Nitromethane Ignition Behind Reflected Shock Waves: Experimental and Numerical Study

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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.

Keywords: Nitromethane, Ignition Delay Time, L9 Taguchi Array, Detailed Kinetics Modeling, Shock Tube.

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 [7-10,11,12]).

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 CH_3NO_2 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 [4] 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 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, Naucr 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 ($\text{CH}_3\text{NO}_2 + 0.75 (\text{O}_2 + 3.76 \text{ N}_2) \rightleftharpoons \text{CO}_2 + 1.5 \text{ H}_2\text{O} + 3.32 \text{ N}_2$). Naucr 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 end wall 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 $A^2\Sigma^+ \rightarrow X^2\Pi$ 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 et al. [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 to 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 NM. Changing only dilution level to 90% Ar results in CH_4 producing around 30 times more OH^* than NM (not shown on Fig. 1). This very low level of NM OH^* emission is the reason for the low SNR of experimental OH^* profiles in this study. Despite the lower-than-normal SNR, the key features were nonetheless adequately resolved for determining ignition delay times.

Figure 1: Computed OH^* profiles using the mechanism of Brequigny et al. [3] at 10 atm, for mixtures of methane and nitromethane diluted in 98% Ar at a) the same temperature (1500 K), and b) the same ignition delay time (1500 K (NM) and 1745 K (CH_4)). The zoomed-in section presents the same results but with the OH^* profiles for NM multiplied by around 300 to clearly visualize the time at which the OH^* ignition peak is reached for the two mixtures.

2.3. Mixture preparation

Mixtures were prepared manometrically in a stainless-steel mixing tank (3.05-m length, 15.24-cm i.d.) equipped with a perforated stinger traversing its center to allow for rapid, turbulent mixing. Nitromethane (>98.5%, Sigma Aldrich), liquid at room temperature, was introduced into a vial and de-gassed several times prior to being evaporated to no more than 60% of its vapor pressure at room temperature. The gases (O_2 (Praxair) and Ar (Acetylene Oxygen Company)) were ultra-high purity grade (99.999%). Mixtures were allowed to rest for at least 2 hours prior to making the first run to further ensure homogeneity through diffusion processes.

A test matrix was developed to minimize the number of experiments yet still validate the model over a wide range of conditions in terms of fuel concentrations, pressures, and equivalence ratios. Three levels of each of the aforementioned variables were assembled into a L9 Taguchi array [30], a method that has been used several times by our group in the past for the efficient, balanced coverage of a wide parameter space [24-32]. Table 1 summarizes the mixtures covered within this L9 array.

Table 1: Mixtures and experimental conditions covered by the L9 array (*: Maximum feasible pressure due to nitromethane vapor pressure limitation).

Mixture#	P (atm)	ϕ	% Ar
1	2	0.5	90
2	2	1.0	95
3	2	2.0	98
4	10	0.5	95
5	10	1.0	98
6	10	2.0	90
7	30	0.5	98
8	10*	1.0	90
9	14*	2.0	95

As indicated in Table 1 for mixtures 8 and 9, due to the relatively low vapor pressure of nitromethane, it was anticipated that for low- and intermediate-dilution levels it would not always be possible to reach a reflected-shock pressure of 30 atm for some mixtures. This limitation is due to the inability of reaching high enough pressures of NM vapor in the mixing tank to allow total mixing tank pressures high enough to fill the shock tube to desired levels. To overcome this limitation, mixtures 8 and 9 were prepared directly in the driven section of the shock tube. Due to the absence of a perforated stinger or any other mixing device, it was found necessary to leave the mixture at rest for at least 10 hours prior to running the experiment (to ensure homogeneity by diffusion process). The measured leak rate of the shock tube was below 1 mTorr/min, which induced an uncertainty in the equivalence ratio of the mixture that is well within the uncertainty in the ignition delay time measurement and temperature determination, and was therefore considered negligible (the uncertainty in the ignition delay time is discussed below). To illustrate this statement, Mix 9 would at worst case be between $\phi = 1.97$ and 1.98 instead of the projected $\phi = 2.0$, for example.

Polycarbonate (lexan) and pre-scored aluminum diaphragms were used. A cross-shaped cutter was employed with polycarbonate diaphragms to facilitate breakage of the diaphragm and prevent diaphragm fragments from tearing off. Helium was used primarily as the driver gas during this study, although air or nitrogen was sometimes added to the helium driver gas for high-pressure experiments, to reduce the speed of the incident shock wave and reach lower temperatures without having to increase the initial pressure in the test section (because of the limitation induced by the low vapor pressure of NM). As can be seen in Table 2, additional mixtures and conditions to the L9 array were also studied. Mixtures 4, 5, and 7 were also investigated at low pressure (~ 2 atm), while a higher dilution level of Ar was investigated and designated as Mix 10.

Table 2: Mixture compositions and conditions investigated for the ignition delay time measurements.

Mixture	ϕ	CH ₃ NO ₂ %	O ₂ %	Ar %	Avg. P ₅ (atm)	T ₅ range (K)
1	0.5	4.0	6.0	90.0	2.1	920-1215
2	1.0	2.857	2.143	95.0	1.9	1215-1495
3	2.0	1.455	0.545	98.0	1.8	1420-1595
4	0.5	2.0	3.0	95.0	2.0	1080-1450
					11.5	955-1210
5	1.0	1.143	0.857	98.0	1.9	1300-1575
					10.4	1255-1485
6	2.0	7.273	2.727	90.0	8.6	890-1010
7	0.5	0.8	1.2	98.0	2.0	1215-1460
					34.3	1185-1375
8	1.0	5.714	4.286	90.0	9.4	895-1055
9	2.0	3.64	1.36	95.0	13.7	875-1080
10	1.0	0.571	0.429	99.0	1.9	1340-1540

3 Experimental Results

3.1 Methods of determination of the ignition delay time

Two definitions of the ignition delay time are used in this study. The first definition corresponds to the time between the passage of the reflected shock wave, indicated by a pressure jump in the signal delivered by the sidewall pressure transducer (defining time 0 in our study), and the intersection of lines drawn along the steepest rate-of-change of OH* de-excitation and a horizontal line which defines the zero-concentration level, as can be seen in Fig. 2 (a) and (b). The moment of ignition was also defined as the top of the ignition peak ($\tau_{\text{ign}100\%}$). Note that due to a continuous increase in the slope of the main ignition peak right after the first OH* peak, the ignition delay time was measured at the peak of the OH* signal only for Mix 7 high-pressure (~ 35 atm) cases (Fig. 3).

As can be seen in Figs. 2 and 3, the OH* profiles of NM vary significantly with the equivalence ratio, the pressure, and the dilution level. Several OH* profiles illustrating these variations are presented and discussed later in this paper. The first peak right after the arrival of the reflected shock wave, observed here with NM, was also observed and discussed with n-nonane in Rotavera et al. [33]. The appearance of this peak was explained by the formation of a methyl radical followed by a series of H-abstractions leading to CH; the latter reacting with O₂ to form OH* as described in Hall and Petersen [28]. Due to the propensity of NM to form CH₃ by thermal dissociation at the high temperatures investigated, this mechanism is believed to be responsible for the first OH* peak observed here.

It is worth mentioning that the width and intensity of this first peak is also subject to experiment-induced broadening. This broadening is due to the passage of the reflected shock wave across the path of the optical setup, as detailed in Rotavera et al. [33]. The importance of this broadening effect varies with the velocity of the reflected shock wave (which varied over a large span during this study due to the large range of conditions investigated). If the response function of the experimental setup were known, it can be used to “correct” the computed result from the model to better compare with the actual experiment. However, characterizing the broadening of the first peak was beyond the scope of this work, so no attempt was made to further analyze the magnitude and shape of the first peak. To document the data behavior and to serve as a qualitative

indication of the evolution of this first peak as a function of the mixture and condition, the evolution with the temperature of the ratio between the maximum intensity of the first peak and the maximum intensity of the second (ignition) peak is provided as supplementary material for each mixture and condition. Note that Mix 6, Mix 8, and Mix 9 do not exhibit any discernable first peak.

Figure 2: Typical sidewall experimental pressure and OH* profiles and methods of determination of the ignition delay time.

Figure 3: Typical sidewall experimental pressure and OH* profiles and method of determination of the ignition delay time for the high-pressure (~ 35 atm) cases with Mix 7.

There are essentially two main sources of uncertainty in the ignition delay time: the uncertainty in the determination of the temperature behind the reflected shock wave (T_5) and the uncertainty associated with the determination of the steepest rate of change or maximum of OH* profiles. Under the present conditions, the experimental setup and method used allow for a determination of T_5 within less than 10 K, which is a typical largest uncertainty with classic hydrocarbons [25-27, 24]. However, due to the low intensity of the OH* profile and associated SNR of some experiments, the total uncertainty in τ_{ign} reported in this study is estimated to be up to 20% (compared to 10% or less in our previous studies). This includes the minimal

temperature variation with facility dP/dt , which was always observed to be less than 2%/ms before the ignition event. All of the ignition delay times presented in the figures below are reported with their respective associated conditions (T_5 , P_5) in the Supplementary Material section.

3.2 Experimental results

Although useful for covering a wide range of conditions in an efficient manner, a minor drawback of a L9 array is that it does not allow direct comparison of the data by varying only one parameter at a time. However, since a few extra conditions and mixtures were studied, it was possible to compare the effects of changing only equivalence ratio, pressure, or dilution level at a number of conditions, and these are shown in the following figures. OH* chemiluminescence profiles are also presented in this section to exhibit the effects of changes in some conditions on the shape of the profiles.

Equivalence ratio effect:

The effect of the equivalence ratio on the ignition delay time of NM is visible in Fig. 4. In this figure, results between $\phi = 0.5$ and 2.0, for mixtures diluted in 98% Ar and at 1.9 atm, are presented for the two kinds of methods used for the ignition delay time measurements. As can be seen, increasing the equivalence ratio leads to a significant increase in the ignition delay time under these conditions. For example, Fig. 4 (a), at a temperature around 1420 K, the ignition delay time is increased by more than a factor 3 when the equivalence ratio is doubled, from 0.5 (135 μ s) to 1.0 (450 μ s). This increase becomes larger than a factor of 13 when comparing the fuel lean (135 μ s) and the fuel rich (1800 μ s) cases at this temperature. A similar behavior is observed for the peak OH* method of determination of the ignition delay time ($\tau_{\text{ign100\%}}$, Fig. 4 (b)).

Figure 4: Effect of the equivalence ratio on the ignition delay time for 98% Ar and reflected-shock pressures around 1.9 atm. (a) using the maximum slope of OH* signal, and (b) using the maximum OH* signal.

To illustrate the variations in the OH* profiles with equivalence ratio, normalized OH* profiles for the 98% Ar mixtures at low pressure are compared in Fig. 5 for (a) a similar temperature (1465 ± 8 K) and (b) a similar ignition delay time using the maximum slope method (445 ± 12 μ s). Profiles were normalized to the highest value reached, whether this value is reached on the first or the second peak. This normalization procedure makes the ignition peak look very small for the $\phi = 2.0$ case in Fig. 5 (b). However, the ignition delay time is still easily identified using both definitions.

Figure 5(a) shows that for a temperature of around 1460 K the second peak, corresponding to the ignition event, is the highest for the fuel lean case, whereas the highest OH* amount is reached at the first peak around $t = 0$ for the stoichiometric case. One can also see that as the equivalence ratio increases, the peak corresponding to the ignition event decreases in intensity and lasts longer (gets wider). Figure 5(b) shows that when matching ignition delay times for different equivalence ratios, the maximum OH* intensity is also reached on the first peak for the stoichiometric and fuel rich conditions, whereas the maximum is reached on the ignition peak for the fuel lean case (but the intensity between the two peaks is relatively close in this case). Again, the intensity of the ignition peak tends to decrease as the equivalence ratio increases, despite the fact that, for a given ignition delay time the temperature increases with the equivalence ratio (OH* intensity is typically increasing with the temperature for a given mixture, as can be seen in Fig. 1 and in Kalitan et al. [34] and de Vries et al. [35]). One can therefore conclude from these observations that the intensity of the OH* ignition peak significantly decreases with the increase in equivalence ratio.

Figure 5: Evolution of the OH* profile with time for (a) similar temperatures and (b) similar ignition delay times using the maximum slope method for mixtures diluted in 98% Ar, around 2 atm, and for equivalence ratios of 0.5, 1.0, and 2.0.

Pressure effect

The effect of pressure on the ignition delay time is visible in Fig. 6 for (a, b) Mix 4, (c, d) Mix 5, and (e, f) Mix 7. For all cases, an increase in pressure induces a decrease in the ignition delay time. However, the

amplitude of this decrease in the ignition delay time seems to be strongly dependent on both the equivalence ratio and the dilution level. The influence of the equivalence ratio on the pressure effect can be observed by comparing results at $\tau_{\text{ign}100\%}$ for Mix 5 (d) and Mix 7 (f). Both mixtures were diluted in 98% Ar, but when the pressure is increased by a factor of around 5 for Mix 5 ($\phi = 1.0$) (from around 1.9 atm to around 10.4 atm), the ignition delay time decreases by a factor between 1.5 (high temperature) and 1.7 (low temperature). For the Mix 7 case ($\phi = 0.5$), despite a larger increase in pressure by a factor of around 17 (from about 2.0 to 34.3 atm), the ignition delay time is decreased by only a factor of around 2.0. The dilution level influence on the pressure effect can be seen by comparing data from Mix 4 (b), 95% Ar, and Mix 7 (f), 98% Ar, both with the same equivalence ratio (0.5). The decrease in the ignition delay time for Mix 7 (described above) is moderate despite the large increase in pressure compared to Mix 4. The ignition delay time is decreased by a factor of around 3 when the pressure increases by a factor close to 6 with Mix 4.

The effects of pressure and temperature on the OH* profile can be observed in Fig. 7. For a mixture at $\phi = 0.5$ and 95% Ar (7a), OH* profiles at identical temperature with pressures around 10 atm and 2 atm and for similar ignition delay times (corresponding to a higher temperature of 1226 K for the 2 atm case) are visible. As can be seen, the shapes of the profiles are somewhat similar regardless of the pressure or the temperature. However, for the high-pressure case the first peak is smaller and the ignition peak is narrower. The experiments were selected in similar fashion for a stoichiometric mixture diluted in 98% Ar (b). In this case, both the first and ignition peaks have the same intensity for each pressure and temperature. Finally, a mixture at $\phi = 0.5$, 98% Ar and at the same temperature (1371 K) was investigated at around 2 and 34 atm (c). As can be seen, the first peak has the highest intensity for the high-pressure case, whereas the highest intensity corresponds to the ignition peak at 2 atm. Note that the difference is not large, especially given the large pressure difference between the two profiles.

Figure 6: Effect of the pressure on the ignition delay time of NM for (a, b) a mixture at $\phi = 0.5$ diluted in 95% Ar, (c, d) a mixture at $\phi = 1.0$ diluted in 98% Ar, and (e, f) a mixture at $\phi = 0.5$ diluted in 98% Ar.

Figure 7: Evolution of the OH* profile with the pressure (a) low- and high-pressure experiments at a similar temperature or a similar ignition delay time at $\phi = 0.5$, 95% Ar, (b) a similar temperature or a similar ignition delay time at $\phi = 1.0$, 95% Ar, and (c) a similar temperature $\phi = 0.5$, 95% Ar.

Dilution level effect

The effect of the dilution level in Ar on the ignition delay time of NM can be seen in Fig. 8 for the low-pressure cases and in Fig. 9 for the intermediate-pressure cases. For nearly all conditions, the decrease in the dilution level leads to a decrease in the ignition delay time. This decrease seems however to be dependent on both the pressure and equivalence ratio. For the low-pressures cases, Fig. 8, the decrease in the ignition delay time is proportionally larger on the low-temperature side than on the high-temperature side. At $\phi = 0.5$ (Fig. 8

(a)), decreasing the dilution level from 98% to 90% of Ar significantly reduces the ignition delay time at around 1220 K, from around 1400 μs for Mix 7 (98% Ar) to 400 μs and 75 μs for Mix 4 (95% Ar) and Mix 1 (90% Ar), respectively. The difference between the mixtures diminishes as the temperature increases, as the ignition delay time is around 2.5 times shorter for Mix 4 than for Mix 1 at around 1450 K, with a factor of 3.5 at 1220 K. A similar observation can be made for the ignition delay time determined at the maximum of the OH* ignition peak (Fig. 8 (b)) and for the stoichiometric cases, Fig. 8 (c, d). As can be seen for the stoichiometric case, ignition delay times for the highly diluted mixtures (Mix 10, 99% Ar) are even lower than for Mix 5 (98% Ar) above 1500 K (although this behavior was not observed with $\tau_{\text{ign}100\%}$, Fig. 8 (d)). For the lowest temperature common to these three mixtures, 1340 K, the ignition delay time decreases from around 2050 μs (2200 μs for $\tau_{\text{ign}100\%}$) (Mix 10, 99% Ar) to around 1215 μs (1530 μs for $\tau_{\text{ign}100\%}$) (Mix 5, 98% Ar) and around 370 μs (430 μs for $\tau_{\text{ign}100\%}$) (Mix 2, 95% Ar).

Figure 8: Effect of the dilution level in Ar on the ignition delay time of NM at around 2 atm for (a, b) $\phi = 0.5$, and (c, d) $\phi = 1.0$.

For the high-pressure case, Fig. 9, a very large difference can be observed for stoichiometric data (a, b), between Mix 5 (98% Ar) and Mix 8 (90% Ar). Note that the two sets of data do not overlap in terms of temperatures within the range of possible observation test times. On the other hand, data at fuel rich

conditions (Fig. 9 (c, d)) are very close to each other despite the change in dilution level (90% Ar for Mix 6 and 95% Ar for Mix 9). Note that this small difference can also be partly due to the difference in pressure between the two sets of data, around 8.6 atm for Mix 6 and around 13.7 atm for Mix 9.

Figure 9: Effect of the dilution level in Ar on the ignition delay time of NM at around 10 atm for (a, b) $\phi = 1.0$, and (c, d) $\phi = 2.0$.

The effect of the Ar dilution on the OH* profiles is visible in Fig. 10 for mixtures at $\phi = 0.5$ at around 2 atm for (a) similar temperatures (1215 ± 4 K) and (b) similar ignition delay times. As can be seen in Fig. 10 (a), the highest intensity in the OH* signal is reached by the ignition peak for all Ar concentrations investigated. However the intensity of the first peak varies greatly with the dilution level. The intensity of the first peak is less than 5% of the ignition peak for the 90% Ar case, and this ratio increases to 10% and 85% for the 95% and 98% Ar dilution cases, respectively. A similar trend is observed for the case where the profiles match a similar ignition delay time (Fig. 10 (b)). In that case, the first peak's intensity is around 4%, 25%, and 75% of the ignition peak for Ar concentrations of 90%, 95%, and 98%, respectively. One can therefore conclude that the intensity of the first peak with regard to the ignition peak increases with the Ar concentration (i.e. more dilution).

Figure 10: Evolution of the OH* profile with time for (a) similar temperatures and (b) similar ignition delay times as a function of the dilution level in Ar for mixtures around 2 atm and for an equivalence ratio of 0.5.

During this study, an attempt was made to determine an ignition correlation for the data determined during this study. It was found that it was not possible to determine such correlation with an acceptable coefficient of correlation value when all the data were taken into account. Ignition correlations were however determined for each dilution level in Ar as can be seen below for the 98% and 90% Ar cases (note that these correlations have been determined using $\tau_{ign100\%}$ to incorporate the 30 atm data for the 98% Ar dilution case):

$$\tau_{ign100\%}(\mu s) = 1.228 \times 10^{-3} \phi^{1.55} P^{-0.26} \exp(37.5/RT) \quad (98\% \text{ Ar}, r^2 = 0.98)$$

$$\tau_{ign100\%}(\mu s) = 1.591 \times 10^{-2} \phi^{-0.72} P^{0.06} \exp(19.8/RT) \quad (90\% \text{ Ar}, r^2 = 0.95)$$

In the above correlations, P is in atm, the ignition activation energy in the exponential term is in kcal/mol, R is the universal gas constant in kcal/mol-K units, and T is the temperature in K. As one can see, the value of the exponent for the equivalence ratio changes from positive (ignition delay time increases as the equivalence ratio increases) to negative when the dilution level decreases from 98% to 90% Ar. An opposite trend is observed with the exponent over the pressure. In addition, there is a marked difference in ignition activation energy (19.8 to 37.5 kcal/mol). This behavior explains why it was not possible to obtain a single ignition correlation for all the data measured in this study, which is not unexpected when looking at ignition delay times over such a wide range of dilution and variation in kinetic behavior [36]. However, the detailed kinetics model is able to replicate the complicated behavior changes over the entire range of experimental conditions, as presented next.

4. Modeling

4.1 Description of the models used

Data from this study were compared to models from the literature. Four models from the literature were considered, although the results from the models from Boyer and Kuo [4] and Tian et al. [14] are not reported in this paper due to their relatively poor performance (ignition delay times are too long by more than an order of magnitude for most of the conditions). The ignition delay time predictions for the more-recent models from Zhang et al. [14] and Brequigny et al. [3] are visible in Figs. 4, 6, 8, and 9. These mechanisms were compared to a mechanism proposed in the present study. The proposed mechanism is based on the recent incremental work by the authors on $\text{H}_2/\text{N}_2\text{O}$ [37], H_2/NO_2 [38], $\text{NH}_3/\text{NO}/\text{N}_2\text{O}$ [26], and $\text{CH}_4/\text{NO}_2/\text{N}_2\text{O}$ [27] (this work being largely based on literature mechanisms [39-43]) and has been extended with the NM sub-mechanisms from Brequigny et al. [3] and some reactions from the recent study of Annesley et al. [22]. Specifically, the recent decomposition rates for nitromethane ($\text{CH}_3\text{NO}_2 \rightleftharpoons \text{CH}_3 + \text{NO}_2$ (R3) and $\text{CH}_3\text{NO}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{NO}$ (R4)) were adopted from Annesley and coworkers. It is important to mention here that the values of k_{R3} and k_{R4} reported in Annesley et al. are based on theoretical computations with Kr as bath gas. According to the principal investigators of the study from Annesley et al., Dr. Tranter and Dr. Klippenstein (private communication), the difference in energy transfer between Kr and Ar induces different values for k_{R3} and k_{R4} . Therefore, their values for k_{R3} and k_{R4} calculated by Dr. Klippenstein with Ar as bath gas were used in this study. These reaction rates are shown in the present paper in Table 3, and the full, detailed kinetics mechanism and its associated thermodynamic data are available as supplementary material.

All the reactions involving the H_2 / hydrocarbons / O_2 sub-systems in the final mechanism come from the initial model of Metcalfe et al. [39]. In case of duplicate reactions for the NM/ NO_x sub-system, the reactions from Mathieu et al. [27] were kept, except for the reactions listed in Table 3. The final mechanism is comprised of 166 species and 1204 reactions. Note that these additions to the CH_4/NO_x mechanism of Mathieu et al. [27] slightly modify its reactivity for CH_4/NO_x data but do not deteriorate the good agreement reached with literature data in Mathieu et al. [27], as is shown later. All calculations shown in figures in this study were performed using the Chemkin Pro software [44]. The “brute force” calculations discussed later were performed using Cantera [45].

Table 3: Reaction rates adopted from Brequigny et al. [3] and Annesley et al. [22] for the cases of duplicate reactions with the model of Mathieu et al. [27] and for the thermal decomposition of nitromethane in Ar as determined theoretically by Annesley et al. [22]. The rate coefficient of each reaction is of the form $k = A T^n \exp(-E_a/RT)$, and units are calories, cm^3 , mol, seconds.

Reaction	Reaction rate			Source
	A	n	E _a	
$\text{HCO} + \text{NO} \rightleftharpoons \text{HNO} + \text{CO}$	1.0×10^8	1.5	-1760	[46]
$\text{CH}_3 + \text{NO}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{NO}$	4.0×10^{13}	-0.2	0	[13]
$\text{CH}_3\text{NO}_2 + \text{OH} \rightleftharpoons \text{CH}_2\text{NO}_2 + \text{H}_2\text{O}$	5.0×10^5	2	1000	[13]
$\text{HNO} + \text{M} \rightleftharpoons \text{H} + \text{NO} + \text{M}$	1.26×10^{16}	-0.43	49480	[13]
$\text{CH}_3\text{NO}_2 \rightleftharpoons \text{CH}_3 + \text{NO}_2$				[22]
0.1 atm	5.176×10^{48}	-10.855	67468	
0.2 atm	4.875×10^{48}	-10.750	67689	
0.5 atm	2.649×10^{48}	-10.545	67936	
1 atm	1.033×10^{48}	-10.330	68069	
2 atm	2.393×10^{47}	-10.050	68131	
5 atm	1.489×10^{46}	-9.575	68083	
10 atm	9.506×10^{44}	-9.135	67940	
20 atm	3.548×10^{43}	-8.630	67701	
50 atm	2.399×10^{41}	-7.885	67261	
100 atm	2.904×10^{39}	-7.245	67799	
$\text{CH}_3\text{NO}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{NO}$				[22]
0.1 atm	2.851×10^{48}	-11.020	66953	
0.2 atm	1.644×10^{48}	-10.880	67057	
0.5 atm	4.932×10^{47}	-10.635	67138	
1 atm	4.932×10^{47}	-10.635	67138	
2 atm	2.333×10^{46}	-10.110	67089	
5 atm	1.349×10^{45}	-9.660	66924	
10 atm	1.002×10^{44}	-9.265	66722	
20 atm	6.266×10^{42}	-8.850	66507	
50 atm	6.266×10^{42}	-8.850	66507	
100 atm	9.078×10^{39}	-7.875	66229	

4.2 Comparison with the Ignition Delay Time Data

As can be seen in Fig. 4 for the equivalence ratio effect at around 1.9 atm (98% Ar), the model of Zhang et al. [14] predicts ignition delay times that are significantly too long, especially for the high-temperature side (up to a factor 4), and the ignition activation energy that can be extracted from the experimental data in Fig. 4 is significantly higher than the activation energy predicted by this model. In comparison, the model from Brequigny et al. is significantly more accurate, with activation energies that are relatively close to the experimental ones. Predictions with the model of Brequigny et al. are generally within reasonable agreement with the data (usually within a factor of around 1.5), except for the fuel rich case at low temperatures where a factor of up to 2 is observed. Results for the fuel-lean mixture are well predicted, especially for the time at which the maximum of the OH* signal is reached. Ignition delay times predicted by the model of the present study are more accurate for the fuel-rich condition, notably for the $\tau_{\text{ign}100\%}$ case. Stoichiometric results are also slightly better predicted (within 25%), especially for the low-temperature side, but the computed results at $\phi = 0.5$ show an ignition delay time that is too short, by a factor up to 1.5 at high temperatures.

The modeling of the pressure effects on Mix 4, 5, and 7 is visible in Fig. 6. Note that the low-pressure data with Mix 5 and 7 have been discussed previously, and Fig. 4 shows the ignition delay time is poorly predicted by the model of Zhang et al. at all conditions investigated except for the Mix 4 results at around 10 atm (Fig. 6 (a and b)). The mechanism of Brequigny et al. presents fair accuracy for all conditions. The mechanism of the present study offers good predictions for all conditions except 30 atm, where the model is over-reactive (a difference by a factor up to 2.5 can be observed with the data). Fuel-lean mixtures are slightly too reactive with the model of the present study, in general.

The modeling of the effect of the dilution level at low pressure is visible in Fig. 8. The less-dilute mixtures are particularly well predicted by the model from the present study, especially when compared to the models from the literature. At $\phi = 1.0$ (Fig. 8 (c)), it is worth noting that at 99% Ar ignition delay times are shorter than at 98% at high temperatures. This behavior is picked up by the model of Brequigny et al. and the model from the present study. For the high-pressure cases, Fig. 9, one can see that the predictions from the model proposed in this study are far superior to the other models and match experiments at all conditions, whereas the other models, including Brequigny et al., are significantly over-predicting the ignition delay time (up to a factor of 10 at high temperatures, Fig. 9 (a) and (c)).

4.3 Comparison with OH* profiles

For all the models considered and for most of the conditions investigated, the first peak of OH* formation near time zero is overestimated, sometimes by more than two orders of magnitude. It is worth mentioning that this level of discrepancy goes much beyond the uncorrected numerical profiles for the first peak, where a correction would be required to account for the time response of the experimental data near time zero as mentioned above. It can be concluded that, since the formation of OH* occurs almost exclusively from the reaction $\text{CH} + \text{O}_2 \rightleftharpoons \text{OH}^* + \text{CO}$ for the present conditions, this discrepancy between the models and the experiments is mainly due to the numerical predictions for the amount of CH radicals formed. This is something that would need to be addressed but is beyond the scope of the present paper.

Consequently to this numerical over-prediction, a direct comparison between the computed and experimental profiles is impossible. One possible way to observe the performance of the models at predicting the OH* profiles is to determine the ratio between the intensity of the first peak and the intensity of the ignition peak for each model. This ratio was then normalized to the highest ratio determined for each model. A similar procedure was followed with the experimental profiles. Due to the uncorrected experimental profiles and very large over-estimation of the first peak intensity from the models, only qualitative information can be obtained from these figures, and results are visible in the supplementary material section. As can be seen, all the trends observed experimentally are predicted by the models.

4.4 Comparison with literature data

To further test the current model, data available in the literature were also analyzed. Literature results were also compared to the predictions from the model of Brequigny et al. and, whenever possible (pyrolysis), to the model from Annesley et al. [22]. The model from Zhang et al. [14] was not considered for data other than decomposition profiles of NM, due to its poor performance against most of the ignition delay time data from the present study, as seen before.

Figure 11 presents the comparison between the evolution of the NM and NO₂ profiles from a highly diluted mixture of NM in Ar at 1180 K and 5.95 atm from Glantzner and Troe [47]. As can be seen, the NM profile is fairly well reproduced from all the models, as a nearly identical NM profile was yielded by the mechanisms. This result indicates that the latest theoretical work on nitromethane decomposition by Annesley et al. is giving satisfactory results.

The NO_2 profile in Fig. 11 is also relatively well predicted by the 4 models: the NO_2 peak is predicted with accuracy by all the models within 5% of the maximum value; but differences can be observed after that. The model of Zhang et al. reproduces with accuracy the experimental trend and the amount of NO_2 formed whereas the other models are within 25% of the experimental value.

Figure 11: Comparison between nitromethane models (this study, Brequigny et al. [3], Annesley et al. [22] and Zhang et al. [14]) and the data from Gläntzer and Troe [47].

Hsu and Lin [48] measured by laser absorption the time evolution of CO and NO concentrations from diluted mixtures of NM in a shock tube. Various dilution levels at sub-atmospheric pressures were investigated. As can be seen in Fig. 12, for a NM concentration of 0.25% in Ar, the NO and CO profiles are largely under-predicted (predicted values are 50-55% lower than the experimental values) by both the model of this study and the model from Brequigny et al.. In comparison, the model from Annesley et al. predicts the NO profile with good agreement, whereas CO is still under-predicted by up to 35%.

Figure 12: Comparison between nitromethane models (this study, Brequigny et al. [3] and Annesley et al. [22]) and the NO and CO profiles from Hsu and Lin [48] (0.25 % NM in Ar, 0.83 atm and around 1055 K).

For a larger concentration of NM (0.4% in Ar, Fig. 13), the models are in better agreement with the experimental data. The CO profile is a bit underestimated by the model from the present study (by less than 20%), whereas the models from Annesley et al. slightly over-predict the amount of CO formed (within 10%). Brequigny et al. under-predicts the CO concentration a bit more than the model of the present study, by up to 30%. The final amount of NO formed is over-estimated by all the models by around 20% but is predicted with fair accuracy by both this study and Brequigny et al. up to around 45 μ s.

Figure 13: Comparison between nitromethane models (this study, Brequigny et al. [3] and Annesley et al. [22]) and the NO and CO profiles from Hsu and Lin [48] (0.4 % NM in Ar, 0.5 atm and around 1386 K).

At the largest NM concentration (0.76% in Ar) investigated by Hsu and Lin, Fig. 14, the NO profile is relatively well predicted, and CO under-predicted, by the present study and Brequigny et al. (around 30% under-prediction), while Annesley et al. over-predicts NO by up to 20% but predicts CO well.

Figure 14: Comparison between nitromethane models (this study, Brequigny et al. [3] and Annesley et al. [22]) and the NO and CO profiles from Hsu and Lin [48] (0.76 % NM in Ar, around 0.67 atm and 1240 K).

Zhang and Bauer [49] determined the amount of (a) CH_3NO_2 , (b) CH_4 , (c) C_2H_4 , and (d) C_2H_6 as a function of temperature behind reflective shock waves for a mixture of 0.67% NM in Ar (Fig. 15). These components were quantified by gas chromatography of gas sampled right after the RSW. To model these data, the mechanisms (this study, Brequigny et al., Annesley et al.) were used at the average pressure of 4.75 atm, and computed values were taken for a test time of 1.5 ms, as in Zhang et al. [15]. As can be seen in Fig. 15 (a), the NM profile is relatively well reproduced by all the models from this study, although differences between the models are visible. The methane profile (Fig. 15 (b)) is significantly over-predicted by around 50% at high temperature by the model from Annesley and coworkers. The CH_4 profile is also over-predicted by the other models, but by less than 20% above 1080 K. Finally, the largest difference between the models is observed for the C_2H_4 (Fig. 15 (c)) and C_2H_6 (Fig. 15 (d)) profiles. The model from Annesley et al. significantly under-predicts the amount of C_2H_4 by a factor up to 5, whereas an under-prediction by less than 30% is observed for the model of the present study. The model of Brequigny et al. is the only model to over-predict the amount of ethylene, by 45% at most. The three models predict the shape of the C_2H_6 profile but ethane is over-predicted in all case at low temperature, from a factor 1.3 (Annesley et al.) to nearly 2 (this study). On the high temperature side, the model of Annesley et al. under-predict the amount of C_2H_6 by around 20% whereas the other models over-estimate it by up to 33% for the model of the present study.

Figure 15: Comparison between nitromethane models (this study, Brequigny et al. [3] and Annesley et al. [22]) and the CH₃NO₂ (a), CH₄ (b), C₂H₄ (c), and C₂H₆ (d) profiles as a function of temperature from Zhang and Bauer [49].

As mentioned before, the present model uses the CH₄/NO_x mechanism presented in Mathieu et al. [27]. To make sure that the modifications made for the nitromethane model do not adversely modify the predictions of the original mechanism, some representative data from the former CH₄/NO_x study [27] have been modeled with the NM models from this study and from Brequigny et al. for comparison. Results are visible in the Supplementary Material Section and show that these experiments are accurately reproduced by the model from the present study.

5-Discussion

Prior to the present study, no ignition delay time data were available to assess the overall validity of detailed kinetics mechanisms for nitromethane. This study observed important differences between mechanisms' predictions, even for recent models such as Zhang et al. (2011) and Brequigny et al. (2015). To help explain these differences, sensitivity and reaction pathway analyses were performed using the model of the present study, the model of Zhang et al., the model of Brequigny et al. and, whenever possible, the model of Annesley and coworkers. The sensitivity analysis was performed on OH* using the Chemkin Pro software [44]. The validity of the sensitivity analysis for ignition delay time using OH* was validated in Mathieu et al. [38] by comparing results with a "brute force" sensitivity analysis for mixtures of H₂/O₂ seeded with NO₂ and diluted in Ar. A "brute force" method was also performed during this study using an earlier version of

the current mechanism (prior to adding the NM dissociation pathways from Annesley et al. [22]) in which the effect on calculated ignition time was determined due to doubling the rate of one reaction in the mechanism, for 24 different reactions, for every experiment. The 24 reactions were chosen from examining H-atom and CH₃ sensitivity coefficient plots for a number of experiments. There is very strong correlation between the relative importance of reactions from the OH* sensitivity and the relative importance of the rate coefficients of reactions on calculated ignition times in the “brute force” analysis.

Due to the large ranges of conditions covered in this study in terms of equivalence ratios, dilution levels, pressures and temperatures, results from the two sensitivity analysis methods show that the reactions that most influence ignition delay time vary depending on experimental conditions. Calculated ignition delay times are much more sensitive to the rates of the dissociation reactions of NM ($\text{CH}_3\text{NO}_2 \rightleftharpoons \text{CH}_3 + \text{NO}_2$ (R1) and $\text{CH}_3\text{NO}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{NO}$ (R3)) than other reactions at low temperatures (below 1000 K), and at even higher temperatures for fuel rich mixtures (mixture 9). At all other conditions, calculated ignition delay times are much more sensitive to the rate of $\text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}$ (R4) than any other reaction, especially in lean and highly diluted mixtures (mixtures 4, 7, and 10). It is interesting to note that above 1000 K, changes in the rate coefficient of the reaction R2 ($\text{CH}_3 + \text{NO}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{NO}$) causes a significantly larger impact than changes in the rates of the initial dissociation reactions. There are a handful of experiments (higher temperatures, stoichiometric, low pressure) at which HCO reactions ($\text{HCO} + \text{M} \rightleftharpoons \text{H} + \text{CO} + \text{M}$ (R5), $\text{HCO} + \text{NO} \rightleftharpoons \text{HNO} + \text{CO}$ (R6)) become very important due to their effect on H-atom concentrations. It is also interesting to note that the impact of changing the rate coefficients of a number of reactions flips from promoting (shortening ignition time) to inhibitive (delaying ignition) for high-pressure conditions (10 atm to 34 atm, compared to 2 atm). This switching behavior is due to recombination reactions ($\text{NO} + \text{O} + \text{M} \rightleftharpoons \text{NO}_2 + \text{M}$ (R7), $\text{H} + \text{CO} + \text{M} \rightleftharpoons \text{HCO} + \text{M}$ (-R5)) reducing radical pools at high pressures, and therefore also changing the net direction of the reaction $\text{NO}_2 + \text{H} \rightleftharpoons \text{NO} + \text{OH}$ (R8), which then removes H-atoms at high pressures instead of producing H-atoms at low pressures.

The sensitivity analysis performed with Chemkin Pro and the mechanism proposed in the present study for the top 10 most-sensitive reactions, on the lowest and highest temperatures investigated for each mixture and pressure conditions, led to a total of 38 different reactions. Many of these reactions have a moderate sensitivity coefficient and, as described above, are condition specific. However, a few reactions were found sensitive in most of the cases. A list of these most-sensitive and -common reactions is provided in Table 4, while the complete results of this sensitivity analysis are provided as supplemental material for all mixtures.

Table 4: List of the 10 most-common sensitive reactions obtained during this study. The order of the reactions corresponds to the order of appearance of the reaction in the model, not to the relative value of the sensitivity coefficient.

Reaction	Reaction number
$\text{CH}_3\text{NO}_2 \rightleftharpoons \text{CH}_3 + \text{NO}_2$	R1
$\text{CH}_3 + \text{NO}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{NO}$	R2
$\text{CH}_3\text{NO}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{NO}$	R3
$\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$	R4
$\text{HCO} + \text{M} \rightleftharpoons \text{H} + \text{CO} + \text{M}$	R5
$\text{HCO} + \text{NO} \rightleftharpoons \text{HNO} + \text{CO}$	R6
$\text{NO}_2 + \text{H} \rightleftharpoons \text{NO} + \text{OH}$	R8
$\text{HCO} + \text{O}_2 \rightleftharpoons \text{CO} + \text{HO}_2$	R9
$\text{CH}_2\text{O} + \text{OH} \rightleftharpoons \text{HCO} + \text{H}_2\text{O}$	R10
$\text{CH}_3 + \text{H} (+\text{M}) \rightleftharpoons \text{CH}_4 (+\text{M})$	R11

To compare the important reactions for the ignition delay time of each mechanism, the sensitivity analysis was conducted for Mix 8 (stoichiometric condition, around 9 atm) at 1055 and 895 K (matching the extremes in temperatures investigated experimentally), which corresponds to the lowest level of dilution investigated (90 % Ar) and to a condition where large differences were observed amongst the models (see Fig. 9).

The sensitivity analysis was conducted on OH* by determining the value of the normalized OH* reaction sensitivities at the time of the second OH* emission peak (σ). The 10 reactions with the largest value of σ were identified for each mechanism, for each experiment. Figure 18 presents the normalized sensitivity coefficient (σ) for the reactions that were common to at least two mechanisms; the other reactions being typically of smaller importance, or are addressed if otherwise. As can be seen in Fig. 18 for the 895 K case, the three mechanisms share the same most-sensitive (promoting) reactions:

(Note that this reaction is written $\text{CH}_3\text{NO}_2 \rightleftharpoons \text{CH}_3 + \text{NO}_2$ in the mechanism of the present study, as in Annesley et al. [22]) As well as the same most-inhibitive reaction:

The two literature mechanisms use basically the same reaction coefficient for R1 (from Glarborg et al. [13], or a very close rate for Brequigny et al.) whereas the reaction coefficient from Annesley et al. is used for the present study. Note that, at this temperature, the reaction R3 ($\text{CH}_3\text{NO}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{NO}$) is among the 10 most-sensitive reactions for the mechanism of the present study, but with a moderate sensitivity coefficient $\sigma = 0.16$. However, this reaction is even less sensitive at higher temperature (1055 K, not among the 10 most-sensitive reactions). The reaction coefficient for R12 is also different between this study (reaction coefficient from Tricot et al. [50]) and the two other models (from Glarborg et al. [13], with slightly more than an order of magnitude difference between the two reaction rates), which explains the large difference in the normalized sensitivity coefficient between this study ($\sigma = -0.33$) and the others ($\sigma = -0.59$ and -0.71 for Brequigny et al. and Zhang et al., respectively). Figure 18 indicates that at 895 K reactions other than R1 have a relatively small sensitivity coefficient for the current model, more so than the other models. For example, the promoting reaction R2 is the reaction with the second largest value of σ for the model of this study and the model of Zhang and coworkers, but large differences are observed between their respective normalized sensitivity coefficients ($\sigma = 0.36$ and 0.95 , respectively).

This reaction also has a relatively large sensitivity coefficient in the model of Brequigny et al. ($\sigma = 0.68$) but is not as important as R10 ($\sigma = 0.80$), which is also an important reaction for the other models.

Note that amongst the models tested herein, R2 and R10 have essentially the same reaction rates under the conditions of the present study. The only other reaction that is common to the 3 mechanisms is the

reaction R13. Note that the sensitivity coefficient for R13 is rather small for all the models, and each model uses the same rate of reaction for R13.

Finally, it is worth mentioning that reaction R9 ($\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$ (R4)) is usually the most-sensitive reaction for the ignition of hydrocarbons at shock-tube conditions [51-52]. However, due to both the low temperatures reached with NM (895 K in the present low-temperature case in Fig. 18) and the importance of R1, the reaction R4 appears only in the top 10 most-sensitive reactions for the model of Brequigny et al. and the model of the present study, with a moderate sensitivity coefficient. Note that the reaction coefficient for R4 used in the model of the present study (taken from the recent work from Kromns et al. [53]) is around 55% slower than the reaction coefficient used in the other mechanisms at this low-temperature condition. For the high-temperature case, 1055 K, R4 is the most-sensitive (promoting) reaction for the model of the present study and for the model of Brequigny and coworkers. This reaction is the second most important promoting reaction for the model of Zhang et al., the most-sensitive (and promoting) reaction being R1 (also a sensitive reaction for the other models, but with a moderate sensitivity coefficient, $\sigma = 0.20$ and 0.25 for the models of this study and Brequigny et al., respectively).

At this temperature, R9 is also a very sensitive reaction that promotes the reactivity of the mixture, for all mechanisms. The reaction coefficient used for this reaction is around two times faster for the model of the present study (reaction coming from the mechanism of Kromns et al. [53]) than for the other models (both using the same rate, from Desain et al. [54])

Among the other sensitive reactions at 1055 K, one can mention that R6 strongly inhibits the reactivity in the model of Zhang et al. ($\sigma = -0.66$) and more moderately in the model of Brequigny et al. ($\sigma = -0.17$), whereas this reaction is not among the 10 most-sensitive reactions for the model of the present study. For the model of the present study and for the model of Brequigny et al., the most important inhibiting reaction is R3 ($\sigma = -0.76$ and -0.78 , respectively, both models using the same rate from Xu et al. [46]), and this reaction is also important for the model of Zhang et al. ($\sigma = -0.47$, using the rate from Dammeier et al. [55]). Note that R3 also has a noticeable importance for the model of the present study and the model of Brequigny et al. at 895 K, whereas R6 was not in the 10 most-sensitive reactions for the model of Zhang and coworkers at low temperature.

Other important reactions from this sensitivity analysis are R2 (promoting, $\sigma = 0.30$ and 0.55 , respectively for the model of this study and from Brequigny et al.), R12 (literature models only) and R14 and R8 (inhibiting with a moderate sensitivity coefficient, this study and Brequigny et al. only, both models sharing the same reaction rates):

From the results of the sensitivity analysis performed under the conditions presented in Fig. 18, it can be concluded that only a few reactions are important to control the ignition of nitromethane (note that, as seen before and in Table 4, a different conclusion could be found for other mixtures and conditions). For the case presented in Fig. 18, many of the sensitive reactions have the same or very similar reaction coefficients in all the models, so a large portion of the noticeable difference between the models must be due to the differences in the reaction coefficients for R4, R9, and R12.

Figure 18: normalized sensitivity coefficient for the model of the present study and the models of Brequigny et al. [3] and Zhang et al. [14] for the two extreme temperatures of Mix 9 (895 and 1055 K).

The reaction pathway analysis module from Chemkin Pro was used to exhibit the differences between the models when predicting NM profiles decomposition from Glántzer and Troe [47]. Results for a reaction time of 40 μs , corresponding to the time at which around 50% of the NM is consumed in Fig. 11, are presented in Fig. 19. As can be seen in this figure, the reaction R1 ($\text{CH}_3\text{NO}_2 (+\text{M}) \rightleftharpoons \text{CH}_3 + \text{NO}_2 (+\text{M})$ or $\text{CH}_3\text{NO}_2 \rightleftharpoons \text{CH}_3+\text{NO}_2$ as written in Annesley et al. [22]) is by far the most important reaction for the NM decomposition under these conditions. It is worth noting that importance of R1 remains very large regardless of the reaction time and the temperature (R1 is actually more important for NM decomposition as the temperature increases). One can notice in Fig. 19 that all the models have a similar molar flux for the NM decomposition through R1, between 87.6 and 92.0%. The models are also in agreement with the small importance of R15 on the NM decomposition profile:

Aside from these two common reactions, some noticeable differences can be observed between models. For example, the models from the present study and from Annesley et al. are the only models where the thermal decomposition of NM is not only due to R1 but also to R3, with a noticeable molar flux (7.1 and 6.5%, respectively):

The second most important pathway for NM decomposition for the models of Zhang et al. and Brequigny et al. is the reaction between NM and the hydroxyl radical leading to water and CH₂NO₂ (R12). This pathway has a molar flux between 3.8 and 3.1% for the two aforementioned models, but it is interesting to mention that the molar flux is only 0.2% for the model of Annesley and coworkers and 2.3 % for the model of the present study.

Nitromethane can also react with the radical H to either produce H₂ and CH₂NO₂ (R16) or methyl and HNO₂ (R17) (and, for the model of this study, HONO (R18)). As can be seen in Fig. 19, the molar flux for R16 is significantly smaller for the model of the present study (<0.1%) than for the other mechanisms (between 1.3 and 2.3%). The other pathway with a hydrogen radical that leads to the formation of a methyl radical and HNO₂(/HONO) was not considered in the model of Annesley et al., whereas only the HNO₂ reaction (R16) was considered in the model of Brequigny et al. and Zhang and coworkers.

Figure 19: Reaction pathway analysis for nitromethane decomposition at 1180 K, 5.95 atm for a mixture of nitromethane diluted in 99.963% Ar. The black numbers correspond to the molar fluxes for the model of the present study; the grey ones for the model of Brequigny et al. [3]; the light grey values are for the model of Zhang et al. [14]; and the italic black ones are for the model of Annesley and coworkers [22].

This molar flux analysis exhibits the very large importance of R1 on the decomposition profile of NM. The reaction rate for R1 determined by Glarborg et al. [13] was used in the models of Zhang et al. and Brequigny and coworkers (although the later essentially used a very close value (Table 3)) while the new rate of Annesley et al. was used in the present study. This new rate in conjunction with R3 (CH₃NO₂ ⇌ CH₃O + NO) provides the same good level of predictions for NM decomposition as per Fig. 11. However, since NM decomposes thermally via R1 and R3 (Fig. 19) and not R1 only, the product composition is different and that should allow for better predictions on intermediate combustion species. More experiments are however

required to fully validate this point. A reaction pathway analysis similar to Fig. 19 was carried out for the other conditions investigated during this study. Results show that, for all the conditions investigated, the NM consumption is largely dominated by its thermal dissociation via R1 and R3.

6-Summary

During this study, new ignition delay time measurements were performed over wide ranges of pressure, temperature, dilution level, and equivalence ratio conditions never investigated before. The results showed that the ignition delay time of nitromethane was sensitive to most of these parameters. The resulting experimental data were used to validate a detailed kinetics mechanism assembled from previous works from the authors and from recent literature work on nitromethane. The model proposed in the present study reproduces with good agreement the experimental data presented herein as well as most of the literature data, although there is still room for improvement.

The numerical chemical analysis showed that a relatively large amount of reactions are important for NM ignition. However, the relative importance of these reactions is strongly condition dependent. The sensitivity analysis performed for several models show that differences between the models are due to a relatively low number of reactions, from both the hydrocarbon and nitromethane/NO_x sub-mechanisms. Among these reactions, the thermal decomposition of nitromethane ((R1) $\text{CH}_3\text{NO}_2 (+\text{M}) \rightleftharpoons \text{CH}_3 + \text{NO}_2 (+\text{M})$) is of primary importance. This reaction was recently updated through high-level calculations by Annesley et al. [22], and a roaming reaction was added to the chemical scheme ((R3) $\text{CH}_3\text{NO}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{NO}$). It can be concluded that the present study improves the overall predictions of nitromethane ignition. However, more data are still needed to further validate the nitromethane sub-mechanism and improve the predictions. The computed OH* profiles also exhibit the need to improve on the CH radical chemistry predictions.

7-Acknowledgments

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