

XII.—*The Hydrides of Boron.*

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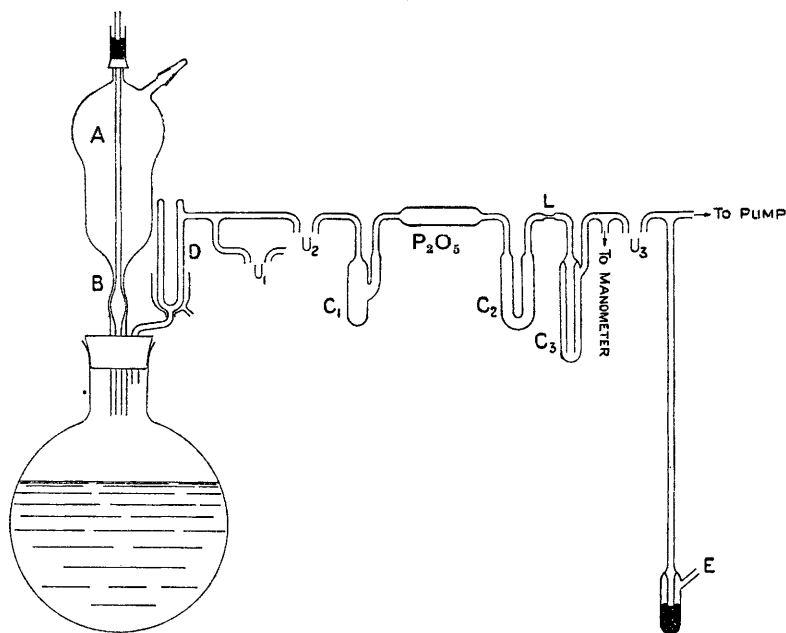
THE investigations of Stock and his collaborators (*Ber.*, 1912 *et seq.*) have definitely shown the existence of a series of boron hydrides of a composition which is unexpected in view of the position of boron in the periodic classification and of the existence of trivalent alkyl compounds. The conclusions of Jones and Taylor (*J.*, 1879, **35**, 41; 1881, **39**, 213), Sabatier (*Compt. rend.*, 1891, **112**, 866), and Ramsay and Hatfield (*P.*, 1901, **17**, 152) as to the existence of BH_3 are without sufficient experimental foundation, yet a doubt remains that the existence of the simpler hydrides might be established if the field of investigation were widened. All previous investigators have used magnesium boride, except Hoffmann (*Chem.-Ztg.*, 1911, **35**, 265), who showed that commercial iron and manganese borides, on reaction with acids, give boron hydrides, which he did not identify. In the case of carbon, different metallic carbides yield different types of hydrocarbons, and it was suspected that other metallic borides might not yield the same hydrides. The suspicion, however, has not been substantiated.

Wöhler and Deville (*Ann. Chim. Phys.*, 1858, **52**, 63), using high temperatures, prepared borides of aluminium which are practically unreactive with acids, but, by using a method similar to that of Stock and Massenez (*Ber.*, 1912, **45**, 3543) for the preparation of magnesium boride, we have prepared an aluminium boride which reacted with acids to give hydrogen containing boron hydride. The same method, with special precautions, led to the preparation of a cerium boride which reacted similarly. In both cases the yield of boron hydride is small, this being particularly so with the aluminium compound. The identity of our boron hydrides with those formed from magnesium boride has been definitely established in the case of gaseous B_4H_{10} , and although the results in the case of the liquid hydrides are not absolutely decisive, the indications are that they are also the same, namely, B_5H_9 and B_6H_{10} .

EXPERIMENTAL.

Preparation of the Aluminium Boride.—Fine aluminium powder (3 parts) and finely powdered boron oxide (1 part) were intimately mixed and fused in small quantities (8–10 g.) in an iron crucible over a large Meker burner. After 3–5 minutes' heating, a bright glow spread through the mass, and at this point the crucible was removed and quickly cooled by plunging its lower portion into water. The product was a greyish, very friable mass.

FIG. 1.



Preparation of the Cerium Boride.—Cerium metal powder ($2\frac{1}{4}$ parts) and powdered boron oxide (1 part) were mixed, and very small quantities fused in a fairly rapid stream of hydrogen. (If large portions were used or if the stream of hydrogen was not rapid, reaction was so vigorous as to melt the bottom of the crucible.) The product, a hard black mass, was powdered in a percussion mortar.

Generating Apparatus.—For the decomposition of the boride, phosphoric acid (d 1.4) at 75° was used. It appears to give better yields than hydrochloric acid, and although some phosphine is formed, this is more readily removed in fractionation than the hydrogen sulphide which results from the use of sulphuric acid.

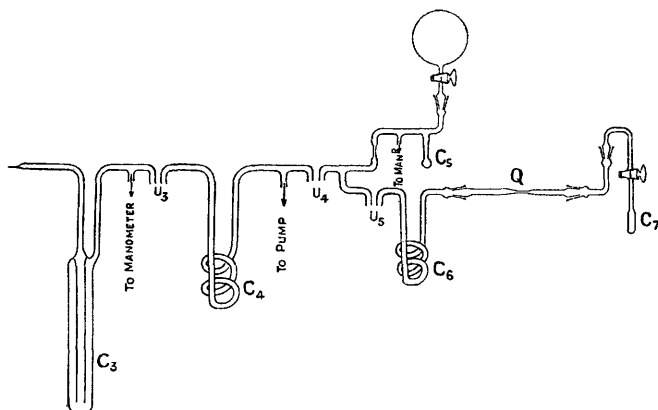
The acid was placed in a 6-litre flask, and the aluminium or cerium boride in A (Fig. 1), which was closed at the top by a mercury seal through which passed a glass rod with a tapered grinding fitting into a constriction at B. By depressing this rod slightly, and either slowly revolving it or tapping A, the powder could be introduced into the acid at a suitable rate. D was a double-surface water-cooled condenser, and C_1 a condenser immersed in liquid ammonia. The liquid ammonia and finally phosphoric oxide remove water. C_2 was the main condenser immersed in liquid air, and containing cotton wool to prevent any boron hydride passing through as a fume or mist. C_3 was another liquid-air condenser, without cotton wool, and connected to a closed U-tube manometer. The issuing hydrogen bubbled out through mercury at E. The whole was connected to the mercury pump. Owing to the hardening action of the boron hydride on tap lubricant, taps were discarded in favour of either U-tube arrangements with greaseless gas valves (see Stock, *Ber.*, 1914, 47, 3109), or simply U-tubes 80 cm. in length with mercury traps at the top, connected to a mercury reservoir. The positions of these tap substitutes are at U_1 , U_2 , and U_3 . In case a larger quantity of gas than could be obtained from one charge of A was required, U_2 would be shut when the powder was exhausted, and the air pumped out through U_1 when fresh powder was introduced.

The boron hydride condensed in C_2 , except some of the higher-boiling product, which condensed in the liquid ammonia. In no case did the issuing hydrogen burn with a green flame. When all the gas had been generated, U_2 was shut, the hydrogen pumped out, and the condensate transferred to the condenser without cotton wool, any boron hydride in the liquid ammonia being transferred also. A constriction at L was then sealed off, U_3 shut, and the glass tubing to the right of it cut and joined to the fractionating and analysing apparatus shown in Fig. 2, all the air being then pumped out.

Fractionation and Analysis.—By blowing liquid air through pentane in a Dewar vessel, a range of temperature up to -120° could be attained, the temperature being measured by a standardised pentane thermometer. Fractionation was carried out at selected temperatures, the pressure shown by the manometer being read; U_3 was opened for a short interval, thus allowing passage to C_4 in liquid air, then closed again, and the manometer re-read, the process being repeated if necessary. The fraction thus removed and condensed in C_4 was then analysed without interfering with the residue of the yield, U_3 being kept shut and C_3 replaced in liquid air. The liquid air was removed from C_4 , and the fraction allowed to vaporise

into the density bulb. Since we were dealing with small quantities, we condensed all the fraction in C_5 by liquid air, shut U_4 and U_5 , and then removed the liquid air. The pressure was read on the manometer, the tap to the density bulb shut, and the small amount of gas in the connecting tubes pumped out and collected. When the bulb was replaced after weighing and the air pumped out, the tap to the bulb was opened and the gas condensed by liquid air in C_7 , where it was reweighed. By removing the liquid air from under C_7 the gas was allowed to stream through a quartz tube Q , which was heated to redness. Unless the passage of the gas is very slow, decomposition is not complete. C_6 was kept in liquid air to collect undecomposed gas. The hydrogen was pumped out and its volume measured. Any undecomposed gas was then transferred by liquid

FIG. 2.



air back to C_7 , and the process repeated. Any solid boron hydride formed in the cooler part of the tube was decomposed by strong heating. Entire decomposition was assured. The deposited boron was estimated both by direct weighing and by titration as boric acid after oxidation by nitric acid. A further study of the composition was afforded by reaction with strong alkali solution, and then decomposition of any hypoborate formed by addition of excess of sulphuric acid; for this purpose, in the case of B_4H_{10} an amount was pumped out and its volume measured, and in the case of the higher-boiling fractions an amount in C_7 was weighed. The reaction is $B_xH_y + 3xH_2O = xH_3BO_3 + \frac{1}{2}(3x + y)H_2$.

The results leave no doubt as to the formation of B_4H_{10} from both the aluminium and the cerium compound. The results given by the liquid fractions are not quite so definite, but indicate B_5H_9 and B_6H_{10} .

Silicon hydrides, phosphine, and carbon dioxide are formed from the aluminium compound and phosphoric acid. Phosphine and carbon dioxide, but no silicon hydrides, are formed from the cerium compound.

Results from Cerium Boride.—280 G. of the boride and 4 litres of phosphoric acid were used. The earlier fractions proved on analysis to be mixtures of phosphine and carbon dioxide, with no trace of boron hydride. The hydride was first detected in a fraction at $-90^{\circ}/<1$ mm. The fraction taken at -80° with a constant vapour pressure (about 1 mm.) gave the following results :

Volume = 12—15 c.c.

(a) Molecular weight, 52.5 (Calc. for B_4H_{10} , 54).

(b) Decomposition by water : 1 vol. \rightarrow 10.7 vols. (Calc., 11 vols.).

(c) Decomposition by heat : 4.5 c.c. (at 765 mm. and 22°) gave 22.3 c.c. of hydrogen (Calc., 22.5 c.c.) and a deposit of boron—(1) by weight = 8.5 mg., (2) by titration = 8.2 mg. (Calc., 8.3 mg.).

The next fractionation, carried out at the temperature of liquid ammonia (-33°), gave 35 mg. of a liquid; the residue (about 10 mg.) was not analysed.

(a) Decomposition by water : 6.4 mg. gave 26.8 c.c. H_2 at *N.T.P.* (Calc. : For B_6H_{10} , 26.1 c.c.; for B_5H_9 , 26.6 c.c.; for B_4H_{10} , 28.9 c.c.).

(b) Decomposition by heat : 28.7 mg. gave 24.6 mg. of boron and 45.5 c.c. or 4.1 mg. of hydrogen (Calc. : For B_4H_{10} , 23.4 mg. B, 5.3 mg. H_2 ; for B_5H_9 , 24.7 mg. B, 4.0 mg. H_2 ; for B_6H_{10} , 24.9 mg. B, 3.8 mg. H_2).

This fraction probably contained some B_4H_{10} , and the analyses are probably those of a mixture of B_4H_{10} , B_5H_9 , and B_6H_{10} —the B_4H_{10} in small amount.

Results from Aluminium Boride.—800 G. of the boride were used. Early fractions contained no boron hydride. The fraction (about 15 c.c.) at b.p. $-80^{\circ}/1$ mm. gave :

(a) Molecular weight, 55.05.

(b) Decomposition by water : 1 vol. \rightarrow 10.8 vols. of H_2 .

(c) „ „ heat : 1 vol. \rightarrow 5.05 vols. of H_2 .

The next fraction was taken at -60° . It was too small to be analysed, but probably contained the last of the B_4H_{10} .

Two fractions were taken at -33° ; the first (10 mg.) was lost, but the second (20 mg.) gave a result agreeing very closely with

B_6H_{10} : 10.45 mg. gave 15.4 c.c. H_2 at *N.T.P.* and 9.0 mg. B (calc. for B_6H_{10} : 15.2 c.c. H_2 , 9.1 mg. B).

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