



Kinetics deconvolution study of multi-component pyrotechnics

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ARTICLE INFO

Keywords:

Pyrotechnics
Chemical kinetics
Deconvolution
Non-linear regression
Variable activation energy

ABSTRACT

This study reports an experimental investigation into the chemical kinetics of several commercial pyrotechnic compositions. A differential scanning calorimeter was utilized to elucidate the thermo-kinetic characteristics of five multicomponent pyrotechnic compositions. The multicomponent nature of practical pyrotechnics results in a complex interaction between the various components as well as condensed phase reactions. The thermo-kinetic study was carried out to approximate the heating experienced by the pyrotechnics before the combustion zone. The chemical kinetic parameters such as overall activation energy (E_a) and pre-exponential factor (A) corresponding to these reactions were estimated using Friedman and Starink method. The large variation in E_a attributed to multiple parallel reactions was addressed through the application of deconvolution techniques utilizing the Frazer-Suzuki function as well as nonlinear mechanistic modelling. The observations from the DSC data and the comparison between the deconvolution techniques provided an insight into the phenomenology of the combustion process of energetic pyrotechnics.

1. Introduction

Pyrotechnics are granular heterogeneous porous composite energetic materials utilized in a wide range of applications. These multi-component energetic materials undergo a complex combustion process involving multiple parallel and competing reactions. The reaction kinetics is typically characterized by an accurate estimate of the ‘kinetic triplet’, which consists of the chemical activation energy (E_a), the pre-exponential factor (A), and the reaction model ($f(\alpha)$). An accurate estimation of the kinetic triplet is essential to obtain reasonable predictions of burning rate, reaction progress, ignition temperature, storage life, and heat generated during the process. Reaction kinetics of energetic materials is often studied by thermal analysis techniques, which simulate the temperature conditions of actual combustion wave. Subsequently, a kinetic analysis may be performed on the experimental data to obtain the kinetic triplet.

The well-known isoconversional methods are most commonly utilized due to their lack of the a priori assumptions. The study by Starink [1] reveals the so-called Type B-1.92 method [1] and Friedman method [2] to be highly accurate. Both techniques evaluate the activation energy (E_a) as a function of reaction progress (α). However, the predictions of the isoconversion methods may not be accurate for cases beyond strictly single step reactions, and additional mechanistic modelling is often necessary. The average E_a value may be used as the nominal activation energy independent of α if the relative variation in

the isoconversional E_a - α relationship is less than 10% [3], signifying a single step reaction [4]. However, in case of complex processes, a large variation in the E_a - α relationship [5,6] as well as dependence of the E_a values on the heating rates [7] has been related to competing or overlapping reactions.

In order to address the meaningfulness of the variable activation energy calculated by an isoconversional technique, a number of single-step reactions may be envisaged with individual constant activation energy values [8]. Thus, in cases involving a complex reaction mechanism, the kinetic analysis must identify the constituent reactions in the overall process in a physically meaningful way. Typically, the experimentally measured overall reaction rate is deconvoluted by representing it as a sum of a set of kinetic equations.

The overlapping curves of a complex process may be deconvoluted using standard statistical functions such as Fraser-Suzuki (FS) function [9–11] shown in Eq. (1), followed by a kinetic analysis of the separated peaks.

$$y = a_0 \exp \left\{ -\frac{\ln 2}{a_3^2} \times \left[\ln \left(1 + 2a_3 x - a_1/a_2 \right) \right]^2 \right\} \quad (1)$$

where a_0 , a_1 , a_2 , a_3 are the parameters corresponding to the amplitude, position, half-width and asymmetry of the curve, respectively. While, x and y indicate arbitrary independent and dependant variable respectively.

Alternatively, nonlinear regression (NLR) techniques are sometimes

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employed which assume a certain reaction scheme, and the overall reaction rate is represented by the sum of each component reaction step [12,13] as shown in Eq. (2).

$$\frac{d\alpha}{dt} = \sum_{i=1}^n c_i A_i \exp\left(\frac{-E_{a,i}}{RT}\right) f_i(\alpha_i) \quad (2)$$

where, $\sum_{i=1}^n c_i = 1$, $\sum_{i=1}^n c_i \alpha_i = \alpha$, and the corresponding kinetic parameters are optimized iteratively to minimize the difference between the experimental and simulated curves.

Numerous investigations on simple binary pyrotechnic compositions [14–20] have been reported in the literature, which typically adopt the simplified Kissinger method [21]. Although, the thermo-kinetic phenomena occurring in composite energetic materials can be expected to be more complex compared to the idealized binary mixtures, relatively fewer investigations [22,23] pertaining to practical multicomponent pyrotechnic compositions or their chemical kinetics can be found.

The current study aims to investigate a set of commercial multicomponent pyrotechnic compositions in order to elucidate their thermo-chemical behavior and extract the thermo-kinetic parameters. The study employs Differential Scanning Calorimetry (DSC) in combination with currently established isoconversional techniques in order to evaluate the E_a - α variation. The broad variation in the E_a - α relationship for each pyrotechnic was addressed by attempting to obtain a meaningful split of the overall reactions into several single step reactions. The study compares the method of deconvolution using the FS function against the so-called Bayesian approach of mechanistic deconvolution. The deconvolution technique fitted a number of FS functions to represent the effective overall reaction rate obtained by averaging the thermograms at several heating rates. As the onset and endset of the process corresponds to a low reactivity, a weightage corresponding to the normalized reaction rate at each point was utilized to allow fitting of the most significant parts of the peak with a higher degree of accuracy. In case of the mechanistic deconvolution, known data relevant to the kinetics under consideration are collected to form the a priori reaction mechanism and adjustable factors associated with the kinetic parameters were numerically optimized.





2. Experimental study

The current study follows the ICTAC Kinetics Committee recommendations for collecting experimental data [24]. The optimal sample mass was pre-determined to be between 1.2–1.5 mg in order to prevent self-heating of the sample while providing sufficient sensitivity to resolve various peaks. The particle size of the samples was closely controlled using a 200 mesh (75 μm) particle sieve. According to the ICTAC Kinetics Committee recommendations for thermal analysis and data processing [25], several distinct steps were followed in this study. The first step is concerned with obtaining good quality experimental kinetic data at multiple heating rates. The second step involves using an isoconversional method to evaluate the E_a - α relationship. The third step is evaluating the kinetic triplet of the single step or multi-step reaction through either model fitting or mechanistic techniques. While the fourth and final step is stated to be validation of the simulated curves against the experimental data.

DSC experiments were carried out with a Mettler Toledo DSC 3 instrument under constant heating rates of 1, 2, 5, 10, 20, 40, and 50 $^{\circ}\text{C}/\text{min}$ with a purge flow of nitrogen maintained at 80 mL/min. The samples were contained within the standard 40 μL aluminum pans sealed with an aluminum lid with a perforation of approximately 0.5 mm diameter. The sample mass was spread across the bottom of the pan in a thin layer to ensure rapid and uniform distribution of heat and minimize the temperature gradients inside the sample. Duplicate experiments were carried out for the extreme heating rates in order to ensure the repeatability of the thermograms and accuracy of the

Table 1

Composition of pyrotechnics used in current study.

Component	Red	Green	Blue	Yellow
KClO ₄	45 %	16 %	48 %	40 %
Mg	20 %	18 %	2.5 %	18 %
SrCO ₃	20 %	–	–	12 %
(C ₂ H ₃ Cl) _n	8 %	8 %	6 %	7 %
C ₁₀ H ₁₁ Cl ₁₇	7 %	8 %	8 %	5 %
CuO	–	–	23 %	–
Ba(NO ₃) ₂	–	50 %	–	–
S	–	–	12.5 %	–
Na ₃ AlF ₆	–	–	–	18 %
Pyrotechnic Flames				

calculated parameters. Furthermore, in case of a thermogram showing peculiar variations, the particular experiment was repeated twice. The resulting minor variation in the appearance of peaks in the thermograms was attributed to the slight inhomogeneity in the sample and small variations in the particle size distribution.

The mass based composition of the pyrotechnics currently being studied has been reported previously [26,27] and reproduced in Table 1. These compositions, typically utilized in display pyrotechnics, have been designated according to the color of the flame they generate.

3. Results and discussion

Typical DSC analysis elucidates the heat flow associated with the chemical reaction occurring within a given sample. The data from the DSC thermograms were used for understanding the chemical kinetics of the pyrotechnics.

3.1. DSC thermogram analysis

Fig. 1 shows the characteristics DSC thermograms obtained at various heating rates for the pyrotechnics under study. Despite utilizing potassium perchlorate as the primary oxidizer and magnesium as the primary fuel, a definite variation in the appearance of the thermograms of each composition was observed. However, certain features of pure component thermochemistry are evident in the DSC thermograms shown in Fig. 1. The phase transition of pure potassium perchlorate was manifested as an endothermic peak between 301–307 $^{\circ}\text{C}$, which is comparable to the values reported in the literature [14,28]. Fig. 1(a)–(d) show the variation of the phase change temperature with heating rates for each pyrotechnic composition.

The oxidizer-fuel reactions in pyrotechnics are typically triggered by melting or decomposition of either the fuel or the oxidizer [15,16]. In the current study, the onset of the primary exothermic peak was typically observed to occur between 360–390 $^{\circ}\text{C}$, significantly lower than the melting point of pure KClO₄ [14], as shown in Fig. 1(a)–(d). This reduction in the temperatures has been attributed [17–19] to the solid-state reactions, increased inter-diffusion of reactive components beyond the Tamman temperature, and inadvertent formation of local hotspots in the sample, as well as crystal defects such as distortions, dislocations, and cracks. Additionally, the primary exothermic event exhibits an appearance of an exothermic peak superimposed with the endothermic peaks corresponding to the decomposition of various additives. This has been further elaborated through the detailed view in Fig. 1(a). This behavior indicates the parallel nature of decomposition process of certain additives.

The extent of reaction (α), which varies from 0 to 1, for each heating

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