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The Behavior of Diboron Tetrachloride toward Some of the Non-metallic Elements[1]

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Diboron tetrachloride reacts readily with chlorine, bromine and oxygen at temperatures below room temperature. Cleavage of the boron-to-boron bond occurs in these three cases, along with the formation of the appropriate boron trihalides. No tendency for diboron tetrachloride to react with iodine, sulfur or white phosphorus was observed.

Although many types of boron compounds have been reported, particularly in recent years, diboron tetrachloride and its derivatives are the only simple substances known to contain boron-to-boron single bonds. It is perhaps not surprising, therefore, that its chemistry is in many ways[2] quite different from that of other boron-containing substances.

The present investigations were undertaken to study the behavior of diboron tetrachloride with some of the non-metallic elements and with their hydrogen compounds. Future papers in this series will deal with the reactions of diboron tetrachloride with amines, with aromatic compounds and with hydrogen.

Diboron tetrachloride is a colorless liquid which is somewhat thermally unstable at room temperature. For this reason, its reactions generally were studied at temperatures of 0° or below. In addition, the sensitivity of diboron tetrachloride to atmospheric oxygen and moisture made it necessary to carry out all investigations in the vacuum system. Due to the low stability of B_2Cl_4, even the precautions mentioned were not sufficient to avoid decomposition completely. For this reason, reactions involving exact whole-number stoichiometries were the exception, rather than the rule.

Diboron tetrachloride reacts readily with the more electronegative elements, even below room temperature, and the reactions result in cleavage of the boron-to-boron bond.

$$B_2Cl_4 + Cl_2 \xrightarrow{-45^\circ} 2BCl_3$$

$$3B_2Cl_4 + 3Br_2 \xrightarrow{-23^\circ} 4BCl_3 + 2BBr_3$$

$$6B_2Cl_4 + 3O_2 \xrightarrow{-78^\circ} 2B_2O_3 + 8BCl_3$$

On the other hand, diboron tetrachloride showed no tendency to react with iodine, sulfur or white phosphorus at room temperature.

Experimental

Apparatus.—With the exception of a Bourdon gauge whose design will be described in a forthcoming publication, standard vacuum apparatus was used in these investigations.

Preparation and Purification of Reagents.—**Diboron tetrachloride** was prepared by the method of Wartik, Moore and Schlesinger.[2] It exhibited a vapor pressure of 44 mm. at 0°.

Chlorine (Matheson Chemical Co.) was purified by fractional condensation, using a series of three U-tubes held at −78.5, −140 and −196° The fraction retained in the −140° trap had a vapor pressure of 63.5 mm. at −78.5°, compared with a reported value[3] of 67.5 mm. at this temperature.

Bromine (Matheson Chemical Co.) was purified by fractional condensation, using a series of three U-tubes held at −22.9°, −78.5° and −196°, respectively. The fraction retained at −78.5° had a vapor pressure of 67.0 mm. at 0.0°, compared with a reported value[4] of 65.9 mm.

Iodine (J. T. Baker Chemical Co.) was subjected to pumping at −22.9° for 0.5 hr. and was used without further purification.

Oxygen (Linde Air Products Co.) was dried by passage through calcium chloride, potassium hydroxide and phosphorus pentoxide columns. No further purification was attempted.

Sulfur (roll) was used without further purification.

Phosphorus (white) was purified by extraction with dry carbon disulfide and then evaporation of the solvent.

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

(2) A. Stock, A. Brandt and H. Fischer, *Ber.*, **58**, 653 (1925); T. Wartik, R. Moore and H. Schlesinger, THIS JOURNAL, **71**, 3265 (1949); G. Urry, T. Wartik, R. Moore and H. Schlesinger, *ibid.*, **76**, 5293 (1954); G. Urry, J. Kerrigan, T. Parsons and H. Schlesinger, *ibid.*, **76**, 5299 (1954); T. Wartik and E. F. Apple, *ibid.*, **77**, 6400 (1955).

(3) M. Trautz and W. Gerwig, *Z. anorg. Chem.*, **134**, 417 (1924).

(4) M. Bouzat and T. Lebaun, *Compt. rend.*, **178**, 635 (1924).

Behavior of B_2Cl_4 with Chlorine.—Gaseous chlorine (1.811 mmoles) was allowed to come into contact with liquid B_2Cl_4 in an ampoule held at −45.2°. A rapid absorption of chlorine, completed in approximately 30 seconds, was observed. (Pressures in this and subsequent experiments involving halogens were measured by means of an all-glass Bourdon gauge.) After the reaction system had been allowed to warm to room temperature, the total gaseous volume was measured, and the gases were then transferred to a tube containing mercury, sealed off and shaken to remove excess chlorine. Following this treatment, 0.700 mmole of trichloroborane (v.p. at −45.2° = 51.0 mm.; reported value[5] 49.0 mm.) was recovered. The amounts of reactants and product involved were: B_2Cl_4 used, 0.358 mmole; Cl_2 used, 0.352 mmole; BCl_3 formed, 0.700 mmole. These results are consistent with the equation

$$Cl_2 + B_2Cl_4 \longrightarrow 2BCl_3$$

Behavior of B_2Cl_4 with Bromine.—Bromine (2.745 mmoles) was sealed in an ampoule with B_2Cl_4 (1.646 mmoles) and allowed to stand at −22.9° for several hours. The contents of the reaction vessel, which were completely volatile, were passed several times through a Pyrex tube containing copper wool. The weight of bromine taken up in the reaction was the difference in weight between the bromine used and that absorbed by the copper. The molar reacting quantities were: B_2Cl_4, 1.646 mmoles; Br_2, 1.557 mmoles. The vapor pressure of the product of this reaction was shown to vary greatly with change in volume, an indication that it was not a single substance. Efforts to separate it into its components by fractional condensation were not successful; a U-trap held at −78.5° (at which temperature trichloroborane should not be retained and tribromoborane should be almost completely non-volatile) retained a material with a vapor pressure of 217 mm. at 0° and allowed the passage of a material with a vapor pressure of 81 mm. at −45°. Each of these vapor pressures was shown to be strongly dependent on volume, indicating that neither of the materials was a pure substance. Similar difficulty attended efforts to separate a prepared mixture of trichloroborane and tribromoborane into its components by fractional condensation.[6] It is therefore likely that the reaction of B_2Cl_4 with bromine produces a number of substances which result from halogen interchange between trichloroborane and tribromoborane, the latter two being formed according to the equation

$$3Br_2 + 3B_2Cl_4 \longrightarrow 2BBr_3 + 4BCl_3$$

Behavior of B_2Cl_4 with Iodine.—After a mixture of B_2Cl_4 and iodine (in excess) had been allowed to stand at room temperature for 0.5 hr. in a sealed tube, 96.5% of the B_2Cl_4 was recovered unchanged. It is likely that the small loss in B_2Cl_4 resulted from its thermal decomposition at room temperature, rather than its reaction with iodine.

Behavior of B_2Cl_4 with Oxygen.—B_2Cl_4 (1.566 mmoles) was condensed in a 250-ml. reaction vessel and held at −196° while 10.35 mmoles of oxygen was admitted. The reaction tube was sealed off and its contents were allowed to stand at −78.5° for 12 hr. A glassy, transparent solid, which did not change in appearance on warming to room temperature, formed. The reaction vessel was connected to the vacuum system, and its residual oxygen content was collected and measured by means of a Toepler pump. Care was taken to trap out gases condensable at −196° during this operation. 9.63 mmoles of unchanged oxygen was recovered. The volatile material condensable at −196° was found to be trichloroborane (v.p. at 0° = 477.8; molecular weight by vapor density = 115.5). It was thus found that 1.566 mmoles of B_2Cl_4 reacted with 0.720 mmole of oxygen to produce 2.017 mmoles of trichloroborane. These values correspond to the equation

$$6B_2Cl_4 + 3O_2 \longrightarrow 2B_2O_3 + 8BCl_3$$

When the reaction between B_2Cl_4 and oxygen was allowed to proceed at or near room temperature, violent inflammation, accompanied by the formation of chlorine, was observed.

Behavior of B_2Cl_4 with Sulfur.—From an equimolar mixture of B_2Cl_4 and roll sulfur which had been allowed to stand at 0° for 15 minutes, it was found possible to recover 98% of B_2Cl_4 used. Here, again, it is probable that thermal decomposition prevented complete recovery of the reagent.

Behavior of B_2Cl_4 with Phosphorus.—From a mixture of B_2Cl_4 and excess white phosphorus which had been allowed to stand in a sealed tube at 0° for 10 minutes, it was found possible to recover 96.4% of the unchanged boron compound, indicating that the latter did not react with phosphorus under the conditions employed.

Discussion

The tendency for B_2Cl_4 to react with the more negative elements (Cl_2, Br_2 and O_2) is perhaps not surprising, in view of the stability of the new bonds formed in these reactions. It was not anticipated, however, that cleavage of the boron-to-boron bond would occur quite as readily as was observed. The reaction of B_2Cl_4 with chlorine takes place quantitatively at −45.2°, with bromine at −22.9° and with oxygen at −78.5°. Failure to obtain a reaction between B_2Cl_4 and iodine at 0° may be due to size restrictions, since the bulky iodine molecule may not be capable of a direct attack on the B_2Cl_4 molecule. It should be noted that, in the other cases where negative elements (sulfur and phosphorus) failed to react with B_2Cl_4, the molecules involved are larger than diatomic. (Aside from iodine, the only diatomic elementary molecule found not to react with B_2Cl_4 is nitrogen.)

An indication of the relative ease of cleavage of the boron-to-boron bond in B_2Cl_4 may be gained from a comparison with halogenation reactions of hexachlorodisilane. The latter does not react with chlorine below 300°,[7] nor with bromine below 500°.[8]

The reaction between B_2Cl_4 and Br_2 seemed to offer promise as a method for the preparation of a pure mixed halide, BCl_2Br. However, redistribution occurred and a mixture, identical with that obtained on mixing BCl_3 with BBr_3, resulted. All efforts to isolate a single mixed halide by fractional condensation techniques failed. Mixed silicon halides, such as $SiCl_3Br$, have, however, been prepared and isolated. This difference in behavior may possibly be accounted for in terms of the formation of unstable dimeric bridge intermediates by the boron halides and not by the silicon halides. Alternately, one might seek an explanation based on resonance stabilization. For the silicon halides, the concept of resonance stabilization need not be invoked, since the silicon atom is surrounded by a complete octet of electrons. In BCl_3 and BBr_3, three π-bonded structures contribute equally to resonance stabilization, while in BCl_2Br, only two such structures are equal. Since, according to Hine,[9] "the greater the number of important contributing structures, and the more nearly equal their contribution, the greater the resonance energy," it is not surprising to observe a lower stability for BCl_2Br than for BCl_3 or BBr_3.

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(5) A. Stock and K. Priess, *Ber.*, **47**, 3109 (1914).

(6) Long and Dollimore (*J. Chem. Soc.*, 4457 (1954)), on the basis of Raman spectra of mixtures of trichloroborane and tribromoborane at room temperature, concluded that all possible halide distributions were represented in the equilibrium mixture.

(7) G. Martin, *ibid.*, **105**, 2836 (1914).

(8) W. Schumb and H. Anderson, THIS JOURNAL, **59**, 651 (1937).

(9) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1956, p. 6.