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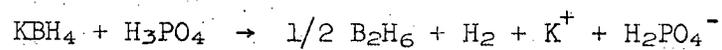
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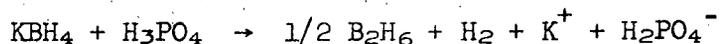
DIBORANE



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DIBORANE



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Diborane can be prepared by a variety of methods, the most common being the reduction of boron trihalides with active metal hydrides^{1,2} and the reaction of hydroborate salts with stannous chloride,³ sulfuric acid,⁴ methanesulfonic acid,⁴ orthophosphoric acid,^{5,6} or polyphosphoric acid.⁶ Although diborane is commercially available in bulk quantities, we have found the reaction of potassium hydroborate (KBH_4) with 85% orthophosphoric acid to be convenient for the rapid preparation in a vacuum line of small quantities of this material. Using this method, diborane is obtained in only fifty percent of the theoretical yield; however, the absence of volatile solvents, the high purity of the product, and the simplicity of the reaction apparatus make this method superior.

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By using approximately 100 percent orthophosphoric acid,⁶ we have increased the yield of diborane to 60-65 percent. However, under these conditions extensive foaming occurs, necessitating the use of an overhead stirrer in the reaction apparatus. We believe the advantage of this increased yield is offset by the relative unavailability of the more concentrated acid and the increased difficulty of stirring.

Caution: This synthesis is not suitable for the preparation of diborane in a flow system at atmospheric pressure because flaming of the reaction mixture and/or the formation of unwanted reduction products (i.e. phosphine) may occur. Inasmuch as diborane reacts violently with oxygen, it must be handled either in a vacuum line or an oxygen-free reaction system at all times.

Procedure

A 200 ml. reaction vessel equipped with an efficient magnetic stirrer and a side-arm addition tube, as shown in the Figure, is connected to a vacuum line in such a way that the volatile reaction products can be removed through a series of four U-tube traps. A plug of glass-wool in the neck of the reaction vessel prevents traces of nonvolatile materials from being carried into the vacuum line. It is also convenient to have a mercury manometer in the system so that gas pressure can be monitored during the reaction. Twenty milliliters of reagent grade orthophosphoric acid (85% H_3PO_4) is poured into the reaction vessel, 1.6 g (0.0297 mole) of fresh carbonate-free KBH_4 * is placed in the

* Metal Hydrides Inc., Beverly, Mass.

side-arm, the side is attached to the reaction vessel as shown in the Figure, and the reaction vessel is evacuated for a period of 0.5 hr. At the end of this time the trap nearest the reaction vessel is cooled to -78° (dry-ice-acetone mixture) and the three remaining traps are cooled to -196° (liquid nitrogen).

Diborane production is begun by carefully rotating and tapping the side-arm until the powdered KBH_4 begins to drop onto the surface of the rapidly stirred acid. Gas evolution begins immediately, and foaming of the reaction mixture occurs. For maximum yield and minimum foaming, care should be taken to avoid the sudden addition of large quantities of KBH_4 . The KBH_4 should be added slowly enough (over a period of 0.5-0.75 hr.) so that the pressure in the reaction system never exceeds 10 mm.

Pumping is continued for at least 0.5 hr. after the last of the KBH_4 has been added, in order to ensure complete removal of the diborane prior to detachment of the reaction vessel from the vacuum line. The condensate in the -78° trap consists mainly of water and traces of trapped diborane, and can be discarded. The diborane, condensed in the -196° traps, is purified by passage through a -111.6° (carbon disulfide slush) into a -196° trap. Traces of material which condense at -111.6° may be discarded. Typically, from six to seven mmoles of B_2H_6 are obtained from this reaction. The reaction may be conveniently scaled up (by no more than a factor of three!) for the preparation of larger quantities, provided that a correspondingly larger reaction vessel is used to accommodate the additional foam.

Properties

Diborane prepared by this method has a vapor pressure at -111.6° of 225 ± 1 mm, a value identical with that reported in the literature.⁷ The infrared spectrum⁸ shows absorptions at 3670 (w), 2625 (s), 2558 (s), 2353 (w), 1853 (m), 1602 (vs), 1197 (s), 1178 (s), 1154 (s), and 973 (m, sh) cm^{-1} . The mass spectrum has peaks from m/e 10-13 and from m/e 21-27, attributable to BH_x^+ and B_2H_x^+ ions, respectively. A small peak at m/e 44 arising from a trace of carbon dioxide (< 0.1%) is also observed in some cases.

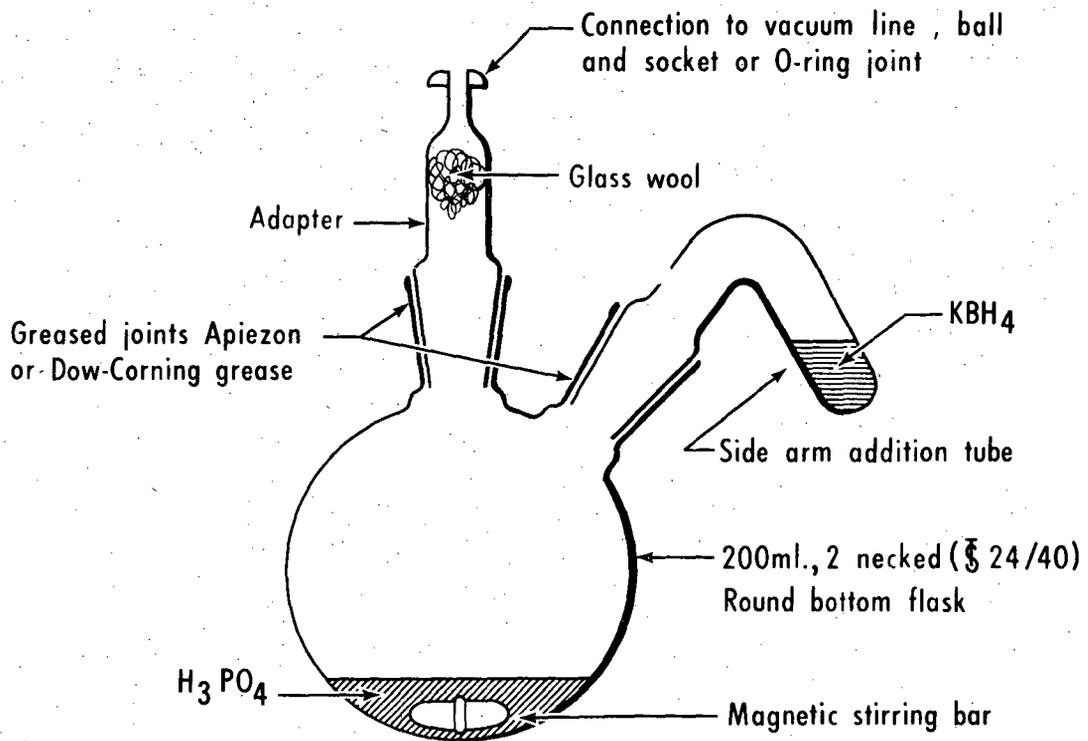
Diborane may be stored in the gas phase at room temperature for several days without appreciable decomposition. On long standing, hydrogen and higher boron hydrides are formed. These decomposition products may be removed by freezing the material at -196° , pumping off the hydrogen, and then distilling the diborane through a -130° trap (n-pentane slush) into a -196° trap.

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Figure Legend

Apparatus for the Preparation of Diborane.



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