Mechanochemical Synthesis of Diborane(6) by the Interaction of Anhydrous Chlorides of Iron (II), Cobalt (II), Nickel (II) with Tetrahydroborates of Alkaline Metals

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Abstract

The reactions of $FeCl_2$, $CoCl_2$, $NiCl_2$ with MBH_4 (M = Li, K, Na) proceeding during mechanical activation of the mixtures of crystal substances in a vacuum vibratory mill were investigated. It was established that the reactions are accompanied by the formation of diborane(6), or B_2H_6, the yield of which depends on the nature of initial reagents, molar ratio of reagents, time of mechanical activation and the mass of ball load. Under the optimal conditions, the yield of B_2H_6 is 30 to 50 %.

INTRODUCTION

In the chemistry of boranes, diborane(6), or B_2H_6, is an important starting compound to synthesize many derivatives of boron hydrides, to obtain pure amorphous boron and nitrogen-containing boron derivatives by means of BN pyrolysis, and to strengthen metal surfaces by boronizing. Many methods to obtain B_2H_6 have been developed, mainly to be performed in organic solvents. Relatively new method to synthesize B_2H_6 without solvents using the mechanochemical procedure is of interest.

Chlorides of Fe(II), Co(II) and Ni(II) in aqueous solutions interact with $NaBH_4$ to form boric acid, sodium chloride, hydrogen and black precipitates containing a metal and boron in the fine state [1, 2]. Under heating of $CoCl_2$, $NiCl_2$ with $NaBH_4$ without solvents, black-coloured products and sodium chloride are formed; H_2 is evolved [3, 4]. It is assumed [1, 4] that both in solution and under heating the reactions proceed through the formation of intermediate unstable tetrahydroborates $M'(BH_4)_2$ where M′ = Fe(II), Co(II), Ni(II). The addition of $NaBH_4$ to a molten eutectic mixture of 33 % $PbCl_2$ + 67 % $FeCl_2$ results in the evolution of diborane(6) [5]. However, the authors of published works do not specify due to what reagent diborane is formed. It should be noted that B_2H_6 was obtained both by heating the mixtures of $PbCl_2$ with $NaBH_4$ and by their mechanical activation (MA) [6]. The reactions of $FeCl_3$ with MBH_4 (M = Li, Na, K) were studied in [7]; it was established that MA results in the formation of B_2H_6 with the yield up to 70–80 %, while diborane(6) was not detected in the gas phase under heating the mixtures of the initial reagents without MA. In diethyl ether, the reaction of $FeCl_3$ with $LiBH_4$ at −45 °C is described by equation [8]

$$3LiBH_4 + FeCl_3 = 1/2H_2 + 1/2B_2H_6 + Fe(BH_4)_2 + 3LiCl \quad (1)$$

It is assumed [8] that $Fe(BH_4)_2$ decomposes in two routes at a temperature above 0 °C:

$$Fe(BH_4)_2 = Fe + H_2 + B_2H_6 \quad (2)$$

$$Fe(BH_4)_2 = Fe + 2B + 4H_2 \quad (3)$$

The authors of [8] point to the possibility of a more complicated interaction mechanism. One can see in the published data that the reactions of transition metal halides with alkaline metal tetrahydroborates are essentially dependent on their conditions. Because of this, it is of some interest to investigate the interaction of anhydrous chlorides of Fe(II), Co(II) and Ni(II) with Na(M?)BH_4 (M = Li, K, Na) under MA for the purpose of obtaining B_2H_6.

TABLE 1

Thermodynamic functions of the reactions of $M'Cl_2$ with MBH_4 calculated using the data of [9] per one mole of MBH_4 according to equation (4), kJ/mol

Function	MBH_4	$FeCl_2$	$CoCl_2$	$NiCl_2$
$-\Delta H^o_{298}$	$LiBH_4$	37.0	44.9	55.8
	$NaBH_4$	31.6	39.5	50.4
	KBH_4	19.8	27.7	38.6
$-\Delta G^o_{298}$	$LiBH_4$	71.6	82.3	94.7
	$NaBH_4$	62.4	77.7	85.5
	KBH_4	52.2	67.4	75.3

Assuming that the reactions follow equation

$$1/2M'Cl_2 + MBH_4 = 1/2H_2 + 1/2B_2H_6 + 1/2M + MCl \quad (4)$$

where M′ = Fe(II), Co(II), Ni(II), M = Li, Na, K, and using thermodynamic data [9], ΔH^o_{298} and ΔG^o_{298} were calculated (Table 1). One can see in the data presented in Table 1 that the reactions are exothermic and thermodynamically possible.

EXPERIMENTAL

The reagents used in the investigation were $LiBH_4$, $NaBH_4$ and KBH_4 with the content of the main compound 96.5, 95.5, 98.6 mass %, respectively. Anhydrous chlorides of Fe(II), Co(II) and Ni(II) were obtained according to the procedure described in [10] by dehydrating the corresponding crystal hydrates under gradual heating in vacuum (~1.5 Pa) to 130−140 °C followed by exposure for 3 h at this temperature. In view of hygroscopicity of the initial reagents, all the operations with them were carried out in a dry box. Mechanochemical reactions were carried out in a vibratory vacuum ball mill [11]. The volume of a cylindrical reactor made of stainless steel was 100 cm^3, its height was 5 cm, the balls loaded into the mill were made of steel, 6 mm in diameter, with the total mass of 100, 200 or 300 g, the frequency of reactor oscillations was 23 Hz, with an amplitude of 6 mm. The synthesis was monitored on the basis of gas evolution; when gas stopped to evolve, MA was ceased. The composition of gas mixtures was identified on the basis of IR spectra recorded with UR-20 spectrophotometer using a gas cell 0.1 m long with windows made of KBr. The presence of B_2H_6 was detected from the observation of characteristic absorption bands (n, cm^{-1}: 2630, 2520, 1915, 1600, 1177, 978) [12]. Total volume of gas evolved was determined by means of gasometry, the volume of B_2H_6 was measured by weighing on the basis of the amount of boron formed after passing the gas through a weighed quartz tube heated to 700 °C, the amount of H_2 was determined as the difference of volumes. The diffraction patterns of powders after MA protected with a fluoroplastic film from atmospheric action were recorded with DRON-3M diffractometer (CuK_a radiation).

RESULTS AND DISCUSSION

Investigating the interaction of metal halides with MBH_4 under MA, we studied the dependence of the yield of B_2H_6 on MA time t, the nature of $M'Cl_2$ and MBH_4, molar ratio of the reagents n (n = mol of MBH_4/mol $M'Cl_2$), the mass of ball load m (Fig. 1). According tot eh data obtained by gasometry and IR spectroscopy, the formed gas phase is composed of H_2 and B_2H_6; no other volatile products were detected. The diffraction patterns of

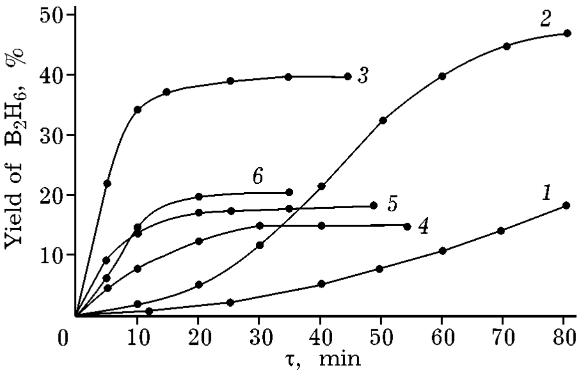

Fig. 1. Kinetic curves for the reactions of B_2H_6 synthesis depending on the nature of MBH_4, molar ratio of reagents n, mass of ball load m:

Curve	Reagents	n	m
1	$CoCl_2 + LiBH_4$	1.1	100
2	$CoCl_2 + LiBH_4$	1.0	200
3	$CoCl_2 + LiBH_4$	1.2	300
4	$CoCl_2 + NaBH_4$	1.3	300
5	$CoCl_2 + NaBH_4$	2.1	300
6	$CoCl_2 + NaBH_4$	5.1	300

the samples obtained by MA of mixtures with $n \gg 2$ exhibit clear reflections corresponding to alkaline metal chlorides. For samples with n much larger or smaller than 2, the reflections of the reagent taken in excess are observed as well. No other reflections were detected. It is possible that other products of reactions may be X-ray amorphous, which was indicated also by the authors of [3]. So, the reactions generally proceed according to equation (4). The yield of B_2H_6 was calculated according to equation (4), in case of a deviation from stoichiometry

TABLE 2

Mechanochemical synthesis of B_2H_6 by the interaction of $FeCl_2$, $CoCl_2$, $NiCl_2$ with MBH_4

Reagent mass, g		n	m, g	t, min	Volume of gas evolved, cm^3			B_2H_6 yield, %
MBH_4	$M'Cl_2$				Total	B_2H_6	H_2	
$LiBH_4$	**$FeCl_2$**							
0.749	2.214	2	100	100	850	0	850	0
$NaBH_4$								
0.633	2.144	1.0	100	150	474	69	405	36.9
0889	1.509	2.0	100	130	863	74	789	28.1
1.969	1.652	4.1	100	140	1100	79	1021	27.1
KBH_4								
2.826	1.867	3.6	100	300	686	33	**653**	10.0
$LiBH_4$	**$CoCl_2$**							
0.607	3.308	1.1	100	145	670	155	415	49.4
0.710	1.015	4.2	100	75	566	84	391	47.9
0.580	3.497	1.0	200	85	719	145	574	48.3
1.956	1.587	7.4	200	45	654	56	598	20.3
0.514	2.666	1.2	300	45	589	104	485	39.5
1.204	1.051	6.8	300	20	523	44	479	24.2
$NaBH_4$								
0.600	2.325	0.9	100	335	376	31	345	17.2
1.096	1.867	2.0	100	260	644	65	579	20.1
0.710	1.802	1.4	200	255	540	42	498	19.9
1.486	1.362	3.8	200	45	481	47	434	20.2
0.720	1.931	1.3	300	170	540	32	508	15.1
0.694	1.136	2.1	300	35	461	40	421	20.7
1.461	0.988	5.1	300	55	523	31	492	18.3
KBH_4								
1.166	1.667	1.7	200	120	605	39	566	16.1
1.122	2.127	1.3	300	80	850	58	792	24.9
$LiBH_4$	**$NiCl_2$**							
0.733	2.320	1.9	100	55	916	87	829	22.9
0.578	1.122	3.1	100	60	572	72	500	36.9
0.513	2.497	1.2	300	60	795	59	736	22.3
0.548	1.324	2.5	300	15	720	65	655	28.3
$NaBH_4$								
0.454	1.399	1.1	100	60	769	0	769	0
0.309	1.863	0.6	300	25	301	2	299	2.0
0.725	1.458	1.7	300	35	800	14	786	6.3
KBH_4								
0.862	1.582	1.3	300	35	380	0	380	0

($n » 2$) according to the amount of the reagent taken in deficiency.

Typical experimental data on the MA synthesis of B_2H_6 are sown in Table 2. According to equation (4), the gas phase should contain identical amounts of H_2 and B_2H_6. However, in fact (see Table 2), the amount of B_2H_6 in the gas phase is much smaller (in some cases down to zero) in comparison with H_2, which suggests that the reactions follow another route, possibly according to equation

$$1/2M'Cl_2 + MBH_4 = H_2 + B + 1/2M' + MCl \quad (5)$$

On the basis of literature data [3, 4], it may be assumed that boron and the correspodning metal are in X-ray amorphous fine state or in the form of "borides" $M' \times 2B$. Calculation of ΔG^o_{298} according to equation (5) gave negative values about ~46 kJ/mol larger in absolute value than those obtained using equation (4) and the data listed in Table 1, that is, reactions according to equation (5) are more probable from the thermodynamic point of view.

According to the data shown in Table 2, a weak dependence of B_2H_6 yields on n is observed for reactions of $FeCl_2$ with $NaBH_4$. The yield of B_2H_6 decreases substantially with KBH_4 used instead of $NaBH_4$. The negative result (the absence of B_2H_6 in the gas phase) with $LiBH_4$ was extremely unexpected. The reactivity of $LiBH_4$ is usually higher than that of other MBH_4 compounds. One can see in the data shown in Table 2 that the yield of B_2H_6 decreases when passing from $LiBH_4$ to KBH_4, other conditions provided identical. In the experiments with $LiBH_4$, a decrease in B_2H_6 yield with an increase in n is observed for the same m.

With $NaBH_4$ used instead of $LiBH_4$, the yield of diborane(6) and the rate of its formation decrease substantially (see Fig. 1). With an increase in m, the reaction rate increases. Such dependence is quite natural because it is known [13] that the input of mechanical energy increases with an increase in the mass of ball load, hence, its fraction is consumed for the activation of reagents. Table 2 also shows the data of MA of $NiCl_2$ mixtures with MBH_4. One can see that for $LiBH_4$ with the same m values, the yield of diborane(6) increases with an increase in n. The yield is 30–36 % with $LiBH_4$, while it decreases sharply for aBH_4 and KBH_4, till complete cessation of B_2H_6 formation.

CONCLUSION

It is shown that the interaction of anhydrous Fe(II), Co(II) and Ni(II) chlorides with MBH_4 (M = Li, Na, K) during mechanical interaction is accompanied by the formation of diborane(6), which depends on the nature of reagents, their molar ratio, duration of mechanical activation, and the mass of ball load. Maximal yields of B_2H_6 are: 36.9 % for the system $FeCl_2 + NaBH_4$, 49.4 % for $CoCl_2 + LiBH_4$, and 36.9 % for $NiCl_2 + LiBH_4$.

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