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An experimental and modeling study of nitromethane+O$_2$+N$_2$ ignition in a shock tube

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Abstract

The ignition of nitromethane/O$_2$/N$_2$ mixtures was investigated via shock tube experiments in the temperature range 947–1333 K at reflected shock pressures near 8, 16 and 32 atm. The ignition was recorded as the intensity maxima of unfiltered luminosity in the range 240–530 nm. Under the experimental conditions of the present study, ignition was found to proceed via a two stage process. Dependencies on concentration, pressure and temperature were examined and discussed. The two ignition stages were separated in time, with individual concentration and temperature dependence. The two experimentally determined ignition stages were found to be pressure independent over the pressure range investigated. The activation energy was derived to be $16.15 \pm 1.57$ kcal mol$^{-1}$ for the first stage ignition and $20.89 \pm 0.82$ kcal mol$^{-1}$ for the second stage ignition. Modeling using the mechanism by Brequigny et al., published in Proceedings of the Combustion Institute (2014) 703–710, could predict the magnitude of the ignition delay times at 8 atm, but it could not reproduce the temperature dependence of the first stage ignition or the pressure independence of both ignition stages. The measurements are discussed in relation to data from the literature.

Keywords: nitromethane, multistage ignition, modeling
1. Introduction

Nitromethane, CH$_3$NO$_2$, is a simple nitrogen containing fuel with high energy content, which is used in mixtures with methanol or as a pure fuel in racing cars and in model engines [1]. It is also considered as a fuel additive [2-4] in engines, promoting their efficiency and reducing soot from their exhaust. Because of the oxygen content in the molecule, nitromethane can act as both a fuel and as an oxidizer in combustion processes, as noted in the study by Fells and Rutherford [5], where the effect of nitromethane addition on the burning rate of methane flames was studied. These dual fuel-oxidizer properties motivate studies of combustion characteristics of nitromethane as a single component as well as in mixtures with other oxidizers. Due to its potential as a monopropellant [6], nitromethane has been extensively studied, focusing on thermal decomposition [7-17], and detonation [18-22]. The combustion chemistry of nitromethane is also of interest from a fundamental research viewpoint since it is the simplest representative for fuel-nitrogen species, and as such can facilitate understanding of the reactions relevant to the mutually sensitized oxidation of hydrocarbons and nitrogen oxides [11].

The decomposition of nitromethane has been investigated mainly by kinetic studies of the thermal decomposition in shock tubes [11-17, 23]. A common experimental approach is to track the formation of NO$_2$, and it is well established that NO$_2$ + ČH$_3$ are the significant decomposition products that then undergo further reactions [12, 13, 16]. It was experimentally shown by Zaslonko et al. [12] that in the temperature and pressure ranges 1030–1580 K and 1.0–2.8 atm, the thermal decomposition produced CH$_3$Ȯ and CH$_3$ONO. The latter was explained as the result of recombination of ČH$_3$ and NO$_2$. In the thermal decomposition study of Hsu and Lin [15] NȮ and CO profiles were measured in the temperature range 940–1520 K at pressures 0.4-1 atm. From the NȮ and CO profiles the authors showed that NO is formed early during the ignition, while CO is formed at a later stage. Kuznetsov et al. [16] monitored the formation of NO$_2$ in nitromethane decomposition through shock tube experiments in the temperature range 1190–1490 K at 1.5 atm. The authors confirmed that the NO$_2$ profile had a convex shape consistent with a typical decomposition product, and that the disappearance of nitromethane and the formation of NO$_2$ coincided. Through theoretical analysis it was also concluded that isomerization of nitromethane to CH$_3$ONO was not competitive compared to the thermal decomposition. The thermal decomposition of nitromethane has been shown to be pressure dependent in the pressure range of 0.1–40 atm [12, 13, 17, 23].

An interesting aspect of nitromethane combustion is that experiments and modeling indicate that it proceeds via two or three steps; detonation has been shown to be a two-step
process [19-22, 24], a similar pattern is seen in low-pressure flames [25] and in the case of flames of liquid nitromethane three reaction zones have been identified [6].

From detonation studies it is known that fuels and mixtures containing NO₂ propagate in a double cellular structure [20-22, 24]. Presles et al. [20, 21] showed a sub-structure within the first part of the main cell during detonation of pure nitromethane and rich nitromethane/O₂ mixtures (1.3 < φ < 1.75) at 390 K and 0.05–1.7 bar. This sub-structure behaved independent of the main cell in terms of velocity and structure. Sturtzer et al. [19] compared their numerical results of pure nitromethane and nitromethane+O₂ detonation with experimental results from Presles et al. [20, 21]. It was suggested that the origin of the double cellular structure is an endothermic step of fuel decomposition into ČH₃ and NO₂, followed by two independent exothermic steps and attributed the reaction NO₂ + Ĥ = NȮ + H₂ as the main exothermic source in the first step of detonation.

Experimental and theoretical studies on nitromethane flames have shown a wide total reaction zone, with the chemistry divided into multiple separated zones [6, 25]. By performing modeling studies Boyer and Kuo [6] identified three reaction zones in a pure liquid nitromethane flame at pressures of 3–6 MPa. Indications of a two stage ignition process for pure nitromethane have been presented [14, 26, 27]. Guirguis et al. [27] noted that in their study of 100% nitromethane pyrolysis behind reflected shock waves, for some of the measurements there were two separated pressure spikes where the second was higher in intensity. The presence of a second pressure spike was however not given any further attention. In light of modeling results for flames from previous studies [6, 28] and detonation studies [20-22, 24], the second pressure spike could indicate that a second stage ignition occurred in the experiments of Gurguis et al. [27].

In the study by Hall and Wolfhard [25] multiple reaction zones in methyl- and ethyl nitrate, methyl nitrite and nitromethane flames were examined at low pressures. It was concluded that these flames had up to three separate reaction zones. The emission from the reaction zones was analyzed and characterized in terms of emitting species. A nitromethane/O₂ flame was analyzed at 323 K and ~0.1 atm, and two reaction zones were detected. A yellow undefined emission was observed in the first reaction zone, and it was argued by the authors that this was likely due to NO₂*.

In the second reaction zone, emissions from C₂*, CH*, CN*, OH*, NH* and NO* were identified. No emission from formaldehyde was observed for nitromethane/O₂ flames.

Laminar burning velocities of nitromethane/air flames have been determined using the Bunsen flame method [29], spherically expanding flames [30], and the heat flux method [28].
In the work of Nauclér et al. [28] laminar burning velocities of nitromethane/air flames were measured using the heat flux method in the temperature range 338–358 K at pressure of 1 atm. The width of the reaction zone of these nitromethane flames was examined using modeling and implications for experimental determinations of laminar burning velocity were discussed. The modeling by Nauclér et al. [28] implied that a two-stage process occurred.

Oxidation studies of nitromethane are not as numerous as compared to detonation and decomposition studies. Oxidation in a static vessel was investigated by Tricot et al. [31] by studying nitromethane explosion limits in the temperature range 700–740 K. Flame structure has been investigated in low-pressure nitromethane/O₂/Ar flames [32, 33].

The ignition of nitromethane in the presence of O₂ has been considered as a one-stage process in studies by Borisov et al. [14] and Kang et al. [26]. A two-stage process in the ignition of nitromethane/O₂ was indicated in the literature [34, 35], and later shown by the authors of the present work [36]. The two-stage ignition process was independently confirmed by Mathieu et al. [37].

Borisov et al. [14] measured the autoignition of nitromethane/O₂ mixtures in a by-pass apparatus with the diluents Ar, N₂ and He at 700–1300 K in order to determine the rate constant for the thermal decomposition of nitromethane. Kang et al. [26] examined the ignition delay times of nitromethane/O₂/Ar mixtures in a shock tube by tracking the von Neuman pressure spike in the temperature-range 1250–1900 K at a pressure of about 0.2 atm for several different nitromethane/O₂/Ar compositions. A correlation between mixture composition and ignition delay times was presented by Kang et al. [26]. The overall activation energy was calculated to be 21.36 ± 0.51 kcal mol⁻¹ through multiple regression analysis. The authors concluded that the presence of oxygen in the NO₂-group in the fuel molecule reduced the role of O₂ as an ignition promoter compared to other hydrocarbon fuels. The decomposition of pure nitromethane, and its ignition in the presence of O₂ was investigated in a shock tube [34] and presented by Djebaili-Chaumiex et al. [35]. Absorption at 235 nm and emission at 235 nm and 306 nm were observed and treated as ignition delay times.

The limited understanding of the ignition of nitromethane in the presence of oxygen calls for further studies. As mentioned above a two-stage behavior was indicated by the present authors in a conference publication [36] where ignition delay times from a shock tube study over 947–1333 K at 8–32 atm were presented. In the present paper, that study is discussed in detail. A characterization of the ignition of nitromethane/O₂ over time is conducted by studying pressure and luminosity profiles to understand the ignition process. Aspects of nitromethane ignition, such as pressure dependence and effects of fuel and oxidizer...
composition at the same equivalence ratio, are examined. A recent kinetic model developed for nitromethane flames [30] was used in an attempt to interpret the ignition characteristics.

2. Experimental details

Experiments were performed in a high-pressure shock tube at NUI Galway. The experimental setup is described in detail in the work of Nakamura et al. [38].

The experimental pressure profiles were recorded using two pressure transducers, one in the endwall and the other at the side wall, 10 mm from the endwall. The measurable time range in this experimental setup is 4000 µs. The ignition was tracked using unfiltered light emission from an optical window at the side wall, 10 mm from the endwall. The window is transparent within a wavelength range of 150–2000 nm and the emission was recorded with a Photodiode array detector (PDA) within the range 240–530 nm. Ignition delay times were measured from the time that the reflected shock wave triggered the pressure transducer at the endwall to the maximum intensities in the luminosity trace. This choice of ignition delay definition is further discussed in Section 4.1.

Four different gas compositions with varying fuel and O\textsubscript{2} content were studied, see Table 1. The gas mixtures were prepared and continuously stirred in a mixing tank at low pressure, at a temperature of 323 K. The shock tube driven section was maintained at the same temperature. Partial pressure was used to control the mixture compositions. An issue when working with nitromethane is the risk of condensation. To avoid this, the liquid nitromethane (Sigma-Aldrich Ireland Limited, 95% purity) was gradually injected into the mixing tank with close monitoring of the pressure. Between each injection the fuel was left to vaporize and equilibrate. The partial pressure of the nitromethane was kept about three times lower than the saturation pressure of nitromethane. The O\textsubscript{2} (99.5%) and N\textsubscript{2} (99.99%) were supplied by BOC Ireland Limited.

The experiments were performed in the temperature range 947–1333 K at approximately 8, 16 and 32 atm. As explained in detail later, the ignition of nitromethane was found to have two separate stages of ignition with the second stage observed to be pressure independent. Therefore experimental results with pressures deviating from the target pressure were included in the presentation of the experimental results. The pressures were within 90–105% of the target pressures, with larger deviations for Mixture 1 at 32 atm, with three deviating pressures at 38.8, 39.5 and 44.9 atm, and Mixture 3 at 8 atm, with two deviating pressure of 9.2 and 9.7 atm.
Traditionally N₂ has been regarded as the final product for nitromethane combustion [1, 7]. For nitromethane flames, NO has been shown to be formed but not consumed [32, 33]. For this reason, NO was chosen as the final product for nitromethane-containing nitrogen in the definition of ϕ, as further discussed in the work of Nauclér et al. [28].

\[ 2 \text{CH}_3\text{NO}_2 + 2.5 \text{O}_2 \rightarrow 2 \text{CO}_2 + 3 \text{H}_2\text{O} + 2 \text{NO} \quad (\text{Eq. 1}) \]

Table 1: Experimental conditions visited with respect to mixture composition and pressure. Mixture components are given as mole%.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>CH₃NO₂</th>
<th>O₂</th>
<th>N₂</th>
<th>φ</th>
<th>Pressure [atm]</th>
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<tr>
<td>1</td>
<td>4</td>
<td>5</td>
<td>91</td>
<td>1</td>
<td>8, 16, 32</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>5</td>
<td>93</td>
<td>0.5</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>10</td>
<td>86</td>
<td>0.5</td>
<td>8, 16</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>2.5</td>
<td>93.5</td>
<td>2</td>
<td>16</td>
</tr>
</tbody>
</table>

The experimental uncertainties, as estimated by Nakamura et al. [38], are ±15 K in reflected shock temperature, \( T_s \), ±15% in ignition delay time, \( \tau \), and ±2% in mixture concentration.

3. Modeling details

The shock tube experiments were modeled using the batch reactor module of CHEMKIN IV [39] at constant volume and at varied pressure conditions. The recent kinetic mechanism for nitromethane combustion by Brequigny et al. [30] was used for the modeling. The mechanism contains 88 species and 701 reactions, of which the nitromethane subset involves 13 reactions. The mechanism is an adaptation of a mechanism by Glarborg et al. [11, 33], to describe oxidation in low-pressure flames validated for pressures in the range 0.5–3.0 bar.

4. Results and discussion

The ignition was investigated for various conditions with respect to composition, equivalence ratio and pressure. The experimental conditions presented in Table 1 are chosen to provide a matrix of parameters covering a relevant range of pressures and mixture compositions. In the following discussion the experimentally measured properties pressure and luminosity, over time, are first evaluated. It is shown that luminosity has two time-separated maxima, which is treated as two separate ignition stages. These stages are discussed separately from both an experimental and a modeling perspective. Correlation equations are
calculated for both of the ignition stages and compared to correlations from the literature [26, 35]. The effects of mixture composition and pressure on ignition delay times are discussed.

4.1 Experimental traces of pressure and luminosity

To accurately define the ignition, profiles of pressure and luminosity over time are explored. Mixtures 1–4 are discussed separately with respect to the characteristics of each mixture. Figures 1–4 are typical examples of the measured pressure and luminosity profiles, clearly illustrating the similarities and differences characterizing the different mixtures. Figure 1 presents the experimental pressure and luminosity profiles of Mixture 1 at $\phi = 1$, at a pressure of 8.2 atm and a temperature of 1115 K. From the pressure trace in Fig. 1, it can be seen that after the distinct pressure rise resulting from the arrival of the shock wave, there is a smooth pressure rise with a maximum. The pressure rise indicates that there is a prolonged activity in the gas mixture after the reflected shock wave reaches the end-plate but the pressure trace cannot be used independently to determine if ignition has occurred. In the luminosity trace in Fig. 1 two luminosity maxima separated in time, are evident. First there is a luminosity maximum shortly after the arrival of the shock wave, with a maximum intensity occurring in a time scale smaller than 40 µs. This is followed by a second luminosity peak with a higher maximum intensity and with a broader distribution over time. The second maximum intensity in light emission roughly coincides in time with the pressure maximum. The difference in intensity between the first and second luminosity maxima can be explained either by a higher concentration of light emitting species during the second luminosity maximum, or by different light emitting species present in the two luminosity maxima.

Mixture 2 has $\phi = 0.5$, with the same oxygen content but with a 50% reduction in nitromethane as compared to Mixture 1. Example pressure and luminosity profiles, representing a measurement for Mixture 2 at 1220 K and 8.5 atm, are shown in Fig. 2. Unlike the pressure in Mixture 1 there is no clearly defined pressure rise after the arrival of the shock wave, indicating that there is no major change in volume during the ignition, or that no ignition occurs. The chemical activity in this mixture is apparently too low to be detected from the pressure traces. However, from the luminosity traces it is evident that ignition does occur. A similar pattern as in the luminosity profiles from Mixture 1 is seen, with two separated maxima. The first maximum occurs shortly after the arrival of the reflected shock wave, while the second maximum is delayed. The second stage has a stronger emission intensity and wider distribution over time. Considering both the pressure and luminosity
traces gives an indication that the lower fuel amount in Mixture 2 decreases the intensity of the luminosity, while preserving similar characteristics over time compared to Mixture 1.

Mixture 3 has $\phi = 0.5$, which is the same as for Mixture 2, with the same nitromethane content as in Mixture 1 but with the $O_2$ content doubled. There is no pressure rise after the arrival of the shock wave for Mixture 3 in the measurements at temperatures $> 1032$ K. Measurements at $984$ K and $1031$ K show a rise in pressure, coinciding in time with the luminosity peaks. Figure 3 shows the pressure and luminosity traces for Mixture 3 at $1031$ K and $8.5$ atm. In the luminosity traces for Mixture 3, it can be seen that both luminosity maxima are close together in time, and are almost indistinguishable. The ignition does not start at the arrival of the shock wave in the measurements at $\leq 1186$ K, but there is a time delay, as can be seen in Fig. 3.

Mixture 4 has $\phi = 2.0$, with the same nitromethane content as Mixture 1 but it contains $50\%$ of the $O_2$ content. This mixture was investigated in the temperature range $1109$–$1780$ K at $32$ atm. As can be seen in Fig. 4 the experimental pressure traces shows no significant pressure rise after the arrival of the shock wave. In the luminosity trace there is a single intensity maximum within the measurable time range. This can be either the first stage ignition with the second ignition stage outside the time restrictions in the present study, or the two maxima collapsed to a luminosity intensity. From the pressure and luminosity traces it cannot be conclusively determined if the ignition of Mixture 4 corresponds to the first or second stages identified in the luminosity profiles of the other mixtures. In the coming sections the information gained from the analysis of the other conditions are used to elucidate the ignition behavior of Mixture 4.

In the experimental pressure profiles of Mixtures 1–3, the pressure rise after the arrival of the shock wave occurs gradually or not at all, in contrast to the sharp pressure rise commonly used to identify ignition in shock tube experiments. Thus, if ignition were to be defined based on the pressure profiles measured in the present study, there would be a high degree of uncertainty. The luminosity profiles have well defined maxima; therefore the experimental ignition is defined as the maxima of the luminosity profiles, with each maximum marking separate ignition events.

In the above it was shown that the ignition of nitromethane in the presence of oxygen exhibits an unusual ignition behavior with two separate ignition stages at the majority of the experimental conditions in the present study, as exemplified by the luminosity profiles in Figs. 1–3. Under these conditions the first stage ignition is fast, with luminosity maximum at $< 40 \mu s$, with the exception of Mixture 3 at $984$ and $1031$ K, while the second stage had a
delayed ignition in all mixtures and experimental conditions. This multi stage ignition is considered analogous to the multi stage chemistry found in flames [6, 25, 28] and in detonations [19]. Both the first and second stages are investigated further.

**Ignition delay determination**

The ignition delay times for first- and second-stage ignition were determined for Mixtures 1–3 in the temperature range 947–1333 K. Figure 5 shows that the ignition delay times for the first stage ignition are the same magnitude for Mixtures 1–3 over the temperature range studied, which indicate that the initial gas mixture composition does not affect the ignition delay times. The activation energy for the first stage ignition is similar for the three mixtures. As a result of experimental uncertainties and the short ignition times of this ignition stage scatter in the results are likely not to be attributed to pressure effects. Mixture 4 show a fast ignition and the results are plotted in Fig. 5 together with the first stage ignition from Mixtures 1–3. The ignition delay times measured for Mixture 4 are of the same order of magnitude as the ignition delay times for Mixtures 1–3, therefore the single stage ignition in Mixture 4 is likely the first stage ignition.

In Fig. 6 the experimental data for the second stage ignition is presented for Mixtures 1–3. The experimental second stage ignition delay decreases with temperature, as the reactivity increases. Reducing the nitromethane content by half has a small activating effect on the second stage ignition by decreasing the ignition delay times. By doubling the O₂ content the effect on the ignition delay was considerably stronger with a reduction of the ignition delay times by ~four times compared to Mixture 1. The effective activation energy of the second stage ignition of Mixture 3 is weaker than that for Mixtures 1–2.

Mixture 1 and Mixture 3 were examined in the pressure range of 7.4–44.9 atm and 7.7–15.6 atm, respectively. For many fuels, the ignition is sensitive to pressure [40]. As a result of the higher concentrations of fuel and O₂ in the gas mixture, ignition is typically faster at higher pressures. However, no change in ignition delay times with pressure is observed for either of the two ignition stages over the pressure range investigated.

**Correlation equations based on mixture composition**

The use of correlation equations allow comparison of datasets obtained at different conditions as the correlations quantify the dependence of the ignition delay on the concentration of fuel, oxidizer and inert gas over a range of conditions. The quality of a correlation depends on the range and quality of data used in deriving it. In the present work
correlation equations were obtained by fitting an expression to the experimental results from Mixtures 1–3 of the present study for both the first (Eq. 2) and second (Eq. 3) stage ignition. Mixture 4 was not included since the single ignition stage cannot be conclusively attributed to one or the other ignition stages identified in the other mixtures. The effect of temperature and mixture composition was evaluated by multiple regression analysis. The concentrations are in mol m\(^{-3}\), temperature in K and R in kcal/kmol.

\[
\tau = 10^{-1.71}e^{-16.15/RT}[CH_3NO_2]^{-0.31}[O_2]^{-0.02}[N_2]^{0.48} \quad \text{(Eq. 2)}
\]

\[
\tau = 10^{-3.38}e^{-20.98/RT}[CH_3NO_2]^{0.59}[O_2]^{-2.35}[N_2]^{1.64} \quad \text{(Eq. 3)}
\]

The overall activation energy, \(E_a\), was determined to be 16.15 ± 1.57 kcal mol\(^{-1}\) for the first-stage ignition and 20.89 ± 0.82 kcal mol\(^{-1}\) for the second stage ignition. The pressure dependence derived from Eq. 2 and Eq. 3 is weak, \(P^{0.15}\) and \(P^{-0.12}\) respectively. It can be seen in Fig. 7 that the correlations from the present study, Eqns. 2 and 3, represent the experimental results satisfactorily, with an exponential agreement. The ignition delay times determined for Mixture 4 were evaluated by comparison to Eqns. 2 and 3. The agreement with the correlation of the first stage ignition, Eq. 2, was good for the measurements at 1109 K and 1258 K, but the measurements at 1509 K and 1779 K did not fit the correlation. However, due to that there are no other mixtures examined in the temperature range 1500–1700 K, it is not possible to evaluate if these measurements are faulty or an accurate description of the first stage ignition at these temperatures. The fit of Mixture 4 were considerably lower than of the second stage ignition, Eq. 3.

The present analysis predicts a promoting effect of \(O_2\) on both ignition stages, as evident from the negative sign on the exponents. \(O_2\) has a minor influence on the first stage ignition, \([O_2]^{-0.02}\). However, the second stage ignition exhibits an unusually large influence of \(O_2\), \([O_2]^{-2.35}\). Commonly the influence of \(O_2\) on ignition is in the order of \([O_2]^{-0.5–1.5}\) [26]. Nitromethane concentration has a positive influence on the ignition in the first stage, \([CH_3NO_2]^{0.31}\), while it has a dampening effect on the second stage ignition, \([CH_3NO_2]^{0.59}\), according to the correlation analysis in Eqns. 2 and 3. Nitrogen is predicted to have a more pronounced dampening effect on the second stage ignition with a positive exponential dependence of 1.64, compared to the first stage ignition with a dependence of 0.48.

The correlations for the first and second ignition stage were compared to correlations from literature [26, 35]. Kang et al. [26] determined the ignition delay at ~0.2 atm by tracking the spike in pressure. The pressure profile presented by Kang et al. has the von Neuman spike, not the gradual increase seen in the present study. As mentioned in the discussion of pressure profiles, the second stage ignition detected by peaks in luminosity, in many cases were
accompanied with a pressure increase. In light of this, the ignition delays from Kang et al., derived from pressure profiles, could be interpreted as the second stage ignition. Any indication of a fast ignition stage, near the arrival of the shock wave in time, is absent in the work by Kang et al. However, this can be a question of detection limits and equipment sensitivity. Their results were presented in the form of a correlation equation Eq. 4, derived from the ignition delay data obtained from mixtures with $\phi \approx 0.8–3.12$. The experimental data was collected for mixture compositions with 8.0–37.8% nitromethane, 8.6–39.5% O$_2$, 33.3–80% Ar in the temperature range 1250-1900 K at ~0.2 atm.

$$\tau = 10^{-1.11} e^{-21.36/RT} [CH_3NO_2]^{0.59} [O_2]^{-0.72} [Ar]^0$$  \hspace{1cm} (Eq. 4)

In the study by Djebailia-Chaumeix et al. [35], the ignition delay times were measured from a delayed emission signal at 235 nm. The correlation, Eq. 5, was derived from ignition delay times for mixture compositions 3.56–6.4% nitromethane, 3.2–12.4% O$_2$, 84–91.97% Ar, and measured at 1040–1380 K at 0.8–2.8 atm.

$$\tau = 10^{-8.43} e^{-15.44/RT} [CH_3NO_2]^{-1.02} [O_2]^{-1.08} [Ar]^{1.42}$$  \hspace{1cm} (Eq. 5)

The similar activation energies determined in the present study and that of Kang et al., with the uncertainty of both $E_a$, supports the hypothesis of the present study that the ignition detected in the pressure profiles by Kang et al. is corresponding to the second stage ignition identified in the present study. The trends in nitromethane and O$_2$, are the same for Eq. 3 and Eq. 4, although with different magnitudes.

The correlation Eq. 5 behaves considerably differently compared to the correlations for the second stage ignition, Eqns. 3 and 4. According to Eq. 5, the ignition is promoted by both oxygen and nitromethane. This behaviour is similar to that of the first stage ignition of the present study, Eq. 2. The activation energy in Eq. 5, is significantly lower than in Eqns. 3 and 4, and is in good agreement with the first stage ignition of the present study, Eq. 2, within its uncertainty.

By comparing the correlations for the second stage ignition, Eqns. 3 and 4, it can be seen that O$_2$ is predicted to have a larger influence on the ignition in the present study, as compared to the analysis by Kang et al. When inserting the experimental results for the second stage ignition into Eq. 4, Mixtures 1 and 2 are well represented, but Mixture 3 is not. This could be attributed to the fact that the equations are generated at different conditions, where Eqn. 4 was calculated from predominantly richer mixtures and higher temperatures than in the present study with one stoichiometric mixture and two mixtures with $\phi = 0.5$, at 947–1333 K. As the activation energies in Eqns. 3 and 4 are in close agreement, the difference in temperature dependency between the studies could be due to differences in mixture composition.
The data from Borisov et al. [14] cannot be directly compared with the correlations obtained in shock tubes. In fact, earlier measurements performed in a by-pass apparatus were affected by significant heat losses during ignition delay as was revealed and discussed by the same authors [41, 42]. Due to heat losses the temperature of the mixture was not equal to the temperature of the walls that affects interpretation of both ignition delays and the apparent activation energy [41, 42].

By interpreting the data in light of the present study, where two ignition stages were observed in the same measurements, it is plausible that discrepancies that exist in the literature [26, 35] could be due to observations of different stages in the ignition.

4.2 Ignition modeling

Possible origin of luminosity

The presence of two luminosity maxima indicate that the ignition of nitromethane in the presence of O₂ occurs in several zones or steps, as previously seen in detonation [19] and flame [6, 25] studies. The possible origins of the luminosity maxima were explored using kinetic modeling and information about the chemiluminescence from exited species in the light emitting wavelength range [43]. When identifying species, considerable experimental work [12, 13, 25, 26, 43-45] and the book of Gaydon [43] was considered. Candidates species were those which emit light within the experimentally detectable range of the present study, 240-530 nm.

In the work of Hall and Wolfhard [25] two zones were detected in a nitromethane/air flame. In the first zone the species C₂*, CH*, CN*, ÓH*, NH* and NO* were observed, but not CH₂O*. In the shock tube study of Kang et al. [26] the authors mention that the species CH₂O*, ÓH*, and NO* were detected through emission after the reflected shock had passed, which was referenced in [26] as a publication in preparation but is, to the best of our knowledge, not yet published. In the shock tube study of nitromethane decomposition by Zaslonko et al. [12] CH₂O* was detected, and used as proof of the presence of CH₃Ó radical early in the ignition. In the combustion of liquid nitromethane strong signals of ÓH* were detected with somewhat smaller signals of CN* [45]. Hu et al. [44] investigated emission from nitromethane/O₂ mixtures in a shock tube and observed emission of CH₃Ó* and ÓH* appearing simultaneously.

NO₂* is a likely candidate for the first stage emission that is detected as it is established in the literature that ground state NO₂ is produced from the thermal decomposition of nitromethane [12, 13], and emits light in the detectable region.
Formaldehyde CH$_2$O* emits light in the range 370-480 nm. It was generally considered that the reaction CH$_3$Ȯ + CH$_3$Ȯ = CH$_2$O* + CH$_3$OH is a source of excited formaldehyde [10].

The presence of significant amounts of ÕH* in the present study were excluded by filtering the luminosity of the experimental measurements of Mixture 3. Unfiltered luminosity was not recorded simultaneously, so the experiments cannot show the absence of luminosity from ÕH radical in the presence of ignition, just the absence of luminosity from ÕH radicals. However, this could also be due to the detection limits or trigger thresholds. As ÕH* radicals have been detected in previous studies, it is included in the discussion of luminosity sources. Precursors to ÕH* are primarily Õ + Ḵ = ÕH* and ČH + O$_2$ = CO + ÕH*, and to a minor extent N$_2$O + Ḵ = N$_2$ + ÕH*.

NO does not decompose at the present temperatures and would therefore not result in one or several concentration maxima with a constrained time interval, but rather be distributed over a wide range in time. The same behavior was also predicted by the model. Considering this NO was excluded as a possible source of the luminosity peaks the species left for consideration are, CN*, NH* and C$_2$*. These species all emit light in the experimentally detectable range of the present study; CN* at 388.3 and 359 nm, NH* at 337 nm, C$_2$* with two swanbands within the detectable region of the present study at 473.7 and 516.2 nm.

The excited species C$_2$* is produced from ČH + Č = C$_2$* + Ḵ and ČH$_2$ + Č = C$_2$* + H$_2$ [46]. Through the reaction ČH + NO = NH* + CO the exited species NH* can be formed [47]. The formation of CN* is, to the best of the authors knowledge, not well established in the literature. Therefore its ground state equivalents are examined further.

Excited species are not present in the chemical kinetic mechanism used to simulate the present results, but the ignition is evaluated using the precursors for the exited species discussed above. Modeling shows two regions of species maxima that could possibly be related to the first- and second-stage ignition, as shown in Fig. 8. The first and second ignition stages are defined as the maximum pressure rises according to the model, and marked in Fig. 8. CH$_3$Ȯ and NO$_2$ peak almost simultaneously at the first ignition stage, with the presence of CH$_3$Ȯ indicating that CH$_2$O* can be formed. CN has a maximum at the second stage ignition, while NH has two maxima corresponding in time with both the first and second stage ignition events. At both ignition stages, maxima from ÕH radical can be found. The radical ČH is of interest as precursor for ÕH* and C$_2$* and NH*. ČH$_2$ acts as a precursor to C$_2$*. The radicals ÕH, ČH and ČH$_2$ have three maxima. First there is a maximum at times < 5 ms, followed by two delayed maxima corresponding in time with the two ignition stages respectively. The first two maxima are predicted to have a lower molar fraction than the third maximum. Atomic
oxygen, Ō, is studied as a precursor to ŌH*, it has a maximum at both ignition stages. The luminosity of both ignition stages is probably emission from a mixture of several of exited species discussed above.

**Definition of ignition delay in the modeling**

The choice of marker to define the ignition delay time is important when evaluating the performance of the mechanism. In light of the previous discussion, several definitions of ignition were tested in our modeling. Precursors to the radicals considered as likely sources of emission have been tested. These include: \(d\over dt\)max, ŌH\(_{\text{max}}\) and ČH+ČH\(_2\)\(_{\text{max}}\), for both ignition stages, [CH\(_3\)Ō\]\(_{\text{max}}\) and [NO\(_2\)]\(_{\text{max}}\) for the first stage ignition, and [CN]\(_{\text{max}}\), [NH]\(_{\text{max}}\) and [N\(_2\)O]\(_{\text{max}}\) for the second stage ignition. The definitions \(d\over dt\)max, ŌH\(_{\text{max}}\) and ČH+ČH\(_2\)\(_{\text{max}}\) were chosen as they have all been established in the literature as markers for ignition, and are formed within the explosion and consumed relatively fast. The results are plotted in Fig. 9 and one can see that there are no major differences in ignition delay time using the different definitions, for either the first or second stage ignition events. The pressure profiles versus time resulted in two pressure rises separated in time; a maximum gradient in pressure \(d\over dt\)max was calculated for both pressure rises. The first maximum for ŌH and ČH+ČH\(_2\) appears at times considerably shorter than the first experimental maximum. This can contribute to the width of the luminosity maximum, but is unlikely to be an appropriate marker for the maximum. Therefore the second maximum was tested as a marker for the first stage ignition. At temperatures > 1150 K, these two first maxima were difficult to distinguish. Therefore the ignition delay times for the first stage ignition were only calculated up to 1150 K for ŌH and ČH+ČH\(_2\). For the second stage ignition the ignition delay time from Ō\(_{\text{lmax}}\) and ŌH\(_{\text{max}}\) were slightly longer compared to predictions using \(d\over dt\)max, [CN/NH]\(_{\text{max}}\) and ČH+ČH\(_2\)__\(_{\text{max}}\), but negligible on the logarithmic scale, as seen in Fig. 8. As there is negligible difference between the definitions for both ignition stages, the choice of ignition marker in modeling the data is of little consequence and does not influence the interpretation of the mechanism’s performance. The maximum pressure gradient \(d\over dt\)max was used for the modeling predictions as the origin of the experimental luminosity was not experimentally proven.
Comparison between experimental results and modeling

When comparing the experimental results with the modeling predictions for the first stage ignition, the activation energy in the predictions is higher for all mixtures examined, as seen in Fig. 5. The predicted first stage ignition ranges between 1–544 µs in the temperature range 1000–1500 K for Mixture 1 at 8 atm, and coincides with the experimental results ~1100 K. There are minor differences between the predicted activation energy of the first stage ignition for the different mixtures, which is slightly lower in Mixture 3 and negligibly higher in Mixture 2 and Mixture 4, as compared to Mixture 1. These differences in activation energy between the different mixtures are small compared to the experimental activation energy.

For Mixtures 1 and 2 the experiments and modeling are in reasonable agreement with the second stage ignition at 8 atm. Moreover, in the simulated second stage ignition the temperature dependence is stronger than observed in the experimental temperature dependence for Mixture 3, as seen in Fig. 6.

The pressure dependence was examined at 8, 16 and 32 atm for Mixture 1. Unlike the pressure independence in the experimental results, the model predicts decreasing ignition delay times (faster reactivity) for both ignition stages with increasing pressure for Mixture 1.

Conclusions

The ignition of nitromethane/O$_2$/N$_2$ mixtures was characterized as a two-stage process under our experimental conditions. The ignition profiles were examined with respect to pressure and luminosity versus time. Some pressure traces showed a continuous rise stretched over time with one maximum, rather than a sharp von Neuman spike, while some traces had no significant pressure rise at all. From the luminosity traces two maxima were identified, the second coinciding in time with the pressure maximum. The luminosity was used to define the experimental ignition, with the ignition delay times taken at the maximum intensity of the luminosity peaks. Firstly, a fast ignition stage occurs, followed by a second stage ignition with higher luminosity intensity and a larger spread over time. The two-stage ignition process, seen also in detonations [19], and possibly corresponding to the occurrence of several reaction zones in modeled flames [6, 28], is thereby proven experimentally in self ignition. Both the first- and second-stage ignition was examined for pressure and mixture composition dependence. An unusual aspect of nitromethane ignition is that over the conditions examined in the current study, there was no pressure dependence in the ignition delay times for either the first- or second-stage ignition. Mixture composition had no measurable effect on the first-stage ignition delay times. However, for the second-stage ignition, the ignition delay time was
decreased by a factor of approximately four by doubling the O₂ content of the mixture, but reducing the nitromethane content by half only marginally reduced the ignition delay times.

Possible exited species generating the emission were identified as possible ignition markers for simulations from a theoretical discussion based on species observed in the literature. It was shown that the definition of ignition did not affect the evaluation of the performance for the mechanism from Brequigny et al. [30].

Modeling could reproduce the magnitude of the first-stage ignition in reasonable agreement, but the temperature dependence was steeper than for the experimental results. For the second stage ignition the model predictions reproduce the temperature dependence well, and also reproduces well the ignition delay times at 8 atm but under-predicts them at 16 and 32 atm. The mechanism could not reproduce the pressure independence seen in the experimental results for either the first- or second-stage ignition. The kinetics of nitromethane/O₂/N₂ ignitions cannot be fully explained, and warrants further investigation.

The experimental temperature and mixture dependence was analyzed in terms of a correlation fit for each ignition stage, Eqns. 2 and 3. From this analysis the first stage ignition was concluded to be mainly promoted by the concentration of nitromethane, suggesting that this ignition stage is controlled by the thermal decomposition of nitromethane and its neighboring chemistry. In the second stage ignition O₂ has a strong promoting effect on the reactivity, while nitromethane has a mild dampening effect on the ignition. From the correlations the overall activation energy was calculated to be 16.15 ±1.57 kcal mol⁻¹ for the first-stage ignition, and 21.45 ±0.82 kcal mol⁻¹ for the second-stage. Compared to the correlation from Kang et al. [26], the second-stage ignition is in the present study predicted to be more influenced by O₂ and diluent concentrations. The activation energy for the second-stage ignition is in good agreement with the activation energy calculated in the work of Kang et al. In the correlation from Djebaili-Chaumiex et al. [35] the activation energy is in good agreement with the first-stage ignition of the present study. In light of the current work, the ignition events detected by Djebaili-Chaumeix et al. and Kang et al. likely belong to the first- and second-stage ignitions, respectively.

The ignition in Mixture 4 was attributed to a first-stage ignition, but the measurement points at 1509 K and 1779 K where differentiated as the ignition delay times do not follow the general trend of first-stage ignition found in the temperature range 947–1333 K.

The chemistry behind ignition of nitromethane/O₂ warrants further studies, in order to elucidate the pressure independence of the ignition and improve capabilities to reproduce this through simulations.
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References

Figure 1: Traces from pressure and light emission from the ignition of Mixture 1 at 1115 K and 8.15 atm.

Figure 2: Traces from pressure and light emission from the ignition of Mixture 2 at 1220 K and 8.5 atm.
Figure 3: Traces from pressure and light emission from the ignition of Mixture 3 at 1031 K and 8.5 atm.

Figure 4: Traces from pressure and light emission from the ignition of Mixture 4 at 1509 K and 16 atm.
Figure 5: The experimental results for the ignition delay times for the first stage ignition with predictions from modeling.

Figure 6: Experimental results and predictions with modeling for the second stage ignition in Mixtures 1-3 at 8, 16 and 32 atm.
Figure 7: The experimental data from the present study presented in the form of Eq. 2 for the first stage ignition and Eq. 3 for the second stage ignition.

Figure 8: Predicted concentrations over time for selected precursors to plausible light emitting species in Mixture 1 at 1100 K and 8 atm.
Figure 9: Comparison of different definitions of the predicted ignition delay time for the first and second stage ignition in Mixture 1.