The Reactions of Diboron Tetrachloride with Some Hydrogen Compounds of Non-metallic Elements and with Dimethyl Sulfide[1]
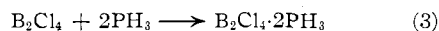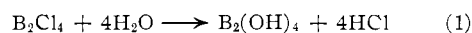
By Thomas Wartik and E. F. Apple

Diboron tetrachloride can be made to react with water, hydrogen sulfide and phosphine without accompanying cleavage of the boron-to-boron bond. Pure sub-boric acid results from reaction with water under the proper conditions. The adducts $B_2Cl_4 \cdot H_2S$ and $B_2Cl_4 \cdot 2H_2S$ exhibited moderate stability at $-78.5°$, but cleavage of the boron-to-boron bond occurred at higher temperatures. $B_2Cl_4 \cdot 2PH_3$ was prepared and exhibited moderate stability at room temperature. The adducts $B_2Cl_4 \cdot SMe_2$ and $B_2Cl_4 \cdot (SMe_2)_2$ were prepared and found to be more stable than the corresponding compounds prepared from dimethyl ether. BCl_2SH, whose oxygen analog has not been reported, was observed as a product of the hydrogen sulfide reaction. Several of its properties are described.
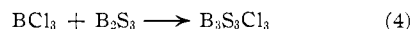
When B_2Cl_4 reacts with non-metallic elements, the only products observed are those which result from cleavage of the boron-to-boron bond.[2] Reaction of hydrogen compounds of the non-metallic elements with B_2Cl_4 is not necessarily accompanied by cleavage of the boron-to-boron bond. In some cases (water[3,4] and ammonia[5]) dehydrohalogenation, without boron-to-boron bond cleavage, occurs. In other cases (hydrogen sulfide and phosphine), the isolation of simple Lewis adducts was possible. Secondary reactions, involving cleavage of the boron-to-boron bond, were observed when B_2Cl_4 was treated with hydrogen sulfide (at room temperature) or with an excess of water (at 100° and above).

At room temperature, B_2Cl_4 reacts with water, excess hydrogen sulfide and excess phosphine according to the equations

$$B_2Cl_4 + 4H_2O \longrightarrow B_2(OH)_4 + 4HCl \qquad (1)$$
$$3B_2Cl_4 + 3H_2S \longrightarrow 4BCl_3 + B_2S_2 + 3H_2 \qquad (2)$$
$$B_2Cl_4 + 2PH_3 \longrightarrow B_2Cl_4 \cdot 2PH_3 \qquad (3)$$

$B_2(OH)_4$, the product of reaction 1, may be dehydrated at about 100°, as described by the authors in a previous publication,[3] to yield a white form of boron monoxide. The latter, on heating to 600°, is converted gradually to a tan solid, presumably the previously reported form of boron monoxide.[6-8]

The reaction of excess hydrogen sulfide with B_2Cl_4 produces, in addition to the products listed in equation 2, substances resulting from secondary reactions between trichloroborane, diboron trisulfide and the excess hydrogen sulfide employed. Trichloroborthiin, $B_3S_3Cl_3$, resulting from the action of BCl_3 on B_2S_3

$$BCl_3 + B_2S_3 \longrightarrow B_3S_3Cl_3 \qquad (4)$$

was obtained in small amounts. BCl_2SH, a previously unreported substance whose oxygen analog is not known, participates in the equilibrium

$$B_2S_3 + 4BCl_3 + 3H_2S \rightleftarrows 6BCl_2SH \qquad (5)$$

BCl_2SH is a colorless liquid which is unstable above 0°. Its vapor pressures between -45.2 and 0° were satisfactorily reproduced by the equation

$$\log P_{mm.} = -\frac{1375.6}{T} + 7.112$$

At $-78.5°$, hydrogen sulfide does not effect boron-to-boron bond cleavage. Instead, white solids with the approximate compositions $B_2Cl_4 \cdot H_2S$ and $B_2Cl_4 \cdot 2H_2S$ were obtained. The latter exhibits a slight dissociation pressure of hydrogen sulfide at $-78.5°$.

Hydrogen iodide did not seem to react with B_2Cl_4 at 0° over a period of 15 minutes.

As an extension of the main investigation, the behavior of dimethyl sulfide with diboron tetrachloride was studied. As is the case with dimethyl ether, two addition compounds, $B_2Cl_4 \cdot Me_2S$ and $B_2Cl_4 \cdot 2MeS$, were observed. Unlike the dietherate, however, $B_2Cl_4 \cdot 2Me_2S$ exhibits no measurable dissociation pressure of dimethyl sulfide at room temperature.

Experimental

Apparatus.—Standard vacuum apparatus was employed in these investigations.

Preparation and Purification of Reagents.—Diboron Tetrachloride was prepared by the method of Wartik, Moore and Schlesinger.[9] It exhibited a vapor pressure of 44 mm. at 0°.

Hydrogen iodide was prepared by the action of iodine on tetralin (Eastman Kodak Co.). The gaseous product was passed through two U-tubes held at $-78.5°$ into a U-tube held at $-196°$. The vapor pressure of the material retained in the $-196°$ bath was 485.8 mm. at $-45.2°$, compared with a reported value[10] of 486.5 mm.

Hydrogen sulfide (Matheson Chemical Co.) was purified by fractional condensation through two U-tubes, held at -111.9 and $-196°$, respectively. The vapor tension of the material retained at $-196°$ was 253.0 mm. at $-78.5°$, compared with a reported value[10] of 259.0 mm.

Phosphine was made by the action of concentrated sodium hydroxide solution on white phosphorus. It was purified by fractional condensation and exhibited a vapor pressure of 174.0 mm. at $-111.9°$, compared with a reported value[11] of 172.5 mm.

Dimethyl sulfide (Eastman Kodak Co.) was dried with anhydrous calcium sulfate and purified by fractional condensation. It exhibited a vapor pressure of 172.0 mm. at 0.0°, compared with a reported value[12] of 168.0 mm.

(1) Presented before the 131st meeting of the American Chemical Society in Miami, Florida, April, 1957.

(2) E. F. Apple and T. Wartik, This Journal, **80**, 6153 (1958).
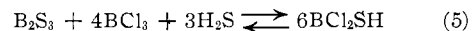
(3) T. Wartik and E. F. Apple, ibid., **77**, 6406 (1955).

(4) A. Stock, A. Brandt and H. Fischer, Ber., **58**, 653 (1925).

(5) G. Urry, T. Wartik, R. Moore and H. Schlesinger, This Journal. **76**, 5293 (1924).

(6) R. Ray and P. Sinha, J. Chem. Soc., 742 (1941).

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

(8) F. A. Kanda, A. J. King. V. A. Russell and W. Katz, This Journal, **78**. 1509 (1956).

(9) T. Wartik, R. Moore and H. Schlesinger, ibid., **71**, 3265 (1949).

(10) G. Maas and H. McIntosh, Proc. Roy. Soc. (Can.), **8III**, 65 (1914).

(11) F. Henning and A. Stock, Z. Physik, **4**, 226 (1921).

(12) H. Thompson and J. Linnett, Trans. Faraday Soc., **31**, 1743 (1935).

Reaction of B_2Cl_4 with Hydrogen Compounds of Non-metallic Elements.—With Hydrogen Iodide.—After B_2Cl_4 had been allowed to stand in contact with an excess of hydrogen iodide at $-78.5°$ for one week, followed by a period of 15 minutes at $0°$, it was found possible to recover 92% of the B_2Cl_4 unchanged. (Failure to effect complete recovery of the B_2Cl_4 probably was due to partial thermal decomposition.)

With Water.—Water (14.06 mmoles) and B_2Cl_4 (3.28 mmoles), on being mixed and allowed to warm in a sealed tube to room temperature, immediately produced a white solid. Standing for an additional 12 hr. at room temperature produced no further visible change, nor was hydrogen found to be present on opening the reaction vessel.

The volatile contents of the latter were found to weigh 0.490 g. Since this volatile matter consisted of a mixture of water and hydrogen chloride, separation by fractional condensation was not attempted. Instead, the mixture was treated with sodium hydroxide solution, in excess, and a volumetric chloride analysis was performed. 12.92 mmoles of hydrogen chloride was found to have been present in the reaction products. Subtraction of the weight of this quantity of hydrogen chloride from the total weight of volatile material gave 0.0196 g. as the weight of water recovered. These data indicate that the molar reaction ratio of water to B_2Cl_4 was 3.96 to 1.00 and that the molar ratio of hydrogen chloride produced to B_2Cl_4 used was 3.94 to 1.00. These findings are consistent with the equation

$$B_2Cl_4 + 4HOH \longrightarrow B_2(OH)_4 + 4HCl$$
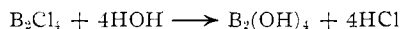
Mixing water (11.37 mmoles) and B_2Cl_4 (2.687 mmoles) and allowing them to remain in a sealed tube at $90°$ for three days resulted in the formation of 0.184 mmole of hydrogen, along with 10.81 mmoles of hydrogen chloride. The quantity of hydrogen produced corresponded to a cleavage of 6.85% of the boron-to-boron bonding in the product. When a lower ratio of water to B_2Cl_4 was employed (2.533 mmoles of the former to 2.450 mmoles of the latter) and the reaction was allowed to proceed for three days at $90°$, 0.631 mmole of hydrogen was produced, along with 1.956 mmoles of trichloroborane and 2.926 mmoles of hydrogen chloride. In this case boron-to-boron bond cleavage occurred to the extent of 28.3%. No unchanged B_2Cl_4 was recovered, and the non-volatile residue was light brown, instead of white.

Virtually complete cleavage of the boron-to-boron bond, in accordance with the equation

$$B_2Cl_4 + 6H_2O \longrightarrow 2H_3BO_3 + 4HCl + H_2$$
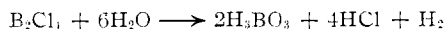
was achieved at $160°$. Water (18.99 mmoles) and B_2Cl_2 (2.575 mmoles) were mixed and allowed to stand in a sealed tube at $160°$ for 14 hr. The production of 2.485 mmoles of hydrogen indicated that the cleavage reaction had proceeded to the extent of 97%.

Some properties of sub-boric acid, $B_2(OH)_4$, will be described below.

With Hydrogen Sulfide.—At temperatures below $-78.5°$ B_2Cl_4 and hydrogen sulfide appear to react to form simple Lewis adducts. The reagents interact in a one-to-one molar ratio at $-78.5°$ to form a white solid, presumably the adduct $B_2Cl_4 \cdot H_2S$. In the presence of an excess of hydrogen sulfide, at $-78.5°$, an adduct of the composition $B_2Cl_4 \cdot 1.83H_2S$ was observed. This material, also a white solid, exhibits a slight dissociation pressure of hydrogen sulfide at $-78.5°$, which fact probably accounts for the deviation from the expected one-to-two ratio.

At temperatures above $-78.5°$, cleavage of the boron-to-boron bond, accompanied by the release of hydrogen, occurs. The following table indicates the extent of cleavage under varying conditions of time and temperature (an excess of hydrogen sulfide was used in all cases).

B_2Cl_4, mmoles	H_2S, mmoles	H_2 formed, mmoles	Temp., °C.	Time, hr.	Cleavage, %
1.598	8.203	0.921	25°	15	57.8
2.120	8.635	1.908	25°	240	90.0
0.904	5.242	0.725	50°	30	80.3
2.958	8.112	2.981	90°	4	100.8
1.585	7.284	1.567	90°	72	98.9

In those reactions where cleavage (as measured by hydrogen release) was essentially quantitative, a yellowish-white solid was produced, along with a mixture of volatile products condensable at $196°$. When the latter were passed through

a U-tube held at $-78.5°$ into another at $-196°$, a liquid was retained at $-78.5°$ which had a vapor pressure of 117.8 mm. at $0°$. This liquid, which exhibited only limited stability at $0°$ and above, was found to be reasonably pure (its vapor pressure at $0°$ was not volume-dependent). Its molecular weight, by vapor density, was 113.9, and it was found to contain 8.72% boron and 24.57% sulfur. The calculated values for BCl_2SH are 114.7, 9.41 and 27.87, respectively. The deviations from the calculated values are not unexpected, in view of the low stability of the substance. Further properties of the previously unreported BCl_2SH are discussed in a later section.

From the volatile reaction products which passed through the U-tube held at $-78.5°$, it was found possible, by further fractional condensation using traps held at $-111.9°$ and at $-196°$, to isolate 2.099 mmoles of reasonably pure hydrogen sulfide (vapor pressure at $-111.9° = 17.2$ mm.; reported value[10] $= 16.8$ mm.). The material retained at $-111.9°$ (3.70 mmoles) did not seem to be a pure substance but behaved very much like a prepared mixture of trichloroborane and hydrogen sulfide. Like the mixture in question, the prepared mixture was a gas at room temperature, a volatile solid at $-78.5°$, an almost entirely non-volatile solid at $-111.9°$, and was not separable by fractional condensation. Phase studies by Martin[13] have shown that compound formation between trichloroborane and hydrogen sulfide does indeed occur at low temperatures. In view of the above, no further attempt was made to obtain separation of this mixture by fractional condensation.

From the solid reaction product, when heated to $60°$ in vacuo, it was found possible to sublime small quantities of a white solid. The latter reacted vigorously with dilute sodium hydroxide solution and was shown to contain 14.43% boron (calculated for $B_3S_2Cl_3$ is 13.81%). In addition, the similarity in volatility ($B_3S_3Cl_3$ is reported to sublime at $50°$)[14] makes it likely that this material was $B_3S_3Cl_3$.

The reaction product not volatile at $60°$ was a yellow solid which was quickly hydrolyzed on exposure to air. Its analysis showed a boron content of 18.5% and a sulfur content of 77.7% (calculated values for B_2S_3 are 18.4 and 81.6%, respectively.) The low sulfur value is probably attributable to partial hydrolysis during handling.

The reaction between excess hydrogen sulfide and B_2Cl_4 at $90°$ was therefore shown to give rise to a complex mixture of products, including B_2S_3, $B_3S_3Cl_3$, BCl_2SH and BCl_3. As will be shown in a later section, equilibria exist involving these three substances and the excess hydrogen sulfide.

With Phosphine.—A mixture of 2.909 mmoles of phosphine and 0.40 mmole of B_2Cl_4 was maintained in a sealed tube at $-78.5°$ (at which temperature a white solid was observed to form immediately) for 8 hr. and at $0°$ for 1 hr. When the reaction tube was opened to the vacuum system, 2.152 mmoles of phosphine (vapor pressure $= 171.6$ mm. at $-111.9°$, reported value[10] $= 172.4$ mm.) was recovered, along with a volatile white solid. The amount of phosphine retained corresponds to the formation of an adduct with the formula $2BCl_4 \cdot 1.86PH_3$. The white solid was shown to consist of two components, the more volatile of which was present in relatively small quantity (by visual estimation) and exhibited a dissociation pressure of 9.8 mm. at $0°$. Since this dissociation pressure differed somewhat from that reported for $BCl_3 \cdot PH_3$ (7.2 mm. at $0°$, calculated from equation given by Gamble and Gilmont),[15] this adduct was prepared from trichloroborane and phosphine and its dissociation pressure at $0°$ was observed to be 9.0 mm.

The major reaction product was a white solid, undoubtedly $B_2Cl_4 \cdot 2PH_3$, with a vapor pressure of about 0.7 mm. at $25°$. It was separated from the more volatile $BCl_3 \cdot PH_3$ by trapping in a $-22.9°$ bath, through which the trichloroborane adduct readily passed. Both of the volatile solids seemed reasonably stable at room temperature. (Owing to the apparent stability of $B_2Cl_4 \cdot 2PH_3$ at room temperature, it is unlikely that the small amount of $BCl_3 \cdot PH_3$ obtained resulted directly from its decomposition. It is thought more probable that the vigor of the initial reaction decomposed some B_2Cl_4, yielding trichloroborane. The latter would then interact with phosphine to form $BCl_3 \cdot PH_3$.) $B_2Cl_4 \cdot 2PH_3$, however, underwent partial decomposition at $65°$, liberating phosphonium chloride (observed dissociation pressure at

(13) D. Martin, THIS JOURNAL, **67**, 1088 (1945).

(14) E. Wiberg and W. Sturm, Z. Naturf., **8b**, 530 (1953).

(15) E. Gamble and P. Gilmont, THIS JOURNAL, **62**, 717 (1940).

$-63.5° = 37.4$ mm.; reported value[16] $= 35.5$ mm.). It was extremely reactive in air, producing a mild explosion immediately upon exposure.

Reaction of B_2Cl_4 with Dimethyl Sulfide.—When a mixture consisting of 1.130 mmoles of B_2Cl_4 and 1.130 mmoles of dimethyl sulfide was allowed to stand at 0° for 0.5 hr., a colorless liquid formed, and both of the reactants were found to have disappeared. However, a small amount of cleavage of the thioether linkage was indicated by the release of 0.111 mmole of methyl chloride (vapor pressure observed $= 35.0$ mm. at $-78.5°$; reported value $= 33.0$ mm.). The liquid, which consisted largely of the adduct $B_2Cl_4 \cdot SMe_2$, was nonvolatile at 0°. After storage at room temperature for 24 hr. it became quite viscous, and after 48 hr. it had changed to a glassy solid. The latter was unstable in air and was readily decomposed by water

From a mixture of B_2Cl_4 (1.130 mmoles) and dimethyl sulfide (2.531 mmoles) which had been allowed to stand for several hours at 0°, it was found possible to recover 0.313 mole of dimethyl sulfide (vapor pressure at 0° $= 180.0$ mm.; reported value[12] $= 172.0$ mm.) and 0.033 mmole of methyl chloride. These results indicate a molar reaction ratio of B_2Cl_4 to dimethyl sulfide of 1.00 to 1.972. The white solid adduct $B_2Cl_4 \cdot 2SMe_2$, on prolonged pumping (24 hr. at room temperature) yielded only a relatively small amount of volatile matter (0.160 mmole), which was shown to be a mixture of dimethyl sulfide and methyl chloride. $B_2Cl_4 \cdot 2SMe_2$ is decomposed rapidly by water and more slowly by air.

Properties of $B_2(OH)_4$.—$B_2(OH)_4$ is a white solid which dissolved in a large excess of water to liberate traces of hydrogen. The rate of hydrogen evolution was increased somewhat by the addition of sulfuric acid and became quite rapid on the addition of sodium hydroxide. The solid inflamed on coming into contact with a watch glass heated by a soft Bunsen flame. On exposure to the atmosphere for 12 hr., the solid still retained strong reducing properties toward solutions of silver nitrate and potassium permanganate, indicating that it has reasonable air stability. The solid seems to be indefinitely stable at room temperature *in vacuo*, since no change (or gas evolution) was noticed in a sample stored under these conditions for several weeks.

In an effort to prepare the previously unreported $BCl(OH)_2$, $B_2(OH)_4$ was exposed to the action of excess chlorine for one day at room temperature. At the end of this time, the only volatile matter which was recovered, in addition to unchanged chlorine, was hydrogen chloride. Although the reaction proceeded only about 50% toward completion in one day, it is probable that cleavage of the boron-to-boron bond did occur but that the intermediate was unstable with respect to elimination of hydrogen chloride.

$$BCl(OH)_2 \longrightarrow HBO_2 + HCl$$
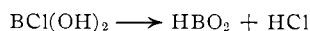
A preliminary report by the authors on the dehydration of $B_2(OH)_4$ has appeared in THIS JOURNAL.[3] Loss of water commences at 90° *in vacuo* and is complete after 4 hr. at 250°. 1.124 mmoles of $B_2(OH)_4$ liberated 2.278 mmoles of water in accord with the equation

$$B_2(OH)_4 \longrightarrow 2BO + 2H_2O$$
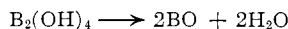
The resulting white boron monoxide, if completely dehydrated, undergoes a gradual transition to a light brown form at about 650° *in vacuo*. If traces of water remain with the monoxide, its conversion to the brown form takes place spontaneously at about 400° and energy is released rapidly enough to heat the solid to incandescence.

Properties of BCl_2SH.—The vapor pressures of BCl_2SH were determined at 0° and below in the usual manner except that, owing to the instability of the compound, the sample was repurified by fractional condensation (a U-trap held at $-78.5°$ retained the BCl_2SH and allowed volatile impurities to pass) and the pressure measuring system was flamed after each vapor pressure determination. The following table lists the observed values, together with those calculated from the equation given earlier.

T, °C.	P_{mm} (obsd.)	P_{mm} (calcd.)
0.0	117.8	119.0
-22.9	41.6	41.0
-30.7	27.2	27.4
-45.2	11.8	10.2

Using the given equation, the extrapolated boiling point was found to be 52°, the molar heat of vaporization 6300 cal., and Trouton's constant 19.4.

An addition compound was formed by treating BCl_2SH (0.972 mmole) with trimethylamine (0.967 mmole) and allowing the mixture to warm slowly to room temperature. A white solid $(BCl_2SH \cdot N(CH_3)_3)$ formed and no excess of either reagent was recovered. The solid released a small amount of methyl chloride (0.104 mmole, vapor pressure $= 36$ mm. at $-78.5°$; reported value $= 33$ mm.) on standing for several hours at room temperature, presumably with the formation of materials such as $(CH_3)_2N=BClSH$. Despite this slow decomposition, the addition compound $BCl_2SH \cdot N(CH_3)_3$ was far more stable than BCl_2SH itself.

Since the major products of the reaction between B_2Cl_4 and excess hydrogen sulfide appear to be diboron trisulfide, trichloroborane and hydrogen according to the equation

$$3B_2Cl_4 + 3H_2S \longrightarrow 3H_2 + B_2S_3 + 4BCl_3$$
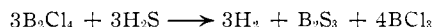
an attempt was made to account for the presence of BCl_2SH among the products. The formation of this substance as a result of the action of trichloroborane and hydrogen sulfide on diboron trisulfide was demonstrated in the following manner. A mixture of diboron trisulfide (0.310 mmole, obtained from the reaction of B_2Cl_4 with hydrogen sulfide as described earlier), trichloroborane (2.754 mmoles) and hydrogen sulfide (3.180 mmoles) was heated in a sealed tube at 90° for three days. A significant part, but not all, of the solid diboron trisulfide had disappeared at the end of this time. The mixture was quickly frozen to $-196°$, the reaction tube was connected to the vacuum system, and its volatile contents were separated by fractional condensation.

In this manner, 0.550 mmole of BCl_2SH (vapor pressure $= 116.2$ at 0°, molecular weight by vapor density $= 114.4$) was recovered. It therefore seems likely that BCl_2SH participates in the equilibrium

$$B_2S_3 + 4BCl_3 + 3H_2S \rightleftharpoons 6BCl_2SH$$
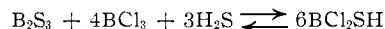
The presence of $B_3S_3Cl_3$ as a product of the reaction between B_2Cl_4 and hydrogen sulfide can readily be explained in terms of

$$BCl_3 + B_2S_3 \rightleftharpoons B_3S_3Cl_3$$
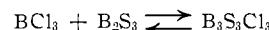
Discussion

Failure to observe reaction between the hydrogen halides and B_2Cl_4 is perhaps surprising, in view of the fact that both hydrogen and the halogens (with the exception of iodine) do undergo reaction. Although only hydrogen iodide was quantitatively tested in this work, previous experience has shown that hydrogen chloride is also without effect on B_2Cl_4.

The substitution of hydroxy groups for chlorine atoms by the action of water on B_2Cl_4 is, of course, entirely analogous to the behavior observed when trichloroborane is treated with water. Despite earlier findings,[4] it was found possible to carry out the preparation of sub-boric acid under such conditions that no hydrogen was liberated, even over relatively long periods of time. Treatment of B_2Cl_4 with a deficiency of water did not result in the formation of isolatable partial hydrolysis products. No satisfactory explanation has been developed for the observation that an equimolar mixture of B_2Cl_4 and water, when heated at 90° for three days, liberates a much higher percentage of the theoretical quantity of hydrogen than that obtained from mixtures employing an excess of water.

In view of the stability of the boron–chlorine bond in trichloroborane toward the action of hydrogen sulfide (no cleavage is reported even at 250°),[17] it seemed unlikely that a thiosub-boric acid,

(16) G. Tammann, *Z. Elektrochem.*, **8**, 158 (1902).

(17) A. Stock and O. Poppenberg, *Ber.*, **34**, 399 (1901).

$B_2(SH)_4$, would result from the treatment of B_2Cl_4 with hydrogen sulfide. This view was borne out. Nevertheless, hydrogen sulfide did react with B_2Cl_4. At low temperatures, simple Lewis adducts were obtained; and at room temperature and above, extensive cleavage of the boron–boron bond occurred. That hydrogen sulfide is far more effective than water in cleaving the boron–boron bond may be seen from the following comparisons. B_2Cl_4 and water (the latter in slight excess) produced no hydrogen over a period of 24 hr. at room temperature, while 57% of the theoretical quantity of hydrogen was released in 15 hr. when hydrogen sulfide was employed under similar conditions. Under conditions where hydrogen sulfide caused quantitative boron–boron bond cleavage (90° for 72 hr.), the use of water released only 6.8% of the theoretical quantity of hydrogen.

In view of the fact that four different boron-containing substances (BCl_3, B_2S_3, BCl_2SH and $B_3S_3Cl_3$) resulted from the quantitative destruction of B_2Cl_4 by hydrogen sulfide, no simple interpretation of the reaction seems feasible. However, since trichloroborane and boron sulfide were the major products, it is likely that BCl_2SH and $B_3S_3Cl_3$ were formed through secondary reaction. Since a mixture of boron sulfide, trichloroborane and hydrogen sulfide was shown to yield BCl_2SH, it is possible that the latter results from exchange between thioboric acid and trichloroborane.

$$2B(SH)_3 + 4BCl_3 \underset{}{\overset{90°}{\rightleftarrows}} 6BCl_2SH$$
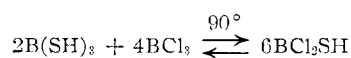
The thioboric acid might result from the action of hydrogen sulfide on boron sulfide.

$$B_2S_3 + 3H_2S \underset{}{\overset{90°}{\rightleftarrows}} 2B(SH)_3$$
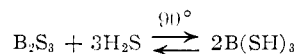
Of particular interest is the fact that BCl_2SH is capable of existence at all, in view of the fact that the oxygen analog, BCl_2OH, has not been prepared.

The Lewis adducts, $B_2Cl_4 \cdot SMe_2$ and $B_2Cl_4 \cdot 2SMe_2$, appear to be more stable than their oxygen analogs. While $B_2Cl_4 \cdot 2OMe_2$ decomposes readily to yield $B_2Cl_4 \cdot OMe_2$ and dimethyl ether at room temperature,[5] no dimethyl sulfide was recoverable from $B_2Cl_4 \cdot 2SMe_2$ at 25°. The increased stability of the alkyl sulfide addition compounds over that of the corresponding etherates is not unexpected, in view of the fact that similar trichloroborane–sulfide complexes (using diethyl sulfide and di-n-butyl sulfide) are more stable to cleavage and dissociation than the analogous trichloroborane–ether complexes.[18]

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The Reaction of Cyanogen with Diboron Tetrachloride and with Boron Halides[1]

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RECEIVED JULY 7, 1958

The reactions of cyanogen with diboron tetrachloride and with boron trihalides did not yield volatile products. With diboron tetrachloride, a brown solid with the empirical composition $B_2Cl_4 \cdot 1.5(CN)_2$ resulted. This material was decomposed by air and by water and absorbed 2 moles of trimethylamine per mole of $B_2Cl_4 \cdot 1.5(CN)_2$. On heating to 400°, it released one mole of BCl_3 per mole of $B_2Cl_4 \cdot 1.5(CN)_2$. The structures of $B_2Cl_4 \cdot 1.5(CN)_2$ and the material obtained through its pyrolysis ($BCl(CN)_3$) are discussed. Cyanogen was found not to react with trifluoroborane, but the adducts $BCl_3 \cdot (CN)_2$, $(BCl_3)_2 \cdot (CN)_2$, $BBr_3 \cdot (CN)_2$ and $(BBr_3)_2 \cdot (CN)_2$ were prepared.

In view of the previously observed reactivities of chlorine and bromine with B_2Cl_4,[2] the possibility of preparing compounds containing boron–cyanide linkages through similar reactions involving the pseudohalogen, cyanogen, suggested itself. Although these studies did not result in the isolation of simple compounds containing the desired boron-cyanide bond, several materials with interesting properties were produced.

With an excess of cyanogen, diboron tetrachloride reacted to form a dark brown material with the empirical composition $B_2Cl_4 \cdot 1.5(CN)_2$. This material was soluble in water and in methanol, and, in each case, a brown solution resulted. It was not soluble in carbon tetrachloride nor in chloroform. $B_2Cl_4 \cdot 1.5(CN)_2$ was not stable in air; on exposure

to the atmosphere for 12 hr. it became completely white.

On heating, $B_2Cl_4 \cdot 1.5(CN)_2$ was converted to a black solid with the empirical composition $BCl(CN)_3$, and trichloroborane was released.

$$B_2Cl_4 \cdot 1.5(CN)_2 \overset{400°}{\longrightarrow} BCl_3 + BCl(CN)_3$$
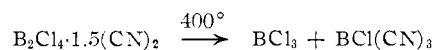
The product of this reaction was considerably more stable than $B_2Cl_4 \cdot 1.5(CN)_2$. No change in color was noticed on exposure to air for a two day period. Heating in air at 500° caused its color to lighten gradually, and at 800° the product was quickly converted to boric oxide.

One mole of $B_2Cl_4 \cdot 1.5(CN)_2$ was observed to absorb 2 moles of trimethylamine without the release of cyanogen or any other volatile material.

As an aid in interpreting the cyanogen experiments, the behavior of this pseudohalogen with