Effect of equivalence ratio on the thermal autoignition of aqueous ammonia ammonium nitrate monofuel

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A B S T R A C T

The combustion of a carbon-free nitrogen-based monofuel consisting of an aqueous ammonium hydroxide/nitrate (AAN) solution was studied at different equivalence ratios ranging between 0.6 and 12. The main oxidizing and reducing agents in AAN are nitric acid and ammonia, respectively. A combined differential thermal/barometric analysis (DTA/DBA) study was used to investigate the effect of the equivalence ratio on the autoignition temperature (AIT) of this monofuel. Increasing the equivalence ratio was found to increase the AIT value and reduce the energy generated during the ignition. Kinetic gas-phase simulations were used to calculate the theoretical AIT values. Good agreement was found at equivalence ratios close to unity. Rate of production and sensitivity analyses were performed to explore the reaction kinetics leading to the thermal auto-ignition. These indicated that reactions reducing nitrogen dioxide to nitrogen oxide and molecular oxygen inhibit the ignition, while reactions between ammonia and high oxidation state NO_x producing amidogen promote it. The results of this study shed light on the influence of non-stoichiometric conditions on the thermal auto-ignition of AAN.

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1. Introduction

Efficient energy storage is widely regarded as an obstacle for wide application of renewable energies [1]. This is due to the need for continuous energy production, which many environmentally friendly sources such as solar are incapable of delivering [2]. The storage of the electrical power as a chemical fuel is an attractive solution to this issue. A widely researched route is hydrogen production via water electrolysis [3]. However, transport of large quantities of pure hydrogen is hazardous [4], and is incompatible with current fuel transport infrastructure [5]. Therefore, the use of H_2 carrier molecules such as hydrocarbons [6] and ammonia [7] has been suggested for hydrogen storage.

In previous work, a complex low-carbon nitrogen-based fuel was investigated [8]. This monofuel was composed of an aqueous solution of urea as a reducer and ammonium nitrate as a net oxidizer (UAN). Kinetic gas-phase simulations were conducted and a combustion mechanism was established [10]. The same mechanism developed for UAN was successfully applied to simulating the ignition of an ammonium hydroxide and ammonium nitrate (AAN) monofuel [11]. Made from mass-produced fertilizers, AAN was previously suggested as a carbon-free hydrogen carrier to be used as

a fuel for energy production on demand [11]. Such nitrogen-based fuels could be used in both continuous (e.g. stationary power generation [8]) and batch combustion processes (e.g. internal combustion engine [9]). Its combustion effluent contains none of the traditional carbon related pollutants (CO, VOCs, and PM). The main products of AAN complete combustion are water and nitrogen (R1). The combustion effluent of UAN has already been shown to reach NO_x emissions below regulatory standard levels without use of catalysis [8], low levels that may be reproduced or even surpassed with AAN,

$$3NH_4NO_3 + 2NH_4OH \rightarrow 4N_2 + 11H_2O. \tag{R1}$$
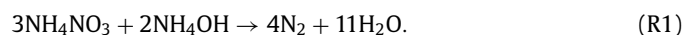
Ammonium nitrate is known to decompose at high temperatures to nitric acid and ammonia (R2). These two products react via ionic ((R3)–(R5)) [12] and homolytic ((R6)–(R9)) [13] mechanisms. It was suggested that the ionic mechanism is dominant at low temperatures, and is overtaken by the homolytic one above 563 K [13],

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

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

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

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

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$$HNO_3 \rightarrow OH + NO_2 \tag{R6}$$

$$NH_3 + OH \leftrightarrow NH_2 + H_2O \tag{R7}$$

$$NH_2 + NO_2 \rightarrow N_2O + H_2O \tag{R8}$$

$$NH_2 + NO_2 \rightarrow H_2NO + NO. \tag{R9}$$

The pre-ignition kinetics of AAN were previously studied at stoichiometric conditions [11]. In that work, nitric acid was found to decompose through three channels ((R6), (R10) and (R11)), of which only (R6) was included in the homolytic mechanism. Dinitrogen tetroxide, created via reaction (R10), generated most of the NO_2 at the investigated condition (R12). Amidogen was mostly produced via a reaction between ammonia and a hydroxyl radical (R13). Finally, water and nitrogen were generally produced by the termination reactions (R14) and (R15), respectively,

$$HNO_3 + HONO \leftrightarrow H_2O + N_2O_4 \tag{R10}$$

$$HNO_3 + NH_2 \leftrightarrow NH_3 + NO_3 \tag{R11}$$

$$N_2O_4 + M \leftrightarrow 2NO_2 + M \tag{R12}$$

$$NH_3 + OH \leftrightarrow NH_2 + H_2O \tag{R13}$$

$$2HONO \leftrightarrow NO + NO_2 + H_2O \tag{R14}$$

$$NH_2 + NO \leftrightarrow H_2O + N_2. \tag{R15}$$

Adding water and nitrogen to the system increases the autoignition temperature (AIT) due to a combined heat sink and mass diffusion effect [11]. This previous work indicated the best agreement between simulations and experiments is at low initial pressures. Therefore, an initial atmospheric pressure was used to mitigate the effect of mass diffusion. The addition of ammonia has been previously shown to inhibit the decomposition of ammonium nitrate [14]. However, how the added ammonia affects the mixture's thermal autoignition is still unknown.

In this system, nitric oxide and ammonia are the oxidizer and reducer (fuel), respectively. Therefore, AAN equivalence ratio (Φ) can be defined as the ratio between the ammonia and nitric acid divided by the stoichiometric ratio, as shown in Eq. (1),

$$\phi = \frac{\frac{n_{NH_3}}{n_{HNO_3}}}{\left(\frac{n_{NH_3}}{n_{HNO_3}}\right)_{Stoichometric}} = \frac{\frac{n_{NH_3}}{n_{HNO_3}}}{\frac{5}{3}} = 0.6 \cdot \frac{n_{NH_3}}{n_{HNO_3}}. \tag{1}$$

Lean and rich mixture conditions are commonly used in combustion processes for a range of purposes [15]. Furthermore, a non-stoichiometric ratio is a useful variable in catalytic ignition and catalytic combustion processes [16]. Therefore, this work focused on investigating the change in AAN AIT as a function of Φ and on simulation-based tools to unveil the effect of Φ on the kinetics of the ignition.

2. Materials and methods

2.1. Experimental

The AAN fuel mixtures were prepared using ammonium nitrate ($\geq$99%, Sigma-Aldrich), ammonium hydroxide (25%, Merck) and ultra-pure water (Milli-Q®). Solutions with equivalence ratios ranging between 0.6 and 12 were tested. To prevent losses of ammonia through evaporation, sample vials equipped with septa (PTFE/silicone, Agilent) were used for storage, and a valve equipped syringe (500R-V-GT, Restek) was used for sample extraction. The tested fuel mass varied from 208.9 mg to 377.3 mg for equivalence ratios of 12–0.6, respectively. The added number of moles of both ammonia (reducer) and nitric acid (oxidizer) in the form of dissolved AN and ammonia was held constant throughout all experiments. Furthermore, the mass of water in each tested sample was unchanged to prevent any effect on the fuel's thermal behavior. Therefore, the change in mixture mass resulted from the decrease in nitric acid and accompanying increase in the lower mass ammonia moles. Nitrogen ($\geq$99.995%, Maxima) was used to evacuate air from the system to remove any residual oxygen. Thus all experiments started with pure nitrogen in the gas-phase at atmospheric pressure.

The experimental system consisted of a thermal analyzer designed for simultaneous differential thermal and barometric analyses (DTA/DBA), described in detail elsewhere [17]. The analyzer included two SS316L cells, 26 ml each, holding 700 µl crucibles (Fig. 1). The two compartments served as "sample" and "reference" cells. A 500 W single zone furnace surrounded the system, while the lines extruding from the furnace were heated using 250 W heating elements. The flow lines were thermally insolated using woven fiberglass to reduce heat losses to the environment. The heating profile was set to reach 303 K, soak for 15 min, and then heat at a rate of 5 K min^{-1} to 773 K.

Temperature and pressure measurements were taken at 1 Hz frequencies using type K thermocouples (CT-TCKB, Controtech) and pressure transducers (G2, Ashcroft), respectively. A running average over 31 data points was used to reduce the signal to noise ratio for the temperature and pressure measurements. The averaged readings from the "reference" cell were subtracted from the "sample" cell, to create the DTA and DBA data, respectively. Their time derivatives at one-second intervals were used to produce the dDTA and dDBA readings. The onset and peak values of the thermal effects were based on the dDTA and dDBA due to their higher sensitivity compared to DTA and DBA data. The onset values were determined by the first instance the dDTA/dDBA data showed successive positive values above the noise levels.

2.2. Chemical kinetic model

A previously developed mechanism for the combustion of nitrogen-based fuels was used in this work. The kinetic and thermodynamic databases, encompassing 246 distinct reactions of 30 species, can be found in the supplementary material. The mechanism was derived from an earlier one used to predict the effluent emissions from UAN combustion [10]. It was also used to successfully predict the AIT of UAN and examine the effect of UAN water content on its ignition at low pressures ($P_i(\text{He}) \leq 2$ MPaG) [18]. After removal of the carbon reaction subset, the mechanism was validated against the AIT of AAN in a nitrogen atmosphere at high pressures [11]. While the ionic reaction subset ((R3)–(R5)) was not included in the mechanism due to the lack of data on ammonia and nitrate ion kinetics, experimental AIT values were successfully reproduced at low pressures ($P_i(\text{N}_2) \leq 2.3$ MPa) [11]. Therefore, no additional modifications were made in the databases. A full