[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

B-Trichloroborazole[1]

BY CHARLES A. BROWN[2] AND A. W. LAUBENGAYER

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The reaction of boron trichloride and ammonium chloride at temperatures above 110° produces B-trichloroborazole as colorless crystals, melting at 84° and subliming readily. This compound is soluble in such anhydrous solvents as benzene, carbon tetrachloride and ether, but reacts vigorously with water and alcohols. Cryoscopic measurements of benzene solutions and vapor density measurements show the molecular formula to be $Cl_3B_3N_3H_3$. This molecule consists of a six-membered ring of alternate boron and nitrogen atoms with one chlorine atom bonded to each boron atom and one hydrogen attached to each nitrogen. The equation determined for the vapor pressure–temperature relations in the solid range 40.7–83.7° is $\log_{10} P_{\text{mm}} = -3.743/T + 11.73$; in the liquid range 86.6–113.3°, $\log_{10} P_{\text{mm}} = -2.497/T + 8.25$. The heats of sublimation and vaporization are 17 and 12.3 kcal./mole, respectively. B-Trichloroborazole undergoes slow irreversible thermal decomposition above 100°, with the evolution of hydrogen chloride and the formation of non-volatile solids. Hydrolysis leads to rupture of the ring with the formation of boric acid and ammonium and chloride ions. The simple synthesis described provides an easy method for preparing cyclic condensed boron–nitrogen systems in good yield.

Wiberg and Bolz[3] first prepared B-trichloroborazole by the thermal decomposition of the addition compound of borazole and hydrogen chloride, $B_3N_3H_6 \cdot 3HCl$. No analyses, physical properties or chemical properties were reported. In further studies of derivatives of borazole, Wiberg and Hertwig[4] prepared N-trimethyl-B-trichloroborazole by the reaction of boron trichloride and monomethylamine at 250°. In a similar manner Jones and Kinney[5] thermally decomposed the addition compound of aniline and boron trichloride to obtain the corresponding substituted borazole. Studies of the reaction of ammonia and boron trichloride at low temperatures[6] indicated a variety of solid products, none of these having been identified as B-trichloroborazole. Recent ultraviolet absorption studies[7] and X-ray diffraction analysis[8] have established the cyclic structure of B-trichloroborazole and the heat of formation has been reported.[9]

Two methods for the preparation of B-trichloroborazole are described in this paper. In either case boron trichloride and ammonium chloride were allowed to react at elevated temperatures. Little, if any, reaction of boron trichloride and ammonia chloride occurs below 110°. Above this temperature hydrogen chloride, B-trichloroborazole and non-volatile products are formed.

Attempts to prepare B-trichloroborazole by the reaction of boron trichloride with ammonia gas resulted in only traces of the desired compound. In this case the products were almost wholly white, non-volatile solids.

Experimental

Preparation. Method 1.—Small quantities of B-trichloroborazole were prepared conveniently in the following manner. Dry, powdered ammonium chloride was placed at one end of a long Pyrex combustion tube and heated by a small electric furnace to 165–175°. A slow stream of boron trichloride and dry nitrogen was passed over the ammonium chloride, and the B-trichloroborazole condensed as needle-like crystals on the cool portions of the tube. A phosphoric oxide drying tower at the outlet side prevented moisture from entering the apparatus. The rate of flow of boron trichloride was adjusted until only a small amount of fuming occurred at the exit, and the reaction was continued until B-trichloroborazole no longer formed. The crude product was removed from the tube, quickly transferred to a vacuum sublimation apparatus, and sublimed at 60–70°.

The unreacted ammonium chloride was recovered, and the yield of B-trichloroborazole was calculated to be 35%, based on the amount of ammonium chloride used. Although the reaction might be written as

$$3NH_4Cl + 3BCl_3 \longrightarrow Cl_3B_3N_3H_3 + 9HCl$$

the principal products are white, non-volatile solids, probably boron amide or boron imide.

By mixing the ammonium chloride with asbestos fibers, placing the mixture between glass wool plugs in the combustion tube, expanding the area of the tube in which the product collects, and running the reaction at 200° it is possible to obtain yields as high as 50%.[10]

Method 2.—B-Trichloroborazole was prepared by refluxing a mixture of chlorobenzene and ammonium chloride in the presence of boron trichloride vapor. The apparatus consisted of a one-liter three-necked flask fitted with a mercury-sealed Hershberg stirrer. One neck of the flask was provided with a water cooled reflux condenser which was attached in turn to a Dry Ice–acetone reflux head. The outlet of the head was connected to a phosphoric oxide drying tower to prevent moisture from entering the apparatus. The third neck of the flask was fitted with an inlet tube which extended to the bottom of the flask. A sealed tube of boron trichloride and a tank of dry nitrogen were attached to this inlet tube.

In a typical run 0.48 mole of dry ammonium chloride and 300 ml. of dry chlorobenzene were placed in the reaction flask. A sealed tube containing 0.48 mole of boron trichloride was attached to the inlet tube. Dry nitrogen was passed through the apparatus to remove moisture, and the reflux head was cooled in a Dry Ice–acetone mixture. The contents of the reaction flask were heated to reflux temperature, accompanied by vigorous stirring. The tube of boron trichloride was opened and the stream of dry nitrogen slowly carried the boron trichloride into the reaction flask. The temperature of the boron trichloride tube was controlled such that a minimum of boron trichloride was lost through the reflux head.

At the end of ten hours all of the boron trichloride had been introduced. The flask was cooled to room temperature and its contents filtered through a sintered glass filter in the absence of moisture. The solvent was removed by vacuum distillation at room temperature, and the crude solid residue was purified by vacuum sublimation. The unreacted ammonium chloride was recovered. The 0.058

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[2] Department of Chemistry, Western Reserve University, Cleveland, Ohio.

[3] E. Wiberg and A. Bolz, *Ber.*, **73**, 209 (1940).

[4] E. Wiberg and K. Hertwig, *Z. anorg. Chem.*, **225**, 141 (1947).

[5] R. G. Jones and C. R. Kinney, THIS JOURNAL, **61**, 1378 (1939).

[6] Martius, *Ann.*, **109**, 79 (1859); Joannis, *Compt. rend.*, **135**, 1106 (1902).

[7] C. Rector, G. Schaeffer and J. Platt, *J. Chem. Phys.*, **17**, 460 (1949).

[8] D. L. Coursen and J. L. Hoard, THIS JOURNAL, **74**, 1742 (1952).

[9] E. R. Van Artsdalen and A. S. Dworkin, *ibid.*, **74**, 3401 (1952).

[10] F. B. Hutto, Jr., Thesis, Cornell University, 1950.

mole of B-trichloroborazole obtained indicate a yield of 36%.[11]

Analysis.—Samples of the compound were boiled in an excess of a 6 *M* aqueous solution of sodium hydroxide. The ammonia liberated was absorbed and titrated in the usual manner. Boron was determined as boric acid by dissolving weighed samples in dilute sodium hydroxide and titrating in the presence of mannitol. Chlorine was determined gravimetrically.

Anal. Calcd. for $Cl_3B_3N_3H_3$: Cl, 57.85; B, 17.65; N, 22.84. Found: Cl, 57.62, 57.80, 57.72; B, 17.88, 17.36, 17.62; N, 22.83, 22.84.

Molecular Formula.—Cryoscopic measurements of benzene solutions were made in a vacuum-type cell in order to preserve anhydrous conditions. The results of these measurements are summarized in Table I and indicate that in benzene solution the molecular form is $Cl_3B_3N_3H_3$, with no apparent association or dissociation in the concentration range investigated.

TABLE I

CRYOSCOPIC MEASUREMENTS OF $Cl_3B_3N_3H_3$

Wt. of sample, g.	Wt. of benzene, g.	Obsd. mol. wt.
0.5446	69.3	181
0.5446	89.8	182
0.5201	61.5	188
0.5201	84.3	183
		Av. 183.4

Calcd. for $Cl_3B_3N_3H_3$ 183.9

Vapor density measurements were obtained using an all-glass "sickle" cell.[12] A sample of 0.0819 g. in a volume of 704.3 ml. gave molecular weights that ranged from 197 at 90.3° to 190 at 132.3°. A second sample of 0.2182 g. in a volume of 668.5 ml. gave molecular weights ranging from 194 at 110.3° to 187 at 141.1°. The measurements indicate that the principal molecular species in the vapor state is $Cl_3B_3N_3H_3$.

Appearance and General Characteristics.—B-Trichloroborazole is a colorless, crystalline solid at room temperature. The crystals belong to the orthorhombic system. Samples stored in sealed tubes for several months at room temperature showed a small amount of decomposition with the formation of a non-volatile solid product. The compound is extremely sensitive to moisture, evolving hydrogen chloride when in contact with moist air. It reacts vigorously with excess water in a highly exothermic manner to give boric acid, ammonium ion and chloride ion.

Melting Point and Density.—The melting point of B-trichloroborazole in sealed, evacuated capillaries was observed to be 83.9–84.5°. Its density was determined pycnometrically to be d_4^{25} 1.5_8, using anhydrous pyridine as the immersion liquid. (The compound reacts slowly with pyridine.)

Solubility.—A qualitative study of the solubility of B-trichloroborazole in various anhydrous liquids was obtained by visual methods. About 5 ml. of solvent was distilled into a bulb containing 0.5 g. of compound. Evidence of solubility was obtained, the solvent removed, and a melting point taken to determine whether any reaction occurred. The compound appeared to be soluble without reaction in benzene, cyclohexane, carbon disulfide, carbon tetrachloride, chloroform, diethyl ether and chlorobenzene. Methyl and ethyl alcohols react vigorously with the evolution of hydrogen chloride. The compound was apparently insoluble in pyridine and nitrobenzene, although some reaction was observed after several days of contact with these liquids.

Saturation Vapor Pressure; Heats of Sublimation and Vaporization.—Vapor pressure–temperature data were obtained for $Cl_3B_3N_3H_3$ using an all-glass "sickle" cell.[12] Typical results are summarized in Table II for the temperature range 40.7 to 113.3°. Above about 100° a slow irreversible decomposition occurs with the formation of hydrogen chloride. A plot of $\log_{10} P$(mm.) *versus* $1/T$ gave two straight lines that intersected at about 86°, approximately the melting point of the compound. However, the direct determination of the melting point (83.9–84.5°) is considered to be more precise.

TABLE II

SATURATION VAPOR PRESSURES OF $Cl_3B_3N_3H_3$

	Pmm	
t, °C.	Obsd.	Calcd.
40.7	0.6	0.6
51.7	1.4	1.6
60.3	3.7	3.1
71.1	6.9	7.1
81.4	12.6	11.6
83.3	15.8	16.7
(melts)		
86.6	19.8	20.5
91.7	25.5	25.6
93.5	27.2	27.7
102.3	39.3	40.0
107.5	51.2	49.3
113.3	61.1	62.1

In the temperature range 40.7 to 83.7° the equation calculated for the sublimation pressures of the solid phase is $\log_{10} P(\text{mm}) = -3.743/T + 11.73$. The average heat of sublimation is 17 kcal./mole. In the range 86.6 to 113.3° the calculated equation for the pressures of the liquid phase is $\log_{10} P(\text{mm}) = -2.497/T + 8.25$, and the average heat of vaporization is 12.3 kcal./mole.

Thermal Decomposition.—Samples of B-trichloroborazole were heated in sealed glass tubes. Decomposition occurred slowly above about 100° with the formation of hydrogen chloride. The evolved gas was identified by vapor density measurements. Although samples were heated as high as 450° for five and one-half hours, only 70 to 85% of the hydrogen and chlorine present was obtained as hydrogen chloride. Powder X-ray diffraction patterns of the solid residue of the decomposition were obtained, but the presence of boron nitride could not be confirmed.

ITHACA, NEW YORK

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[11] The use of a modification of this method to obtain B-trichloroborazole, an intermediate in the synthesis of borazole, has been reported by R. Schaeffer, M. Steindler, L. Hohnstedt, H. S. Smith, Jr., L. B. Eddy and H. I. Schlesinger, THIS JOURNAL, **76**, 3308 (1954). They obtained an initial yield of about 40% B-trichloroborazole and, when more of the reagents were added to the residues from the initial reaction, the yield is reported to approach 90%.

[12] A. W. Laubengayer and F. B. Schirmer, THIS JOURNAL, **62**, 1578 (1940).