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Kinetic Analysis of the Thermal Decomposition of Three LOVA Gun Propellants Based on RDX and Nitrocellulose

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Abstract

The undesired ignition of ammunitions during their different stages of life can lead to hazardous situations for goods and people. To tackle this, projects of Low-Vulnerability Ammunitions (LOVA) have been developed. However, this loss of sensitivity can lead to ignition issues. The study of thermal decomposition is essential to reach a better understanding of ignition phenomena. This paper is about the thermal decomposition of three LOVA gun propellants based on RDX and nitrocellulose. Decomposition is studied by ThermoGravimetric Analysis (TGA) between 30 and 300 °C, under argon atmosphere and five heating rates (0.3, 0.5, 0.8, 1.0, 1.2 K/min). A kinetic analysis method, considering ICTAC recommendations, is developed in this paper and applied to TGA results. The latter allows to determine global kinetic parameters (pre-exponential factor, activation energy and reaction model based on the truncated Sestak-Berggren equation) to obtain a decomposition law depending on temperature and extent of conversion. Models with three kinetic steps are obtained. Their integration provides mass loss curves in good agreement with the TGA results. This study is part of a wider project which aims to model ignition and combustion processes of low-vulnerability gun propellants using detailed kinetics chemistry for the gas phase.

Introduction

Gun propellants are energetic materials employed in the defense area for the propelling of projectiles. They present the particularity to release an important quantity of hot gases in a very short period of time. Two aspects of energetic materials are of great importance and are related: safety and performance. The first one has especially been at concern since several decades. Indeed, some severe accidents have been caused by the undesired ignition of ammunitions such as the fire of the aircraft carrier USS Forrestal in the 1967. To tackle this, projects of Low-Vulnerability Ammunitions (LOVA) have been developed. This new kind of ammunition is less sensitive and this loss of sensitivity directly impact their ignition performances. The study of their ignition characteristics is then essential.

Among the several and complex processes involved in the ignition of a propellant, thermal decomposition is of great importance since it produces the first reactants of exothermic reactions. However, its understanding is still limited. Indeed, decomposition is often considered to occur in the liquid and the gas states. Although the gas state decomposition has been extensively studied, like for RDX [1], it is not the case of the liquid one due to experimental difficulties: the foam zone in which it occurs is very thin, in the order of some microns at atmospheric pressure for RDX, heterogeneous and present steeper gradients [1]. Therefore, just a few studies have been conducted [2] and global approaches are often adopted to model it [1], [3], [4]. Furthermore, for composite propellants like RDX/GAP/BTTN [1], the knowledge of a mechanism for each ingredient is required. This can be problematic when the decomposition process of an ingredient is not or poorly understood like nitrocellulose.

This paper deals with the thermal decomposition of three LOVA gun propellants based on RDX and nitrocellulose. Laser ignition experiments have been performed previously on these materials enabling the determination of ignition delays or probabilities [5]. In this study, thermal decomposition phenomenon is investigated by TGA in low heating rate conditions at atmospheric pressure. Here, a kinetic analysis method is developed to determine global parameters based on TGA experiments. A law of decomposition can thus be obtained, that is particularly useful for the numerical modelling of ignition and combustion processes. Results of modelling are finally presented and discussed in the last section.

Materials and Methods

Materials

The gun propellants studied were produced at the French-German Institute of Saint-Louis. These white pellets are cylindrical (3 mm diameter, 5 mm long), perforated by a central hole (0.5 mm diameter) and have an average mass of 40 mg. The propellants are composed of same ingredients but with different proportions:

- 95/05 (**P1**): RDX (wt 94,7 %), Nitrocellulose (wt 05 %) et Centralite I (wt 0,3 %)
- 90/10 (**P2**): RDX (wt 89,7 %), Nitrocellulose (wt 10 %) et Centralite I (wt 0,3 %)
- 85/15 (**P3**): RDX (wt 84,7 %), Nitrocellulose (wt 15 %) et Centralite I (wt 0,3 %)

The materials were used as received, only a heating of at least 24 h at 50 °C was performed to remove discrepancies due to humidity.

Characterization

The thermal decomposition of the propellants was studied by thermogravimetric analysis with a TGA Setaram Setsys 16/18. The samples are placed into an open pan in alumina and are heated under a dynamic atmosphere of argon (30 mL.min⁻¹) from ambient to 300 °C. In compliance with ICTAC recommendations, for each propellant, five heating conditions were tested [6]. The constant heating rates were chosen to avoid thermal runaway and are, therefore, rather small. The experimental conditions tested are summarized in Table 1.

Table 1: Experimental conditions of TGA characterization

	P1	P2	P3
Mass	2.27 ± 0.12 mg	2.15 ± 0.13 mg	2.13 ± 0.11 mg
Atmosphere	Argon		
Heating conditions β	0.3 ; 0.5 ; 0.8 ; 1.0 ; 1.2 °C/min T = [30-300°C]		

Kinetic analysis method

To model the decomposition kinetics of these three propellants, a kinetic analysis method, based upon ICTAC recommendations [6], [7] has been designed and is presented below.

The kinetics of the thermal decomposition in the condensed phase is commonly described by the following equation of rate:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) = A \cdot \exp\left(-\frac{E}{R \cdot T}\right) \cdot f(\alpha) \quad (1)$$

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 , $f(\alpha)$) is often called the kinetic triplet and is sufficient to entirely describe the kinetics of decomposition.

TGA instrument tracks the mass of the solid according to the time which enables to follow the decomposition. The extent of conversion is therefore defined by:

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

with m_0 the initial mass of the sample and m_{final} the final mass. It can however be defined by any physical property which follows the studied process.

The reaction model is a function of α which can have various expressions and can represent different physical processes such as nucleation with the JMA model, for example.

To summarize, for a given temperature profile, the conversion rate $\frac{d\alpha}{dt}$ can be entirely determined if A , E and $f(\alpha)$ are known.

Theoretically, the rate equation (1) is only valid under the assumption that the studied process can be described by a single reaction or kinetic step [7]. However, the processes in condensed phase usually require several steps. It is thus necessary to determine as many kinetic triplets as steps.

Determination of E

Isoconversional methods are “model-free” ones, that is to say, they allow to determine kinetic parameters without assumptions on the expression of $f(\alpha)$. They also offer the particularity to obtain E_α depending on α . Indeed, according to the equation (3), at constant extent of conversion, the rate only depends on the temperature:

$$\left[\frac{\partial \ln \left(\frac{d\alpha}{dt} \right)}{\partial T^{-1}} \right]_\alpha = -\frac{E_\alpha}{R} \quad (3)$$

This equation means that, at constant α , the plot of $\ln \left(\frac{d\alpha}{dt} \right)$ vs T_α^{-1} for each experiment represents a straight line with a slope of $-\frac{E_\alpha}{R}$. The influence of α on E_α enables to detect a change in the process behavior, and thus, the presence of a multi-step phenomenon. In practice, activation energy is observed on $\alpha = [0.1; 0.9]$. If on this interval the variations of E_α are higher than $\pm 10\%$ of the average value, the process is considered as a multi-step one.

Differential method of Friedman is one of the most famous isoconversional method recommended by ICTAC and is defined by equation (4) [8]:

$$\ln \left(\frac{d\alpha}{dt} \right)_{\alpha,i} = \ln[f(\alpha) \cdot A_\alpha] - \frac{E_\alpha}{R \cdot T_{\alpha,i}} \quad (4)$$

with i referring to the i^{th} temperature program. By plotting $\ln \left(\frac{d\alpha}{dt} \right)_{\alpha,i}$ vs $T_{\alpha,i}^{-1}$ we can get E_α .

Determination of A

A way to determine the pre-exponential factor is to employ the kinetic invariants. This method makes use of what is called the compensation effect, which states that for a given experiment, if we assume different forms of the reaction model $f(\alpha)$, kinetic parameters A and E will be very different from a model to another. Nonetheless, these couples will all demonstrate a strong correlation known as compensation effect:

$$\ln(A_j) = a \cdot E_j + b \quad (5)$$

with j referring to the j^{th} reaction model $f_j(\alpha)$. The coefficients a and b depend on the considered experiment ($\beta = 0.3; 0.5; 0.8; 1$ or 1.2 K/min). This method can be used in association with the isoconversional methods to obtain A vs α [6]. For each experiment i , coefficients a_i and b_i are calculated. By replacing E_j by E_α in (5), we have $A_{\alpha,i}$ for each test. A_α is then obtained by computing the average of $A_{\alpha,i}$.

Determination of $f(\alpha)$

The last element of the kinetic triplet is the reaction model $f(\alpha)$. To obtain it, ICTAC recommends to use a linear “model-fitting” method or reconstruction methods in the case of a single step process. Otherwise, a nonlinear model fitting method is required [6].

No matter the case, single or multi step process, we chose to adopt a nonlinear model-fitting approach to deal with this part. At this stage of the analysis, it is necessary to estimate the number of steps to take into account. For that, we can proceed in two ways:

1. A visual inspection of the experimental derivatives (DSC or DTG) can provide information on the nature of the process: each peak or shoulder reveals the presence of an important phenomenon to consider [6].
2. An inspection of the isoconversional activation energy profile can also reveal the presence of different phenomena as explained above [6], [7].

One should always consider a minimum number of steps which can be justified by the aforesaid observations of derivatives and energy profiles or by physical/chemical arguments from other characterizations (DSC, mass spectrometer, etc.). This prevents from obtaining a model purely mathematical.

Thus, each kinetic step k taken into account is represented by its own conversion α_k . Each step has a weight w_k in the global process which is also estimated by the observation of the experimental curves and the isoconversional energy:

$$\alpha_{tot} = \sum_{k=1}^{N_{steps}} w_k \cdot \alpha_k \quad (6)$$

$$\frac{d\alpha_{tot}}{dt} = \sum_{k=1}^{N_{steps}} w_k \cdot \frac{d\alpha_k}{dt} \quad (7)$$

Finally, a kinetic triplet $(A_k, E_k, f_k(\alpha_k))$ is associated to each step k .

$$\frac{d\alpha_k}{dt} = A_k \cdot \exp\left(-\frac{E_k}{RT}\right) \cdot f_k(\alpha_k) \quad (8)$$

It is assumed here that the reaction model has the following form:

$$f_k(\alpha_k) = z_k \cdot \alpha_k^{m_k} \cdot (1 - \alpha_k)^{n_k} \quad (9)$$

This model is a truncated form of the Sestak-Berggren equation which allows to mathematically represent several classic reaction models by adjusting the parameters z_k , m_k et n_k [9].

Finally, for each step k , the unknowns are:

- w_k the weight of the step k
- A_k and E_k , Arrhenius parameters of the step k
- z_k , m_k et n_k reaction model parameters of the step k

These unknowns are determined by an iterative method of optimization (nonlinear model-fitting). The objective function to minimize is:

$$RSS = \sum_{i=1}^{N_{exp}} (\alpha_{exp,tot}^i - \alpha_{calc,tot}^i)^2 \quad (10)$$

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 i^{th} experience obtained by integration of equations (8) and calculated with equation (6). The numerical scheme is a third order BDF. Optimization is performed on MATLAB software [10], [11] and is based on the simplex method [12].

The optimization process is built upon different levels with the main being the one of weights w_k . For each set of values w_k tested by the algorithm, all of the other unknowns are optimized by kinetic step k . A detailed diagram is available Figure 1.

Model-fitting kinetic processing

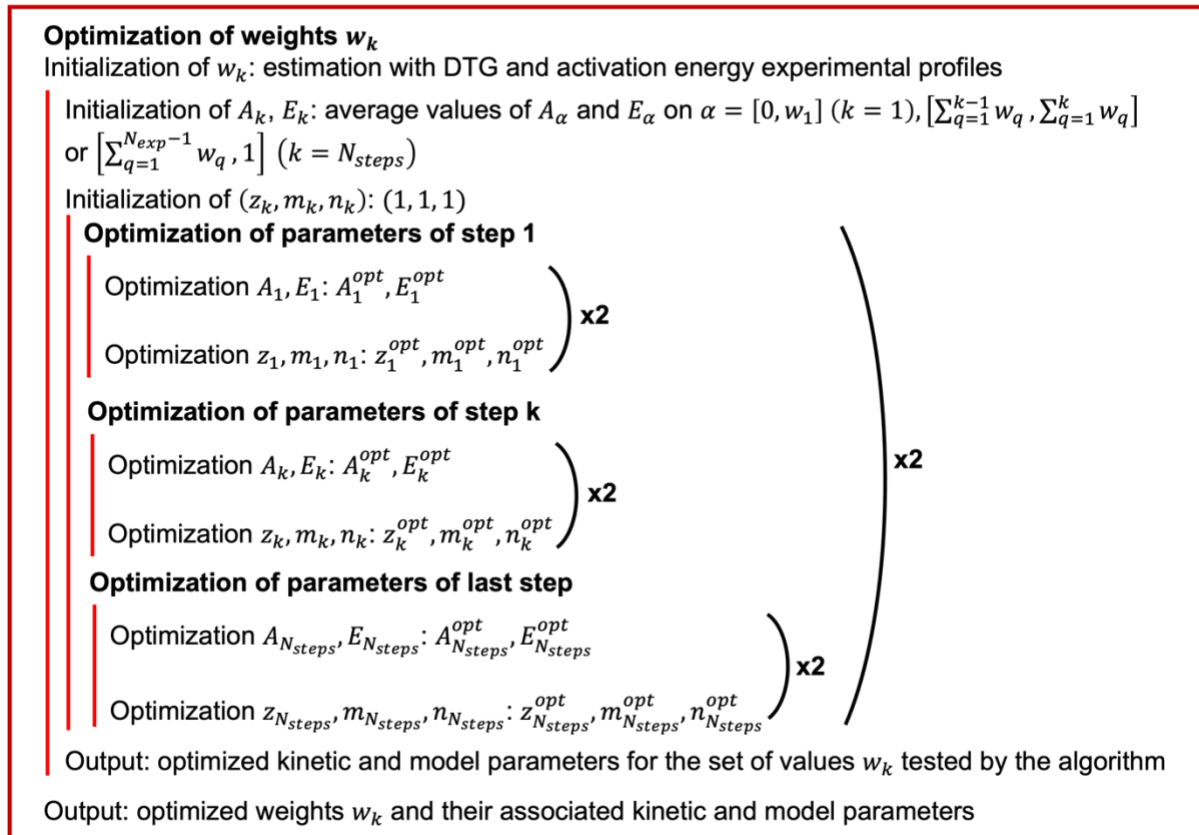


Figure 1: Optimization procedure of the global parameters

Results and discussion

The experimental non dimensional mass losses and their first derivatives are presented in Figure 2. The final extents of decomposition between 30 and 300 °C are:

- 0.9864 ± 0.0034 for P1
- 0.9703 ± 0.0100 for P2
- 0.9413 ± 0.0165 for P3

A first observation is that the higher the nitrocellulose rate, the lower and more imprecise the final extent of decomposition. Indeed, several studies have already noticed the presence of a residue in the decomposition products of the nitrocellulose. This has been observed in particular for low pressure conditions, temperatures near the decomposition one or at high temperatures under short times of exposure [13]–[15].

The inspection of mass losses does not really provide clues to determine the number of kinetic steps to consider. However, the inspection of the first derivatives is more informative. Indeed, they globally consist in a shoulder (S) and a principal peak (Pk), which means it is necessary to consider at least two steps, *a priori*.

- For a same propellant, the higher the heating rate the clearer the shoulder S is. This is particularly perceptible on Figure 2d and 2e: the temperature shifts of Pk and S on the right with the increase in the heating rate are not the same. Furthermore, for a same heating rate, the less the rate of nitrocellulose, the less clear the shoulder S is, which would mean the shoulder S directly refers to the decomposition of nitrocellulose. This is consistent with the observations of Jing *et al.* who have studied the decomposition of a RDX/NC propellant by DSC at 10 K/min under nitrogen. In these conditions, they obtained two peaks slightly overlapped, the first one corresponding to nitrocellulose decomposition and the second one to RDX one [16]. Thus the peak Pk could represent the decomposition of RDX.
- The inspection of the main peak Pk reveals that it has very different shapes depending on the propellant and that it seems to result from the layering of at least two peaks: a low intensity peak (Pk1) and a high intensity peak (Pk2). For P1, by inspecting curves $\beta = 0.5$ to $\beta = 1.2$ K/min, Pk1 appears before Pk2 and they merge more and more into each other as β increases. For P2, Pk2 appears before Pk1 for low β before merging with it as β increases. Finally for P3, both are mixed up at low β . As heating rate increases, Pk1 shifts before Pk2. Therefore, the mass loss related to the main peak seems to be composed of at least two kinetic steps, the relative position of each one with respect to the other depends on the rate of nitrocellulose, at equal heating rate.

Finally, the inspection of experimental curves leads to consider at least three kinetic steps: one associated with the shoulder S and two with the peak Pk.

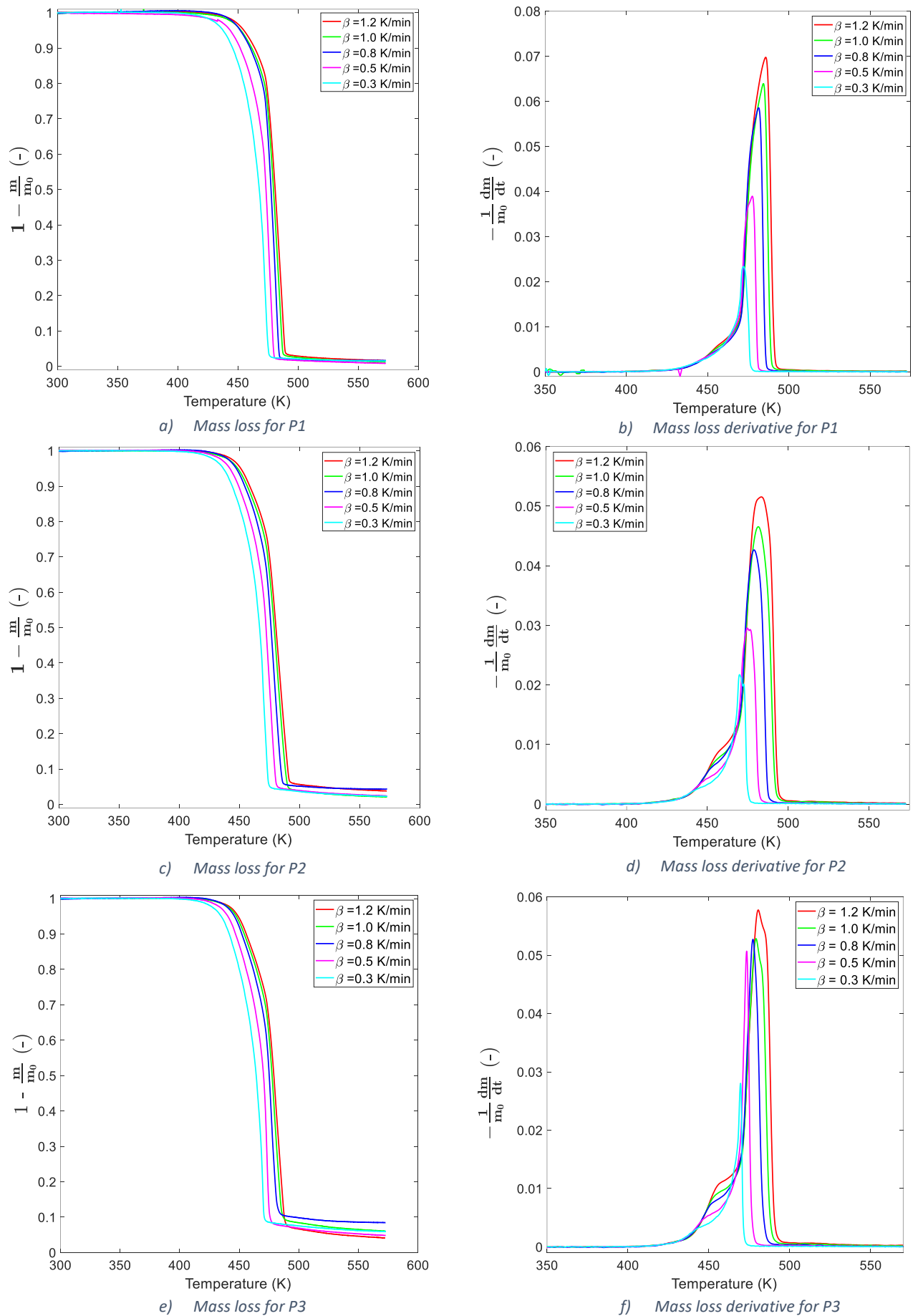


Figure 2: Non dimensional mass losses and their derivatives under argon atmosphere for the three propellants

The activation energy profiles are obtained by Friedman method. Only the variations for $\alpha = [0.1; 0.9]$ are studied, activation energy E_a being submitted to large fluctuations beyond this interval [7]. The profiles are qualitatively similar for the three propellants, and so, only the profile for P1 is presented Figure 3 for the sake of concision.

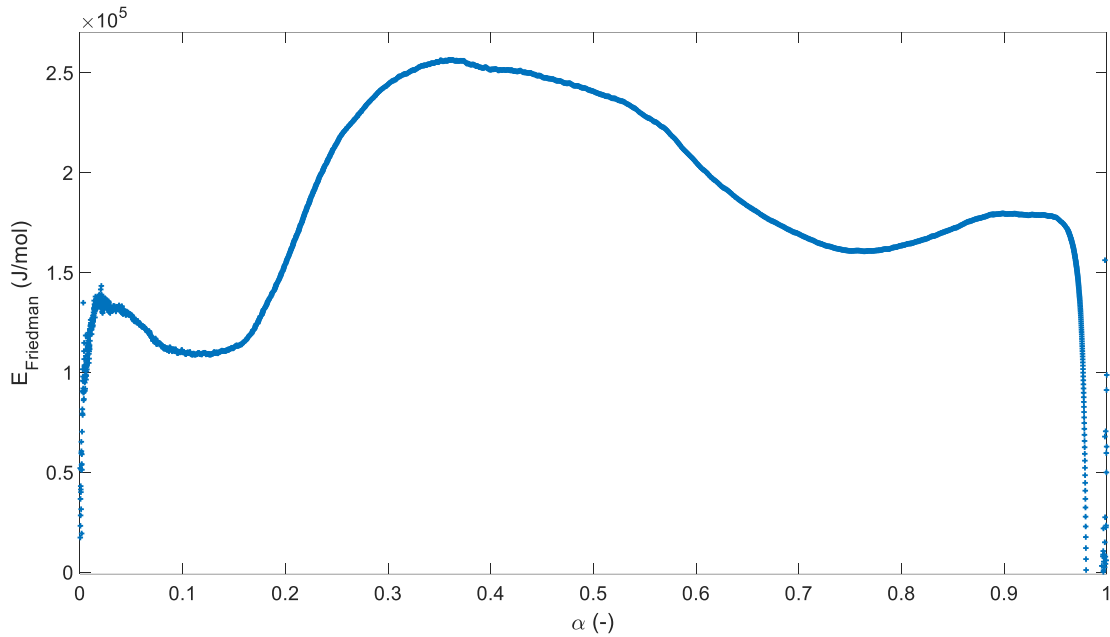


Figure 3: Isoconversional activation energy of Friedman for P1 under argon

The profiles are divided in three zones more or less stable separated by two zones of large fluctuations. Therefore the variations of E_a with α are higher than $\pm 10\%$ of the average value and several steps have to be considered [7]. The areas of large fluctuations can be due to overlapped kinetics (competitive/parallel) but also to the fact that a same kinetic event can happen at different extents of conversion with the heating rate. Here we assume three steps of decomposition which correspond to the three zones of stability. The initial weights are chosen as the extents of conversion between two zones: 0.25, 0.40 and 0.35 for P1, for example. The optimized parameters for each step of each propellant are presented Table 2.

Table 2 : Optimized parameters for the thermal decomposition of the three propellants under argon

	w_i	A_i (s ⁻¹)	E_i (J/mol)	z_i	m_i	n_i
P1						
Step 1	0.3129	$3.7903 \cdot 10^{10}$	109600	0.0323	0.1597	0.1896
Step 2	0.3085	$3.7355 \cdot 10^{18}$	183190	0.1746	0.7712	0.6249
Step 3	0.3785	$1.8724 \cdot 10^{19}$	191680	0.5057	0.9273	1.5003
P2						
Step 1	0.2277	$1.5335 \cdot 10^{13}$	129600	0.0344	0.1421	0.5967
Step 2	0.6619	$9.6985 \cdot 10^{16}$	169470	0.0810	0.5576	0.5708
Step 3	0.1104	$1.6372 \cdot 10^{14}$	147230	3.6951	1.0900	4.0368
P3						
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

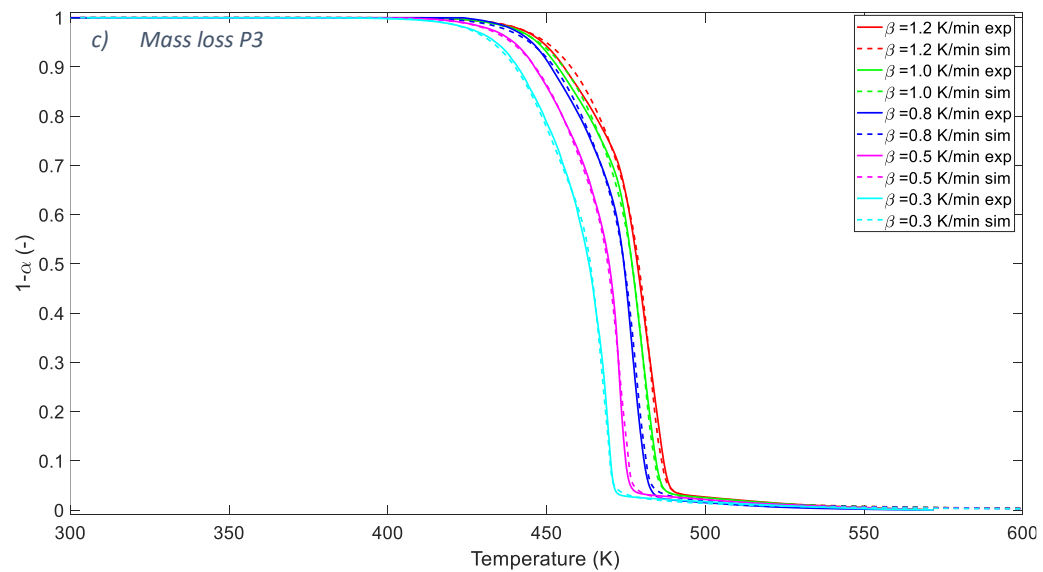
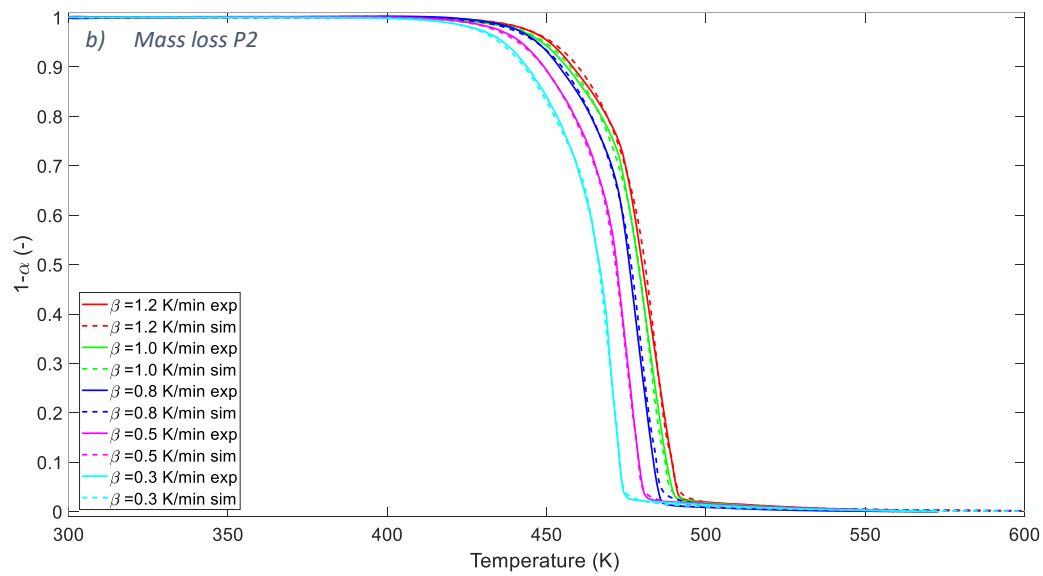
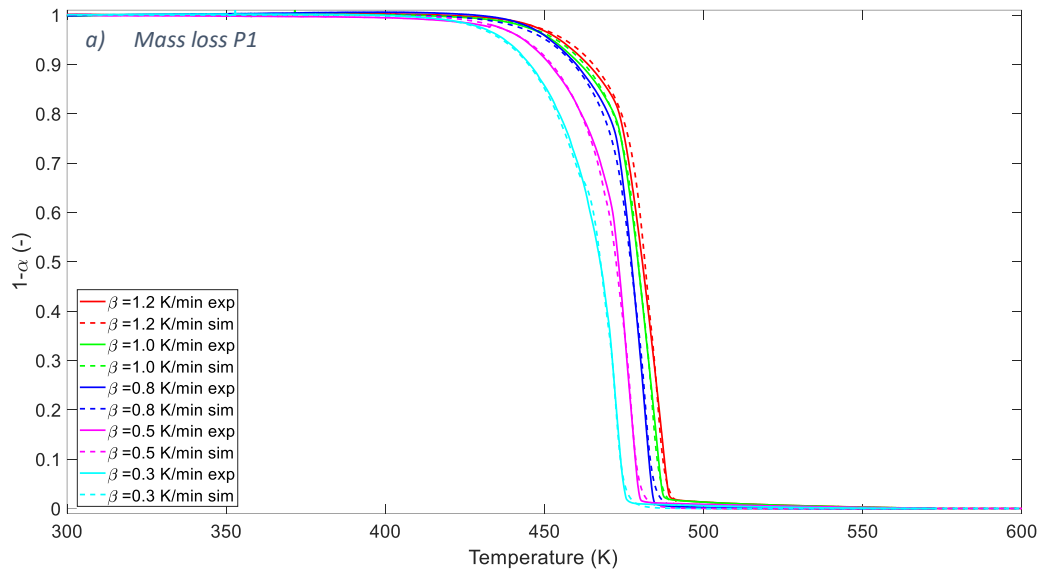


Figure 4: Experimental (straight lines) and simulated (dots) conversions for the three propellants under argon

Figure 4 displays the simulated and experimental profiles of mass loss for the three propellants. The experimental curves are rather satisfactorily reproduced by the simulation although some differences can be noticed. In order to quantify these differences, the relative errors between experiments and simulations have been plotted. However, only the ones for P3 are presented, the analysis being very similar for the three propellants.

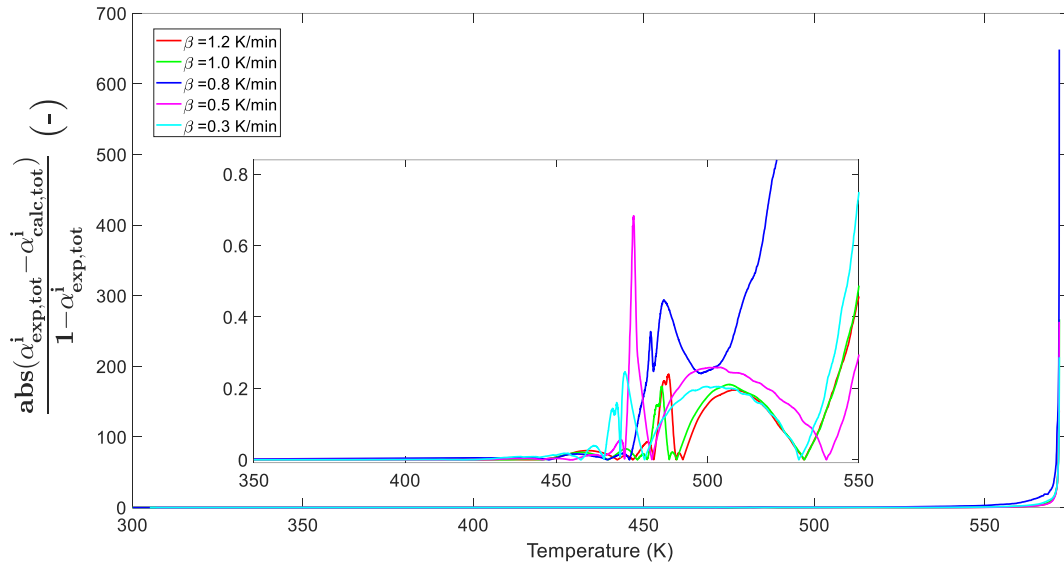


Figure 5: Relative error between simulated and experimental conversions for P3

Three zones of large errors are noticeable:

- The first one is near the maximum of the derivatives. Since it is very important, a slight shift of abscissa causes a high shift of ordinate.
- The second area begins around 500 K and relates to the difficulty of the model to reproduce the curves feet for the extent of conversion.
- Finally, the difficulty of the model to converge to a conversion of 1 is responsible of the exuberant error at the end of the curves. Indeed, after 0.99 the simulated conversion hardly varies anymore whereas the experimental one is near 1 with a high numerical precision (0.99999).

Apart from these three zones, the relative error is less than 5 %.

It would be difficult to improve our modelling of the decomposition process based uniquely on the TGA experiments. Indeed, more detailed knowledge of the kinetic mechanism would be required to identify the main species involved in the decomposition process and thus to adjust the number and the weights of kinetic steps.

Conclusion

This paper describes the study of the thermal decomposition of three LOVA gun propellants based on RDX/nitrocellulose. For that, TGA experiments have been performed at low heating rates under argon atmosphere. From these results a kinetic analysis method has been developed 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 numerically model decomposition. This modelling will be then compared to experimental results obtained in our own experimental set-up.

Acknowledgements

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