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A NUMERICAL METHOD OF COMPUTING THE KINETIC PARAMETERS

Exothermic decomposition of energetic materials via the exothermic rate equation

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Abstract

A numerical method of computing the kinetic parameters (the activation energy (E), the pre-exponential constant (A) and the reaction order (n)) of exothermic decomposition of energetic materials via the exothermic rate equation is presented. The values of E, A and n are reported for the exothermic decomposition of six typical energetic materials, 1,6-diazido-2,5-dinitrazahexane (I), 1,5-diazido-3-nitrazapentane (II), 2,2,4,7,9,9-hexanitro-5-methyl-4,7-dinitrazadecane (III), 2,2,2-trinitroethyl-4,4,4-trinitrobutyrate (IV), 1,4-dinitro-2,3-dioxo-1,4-dinitrazacyclohexane (V) and 1,3,5-trianitro-1,3,5-triazafurazano[3,4-f]cycloheptane (VI).

Keywords: decomposition reaction, DSC, energetic materials, exothermic rate equation, kinetic parameters, numerical method

Introduction

Compounds I–VI can be used as high explosives or energetic ingredients of propellants. Their kinetic behaviour has not yet been reported. The aim of this work is to present a numerical method of computing the kinetic parameters via the exothermic rate equation and to report the values of E, A and n for the exothermic decomposition of compounds I–VI.

Experimental

Materials

The following six energetic compounds used in this work were prepared and purified at our Institute.

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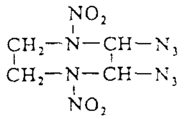
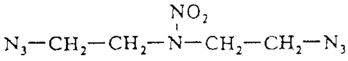
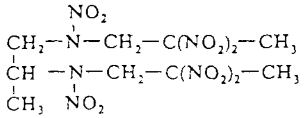


I

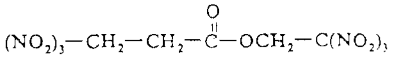


$N_3-CH_2-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-N_3$

II

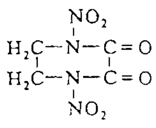


III

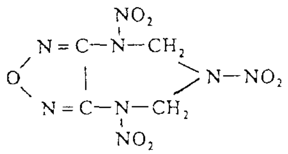


$(NO_2)_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OCH_2-C(NO_2)_3$

IV



V



VI

The structures of compounds I–VI were characterized by elemental analyses, molecular weight determination, IR spectrometry, mass spectrometry and nuclear magnetic resonance spectrometry. Their purities were more than 99.5%. The compounds were kept in a vacuum desiccator before use.

Experimental equipment and conditions

DSC experiments on compounds I–VI were carried out with a model CDR-1 thermal analyser made in the Shanghai Balance Instrument Factory, using a Ni/Cr-Ni/Si thermocouple plate, under static air conditions, at four different heating rates in the range 0.5–20 deg·min^{-1}. Aluminium oxide was used as reference material. DSC curves were obtained for both a sealed cell made of stainless steel and an aluminium cell with a rolled-up side. The heating rate was calculated according to the actual rate of temperature rise from 50°C to the temperature at the end of the decomposition. The amount of sample used was about 0.7 mg.

DSC curves for the exothermic decompositions of compounds I–VI are shown in Fig. 1. The DSC curve of II was obtained with the sealed cell of stainless steel; the DSC curves of the others were obtained with the aluminium cell with a rolled-up side.

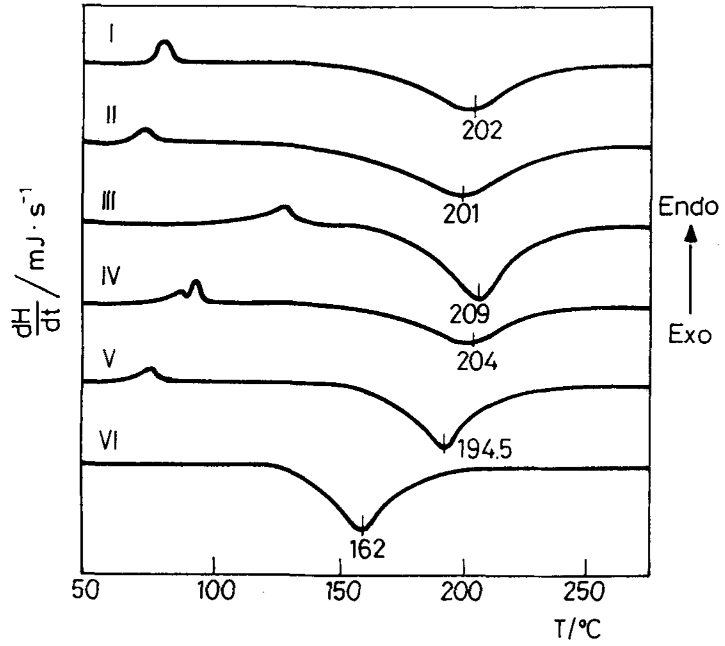


Fig. 1 DSC curves of thermal decomposition of compounds I–VI at a heating rate of 5 deg·min^{-1}

Analysis of kinetic data

According to our previous papers [1, 2], the exothermic rate equation used to determine non-isothermal kinetic parameters from a single non-isothermal DSC curve is

$$\ln\frac{\mathrm{d}H_t}{\mathrm{d}t} = \ln\left\{AH_0 f(\alpha)\left[1+\frac{E}{RT}\left(1-\frac{T_0}{T}\right)\right]\right\} - \frac{E}{RT} \qquad (1)$$

where H_0 is the total exothermicity of the substance (corresponding to the total area under the DSC curve; T_0 is the initial point at which the DSC curve deviates from the baseline; and H_t, α, T, $f(\alpha)$, t, R, A and E have the usual meanings [1, 2].

In order to obtain the kinetic parameters, we took the minimal values of the evaluation functions Ω $(E, A, \ldots)$:

$$\Omega = \sum_{i=1}^{l}\left\{\ln\left(\frac{\mathrm{d}H_t}{\mathrm{d}t}\right)_i - \ln\left\{AH_0 f(\alpha_i)\left[1+\frac{E}{RT_i}\left(1-\frac{T_0}{T_i}\right)\right]\right\} - \frac{E}{RT_i}\right\}^2 \qquad (2)$$

The kinetic parameters, the conditions of taking the minimal values of the function Ω (E, A,...), the fifteen normal equations for computing the kinetic parameters obtained from Eq. (2) and all the forms of $f(\alpha)$ listed in Table 1 are presented in Table 2.

Table 1 Kinetic functions used for the present analysis

Function no.	Function form (differential form), $f(\alpha)$
1	$(1-\alpha)^n$
2	α^m
3	$[1-\ln(1-\alpha)]^k$
4	$\alpha^m(1-\alpha)^n$
5	$\alpha^m[1-\ln(1-\alpha)]^k$
6	$(1-\alpha)^n\,[1-\ln(1-\alpha)]^k$
7	$\alpha^m(1-\alpha)^n\,[1-\ln(1-\alpha)]^k$
8	$[-\ln(1-\alpha)]^k$
9	$\alpha^m[-\ln(1-\alpha)]^k$
10	$(1-\alpha)^n[-\ln(1-\alpha)]^k$
11	$\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^k$
12	$(1-\alpha)^n[1-(1-\alpha)^{1/3}]^k$
13	$(1-\alpha)^n[1-(1-\alpha)^{1/2}]^k$
14	$(1-\alpha)^n[(1-\alpha)^{-1/3}-1]^k$
15	$(1+\alpha)^n[(1+\alpha)^{1/3}-1]^k$

Table 2 Normal equations corresponding to the fifteen differrential mechanism functions in Table 1

Function no.	Kinetic parameters	Condition of taking the minimal values of function Ω (E, A,...)	Corresponding normal Eqs
1	A	$\partial\Omega / \partial A = 0$	$\begin{bmatrix} l & a_1 \\ a_1 & \theta_1 \\ q & r_1 \end{bmatrix}\begin{bmatrix} Z \\ n \end{bmatrix} = \begin{bmatrix} B \\ F_1 \\ G \end{bmatrix}$
	n	$\partial\Omega / \partial n = 0$	
	E	$\partial\Omega / \partial E = 0$	
2	A	$\partial\Omega / \partial A = 0$	$\begin{bmatrix} l & a_2 \\ a_2 & \theta_2 \\ q & r_2 \end{bmatrix}\begin{bmatrix} Z \\ m \end{bmatrix} = \begin{bmatrix} B \\ F_2 \\ G \end{bmatrix}$
	m	$\partial\Omega / \partial m = 0$	
	E	$\partial\Omega / \partial E = 0$	
3	A	$\partial\Omega / \partial A = 0$	$\begin{bmatrix} l & a_3 \\ a_3 & \theta_3 \\ q & r_3 \end{bmatrix}\begin{bmatrix} Z \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_3 \\ G \end{bmatrix}$
	k	$\partial\Omega / \partial k = 0$	
	E	$\partial\Omega / \partial E = 0$	

Table 2 Continued

Function no.	Kinetic parameters	Condition of taking minimal values of function Ω (E, A,...)	Corresponding normal Eqs
4	A	$\partial\Omega / \partial A = 0$	$\begin{bmatrix} l & a_1 & a_2 \\ a_1 & \theta_1 & \theta_4 \\ a_2 & \theta_4 & \theta_2 \\ q & r_1 & r_2 \end{bmatrix} \begin{bmatrix} Z \\ n \\ m \end{bmatrix} = \begin{bmatrix} B \\ F_1 \\ F_2 \\ G \end{bmatrix}$
	n	$\partial\Omega / \partial n = 0$	
	m	$\partial\Omega / \partial m = 0$	
	E	$\partial\Omega / \partial E = 0$	
5	A	$\partial\Omega / \partial A = 0$	$\begin{bmatrix} l & a_2 & a_3 \\ a_2 & \theta_2 & \theta_6 \\ a_3 & \theta_6 & \theta_3 \\ q & r_2 & r_3 \end{bmatrix} \begin{bmatrix} Z \\ m \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_2 \\ F_3 \\ G \end{bmatrix}$
	m	$\partial\Omega / \partial m = 0$	
	k	$\partial\Omega / \partial k = 0$	
	E	$\partial\Omega / \partial E = 0$	
6	A	$\partial\Omega / \partial A = 0$	$\begin{bmatrix} l & a_1 & a_3 \\ a_1 & \theta_1 & \theta_5 \\ a_3 & \theta_5 & \theta_3 \\ q & r_1 & r_3 \end{bmatrix} \begin{bmatrix} Z \\ n \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_1 \\ F_3 \\ G \end{bmatrix}$
	n	$\partial\Omega / \partial n = 0$	
	k	$\partial\Omega / \partial k = 0$	
	E	$\partial\Omega / \partial E = 0$	
7	A	$\partial\Omega / \partial A = 0$	$\begin{bmatrix} l & a_1 & a_2 & a_3 \\ a_1 & \theta_1 & \theta_4 & \theta_5 \\ a_2 & \theta_4 & \theta_2 & \theta_6 \\ a_3 & \theta_5 & \theta_6 & \theta_3 \\ q & r_1 & r_2 & r_3 \end{bmatrix} \begin{bmatrix} Z \\ n \\ m \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_1 \\ F_2 \\ F_3 \\ G \end{bmatrix}$
	n	$\partial\Omega / \partial n = 0$	
	m	$\partial\Omega / \partial m = 0$	
	k	$\partial\Omega / \partial k = 0$	
	E	$\partial\Omega / \partial E = 0$	
8	A	$\partial\Omega / \partial A = 0$	$\begin{bmatrix} l & a_4 \\ a_4 & \theta_7 \\ q & r_4 \end{bmatrix} \begin{bmatrix} Z \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_4 \\ G \end{bmatrix}$
	k	$\partial\Omega / \partial k = 0$	
	E	$\partial\Omega / \partial E = 0$	
9	A	$\partial\Omega / \partial A = 0$	$\begin{bmatrix} l & a_2 & a_4 \\ a_2 & \theta_2 & \theta_9 \\ a_4 & \theta_9 & \theta_7 \\ q & r_2 & r_4 \end{bmatrix} \begin{bmatrix} Z \\ m \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_2 \\ F_4 \\ G \end{bmatrix}$
	m	$\partial\Omega / \partial m = 0$	
	k	$\partial\Omega / \partial k = 0$	
	E	$\partial\Omega / \partial E = 0$	
10	A	$\partial\Omega / \partial A = 0$	$\begin{bmatrix} l & a_1 & a_4 \\ a_1 & \theta_1 & \theta_8 \\ a_4 & \theta_8 & \theta_7 \\ q & r_1 & r_4 \end{bmatrix} \begin{bmatrix} Z \\ n \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_1 \\ F_4 \\ G \end{bmatrix}$
	n	$\partial\Omega / \partial n = 0$	
	k	$\partial\Omega / \partial k = 0$	
	E	$\partial\Omega / \partial E = 0$	
11	A	$\partial\Omega / \partial A = 0$	$\begin{bmatrix} l & a_1 & a_2 & a_4 \\ a_1 & \theta_1 & \theta_4 & \theta_8 \\ a_2 & \theta_4 & \theta_2 & \theta_9 \\ a_4 & \theta_8 & \theta_9 & \theta_7 \\ q & r_1 & r_2 & r_4 \end{bmatrix} \begin{bmatrix} Z \\ n \\ m \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_1 \\ F_2 \\ F_4 \\ G \end{bmatrix}$
	n	$\partial\Omega / \partial n = 0$	
	m	$\partial\Omega / \partial m = 0$	
	k	$\partial\Omega / \partial k = 0$	
	E	$\partial\Omega / \partial E = 0$	

Table 2 Continued

Function no.	Kinetic parameters	Condition of taking the minimal values of function Ω $(E, A,\ldots)$	Corresponding normal Eqs
12	A	$\partial\Omega / \partial A = 0$	$\begin{bmatrix} l & a_1 & a_5 \\ a_1 & \theta_1 & \theta_{11} \\ a_5 & \theta_{11} & \theta_{10} \\ q & r_1 & r_5 \end{bmatrix} \begin{bmatrix} Z \\ n \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_1 \\ F_5 \\ G \end{bmatrix}$
	n	$\partial\Omega / \partial n = 0$	
	k	$\partial\Omega / \partial k = 0$	
	E	$\partial\Omega / \partial E = 0$	
13	A	$\partial\Omega / \partial A = 0$	$\begin{bmatrix} l & a_1 & a_6 \\ a_1 & \theta_1 & \theta_{13} \\ a_6 & \theta_{13} & \theta_{12} \\ q & r_1 & r_6 \end{bmatrix} \begin{bmatrix} Z \\ n \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_1 \\ F_6 \\ G \end{bmatrix}$
	n	$\partial\Omega / \partial n = 0$	
	k	$\partial\Omega / \partial k = 0$	
	E	$\partial\Omega / \partial E = 0$	
14	A	$\partial\Omega / \partial A = 0$	$\begin{bmatrix} l & a_1 & a_7 \\ a_1 & \theta_1 & \theta_{15} \\ a_7 & \theta_{15} & \theta_{14} \\ q & r_1 & r_7 \end{bmatrix} \begin{bmatrix} Z \\ n \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_1 \\ F_7 \\ G \end{bmatrix}$
	n	$\partial\Omega / \partial n = 0$	
	k	$\partial\Omega / \partial k = 0$	
	E	$\partial\Omega / \partial E = 0$	
15	A	$\partial\Omega / \partial A = 0$	$\begin{bmatrix} l & a_8 & a_9 \\ a_8 & \theta_{16} & \theta_{18} \\ a_9 & \theta_{18} & \theta_{17} \\ q & r_8 & r_9 \end{bmatrix} \begin{bmatrix} Z \\ n \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_8 \\ F_9 \\ G \end{bmatrix}$
	n	$\partial\Omega / \partial n = 0$	
	k	$\partial\Omega / \partial k = 0$	
	E	$\partial\Omega / \partial E = 0$	

Notation:

$$y_i = \ln\left(\frac{dH_t}{dt}\right)_i;$$

$$a_1 = \sum_{i=1}^{l} \ln(1-\alpha_i);$$

$$a_2 = \sum_{i=1}^{l} \ln\alpha_i;$$

$$a_3 = \sum_{i=1}^{l} \ln[1-\ln(1-\alpha_i)];$$

$$a_4 = \sum_{i=1}^{l} \ln[-\ln(1-\alpha_i)];$$

$$a_5=\sum_{i=1}^{l}\ln\left[1-(1-\alpha_i)^{1/3}\right];$$

$$a_6=\sum_{i=1}^{l}\ln\left[1-(1-\alpha_i)^{1/2}\right];$$

$$a_7=\sum_{i=1}^{l}\ln\left[(1-\alpha_i)^{-1/3}-1\right];$$

$$a_8=\sum_{i=1}^{l}\ln(1+\alpha_i);$$

$$a_9=\sum_{i=1}^{l}\ln\left[(1+\alpha_i)^{1/3}-1\right];$$

$$b=\sum_{i=1}^{l}y_i;$$

$$c=\sum_{i=1}^{l}\frac{1}{T_i};$$

$$D_i=\ln\left[1+\frac{E}{RT_i}\left(1-\frac{T_o}{T_i}\right)\right];$$

$$d=\sum_{i=1}^{l}D_i;$$

$$\theta_1=\sum_{i=1}^{l}\ln^2(1-\alpha_i);$$

$$\theta_2=\sum_{i=1}^{l}\ln^2\alpha_i;$$

$$\theta_3=\sum_{i=1}^{l}\ln^2[1-\ln(1-\alpha_i)];$$

$$\theta_4 = \sum_{i=1}^{l} \ln\alpha_i \cdot \ln(1-\alpha_i);$$

$$\theta_5 = \sum_{i=1}^{l} \ln[1-\ln(1-\alpha_i)] \cdot \ln(1-\alpha_i);$$

$$\theta_6 = \sum_{i=1}^{l} \ln[1-\ln(1-\alpha_i)] \cdot \ln\alpha_i;$$

$$\theta_7 = \sum_{i=1}^{l} \ln^2[-\ln(1-\alpha_i)];$$

$$\theta_8 = \sum_{i=1}^{l} \ln(1-\alpha_i)\ln[-\ln(1-\alpha_i)];$$

$$\theta_9 = \sum_{i=1}^{l} \ln\alpha_i \cdot \ln[-\ln(1-\alpha_i)];$$

$$\theta_{10} = \sum_{i=1}^{l} \ln^2\left[1-(1-\alpha_i)^{1/3}\right];$$

$$\theta_{11} = \sum_{i=1}^{l} \ln(1-\alpha_i) \cdot \ln\left[1-(1-\alpha_i)^{1/3}\right];$$

$$\theta_{12} = \sum_{i=1}^{l} \ln^2\left[1-(1-\alpha_i)^{1/2}\right];$$

$$\theta_{13} = \sum_{i=1}^{l} \ln(1-\alpha_i) \cdot \ln\left[1-(1-\alpha_i)^{1/2}\right];$$

$$\theta_{14} = \sum_{i=1}^{l} \ln^2\left[(1-\alpha_i)^{-1/3}-1\right];$$

$$\theta_{15} = \sum_{i=1}^{l} \ln(1-\alpha_i) \cdot \ln\left[(1-\alpha_i)^{-1/3}-1\right];$$

$$\theta_{16} = \sum_{i=1}^{l} \ln^2(1+\alpha_i);$$

$$\theta_{17} = \sum_{i=1}^{l} \ln^2\left[(1+\alpha_i)^{1/3} - 1\right];$$

$$\theta_{18} = \sum_{i=1}^{l} \ln(1+\alpha_i)\cdot\ln\left[(1+\alpha_i)^{1/3} - 1\right];$$

$$f_1 = \sum_{i=1}^{l} y_i\cdot\ln(1-\alpha_i);$$

$$f_2 = \sum_{i=1}^{l} y_i\cdot\ln\alpha_i;$$

$$f_3 = \sum_{i=1}^{l} y_i\cdot\ln[1-\ln(1-\alpha_i)];$$

$$f_4 = \sum_{i=1}^{l} y_i\cdot\ln[-\ln(1-\alpha_i)];$$

$$f_5 = \sum_{i=1}^{l} y_i\cdot\ln\left[1-(1-\alpha_i)^{1/3}\right];$$

$$f_6 = \sum_{i=1}^{l} y_i\cdot\ln\left[1-(1-\alpha_i)^{1/2}\right];$$

$$f_7 = \sum_{i=1}^{l} y_i\cdot\ln\left[(1-\alpha_i)^{-1/3} - 1\right];$$

$$f_8 = \sum_{i=1}^{l} y_i\cdot\ln(1+\alpha_i);$$

$$f_9 = \sum_{i=1}^{l} y_i\cdot\ln\left[(1+\alpha_i)^{1/3} - 1\right];$$

$$g_1 = \sum_{i=1}^{l} \frac{\ln(1-\alpha_i)}{T_i};$$

$$g_2 = \sum_{i=1}^{l} \frac{\ln\alpha_i}{T_i};$$

$$g_3 = \sum_{i=1}^{l} \frac{\ln[1-\ln(1-\alpha_i)]}{T_i};$$

$$g_4 = \sum_{i=1}^{l} \frac{\ln[-\ln(1-\alpha_i)]}{T_i};$$

$$g_5 = \sum_{i=1}^{l} \frac{\ln[1-(1-\alpha_i)^{1/3}]}{T_i};$$

$$g_6 = \sum_{i=1}^{l} \frac{\ln[1-(1-\alpha_i)^{1/2}]}{T_i};$$

$$g_7 = \sum_{i=1}^{l} \frac{\ln[(1-\alpha_i)^{-1/3}-1]}{T_i};$$

$$g_8 = \sum_{i=1}^{l} \frac{\ln(1+\alpha_i)}{T_i};$$

$$g_9 = \sum_{i=1}^{l} \frac{\ln[(1+\alpha_i)^{1/3}-1]}{T_i};$$

$$h_1 = \sum_{i=1}^{l} D_i \cdot \ln(1-\alpha_i);$$

$$h_2 = \sum_{i=1}^{l} D_i \cdot \ln\alpha_i;$$

$$h_3 = \sum_{i=1}^{l} D_i \cdot \ln[1-\ln(1-\alpha_i)];$$

$$h_4 = \sum_{i=1}^{1} D_i \cdot \ln[-\ln(1-\alpha_i)];$$

$$h_5 = \sum_{i=1}^{1} D_i \cdot \ln\left[1-(1-\alpha_i)^{1/3}\right];$$

$$h_6 = \sum_{i=1}^{1} D_i \cdot \ln\left[1-(1-\alpha_i)^{1/2}\right];$$

$$h_7 = \sum_{i=1}^{1} D_i \cdot \ln\left[(1-\alpha_i)^{-1/3}-1\right];$$

$$h_8 = \sum_{i=1}^{1} D_i \cdot \ln(1+\alpha_i);$$

$$h_9 = \sum_{i=1}^{1} D_i \cdot \ln\left[(1+\alpha_i)^{1/3}-1\right];$$

$$Q_i = \frac{1}{RT_i}\left[\frac{1-\dfrac{1-T_o}{T_i}}{1+\dfrac{E}{RT_i}\left(1-\dfrac{T_o}{T_i}\right)}\right];$$

$$r_1 = \sum_{i=1}^{1} Q_i \cdot \ln(1-\alpha_i);$$

$$r_2 = \sum_{i=1}^{1} Q_i \cdot \ln\alpha_i;$$

$$r_3 = \sum_{i=1}^{1} Q_i \cdot \ln[1-\ln(1-\alpha_i)];$$

$$r_4 = \sum_{i=1}^{1} Q_i \cdot \ln[-\ln(1-\alpha_i)];$$

$$r_5 = \sum_{i=1}^{l} Q_i \cdot \ln\left[1 - (1 - \alpha_i)^{1/3}\right];$$

$$r_6 = \sum_{i=1}^{l} Q_i \cdot \ln\left[1 - (1 - \alpha_i)^{1/2}\right];$$

$$r_7 = \sum_{i=1}^{l} Q_i \cdot \ln\left[(1 - \alpha_i)^{-1/3} - 1\right];$$

$$r_8 = \sum_{i=1}^{l} Q_i \cdot \ln(1 + \alpha_i);$$

$$r_9 = \sum_{i=1}^{l} Q_i \cdot \ln\left[(1 + \alpha_i)^{1/3} - 1\right];$$

$$P = \sum_{i=1}^{l} Q_i \cdot y_i;$$

$$q = \sum_{i=1}^{l} Q_i;$$

$$S = \sum_{i=1}^{l} D_i \cdot Q_i;$$

$$W = \sum_{i=1}^{l} \frac{Q_i}{T_i};$$

$$B = b + \frac{E}{R} c - d;$$

$$F_j = f_j + \frac{E}{R} g_j - h_j; \quad (j = 1, 2, 3, \ldots, 9)$$

$$Z = \ln(AH_o) = \ln A + \ln H_o;$$

$$G = P + \frac{E}{R} W - S.$$

Table 3 DSC data on compound I

Data point	Temperature T/K	Reaction depth H_t / H_o	Exothermic rate dH_t/dt(mJ/s)	$d(H_t/H_o)$ /$dT \times 10^3$ (K^{-1})
1	447.2	0.0261	0.9807	3.907
2	451.2	0.0456	1.392	5.547
3	455.2	0.0711	2.102	8.373
4	458.2	0.0978	2.862	11.40
5	460.7	0.1344	3.899	15.53
6	463.2	0.1733	5.021	20.00
7	465.7	0.2167	6.202	24.71
8	468.2	0.2711	7.585	30.21
9	469.7	0.3256	8.830	35.17
10	470.7	0.3861	10.04	40.00
11	472.7	0.4522	11.14	44.39
12	474.7	0.5217	11.83	47.13
13	475.7	0.5806	12.05	48.00
T_o=430.2 K;	H_o=3012 mJ;	φ=0.0833 °C·s^{-1}		

Table 4 DSC data on compound II

Data point	Temperature T/K	Reaction depth H_t / H_o	Exothermic rate dH_t/dt(mJ/s)	$d(H_t/H_o)$ /$dT \times 10^3$ (K^{-1})
1	436.2	0.0042	0.2042	0.4508
2	446.2	0.0148	0.8502	1.877
3	452.2	0.0325	1.630	3.599
4	456.2	0.0549	2.684	5.927
5	460.2	0.0878	4.140	9.142
6	465.2	0.1402	6.326	13.97
7	468.2	0.1993	9.007	19.89
8	471.2	0.2880	12.89	28.45
9	475.2	0.4041	17.07	37.69
10	477.2	0.5021	19.86	43.84
11	480.2	0.6157	20.92	46.19
T_o=418.2 K;	H_o=2378 mJ;	φ=0.1905 °C·s^{-1}		

Table 5 DSC data on compound III

Data point	Temperature T/K	Reaction depth H_t / H_o	Exothermic rate dH_t/dt(mJ/s)	$d(H_t/H_o)$ /dT×10^3 (K^{-1})
1	454.9	0.0169	0.6150	4.004
2	459.7	0.0447	1.213	7.900
3	461.6	0.0623	1.531	9.970
4	465.2	0.1074	2.289	14.90
5	468.8	0.1733	3.397	22.12
6	472.1	0.2560	4.326	28.17
7	474.8	0.3412	5.255	34.21
8	477.2	0.4299	6.063	39.47
9	479.6	0.5286	6.569	42.77
10	481.4	0.6062	6.678	43.48
T_o=445.0 K;	H_o=1843 mJ;	φ=0.0833 °C·s^{-1}		

Table 6 DSC data on compound IV

Data point	Temperature T/K	Reaction depth H_t / H_o	Exothermic rate dH_t/dt(mJ/s)	$d(H_t/H_o)$ /dT×10^3 (K^{-1})
1	443.4	0.0327	0.2301	3.433
2	449.1	0.0572	0.3598	5.369
3	453.8	0.0881	0.5188	7.741
4	459.0	0.1378	0.8117	12.11
5	463.8	0.2069	1.176	17.54
6	467.3	0.2765	1.540	22.97
7	471.2	0.3771	1.958	29.22
8	474.6	0.4826	2.192	32.71
9	477.7	0.5841	2.305	34.40
10	481.1	0.7085	2.544	37.95
T_o=422.2 K;	H_o=804 mJ;	φ=0.0833 °C·s^{-1}		

Once the value of E has been calculated from $\partial\Omega/\partial E = 0$, the corresponding values of A, n, m and k can then be obtained from $\partial\Omega/\partial A = 0$, $\partial\Omega/\partial n = 0$, $\partial\Omega/\partial m = 0$ and $\partial\Omega/\partial k = 0$. In the iterative computation process of combined dichotomous and least-squares methods, we take $AA = 10^{-1}$, $BB = 10^{10}$, $H = 50.0$, $E_1 = 10^{-10}$ and $E_2 = 10^{-5}$, where E is the root of the equation

Table 7 DSC data on compound V

Data point	Temperature T/K	Reaction depth H_t / H_o	Exothermic rate dH_t/dt(mJ/s)	$d(H_t/H_o)$ /dT×10^3 (K^{-1})
1	448.7	0.0413	1.234	6.079
2	452.7	0.0708	1.883	9.273
3	456.2	0.1091	2.669	1.315
4	458.2	0.1381	3.287	16.20
5	459.7	0.1639	3.837	18.90
6	461.2	0.1939	4.347	21.41
7	462.7	0.2284	5.046	24.85
8	464.2	0.2679	5.694	28.05
9	465.2	0.2971	6.243	30.74
10	466.2	0.3304	6.648	32.74
11	467.2	0.3643	7.084	34.89
12	468.2	0.4004	7.569	37.28
13	469.2	0.4388	7.987	39.34
14	470.2	0.4790	8.414	41.40
15	471.2	0.5209	8.640	42.55
16	472.2	0.5639	8.778	43.23
17	472.9	0.5965	8.841	43.54
T_o=429.7 K;	H_o=2437 mJ;	φ=0.0833 °C·s^{-1}		

$\partial\Omega/\partial E = 0$, $[AA,BB]$ is the root interval of the equation $\partial\Omega/\partial E = 0$, H is the step size, and E_1 and E_2 are two constants of the control precision. When the value of a certain point on the left side of the equation $\partial\Omega/\partial E = 0$ is less than E_1 or half of the small interval length is less than E_2, this point or the intermediate point of the small interval is the solution of the equation $\partial\Omega/\partial E = 0$.

For example, by substituting the original data for the energetic materials listed in Tables 3–8, and all the forms of $f(\alpha)$ in Table 1, into all the normal equations in Table 2, the corresponding values of E and A and the probable mechanism functions are obtained by the method of logical choices [1]. These values of E and A are in agreement with the calculated values obtained by Kissinger's method and by means of the integral and differential methods [1, 3] (for data, see Table 9). This fact shows that our numerical method is suitable for computing the values of E, A and n for the exothermic decomposition of energetic materials.

Table 8 DSC data on compound VI

Data point	Temperature T/K	Reaction depth H_t / H_o	Exothermic rate dH_t/dt(mJ/s)	$d(H_t/H_o)/dT \times 10^3$ (K^{-1})
1	428.9	0.0218	0.3515	6.852
2	430.9	0.0385	0.5356	10.44
3	432.4	0.0565	0.7030	13.70
4	433.7	0.0766	0.9498	18.52
5	434.7	0.0971	1.167	22.76
6	435.7	0.1227	1.519	29.61
7	436.7	0.1550	1.849	36.05
8	437.4	0.1847	2.251	43.88
9	438.2	0.2199	2.602	50.73
10	438.7	0.2468	2.954	57.59
11	439.2	0.2768	3.209	62.56
12	439.7	0.3096	3.540	69.00
13	440.2	0.3457	3.833	74.71
14	440.7	0.3846	4.017	78.30
15	441.2	0.4261	4.448	86.70
16	441.7	0.4693	4.506	87.85
17	442.1	0.5136	4.565	88.99
T_o=419.4 K;	H_o=616 mJ;	φ=0.0833 °C·s^{-1}		

Table 9 Calculated values of kinetic parameters of exothermic decompositions of compounds I–VI

	Kissinger method				Integral method		Differential method		This work		
φ	T_m	E_k	$\log A_k$	r_k	E	$\log A$	E	$\log A$	E	$\log A$	n^*
Compound I											
2.00	192	148.8	14.2	0.998	142.2	12.4	152.0	13.5	146.5	13.2	0.38
5.00	202										
10.43	231										
20.00	240										
Compound II											
2.14	191	168.4	16.8	0.995	160.2	14.5	171.9	15.8	172.3	16.1	0.51
5.42	201										
11.43	227										
23.00	237										

Table 9 Continued

	Kissinger method				Integral method		Differential method		This work		
φ	T_m	E_k	$\log A_k$	r_k	E	$\log A$	E	$\log A$	E	$\log A$	n^*
Compound III											
2.09	202	185.0	17.9	0.996	182.0	17.1	173.0	16.1	172.5	16.0	0.99
5.25	209										
10.51	237										
21.10	245.5										
Compound IV											
2.09	195	113.7	10.1	0.999	110.1	8.8	116.0	9.4	118.2	10.0	0.55
5.24	204										
10.77	235										
22.14	249										
Compound V											
2.31	187	154.9	15.1	0.999	154.3	13.7	152.5	13.5	154.2	14.2	0.70
5.83	194.5										
11.00	204										
22.50	237										
Compound VI											
2.15	158	282.8	32.1	0.999	291.0	31.4	294.5	31.8	287.2	31.3	0.40
5.08	162										
10.87	166										
23.88	172										

Notation:

*: The values of n in the most probable mechanism function formula $f(\alpha) = 1-\alpha)^n$; φ, heating rate (°C·min^{-1}); T_m, maximum peak temperature (°C); E, apparent activation energy (KJ·mol^{-1}); A, pre-exponential constant (s^{-1}); r, linear correlation coefficient; n, reaction order. Subscript k, data obtained by Kissinger's method [4].

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Zusammenfassung — Es wird eine numerische Methode zur Berechnung der kinetischen Parameter (der Aktivierungsenergie (E), des präexponentiellen Faktors (A) und der Reaktionsordnung (n)) der exothermen Zersetzung energiereicher Substanzen über die exotherme Geschwindigkeitsgleichung vorgestellt. Die Werte von E, A und n werden für die exotherme Zersetzung von sechs typischen energiereichen Substanzen angegeben: 1,6-Diazido-2,5-dinitrazahexan (I), 1,5-Diazido-3-nitrazapentan (II), 2,2,4,7,9,9-Hexanitro-5-methyl-4,7-dinitrazadekan (III), 2,2,2-Trinitroethyl-4,4,4-trinitrobutyrat (IV), 1,4-Dinitro-2,3-dioxo-1,4-dinitrazacyclohexan (V) und 1,3,5-Trinitro-1,3,5-triazafurazano[3,4-f]cycloheptan (VI).