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Borazine and Its Derivatives: Synthesis, Mechanochemical Synthesis Reactions and Outlooks for Technological Applications

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Abstract

Review of publications on chemistry, properties and outlooks of the use of boron and nitrogen containing compound borazine (borazol), or *cyclo*-$H_3B_3N_3H_3$ and some its derivatives, as well as the starting compounds for synthesis, since 1926 (the date of borazine discovery) till now is presented. It is shown that the information described in classical works is in many aspects urgent also at present. With the use of borazine, promising methods were developed for obtaining insulating layers and films based on boron nitride h-BN and carbonitroborides through thermal or plasmachemical decomposition of vapours, as well as coatings composed of condensed heterocyclic borazine derivatives. The data obtained by the authors of the review on solid-phase mechanochemical methods of the synthesis of borazine and its derivatives – N-trimethylborazine and N-triethylborazine are presented. Advantages and possibilities of technical implementation of these methods in comparison with other known methods are substantiated.

Key words: borazine, borazine derivatives, mechanochemical synthesis, physicochemical properties, application

INTRODUCTION

The subject considered in the present work is borazine or *cyclo*-$H_3B_3N_3H_3$ ($B_3N_3H_6$), which is a six-membered heterocyclic boron and nitrogen containing compound with B and N atoms alternating in the cycle. The trivial name of this compound is also used: borazol (as a structural analogue of benzene) and the system name according to IUPAC nomenclature *s*-triazatriborine. Homoatomic cycles formed by boron atoms similarly to organic ones, for example C_6H_6, C_6H_{12}, C_5H_5 *etc.*, are not typical for the chemistry of boron. Chemistry of different-type heteroatomic cycles with boron atoms has developed into an extensive area of modern inorganic and hetero-organic chemistry [1–3]. In addition to boron atoms, heterocycles can contain C, O, N, P, Si, S atoms in different combinations. Examples of the structure of these molecules are presented in Fig. 1. Numerous derivatives of $B_3N_3H_6$ with a common name Borazines are known, first of all the products of hydrogen substitution in the $[B_3N_3]$ heterocycle by the atoms of elements or organic radicals (R); condensed heterocycles are also known [4].

The foundations of the chemistry of boranes were formed by the classical works of A. Stock in 1912, later on generalized in monograph [5]. The development of modern chemistry of boranes and their derivatives started in late 1940es. Boron compounds are used in various areas of materials science, in catalyst, inorganic and organic synthesis, biochemistry, medicine, agriculture *etc.* Some boranes and their derivatives are manufactured on the industrial scale, so their application for technical and experimental purposes is possible.

Classification of chemical binding in borane structure was considered in review [6]. The first type of boranes and their derivatives includes

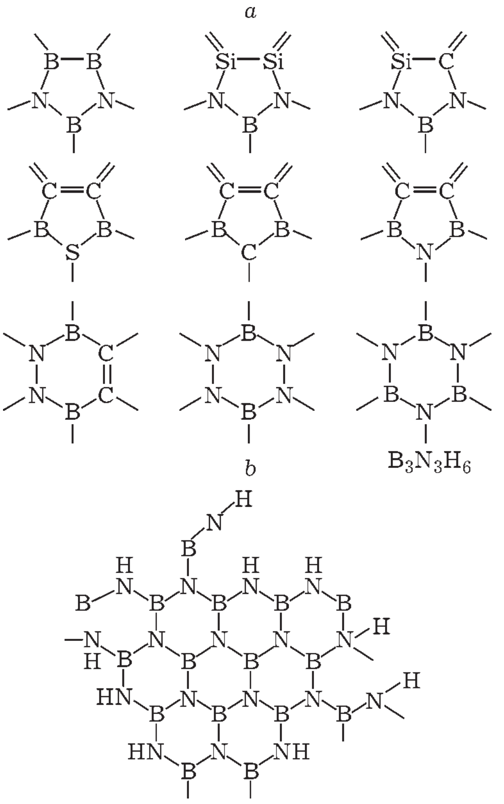


Fig. 1. Schematic sketch of the molecules of heterocyclic boron compounds (*a*) and two-dimensional product of borazine condensation (*b*).

the simplest representatives, such as borane BH_3, its adducts with Lewis bases $BH_3 \cdot L$, tetrahydroborate anion BH_4^-, diborane(6) B_2H_6. The compounds of this class serve as the starting components for the synthesis of complicated borane compounds including borazines. The second type includes cluster hydrides of boron: boranes B_3H_9, $B_{10}H_{14}$, decaborane (14) and its derivatives, for example $B_{10}H_{12}L_2$, polyhedral anions having the composition $B_nH_n^{2-}$, for example $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, *ortho*-, *meta*-, *para*-carboranes(12) $B_{10}C_2H_{12}$ and their derivatives $B_9C_2H_{12}^-$, π-complexes of transition metals (M) with the composition $[M^{III}(\pi\text{–}\eta^5\text{-}B_9C_2H_{11})_2]^-$, metal boranes $Sn^{II}B_9C_2H_{11}$, cluster polymers *etc.* [2, 6–13]. The third type of borane derivatives incorporates heterocycles (see Fig. 1) including $B_3N_3H_6$ and its analogues.

The date of the start of development of borazine chemistry is considered to be 1926 when A. Stock and E. Pohland published a work describing its synthesis and investigation of its properties [14]. The next two decades 1930–1950 are marked with extensive efforts in borazine chemistry. The primary information on the synthesis of borazine, its physicochemical properties and derivatives was collected and generalized in monograph [5] and review [15]. The similarity of the physical properties of $B_3N_3H_6$ with the properties and structure of C_6H_6 was stressed, so borazine was called inorganic benzene. The initial ideas about the structure of $B_3N_3H_6$ molecule were based on its physical and chemical properties [4, 5]. Later on, the structure of borazine was determined by means of electron diffraction, XSA and vibrational spectroscopy [16, 17]. The overall results of the initial stage of development of borazine chemistry (1926–1960) were generalized in review [4] where the information about more than 190 its derivatives was presented, demonstrating the onrush of borazine chemistry. It is noteworthy that a list of 194 publications was cited in that review. This information is of interest also under modern conditions. The authors of the review describe the use of borazine as an additive to fuel, as a component of polymer materials, and the vapour of this compound is used in counters for neutron detection in atomics. Later works report the application of borazine for layer deposition and for obtaining fibres composed of BN and BCN, formation of condensed structures (see Fig. 1), polymers, ceramics and nanosystems [3, 18–20].

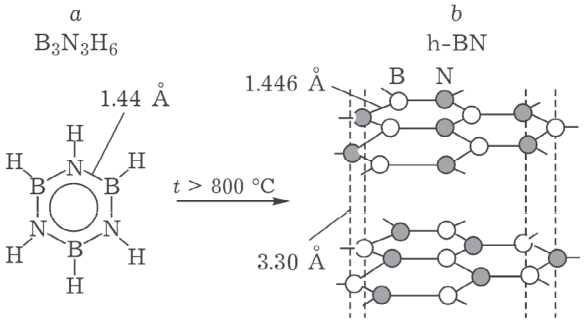
The first classical method of $B_3N_3H_6$ synthesis is based on the reaction of B_2H_6 with NH_3 under heating the gas mixture in a tight apparatus [5, 14, 15]. As a result, borazine was obtained and its properties were determined, but it is difficult to use this method because of the high reactivity and toxicity of B_2H_6. Technologically, it may be implemented in the case if modern apparatus arrangement of the process is realized on the basis of stationary production of diborane. Borazine synthesis methods using boron halides BX_3, alkyl amines R_3N *etc.* are known [14]. Reactions are carried out in the inert atmosphere in organic solvents (diglyme, triglyme, tetraglyme, ethers, THF, chlorobenzene *etc.*), their preparation and regeneration are complicated procedures; in addition, it is possible to introduce admixtures with them.

Efficient methods may be solid-phase reactions activated by the mechanical action on the mixtures of starting reactants – simple and commercially available substances, in particular $NaBH_4$, NH_4Cl and their analogues [21–24]. Reactions involving mechanical activation (MA), as a rule, are carried out without solvents, which simplifies complete synthesis cycles and improves the purity of the products. This is a substantial advantage of these reactions. The modern state of mechanochemistry was considered in review [25]. In the present work we discuss the principles of synthesis and application of borazines with focus on MA reactions.

BORAZINE AND ITS DERIVATIVES. PRINCIPLES OF SYNTHESIS AND APPLICATION

The first works on chemistry and synthesis of borazine according to the reaction of B_2H_6 with NH_3 stated the complicated character of the formation of this heterocycle from the simplest starting components and specificity of B–N chemical bond in $B_3N_3H_6$ molecule [5, 14, 15, 26]. The electron configuration of boron atom ($Z = 5$) is $1s^22s^22p^1$. In the formation of compounds, the valence electrons form energetically more stable configuration $1s^22s^12p^2$ in which boron possesses four valence atomic orbitals (AO) – $2s$, $2p_x$, $2p_y$, $2p_z$ – and only three valence electrons [6, 7, 27]. The electrons of boron atom are localized in the strong field of the nucleus, thus the $2p_z$ AO is vacant. This feature allows the light-weight element boron with the simplest electronic structure of the atom to form very complicated compounds with many types of chemical bonding and structures [6]. Boron atom is able to form σ-bonds with the participation of AO having the sp^2 configuration and at the same time π-bonds in which the vacant $2p_z$ AO is involved, for example in molecules BX_3 (where X is a halogen) *etc.* The vacant AO provides the electro acceptor ability of boron atom in molecules BX_3, BR_3 (R = H, alkyl, aryl *etc.*). Its interaction with unshared electron pairs of donor molecules leads to the formation of molecular complexes, for example $BH_3 \cdot NH_3$, $BH_3 \cdot R_3N$, $BX_3 \cdot NH_3$, $BF_3 \cdot Me_2O$. These compounds are known as initial or intermediate products of borazine synthesis processes [4, 5, 14, 15].

Borazine and isoelectronic benzene C_6H_6 are close to each other in molecular structure: both have D_{3h} symmetry, bond lengths in $B_3N_3H_6$ molecule are, Å: B–N 1.44, N–H 1.02, B–H 1.20, in C_6H_6 C–C 1.397, C–H 1.084 Å. The melting point of borazine is −58.0 °C, boiling point 53.0 °C [5].In H-substituted borazines, the length of B–N bonds varies within the range 1.413–1.42 Å, while the length of bonds in benzene in the structures of layers of hexagonal boron nitride h-BN is 1.446 Å [4, 7, 26]. Aromaticity, that is, delocalization of electrons over the atoms of the cycle, is characteristic of borazines to a lesser extent than of benzene [6, 7]. Nevertheless, elements of π-bonding are realized also in the cycles of borazine [18, 20]. Identical stoichiometry, similarity of size and analogy of the elements of structure of borazine molecules and h-BN can become a favourable circumstance for the design of materials based on boron nitride and its derivatives (Fig. 2). Borazine molecule is a structural blank for h-BN. Thermodynamic probability of the formation of h-BN is high because the standard heat of its formation $-\Delta H^{\circ}_{f\,298} = 251.14$ kJ/mol. It is known that ceramic parts and films made of BN possess valuable dielectric characteristics [26]. Borazine is thermally stable in the gas phase, but it



c
Layer structure h-BN

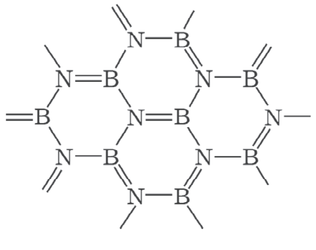


Fig. 2. Details of the structure of borazine molecule $B_3N_3H_6$ (*a*), hexagonal boron nitride h-BN (*b*) and layer structure in h-BN (*c*).

slowly polymerizes in the liquid phase when stored for a long time at room temperature [5, 29].

The classical principle of the synthesis of $B_3N_3H_6$ from NH_3, B_2H_6 or other boranes [5, 14, 15] is important because the details of its mechanism are essential for synthesis methods that are under development at present. Ammonia interacts with boranes to form nonvolatile products such as $B_2H_6 \cdot 2NH_3$, $B_4H_{10} \cdot 4NH_3$, $B_5H_9 \cdot 4NH_3$. Their heating in a tightly closed apparatus leads to complicated overall reactions like

$$3(B_2H_6 \cdot 2NH_3) = 2(cyclo\text{-}B_3N_3H_6) + 12H_2 \qquad (1)$$

When this process is carried out at a temperature of 180–220 °C for 0.3–3 h, the yield of borazine is 23–41 % [15]. Side products are also formed; they contain B, H, N, so the yields decrease. The final stage of the formation of heterocycle takes place at increased temperature similarly to the case of the formation of organic cyclic structures like C_6H_6 and others from non-cyclic hydrocarbons CH_4, C_2H_2 [28].

There are many reactions involving the synthesis of borazine derivatives like $(XBNR)_3$ where X stands for halogens, R = H or organic radicals, more frequently Me, Et, Bu, Ph [2, 4, 18, 29]. The authors of [4, 29] described the syntheses of some of these compounds including the following stages:

$$BX_3 + NR_3 \rightarrow X_3B \cdot NR_3$$
$$X_3B \cdot NR_3 \rightarrow X_2BNR_2 + RX \qquad (2)$$
$$3(X_2BNR_2) \rightarrow cyclo\text{-}(XBNR)_3 + 3RX$$

The second and the third stages usually proceed in reaction mixture under heating.

Examples may also be the syntheses of borazine derivatives from BCl_3 and NH_4Cl in boiling chlorobenzene C_6H_5Cl (boiling point 132 °C) and from BCl_3 and aniline $Ph\text{-}NH_2$ [2, 29, 30]:

$$3BCl_3 + 3NH_4Cl \rightarrow cyclo\text{-}(ClBNH)_3 + 9HCl \qquad (3)$$
$$3BCl_3 + 6PhNH_2 \rightarrow cyclo\text{-}(ClBNPh)_3 + 3PhNH_2 \cdot HCl \qquad (4)$$

Borazine derivative $cyclo\text{-}(ClBNPh)_3$ was obtained as long ago as in 1889 according to reaction (4), but this discovery was not noted by contemporaries [2]. Reactions like (3) and (4) are interesting because they proceed without participation of hydride atoms $H^{\delta-}$.

A nodal event in the development of modern chemistry of boranes was the discovery of metal tetrahydroborates by Schlesinger and Brown [31–34] in the interaction between B_2H_6 and organometallic compounds MR_n:

$$Al(CH_3)_3 + 2B_2H_6 \rightarrow Al(BH_4)_3 + 2B(CH_3)_3 \qquad (5)$$

Tetrahydroborates $LiBH_4$ and $Be(NH_4)_2$ were synthesized similarly. During the development of the chemistry of metal tetrahydroborates, the methods of the synthesis of borohydrides of alkaline metals ($M'BH_4$): $LiBH_4$, $NaBH_4$ and KBH_4 were developed (1940–1950). Reviews and monographs were published on this subject [1, 30, 35–38]. For example, the authors of [30] considered the principles and apparatus arrangement for the production of $M'BH_4$.

Reactions of the synthesis of $M(BH_4)_n$ can be related to the following classes:

A. Formation of BH_4^- anion [30, 35, 37]:

$$2LiH + B_2H_6 \rightarrow 2LiBH_4;\ \text{in ether, } LiBH_4 \text{ is solvated} \qquad (6)$$
$$4M'H + B(OCH_3)_3 \rightarrow M'BH_4 + 3MOCH_3;\ M' = Li, Na \qquad (7)$$
$$Na_2B_4O_7 + 7SiO_2 + 16Na + 8H_2 \rightarrow 4NaBH_4 + 7Na_2SiO_3 \qquad (8)$$

Reaction (8) is carried out at 450–500 °C and the pressure of H_2 equal to 3 atm, the yield is 90 %. Liquid ammonia is used to isolate $NaBH_4$ from the reaction mixture [30].

B. Reaction of BH_4^- anion exchange [23, 35, 37, 39, 40]:

$$NaBH_4 + LiCl \rightarrow LiBH_4 + NaCl;\ \text{THF, dimethylformamide} \qquad (9)$$
$$NaBH_4 + KOH \rightarrow KBH_4 + NaOH;\ \text{aqueous medium, KOH in excess} \qquad (10)$$
$$4NaBH_4(s) + ZrCl_4(s) \rightarrow Zr(BH_4)_4(\text{liquid, vapour}) + 4NaCl(s) \qquad (11)$$

Covalent bonding type is realized in $M(BH_4)_n$ structures with the participation of bridging H atoms according to the scheme M–H–BH (M = Be, Al, Zr, Hf, Th, Ti(III), U(IV)) with the formation of volatile non-ionic compounds $M(BH_4)_n$ [36, 39, 40]. Compounds $M'BH_4$ (M′ = Na, K, Rb, Cs) belong to the ionic type.

At present, $LiBH_4$, $NaBH_4$, KBH_4 are manufactured on an industrial scale and are commercially available [41]. For the synthesis of borane compounds under MA conditions it is reasonable to use more stable, relatively cheap and handy $NaBH_4$ as a carrier of $H^{\delta-}$.

Reaction sequences with $M'BH_4$ are important for the synthesis of borazines [2, 24, 42]:

$$M'BH_4 + NH_4Cl \xrightarrow{25\ ^\circ C} [NH_4BH_4](s) + M'Cl \qquad (12)$$

$$NH_4BH_4 \xrightarrow{106\ ^\circ C} H_2B(NH_3)_2BH_4(s) + 2H_2 \qquad (13)$$

$$\mathrm{H\text{-}B(NH\text{-}\ )\text{-}BH\text{-}} \xrightarrow{120-140\ ^{\circ}\mathrm{C}} cyclo\text{-}\mathrm{B_3N_3H_6}\ \text{(vapour)} + \mathrm{(BHNH)}_n + \mathrm{H} \quad (14)$$

Tetrahydroborates $M'BH_4$ are carriers of active hydride hydrogen $H^{\delta-}$. This feature found application in selective substitution of elements bound to boron or nitrogen atoms of borazine for H atoms [4]:

$$2R_3N_3B_3Cl_3 + 6M'BH_4 \rightarrow 2R_3N_3B_3H_3 + 3B_2H_6 + 6M'Cl$$

$$3BCl_3 + 3NH_3 \rightarrow cyclo\text{-}2,4,6\text{-}Cl_3B_3N_3H_3 + 6HCl \quad (15)$$

$$2Cl_3B_3N_3H_3 + 6NaBH_4 \rightarrow 2B_3N_3H_6 + 3B_2H_6 + 6NaCl;\ \text{diglyme, yield } 46\ \%.$$

Reaction (15) with varying R and X is typical for the synthesis of borazine derivatives.

Alkylaminoboranes $R_{3-n}H_nN \cdot BH_3$ serve as the starting and sometimes intermediate compounds in the synthesis of borazine derivatives. An example of these processes is the sequence of reactions (2). These compounds were described for the first time by Wiberg in 1948 [43], discussed in reviews [44, 45] and monographs [1, 29, 30, 46]. Many methods of the synthesis of $R_3N \cdot BH_3$ are based on reactions performed in organic solvents. At present, some $R_3N \cdot BH_3$, their solutions and derivatives are manufactured on a commercial scale [41].

Taking into account the applied significance of complexes $L \cdot BH_3$, efficient mechanochemical methods of their synthesis were developed, possessing the above-indicated advantages [47, 48]. The features of the synthesis of $R_3N \cdot BH_3$ were studied during MA according to the reactions of the type

$$R_3N \cdot HCl(s) + M'BH_4(s) \rightarrow R_3N \cdot BH_3(\text{liquid, vapour}) + M'Cl(s) + H_2 \quad (16)$$

where R = Me, Et; M′ = Li, Na, K; apparatus is a rotary vacuum ball or vibratory mill, t = 70–100 °C, MA duration τ = 3–6 h, $R_3N \cdot BH_3$ yield varies within the range 74–87 % depending on R_3N, M′, t, τ [48]. By means of MA according to reaction (16) complexes $L \cdot BH_3$ were synthesized, with $L = Me_2HN$, Et_2HN, $(C_4H_9)HN$, $(C_6H_5CH_2)_3N$, C_5H_5N, tribenzylamine, N_2H_4 with the yield of 34–98 % [22–24, 47–54]. These complexes may be the initial compounds for the synthesis of borazines. Volatile compounds $L \cdot BH_3$ containing simple radicals Me and Et are suitable for depositing carbonitroboride films and coatings like $B_xC_yN_z$ on substrates from the gas phase [22–24].

SOLID-PHASE REACTIONS OF BORAZINE SYNTHESIS

Let us pass to the consideration of solid-phase reactions of borazine synthesis. The first reaction of this type was performed by H. Schelisnger [55], and then reproduced and improved by V. I. Mikheeva and V. Yu. Markina [56]:

$$3LiBH_4(s) + 3NH_4Cl(s) \rightarrow cyclo\text{-}H_3B_3N_3H_3(\text{vapour}) + 3LiCl(s) + 9H_2 \quad (17)$$

The reaction is carried out in a flask under stirring the mixture of reagents at 250–300 °C. Due to the formation of side products, the yields (18–42 %) are poorly reproducible. The use of $LiBH_4$ has some disadvantages: a) lithium is a rare alkaline metal, its compounds are expensive, recovery is necessary; b) LiBH4 is a substance inflammable when in contact with moisture, so special precautions are to be taken in the case if large amounts of reagents are involved. For these reasons, laboratory process (17) with $LiBH_4$ did not win technological application. It is reasonable to perform syntheses using the commercially available compound $NaBH_4$. However, $NaBH_4$ is less active in reactions than $LiBH_4$. In the version with $NaBH_4$, MA of the reagent mixture in mills is required. Information about mechanochemical syntheses of borazine from $NaBH_4$ and NH_4Cl was presented in [21–24, 42, 57–60]. Synthesis proceeds similarly to reaction (17):

$$3NaBH_4(s) + 3NH_4Cl(s) \rightarrow B_3N_3H_6(\text{vapour}) + 3NaCl(s) + 9H_2,\ -\Delta H^{\circ}_{298} = 233.63\ \text{kJ/mol} \quad (18)$$

The first laboratory set-up for borazine synthesis and operation mode for MA according to reaction (18) were described in detail in [58]. The reagents used in the syntheses were $NaBH_4$ of 96.5 % purity and NH_4Cl of Kh. Ch. reagent grade (chemically pure) at the molar ratio $NaBH_4/NH_4Cl$ = 0.31. Under optimized conditions, the yield of borazine reaches 38 % with respect to $NaBH_4$. The characteristics of thus obtained borazine are: T_m = (−58±1) °C; IR spectrum, ν, cm^{-1}: 3450, 2535, 1465, 1070, 920, 700, 520 and 402 – correspond to the published data [61, 62]. The yield is close to that achieved in the classical works. A disadvantage of the set-up with oscillating reactor [58] is the possibility to disturb impermeability. To eliminate it, borazine synthesis mode with preliminary MA of the mixture of $NaBH_4$ with NH_4Cl at room temperature was developed [24, 60]. The mixture was subjected to MA in a tightly closed rotating ball mill without connecting it at the MA stage to the gas withdrawal system. The set-up in which the synthesis principle with preliminary MA of the mixture was described in [60]. It was used for technological syntheses of borazine at the Novosibirsk Capacitor Plant (MEI USSR). A typical synthesis mode involved charging 250 g of $NaBH_4$ and 500 g of NH_4Cl into the reactor (molar ratio $NH_4Cl/NaBH_4$ = 1.5), MA duration was 1.5 h. Then reactor temperature was gradually increased to 270 °C. The resulting mixture of vapour and gases was passed through cooled condenser traps. The yield of the raw product containing 0.2 % B_2H_6 and 0.1 % NH_3 is 34–51 g (22–30 %) [60]. After repeated recondensation at −78 °C, no foreign admixtures were detected. Replacement of $NaBH_4$ by $LiBH_4$ or KBH_4 has no substantial effect on the yield.

For the synthesis of larger (up to 150 g) amounts of borazine according to reaction (18), a vacuum vibratory set-up with the vertical arrangement of units was developed [63, 64]. Due to the complicated maintenance, it was replaced by a simpler set-up [60].

The possibility of the mechanochemical synthesis of borazine at lower temperatures (~80 °C) was demonstrated in [65]:

$$4LiBH_4(s) + (NH_4)_2ZnCl_4(s) = 2/3B_3N_3H_6(\text{vapour}) + B_2H_6 + 4LiCl + Zn + 7H_2 \quad (19)$$

Thermal or plasmachemical decomposition of borazine vapour was used to obtain insulating films composed of BN [24, 66–69] according to reaction

$$B_3N_3H_6(\text{vapour}) \xrightarrow{600-800\ ^\circ\text{C}} 3BN(s) + 3H_2(g) \quad (20)$$

Increased attention to the use of borazine to obtain inorganic polymers and films is stressed in [70]; described is the method of borazine synthesis in solution according to reaction

$$3(NH_4)_2SO_4 + 6NaBH_4 \rightarrow 2B_3N_3H_6 + 3Na_2SO_4 + 18H_2 \quad (21)$$

At the molar ratio of BH_4^-/NH_4^+ = 0.65 in tetraglyme, temperature 120–140 °C and τ = 3 h the yield of borazine was 10–20 g (58–60 % with respect to BH_4^-). It is possible to use acid salts $(NH_4)HSO_4$ and $(NH_4)_2HPO_4$ in reaction (21), but the results are worse because SO_4^{2-} and PO_4^{3-} form undesirable gases in contact with BH_4^-: H_2S and PH_3 [9, 37].

MECHANOCHEMICAL METHODS OF THE SYNTHESIS OF N-TRIMETHYLBORAZINE AND N-TRIETHYLBORAZINE

The necessity to develop mechanochemical methods of the synthesis of non-ionic N-trimethylborazine (TMB) or *cyclo*-$(CH_3NBH)_3$, and N-triethylborazine (TEB), or *cyclo*-$(C_2H_5NBH)_3$ was dictated by the possibility to deposit carbonitride layers and films with the composition $B_xC_yN_z$ (ideally BCN) on substrates using thermal or plasmachemical decomposition of their vapour [71–73]. The primary information on obtaining boron carbonitride (BCN), a valuable electric insulating material, by means of high-temperature metal ceramics was published in [74]. The technology of obtaining metal ceramics is unsuitable for manufacturing the films for microelectronic devices, so attention is paid to the use of TMB vapour. The stoichiometric composition of TMB holds up the atomic composition (BCN) and possibly the elements of its structure, similarly to the resemblance of compositions and structures of borazine with h-BN marked above (see Fig. 3). As far as TEB is concerned, it should be noted that its stoichiometry does not meet the composition (BCN) in carbon content. The effect of this feature on the properties of resulting films needs more detailed investigation.

The problem of the synthesis of alkyl derivatives of borazines $R_3N_3B_3R'_3$ was considered in [2, 4, 29]. TMB was obtained for the first time according to the sequence of transformations of B_2H_6 and methylamine $H_3C{-}NH_2$ under heating in the absence of the air [75, 76]:

$$B_2H_6(g) + 2CH_3NH_2(\text{vapour}) \rightarrow 2CH_3NH_2 \cdot BH_3(s)$$
$$3CH_3NH_2 \cdot BH_3 \xrightarrow{100\ ^\circ\text{C}} (CH_3NHBH_2)_3 + 3H_2$$
$$(CH_3NHBH_2)_3 \xrightarrow{200\ ^\circ\text{C}} cyclo\text{-}(CH_3NBH)_3 + 3H_2 \quad (22)$$

Remarkable features of the process are the formation of monomethylaminoborane $CH_3NH_2 \cdot BH_3$ at the first stage and the formation of TMB cycle at 200 °C at the last one (a usual condition for the formation of heterocycle $[B_3N_3]$). Provided that B_2H_6 is available, the synthesis according to reactions (22) can be used for technological purposes.

Almost simultaneously, a method of the synthesis of TMB through the interaction of $LiBH_4$ with methylamine hydrochloride $CH_3NH_2 \cdot HCl$ in diethyl ether in which $LiBH_4$ is soluble was proposed [77, 78], while $NaBH_4$ and KBH_4 are insoluble in ether. The first stage of the process is

$$LiBH_4 + CH_3NH_2 \cdot HCl \xrightarrow{25\ ^\circ C} CH_3NH_2 \cdot BH_3 + LiCl + H_2$$

After evaporation of ether, the reaction mass was heated to 250 °C. Thus methylaminoborane was transformed into volatile TMB. The synthesis of TMB using $NaBH_4$ in boiling triglyme was also reported [78]. It is interesting that this work was published as early as in 1960 in Chemistry and Industry (the USA). In the sequences of reactions (22) and (23) TMB molecules are formed during pyrolysis of $CH_3NH_2 \cdot BH_3$ which is formed at the first stage of synthesis and relates to alkylaminoboranes $R_{3-n}H_n \cdot BH_3$ with $n = 2$. It was demonstrated above that $R_3N \cdot BH_3$ is easily obtained by means of MA from crystal borohydrides of alkaline metals and $R_3N \cdot HCl$ without using B_2H_6 and organic solvents. The conditions of the synthesis of $CH_3NH_2 \cdot BH_3$ by means of MA from $MeNH_2 \cdot HCl$ and $M'BH_4$ for M′ = Na, Li, K:

$$CH_3NH_2 \cdot HCl(s) + M'BH_4(s) \rightarrow CH_3NH_2 \cdot BH_3(s) + M'Cl(s) + H_2(g) \quad (24)$$

were studied in [80]. The reaction was carried out in a vibratory ball mill [23, 24]. The next stage

$$3CH_3NH_2 \cdot BH_3 \rightarrow (CH_3NBH)_3 + 6H_2 \quad (25)$$

was performed under stepwise temperature rise up to 100 and 250 °C with gas removal.

The synthesized TMB was identified on the basis of melting point (−7 °C), pressure of saturated vapour at 25 °C (11.7 mm Hg), density of the liquid phase at 20 °C (0.850 g/cm^3), refractive index ($n_D^{20} = 1.440$) and IR spectrum corresponding to the characteristics reported in [75, 77, 80–83]. The yields of TMB with $LiBH_4$, $NaBH_4$, KBH_4 are 60, 34 and 36 %, respectively.

Similarly to the synthesis of TMB according to reactions (24) and (25), the synthesis of TEB under MA of the mixture of ethylamine hydrochloride $EtNH_2 \cdot HCl$ with $M'BH_4$ for M′ = Li, Na, K was investigated for the sequence

$$EtNH_2 \cdot HCl + M'BH_4 \rightarrow EtNH_2 \cdot BH_3 \rightarrow (EtNHBH_2)_n \rightarrow cyclo\text{-}(EtNBH)_3 \quad (26)$$

The effect of the molar ratio $n = M'BH_4/EtNH_2 \cdot HCl$, process duration τ, nature of $M'BH_4$ and MA conditions was studied. Stage-by-stage pyrolysis of the products of MA reaction at 90 °C and then at 240 °C leads to the formation of TEB. The maximal yields of TEB were 79, 60 and 74 % for $LiBH_4$, $NaBH_4$ and KBH_4, respectively, and for $n = 1.3–1.7$. The product was characterized on the basis of melting point −48 °C, density of the liquid 0.836 g/cm^3 at 20 °C, refractive index $n_D^{20} = 1.4365$ and pressure of saturated vapour 3.0 mm Hg at 24 °C, which correspond to literature data for TEB [78]. The IR spectra of synthesized TMB and TEB are presented in Fig. 3. These spectra confirm the nature of the substances and are suitable for analytical purposes. Investigation of the synthesis of TMB and TEB provides evidence of the efficiency of MA method and its promising character for obtaining the considered substituted borazines.

For the synthesis of h-BN, interesting reactions may be thermolysis of hexahydroborazine (called also hexahydroborazole or cyclotriborazene), *cyclo*-$H_6B_3N_3H_6$, that is, hydro-

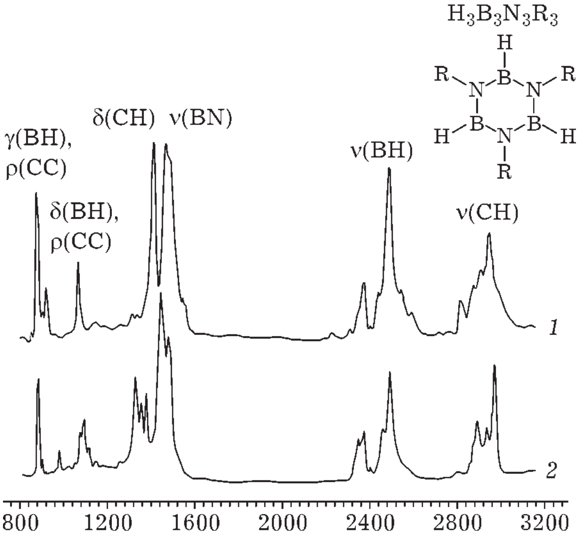


Fig. 3. IR spectra of TMB (*1*), TEB (*2*) and a scheme of $H_3B_3N_3R_3$ molecules. Spectrophotometer: UR-20; samples: films pressed between discs made of KBr. Band positions, ν, cm^{-1}: TMB – ν(CH) 2948 m, 2818 w; ν(BH) 2491 s; ν(BN) 1470 v.s; δ(CH) 1410 v.s; ρ(CH), δ(BH) 1070 m; ρ(BH), ρ(CN) 878 s; TEB – ν(CH) 2970 s, 2935 m, 2893 m, 2875 sh.; ν(BH) 2492 s; ν(BN) 1443 v.s; δ(CH_3) 1480 s, 1379 s; δ(CH_2) 1443 v.s; ρ(CC) 1118 w, 1093 m, 886 s; δ(BH) 1079 w; γ(BH) 982 w, 886 s.

genated derivative of borazine [84–87]. Its synthesis [84] is described by the following reactions:

cyclo-$B_3N_3H_6 + 3HCl \rightarrow B_3N_3H_6 \cdot 3HCl$,
diethyl ether
$B_3N_3H_6 \cdot 3HCl + 3NaBH_4 \rightarrow$ *cyclo*-$B_3N_3H_{12}$
$+ 3NaCl + 3/2B_2H_6$, diglyme

More complicated versions were described in [86]. The stability of *cyclo*-$B_3N_3H_{12}$ crystals in the air, notable pressure of its saturated vapour at 45–75 °C and the ability to sublime in vacuum around 100 °C were observed. At ~130 °C, its decomposition with the evolution of hydrogen starts [85].

CONCLUSION

Analysis of publications on the chemistry of borazine and its derivatives over the period from the date of their discovery till present days reveals that enormous fundamental information has already been accumulated, which is of interest for modern programmes of innovation studies and developments. The information published in the first classical works and subsequent ones concerning synthesis procedures, conditions and foundations of the mechanisms of these reactions is to be used because these data did not change substantially. The possibility to use borazine vapour for depositing insulating layers and films composed of boron nitride h-BN from the gas phase, and also the vapour of N-trimethylborazine and N-triethylborazine in the plasmachemical processes of deposition of insulating carbonitroboride films of substrates was revealed. Efficient mechanochemical methods of the synthesis of borazine and its derivatives from simple commercially available starting reagents were developed. Other methods of the synthesis of these compounds are also known; they may be used under the proper conditions and apparatus arrangement. Such a situation makes it reasonable to include the set of problems outlined above into the programmes of innovation research and technological developments in order to use them for the sake of Russia.

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