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Research article

Auto-ignition of a carbon-free aqueous ammonia/ammonium nitrate monofuel: A thermal and barometric analysis

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ABSTRACT

A carbon-free aqueous solution of ammonium hydroxide and ammonium nitrate (AAN) was studied using differential thermal and barometric analyses under initial N_2 pressure of up to 4.6 MPa. The suggested nitrogen-based monofuel exhibited three distinct exothermic processes during heating. Their onset temperatures increased as the initial nitrogen pressure was raised. In addition, a higher extent of reaction was observed at high nitrogen pressures. This result was attributed to the effect of mass diffusion in the system, which decreased at higher pressures. Using a modified mechanism for the combustion of nitrogen-based fuels, the thermal ignition process was simulated. The resulting auto-ignition temperature values were shown to be in good agreement with experiments at initial nitrogen pressures of up to 2.3 MPa. Above this pressure, the agreement between experimental and model results was hampered by mass diffusion effects. Using the modified mechanism, the main chemical pathways prior to auto-ignition of AAN were identified and the reactions leading to ignition were discussed. This paper presents for the first time the auto-ignition of AAN and explores the combustion chemistry of this carbon-free monofuel.

1. Introduction

While improvements have been made in the field of renewable energies, intermittent production is still limiting any wide-spread application. Renewable hydrogen generation by water electrolysis is a possible large scale energy storage solution, but molecular hydrogen transportation requires specialized infrastructure and involves inherent safety hazards [1]. Transforming produced hydrogen into a storable and transportable liquid is attractive due to higher energy density and simpler infrastructure [2]. While carbon-based synthetic fuels are possible (i.g. methanol economy), nitrogen-based fuels can alternatively be used as effective hydrogen carriers as well [3]. Previously, urea ammonium nitrate (UAN), a low-carbon nitrogen-based monofuel, was investigated under various conditions [4]. In the present work, a solution of aqueous ammonia and ammonium nitrate (AAN), both mass-produced fertilizers, is proposed as an alternative carbon-free monofuel. In this material, the oxidizer and reducer are both in the same phase. The ideal overall stoichiometric combustion reaction for AAN produces only nitrogen and water (R1), both safe, and environmentally harmless.

$$3NH_4NO_3 + 2NH_4OH + 4H_2O \rightarrow 4N_2 + 11H_2O \tag{R1}$$

However, in practice, traces of pollutants can be produced during AAN's combustion.

Ammonium nitrate (AN) is known to decompose into nitric acid and ammonia (R2) in the gas phase at elevated temperatures [5]. Below 563 K the immediate decomposition products of AN react mainly through an ionic mechanism as detailed in reactions R3–R5 [6]. Above that temperature, a homolytic mechanism comprising primarily of reactions R6–R9 becomes dominant [7]. Ammonium hydroxide (AH) simply decomposes into water and ammonia, which in turn, are expected to react through reactions R4 and R7. Although these mechanisms explain some of the chemistry involved in AN decomposition, they are not complete [8] and do not address the effects of the added ammonia and water in our system.

$$NH_4NO_3 \leftrightarrow HNO_3 + NH_3 \tag{R2}$$

$$2HNO_3 \leftrightarrow H_2O + NO_2^+ + NO_3^- \tag{R3}$$

$$NH_3 + NO_2^+ \rightarrow N_2O + H_3O^+ \tag{R4}$$

$$NO_3^- + H_3O^+ \leftrightarrow HNO_3 + H_2O \tag{R5}$$

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$$HNO_3 \rightarrow OH + NO_2 \quad (R6)$$

$$NH_3 + OH \leftrightarrow NH_2 + H_2O \quad (R7)$$

$$NH_2 + NO_2 \rightarrow N_2O + H_2O \quad (R8)$$

$$NH_2 + NO_2 \rightarrow H_2NO + NO \quad (R9)$$

While some previous work has been performed on the characterization of AN with ammonia in a non-aqueous system [9], no thermal analysis was ever performed above atmospheric pressure at stoichiometric compositions. Moreover, to the best of our knowledge no differential barometric analysis was ever reported for this composition. Conditions above atmospheric pressure are important since AAN's stoichiometric combustion is expected to take place at high pressures [4]. Based on earlier work with UAN, high pressure combustion has a dramatic effect on the combustion efficiency, especially below 4.6 MPa. We believe a similar effect is expected for AAN. Furthermore, the kinetics of AAN's gas-phase reactions prior to its ignition have not been fully explored. Understanding the chemistry of AAN at high temperature and pressure can enable improved design of the thermal auto-ignition process and catalytic ignition of this fuel. Therefore, the main objective of this work is to explore the thermal decomposition of AAN at initial N_2 pressures of up to 4.6 MPa, to simulate the chemical changes the fuel undergoes during heating, and suggest a realistic mechanism leading to AAN's auto-ignition.

2. Materials and methods

2.1. Experimental

The aqueous AAN monofuel consisted of AN (≥99%, Sigma-Aldrich), water (Milli-Q® ultrapure water), and AH (25%, Merck). The component mole ratio was approximately 3(AN):2(AH):4(H_2O). The monofuel was subsequently filtered using a 0.45 μm syringe filter (SLHV033RS, Millex). Nitrogen (≥99.995%, Maxima) was used to apply the initial diluent pressure in all experiments.

The thermal analyzer used for the experiments is discussed in detail elsewhere [10] and is described here only in brief. The system encompassed two cells, approximately 26 ml each, heated concurrently in a single zone furnace (500 W). The analyzer was first heated to 303 K and held there for 15 min, then heated to 773 K at a rate of roughly 5 K min^{-1}. Temperature and pressure measurements were taken once a second using thermocouples (type K) and pressure transducers (G2, Ashcroft). The compartments were washed with nitrogen to evacuate residual air. Identical 700 μl SS 316L crucibles were placed in each cell, with an average 301 ± 2 mg of AAN placed in one of them (sample crucible). Each experiment was repeated at least 4 times to reach acceptable standard deviations. The differential thermal analysis (DTA), differential barometric analysis (DBA), dDTA, and dDBA curves were calculated by averaging 30 successive data points to improve the signal to noise ratio.

2.2. Chemical kinetic model

The kinetic and thermodynamic data used in this work was derived from a previously developed and validated mechanism for the combustion of an aqueous solution of urea and ammonium nitrate (UAN) [11, 12]. The previous mechanism was modified to remove the carbon dataset and associated thermodynamic properties. The resulting mechanism was composed of 246 distinct reactions between 30 species (see Supplementary material). Although the ionic reaction set (R3–R5) was not included due to lack of kinetic data from the literature, good agreement was achieved at low-pressures (P < 3 MPa) for the auto-ignition temperature nevertheless (Section 3.2).

Simulations were performed with the CHEMKIN-PRO™ software package [13]. To approximate the experimental conditions a closed homogeneous reactor model was selected. The products of reaction R10 were used as the gaseous inlet composition. A similar assumption was shown to be valid in previous work [11,12].

$$3NH_4NO_{3(aq)} + 2NH_4OH_{(aq)} + 4H_2O_{(l)} \rightarrow 3HNO_{3(g)} + 5NH_{3(g)} + 6H_2O_{(g)} \quad (R10)$$

Heating profiles were adjusted to achieve a 5 K min^{-1} heating rate in the simulations, starting at a temperature of 303 K. The reactor volume was set as ~26 ml and the initial pressures used in the simulations were set to account for the vapor pressure of AAN at 303 K [14], as well as the partial pressure of the immediate decomposition products in accordance with reaction R10 (Table S1 in the Supplementary material).

2.3. Theoretical diffusion calculations

Mass diffusivities were calculated for nitric acid and ammonia, the immediate reactive thermal decomposition products of AN and AH. The Hirschfelder-Bird-Spotz equation [15,16] using the Brakow correction for polar compounds [16,17] was used. The mass diffusion values were calculated at the auto-ignition pressure and temperature measured at each initial N_2 pressure. The species assumed to be present in the mixture were nitrogen, water, nitric acid, and ammonia (products of reaction R10). While other species are likely to be present at the ignition, the calculations were used only to demonstrate the impact of pressure on the mass diffusion of reactants. Therefore, the main component composition was assumed to be sufficient.

While Lennard-Jones molecular diameter (σ) and interaction potential (ε) values were available for nitrogen and water [16], for nitric acid and ammonia the values had to be estimated using empirical relations [16] based on their critical parameters and boiling conditions [18]. Finally, the molecular diffusion volume for nitric acid was estimated using the atomic diffusion-volume increments method [16]. Both the binary and mixture mass diffusions are listed in Table S2.

3. Results and discussion

3.1. Thermal decomposition of AAN

Three exothermic processes were detected during differential thermal and barometric analysis of AAN. These were designated as pre-ignition, auto-ignition, and post-ignition effects. The onset temperatures and pressures were determined and marked by X in Fig. 1a and b. The onset of each process was determined by differential analysis (dDTA and dDBA), as can be seen in Fig. 1.

An endotherm spread up to a temperature of about 473 K was detected prior to the exotherms and is associated with both the vaporization of water and ammonia from the liquid phase, as well as the

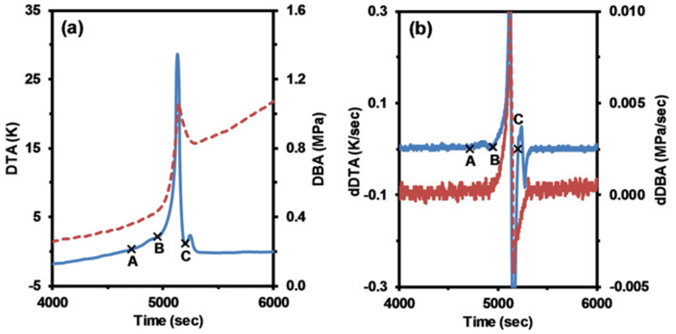

Fig. 1. The exothermic processes as detected at an initial N_2 pressure of 0.6 MPa through: (a) DTA (solid line) and DBA (dotted line) data, and (b) dDTA (solid line) and dDBA (dotted line) data.