



Full Length Article

Nitromethane ignition behind reflected shock waves: Experimental and numerical study

O. Mathieu^{a,*}, B. Giri^b, A.R. Agard^b, T.N. Adams^b, J.D. Mertens^b, E.L. Petersen^a^aTexas A&M University, Department of Mechanical Engineering, College Station, TX, USA^bTrinity College, Department of Engineering, Hartford, CT, USA

ARTICLE INFO

Article history:

Received 17 March 2016

Received in revised form 10 May 2016

Accepted 12 May 2016

Keywords:

Nitromethane

Ignition delay time

L9 Taguchi array

Detailed kinetics modeling

Shock tube

ABSTRACT

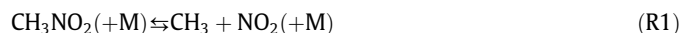
Ignition delay times for nitromethane have been measured behind reflected shock waves over wide ranges of temperature (875–1595 K); pressure (2.0–35 atm); equivalence ratio (0.5, 1.0, and 2.0); and dilution (99, 98, 95, and 90% Ar by volume) using a L9 Taguchi array. Emission from excited-state hydroxyl radicals (OH*) was the primary diagnostic for determining the ignition delay times from the experiments. Results showed that nitromethane's ignition delay time is very sensitive to most of the experimental parameters that were varied. In addition, the OH* profile for nitromethane presents an interesting double feature, with the relative intensity between the two peaks varying greatly depending on the experimental conditions. A detailed chemical kinetics mechanism was assembled from previous work by the authors and from sub-mechanisms from the literature. The latest theoretical work on nitromethane decomposition was used, and the final mechanism satisfactorily reproduces the ignition delay time data from the present study, as well as nitromethane and CH₄/NO_x ignition delay time data available from the literature.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Due to its various properties as a fuel component, there is significant interest in the detailed understanding of nitromethane's combustion chemistry. When blended with gasoline, nitromethane (NM) leads to an increase in octane sensitivity (sensitivity = RON-MON) [1], which can be beneficial for preventing knock in modern, direct-injected, boosted gasoline engines [2]. NM also has a high lubricity, which makes it an interesting fuel component for model and racecar engines [3]. Additionally, the relatively small size of the NM molecule with regards to its oxygen content (CH₃NO₂) allows for the introduction of more fuel into the cylinder for a given quantity of air, which, despite the lower energy density of NM compared to a regular gasoline fuel, leads to a higher energy output, useful for racecar engines. Finally, NM is often used as a reference component to understand the combustion mechanism of propellants [4,5] and is itself a candidate liquid monopropellant [6]. Despite these various areas of interest, as described in more detail below, the combustion chemistry of nitromethane has been investigated in only a limited number of studies [3] (detonations studies are, in contrast, more common [7–12]).

A detailed kinetics mechanism was proposed in the study of Glarborg et al. [13] in 1999, and this model was able to predict with fair accuracy the available literature shock-tube data on nitromethane decomposition. In their study, the pre-1999 experimental work was used to re-evaluate the reaction rates of the following important reactions:



According to Glarborg et al., the reactions $\text{CH}_3\text{NO}_2 \rightleftharpoons \text{CH}_3\text{ONO}$ and $\text{CH}_3 + \text{NO}_2(+\text{M}) \rightleftharpoons \text{CH}_3\text{ONO}(+\text{M})$ can be considered negligible under practical combustion conditions. In addition, the formation of NO directly from CH₃NO₂ decomposition was not considered.

Over the past few years, detailed kinetics mechanisms on NM combustion have seen constant improvement in the literature. These contemporary kinetics mechanisms for NM [3,4,14,15] all rely on the rate for R1 estimated by Glarborg and coworkers [13]. In the study from Boyer and Kuo [5] for example, the flame structure of NM at high pressure was investigated numerically using a detailed kinetics model they developed. Flame species formed in a premixed flame of NM in Ar were identified by Tian et al. [14], and a detailed kinetics mechanism was validated with these data. However, as pointed out by Brequigny et al. [3], these

* Corresponding author.

E-mail address: olivier.mathieu@tamu.edu (O. Mathieu).

two mechanisms are limited as they are either designed for high pressure only (20–150 atm) [4] or have only been validated with a single equivalence ratio [14]. A more-comprehensive mechanism based on the one from Glarborg et al. [13] was then developed by Zhang et al. [15], who validated a chemical scheme against species and temperature profiles from laminar flames at different equivalence ratios (1.0, 1.45, and 2.0). This mechanism was recently improved by Brequigny et al. [3] who also measured the laminar flame speed of NM between 0.5 and 3 bar. The maximum flame speed was observed for lean mixtures in the study of Brequigny et al., around $\phi = 0.7$ – 0.8 , and their model was able to predict this result. However, Nauc ler et al. [16] analyzed the results of Brequigny et al. and showed that this result was due to the equation Brequigny et al. used for determining the equivalence ratio ($\text{CH}_3\text{NO}_2 + 0.75 (\text{O}_2 + 3.76 \text{N}_2) \rightleftharpoons \text{CO}_2 + 1.5 \text{H}_2\text{O} + 3.32 \text{N}_2$). Nauc ler et al. used a different set of ideal products to determine the equivalence ratio ($\text{CH}_3\text{NO}_2 + 1.25 \text{O}_2 \rightleftharpoons \text{CO}_2 + 1.5 \text{H}_2\text{O} + \text{NO}$) and found that the maximum flame speed was then obtained on the fuel-rich side (at an equivalence ratio of around 1.2), in agreement with results generally observed with other hydrocarbons [17,18].

To further refine and validate NM detailed kinetics mechanisms over wide ranges of conditions, more experimental data was necessary. Ignition delay time measurements in shock tubes, thanks to their accuracy and the simplicity of their modeling, are extremely valuable to rapidly assess the global accuracy of a mechanism and to help improve predictions. Unfortunately, to date there are no ignition delay time data available in the literature (except for the ignition delay time measurements by Kang et al. [19], for which the pressure condition was not reported, making these data rather difficult to use to validate a kinetics model).

In addition to this lack of data, previous mechanisms for NM do not include the latest developments for NM chemistry, based on recent theoretical and experimental studies [20–22]. As summarized by Annesley et al. [22], results from shock tubes and infrared multi-photon dissociation experiments historically disagree with each other in that only CH_3 and NO_2 have been detected in shock-tube NM decomposition, whereas the formation of NO , accounting for up to 40% of the NM consumption [23], was also observed with infrared multi-photon dissociation techniques. Theoretical studies identified a roaming isomerization of NM ($\text{CH}_3\text{NO}_2 \rightarrow [\text{CH}_3\text{ONO}^*] \rightarrow \text{CH}_3\text{O} + \text{NO}$) competing with the simple bond fission pathway ($\text{CH}_3\text{NO}_2 \rightleftharpoons \text{CH}_3 + \text{NO}_2$). The branching ratio between these two pathways was predicted to be strongly pressure dependent between 1 and 200 Torr above 1000 K, transitioning from roaming dominated to bond fission dominated [20]. Annesley et al. [22] investigated both theoretically and experimentally (in a shock tube at pressures between 30 and 120 Torr) the competition between roaming mediated isomerization and thermal dissociation of NM. Their result was consistent with the previous theoretical work, although the pressure dependence of the branching ratio is not as strong as predicted by Zhu et al. [20].

To help improve understanding of NM combustion, the scope of the present study was twofold. First, new experimental measurements were performed under conditions never before investigated. Ignition delay times (τ_{ign}) were measured over large ranges of temperature, pressure, dilution, and equivalence ratio in a shock tube. A test matrix was developed to limit the number of experiments while still validating the model over a wide range of conditions. The second main aspect of this study was to propose a detailed kinetics mechanism capable of reproducing the results from the present study along with other nitromethane data and hydrocarbon/ NO_x ignition delay time data from the literature. The first part of the paper details the experimental setups used during this study. The experimental results obtained with these setups are then presented and compared with detailed kinetics models from the literature and with a detailed mechanism proposed in this

study. Finally, the experimental results are explained by numerical analysis using the mechanism.

2. Experimental setup

2.1. Description of the apparatus

Ignition delay times (τ_{ign}) were measured in a high-pressure shock tube. The driver section is 2.46 m long (76.2-mm i.d.), and the driven section is 4.72 m long (152.4-mm i.d.). Test pressure in the shock tube was monitored by one PCB 134A transducer located at the endwall and one Kistler 603 B1 transducer located at the sidewall. More details and schematics of the shock-tube setup can be found in Aul et al. [24].

The measurement section is equipped with 5 pressure transducers (PCB P113A) equally spaced by 406 mm and mounted flush with the inner surface. The last transducer is located 16 mm before the shock-tube endwall. These transducers delivered a signal upon the passage of the incident shock wave, and its velocity was determined using four Fluke PM-6666 timer/counter boxes. A curve fit of these four velocities was then extrapolated to determine the incident wave speed at the endwall location. Post reflected-shock conditions were obtained using this extrapolated wave speed in conjunction with one-dimensional shock relations and the initial conditions at the test region. This method was proven to maintain the uncertainty in the temperature determination behind reflected shock waves (T_5) below 10 K as shown in Petersen et al. [25].

2.2. Optical diagnostic

Ignition delay times were determined using the chemiluminescence emission from the $\text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi$ transition of the excited-state hydroxyl radical (OH^*) at 307 ± 10 nm. During this study, an unusually low level of OH^* chemiluminescence was observed, leading to a relatively low signal-to-noise ratio (SNR) compared to former studies from our group [26,27]. To illustrate this low level of OH^* chemiluminescence, the most recent NM mechanism from Brequigny et al. [3] was coupled with the OH^* sub-mechanism used in Mathieu and Petersen [26] (comprised of the OH^* mechanism from Hall and Petersen [28], along with the reaction $\text{N}_2\text{O} + \text{H} \rightleftharpoons \text{N}_2 + \text{OH}^*$ from Hidaka et al. [29]). Numerical OH^* profiles are then compared between NM and CH_4 for similar equivalence ratios, temperatures, ignition delay times, and pressures. Results are visible in Fig. 1 for (a) mixtures of CH_4 and CH_3NO_2 at 1500 K (10 atm, $\phi = 1$, 98% Ar); and (b) for the same mixtures and the same conditions except that the CH_4 mixture is now at 1745 K. As can be seen in Fig. 1(a), the computed OH^* profile from nitromethane combustion presents a double peak; the first peak is always found around time zero and is, by far, the largest intensity (as per the model). The second peak at around 200 μs in Fig. 1 corresponds to the maximum OH^* intensity for the main ignition event, is a much smaller intensity, and can barely be seen on the scale. However, only one peak is resolved at around 3250 μs for the ignition of CH_4 . This time difference for the ignition peaks illustrates the large difference in reactivity between methane and nitromethane. As shown later in the paper, these two peaks for NM were also observed experimentally, and the origins and respective amplitudes of these peaks are discussed. Since ignition delay time measurements in shock tubes are limited by a maximum observation test time (around 100–1500 μs in this study), the respective amount of OH^* produced by CH_4 and NM (the second peak for the latter) are also compared at conditions for which the maximum OH^* occurs at the same time. Fig. 1 shows that at 10 atm, 98% Ar, and $\phi = 1.0$, this is achieved by increasing the CH_4 temperature to 1745 K, at which CH_4 produces around 300 times more OH^* than

Download English Version:

<https://daneshyari.com/en/article/6633511>

Download Persian Version:

<https://daneshyari.com/article/6633511>

[Daneshyari.com](https://daneshyari.com)