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

KNOXVILLE, TENNESSEE

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

The Ammonolysis of Boron Triiodide in Liquid Ammonia

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

RECEIVED JANUARY 21, 1956

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.

KNOXVILLE, TENNESSEE

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

[2] W. J. McDowell and C. W. Keenan, THIS JOURNAL, **78**, 2065 (1956).

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

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