



Thermal history method for identification of autocatalytic decomposition reactions of energetic materials



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ABSTRACT

The thermal stability during the autocatalytic decomposition of a material depends on the intrinsic properties of the substance such as its kinetic triplet, in addition to its thermal history. In this reported study, simulations were conducted on select substances using the first-order reaction model (F1) and the general autocatalytic reaction model (Cn). Through changing the initial conversion rate, the thermal history's influence on the dynamic differential scanning calorimetry (DSC) curves was investigated based on the n-order reaction and autocatalytic reaction. A thermal history method for determining the autocatalytic decompositions of four energetic materials were established using the results of Roudit et al. and a simulated combustion. The isothermal DSC measurements and Swiss method were also employed to validate the reliability of the proposed thermal history method. Results of the simulations and experiments indicated that the influence on the dynamic DSC curves was significant based on data in the autocatalytic reactions. Thermal stability was decreased with a lower initial temperature and peak temperature. The influence was more significant on the energetic materials with greater autocatalytic potential. The results of this study indicated that the proposed thermal history method can be successfully used to quickly and effectively identify the autocatalysis characteristics of energetic materials.

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1. Introduction

Many energetic materials have been found to decompose autocatalytically (Long et al., 2002; Batten, 1985; Li and Koseki, 2005; Pourmortazavi et al., 2012). These materials are vulnerable to a number of unspecified external factors, which can cause them to ignite and explode a very dangerous situation. Autocatalytic decomposition is a reaction that is catalyzed by reaction products (Stoessel, 2009). Energetic materials experienced thermal history may contain decomposition products, which can trigger their thermal decomposition.

Roudit et al. (Roudit et al., 2013) reported that for autocatalytic and “nth order” reactions, the influence of the reaction progress at the beginning of the thermal experiment on the thermal behavior was different. The influence was significant for materials that decomposed according to autocatalytic models, but was negligible for materials that decomposed by first-order kinetics. Using the results of Roudit et al., simulations were also conducted

in this study using the first-order reaction model (F1) and the general autocatalytic reaction model (Cn). Based on all the aforementioned results, a new method termed the thermal history method was established and used to investigate the thermal behavior of four energetic materials.

2-Ethylhexyl nitrate (EHN) is an additive used in liquid propellants, which is a typical –O–NO₂ type compound (Yang et al., 2015; Suppes et al., 1997; Oxley et al., 2001; Bornemann et al., 2002; Chen et al., 2012). Pentaerythritol tetranitrate (PETN) (Huang and Wu, 1992; Hu et al., 2003) and nitrocellulose (NC) (Lee et al., 2002) are the nitrate explosives. PETN is a high explosive, while NC is commonly used as a component in single, double and triple-based powder and mixed explosives. Cyclotetramethylene tetramine (HMX) is a high explosive used as an important component in solid-propellant (Mccoy, 1999). These four substances are widely used energetic materials, whose thermal decomposition characteristics have always been an important issue. The thermal behavior of these four energetic materials was examined in this reported study using the thermal history method.

Until recently, the most reliable tool for the identification of autocatalytic decomposition was isothermal DSC measurement (Vyazovkin et al., 2011). In 2002, another identification method

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(Bou-Diab and Fierz, 2002) was reported by the Swiss Institute for the Promotion of Safety and Security (Swiss method). The Swiss method consists of fitting a first order kinetic model to the measured dynamic DSC curve and determining the apparent activation energy. These two methods were also conducted in this paper for the verification of the reliability of the thermal history method.

2. Simulation of the influence of thermal history on thermal decomposition

To illustrate in more detail the influence of the thermal history on the course of the decomposition and the dependence on the form of the $f(\alpha)$ (where α represents the conversion rate) function simulations of two commonly applied functions were performed:

First-order reaction F1 : $f(\alpha) = 1 - \alpha$.

General autocatalytic model Cn: $f(\alpha) = (1 - \alpha)^n (1 + k_{\text{cat}} \alpha)$. Parameter k_{cat} is the autocatalytic factor. As the k_{cat} value is increased, the autocatalytic characteristics of the material become increasingly apparent.

Dynamic DSC curves represent the relationship between exothermic rate (q) and temperature (T).

$$q = \frac{QVd}{M} \frac{d\alpha}{dT/\beta} \quad (1)$$

where Q is the enthalpy of the thermal decomposition reaction in J mol^{-1} , V is the volume of material loaded in cm^{-3} , d is the loading density in g cm^{-3} , M is the mole mass of materials in g mol^{-1} , and $d\alpha/dT$ is the reaction rate. The $d\alpha/dT$ versus T curve was used to represent dynamic DSC curve in this study since Q , V , d , M , β were held constant.

For the simulations the following input parameters were used: $A = 1 \times 10^{10} \text{ s}^{-1}$, $E = 100 \text{ kJ mol}^{-1}$, $\beta = 10 \text{ }^\circ\text{C min}^{-1}$, $n = 1$, $k_{\text{cat}} = 10, 25, 100$. The initial conversion (α_0) were 0, 0.05, 0.1, 0.2, 0.3, and 0.4 when the temperature was 300 K, which were used as the initial value for the curves. Wherein, the α_0 was that some material had been converted to reaction products at the beginning of the thermal experiment, which also represented the thermal history. Fig. 1 shows the simulated DSC curves based on the different models.

As can be seen from Fig. 1, with the increase of α_0 , the T_{onset} and T_{peak} did not change based on the F1 model and the peak heights decreased and the peak widths were constant, which resulted in a decrease in the ratio of the peak height to the peak width. In this section, the T_{onset} was defined as the temperature which was taken from the $d\alpha/dT$ versus T curves in Fig. 1 when the $d\alpha/dT$ rose to 0.001. According to the Cn model, the T_{onset} and T_{peak} decreased with the increase of α_0 , which was very different from the results obtained with the F1 model. The peak height decreased and the peak widths increased, which led to a decrease of the ratio of the peak height to the peak width. The results of the simulation indicated that influence of thermal history was significant for materials that decomposed according to the Cn model, but was negligible for materials that decomposed according to the F1 model in terms of T_{onset} and T_{peak} .

As shown in Fig. 1, the larger the value of k_{cat} was, the more acute the peaks became and the greater the autocatalytic potential was. With the increase of k_{cat} value, the rate of change of T_{onset} and T_{peak} increased. We concluded that the greater the autocatalytic potential was, the more significant the influence of thermal history was.

3. Experimental

3.1. Material

All reagents and materials in this investigation were used as received without further purification. The EHN (97 wt. %) employed was the Aladdin reagent. The NC (containing 13.78% nitrogen), HMX, PETN were industrial products, provided by Nanjing University of Science and Technology.

3.2. Apparatus and experimental conditions

All the experiments were conducted using a DSC1 instrument, which was manufactured by Mettler Toledo Company, Switzerland. The sensitivity tested in the TAWN method is 11.9. The test samples were sealed in stainless steel crucibles, and an empty crucible was used as reference. All of the DSC experiments were performed under a dry nitrogen atmosphere with the flow rate of 40 ml min^{-1} . Before the DSC experiments, indium and zinc were used for the calibration of the instrument.

3.3. The thermal history method

To obtain a certain thermal history of materials, the thermal history method was used in this paper. This method consisted of the follows:

Step (1) The first dynamic DSC curve (numbered –1) was collected at the heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ with a temperature range of 50–400 $^\circ\text{C}$. T_{onset} , T_{peak} and the decomposition enthalpy change (ΔH_r) were obtained.

Step (2) Under the same experimental conditions, the sample was heated to the interruption temperature (T_i) and was then cooled to 50 $^\circ\text{C}$. Next, a complete dynamic DSC test was conducted for the cooled sample to collect the second dynamic DSC curve. Three interruption temperatures were selected between T_{onset} and T_{peak} for each of the four energetic materials to repeat the experiment. The curves were numbered 2#, 3# and 4# corresponding to the different interruption temperatures.

According to the results of simulations the above, if the T_{onset} and T_{peak} of the second DSC curve changed significantly from that of the first DSC curve, the decomposition of the sample was considered to be an autocatalytic reaction. If this condition did not exist, the sample's reaction was considered to be an "nth order" reaction.

3.4. The Swiss method

The beginning of the reaction determines the behavior of the reaction mass under adiabatic conditions. It can be shown that at small conversion any reaction's kinetics can be described by a first order reaction. The measured heat release rate q at the beginning of a reaction ($\alpha < 0.1$) can be described as follows:

$$q = q_0 \exp\left(-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)(1 - \alpha) \quad (2)$$

where T_0 is the onset temperature, K; q_0 is the heat release rate at the onset temperature, W kg^{-1} ; E is the activation energy, kJ mol^{-1} ; R is the ideal gas constant, $\text{kJ mol}^{-1} \text{ K}^{-1}$; T is the temperature, K; α is the extent of conversion.

The DSC signal baseline for a material must either be known or be based on a reasonable assumption. In this study, the DSC data were analyzed using AKTS software from which the interrelation

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