



Short communication

Decomposition of NH_3BH_3 at sub-ambient pressures: A combined thermogravimetry–differential thermal analysis–mass spectrometry study

Orielle Palumbo^{a,b,*}, Annalisa Paolone^{a,c}, Pasquale Rispoli^a, Rosario Cantelli^{a,d}, Tom Autrey^e

^a “Sapienza” Università di Roma, Dipartimento di Fisica, Piazzale A. Moro 2, I-00185 Roma, Italy

^b CNR-ISC, Istituto dei Sistemi Complessi, via dei Taurini 19, 00185 Roma, Italy

^c Laboratorio Regionale SuperMAT, CNR-INFN, Salerno, Italy

^d CNR-INFN, Piazzale A. Moro 2, I-00185 Roma, Italy

^e Pacific Northwest National Laboratory, 908 Battelle Blvd., Richland, WA 99352, USA

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ABSTRACT

We report a systematic study of the isothermal decomposition of ammonia borane, NH_3BH_3 , at 363 K as a function of argon pressure ranging between 50 and 1040 mbar using thermogravimetry and differential thermal analysis coupled with mass analysis of the volatile species. During thermal aging at 363 K, evolution of hydrogen, aminoborane and borazine is monitored, with the relative mass loss strongly depending on the pressure in the reaction chamber. Furthermore, the induction period required for hydrogen release at 363 K decreases with decreasing pressure.

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1. Introduction

Ammonia borane (NH_3BH_3) has attracted recent interest as a potential hydrogen storage material for fuel cell power applications [1–4]. While ammonia borane (AB) is stable at room temperature in the solid phase, hydrogen is released when AB is dissolved in solution in the presence of catalysts [5–11] and at moderate temperatures in ionic liquids [12], or embedded in mesoporous scaffolds [13,14]. Dehydrogenation of neat solid-state AB occurs rapidly upon melting (>393 K); however, the partial release, up to 1 equiv. or 6 wt% hydrogen is released from the solid phase of AB during long isothermal aging at temperatures between 343 and 363 K [15,16]. During the decomposition formation of the volatile impurities, borazine, $[(\text{BHNH})_3]$, diborane $[\text{B}_2\text{H}_6]$ and aminoborane $[\text{BH}_2=\text{NH}_2]$ are observed in the evolved hydrogen gas. Under non-isothermal conditions, i.e., ramped temperature programmed desorption (TPD) up to 500 K, TG/DSC/MS studies suggest that the relative impurity quantities in the evolved hydrogen and the final mass loss are highly dependent on the thermal history of the sample. For example, the yield of borazine is reported to increase with an increase in the TPD ramp rate, ranging from 3.5% at 0.5 K min^{-1}

to 6.5% at 5 K min^{-1} , compared to 4.0% under isothermal conditions at 363 K [15]. The higher borazine yields at the greater ramp rates is also consistent with the report of greater observed mass loss. To date there has been no forthcoming explanation for the change in the distribution of products as a function of temperature ramp rate or any insight into the product distribution as a function of reactor pressure. More detailed insight into the decomposition mechanism and the role of external variables (e.g., pressure and temperature) on the outcome of the impurities formed in the released gas are highly desirable in order to lower the dehydrogenation temperature and to avoid the formation of undesirable products such as borazine and diborane.

It is the aim of the present investigation to gain further insight into the dependence of the decomposition process on variable pressure conditions at a constant temperature. We report a systematic study of the decomposition of ammonia borane at the fixed temperature of 363 K and at various argon pressures in the analysis chamber ranging from ~50 to 1040 mbar. This study was carried out by means of concomitant measurements of thermogravimetry (TGA), differential thermal analysis (DTA) and mass spectrometry (MS).

2. Experimental

Ammonia borane (NH_3BH_3) was prepared according to literature procedures [17] and purified by vacuum sublimation

* Corresponding author at: “Sapienza” Università di Roma, Dipartimento di Fisica, Piazzale A. Moro 2, I-00185 Roma, Italy. Tel.: +39 06 49914400; fax: +39 06 4957697.
E-mail address: oriele.palumbo@roma1.infn.it (O. Palumbo).

(~ 0.013 mbar at 60°C). Simultaneous TGA–DTA experiments were performed using a Setaram Setsys Evolution 1200 TGA System. After mounting the sample in an Al_2O_3 crucible, the system was evacuated and subsequently flooded with high purity argon. The TGA–DTA curves were measured on 2–5 mg of NH_3BH_3 powder during isothermal heating at $T=363$ K, and at various argon pressures in the analysis chamber ranging from ~ 50 to 1040 mbar, and precisely at: 52, 140, 270, 860 and 1039 mbar. In each experiment the starting material was the as-received AB powder. The argon pressure inside the chamber was set under dynamic conditions with a gas flow rate of 40 ml min^{-1} , by using a dry rotative pump connected with the chamber through a needle valve.

Since we observed a slight dependence of the decomposition time on the sample mass (results will be published elsewhere) the presently reported experiments were carried out on samples with very close mass values.

Concomitant MS analysis of the released gas was carried out by a Pfeiffer Prisma analyzer connected to the experimental cell; the pressure reduction necessary for the quadrupole operation was obtained by means of a needle valve. To identify all possible gaseous products, survey scans in the mass range of 1–100 amu were recorded over all the above processes.

3. Results and discussion

The isothermal decomposition of AB at 363 K was previously investigated by solid-state ^{11}B NMR spectroscopy. The results showed that the decomposition of ammonia borane can be described by an induction, nucleation and growth mechanistic pathway [18]. During the induction period where the dihydrogen bonding network is disrupted, little hydrogen is released; however, concomitantly with the initial hydrogen release, additional solid phase species are observed: the diammoniate of diborane (DADB), $[(\text{NH}_3)_2\text{BH}_2]^+[\text{BH}_4]^-$, and two other species suggested to be the linear $(\text{NH}_3\text{BH}_2\text{NH}_2\text{BH}_3)$ and cyclic dimer $(\text{NH}_2\text{BH}_2)_2$ of aminoborane. At longer reaction times the ^{11}B NMR spectrum shows the formation of a complex polymeric aminoborane (PAB) containing both BH_2N_2 and BHN_3 species [16].

Fig. 1 shows the curves of the relative mass loss and heat flow simultaneously measured during the aging of AB at a comparable temperature, $T=363$ K, to the ^{11}B NMR experiments but at variable pressures.

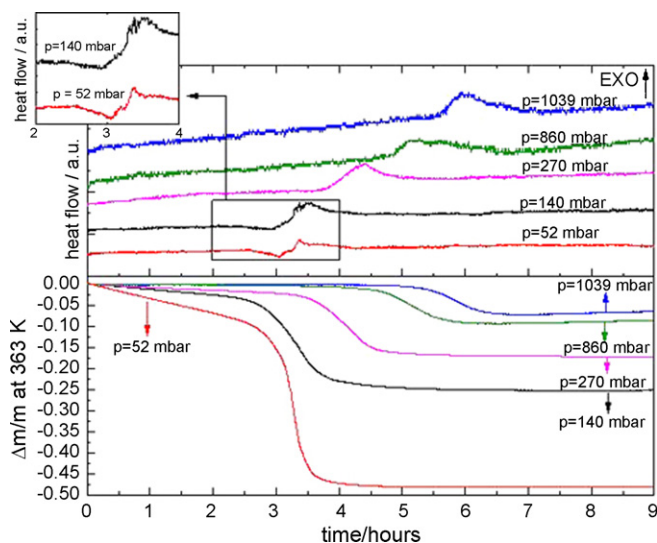


Fig. 1. Time dependence of relative mass variation and DTA signal during ageing at 363 K at various pressures.

At pressures, p , ranging between 140 and 1040 mbar, the temperature-induced decomposition is revealed as a weight loss (bottom panel in Fig. 1) accompanied by an exothermic process in the calorimetry curve (upper panel in Fig. 1).

It can be noted that when pressure is lowered the weight loss increases and concomitantly the aging time decreases. Indeed, at $p=1039$ mbar the total weight loss is about 7% and is reached after about 7 h aging. On the other hand, at $p=140$ mbar the total weight loss is 24% and is reached in about 4 h. At the lower pressures, while the higher weight loss could be due to some sublimation of the AB, the shorter times associated with the onset of the exothermic peak clearly indicates that the induction period preceding hydrogen release is remarkably reduced.

The decrease in the induction period is surprising result and even more apparent at $p=52$ mbar, where the observed mass change decreases in about 3.5 h reaching a final weight loss of about 49%.

At the lower pressures the decomposition is anticipated by an endothermic process (upper panel in Fig. 1). In the calorimetry curve measured during aging at 140 mbar, this process appears only as a small dip as it is mainly compensated by the subsequent exothermic peak. But on further lowering pressure, the endothermic process becomes more prominent and appears as the main feature of the calorimetry signal measured at 52 mbar (see insert in Fig. 1). This endothermic peak is likely due to AB sublimation, and is consistent with its measurable vapour pressure (<1 mbar at room temperature) [19,20]. Actually, sublimation of NH_3BH_3 without decomposition during heating under vacuum is widely reported in literature [21–23] and is a method commonly used as a purification procedure to obtain solid AB samples.

Indeed, at the end of the experiments carried out at lower pressures, the presence of a white layer covering the sides of the reaction vessel was observed. Likely, AB deposition on the wall of cell and vacuum line occurs before reaching the mass spectrometer.

In order to ascertain the nature of this powder, and thus the occurrence of sublimation during isothermal aging carried out at lower pressures, a comparative experiment was performed in a quartz tube by aging a few mg of AB around 360 K with an argon pressure of about 140 mbar for 150 min. During aging, the formation of a white layer was observed on a copper plate placed a few centimeters from the powder crucible. The DTA spectrum obtained by heating this powder to 670 K at a temperature rate of 5 K min^{-1} in an argon pressure showed the same features displayed by the starting AB powder (Fig. 2), as both measured by ourselves and reported in literature [15]. This result confirms the occurrence of sublimation of ammonia borane during aging at lower pressures.

A concomitant mass analysis of the volatile species released during the TGA–DTA measurements was carried out during all the agings at different pressures and is shown in Fig. 3. Near ambient pressure ($p=1039$ and 860 mbar) the mass spectrum shows a well developed hydrogen ($m/z=2$) emission and a further signal is recorded at $m/z=41$. These peaks show a strong time-correlation with the observed mass loss in the TGA (Fig. 1).

At pressures lower than 860 mbar, the emissions of $m/z=2$ and 41 are still the most predominant peaks observed. Moreover, emissions at $m/z=78$ and 80, m/z between 27 and 29, and m/z between 10 and 13 and between 23 and 26 are also detected, consistently with the reported mass spectrum of borazine $(\text{BHNH})_3$, aminoborane (BH_2NH_2) and diborane (B_2H_6) , respectively [15,24,25]. Emission at $m/z=42$ is also observed. This signal has been previously assigned [15] to aminodiborane $(\text{BH}_2\text{NH}_2\text{BH}_3)$.

The intensity of the signal at $m/z=11$ increases in the mass spectrum measured at $p=140$ and 52 mbar and is likely due to a contribution coming from some B+ possibly present in gas phase. This presence would be in agreement with the suggested sublimation of AB at lower pressures.

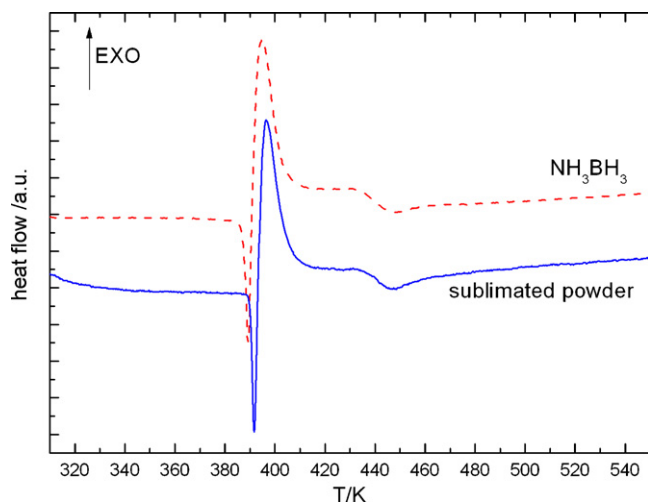


Fig. 2. DTA signals of ammonia borane and of the white powder removed from the copper shutter, measured during heating up to 670 K at a temperature rate of 5 K min^{-1} in an argon pressure.

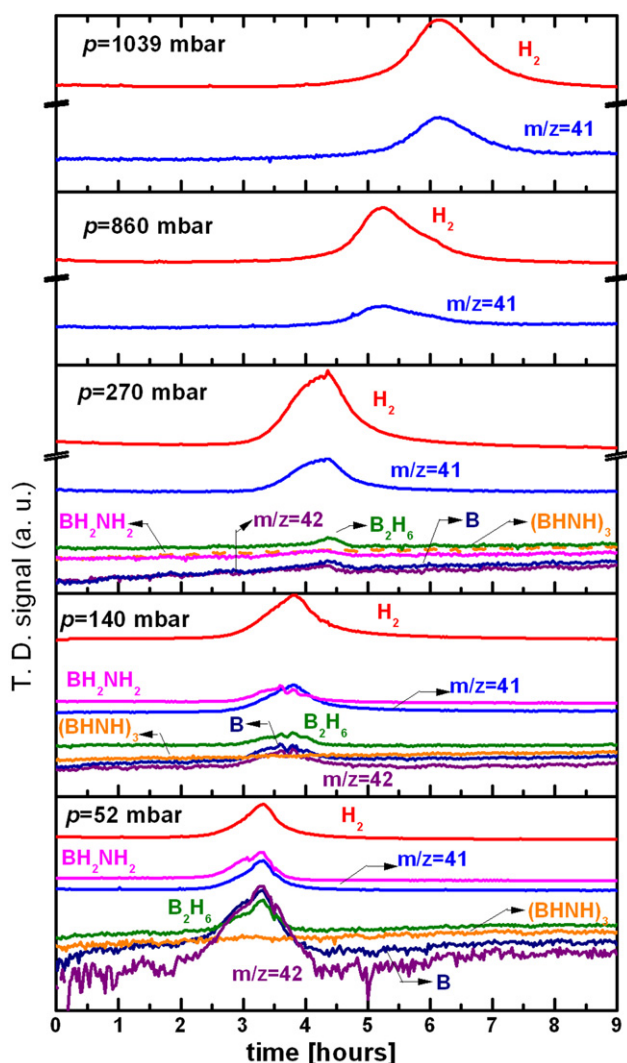


Fig. 3. Mass spectrometry results: time dependence of gas evolution during aging at 363 K at various pressures; hydrogen (H_2), $m/z=2$; unknown, $m/z=41$; borazine ($(\text{BHNH})_3$), $m/z=78$ and $m/z=80$; monomeric aminoborane (BH_2NH_2), m/z between 27 and 29; diborane (B_2H_6) m/z between 10 and 13, and m/z between 23 and 26; aminodiborane ($\text{BH}_2\text{NH}_2\text{BH}_3$), $m/z=42$; boron (B^+) $m/z=11$.

The peak in the signal at $m/z=41$ is observed concomitantly with the measured mass loss in each annealing, whatever the pressure is. The attribution of this signal is rather difficult and at the present we are not able to attribute it to some evolving species, and either not to say if it comes from the solids products as an in-equilibrium gas phase. Future work will be devoted to the investigation of its nature by using other independent techniques.

The data reported in the present work indicate that the isothermally induced decomposition of AB is significantly influenced by the pressure at which this process is carried out. In particular the measured thermogravimetric curves show that, in isothermal agings at pressures below 800 mbar the induction period is appreciably reduced, leading to the release of the first equivalent of hydrogen from AB at shorter reaction times.

A possible explanation for the observed reduction of the induction time may be suggested by the fact that as the pressure of the reactor is lowered, sublimation becomes a more important physical process. During sublimation, defects resulting in the disruption of the dihydrogen bonding network are likely to be introduced into the crystal structure of the solid AB. Previous work has shown that the disruption of the dihydrogen bonds in AB facilitates the isomerisation of AB to the diammoniate of diborane (DADB), followed immediately by the release of molecular hydrogen. As such, at a given temperature, e.g., 363 K, a lowering of the reaction pressure results in enhanced rates of sublimation. As sublimation occurs, defects are introduced thereby decreasing the induction period leading to the critical nucleation event, formation of DADB. Once DADB is formed the release of molecular hydrogen from solid AB follows.

Moreover, the pressure in the reactor also influences the nature of the outcoming gas during the isothermal decomposition. One can speculate that in experiments performed by using a capillary close to the sample in order to connect the TGA/DTA cell to the mass spectrometer, this setup can locally decrease the pressure and influence the released gases composition. This phenomenon is enhanced in systems having high vapour pressures, as NH_3BH_3 , where sublimation takes a major role at low pressure. This hypothesis can help explain the scattering of results existing among the various laboratories in measuring the volatile products by the above-mentioned capillary technique.

4. Conclusions

The present work reports a systematic investigation of the influence of pressure on the thermally induced decomposition of NH_3BH_3 . At high pressures, the mass decrease during aging at 363 K is consistent with the transformation of NH_3BH_3 into NH_2BH_2 , while on decreasing the argon pressure, the weight loss increases and concomitantly the aging time decreases. Simultaneous mass spectrometry analysis shows the presence of aminoborane (BH_2NH_2) and a slight emission of diborane (B_2H_6) and borazine ($(\text{BHNH})_3$) in the gas phase. The presently reported experiments show for the first time the dependence of the decomposition process at variable pressure conditions and constant temperature, and provide indications about the outcome of the impurities formed in the released gas. These data may be useful for applications, in order to avoid the formation of unwanted products such as borazine and diborane.

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