

Study of overdriven detonations of H₂-NO₂/N₂O₄ mixtures

Jocelyn Luche, Daniel Desbordes, Henri Noël Presles

Laboratoire de Combustion et de Détonique, UPR 9028 CNRS, ENSMA, BP 40109, 86961
Futuroscope Chasseneuil, France

Corresponding author, Jocelyn Luche: jocelyn.luche@lcd.ensma.fr

1. Introduction

The specific features of self-sustained detonations of a mixture of fuel with NO₂ as oxidizer is the appearance of two main exothermic reaction steps during the heat release process behind the leading shock wave. These two steps find their expression in the existence of a double detonation cellular structure (λ_1 and λ_2) for the stoichiometric and rich mixtures (and probably for the very lean mixtures). These two structures are correlated to the two calculated characteristic chemical induction lengths (Li_1 and Li_2) consequence of the existence of two local maximum reaction rates during the heat release behind the leading shock wave (Lamoureux et al., 2001; Joubert, 2001; Joubert et al., 2003; Desbordes et al., 2004). In particular in H₂-NO₂/N₂O₄ systems, for equivalence ratio $\phi \geq 1$ in the range $0.5 < \phi < 2.0$, each two cells λ_1 and λ_2 of the first and second reaction steps varies proportionally to Li_1 and Li_2 (calculated in the ZND frame with a detailed chemical kinetics (Joubert et al., 2003)) by a quasi constant factor k ($\lambda_i = k Li_i$) of about 15-20. In order to estimate, in these conditions, the post-shock temperature dependency of Li_i (and λ_i), overdriven detonation of different overdriven degrees, D/D_{CJ} , are considered numerically and experimentally. For these different detonation propagation regimes, the comparison between calculations and experiments of the $Li_i/Li_{i,CJ}$ (D/D_{CJ}) and $\lambda_i/\lambda_{i,CJ}$ (D/D_{CJ}) dependencies can provide global activation energy Ea_i of each reaction step assuming that $Li_i \sim \lambda_i \sim \exp(Ea_i/RT)$. Experimentally, quasi-steady overdriven detonation in rich H₂-NO₂/N₂O₄ mixtures are obtained by using the shock tube technique explained in details in Desbordes and Lannoy, 1990.

2. Experimental set-up

Detonations of H₂-NO₂/N₂O₄ mixtures were conducted experimentally at ambient initial temperature $T_0 = 293K$ in a steel detonation tube (52 mm internal diameter) consisting of two parts separated by a thin Mylar foil (thickness of 40 μ m). The first part A, the driver section, of 6 m long allows initiating and stabilizing a quasi-CJ detonation wave in stoichiometric C₂H₄/O₂ mixture at various initial pressure $P_{0,A}$. Provided that $P_{0,A}$ is large enough in comparison with $P_{0,B}$ (the initial pressure of the part B), the Mylar foil rupture caused by this detonation wave involves the creation of a quasi-steady overdriven detonation wave in the second part (part B), the driven section of 1 m long. This section contains the H₂-NO₂/N₂O₄ mixture at equivalence ratio $\phi = 1.2$ and initial pressures $P_{0,B} = 0.4$ bar and 0.5 bar.

Instrumentation includes pressure transducers in order to characterize the detonation propagation regimes (detonation pressure jump P and velocity D) in the first and the second part of the tube and smoked foil plates in the driven section in order to record cellular

structure of the overdriven detonation wave in H_2 - NO_2/N_2O_4 mixtures. For fixed initial pressure $P_{0,B}$ of H_2 - NO_2/N_2O_4 , initial pressure $P_{0,A}$ of $C_2H_4 + 3O_2$ mixtures was determined with respect to the expected overdriven degree D/D_{CJ} of the detonation regime in H_2 - NO_2/N_2O_4 mixtures given by the detonation polar analysis in the P_1, U_1 plane on Fig. 1 (see Desbordes and Lannoy, 1990).

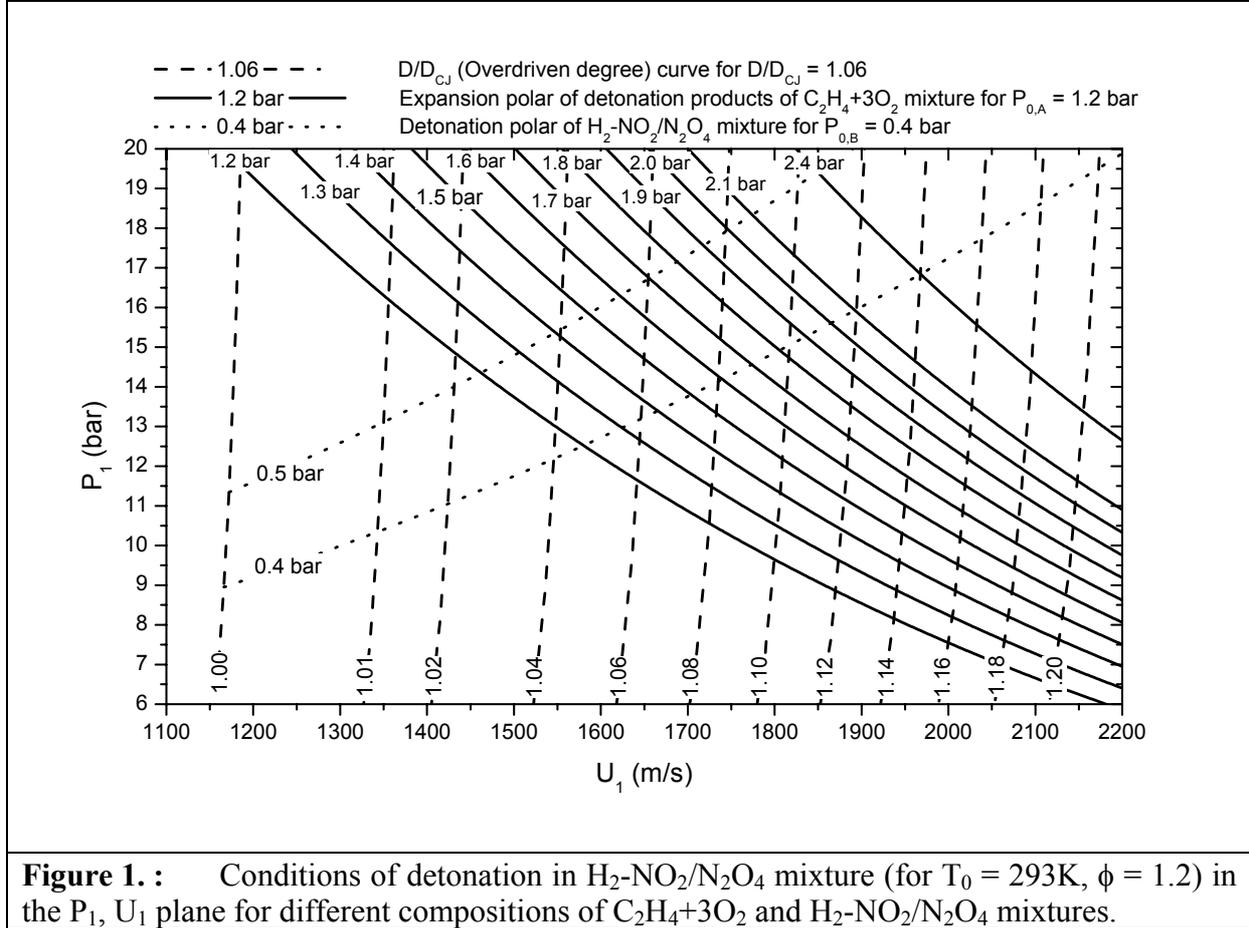


Figure 1. : Conditions of detonation in H_2 - NO_2/N_2O_4 mixture (for $T_0 = 293K, \phi = 1.2$) in the P_1, U_1 plane for different compositions of $C_2H_4 + 3O_2$ and H_2 - NO_2/N_2O_4 mixtures.

3. Results

Steady overdriven detonations are obtained in H_2 - NO_2/N_2O_4 mixtures quasi instantaneously by choosing adequate condition of initial pressure $P_{0,A}$ in the driver section. Typical smoked foil records of cellular structure in H_2 - NO_2/N_2O_4 mixture at $\phi = 1.2, P_{0,B} = 0.4$ bar are displayed in Fig. 2 for the CJ detonation regime (Fig. 2a) and two steady overdriven detonation regimes characterized by their overdriven degree (D/D_{CJ} ratio) $D/D_{CJ} = 1.07$ (Fig. 2b) and $D/D_{CJ} = 1.12$ (Fig. 2c).

The two nets of cellular structure of size λ_1 (small) and λ_2 (large) appear clearly. The λ_1 cell widths are deduced from these records and are equal to 1.4 mm, 0.32 mm and 0.18 mm for $D/D_{CJ} = 1.00, D/D_{CJ} = 1.07$ and $D/D_{CJ} = 1.12$ respectively while the λ_2 cell widths are found to be equal to 42.9 mm ($D/D_{CJ} = 1.00$), 13.7 mm ($D/D_{CJ} = 1.07$) and 10.2 mm ($D/D_{CJ} = 1.11$).

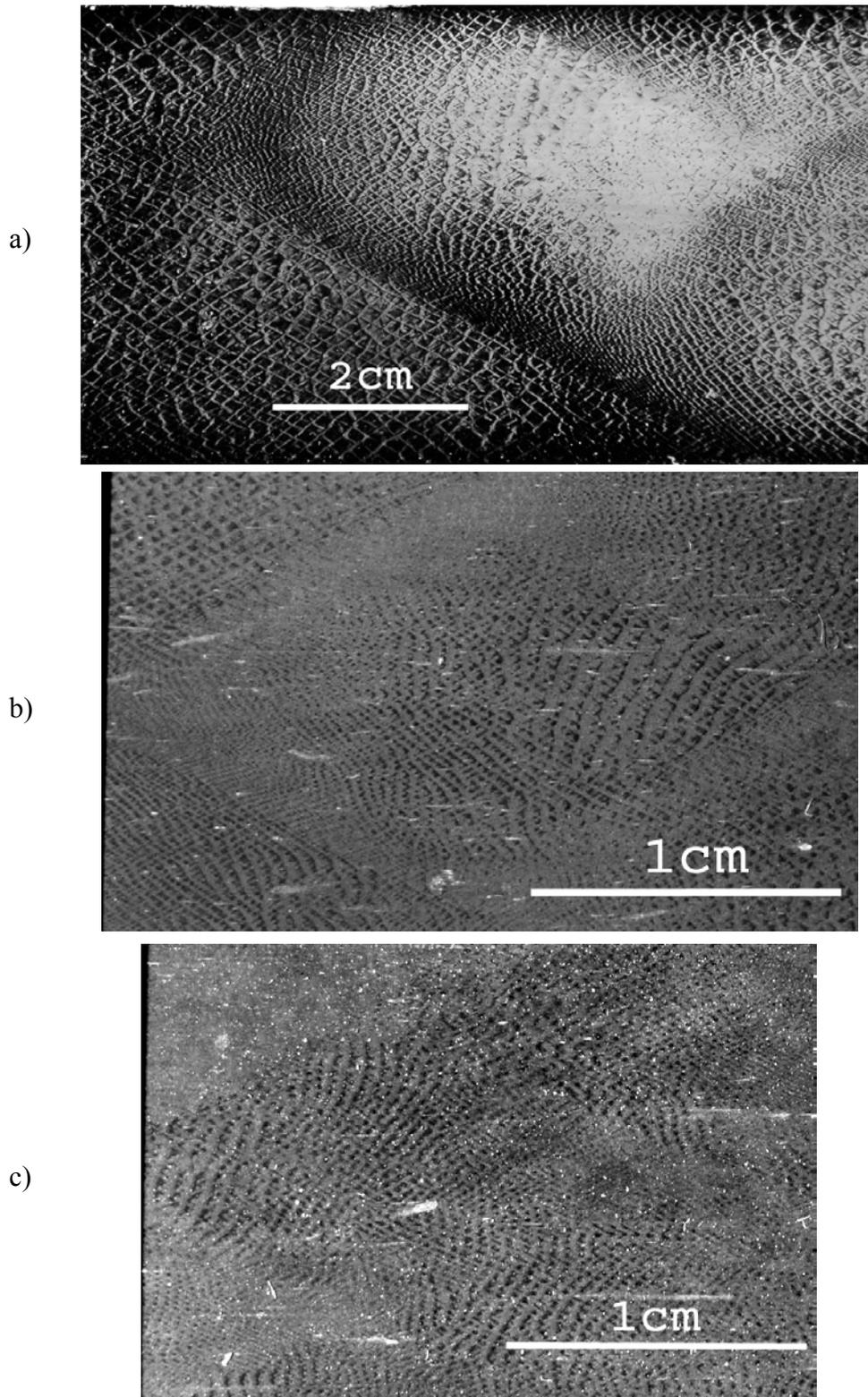


Figure 2. : Typical smoked foil records for CJ detonation regime (a) and for 2 steady overdriven detonation conditions: $D/D_{CJ} = 1.07$ (b) and $D/D_{CJ} = 1.12$ (c) in H_2-NO_2/N_2O_4 mixture at $\phi = 1.2$, $P_{0,B} = 0.4$ bar and $T_0 = 293K$.

As previously observed in single detonation cellular system (Vasiliev and Nikolaev, 1978; Gravrilenko and Prokhorov, 1983; Huang and Xu, 1987; Desbordes, 1988; Desbordes et al., 1990; Meltzer et al., 1990), the cell sizes λ_1 and λ_2 drastically decreased as D/D_{CJ} ratio increased. As D/D_{CJ} increased from 1 to about 1.1, cellular structure sizes decrease from 1 to roughly 0.3. The overdriven cell sizes have decreased drastically up to a factor around of 10 in comparison of those measured in the quasi-CJ detonation regime.

Experimental values $\lambda_i/\lambda_{i,CJ}$ vs. D/D_{CJ} and numerical values $L_i/L_{i,CJ}$ vs. D/D_{CJ} for $P_{0,B} = 0.4$ bar and $P_{0,B} = 0.5$ bar in H_2-NO_2/N_2O_4 mixtures are reported for each reaction step (λ_1, L_{i_1} and λ_2, L_{i_2}) in Fig. 3 and Fig. 4 respectively. Chemical induction lengths (L_{i_1} or L_{i_2}) are numerically derived from the calculated induction times of the detailed chemical kinetic mechanism (Joubert et al., 2003) computed with the STANJAN code of the CHEMKIN II package (Kee et al., 1993; 1994).

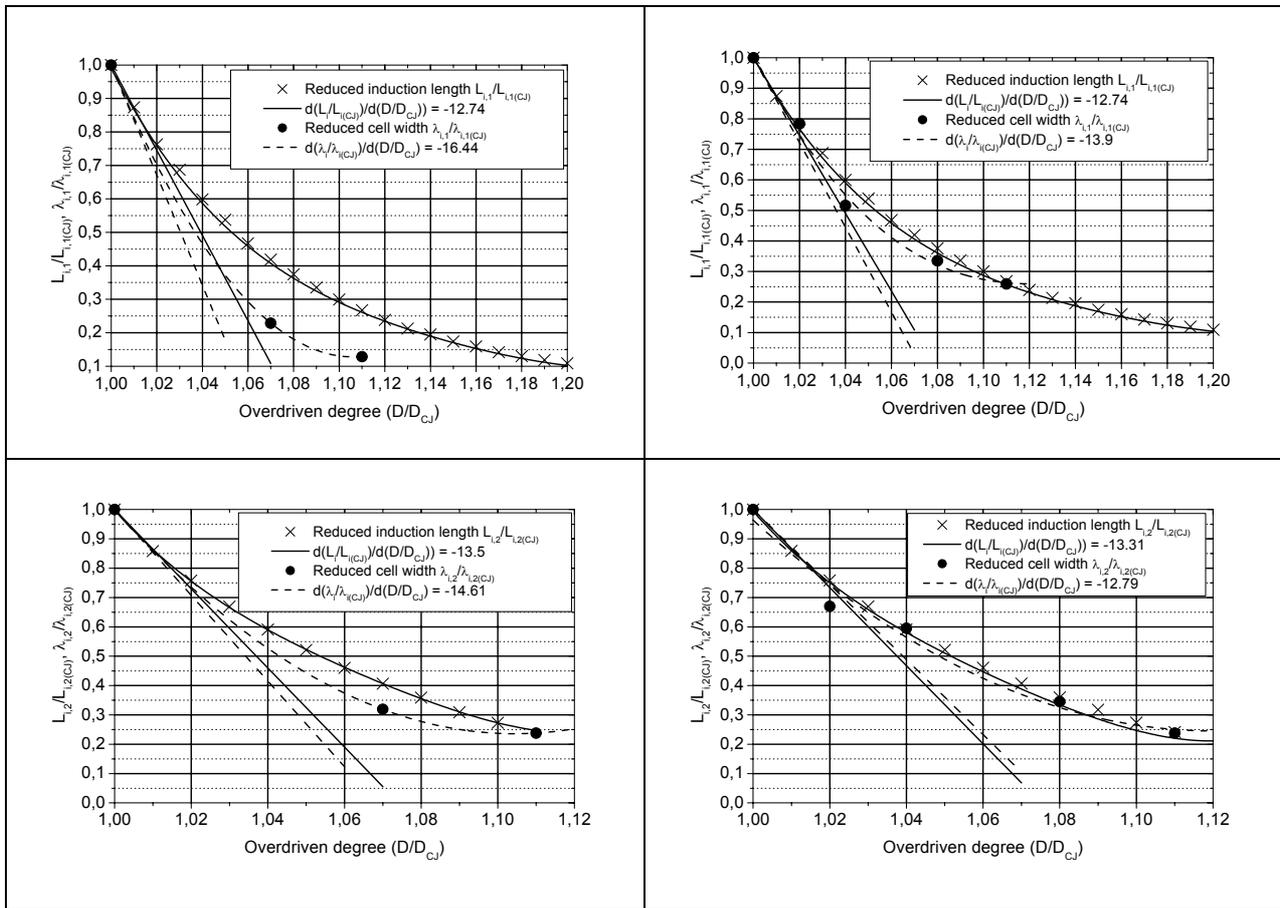


Figure 3. : Experimental values $\lambda_i/\lambda_{i,CJ}$ vs. D/D_{CJ} and numerical values $L_i/L_{i,CJ}$ vs. D/D_{CJ} for H_2-NO_2/N_2O_4 mixture at $\phi = 1.2$, $P_{0,B} = 0.4$ bar and $T_0 = 293K$ ($i = 1$ and 2).

Figure 4. : Experimental values $\lambda_i/\lambda_{i,CJ}$ vs. D/D_{CJ} and numerical values $L_i/L_{i,CJ}$ vs. D/D_{CJ} for H_2-NO_2/N_2O_4 mixture at $\phi = 1.2$, $P_{0,B} = 0.5$ bar and $T_0 = 293K$ ($i = 1$ and 2).

Agreements between numerical $L_i/L_{i,CJ}$ (D/D_{CJ}) and experimental $\lambda_i/\lambda_{i,CJ}$ (D/D_{CJ}) curves are quite good with only a small difference between these results essentially due to the measure

uncertainty on detonation cellular widths. In a general way, the size λ_i of the detonation structure of a chemical system depends on the local detonation velocity D by the approximate relationship:

$$\frac{\lambda_i}{\lambda_{i,CJ}} \cong \frac{Li_i}{Li_{i,CJ}} \cong \frac{D}{D_{CJ}} \exp\left(\frac{Ea_i}{RT_{ZND}} \left[\left(\frac{D_{CJ}}{D}\right)^2 - 1\right]\right)$$

where $\lambda_i = \lambda_{i,CJ}$ when $D = D_{CJ}$, Ea_i being the activation energy of the step (i).

The slope of the curve $\lambda_i/\lambda_{i,CJ} = f(D/D_{CJ})$ deduced of this expression is approximately equal to $-2Ea_i/RT$. In the particular case $D/D_{CJ} = 1.0$, the slope of the curves $\lambda_1/\lambda_{1,CJ} = f(D/D_{CJ})$ corresponds to $-2Ea_1/RT_{ZND}$ and that of $\lambda_2/\lambda_{2,CJ} = f(D/D_{CJ})$ corresponds to $-2Ea_2/RT_1$, T_1 being the temperature at the end of the first exothermic step and at the beginning of the second exothermic step. So, it is possible to deduce the reduced activation energy (Ea_i/RT) and the activation energy (Ea_i) from the two curves, each of them can be associated respectively with the two characteristic chemical steps during the process of heat release. Those results are presented in Table 1.

$P_{0,B} = 0.4$ bar	Slope of $Li_i/Li_{i,CJ}$ (D/D_{CJ}) curves	T	Ea_i/RT	Ea_i (kcal/mol)
Fig 3a	-12.74	$T_{ZND} \approx 1725K$	≈ 6.37	≈ 21.8 (i = 1)
Fig 3b	-13.50	$T_1 \approx 2938K$	≈ 6.75	≈ 39.4 (i = 2)
$P_{0,B} = 0.5$ bar	Slope of $Li_i/Li_{i,CJ}$ (D/D_{CJ}) curves	T	Ea_i/RT	Ea_i (kcal/mol)
Fig 4a	-12.74	$T_{ZND} \approx 1733K$	≈ 6.37	≈ 21.9 (i = 1)
Fig 4b	-13.31	$T_1 \approx 2946K$	≈ 6.66	≈ 39.0 (i = 2)

Table 1. : Activation energies (Ea_i) of the two exothermic reaction steps for H_2 - NO_2/N_2O_4 mixture deduced from the results of the $Li_i/Li_{i,CJ} = f(D/D_{CJ})$ curves at $\phi = 1.2$, $P_{0,B} = 0.4$ bar and 0.5 bar, $T_0 = 293K$

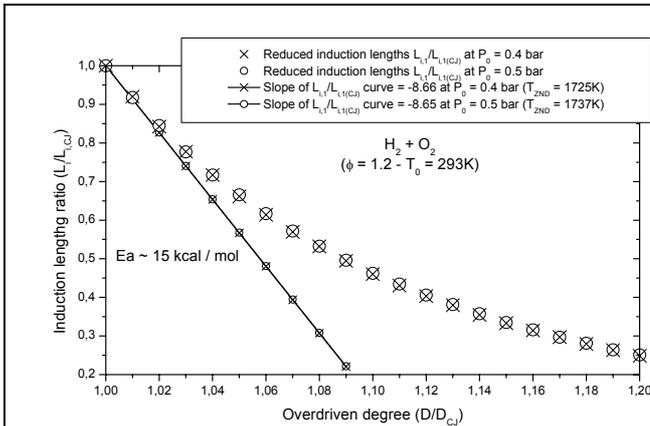


Figure 5. : Experimental values $\lambda_i/\lambda_{i,CJ}$ vs. D/D_{CJ} and numerical values $Li_i/Li_{i,CJ}$ vs. D/D_{CJ} for H_2 - O_2 mixture at $\phi = 1.2$, $T_0 = 293K$, $P_0 = 0.4$ bar and 0.5 bar.

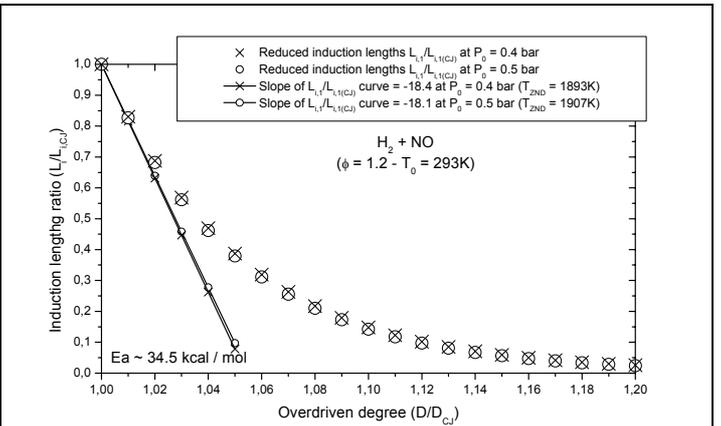


Figure 6. : Experimental values $\lambda_i/\lambda_{i,CJ}$ vs. D/D_{CJ} and numerical values $Li_i/Li_{i,CJ}$ vs. D/D_{CJ} for H_2 - NO mixture at $\phi = 1.2$, $T_0 = 293K$, $P_0 = 0.4$ bar and 0.5 bar.

The activation energy (respectively $E_{a1} \sim 21.8$ kcal/mol at $P_{0,B} = 0.4$ bar and $E_{a1} \sim 21.9$ kcal/mol at $P_{0,B} = 0.5$ bar) of the first exothermic step ($H_2+NO_2 \rightarrow NO+H_2O$) presents a value close to the computed one for a H_2/O_2 mixture, *i.e.* $E_a \sim 19$ kcal/mol according to the study of Desbordes et Lannoy (1990) or a value close to the numerical one deduced from the $Li_i/Li_{i,CJ} = f(D/D_{CJ})$ curves on Fig. 5 (with $E_a \sim 15$ kcal/mol) for a H_2/O_2 mixture in the same conditions. The activation energy (respectively $E_{a1} \sim 39.4$ kcal/mol at $P_{0,B} = 0.4$ bar and $E_{a2} \sim 39.0$ kcal/mol at $P_{0,B} = 0.5$ bar) of the second exothermic step ($H_2+NO \rightarrow \frac{1}{2}N_2+H_2O$) presents a value close to the computed one for a H_2/NO mixture ($E_a \sim 34.5$ kcal/mol deduced from $Li_i/Li_{i,CJ} = f(D/D_{CJ})$ curves on Fig. 6) at $\phi = 1.2$ and $T_0 = 293K$.

4. Conclusion

The study of different overdriven detonation regimes in H_2-NO_2/N_2O_4 mixture of equivalence ratio $\phi = 1.2$ has revealed two cellular structures of different size λ_1 and λ_2 which decreases drastically when overdriven degree (D/D_{CJ}) increases. A quite good agreement between numerical $Li_i/Li_{i,CJ} (D/D_{CJ})$ and experimental $\lambda_i/\lambda_{i,CJ} (D/D_{CJ})$ curves is observed for both cellular structures. The deduced activation energy of the first exothermic step ($H_2+NO_2 \rightarrow NO+H_2O$), $E_{a1} \sim 21.8$ kcal/mol, is close to the value of the activation energy ($E_a \sim 15 - 19$ kcal/mol) of H_2/O_2 mixture and the activation energy of the second exothermic step ($H_2+NO \rightarrow \frac{1}{2}N_2+H_2O$), $E_{a2} \sim 39.0$ kcal/mol, is close to the activation energy for H_2/NO mixture ($E_a \sim 34.5$ kcal/mol). This study confirms the existence for overdriven detonation regime of two detonation cell structures and two exothermic reaction steps that we had already identified in quasi-CJ detonation regime.

References

- D. Desbordes 1988, "Transmission of Overdriven Plane Detonations: Critical Diameter as a Function of Cell Regularity and Size", *Dynamics of Explosions: Progress in Astronautics and Aeronautics*, AIAA, New York, 114: 170-185.
- D. Desbordes and A. Lannoy 1990, "Effects of a Negative Step of Fuel Concentration on Critical Diameter of Diffraction of a Detonation", *Dynamics of Detonations and Explosions: Detonations: Progress in Astronautics and Aeronautics*, AIAA, New York, 133: 170-186.
- D. Desbordes, H. N. Presles, F. Joubert, C. Gbagdo Douala 2004, "Etude de la détonation de mélanges pauvres H_2-NO_2/N_2O_4 ", *C. R. Mécanique* 332: 993-999.
- T. P. Gravrilenko and E. S. Prokhorov 1983, "Overdriven Gaseous Detonations", *Shock Waves, Explosions and Detonations: Progress in Astronautics and Aeronautics*, AIAA, New York, 87: 244-250.
- Z. W. Huang, and B. Xu 1987, "relation between Cell Size and Detonation Parameters in Overdriven Gaseous Detonations", *Combustion and Flame*, 67(2): 95-98.

- F. Joubert, D. Desbordes, H. N. Presles 2003, "Structure cellulaire de la détonation des mélanges H_2 - NO_2/N_2O_4 ", *C. R. Mécanique*, 331: 365-372.
- F. Joubert 2001, "Etude de la détonation de mélanges réactifs gazeux constitués d'un combustible (H_2 , CH_4 , C_2H_6 , C_2H_4) et d'un oxyde d'azote, N_2O et NO_2/N_2O_4 ", *Thèse de l'université de Poitiers*.
- R. J. Kee, F. M. Rupley, J. A. Miller 1993, "The Chemkin thermodynamic data base", Sandia Report, SAND87-8215B, UC-4.
- R. J. Kee, F. M. Rupley, J. A. Miller 1994, "Chemkin-II: A Fortran chemical kinetics package for the analysis of gas phase chemical kinetics", Sandia Report, SAND89-8009B, UC-706.
- N. Lamoureux, C. Matignon, M. O. Sturtzer, D. Desbordes, H. N. Presles 2001, "Interprétation de la double structure observée dans l'onde de détonation du nitrométhane gazeux", *C. R. Acad. Sci. Paris, Série IIB*, 687-692.
- J. Meltzer, J. E. Sheperd, R. Akbar and A. Sabet 1990, "Mach Reflection of Detonation Waves", *Progress in Astronautics and aeronautics*, 153: 78-94.
- A. A. Vasiliev and Yu. Nikolaev 1978, "Closed Theoretical model of detonation cell", *Acta Astronaut.*, 5: 983-996.