Thermal analysis of the decomposition of a LOVA gun propellant based on RDX and Nitrocellulose

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1   Introduction

Ignition and combustion phenomena of solid propellants involve several complex processes that have to be studied to improve their understanding. Among them, thermal decomposition is of great importance since it produces the reactants of the first exothermic reactions. For this reason, it has been extensively studied, in particular for RDX monopropellants.

Decomposition can occur in different states: solid, liquid or gas. Regarding decomposition of RDX in the solid state, it is neglected due to its low melting temperature causing short residence times [1,2]. In the liquid state, decomposition of RDX occurs in the so called foam layer composed of both liquid and gas bubbles. This zone is experimentally difficult to study due to its thinness (some microns at atmospheric pressure), heterogeneity and steeper gradients, and therefore, global approaches are usually adopted to deal with the decomposition [2]. More recently, Khichar has succeeded in developing a detailed mechanism in condensed phase considering five different pathways and has used it in a 1D steady-state combustion modelling [3]. Finally, decomposition of RDX is especially well addressed in the gas phase, with several detailed combustion mechanisms, like the one of Yetter and Chakraborty [2].

RDX composite propellants have also been addressed, such as RDX/GAP, RDX/TAGzT or RDX/GAP/BTTN [2,4,5]. BTTN and RDX decomposition is assumed in both gas phase and condensed phase whereas GAP decomposition is only considered for the condensed phase. In this case, distinct mechanisms exist for each ingredient and are assembled to form a unique mechanism [4]. Therefore, decomposition of composite propellants requires the knowledge of a mechanism for each ingredient. However, it is not possible for some common composite propellants like RDX/nitrocellulose. Indeed, decomposition of nitrocellulose is poorly understood and no kinetics scheme exists.

This work focuses on the study of the thermal decomposition of a LOVA gun propellant based on RDX and nitrocellulose. The pyrolysis products of these materials have previously been investigated under fast heating rates conditions. Laser ignition experiments have also been performed on these materials in a pressurized closed reactor [6]. Here, a kinetic analysis method is proposed to obtain global kinetic parameters based on TGA experiments. Results of the modelling are presented in section 3.

2   Experimental Details

Material

Material of interest is a white cylindrical LOVA gun propellant with a central perforation of 0.5 mm diameter. The average mass, diameter and length are respectively 40 mg, 3 mm and 5 mm. It is mainly composed of RDX (85 wt%) and nitrocellulose (15 wt%). These pellets were produced at the French-German Institute of Saint Louis and used as received. They only suffered heating at 50 °C during 24 h before tests.

Characterization

The decomposition of the propellant is studied by thermal analysis thanks to a Setaram Setsys 16/18 TGA instrument. Samples of 2.13 ± 0.11 mg are placed in an alumina open pan and are heated under an argon dynamic flow of 30 mL.min^{-1} from 30 to 300 °C. In accordance with ICTAC recommendations [7,8] five different non isothermal heating rates β were chosen so as to avoid thermal runaway: 0.3, 0.5, 0.8, 1.0 and 1.2 K/min.

Kinetic analysis method

In order to study the thermal decomposition of our materials, a kinetic analysis method has been developed and is presented below.

The kinetics of thermal decomposition in condensed phase is commonly defined by the equation of rate [7,8,9]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A\,exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{1}$$

with α the extent of conversion reactive/product, t the time, T the temperature, $k(T)$ the rate constant of Arrhenius, A the pre-exponential factor, E the activation energy, R the ideal gas constant and $f(\alpha)$ the reaction model. A, E and $f(\alpha)$ is often called the kinetic triplet and is sufficient to entirely describe the kinetics of decomposition.

In our case, TGA instrument follows the mass loss of the sample:

$$\alpha = \frac{m_0 - m(t)}{m_0 - m_{final}} \tag{2}$$

with m_0 the initial mass of the sample and m_{final} the final mass.

Actually, the rate equation is only valid for a single-step kinetics. If it is not the case, each step k is characterized by its own extent of conversion and kinetic triplet [7,8]:

$$\frac{d\alpha_k}{dt} = A_k\,exp\left(-\frac{E_k}{RT}\right)f_k(\alpha_k) \tag{3}$$

They are linked to the total extent of conversion α_{tot} by their weight w_k:

$$\alpha_{tot} = \sum_{k=1}^{N_{steps}} w_k \alpha_k \quad \frac{d\alpha_{tot}}{dt} = \sum_{k=1}^{N_{steps}} w_k \frac{d\alpha_k}{dt} \tag{4}$$

In this paper we assume a truncated form of Sestak-Berggren equation for $f_k(\alpha_k)$ as it enables to represent several common models (Diffusion, Avrami-Erofeev) by adjusting its parameters z_k, m_k and n_k [9]:

$$f_k(\alpha_k) = z_k \alpha_k^{m_k}(1 - \alpha_k)^{n_k} \tag{5}$$

Finally, for each step, 6 unknowns have to be determined: w_k, A_k, E_k z_k, m_k and n_k. It is achieved thanks to an iterative method of optimization (non-linear model-fitting) whose objective function is:

$$RSS = \sum_{i=1}^{N_{exp}} \left(\alpha_{exp,tot}^i - \alpha_{calc,tot}^i\right)^2 \tag{6}$$

where $\alpha_{exp,tot}^i$ is the total extent of conversion obtained experimentally by TGA for each experience i. $\alpha_{calc,tot}^i$ is the total conversion of the ith experience obtained by integration of equations (3) and calculated with equation (4).

The application of this optimization process requires the use of initial guesses for the unknowns. The visual inspection of the first derivative of the mass loss can help to identify the minimum number of steps to include in the analysis: each peak or shoulder can indicate the presence of an important process to take into account.

The isoconversional method of Friedman (7) is then applied after a pre-processing of the raw data of mass loss [10]. Isoconversional methods enable to obtain the variation of E_α with α which is a key clue to identify if a process can be treated as a single-step one or not: its variation must not exceed ± 10 % of its mean value on $\alpha = [0.1, 0.9]$. Therefore, Friedman method enables to select the number of steps and to estimate their weights w_k along their activation energies E_k [8].

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[f(\alpha)A_\alpha] - \frac{E_\alpha}{RT_{\alpha,i}} \tag{7}$$

To obtain initial guesses for the pre-exponential factors A_k, we make use of compensation effect. For given conditions (atmosphere, heating rate), the introduction of different reaction models $f_j(\alpha)$ in (1) will provide very different couples (A_j, E_j) by fitting to experimental data. However, those couples will demonstrate a strong correlation known as the compensation effect [7]:

$$\ln(A_j) = aE_j + b \tag{8}$$

where j refers to the jth reaction model assumed and (a,b) to the parameters of the correlation obtained for a heating rate β_i. Thus, the substitution of Friedman activation energies E_α into (8) can provide A_α vs α as initial guesses for A_k.

Finally, model parameters z_k, m_k and n_k are initialized at 1.

The optimization process is built upon different levels with the main being the one of the weights w_k. For each set of values w_k tested by the algorithm, all the other unknowns are optimized by kinetic step k.

3   Results and discussion

The nondimensional mass losses obtained under argon and their first derivatives are presented Figures 1 and 2. The mean extent of decomposition is 0.941 ± 0.017, the presence of a solid residue can be due to the nitrocellulose as already noticed by several authors [11,12]. The inspection of derivatives exhibits the presence of a peak and a shoulder, which is more significant as heating rate increases: a minimum of two steps is required for our model. Higher heating rates reveal a flattened peak which indicates a possible third important process.
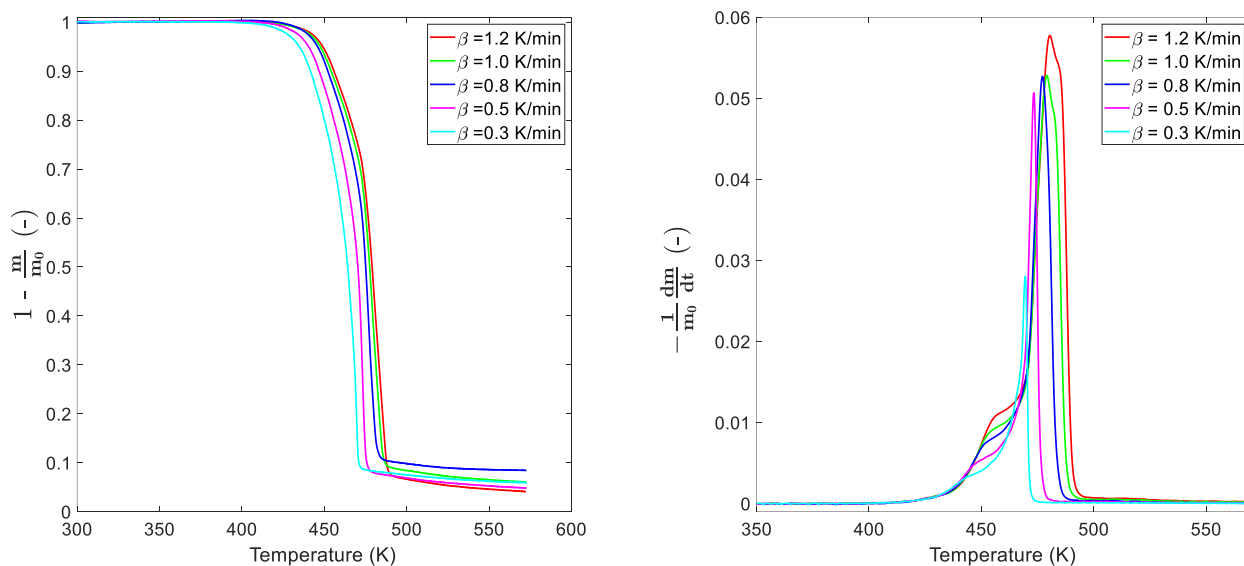
Figure 1: Nondimensional mass loss under argon and Figure 2: Nondimensional mass loss derivative under argon

The application of the Friedman method provides the activation energy profile presented Figure 3. Between 10 and 90 % of conversion, three zones of stability are separated by zones of great variations. Therefore, three steps are considered for the analysis with initial weights of 0.3, 0.4 and 0.3 which correspond to conversions between two stable zones. The optimized parameters obtained for each step are presented in Table 1.
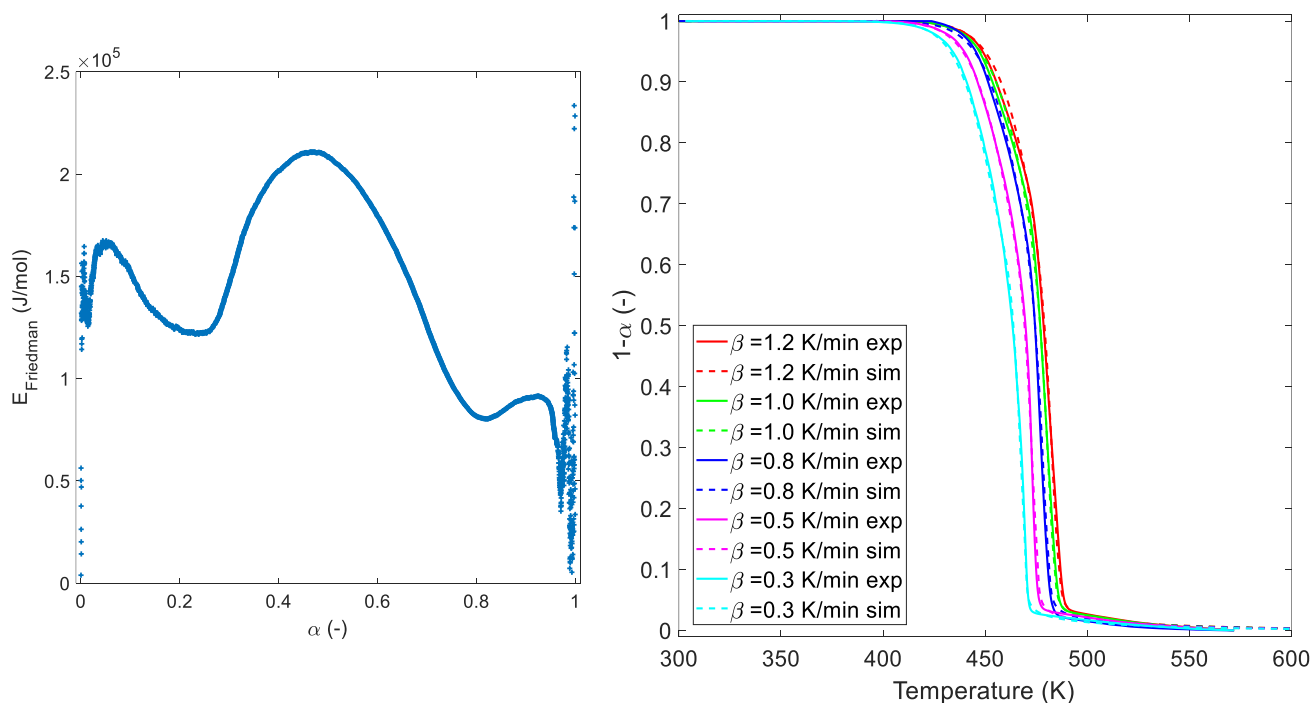

Figure 3: Isoconversional activation energy of Friedman under argon and Figure 4: Experimental and simulated extents of conversion under argon

Table 1: Optimized parameters for the thermal decomposition under argon

	w_l	A_l (s^{-1})	E_l (J/mol)	z_l	m_l	n_l
Step 1	0.3344	$3.3738 \cdot 10^{12}$	124480	0.0375	0.1987	0.5961
Step 2	0.5628	$1.3069 \cdot 10^{16}$	161300	0.1243	0.6943	0.5358
Step 3	0.1028	$2.7678 \cdot 10^{14}$	148440	3.4025	1.0831	4.7657

The comparison between simulated and experimental mass losses is available Figure 4. The reproduction of experimental curves is rather satisfactory even if some differences are noticeable. The relative error is presented Figure 5. Three zones of important errors are observable. The first one is close to the maximum peak derivation. Since the derivative is very important, a slight shift of abscissa causes a high shift of ordinate. The second zone which starts around 500 K corresponds to the difficulty of the model to reproduce the conversion curves feet. Finally, the exuberant error observed after the second zone is due to the difficulty of the model to converge to an extent of conversion of 1. Indeed, after 0.99 the variations of the model are almost non-existent whereas the experimental conversions reach values very close to 1 (0.99999). Except these three zones, the relative error is less than 5 % which corresponds to 60-70 % of the decomposition. A fourth step could help the model to reduce these differences.

Finally, it would be difficult to provide a more detailed model and associate particular reactions only using TGA experiments. Nevertheless, similarities can be observed between steps and initial mass fractions of propellant ingredients: the fraction of step 3 (0.1028*0.941) added to the fraction of residue (0.059) gives a fraction very close to the initial nitrocellulose part (0.15).
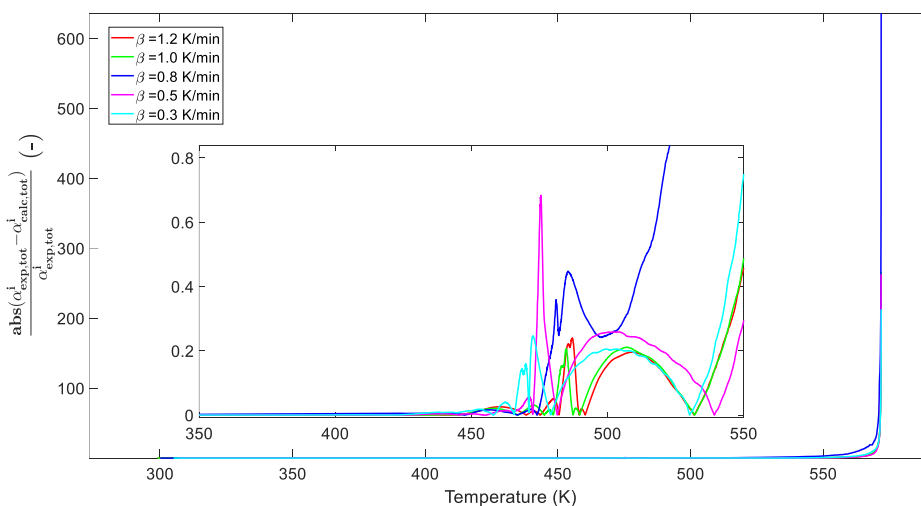

Figure 5: Relative error between calculated and experimental conversions

4 Conclusion

This paper has focused on the thermal decomposition of a LOVA gun propellant composed of RDX and nitrocellulose. Decomposition has been studied thanks to TGA at low heating rates and under argon. For that, a kinetic analysis method, based on ICTAC recommendations, has been developed. This

method employed TGA results to obtain global kinetic parameters. Its application to our materials has enabled to reproduce satisfactorily mass loss profiles by modelling the process with three kinetic steps.

This work is part of a wider project aiming to numerically model ignition and combustion phenomena of LOVA gun propellants. Kinetic parameters obtained here will be used to model decomposition. This modelling will be then compared to experimental results obtained in our own experimental set-up.

Acknowledgements

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