## Summary

The preparation of $B_5H_{11}$ in quantities suitable for experimental work has been accomplished by the use of a flow method involving diborane. Measurements upon a sample unusually free from $B_5H_9$ gave $-123.3°$ for the melting point and 53.0 mm. for the vapor tension at 0°.

The thermal decomposition of $B_5H_{11}$ at first gives hydrogen, diborane, tetraborane and smaller quantities of a probable octaborane. Further heating produces non-volatile solids, $B_5H_9$ and $B_{10}H_{14}$. A ten-fold excess of hydrogen added at the start hinders so effectively the formation of substances less volatile than $B_5H_{11}$ that it is possible to prepare diborane and tetraborane from $B_5H_{11}$ practically without loss. The equilibrium system involving hydrogen, $B_5H_{11}$, tetraborane and diborane was studied to some extent at a temperature of 100°. Any one of these three boron hydrides may be prepared in quantity from one of the others, by a suitable adjustment of the experimental conditions. The preparation of useful quantities of tetraborane from diborane therefore is feasible.

Improvements in the method of preparing $B_5H_9$ by long heating of diborane have increased the yields to 33%.


CHICAGO, ILLINOIS RECEIVED JUNE 9, 1933
PUBLISHED OCTOBER 6, 1933

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CHICAGO]

# Hydrides of Boron. III. Dimethoxyborine

BY ANTON B. BURG AND H. I. SCHLESINGER

Linkages between boron atoms seldom occur in compounds of boron with elements other than hydrogen. A striking contrast to this situation is presented by the boron hydrides, in all of which the boron atoms are linked together. The tendency for such linking is so strong that monoborine ($BH_3$) seems incapable of existence and the simplest hydride is diborane ($B_2H_6$), a circumstance not easily explained by any generally acceptable theory of valence. Substitution of halogens for hydrogen in diborane leads to compounds of the type $B_2H_5X$[1] and possibly $B_2H_4X_2$, but further substitution leads only to the boron trihalide. The only known simple derivative of monoborine, aside from those in which all of the hydrogen is replaced, is phenylborine ($C_6H_5BH_2$),[2] a compound which has been studied very little. It is thus of considerable interest to prepare compounds of the types $HBR_2$, $H_2BR$, $HBX_2$, and $H_2BX$, in the hope that a compound showing a tendency toward association by boron linkages may be obtained. Such work might lead to a better understanding of the factors which stabilize the boron to boron bond.

(1) Stock, Kusz and Priesz, *Ber.*, **47**, 3115 (1914); Stock and Pohland, *ibid.*, **59B**, 2223 (1926).
(2) Pace, *Atti. accad. Lincei*, [VI] **10**, 195 (1929).

This paper describes the preparation of dimethoxyborine, $(CH_3O)_2BH$, by the reaction of diborane with methyl alcohol. It is a colorless liquid, whose normal boiling point is 25.9° (vapor tension 275 mm. at 0°). In the vapor phase at room temperature it shows a normal value of the molecular weight (73.9), and the only indications of association at lower temperatures are too uncertain to be considered. It is not spontaneously inflammable in air, but is rapidly hydrolyzed according to the equation $(CH_3O)_2BH + 3HOH \longrightarrow B(OH)_3 + 2CH_3OH + H_2$. Its odor is a composite of methyl alcohol and diborane.

Dimethoxyborine decomposes reversibly, according to the equation $6(CH_3O)_2BH \rightleftarrows B_2H_6 + 4(CH_3O)_3B$. No intermediate compound, such as monomethoxyborine or methoxydiborane, could be isolated. The equilibrium point favors the decomposition under all easily attained conditions. The rate of decomposition in the gas phase is comparatively low, and depends but little upon changes of pressure. In the liquid state at temperatures above 0°, the decomposition is so rapid that special precautions are necessary for obtaining trustworthy measurements of the vapor tension.

In all of this work, the only indication of the existence of monomethoxyborine was an unstable, non-volatile white solid, which was formed as a by-product of the preparation of dimethoxyborine. It decomposed on standing at room temperature, to give diborane, dimethoxyborine, and trimethyl borate, in proportions represented by the formula $(CH_3OBH_2)_x$. The substance may have been a polymer of monomethoxyborine, which could be explained as a complex compound in which oxygen in one molecule occupies the fourth position in the coördination sphere of the boron in another. This is not certain, for other explanations are possible.

## Experimental

**Preparation.**—The reaction used for the preparation is represented by the equation $4CH_3OH + B_2H_6 \longrightarrow 2(CH_3O)_2BH + 4H_2$. The methyl alcohol used for the purpose was treated with barium oxide to remove water, and its purity was checked by the vapor tension at 0° (29.6 mm.). The exact proportions of the two substances apparently were not critical, for the yields were about equally good whether the excess of diborane was four-fold or twenty-fold. The yields varied between 75 and 90% of the methyl alcohol; trimethyl borate was obtained as a by-product. The details of our largest-scale preparation were as follows.

Approximately 500 cc.[3] of pure diborane and 270 cc. of methyl alcohol were condensed together upon the outer wall of a 3-cm. wide test-tube, which was sealed into the top of a one-liter flask[4] connected to the vacuum apparatus. Then the two substances were allowed to warm and a rapid effervescence occurred. The hydrogen was pumped off through a trap immersed in liquid nitrogen, and the process was repeated until no further hydrogen was produced. Then the excess diborane was isolated by trapping

(3) All volumes given in this paper refer to gases at standard conditions.

(4) This reaction vessel is like that used by Stock and Somieski, *Ber.*, **50**, 1742 (1917), for the halogenation of silane.

out the less volatile substances at a temperature of $-145°$, and two more 270-cc. portions of methyl alcohol were treated with it as before. The dimethoxyborine was purified by fractional condensation, using baths at $-90°$ (to trap out methyl borate completely) and $-120°$. The fraction condensed at $-120°$ showed a vapor tension of 275 mm. at 0°; further distillation did not change the value; yield, 300 cc.

**Analysis.**—A sample was analyzed by hydrolysis with a slight excess of water, according to the equation $(CH_3O)_2BH + 3HOH \longrightarrow B(OH)_3 + 2CH_3OH + H_2$. The hydrogen was pumped out and measured. The methyl alcohol was separated from the residual water by distillation methods, and measured as a gas. The boric acid was titrated with 0.1 *N* barium hydroxide, in the presence of excess mannite. A sample whose volume was 8.85 cc. gave 8.95 cc. of hydrogen, 17.5 cc. of methyl alcohol, and 8.85 cc. of boric acid (calculated as a gas). These values check the above equation, leaving no doubt of the identity of the substance.

**Solid By-Product of the Preparation.**—An unstable white solid was formed as a by-product of the experiment described above. It seemed to be entirely non-volatile at room temperature, but decomposed on heating. The volatile substances were removed completely from the reaction vessel, and the solid was allowed to stand for twelve hours at room temperature. During this time it disappeared completely, and in its place was found 16.0 cc. of diborane, 18.0 cc. of dimethoxyborine, and 6.6 cc. of trimethyl borate. These quantities correspond to the formula $(CH_3OBH_2)_x$, within the probable error.

At first glance this substance appears to be a polymer of monomethoxyborine, which is easily explained as a complex compound in which oxygen in one molecule occupies the fourth position in the coördination sphere of boron in another. But we might also regard it as a complex compound of the type $(CH_3OBH_3)_2BOCH_3$, or $(CH_3OBH_3)BH(OCH_3)$. These possibilities are less probable, in that they require that the hypothetical $BH_3$ form complex compounds with oxygen, but the present state of our knowledge does not allow us to eliminate them.

**The molecular weight** was determined by weighing a measured volume of the gas, in a small bulb closed by a stopcock (the substance reacts slightly with grease, but the effect is not serious): first sample, 18.32 cc. weighed 0.0604 g., m. w. = 73.8; second sample, 37.90 cc. weighed 0.1256 g., m. w. = 74.2. The theoretical value for the monomer is 73.9.

**The melting point** was determined by the aid of the magnetic device of Stock.[5] The temperature was measured by the carbon tetrafluoride vapor tension thermometer. The average value was $-130.6°$.[6]

**The vapor tensions** were measured with particular care, on account of their possible relation to association in the liquid state at low temperatures. A 200-cc. sample was purified as thoroughly as possible by the aid of a simple reflux fractionating tube[7] (reflux temperature, $-78.5°$) and stored at liquid air temperature. Almost all of the measurements were made upon fresh small samples from this large supply. The tensions at temperatures below $-40°$ were registered upon a mercury manometer whose arms were 16 mm. in internal diameter, and measured by a precision cathetometer (probable error not greater than 0.01 mm.). At higher temperatures it was necessary to work more rapidly than the use of the cathetometer would allow. The values given in Table I are either averages of several points near together, or selections from a number of mutually consistent values.

(5) Stock, *Ber.*, **50**, 156 (1917).

(6) It was noted that slightly different values were obtained, depending upon whether the same sample was melted on the plunger and re-frozen before the determination, or condensed directly as a solid, during a very slow distillation. In the former case, the average was $-130.2°$; in the latter, $-131.0°$. The difference is greater than the probable error, but its meaning is not apparent.

(7) Burg, article to be published in an early number of THIS JOURNAL.

TABLE I

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $t$, °C..... | −95.8 | −86.7 | −70.9 | −64.7 | −56.1 | −46.3 | −36.0 | −28.2 |
| $p$, mm..... | 0.18 | 0.52* | 2.66 | 4.58 | 9.60 | 19.85* | 39.2 | 64.3 |
| $t$, °C..... | −20.5 | −11.5 | −8.9 | 0.00 | 6.8 | 8.9 | 12.0 | 13.8 |
| $p$, mm..... | 100.5 | 158 | 180 | 275* | 366 | 403 | 453 | 490 |

The values marked with an asterisk were used in calculating the constants for the equation

$$\log_{10} p = -(1849.0/T) + 175 \log_{10} T - 0.008221\ T + 7.1895$$

which represents the other values reasonably well. From this equation we calculate the boiling point to be 25.9°, the molal heat of vaporization, 6138 cal., and the Trouton constant, 20.5 cal./deg. The curve representing the relation of log $p$ to $1/T$ (Fig. 1)[8] is definitely concave downward, but this

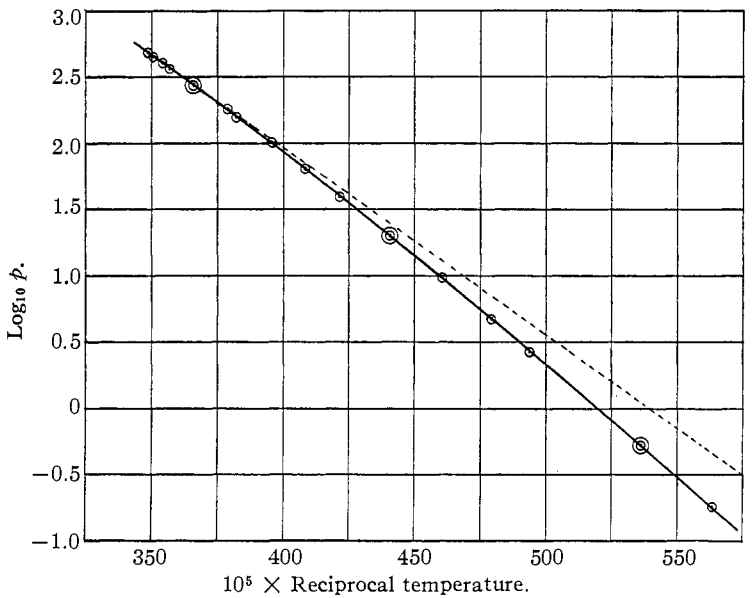


Fig. 1.—Vapor tensions of dimethoxyborine.

curvature is not much more pronounced than that observed in many other volatile oxygen compounds. We cannot attribute it to any tendency toward formation of linkages between boron atoms.

### The Equilibrium with Diborane and Trimethyl Borate

**The Decomposition.**—Dimethoxyborine decomposes to form diborane and methyl borate, without indication of any other substance. The change of volume in the process, indicated by the equation $6(CH_3O)_2BH \rightleftarrows B_2H_6 + 4(CH_3O)_3B$, makes it possible to follow the change roughly by

(8) The dotted line represents the Clapeyron equation, drawn through the point for 0°, with a slope corresponding to a normal value for the Trouton constant. The points used for calculating the Nernst equation are doubly circled.

measurements of the total gas volume. Table II gives the results of an experiment in which 31.8 cc. of pure dimethoxyborine was placed in a U-tube with adjacent manometer (total available space, 105 cc.), and the volumes determined from time to time by measurement of the pressure and of the temperature, which varied one or two degrees from the average, 20°.

TABLE II

| | | | | | | |
|---|---|---|---|---|---|---|
| Time, hours..... | 0 | 20.0 | 26.5 | 44.5 | 57.5 | 68.0 |
| Volume, cc..... | 31.8 | 30.8 | 30.4 | 29.8 | 29.5 | 29.3 |

At the end of the experiment, the residual substance and the products were isolated, and it was found that 14.7 cc., or 46%, of the sample had decomposed to form 9.8 cc. of trimethyl borate[9] and 2.5 cc. of diborane, in good agreement with the equation given above and with the observed decrease of volume. The remaining 17.1 cc. of dimethoxyborine was allowed to stand for two hundred and thirty-four hours in a space of 1200 cc. at room temperature. The result was 65% decomposition. In another experiment, a 43.9-cc. sample was allowed to stand for fifteen hours in the 1200 cc. space at room temperature, and was 9% decomposed. In this case the pressure was only one-tenth as high as in the experiment recorded in Table II, but the rate of decomposition was two-thirds as rapid.

The decomposition is far more rapid if the substance is placed in the reaction vessel in which the preparation was carried out, after the disappearance of the white solid. Under such conditions a 300-cc. sample in a space of 1100 cc. was 30% decomposed in one hundred and ten minutes at room temperature. The rate was about seventeen times as rapid as that observed in the experiment recorded in Table II, which occurred at about the same pressure. The catalytic activity of the reaction chamber was destroyed by heating at high vacuum.

**The Reverse Reaction.**—As a test of the reversibility of the decomposition of dimethoxyborine, 17.2 cc. of diborane and 9.75 cc. of methyl borate (both very carefully purified) were placed together in a space of 105 cc., and left for forty hours in the vapor state at room temperature. The components of the mixture were separated again, and there was isolated 0.15 cc. of a gas having a vapor tension of 1.2 mm. at −78.5°. The process was repeated, this time for seventy-eight hours, and 0.30 cc. of the product was obtained. In ninety-eight hours, 0.40 cc. was produced. The three samples were combined and purified as thoroughly as possible. From two values of the vapor tension, 46 mm. at −33.8° and 17.2 mm. at −48.5°, the substance was indicated to be dimethoxyborine. All doubt was removed by an analysis, in which the 0.78-cc. sample was hydrolyzed to produce 0.8 cc. of hydrogen and 0.75 "cc." of boric acid (methyl alcohol not determined).

(9) Identified by the 35.5 mm. vapor tension at 0°, and the value −29° for the melting point. *Cf.* Wiberg and Sütterlin, *Z. anorg. allgem. Chem.*, **202**, 15 (1931).

The decomposition of dimethoxyborine is thus shown to be appreciably reversible. This reaction is not recommended as a means of preparation, even though the yields would be practically quantitative, for any attempts to increase the rate of reaction by heating would be likely to result in some formation of $B_5H_{11}$ and $B_4H_{10}$, either of which would be very hard to remove from the product.

We are planning to study further the chemical properties of dimethoxyborine, as well as the reaction of a variety of alcohols with various boron hydrides. We have recently found that boron trimethyl, like boron trihalides and trimethyl borate, reacts with diborane. We hope in the near future to be able to report on some new derivatives of diborane, obtained by this method.

## Summary

Dimethoxyborine, a compound of the new type $HBX_2$, has been prepared by the reaction of diborane with methyl alcohol. A white, non-volatile, unstable solid which may be a complex polymer of monomethoxyborine, was obtained as a by-product.

Dimethoxyborine shows no tendency toward association, beyond that common to most volatile oxygen compounds. Its vapor tensions were measured with some care, and expressed by an equation of the Nernst approximation type.

The substance decomposes very easily to form diborane and trimethyl borate. This reaction is reversible to an appreciable extent.

CHICAGO, ILLINOIS RECEIVED JUNE 9, 1933
PUBLISHED OCTOBER 6, 1933

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# The Quantum Yields of the Photochemical Reactions of Phosgene

BY C. W. MONTGOMERY AND G. K. ROLLEFSON

In the previous work which has been reported[1] on the photochemical oxidation of phosgene, the phosgene-sensitized oxidation of carbon monoxide, and the photochemical reaction of phosgene with hydrogen, kinetic studies of the reactions have been carried out and an attempt has been made to arrive at well-correlated and self-consistent reaction mechanisms in the three cases. This program has been completely successful from the kinetic standpoint with one exception (for a discussion of this case see (1b).

## Quantum Yields of the Phosgene Reaction

In order to gain further confirmation of the mechanisms already proposed, for certain photochemical reaction of phosgene it is still necessary

(1) (a) Rollefson and Montgomery, THIS JOURNAL, **55**, 142 (1933); (b) **55**, 4029 (1933); (c) **55**, 4036 (1933).