

PHYSICAL METHODS
OF INVESTIGATION

Vaporization and Thermal Decomposition of B,B',B''-Tribromoborazine

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Abstract—Vapor pressure as a function of temperature above solid and liquid (BrBNH)₃ and the thermodynamic parameters of (BrBNH)₃ sublimation and vaporization have been determined using static tensimetry with membrane null-manometer. The thermal decomposition of tribromoborazine has been studied in the saturated and unsaturated vapor regions. Irreversible decomposition occurred at noticeable rates at temperatures higher than 343 K and was accompanied by HBr evolution. In the unsaturated vapor region, thermal decomposition has far lower rates than in the saturated vapor region because of diffusion limitations. The activation energy of condensed-phase thermal decomposition of B,B',B''-tribromoborazine is 65 ± 3 kJ/mol, and this value proves that tribromoborazine decomposition at low temperatures is not accompanied by opening of the boron–nitrogen cycle.

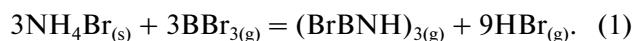
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Boron and nitrogen compounds have been used since long ago as precursors for the synthesis of inorganic polymers and boron nitride for use in industries and microelectronics. For example, cubic boron nitride is used as a diamond substitute in drilling and cutting tools. Hexagonal BN is one of the few analogues of graphite.

B,B',B''-Trihaloborazines are suitable precursors for both boron nitride and various boron–nitrogen inorganic polymers. This is due to the good volatility and sufficient thermal stability of trihaloborazines. Their use as precursors in vapor phase deposition reactions opens ample opportunities for preparing nanostructured BN and inorganic polymers as thin graphene-like surface films [1], catalysts [2], ceramic coatings [3], matrices [4], and nanotubes [5]. However, the processes involved in trihaloborazine heating that yield diverse inorganic polymers and boron nitride, yet remain poorly studied. Here, we study the volatility and thermal decomposition of B,B',B''-tribromoborazine.

EXPERIMENTAL

We chose to study B,B',B''-tribromoborazine (hereafter, tribromoborazine). (BrBNH)₃ was prepared using the hot tube method [6] by reaction (1) at 473–493 K.



Nitrogen was used as a carrier gas. Ammonium bromide (pure grade) was resublimed under vacuum before use. Boron tribromide was synthesized and purified using routine procedures [7]. The tribromoborazine produced by reaction (1) was condensed in the

cold part of the system at room temperature and then purified by repeated vacuum resublimation at 318–328 K. The compound was obtained as colorless needlelike crystals. In view of the irreversible reaction of (BrBNH)₃ with atmospheric moisture, all manipulations (purification, packing, and sampling) were carried out in whole-sealed evacuated glass systems, which were fully air-tight.

The mass-spectrometric study of the vapor over tribromoborazine was carried out on an MX-1321 instrument; the ionizing electron energy was 30 and 70 eV, and the vaporizer temperature was 393 K.

The (BrBNH)₃ vapor pressure was measured as a function of temperature by static tensimetry method with a glass membrane null-manometer [8, 9]. The instruments were made of molybdenum glass. Pressure was measured on an MChR-3 mercury gage accurate to 0.1 mmHg. Temperature was monitored by two thermocouples (Chromel–Alumel); thermo-emf was measured on a Shch-1516 digital voltmeter; the temperature measurement accuracy was ±0.05 K. The volume of the membrane chamber was found as the difference between the weights of the water-filled and empty system. The volume measurement error was ±0.02 mL, which amounts (for the instrument volume of 18.86 and 37.28 mL) to 0.1 and 0.05% for the first and second set of runs, respectively.

RESULTS AND DISCUSSION

Tribromoborazine vaporization processes. A representative mass spectrum of vapor above tribromoborazine is displayed in Table 1. The major process is the vaporization of (BrBNH)₃ in the form of monomeric molecules accompanied by partial thermal dissocia-

Table 1. Mass spectrum of B,B',B''-tribromoborazine recorded with 30-eV ionizing electron energy and a vaporizer temperature of 393 K

Ion	m/z	$I_{rel}, \%$
$B_3N_3H_3^+$, $B_3N_3H_2^+$, $B_3N_3H^+$	73–78	11.2
Br^+	79, 81	39.9
HBr^+	80, 82	*
$Br_2B_2NH_2^+$	129–133	22.3
$BrB_3N_3H_3^+$	155–160	34.8
$Br_2B_3N_2^+$	218–223	9.4
$Br_2B_3N_3H_3^+$	233–241	84.4
$(BrBNH)_3^+$	313–321	100.0

* The ion peak intensity noticeably exceeds the overall intensity of $(BrBNH)_3^+$ peaks.

tion with hydrogen bromide evolution (with a vaporizer temperature of 393 K). The hydrogen bromide peak intensity noticeably exceeds the overall intensity of ion peaks that refer to a molecular ion as judged from their weight-to-charge ratios. The other ions in the mass spectrum are likely fragments of the $(BrBNH)_3^+$ molecular ion. Thus, HBr is the major volatile product of tribromoborazine decomposition.

Two runs were carried out to study tribromoborazine vaporization. In the first run, to a system of 18.86 mL in volume, 24.7 mg tribromoborazine was placed under vacuum. Then, the instrument was transferred to a furnace and vapor pressure was measured as a

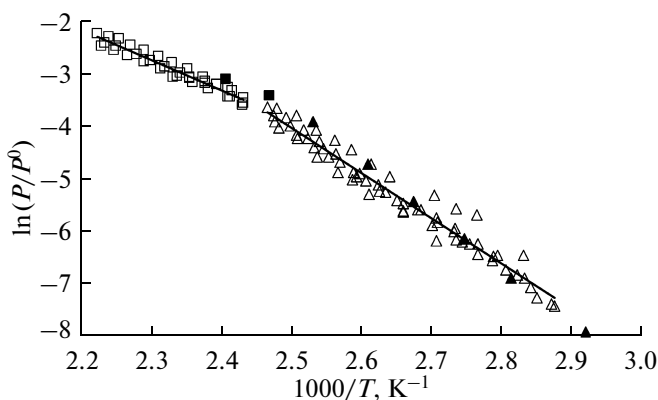


Fig. 1. $\ln(P/P_0) = f(1/T)$ for sublimation (triangles) and vaporization (squares) of tribromoborazine (white symbols refer to this work, and black symbols are data taken from [10]).

function of temperature in the heating–exposure–cooling mode. The heating rate was ~ 2 K/min. Exposure lasted 2–3 h for each set of measurements; the exposure temperature was increased systematically from set to set. Cooling was slow (for several hours). In experiments designed in this way, a considerable portion of $(BrBNH)_3$ underwent irreversible thermal decomposition, which manifested itself as an irreversible increase in pressure in the system. Noticeable tribromoborazine decomposition rates were found at temperatures above 343 K.

In the second run, to a system of 37.28 mL in volume, 37.7 mg tribromoborazine was placed under vacuum. The first sets of measurements in the second run were carried out in the heating–rapid cooling mode. The heating rate was ~ 2 K/min. Rapid cooling was provided by withdrawing the instrument from the furnace. In experiments designed in this way, $(BrBNH)_3$ decomposition occurred to a small extent.

For the reason that, in each set of measurements, equilibrium volatilization of tribromoborazine was to some extent accompanied by its irreversible thermal decomposition, the overall pressure in the system increased from set to set. For deriving the $(BrBNH)_3$ saturated vapor pressure versus temperature dependence, it is necessary to subtract the partial pressure of decomposition products from the overall pressure. On the assumption that hydrogen bromide was the only volatile decomposition product, its partial pressure was estimated from the thermal gas expansion line at low temperatures (within 343 K), where the tribromoborazine saturated vapor pressure was less than 0.1 mmHg [10]. The vapor pressure of HBr estimated from the thermal expansion line was further refined by the consecutive approximations method [9]. The resulting log plot of tribromoborazine saturated vapor pressure versus reciprocal temperature is shown in Fig. 1. For comparison, the same figure displays data taken from [10]; there is a satisfactory agreement between these data. We appreciably expanded the temperature range of tribromoborazine vaporization relative to that used in [10].

The enthalpies and entropies of sublimation and vaporization were derived from the measured vapor pressure versus temperature relationship as follows

$$\ln\left(\frac{P}{P_0}\right) = -\frac{A}{T} + B = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}. \quad (2)$$

The combined data of five sets of the two runs were treated in a similar way; the resulting thermodynamic parameters of sublimation and vaporization are listed in Table 2.

Thermal decomposition of tribromoborazine was studied both in the saturated and unsaturated vapor regions.

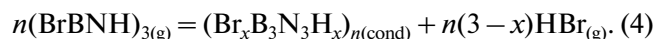
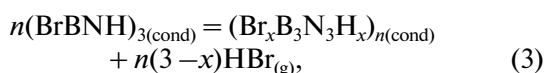
Determination of composition of the condensed phase. Assuming that HBr is the only volatile product of thermal decomposition of tribromoborazine, we

Table 2. Parameters of Eq. (2) and the thermodynamic parameters of (BrBNH)₃ vaporization and sublimation

Parameter	Sublimation		Vaporization	
	this work	[10]	this work	[10]
<i>A</i>	8.65 ± 0.37	10.35 ± 0.07	5.76 ± 0.48	5.64 ± 0.61
<i>B</i>	17.61 ± 1.12	22.31 ± 0.18	10.52 ± 1.13	10.53 ± 1.61
ΔH°_t , kJ/mol	71.9 ± 3.5	86.1 ± 0.6	47.9 ± 4.0	46.9 ± 5.0
ΔH°_t , J/mol K	146.4 ± 9.3	185.5 ± 1.5	87.4 ± 9.4	87.6 ± 13.4
Number of datapoints	65	30	36	5
Temperature range, K	347–405	342–402	411–450	402–415
T_{triple} , K			407.3	399.8
T_{boil} , K*			548	536 ± 42

Note: *Obtained by extrapolation.

may write the following reaction equations for (BrBNH)₃ decomposition in the condensed phase (3) and in the vapor phase (4).



The parameter *x* in Eqs. (3) and (4) characterizes the composition of the nonvolatile product of thermal decomposition of tribromoborazine (Br_{*x*}B₃N₃H_{*x*})_{*n*}. The *x* value varies from three for pure tribromoborazine to zero for complete (BrBNH)₃ decomposition to boron nitride.

In this work, *x* was calculated on the basis of variations in hydrogen bromide and tribromoborazine amounts in the system. Measurements in the unsaturated vapor region (where all tribromoborazine is volatilized) allow the hydrogen bromide and tribromoborazine amounts in the system to be calculated from the Mendeleev–Clapeyron equation: $\frac{P}{T} = \frac{nR}{V}$. The HBr amount was derived from the thermal gas expansion line in the low-temperature region (below 343 K), where the tribromoborazine saturated vapor pressure is less than 0.1 mmHg. The total HBr and (BrBNH)₃ amount was determined immediately after the yield to unsaturated vapor.

The *P/T* versus temperature plot for two consecutive sets of measurements is shown in Fig. 2. Initial $\frac{P}{T}(\text{BrBNH})_3$ and $\frac{P}{T}\text{HBr}$ values were calculated in the first set of measurements; $\frac{P'}{T}(\text{BrBNH})_3$ and $\frac{P'}{T}\text{HBr}$ values after temperature-controlled exposure were calculated from the subsequent set of measurements. The decomposed tribromoborazine amount was found

from Eq. (5); the evolved HBr amount was found from Eq. (6); and *x* was found from Eq. (7).

$$\Delta n_{(\text{BrBNH})_3} = \left(\frac{P}{T}(\text{BrBNH})_3 - \frac{P'}{T}(\text{BrBNH})_3 \right) \frac{V}{R}, \quad (5)$$

$$\Delta n_{\text{HBr}} = \left(\frac{P}{T}\text{HBr} - \frac{P'}{T}\text{HBr} \right) \frac{V}{R}, \quad (6)$$

$$x = 3 - \frac{\Delta n_{\text{HBr}}}{\Delta n_{(\text{BrBNH})_3}}. \quad (7)$$

The results of *x* determination for various conditions are listed in Table 3.

In run 1, we studied (BrBNH)₃ thermal decomposition in the saturated vapor region (in the presence of a condensed tribromoborazine phase in the system). In this case, the variation of *x* in each set of measure-

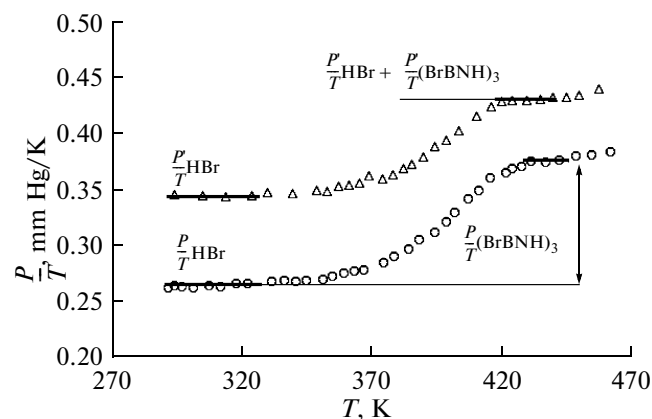


Fig. 2. Example determination of tribromoborazine and hydrogen bromide in the unsaturated vapor region from *P/T* versus temperature curve. Circles refer to the first set of measurements and triangles to the second set of measurements. For explanations, see the text.

Table 3. Determination of the composition of a condensed phase (parameter x) for tribromoborazine decomposition (reaction (4))

Run no.	T , K	t , h	$\Delta n(\text{BrBNH})_3$, mmol	$\Delta n(\text{HBr})$, mmol	$\frac{\Delta n_{\text{HBr}}}{\Delta n_{(\text{BrBNH})_3}}$	x
1	353–443	12 ^a	0.046 ± 0.002	0.080 ± 0.002	1.74 ± 0.06	1.26 ± 0.06
1	660 ± 5	99 ^b	0.078 ± 0.002^c	0.209 ± 0.002	2.68 ± 0.03	0.32 ± 0.03
2	573 ± 4	6.5 ^a	0.042 ± 0.002	0.073 ± 0.002	1.74 ± 0.09	1.26 ± 0.09
		13.2	0.055 ± 0.001	0.105 ± 0.001	1.91 ± 0.05	1.09 ± 0.05
		37.1	0.083 ± 0.002	0.179 ± 0.001	2.16 ± 0.04	0.84 ± 0.04
		39.8	0.095 ± 0.002	0.206 ± 0.001	2.17 ± 0.04	0.83 ± 0.04

Note: ^a Overall exposure time. ^b Until P/T in the system ceases to increase. ^c At the end of the run, there is no tribromoborazine in the system.

ments cannot be determined. However, after the measurements in the saturated vapor region are over (the total exposure time is longer than 12 h at temperatures of 353–443 K), the system was heated to yield to unsaturated vapor; this allowed us to determine x to be 1.26 ± 0.06 . Thus, when tribromoborazine is decomposed in a condensed phase at temperatures up to 443 K, the composition of the solid decomposition product is formulated as $(\text{Br}_{1.26}\text{B}_3\text{N}_3\text{H}_{1.26})_n$, which indicates its polymeric nature.

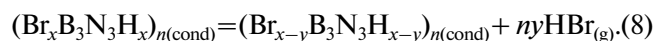
In run 2, we studied the decomposition of gaseous tribromoborazine; the measurement protocol was as follows: rapid heating—exposure—rapid cooling. The heating rate was 4–5 K/min; the exposure temperature was chosen such that $(\text{BrBNH})_3$ fully vaporized (the unsaturated vapor region). Two consecutive sets of measurements were carried out as follows: the system was rapidly heated to a certain temperature and then exposed for several hours, after which the instru-

ment was taken off the furnace and rapidly cooled in air. Then, a second rapid heating and exposure were carried out.

Noteworthy, in run 2 sets of measurements were carried out prior to unsaturated vapor measurements, to measure saturated vapor pressure as a function of temperature; for this reason, the initial x value in run 2 was 1.26 ± 0.09 . This value well agrees with the value of 1.26 ± 0.06 , which was obtained after condensed-phase tribromoborazine decomposition (in run 1). Interestingly, short-time borazine thermolysis (for 30 min or less) at 613–653 K yields a compound of composition $(\text{H}_{1.2}\text{B}_3\text{N}_3\text{H}_{1.2})_n$ as a nonvolatile product; this compound has a polymeric nature [11].

Noteworthy, at a fixed temperature (573 ± 4 K) the x value depends on the exposure time (Table 3) and given log-tern exposure, it approaches some constant value of ~ 0.8 .

According to the results of measurements, the amounts of evolved HBr and decomposed $(\text{BrBNH})_3$ are linear functions of time (Fig. 3), and their ratio also changes with time (Table 3). Thus, the evolved HBr amount increases with time from 1.74 to 2.17 mol per tribromoborazine mole. In our opinion, the increased amount of HBr evolved per $(\text{BrBNH})_3$ mole is due to the slow thermal decomposition of condensed $(\text{Br}_x\text{B}_3\text{N}_3\text{H}_x)_n$ with hydrogen bromide evolution:



Thus, hydrogen bromide appears in the system due to at least two processes: rapid borazine decomposition (reactions (3), (4)) and a relatively slow decomposition (aging) of the polymer (process (8)). Even after 39.8 h of exposure at 573 K, a noticeable amount of undecomposed tribromoborazine (22.6% of the initial weight) remains in the system.

The complete conversion of gaseous tribromoborazine to boron nitride in a closed system is hardly

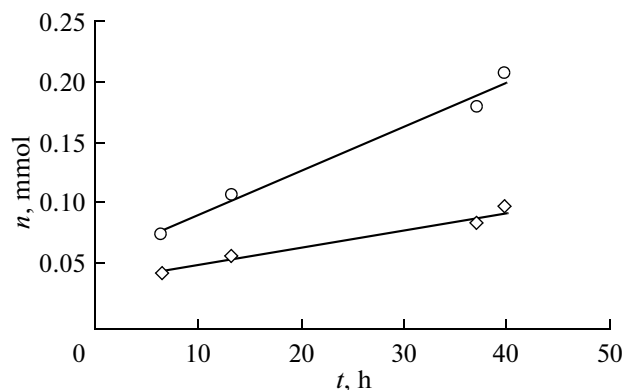


Fig. 3. Evolved HBr amount (circles) and consumed tribromoborazine amount (rhombs) versus time at an exposure temperature of 573 ± 4 K.

achievable even at elevated temperature. Exposure at 660 ± 5 K for 99 h (until HBr evolution ceases) in the first run yields a condensed phase of composition $(\text{Br}_{0.32}\text{B}_3\text{N}_3\text{H}_{0.32})_n$ but not pure boron nitride. Tribromoborazine is completely decomposed in the course of the run. This behavior is typical of borazine, too: exposure of $(\text{HBNH})_3$ for 48 h at 748 K (until hydrogen evolution ceases) yields a condensed phase of composition $(\text{H}_{0.45}\text{B}_3\text{N}_3\text{H}_{0.45})_n$ [11]. For tribromoborazine, similar conversion is achieved at a temperature 90 K lower than for borazine.

Kinetics of tribromoborazine decomposition. Static tensimetry method with membrane null-manometer is usable for kinetic studies of processes in which the number of gas moles changes. The volume V of the system is a fixed value during the run; therefore, a conventional reaction rate v_{conv} may be taken to be an increment in the quotient $\frac{P}{T}$ in unit time, which is directly proportional to the increase in hydrogen bromide concentration in the system: $v_{\text{conv}} = \frac{\Delta(P/T)}{\Delta t}$.

The HBr evolution rate from $(\text{Br}_x\text{B}_3\text{N}_3\text{H}_x)_{n(\text{cond})}$ at 573 K is relatively low; therefore, we may state that hydrogen bromide evolution by reaction (8) will be insignificant at low temperatures. This allows using the initial rates method for estimating the activation energy of the condensed-phase thermal decomposition of tribromoborazine at relatively low temperatures (353–443 K). In using the initial rates method for $(\text{BrBNH})_3$ thermal decomposition in the saturated vapor region, we made the following assumptions: the tribromoborazine concentration in condensed phase remains practically unchanged during the run; the product $(\text{Br}_x\text{B}_3\text{N}_3\text{H}_x)_{n(\text{cond})}$ does not experience further decomposition at noticeable rates; and the contribution of gas-phase tribromoborazine decomposition is negligible and ignored. Five sets of vapor pressure measurements as a function of time have been carried out at 353, 384, 404, 419, and 443 K; the log plot of the conventional rate versus reciprocal temperature is seen in Fig. 4. We note that points referring to the decomposition of solid and liquid tribromoborazine fall on one straight line. According to this work, the activation energy of the condensed-phase thermal decomposition of $(\text{BrBNH})_3$ (process (3)) is 65 ± 3 kJ/mol. Data from [11] give an estimate of 220 kJ/mol for the activation energy of thermal decomposition of borazine, implying the greater ease of $(\text{BrBNH})_3$ decomposition relative to $(\text{HBNH})_3$. In our opinion, the reason for this is the easier elimination of HBr compared to H_2 due to the greater negative charge on the bromine atom.

After $(\text{BrBNH})_3$ was completely evolved to the gas phase, the decomposition reaction rate substantially

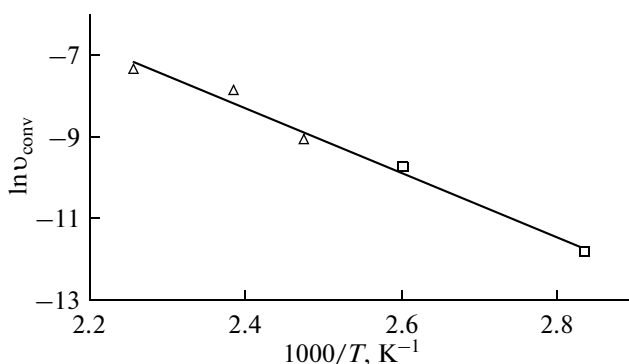


Fig. 4. Log conventional rate versus reciprocal temperature for tribromoborazine decomposition in a liquid phase (triangles) and solid phase (squares).

slowed down and was virtually independent of decomposition temperature. Our estimate of the activation energy of gas-phase tribromoborazine decomposition in the range 473–573 K is 5 ± 2 kJ/mol, indicating that the reaction rate is controlled by tribromoborazine diffusion to the walls of the vessel. An estimate of 2.5 kJ/mol was obtained for the activation energy with diffusion rate control from the diffusivity versus temperature dependence at the temperatures of our runs [12].

Suggested decomposition scheme. The small value of the activation energy of condensed-phase thermal decomposition of tribromoborazine (65 ± 3 kJ/mol) suggests that, unlike for borazine, tribromoborazine thermal decomposition preserves the B_3N_3 heterocycle core. Tribromoborazine thermal decomposition is likely a polycondensation reaction, where polymer compounds $(\text{Br}_x\text{B}_3\text{N}_3\text{H}_x)_{n(\text{cond})}$ are formed at the first stage to slowly lose hydrogen bromide in the course of further crosslinking of polymeric fragments. Our suggested scheme of tribromoborazine decomposition is displayed in Fig. 5. This scheme comprises the rapid addition of tribromoborazine molecules to a growing polymer network and a slower release of hydrogen bromide upon further polymer crosslinking.

In summary, we used static tensimetry method to determine saturated and unsaturated vapor pressures of $(\text{BrBNH})_3$ as a function of temperature, and the parameters of tribromoborazine sublimation and vaporization have been determined. Noticeable rates of tribromoborazine decomposition with HBr gas evolution are observed at temperatures higher than 343 K. The other decomposition products are nonvolatile and have a polymeric nature. At 573 K polymers continue releasing hydrogen bromide, may be, due to the crosslinking of polymer chains. We failed to provide complete HBr release even upon a long-term exposure of the closed system at 660 K. Likely, complete removal of HBr at these temperatures is achievable only under unequilibrium conditions. Our estimate of

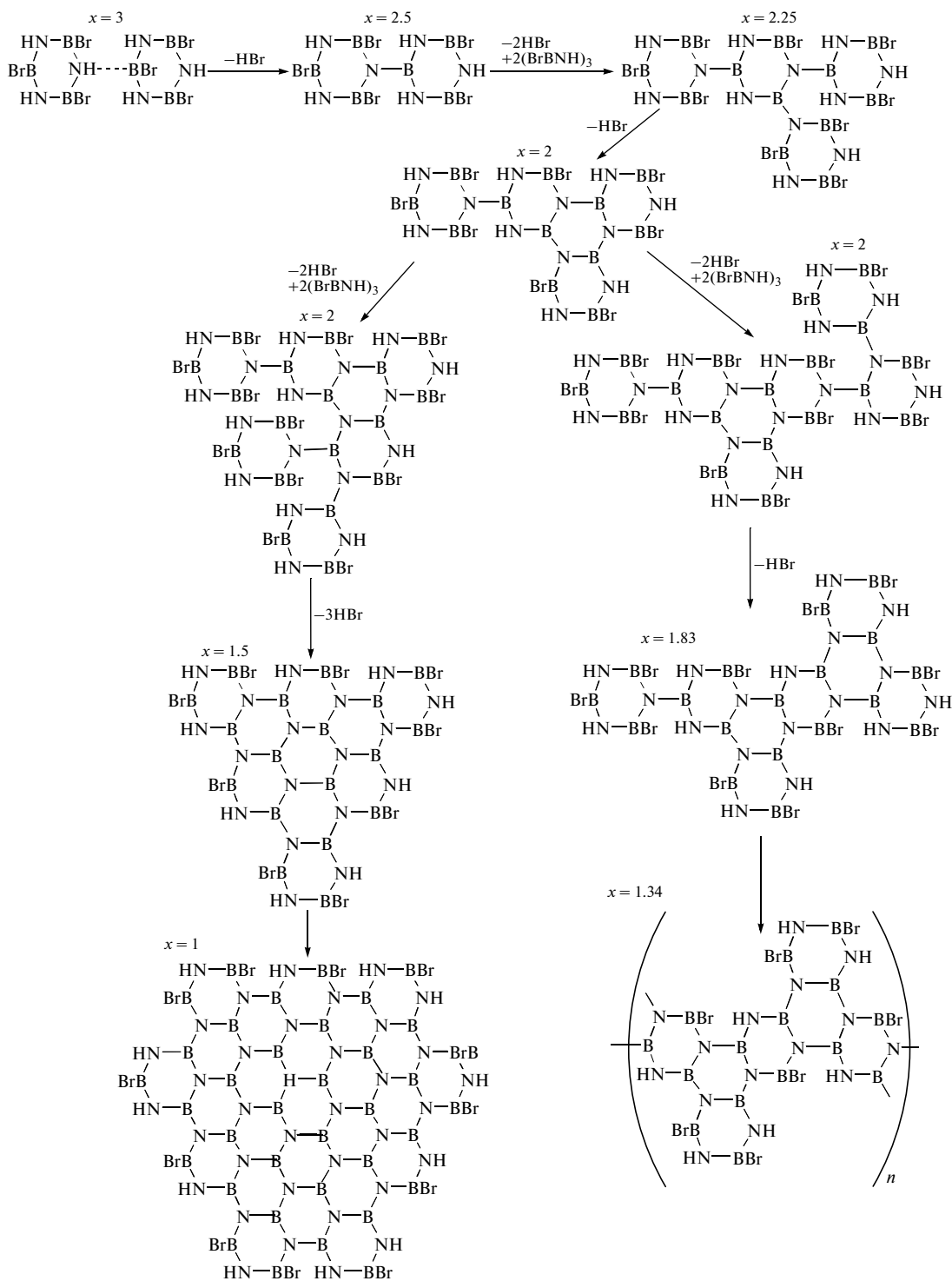


Fig. 5. Suggested scheme of tribromoborazine thermolysis: the initial polycondensation step (top), and formation of 2D sheets (left) and linear polymers (right). The x value is given for each structure.

the activation energy for tribromoborazine thermal decomposition in a condensed phase is 65 ± 3 kJ/mol, which is an indirect indication of the preservation of the heterocycle core upon the thermal decomposition.

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REFERENCES

1. K. B. Shelimov and M. Moskovits, *Chem. Mater.* **12**, 250 (2000).
2. G. Postole, M. Caldararu, N. I. Ionescu, et al., *Thermochim. Acta* **434**, 150 (2005).
3. K. N. Chaitanya, R. Schaeffer, and R. T. Paine, *J. Am. Chem. Soc.* **109**, 5556 (1987).
4. K. J. L. Paciorek, S. R. Masuda, and H. Rainhold, *Chem. Mater.* **3**, 88 (1991).
5. F. Müller, K. Stöwe, and H. Sachdev, *Chem. Mater.* **17**, 3464 (2005).
6. C. A. Brown and A. W. Laubengayer, *J. Am. Chem. Soc.* **77**, 3699 (1955).
7. *Handbuch der praeparativen anorganischen Chemie*, Ed. by G. Brauer (Ferdinand Enke, Stuttgart, 1975–1981; Mir, Moscow, 1985).
8. A. V. Suvorov, *The Thermodynamic Chemistry of Vapor State* (Khimiya, Leningrad, 1970) [in Russian].
9. E. I. Davydova, T. N. Sevastianova, A. V. Suvorov, and A. Y. Timoshkin, *Coord. Chem. Rev.* **254**, 2031 (2010).
10. A. W. Laubengayer and C. W. J. Scafie, *J. Chem. Eng. Data* **11**, 172 (1966).
11. A. W. Laubengayer, P. C. Jr. Moews, and R. F. Porter, *J. Am. Chem. Soc.* **83** (6), 1337 (1961).
12. B. P. Nikol'skii, *Physical Chemistry* (Khimiya, Leningrad, 1987) [in Russian].