

Fig. 2.—Dependence of the association constant of $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{Pi}^-$ on the macroscopic dielectric constant of the solvent. Point numbers correspond to those given to the solvent in Table III.

It may be significant that the enhancement of the dielectric constant of ethylene chloride in the

presence of the picrate (from 10.23 to 11.2) is less than that in the presence of the perchlorate (from 10.23 to 12.4). Results available at present are insufficient to warrant a conclusion regarding the dependence of the magnitude of this enhancement on the properties of the ions of the dissolved salt. In view of our interpretation of this enhancement it seems reasonable to predict that it (this enhancement) will be found to increase (1), with decrease in the size of ions of like charge and (2), with increase in the charge of ions of the same size.

The slope of the straight line in Fig. 2 is not alone sufficient in this case to permit evaluation of the a -parameter of this picrate. As seen from equation 4 the slope is

$$d \log K_A/d(100/D) = (0.4343/100)(\epsilon^2/akT + \mu\epsilon/d^2kT)$$

The linearity between $\log K_A$ and $100/D$ does, however, warrant the conclusion that the a -parameter of this picrate has the same value in each of the seven solvents. If this were not so, the change in the value of ϵ^2/akT (with change in D) would need to be equal and opposite in sign to that of $\mu\epsilon/d^2kT$; a restriction which seems extremely unlikely. It seems far more reasonable to presume that the value of μ , the dipole moment of the picrate ion and of the d -parameter of this picrate are constant, independent of the dielectric constant of the solvent

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The Preparation of Boron Monoxide and its Conversion to Diboron Tetrachloride¹

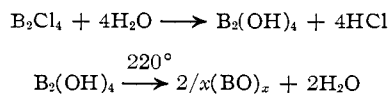
BY A. L. McCLOSKEY, R. J. BROTHERTON AND J. L. BOONE

RECEIVED MAY 12, 1961

Tetrahydroxydiboron was prepared by hydrolysis of tetra-(dimethylamino)-diboron in aqueous hydrochloric acid solution and by neutral hydrolysis of tetraisopropoxy or tetraethoxydiboron. The anomalous hydrolysis of tetramethoxydiboron is also discussed. Boron monoxide was prepared by dehydration of tetrahydroxydiboron and its possible structure discussed. Boron monoxide was converted to diboron tetrachloride by reaction with boron trichloride at approximately 200°. This conversion completes a series of reactions which establishes the integrity of the boron-boron bond in a number of related compounds.

Introduction

Wartik and Apple prepared tetrahydroxydiboron, $\text{B}_2(\text{OH})_4$, by the hydrolysis of diboron tetrachloride and converted it into boron monoxide, $(\text{BO})_x$, by dehydration at 220°. The boron mon-



oxide prepared by this procedure was white, or colorless, and was stable in vacuum up to about 500°. However, at 650° it was converted to an amber form which was assumed to be the same as

the boron monoxide reported from the reaction of zirconium oxide with elemental boron at elevated temperature.³ More recently boron monoxide was reported as a product of the reaction of boric oxide with elemental boron, and presumably this is also a high-temperature form.⁴ However, a number of inconsistencies exist concerning the nature of the so-called low-temperature and high-temperature modifications and the relation between these forms is not well understood.

Work has now been performed which gives a better insight into the boron monoxide prepared directly from compounds known to contain boron-boron bonds. Since very little information was available concerning this substance, it was essential that a comparison be made between previously reported boron monoxide and that available

(1) The research reported in this document was supported by Wright Air Development Division, Air Research and Development Command, United States Air Force, under contract AF 33(616)-5931. A portion of this research was reported in a preliminary communication, A. L. McCloskey, J. L. Boone and R. J. Brotherton, *J. Am. Chem. Soc.*, **83**, 1766 (1961).

(2) T. Wartik and E. F. Apple, *ibid.*, **77**, 6400 (1955).

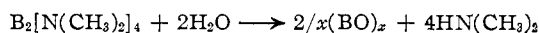
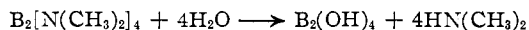
(3) E. Zintl, W. Morawietz and E. Gastinger, *Z. anorg. u. allgem. Chem.*, **245**, 8 (1940).

(4) F. A. Kanda, A. J. King, V. A. Russell and W. Katz, *J. Am. Chem. Soc.*, **78**, 1509 (1956).

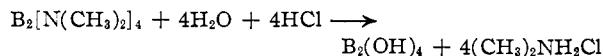
from new sources of diboron compounds. Tetrahydroxydiboron has been prepared by the hydrolysis of tetra-(dimethylamino)-diboron $B_2[N(CH_3)_2]_4$,⁵ tetraethoxydiboron, $B_2(OC_2H_5)_4$,⁶ or tetraisopropoxydiboron, $B_2[OCH(CH_3)_2]_4$,⁶ and dehydrated to boron monoxide. Reaction with water converts this oxide back to tetrahydroxydiboron, while reaction with boron trichloride converts it into another simple diboron compound, diboron tetrachloride.

Discussion

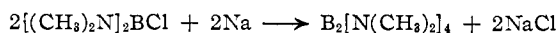
The hydrolysis of tetra-(dimethylamino)-diboron was expected to yield tetrahydroxydiboron or boron monoxide according to the equations



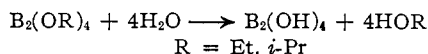
However, extensive studies have shown that with water in either diethyl ether or diglyme solution approximately one mole of amine was retained per mole of starting diboron compound. Dimethylamino groups were also retained when tetra-(dimethylamino)-diboron was dissolved in excess water.⁷ Acid hydrolysis (analogous to the previously described alcoholysis reaction)⁶ with stoichiometric amounts of aqueous hydrochloric acid



produced tetrahydroxydiboron in 56% yield. Indications were that the yield was controlled by the solubility of tetrahydroxydiboron in the water-amine hydrochloride solution, and a different solvent may allow a more efficient separation. This procedure has proved to be a very convenient method for the preparation of tetrahydroxydiboron, and subsequently boron monoxide, since tetra-(dimethylamino)-diboron is readily available from the reduction of chloro-bis-(dimethylamino)-borane with sodium.^{5,7}



The aqueous hydrolysis of tetraethoxydiboron or tetraisopropoxydiboron at 0° produced tetrahydroxydiboron in quantitative yield. The hy-



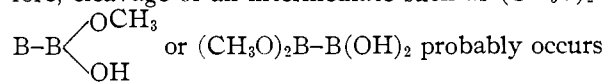
drolysis of tetramethoxydiboron was anomalous, however, and no conditions could be found which would allow hydrolysis without extensive boron-boron cleavage and the accompanying formation of hydrogen gas. When tetramethoxydiboron

(5) R. J. Brotherton, A. L. McCloskey, L. L. Petterson and H. Steinberg, *J. Am. Chem. Soc.*, **82**, 6242 (1960).

(6) R. J. Brotherton, A. L. McCloskey, J. L. Boone and H. M. Manasevit, *ibid.*, **82**, 6245 (1960).

(7) Recently H. Noth and W. Meister, *Chem. Ber.*, **94**, 509 (1961), in an independent investigation also found that the dimethylamino groups were incompletely hydrolyzed in water solution. They reported complete hydrolysis to tetrahydroxydiboron in excess methanol-water solution, but this compound was not isolated or characterized by elemental analysis. Dehydration gave boron monoxide, but this material was also not characterized.

was added to either stoichiometric or excess amounts of water (10 min., 25°), 32–42% of the theoretical amount of hydrogen was formed. When it was added to stoichiometric amounts of water in tetrahydrofuran (50 min., 25°), no hydrogen was evolved, but a white precipitate rapidly formed. However, after all volatile material was removed by high vacuum distillation at 25° and excess water was added, 33% of the calculated hydrogen was evolved in 5 min. at 25°. Tetrahydroxydiboron itself does not generate appreciable amounts of hydrogen in water, methanol or a mixture of these reagents during 1 hr. at 25°, and therefore, cleavage of an intermediate such as $(CH_3O)_2-$



at some early stage in the hydrolysis. The reason for the difference between this and the ethoxy case is not understood.

Tetrahydroxydiboron prepared either from tetra-(dimethylamino)-diboron or tetraethoxydiboron was comparable in all respects to that reported by Wartik.² It could be dehydrated to boron monoxide, or it could be dissolved in water or aqueous methanol with essentially no hydrogen evolution.

Boron monoxide, prepared from the above tetrahydroxydiboron in quantitative yield at 250° at reduced pressure,² was found to rapidly absorb water from the air, being transformed completely to $B_2(OH)_4$ in about 1.5 hr. under condition of 50% relative humidity at room temperature. Initial studies of the reactivity of boron monoxide involved a search for solvents in which it would be soluble either with or without reaction. Small amounts of boron monoxide placed in refluxing methanol, ethanol, isopropyl alcohol or *t*-butyl alcohol dissolved without any apparent cleavage of the boron-boron bond. Although boric oxide is soluble in methyl borate, presumably due to the formation of various methoxy-boric anhydrides such as trimethoxyboroxine, boron monoxide would not dissolve to any appreciable extent in this same material. It was also found to be insoluble in dimethylamine refluxing at atmospheric pressure.

The reaction of boron monoxide, prepared as described above, with boron trichloride led to a unique and useful synthesis of diboron tetrachloride, B_2Cl_4 . Stock⁸ originally prepared diboron tetrachloride, B_2Cl_4 , in small quantities by an arc reaction in which zinc electrodes were immersed in liquid boron trichloride. Schlesinger and co-workers^{9,10} have obtained diboron tetrachloride in higher yields by passing gaseous boron trichloride through a glow discharge between mercury electrodes at 1–2 mm. pressure. Subsequent modifications of this general discharge method utilizing gaseous boron trichloride have not resulted in significantly higher yields.^{11–13}

(8) A. Stock, A. Brandt and H. Fischer, *Ber.*, **53B**, 653 (1925).

(9) T. Wartik, R. Moore and H. I. Schlesinger, *J. Am. Chem. Soc.*, **71**, 3265 (1949).

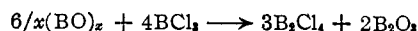
(10) G. Urry, T. Wartik, R. E. Moore and H. I. Schlesinger, *ibid.*, **76**, 5293 (1954).

(11) J. Frazer and R. Holzmann, *ibid.*, **80**, 2907 (1958).

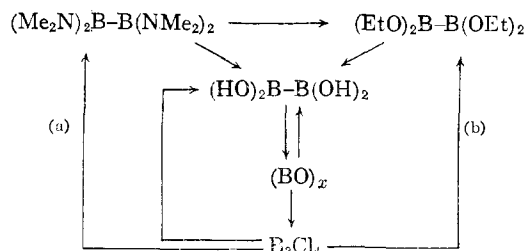
(12) A. Holliday and A. Massey, *ibid.*, **80**, 4744 (1958).

(13) A. Holliday and A. Massey, *J. Chem. Soc.*, 43 (1960).

Diboron tetrachloride has now been prepared by passing boron trichloride vapor over boron monoxide at 200°. The other product of this re-

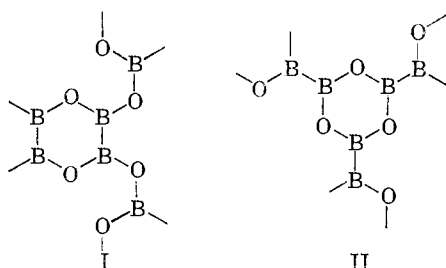


action was not isolated, but it was probably either boric oxide or a mixed compound of boric oxide and boron trichloride. This exchange conversion constitutes additional evidence for the integrity of the boron-boron bond in the following group of compounds, all of which have been related by interconversion as shown. Reactions a and b have been described previously.¹⁰



Although the structure of boron monoxide has not been determined, all chemical evidence indicates that it must have one boron-boron bond for each two boron atoms and that every boron atom must be attached to at least two oxygen atoms. Boron monoxide vaporization at 1300–1500° into gaseous B_2O_2 is further evidence for the presence of the boron-boron bond. Only at even higher temperatures was this bond ruptured to give appreciable quantities of the simple BO species.^{14–17}

Polymeric boron monoxide structures similar to those proposed by Wartik and Apple are possible.² However, in addition to the linear chains of six-membered B_4O_2 rings, a three dimensional structure composed of these rings is also possible (I). The four-membered B_2O_2 rings proposed by



these authors would probably be highly strained and six-membered, boroxole rings in a three dimensional structure are more probable (II). It is reasonable that the true structure might even vary with respect to ring size and composition. The possibility of tetracoördination about the boron atom similar to that found in crystalline boric oxide should not be overlooked.^{18,19}

(14) M. G. Inghram, R. F. Porter and W. A. Chupka, *J. Chem. Phys.*, **25**, 498 (1956).

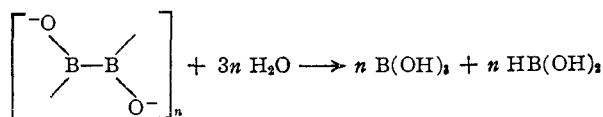
(15) A. W. Searcy and C. E. Myers, *J. Phys. Chem.*, **61**, 957 (1957).

(16) M. D. Scheer, *ibid.*, **62**, 490 (1958).

(17) J. R. Soulen and J. L. Margrave, *J. Am. Chem. Soc.*, **78**, 2911 (1956).

Although the nature of the boron monoxide prepared by dehydration of tetrahydroxydiboron is becoming more clearly understood, its relation to the so-called high-temperature boron monoxide has not been clarified. The colorless form of boron monoxide prepared by Wartik and Apple was reported to change to an amber form at 650°. However, with small amounts of water present, the conversion occurred at 400° and was highly exothermic. This energy evolution may have resulted from hydrolysis of some of the boron-boron bonds by the water remaining in the sample. The high-temperature, amber material was hard and brittle and much less soluble in water and methanol than the original boron monoxide, but the solutions still decolorized permanganate.

The boron monoxide reported by Kanda, *et al.*, from the reaction of boron and boric oxide at 1350° was also an amber glassy substance.⁴ However, this material exhibited chemical properties different from that prepared from tetrahydroxydiboron.² For example, the former reacted with water and alcohols to produce hydrogen and boron hydrides (specifically tetraborane) with a loss of as much as 30% of the boron monoxide.^{4,20} In several cases it was found to be pyrophoric on exposure to air. At temperatures above 450° it disproportionated into boric oxide and a black non-reducing solid which was assumed to be boron. These properties do not appear to be consistent with the boron monoxide observed here or elsewhere. The formation of boron-hydrogen bonds by solvolysis without breaking boron-boron bonds appears to be impossible, as does the attachment of more than one hydrogen atom to a boron atom under the conditions of the hydrolysis, as in the reaction



A reaction of this type would be very similar to that described by Shapiro and Weiss for the alcoholysis of boron hydrides.²¹ The boron-boron bond in the boron monoxide prepared from diboron compounds is not cleaved by water, and the loss of 30% of Kanda's material in water leads one to infer that it may contain as much as 30% of some other substance responsible for the boron hydrides and hydrogen. The formation of these materials is reminiscent of the reaction of magnesium boride with water and acids, and one is tempted to assume that this impurity is some species or mixture of materials with similar, extensive boron-boron bonding.

Experimental

Procedure and Analyses.—Standard vacuum-line apparatus and techniques were used whenever high-vacuum operations are indicated. Carbon and hydrogen analyses were

(18) S. V. Berger, *Acta Chem. Scand.*, **7**, 611 (1953).

(19) F. Dacheille and R. Roy, *J. Am. Cer. Soc.*, **42**, 78 (1959).

(20) F. A. Kanda, German Patent 1,040,520, October 9, 1958. British Patent 842,558, July 27, 1960.

(21) I. Shapiro and H. G. Weiss, *J. Phys. Chem.*, **63**, 1319 (1959).

done by Dr. Adelbert Elek, Los Angeles, California. Boron analyses were performed by the Parr bomb fusion method,²² since boron-boron compounds are not easily hydrolyzed to boric acid by normal hydrolysis techniques.

The Preparation of Tetrahydroxydiboron by the Acid Hydrolysis of Tetra-(dimethylamino)-diboron.—A solution of 28.5 ml. of 6.19 *N* hydrochloric acid was added slowly over a 45-minute period to a mixture of 8.40 g. (42.4 mmoles) of tetra-(dimethylamino)-diboron⁶ and 10.0 ml. of water at 0°. The resulting solid was filtered and dried to give 2.89 g. of crude tetrahydroxydiboron which retained small amounts of nitrogen. This crude product was washed with 10 ml. of 0.068 *N* hydrochloric acid and the residue dried to give 2.14 g. (56.3% yield) of tetrahydroxydiboron.

Anal. Calcd. for B₂O₄H₄: B, 24.20. Found: B, 23.91; N, < 0.3.

Attempted isolation of tetrahydroxydiboron in reactions of the type described above by sublimation or by chloroform extraction of the dimethylamine hydrochloride which is formed simultaneously gave products containing significant amounts of nitrogen. Acid hydrolysis in ether solvents also gave insoluble, partially hydrolyzed materials containing nitrogen.

Neutral Hydrolysis of Tetra-(dimethylamino)-diboron.—Tetra-(dimethylamino)-diboron (1.31 g., 6.6 mmoles) was added to 0.475 g. (26.4 mmoles) of water in 35 ml. of diglyme at room temperature. The resulting dimethylamine was bubbled into standard acid in a stream of dry nitrogen. Initial amine evolution was rapid giving 75% of the theoretical dimethylamine in 2 hr., but 4 additional hr. gave only an additional 3.5%. No further amine evolution could be detected, and the reaction mixture was filtered to give 0.73 g. of a white solid which reduced silver nitrate and appears from the following analyses to be mostly trihydroxy-(dimethylamino)-diboron or a material with approximately the same empirical formula.

Anal. Calcd. for B₂(OH)₃NMe₂: B, 18.57; C, 20.57; H, 7.78. Found: B, 18.6; C, 17.65; H, 6.76.

When 0.207 g. of this solid was added to 4 ml. of water at room temperature, the solid dissolved completely, but no amine evolution was detected in 10–15 minutes. The water was evaporated at 0.5 mm. to give 0.16 g. of a white solid which reduced silver nitrate and contained 18.04% boron, 14.79% carbon and 6.03% hydrogen. In an attempt to prepare boron monoxide directly, tetra-(dimethylamino)-diboron (4.83 g., 24.4 mmoles) was added to 0.85 g., (47.2 mmoles) of water in 90 ml. of diethyl ether at room temperature. When the resulting dimethylamine was swept into standard acid with dry nitrogen for 20 hr. (until no additional dimethylamine evolution could be detected), 77% of the theoretical dimethylamine was evolved. The reaction mixture was filtered to give 1.76 g. of a white solid containing 18.0% boron (the theoretical boron content of boron monoxide is 40.4%).

The Preparation of Tetrahydroxydiboron by the Hydrolysis of Tetraethoxydiboron and Tetraisopropoxydiboron.—Tetraethoxydiboron⁸ (1.248 g., 6.2 mmoles) was cooled to 0°, and 0.45 g. (25.0 mmoles) of water was added. The reaction mixture, which slowly solidified, was held at 0° for 1 hr., and additional water (about 1 g.) was added. The solid did not dissolve completely in the excess water, and after 10 minutes at room temperature, the excess water and ethanol were removed by vacuum evaporation to give a quantitative yield (0.56 g.) of tetrahydroxydiboron as a white powdery solid.

Anal. Calcd. for B₂O₄H₄: B, 24.19. Found: B, 23.77.

A quantitative yield of tetrahydroxydiboron was also obtained by a comparable hydrolysis of tetraisopropoxydiboron.

Hydrolysis of Tetramethoxydiboron in Excess Water.—Tetramethoxydiboron⁸ (255.2 mg., 1.753 mmoles) was purified in a vacuum line by fractional condensation at -45° and distilled into a 15-ml. flask containing excess water (3.0 g., 167 mmoles) at -195°. The isolated system was warmed rapidly to 25° and held at that temperature for 10 minutes before cooling to -78°. The resulting hydrogen was collected in a Toepler pump and measured at 16.4 cc. (0.732 mmole) or 41.8% of that calculated for complete cleavage of

the boron-boron bonds. Rewarming to 25° for an additional 90 minutes increased the total hydrogen to 18.0 cc. (0.804 mmole; 45.9%).

Hydrolysis of Tetramethoxydiboron with a Stoichiometric Amount of Water.—Tetramethoxydiboron (250.2 mg., 1.718 mmoles) was purified as in the preceding experiment and condensed onto 123.5 mg. (6.853 mmoles) of water at -195°. Rapid warming to 25° for ten minutes gave 0.557 mmoles of hydrogen (32.4%). An additional 45 minutes at 25° increased the total to 0.648 mmole (37.7%).

Hydrolysis of Tetramethoxydiboron in Ether Solvents.—Tetramethoxydiboron (190.8 mg., 1.310 mmoles) was added at -78° to 192.0 mg. (10.65 mmoles) of water in 10.0 ml. of diethyl ether. When the system was warmed rapidly to ca. 25° in a water bath, solids formed immediately with some hydrogen evolution. The flask was cooled to -78° after 10 minutes at 25°, and the hydrogen was collected in a Toepler pump (0.111 mmole, 8.4%). Additional periods of warming at 25° for 15 and 25 minutes brought the total hydrogen evolved to 14.9 and 19.9%, respectively. When tetramethoxydiboron (182.5 mg., 1.253 mmoles) was mixed with an approximately stoichiometric amount of water (93.0 mg., 5.167 mmoles) in 5.0 ml. of tetrahydrofuran and rapidly warmed from -78 to 25°, a clear solution formed initially but clouded quickly to give a white precipitate. During 50 minutes at 25°, only 0.5% of the calculated hydrogen was formed (0.006 mmole). However, when all volatile material was removed under high vacuum at 25° and an additional 2.0 grams of water was added at that temperature, 33.0% (0.415 mmole) of the calculated hydrogen was evolved in five minutes.

The Reactions of Tetrahydroxydiboron with Water and Methanol.—A solution of tetrahydroxydiboron was prepared by dissolving 25.0 mg. (0.467 mmole) of boron monoxide in 3.00 ml. of water at 25°. Only traces of hydrogen were formed during 3 hr. at this temperature (approximately 0.1% of that calculated for complete B-B cleavage).

The tetrahydroxydiboron above was dried at 25° under high vacuum and 60 mg. (1.87 mmoles) of methanol was added. Hydrogen evolution during 1 hr. at 25° was very slight under these conditions. Water (3.00 ml.) was added to the mixture at 25°; the resulting solution generated 1.5% (0.007 mmole) of the calculated hydrogen in 1 hr.

Boron Monoxide.—Tetrahydroxydiboron (0.538 g.) was heated to 250° at 0.5 mm. pressure and maintained at this temperature for 5 hr. to give 0.321 g. (99.7% yield) of boron monoxide as a fluffy white solid.

Anal. Calcd. for (BO)₂: B, 40.37. Found: B, 39.9; N, 0.0.

A 10.8-mg. sample of boron monoxide rapidly absorbed water from the laboratory atmosphere (50% relative humidity) and was completely converted to tetrahydroxydiboron in less than 2 hr. Tetrahydroxydiboron showed no weight increase when allowed to stand in the atmosphere in a similar manner.

Apparent Solubilities of Boron Monoxide.—Boron monoxide was added to various solvents at room temperature (except for dimethylamine) and the mixtures warmed slowly to reflux temperatures in a dry nitrogen atmosphere. The results are summarized as follows.

The Conversion of Boron Monoxide to Diboron Tetrachloride.—An approximately thirtyfold excess of boron trichloride was passed over 80.6 mg. of very finely divided boron monoxide at 200° and a pressure of about 450 mm. for 35 minutes. (The entire operation was performed in a standard high-vacuum system.) The boron trichloride was distilled from a reservoir at 0°, through a heated U-tube containing the boron monoxide suspended on top of a glass wool plug and into a receiver maintained at -3°. (Heating the boron monoxide at about 250° under vacuum for 5 hr. beforehand insured complete dehydration.) The retention time of the gas stream in the hot zone was estimated at two to three minutes. The products were fractionated to remove excess boron trichloride and to isolate any less volatile components. Between -45 and -85°, a sample (0.058 mmole) was collected which had a vapor pressure and infrared spectrum corresponding to those of diboron tetrachloride. An additional 0.134 mmole of diboron tetrachloride was isolated after two additional passes of the boron trichloride were made through the remaining boron monoxide under the same conditions as above except for a slightly higher temperature (236°). No attempt was made to force

(22) D. L. Hunter, L. I. Petterson and H. Steinberg, *Anal. Chim. Acta*, **21**, 523 (1959).

TABLE I

Solvent	Mg. (BO) ₂ added per ml. of solvent	Solubility	Notes
Methanol	11.0	Soluble at room temperature	Reduced AgNO ₃ readily after 2 hr. at 64° and 20 hr. at room temperature
Absolute ethanol	9.2	Dissolved rapidly on warming	Reduced AgNO ₃ readily after 5 hr. at 78°
Isopropyl alcohol	10.9	Dissolved rapidly on warming	Reduced AgNO ₃ readily after 5 hr. at 82°
<i>t</i> -Butyl alcohol	9.0	Dissolved slowly at 82°	Reduced AgNO ₃ readily after 2 hr. at 82°
Dimethylamine	2.7	Apparently insoluble	Added at -80° and warmed to 7°
Di-isopropylamine	5.4	Appeared to be slightly soluble at 83°
Methyl borate	2.6	Insoluble at 65°	Liquid layer did not reduce AgNO ₃
Methyl borate + 1% methanol	2.6	Soluble at reflux

the reaction to completion nor to analyze the residue for boron monoxide.

The infrared spectrum of the diboron tetrachloride corresponded closely with that of the pure material²³ with the strongest absorptions at 10.9 and 13.7 μ . Weak bands at 10.1 and 10.5 μ were attributed to small amounts of boron trichloride. The observed vapor pressures of the product are compared with those reported in the literature for pure diboron tetrachloride.⁵

(23) M. J. Linevsky, E. R. Shull, D. E. Mann and T. Wartik, *J. Am. Chem. Soc.*, **75**, 3287 (1953); D. E. Mann and L. Fano, *J. Chem. Phys.*, **26**, 1665 (1957).

Temp., °C.	Vapor pressure, mm.	
	Obsd.	Lit.
-30	6	6.8
-45	2.3	2.3

A sample of the diboron tetrachloride was hydrolyzed in a sealed Pyrex tube with excess water (16 hr. at 190°). Hydrogen was measured in the vacuum line and hydrogen chloride and boric acid were titrated with standard sodium hydroxide.

Anal. Calcd. H₂/B(OH)₃/HCl for B₂Cl₄: 1.00/2.00/4.00.
Found: 1.00/2.16/4.08.