

Ignition of nitromethane+O₂+N₂ in a shock tube

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Abstract

The ignition of nitromethane+O₂+N₂ mixtures was investigated using shock tube experiments in the temperature range 1108–1300 K and reflected shock pressures around 8, 16 and 32 atm. During the present study the ignition was examined by pressure and luminosity profiles over time. The temperature and pressure dependence as well as the effect of mixture composition on ignition delays of nitromethane in the presence of oxygen are discussed. Under the experimental condition of the present study, the ignition proceeds through a two stage process. New measurements are compared to data from the literature.

Introduction

Nitromethane is used as a fuel in racing cars as well as in model engines. Despite its practical applications, engine relevant studies of nitromethane combustion are scarce. One important property of a fuel is its ignition characteristics, which give important information when it comes to a potential fuels' suitability for use, especially in combustors. Ignition is highly governed by the specific chemistry of the fuel, with controlling characteristics being activation energy, ignition profiles of various properties and species over time and ignition delay times.

The chemistry controlling the ignition of nitromethane can be investigated in kinetic studies using shock tubes. The thermal decomposition of nitromethane without the presence of an oxidizer has been examined in several shock tube studies [1–6]. Glänzer and Troe [2] examined CH₃NO₂ and NO₂ concentration profiles using shock waves in the temperature range 900–1500 K from 0.1–20 atm with varying concentrations of Ar bath gas. It was experimentally shown by Zaslanko et al. [1] that in the temperature and pressure ranges 1030–1580 K and 1.0–2.8 atm, the thermal decomposition produced CH₃O and CH₃ONO. The latter was explained as the result of recombination of CH₃ and NO₂. Kuznetsov et al. [5] monitored the formation of NO₂ in nitromethane decomposition through shock tube experiments in the temperature range 1190–1490 K and at 1.5 atm. The authors confirmed that the NO₂ profile had a convex shape consistent with a typical decomposition product, and that the disappearance of nitromethane and the formation of NO₂ coincided. Through theoretical analysis it was also concluded that isomerization of nitromethane to CH₃ONO was not competitive compared to the thermal decomposition. The thermal decomposition of nitromethane was shown to be pressure dependent in studies covering a pressure range from 0.1–40 atm [1, 2, 6]. In the thermal decomposition study of Hsu and Lin [4] NO and CO profiles were measured in the temperature range 940–1520 K and at pressures 0.4–1 atm. From the NO and CO profiles the

authors showed that NO is formed early during the ignition, while CO is formed at a later stage.

In its chemical structure nitromethane contains two oxygen atoms in a nitrogen dioxide group (NO₂). Because of the oxygen content, nitromethane can act both as a fuel and as an oxidizer in combustion processes. This aspect of nitromethane combustion was noted in the study of Fells and Rutherford [7], where the effect of nitromethane addition to methane on the burning rate of methane flames was examined.

The ignition of nitromethane in the presence of O₂ has only been previously examined in the studies of Borisov et al. [3] and Kang et al. [8]. In [3] the autoignition was measured in a by-pass apparatus for nitromethane in the presence of O₂ and the diluents Ar, N₂ and He to determine the rate constant for the thermal decomposition of nitromethane. Kang et al. [8] examined the ignition delay times of nitromethane+O₂+Ar mixtures by tracking the von Neuman pressure spike in the temperature-range 1250–1900 K and pressure of about 0.2 atm for several different nitromethane+O₂+Ar compositions. The von Neuman spike is the rapid rise in pressure typically occurring at ignition of explosives in a shock tube. The authors mention that the species CH₂O, OH, and NO were detected through emission after the reflected shock had passed, referenced in [8] as a coming publication but is, to the best of the authors knowledge, not yet published. A correlation between mixture composition and ignition delay times was presented by Kang et al. [8]. The overall activation energy was found 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. All of the mixtures investigated by Kang et al. [8] were measured at different equivalence ratios (ϕ). As ϕ is independently a factor affecting the ignition, the effect of mixture composition on ignition is warranted to be revisited.

In the current study the ignition of nitromethane+O₂+N₂ mixtures has been examined through shock tube experiments. Different aspects of

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nitromethane ignition, pressure dependence and effects of fuel and oxidizer composition at the same equivalence ratio, were examined.

Experiments

Experiments were performed in the high pressure shock tube at the National University of Ireland, Galway. The experimental setup is described in detail in the work of Nakamura et al. [9]. The gas mixture and driven section of the shock tube was kept at 323 K to avoid condensation of the fuel.

The experiments were performed in the temperature range 1100–1300 K at approximately 8, 16 and 32 atm. The ignition was tracked using unfiltered light emission from an optical window at the sidewall, 10 mm from the endwall, transparent within a wavelength range of 150–2000 nm and recorded with a Photodiode array detector (PDA) within the range 240–530 nm. The ignition delay was measured from the time that the reflected shock wave triggered the pressure transducer at the endwall to the maximum intensity of light emission peak. The pressure profile of the ignition was also recorded by two pressure transducers on the endwall and at the sidewall, 10 mm from the endwall. The pressure transducers are Kistler 603B made by Kistler Group, Inc (endwall) and Model 113B24 made by PCB Piezotronics, Inc (sidewall).

The nitromethane was from Sigma-Aldrich Ireland Limited at 95 % purity. The O₂ (99.5 %) and N₂ (99.99%) were supplied by BOC Ireland Limited.

Three different gas compositions with varying fuel and O₂ content were examined. The gas mixtures were prepared and kept in a mixing tank at low pressure, at 323 K with continuous stirring. Partial pressure was used to control the mixture compositions. An issue with nitromethane is the risk of condensation. To avoid this, the liquid nitromethane was gradually injected to the mixing tank at continuous monitoring of the pressure. Between each injection of nitromethane the fuel was left to vaporize and equilibrate 5–30 min. The partial pressure of the nitromethane was kept about three times lower than the saturation pressure of nitromethane. The three mixture compositions are presented in Table 1.

Uncertainty limits of the measurements are ± 15 K in reflected shock temperature, T₅, ± 15 % in ignition delay time, τ , and ± 2 % in mixture concentration, as estimated in Nakamura et al. [9].

The second stage ignition will in the present paper be shown 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 [10]. For nitromethane flames, NO has been shown to be formed but not consumed [11, 12]. For this reason, NO was

chosen as the final product for nitromethane-containing nitrogen in the definition of ϕ .

Table 1: Mixture compositions in mole % of the nitromethane+O₂+N₂ mixtures examined in the present study.

Mixture	CH ₃ NO ₂	O ₂	N ₂	ϕ
1	4	5	91	1.0
2	2	5	93	0.5
3	4	10	86	0.5

Results and Discussion

Ignition profiles over time of nitromethane+O₂+N₂ mixtures

To accurately define the ignition of a fuel, first the ignition profiles versus time need to be explored. Both pressure and luminosity are utilized to investigate the ignition characteristics of nitromethane/O₂/N₂ mixtures. Mixtures 1–3 are in the following discussed separately with respect to the characteristics of each mixture while Figs. 1–3 are typical examples of measurement results, respectively, clearly illustrating the similarities and differences between the mixtures. In Figs. 1-3 the luminosity is multiplied by a factor of 20. In the following discussion the ignition of Mixtures 1–3 will be described as a two stage process. In Figs. 1–3 this can be identified from the luminosity trace over time as two separate intensity maxima.

Figure 1 presents an example of the ignition of Mixture 1, at $\phi = 1.0$ and 8.15 atm and 1115 K, with the experimental pressure and luminosity profiles over time. From the pressure trace in Fig. 1, it can be seen that after the arrival of the shock wave there is no von Neuman spike for either the first or second stage ignitions. Neither of the ignition stages is distinguishable from the pressure trace. Once the sidewall pressure transducer is activated, there is a continuous increase in pressure which reaches a plateau. The plateau coincides in time with the maximum of the second luminosity maximum. The pressure rise observed indicated that there is a prolonged activity in the gas mixture after the reflected shock wave reaches the end-plate but the pressure trace cannot independently be used to determine if ignition occurred in Mixture 1.

In the luminosity traces for Mixture 1, two ignition stages separated in time were detected. There is a fast ignition as a first stage, starting simultaneously with the arrival of the shock wave, with a maximum intensity occurring on a time scale smaller than 50 μ s. This is followed by a separate luminosity peak with a higher maximum luminosity intensity and broader distribution over time, here defined as the second stage ignition. The difference in intensity between the first and second stage ignition can be explained by the larger amount of light emitting species present during the second stage or different light emitting species present in the two ignition stages.

Mixture 2 was prepared at $\phi = 0.5$ with the same oxygen content but 50% less nitromethane compared to Mixture 1. An example pressure trace, representing the measurements for Mixture 2, is shown in Fig. 2. Unlike the pressure in Mixture 1 there is no clearly defined pressure rise after the arrival of the shock wave.

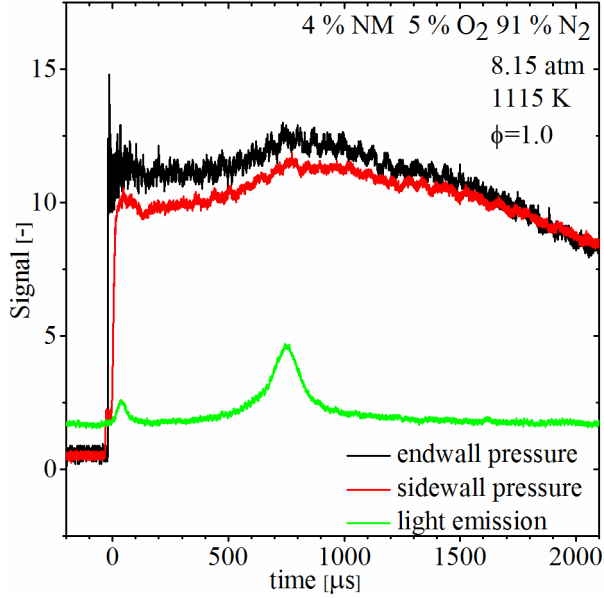


Figure 1: Traces from pressure and light emission from the ignition of mixture 1 at 1115 K and 8.15 atm.

The lack of pressure rise in Mixture 2 indicates that there is no major change in volume during the potential ignition, or no ignition occurs. The chemical activity in this mixture is likely too low to be detected from the pressure trace. From the luminosity traces recorded for Mixture 2, a similar pattern as in the luminosity from Mixture 1 is seen, with two separated ignition stages. The first stage starts with the arrival of the reflected shock wave, while the second stage of ignition is delayed. The second stage has a larger 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 ignition, while preserving similar ignition characteristics over time compared to Mixture 1.

Mixture 3 was also prepared at $\phi = 0.5$, same as Mixture 2, with the same nitromethane content as in Mixture 1 but with double the O_2 content. Figure 3 shows the pressure and luminosity traces for Mixture 3 at 1031 K and 8.47 atm. For Mixture 3 there is no defined pressure rise in the measurements at temperatures >1032 K. Measurements at 984 K and 1031 K show clear rise in the pressure traces. From the pressure traces, with exception for the measurements at 984 K and 1031 K, no clear indication of ignition can be seen. In the luminosity traces for Mixture 3, it can be seen that both ignition stages are close together in time, almost indistinguishable, with only a small bump on the side of the luminosity distribution indicating the

presence of the first ignition stage. The ignition does not start at the arrival of the shock wave in the measurements at ≤ 1186 K, but there is a time delay, as can be seen in Fig. 3. For the measurements at 984 K and 1031 K, the inclinations of the luminosity and pressure rise coincide in time.

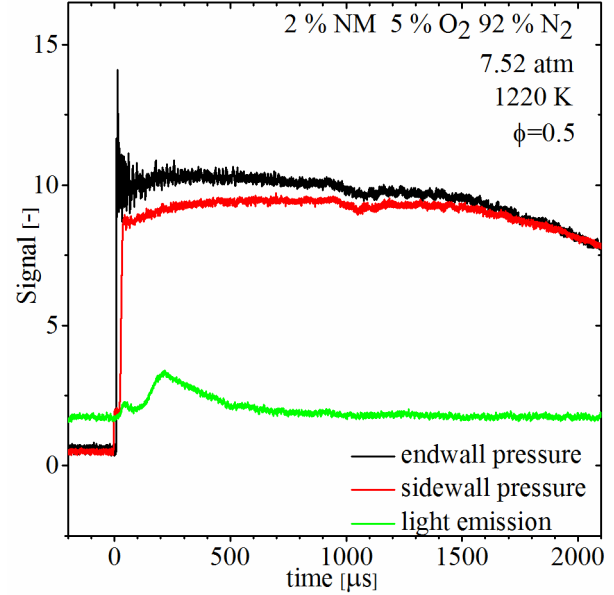


Figure 2: Traces from pressure and light emission from the ignition of mixture 2 at 1220 K and 8.52 atm.

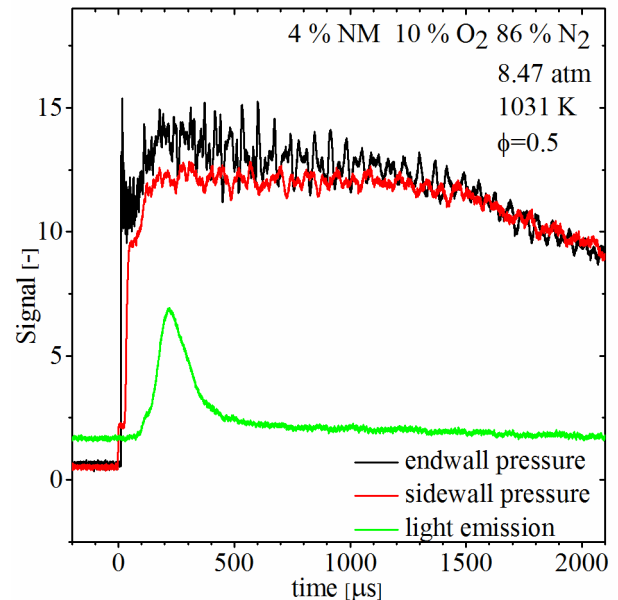


Figure 3: Traces from pressure and light emission from the ignition of mixture 3 at 1031 K and 8.47 atm.

Guirguis et al. [13] 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. In light of the present study, this could indicate that a second stage ignition occurred in these cases, for pure nitromethane ignition.

As the experimental pressure traces cannot be used to determine if ignition has occurred for Mixtures 1–3, with two exceptions, Mixture 3 at 984 and 1031 K, the luminosity is used to define the ignition delay times for all measurements in the present study.

Ignition of nitromethane in the presence of oxygen exhibits an unusual ignition behavior, with two separated ignition stages under the experimental conditions in the present study, as exemplified by the luminosity profiles in Figs. 1–3. Under these conditions the first stage ignition was fast, with luminosity maximums at $< 50 \mu\text{s}$, 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. Therefore the second stage is investigated further for temperature dependence.

Temperature and pressure dependence of the second stage ignition

All three mixtures were investigated for temperature dependence and the pressure dependence was examined for Mixture 1. In Fig. 4 the experimental data for the second stage ignition is presented for Mixture 1 at 8, 16 and 32 atm over the temperature range 1108–1300 K. The experimental second stage ignition delay is decreasing with temperature, as the reactivity is increasing.

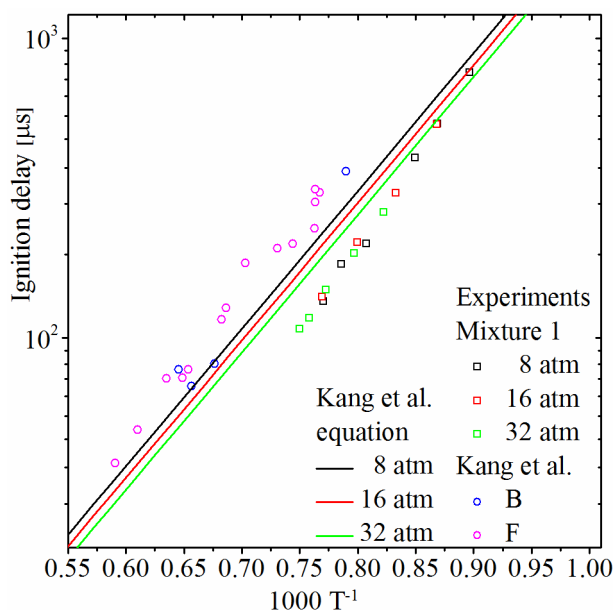


Figure 4: Experimental results for Mixture 1 at 8 atm, 16 atm and 32 atm with prediction from the Kang et al. [8] equation and experimental results from the same work.

For many fuels, the ignition is sensitive towards pressure [14]. Typically the ignition of fuels is faster with increasing pressure. This can be explained by the higher concentrations of fuel and O_2 in the gas mixture.

An unusual aspect with the examined nitromethane ignition is that it showed no pressure dependence over the conditions examined in the current study. The pressure dependence was examined for Mixture 1 by

performing measurements at 8, 16 and 32 atm. To confirm that the pressure independence is valid at other mixture compositions, Mixture 3 was studied at 984–1198 K at 8 atm and two temperatures, 1086 K and 1149 K at 16 atm, resulting in no change in ignition delay with pressure.

The experimental results by Kang et al. [8] were measured at ~ 0.2 atm and ϕ close to 1 in two of their measurement series. The measurement series B and F have the compositions nitromethane/ O_2 / Ar , $\text{B}=0.482:0.635:0.553$ and $\text{F}=0.353:0.471:0.824 \text{ mol m}^{-3}$ at $\phi = 0.94$ and 0.96 , respectively. These two measurement series, B and F, are compared to the experimental results of the present study in Fig. 4, to explore similarity in the effective activation energy. The values for ignition delay times from Kang et al. [8], plotted in Fig. 4, were obtained through data digitizing in the present study.

The correlation equation from Kang et al. [8] was derived from five rich flames with $\phi \approx 1.25$ – 3.12 , and four lean and near stoichiometric flames with $\phi \approx 0.80$ – 0.96 . The temperature region for the equation is 1250–1900 K, with only overlapping temperature region of 1250–1300 K between the present study and Kang et al. [8].

Predictions from the Kang et al. [8] equation for Mixture 1 results in higher ignition delay times, with a weaker temperature dependence as compared to the experimental results for Mixture 1 as shown in Fig. 4. The pressure dependence in the predictions is mild. Over the range of measured pressures, the second stage ignition did not change with pressure for the examined temperatures. The first stage ignition was $< 50 \mu\text{s}$ at all pressures examined.

Effect of initial gas mixture composition

To investigate the effect of fuel and oxidizer on the ignition, the temperature dependence of the second stage ignition was studied for three gas mixtures. The stoichiometric Mixture 1 is compared to two Mixtures, 2 and 3, with the same $\phi = 0.5$ but with reduced nitromethane in Mixture 2 and increased O_2 content in Mixture 3, as compared to Mixture 1. As can be seen in Fig 5, 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 O_2 content the effect on the ignition delay was considerably stronger with a reduction of the ignition delay times by ~ 4 times compared to Mixture 1. The effective activation energy of the second stage ignition of Mixture 3 is weaker than for Mixtures 1–2.

Predictions from the equation by Kang et al. [8] for ignition delays related to mixture composition for the mixtures of the present study were compared to the experimental results of the present study in Fig. 6. The predictions are higher than the experimental results from the present study with slightly weaker temperature dependence. The effect of mixture composition follows the same general trend but the magnitude of the effects was different. In the conclusions of Kang et al. [8] it

was stated that nitromethane has a dampening effect on the ignition resulting in longer ignition delay times with higher nitromethane content, consistent with the findings of the present study. However, in the experimental results of the present study, the O₂ content had a more pronounced effect on the ignition delay times than in Kang et al. [8].

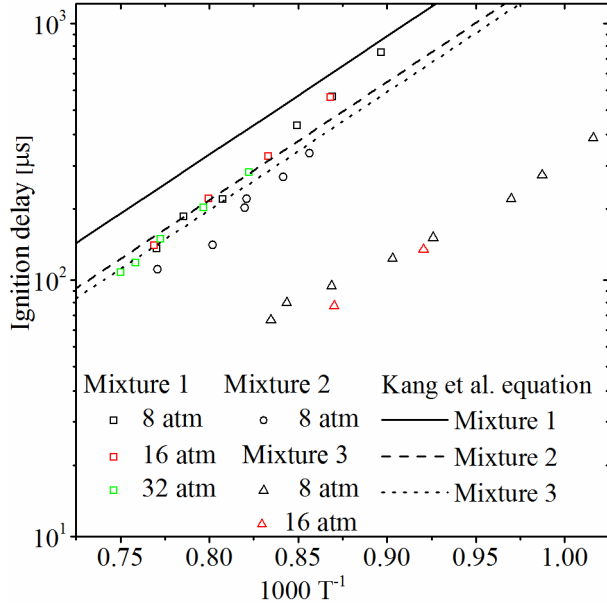


Figure 5: Experimental results with predictions from Kang et al. [8] equation for Mixtures 1–3 at 8 atm, 16 atm and 32 atm.

By multiple regression analysis the effect of temperature and mixture composition was evaluated for the experimental results from the present study. The concentration is in mol m⁻³, temperature in K and R in kcal K⁻¹ mol⁻¹. The overall activation energy, E_a, was determined to be 21.45 (±1.67) kcal mol⁻¹ in the present study. This is within the uncertainty of the overall activation energy in Kang et al. [8] which was calculated to be 21.36 (±0.51) kcal mol⁻¹. The analysis predicts a large influence of O₂, [O₂]^{-2.32}, commonly the influence on ignition is in the order of [O₂]^{-0.3>-1.5} [8].

$$\tau = 10^{-3.38} e^{-E_a/RT} [\text{CH}_3\text{NO}_2]^{0.57} [\text{O}_2]^{-2.32} [\text{N}_2]^{1.66} \quad (\text{Eq. 1})$$

The experimental results of the present study are presented in two correlation forms with exponent coefficients from Eq. 1 and the Kang et al. [8] equation in Fig. 6. There it can be seen that the correlation in Eq.1 represents the experimental result satisfactory, with a close linear agreement. The experimental results for Mixtures 1-2 are also well represented by the Kang et al. [8] correlation, but for Mixture 3 the experimental results do not fit in the correlation form. There is an agreement between the two correlation equations, which coincide as can be seen in Fig. 6.

From Eq. 1 it can be seen that O₂ is predicted to have a larger influence on the ignition as compared to the analysis by Kang et al. [8]. The difference between

the Kang et al. [8] equation and the fit of the experimental data for Mixture 3 in the present study could be attributed to that the equations were generated at different conditions. The correlation of Kang et al. [8] was calculated from predominantly richer mixtures and higher temperatures, than in the present study with one stoichiometric mixture and two mixtures at $\phi = 0.5$ and at 1100–1300 K. As the activation energies in the present study and Kang et al. [8] are in close agreement, the difference in temperature dependency between the studies could be an effect of mixture concentrations.

The experimental results from Borisov et al. [3] for the mixture of nitromethane:O₂:N₂, 0.20:0.17:0.63 was inserted into both correlations, Eq. 1 and Kang et al. [8], and compared with the experimental results of the present study. From analysis of the Borisov et al. [3] data, a better fit to the correlation from Kang et al. [8] than to Eq. 1 was obtained.

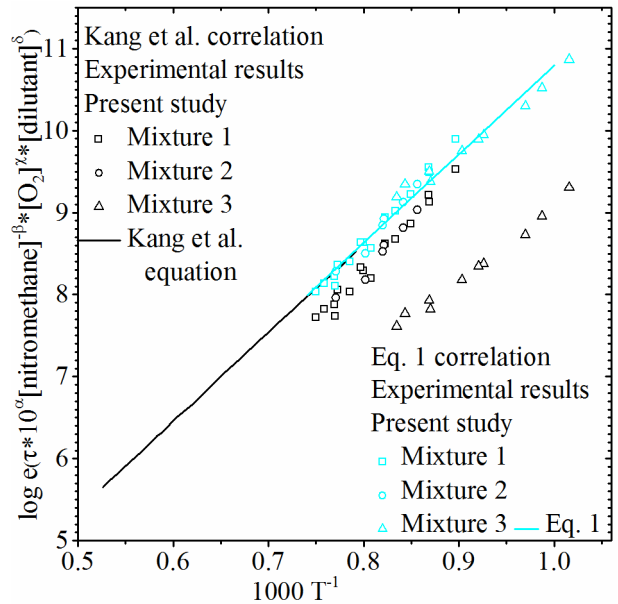


Figure 6: The experimental data from the present study in the form of the correlation function from Kang et al. [8] and the correlation function presented in Eq. 1.

Conclusions

The ignition of nitromethane+O₂+N₂ mixtures was characterized as a two stage process under the experimental conditions in the present study. The ignition was defined as the maximum intensity of the luminosity peaks. First a fast ignition occur at times < 50 μs, followed by a temperature dependent second stage ignition with higher luminosity intensity and a larger spread over time. The second stage ignition was examined for pressure and mixture dependence. It was found that ignition delays of the second stage were independent of pressure. The second stage ignition was decreased by a factor of ~4 by doubling the O₂ content of the mixture, but .reducing the nitromethane content by half reduced the ignition delay times marginally. The temperature and mixture dependence was analyzed in terms of a correlation fit, Eq. 1, with a larger O₂ and diluent influence as compared to the correlation from

Kang et al. [8]. From the correlation the overall activation energy was calculated to be 21.45 (± 1.67) kcal mol⁻¹, in good agreement with Kang et al. [8]. The agreement of the experimental results in the present study and experimental results from Borisov et al. [3] was compared through correlations from Eq. 1 and Kang et al. [8]. The results motivate continued work, with a reexamination of the unusual O₂ dependence in Eq. 1 by further studies of Mixture 3.

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