Mechanochemical Synthesis of N-trimethylborazine through the Interaction of Methylamine Hydrochloride with Alkaline Metal Tetrahydroborates

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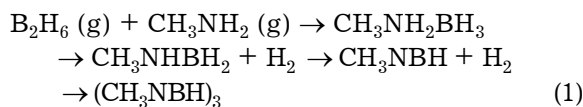
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Abstract

Reactions of CH_3NH_2HCl with MBH_4 (M = Li, Na, K) proceeding during mechanical activation of the mixtures of crystal substances in a vacuum ball vibratory mill are investigated. It is established that the stage-by-stage pyrolysis of reaction products at $100\,^{\circ}C$, then at $200\,^{\circ}C$ results in the formation of N-trimethylborazine $(CH_3NBH)_3$. Maximal yields of N-trimethylborazine with $LiBH_4$, $NaBH_4$ and KBH_4 are 60, 34 and 36 %, respectively. Melting points, saturated vapour pressure, density, refractive index of N-trimethylborazine are determined; the IR spectrum is reported.

Keywords: mechanochemical synthesis, alkaline metal tetrahydroborates, methylamine hydrochloride trimethylborazine
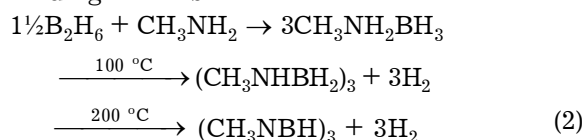
INTRODUCTION

For the synthesis of BCN films by means of thermal or plasma decomposition of vapour, the compound used as precursor is volatile N-trimethylborazine $(CH_3NBH)_3$ (TMB) in which CH_3 groups are bound with nitrogen atoms [1, 2].
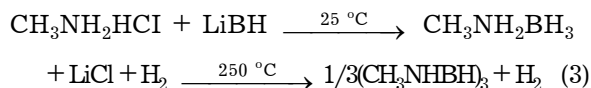
TMB was synthesized for the first time by heating a mixture of volatile diborane(6), B_2H_6, and methylamine (CH_3NH_2) at $200\,^{\circ}C$ without access for air [3–5] according to reaction

$$B_2H_6\,(g) + CH_3NH_2\,(g) \rightarrow CH_3NH_2BH_3$$
$$\rightarrow CH_3NHBH_2 + H_2 \rightarrow CH_3NBH + H_2$$
$$\rightarrow (CH_3NBH)_3 \quad (1)$$

According to the data reported in [5], the reaction proceeds through the stage of formation of methylaminoborane; the latter compound is transformed at $100\,^{\circ}C$ into the trimer product $(CH_3NHBH_2)_3$. Heating of the latter up to $200\,^{\circ}C$ leads to the formation of TMB according to the scheme

$$1\tfrac{1}{2}B_2H_6 + CH_3NH_2 \rightarrow 3CH_3NH_2BH_3$$
$$\xrightarrow{\,100\,^{\circ}C\,} (CH_3NHBH_2)_3 + 3H_2$$
$$\xrightarrow{\,200\,^{\circ}C\,} (CH_3NBH)_3 + 3H_2 \quad (2)$$

Later on, a more convenient method was proposed to synthesize TMB: through the reaction of $LiBH_4$ with CH_3NH_2HCl in diethyl ether in which $LiBH_4$ dissolved [6, 7]. After the initial stage, which is the synthesis of $CH_3NH_2BH_3$, the ether was evaporated in vacuum, and the reaction mixture was subjected to pyrolysis at $250\,^{\circ}C$. The sequence describing the synthesis of TMB is represented by the following scheme:

$$CH_3NH_2HCl + LiBH \xrightarrow{\,25\,^{\circ}C\,} CH_3NH_2BH_3$$
$$+ LiCl + H_2 \xrightarrow{\,250\,^{\circ}C\,} 1/3(CH_3NHBH)_3 + H_2 \quad (3)$$

The single-stage synthesis of TMB using $NaBH_4$ in boiling bed was proposed in [8].

One can see in the data listed above that methylaminoborane or the products of its pyrolysis are to be obtained for the synthesis of TMB.

The above-considered methods of TMB synthesis have several essential shortcomings, such as the use of gaseous toxic diborane(6) and diethyl ether as the reaction medium.

The goal of the present work was to investigate the possibility to carry out the synthesis of TMB without using diborane(6) and diethyl ether. It is known [9] that the use of mecha-

nochemical activation (MA) is efficient in the synthesis of borazine $B_3N_3H_6$ by the interaction of $NaBH_4$ with NH_4Cl. In this connection, in the present work we studied the conditions of synthesis of $CH_3NH_2BH_3$ or the products of its decomposition by means of the reaction of the tetrahydroborates of alkaline metals (lithium, sodium and potassium) with methylamine hydrochloride during MA.

EXPERIMENTAL

The reagents used in the work were $LiBH_4$, $NaBH_4$ and KBH_4 with the content of the major compound 95.2, 96.0 and 98.4 mass %, respectively, and CH_3NH_2HCl of "ch" reagent grade. Before using, the salts were dried in vacuum (1.3 Pa) at 50 °C for 3−4 h. Due to the hygroscopic properties of the reagents, operations with them were carried out in the dry chamber in the atmosphere of nitrogen. Mechanical activation of the mixture of initial solid reagents CH_3NH_2HCl and MBH_4 was carried out in a ball vibratory mill [10, 11]. Steel balls 6 mm in diameter, their total mass being 100, 200 or 300 g, were charged into the reactor made of stainless steel 100 cm^3 in volume and 5 cm high; the weighed portions of initial reagents were added. The reactor was sealed and connected to the system of gas pressure measurement. Mechanical activation of the reagents was carried out at 23 Hz and the amplitude 6 mm. The end of the MA process was monitored as the moment when gas evolution stopped. As a rule, the amount of gas evolved exceeded the calculated value (see eq. (3)), which is likely to be connected with the partial decomposition of methylaminoborane. It should be noted that pure methylaminoborane could not be obtained by MA of the mixture of CH_3NH_2HCl with $NaBH_4$ in the vibratory mill [12].

After MA was over, the reaction mass together with the balls was transferred from the reactor into the ampoule for pyrolysis; the ampoule was 50 cm long. The ampoule was mounted into a vertical two-region furnace (the height of the lower region was 15 cm, the upper zone 35 cm), evacuated to the residual pressure of 1.5 Pa, then filled with gaseous nitrogen to the atmospheric pressure, and connected with the

bubbler. The upper part of the ampoule was quickly heated to 250 °C. The lower part of the ampoule, in which the reaction mixture was situated, was gradually heated to 100 °C and kept at this temperature till gas evolution stopped (~0.5 h). Products were fractionated by their distillation into the trap cooled to −45 °C. The yield of TMB was calculated using equation (3), and in the case of deviation from the stoichiometry the yield was calculated with respect to the reagent taken in deficiency. The compound was identified on the basis of melting point (−7 °C), saturated vapour pressure at 25 °C (11.7 mm), density at 20 °C (0.850 g/cm^3), refractive index $n_D^{20} = 1.4400$, which corresponds to the literature data [3, 6].

Refractive index was measured with a IRF-22 diffractometer.

The IR spectrum of TMB was recorded with a UR-20 spectrophotometer (Fig. 1). The sample was prepared in the form of a film pressed between two discs made of KBr. No measures protecting the sample from the atmosphere were taken. The assignment of frequencies was made in agreement with the data of [13−15].
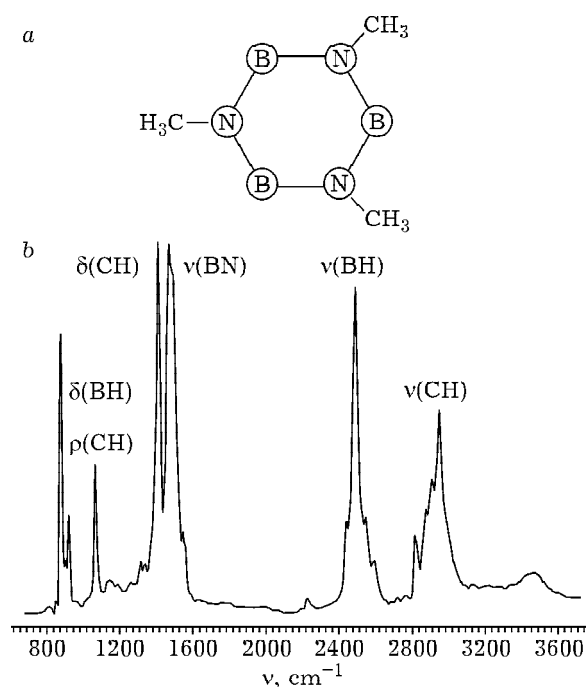

Fig. 1. Structure of $(CH_3NBH)_3$ molecule (*a*) and its IR spectrum (*b*).

TABLE 1

Mechanochemical synthesis of $(CH_3NBH)_3$ through the interaction of $CH_3NH_2 \cdot HCl$ with MBH_4

Exp. No.	Reagent mass, g		n	m, g	Time, h	Reactor	Yield of $(CH_3NBH)_3$	
	MBH_4	$CH_3NH_2 \cdot HCl$				volume, cm^3	g	%
				$LiBH_4$				
1	1.454	2.932	1.54	100	2.0	100	0.81	45.6
2	1.721	3.049	1.75	100	2.0	100	0.83	45.3
3	2.899	2.724	3.3	100	2.0	100	0.99	60.2
4	1.273	2.653	1.48	200	1.5	100	0.64	40.1
5	1.530	3.117	1.52	300	1.3	100	0.94	37.1
6	2.312	9.877	0.73	200	3.0	180	1.93	40.5
7	2.598	9.964	0.81	200	2.5	180	2.74	51.2
				$NaBH_4$				
8	2.305	2.698	1.53	100	3.0	100	0.45	27.6
9	2.669	3.095	1.54	100	2.5	100	0.56	30.0
10	3.399	2.446	2.5	100	3.0	100	0.40	26.7
11	3.605	2.030	3.2	100	3.0	100	0.42	34.0
12	2.697	2.321	2.1	200	2.5	100	0.44	31.7
13	2.709	2.627	1.8	300	2.5	100	0.49	30.8
14	6.424	9.023	1.3	200	2.0	180	1.45	24.2
15	5.806	9.499	1.1	200	2.0	180	1.63	24.2
				KBH_4				
16	3.016	2.636	1.44	100	3.5	100	0.58	36.3
17	2.912	2.537	1.44	200	3.0	100	0.44	28.7
18	2.485	2.839	1.1	300	2.0	100	0.45	26.0
19	2.899	2.493	1.96	100	6.0	180	0.34	22.4
20	2.652	2.503	1.33	200	4.0	180	0.25	16.9

The major bands of the compound $(CH_3NBH)_3$, ν, cm^{-1}: $\nu(CH)$ 2948 m., 2818 w.; $\nu(BH)$ 2491 s., $\nu(BN)$ 1470 v.s., $\delta(CH)$ 1410 v.s., $\rho(CH)$, $\delta(BH)$ 1070 m., $\rho(BH)$, $\rho(CN)$ 878 m.

RESULTS AND DISCUSSION

While synthesizing TMB, we studied the effect of the molar ratio of the reagents n (mol MBH_4/mol CH_3NH_2HCl), time of mechanical activation τ, nature of MBH_4 and the mass of ball load m. The results obtained are listed in Table 1.

With $LiBH_4$ (in the reactor 100 cm^3 in volume) with the total ball mass equal to 100 g, we observe an increase in the yield of TMB and an increase in n (see Table 1, exp. Nos. 1–3). For $n = 3.3$, the yield of TMB reaches 60 %. An increase in the total ball mass (exp. Nos. 4, 5) leads to a decrease in MA time, but the yield of TMB somewhat decreases (exp. Nos. 1, 4, 5).

With $NaBH_4$, the yield of TMB turned out to be lower than that achieved with LiBH4. It should also be stressed that the yield of TMB is only weakly dependent on the n value (see Table 1, exp. Nos. 8–11). With an increase in ball load (exp. Nos. 12, 13) we observe a trend to decrease the yield of TMB and shorten the time of MA.

With KBH4 and NaBH4 used in the syntheses, the yields of TMB were approximately the same, however, in the case of the mixture with KBH_4 the yield decreases with an increase in the total mass of balls, while the duration of MA is somewhat longer than that for the mixture with $NaBH_4$. A decrease in the yield of TMB with an increase in total bass mass is likely to be connected with the high temperature developed in the reactor [10, 11], which, in turn,

leads to the formation of side products decreasing the yield of the target product.

Results on the synthesis of TMB using KBH_4 turned out to be unexpected. It was shown in [12] that, while $NaBH_4$ and CH_3NH_2HCl interact in tetrahydrofuran forming $CH_3NH_2BH_3$ with the yield 50−80 % (time of reagent mixing: 4−5 h), in the case of KBH_4 the reaction proceeds by only 3 % after mixing for 24 h. The data obtained provide evidence of the efficiency of the use of MA for the reaction of KBH_4 with methylamine hydrochloride resulting in the formation of methylaminoborane, the products of its decomposition (similar to those formed in the reaction with the use of $NaBH_4$ [12]) and finally TMB with rather high yield.

To test the assumption that methylaminoborane is a precursor for the synthesis of N–trimethylborazine, we synthesized this compound using the data reported in [2] through the interaction of methylamine hydrochloride with $NaBH_4$ in tetrahydrofuran.

The weighed portion of methylaminoborane of 2.64 g was subjected to pyrolysis as described above. The amount of TMB obtained was 1.09 g. The yield was 45.4 %, which is comparable with the data obtained using the mechanochemical method (see Table 1, exp. Nos. 9−13). So, it was confirmed that methylaminoborane is the precursor for the formation of TMB. It is necessary to stress that the 45 % yield of the target product points to the complicated character of the process of transformation of the linear molecules of methylaminoborane into the cyclic molecules (TMB), which is due to the formation of side products. Similar results were also observed for the synthesis of borazine $(BNH_2)_3$ [9].

In order to obtain a large amount of TMB, we carried out test experiments using the reactor 180 cm^3 in volume, 5 cm high, and containing the ball load of 200 g. As a result, TMB was obtained in large amount but with smaller yield (exp. Nos. 6, 7, 14, 15, 19, 20).

CONCLUSION

It was demonstrated that the interaction of methylamine hydrochloride with tetrahydroborates of alkaline metals (lithium, sodium, potassium) under mechanical activation is accompanied by the formation of the products the stage-by-stage pyrolysis of which at 100 and 250 °C leads to the formation of N-trimethylborazine. The mechanochemical method of synthesis allowed one to exclude the use of diborane(6) and diethyl ether as the reaction medium, and to use in addition to $LiBH_4$ cheaper and more convenient $NaBH_4$ and KBH_4. The maximal yields of N-trimethylborazine achieved with $LiBH_4$, $NaBH_4$ and KBH_4 are 60.2, 34.0 and 36.3 %, respectively.

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