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Improved Arc Process for the Preparation of Diborane. Purification of Diborane[1]

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Optimum conditions for operating the arc method for the preparation of diborane are very briefly outlined as are improvements in the procedure which reduce the amount of liquid nitrogen and decrease greatly the time required for the generation of diborane. The use of pyridine in separating diborane from hydrogen halides and other impurities is described.

To meet our requirements for diborane, in the initial phases of the investigation described in a general way in paper I of this series, we reinvestigated and improved the procedure for preparing diborane by the passage of an electrical discharge through a mixture of hydrogen and boron tribromide vapor.[2] Because still more satisfactory methods were later developed,[3] the modified arc process is described only very briefly. In general the apparatus was much like that described by Schlesinger and Burg[2a] except as pointed out below.

The most important changes we have made in the procedure are the following: (1) The amount of liquid nitrogen required has been greatly decreased by carrying out the condensation of the major portion of the initial reaction product with solid carbon dioxide instead of with liquid nitrogen. Bromodiboranes and unchanged boron tribromide were thus condensed while hydrogen and hydrogen bromide passed on. The trap used for the condensation should be so designed that relatively large amounts of material can be condensed without clogging the system.

(2) The time required for conversion of the bromodiboranes to diborane according to the equation

$$3B_2H_{6-x}Br_x \rightleftarrows \frac{6-x}{2}(B_2H_6) + xBBr_3$$

has been greatly reduced. This result was achieved by heating the original −80° condensate to 100°. For this purpose the condensate was distilled into a fractionating apparatus consisting of a boiler and a vertical, air-cooled condenser the upper part of which carried a cup-like cold finger filled with solid carbon dioxide. The diborane passed by the cold finger and through a −80° trap (to complete its separation from higher boiling materials) into liquid nitrogen traps. The unchanged bromodiboranes, returned to the boiler by the cold finger, reacted further according to the equation given because of the removal of diborane.

(3) Diborane prepared by the arc process is always contaminated with hydrogen halides which are difficult to remove by physical means. The separation may be very satisfactorily effected by adding small quantities of pyridine to the impure diborane.

$$B_2H_6 + 2C_5H_5N \longrightarrow 2C_5H_5N{:}BH_3$$
$$C_5H_5N{:}BH_3 + 3HX \longrightarrow C_5H_5N{:}BX_3 + 3H_2$$

At the cost of 2 to 3% of the diborane, hydrogen halides are rapidly and quantitatively removed.[4]

Studies on the process as a whole indicated that the optimum conditions are high flow rate (700 ml. per minute of hydrogen saturated with boron tribromide at 25°), low pressure (15 mm.) in the discharge chamber, a separation of about 7 cm. of the water-cooled copper electrodes and a current of 40–50 ma. at 12,000 volts. Under these conditions a conversion of about 10% of the boron bromide with a yield of about 300 cc./hr. of diborane (gas at S.T.P.) or about 85% may be attained. If either the pressure or the current rises much above the values given, boron is deposited and both conversion and yield drop sharply.

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(1) New Developments in the Chemistry of Diborane and the Borohydrides. II. For paper I, see THIS JOURNAL, **75**, 186 (1953).

(2) (a) H. I. Schlesinger and A. B. Burg, *ibid.*, **53**, 4321 (1931); (b) A. Stock and W. Sutterlein, *Ber.*, **67**, 407 (1934).

(3) Reference 1 and paper IV: H. I. Schlesinger, H. C. Brown, J. R. Gilbreath and J. J. Katz, THIS JOURNAL, **75**, 195 (1953).

(4) Diborane may be purified from volatile impurities which do not react with pyridine by converting the diborane to the non-volatile pyridine borine. The volatile impurities are removed and the diborane is regenerated from the pyridine borine, *e.g.*, by the addition of boron fluoride etherate.