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Non-isothermal Decomposition Kinetics of $Cu(NH_3)_2(FOX\text{-}7)_2$

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Abstract: For fully understanding the thermal properties of Cu-FOX-7 complexes [FOX-7=1,1-diamino-2,2-dinitroethylene], thermal decomposition behavior of $Cu(NH_3)_2(FOX\text{-}7)_2$ was studied with DSC and TG-DTG methods. The kinetic equation of the first exothermic decomposition process is $\frac{d\alpha}{dT}=\frac{10^{15.12}}{\beta}4\alpha^{3/4}\exp(-1.429\times10^5/RT)$. The self-accelerating decomposition temperature and critical temperature of thermal explosion are 145.5, 156.2 ℃, respectively. The thermal stability of $Cu(NH_3)_2(FOX\text{-}7)_2$ is much lower than that of FOX-7. The specific heat capacity of $Cu(NH_3)_2(FOX\text{-}7)_2$ was determined with a micro-DSC method. Molar heat capacity is 447.3 $J\cdot mol^{-1}\cdot K^{-1}$ at 25 ℃. Adiabatic time-to-explosion was also estimated to be about 9.5 s. The thermal stability of $Cu(NH_3)_2(FOX\text{-}7)_2$ is much lower than that of (FOX-7).

Key words: physical chemistry; 1,1-diamino-2,2-dinitroethylene(FOX-7); copper complex; non-isothermal decomposition kinetics

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1 Introduction

1,1-Diamino-2,2-dinitroethylene (FOX-7) is a novel high-energy material with high thermal stability, low sensitivity to impact and friction, and have been studied a lot[1-8]. FOX-7 is a representative "push-pull" nitro-enamine, and possesses a highly polarized carbon-carbon double bond with positive and negative charges being stabilized by the amino group and nitro group respectively, and presents certain acidic properties [9-11]. Its energetic salts, such as potassium salt, rubidium salt, cesium salt and guanidine salt, have been reported[11-13]. Other salts and metal complexes of FOX-7 also are synthesized throng replacement reaction[14-17]. $Cu(NH_3)_2(FOX\text{-}7)_2$ is a new typical FOX-7 complex, and its synthesis and crystal structure have been reported[14-15] recently. In this paper, non-isothermal decomposition kinetics, specific heat capacity and adiabatic time-to-explosion of $Cu(NH_3)_2(FOX\text{-}7)_2$ will be studied to further evaluate its thermal stability.

2 Experimental

2.1 Sample

$Cu(NH_3)_2(FOX\text{-}7)_2$ was prepared according to Ref.[14]. $Cu(NH_3)_2(FOX\text{-}7)_2$ is purple. Crystal data of $Cu(NH_3)_2(FOX\text{-}7)_2$: monoclinic, space group $P2_1/c$, a=0.68818(7) nm, b=0.73083(8) nm, c=1.31966(14) nm, β=95.986°, V=0.66009(12) nm^3, D_c=1.972 $g\cdot cm^{-3}$, μ=0.862 mm^{-1}, $F(000)$=199, Z=2, R_1=0.0344, wR_2=0.0989. The molecular structure of $Cu(NH_3)_2(FOX\text{-}7)_2$ is shown in Figure 1.

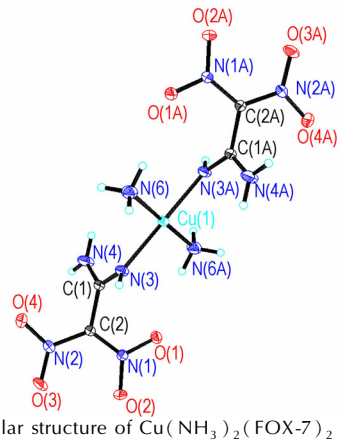

Fig.1 Molecular structure of $Cu(NH_3)_2(FOX\text{-}7)_2$

2.2 Apparatus and experiment conditions

The DSC experiments were performed using a DSC200 F3 apparatus (NETZSCH, Germany) under a nitrogen atmosphere at a flow rate of 80 $mL\cdot min^{-1}$. The sample was about 0.4 mg. The heating rates were 5.0, 7.5, 10.0, 12.5 ℃ $\cdot min^{-1}$, respectively. The temperature range was from room temperature to 300 ℃.

The TG/DTG experiment was performed using a SDT-Q600 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 100 $mL\cdot min^{-1}$. The sample was 0.32 mg. The heating rate was 5 ℃ $\cdot min^{-1}$ and the temperature range was from room temperature to 350 ℃.

The specific heat capacity was determined using a Micro-DSC Ⅲ apparatus (SETARAM, France). The sample was 383.62 mg; heating rate was 0.15 ℃ $\cdot min^{-1}$; temperature range was from 10 ℃ to 80 ℃.

3 Results and discussion

3.1 Thermal decomposition behavior

Typical DSC and TG-DTG curves of $Cu(NH_3)_2(FOX\text{-}7)_2$

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sample at a heating rate of 5.0 ℃ · min^{-1} are shown in Figure 2 and Figure 3.

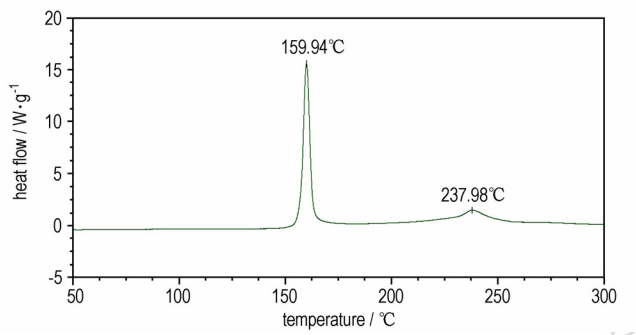

Fig. 2 DSC curve of $Cu(NH_3)_2(FOX\text{-}7)_2$ at 5.0 ℃ · min^{-1}

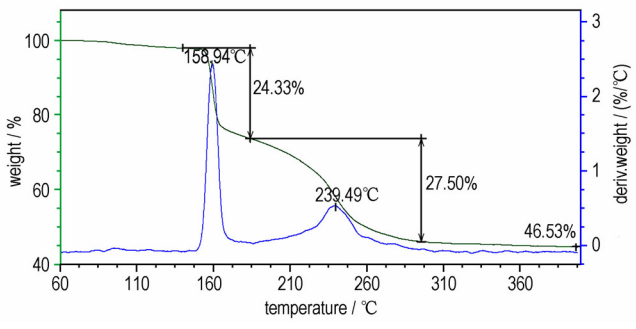

Fig. 3 TG/DTG curves of $Cu(NH_3)_2(FOX\text{-}7)_2$ at 5.0 ℃ · min^{-1}

From Figure 2 and Figure 3, the thermal decomposition of $Cu(NH_3)_2(FOX\text{-}7)_2$ can be divided into two exothermic processes. The first is an intensive exothermic decomposition process, which occurs at 160 ~ 185 ℃ with a mass loss of about 24.3%. The extrapolated onset temperature, peak temperature and decomposition heat of $Cu(NH_3)_2(FOX\text{-}7)_2$ are 157.2, 159.9 ℃ and 758.4 J · g^{-1}, respectively. The second is a slow exothermic decomposition process with a mass loss of about 27.5 % at the temperature range of 185 ~ 300 ℃, and the peak temperature is 238.0 ℃. The final residue at 400 ℃ is about 46.5 %.

3.2 Non-isothermal decomposition kinetics

In order to obtain the kinetic parameters (the apparent activation energy (E) and pre-exponential constant (A)) of the first exothermic decomposition process, a multiple heating method (Kissinger method [18] and Ozawa method [19]) was employed. The determined values of the beginning temperature (T_0), extrapolated onset temperature (T_e) and peak temperature (T_p) at the different heating rates are listed in Table 1. The values of T_{00} and T_{e0} corresponding to $\beta \to 0$ obtained by Eq. (1) are also listed in Table 1 [20].

$$T_{0i \text{ or } ei} = T_{00 \text{ or } e0} + n\beta_i + m\beta_i^2, \quad i = 1 \sim 4 \qquad (1)$$

where n and m are coefficients.

The calculated values of kinetic parameters (E and A) are also listed in Table 1. The apparent activation energy obtained by Kissinger method is consistent with that obtained by Ozawa method. The linear correlation coefficients (r_k, r_o) are all close to 1.

Table 1 T_0, T_e, T_p, T_{00}, T_{e0} and kinetic parameters of $Cu(NH_3)_2(FOX\text{-}7)_2$ at various heating rates

β/℃ · min^{-1}	T_0/℃	T_e/℃	T_p/℃	T_{00}/℃	T_{e0}/℃	E_k/kJ · mol^{-1}	log(A/s^{-1})	r_k	E_o/kJ · mol^{-1}	r_o
5.0	150.2	157.2	159.9							
7.5	153.0	161.7	164.2	143.0	145.5	142.9	15.12	0.9999	142.8	0.9998
10.0	157.6	165.1	167.3							
12.5	160.4	167.7	169.6							

Note: Subscript k, data obtained by Kissinger method; subscript o, data obtained by Ozawa method.

T versus α (the conversion degree) curves at different heating rates are shown in Figure 4. The values of E for any given value of α were obtained and shown in Figure 5. The values of E steadily distribute from 129 kJ · mol^{-1} to 139 kJ · mol^{-1} in the α range of 0.05 ~ 0.95, and the average value of E is 136.2 kJ · mol^{-1}, which is in approximate agreement with that obtained by Kissinger method and Ozawa method from only peak-temperature values. So, the values were used to check the validity of E by other methods.

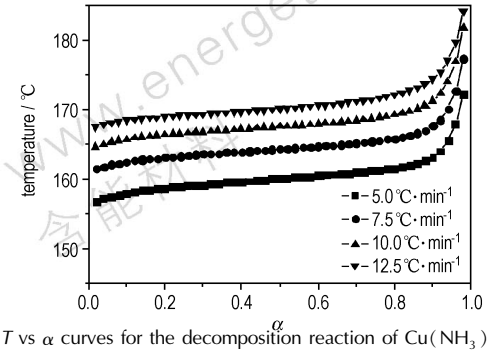

Fig. 4 T vs α curves for the decomposition reaction of $Cu(NH_3)_2(FOX\text{-}7)_2$ at different heating rates

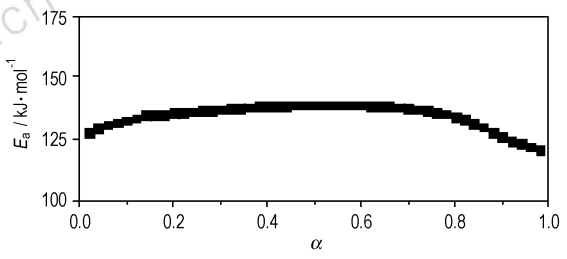

Fig. 5 E_a vs α curve for the decomposition reaction of $Cu(NH_3)_2(FOX\text{-}7)_2$ by Ozawa method

The integral equations (The general integral equation, universal integral equation, MacCallum-Tanner equation, Šatava-Šesták equation and Agrawal equation) were cited to obtain the values of E, A and the most probable kinetic model function [$f(\alpha)$] from each DSC curve. Forty-one types of kinetic model functions taken from Ref. [20] and experimental data form each DSC curve were put into the above five integral equationsfor calculating, respectively. So, the most probable kinetic model function is classified as $f(\alpha) = 4\alpha^{3/4}$ (Mampel power law, $n = 1/4$), according to the unanimity rule of cal-

culation results from each model equation[20]. The kinetic equation can be described as:

$$\frac{d\alpha}{dT}=\frac{10^{15.12}}{\beta}4\alpha^{3/4}\exp(-1.429\times10^{5}/RT) \quad (2)$$

3.3 Self-accelerating decomposition temperature and critical explosion temperature

The self-accelerating decomposition temperature (T_{SADT}) and critical temperature of thermal explosion (T_b) are two important parameters for energetic materials, which are required to ensure safe storage and process operations and then to evaluate the thermal stability. T_{SADT} and T_b can be obtained by Eq. (3) and Eq. (4)[20-21], respectively.

$$T_{SADT}=T_{e0} \quad (3)$$

$$T_b=\frac{E_O-\sqrt{E_O^2-4E_ORT_{e0}}}{2R} \quad (4)$$

T_{SADT} and T_b for $Cu(NH_3)_2(FOX\text{-}7)_2$ are 145.5 ℃ and 156.2 ℃ respectively, which are much lower than those of FOX-7 (206.0 ℃ and 207.1 ℃[3]).

3.4 Specific heat capacity

Fig. 6 shows the determination result of $Cu(NH_3)_2(FOX\text{-}7)_2$, using a continuous specific heat capacity mode of Micro-DSC Ⅲ. In determined temperature range, specific heat capacity presents a good linear relationship with temperature. Specific heat capacity equation of $Cu(NH_3)_2(FOX\text{-}7)_2$ is:

$$C_p=0.3468+2.6667\times10^{-3}T\ (283.0\ K<T<343.0\ K) \quad (5)$$

The molar heat capacity of $Cu(NH_3)_2(FOX\text{-}7)_2$ is 447.3 J·mol^{-1}·K^{-1} at 25 ℃.

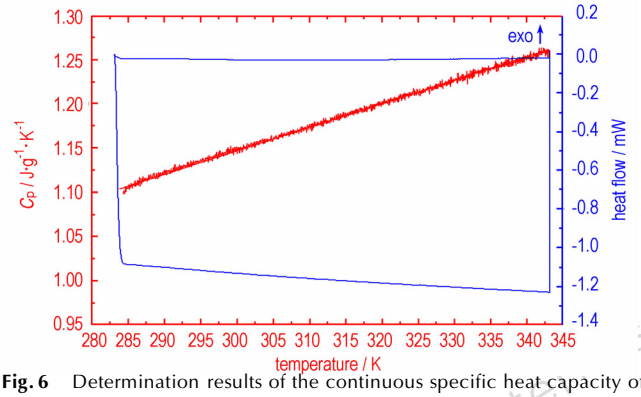

Fig. 6 Determination results of the continuous specific heat capacity of $Cu(NH_3)_2(FOX\text{-}7)_2$

3.5 Adiabatic Time-to-explosion

The adiabatic time-to-explosion is also an important parameter for evaluating the thermal stability of energetic materials and can be calculated by Eq. (6) and Eq. (7)[20,22-25].

$$C_p\frac{dT}{dt}=QA\exp(-E/RT)f(\alpha) \quad (6)$$

$$\alpha=\int_{T_0}^{T}\frac{C_p}{Q}dT \quad (7)$$

After integrating of Eq. (6), the adiabatic time-to-explosion equation can be obtained as:

$$t=\int_0^t dt=\int_{T_0}^{T}\frac{C_p\exp(E/RT)}{QAf(\alpha)}dT \quad (8)$$

where the limit of temperature integration is from T_{00} to T_b.

The conversion degree (α) of energetic materials from the beginning thermal decomposition to thermal explosion in the adiabatic conditions is too small (0.007) to obtain the most probable kinetic model function[$f(\alpha)$] in the process. So, we used Reaction-order model [$f(\alpha)=(1-\alpha)^n$] to estimate the adiabatic time-to-explosion and supposed different rate orders (n=0, 1, 2)[20,26]. t_0=9.45 s, t_1=9.52 s and t_2=9.59 s from Eq. (8) were obtained directly according to the above data. As a rule, the rate order (n) of energetic materials ranges from 0 to 2, therefore the adiabatic time-to-explosion of $Cu(NH_3)_2(FOX\text{-}7)_2$ is about 9.5 s. Although it is a short time, the result can be proved credible according to the intense change of DSC curves in the first exothermic decomposition process.

4 Conclusions

(1) The thermal decomposition of $Cu(NH_3)_2(FOX\text{-}7)_2$ presents two continuous exothermic processes. The kinetic equation of the first decomposition process is $\frac{d\alpha}{dT}=\frac{10^{15.12}}{\beta}4\alpha^{3/4}\exp(-1.429\times10^{5}/RT)$.

(2) The self-accelerating decomposition temperature and critical temperature of thermal explosion are 145.5 and 156.2 ℃, respectively. Specific heat capacity equation of $Cu(NH_3)_2(FOX\text{-}7)_2$ is $C_p=0.3468+2.6667\times10^{-3}T$ (283.0 K $<T<$ 343.0 K) and the molar heat capacity is 447.3 J·mol^{-1}·K^{-1} at 25 ℃. Adiabatic time-to-explosion of $Cu(NH_3)_2(FOX\text{-}7)_2$ was estimated to be about 9.5 s.

(3) Results show that the thermal stability of $Cu(NH_3)_2(FOX\text{-}7)_2$ is much lower than that of FOX-7.

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$Cu(NH_3)_2(FOX\text{-}7)_2$ 的非等温分解动力学

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摘　要：利用 DSC 和 TG-DTG 法研究了 $Cu(NH_3)_2(FOX\text{-}7)_2$ 的热分解行为。第一放热分解过程的非等温分解动力学方程为 $\frac{d\alpha}{dT}=\frac{10^{15.12}}{\beta}4\alpha^{3/4}\exp(-1.429\times10^5/RT)$。$Cu(NH_3)_2(FOX\text{-}7)_2$ 的自加速分解温度和热爆炸临界温度分别为 145.5 ℃和 156.2 ℃。利用微量热法研究了 $Cu(NH_3)_2(FOX\text{-}7)_2$ 的比热容，25 ℃时的摩尔热容为 447.3 J·mol^{-1}·K^{-1}。同时估算了 $Cu(NH_3)_2(FOX\text{-}7)_2$ 的绝热至爆时间大约为 9.5 s。$Cu(NH_3)_2(FOX\text{-}7)_2$ 的热稳定性远低于母体化合物 FOX-7。

关键词：物理化学；1,1-氨基-2,2-硝基乙烯（FOX-7）；铜配合物；非等分解温动力学
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