

Thermal decomposition of cyclotriborazane

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Abstract

Cyclotriborazane (CTB), $B_3N_3H_{12}$, is a crystalline white solid, which decomposes above 400 K to hydrogen and a few other products, depending on the reaction conditions. In this work we present investigations of the thermal decomposition of both the neat compound and CTB dissolved in diglyme and tetraglyme. Several thermophysical and analytical methods, such as differential scanning calorimetry (DSC), thermogravimetry (TG), mass spectroscopy (QMS), and ^{11}B nuclear magnetic resonance spectroscopy (NMR) have been used for this investigation. The decomposition of the neat substance releases 3.1 mol H_2 /mol CTB and leads to a polymeric products and borazine. In open vessels, sublimation as a competing process also occurs. The enthalpy of the decomposition process ($\Delta_R H_s$) has been determined as $\Delta_R H_s = -34.0 \pm 2.9$ kJ/mol.

In contrast to the thermal decomposition of the pure substance, the decomposition in polyethers, such as diglyme and tetraglyme, leads above 370 K to borazine and small amounts of soluble oligomeric borazine species. Also BH_3 group containing species are occurring as intermediates. In these systems no precipitation was detected. DSC measurements show for the decomposition in solution several strong exothermic effects. The overall decomposition enthalpy in diglyme is given by $\Delta_R H_d = -32.0 \pm 2.8$ kJ/mol and in tetraglyme by $\Delta_R H_t = -48.0 \pm 4.7$ kJ/mol. The enthalpy of solution of cyclotriborazane was determined in diglyme and in tetraglyme with the values $\Delta_D H_d = -2.1 \pm 0.2$ kJ/mol and $\Delta_D H_t = -4.6 \pm 0.5$ kJ/mol, respectively.

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1. Introduction

In several papers thermal dehydrogenation reactions of compounds, containing only boron, nitrogen, and hydrogen, called “BNH-compounds”, were reported [1–5]. These compounds are among others useful as hydrogen generating material [6–8]. It is known that, depending on the decomposition conditions, different products besides hydrogen are formed [1,5,9,10].

The best known species of these hydrogen generating BNH compounds is ammonia borane, BH_3NH_3 . During its thermal decomposition, ammonia borane releases hydrogen in two steps. The first one occurs at 340 K resulting in the production of polymeric $(BH_2NH_2)_n$, followed by the conversion to $(BHNH)_n$ at 380 K [5,11]. A complete decomposition of ammonia borane to $(BHNH)_n$ provides 13 wt.% usable hydrogen. Unfortunately, the thermal decomposition leads mainly to inert polymeric solids

[4,5,12,13]. Several groups try to develop processes that allow to convert the polymeric residues back into ammonia borane [14,15]. But, beside the unfavorable thermodynamics, the rehydrogenation of the products poses a particular challenge because of the inertness of the polymeric compounds. The polymers formed are insoluble in organic solvents and a significant effort is needed for the digestion of the material.

Therefore, it was our interest, to avoid the formation of any polymeric products during the hydrogen release to get an improvement in the reactivity. From this point of view, cyclotriborazane (“inorganic cyclohexane”) seems to be an interesting alternative hydrogen generating material, which partly results in borazine (“inorganic benzene”) during the release of hydrogen [16,17]. Although from cyclotriborazane only 7 wt.% of usable hydrogen are released, which is only half of the amount of what can be obtained from ammonia borane, its complete conversion to the reactive borazine would improve the chemical situation in comparison to the inert polymer strongly.

Different groups calculated a free enthalpy for the dehydrogenation in the range of -150 to -155 kJ/mol [18,19] for borazine and the polymeric products and therefore assumed the

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impossibility to reload these products with molecular hydrogen directly. However, an indirect hydrogenation is not excluded. Therefore it is essential, that the product has still a high reactivity, like borazine.

Another interesting point is, that the decomposition temperature of cyclotriborazane is moderate enough to perform the reaction in the dissolved state as well [16]. Because of its ability to stabilize BNH compounds and to support reactions with hydrogen transfer in general, glymes in particular need to be considered as favorable solvents for this type of reaction [20]. The experiment can be easily performed in solution because cyclotriborazane and borazine show both sufficient solubility in glymes [10,16]. Also, many reactions with hydrogen transfer work better in glymes, than in other organic solvents [20,21] and decomposition experiments with ammonia borane and the currently most commonly used synthesis of borazine [22] has been already successfully performed in these solvents.

The dehydrogenation of ammonia borane in diglyme to borazine had been described in Ref. [10] and the occurrence of cyclotriborazane had been mentioned as an intermediate, but further detailed research of this reaction system, especially with respect to thermo-physical quantities, such as reaction and solution enthalpies was done so far only theoretically [8,23–25]. It can be assumed that if the presence of the solvent controls the type of products formed the knowledge of the thermodynamic data in conjunction with structural information should support the basic mechanistic ideas. A special interest lies in the stability of the BN-ring with and without “solvent support”.

2. Experimental

All synthesis and investigations were performed under argon atmosphere. All precautions in respect of air and moisture sensitive reagents have been taken. All chemicals used were obtained from Aldrich. Solvents were dried over sodium and the used sodium borohydride pellets were pulverized under inert gas shortly before use.

Cyclotriborazane was synthesized as reported in Ref. [16] and was further purified by vacuum sublimation. The products were analyzed by XRD, ^{11}B , and ^1H NMR and the obtained data show very good coincidence with the literature values [1,2,10,16].

All DSC measurements were performed using a differential scanning calorimeter, type C-80 from Setaram. In some measurements, the used Hastelloy C-276 high pressure vessels have been connected to a pressure detector PA-21S/80400.3 from Keller. For the determination of the enthalpy of solution, reversal mixing vessels were used.

DTA/TG/QMS investigations were carried out at the “Fraunhofer Institut für keramische Technologien und Sinterwerkstoffe, Dresden” with a differential thermo analyzer STA 429 from Netzsch. The Netzsch 403-3 ceramic blend was coupled to a Balzers QMG 421 quadrupole mass spectrometer. All enthalpies determined are integral molar and referred to 1 mol pure cyclotriborazane. For elemental analyzes a CHN O-Rapid from Heraeus was used. X-ray diffraction measurements

were carried out, using the Siemens D5000 Diffractometer. NMR spectra were obtained by using the 400 MHz spectrometer DPX-400 from Bruker. Samples were run in 10 mm tubes, each containing a 2 mm diameter reference tube, filled with 0.19 M $\text{BF}_3\cdot\text{OEt}_2$ in CDCl_3 (0 ppm) as external standard. For quantitative NMR measurements, different diglyme and tetraglyme solutions with known concentrations of cyclotriborazane and borazine were prepared and used to compare the peak areas of each signal. For further confirmation the $\text{BF}_3\cdot\text{OEt}_2$ signal areas were used for integration likewise. Both methods gave consistent results. Because the nature of the other species is not known in detail, it was not possible to create a similar reference for the interpretation of their signals. Thus, only the quantitative analysis of borazine and cyclotriborazane was carried out.

2.1. Decomposition of the solid cyclotriborazane

- In a typical experiment a 25 ml Schlenk vessel was connected to a cooling trap (195 K). 0.67 g (7.7 mmol) cyclotriborazane were heated up to 470 K and the sample was held for additional 6 h at this temperature before it was slowly cooled down. The residues in the vessel as well as the residues in the cooling trap were analyzed by XRD and ^{11}B NMR.
- A second kind of heating experiment was performed, using open vessels of a DTA/TG apparatus. Two to three milligrams of cyclotriborazane were heated up to 560 K and all volatile components were transferred to a mass spectrometer by a helium gas stream.
- For the DSC measurements, approximately 20 mg (0.23 mmol) of cyclotriborazane in Hastelloy vessels were heated up to 530 K with a heating rate of 1 K/min. During some measurements, a pressure detector was used. After completion of the heating program, the vessels were cooled down and the products were analyzed by XRD and ^{11}B NMR.

2.2. Decomposition in glymes

- A DSC vessel was filled with 0.5 ml of an 0.3 M solution of cyclotriborazane in diglyme and heated up to 490 K. After the subsequent cooling to room temperature, the products were analyzed by ^{11}B NMR. Further decomposition experiments were performed with various heating rates between 0.05 and 1 K/min. Similar procedures were also carried out with tetraglyme as the solvent.
- In another kind of experiments, the prepared solution was quenched during the reaction at specific temperatures and ^{11}B spectra of the quenched system were taken. Likewise procedures, using tetraglyme as solvent were carried out.
- For the enthalpy of solution in diglyme and tetraglyme, about 2 mg of cyclotriborazane were dissolved in 2 ml glyme (0.01 M solution). For each value about five measurements were taken. Measurements in normal air and under argon atmosphere were used to determine the air sensitivity of the samples.

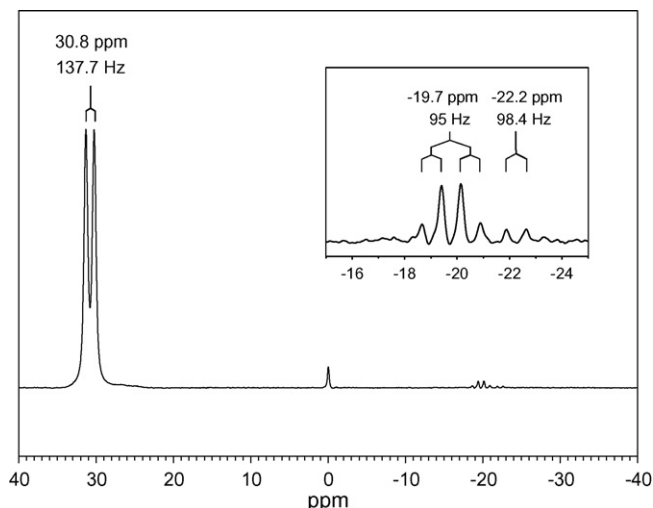


Fig. 1. Undecoupled ^{11}B spectrum of the products collected by the cooling trap after the thermal decomposition of neat cyclotriborazane. The spectrum shows three different signals: a doublet at 30.8 ppm, $J = 137.7$ Hz (Lit.: 29.1–30.5 ppm, $J = 133$ –139 Hz [10]) resulting from borazine, a quartet at -19.7 ppm ($J = 95$ Hz) caused by unknown compounds containing a BH_3 group, a doublet at -22.2 ppm ($J = 98.4$ Hz) indicating the presence of the BH group in another unidentified compound. The chemical shifts are referenced to $\text{BF}_3 \cdot \text{OEt}_2$.

3. Results

3.1. Decomposition of the solid cyclotriborazane

- (a) The thermal decomposition in Schlenk vessels starts, depending on the heating rate, at about 420 K and an extensive evolution of hydrogen and some other products that were eliminated from the gas phase by condensation was observed. At a temperature of about 430 K the sublimation of cyclotriborazane as a competitive effect was noticed. Therefore the not all of cyclotriborazane used was finally decomposed.

The end of the reaction in these experiments was indicated, by the end of any gas evolution. An amorphous and insoluble white solid remained in the vessel. Elemental analysis showed that the remaining hydrogen content is 6.4 wt.% which corresponds to a formula of $[\text{BNH}_{1.7}]_x$. The solid residue possesses most likely a similar polymeric structure, as the ones reported by several other groups for the decomposition of ammonia borane and related compounds [5,26].

The cooling trap gave 0.3 ml of a white clouded liquid. ^{11}B NMR of the filtered liquid indicates the presence of borazine and slight amounts of impurities (Fig. 1). Assuming, that borazine is the only liquid species, the yield is about 40 mol% in respect to the amount of cyclotriborazane used.

- (b) In open vessels, the sublimation of cyclotriborazane increases strongly. TG data showed a weight loss of about 85 wt.% and the DTA plots obtained show a strong endothermic effect, superposing the decomposition effect of cyclotriborazane.

In a measurement of the mass spectra as a function of the temperature, the intensity of all signals present increased

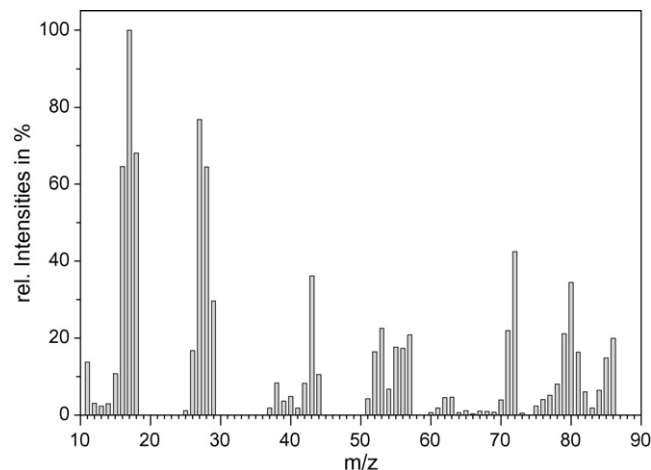


Fig. 2. Mass spectrum of the volatile compounds of the thermal decomposition of cyclotriborazane, recorded at 428 K: the most intensive mass numbers are $m/z = 17$ (ammonia) and $m/z = 27$ (diborane and BNH_2). In addition to these signals, the ones of borazine ($m/z = 80$) and cyclotriborazane ($m/z = 86$) and its fragmentation products were detected.

equivalently and reached their maxima at the same temperature. This behavior makes it hard to assign the release of the detected species to the different thermal effects (see Section 2.1c). The mass spectrum shows the occurrence of large amounts of ammonia, diborane, borazine, and sublimed cyclotriborazane (Fig. 2).

- (c) The DSC measurements show at least three different exothermic effects above 420 K taken at an heating rate of 1 K/min (Fig. 3).

The first two DSC signals vary in their intensities, but the third one was always constant. The integration of the third DSC signal typically yielded a value varying from -16 to -17 kJ/mol. All effects together reach a value of about -42 to -47 kJ/mol which corresponds to an enthalpy of decomposition $\Delta_R H_s = -34.0 \pm 2.9$ kJ/mol after the pressure correction was applied. The steep pressure rise beyond 450 K indicates a strong formation of gaseous products. Analyzing the overall pressure increase results in an amount of 3.1 mol per mol cyclotriborazane of gaseous species

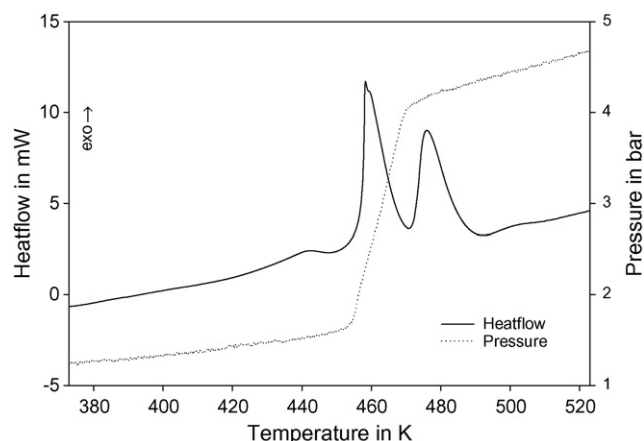


Fig. 3. Thermal decomposition of cyclotriborazane: plotted is the DSC signal and corresponding pressure development.

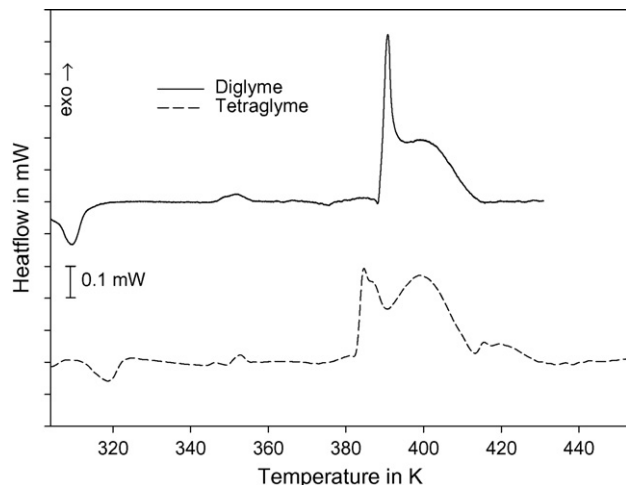


Fig. 4. DSC plots of the thermal decomposition of cyclotriborazane in diglyme and tetraglyme: these experiments were done with a heating rate of 0.05 K/min. Both plots show a remarkable analogy in their occurring effects. The signals are shifting to higher temperatures with increasing heating rates. For the onset temperatures of the main effect a shift from 375 to 400 K was found, when the heating rate is increased to 1 K/min.

released. The only non-gaseous product obtained was an amorphous white solid. Elemental analysis showed that it possesses a hydrogen content of 4.8 wt.% which corresponds to the formula $[\text{BNH}_{1.3}]_x$. No borazine or other species were detected during this type of experiment.

3.2. Decomposition in glymes

- (a) The thermal decomposition in diglyme and tetraglyme are similar in respect to their thermal effects (see Fig. 4). Both show an endothermic effect, occurring between 310 and 330 K, depending on the heating rate. Various heating and cooling cycles at different rates indicate a phase transition to be responsible for this effect. However, it was not possible to determine the nature of this effect in detail. The ^{11}B NMR measurements showed no change in the electronic shielding around the boron nuclei. Another DSC signal, which was not caused by a reversible effect, occurred at 350 K. It corresponds to a value of about -2 to -3 kJ/mol.

Right after a small precursory exothermic effect starting at about 370 K, at least two overlapping signals, indicating the main reaction, were detected, whose onset temperatures at the given rate of 0.05 K/min are about 380 K. These reactions could not be separated by varying the heating regime because of their similar onset temperatures and overlapping shapes. After pressure correction, the overall enthalpy for these effects was determined to be $\Delta_{\text{R}}H_{\text{d}} = -32.0 \pm 2.8$ kJ/mol in diglyme and $\Delta_{\text{R}}H_{\text{t}} = -48.0 \pm 4.7$ kJ/mol in tetraglyme. During both reactions a pressure increase, proportional to the heat release, was found.

- (b) ^{11}B spectra of the products after the calorimetric experiments in diglyme as well as in tetraglyme showed that cyclotriborazane during the process was completely decomposed. The main product beside small amounts of soluble

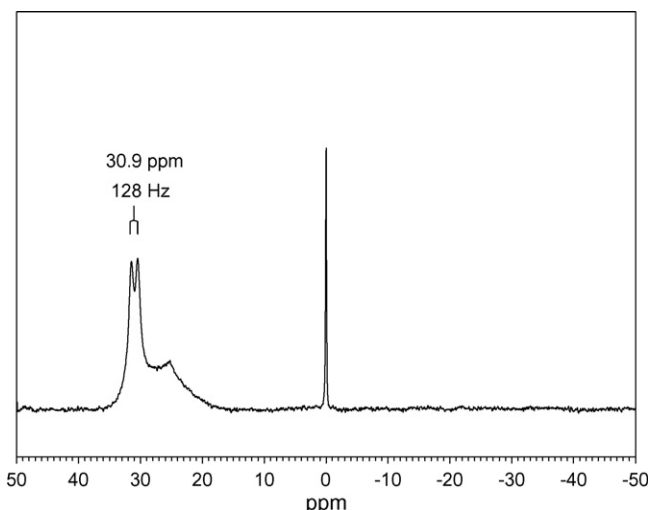


Fig. 5. ^{11}B spectrum of the thermal decomposition products of cyclotriborazane: The spectrum shows no signal of cyclotriborazane (-11.2 ppm, $J = 104$ Hz [10]) anymore, but the one of the product borazine (30.9 ppm). The broad signal between 20 and 30 ppm is caused by the reaction of borazine with itself to oligomeric species. No precipitation or clouding occurred.

oligomeric species was borazine. No precipitation or clouding effects occurred during the heating process (Fig. 5).

Quenched reactions at about 410 K also showed the occurrence of BH_3 species as an intermediate with a chemical shift of about -22 ppm. This shift is similar to what was reported for ammonia borane (-22.6 ppm [27]). Beside this compound, a location at the end of any open BN chain would result in a similar chemical shift and needs to be considered as well. The occurrence of a boron containing species besides cyclotriborazane and borazine indicates a more difficult reaction scheme than a simple dehydrogenation, but we did not succeed in assigning possible reactions steps to the various peaks in the DSC plots.

- (c) The thermal effect during the dissolving of cyclotriborazane in diglyme is smaller ($\Delta_{\text{D}}H_{\text{d}} = -2.1 \pm 0.2$ kJ/mol) than in tetraglyme ($\Delta_{\text{D}}H_{\text{t}} = -4.6 \pm 0.5$ kJ/mol). Remarkably, noticeable higher effects were observed in air than in argon (-2.8 ± 0.1 kJ/mol in diglyme and -7.7 ± 1.1 kJ/mol in tetraglyme). During the experiments in air the thermal effects were more pronounced and lasted longer than under argon and resulted in a slight clouding.

4. Discussion

The thermal decomposition of solid cyclotriborazane takes place in a sequence of at least three exothermic steps as was confirmed by our calorimetric measurements. The main products are polymeric species with a formula of about $[\text{BNH}_2]_x$, but generally the non-polymeric, liquid cyclic trimer $[\text{BNH}_2]_3$ – borazine – is also created in significant amounts. The yield of 40% is lower than it was reported in Ref. [16], but this might be an effect of the different set up and the partial sublimation of the cyclotriborazane out of the heated zone. The mass spectra of the gas phase during this reaction show, amongst others, high concentrations of ammonia, diborane, and monomeric BNH_2 . Parts

of the spectra resemble the one of cyclotriborazane, mentioned in Ref. [10], but other mass numbers in the spectra indicate also the formation of borazine, which would be the preferred product of the reaction. It is also apparent, that besides the cracking pattern of cyclotriborazane and borazine additional peaks are found that most likely result from compounds created by the ring opening of the cyclotriborazane during the dehydrogenation. In contrast to these results, no borazine was found during and after the C80 measurements. Most likely, the vessel material, Hastelloy C-276, an alloy of nickel, molybdenum, chromium, iron, and tungsten, supports the dehydrogenation of borazine, which was probably formed during the reaction. Further hydrogen release by borazine leads to polymeric solid products as described in Ref. [28]. Similar reactions in the presence of metals are reported [29]. The amounts of the gaseous products released, calculated from the pressure measurements, and the elemental analyses of the solid residues, both showed that the hydrogen evolution agrees to the formula $[\text{BNH}_{1.3}]_x$ for the residue. This formula corresponds to a lower amount of hydrogen than the one that was found in the experiments conducted in the glass apparatuses and thus would be consistent with the view that additional hydrogen is released from polymerizing borazine.

The measured enthalpies of solution under argon atmosphere are exothermic and indicate attractive interactions between cyclotriborazane and the glymes. It is conceivable, that the oxygen atoms of the glyme molecules coordinate around the nitrogen–hydrogen groups (in analogy to ammonium 18-crown-6 etherate [30]) by forming hydrogen bonds. The more exothermic value in tetraglyme compared to diglyme is probably a result of better solvation, because of the hydrogen bonds that are formed between the two additional oxygen atoms in the solvent molecule and cyclotriborazane. Solutions of cyclotriborazane in glymes, if stored under argon, are stable for a long period of time. A 0.8 M solution of cyclotriborazane has been stored for 3 weeks without clouding. ^{11}B spectra taken after this period indicated no additional signals than the one of the pure substance. In contrast to that, the dissolving effects under air were stronger and a beginning of clouding indicated that a further reaction took place. This reaction is not ascribable to autoxidation or to simple self-assembling of cyclotriborazane, because of the stability of the solution under argon, as long as no moisture is present. Instead, the cyclotriborazane, if dissolved in organic liquids, is very sensitive towards moisture in normal air and reacts easily—in contrast to the neat substance which is not even attacked by cold water. The inertness of the pure cyclotriborazane against water has been reported in Refs. [2,16] and explained to be a wetting effect. A similar behavior was recognized in earlier experiments with several BNH compounds which decomposed in the presence of ordinarily moist air if they were dissolved in organic solvents. In contrast to that, solid BNH compounds are fairly stable in moist air. Passivation effects due to the formation of various hydrolysis products are likely.

The thermal decomposition in diglyme does not lead to insoluble components. Only the desired product borazine and soluble oligomers, polyborazylene [17,31], were obtained. Assuming, the NMR sensitivity in our measurements of the oligomer is

comparable to the one of borazine, a yield of 70% borazine can be calculated. In Ref. [15] it has been reported, that polyborazylene can be produced by further dehydrogenation of borazine. Although we did not find any evidence, that under these conditions this reaction is exclusively responsible for the formation of these species, we found, that it is possible to suppress the amount of oligomers formed by lowering the cyclotriborazane concentration and the temperature during the reaction.

Very similar results gave the experiments we performed with tetraglyme as solvent and therefore we conclude that similar results would be obtained in other glymes as well. Obviously, the number of collisions of the BNH molecules with each other, which are necessary for polymerization process to occur, are efficiently suppressed by the presence of the glyme molecules, which may be due to the strong interaction of the solvent molecules with the BNH compounds. In this way, glymes stabilize them—especially the reactive borazine, which has a high tendency to undergo self-polymerization. It even seems to stabilize the unstable open chained intermediates, like the BH_3 group that was detected in some ^{11}B spectra suggests. Remarkably, the hydrogen release temperature is much lower, i.e. by 30 K when heated with 1 K/min, than the one for the neat substance. Obviously the glyme molecules support the decomposition of cyclotriborazane in a similar way, as they facilitate hydrogenations of organic compounds by supporting the hydrogen transfer [20]. For example they could promote the formation of the BH_3 species. The BH_3 occurrence shows, that the dehydrogenation is not just a simple intramolecular elimination of hydrogen, but rather a complex reaction system. Some recently performed screening experiments showed that the occurrence of this species has a significant influence on the decay rate of cyclotriborazane, but more research is needed to answer the question about the role of the BH_3 species.

The enthalpies determined by the DSC experiments show a stronger exothermic reaction in solution than it does in the solid state. Unfortunately, the enthalpy of reaction of -34.0 kJ/mol for the decomposition of the solid cyclotriborazane includes not only the contribution of the reaction to borazine but also the contribution by the hydrogen releasing polymerization. It can be expected, that the polymerization of borazine is exothermic like dehydrogenation reactions of other BNH compounds and that therefore the enthalpy for the technically preferred reaction to borazine is less exothermic.

In Ref. [19] the reaction enthalpy $\text{B}_3\text{N}_3\text{H}_{12}(\text{s}) \rightarrow \text{B}_3\text{N}_3\text{H}_6(\text{l}) + \text{H}_2(\text{g})$ has been predicted to be approximately -4.2 kJ/mol at 298 K. If these results describe the situation at 298 K correctly, one needs to conclude from our experiments that a change of the reaction to a more exothermic behavior at higher temperatures, i.e. above 400 K, occurs.

In solution, the enthalpy values we measured show only small differences in comparison to the solid decomposition. The slightly higher values in tetraglyme are based on the influence of the solvent and its ability to coordinate around the BNH species. Because of its less exothermic behavior, weaker solvation, and consequently its less negative free enthalpy, diglyme might be the more favorable solvent in respect to possible rehydrogenation procedures.

In this paper we investigated the thermal decomposition of cyclotriborazane to borazine in solid and in liquid phase. Undoubtedly, the dehydrogenation of cyclotriborazane at least in glymes is not just a simple intermolecular hydrogen elimination, unlikely the corresponding organic compounds, but a reaction that includes several decomposition pathways as can be seen from the presence of the unexpected BH_3 species; a topic that needs to be considered and investigated in the future.

In general, the comparison with experiments of the hydrogen decomposition in the gas phase would be of great interest, since they would allow to identify the influence of the solvent decisively. On the one hand, the calculated enthalpy values could be confirmed and on the other hand the formation of oligomers could be suppressed by lowering the cyclotriborazane partial pressure in a similar way as it was done in solution. For the possible use of a heterogeneous catalyst, the suppression of the formation of the oligomers is important since they would adhere to the surface of the catalyst and cause its inactivation.

5. Conclusion

It has been shown, that the thermal decomposition of neat cyclotriborazane mainly results in the formation of polymeric products, having the average formula $[\text{BNH}_2]_x$, but depending on the conditions, a formation of borazine in substantial amounts is also possible. The polymeric residues can be avoided by using glymes as a solvent. The influence of the solvent on the reaction is best seen by the lowered temperatures at which the hydrogen release takes place. An approximately 70% yield of borazine had been obtained. NMR, QMS, and DSC experiments show, that the decomposition is not a simple dehydrogenation, but a more complex reaction system and an open chained, BH_3 group containing intermediate was detected.

Comparing the experimentally determined values of the reaction enthalpies to calculations of the decomposition without solvent, significant differences are found, which can be predominantly attributed not only to the reaction conditions present, such as the temperature and the concentration, but also to the different interactions of the dissolved species with the glyme molecules.

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