Mechanochemical Synthesis of Diborane(6) in the Solid Phase by the Interaction of Tetrahydroborates of Alkaline Metals with Cadmium Bromide and Iodide

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Abstract

Reactions of CdX (X = Br, I) with MBH_4 (M = Li, Na, K) under mechanical activation (MA) of the mixtures of crystalline compounds in vacuum vibratory mill are investigated. It is discovered that the reactions are accompanied by the formation of B_2H_6; its yield depends on the nature of CdX_2, MBH_4 and correlates with the calculated ΔG°_{298} values. It is shown that the mechanochemical synthesis of B_2H_6 depends on temperature within the range 50–120 °C. Under thermal initiation, the reactions of CdX_2 with MBH_4 proceed with the formation of H_2, except for the reaction of CdI_2 with KBH_4, which results in the formation of H_2 and B_2H_6.

INTRODUCTION

Diborane(6), B_2H_6, is the initial compound for the synthesis of various derivatives of boron hydrides and for obtaining pure boron [1]. Many methods of diborane(6) synthesis have been developed, but they are performed mainly in organic solvents [1]. A promising relatively new method is mechanochemical synthesis. Under mechanical activation (MA), reactions between initial crystalline reagents occur without using organic solvents as a reaction medium, which simplifies the process. In addition, this method allows one to broaden the possibilities of B_2H_6 synthesis due to the use not $LiBH_4$ but more convenient compounds $NaBH_4$ and KBH_4, which exhibit a very limited solubility in organic solvents. As a rule, reactions between the chlorides of polyvalent metals and tetrahydroborates of alkaline metals MBH_4 (M = Li, Na, K) were used for mechanochemical synthesis [2]. The authors of [3] investigated mechanochemical reactions of lead halides with MBH_4 and discovered a complicated dependence of the yield of B_2H_6 on the nature of halide ion.

Solid-phase reactions of $CdCl_2$ with MBH_4 have been conducted by means of MA with a 35–95 % yield of B_2H_6, depending on conditions [4]. Under heating, reactions in mixtures of $CdCl_2$ with MBH_4 proceed mainly with the formation of hydrogen in the gas phase; only in the case of $LiBH_4$ a small amount of B_2H_6 is formed.

The goal of the present work was to investigate the solid-phase reactions of $CdBr_2$ and CdI_2 with MBH_4 for obtaining B_2H_6, both by means of MA and under heating.

Taking into account the results of [4], we may assume that the reactions of CdX_2 (X = Cl, Br, I) with MBH_4 (M + Li, Na, K) can proceed according to the equations:

$$CdX_2 + 2MBH_4 = H_2 + B_2H_6 + Cd + 2MX \quad (1)$$

$$CdX_2 + 2MBH_4 = 4H_2 + 2B + Cd + 2MX \quad (2)$$

Calculation of thermodynamic functions was performed for these reactions (Table 1). One

TABLE 1

Thermodynamic functions for the reactions of CdX_2 with MBH_4 calculated per one mole of MBH_4 using the data from [5]

Thermodynamic function	MBH_4	Reaction (1)			Reaction (2)		
		$CdCl_2$	$CdBr_2$	CdI_2	$CdCl_2$	$CdBr_2$	CdI_2
ΔH°_{298}, kJ/mol	$LiBH_4$	−12.4	7.1	32.2	−35.4	−15.9	9.2
	$NaBH_4$	−7.0	5.3	22.9	−30.0	−17.7	−0.1
	KBH_4	4.8	10.0	20.3	−18.2	−13.0	−2.7
ΔS°_{298}, kJ/(mol K)	$LiBH_4$	133.0	135.9	138.9	219.4	222.4	225.3
	$NaBH_4$	120.0	123.1	125.0	206.4	209.5	211.4
	KBH_4	125.5	127.1	127.5	211.9	213.5	213.9
$-\Delta G^\circ_{298}$, kJ/mol	$LiBH_4$	52.1	33.4	9.2	100.8	82.2	58.0
	$NaBH_4$	42.8	31.4	14.4	91.6	80.2	63.1
	KBH_4	32.6	27.9	17.7	81.4	76.7	66.5

can see that reactions according to eqn. (1) are possible from the thermodynamic point of view, but they are less probable than those proceeding according to eqn. (2); reactions with $CdCl_2$ are more probable than those with $CdBr_2$ and CdI_2.

EXPERIMENTAL

Reagents used in the present study included $LiBH_4$, $NaBH_4$ and KBH_4 containing 95, 96 and 98 % of the main compound, respectively; anhydrous $CdBr_2$ and CdI_2 of "ch." grade (pure). Mechanochemical reactions of $CdBr_2$ and CdI_2 with MBH_4 were performed in a vibratory vacuum ball mill [6] (reactor volume: 100 cm^3; height: 5 cm; ball load: steel balls 6 mm in diameter, with the total mass of 200 and 300 g; the frequency of vibrations of the reactor: 23 Hz; amplitude: 6 mm). The synthesis conditions have been described in detail in [7]. Loading and sampling procedures were performed in a chamber in dry nitrogen.

The IR spectra of the formed gas mixtures were recorded with UR-20 spectrophotometer. The presence of B_2H_6 in the gas phase was detected with the help of characteristic absorption bands (ν, cm^{-1}: 2630, 2520, 1915, 1600, 1177, 978) [8]. Total amount of the evolved gas (H_2 and B_2H_6) was determined by means of gasometry; the amount of B_2H_6 was measured by weighing the amount of boron obtained by pyrolysis of B_2H_6 passed through a weighed glass tube heated to 700 °C; the amount of H_2 was determined as a difference.

X-ray diffraction patterns of the powders protected from the atmosphere with a film made of fluoroplastics were recorded with X-ray diffractometer DRON-3M (CuK_α radiation). Reactions of $CdBr_2$ and CdI_2 with MBH_4 under heating were studied by means of thermographing. Thermogasovolumograms were recorded with a set-up described in [9], using Chromel-Alumel thermocouples (with Al_2O_3 as reference, heating rate 6−7 °C/min). Samples were heated in glass ampoules at the initial pressure of 1.3 Pa. The composition of gas phase after thermographing was determined using the method described above.

RESULTS AND DISCUSSION

When investigating the interaction of $CdBr_2$ and CdI_2 with MBH_4 during MA, we studied the effect of time of MA (τ), ball load mass (m), nature of MBH_4 and CdX_2, reagents molar ratio n ($n = n_1$ mole of MBH_4 $/n_2$ mole of CdX_2) and temperature (t) on the yield of B_2H_6. The data on mechanochemical synthesis of B_2H_6 using $CdBr_2$ and CdI_2 are shown in Tables 2 and 3. According to the IR spectroscopic and gasometric analysis, after MA of the reagents mixture the gas phase is composed of H_2 and B_2H_6. The yield of B_2H_6 was calculated using eqn. (1); in case of deviations from stoichiometry ($n = 2$), calculation was performed with respect to the reagent taken in deficiency. In agreement to eqn. (1), the amount of H_2 in the gas phase should be equal to that of B_2H_6;

TABLE 2

Mechanochemical synthesis of B_2H_6 in the solid phase by the interaction of $CdBr_2$ with MBH_4

Experiment No.	Reagents mass, g		n	m, g	t, °C	τ, min	Volume of the evolved gas, cm^3			The B_2H_6 content in the gas phase, %	Yield, %	g_m, mol/MJ
	MBH_4	$CdBr_2$					Total	B_2H_6	H_2			
	$LiBH_4$											
1	0.362	1.576	2.9	200	50	255	89	21	68	21.2	16.0	0.026
2	0.901	3.156	3.6	200	80	230	298	116	182	39.0	44.8	0.158
3	0.303	4.040	0.9	300	80	190	373	131	242	35.1	84.1	0.017
4	0.355	1.556	2.9	300	80	180	271	105	166	38.8	82.3	0.014
5	0.358	1.521	2.9	300	120	90	420	111	309	26.3	88.5	0.030
	$NaBH_4$											
6	0.546	1.065	3.7	200	50	285	137	21	116	15.2	24.0	0.023
7	0.442	1.098	2.9	200	80	205	247	67	180	27.9	76.2	0.102
8	0.826	1.528	3.9	200	80	255	286	93	193	32.6	74.3	0.114
9	0.570	2.095	1.9	300	80	235	355	127	228	35.8	73.7	0.013
10	0.565	1.025	3.9	300	120	65	235	71	164	30.3	84.4	0.026
	KBH_4											
11	0.549	1.090	2.6	200	50	315	104	16	88	15.2	17.7	0.016
12	1.025	1.872	2.7	200	80	210	182	41	141	22.4	26.5	0.060
13	1.245	1.891	3.4	200	80	230	197	40	157	20.3	25.8	0.055
14	1.251	2.083	3.0	300	80	225	295	86	209	29.0	49.9	0.009
15	1.311	2.058	3.2	300	120	125	471	117	354	24.8	68.9	0.023

*The ratio of the volume of B_2H_6 evolved to the total volume of the evolved gas.

TABLE 3

Mechanochemical synthesis of B_2H_6 in the solid phase by the interaction of CdI_2 with MBH_4

Experiment No.	Reagents mass, g		n	m, g	t, °C	τ, мин	Volume of the evolved gas, cm^3			The B_2H_6 content in the gas phase, %	Yield, %
	MBH_4	CdI_2					Total	B_2H_6	H_2		
	$LiBH_4$										
1	0.955	3.148	5.0	200	50	310	128	–	128	–	0
2	0.926	3.188	4.9	200	80	240	131	–	131	–	0
3	0.923	4.454	3.5	300	80	215	119	–	119	–	0
4	0.632	6.463	1.7	300	120	240	313	37	276	11.9	11.4
5	0.971	4.560	3.6	300	120	260	301	47	254	15.6	16.6
6	0.958	3.077	5.2	300	120	250	313	51	262	16.2	27.0
	$NaBH_4$										
7	1.131	2.283	4.8	200	50	225	143	–	143	–	0
8	1.258	2.309	5.3	200	80	160	131	–	131	–	0
9	0.482	3.422	1.4	300	80	250	101	14	87	14.0	9.9
10	1.077	2.158	4.8	300	80	220	218	12	206	5.5	9.1
11	0.998	2.021	4.8	300	120	215	376	70	306	18.6	56.7
	KBH_4										
12	1.532	3.492	2.6	200	80	230	141	–	141	–	0
13	1.787	3.285	3.7	300	80	250	153	–	153	–	0
14	1.709	3.531	3.3	300	120	130	276	53	223	19.2	24.6
15	1.798	3.547	3.4	300	140	150	567	140	427	24.7	65.0

however, in fact, B_2H_6 content is lower than H_2 (see Tables 2 and 3), which indicates that reactions proceed also according to eqn. (2). The yield of B_2H_6 in the interaction of CdX_2 with MBH_4 under identical synthesis conditions (τ, m, t) is almost independent of n (compare experiments 3 and 4, 7 and 8, 12 and 14 in Table 2; experiments 4–6 in Table 3). The yield of B_2H_6 is substantially dependent on the nature of MBH_4 and especially on the nature of CdX_2 (see Tables 2 and 3); in the general form, it correlates with the calculated ΔG°_{298} (see Table 1).

The dependence of the yield of B_2H_6 on τ, m and t in reactions between $CdBr_2$ and MBH_4 is shown in Fig. 1. The yield increases with increasing m. At least two reasons explain this phenomenon. It is known [10] that in this case the mechanical energy input to the system increases; a part of that energy is consumed for chemical reaction; in addition, temperature in the reactor rises: with a 200 g ball load, it reaches 50 °C after ~30 min; with 300 g, it reaches 80 °C. Thermodynamic calculations also suggest expectation for an increase in the yield of B_2H_6 (see Table 1). For the indicated reactions, ΔG°_{298} is negative, while ΔS°_{298} is positive. Because of this, the absolute value of ΔG°_{298} will increase with temperature rise.

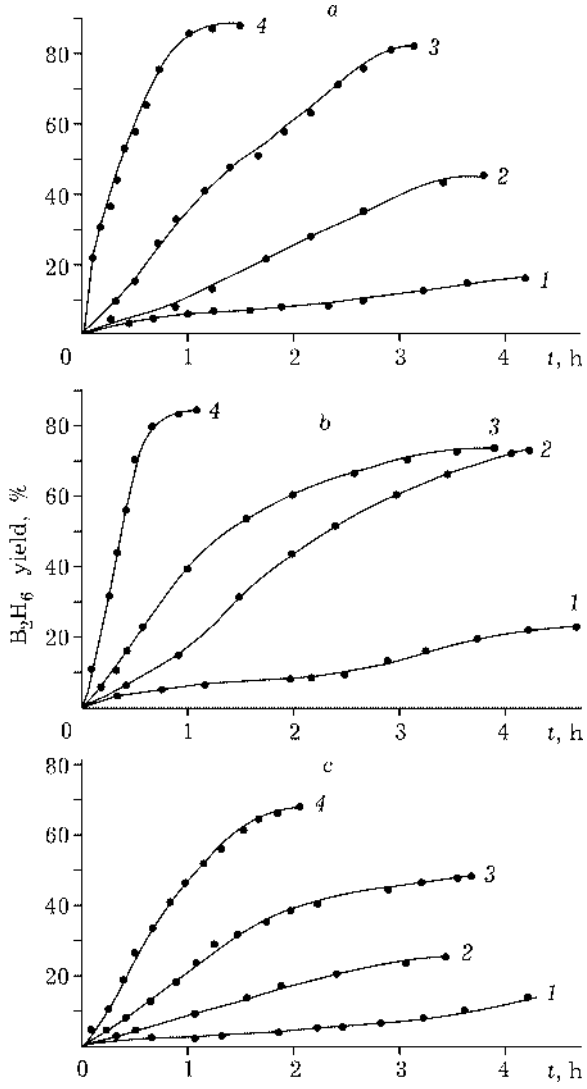

Fig. 1. Yield of B_2H_6 in mechanochemical reactions $CdBr_2$ + $LiBH_4$ (*a*), $CdBr_2$ + $NaBH_4$ (*b*), and $CdBr_2$ + KBH_4 (*c*). *m*, g: 200 (*1*, *2*), 300 (*3*, *4*); *t*, °C: 50 (*1*), 80 (*2*, *3*), 120 (*4*).

It was demonstrated in [4] that in case of MA of mixtures composed of $CdCl_2$ and MBH_4, the liberation of B_2H_6 is preceded by the formation of $Cd(BH_4)_2$, which decomposes at ~80 °C. Because of this, a low yield of B_2H_6 at the temperature of 50 °C (m = 200 g) could be explained by possible formation of $Cd(BH_4)_2$ in these reactions. To check this assumption, we activated reagent mixtures corresponding to experiments 1, 6 and 11 (see Table 2) for 2 h; then the mixtures were heated to 80 °C and kept for 2–3 h. However, we observed only insignificant increase in the yield of B_2H_6 (within several per cent).

One can see in the data shown in Table 3 that no B_2H_6 is formed under the activation of CdI_2 with MBH_4 (m = 200 g). However, if the activated mixtures (see Table 3, experiments 1, 2, 7, 8 and 12) are heated to ~400 °C, we observe the liberation of B_2H_6. Its yield is 28, 30, and 64 % for M = Li, Na and K, respectively. It should be noted that up to 100–105 °C B_2H_6 is absent from the gas phase; its emission occurs mainly within the temperature range 110–180 °C. The activated mixtures of CdI_2 with $NaBH_4$ and KBH_4 (m = 200 g, t = 50 °C, τ = 2 h) were investigated by means of XPA. Reflections were identified using the data of [11]. Along with reflections corresponding to the initial reagents, the X-ray diffraction patterns of the mixture of CdI_2 with $NaBH_4$ contain weak reflections with d = 3.207, 2.440, 2.415 and 2.026 Å, which can be related to the reaction product. The diffraction patterns of the mixture of CdI_2 with KBH_4 exhibit only reflections related to the initial reagents. On the basis of the obtained data it may be assumed that the MA of mixtures of CdX_2 with MBH_4

results in the formation (or creates conditions for the formation) of intermediate complex compounds differing in composition and thermal stability; they contain the cations of alkaline metals, cadmium, BH_4^- group and halide ion.

It is recommended [12] to characterize mechanochemical reactions by energy yield g_m (mol/MJ). The g_m values were calculated for the mechanochemical reactions of $CdBr_2$ with MBH_4 (Table 2) using the equation

$$g_m = a/(I\tau),$$

where a is the amount of the formed B_2H_6, mole; I is the power consumed inside the reactor of the vibratory mill, W; τ is the time of mechanical activation, h. The I values were taken from [13]: for the ball load of 200 g, power is 2.38 W; for 300 g, it is 30.8 W. The data for g_m are listed in Table 2; it follows from those data that it is most profitable from the energy viewpoint to conduct the process with m = 200 g, since under these conditions g_m is maximal. For comparison, it can be noted that for the mechanochemical reaction of $CdCl_2$ with $NaBH_4$ g_m = 0.61 mol/MJ for m = 200 g and 0.09 mol/MJ for m = 300 g [13].

The interaction of MBH_4 with $CdBr_2$ and CdI_2 under heating was investigated by means of DTA with simultaneous recording of gas liberation and the analysis of gas phase for the B_2H_6 content. Thoroughly mixed reagents, separately crushed to powders preliminarily and mixed at the equimolar ratio (n = 2), were subjected to thermal analysis. The samples were heated to 400–500 °C, till the finish of gas emission. All thermograms exhibited endo effects on heating curves at 320 °C, which corresponds to the melting point of metal cadmium. Gas liberation starts at 30–50 °C; only for the CdI_2 – KBH_4 mixture it starts at about 120 °C. Intensive gas liberation in mixtures of MBH_4 with CdI_2 starts at 281, 272, 297 °C, while for CdI_2 it starts at 277, 240, 190 °C for M = Li, Na, K, respectively, which can be due to $LiBH_4$ melting (t_{melt} = 284 °C) or to the formation of the corresponding eutectics, for example $CdBr_2$ – KBr (t_{melt} = 297 °C), CdI_2 – NaI (t_{melt} = 287 °C), CdI_2 – KI (t_{melt} = 210 °C) [14]. Heating of the mixture of CdI_2 with KBH_4 results in the liberation of B_2H_6 with a yield of 48 %; its content in the gas phase is 20 %, which means that the reaction follows eqns. (1) and (2). Heating of other mixtures is accompanied only by the evolving of H_2, which means that the reactions follow only eqn. (2). It should be noted that in [4] it was discovered in thermal analysis studies of the samples of $CdCl_2$ with MBH_4 that the reactions of $CdCl_2$ with $NaBH_4$ and KBH_4 proceed with the formation of H_2, while with $LiBH_4$ they result in the formation of H_2 and B_2H_6, the content of the latter in the gas phase being about 13 %.

Comparing the ΔG°_{298} values listed in Table 1 one can see that the reactions according to eqn. (1) leading to the formation of B_2H_6 are thermodynamically less probable than the reaction according to the eqn. (2). However, it is the formation of B_2H_6 which is observed in the reactions of MBH_4 with CdX_2 during MA. With the thermal initiation of reactions of $CdBr_2$ and CdI_2 with MBH_4, the interaction is accompanied mainly by the liberation of H_2 into the gas phase, which means that the reactions mainly proceed *via* eqn. (2). Hence, MA is a soft activating factor, allowing one to perform reactions between crystal compounds toward the synthesis of thermodynamically unstable B_2H_6, for which ΔG°_{298} = 89.4 kJ/mol. The dependence of the synthesis of B_2H_6 on temperature is shown in Tables 2 and 3. A similar dependence was also observed for the mechanochemical reaction $SnCl_2$ + KBH_4 in [15].

CONCLUSION

Thus, the performed investigations demonstrated that B_2H_6 can be obtained by means of MA of the mixtures of CdX_2 (X = Br, I) with MBH_4. The yield of B_2H_6, reaching a maximum of 88 %, depends on the nature of CdX_2 and MBH_4; it generally correlates with the calculated ΔG_{298}. A feature of these reactions is temperature dependence. With thermal initiation, the reactions of CdX_2 with MBH_4 proceed with the formation of H_2, except for the reaction of CdI_2 with KBH_4, which proceeds with the formation of H_2 and B_2H_6 (the yield being 48 %).

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