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Abstract

Full Text

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ON THE PRODUCTION OF DIBORANE BY REDUCTION OF BORON TRIFLUORIDE ETHERATE WITH CALCIUM HYDRIDE

(Presented by Academician I. I. Chernyaev, November 10, 1959)

The reduction of boron halide compounds by calcium hydride is a little-studied reaction.

According to Hurd' s data ([1]), vapors of boron trichloride at temperatures above 200° in the presence of hydrogen give gaseous products containing diborane. Hagemüller and de Pape ([2]), studying the interaction of gaseous boron trifluoride with calcium hydride, established the formation of diborane at 225–300°, but at this temperature the reaction proceeded incompletely.

Fig. 1. Thermogram of a mixture of calcium hydride with boron trifluoride etherate

At 300–700° the main product of the reaction is higher boranes and boron, and at a still higher temperature—calcium boride, CaB_6. The authors regard the reduction reaction of boron trifluoride by calcium hydride as a new method for obtaining boron (at 300°) and calcium boride (at 700°).

The aim of the present work was to find conditions for the reduction of boron trifluoride etherate by calcium hydride that ensure the production of diborane, and it is a continuation of our studies on the reaction of boron trifluoride with lithium hydride ([3–5]). The investigation of the reaction of BF_3 etherate with calcium hydride was preceded by a thermographic study of this reaction using N. S. Kurnakov' s pyrometer with differential recording and simultaneous analysis of the evolved gases.

Thermographic analysis showed that the evolution of diborane practically coincides with the onset of boiling of boron trifluoride etherate (120°), and the

Fig. 2. Apparatus for obtaining diborane

Figure 2: Fig. 2. Apparatus for obtaining diborane

greatest amount of it is evolved at a molar ratio $CaH_2 : BF_3$ close to 3 : 2, probably according to the equation

$$3CaH_2 + 2BF_3 \cdot (C_2H_5)_2O = B_2H_6 + 3CaF_2 + 2(C_2H_5)_2O.$$

In addition to the thermal effect corresponding to this reaction (masked by the superposition of the thermal effect of boiling of the etherate), on all thermograms (Fig. 1) an endothermic effect is observed at 250–322°, corresponding to the decomposition of calcium borofluoride $Ca(BF_4)_2$ (decomp. temp. 260–295° ([6])); $Ca(BF_4)_2 \rightarrow CaF_2 + 2BF_3$, and an exothermic effect at 300–333° of the reaction of formation of elemental boron according to the equation:

$$3CaH_2 + 2BF_3 = 3CaF_2 + 2B + 3H_2.$$

The synthesis of diborane was carried out at a temperature close to the boiling point of the etherate, in an apparatus consisting of a reactor equipped with a mechanical stirrer with a mercury seal, a reflux condenser, a dropping funnel, a nitrogen inlet, and a thermometer (Fig. 2). Calcium hydride powder (150 mesh) was placed in the reactor, and boron trifluoride etherate was gradually added. Upon heating the mixture to 110–120°, vigorous evolution of diborane began; the diborane was absorbed by a benzene solution of *p*-toluidine.

Fig. 2. Apparatus for obtaining diborane

The yield of diborane was calculated in two ways: from the amount of it bound by the amine, and from the consumption of calcium hydride in the reaction medium.

The ratio of the reactants has a decisive effect on the yield of diborane (Table 1). With an insufficient amount of boron trifluoride etherate, approximately 1–2 hours after the onset of diborane evolution, a spontaneous exothermic reaction develops in the reaction mixture, as a result of which the temperature of the mixture rises to 450–500°. In this case the reaction mixture turns black and the yield of diborane drops sharply (experiments 1 and 2). The greatest yield is achieved with an excess of etherate of up to 60% (experiments 4 and 6). Elemental bromine and iodine do not exert an activating effect on the reaction under study.

In the solid reaction products, chemical and X-ray diffraction (Debye) methods revealed CaF_2, $Ca(BF_4)_2$, CaH_2, and elemental boron. The presence of $Ca(BF_4)_2$ was also confirmed by the thermographic method. The formation of calcium borofluoride may be represented by the scheme: $CaF_2 + 2BF_3 = Ca(BF_4)_2$.

Calcium borohydride $Ca(BH_4)_2$ was not detected chemically in the reaction products. The diborane formed was identified in the form of its compounds with *p*-toluidine and trimethylamine by the contents of boron and hydride hydrogen and by the melting point.

$CH_3C_6H_4NH_2 \cdot BH_3$.	Found, %:	B 8.98; 9.12;	H_{hydr} 2.47; 2.39
	Calculated, %:	B 8.95;	H_{hydr} 2.489

M.p. 59-60° (literature value 60° (7)).

Found, %: B 14.95; 14.70; H_{hydr} 4.130; 4.125
$(CH_3)_2N \cdot BH_3$. Calculated, %: B 14.85; H_{hydr} 4.128

M.p. (after sublimation) 94° (literature data 94° [8]).

Table 1

Data on the study of the reaction of calcium hydride with boron trifluoride etherate

Exp. No.	Taken, g (mol.) CaH_2	Taken, g (mol.) $BF_3 \cdot (C_2H_5)_2O$	Molar ratio CaH_2 : BF_3	Yield of B_2H_6, %, calculated from $CH_3C_6H_4NH_2 \cdot BH_3$	Yield of B_2H_6, %, calculated from CaH_2	Obtained *n*-$CH_3C_6H_4NH_2 \cdot BH_3$, g	Obtained *n*-$CH_3C_6H_4NH_2 \cdot BH_3$, m.p., °C	Obtained *n*-$CH_3C_6H_4NH_2 \cdot BH_3$, H_{hydr} content, %	Reaction temp., °C
1	12.6(0.3)	35.5(0.25)	3 : 2.5	Not det.	22	–	–	–	120°, then up to 450°
2	13.6(0.32)	35.5(0.25)	3.2 : 2.5	Not det.	62	–	–	–	Same
3	10.22(0.23)	32.7(0.23)	1 : 1	Not det.	20	–	–	–	Same
4	4.2(0.1)	14.3(0.1)	1 : 1	Not det.	100	–	–	–	120°
5	6.32(0.15)	14.2(0.1)	3 : 2	65	73	20.61	58–60	2.47	120°
6	6.33(0.15)	21.3(0.15)	1 : 1	95	100	22.45	58–59	2.39	Same

Exp. No.	Taken, g (mol.) CaH_2	Taken, g (mol.) $BF_3 \cdot (C_2H_5)_2OBF_3$	Molar ratio CaH_2 :	Yield of B_2H_6, %, calculated from CaH_2	Yield of B_2H_6, %, calculated from $CH_3C_6H_4 - NH_2 \cdot BH_3$	Obtained n-$CH_3C_6H_4NH_2 \cdot BH_3$, g	Obtained n-$CH_3C_6H_4NH_2 \cdot BH_3$, m.p., °C	Obtained n-$CH_3C_6H_4NH_2 \cdot BH_3$, hydride content, %	Reaction temp., °C
7	6.32(0.15)	35.3(0.15)	3 : 5	75	70	30.60	58–59	2.28	Same

The results of the present work show that diborane can be obtained in good yield by reducing boron trifluoride etherate with calcium hydride.

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Note: Figure translations are in progress. See original paper for figures.