A novel application of an isoconversional method for thermal decomposition kinetics of heavily aluminized RDX

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1 Introduction

The understanding of the response of propellants and energetic materials is of broad interest to the energetic materials community for the purposes of safe handling, storage methods, and comprehension of reaction violence. In particular accurate kinetics are essential for predicting the chemical reactive response of energetic materials.

Several approaches to determine the reaction profile of energetic materials have been proposed. The first one develops detailed mechanism that covers more than hundred reactions [1]. Most of such high energy materials have complex reaction profile which cannot be described by a single reaction step. Nevertheless, the kinetics composed of too many specific reactions are not suitable for efficient computational chemistry for its exhaustively demanding computing time. The second one assumes only a few reaction steps which have dominance on the global chemical reaction. Tarver and coworkers have proposed such reactive flow kinetics for a series of common energetic materials [2-3]. Lastly, the approach is an enhancement to isoconversional approach of Friedman [4]. This approach addresses activation energy and frequency factor which vary with each degree of conversion that reacts in sequence. Recently this last method has gained much attention thanks to a noticeable progress in the integral method [5] and the availability on the kinetics analysis software [6]. For this reason, we focus on this last approach for building the chemical reaction kinetics.

To obtain kinetics of reactive materials based on thermal stimulus, several types of thermal decomposition experiments such as TGA, STEX, ODTX and DSC have been in use. These experiments have distinct scales of the device and the amount of target samples used.

In this paper, DSC experiments are conducted to extract kinetics of a multi-purpose energetic material which is comprised of 50% RDX (cyclotrimethylene-trinitramine) and 35% aluminum powder with 15% HTPB (hydroxyl-terminated polybutadiene) binder, and its initial density after pressing is 1.78 g/cc. The DSC has been mainly used to measure the thermal decomposition characteristics of energetic materials [6-9] The use of isoconversional method to extract the kinetics does not require any sort of numerical fittings. Because the scheme is essentially a single step with a multiple set of

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Arrhenius parameters that evolve with the reaction progress, there is an obvious computational advantage over any competing multi-step kinetics.

To validate the present kinetics, a thermal decomposition experiment is performed to compare the simulation result that utilizes the present kinetics. Results confirm the applicability of the kinetic scheme to the practical thermal stimulus test for the considered energetic material.

2 DSC experiments and kinetics calculation

2.1 Differential scanning calorimetry

DSC experiments are carried out on Mettler Toledo DSC821e. The sample masses are in the range of 2.50 ~ 2.55 mg. The four heating rates of 0.5, 1.0, 2.0 and 4.0℃/min are used. The temperature range of 30 ~ 450℃ is covered at all heating rates. For all DSC signals, positive going feature corresponds to exothermic process. The aluminum sealed closed pans are used: to endure the pressure generated by exothermic reaction of energetic materials, closed pans must be adopted for the present experiment. Since evaporation is faster than decomposition in the sample in an open pan DSC [10], one must consider the closed pan DSC in order to observe the exothermic chemical reaction.

2.1 Kinetics calculation

The DSC traces have the form of Fig. 1 where the reaction rate $d\alpha/dt$ and the mass fraction of product α are obtained from equations below:

$$\frac{d\alpha}{dt} = S(t) - B(t) / \int_{t_0}^{t_{end}} [S(t) - B(t)]dt \tag{1}$$

$$\alpha(t) = \int_{t_0}^{t} S(t) - B(t)dt / \int_{t_0}^{t_{end}} [S(t) - B(t)]dt \ \ (0 \le \alpha \le 1) \tag{2}$$

$$B(t) = [1 - \alpha(t)](a_1 + b_1 t) + \alpha(t)(a_2 + b_2 t) \tag{3}$$

Here $S(t)$ is DSC data as a function of time t. $B(t)$ is called baseline which is a reference line for determining the magnitude of heat flow. The determination of baseline is conducted using AKTS-Thermokinetics Software [6].

The DSC signals of heavily aluminized RDX are plotted in Fig. 2. In this figure, as heating rate increases, the temperature range during which the chemical reaction occurs becomes narrower, and the peak value of signal becomes higher. Also the reaction begins at a higher temperature and terminates at a higher temperature. And From DSC signals, the heat of reaction is calculated as 1024.3J/g.

As DSC experiment is conducted with a certain heating rate, relationship between $d\alpha/dt$ and temperature can be obtained. Then isoconversional method is applied to DSC data with several heating rates usually 4~5 heating rates, to extract the kinetics parameter [6-9].

In the Friedman isoconversional method, reaction rate of materials is given in the Arrhenius form

$$\frac{d\alpha}{dt} = [A_\alpha f(\alpha)]\exp(\frac{-E_\alpha}{RT(t)}) \tag{4}$$

Here $R, t, T, A_\alpha, E_\alpha$ are universal gas constant, time, temperature, frequency factor and activation energy at product mass fraction α respectively. $f(\alpha)$ is commonly used as a set of functions reflecting the reaction mechanism. In the present work, activation energy and frequency factor are calculated without the assumption of $f(\alpha)$. We take a logarithm of both sides of Eq. (4):

$$\ln\frac{d\alpha}{dt} = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT} \tag{5}$$

In an Arrhenius plot, $-E_\alpha / R$ is slope and $\ln[A_\alpha f(\alpha)]$ is the intercept with vertical axis $\ln[d\alpha/dt]$. The Friedman analysis of the aluminized RDX with four heating rates is presented in Fig. 3. Dotted line represents the connection of the same α points of each result. The line indicates that α=0.95 is plotted as represented in Fig. 3. The slope and intercept with a vertical axis of dotted lines mean

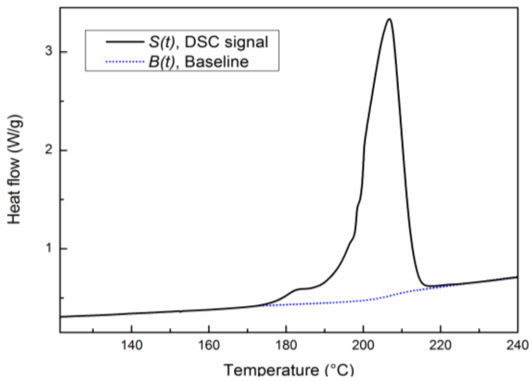

Figure 1. DSC signals and baseline.

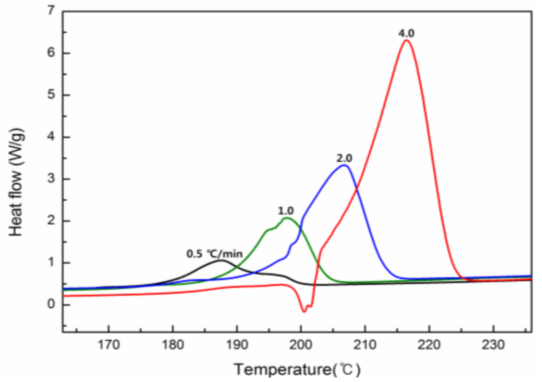

Figure 2. DSC signals of heavily aluminized RDX.

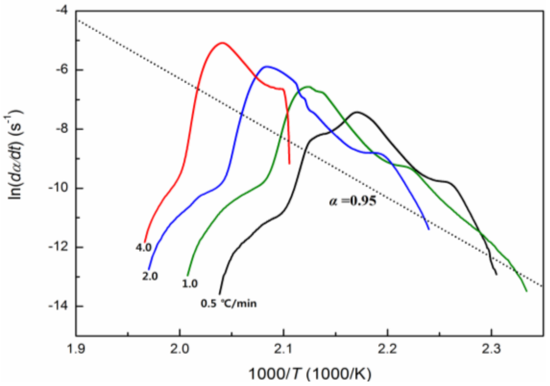

Figure 3. Friedman analysis of heavily aluminized RDX.

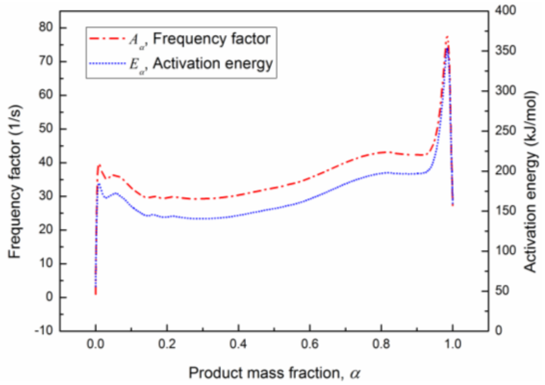

Figure 4. Frequency factor and activation energy of heavily aluminized RDX.

activation energy and frequency factor at α, respectively. Similarly the Arrhenius parameters in a full reaction process with the product mass fraction, α being between the value of 0 and 1 can be obtained. The activation energy and frequency factor with α extracted from the Friedman analysis are presented in Fig. 4. The obtained sets of activation energy and frequency factor are varied with α. This implies that the extracted kinetics describe full chemical reaction process elaborated through a set of Arrhenius parameter, because a set of Arrhenius parameters represents a specific profile of a reaction process. The presented kinetic scheme is extracted theoretically without the artificial numerical fitting procedure.

3 Kinetics validation

The governing equations of constant volume reaction are summarized as follows:

$$\frac{dT}{dt} = \dot{w} \tag{6}$$

$$\frac{d\alpha}{dt} = A_\alpha \exp\left(\frac{-E_\alpha}{RT}\right) \tag{7}$$

where $\dot{w}$ is heating rate. In the DSC experiment, the heat generated from reaction is emitted to the reference materials immediately, and such the enthalpy of reaction is neglected in Eq. (6). The Arrhenius parameters in Fig. 4 are used in the validation calculation. The comparisons of DSC experiments and simulations are plotted in Fig. 5 and 6 where results of DSC experiments are obtained from Eq. (1-3). In Fig. 5, similarity between simulation and experiment is observed except around 203℃ of 4.0℃/min heating rate. Here, a slope discontinuity is occurred. There is similarity for product mass fraction results, except for 203℃ of 4.0℃/min heating rate. The good conformity between simulation and experiment suggests that the obtained kinetic scheme is capable of describing

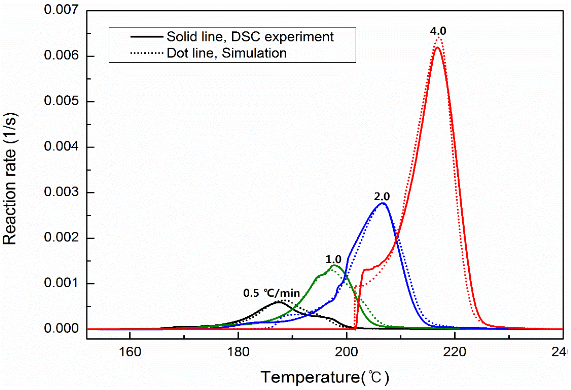

Figure 5. Reaction rate comparison between experiment and simulation.

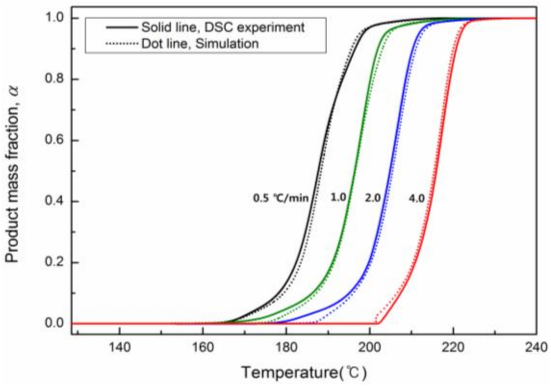

Figure 6. Product mass fraction comparison between experiment and simulation.

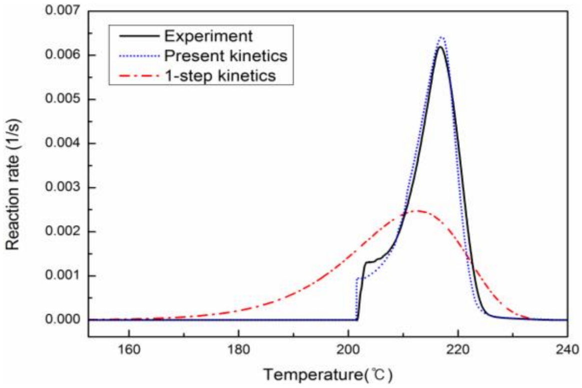

Figure 7. Reaction rate at 4.0℃/min (experiment, present kinetics, 1-step kinetics).

a reaction process from the initial to a final state of the aluminized RDX reaction. In Figure 5, the slope discontinuities are evident at different heating rates including the 4.0℃/min. The existence of reaction rate discontinuities is representative of a rather complex chemical processes that cannot be modeled by a single step kinetic illustrated by a smooth bell-shape curve.

A single step method as opposed to the present kinetics is considered at 4.0℃/min case of heating rate. The corresponding one-step reaction is given by

$$\frac{d\alpha}{dt} = A_0 \exp(\frac{-E_0}{RT}) \tag{8}$$

where the values of $A_0 = \exp(42)$ and $E_0 = 200\text{kJ/mol}$ are used. The results are plotted in Fig. 7. One can see that accurate reproduction of experimental values are simply impossible using such a single step kinetic. The deficiency of the full parameters of the Arrhenius expression to describe the slope discontinuity explains the necessity of considering the present method for reaction process.

In comparison to a single step or multiple step reaction scheme, the present kinetics extracted from the closed pan DSC require just two reaction parameters that evolve with time from initial to a final product state of the energetic sample. Thus with good accuracy, there is a definite advantage of the present scheme in full scale hydrodynamic simulation of the reactive response of energetic materials.

4 A thermal decomposition test and simulation

4.1. Governing equations and numerical method

To show validity and applicability of the extracted kinetics scheme to a practical thermal experiment, we conduct the thermal decomposition test. The governing equations are as follows

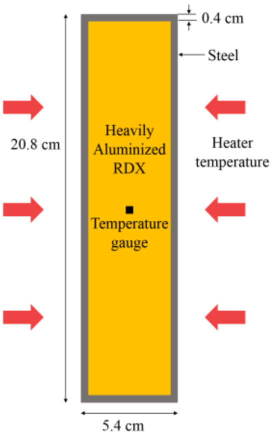

Figure 8. Schematic of thermal decomposition test

Table 1: Comparison of explosion time and temperature between experiment and simulation

	Explosion time	Explosion temperature
Experiment	21.55 hour	165.3 ℃
Simulation	21.61 hour	165.6℃

$$\rho C\frac{\partial T}{\partial t}=k(\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2})-\frac{\partial \alpha}{\partial t}Q \tag{9}$$

$$\frac{d\alpha}{dt}=A_\alpha \exp(\frac{-E_\alpha}{RT}) \tag{10}$$

Here ρ, C and k are density, specific heat and thermal conductivity respectively. Equation (9) is the energy balance. To describe the heating process, heat conduction must be considered in the governing equation.

In this experiment, the energetic materials do not ‘flow’ during the constant heating process. Thus mass and momentum are unchanged. The kinetic parameters of Fig.4 is used in the rate equation. The cylindrical 2nd order central difference scheme is used for the spatial discretization, and a 3rd order Runge-Kutta method is used for time integration.

4.2. Simulation set up and results

The slow cookoff test is a standardized experiment for monitoring the violence of reaction of insensitive munitions [11]. The obtained temperature with respect to time until a thermal runaway is observed provides classification to the reaction violence being a deflagration or detonation.

The schematic of the simulation is given in Fig. 8. The inside of cylindrical steel case is filled with the aluminized RDX. The temperature of the charge is measured at the center. The thickness of the case is 0.4 cm. The width and length of the charge are 4.5 cm and 20.0 cm, respectively. The initial temperature of aluminized RDX is 30.8 ℃and then it is heated to 108℃within 1 hour. The heater temperature is maintained at 108℃ for 7 hours to allow temperature to equilibriate before the final

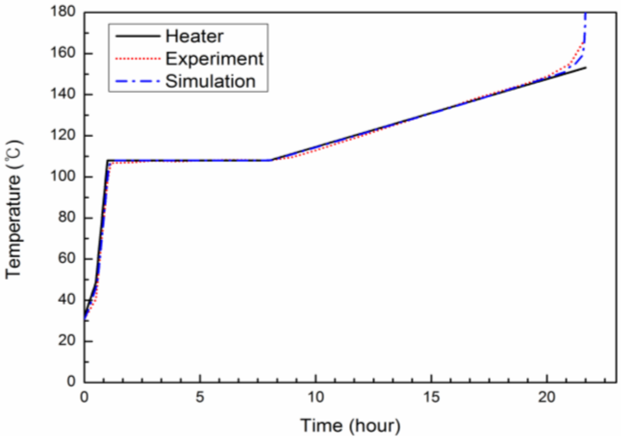

Figure 9. Temperature histories of slow cook-off test (heater, simulation, experiment)

runaway to occur. Then the heating rate of 3.3℃/hour is used until explosion is witnessed.

The temperature histories are plotted in Fig. 9, and corresponding explosion time and temperature are listed in Table 1. We report a very good agreement between experiment and simulation by using the present chemical kinetics.

5 Conclusion

A chemical kinetic scheme for a heavily aluminized RDX is constructed based on the DSC experiment and the Friedman isoconversional method. The obtained kinetics with Arrhenius terms that are parametrized by the reaction progress are validated against the experimental data. In the general reactive flow simulation of energetic materials, the present approach possesses considerable advantage in terms of computational efficiency as it closely resembles the single step global reaction model while it utilizes innumerable set of Arrhenius parameters that are directly obtained from the instantaneous progress of the reaction. Additional energetic materials are being considered for constructing a reliable reaction model based on the present isoconversional method.

Acknowledgments

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