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Confined rapid thermolysis studies of ammonia borane

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ABSTRACT

Thermochemical calculations of ammonia borane (AB, H_3NBH_3), which has a hydrogen content of 19.6% by weight, indicate that it has the potential to boost specific impulse in chemical propulsion applications due to its high hydrogen content and the moderate exothermicity of decomposition. Research to date on AB decomposition has focused on relatively slow heating rates. These studies have shown that the mass lost due to decomposition increases with increasing heating rate. This trend has been confirmed in this work, as mass loss continues to increase up to 50 K/min, the limit of most TGA/DSC instruments. In this research effort, confined rapid thermolysis was used to examine the decomposition of AB under isothermal conditions. Fourier transform infrared (FTIR) spectroscopy and time-of-flight mass spectrometry (ToF-MS) were employed to identify the gaseous products, which include H_2, NH_3, H_2NBH_2, and c-$N_3B_3H_6$. The decomposition resulted in significant condensed-phase products as well, which were pressed into a KBr pellet and examined with FTIR spectroscopy. FTIR transmission spectra of the condensed-phase products with several heating durations show the disappearance of absorption bands of AB and appearance of bands attributed to polymeric species. Condensable gas-phase products were also collected from the stream of decomposition products, and FTIR spectroscopy showed they have absorption bands similar to the polymeric species, indicating that the H_2NBH_2 will readily condense out of the gas-phase products and polymerize at low temperatures.

1. Introduction

Future space missions with chemical propulsion systems will require the development of propellants with increased performance. To increase the energy density (per unit mass) over current hydrocarbons, earlier studies identified hydrogen, beryllium, boron, or some combination thereof as elements of future fuels [1]. Molecular hydrogen has been used successfully as a liquid fuel for rocket propulsion. However, it requires cryogenic facilities, which complicates handling and rocket design. Beryllium and its compounds have generally been deemed too toxic to be viable fuels. Boron, however, is of strong interest due its high combustion enthalpy on both a mass and volume basis. It is typically introduced as a particle with a passivation layer, and as such there are significant difficulties with ignition and complete combustion [2]. Similarly, boranes (B_xH_y) have been of interest for years as a propellant fuel because of their high energy density. The liquid pentaborane (B_5H_9) has 60% greater energy density than conventional jet fuel [1]. However, problems with the pyrophoricity and toxicity of boranes ultimately proved them too dangerous for widespread use.

Recently, ammonia borane (AB, NH_3BH_3), a solid compound at room temperature, has been the subject of vigorous study to examine its potential for storing hydrogen at high densities. AB contains 19.6% hydrogen by mass. The initial studies on AB decomposition [3,4] showed that it would slowly decompose to produce hydrogen gas. Unlike the previously investigated borane fuels (B_2H_6, B_5H_9), AB is not known to have significant toxicity or safety problems, and it does not require any special storage conditions [5].

Increasing specific impulse (I_{sp}) is one of the main objectives in developing novel rocket propellants for deep space travel. Since I_{sp} is proportional to the square root of chamber temperature divided by the average molecular weight of the products, AB is of interest because it undergoes an exothermic decomposition to release H_2 [6]. Thermochemical calculations and preliminary laboratory scale motor tests confirm that AB can indeed improve specific impulse in a paraffin-fueled hybrid rocket motor [7]. However, this study also showed that significant additions of AB result in a considerable quantity of condensed-phase products accumulating on the solid-fuel surface, leading to a decreased regression rate. To understand the chemistry related to these results, a better understanding of AB decomposition is required.

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1.1. Previous studies on AB decomposition

Contemporary AB research, recently reviewed by Staubitz et al. [8], is primarily concerned with generating hydrogen for use in proton-exchange fuel cells, and using catalysis or other methods to provide increased hydrogen release at low temperatures. The thermal decomposition of AB, first studied by Hu et al. [9], has recently been investigated in a series of publications emanating from a group at Freidberg University of Mining and Technology [6,10,11]. These studies rely mostly on combination of TGA/DSC experiments.

The first of these studies [6] shows that for sufficiently slow heating rates (0.05 K/min), or isotherms above 70 °C for sufficient time (∼30 h), AB fully completes the first decomposition step below its melting temperature (104 °C) [6], demonstrating that at the low limit of heating rate, AB can fully undergo its first exothermic decomposition step without changing phase. Following the lengthy isotherms ranging from 70 to 90 °C, the resulting condensed-phase product was determined to be polymeric aminoborane $[(NH_2BH_2)_x]$ [6]. At increased heating rates, the compound will melt prior to the bulk of the decomposition, with gas release resulting in a vigorous foaming.

Additionally, the investigations of Wolf et al. [6] and Baitalow et al. [10] at slow heating rates (≤5 K/min) show that the percent mass loss increased with an increasing heating rate, while the volume of evolved gas (as measured by water displacement) was independent of heating rate. Assuming hydrogen was the only product released into the gas phase, Baitalow et al. measured approximately 2.2 mol H_2/mol of AB when heating up to 190 °C, corresponding to a total mass loss of 14.3% for all heating rates [10]. At a heating rate of 1 K/min, the gravimetric mass loss recorded was roughly 15%, corresponding closely with their volumetric measurement of hydrogen. However, at a heating rate of 5 K/min, the gravimetric mass loss was approximately 23%, about 1.6 times the mass of the measured hydrogen [10]. This result from Baitalow et al. [10] demonstrates that a certain percentage of the decomposition gases are either condensable at room temperature or are water-soluble. Furthermore, the amount of these condensable/water-soluble products increases with increasing heating rate. Gas-phase FTIR/MS studies performed in conjunction with these TGA/DSC studies give evidence that these products consist of monomeric aminoborane (BH_2NH_2), borazine (c-$[BHNH]_3$), and small amounts of other BNH_x species [10].

Stowe et al. [12] have studied the mechanism of thermal decomposition of AB below its melting point by probing the solid phase using nuclear magnetic resonance (NMR) spectroscopy. Using the NMR data, they have proposed a mechanism through which the AB can react to form polymeric amino-borane (PAB) and release hydrogen into the gas phase. The NMR spectra show the reaction is initiated with the formation of a “mobile” phase of AB, which then leads to the formation of an ionic compound, the diamoniate of diborane or DADB $[(NH_3)_2BH_2]^+[BH_4]^-$. It is suggested that the more reactive DADB will react with the surrounding AB, resulting in hydrogen release and amino-borane polymerization.

Another detailed study of AB decomposition has recently been published by Frueh et al. [13], in which materials characterization techniques are used in addition to TGA/DSC analysis to understand the chemical pathways of AB decomposition. This study claims to observe a third hydrogen release at a temperature of 1170 °C, with significantly slower reaction rate than the first two hydrogen releases. The resulting material after prolonged heating was determined to be hexagonal boron nitride through the use of several material characterization techniques [13].

1.2. Objective of this work

For energetic materials, the kinetic decomposition pathways may be highly dependent on the heating rate. For example, Oyumi and Brill found that with RDX decomposition, changing the external heating rate results in a shift from CH_2O and N_2O as the main decomposition products at low heating rates to HCN and NO_2 at high heating rates [14]. Therefore, to understand the decomposition behavior of propellant ingredients, it is widely recognized that the process must be studied using both slow and rapid heating conditions. Previous works [6,9–11] have only examined decomposition at slow heating rates (≤10 K/min), where the time scale for reaction is on the same order as the time scale for heating. In this work, the decomposition of AB is studied using confined rapid thermolysis (CRT). In this experiment, the sample is heated at rates of approximately 2000 K/s to a set temperature where diagnostics of the isothermal decomposition are performed. TGA/DSC experiments are also performed to investigate changes in mass loss and heat release with increased heating rate.

2. Experiment

2.1. Sample

The ammonia borane used in this study was purchased from Boroscience International. The material was specified to be 98% pure by the supplier using proton and ^{11}B NMR spectroscopy. Its physical appearance is that of a white powder.

2.2. CRT with gas-phase diagnostics

The CRT experiment was previously described in [15]. In this experiment, a small amount of material (∼0.5 mg) is heated in a narrow space between two flat surfaces. Two copper rods, 53 mm in height and 15.6 mm in diameter, are heated to a preset isothermal condition, using high-watt density cartridge heaters. The copper rods are then compressed against the sample holder, consisting of a retaining ring and thin metal foils, using a pneumatic piston cylinder. The sample holder maintains a sealed 300 μm gap between the heaters, except for a rectangular slit that allows decomposition gases to escape into the cool atmosphere and into the modulated beam of the FTIR. The CRT apparatus is used in conjunction with two diagnostic tools to examine the gas-phase species: rapid scanning FTIR transmission spectroscopy, and time-of-flight mass spectrometry (ToF-MS). These two diagnostic tools complement one another and are most effective when used in conjunction.

For the CRT/gas-phase FTIR spectroscopy, the setup is contained in a constant pressure chamber filled with N_2. The modulated FTIR beam, which enters and exits the chamber via ZnSe windows, passes through the decomposition gases that emanate from a rapidly heated sample. The Bruker IFS 66/S FTIR spectrometer is programmed to acquire the transmissivity spectrum with a spectral resolution of 2 cm^{-1} and a temporal resolution of 50 ms.

As previously described by Chowdhury et al. [16], the ToF-MS measurements take place with an identical CRT heating system inside a low-pressure chamber. A commercially available ToF-MS spectrometer is used. Several stages of vacuum are used to generate a molecular beam from the evolved decomposition gases. The gases first pass through a 100 μm orifice into the first stage, pumped down to 10^{-4} Torr. Subsequently, the gases pass through a 1 mm Ni skimmer to the second stage, pumped to 10^{-6} Torr, and a 0.5 mm slit to a third stage, pumped to 10^{-7} Torr. Next, an electron beam, with an impact ionization energy set at 70 eV, is incident on the molecular beam for a period of 3 μs. The resulting positive ions created by the interaction of the two beams are accelerated across