

Impact of Nitromethane Addition on the Detonation Properties of n-Heptane / Oxygen Mixtures

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1 Introduction

A gas phase detonation can be initiated either very quickly by a strong shock wave, such as the one generated by high explosives, or by a low energy source which ignites a flame leading to a precursor shock at the end of a multistage acceleration mechanism. In both processes, the detonation is obtained if the shock wave intensity is sufficient to ignite the explosion in unburned gases. The conditions of shock-to-detonation transition (SDT) are important to know in order to design Pulsed Detonation Engines or Rotating-Detonation-Engines. In this type of engines, the ignition energy must be small and the deflagration-to-detonation Transition (DDT) must be very quick. In this context, n-heptane/O₂ mixtures appear to be of great interest, since n-heptane sensitivity to detonation is nearly the same as for light alkenes [1]. Obviously, an increase in the reactivity of unburned gases behind the precursor shock induces a faster transition to detonation, it is then important to study ignition improvers. The effect of additives on the sensitization of ignition or detonation of hydrocarbon/oxidant mixtures has been previously studied by several researchers: hydro-peroxides [2-5], dimethyl ether [6], aluminium alkyl derivatives [7], nitrates such as the isopropyl nitrate [8]. These various compounds are relatively unstable leading to difficulties of storage. Nitromethane presents the advantage to be a stable liquid.

A large amount of work has been devoted to studying the kinetics of NM decomposition at relatively low pressure and temperature [9-11]. The thermal decomposition of NM in shock waves has been performed by several authors [12-15]. In our previous work [16], a bimolecular initiation step was proposed based on NM decomposition profiles obtained behind reflected shock waves, both for pyrolytic and oxidation conditions. Concerning the oxidation of NM behind shock waves, very few studies have been reported in the literature [16-20]. Kang et al. [18] have given a relation between the ignition delay time, temperature and densities of NM and O₂. Recently, a NM low pressure flame study was performed and a kinetic model was proposed [19] which was modified to take into account the pressure based on expanding flame speed measurements [20].

This work aims at exploring the kinetic role of nitromethane added to n-heptane on the shock-to-detonation transition.

2 Experimental setup and methodology

The shock tube to study the onset of the detonation behind an incident shock wave is shown in Fig. 1. The test section to study the shock-to-detonation transition (SDT) was located at 3.20 m from double

diaphragm which separated driver and driven tube, referred to as the measurement zone. It was equipped with four pressure gauges (C_1 to C_4) of very small sensitive surface (0.5 mm^2). The gauges were flush mounted with inside the wall every 150 mm. The precision on the shock wave velocity was better than 0.4%. The traces of the detonation passage were recorded on a soot foil ($21 \text{ cm} \times 17 \text{ cm}$) located 270 mm behind the last pressure gauge (C_4) of the measurement zone. For more details see [1].

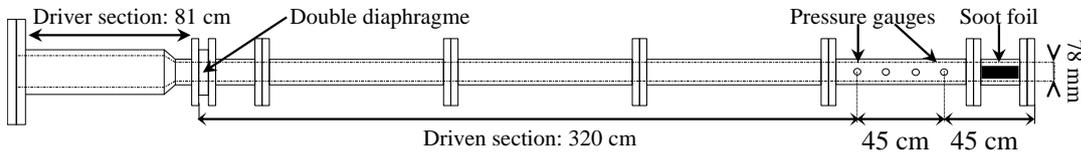


Figure 1. Sketch of the shock tube used for the detonation study.

3 Methodology

Following the analysis developed in [1], the SDT can be observed in the driven tube if the pressure P_2 and the temperature T_2 behind the precursory shock wave are quite high to initiate the explosive reaction. In this case, the particles near the contact surface are heated from the shock wave formation up to the ignition point. A combustion wave (CW) propagates from this point in the mixture initially at P_2 and T_2 . In these conditions, CW becomes quasi-instantaneously a detonation wave which propagates at very high velocity $V_{CW} \approx D_{CJ}(2)$ where $D_{CJ}(2)$ is the velocity of a Chapman- Jouguet detonation for a mixture initially at P_2 and T_2 . The CW quickly merges with PSW as shown in Fig. 2. Beyond merging point (MP), the velocity of the “Overdriven Detonation” (V_{OD}) decreases to the self-sustained detonation velocity D_{exp} close to the value $D_{CJ}(1)$: $D_{exp} < D_{CJ}(1) \leq V_{OD} < D_{CJ}(2)$.

In fact, the conditions of the SDT can be determined by plotting the curve V_{SW} (Fig. 5) versus P_4/P_1 , since the shock wave strength ($I_{PSW} = (P_2 - P_1)/P_1$) depends on the ratio of initial pressures P_4/P_1 in driver and driven tube respectively. The critical pressure and temperature ($P_{2,c}$ and $T_{2,c}$) of the SDT are then easily deduced.

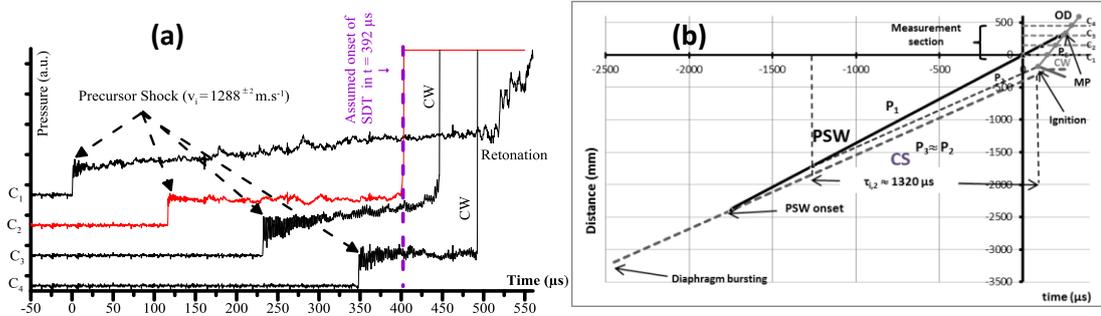


Figure 2. Recording (a) and trajectories of the waves (b) in the shock tube. PSW: Precursory Shock Wave; CS: Contact surface; CW: Combustion Wave; OD: Overdriven Detonation; C_1 - C_4 : Location of pressure gauges; $\tau_{1,2}$: particle heating time. MP: merging point between PSW and CW. P_i : pressure of gases in state i.

By increasing progressively P_4/P_1 , four characteristic situations are observed according the location of the merging point (MP) as shown in Fig. 3-b: (i) MP is beyond the gauge C_4 and the mean wave front velocity (V_{SW}) between C_1 and C_4 is equal to V_{PSW} , (ii) MP is located between C_1 and C_4 and $V_{PSW} < V_{SW} < V_{OD}$, (iii) MP is located just before C_1 : $V_{SW} = V_{OD}$. (iv) MP is located away ahead C_1 and the velocity V_{SW} is stabilized at a velocity very close to $D_{CJ}(1)$.

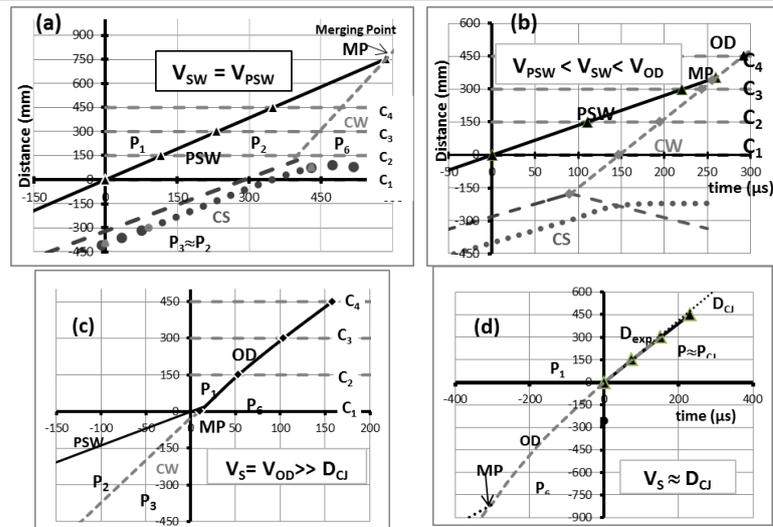


Figure 3. Different types of records in the test zone to determine the conditions of Shock Wave to Detonation Transition (SDT).

4 Results

4.1 Nitromethane Decomposition and Oxidation

The first step of this study is to be able to simulate accurately the kinetic decomposition and oxidation of mildly diluted NM/O₂ mixtures. The second step is to build a model that describes both n-heptane and NM oxidation. The first step relies on the experimental work of [16] for the validation since NM profiles versus time are available both in pyrolysis and oxidation over a wide range of P, T and composition conditions. The NM specific steps can be found in the earlier work of [16] or the more recent work of [20]. As for n-heptane, the kinetic used was the same as [1] developed by [26]. Therefore, 2 different detailed kinetic mechanisms were built that differ by their NM sub-mechanism: MechB (NM based on [20]) and MechDC (NM based on [16]). An example of the comparison between the NM experimental profile and the simulated one is given Fig. 4. As one can see the model MechDC captures more accurately the NM profile decomposition behind reflected shock than MechB. In this example, the explosive oxidation of NM/O₂/Ar mixture at 1202 K and 0.853 bar occurs at around 200 μs. The identification of the onset of the exothermal reaction is based on the simulated T profiles. The simulated ignition delay time is shorter than the experimental one for both models and will need further improvement. Nevertheless, since NM concentration evolution is better captured by the mechanism of MechDC, the ignition delay times needed to analyse the SDT and the the ignition delay in a detonation will be estimated using this mechanism.

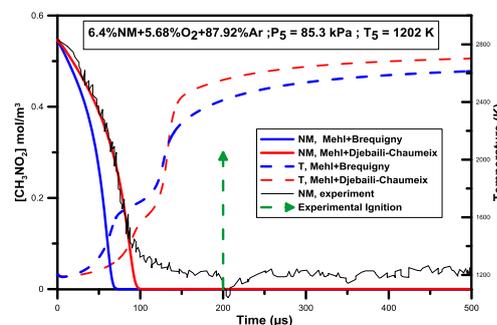


Figure 4. Experimental and computed Profiles of NM behind RSW propagating in 6.4%NM-5.68%O₂-87.92%Ar mixture at P₅ = 85.3 kPa and T₅=1202 K.

4.2 Detonation of nitromethane/ oxygen mixtures

The detonation of three different mixtures has been investigated labelled M1 (0.5Ar+0.285NM + 0.215O₂), M2 (0.5Ar+ 0.308NM+0.192O₂) and M3 (0.571NM+ 0.243O₂) mixtures. The experiments were performed at P₁ ranging from 0.784 to 8.25 kPa and at ambient temperature. The mixture is submitted to the incident shock wave as described previously. P₂ and T₂ are deduced from V_{SW} recorded between 3.2 m and 3.65 m from the diaphragm which separates driver and driven gases. When the SDT is observed in the measurement zone, V_{CW} can be much higher than D_{CJ}(1), as shown in Fig. 5 for the diluted stoichiometric mixture M1. In this case, T_{2,c} and P_{2,c} are equal to 840 K and 40.6 kPa respectively for P₁ = 2.4 kPa and T₁=295 K. In the transition zone, the pressure P₆ behind CW reaches about 350 times P₁. At very low initial pressures, the gap between D_{exp} and D_{CJ}(1) becomes important (about 10% at P₁ =2 kPa). The cell sizes have been recorded on a soot foil. With the NM-0.75O₂ mixtures some substructures were observed inside the main cell in agreement with the Manzhelii criterion [21]. For these mixtures, the ratio Ta/T_{ZND} (Ta being the activation temperature and T_{ZND} the Zeldovich-Von Neumann-Doering temperature behind the leading shock) is less than 5.5. In some cases, these substructures remain visible in the whole main cell as it was reported by Presles et al. [22]. By using [16] kinetic model, Sturzer et al. [23] showed that these substructures are due to the release of chemical energy in two steps. In Fig. 6, the cell sizes of stoichiometric NM/O₂ mixtures have been compared to those of C₇H₁₄/O₂ mixtures and other systems summarized in [24]. From this diagram, the detonation sensitivity of NM/O₂ mixtures is close to that of n-heptane /O₂ mixtures and are much less sensitive than hydrazine and UDMH mixtures.

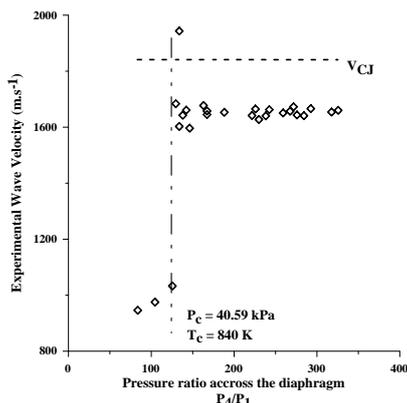


Figure 5. Determination of critical pressure P_C and temperature T_C for SDT in 28.55% NM-21.45% O₂-50% Ar mixture at P₁= 2.4 kPa.

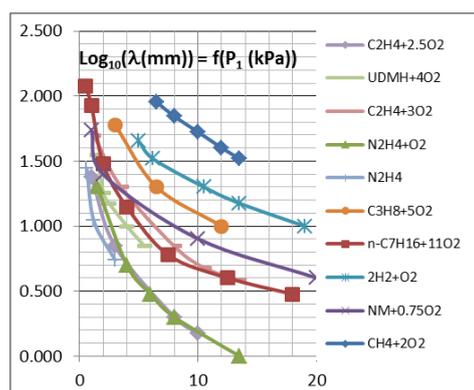


Figure 6. Log₁₀(λ) versus the initial pressure of NM/0.75O₂ and n-C₇H₁₆/O₂ mixtures, compared with the cell size of various fuel/O₂ mixtures summarized by Abid et al. [24]

4.3 Effect of NM addition on the SDT in C₇H₁₆/O₂ mixtures

The ability of the explosive mixture to detonate has been studied as a function of I_{PSW}. The critical conditions P_{2,c} and T_{2,c}, as well as detonation cell sizes (Fig. 7) have been determined for a series of experiments with the stoichiometric mixtures at T₁≈295 K, and P₁≈2.0 and 4.0 kPa. The content of NM in the stoichiometric mixture varies from 1 to 20 mol%. The detonation parameters as well as the cell size (Fig. 8) are practically not modified by the introduction of 1% to 20% NM in the mixture at constant stoichiometry. So, if there is any effect on the SDT, it would be due to the chemical mechanism during the transition period. The conditions of SDT in the measurement section are reported in table 1 for 0, 1, 5, and 20 mol% NM in fuel mixtures at P₁ = 2.0 and 4.0 kPa. the critical pressure P₂⁻ correspond to the case where the merging point is located inside of the measurement zone (Fig. 3-b). P₂⁺ corresponds to merging point well before the measurement zone (fig. 3-d), hence V_{CW} tends to the self-sustained detonation velocity D_{exp}.

The ignition delay times τ_{i,2} have been computed by taking into account oxidation of n-heptane and nitromethane at high (T₂>1000 K) and at low (T₂<1000 K) temperatures. The results are given in

Table 1. These delay times are compared with particles heating times $\tau_{2,meas}$ located near contact surface (CS) between driver gas and driven gases. The computed delay is too long to be compatible with experimental delay times. This conclusion enhances the assumptions about the importance of the variation of the thermodynamic state (especially the gradient of temperature) resulting from the turbulence which develops in the boundary layer behind the PSW, as described by [25].

Table 1: mean ignition delay times $\tau_{i,2}$ computed under T_2, P_2 conditions, and ignition delay times, $\tau_{2,meas}$, deduced from trajectories of the waves. $\tau_{2,vN}$: auto-ignition delay time under von Neuman assumptions.

P_1 (kPa)	% _{NM}	P_2^- (kPa)	P_2^+ (kPa)	T_2^- (K)	T_2^+ (K)	$\tau_{i,2}$ (ms)	$\tau_{2,meas}$ (ms)	$\tau_{2,vN}$ (m μ)
2.0	0	59.2	61.4	1010 \pm 4	1031 \pm 4	13.6	1.82 \pm 0.13	7.78
	1	57.4	61.8	998 \pm 5	1047 \pm 5	11.4	1.80 \pm 0.13	7.80
	5	58.0	62.8	1000 \pm 5	1051 \pm 7	7.03	1.80 \pm 0.13	7.41
	20	58.0	67.6	1002 \pm 5	1095 \pm 5	2.92	1.73 \pm 0.12	5.89
4.0	0	93.2	96.0	882 \pm 2	900 \pm 4	44.3	2.10 \pm 0.15	3.13
	1	84.8	94.0	839 \pm 5	892 \pm 5	40.3	2.15 \pm 0.15	3.12
	5	96.0	100.0	900 \pm 4	916	22.02	2.06 \pm 0.14	2.96
	20	96.8	104.8	901 \pm 7	942	9.41	2.03 \pm 0.14	2.33

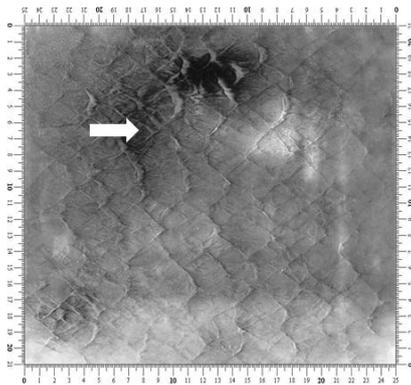


Figure 7. Detonation cellular structures in 20 mol% NM in n-heptane/O₂ mixture, initially at $P_1=2.0$ kPa and $T_1\approx 295$ K

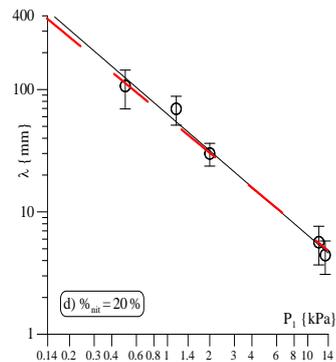


Figure 8. Evolution of the cell width λ with P_1 for 20% NM in fuel (circles and dashed line) compared with evolution of λ in n-heptane/O₂ mixture (continuous line)

Finally, the SDT is not accelerated by addition of NM to n-heptane. Other additives such as hydrazine would be probably more efficient but they are more unstable than NM. The SDT could be reduced by coupling electric discharge with the passage of PSW to earlier initiate the ignition behind the shock of moderate intensity.

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