N-脒基脲二硝酰胺放热分解反应的动力学行为

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摘要： 用 DSC 和微热量仪研究了 *N*-脒基脲二硝酰胺(GUDN)的放热分解反应动力学行为和比热容, 计算得到程序升温下 GUDN 主放热分解反应的动力学参数(活化能 E_a 和指前因子 *A*)、自加速分解温度(T_{SADT})、绝热条件下达到最大分解反应速率的时间(t_{TMRad})和至爆时间(t_{Tlad}). 结果表明, 在非等温 DSC 条件下, GUDN 的热分解过程可用经验级数自催化动力学方程 $d\alpha/dt=10^{18.49}\exp(-195500/RT)(1-\alpha)^{0.81}+10^{18.00}\exp(-177000/RT)\alpha^{1.29}(1-\alpha)^{0.71}$ 描述. 热分解转热爆炸的临界温升速率为 0.1236 K·h⁻¹. 所得的 T_{SADT}、t_{TMRad} 和 t_{Tlad} 值分别为 473.95 K、2.24 s 和 3.51 s.

关键词： *N*-脒基脲二硝酰胺; 自催化分解; 动力学参数; 临界温升速率; 热爆炸; 非等温 DSC

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Kinetic Behaviour of the Exothermic Decomposition Reaction of *N*-Guanylurea Dinitramide

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Abstract： The kinetic behaviour of the exothermic decomposition reaction and the specific heat capacity of *N*-guanylurea dinitramide (GUDN) were determined by DSC and mircocalorimeter. Its kinetic parameters of the major exothermic decomposition reaction in a temperature-programmed mode [the apparent activation energy (E_a) and pre-exponential factor (*A*)], self-accelerating decomposition temperature (T_{SADT}), time to maximum rate (t_{TMrad}), and time-to-ignition (t_{Tlad}) under adiabatic conditions were calculated. The results showed that under non-isothermal DSC conditions, the thermal decomposition of GUDN could be described by the empiric-order autocatalytic equation: $d\alpha/dt=10^{18.49}\times\exp(-195500/RT)(1-\alpha)^{0.81}+10^{18.00}\exp(-177000/RT)\alpha^{1.29}(1-\alpha)^{0.71}$, and the value of the critical rate of temperature rise in GUDN was 0.1236 K·h⁻¹ when the decomposition reaction converted into thermal explosion. The values of T_{SADT}, t_{TMRad}, and t_{Tlad} were 473.95 K, 2.24 s, and 3.51 s, respectively.

Key Words： GUDN; Autocatalytic decomposition; Kinetic parameters; Critical rate of temperature rise; Thermal explosion; Non-isothermal DSC

N-Guanylurea dinitramide (GUDN) is a new energetic oxidizer with higher energy and lower sensitivities. Its crystal density is 1.755 g·cm⁻³, detonation velocity is about 8210 m·s⁻¹, specific impulse and pressure exponent are 213.1 s and 0.73[1], respectively. Therefore, it has the potential for possible use as an energy ingredient of propellants and explosives from the point of view of the above-mentioned high performances. A number of papers have reported on its preparation[2,3] and properties[4−13], however, its kinetic parameters and critical rate of temperature rise of thermal explosion for the autocatalytic decomposing reaction have not been described unequivocally. The aim of the present work is to obtain more detailed information on the auto-

catalytic decomposition of GUDN to fit kinetic models of the reaction and to estimate kinetic parameters, self-accelerating decomposition temperature (T_{SADT}), time to maximum rate (t_{TMRad}) and time-to-ignition (or explosion)(t_{Tiad}) under adiabatic conditions and the critical rate of temperature rise of thermal explosion. This is quite useful in the evaluation of its thermal stability under non-isothermal condition and in the study of its thermal changes at high temperature.

1 Theoretical and method

1.1 Basic theory of decomposition reaction

The enthalpy (q_1) of thermal decomposition reaction per unit time for energetic materials (EMs) can be expressed by the equation:

$$q_1 = \frac{QVd}{M}\frac{d\alpha}{dt} \tag{1}$$

where Q is the enthalpy of the thermal decomposition reaction in J·mol^{-1}, V the volume of EMs loaded in cm^3, d the loading density in g·cm^{-3}, M the mole mass of EMs in g·mol^{-1} and $d\alpha/dt$ the reaction rate in s^{-1}.

The thermal decomposition, as an autocatalytic reaction, can be described by the following equations:

$$A \xrightarrow{k_1} B \tag{2}$$

$$A+B \xrightarrow{k_2} 2B \tag{3}$$

where A represents the initial reactant and B the thermal decomposition product. The rate expression that corresponds to this scheme is

$$\frac{d\alpha}{dt} = k_1(1-\alpha)^m + k_2\alpha^n(1-\alpha)^p \tag{4}$$

where α stands for the conversion degree, for DSC curve, $\alpha = H/H_o$, H_o is the total exothermicity of the EMs (corresponding to the global area under the DSC curve) and H is the reaction heat in a certain time (corresponding to the partial area under the DSC curve); $k_1 = A_1\exp(-E_{a1}/RT)$, $k_2 = A_2\exp(-E_{a2}/RT)$, where A_1 and A_2 are the pre-exponential factors, E_{a1} and E_{a2} the activation energies for the autocatalytic reaction, R is the gas constant, T the temperature, t the time; m, n and p are the apparent reaction orders.

Substituting Eq.(4) into Eq.(1) gives

$$q_1 = \frac{QVd}{M}\left[A_1\exp\left(-\frac{E_{a1}}{RT}\right)(1-\alpha)^m + A_2\exp\left(-\frac{E_{a2}}{RT}\right)\alpha^n(1-\alpha)^p\right] \tag{5}$$

At the same time, the amount of heat (q_2) transferred by the wall of the reactor to surrounding medium in unit time is

$$q_2 = k'(T-T_c)S \tag{6}$$

where k' is an overall heat transfer coefficient in J·cm^{-2}·K^{-1}·s^{-1}; T_c the temperature of the reaction wall and surroundings according to the linear relationship $T_c = T_o + \beta t$, where β is the heating rate K·min^{-1}, T_o the initial temperature at which the DSC curve deviates from the baseline in K; S the external surface of the loaded sample in cm^2.

1.2 Transition from decomposition to thermal explosion

With the boundary conditions of thermal explosion, Eq.(5) becomes

$$q_1|_{T_b} = \frac{QVd}{M}[k_{1b}(1-\alpha_b)^m + k_{2b}\alpha_b^n(1-\alpha_b)^p] \tag{7}$$

where α_b is the value of α corresponding to T_b, $k_{1b} = A_1\exp(-E_{a1}/RT_b)$, $k_{2b} = A_2\exp(-E_{a2}/RT_b)$, where T_b is the critical temperature of thermal explosion of EMs in K and Eq.(6) becomes

$$q_2|_{T_b} = k'(T_b - T_{e0})S \tag{8}$$

where T_{e0} is the onset temperature in the DSC curve under linear temperature increase condition when β tends to zero.

According to the q_1–T and q_2–T relations, the sufficient and essential conditions from thermal decomposition to thermal explosion can be expressed as

$$\left| q_1|_{T_b} = q_2|_{T_b} \right. \tag{9}$$

$$\left| \frac{dq_1}{dT}\right|_{T_b} = \frac{dq_2}{dT}\bigg|_{T_b} \tag{10}$$

Differentiation of Eq.(5) with respect to t gives

$$\frac{dq_1}{dT}\bigg|_{T=T_b, \alpha=\alpha_b} = QVd\left[\frac{(dT/dt)_{T_b}}{RT_b^2}(k_{1b}E_{a1}(1-\alpha_b)^m + k_{2b}E_{a2}\alpha_b^n(1-\alpha_b)^p) + \right.$$
$$(k_{1b}(1-\alpha_b)^m + k_{2b}\alpha_b^n(1-\alpha_b)^p)(k_{2b}n(1-\alpha_b)^p\alpha_b^{n-1} - k_{2b}p(1-\alpha_b)^{p-1}\alpha_b^n - $$
$$\left. k_{1b}m(1-\alpha_b)^{m-1})\right]\Big/ M(dT/dt)_{T_b} \tag{11}$$

where $(dT/dt)_{T_b}$ is the increasing rate of temperature in EMs when thermal decomposition converts into thermal explosion. This is difficult to solve directly from conventional experiments.

Differentiation of Eq.(6) with respect to t gives

$$\frac{dq_2}{dT}\bigg|_{T=T_b} = \frac{k'S}{(dT/dt)_{T_b}}\left[\left(\frac{dT}{dt}\right)_{T_b} - \beta\right] \tag{12}$$

Combining Eqs.(7)–(9), yields

$$\frac{QVd}{M}[k_{1b}(1-\alpha_b)^m + k_{2b}\alpha_b^n(1-\alpha_b)^p] = k'S(T_b - T_{e0}) \tag{13}$$

Combining Eqs.(10)–(12), yields

$$QVd\left[\frac{(dT/dt)_{T_b}}{RT_b^2}(k_{1b}E_{a1}(1-\alpha_b)^m + k_{2b}E_{a2}\alpha_b^n(1-\alpha_b)^p) + \right.$$
$$(k_{1b}(1-\alpha_b)^m + k_{2b}\alpha_b^n(1-\alpha_b)^p)(k_{2b}n(1-\alpha_b)^p\alpha_b^{n-1} - k_{2b}p(1-\alpha_b)^{p-1}\alpha_b^n - $$
$$\left. k_{1b}m(1-\alpha_b)^{m-1})\right]\Big/ M(dT/dt)_{T_b} = \frac{k'S}{(dT/dt)_{T_b}}\left[\left(\frac{dT}{dt}\right)_{T_b} - \beta\right] \tag{14}$$

As the thermal explosion starts, $(dT/dt)_{T_b} \gg \beta$, and Eq.(14) may be simplified to the following form:

$$QVd\left[\frac{(dT/dt)_{T_b}}{RT_b^2}(k_{1b}E_{a1}(1-\alpha_b)^m + k_{2b}E_{a2}\alpha_b^n(1-\alpha_b)^p) + \right.$$
$$(k_{1b}(1-\alpha_b)^m + k_{2b}\alpha_b^n(1-\alpha_b)^p)(k_{2b}n(1-\alpha_b)^p\alpha_b^{n-1} - k_{2b}p(1-\alpha_b)^{p-1}\alpha_b^n - $$
$$\left. k_{1b}m(1-\alpha_b)^{m-1})\right]\Big/ M(dT/dt)_{T_b} = k'S \tag{15}$$

Combining Eqs.(13) and (15), we get

$$\left(\frac{dT}{dt}\right)_{T_b} = \{(T_b - T_{e0})(k_{1b}(1-\alpha_b)^m + k_{2b}\alpha_b^n(1-\alpha_b)^p)(k_{2b}n(1-\alpha_b)^p\alpha_b^{n-1} - $$
$$k_{2b}p(1-\alpha_b)^{p-1}\alpha_b^n - k_{1b}m(1-\alpha_b)^{m-1})\}/\{(k_{1b}(1-\alpha_b)^m + k_{2b}\alpha_b^n(1-\alpha_b)^p - $$
$$(T_b - T_{e0})(k_{1b}\frac{E_{a1}}{RT_b^2}(1-\alpha_b)^m + k_{2b}\frac{E_{a2}}{RT_b^2}\alpha_b^n(1-\alpha_b)^p\} \tag{16}$$

Equation (16) is the relation formula for estimating the critical rate of temperature rise in EMs when the apparent empiric-order autocatalytic decomposition converts into thermal explosion.

Once the values of E_{a1}, E_{a2}, A_1, A_2, T_{e0}, T_b, α_b, m, n, and p have been calculated from an analysis of the DSC curves under the

same experimental conditions, the corresponding value of $(dT/dt)_{T_b}$ can then be obtained from Eq.(16).

1.3　Method of computing kinetic parameters

In order to obtain the values of A_1, A_2, E_{a1}, E_{a2}, α_b, m, n, and p needed for solving Eq.(16) obtained from Eq.(4), combing Eq.(4) and $\alpha = H/H_0$, we obtain

$$\frac{dH}{dt}=H_0A_1e^{-E_{a1}/RT}(1-\alpha)^m+H_0A_2e^{-E_{a2}/RT}\alpha^n(1-\alpha)^p \qquad (17)$$

Where $\left(\dfrac{dT}{dt}, T, \alpha\right)$ is a three-dimension data vector, $(A_1, A_2, E_{a1}, E_{a2}, m, n, p)$ is a seven-dimension vector about parameters which would be estimated.

Setting

$$\zeta=(T, \alpha) \qquad (18)$$

and

$$\theta=(A_1, A_2, E_{a1}, E_{a2}, m, n, p)=(\theta_1, \theta_2, \theta_3, \theta_4, \theta_5, \theta_6, \theta_7) \qquad (19)$$

the Eq.(17) may be denoted as

$$\frac{dH}{dt}=f(T, \alpha, A_1, A_2, E_{a1}, E_{a2}, m, n, p)=f(\zeta, \theta) \qquad (20)$$

Substituting the original data

$$\left[\left(\frac{dT}{dt}\right)_i, T_i, \alpha_i\right] \qquad i=1, 2, \cdots, L$$

into Eq.(20) gives

$$\frac{dH}{dt}=f(T_i, \alpha_i, A_1, A_2, E_{a1}, E_{a2}, m, n, p)=f(T_i, \alpha_i, \theta) \quad i=1, 2, \cdots, L \quad (21)$$

In order to analyze the non-linear function $f(T_i, \alpha, \theta)$ about $\theta=(A_1, A_2, E_{a1}, E_{a2}, m, n, p)$, the Taylor expansion of Eq.(21) at the initial point $\theta^{(0)}=(A_1^{(0)}, A_2^{(0)}, E_{a1}^{(0)}, E_{a2}^{(0)}, m^{(0)}, n^{(0)}, p^{(0)})$ and reserving the first item and the second item is used

$$\frac{dH}{dt}=f(\zeta, \theta^{(0)})+\frac{\partial f(\zeta, \theta)}{\partial A_1}\bigg|_{\theta=\theta^{(0)}}(A_1-A_1^{(0)})+\frac{\partial f(\zeta, \theta)}{\partial A_2}\bigg|_{\theta=\theta^{(0)}}(A_2-A_2^{(0)})+$$
$$\frac{\partial f(\zeta, \theta)}{\partial E_{a1}}\bigg|_{\theta=\theta^{(0)}}(E_{a1}-E_{a1}^{(0)})+\frac{\partial f(\zeta, \theta)}{\partial E_{a2}}\bigg|_{\theta=\theta^{(0)}}(E_{a2}-E_{a2}^{(0)})+$$
$$\frac{\partial f(\zeta, \theta)}{\partial m}\bigg|_{\theta=\theta^{(0)}}(m-m^{(0)})+\frac{\partial f(\zeta, \theta)}{\partial n}\bigg|_{\theta=\theta^{(0)}}(n-n^{(0)})+$$
$$\frac{\partial f(\zeta, \theta)}{\partial p}\bigg|_{\theta=\theta^{(0)}}(p-p^{(0)}) \qquad (22)$$

where $\frac{dH}{dt}$ is a linear function as $(A_1-A_1^{(0)})$, $(A_2-A_2^{(0)})$, $(E_{a1}-E_{a1}^{(0)})$, $(E_{a2}-E_{a2}^{(0)})$, $(m-m^{(0)})$, $(n-n^{(0)})$ and $(p-p^{(0)})$.

Setting

$$\theta^{(l+1)}=\theta^{(0)}+\gamma^{(l)} \qquad (l=0, 1, 2, \cdots)$$

and substituting the origins data $\left[\left(\dfrac{dH}{dt}\right)_i, T_i, \alpha_i\right]$ into Eq.(22) give

$$\left(\frac{dH}{dt}\right)=f(T_i, \alpha_i, \theta^{(l)})+\sum_{j=1}^{7}\frac{\partial f(T_i, \alpha_i, \theta)}{\partial\theta_j}\bigg|_{\theta=\theta^{(l)}}(\theta_j^{(l+1)}-\theta_j^{(l)}) \qquad (23)$$

Then the mean-square procedure is applied by taking minimal values of evaluation function

$$SS(\theta)=\sum_{i=1}^{L}\left[\left(\frac{dH}{dt}\right)_i-f(T_i, \alpha_i, \theta^{(l)})-\sum_{j=1}^{7}\frac{\partial f(T_i, \alpha_i, \theta)}{\partial\theta_j}\bigg|_{\theta=\theta^{(l)}}(\theta_j-\theta_j^{(l)})\right]^2$$
$$\overset{\text{note}}{=}\sum_{i=1}^{L}\left[\left(\frac{dH}{dt}\right)_i-f(T_i, \alpha_i, \theta^{(l)})-\sum_{j=1}^{7}X_{ij}^{(l)}\gamma_j^{(l)}\right]^2 \qquad (24)$$

Letting

$$Y^{(l)}=\begin{bmatrix}\left(\dfrac{dH}{dt}\right)_1-f(T_1, \alpha_1, \theta^{(l)}) \\ \left(\dfrac{dH}{dt}\right)_2-f(T_2, \alpha_2, \theta^{(l)}) \\ \cdots \\ \left(\dfrac{dH}{dt}\right)_L-f(T_L, \alpha_L, \theta^{(l)})\end{bmatrix} \qquad X^{(l)}=\begin{bmatrix}X_{11}^{(l)}\cdots X_{17}^{(l)} \\ X_{21}^{(l)}\cdots X_{27}^{(l)} \\ \cdots \\ X_{L1}^{(l)}\cdots X_{L7}^{(l)}\end{bmatrix}$$

$$\gamma^{(l)}=\begin{bmatrix}\gamma_1^{(l)} \\ \gamma_2^{(l)} \\ \vdots \\ \gamma_7^{(l)}\end{bmatrix}=\begin{bmatrix}\theta_1-\theta_1^{(l)} \\ \theta_2-\theta_2^{(l)} \\ \vdots \\ \theta_7-\theta_7^{(l)}\end{bmatrix}$$

where $\gamma_j^{(l)}=\theta_j-\theta_j^{(l)}$, $X_{ij}^{(l)}=\dfrac{\partial f(T_i, \alpha_i, \theta)}{\partial\theta_j}\bigg|_{\theta=\theta^{(l)}}$

Under the condition of the existence of $(X^{(l)'}X^{(l)})$, we have

$$(X^{(l)'}X^{(l)})\gamma^{(l)}=X^{(l)}Y^{(l)} \qquad l=0, 1, 2, \cdots \qquad (25)$$

Letting $A_1^{(0)}$, $A_2^{(0)}$, $E_{a1}^{(0)}$, $E_{a2}^{(0)}$, $m^{(0)}$, $n^{(0)}$, and $p^{(0)}$ as an initial values and using these values, the value of $\theta^{(1)}=\theta^{(0)}+\gamma^{(0)}$ may be calculated. This modified value of $\theta^{(1)}$ is used as an initial value for the next calculation which yields another modified value of $\theta^{(2)}=\theta^{(1)}+\gamma^{(1)}$. Thus after satisfying the condition of Eq.(26) seven consistent estimation values in Eq.(27) will be obtained.

$$|\theta_j^{(l+1)}-\theta_j^{(l)}|<\delta \qquad (j=1, 2, \cdots 7) \qquad (26)$$

where $\delta=0.003$[14].

$$\hat{\theta}=\theta^{(l+1)}=(A_1^{(l+1)}, A_2^{(l+1)}, E_{a1}^{(l+1)}, E_{a2}^{(l+1)}, m^{(l+1)}, n^{(l+1)}, p^{(l+1)}) \qquad (27)$$

1.4　Estimation of adiabatic time-to-explosion

If $E_{a1}\approx E_{a2}$, $A_1\approx A_2$ and $m\approx p\approx 1$ in Eq.(4), and the catalyst concentration achieves a stationary state:

$$\alpha_{cat}\approx\text{const.} \qquad (28)$$

Eq.(4) becomes

$$\frac{d\alpha}{dt}=(k_1+k_2\alpha)(1-\alpha)\equiv k(1-\alpha) \qquad (29)$$

Under the adiabatic condition, the differential equation[15,16] describing the time-temperature relation of this one-order exothermal decomposition with an Arrhenius temperature dependence is

$$C_p\frac{dT}{dt}=Q(1-\alpha)A\exp(-E/RT) \qquad (30)$$

where C_p, Q, A and E are the specific heat capacity, heat of reaction, pre-exponential constant and activation energy, respectively, R is the gas constant, T is the absolute temperature, t is the time, α is the fraction of substance decomposed and can be expressed as a function of temperature

$$\alpha=\int_{T_0}^{T}\frac{C_p}{Q}dT=\int_{T_0}^{T}\frac{a+bT}{Q}dT \qquad (31)$$

where $C_p=a+bT$, on rearranging and integrating Eq.(30), we obtain

$$t=\frac{1}{QA}\int_{T_0}^{T}\frac{a+bT}{1-\alpha}e^{E/RT}dT$$
$$=\frac{1}{QA}\int_{T_0}^{T}\frac{(a+bT)e^{E/RT}}{\left[1-\int_{T_0}^{T}\frac{(a+bT)}{Q}dT\right]}dT$$
$$=\frac{1}{QA}\int_{T_0}^{T}\frac{(a+bT)e^{E/RT}}{\left[1-\frac{1}{Q}\int_{T_{(0\,or\,b)}}^{T_{p0}}(a+bT)dT\right]}dT$$

$$= \frac{1}{QA} \int_{T_0}^{T} \frac{(a+bT)e^{E/RT}}{\left\{ 1 - \frac{1}{Q} \left[a(T_{p0} - T_{00\,or\,e0}) + \frac{b}{2}(T_{p0}^2 - T_{00\,or\,e0}^2) \right] \right\}} dT \quad (32)$$

Once the values of a, b, Q, A, E, T_{e0}, and T_{p0}, have been calculated from an analysis of the DSC curves, the correspondent value of t can then be obtained from Eq.(32).

2 Experimental

2.1 Materials

GUDN was prepared according to the method reported in the literature[1]. It is a pale yellow crystal. m.p.= 214 ℃ (decomposition). For GUDN($C_2H_7O_5N_7$) M_r=209.15, w_i (calculated): 11.48%C, 3.34% H, 46.89% N; w_i(found): 11.14% C, 3.34% H, 46.99%N. IR spectrum(KBr) ν/cm^{-1}: 1743 (—C(NH)—), 1688(—C(O)—), 1523, 1444 (—NO$_2$—). UV-Vis spectrum(H$_2$O), λ_{max}: 282.5, 212.0 nm. The analytical results show that it has the composition of $C_2H_7O_5N_7$.

2.2 Instruments and conditions

In the present experiments, the initial data needed for calculating all the kinetic parameters were obtained using a differential scanning calorimeter (TA, USA) with an aluminum cell. The conditions of the DSC analyses were: sample mass, about 1 mg; heating rates, 2.5, 5, 10 and 15 K·min^{-1}; atmosphere, N$_2$ gas; reference sample, α-Al$_2$O$_3$. DSC curves obtained under the same conditions overlap with each other, indicating that the reproducibility of tests is satisfactory.

Specific heat capacity of GUDN was determined by a mircocalorimeter Micro-DSC III (SETARAM, France). The mircocalorimeter was calibrated by Joule effect before each experiment. The solution enthalpy of KCl in deionized water was determined at 298.15 K with the value of (17.266±0.074) kJ·mol^{-1}, close to the literature value of (17.241±0.018) kJ·mol^{-1} [17], indicating that the calorimetric system was reliable. The specific heat capacity of standard sample α-Al$_2$O$_3$, m=320.60 mg, was determined at 298.15 K with the value of 79.44 kJ·mol^{-1}, close to the literature of 79.02 kJ·mol^{-1} [18], indicating that the calorimetric system was accurate.

The conditions of the mircocalorimeter analyses were: atmosphere, N$_2$ gas; sample mass, 608.46 mg; the range of temperature, 283–353 K, heating rates, 0.15 K·min^{-1}.

3 Results and discussion

3.1 Decomposition kinetics of GUDN

The typical DSC curve of GUDN is shown in Fig.1. The DSC curve shows that only one exothermic peak before 250 ℃. A major exothermic peak at 219.17 ℃ is due to the decomposition of GUDN in molten state.

The original data $(T_i, \alpha_i, i =1, 2, \cdots, 13)$ taken from the DSC curve at a heating rate of 10 K·min^{-1} are shown in Table 1. The measured values of β_i and T_{ei} (i=1, 2, $\cdots$, 4), the calculated value of E_{oe} and E_{op} by the Ozawa's method[19], the values of E_{Kp} and A_K by the Kissinger's method[20], the value (T_{e0}) of T_e, which is self-accelerating decomposition temperature (T_{SADT}), corresponding to
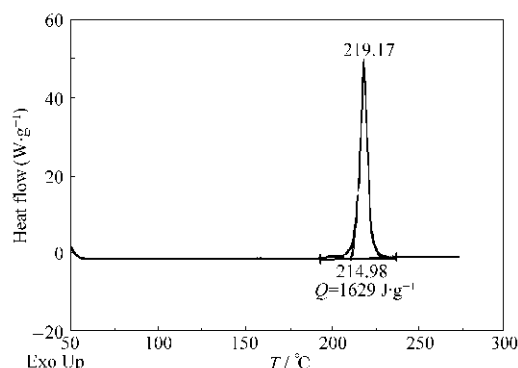

Fig.1 DSC curve for GUDN at a heating rate of 10 K·min^{-1}

Table1 Basic data of the major exothermic decomposition of GUDN determined by DSC^a

Datrum point	T_i/K	α_i	$(dH_i/dt)_i$/(mJ·s^{-1})	$10^3(d\alpha/dT)_i$/(K^{-1})
1	467.15	0.00001	0.0724	0.4457
2	469.15	0.0001	0.0867	0.5341
3	471.15	0.0004	0.1088	0.6704
4	473.15	0.0010	0.1417	0.8730
5	475.15	0.0021	0.1902	1.171
6	477.15	0.0037	0.2619	1.613
7	479.15	0.0066	0.3881	2.390
8	481.15	0.0117	0.6584	4.055
9	483.15	0.0216	1.250	7.698
10	485.15	0.0420	2.571	15.84
11	487.15	0.0837	5.280	32.52
12	489.15	0.1619	10.88	67.02
13	491.15	0.2916	24.60	151.2

$^a T_e$=180 ℃; H_0=974.14 mJ; β=0.1666 K·s^{-1}

$\beta \to 0$ obtained by Eq.(33) taken from literature[21], the value (T_{p0}) of corresponding to $\beta \to 0$, the value of T_b obtained by Eq.(34) taken from literature[21], and the value of α_b corresponding to T_b are shown in Table 2.

$$T_{ei} = T_{e0} + b\beta_i + c\beta_i^2, \quad i=1, 2, \cdots 4 \quad (33)$$

$$T_b = \frac{E_{oe} - \sqrt{E_{oe}^2 - 4E_{oe}RT_{e0}}}{2R} \quad (34)$$

The calculated values of E_{a1}, E_{a2}, A_1, A_2, m, n, and p by the above-mentioned method are given in Table 3. By substituting the values of T_{e0}, T_b, and α_b in Table 2, and E_{a1}, E_{a2}, A_1, A_2, m, n, and p in Table 3 into Eq.(16), the value of $(dT/dt)_{T_b}$ listed in Table 3 is obtained.

The results in Tables 2 and 3 show that: (1) under our non-isothermal DSC conditions, the thermal decomposition of GUDN can be described by the empiric-order autocatalytic equation:

$$\frac{d\alpha}{dt} = 10^{18.49} \exp\left(-\frac{195500}{RT}\right)(1-\alpha)^{0.81} +$$
$$10^{18.00} \exp\left(-\frac{177000}{RT}\right)\alpha^{1.29}(1-\alpha)^{0.71} \quad (35)$$

(2) The value of the critical rate of temperature rise in GUDN is 0.1236 K·h^{-1} when the decomposition reaction converts into thermal explosion; (3) Because $(dT/dt)_{T_b} \gg \beta$, we conclude that in

Table 2   The calculated values of the critical temperature (T_b) of thermal explosion for GUDN[a]

Measured values			Calculated values							
β/(K·min^{-1})	T_e/K	T_p/K	E_{oe}/(kJ·mol^{-1})	E_{op}/(kJ·mol^{-1})	E_{Kp}/(kJ·mol^{-1})	A_K/s^{-1}	T_{SADT}/K	T_{p0}/K	T_b/K	α_b
2.5	478.01	482.21	231.10	233.82	237.76	$10^{23.43}$	473.95	478.25	482.32	0.02
5	486.86	491.01								
10	488.13	492.32								
15	492.41	496.76								

[a]β, heating rate; T_e, onset temperature in the DSC curve; T_p, maximum peak temperature; E_{oe}, E_{op}, apparent activation energy obtained by Ozawa's method; E_{Kp}, apparent activation energy obtained by Kissinger's method; A_K, pre-exponential constant obtained by Kissinger's method; $T_{SADT} \overset{\text{def}}{=\!=} T_{e0}$, the value of T_e corresponding to $\beta \rightarrow 0$; T_{p0}, the value of T_p corresponding to $\beta \rightarrow 0$; α_b, the value of α corresponding to T_b

Table 3   Results for analyzing the data in Tables 1 and 2 by Eqs.(4) and (16)

E_{a1} (kJ·mol^{-1})	E_{a2} (kJ·mol^{-1})	A_1 s^{-1}	A_2 s^{-1}	m	n	p	RSS[a]	$(dT/dt)_{T_b}$ (K·h^{-1})
195.50	177.00	$10^{18.49}$	$10^{18.00}$	0.81	1.29	0.71	0.7609	0.1236

[a] the residual sum of squares

the derivation process of Eq.(16), the assumption of adopting $\dfrac{(dT/dt)_{T_b} - \beta}{(dT/dt)_{T_b}} = 1$ is rational.
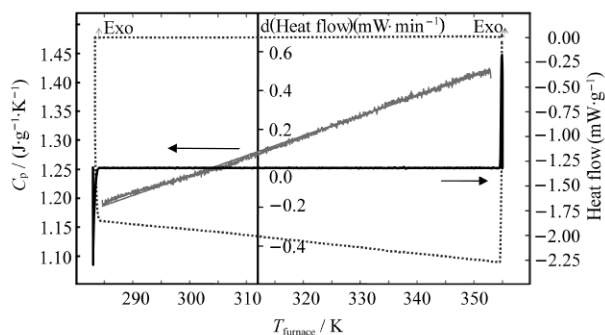
3.2   The value of C_p for GUDN

The determination and linear-fit result of the specific heat capacity (C_p) of GUDN are shown in Fig.2. The result shows, the equation of specific heat capacity of GUDN with temperature is $C_p = 0.2068579 + 0.003439981T$ in the temperature range of 283.3 − 354.9 K.

3.3   Time-to-maximum rate and time-to-explosion under adiabatic condition

The adiabatic time-to-explosion (t_{TIad}) and adiabatic time-to-maximum rate (t_{TMRad}) are the time of energetic material thermal decomposition achieving to explosion and maximum rate under the adiabatic conditions and are two important parameters of assessing the stability and the security of energetic materials.

By substituting the values of $C_p = 0.2068579 + 0.003439981T$, differential mechanism function $f(\alpha) = (1-\alpha)$, $E = E_K = 237706$ J·mol^{-1}, $A = A_K = 10^{23.43}$ s^{-1}, decomposition heat $Q = 1629$ J·g^{-1}, $R = 8.314$ J·mol^{-1}·K^{-1}, α, conversion degree, $\alpha = \int_{T_0}^{T} \dfrac{C_p}{Q} dT$, integral upper limit, $T = T_{p0} = 478.25$ K for t_{TMRad}, $T = T_b = 482.32$ K for t_{TIad} and integral lower limit, $T_0 = T_{e0} = 473.85$ K into Eq.(32), the values

of t_{TMRad} of 2.24 s and t_{TIad} of 3.51 s of GUDN are obtained.

4   Conclusions

(1) Under our non-isothermal DSC conditions, the thermal decomposition of GUDN can be described by the empiric-order autocatalytic equation:

$$\frac{d\alpha}{dt} = 10^{18.49} \exp{-195500/RT}(1-\alpha)^{0.81} +$$
$$10^{18.00} \exp{-177000/RT} \alpha^{1.29}(1-\alpha)^{0.71}$$

(2) The value of the critical rate of temperature rise in GUDN is 0.1236 K·h^{-1} when the decomposition reaction converts into thermal explosion.

(3) The equation of specific heat capacity of GUDN with temperature is $C_p = 0.2068579 + 0.003439981T$ in the temperature range of 283.3 − 354.9 K. The values of T_{SADT}, t_{TMRad}, and t_{TIad} are 473.95 K, 2.24 s, and 3.51 s, respectively.

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Fig.2   Determination curve of the continuous specific heat capacity of GUDN

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