experiments, in which both chromium and titanium were associated with the iron, were carried out.[12]

In addition to the work that has just been recorded, an attempt was made to substitute the air-bubbling process for the treatment with bismuth oxide in Newton's method[13] for determining iron, wherein the ferric salt is deoxidized by means of a previously prepared solution of titanous sulfate, the rest of the procedure being the same as that of the Gooch and Newton[4] process. Strangely enough, it was found that the outcome of the experiments depended somewhat upon the way in which the titanic sulfate had been reduced, in order to obtain the desired reagent. When the necessary valence change was brought about with the aid of a reductor,[14] the resulting solution could be used in the procedure and relied upon to yield a result in satisfactory agreement with the standard value.[15] When, on the other hand, the refined electrolytic process[7] was employed for the deoxidation of the titanic compound, the solution so obtained gave rise to results that were noticeably too low. It would seem, therefore, that the matter requires further investigation.

Summary

As the differential oxidizing agent ordinary air has been substituted, with a fair degree of success, for bismuth trioxide in the Gooch and Newton process for estimating iron in the presence of titanium.

[12] Unpublished experiments by B. W. Allan.

[13] Newton, *Am. J. Sci.*, [4] **25**, 343 (1908).

[14] Van Brunt, THIS JOURNAL, **36**, 1426 (1914); Bray, Simpson and MacKenzie, *ibid.*, **41**, 1363 (1919); Lundell and Knowles, *ibid.*, **45**, 2620 (1923).

[15] Reductor values taken as correct.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Hydrides of Boron. IV. The Methyl Derivatives of Diborane

BY H. I. SCHLESINGER AND A. O. WALKER[1]

Although diborane has an atomic arrangement similar to that of ethane, as shown by x-ray data[2] taken at low temperatures, the bonds in the two compounds must differ in certain fundamental respects, for the molecule of diborane does not contain enough valence electrons to establish doublet bonds between the atoms involved. Many suggestions have been made concerning the structure of diborane;[3] although all of these lack the support of an adequate experimental basis, those assuming some type of single electron bond between boron and hydrogen seem at present most satisfactory as working hypotheses. To account for the molecular formula of diborane, four of the six hydrogen atoms are usually thought of as bound by ordinary doublet bonds; each of the two remaining hydrogen atoms is bound by a single electron bond to each of the two boron atoms.[4]

For a molecule so constituted, one need not assume that the same two hydrogen atoms are at all times held by single electron bonds. The situation is, however, different in a compound in which four of the hydrogen atoms are replaced by other atoms or groups, for boron compounds containing no boron to hydrogen linkages have, in general, formulas consistent with the ordinary present-day concepts of valence.

The present investigation was undertaken to obtain data which might be of value in deciding to what extent the idea of the single electron bond might aid in suggesting new lines of investigation and in interpreting observations in the chemistry of the boron hydrides. It was hoped that the methyl derivatives might be stable enough to allow the preparation and isolation of all of those capable of existence. Should there be marked differences in properties and stability of the tetra-

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[1] Taken from a dissertation submitted by A. O. Walker to the Faculty of the Division of the Physical Sciences of the University of Chicago in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Mark and Pohland, *Z. Krist.*, **62**, 103 (1925).

[3] Eastman, THIS JOURNAL, **44**, 438 (1922); Robinson, *Trans. Faraday Soc.*, **18**, 298 (1922); Main-Smith, *Chem. News*, **135**, 81 (1927); Sugden, *J. Chem. Soc.*, 1173 (1927); Wiberg, *Z. anorg. allgem. Chem.*, **173**, 199 (1928); Sidgwick, "The Electronic Theory of Valency," Oxford Press, 1927; Pauling, THIS JOURNAL, **53**, 3225 (1931).

[4] According to Mullikan, *Phys. Rev.*, **43**, 765 (1933), a molecule so constituted should possess magnetic properties which a preliminary investigation, carried out in this Laboratory, fails to disclose. Since the work has not yet been extended to low temperatures, and since the theoretical basis for the conclusion is as yet uncertain, this discrepancy will, for the present, be neglected.

and pentamethyl derivatives, or should the latter prove incapable of existence, this result would itself have some bearing on the problem in question; further detailed study of these compounds might ultimately lead to a far better understanding of the nature of the anomalous valence relations in the boron hydrides.

The first preparative method employed was the methylation of monobromodiborane with zinc methyl. The reaction produced a small amount of a substance which later work indicated to have been dimethyldiborane, but which could not be isolated on account of the very low yield and the formation of several other products. The direct methylation of diborane by zinc methyl was then attempted. This reaction also yielded some methyl derivatives but a separation could not be effected.

Finally, as suggested by the preparation of the halogen derivatives of diborane by the action of boron halide on diborane,[5] the reaction of diborane with boron trimethyl was studied. The experimental results can be expressed by the following equations

$$5B_2H_6 + 2B(CH_3)_3 \longrightarrow 6B_2H_5CH_3 \qquad (1)$$

$$2B_2H_6 + 2B(CH_3)_3 \longrightarrow 3B_2H_4(CH_3)_2 \qquad (2)$$

$$B_2H_6 + 2B(CH_3)_3 \longrightarrow 2B_2H_3(CH_3)_3 \qquad (3)$$

$$B_2H_6 + 4B(CH_3)_3 \longrightarrow 3B_2H_2(CH_3)_4 \qquad (4)$$

The various methyl derivatives, boron trimethyl and diborane are components of a very complex system of reversible reactions. The equilibria in this case are more favorable to the formation of the derivatives than in the case of the system diborane–boron trichloride.[5] If an excess of diborane is used, the monomethyl and the dimethyl derivatives are formed. An excess of boron trimethyl favors the formation of the trimethyl and tetramethyldiborane.

These results indicate that if pentamethyldiborane is capable of existing it should be obtainable by the use of a large excess of boron trimethyl. But even when ten mols of boron trimethyl was treated with one mol of diborane, no substance less volatile than tetramethyldiborane was obtained.

Dimethyldiborane, prepared according to the reaction mentioned, appears to have an unsymmetrical structure in which both of the methyl groups are attached to the same boron atom, for, when hydrolyzed, it yields one mol of boric acid, one mol of dimethylboric acid and four mols of hydrogen.[6] In the trimethyl derivative, two of the methyl groups are shown to be attached to one of the boron atoms and the third to the other, for hydrolysis yields no boric acid and but one mol of dimethylboric acid. Tetramethyldiborane yields two mols of dimethylboric acid and hence has a symmetrical structure. In the hydrolysis of the monomethyl- and trimethyldiborane, a white solid, probably monomethylboric acid, which was absent in the products of the hydrolysis of the dimethyl- and tetramethyldiborane, was obtained. Due to the fact that it is not very volatile and, therefore, is difficult to investigate in the vacuum system, the substance was not further studied. The dimethylboric acid formed in the hydrolysis of the methyl derivatives was isolated and shown to be formed in the calculated quantities.

Monomethyldiborane is by far the least stable of the four methyl derivatives prepared, having a marked tendency to revert to diborane and boron trimethyl, as well as to go over into the more highly methylated derivatives. This observation, together with the facts that we have thus far been able to obtain only the unsymmetrical dimethyldiborane and that tetramethyldiborane does not react further with boron trimethyl, suggests the following generalizations.

(1) Boron derivatives of this type are more stable when two of the three hydrogen atoms are replaced by methyl (or ethyl[7]) radicals, than if only one hydrogen atom is replaced. In this connection it is suggestive to note that Burg and Schlesinger[8] have found that dimethoxyborine ($(CH_3O)_2BH$) is more stable than the corresponding monomethyl derivative.

(2) It appears that the boron–boron linkage in compounds of this type can exist only when each boron atom is also attached to at least one hydrogen atom. More broadly stated, this observation lends support to the view mentioned in the introductory paragraph that (at any moment) two of the hydrogen atoms in diborane are held by a type of bond different from that which holds the other four hydrogen atoms. It must be admitted, how-

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[5] Schlesinger and Burg, THIS JOURNAL, **53**, 4321 (1931).

[6] That the formation of dimethylboric acid in this hydrolysis is not due to a primary hydrolysis yielding monomethylboric acid followed by a secondary reaction of the latter to give the dimethyl derivative, is shown by the fact that hydrolysis of monomethyldiborane gives monomethylboric acid but no dimethylboric acid, and that only one mol of dimethylboric acid is obtained from trimethyldiborane.

[7] Ethyl derivatives, prepared recently in this Laboratory, behave in a fashion entirely analogous to that of the methyl derivatives.

[8] Burg and Schlesinger, THIS JOURNAL, **55**, 4020 (1933).

ever, that substitution of four methyl groups for four hydrogen atoms in diborane may so alter the character of the molecule as to prevent further substitution. It is hoped that detailed study, already begun, of the properties of the various alkyl derivatives will throw additional light on the problem.

Experimental

A. Description of Apparatus.—The apparatus and the technical methods used in this work were essentially the same as those used by Stock[9] in his work on the hydrides of boron and silicon. The apparatus, as represented in Fig. 1, is of a simplified design especially suited to the work here described. It differs from other forms mainly in the easy reversibility of the fractional condensation system, and in the relegation of more purposes to the seal-off system SO, Fig. 1, which is used as a point of attachment for the melting point tube, the weighing tubes or bulbs and various special forms of apparatus for carrying out reactions. The tube T_1, which was used for measuring the volumes of gaseous samples, was calibrated with water and also with pure carbon dioxide. Volume corrections for the variation of the mercury level in the manometer were made on the basis of the known internal diameter of the manometer tubing.

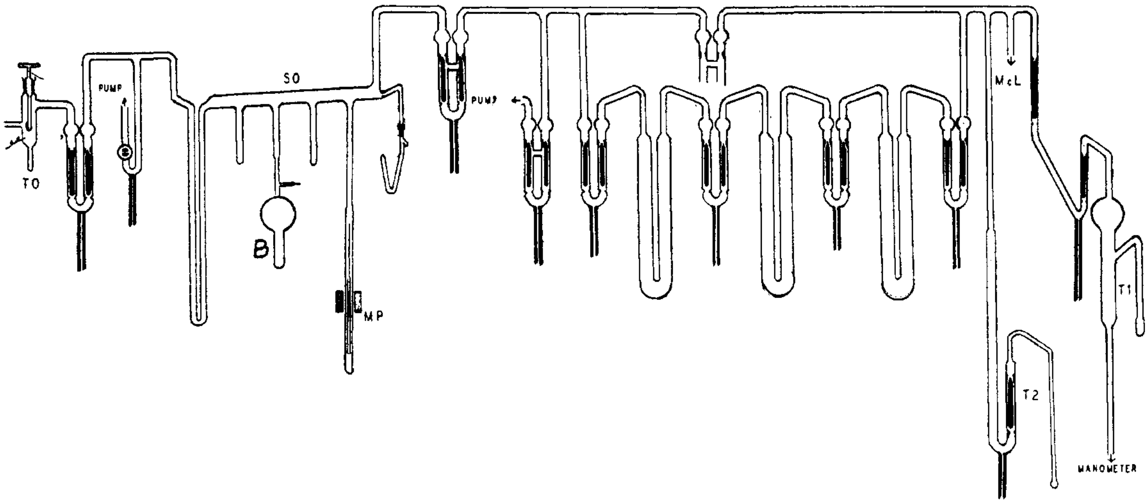

Fig. 1.

The different substances were purified by fractional condensation, such as described by Stock.[10] The mixture to be fractionated is condensed in the tube T_1 by means of liquid nitrogen. By a slow lowering of the bath, the mixture is gradually warmed and the vapors are allowed to pass through a series of U-tubes, each at a temperature lower than the preceding. Thus the more volatile components of the mixture condense in the farthest tube while the less volatile substances are held in the nearer tubes.

Vapor tensions were determined in the tube T_1 and also in T_2, the volume of the latter being about 5% of that of T_1. A pure sample exhibits the same tension regardless of the volume of the vapor phase, while an impure sample shows different tensions when measured in systems of different volumes.

B. Analytical Methods.—Two procedures were followed in the determination of the composition of these compounds. The first method was to hydrolyze the sample and determine the hydrogen, boric acid and dimethylboric acid produced. The second method was to oxidize the sample with concentrated nitric acid and measure the amount of carbon dioxide and boric acid formed.

Hydrolysis Method.—A sample is sealed off in a bulb (B Fig. 1) with an excess of water and allowed to warm to room temperature. After standing at room temperature for a short time the bulb is sealed into the tube opener and the tubulature of the bulb is immersed in liquid nitrogen and allowed to stand for at least an hour to ensure complete condensation of all condensable materials. The tip of the bulb is then broken and the hydrogen is passed through a U-tube immersed in liquid nitrogen and brought into a eudiometer by means of a Toepler pump.

The bulb, which contains the boric acid, dimethylboric acid and water, is next warmed to room temperature and the dimethylboric acid is transferred to the vacuum system where it is purified and its volume measured. The boric acid is washed into a flask and titrated[11] with barium hydroxide in the presence of mannite, with phenolphthalein as the indicator.

Oxidation Method.—A sample is sealed off in a bulb containing concentrated nitric acid and is heated at 250° for two hours. In the vacuum apparatus the nitrogen dioxide is condensed in a tube at −120° and the carbon dioxide and nitrous oxide at −184°, while the nitric oxide is pumped off. The mixture of nitrous oxide and carbon dioxide is passed over a heated copper spiral; the carbon dioxide is then recondensed and its volume measured in the usual way. The boric acid in the original bulb is washed into a flask and titrated.

Molecular weights were calculated from vapor densities. Attention is called to the fact that the quantities of the compounds available for these measurements were in some

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(9) A. Stock, *Ber.*, **54A**, 142 (1921).

(10) A. Stock, *ibid.*, **50**, 998 (1917).

(11) Stock and Kuss, *ibid.*, **56**, 789 (1923).

cases as small as 0.0177 g. and never larger than 0.0312 g. Under these circumstances the agreement between the calculated and the observed values reported below must be considered quite satisfactory.

C. Preparation of the Methyl Derivatives of Diborane.—Three experiments may be cited as typical of the proportions of the reagents used and of the yields obtained. When diborane and boron trimethyl were mixed in the proportion of five mols to one and allowed to react for twelve hours at room temperature there was a decrease in (gas) volume of about 5.7%. This change in volume corresponds to a conversion of 60% of the boron trimethyl to dimethyldiborane and 40% to the monomethyl derivative. With equal volumes of the two reagents, for which the most precise measurements were made, the product consisted of 8.1% monomethyldiborane, 81.6% dimethyldiborane, 8.0 and 2.3% of the tri- and tetramethyl derivatives, respectively. With one mol of diborane and four mols of boron trimethyl, the products were exclusively trimethyl and tetramethyldiborane.

(1) **Isolation of Monomethyldiborane.**—The mixture resulting from the first reaction described in the previous section was passed through a U-tube cooled to −160°, to separate the excess diborane from the products of the reaction. The condensate in the −160° tube was then passed through a U-tube cooled to −140°. The fraction which passed through the latter tube was then subjected to the fractionation twice more. In all of these fractionations the pressure was less than one millimeter of mercury. The material finally obtained exerted a vapor tension of 55 mm. at −78.5°. It was so unstable that its vapor tension at −78.5° rose to 65 mm., as a result of exposure of the vapor to room temperature for one minute.

Two samples of this material with vapor tension of 55 mm. at −78.5° were then analyzed by the hydrolysis method previously described. The observed quantities are compared with those calculated from the equation: $B_2H_5CH_3 + 5H_2O \longrightarrow B(OH)_3 + CH_3B(OH)_2 + 5H_2$.

Sample	H_2 calcd.	H_2 found	$B(OH)_3$ calcd.	$B(OH)_3$ found
0.201[12]	1.005	0.992	0.201	0.202
.235	1.175	1.168	.235	.231

(2) **Isolation of Dimethyldiborane.**—The mixture from the reaction of equal volumes of diborane and boron trimethyl was passed through a series of U-tubes surrounded by baths at −112, −120 and −196°. The material collected in the −120° tube was then refractionated through the same cooling baths. The final product thus obtained was separated by distillation into several portions, each of which exhibited a vapor tension of 10 mm. at −78.5°, thus indicating that the product was homogeneous and probably pure.

The observed molecular weights were 54.0 and 54.6; the theoretical value 55.7.

The vapor tension of this material was measured at several temperatures between −78.5 and −44.5°. The values fit satisfactorily the equation $\log P = (-1212/T) + 7.363$, as can be seen from the calculated temperatures given in the table. From the equation the heat of vaporization is seen to be 5540 cal., the boiling point −2.6°, and the Trouton constant 20.2.

V. t., mm.	10	31	38	42	50
T (abs.), obsd.	194.6	206.7	209.2	212.0	213.6
T (abs.), calcd.	191.5	206.5	209.6	211.2	214.0
V. t., mm.		64	69	103.5	113
T (abs.), obsd.		218.0	219.6	226.5	228.6
T (abs.), calcd.		218.1	219.4	226.7	228.3

Two samples of this material were then analyzed by the two methods already described

$$B_2H_4(CH_3)_2 + 4H_2O \longrightarrow 4H_2 + B(OH)_3 + BOH(CH_3)_2 \quad (1)$$

Sample	H_2 calcd.	H_2 found	$B(OH)_3$ calcd.	$B(OH)_3$ found	BOH-$(CH_3)_2$ calcd.	BOH-$(CH_3)_2$ found
0.291[12]	1.166	1.165	0.291	0.285	0.291	0.290
.478	1.910	1.890	.478	.469	.478	.472

$$B_2H_4(CH_3)_2 + 12O \longrightarrow 2CO_2 + 2B(OH)_3 + 2H_2O \quad (2)$$

Sample	CO_2 calcd.	CO_2 found	$B(OH)_3$ calcd.	$B(OH)_3$ found
0.342[12]	0.685	0.684	0.684	0.678
.375	.750	.748	.750	.737

The values of the melting point, determined by the method of Stock,[13] were found to be as follows for four carefully purified samples: −150.2, −150.1, −150.2 and −150.2°, average −150.2°. In all cases the melting point rose about two degrees if the material was allowed to warm up for only a short time. This was undoubtedly due to the formation of heavier derivatives.

Isolation of Dimethylboric Acid.—The water and volatile materials from the hydrolysis of the dimethyldiborane were passed through a U-tube cooled to −50° and condensed in a U-tube at −70°. The process was repeated several times with the −70° condensate, finally yielding a product which had a vapor tension of 36 mm. at 0°. The molecular weights were found to be 54.6 and 56.4: the theoretical value 57.8.

ANALYSES BY OXIDATION

Sample	CO_2 calcd.	CO_2 found	$B(OH)_3$ calcd.	$B(OH)_3$ found
0.468[12]	0.936	0.944	0.468	0.460
.437	.875	.876	.437	.429

(3) **Isolation of Trimethyldiborane.**—The condensate obtained in the U-tube cooled to −112° in the process of purification of the dimethyldiborane, was passed through a series of U-tubes surrounded by baths at −90, −100 and −196°. The condensates in the −90° and the −196° tubes were removed and the condensate in the −100° tube was then passed through the series again. Several repetitions of this process yielded a homogeneous product.

The observed molecular weights of this material were 68.5 and 69.2; the theoretical value 68.7.

The vapor tensions were determined at several temperatures between −78.5 and 0°. The values fit satisfactorily the equation $\log P = (-1527/T) + 7.673$. From the equation the heat of vaporization is found to be 6980 cal., the boiling point 45.5° and the Trouton constant 21.9.

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[12] All quantities in this and subsequent analytical tables are expressed in millimoles.

[13] Stock, *Ber.*, **50**, 156 (1917).

V. t., mm.	2.0	3.1	4.2	9.4
T (abs.), obsd.	211.7	212.3	216.5	227.5
T (abs.), calcd.	207.1	212.6	216.6	227.9
V. t., mm.	22.6	50.0	53.5	123.0
T (abs.), obsd.	241.1	256.1	257.6	273.1
T (abs.), calcd.	241.6	255.6	256.9	273.5

Analyses.—$B_2H_3(CH_3)_3 + 3H_2O \longrightarrow 3H_2 + BOH(CH_3)_2 + BCH_3(OH)_2$.

Sample	H_2 calcd.	H_2 found	$BOH(CH_3)_2$ calcd.	$BOH(CH_3)_2$ found
0.278[12]	0.836	0.836	0.278	0.277
.261	.783	.782	.261	.260

$B_2H_3(CH_3)_3 + 15O \longrightarrow 3CO_2 + 2B(OH)_3 + 3H_2O$

Sample	CO_2 calcd.	CO_2 found	$B(OH)_3$ calcd.	$B(OH)_3$ found
0.184[12]	0.553	0.556	0.368	0.367
.207	.620	.616	....	....

The melting points of three different samples are −122.9, −122.9 and −122.9°, av. −122.9°.

(4) **Isolation of Tetramethyldiborane.**—The condensate obtained in the −90° U-tube in the process of isolation of the trimethyldiborane was passed through a series of U-tubes surrounded by baths at −70, −78.5 and −196°. The condensate in the −78.5° tube was then passed through this series until a sample having a vapor tension of 54 mm. at 0° was obtained. The material collected on the walls of the tube as long needles. Pumping this material for 45 minutes at −78.5° removed traces of trimethyldiborane, and reduced the 0° tension to 48 mm. Even very brief exposure to higher temperatures brought the 0° tension back to 54 mm. The impurity responsible for this change can be removed only by the procedure just mentioned. Although the amount of this impurity is very small, all vapor tensions recorded were obtained with the specially purified samples.

The values for the molecular weight were 83.4 and 84.5; the theoretical value 83.7.

The vapor tension of this material was determined at several temperatures between −51.2 and 0°. The data fit the equation $\log P = (-1643/T) + 7.687$. From this equation the heat of vaporization is seen to be 7525 cal., the boiling point 68.6° and Trouton's constant 22.

V. t., mm.	2	7	18	25	28	48
T (abs.), obsd.	221.9	240.1	255.1	261.6	264.1	273.1
T (abs.), calcd.	222.3	240.0	255.4	261.2	263.3	273.4

Analyses. $B_2H_2(CH_3)_4 + 2H_2O \longrightarrow 2H_2 + 2BOH(CH_3)_2$.

Sample	H_2 calcd.	H_2 found	$BOH(CH_3)_2$ calcd.	$BOH(CH_3)_2$ found
0.379[12]	0.758	0.759	0.758	0.756
.367	.734	.732	.734	.731

The melting points of three samples of this material were −72.5, −72.5 and −72.5°, av. −72.5°.

We take pleasure in acknowledging the invaluable assistance and suggestions of Dr. A. B. Burg and Mr. Leo Horvitz, as well as the aid furnished by a grant from the National Research Council for liquid nitrogen extensively used in this work.

Summary

1. Four methyl derivatives of diborane ($B_2H_5CH_3$, $B_2H_4(CH_3)_2$, $B_2H_3(CH_3)_3$ and $B_2H_2(CH_3)_4$) have been prepared by the reaction of boron trimethyl with diborane. Vapor densities, vapor tensions and freezing points, together with some other derived physical constants of these compounds, have been determined.

2. A study of the products of the reaction of the methyl derivatives with water indicates that tetramethyldiborane has a symmetrical structure, that in dimethyldiborane both methyl groups are attached to the same boron atom and that in trimethyldiborane one boron atom holds two while the other boron atom is combined with one methyl group.

3. Treatment of the lower methyl derivatives with excess of boron trimethyl leads to the formation of the higher derivatives; in the absence of boron trimethyl the higher derivatives decompose into the lower ones and ultimately into boron trimethyl and diborane.

4. Nevertheless, even with large excess of boron trimethyl, no indications of the formation of penta- or hexamethyl derivatives were observed.

5. The bearing of these observations on the question of the structure of diborane has been discussed.

6. In the course of the investigation dimethylboric acid, formed by the action of water on the three higher methyl derivatives, has been isolated and characterized.

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