Double cellular structure in the detonation of mixtures or compounds containing the NO₂ group

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Introduction

Experimental observations of the detonation structure of gaseous nitromethane (NM) and nitromethane-oxygen mixtures revealed the existence of a double celullar structure /1/ for the equivalence ratio Φ such as $1.3 \le \Phi \le 1.75$. Calculations of the reaction zone in the ZND model using a detailed chemical scheme for the NM decomposition and oxidation showed /2/ that the chemical energy is released in two main reaction steps on this range of equivalence ratio, leading to the determination of two different induction lengths.

The comparison of experimental and numerical results shows that the double cellular structure founds its origin in this special two steps chemical kinetics. To our knowledge this study was the first dealing experimentally and numerically with a non monotonous chemical heat release inside the reaction zone of a detonation wave. The NO₂ group, by its specific decomposition, is clearly responsible for the two successive exothermic steps. This work reinforces the idea, developed and checked with classical reactive mixtures, that the cellular structure of the detonation is the consequence of the local high chemical heat release rate of Arrhenius type.

That was the starting point of a thorough study of the detonation of three gaseous mixtures made of a fuel (H₂, CH₄ and C₃H₆) and of the oxidizer NO₂ /3/. In these mixtures, unlike nitromethane, fuel and oxidizer do not belong to the same molecule.

Numerical and experimental studies of the detonation in these mixtures have been performed with respect to the equivalence ratio Φ (2 \geq $\Phi \geq$ 0.5) and the initial pressure P₀ (2 \geq P₀ \geq 0.5bar) at ambient temperature (T₀=293K). As similar results were obtained with these three mixtures we are going to present only those related to H₂.

Experimental results

The experimental study has been conducted with a stainless steel tube of 7m length and 52mm internal diameter equipped with pressure and ionization gages. We used the soot tracks method to record the cellular structure of the detonation /4/.

Analysis of all the records shows that a double cellular structure of very different characteristic sizes exist in the detonation of the mixtures H₂-NO₂/N₂O₄ for $2 \ge \Phi \ge 1$ (Fig 1). Each main cell of size λ_2 contains a set of smaller cells whose size increases continuously along the main one due to the fact they are submitted to the variation of the local velocity of the detonation front. The characteristic size λ_1 of these cells is measured in the middle of the large ones where the detonation velocity D is close to D_{CJ}/5/. For $\Phi < 1$ (Fig 2) only one set of cellular structure remains.

Figure 1 : Picture of the cellular structure of the detonation of the mixture H_2 -(NO₂/N₂O₄), Φ =1.25, P₀=1bar and T₀=293K.

Figure 2 : Picture of the cellular structure of the detonation of the mixture H_2 -(NO₂/N₂O₄), Φ =0.9, P₀=1bar and T₀=293K.



Numerical study of the reaction zone of the detonation wave

We performed 1D plane calculations of the reaction zone of the self-sustained detonation wave in gaseous H₂-NO₂/N₂O₄ mixture for $0.5 \le \Phi \le 2$ with the ZND model and detailed chemical scheme of NM decomposition and oxidation /6/ to whom we added the chemical reaction between N₂O₄ and NO₂ /7/. Chemical equations are solved using CHEMKIN code /8/9/ along the Rayleigh-Mickelson line from the ZND state towards the CJ one. Measured values of the detonation velocity being close to calculated ones (D_{CJ}), the overall chemical energy is released inside the reaction zone in accordance with the CJ assumption which justifies the above calculations.

Analysis of the evolution of the temperature inside the reaction zone shows two different trends depending on whether the value of the equivalence ratio Φ is higher or smaller than 1. Examples of time evolution of the temperature inside the reaction zone representative of these different trends are displayed on Fig 3 and 4 and Fig 5 for the equivalence ratio Φ respectively equal to 1.5 and 0.5. They show that between the ZND and CJ states temperature undergoes negative and positive variations.

In Fig 3 the time evolution of the temperature displays two inflexion points corresponding to local maxima of heat release rate (maxima of dT/dt=T') during the two main exothermic chemical reactions. These points are used to define two induction times:

- τ_{i1} between the ZND state (time origin) and the first inflexion point (order of 10^{-7} s). - τ_{i2} between the time origin and the 2^{nd} inflexion point. This time is about one order of magnitude larger than τ_{i1} .

 τ_{i1} is defined whatever the equivalence ratio of the mixture, while τ_{i2} can be defined only for $\Phi \ge 1$. So for lean mixture (Fig 5, $\Phi = 0.5$) only one induction time can be determined.

Fig 4 (Φ =1.5) and Fig 5 (Φ =0.5) show the evolution inside the reaction zone of:

- The temperature,

- The initial chemical species,

- The main chemical species useful to understand the main steps of the temperature variation.

In the case of $\Phi=1.5$ (Fig 4) the chemical reaction NO₂+H \rightarrow NO+OH is the source of the first exothermic step, NO being the oxidizer of the second one. When $\Phi=0.5$ (Fig 5) the respective contribution of oxygen provided by NO₂ and NO are not clearly separated.

Figure 3 : Time evolution of the temperature T and its derivative T' between the ZND and CJ states of the detonation of the mixture H₂-(NO₂/N₂O₄), Φ =1.5, P₀=1 bar and T₀=293K.

Figure 4 : Evolution of the molar composition of a few chemical species and temperature inside the reaction zone of the detonation of the mixture H₂-(NO₂/N₂O₄), Φ =1.5, P₀=1 bar and T₀=293K (D_{CJ}=2890m/s).

Figure 5 : Evolution of the molar composition of a few chemical species and temperature inside the reaction zone of the detonation of the mixture H₂-(NO₂/N₂O₄), Φ =0.5, P₀=1 bar and T₀=293K (D_{CJ}=2190m/s).



Induction lengths Li_1 et Li_2 are obtained by integration of the particle velocity relative to the leading shock.

The comparison between the calculated L_{ij} (j=1,2) and the measured values of λ_j (j=1,2) shows (Fig 6) that these two groups of data can be correlated through the relation $\lambda_j = k_j L_{ij}$ (j=1,2) with $k_1=15$ and $k_2=20$.

Figure 6 : Chemical induction lengths Li_1 and Li_2 and cells sizes λ_1 and λ_2 of the detonation of the mixture H_2 -(NO₂/N₂O₄) with respect to the equivalence ratio (P₀=1bar).



Conclusion

This study shows that the oxidizer NO₂ mixed with H₂ is responsible, by its specific decomposition, for a chemical heat release in two steps in the reaction zone of the detonation. The chemical reaction NO₂+H \rightarrow NO+OH has been identified as mainly responsible for the first exothermic step, NO being the oxidizer of the second one.

The comparison between experimental and numerical results clearly confirms that this specific heat release is responsible for the double cellular structure in the detonation wave. This results are similar to those previously obtained with nitromethane.

So the behaviour of the oxidizer NO₂, being either a free molecule in a reactive mixture or included inside a propellant, appears to be the same in the reaction zone of a detonation wave.

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