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Thermal behavior and safety of 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowutrzitane

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Abstract The thermal decomposition behaviors of 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowutrzitane (TEX) were studied by using a C-500 type Calvet microcalorimeter at five heating rates. The kinetic and thermodynamic parameters of exothermic decomposition reaction were obtained. The specific heat capacity of TEX was determined with a Micro-DSC III calorimeter, the specific heat capacity equation and the molar specific heat capacity were also obtained. The self-accelerating decomposition temperature, adiabatic decomposition temperature rise, and critical temperature of thermal explosion are 512.69, 7115.59, and 527.42 K, respectively. The adiabatic time-to-explosion is calculated to be a certain value between 53.69 and 54.05 s.

Keywords 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowutrzitane · Thermal behavior · Specific heat capacity · Thermal hazard

Introduction

To meet on the demands of the various weapon and equipment development, new materials have focused not only on high energy but also on low sensitivity to external stimuli [1–4]. 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowutrzitane(TEX) is a new highly energetic and insensitive explosive with a cage structure. TEX has a high density ($\rho = 1.99$ g cm^{-3}), high thermal stability (decomposition sets on above 240 °C), and low sensitivity to external stimuli (impact sensitivity $H_{50} = 23$ J, friction sensitivity >360 N, sensitivity to electric spark 6.7 J). In addition, it exhibits desirable explosion parameters such as a high detonation rate (8170 ms^{-1}) and a high detonation pressure ($p_{\mathrm{cj}} = 31.4$ GPa) [5–8]. Many papers have been concerned with the synthesis and properties, and applications in explosives [9–13], but the studies of thermal behavior and safety have not been reported by using microcalorimetry method.

In the present paper, the thermal decomposition behaviors of TEX were investigated by a C-500 type Calvet microcalorimeter at five heating rates. The self-accelerating decomposition temperature, the adiabatic decomposition temperature rise, the critical temperature of thermal explosion, and the adiabatic time-to-explosion are also obtained at the same time. The results can provide helpful information for its applications in explosive and propellant in the future.

Experimental

Sample

The sample(TEX) used in the investigation was prepared by Beijing Institute of Technology and Xi'an Modern Chemistry Research Institute and kept under vacuum before use. Its purity was higher than 99.5 %.

Equipment and conditions

The specific heat capacity of TEX was determined with a Micro-DSC III calorimeter (SETARAM, France). The

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thermal decomposition processes were measured by using a C-500 type Calvet microcalorimeter (SETARAM, France), which has a high sensitivity and was equipped with two 10 mL-vessels. The precision of enthalpy measurement was better than 0.5 % after calibration with the standard materials of In and Sn.

Results and discussion

Thermal decomposition behavior

The heat flow curves of TEX at different heating rates are shown in Fig. 1, which shows only one exothermic peak. The characteristic temperatures obtained by heat flow curves at different heating rates are listed in Table 1.

In order to obtain the apparent activation energy (E) and the pre-exponential constant (A) of the thermal decomposition for TEX, The multiple heating methods (Kissinger method and Ozawa method) [14–16] were employed. Kissinger equation and Ozawa equation are as follow [17, 18]

$$\ln\left(\frac{\beta_{\mathrm{i}}}{T_{\mathrm{pi}}^{2}}\right) = \ln\frac{AR}{E} - \frac{E}{R}\frac{1}{T_{\mathrm{pi}}} \tag{1}$$

$$\lg\beta_{\mathrm{i}} = \lg\left(\frac{AE}{RG(\alpha)}\right) - 2.315 - 0.4567\frac{E}{RT_{\mathrm{pi}}} \tag{2}$$

where β_{i} is the linear heating rate(K min^{-1}), T_{pi} represents the peak temperature of the thermal decomposition process (K), R is the gas constant (J mol^{-1} K^{-1}).

From the original data in Table 1, the values of E and A obtained by Kissinger method (with a subscript of k) and Ozawa method (with a subscript of o) are listed in Table 2.

From Table 2, one can see that the apparent activation energy obtained by Kissinger method is in good agreement with that obtained by Ozawa method, and the linear correlation coefficients are all close to one, which means that the results is reliable.

The specific heat capacity of TEX

Figure 2 shows the determination results of specific heat capacity of TEX using continuous specific heat capacity mode of a Micro-DSC III apparatus. The sample mass was 413.71 mg and the heating rate was 0.2 °C min^{-1} from 10 to 80 °C. In determined temperature range, specific heat capacity of TEX presents a good linear relationship with temperature and the

Table 1 Original data of the thermal decomposition reaction of TEX at different heating rates

β/°C min^{-1}	T_{e}/°C	T_{P}/°C	ΔH/J g^{-1}
0.2	246.23	265.70	−6487.51
0.3	250.05	272.23	−6579.50
0.4	252.51	275.62	−6601.08
0.5	254.94	278.57	−6473.03
0.6	258.08	282.81	−6448.30

β is the heating rate, T_{p} is the peak temperature, T_{e} is the onset temperature, and ΔH is the enthalpy of decomposition reaction

Table 2 Kinetic parameters obtained by Kissinger method and Ozawa method

Kissinger method			Ozawa method	
E_{k}/kJmol^{-1}	lg(A_{k})	r_{k}	E_{o}/kJmol^{-1}	r_{o}
156.65	11.54	0.995	157.61	0.996

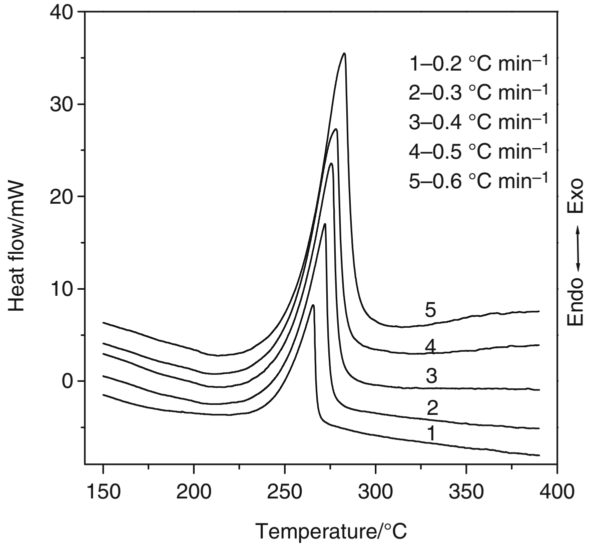

Fig. 1 The heat flow curves of TEX at different heating rates

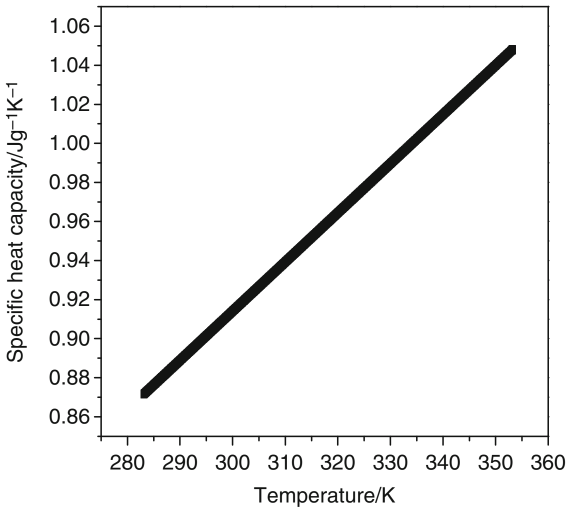

Fig. 2 Specific heat capacity of TEX as a function of temperature

linear correlation coefficient is 0.9993. The equation [19, 20] describing the relationship can be written as

$$C_p(\mathrm{J\ g^{-1}\ K^{-1}}) = 0.196 + 2.414 \times 10^{-3}\, T \quad (283.15\,\mathrm{K} < T < 353.15\,\mathrm{K}) \tag{3}$$

The molar specific heat capacity is 0.916 J g^{-1} K^{-1} at 298.15 K.

Self-accelerating decomposition temperature (T_{SADT})

The value T_{e0} and T_{p0} of T_e and T_p corresponding to$\beta \rightarrow 0$ can be obtained by substituting the T_{ei} and T_{pi} from Table 1 into Eq. 4 and the self-accelerating decomposition temperature (T_{SADT}) [21, 22] can be also obtained by Eq. 5.

$$T_{(\mathrm{e,p})\mathrm{i}} = T_{(\mathrm{e,p})_0} + b\beta_\mathrm{i} + c\beta_\mathrm{i}^2 \quad \mathrm{i} = 1, 2, 3, 4, 5 \tag{4}$$

$$T_{\mathrm{SADT}} = T_{e0} \tag{5}$$

where b and c are coefficients.

The values of T_{e0} (T_{SADT}) and T_{p0} are 512.69 and 526.89 K, respectively.

Thermodynamic parameters of activation reaction

With the help of the data in Table 2, the entropy of activation ($\Delta S^{\neq}$), the enthalpy of activation ($\Delta H^{\neq}$), and the Gibbs free energy of activation ($\Delta G^{\neq}$) [23] are obtained by Eqs. 5–7 taken from as 40.19 $\mathrm{Jmol^{-1}\ K^{-1}}$, 152.27 kJ $\mathrm{mol^{-1}}$, and 131.09 kJ $\mathrm{mol^{-1}}$ corresponding to $T = T_{po} = 526.89$ K, $E = E_k = 156650$ $\mathrm{Jmol^{-1}}$, $A = A_k = 10^{15.14}\ \mathrm{s^{-1}}$. The value of $\Delta G^{\neq}$ is positive, showing that the thermal decomposition reactions of TEX will not take place until the proper temperature is reached.

$$A_k = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \tag{6}$$

$$\Delta H^{\neq} = E_k - \mathrm{RT} \tag{7}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{8}$$

where k_B is the Boltzmann constant and h is the Planck constant.

Adiabatic decomposition temperature rise (ΔT_{ad})

The adiabatic decomposition temperature rise is defined as ΔT_{ad}. It can be obtained by Eq. 9 [19].

$$\Delta T_{\mathrm{ad}} = \frac{-H_d}{C_p} = \frac{Q_d}{C_p} \tag{9}$$

where H_d is the quantity of heat released from the thermal decomposition, and C_p is the specific heat capacity of TEX.

The specific heat capacity of TEX was $C_p = 0.916$ J g^{-1} K^{-1} at 298.15 K, H_d was obtained from the average of ΔH at different heating rates, and the value is −6517.88 J g^{-1}.

$$\Delta T_{\mathrm{ad}} = \frac{-H_d}{C_p} = \frac{Q_d}{C_p} = 7115.59\,\mathrm{K}$$

Critical temperature of thermal explosion (T_b)

The critical temperature of Thermal explosion (T_b) is an important parameter of evaluating the safety and elucidating transition tendency from thermal decomposition to thermal explosion for small-scale EMS.

For TEX, the value of T_b obtained from Eq. 10 [19, 20] using the value of T_{e0}, and the value T_b is 527.42 K.

$$T_b = \frac{E_o - \sqrt{E_o^2 - 4E_oRT_e}}{2R} \tag{10}$$

Adiabatic time-to-explosion

Energetic materials need a time from the beginning thermal decomposition to thermal explosion in the adiabatic conditions. The time is named the adiabatic time-to-explosion. The adiabatic time-to-explosion is an important parameter for assessing their thermal stability and the safety. It can be calculated by the following Eqs. 11–14 [21, 23–25].

$$C_p \frac{\mathrm{d}T}{\mathrm{d}t} = QA \exp\left(\frac{-E}{RT}\right) f(\alpha) \tag{11}$$

$$f(\alpha) = (1 - \alpha)^{\mathrm{n}} \tag{12}$$

$$\alpha = \int \frac{C_p}{Q}\, \mathrm{d}T \tag{13}$$

$$C_p = a + bT \tag{14}$$

where t is the adiabatic time-to-explosion(s), C_p is the specific heat capacity (J g^{-1} K^{-1}), A is the pre-exponential constant (s^{-1}), Q is the exothermic value (J g^{-1}), E is the apparent activation energy (J $\mathrm{mol^{-1}}$), R is the gas constant (J $\mathrm{mol^{-1}}$ K^{-1}), α is the fraction of conversion, $f(\alpha)$ is the decomposition reaction mechanism function and the limit of temperature integral is from T_{e0}(K) to T_b(K).

The combination of Eqs. 11–14 can give the following equation:

$$\begin{aligned} t &= \int_0^t \mathrm{d}t = \int_{T_0}^{T} \frac{C_p \exp(E/RT)}{QAf(\alpha)} \mathrm{d}T \\ &= \frac{1}{QA} \int_{T_0}^{T} \frac{(a + bT)\exp(E/RT)}{(1-\alpha)^{\mathrm{n}}} \mathrm{d}T \\ &= \frac{1}{QA} \int_{T_0}^{T} \frac{(a + bT)\exp(E/RT)}{\left[1 - \frac{1}{Q}\int_{T_0}^{T}(a + bT)\mathrm{d}T\right]^{\mathrm{n}}} \mathrm{d}T \end{aligned} \tag{15}$$

For TEX, C_p (J g^{-1} K^{-1}) $= 0.196 + 2.414 \times 10^{-3}$ T, $Q = 6511.88$ J g^{-1}, $A = 10^{11.54}$ s^{-1}, $E = 156650$ J mol^{-1}, $T_{e0} = 512.69$ K, $T_b = 527.42$ K, then $t = 53.69$ s ($n = 0$), $t = 53.88$ s ($n = 1$), and $t = 54.05$ s ($n = 2$). We can see that the adiabatic time-to-explosion is little affected by the reaction order, so the adiabatic time-to-explosion of TEX is a certain value between 53.69 and 54.05 s.

Conclusions

1. The thermal decomposition behaviors of TEX were studied by a C-500 type Calvet microcalorimeter at five heating rates and the values of enthalpy were calculated accurately. The apparent activation energy (E) and the pre-exponential constant (A) of the thermal decomposition for TEX were determined by using Kissinger method and Ozawa method.
2. The standard molar specific heat capacity of TEX is 0.916 J g^{-1} K^{-1} at 298.15 K, and the equation describing values of the specific heat capacity versus temperatures is C_p (Jg^{-1} K^{-1}) $= 0.196 + 2.414 \times 10^{-3}$ T (283.15 K $< T <$ 353.15 K).
3. The values of the thermodynamic parameters of activation reaction $\Delta S^{\neq}$, $\Delta H^{\neq}$, $\Delta G^{\neq}$ are 40.19 J mol^{-1} K^{-1}, 152.27 kJ mol^{-1}, and 131.096 kJ mol^{-1}, respectively.
4. The self-accelerating decomposition temperature, the adiabatic decomposition temperature rise, and the critical temperature of thermal explosion of exothermic decomposition reaction are 512.69, 7115.59, and 527.42 K, respectively. The adiabatic time-to-explosion of exothermic decomposition reaction is a certain value between 53.69 and 54.05 s.

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