# Influence of Ar Dilution on Detonation Regime in H<sub>2</sub>-NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> Mixtures

## Jocelyn Luche, Henri Noël Presles and Daniel Desbordes

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

Previous studies have shown that the detonation in gaseous nitromethane, nitromethaneoxygen mixtures (Presles et al., 1996) and  $H_2/CH_4/C_2H_6 - NO_2/N_2O_4$  mixtures (Joubert, 2001) exhibits a double cellular structure on large range of equivalence ratio. Calculations of the reaction zone in all these mixtures through the ZND model and using a detailed chemical scheme (involving 69 chemical species among 368 reversible reactions, Djebailï Chaumeix et al., 1997) have shown that for the same range of equivalence ratio, chemical energy is released in two main exothermic steps of very different characteristic induction lengths (Lamoureux et al. 2001, Joubert et al., 2003).

It is well known that monoatomic (Ne, Ar, Kr) dilution of reactive mixtures with  $O_2$  as the oxidizer leads to improvement of the regularity of the cellular structure and also to a great evolution of the value of the proportionality coefficients between parameters representative of the detonability (point source critical initiation energy, critical diameter of detonation diffraction) and cell size.

To determine what could be the effect of argon dilution on the detonation of reactive systems exhibiting a non-monotonous heat release, we studied detonation in  $H_2$ -NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> mixtures with respect to Ar dilution.

#### 2. Frame of the study

This work has been conducted with the H<sub>2</sub>-NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> mixture of equivalence ratio  $\phi = 1.2$ , at ambient initial conditions (initial temperature T<sub>0</sub> = 293K and pressure P<sub>0</sub> = 1bar). The detonation of this mixture exhibits a very clear double cellular structure. This mixture has been progressively diluted with Ar up to 60%.

#### 3. Calculations

Computations of the detonation reaction zone (see Introduction) in all these mixtures (Fig. 1) show that their energy is released in two main steps of characteristic induction lengths  $Li_1$  and  $Li_2$ . Increase of Ar dilution up to 60% has nearly no effect on  $Li_1$ . Indeed the ratio between the largest and the smallest values is less than one order of magnitude (*e.g.*  $3.10^{-5}$  m  $\leq Li_1 \leq 6.10^{-5}$  m). Conversely, the second exothermic step induction length  $Li_2$  is strongly affected by Ar dilution higher than 30% (*e.g.*  $5.10^{-4}$  m  $\leq Li_2 \leq 2.10^{-1}$  m).

#### 4. Experimental set-up

Experimental studies of the detonation of H<sub>2</sub>-NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> mixtures at  $\phi = 1.2$  diluted by different molar fraction of Argon (from 0% to 60%) at P<sub>0</sub> = 1 bar, T<sub>0</sub> = 293K were conducted in a steel detonation tube (9 m length and 52 mm internal diameter). This tube is equipped with pressure gages to characterize detonation propagation modes and smoked plates (Denisov and Troshin, 1960) to record the detonation cellular structure.



## 5. Results

The measured detonation velocities  $(D_{exp})$  are compared to the computed ones  $(D_{CJ})$  on Fig. 2 with respect to Ar dilution in H<sub>2</sub>-NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> mixtures.

For Ar  $\leq$  50% a multi-headed detonation propagates with a velocity (D<sub>exp</sub>) close to the theoretical one (D<sub>CJ</sub>) (discrepancy lower than 3%). All these detonations present a double cellular structure (Fig. 3a: 0% Ar, Fig. 3b: 10% Ar and Fig. 3c: 30% Ar).

For Ar  $\geq 52.5\%$ , the detonation is steady self-sustained and presents a single cellular structure (*e.g.* Fig. 3d: 52.5% Ar and Fig. 3e: 60% Ar). Its velocity is lower by about 25% (symbolized by dash lines on Fig. 2) to 30% (symbolized by dot lines on Fig. 2) than the theoretical one (symbolized by a full line on Fig. 2). Those results show that a small increase of Argon molar fraction (from 50% to 52.5%) is responsible for a sudden variation of detonation wave propagation regime, *i.e.* from a quasi-CJ regime to a regime which can be qualified as "non-ideal" one since  $D_{exp} \ll D_{CJ}$ . According to a previous study (Desbordes et al., 2004), this last result can be explained by the fact that detonation wave propagation is only supported by a part of the available chemical energy provided mainly by the first exothermic step. In fact, the detonation tube diameter is too small for the heat of the second exothermic step to be released inside the detonation reaction zone.

Simple calculations (Fig. 4) of  $\frac{Q_{exp}}{Q_{CJ}}$  ratio (where  $\frac{Q_{exp}}{Q_{CJ}} \approx \left(\frac{D_{exp}}{D_{CJ}}\right)^2 \approx \frac{P_{exp}}{P_{CJ}}$  deduced from approximated relations of sonic state of detonation wave  $D \approx \sqrt{2(\gamma^2 - 1)Q}$  and  $P \approx 2\rho_0 (\gamma - 1)Q$ ) taking into account the detonation velocity and pressure deficits clearly show that for Ar  $\geq 52.5\%$  only a part of the global chemical energy ( $Q_{exp} \approx 0.5 \times Q_{tot}$  corresponding approximately to the energy of the first exothermic step) is released inside the reaction zone. Conversely, up to 50% Ar dilution, those computations show that the detonation wave is supported by the chemical energy released by the both exothermic steps ( $Q_{exp} \approx Q_{tot}$ ).

In the non-ideal detonation regime, the single cellular structure contains itself a substructure which appears only in the first part of the main cells. In fact, this sub-structure is similar to that observed in the detonation cells of  $C_nH_m/O_2/N_2$  mixtures of high reduced activation energy (Ea/RT > 6) (Manzhaleï, 1977).







**Figure 3.:** Smoked plate records of cellular structure in H<sub>2</sub>-NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub>/Ar mixtures at  $\phi$ =1.2, P<sub>0</sub>=1bar, T<sub>0</sub>=293K for various values of Ar dilution: a) 0%, b) 10%, c) 30%, d) 52.5% and e) 60%

Comparison of the evolution of the cell sizes and the computed induction lengths with respect to Ar dilution will be discussed in the final paper.



As we recorded the profile of the detonation pressure (Fig. 5) in each experiment we have made a similar analysis based on pressure (up to 50% Ar dilution  $P_{exp} \approx P_{CJ}$  and for Ar  $\geq$  52.5%  $P_{exp} \approx 0.45$  or  $0.55 \times P_{CJ}$ ) and the results so obtained confirm those based on detonation velocity.

# 4. Conclusion

The study of the influence of Argon dilution on the detonation in H<sub>2</sub>-NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> mixture of equivalence ratio  $\phi = 1.2$  has revealed new results. Up to Argon dilution of 50% the detonation regime is close to the CJ one and exhibits a double cellular structure. For just higher Ar dilution the detonation regime suddenly becomes very non-ideal and exhibits a single cellular structure. This regime is supported only by the chemical energy released by the first exothermic step. In that case, as Ea/RT > 6, a sub-structure exists in the first half of the detonation cells.

# References

Denisov, Y. N. and Troshin, Y. K., "Structure of gaseous detonation in tubes", Soviet. Phys. Tech. Phys. 5 b (1960), 419-431.

Desbordes, D., Presles, H. N., Joubert, F., Gbagdo Douala, C., « Etude de la détonation de mélanges pauvres H<sub>2</sub>-NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> », *C. R. Mecanique* 332 (2004), 993-999.

Djebaïli Chaumeix, N., Abid, S., Paillard, C. E., "Shock tube study of the nitromethane decomposition and oxydation", Shock Waves 1 (1997), 121-126.

Joubert, F., « Etude de la détonation de mélanges réactifs gazeux constitués d'un combustible (H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>) et d'un oxyde d'azote, N<sub>2</sub>O et NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> », *Thèse de l'université de Poitiers* (2001).

Joubert, F., Desbordes, D., Presles, H. N., « Structure cellulaire de la détonation des mélanges H<sub>2</sub>-NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> », *C. R. Mecanique* 331 (2003), 365-372.

Lamoureux, N., Matignon, C., Sturtzer, M. O., Desbordes, D., Presles, H. N., « Interprétation de la double structure observée dans l'onde de détonation du nitrométhane gazeux », *C. R. Acad. Sci. Paris*, Série IIB (2001), 687-692.

Manzhaleï, V. I., « Sur la structure fine de la détonation dans les gaz », *Fiz. Gor. I. Vzviva.* 3 (1977), 470-473.

Presles, H. N., Desbordes, D., Guirard, M., Guerraud, C., "Gaseous nitromethane and nitromethane-oxygen mixture, a new detonation structure", *Shock Waves* 6 (1996), 111-114.