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Calorimetric process monitoring of thermal decomposition of B–N–H compounds[☆]

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Abstract

Borazane BH_3NH_3 is a crystalline solid with a high hydrogen content. It decomposes thermally activated already at temperatures below 410 K.

The thermal decomposition of BH_3NH_3 was studied by thermogravimetry (TG), differential scanning calorimetry (DSC), volumetric measurements and coupled TG/FTIR. Measurements were performed under isothermal conditions and in scanning mode.

The enthalpy change at the exothermic decomposition reaction $\Delta_r H$ was determined by use of DSC-technique. At different heating rates and temperatures a value of $\Delta_r H = -(21.7 \pm 1.2)$ kJ/mol BH_3NH_3 was obtained.

It can be pointed out that under appropriate conditions borazane decomposes completely below the melting temperature of $T = 385$ K given in the literature. As a consequence of the low decomposition rate a separation of different steps is possible only at low heating rates.

The decomposition reaction is accompanied by hydrogen evolution. During this first decomposition step borazane releases approximately 1 mol H_2 per mol BH_3NH_3. The other decomposition products are a solid residue of polymeric aminoborane $(BH_2NH_2)_x$ and a small amount of the volatile borazine $B_3N_3H_6$. The solid aminoborane was characterised by X-ray powder diffraction measurements, IR-spectroscopy and elemental analysis. The small amount of borazine formed was detected by the coupled TG/FTIR-investigations.

The mass of the hydrogen released below $T = 385$ K is about 6.5% of the initial sample mass. Due to the significant amount of evolved hydrogen and the exothermic character of the decomposition process the use of borazane as a source for hydrogen seems to be possible and interesting.

Keywords: Borazane; Borazine; Thermal decomposition; DSC; TG; Volumetric measurements and coupled TG/FTIR

1. Introduction

Borazane BH_3NH_3 is at ambient temperature and atmospheric pressure a white crystalline solid with a relatively high hydrogen content (about 20 mass% H_2). It is well-known [1] that borazane decomposes thermally activated already at temperatures below 410 K. The decomposition takes place under hydrogen

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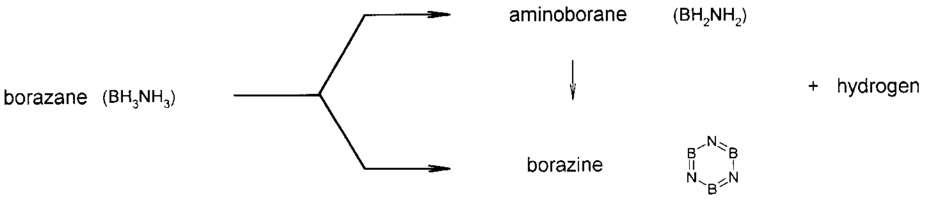

Fig. 1. The thermal decomposition of borazane under hydrogen release and formation of aminoborane and borazine.

release and formation of aminoborane BH_2NH_2 and borazine $B_3N_3H_6$ according to the reaction equations in Fig. 1.

Which of the decomposition products are formed preferentially as a function of temperature and pressure is unknown. Usually for the decomposition two steps are observed [1]. Both steps of the decomposition and with it of the hydrogen release should be exothermic. This was surprising compared with the well studied decomposition of metalhydrides.

In our previous investigations two overlapping exothermic steps of the thermal decomposition of borazane were detected by means of differential scanning calorimetry (DSC) technique as the temperature was increased to 453 K at heating rates higher than 1 K/min [2]. Further we have proved that these two exothermic effects could be separated at heating rates far below 1 K/min. In contrast to these observations for the thermal decomposition, for borazane a melting temperature of 380 K is given in [1].

Because of the relatively high hydrogen content, the medium temperatures at the thermal decomposition and the exothermic character of the decomposition process borazane seems interesting as a source for hydrogen, also for technical applications. The aim of the present work is to investigate at the decomposition of borazane the sequence of the thermal events in dependence on the heating rate and to find out thermal conditions for a separation of the different processes.

The first step of the thermal decomposition of borazane is studied by DSC, thermogravimetry (TG), FTIR, volumetric measurement and coupled techniques at temperatures lower than 410 K. The decomposition is investigated at low heating rates or at isothermal conditions, in order to allow a clear separation of different processes. The decomposition enthalpy $\Delta_r H$ and the corresponding amount of evolved hydrogen are measured in dependence on temperature and time. Additionally, the solid and gaseous products of the first decomposition step are analysed by means of the different methods.

2. Experimental

Borazane was synthesised by the reaction of ammonium carbonate and sodium boronhydride in a solution of tetrahydrofuran corresponding to [3–5]. Sample purity was controlled by X-ray powder diffraction measurements, IR and elemental analysis.

The calorimetric investigations were performed in a Setaram DSC (Model C 80) with a sample mass of about 20 mg. This instrument was running at the measurements in scanning (heating rates 0.05–1 K/min) and in isothermal ($343 \leq T$ (K) ≤ 363) mode.

Volumetric data were collected by coupling the C 80 calorimeter with an equipment for gas-volumetric measurements. Values of heat flow and the evolved hydrogen were recorded simultaneously. Only gases, which are not condensable at room temperature, were detected by this arrangement.

TG measurements were carried out by use of a Setaram TG/DSC with a sample mass of about 3–6 mg. The thermal activated decomposition of borazane was investigated in argon atmosphere (flow rate about 1 l/h) with a constant heating rate or at isothermal conditions.

For the determination of the gaseous decomposition products a coupled TG/FTIR technique increases the usefulness of mass loss data because of qualitative online analysis of volatile products related to the detected steps by the TG analysis. The used coupling system TGA/SDTA 851^e (Mettler-Toledo) and Protege 460 (Nicolet Instrument) provides an optimised interface between the two instruments to get qualitative and quantitative results with a high accuracy and resolution for the thermal decomposition of borazane. Briefly, gram–schmidt curves represent summarised changes in measured intensities covering the range 4000–400 cm^{-1} as function of time and temperature. Chemigrams are changes in spectral regions only characteristically for specified components depending on time and temperature. They can be generated by computer assisted analysis using subtraction routines and single spectra evaluation in comparison to a database of pure component spectra. They represent relative changes in concentration of the specified component over the covered range of time and temperature.

Investigations were performed in isothermal and scanning mode. Experimental conditions, such as temperature, heating rate and sample mass are comparable with experimental conditions in the DSC C 80.

The gas cell and transfer line were thermostated to prevent condensation effects. The temperature was set to 1 K above the temperature of the TG/SDTA instrument. In the range of 4000–400 cm^{-1} spectral data were collected with 16 scans/min, a resolution of 4 cm^{-1} and a flow rate of argon of 30 ml/min.

3. Results and discussion

Typical results from the calorimetric investigations of the borazane decomposition in the temperature range from ambient temperature to 410 K are given in Fig. 2. Measurements with heating rates of 1 and 0.05 K/min are presented.

With a heating rate of 1 K/min (dashed line in Fig. 2), beginning near $T = 368$ K, an exothermic process is detected, which indicates the beginning decomposition of borazane. Immediately after beginning of the decomposition, only few degrees higher, an endothermic effect overcompensates the exothermic decomposition process. The endothermic event seems to be in accordance with the melting process of borazane, which by our thermomicroscopic investigations was confirmed also. A strong exothermic heat power with the maximum near $T = 386$ K appears again after the melting process. With approximation of the temperature to $T = 398$ K a renewed rise of the exothermic heat power begins. The residual power at the minimum is higher than expected for the base line, that means, that a further decomposition step started before the first step is closed completely. From the observed sequence of the thermal events the conclusion follows, that the small decomposition rate of borazane compared with the used heating rate is the reason for the observation of the melting process. A melting temperature for still existing borazane should be existing only at higher heating rates. The small decomposition rate of the borazane has also as a consequence, that the second decomposition process begins immediately after melting before the decomposition of borazane is finished completely. Therefore a more quantitative thermodynamic or kinetic evaluation of the measured DSC curves seems possible after a separation of the thermal events by use of much smaller heating rates only.

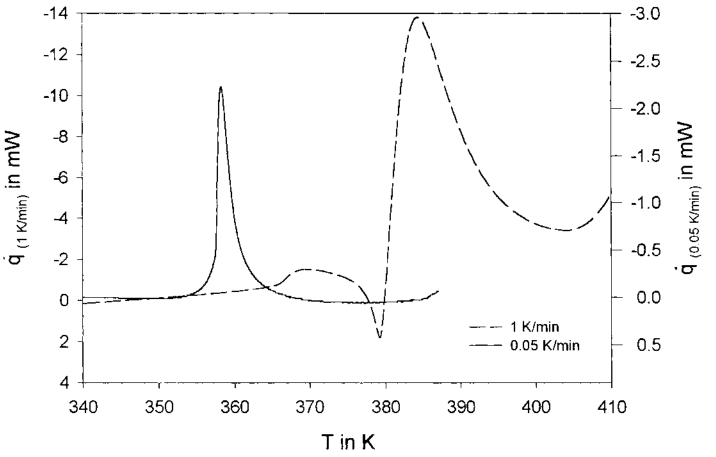

Fig. 2. DSC C 80 curves of thermal decomposition of BH_3NH_3: (—) heating rate 0.05 K/min, (- - -) heating rate 1 K/min.

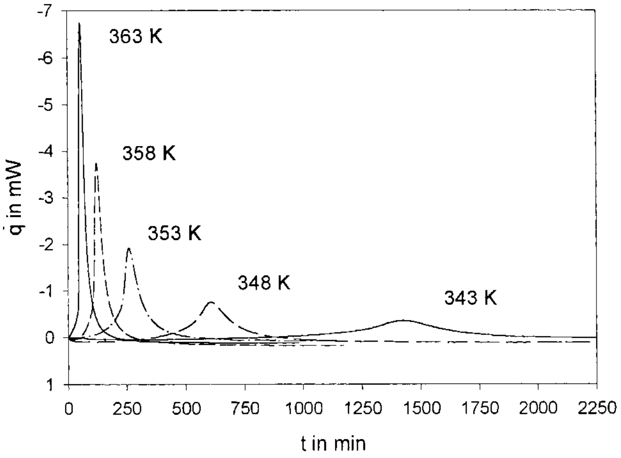

Fig. 3. DSC C 80 curves of thermal decomposition of BH_3NH_3 at isothermal temperatures between 343 and 363 K.

Using a heating rate of 0.05 K/min (solid line in Fig. 2), the first decomposition step could be obtained at significantly lower temperatures completely. The exothermic effect begins at about 355 K and is completed already below the apparent melting temperature. No sign of an endothermic event was detectable. At low heating rate borazane decomposes below its melting point completely. At a heating rate of 0.05 K/min both thermal events from the decomposition can be obtained clear separated one from the other.

Additionally the first decomposition step was studied with DSC operating in the isothermal mode at temperatures between 343 and 363 K. Isothermal measurements are suitable for the investigation of the slow decomposition reaction of borazane in the solid state below the melting temperature. Fig. 3 shows typical calorimetric curves obtained at different temperatures. A single exothermic peak was detected in all cases. The rate of decomposition strongly depends on the temperature. The maximum heat power of the decomposition reaction is reached after approximately 40 min at a temperature of $T = 363$ K and after more than 24 h at $T = 343$ K. The mean enthalpy of decomposition reaction is nearly independent of the temperature and is equal to $\Delta_r H = -(21.7 \pm 1.2)$ kJ/mol BH_3NH_3. The complete decomposition of the borazane sample during the first decomposition step was confirmed by means of X-ray diffraction analysis (XRD) analysis.

The solid residue remaining after the decomposition was analysed by use of XRD, IR spectroscopy and elemental analysis. The results were compared with data from [6,7]. It was found that polymeric aminoborane $(BH_2NH_2)_x$ is probably the main component of the solid residue. The residue usually shows an amorphous character in the XRD analysis.

By means of several methods the thermal decomposition of borazane below $T = 373$ K was studied to get information about the gaseous decomposition products. In order to provide a better and easier comparison in the following the results from the isothermal measurements at $T = 363$ K are presented and discussed.

Fig. 4 shows a typical isothermal calorimetric curve at $T = 363$ K together with the corresponding curve from the volumetric measurement for the evolution of hydrogen. It should be possible to exclude that other volatile gaseous decompositions products are measured.

Through a comparison of both curves in Fig. 4 is clearly evident, that the first exothermic step of decomposition is accompanied by a simultaneous release of hydrogen. The rate of gas evolution roughly correlates with the recorded heat flow. Some obvious differences are probably due to additional exothermic processes during the decomposition, e.g. the polymerisation of intermediate decomposition products appears to be such an additional process.

From the volumetric measurements follow that borazane release a defined amount of hydrogen. The decomposition under isothermal conditions at temperatures from 343 to 363 K yields approximately

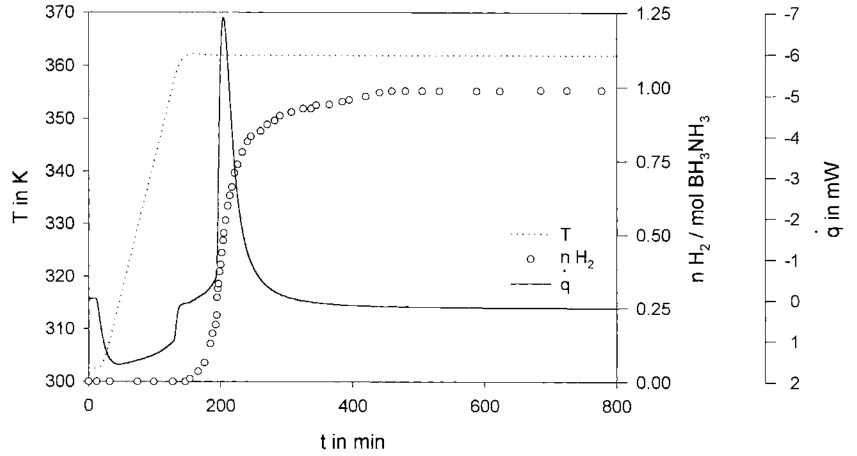

Fig. 4. Volumetric measurement at isothermal temperature 363 K: (—) heat flow, (• • •) temperature, (°) evolved hydrogen.

1.0 mol H_2/mol BH_3NH_3. The final value was attained after approximately 6 h at 363 K and after more than 40 h at 343 K. Longer decomposition runs do not result in a further increase of the detected hydrogen amount.

Simultaneous TG/DSC measurements are sensitive to the formation of evolved gaseous products. The TG/DSC curves for the isothermal decomposition of borazane at $T = 363$ K are shown in Fig. 5. A single significant step of mass loss is observable. It is clearly associated with the exothermic event of the DSC curve. The final mass loss at the decomposition in the first step is about $\Delta m = (10.0 \pm 0.1)\%$ of the initial sample mass. The release of 1.0 mol H_2/mol BH_3NH_3, which follows from the volumetric investigations, corresponds to a value for the mass loss of 6.5 mass% only. Obvious, borazane evolves additional volatile product, which condense near room temperature. Therefore the detection of this product with the used volumetric equipment was impossible and an identification of the gaseous products immediately after its formation seems necessary. For this purpose the FTIR analysis of the gas phase may be useful.

Simultaneous TG–FTIR measurements allow the identification of the individual gaseous substances together with an assignment of the identified compo-

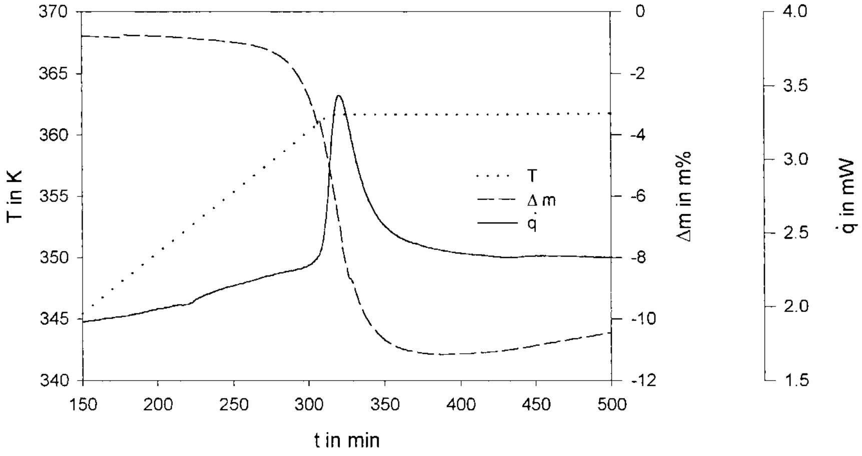

Fig. 5. TG/DSC curves of BH_3NH_3 at isothermal temperature 363 K: (—) heat flow, (• • •) temperature, (— —) mass loss.

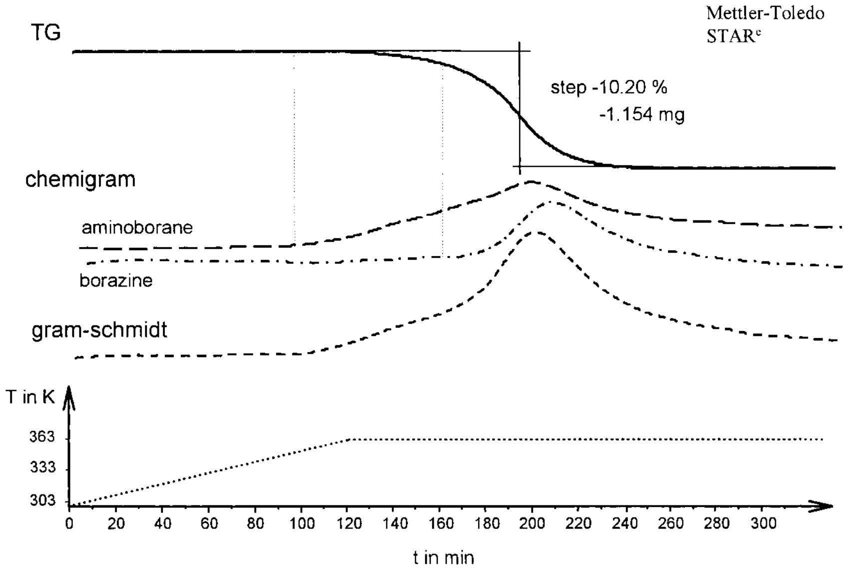

Fig. 6. TG/FTIR-investigations to characterisation of evolved gas phase: (—) mass loss, (• • •) temperature, (— —) chemigram aminoborane, (·–·–) chemigram borazine, (- - -) gram–schmidt.

nents to particular decomposition steps in the TG curve. Results of the TG–FTIR investigations of the decomposition of borazane are given in Fig. 6. The sample was heated up to 363 K with a rate of 0.5 K/min and then was held at this temperature for 200 min. A single significant step of mass loss was detected, slightly beginning already at 340 K. The final mass loss is about $\Delta m = (10.2 \pm 0.1)\%$ of the initial sample mass, being in a good agreement with TG/DSC data. Using comparisons with known spectra data [8,9] monomeric aminoborane BH_2NH_2 and borazine $B_3N_3H_6$ could be identified in the evolved gas phase. It was reported in [9] that the monomeric aminoborane is unstable at room temperature and undergoes a conversion in non-volatile oligomers. Borazine is a high volatile liquid with a boiling point at $T = 328$ K.

Because of partially overlapping spectral regions characterising NH- and BH-bondings for both monomeric aminoborane and borazine, the corresponding chemigrams may be influenced by each other. However, it can be clearly seen in Fig. 6 that the formation of borazine will be initiated after forming monomeric aminoborane. At $T = 363$ K the maximum of decomposition forming hydrogen, monomeric aminoborane and borazine will be reached after 70 min.

Probably BH_2NH_2 may be a reactive intermediate during the formation of borazine at the thermal decomposition of borazane. But more exact details about the decomposition mechanism could not yielded after these investigations.

4. Conclusion

This paper represents results of the investigations of the thermal decomposition of borazane up to $T = 410$ K. Measurements are performed in scanning mode with heating rates between 0.05 and 1 K/min or at isothermal conditions from 343 to 363 K. The decomposition was investigated by means of DSC, volumetric measurements, TG/DSC and TG/FTIR. Borazane could be totally decomposed below its apparent melting point at $T = 385$ K. For this purpose a low heating rate of 0.05 K/min or isothermal conditions must be applied, because the decomposition speed is very slow. The DSC measurements are characterised by a single exothermic peak, which occurs completely below $T = 385$ K and corresponds to the first decomposition step. For the enthalpy change at the decomposition reaction a value of $\Delta_r H = -(21.7 \pm 1.2)$ kJ/mol BH_3NH_3 was determined. The exothermic decomposition process is accompanied by hydrogen evolution. The amount of released hydrogen is independent of the temperature and is equal to 1.0 mol H_2/mol BH_3NH_3.

It seems probable that several reactions take place simultaneously. The main product is a polymeric aminoborane $(BH_2NH_2)_x$. This solid product was characterised by means of IR-spectroscopy, elemental analysis and XRD analysis. A second decomposition product is borazine $B_3N_3H_6$ as follows from the combined TG–FTIR measurements. At the chosen conditions for the thermal decomposition of borazane a very small amount of borazine seems to be formed only.

Additionally, monomeric aminoborane was found in the evolved gas phase. FTIR measurements prove that the formation of borazine will be initiated after forming monomeric aminoborane.

To verify the applicability of the investigated substances as a possible source of hydrogen and energy, further processes of the hydrogen evolution also at higher temperatures must be investigated.

Acknowledgements

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