Effect of two Additives (CH_3NO_2 and H_2O_2) on the Detonation Properties of Gaseous Stoichiometric n-C_7H_{16} / O_2 Mixtures

Bruno Imbert, Laurent Catoire, Nabiha Chaumeix, Gabrielle Dupré, Claude Paillard

Laboratoire de Combustion et Systèmes Réactifs (L.C.S.R.) / C.N.R.S.
and University of Orleans
1C, avenue de la Recherche Scientifique, F - 45071 Orléans cedex 02, France
paillard@cnrs-orleans.fr

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Aims of this study:

Pulsed detonation engines (P.D.E.) are a type of propulsion mode for future hypersonic flight or low cost launchers. They rely on a detonation operating cycle (at a rate higher than 100 Hz), which requires a rapid Deflagration- to- Detonation Transition (D.D.T.).
To make easier, and safer, the fuel storage, and its transportation, it can be convenient to use for P.D.E. systems, liquid hydrocarbon based mixtures, rather than gaseous ones. Consequently, n-heptane detonation properties may be of fundamental interest for this kind of applications.

We have presented recently, an experimental study dealing with the detonation properties of n-heptane/oxygen gaseous mixtures, diluted or not in argon (Imbert *et al*. 2003 and 2004).
It has been shown that the stoichiometric C_7H_{16} / O_2 mixture cell width λ_{exp} varies in the same way than oxygen / light alkenes (ethylene or propene) ones. That involves, for a mixture initially at the ambient temperature T_1 and pressure P_1, a critical initiation energy $E_c \propto \lambda_{exp}^3$, about hundreds of mJ in oxygen, and hundreds of kJ in air (case closer to a practical application).

As the direct initiation can’t be considered for a repeated use on long distance flies, it appears necessary to promote the D.D.T. in order to reduce both “run up” transition distance and time.
Traditional mechanical systems intended to this goal generally requires obstacles: Shchelkin spirals, periodic plates with adapted blockage ratio, *etc*. These processes are proved to be particularly efficient to accelerate the flame (Sorin *et al*., 2003, *etc*.), but have nevertheless the drawback to hinder the thrust tube. The embarrassment, thus caused, slows down the burnt gases exhaust, as well as the fuel / air filling and mixing, and consequently reduces both the cycle maximum frequency, and the P.D.E. propulsion mechanical performances.

This work presents, like an alternative possibility, the combustion kinetics promotion by a chemical additive effect. This process does not present such a drawback, and logically enables to change the typical kinetic sizes, which characterize the mixture sensitivity to detonation, through:

- the induction time τ_i, and distance Δ_i, as described by the one-dimensional model Z.N.D.;
- the cell size λ (assuming a proportionality factor $A = \lambda / \Delta_i$ varying little with the additive fraction).

Indeed, several former experimental and numerical studies prove the additive effect on the gaseous
fuel / oxidizer mixtures auto-ignition delays. According to its chemical nature, the additive may:

- promote the D.D.T., i.e. to sensitize the detonation, and to shorten the ignition delays τ, like:
  - nitrates (Zhang *et al.*, 2001);
  - aluminum alkyl (Ryan *et al.*, 1995);
  - peroxides (Inomata *et al.*, 1990);
  - dimethyl ether (Karpuk *et al.*, 1991);
- inhibite it, and to reduce accidental detonation risks: halogenated compounds (Evariste *et al.*, 1996).

This study tries to characterize the additive effect, on gaseous heptane based mixtures ignition and detonation, of two possible reactive molecules:

- nitromethane (CH_3NO_2), liquid explosive, which vapor can explode in gas phase, only, or with oxygen, and which can be used as a doping agent for car gasoline. The effect of the addition of nitromethane has been studied experimentally.
- hydrogen peroxide (H_2O_2), object of many researches in aeronautics, nowadays, as a “green” monopropellant or a storable oxidant, in order to reduce propulsion pollution. This additive effect has been studied numerically.

Influence of the nitromethane as an additive:

The additive effect on the detonation cell sizes λ_{exp} of n - heptane based mixtures is studied behind incident shock waves in a stainless-steel shock tube (78 mm i.d.) which has (figure 1):

- a 1 m long driver section filled with helium, at the pressure $P_4 \in$ [1 bar; 16 bar]
- a test section, about 4.50 m long, in which:
  - reactive mixtures are initially introduced at the total pressure $P_1 \in$ [200 Pa; 14 kPa], and $T_1 \approx 20°C$;
  - several diagnostic instruments (4 piezoelectric pressure transducers and a soot foil) are located close to the endwall, to get the maximum possible predetonation length $L_{DDT, max}$ here at about 3.20 m:

Experiments have been done for four additive amounts ($\%_{Nit}$ = 0; 1 %; 5 % and 20 %), with:

$\%_{Nit} = 100 \cdot \dfrac{X_{CH_3NO_2}}{X_{CH_3NO_2} + X_{C_7H_{16}}}$, and X_S the specie S mole fraction in the gaseous mixture.

Nitromethane is introduced in so small quantities ($X_{CH3NO2} \leq 2$ %) that it has only very little effect on detonation speeds, and thermodynamic parameters (fig. 2 and table 1). Consequently, heptane-based mixtures sensitivity to detonation enhancement depends only on the combustion kinetics improvement.

The relative C-N bond weakness ($E_{C-N} = 305$ kJ.mol^{-1}), enables this additive to dissociate in a quite fast and easy way, in two fairly reactive radicals according to: $CH_3NO_2 + M \Leftrightarrow °CH_3 + °NO_2 + M$.

Because of this, we can expect a shortening of the induction period Δ_i behind the leading shock (according to the Z.N.D. model), and thus, a cell width λ decrease (provided that A factor varies little).

Actually, the cellular structure characteristics (general aspect, as well as cell sizes L and λ) are the same, with or without nitromethane. For example, the pattern printed on the soot foil (figure 3):

- remains weakly regular, according to Libouton *et al.* (1981) classification;

- does not reveal additional substructures, which could be due to the nitromethane decomposition mechanism in two stages, as Presles *et al.* (1996) observed it in a rich CH_3NO_2 / O_2 mixture ($\Phi \geq 1.3$);
- is linked to a cell size ratio L / λ ≈ 1.4, and an opening angle seen from the apex close to 70°.

Above all, the power type empirical law $\frac{\lambda_{exp}}{\lambda_0} \approx \left(\frac{P_1}{P_0}\right)^{-n_\lambda}$ which best describes the evolution of the cell size $\lambda_{cor} \approx \lambda_{exp}$ versus the initial pressure P_1, does not seem to depend on the additive amount $\%_{Nit}$, com- pared to the measurement uncertainties $\Delta\lambda_{exp} \approx 0.3 \times \lambda_{exp}$ (95 % interval confidence) (fig. 4 and table 2)

Consequently, CH_3NO_2 appears to have very little effect, as an additive, on the thermodynamic and kinetic detonation characteristics of stoichiometric C_7H_{16} / O_2 mixtures. This explosive molecule, however reactive when it is alone, does not seem to be selected to sensitize this kind of mixtures.

This observation confirms the remark of Akbar *et al.* (2000), who have studied the nitrate based sensitizers on hydrocarbon fuel JP-10. They have shown that it is not possible to largely increase these mixtures sensitivity to detonation, by adding a small amount of nitrate, since its typical cell size is comparable with that of the main mixture, for similar conditions.

Influence of hydrogen peroxide (H_2O_2) as an additive:

Golovitchev *et al.* (1996) have shown in a numerical and experimental study, that H_2O_2 shortens the ignition delay of gaseous CH_4 / O_2 mixtures. Agarwal and Assanis (2001) have concluded the same, thanks to their experiments. Recently, Frolov *et al.* (1999 and 2002), have shown numerically, that the addition of 20 % and of 60 % H_2O_2, with respect to O_2, on iso-octane, enables to reduce the detonation cell width λ of C_8H_{18} / air mixtures by factors close to 10 and 100, respectively.

In this study, Rente and Golovitchev (2001) reduced kinetic model, has enabled to simulate with Chemkin III, the peroxide effect on induction delays τ_i, for stoichiometric n-C_7H_{16} / "air" mixtures defined by: C_7H_{16} / O_2 / H_2O_2 / N_2 with: $\frac{X_{N_2}}{X_{O_2}} = 3.76$, and $\%_{Per} = 100 \cdot \frac{X_{H_2O_2}}{X_{H_2O_2} + X_{O_2}} = 0$; 1 %; and 5 %.

H_2O_2 efficiently promote the heptane combustion (figure 5), as an oxidizing additive: a relative little fraction $\%_{Per} = 1$ % seems to reduce the ignition time τ by a factor 4 (1,4 ms → 350 µs), without changing the final °OH mole fraction X_{OH}, at the thermodynamic equilibrium (only 2 % of relative rise). This spectacular result can be interpreted by a highly eased initiation stage, which quickly reveals a plate of radicals OH, which result from the homolytic bond O-O break ($E_{O\text{-}O}$ = 142 kJ.mol^{-1}) according to: $H_2O_2 + M \Leftrightarrow {}^\circ OH + {}^\circ OH + M$. The initial amount of °OH ($X_{OH} \approx 8 \times 10^{-7}$) shortens the initiation period, and quickly propagates the reaction, once the first active species resulting from C_7H_{16} have been formed.

Table 3 summarizes calculated shortening factors τ_{ref} / τ, for very wide conditions (T ∈ [800 K ; 1500 K], P ∈ {5 bar; 40 bar}). They seem maximum for temperatures close to the upper Negative Coefficient Temperature (N.C.T.) region limit (T ∈ [1000 K ; 1100 K]), and raise with $\%_{Per}$.

This kinetic result which seems to particularly encourage the use of H_2O_2 as a D.D.T. sensitizer, can be confirmed by the cell width λ analysis, typical of the established self-sustained detonation.

Although Gavrikov *et al.* (2000) expression seems to predict for mixtures C_7H_{16} / O_2 / Ar, a cell width λ_{Gav}, and thus, a correlation factor A_{Gav} approximately nine times smaller than the real one, it well reproduces these two parameters evolution, versus the initial combustible mixture physicochemical characteristics (Imbert *et al.*, 2004). Consequently, as all these values (required, and associated to the reference mixture) are approximately nine times too small, it is possible to define a "normalized proportionality factor" $A_{norm} = A_{Gav} / A_{Gav, ref}$, which analysis becomes then relevant (table 4).

The induction distance $\Delta_i = \tau_i \cdot u_{VN}$ fall, and the slight A_{norm} factor decrease, must contribute to significantly reduce the size λ linked to doped mixtures, and thus enhance their sensitivity to detonation.

It must be pointed out that the additional role of H_2O, which goes with H_2O_2 in great quantity, for stability reasons, and which can act as a thinner from a kinetic point view, is neglected in this simulation.

As Landry *et al*. (2003) have experimentally shown that the addition in $C_{10}H_{22}$ / O_2 mixtures, of H_2O_2 / H_2O (50 % - 50 % in weight) make the run up distance L_{DDT} grow, because of the dilution effect, the simulation must be kept on, in the future, by considering the additional effect of a H_2O.

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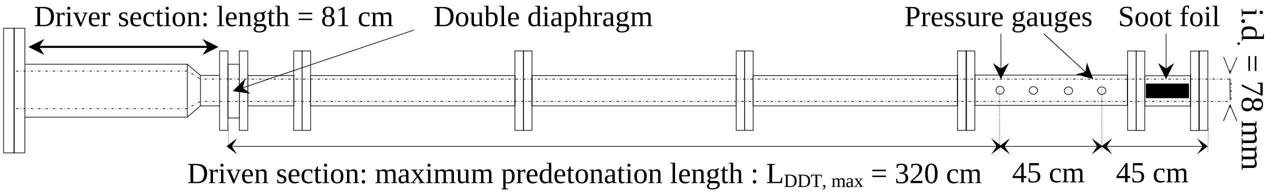


Figure 1 : Simplified sketch of the shock tube used for this study.

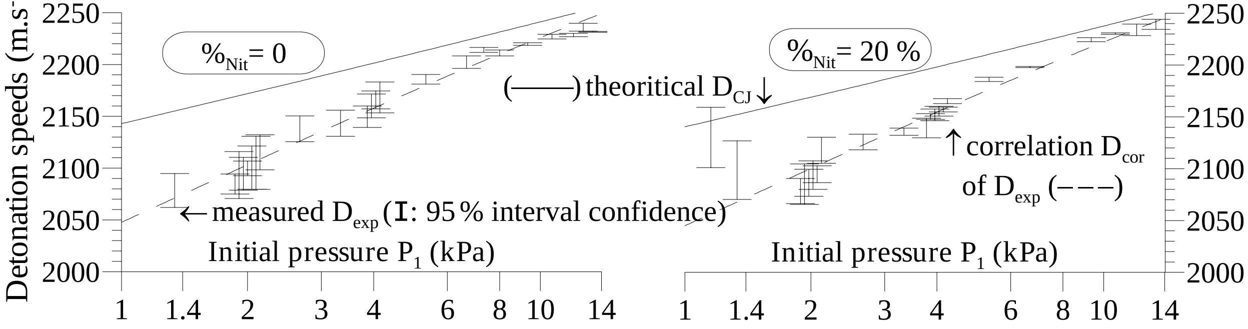
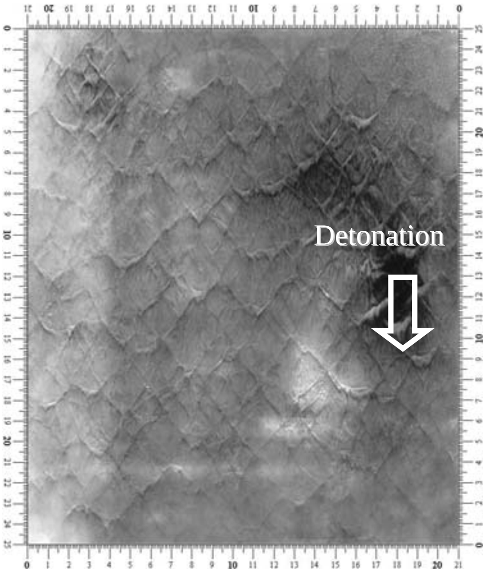


Figure 2 : Evolution of detonation speeds D_{CJ}, D_{exp} and D_{cor} versus the initial pressure P_1 of the stoichio- metric C_7H_{16} / CH_3NO_2 / O_2 mixture (T_1 = 20°C), for $\%_{Nit}$ = 0 and $\%_{Nit}$ = 20 % (log.-normal plot).



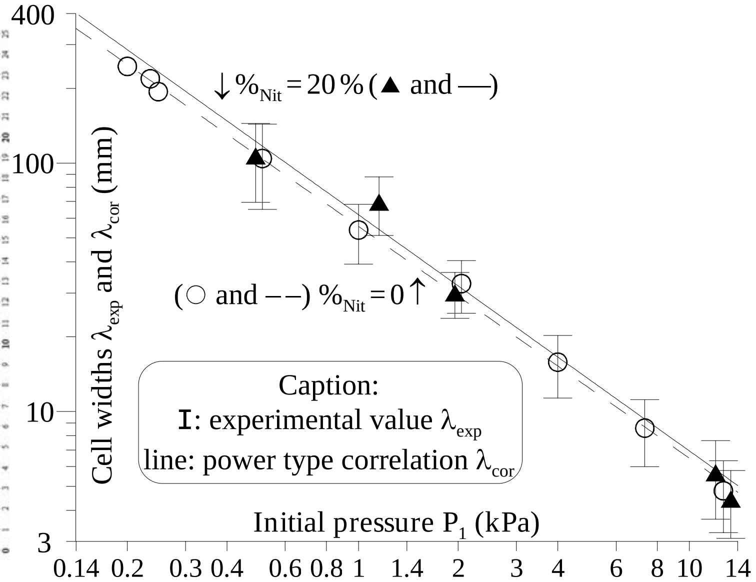


Figure 3 (on the left) and **4** (on the right): Cellular structure characteristics of the detonation of stoichiometric mixture C_7H_{16} / CH_3NO_2 / O_2, initially at temperature T_1=20°C, and pressure P_1:

- Fig. 3: cellular pattern printed on a soot foil, for P_1 = 2,0 kPa and $\%_{Nit}$ = 20 %;
- Fig. 4: evolution of cell widths λ_{exp} and λ_{cor} versus P_1 for $\%_{Nit}$ = 0 and $\%_{Nit}$ = 20 % (log.-log. plot)

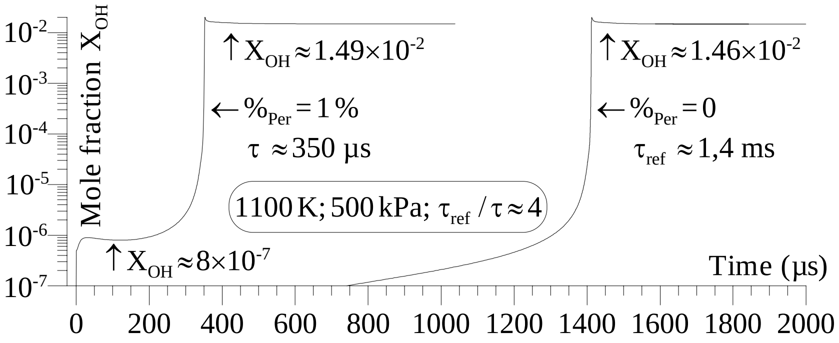
P_1 (kPa)	$\%_{Nit}$ (%)	D_{CJ} (m.s^{-1})	T_{CJ} (K)	P_{CJ} (kPa)	D_{cor} (m.s^{-1})	T_{VN} (K)	P_{VN} (kPa)	u_{VN} (m.s^{-1})
2.0	0 (ref)	2172	3175	70.0	2102	1654	126.4	187.6
2.0	20	2169	3171	70.5	2098	1651	127.4	185.6
4.0	0 (ref)	2201	3284	143.5	2157	1716	266.5	189.5
4.0	20	2198	3279	144.5	2154	1713	268.6	187.4

$\%_{Nit}$ (%)	λ_0 (mm)	n_λ	P_{lim} (Pa)
0 (ref)	0.76	0.93	194
1	0.76	0.95	229
5	0.60	1.02	276
20	0.66	0.99	253

Tables 1 (on the left) and **2** (on the right): Evolution, versus the nitromethane amount $\%_{Nit}$ of stoichiometric mixture C_7H_{16} / CH_3NO_2 / O_2, initially at temperature T_1 = 20°C and pressure P_1, of the:

- theoretical D_{CJ} and semi-empirical D_{cor} detonation speed (see figure 2);
- final thermodynamic state on Chapman Jouguet surface (T_{CJ}, P_{CJ} calculated from D_{CJ}) ;
- von Neumann state (T_{VN}, P_{VN}), and unburned gas speed u_{VN} in the leading shock referential ($\Leftarrow D_{cor}$);
- power type law coefficients (extrapolated cell width λ_0 at pressure P_0 = 100 kPa, and exponent n_λ);
- calculated detonation limit pressure P_{lim}, in the shock tube (i.d. = 78 mm) so that $\lambda_{cor}(P_{lim}) = \pi\cdot\{\text{i.d.}\}$;

τ_{ref} / τ	$\%_{Per}$ = 1 %		$\%_{Per}$ = 5 %	
P T	500 kPa	4.0 MPa	500 kPa	4.0 MPa
800 K	1.3	1.3	2.1	1.5
900 K	2.8	1.3	8.5	2.0
1000 K	4.0	2.4	15.0	6.3
1100 K	4.0	3.6	15.0	12.6
1300 K	2.0	2.5	5.0	8.0
1500 K	1.3	1.6	2.0	4.0



$\%_{Per}$ (%)	D_{CJ} (m s^{-1})	T_{VN} (K)	τ_i (µs)	Δ_i (mm)	A_{norm}	λ_{norm}
0 (ref)	1796	1540	3.7	1.00	1.00	1.00
1	1797	1540	2.6	0.70	0.91	0.64
5	1800	1540	1.3	0.35	0.77	0.27

Figure 5, **tables 3** (up) and **4** (bottom):

Kinetic characteristics of stoichiometric n-heptane / air mixture with hydrogen peroxid in small amounts:
C_7H_{16} / H_2O_2 / O_2 / N_2; X_{N2} / X_{O2} = 3.76; $\%_{Per} \leq 5$ %

Fig. 5: °OH mole fraction profiles (T = 1100 K; P = 500 kPa; $\%_{Per}$ = 0 and 1 %; normal -log. plot).
Table 3: computed shortening factors τ_{ref} / τ for the ignition delays τ behind a shock wave.
Table 4: theoretical detonation speed D_{CJ}, von Neumann temperature T_{VN}, induction time τ_i, distance Δ_I, normalized A factor (A_{Gav} / $A_{Gav,\,ref}$ computed according to Gavrikov *et al.*), and cell width (λ / λ_{ref}).