Experimental Study of Nitromethane Oxidation: CO and H₂O Time-Histories Behind Reflected Shock Waves

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1 Introduction

Nitromethane (NM) is recently receiving a lot of attention in the combustion community [1-5] for a variety of reasons: from a pure fundamental research viewpoint, since NM can help in understanding the mutual sensitization between hydrocarbons and NOx; to very practical applications since NM can be used as a monopropellant, an automotive fuel additive, or even for race and modeling engines (see references in [3-5]). Despite notable progress, this recent research work on NM exhibits a lack of understanding on NM combustion chemistry. For instance, the model developed by Brequigny et al. [1] was not able to reproduce accurately the flame speed data of Nauclér et al. [2]. Although these discrepancies could have been induced by the differences in the techniques used to measure the laminar flame speeds (spherical flames in a closed vessel for Brequigny et al., flat flames on a perforated plate burner for Nauclér et al.). More recently, discrepancies also appeared for ignition delay time (τ_{ign}) measurements in shock tubes. In the study of Mathieu et al. [4], the model from Brequigny et al. was improved, notably by using the new NM decomposition rates from Annesley et al. [3]. The updated model presented an overall better accuracy than the model of Brequigny et al. against ignition delay time data obtained over wide ranges of pressures, dilution levels (in Ar), and equivalence ratios. This improved agreement was essentially observed for the low-dilution/high-pressure cases. On the other hand, the recent study on NM ignition from Nauclér et al. [5] investigated NM mixtures at higher pressures and lower dilution levels (in N_2), and the comparison between their data and the models showed that the Brequigny's model was performing better at reproducing τ_{ign} .

This current situation indicates that more data are needed to further develop and validate a detailed NM combustion chemistry model. While global kinetics data such as laminar flame speeds and ignition delay times are useful to validate the overall reactivity of a model, they typically involve a large amount of reactions, which often prevents one from adjusting confidently the key reaction(s). The current situation with recent studies illustrates this statement. In contrast, following the formation and/or consumption of individual chemicals during the combustion process typically involves a much lower number of reactions, thus allowing more easily the identification of the appropriate reaction rates to adjust. The goal of the present study was therefore to obtain these kind of data by measuring behind reflected shock waves the

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time histories of CO, an intermediate species, and H_2O , a final product, with laser absorption techniques. The techniques used to measure the time histories of CO and H_2O are described below, followed by the presentation of the data. These data are then compared to modern detailed kinetics mechanisms.

2 Experimental setup

2.1 Shock tubes

Experiments were conducted in two different shock tubes. The two facilities are similar, but with slightly different dimensions. Both tubes are single-diaphragm, made of stainless steel, with a 7.62-cm i.d. driver section (2.46-m long) for the CO diagnostic shock tube (COST); 3-m long for the water diagnostic shock tube (WDST)) with a large-diameter driven section (15.24-cm i.d., 4.72-m long for the COST; 16.2-cm i.d., 6.78-m long for the WDST). In both cases, PCB P113A piezoelectric pressure transducers were used along the driven section to measure the incident-wave velocities. A curve fit of the measured velocities was used to determine the incident wave speed at the endwall location and the post reflected-shock conditions using 1-D shock relations and initial conditions in the test region. Test pressure was monitored by a Kistler 603 B1 transducer located at the sidewall, in the same plane as the observation windows (sapphire, 16 mm from the endwall). More details on the shock tubes can be found in the literature [6,7]. Non-ideal boundary-layer effects measured by the change in pressure (dP/dt) behind the reflected shock wave were determined to be less than 2%/ms in each facility. Test mixtures were prepared using the partial pressure method in a stainless steel mixing tank shared by the two facilities. Gases were high purity (99.994% purity for O_2 , 99.9999% for Ar). Nitromethane (98+%) was purchased from Alfa Aesar.

2.2 Laser diagnostics

The Beer-Lambert relation describes the attenuation of a monochromatic light source by $I/I_0 = \exp(-k_\nu P_{abs}L)$, where I_0 and I are the transmitted and incident intensities, k_ν is the spectral absorption coefficient, P_{abs} is the partial pressure of the absorbing species, and L is the path length. If k_ν can be calculated and I/I_0 can be measured, the concentration of a species of interest can be obtained. In this study, k_ν was calculated using the spectroscopic linestrengths from the HITRAN 2004 database [8]. Note that k_ν is function of temperature. To account for the change in k_ν during an experiment, the simulated temperature rise was used to correct the absorption coefficient. This procedure was described in Mathieu et al. [12].

• CO diagnostic

A quantum cascade laser (QCL) from Alpes Lasers was used to generate light at 4566.17 nm to access the fundamental R(12) transition of the v"=0 band of CO. This line has been well-characterized by Ren et al. [9]. Two InSb detectors (Teledyne Judson J10D) were used to monitor the incident and transmitted intensities, I_0 and I. To minimize broadband light emission from striking the detector on the transmitted side, multiple irises were used to aid the bandpass filters in reducing emission levels. Prior to each experiment, the laser was scanned over the selected transition via a removable absorption cell containing a CO/Ar mixture and placed at the center of the transition. A thorough description of the CO diagnostic can be found elsewhere [10].

• *H*₂*O* diagnostic

A tunable diode laser (TDL) from Toptica Photonics was used to generate light at 1388.140 nm to access the H_2O transition at 1388.1389 nm within the v_1+v_3 fundamental band. The slight shift in wavelength is to account for the pressure shift of the line center. This line shift was calculated according to Li et al. [11]

and was also measured by successively changing the laser wavelength over the course of nearly identical shock experiments in a mixture with a known amount of H₂O; the calculations and experiment were in excellent agreement. The laser wavelength was monitored using a Burleigh WA-1000 wavemeter, with an uncertainty of ±0.0005 nm. Two InGaAs detectors (Newport 2317NF) were used to measure the incident and transmitted intensities, I_0 and I. A thorough description of the H₂O diagnostic can be found elsewhere [12].

3 Experimental results

Experiments were carried out behind reflected shock waves. To mitigate the influence of the exothermicity on the results and still obtain a good absorption signal, we studied mixtures diluted in 99% Ar. The conditions investigated during this study are summarized in Table 1.

Diagnostic	NM (mole %)	O ₂ (mole %)	Ar (mole %)	Equiv. ratio	Temp. (K)	Pressure (atm)
CO	0.5714	0.4286	99.0	1.0	1375-1630	1.05 ± 0.10
H ₂ O	0.40	0.60	99.0	0.5	1210-1496	0.85±0.10
	0.5714	0.4286	99.0	1.0	1290-1610	0.80 ± 0.12
	0.7273	0.2727	99.0	2.0	1430-1690	1.0±0.10

Table 1: Mixtures and conditions investigated

Typical profiles obtained for CO and H_2O are presented in Fig. 1, for the stoichiometric case at around 1370 K. As can be seen, both profiles present an interesting shape with two growth periods. First, the concentration of the two species sharply rise right after the passage of the reflected shock wave, then their concentrations rise slowly until reaching a maximum at around 800 μ s. After this time, H_2O , which is a final product, stabilizes on a plateau, whereas CO is slowly consumed. It is visible in Fig. 1 that the timing of the first rise does not vary with the temperature for both species, but the timing of the second rise does.



Figure 1. Left: CO and H₂O profiles for a stoichiometric mixture at 1467±2 K; center: H₂O profiles for a mixture at ϕ = 0.5; right: CO profiles for a mixture at ϕ = 1.0.

CO and H₂O Time Histories from Nitromethane

The time at which the CO and H₂O profiles reach their maximum on the second hump (called τ_{max} herein) is plotted for each temperature investigated in Fig. 2. As can be seen, this timing increases exponentially as the temperature decreases. For the stoichiometric case, CO and H₂O appear to have the same timing below about 1500 K. Above this temperature, CO tends to reach its maximum a little before H₂O. Concerning the H₂O data, one can see that the increase in the equivalence ratio is associated with a noticeable increase in τ_{max} . For example, at around 1470 K, τ_{max} is longer at $\phi = 2.0$ and 1.0 than at $\phi = 0.5$ by factors of around 5.3 and 1.65, respectively. The evolution with the temperature of the maximum mole fraction of H₂O and CO (at τ_{max}) is visible in Fig. 2, right. As can be seen, the maxim amount of CO produced is increasing with the temperature, whereas an opposite trend is observed with water. The equivalence ratio has a large effect on the maximum amount of water formed, with a maximum mole fraction of water that increases with ϕ .



Figure 2. Left: Evolution of the time at which CO and H_2O reach their maximum mole fractions; right: Evolution of the maximum mole fractions of CO and H_2O with the temperature. Lines: models (continuous: Mathieu et al. [4], dashed: Brequigny et al. [1])

4 Models comparison

The two most recently published models for NM (namely, Brequigny et al. [1] and Mathieu et al. [4]) were used in this study. The comparison of their performances with the data obtained herein is visible in Fig. 2. As can be seen, the time at which the maximum amount of CO is reached is relatively well predicted by both models, the model from Mathieu et al. being moderately over-reactive, whereas the model of Brequigny et al. is slightly under-reactive. The timing for the maximum amount of H₂O is however very well predicted by the model of Mathieu et al. over the entire range of conditions investigated. On the other hand, the predicted delay is too long for the model of Brequigny et al., by a factor up to 2. The maximum amount of both CO and H₂O is also more accurately predicted by the model of Mathieu et al., over the entire range of conditions investigated.

Some examples of profile comparisons between the models and the experiment are provided in Fig. 3. Concerning the H_2O profiles, it is visible that the better predictions from the model from Mathieu et al. observed in Fig. 2 lead to a better prediction of the profile shape, overall. However, the first rise in H_2O mole fraction is over-estimated by the model, while the model of Brequigny et al. tends to do a better job

at predicting the mole fraction after the first rise. A similar observation can be made for the CO profiles. In this case, this over-estimation of the first rise mole fraction in CO leads to predictions that are consistently above the experimental profiles, until the maximum mole fraction is reached. This maximum in mole fraction of CO is however closer to the data than the value computed by the model of Brequigny et al.



Figure 3. Left: Evolution with time of the H_2O mole fraction; right: Evolution with time of the CO mole fraction. Lines: models (continuous: Mathieu et al. [4], dashed: Brequigny et al. [1])

This over-prediction of the H₂O and CO mole fractions at the first peak level by the model of Mathieu et al. can be explained by the choice in some reaction rates. Compared to the model of Brequigny et al., Mathieu and coworkers used the reaction rate for NM decomposition recently published by Annesley et al. [3]. Once NM is (mostly) decomposed to CH_3 and NO_2 at the very beginning of the experiment, these two radicals will then react together via $CH_3 + NO_2 \rightleftharpoons CH_3O+NO$ (R1). The methoxy radical will then produce formaldehyde (CH₂O) and eventually CO, with the intermediate formation of water via $CH_2O+OH \Rightarrow HCO+H_2O$ (then HCO+M \Rightarrow H+CO+M, along with HCO+NO \Rightarrow HNO+CO). As can be seen, the reaction $CH_3 + NO_2 \rightleftharpoons CH_3O+NO$ is playing a paramount importance in the predictions of CO and H_2O at the first peak level. As noted by Annesley et al. [3], there is currently a large uncertainty in the rate of this reaction. Therefore the use of the accurate NM decomposition rate of Annesley et al. is counterbalanced by the inaccurate reaction rate of R1 in the model of Mathieu at al., whereas the outdated decomposition rate of NM in Brequigny et al. offers apparently closer predictions of the first peak by counterbalancing R1. One can therefore conclude that improved predictions of NM combustion chemistry could be obtained once an accurate reaction rate for $CH_3 + NO_2 \leftrightarrows CH_3O+NO$ is obtained. CO and H_2O profiles with a reaction rate for R1 multiplied and divided by 2 are visible in Fig. 3. Note that this reaction is also very important for the predictions of the mutual sensitization of NOx and hydrocarbons.

5 Conclusions

The recent literature on nitromethane combustion exhibits discrepancies between experimental results and models coming from different groups. To identify and reduce these discrepancies, new time history profiles of H₂O and CO were obtained by laser absorption techniques in shock tubes. A peculiar shape of the profiles was found for both species, where a rapid formation of H₂O and CO occurs right after the beginning of the experiment. This initial formation is followed by another growth on their mole fractions at a later time that varies with the temperature. Modern detailed kinetics models capture this unique profile but could still be improved. This study shows that an accurate determination of the rate of reaction for CH₃ + NO₂ \leftrightarrows CH₃O+NO is necessary to obtain better predictions for NM combustion.

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