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Thermal behavior of 3,4,5-triamino-1,2,4-triazole dinitramide

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Abstract The thermal decomposition behavior of 3,4,5-triamino-1,2,4-triazole dinitramide was measured using a C-500 type Calvet microcalorimeter at four different temperatures under atmospheric pressure. The apparent activation energy and pre-exponential factor of the exothermic decomposition reaction are 165.57 kJ mol^{-1} and $10^{18.04}$ s^{-1}, respectively. The critical temperature of thermal explosion is 431.71 K. The entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), and free energy of activation ($\Delta G^{\neq}$) are 97.19 J mol^{-1} K^{-1}, 161.90 kJ mol^{-1}, and 118.98 kJ mol^{-1}, respectively. The self-accelerating decomposition temperature (T_{SADT}) is 422.28 K. The specific heat capacity of 3,4,5-triamino-1,2,4-triazole dinitramide was determined with a micro-DSC method and a theoretical calculation method. Specific heat capacity (J g^{-1} K^{-1}) equation is $C_{\mathrm{p}} = 0.252 + 3.131 \times 10^{-3}\, T$ (283.1 K < T < 353.2 K). The molar heat capacity of 3,4,5-triamino-1,2,4-triazole dinitramide is 264.52 J mol^{-1} K^{-1} at 298.15 K. The adiabatic time-to-explosion of 3,4,5-triamino-1,2,4-triazole dinitramide is calculated to be a certain value between 123.36 and 128.56 s.

Keywords 3,4,5-Triamino-1,2,4-triazole dinitramide · Thermal behavior · Specific heat capacity · Adiabatic time-to-explosion

Introduction

The most accepted definition of an ionic liquid is a salt with melting point below 373.15 K [1–3]. Ionic liquids attract increasing attention among academic and industrial chemists for their unique properties. The chemical and thermodynamic stabilities of these compounds, combined with their low vapor pressures and low melting points, have put them forth as potential replacements of many noxious organic solvents used in the chemical industry.

Recently, many studies in developing energetic salts and energetic ionic liquids based on 1,2,3-triazole and 1,2,4-triazole as cations and nitrates, perchlorates, and dinitramides as anions have been made [4–6]. On the thermal aspect, kinetic and thermodynamic of 3,4,5-triamino-1,2,4-triazole dinitramide is a basic task in the content of thermal process. The thermal behavior of materials may be determined in a short time using thermal analysis techniques such as DSC, TG-DTG, but more intensive and precise thermal analysis can be carried out by using microcalorimeter.

In this study, C-500 Calvet microcalorimeter was applied for researching the thermal decomposition behavior of 3,4,5-triamino-1,2,4-triazole dinitramide at four different heating rates, and the data were analyzed to obtain the critical temperature of thermal explosion (T_{b}); the self acceleration decomposition temperature (T_{SADT}) is obtained at the same time.

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Experimental

Materials and measurements

3,4,5-Triamino-1,2,4-triazole dinitramide used in this research was prepared by Beijing Institute of Technology and Xi'an Modern Chemistry Research Institute, and its purity was more than 99.5%. The sample was kept in a vacuum drying vessel before use.

The thermal decomposition behavior was measured using a C-500 type Calvet microcalorimeter (Setaram, France), which had a high sensitivity and equipped with two 10 mL-vessels. The precision of enthalpy measurement was less than 0.5% after adjusting. The four different heating rates were 1.67×10^{-3} K s^{-1} (0.10 K min^{-1}), 5.00×10^{-3} K s^{-1} (0.30 K min^{-1}), 6.67×10^{-3} K s^{-1} (0.40 K min^{-1}), 8.33×10^{-3} K s^{-1} (0.50 K min^{-1}), respectively. Sample used was about 10 mg, and the reference sample was α-Al_2O_3. Each process was repeated three times, and the heat flow curves under same conditions overlap with each other, indicating that the reproducibility of test is satisfactory.

The measurement of specific heat capacity (C_p) was performed using a Micro-DSCIII apparatus (Setaram, France). The amount of sample was 391.93 mg. The heating rate was 0.15 K min^{-1} from 283.1 to 353.2 K.

Results and discussion

Thermal decomposition behavior

The thermal decomposition of 3,4,5-triamino-1,2,4-triazole dinitramide is composed of one exothermic process with a peak temperature at different heating rates. The peak temperatures obtained by using microcalorimeter at different heating rates are listed in Table 1. In Table 1, β is the heating rate, T_p the peak temperature, T_e the onset temperature, and ΔH the enthalpy of decomposition reaction.

In order to obtain the kinetic parameters [the apparent activation energy (E) and the pre-exponential constant (A)] of the decomposition reaction for 3,4,5-triamino-1,2,4-triazole dinitramide, multiple heating methods (Kissinger method and Ozawa method) were employed. Kissinger and Ozawa equations are as follows [7–14]

$$\ln\left(\frac{\beta_i}{T_{pi}^2}\right) = \ln\frac{AR}{E} - \frac{E}{R}\frac{1}{T_{pi}} \quad [i = 1, 2, \ldots, 4] \tag{1}$$

$$\log\beta_i = \log\left(\frac{AE}{RG(\alpha)}\right) - 2.315 - 0.4567\frac{E}{RT_i} \quad [i = 1, 2, \ldots, 4] \tag{2}$$

where β_i is the linear heating rate, T_{pi} represents the peak temperature of the decomposition process, R is the gas constant.

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.

With the data listed in Table 2, the entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), and free energy of activation ($\Delta G^{\neq}$) corresponding to $T = T_p$, $E = E_k$, and $A = A_k$ obtained by Eqs. 3–5 are 97.19 J mol^{-1} K^{-1}, 161.90 kJ mol^{-1}, and 118.98 kJ mol^{-1}, respectively.

$$A = \frac{k_B T}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right) \tag{3}$$

$$\Delta H^{\neq} = E - RT \tag{4}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{5}$$

where k_B is the Boltzmann constant (1.3807×10^{-23} J K^{-1}), and h is the Plank constant (6.626×10^{-34} J s^{-1}).

Critical temperature of thermal explosion (T_b) and self-accelerating decomposition temperature (T_{SADT})

The value T_{e0} (T_{SADT}) of T_e corresponding to $\beta = 0$ can be obtained by substituting the T_e and β from Table 1 into the Eq. 6 [7–11, 15, 16].

$$T_{(o,e,p)i} = T_{(o,e,p)0} + b\beta_i + c\beta_i^2 + d\beta_i^3 \quad [i = 1, 2, \ldots, 4] \tag{6}$$

where b, c, and d are coefficients.

The value of T_{e0} (T_{SADT}) is obtained as 422.28 K. The critical temperature of thermal explosion T_b obtained from Eq. 7 taken from Refs. [7–11, 15, 16] is 431.71 K, where $E_o = E_{op}$.

Table 1 Original data of the thermal decomposition reaction of 3,4,5-triamino-1,2,4-triazole dinitramide at different heating rates

β/K min^{-1}	T_0/K	T_e/K	T_p/K	$-\Delta H$/kJ mol^{-1}	Average value of $-\Delta H$/kJ mol^{-1}
0.10	387.93	425.95	432.15	812.17	831.78
0.30	395.51	432.44	442.13	894.33	
0.40	397.64	435.24	444.97	860.70	
0.50	399.86	437.78	447.12	759.93	

Table 2 Kinetic parameters obtained from the data in Table 1

E_k/kJ mol^{-1}	log A_k/s^{-1}	r_k	E_{op}/kJ mol^{-1}	r_{op}
165.57	18.04	0.999	164.40	0.999

$$T_b = \frac{E_o - \sqrt{E_o^2 - 4E_oRT_{SADT}}}{2R}. \tag{7}$$

Specific heat capacity (C_p)

Figure 1 shows the determination results of 3,4,5-triamino-1,2,4-triazole dinitramide using a continuous specific heat capacity mode of a Micro-DSCIII apparatus. In determining temperature range, specific heat capacity of 3,4,5-triamino-1,2,4-triazole dinitramide presents a good linear relationship with temperature. Specific heat capacity (J g^{-1} K^{-1}) equation is shown as:

$$C_p = 0.252 + 3.131 \times 10^{-3}\,T \quad (283.1\,\mathrm{K} < T < 353.2\,\mathrm{K}). \tag{8}$$

The molar heat capacity of 3,4,5-triamino-1,2,4-triazole dinitramide is 264.52 J mol^{-1} K^{-1} at 298.15 K. Although only a 70.0 K range was taken in the determination process, the specific heat capacity equation obtained was a stable and continuous equation, which can provide a reference and some help for wide temperature applications.

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 [7, 9–11, 16, 17]. Ordinarily, the heating rate ($\mathrm{d}T/\mathrm{d}t$) and critical heating rate $(\mathrm{d}T/\mathrm{d}t)_{T_b}$ in a thermal decomposition reaction were used to estimate the thermostability of energetic materials. However, the adiabatic time-to-explosion (t) can be calculated by the following Eqs. 9–12 [7, 18–24] if a series of experimental data were obtained. Thereby, as an important parameter, it is easier to estimate the thermostability of energetic materials according to the length of the adiabatic time-to-explosion.

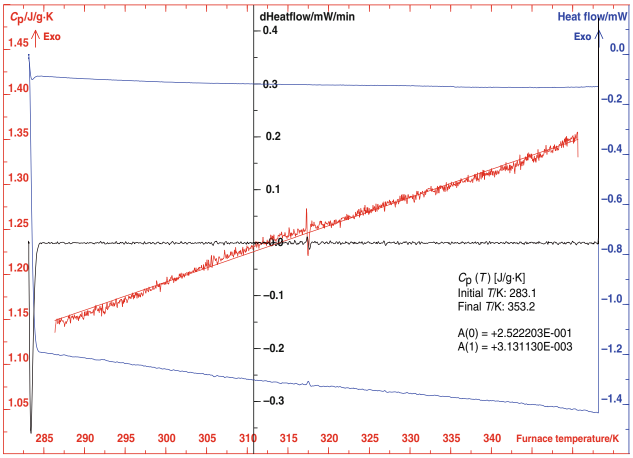

Fig. 1 Determination results of the continuous specific heat capacity

$$C_p\frac{\mathrm{d}T}{\mathrm{d}t} = QA\exp(-E/RT)f(\alpha) \tag{9}$$

$$f(\alpha) = (1-\alpha)^n \tag{10}$$

$$\alpha = \int \frac{C_p}{Q}\mathrm{d}T \tag{11}$$

$$C_p = a + bT \tag{12}$$

where C_p is the specific heat capacity (J mol^{-1} K^{-1}), T is the absolute temperature (K), t is the adiabatic decomposition time (s), Q is the exothermic energy (J mol^{-1}), A is the pre-exponential factor (s^{-1}), E is the apparent activation energy of the thermal decomposition reaction (J mol^{-1}), R is the gas constant (J mol^{-1} K^{-1}), $f(\alpha)$ is the most probable kinetic model function and α is the conversion degree, a and b are coefficients.

The combination of Eqs. 9–12 can give the following equation:

$$\begin{aligned} t = \int_0^t \mathrm{d}t &= \int_{T_{o0}}^{T} \frac{C_p\exp(E/RT)}{QAf(\alpha)}\mathrm{d}T \\ &= \frac{1}{QA}\int_{T_{o0}}^{T} \frac{(a+bT)\exp(E/RT)}{(1-\alpha)^n}\mathrm{d}T \\ &= \frac{1}{QA}\int_{T_{o0}}^{T} \frac{(a+bT)\exp(E/RT)}{\left[1-\frac{1}{Q}\int_{T_0}^{T}(a+bT)\mathrm{d}T\right]^n}\mathrm{d}T. \end{aligned} \tag{13}$$

The limit of the temperature integral in Eq. 13 is from T_{o0} to T_b.

(1) When $n = 0$

$$t_0 = \frac{1}{QA}\int_{T_{o0}}^{T_b}(a+bT)\exp(E/RT)\mathrm{d}T. \tag{14}$$

(2) When $n = 1$

$$t_1 = \frac{1}{QA\left\{1-\frac{1}{Q}\left[a(T_{o0}-T_b)+\frac{b}{2}\left(T_{o0}^2-T_b^2\right)\right]\right\}} \times \int_{T_{o0}}^{T_b}(a+bT)\exp(E/RT)\mathrm{d}T. \tag{15}$$

(3) When $n = 2$

$$t_2 = \frac{1}{QA\left\{1-\frac{1}{Q}\left[a(T_{o0}-T_b)+\frac{b}{2}\left(T_{o0}^2-T_b^2\right)\right]\right\}^2} \times \int_{T_{o0}}^{T_b}(a+bT)\exp(E/RT)\mathrm{d}T. \tag{16}$$

We can directly get $t_0 = 123.36$ s, $t_1 = 125.94$ s, and $t_2 = 128.56$ s from Eqs. 14–16, so the adiabatic time-to-explosion of 3,4,5-triamino-1,2,4-triazole dinitramide is a certain value between 123.36 and 128.56 s.

Conclusions

The thermal decomposition behavior of 3,4,5-triamino-1,2,4-triazole dinitramide was measured using a C-500 type Calvet microcalorimeter at four different temperatures under atmospheric pressure. The apparent activation energy and pre-exponential factor of the exothermic decomposition reaction are 165.57 kJ mol^{-1} and $10^{18.04}$ s^{-1}, respectively. The critical temperature of thermal explosion is 431.71 K. The entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), and free energy of activation ($\Delta G^{\neq}$) are 97.19 J mol^{-1} K^{-1}, 161.90 kJ mol^{-1} and 118.98 kJ mol^{-1}, respectively. The self-accelerating decomposition temperature (T_{SADT}) is 422.28 K.

The specific heat capacity of 3,4,5-triamino-1,2,4-triazole dinitramide was determined with a micro-DSC method and a theoretical calculation method. Specific heat capacity (J g^{-1} K^{-1}) equation is $C_{\mathrm{p}} = 0.252 + 3.131 \times 10^{-3}\,T$ (283.1 K $< T <$ 353.2 K). The molar heat capacity of 3,4,5-triamino-1,2,4-triazole dinitramide is 264.52 J mol^{-1} K^{-1} at 298.15 K. The adiabatic time-to-explosion of 3,4,5-triamino-1,2,4-triazole dinitramide was calculated to be a certain value between 123.36 and 128.56 s.

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