

including the use of the universal stage was shown.

4. Some attempt was made to explain the data

in terms of structure and chemical constitution.

STATE COLLEGE, PA.

RECEIVED DECEMBER 12, 1939

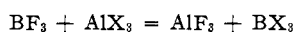
[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 80]

The Reaction of Boron Fluoride with Aluminum Chloride or Bromide

BY E. LEE GAMBLE, PAUL GILMONT AND JOHN F. STIFF

Discussion

The comparative lack of volatility of aluminum fluoride (melting point 1040°) with respect to the other halides of aluminum may be taken advantage of for the preparation of various volatile halides. For example, this paper describes the preparation of boron chloride and of boron bromide by the action of boron fluoride on the corresponding aluminum halide.



The ease with which the reactants are obtainable and the differences in volatility make this a simple means of preparation. It is possible that mixed fluorohalides of aluminum are intermediate products of this reaction, but they have not been isolated in a state of purity. The action of boron fluoride on aluminum iodide has produced small amounts of boron iodide but as yet the yields have been quite low. The development of this preparation is to be continued. Boron chloride or bromide is also produced when potassium fluoborate is heated with aluminum chloride or bromide but the yields obtained are not as satisfactory as when boron fluoride is used.

No fluorochlorides or fluorobromides of boron have ever been reported, nor have any been detected in this investigation. To determine whether the known fluorochlorides of silicon¹ could be prepared by this type of reaction, sodium fluosilicate was heated with aluminum chloride, the volatile products obtained proved to be only silicon tetrachloride and tetrafluoride, containing none of the fluorochlorosilanes.

The conversion of volatile fluorides into chlorides or bromides by means of aluminum chloride or bromide should prove to be somewhat general. From one point of view, the results of this reaction may be looked upon as the reverse of those of the Swarts reaction for the production of fluorides

or mixed fluorohalides by means of antimony fluoride.²

Many of the methods described in the literature for the preparation of the boron halides have been repeated in this Laboratory.³ It is felt that the preparation of boron bromide from boron fluoride and aluminum bromide is a simpler method than any hitherto described. Also, the preparation of boron chloride by this method may prove convenient.

Experimental

Reagents.—Potassium fluoborate was prepared by dissolving boric acid in 48% hydrofluoric acid and adding potassium carbonate. The product was recrystallized from hot water and dried at 110°.⁴ Boron fluoride was prepared by the action of hot concentrated sulfuric acid on a mixture of potassium fluoborate and boric oxide.⁵ The aluminum bromide was prepared by slowly adding bromine to an excess of aluminum, in an ordinary distilling flask cooled by water.

Reactions with Boron Fluoride.—The flask in which the reactions were carried on was dumbbell-like in appearance and was constructed by sealing a 1-liter round-bottomed flask to the bottom of a half-liter distilling flask by means of 25 cm. of 30-mm. tubing. The tube for the introduction of the boron fluoride passed through a one-hole cork stopper in the distilling flask and extended to the middle of the larger flask. The smaller flask served as a condenser to prevent large quantities of the aluminum halide from distilling over with the product. A weighed quantity of aluminum chloride was poured into the reaction flask, or aluminum bromide was distilled in from the flask in which it was prepared, and its weight determined by difference. The boron fluoride generator was connected to the reaction flask by means of a small bubbler containing concentrated sulfuric acid. The rate of flow of the boron fluoride was comparatively rapid, about thirty minutes for 2 moles of gas. After the apparatus was swept out with boron fluoride, the large flask containing the

(2) F. Swarts, *Acad. roy. de Belgique*, **24**, 309 and 474 (1892); *Bull. soc. chim.*, [4] **35**, 1557 (1924).

(3) An effort was made to see whether, in the preparation of boron trichloride [BCl₃] by relatively low temperature reactions, some B₂Cl₄ was not formed at the same time. Careful distillation of the reaction products produced only negative results.

(4) "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 24.

(5) Ref. 4, p. 23.

(1) W. C. Schumb and E. L. Gamble, *THIS JOURNAL*, **56**, 3943 (1932); H. S. Booth and C. F. Swinehart, *ibid.*, **57**, 1333 (1935).

aluminum halide was heated gently by means of a free flame whereupon the reaction soon started. For the preparation of boron chloride gentle heating was found desirable as long as the reaction took place. Then, using two burners, both flasks were heated strongly with a stream of boron fluoride still passing through the reaction flasks. After continued heating, the aluminum fluoride fell from the sides of the flask as a light white powder. For the preparation of the boron bromide the aluminum bromide was refluxed gently in a stream of boron fluoride. The contents of the flask soon solidified and again the mass was strongly heated in boron fluoride. The effluent gases were passed into a U-tube cooled with solid carbon dioxide and alcohol, protected by a drying tube. When the reaction was over the U-tube was sealed off and its contents distilled. In the preparation of boron bromide small amounts of bromine were obtained but were readily removed by shaking with mercury. A little metallic aluminum added to the preparation flask decreased the amount of bromine formed. In order completely to remove boron fluoride from boron chloride or bromide, distillation in a good column was desirable. From one-half a mole of aluminum chloride and two moles of boron fluoride 80% yields of boron chloride have been obtained. Using comparable amounts of reactants, 70% yields of boron bromide have been obtained.

Pure aluminum fluoride was not obtained as the by-product of the reaction, appreciable amounts of chloride or bromide being present. Analysis has shown the amount of bromine to be as high as 40% (theoretical for AlF_2Br is

55%); but this was decreased very markedly when the solid product was heated strongly in a stream of boron fluoride.

Reaction with Potassium Fluoborate.—When either aluminum chloride or bromide was heated with potassium fluoborate, some boron chloride or bromide, together with boron fluoride, was formed. An excess of the aluminum halide increases the percentage conversion of the fluoborate.

In an apparatus somewhat similar to that described above, one mole of aluminum chloride and one-half a mole of potassium fluoborate were heated by means of an oil-bath for four hours, with the temperature slowly increasing from 150 to 175°. The product was condensed in liquid nitrogen. The recovery of pure boron chloride was 0.26 mole, a yield of 56%, based on the potassium fluoborate used. Under comparable conditions yields of around 30% of boron bromide have been obtained.

Summary

Boron fluoride and potassium fluoborate have been found to react with aluminum chloride or bromide to produce good yields of boron chloride or bromide. The conditions of the reactions are given and the use of boron fluoride is particularly recommended as a means of preparing boron bromide. No fluorochlorides or fluorobromides of boron have been isolated in this investigation.

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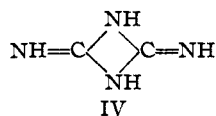
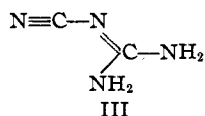
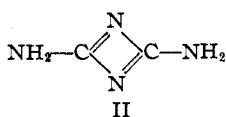
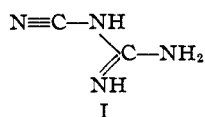
RECEIVED FEBRUARY 19, 1940

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 767]

The Crystal Structure of Dicyandiamide

By E. W. HUGHES

Several different structures have been proposed for the dimer of cyanamide but no absolutely conclusive evidence has ever been given for any one of them. In past years many people have preferred the cyanoguanidine¹ structure I.



But even fairly recently² arguments have been advanced in favor of the cyclic structure II. The closely related alternatives III and IV, which

(1) For a good summary of the arguments, as well as one of the more important original investigations, see Hale and Vibrans, *THIS JOURNAL*, **40**, 1046 (1918).

(2) Bell, *Sci. Proc. Roy. Dublin Soc.*, **18**, 207 (1926).

differ from I or II only in the disposition of hydrogens and double bonds, also have been proposed. I have made an X-ray examination of crystalline dicyandiamide for the purpose of resolving this long-standing controversy, with the results reported below.

Several previous crystallographic investigations have been recorded. In 1911 Heydrich³ reported the crystals as monoclinic holohedral with $a : b : c = 1.1109 : 1 : 1.4213$, $\beta = 115^\circ 20'$. He also found strong positive birefringence and that the acute bisectrix makes an angle of about 11° with c in the acute angle β' . The cleavage on $\{100\}$ is excellent and that on $\{001\}$ is good. In 1927 Baier⁴ made an independent examination. Although he chose a different axial system, with $\beta = 90^\circ 31'$, his axial ratios, $a : b : c = 1.0021 :$

(3) Heydrich, *Z. Krist.*, **48**, 278 (1910-1911).

(4) Baier, *ibid.*, **65**, 719 (1927).