_3N{:}BF_3$	−46.1		−26.6	27
	$Me_3N + BCl_3 = Me_3N{:}BCl_3$			(−30.5)[c]	

[a] With respect to Me_3N as a reference base, BF_3 appears to be "weaker" than BH_3 by about 5 kcal., as an acid. Reaction (5) is strictly hypothetical; $OC{:}BF_3$ has not yet been prepared although serious attempts to do so have been made. We doubt that direct addition can lead to this substance. [b] Data in this paper. [c] Estimated values.

correspond to the equations as originally designated are given in Table IV, along with other closely related values which are of interest.

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(25) A. B. Burg, *ibid.*, **74**, 3482 (1952).

(26) A. B. Burg and A. A. Green, *ibid.*, **65**, 1838 (1943).

(27) Unpublished data by McCoy and Bauer.

ITHACA, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TENNESSEE]

Some Reactions of Monoammonia-boron Trifluoride with Solutions of Alkali Metals in Ammonia

BY W. J. MCDOWELL[1] AND C. W. KEENAN

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The reactions of the alkali metals, lithium, sodium, potassium and cesium, with liquid ammonia solutions of $BF_3{\cdot}NH_3$ have been studied. Differences in the stoichiometry of reaction for these metals have been observed: the mole ratio of metal:$BF_3{\cdot}NH_3$ is 3.0 for lithium, 2.5 for sodium and 1.0 for both potassium and cesium. The products of the reaction of $BF_3{\cdot}NH_3$ with potassium have been studied and proposals have been made as to the nature of the products of the reactions with the other metals.

Introduction

This study was undertaken to extend the knowledge of the chemistry of boron compounds in liquid ammonia. Kraus and Brown[2] have described the reaction between sodium and $BF_3{\cdot}NH_3$ in this solvent. They found that hydrogen was evolved in stages and interpreted this as indicating that all the fluoride ligands are not solvolyzed with equal ease. Further, from the fact that the solvolysis of the ethylamine derivative of BF_3 may go to completion, as indicated by the reaction of lithium with a solution of BF_3 in ethylamine, they concluded that a liquid ammonia solution of $BF_3{\cdot}NH_3$ should be completely ammonolyzed.

Our investigation has revealed some unexpected and interesting chemical properties of the $BF_3{\cdot}NH_3$–liquid ammonia system.

Experimental

Apparatus.—Most of the reactions in liquid ammonia were carried out in an apparatus similar to one which has been described.[3]

All of the reaction products were handled in a dry box filled with anhydrous, oxygen-free nitrogen.

X-Ray powder diffraction photographs were made of several of the products with a Model 795 Picker–Waite diffraction unit. The samples were enclosed in thin-walled Pyrex capillaries and exposed in a 70 mm. camera to radiation from a tube equipped with a copper target and a nickel filter. An accelerating voltage of 45 kv., a filament current of 9 ma., and an exposure time of 1 hr. were used for all samples.

Reagents.—The ammonia used in all quantitative reactions was purified from commercial material (99.9%) by distilling and storing in small cylinders containing sodium amide.

The $BF_3{\cdot}NH_3$ was prepared by the addition of ammonia to boron trifluoride etherate as described by Kraus and Brown.[2] The white precipitate was allowed to settle and the excess ether removed by decantation. The product was washed twice with fresh ether and then freed of ether by evacuation.

Anal. Calcd. for $BF_3{\cdot}NH_3$: B, 12.8; F, 67.2; N, 16.5. Found: B, 12.4; F, 67.9; N, 16.4.

All other chemicals used were reagent grade except the cesium which was distilled from C.P. material.

The Analysis of Boron Compounds Containing Fluorine.—The method of Pflaum and Wenzke,[4] modified to exclude the sodium peroxide fusion, was used to analyze compounds containing boron and fluorine.

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[1] Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[2] C. A. Kraus and E. H. Brown, THIS JOURNAL, **51**, 2690 (1929).

[3] G. W. Watt and C. W. Keenan, *ibid.*, **71**, 3833 (1949).

[4] D. J. Pflaum and H. H. Wenzke, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 392 (1932).

Results

Solubility of $BF_3 \cdot NH_3$ in Liquid Ammonia.—The compound $BF_3 \cdot NH_3$ appeared to be soluble in liquid ammonia at −33° to the extent of about 10 g. per 100 ml. The solutions obtained, even the very dilute ones, were always slightly turbid.

Reactions with Alkali Metals.—In most of the reactions described 0.5000–1.5000 g. of $BF_3 \cdot NH_3$ was dissolved in about 50 ml. of liquid ammonia. The alkali metal was added sometimes as weighed pieces, but more commonly as a standard solution. In making up the solutions about six moles of metal per mole of $BF_3 \cdot NH_3$ to be titrated was dissolved in 20.0 to 30.0 ml. of solution.

Reaction with Lithium.—This metal was introduced into the buret in a nitrogen atmosphere due to the deliquescent behavior of lithium in ammonia. The results of four titrations are given in Table I. In reaction no. 2 an excess of lithium was added and the solution was back titrated with a standard ammonium iodide solution. In reactions no. 3 and 4 excess titrant was added after the appearance of the third end-point and the excess was measured by back-titration with ammonium iodide. In both forward and back titrations the deep blue color characteristic of dilute alkali metal solutions in ammonia served as its own indicator.

The behavior of the titration reactions with lithium was most unusual. In two of the forward titrations three end-points were observed. The first, which occurred at very nearly one equivalent of lithium per mole of $BF_3 \cdot NH_3$ (see Table I) faded within 15 or 20 minutes after it was first observed. When this occurred the titration was begun again. The ensuing reaction was as rapid as when the first metal was added. The second end-point (at about 2.5 equivalents per mole) did not fade for about 40 minutes. When the second end-point had faded, the titration was begun again and again the reaction proceeded rapidly. The third end-point (three equivalents per mole) did not fade after 2 hr. The back titrations, where done, agreed well with the last end-point of the forward reaction.

Table I

Summary of Stoichiometry[a] Calculations for Reactions of $BF_3 \cdot NH_3$ with Lithium

Reaction no.	1st end-point	2nd end-point	3rd end-point	By back-titration
1	1.13	Not obsd.	3.09	..
2	..	..	..	3.00
3	1.17	2.44	2.68	2.95
4	1.03	2.46	2.96	2.96
Av.	1.11	2.45	2.91	2.97

[a] Given as a ratio equivalents Li per mole $BF_3 \cdot NH_3$.

From reaction no. 1 an ammonia soluble and an ammonia insoluble product were recovered quantitatively. X-Ray analysis indicated that lithium fluoride was the major constituent of the insoluble portion and a small amount of LiF was found in the ammonia soluble portion. (The three strongest lines for LiF were present and there were no extraneous lines.) The ammonia-soluble portion, sampled immediately after all solvent ammonia was removed, was analyzed for nitrogen by the Kjeldahl method.

Anal. Calcd. for $(NH_2)_2B(NH)B(NH)$: N, 74.3. Found: N, 75.0. Calcd. total wt. of products $(NH_2)_2B(NH)B(NH)$ plus LiF: 0.405 g. Found: 0.402 g.

Reaction with Sodium.—Five reactions with sodium were carried out. The details are summarized in Table II. As noted in the table, two end-points were observed. Although the first one persisted for approximately 20 minutes, after it faded the reaction again went as rapidly as titrant could be added.

The products of the reaction consisted of a finely divided white precipitate and an ammonia soluble product. X-Ray and chemical analysis of the insoluble product indicated that it was largely sodium fluoride.

Anal. Calcd. for NaF: Na, 54.8; F, 45.2. Found: Na, 48.9; F, 42.4.

X-Ray analysis also showed that there was some sodium fluoride in the ammonia soluble product.

The total product weight was determined for reactions no. 1 and 2, Table II.

Table II

Summary of Reactions of Sodium with $BF_3 \cdot NH_3$ Solution

Reaction no.	Conditions	Equiv. Na/mole $BF_3 \cdot NH_3$	Equiv. H_2/mole $BF_3 \cdot NH_3$
1[a]	$BF_3 \cdot NH_3$ titrated with Na	2.45	2.60
2[a]	$BF_3 \cdot NH_3$ titrated with Na	2.55	2.51
3[b]	2-fold excess of Na	2.64	2.20
4[b]	2-fold excess of Na	2.59	2.87
5[b]	4-fold excess of Na	1.76	2.07
Av. (excluding no. 5)		2.55	2.54

[a] Two end-points observed: first at a 1 to 1 ratio which faded after 20 min.; second (recorded here) did not fade after 1.5 to 2 hr. [b] $BF_3 \cdot NH_3$ added from side arm into 1 to 2 *N* solution of Na; H_2 evolved in two stages: first, immediately on addition; second, began after 20 min. Reaction time allowed 2 to 5 hr. Excess Na titrated rapidly with NH_4I solution to determine equiv. of Na used.

Anal. Calcd. total wt. of products $(NH_2)_2B(NH)BF(NH_2)$ plus NaF: 1.327, 0.980 g. Found: 1.337, 0.961 g.

In reactions no. 3, 4 and 5 solid $BF_3 \cdot NH_3$ was added to a solution containing excess sodium. During the immediate violent reaction an estimated one equivalent of hydrogen was evolved per mole of $BF_3 \cdot NH_3$. After this first violent evolution of gas, the mixture remained 20 minutes without apparent reaction. A slow evolution of hydrogen then began which lasted from 1 to 1.5 hr. The excess sodium was then titrated with ammonium iodide solution.

Reaction with Potassium.—No reactions between $BF_3 \cdot NH_3$ and potassium were found described in the literature, but the reaction of potassium was expected to proceed in the same manner as that of sodium. This was found not to be the case. Eight reactions of $BF_3 \cdot NH_3$ with potassium were run and in each case one equivalent of potassium reacted per mole of $BF_3 \cdot NH_3$ and one equivalent of hydrogen (within the error of the measurements) was evolved.

The most important data from these reactions are recorded in Table III.

Table III

Summary of Reactions of Potassium with $BF_3 \cdot NH_3$ Solutions

Reaction no.	Mmoles $BF_3 \cdot NH_3$	Meq. K	Meq. H_2	Comments
1	4.75	Excess	4.64	Reactants placed together; NH_3 condensed on them; excess K remained
2	11.8	13.3	11.9	Potassium added in pieces to $BF_3 \cdot NH_3$ soln.
3	16.95	17.05	15.5	Potassium soln. titrated into $BF_3 \cdot NH_3$ soln.
4	3.27	3.30	3.17	Same as 3
5	14.7	14.7	12.1	Equiv. amount of solid potassium added
6	18.9	Excess	20.6	Excess potassium remained 16 hr. without reacting
7	18.9	18.9	20.0	See Table IV for details
8	14.4	14.4	15.2	See Table IV for details

The data for potassium added in reactions No. 3 and 4 are based on one-drop end-points which persisted for 20 minutes. An excess of three drops faded after an additional 45 minutes, but an excess of six drops produced a color which lasted for 24 hr., at which time observation was discontinued.

Reactions no. 7 and 8 were carried out in a small tared Faraday-type tube. The purpose was to recover the products quantitatively in order to get precise gravimetric data, inasmuch as (1) great difficulty was experienced in determining boron and fluorine in the same sample with satisfactory precision and (2) results from previous reactions indicated that two products were formed (one a potassium compound, the other a boron compound) which could not be separated on the basis of their solubilities in liquid ammonia. Details are given in Table IV. The X-ray powder diffraction data for the total product showed that KF was one of the products. Literature for KF, 3.08 (m), 2.66 (s), 1.88 (s), 1.54 (m), 1.19 (m); found, 7.25 (w), 3.58 (w), 3.31 (w), 3.10 (m), 2.67 (s), 2.36 (w), 2.21 (w), 1.89 (s), 1.54 (m).

TABLE IV

TOTAL PRODUCT AND REACTANT WEIGHTS OF REACTION OF $BF_3 \cdot NH_3$ AND POTASSIUM

Item	Reaction no. 7	No. 8
Wt. $BF_3 \cdot NH_3$, g.	1.6037	1.2203
Wt. potassium, g.	0.7388	0.5629
Total product, wt., g.	2.3175	1.7573
Theoretical wt. of KF + BNH_2F_2, g.	2.3235	1.7688

Anal. Calcd. total products $B(NH_2)F_2$ plus KF: B, 8.80; F, 46.4; N, 11.4. Found: B, 8.51; F, 46.3; N, 11.9.

Reaction with Cesium.—Because of the instability of liquid ammonia solutions of cesium, reactions involving this metal were brought about by breaking a glass bulb of the metal immersed in a solution of $BF_3 \cdot NH_3$. The excess cesium was titrated with a standard solution of ammonium iodide. The results of two runs can be summarized as follows: meq. Cs, 1.50, 2.27; mmols. $BF_3 \cdot NH_3$, 0.50, 1.65; meq. NH_4I, 0.914, 0.57. Calculated ratios of $Cs/BF_3 \cdot NH_3$ are 1.17 and 1.03, respectively.

Reaction with Potassium Amide.—In an attempt to determine if $BF_3 \cdot NH_3$ existed in liquid ammonia as a monobasic complex acid which was attacked by the potassium solution or if it solvolyzed to produce ammonium fluoride which then reacted with the potassium solution, two titrations of $BF_3 \cdot NH_3$ with potassium amide were performed.

The experimental procedure was the same as for a titration with a solution of the metal except that a spiral of freshly oxidized iron wire was added to the buret and the potassium allowed to convert to the amide. Triphenylmethane was used as an indicator for these acid–base titrations.

In the first reaction only a little over one equivalent of potassium amide was added per mole of $BF_3 \cdot NH_3$. No end-point was reached. An insoluble product was obtained which X-ray analysis showed to be largely potassium fluoride. The soluble product was not identified.

The second reaction was carried to an end-point which faded slowly but lasted for about 10 minutes. At this point 2.6 equivalents of potassium amide had been added per mole of $BF_3 \cdot NH_3$. X-Ray analysis indicated that the ammonia-insoluble product was largely potassium fluoride and that the ammonia-soluble product contained a small amount of potassium fluoride. This interpretation of the X-ray data was confirmed by chemical analysis.

Anal. Calcd. for KF: F, 32.7; K, 67.3. Found in the ammonia-insoluble portion: F, 32.9; K, 65.2; B, 0.30. Found in the ammonia-soluble portion: F, 28.9; N, 34.6; B, 16.8; K, 9.42.

The insoluble material recovered on the filter appeared to be nearly pure potassium fluoride and by weight amounted to 2.4 equivalents per mole of $BF_3 \cdot NH_3$.

Two reactions were carried out in which a weighed quantity of $BF_3 \cdot NH_3$ was added to a large excess of potassium amide followed by titration of the excess amide with ammonium iodide. Both reactions indicated that three equivalents of amide reacted per mole of $BF_3 \cdot NH_3$, although a mechanical failure of the apparatus ruined one of the runs. Data from one reaction, in mmols.: KNH_2, 44.6; $BF_3 \cdot NH_3$, 10.3; NH_4I, 13.7. Mole ratio $KNH_2/BF_3 \cdot NH_3$ is 3.00. Calcd. wt. KF, 1.795 g.; wt. insol. product, 1.804. Calcd. wt. $B_2(NH)_3$, 0.344 g.; wt. sol. product after 2 hr. evacuation at room temperature, 0.327.

Ion-exchange Studies.—As pointed out above, the reaction of potassium and $BF_3 \cdot NH_3$ in ammonia apparently gave two products, KF and BNH_2F_2. Since these could not be separated cleanly by filtration, an experiment with an exchange resin was planned in order to investigate the ionic species in solution. Although the boron containing group should certainly be neutral or negative,[5] there is at least one intriguing report[6] which states that boron can be removed from certain solutions by a *cation* exchanger.

Accordingly, an experiment was carried out in the apparatus diagrammed in Fig. 1. A glass tube D was filled with 11.7 g. of Dowex-50 (cation resin) and packed with glass wool on either end. The resin had previously been put into the ammonium form in aqueous medium, dried 16 hr. *in vacuo* over magnesium perchlorate, then exposed in turn to gaseous and liquid ammonia and finally washed copiously with liquid ammonia. Tube D was then attached by means of short sections of Tygon tubing to the reaction vessel A and the eluate collector E. A sealed glass bulb B, containing 0.4380 g. of $BF_3 \cdot NH_3$ was placed on the coarse in-line frit at the bottom of vessel A. A tared vessel F was provided so that the eluate solution could be collected, evaporated to dryness and weighed. A glass frit in the line between E and F ensured that no resin could be carried into F.

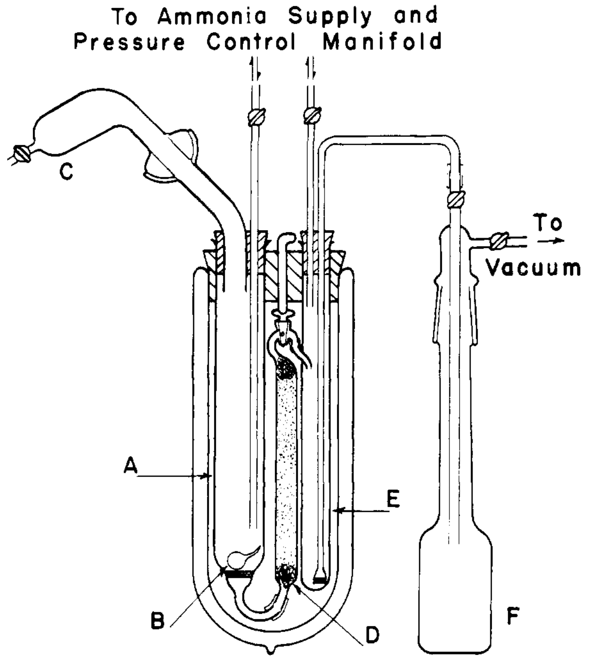

Fig. 1.—Apparatus for operation of ion-exchange column in liquid ammonia.

The complete apparatus (vessels C, A, D, E and F) was flushed with gaseous ammonia, then 0.1901 g. of potassium was placed in Tube C, and liquid ammonia at −33° was placed in the unsilvered Dewar flask shown in the figure. After enough ammonia was condensed to fill tube D and partially fill vessel A, the bulb B was broken and the solid potassium in C tumbled into the solution. After the reaction was over (hydrogen gas being liberated through the stopcock in C), the stopcock between D and E was opened slightly and the solution in A was slowly delivered *via* D into E. Periodically the column operation was interrupted and the eluate solution was drawn over into F. A slight precipitate in A was dissolved by condensation of fresh ammonia and finally the column was washed with five portions (approx. 11 ml. each) of fresh ammonia.

The solid recovered in flask F weighed 0.4457 g., gave no flame test for potassium and had the same X-ray powder diffraction pattern as had the $BF_3 \cdot NH_3$ originally placed in bulb B.[7] Some details on subsequent treatment of the resin have been reported previously.[7]

Discussion

In summary, it may be said that cesium and potassium react in the amount of 1.0 equivalent per mole of $BF_3 \cdot NH_3$, that sodium reacts in the amount of 2.5 equivalents per mole of $BF_3 \cdot NH_3$ with a transient end-point observed at 1.0 equivalent per mole and that lithium reacts in the amount of 3.0

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[5] C. A. Wamser, THIS JOURNAL, **73**, 409 (1951).

[6] D. I. Ryabchikov and V. V. Danilova (Acad. Sci., U.S.S.R.), *Zhur. Anal. Khim.*, **5**, 28 (1950).

[7] C. W. Keenan and W. J. McDowell, THIS JOURNAL, **75**, 6348 (1953).

equivalents per mole of $BF_3 \cdot NH_3$ with transient end-points at 1.0 and 2.5 equivalents per mole. Potassium amide was also observed to react with $BF_3 \cdot NH_3$ in the amount of 3.0 equivalents per mole when present in excess. These observations have been reported previously.[8]

The products of the reaction of potassium with $BF_3 \cdot NH_3$ are almost certainly potassium fluoride and a compound of the composition $B(NH_2)F_2$. The proposed over-all reaction is

$$BF_3 \cdot NH_3 + K \longrightarrow B(NH_2)F_2 + KF + {}^1/_2H_2$$

The fact that we find $B(NH_2)F_2$ unsolvated whereas BF_3 is solvated may be explained by noting that the amide ion has two pairs of electrons to share. The basic character of this compound is revealed by its behavior when passed through the ammonium resin in a solution containing potassium

$$K^+F^- + NH_4R \longrightarrow KR + NH_4{}^+F^-$$
$$NH_4{}^+F^- + B(NH_2)F_2 \longrightarrow BF_3 \cdot NH_3 + NH_3$$

Since the stoichiometry of the reaction of cesium with $BF_3 \cdot NH_3$ is the same as that of potassium, it would seem reasonable to assume that the reaction is analogous. However, no other supporting data have been obtained.

The products of the reaction of sodium with $BF_3 \cdot NH_3$ were not established except for the fact that sodium goes to sodium fluoride. The stoichiometric relationship at the final end-point indicates that two moles of $BF_3 \cdot NH_3$ react with five equivalents of sodium. One reaction based on this ratio would be

$$2BF_3 \cdot NH_3 + 5Na + 2NH_3 \longrightarrow (NH_2)_2B(NH)BF(NH_2) + 5NaF + {}^5/_2H_2$$

A salt of a water system compound somewhat analogous to the proposed product is known.[9] The corresponding acid has the formula: (OH)FBOBF(OH). Some substantiation for the above proposed reaction is that the total product weights of two reactions (weighed in ammonia atmosphere immediately after evaporation of the solvent) agree well with the theoretical weights calculated from the above equation.

That the transient end-point observed at one equivalent of sodium may indicate the formation of the compound $B(NH_2)F_2$, proposed for the reaction with potassium, has been considered. One reaction of $BF_3 \cdot NH_3$ with one equivalent of potassium followed by titration with sodium was carried out to test this idea, but the sodium did *not* react with the reaction products of potassium and $BF_3 \cdot NH_3$.

When lithium reacts with all three fluorides of $BF_3 \cdot NH_3$, X-ray analysis shows that one of the products is lithium fluoride. If we assume that the other product results from removal of hydrogen and fluorine from the final boron–fluoride compound proposed for the reaction with sodium we have

$$(NH_2)_2B(NH)B(NH)$$

The existence of this compound is substantiated by the nitrogen analysis of the ammonia-soluble product and by the total weight of the products.

Assuming that the transient end-points observed in the titration with lithium correspond to the permanent end-point compounds proposed for sodium and potassium, the stepwise removal of fluorine from $BF_3 \cdot NH_3$ would be

$$2BF_3 \cdot NH_3 \longrightarrow 2B(NH_2)F_2 \longrightarrow (NH_2)_2B(NH)BF(NH_2) \longrightarrow (NH_2)_2B(NH)B(NH)$$

The latter compound could lose ammonia, on evaporation of the solvent ammonia, to form boron imide. The ammonia-soluble products of all reactions were observed to lose ammonia upon evacuation or standing at room temperature in an inert atmosphere.

The over-all reaction of potassium amide with $BF_3 \cdot NH_3$ indicated by the data is

$$BF_3 \cdot NH_3 + 3KNH_2 \longrightarrow 3KF + B(NH_2)_3 + NH_3$$

Although the analytical data indicated that the soluble product after evacuation was boron imide, the fact is that practically all the boron appeared in the filtrate. It may be assumed that boron imide is not formed in ammonia solution, but only upon evaporation of the solvent ammonia. The amide is soluble whereas the imide is very slightly soluble, as stated by Joannis. It seems probable that the compound formed in ammonia solution is either the amide $B(NH_2)_3$ proposed by Joannis[10] or the compound $(NH_2)_2B(NH)B(NH)$, proposed herein as a product of the reaction of $BF_3 \cdot NH_3$ and lithium. These reactions show that the compound $BF_3 \cdot NH_3$ is capable of being completely solvolyzed in a solution containing potassium ions.

The most interesting aspect of this research was the discovery of the different alkali metal–$BF_3 \cdot NH_3$ reaction ratios. Watt[11] states that "The process of reduction by means of solutions of metals in ammonia consists in the addition of one or more electrons to an atom, group of atoms or an ion. The metal cation is present in solution but does not usually influence the course of the primary reduction reaction." Burgess and Holden[12] found that the iron-catalyzed reaction of potassium with ammonia was faster than the reaction of sodium with ammonia. This example has been cited as a case in which these alkali metal solutions are not identical, but it is to be emphasized that here Burgess and Holden were dealing merely with reactions of different rates, not different stoichiometry.

Only in the case of some organic reactions are there indications of gross differences in the reactivity of different alkali metal–ammonia reducing systems. Wilds and Nelson[13] reported that a lithium–alcohol–ammonia system is a better reducing medium for phenolic ethers than is a sodium–alcohol–ammonia system. Even here, however, the only thing shown was a difference in the yield of the same end-product.

Previous reduction reactions evidently have involved only compounds which could be reduced similarly by all of the alkali metals. $BF_3 \cdot NH_3$ is a

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[8] C. W. Keenan and W. J. McDowell, This Journal, **76**, 2839 (1954).

[9] H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 153.

[10] A. Joannis, *Compt. rend.*, **135**, 1106 (1902).

[11] G. W. Watt, *Chem. Revs.*, **46**, 290 (1950).

[12] W. M. Burgess and F. R. Holden, This Journal, **59**, 462 (1937).

[13] A. L. Wilds and N. A. Nelson, *ibid.*, **75**, 5360 (1953).

borderline case which reveals clearly that there can be differences in the reaction mechanisms of ammonia solutions of the different alkali metals.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TENNESSEE]

The Ammonolysis of Boron Triiodide in Liquid Ammonia

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The ammonolysis of boron triiodide yields ammonium iodide and boron imide. The latter does not react with potassium solutions in ammonia at −33 or at 25°.

Introduction

A study[2] of the chemistry of monoammonia–boron trifluoride in liquid ammonia at −33° revealed that this compound does not always react as though it were completely solvolyzed. It was of interest to extend the investigation to the other halides; boron triiodide was studied in order to test the prediction of Joannis[3] that the triiodide would behave as do the trichloride and tribromide. His prediction was largely borne out by our work.

We find that the reaction proceeds as

$$2BI_3 + 9NH_3 \longrightarrow B_2(NH)_3 + 6NH_4I$$

Joannis found that the amide was formed in the case of the trichloride and tribromide. Possibly the reaction with the iodide is so exothermic that the imide is formed directly.

Experimental

Boron Triiodide.—Boron triiodide was prepared by the method reported by Schumb, Gamble and Banus.[4] All transfers, filtrations and resublimations were done under dry nitrogen. The final product was transferred to glass capsules, sealed and stored in a refrigerator. The purified product was a glistening white, crystalline material.

Anal. Calcd. for BI_3: B, 2.76; I, 97.24. Found: B, 2.97; I, 97.66.

It was found important in this preparation to exclude *all* moisture and to avoid heating the compound above its melting point after it had been separated from a large excess of iodine. The compound could not even be allowed to stand for long periods (days) at room temperature in sealed tubes without discoloration.

Reactions with Liquid Ammonia.—The reactions were carried out in a bulb which was fitted with a ground glass cap and a stopcock. A sample of boron triiodide was placed in the tared bulb in an anhydrous nitrogen atmosphere; then the bulb was reweighed. Especially purified anhydrous ammonia gas was admitted to the bulb through a previously flushed system, and finally liquid ammonia was caused to condense by cooling the bulb in a Dry Ice–acetone bath. Dilution of the incoming gaseous ammonia by the nitrogen retained in the bulb apparently inhibited the initial reaction, but the first drop of liquid to condense on the solid material reacted with extreme violence. The reaction products were not totally soluble in ammonia and a flocculent white precipitate settled out. After approximately 3 ml. of liquid ammonia was condensed in the tube, the tube was transferred to a bath of liquid ammonia and allowed to remain 4 to 6 hr. The ammonia in the reaction tube was finally allowed to boil away through a mercury trap. The bulb and contents were then evacuated to constant weight at room temperature. The results of four such runs may be seen in Table I.

TABLE I

RESULTS OF REACTION OF BORON TRIIODIDE WITH LIQUID AMMONIA

BI_3, g.	Product, g.	Moles NH_3 per mole BI_3
0.3484	0.4172	4.55
.3907	.4674	4.52
.5800	.6731	4.49
.4965	.5916	4.41

The ratio of 4.5 moles of ammonia per mole of boron triiodide, obtained by weighing the product, was confirmed by chemical analysis of the product.

Calcd. from ratio: NH_3, 16.36. Found: NH_3, 16.2.

An X-ray diffraction analysis of the product revealed that ammonium iodide was present.

Reactions with Potassium in Liquid Ammonia.—In order to confirm the findings described above and to determine if any of the reaction products other than the ammonium iodide were capable of undergoing reduction, three reactions of these products with metallic potassium were carried out.

In the first two of these reactions an apparatus similar to that described by Watt and Keenan[5] was employed.

The entire apparatus was placed within a dry box and loaded with a weighed sample of boron triiodide. All openings to the apparatus were plugged before it was removed and attached to a system for introduction of ammonia and collection of gaseous reaction products. Ammonia was introduced and condensed as described above except that only a liquid ammonia coolant bath was used.

Approximately 30 ml. of ammonia was condensed on the triiodide in the reactor tube and the resulting mixture was titrated with a standard solution of potassium while being stirred with a slow stream of gaseous ammonia. In both reactions a very sharp end-point was found at 3 equivalents of potassium per mole of boron triiodide. The blue color caused by the slight excess of potassium at the end-point lasted for over an hour indicating that no further reaction was likely.

The gaseous reaction product was collected and shown to be hydrogen. An ammonia-soluble solid product was washed through the in-line filter and collected in a tared flask. A sparingly soluble solid product was caught on the in-line filter. The products were freed of ammonia by evaporation at room temperature, evacuated and weighed. X-Ray and chemical analyses indicated that the ammonia-soluble product was almost pure potassium iodide. The exact composition of the insoluble product was not established. No sharp lines were obtained by X-ray diffraction, only two broad halos. Spot analyses showed that the material contained nitrogen and boron but no potassium and iodine. These data indicate that boron imide is formed, since Joannis[3] states that the amide is ammonia soluble while the imide is ammonia insoluble.

In a third reaction the insoluble product was exposed to a liquid ammonia solution of potassium for 4 hr. at 25° in a sealed tube. There was no apparent change in the material and its X-ray diffraction pattern (two halos) was the same as before exposure to potassium.

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