

# Mechanochemical Synthesis of Diborane(6) by Reactions of Alkaline Tetrahydroborates with Iron (III) Chloride

KLAVDIY G. MYAKISHEV and VLADIMIR V. VOLKOV

*Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 3, Novosibirsk 630090 (Russia)*

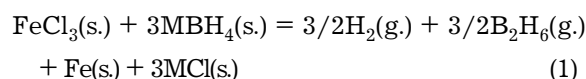
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## Abstract

Reactions of  $\text{FeCl}_3$  with  $\text{MBH}_4$  ( $M = \text{Li, Na, K}$ ) which take place during mechanical activation (MA) of mixtures of crystalline substances in a vibratory vacuum mill have been studied. The reactions form diborane(6) or  $\text{B}_2\text{H}_6$ ; the product yields depend on the nature of  $\text{MBH}_4$ , on the molar ratio of reagents, and on the mechanical activation time. Under optimal conditions, the yield of  $\text{B}_2\text{H}_6$  is 81.5, 79.5, and 73.5% when  $\text{LiBH}_4$ ,  $\text{NaBH}_4$ , and  $\text{KBH}_4$ , respectively, are used. When mixtures of  $\text{FeCl}_3$  with  $\text{MBH}_4$  are heated without MA, reactions occur with liberation of  $\text{H}_2$ , while  $\text{B}_2\text{H}_6$  is not formed.

## INTRODUCTION

Diborane(6), or  $\text{B}_2\text{H}_6$ , is a substrate for the synthesis of boron hydrides. Of many synthetic procedures leading to  $\text{B}_2\text{H}_6$  [1], mechanical activation is preferable from ecological viewpoint. This method gave high yields of  $\text{B}_2\text{H}_6$  as a result of solid-phase reactions between anhydrous transition metal halides and  $\text{MBH}_4$  ( $M = \text{Li, Na, K}$ ) avoiding the use of organic solvents as reaction media [2]. In this respect, it is of interest to examine feasibility of solid-phase reactions with iron (III) chloride according to the following scheme:



Thermodynamic data of [3] were used to calculate  $\Delta G_{298}^\circ$  for reactions (1) with  $\text{LiBH}_4$ ,  $\text{NaBH}_4$ , and  $\text{KBH}_4$ , and this resulted in  $-110.3$ ,  $-101.1$ , and  $-90.9$  kJ/mol  $\text{MBH}_4$ , respectively. The reactions are thermodynamically feasible.

As is known, the reaction of iron (III) chloride with  $\text{LiBH}_4$  in ether forms  $\text{B}_2\text{H}_6$  [4].

This compound was also generated by passing iron (III) chloride vapours through  $\text{NaBH}_4$  or by adding  $\text{NaBH}_4$  to a  $\text{FeCl}_3$  melt [1, p. 178].

To obtain diborane(6), in this work we investigated the interaction of anhydrous  $\text{FeCl}_3$  with  $\text{MBH}_4$  ( $M = \text{Li, Na, K}$ ) induced by mechanochemical activation (MA) or by heating.

## EXPERIMENTAL

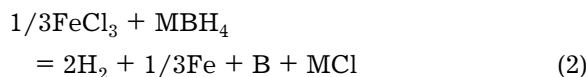
Anhydrous iron (III) chloride was of pure grade;  $\text{LiBH}_4$ ,  $\text{NaBH}_4$ , and  $\text{KBH}_4$  contained 96.5, 95.5, and 98.6 % main substance, respectively. In view of their hygroscopicity, the starting reagents were handled in a box with dry nitrogen. Mechanochemical reactions were conducted in a vibratory vacuum ball mill [5]. The cylindrical reactor (5 cm in height, 100 cm<sup>3</sup> capacity) was charged with steel balls 6 mm in diameter (total weight 100 g); reactor vibration frequency was 23 Hz, vibration amplitude 6 mm. The synthesis was monitored according to the liberation of  $\text{H}_2$  and  $\text{B}_2\text{H}_6$ . The gas mixtures formed by reactions of  $\text{MBH}_4$  with  $\text{FeCl}_3$

in the course of MA were identified by IR and mass spectroscopy. IR spectra were recorded on a UR-20 spectrophotometer using a gas cell (0.1 mm in length) with KBr windows. The presence of  $B_2H_6$  was inferred from the characteristic absorption bands ( $\nu$ ,  $cm^{-1}$ : 2630, 2520, 1915, 1600, 1177, 978) [6]. Mass spectra were measured on an MI-1201 mass spectrometer. Apart from  $B_2H_6$ , no other volatile products such as HCl or  $BCl_3$  have been detected in the gas phase. The total volume of the evolved gas was determined by gasometry; the volume of  $B_2H_6$  was evaluated by the weight method from the amount of boron formed by passing the gas through a weighed quartz tube heated to 700 °C; the amount of  $H_2$  was determined from the volume difference. After MA, the diffraction patterns of powders covered with a Teflon film for protecting them from contact with atmosphere were recorded on a DRON-3M diffractometer ( $CuK\alpha$  radiation). Thermal gas volumetric patterns were measured on a device described in [7] using chromel-alumel thermocouples ( $Al_2O_3$  as a standard, heating rate 6–7 °C/min). The samples were heated in glass ampules at a standard pressure of 1.3 Pa. After thermography, the composition of the gas phases was determined by the method described above.

## RESULTS AND DISCUSSION

In the course of this study, we investigated the effects of MA time ( $\tau$ ), the nature of  $MBH_4$ , and the molar ratio of reagents  $n$  ( $n$  = moles of  $MBH_4$ /moles of  $FeCl_3$ ) on the yield of  $B_2H_6$ . When the reagents were taken in a stoichiometric ratio,  $n = 3$  according to Eq. (1). Gasometric and IR and mass spectrometric measurements indicated that the gas phase formed in the reaction consisted of  $H_2$  and  $B_2H_6$ . No other volatile products such as higher boranes,  $BCl_3$ , or HCl have been detected. The diffraction patterns of the samples of reagent mixtures recorded after MA showed clear-cut reflections corresponding to alkaline chlorides. Consequently, the reactions in general occur by Eq. (1). The yields of  $B_2H_6$  were calculated from Eq. (1) or from the amount of the reagent taken in deficiency when the reagents

were taken in amounts other than stoichiometric. Table 1 lists typical data on MA synthesis of  $B_2H_6$ . According to Eq. (1), the gas phase should contain equal amounts of  $H_2$  and  $B_2H_6$ . The content of  $B_2H_6$  is actually smaller than that of  $H_2$  (see Table 1), indicating that the reactions (partially) follow another route, possibly



Calculation of  $\Delta G_{298}^0$  by Eq. (2) gave  $-156.4$ ,  $-147.1$ ,  $-136.9$  kJ/mol for  $LiBH_4$ ,  $NaBH_4$ , and  $KBH_4$ , respectively; therefore, reactions (2) are thermodynamically more favorable than reactions (1).

The content of diborane(6) in the gas phase, as well as the yield of  $B_2H_6$ , increases with decreasing  $n$ , *i. e.*, with the increasing content of  $FeCl_3$ , the yield of  $B_2H_6$  reaches 70–80 % when  $n \approx 1$  (see Table 1). It is noteworthy that the yields of  $B_2H_6$  and the conversion of the starting boron become equal near  $n = 3$  corresponding to the stoichiometry of reaction (1). The yield of  $B_2H_6$  in these reactions generally correlates with the calculated values of  $\Delta G_{298}^0$ , increasing slightly from  $KBH_4$  to  $NaBH_4$  and  $LiBH_4$ . The dependence of the yield of  $B_2H_6$  on the MA time is illustrated by the history of the gas liberation curves shown in Fig. 1. It can be seen that when  $n > 3$  (curves 1–3) the rate of formation of  $B_2H_6$  from  $KBH_4$  is much smaller than in the cases of  $NaBH_4$  and  $LiBH_4$ . For the latter two compounds, the rates differ insignificantly. For  $n \approx 1$  (curves 4–6), the rate of formation of  $B_2H_6$  from  $NaBH_4$  is much higher than from  $LiBH_4$  and  $KBH_4$ . Thus a significant excess of  $FeCl_3$  over stoichiometry in the reaction mixture favors reaction (1), and the yields of  $B_2H_6$  reach 70–80 %, permitting the use of these reactions for the synthesis of diborane(6) on a scale other than laboratory.

Based on the data of [1], one would expect that  $B_2H_6$  will be formed by heating mixtures of  $FeCl_3$  with  $MBH_4$ . Thermography together with simultaneous gas liberation measurements was carried out for  $FeCl_3$  thoroughly mixed with  $LiBH_4$ ,  $NaBH_4$ , and  $KBH_4$ . Our study showed that after heating to 600–700 °C, gas liberation

TABLE 1  
Mechanochemical synthesis of B<sub>2</sub>H<sub>6</sub> by reactions of FeCl<sub>3</sub> with MBH<sub>4</sub>

Run No.	Reagent mass, g		<i>n</i>	$\tau$ , min	Volume of liberated gas, cm <sup>3</sup>			Volume of B <sub>2</sub> H <sub>6</sub> , calculated by Eq. (1), cm <sup>3</sup>	Content of B <sub>2</sub> H <sub>6</sub> in the gas phase*, %	Yield of B <sub>2</sub> H <sub>6</sub> , %	Conversion of starting boron, %
	MBH <sub>4</sub>	FeCl <sub>3</sub>			Total	B <sub>2</sub> H <sub>6</sub>	H <sub>2</sub>				
LiBH <sub>4</sub>											
1	0.890	0.825	8.1	140	504	75	429	171	14.9	43.9	16.4
2	0.811	0.913	6.6	120	566	90	476	189	15.9	47.6	21.6
3	0.438	1.363	2.4	110	560	127	423	226	23.1	56.2	56.3
4	0.309	1.501	1.5	90	368	111	257	159	30.2	69.8	69.9
5	0.325	2.151	1.1	120	523	137	386	168	26.3	81.5	81.5
NaBH <sub>4</sub>											
6	0.790	0.496	6.9	80	266	43	223	102	16.0	41.9	18.3
7	0.458	0.539	3.7	80	260	47	213	112	18.0	41.8	34.4
8	0.210	0.376	2.4	80	151	29	122	62	19.4	46.8	46.8
9	0.159	0.451	1.5	80	116	31	85	40	26.6	65.5	65.5
10	0.145	0.774	0.8	70	105	34	71	43	32.4	79.5	79.5
KBH <sub>4</sub>											
11	1.457	0.402	10.9	130	217	34	183	83	15.7	40.8	11.1
12	0.624	0.382	4.9	130	211	34	177	79	16.1	43.3	26.1
13	0.477	0.525	2.7	130	266	42	224	99	15.7	42.1	42.1
14	0.460	0.790	1.8	120	246	53	193	96	21.5	55.2	55.2
15	0.353	1.501	0.7	100	266	54	212	73	22.0	73.5	73.5

\*The ratio of the volume of liberated B<sub>2</sub>H<sub>6</sub> to the total volume of the liberated gas.

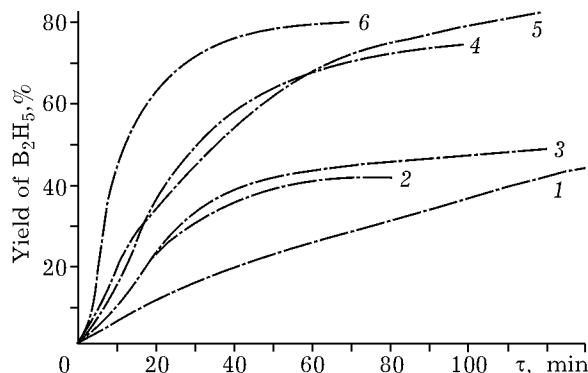


Fig. 1. Kinetic curves for the synthesis of  $B_2H_6$  depending on the nature of  $MBH_4$  and the molar ratio of reagents  $n$ :

Curve	Reagents	$n$	Run No. in Table 1
1	$KBH_4 + FeCl_3$	4.9	12
2	$NaBH_4 + FeCl_3$	3.7	7
3	$LiBH_4 + FeCl_3$	6.6	2
4	$KBH_4 + FeCl_3$	0.7	15
5	$LiBH_4 + FeCl_3$	1.1	5
6	$NaBH_4 + FeCl_3$	0.8	10

started at 45 °C for mixtures of  $FeCl_3$  with  $LiBH_4$  and  $NaBH_4$  and at 60 °C for mixtures with  $KBH_4$ . Analysis showed that the gas phase contained  $H_2$  but no  $B_2H_6$ ; *i. e.*, reactions with heating follow route (2). Similar results were obtained for reactions of  $NaBH_4$  with  $CoCl_2$  [8] and  $NiCl_2$  [9], which also liberated  $H_2$  upon heating. The difference between our results and the data of [1] is probably explained by the difference in synthetic conditions.

A comparison of the experimental and theoretical values of  $\Delta G_{298}^0$  for reactions (1) and (2) indicates that reaction (1) is preferable under conditions of mechanochemical activation, although it is thermodynamically less favour-

able. The case is similar for related systems, for which mechanochemical activation initiated thermodynamically less favourable processes, in particular, the formation of thermodynamically unstable  $B_2H_6$  [2, 10].

## CONCLUSIONS

Thus mechanochemical activation of  $FeCl_3$  with  $LiBH_4$ ,  $NaBH_4$ , and  $KBH_4$  forms diborane(6), the yields being 73.5, 79.5, and 81.5 %, respectively, under optimum conditions. These rather high yields of diborane(6) allow one to replace  $LiBH_4$  by  $NaBH_4$  and  $KBH_4$ , which are less expensive and more convenient to handle, while  $FeCl_3$  is ecologically preferable to other metal halides such as Cd, Cr, or Pb halides [2].

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