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Thermal decomposition of ammonia–borane under pressures up to 600 bar

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Abstract

The thermal decomposition of ammonia–borane BH_3NH_3 in the temperature range up to 450 K has been studied by differential scanning calorimetry (DSC) and volumetric analysis of the released volatile decomposition products. Measurements were performed in a transitiometer ST6-VI under pressures up to 600 bar and in a DSC C-80 in the pressure range 1–100 bar hydrogen. Above 360 K ammonia–borane undergoes an exothermic decomposion, which proceeds in two steps with rising temperature. The decomposition is accompanied by hydrogen release. Formation of further volatile products, beside hydrogen, seems to be negligible. The heat evolution and hydrogen release terminates near 430 K. The final amount of released hydrogen is approximately equal to 2 mol H_2/mol ammonia–borane. Variation of pressure does not influence significantly the reaction enthalpy and hydrogen release. The transitiometer ST6-VI is well-suitable for the monitoring of solid–gas reaction under high-pressure conditions. This instrument enables a reliable determination of the reaction heat and the amount of gas release/gas uptake.

Keywords: Ammonia–borane; Thermal decomposition; DSC; Volumetric measurements

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1. Introduction

Decomposition reactions, which proceed under uptake or release of gaseous reaction products, are in principle influenced by the pressure of the gas phase in the reaction system. The variation of pressure might lead to a larger or smaller shift of the reaction equilibrium, depending on the corresponding thermodynamic and kinetic parameters for the reaction. Example for such reactions is the reversible hydrogen uptake/hydrogen release in hydrogen storage materials.

The most common detection methods in studying the reversible hydrogen exchange under different pressures involve volumetric or gravimetric measurements. These methods deliver important data regarding the hydrogen storage capacity. But it is often of great interest to obtain additionally values of the reaction enthalpy both for the hydrogen uptake and the hydrogen release direction. Calorimetry is the method of choice for obtaining such enthalpy values in a wide range of pressures. Furthermore, the calorimetric monitoring is a well-suitable tool for a quick obtaining of preliminary information about the occurrence of several reaction steps in case of a more complicated reaction pathway.

The aim of the presented work is to illustrate the performance of the high-pressure transitiometer ST6-VI from BGR-TECH (Poland) for reaction monitoring. It is constructed according to the principles of scanning transitiometry, previously described [1]. This instrument enables the simultaneous monitoring of the calorimetric signal and the volume change of the reaction system. From the volume change the released or consumed amount of gaseous reaction products can be determined. Beside usual temperature

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scans, the transitiometer allows the performance of pressure scans, which might be a favorable experimental tool for the monitoring of reversible processes in solid–gas systems.

This paper presents results of investigations of the thermal decomposition of solid ammonia–borane BH_3NH_3, also known as borazane. Measurements were made with the transitiometer ST6-VI in the high-pressure range and with a DSC C-80 device from Setaram in the low-pressure range. The thermal decomposition of ammonia–borane at ambient pressure is already well investigated [2–7]. Due to the exothermic decomposition enthalpy, it could be expected that an increase of pressure in the range below 1000 bar does not influence significantly the reaction enthalpy and amount of released hydrogen. Thus, ammonia–borane seems to be a viable calibration substance for a performance check of the transitiometer ST6-VI.

2. Experimental

2.1. Instruments

A detailed scheme of the transitiometer ST6-VI is represented in Fig. 1. It consists of two main parts, a calorimetric block and a high-pressure piston pump connected to the reaction vessel. The instrument is equipped with high-pressure vessels made from 316 stainless steel. The ammonia–borane sample was placed in a Teflon tubing sealed at both ends with Teflon plugs. The reaction vessel is connected through a stainless steel high-pressure capillary tube to the piston pump. The piston pump is driven by a computer-controlled stepper motor through a gear box.

Mercury was used as pressure transmitter. Thanks to the mercury column volatile reaction products, which were released during the decomposition of ammonia–borane, remain inside the calorimetric vessel. Because the pressure detector and the stepper motor are connected to the computer, any of the three variables – temperature, pressure or volume – can be changed stepwise or scanned continuously. Thus, beside the usual temperature scans at isobaric conditions, the transitiometer ST6-VI allows the performance of pressure scans at isothermal conditions, which could be of special interest during the investigation of solid–gas reactions. Changes of the volume in the system are determined simultaneously to the calorimetric output by counting and recording the number of steps of the stepper motor controlling the piston displacement of the pump. The resolution of volumetric measurements is $(5.24 \pm 0.04) \times 10^{-6}\ \mathrm{cm^3}$/motor step. However, the practical resolution was $7 \times 10^{-4}\ \mathrm{cm^3}$ due to the sensitivity of the pressure detection. A detailed description of the transitiometer ST6-VI is given in [8]. Measurements of the thermal decomposition of ammonia–borane were carried out in the pressure range up to 600 bar at a heating rate of $0.15\ \mathrm{K\ min^{-1}}$. Typical sample mass was about 50 mg. Experiments were performed on a ST6-VI device placed in the Blaise Pascal University in Clermont-Ferrand, France.

In the DSC C-80 from Setaram ammonia–borane was decomposed under hydrogen atmosphere in the pressure

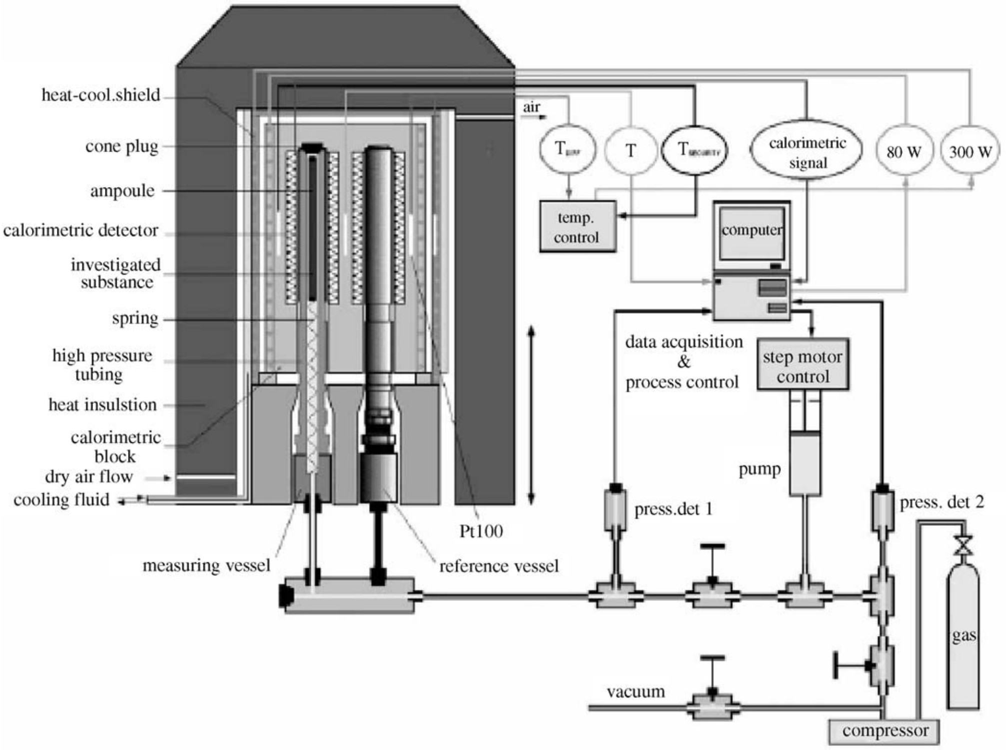

Fig. 1. A diagram of the transitiometric technique used in the present study.

range 1–100 bar at a heating rate of 0.15 K min^{-1}. High-pressure gas circulation vessels made from hastelloy 78206 alloy were used. The reaction vessel was connected through a capillary tube to a pressure detector placed outside the DSC C-80. The amount of released gaseous products was calculated from the variation of pressure after the correction for pressure change due to the thermal expansion. Volatile decomposition products, which condense at room temperature, were not detected by this equipment. The internal volume of the reaction system was calibrated using hydrogen feed with a definite gas flow rate. Typical sample mass at experiments was about 50 mg.

2.2. Materials

Ammonia–borane BH_3NH_3 (+90%, KatChem, Czech Republic) was re-crystallized from diethyl ether by Soxthlet extraction. All purification steps and the sample preparation for calorimetric measurements were performed under argon using Schlenk technique.

The purity of the used ammonia–borane sample was proved by elemental analysis, powder X-ray diffraction analysis and ^{1}H NMR, ^{11}B NMR measurements in acetonitrile. Boron content was determined photometrically, nitrogen content by means of an Herraeus Analyser CHN-O-Rapid instrument, the content of hydridic hydrogen by volumetric determination of the gas release at the acidic hydrolysis (1 M aqueous HCl).

3. Results and discussion

3.1. High-pressure transitiometer

Ammonia–borane BH_3NH_3 was used to check the performance of the high-pressure transitiometer ST6-VI. Obtained results for the thermal decomposition of ammonia–borane under 600 bar in the temperature ranges up to 453 K were represented in Fig. 2. Decomposition temperature was increased with a heating rate of 0.15 K min^{-1}. Fig. 2 shows the heat flow data obtained after the subtraction of the constructed baseline from the recorded calorimetric curve. First thermal event starts near 360 K. There are two significant exothermic events assigned to two decomposition steps. Both exothermic events are not completely separated due to the low reaction rate. The appearance of two decomposition steps is in agreement with known investigations of the thermal decomposition of ammonia–borane [4–6]. As expected, no signs of an endothermic melting process were obtained. This fact confirms earlier observations [6,7] that at sufficiently low heating rates ammonia–borane is completely decomposed already below the apparent melting point reported in the literature [2,3].

Both exothermic steps of the thermal decomposition of ammonia–borane are accompanied by release of volatile products as shown in Fig. 2. The amount of released products was calculated from the detected variation of volume after correction for thermal expansion. Just as in case of calorimetric monitoring of the ammonia–borane decomposition, both steps of gas evolution are not clearly separated. Gas evolution is terminated near 430 K, the final value amounts to approximately 2.0 mol volatile products/mol ammonia–borane. In each decomposition step roughly 1 mol volatile products/mol ammonia–borane was released.

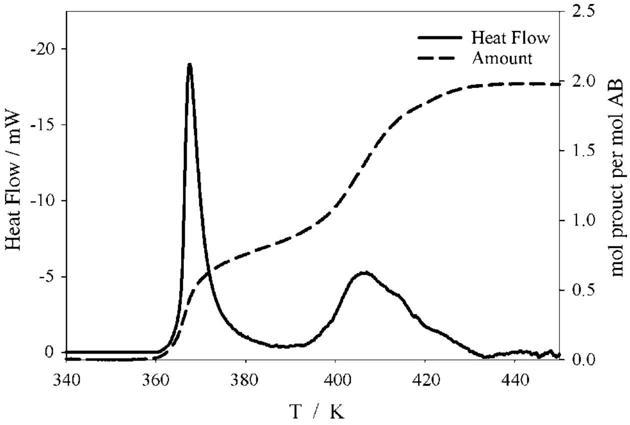

Fig. 2. Temperature dependence of the heat flow (–) and the amount of released volatile products (– –) at the thermal decomposition of ammonia–borane BH_3NH_3 (transitiometer ST6-VI, 600 bar, mercury as pressure transmitter, heating rate 0.15 K min^{-1}).

It is well known that the thermal decomposition of ammonia–borane is accompanied by release of hydrogen [4–7]. The amount of released hydrogen was exclusively recorded by means of gas-volumetric measurements at atmospheric pressure. It was shown that the amount of released hydrogen is not significantly influenced by experimental conditions, for example it is nearly independent on the heating rate used. The final amount of released hydrogen, which was achieved at temperatures near 473 K in earlier investigations, is approximately equal to 2.2 ± 0.1 mol hydrogen/mol ammonia–borane [5,6].

As has been shown by means of mass spectrometry and FT-IR spectroscopy [6], in addition to hydrogen some further gaseous products, such as monomeric aminoborane BH_2NH_2 and borazine $(BHNH)_3$ (which is the B–N-analog of benzene), were released during the thermal decomposition of ammonia–borane. Contrary to the release of hydrogen, the final amount of these additional volatile products strongly increases with rising heating rate.

The variation of the volume of the reaction system detected in the transitiometer ST6-VI includes contributions of all volatile reaction products. Due to the use of mercury as pressure-transmitter, all volatiles remain in the hot reaction area inside the calorimetric vessel. The great advantage of this technique is that both the thermal behavior of the solid sample and the formed gaseous products could be monitored. The final amount of volatile products detected at the thermal decomposition of ammonia–borane in the transitiometer

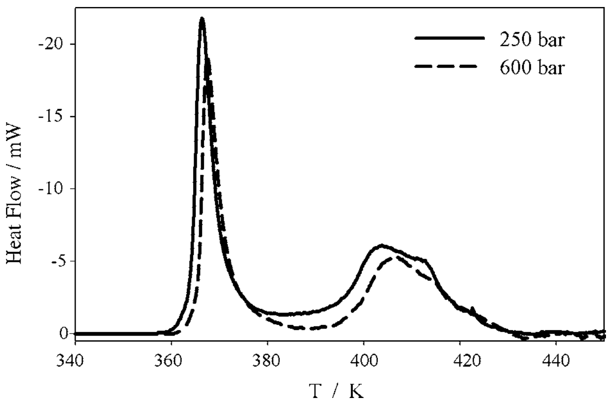

Fig. 3. Comparison between the temperature dependence of the heat flow obtained at the thermal decomposition of ammonia–borane BH_3NH_3 at 250 bar (–) and 600 bar (– –) (transitiometer ST6-VI, mercury as pressure transmitter, heating rate 0.15 K min^{-1}).

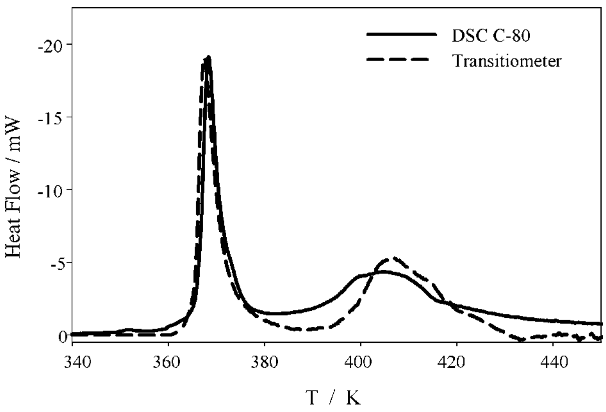

Fig. 5. Comparison between the temperature dependence of the heat flow obtained at the thermal decomposition of ammonia–borane BH_3NH_3 in the DSC C-80 at 50 bar hydrogen (–) and in the transitiometer ST6-VI at 600 bar (– –) (heating rate 0.15 K min^{-1}).

ST6-VI is nearly equal to the release of hydrogen, which was obtained in [6] by gas-volumetric measurements in a similar temperature range. Consequently, hydrogen should be the prevailing volatile reaction product in experiments performed in the transitiometer ST6-VI. The amount of further volatile products seems to be negligible. This conclusion was confirmed by the gravimetrically determined mass loss of the solid residue, which was recovered from the reaction vessel after the decomposition experiment in the transitiometer was finished.

In order to prove the consistency of the results obtained in the transitiometer ST6-VI at the monitoring of the thermal decomposition of ammonia–borane, isobaric measurements were performed at different pressures. As shown in Fig. 3, the variation of pressure from 250 to 600 bar does not influence significantly the detected heat flow data. The same conclusion is given for the comparison of the amount of released volatile products, obtained at 250 and 600 bar (Fig. 4). It should be noted that the variation of volume, which is caused by the release of volatile products, became smaller at greater pressure, while the variation of volume caused by thermal expansion of mercury remains similar. Nevertheless, a reliable monitoring of the release of gaseous products is still possible at higher pressures due to the high resolution of volumetric measurements in the transitiometer ST6-VI.

3.2. DSC C-80

In order to make an additional inspection of the performance of the transitiometer ST6-VI for reaction monitoring, we have measured the thermal decomposition of ammonia–borane in a DSC C-80 under pressures up to 100 bar. Heating rate, preparation and mass of the ammonia–borane sample were the same, as in case of the transitiometer ST6-VI.

Comparisons of experimental plots, which were obtained in a typical measurement in the DSC C-80, with results obtained for the decomposition of ammonia–borane in the transitiometer ST6-VI under 600 bar were represented in Figs. 5 and 6. The agreement between data detected in the

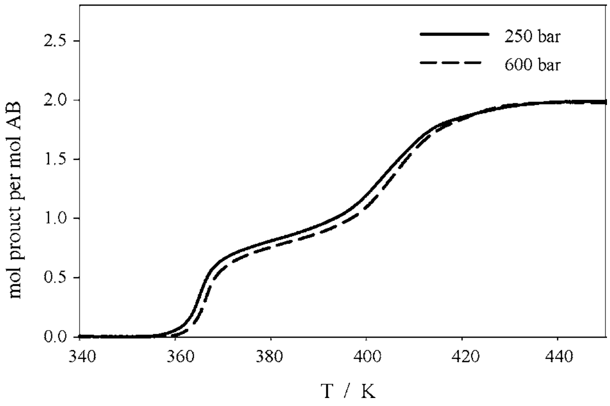

Fig. 4. Comparison between the temperature dependence of the amount of released volatile products measured at the thermal decomposition of ammonia–borane BH_3NH_3 at 250 bar (–) and 600 bar (– –) (transitiometer ST6-VI, mercury as pressure transmitter, heating rate 0.15 K min^{-1}).

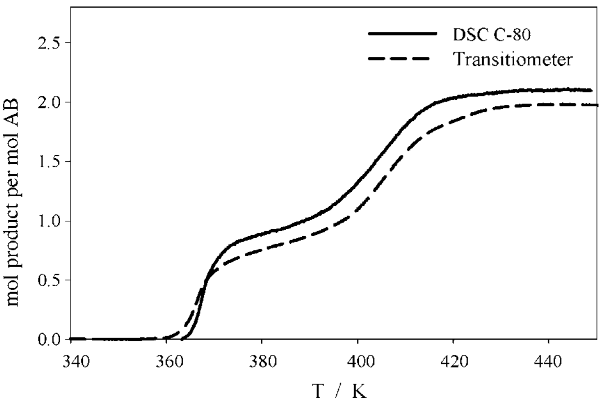

Fig. 6. Comparison between the temperature dependence of the amount of released volatile products obtained at the thermal decomposition of ammonia–borane BH_3NH_3 in the DSC C-80 at 50 bar hydrogen (–) and in the transitiometer ST6-VI at 600 bar (– –) (heating rate 0.15 K min^{-1}).

Table 1
Reaction enthalpy and final amount of released volatile products at the thermal decomposition of ammonia–borane in the transitiometer ST6-VI and DSC C-80 (heating rate 0.15 K min^{-1})

Pressure	$\Delta_R H$ (kJ mol^{-1})	mol product/mol ammonia–borane
Transitiometer ST6-VI		
600 bar mercury as pressure transmitter	−50	2.0
250 bar mercury as pressure transmitter	−65	2.0
250 bar mercury as pressure transmitter	−70	1.8
DSC C-80		
80 bar H_2	−70	2.1
60 bar H_2	−65	2.2
50 barH_2	−55	2.3
10 bar H_2	−60	2.2
1 bar H_2	−60	2.2

DSC C-80 and in the transitiometer is sufficiently high, both in case of the reaction heat flow and the amount of released gaseous products.

It should be noted that the technique used in the DSC C-80 is quite different from transitiometer technique. The amount of released gaseous products was calculated from the variation of pressure in a reaction system with definite volume. In order to compensate the low resolution of the pressure sensor used in these experiments, we have chosen a reaction system with a low internal volume and, consequently, with a great pressure variation during the thermal decomposition. The range of pressure variation was usually 5–20 bar.

Due to the fact that the pressure detector was placed outside the DSC C-80, the release of gaseous products, which condense at room temperature, does not contribute to the pressure variation detected in the C-80 experiments. The above-mentioned monomeric aminoborane BH_2NH_2 and borazine $(BHNH)_3$ are such products. Borazine is a volatile liquid with a boiling point at 328 K. Monomeric aminoborane is an unstable gas at room temperature and undergoes a rapid oligomerization under formation of solid deposits [9]. From this point of view, the obtained good agreement between the final amount of gaseous products detected in the transitiometer ST6-VI and in the DSC C-80 confirms the conclusion that the thermal decomposition of ammonia–borane at a heating rate as low as 0.15 K min^{-1} is accompanied by the release of negligible amount of further gaseous decomposition products, beside hydrogen.

The values of the decomposition enthalpy and the final amount of released volatile decomposition products, which were obtained in different experiments in the transitiometer ST6-VI (under pressures 250 and 600 bar) and in the DSC C-80 (under initial pressures ranged from 1 to 80 bar) were listed in Table 1. There is a good agreement between different devices and pressures.

4. Conclusions

The thermal decomposition of ammonia–borane BH_3NH_3 in the temperature range up to 453 K was monitored in the high-pressure transitiometer ST6-VI under pressures up to 600 bar. Calorimetric measurements show two partially overlapping exothermic events assigned to two decomposition steps. Both steps of the thermal decomposition are accompanied by a stepwise release of volatile reaction products. Gas evolution is terminated near 430 K, the final value amounts to approximately 2 mol gaseous products/mol ammonia–borane. In principle, the used transitiometry technique allows the monitoring of the thermal behavior of the released gaseous reaction products. But the formation of further volatile products, beside hydrogen, seems to be negligible. Possibly, this is caused by the low heating rate of 0.15 K min^{-1} only.

Experimental results obtained in the transitiometer ST6-VI agree with general conclusions made from earlier investigations of the thermal decomposition of ammonia–borane. In order to perform a quantitative comparison between experiments in different devices and under different pressures, the thermal decomposition of ammonia–borane was additionally investigated in a DSC C-80 in the pressure range 1–100 bar and with the same ammonia–borane sample and at the same heating rate of 0.15 K min^{-1}, as in case of experiments in the transitiometer ST6-VI. There is a good agreement between the results obtained for the ammonia–borane decomposition in the transitiometer ST6-VI (under pressures 250 and 600 bar) and in the DSC C-80 (under pressures 1–100 bar). Thus, the good performance of the transitiometer ST6-VI was proved using ammonia–borane as calibration substance. This instrument is well suitable for the monitoring of solid–gas reaction under high-pressure conditions. It enables a reliable determination of the reaction heat and the amount of gas release/gas uptake.

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