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Non-isothermal Decomposition Kinetics, Specific Heat Capacity and Adiabatic Time-to-explosion of Cu(pn)$_2$(FOX-7)$_2$

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Abstract: The energetic complex [Cu(pn)$_2$(FOX-7)$_2$] (pn=1,3-diaminopropane) was synthesized by the reaction of K(FOX-7)·H$_2$O and Cu(NO$_3$)$_2$·3H$_2$O in 1,3-diaminopropane solution. The thermal decomposition behavior was studied by differential scanning calorimetry (DSC) and thermogravimetry/derivative thermogravimetry (TG/DTG), the specific heat capacity was determined with a micro-DSC and the adiabatic time-to-explosion and the impact sensitivity were studied as well. Results show that the non-isothermal decomposition kinetic equation of the first decomposition process is $d\alpha/dT=(10^{17.83}/\beta)3\alpha^{2/3}\exp(-1.635\times10^5/RT)$. The self-accelerating decomposition temperature and critical temperature of thermal explosion are 145.6 ℃ and 146.7 ℃, respectively. The molar heat capacity is 653.79 J·mol^{-1}·K^{-1} at 298.15 K. Adiabatic time-to-explosion is about 77 s, and the characteristic drop height (H_{50}) of Cu(pn)$_2$(FOX-7)$_2$ is 71 cm (>14 J) (RDX, >7.5 J), which indicating Cu(pn)$_2$(FOX-7)$_2$ is relatively less sensitive.

Key words: 1,1-diamino-2,2-dinitroethylene (FOX-7); copper complex; 1,3-diaminopropane; non-isothermal decomposition kinetics; adiabatic time-to-explosion

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1 Introduction

1,1-Diamino-2,2-dinitroethylene (FOX-7) is a high-energy material with high thermal stability and low sensitivity to impact and friction[1-2]. Since first reported in 1998, FOX-7 has been considered as a research emphasis of energetic materials and will be used in insensitive ammunition and solid propellant. FOX-7 is a representative "push-pull" nitro-enamine, which 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[3-9]. Many researches have been studied on the synthesis[5-6], mechanism[4], molecule structure[2], theoretical calculation[11], thermal behavior[12], explosive performance and application[28] of FOX-7. Existing in manifold tautomers and resonances, FOX-7 can react with some nucleophiles to prepare many new energetic derivatives[11]. Some energetic salts, such as potassium salt, rubidium salt, cesium salt and guanidine salt, have been reported[11-12]. Other salts and metal complexes of FOX-7 also can be synthesized through replacement reaction, such as Cu(NH$_3$)$_2$(FOX-7)$_2$, Cu(CH$_3$NH$_3$)$_2$(FOX-7)$_2$, [Cu(en)$_2$(FOX-7)$_2$(H$_2$O)]·H$_2$O, [Cu(phen)$_2$FOX-7]Cl·3H$_2$O, Zn(NH$_3$)$_2$(FOX-7)$_2$ and Zn(en)$_2$(FOX-7)$_2$[14-17].

Many energetic Cu(Ⅱ) complexes were often used as detonating explosive or combustion catalyst of solid propellant[18-21], so we hope that Cu-FOX-7 complexes can also be used as energetic catalyst. Cu(pn)$_2$(FOX-7)$_2$ is a new typical FOX-7 complex, and its synthesis and crystal structure have been reported[16]. In this paper, we studied the decomposition kinetics of Cu(pn)$_2$(FOX-7)$_2$, determined specific heat capacity and calculated adiabatic time-to-explosion for further estimating its thermal stability.

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2 Experimental

2.1 Synthesis

All chemicals used in synthesis were analytical-grade commercial products. FOX-7 came from Xi'an Modern Chemistry Research Institute (purity>99%). K(FOX-7)·H$_2$O was prepared according to the ref. [13].

Cu(pn)$_2$(FOX-7)$_2$ (pn=1,3-diaminopropane) was prepared according to ref. [16] as follows: K(FOX-7)·H$_2$O (2 mmol) and Cu(NO$_3$)$_2$·3H$_2$O (1 mmol in 3 mL water) were stirred in 1,3-diaminopropane solution (78 mmol) for 30 min to give a clear solution at room temperature. Gradually purple crystals slowly appeared and were identified as Cu(pn)$_2$(FOX-7)$_2$. (yield 46%, 0.233 g). IR (KBr, ν/cm^{-1}): 3408, 3294, 3226, 2931, 2359, 2025, 1659, 1500, 1344, 1281, 1132, 1029, 926, 829, 741, 681, 501. Anal. Calcd. (%) for C$_{10}$H$_{26}$N$_{12}$O$_8$Cu: C 23.21, H 5.32, N 33.68; found: C 23.14, H 5.57, N 33.22.

2.2 Physical Measurements

The DSC experiments were performed using a DSC200 F3 apparatus (NETZSCH, Germany) under a nitrogen atmosphere at a flow rate of 80 mL·min^{-1}. The heating rates were 5.0, 7.5, 10.0 ℃·min^{-1} and 12.5 ℃·min^{-1} from ambient temperature to 350 ℃, respectively. The TG/DTG experiment was performed using a SDT-Q600 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 100 mL·min^{-1}. The heating rate was 5.0 ℃·min^{-1} from ambient temperature to 350 ℃. The specific heat capacity was determined using a

Micro-DSC Ⅲ apparatus (SETARAM, France). The heating rate used was 0.15 ℃ · min^{-1} from 10 ℃ to 80 ℃. The sample mass was 115.7 mg.

The impact sensitivity was determined by using a ZBL-B impact sensitivity instrument (NACHEN, China). The mass of drop hammer is 2.5 kg. The sample mass for every test is 30 mg.

3 Results and Discussion

3.1 Thermal Decomposition Behavior

DSC curves of Cu(pn)$_2$(FOX-7)$_2$ at various heating rates are shown in Fig. 1. TG-DTG curve of Cu(pn)$_2$(FOX-7)$_2$ sample at a heating rate of 5.0 ℃ · min^{-1} is given in Fig. 2.

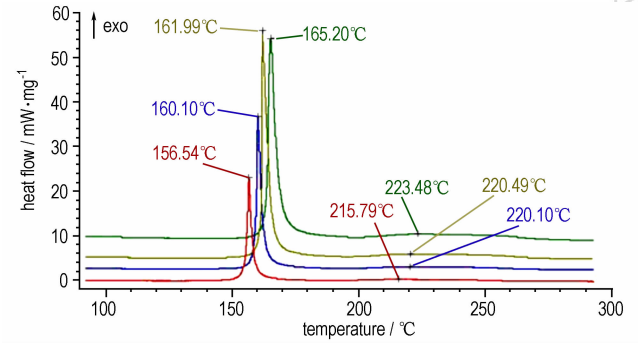

Fig. 1 DSC curves of Cu(pn)$_2$(FOX-7)$_2$

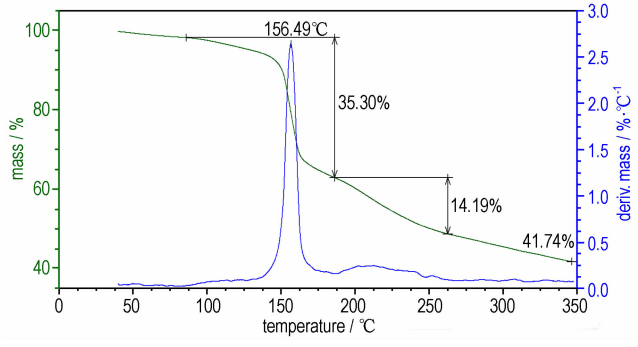

Fig. 2 TG/DTG curve of Cu(pn)$_2$(FOX-7)$_2$ at 5 ℃ · min^{-1}

Fig. 1 shows that the DSC curves of Cu(pn)$_2$(FOX-7)$_2$ exhibit two exothermic peaks, which are in agreement with the results of TG/DTG, and the peak temperatures go up with the increase of heating rate. Fig. 2 illustrates that the thermal decomposition of Cu(pn)$_2$(FOX-7)$_2$ can be divided into two decomposition processes. The first is an intense decomposition process, which occurs at 140 – 185 ℃ with a mass loss of 35.30%. The extrapolated onset temperature, peak temperature and heat of decomposition are 155.47 ℃, 156.49 ℃ and 816.5 J · g^{-1} at the heating rate of 5.0 ℃ · min^{-1}. The second stage is a slow decomposition process at the temperature range of 185–270 ℃ with a mass loss of about 14.19%. The peak temperature is 215.8 ℃ at a heating rate of 5.0 ℃ · min^{-1}. The final residue at 350 ℃ is about 41.74%. Comparing with the thermal decomposition of Cu(NH$_3$)$_2$(FOX-7)$_2$[14], they exhibits similar thermal decomposition processes, but the thermal stability of Cu(pn)$_2$(FOX-7)$_2$ is slightly lower than that of Cu(NH$_3$)$_2$(FOX-7)$_2$, which is due to the introduce of long carbon chain.

3.2 Non-isothermal Decomposition Kinetics

In order to obtain the kinetic parameters (the apparent activation energy (E) and pre-exponential factor (A)) of the first exothermic decomposition process, Kissinger method[21] and Ozawa method[22] were 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}[22] corresponding to $\beta \to 0$ obtained by Eq. (1) are also listed in Table 1.

$$T_{0i \text{ or } ei} = T_{00 \text{ or } e0} + n\beta_i + m\beta_i, \quad i = 1-4 \tag{1}$$

where n and m are coefficients.

The calculated kinetic parameters (E and A) in Table 1 show that the E obtained by Kissinger method is consistent with that by Ozawa method. The linear correlation coefficients (r) are all close to 1. So, the result is credible.

T versus α (the conversion degree) curves at different heating rates are shown in Fig. 3. The values of E_O for any given value of α were obtained and shown in Fig. 4. The values of E_O steadily distribute from 142 to 158 kJ · mol^{-1} in the α range of 0.175–0.875, and the average value of E_O is 151.9 kJ · mol^{-1}, which is in approximate agreement with that obtained by Kissinger method and Ozawa method from only peak temperature values (163.5 and 162.3 kJ · mol^{-1}, respectively). So, the values were used to check the validity of E by other methods.

The integral equations (The general integral equation, The 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[24]. Forty-one types of kinetic model functions taken from Ref. [24] and experimental data form each DSC curve were put into the above five integral equations for calculating, respectively. The values were obtained and shown in Table 2. So, the most probable kinetic

Table 1 The values of T_0, T_e, T_p, T_{00}, T_{e0} and kinetic parameters of the first exothermic decomposition process for Cu(pn)$_2$(FOX-7)$_2$ determined from DSC curves at various heating rates (β)

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	147.3	155.5	156.6							
7.5	150.4	159.3	160.1							
10.0	152.9	161.7	162.0	139.8	145.6	163.5	17.83	0.9908	162.3	0.9915
12.5	155.1	163.6	165.2							

Note: Subscript K, data obtained by Kissinger method; subscript O, data obtained by Ozawa method.

model function is classified as $f(\alpha)=3\alpha^{2/3}$ (No. 23 equation, Mampel power law, $n=1/3$), according to the unanimity rule of calculation results from each model equation[24]. The kinetic equation can be described as:

$$\frac{d\alpha}{dT}=\frac{10^{17.83}}{\beta}3\alpha^{2/3}\exp(-1.635\times10^5/RT) \quad (2)$$

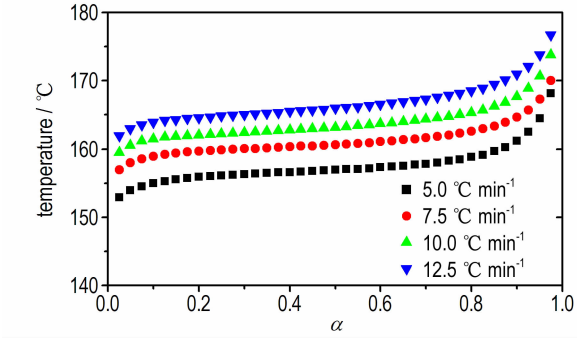

Fig. 3 T vs α curves for the decomposition reaction of $Cu(pn)_2(FOX\text{-}7)_2$ at different heating rates

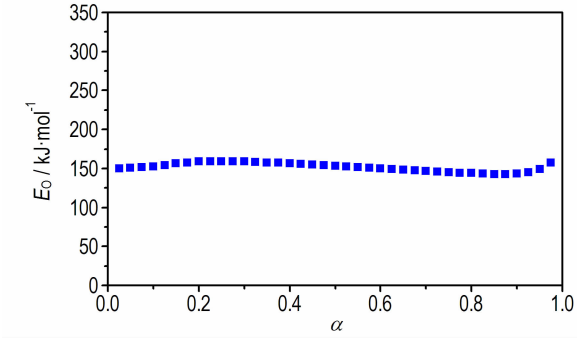

Fig. 4 E_O vs α curve for the decomposition reaction of $Cu(pn)_2(FOX\text{-}7)_2$ by Ozawa method

Table 2

β /℃ · min^{-1}	Eq.	E /kJ · mol^{-1}	log /(A/s^{-1})	r
	the general integral equation	189.9	21.0	0.9665
	the universal integral equation	187.3	19.4	0.9656
5.0	MacCallum-Tanner equation	189.8	20.9	0.9688
	Šatava-Šesták equation	187.4	20.7	0.9688
	Agrawal equation	189.9	21.0	0.9665
	the general integral equation	180.5	19.8	0.9694
	the universal integral equation	178.0	18.2	0.9687
7.5	MacCallum-Tanner equation	180.4	19.8	0.9716
	Šatava-Šesták equation	178.5	19.6	0.9716
	Agrawal equation	180.5	19.8	0.9694
	the general integral equation	154.7	16.7	0.9785
	the universal integral equation	152.2	15.1	0.9778
10.0	MacCallum-Tanner equation	154.4	16.6	0.9803
	Šatava-Šesták equation	154.0	16.6	0.9803
	Agrawal equation	154.7	16.6	0.9785
	the general integral equation	133.7	14.1	0.9743
	the universal integral equation	131.3	12.6	0.9734
12.5	MacCallum-Tanner equation	133.3	14.0	0.9768
	Šatava-Šesták equation	134.1	14.1	0.9768
	Agrawal equation	133.7	14.1	0.9743
	mean	163.9	17.5	

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 required to ensure safe storage and process operations for energetic materials and then to evaluate the thermal stability[24-25]. T_{SADT} and T_b can be obtained by Eq. (3) and Eq. (4), 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 $Cu(pn)_2(FOX\text{-}7)_2$ are 145.6 ℃ and 146.7 ℃, respectively, which are similar with those of $Cu(NH_3)_2(FOX\text{-}7)_2$ as 145.5 ℃ and 156.2 ℃[26], but much lower than those of FOX-7 as 206.0 ℃ and 207.1 ℃[27]. Admittedly, the thermal stability of FOX-7 all declines when it becomes salts or complexes, and the decomposition process also becomes severe.

3.4 Specific Heat Capacity

Figure 5 shows the result of $Cu(pn)_2(FOX\text{-}7)_2$ measured by a continuous specific heat capacity mode of Micro-DSC Ⅲ. In determined temperature range, specific heat capacity presents a good quadratic relationship with temperature. Specific heat capacity equation of $Cu(pn)_2(FOX\text{-}7)_2$ is:

$$c_p=-2.6824+1.9441\times10^{-2}T-2.0494\times10^{-5}T^2$$
$$(285.0\ K<T<350.0\ K) \quad (5)$$

where c_p is the specific heat capacity in J · g^{-1} · K^{-1}.

The molar heat capacity of $Cu(pn)_2(FOX\text{-}7)_2$ is 653.79 J · mol^{-1} · K^{-1} at 298.15 K.

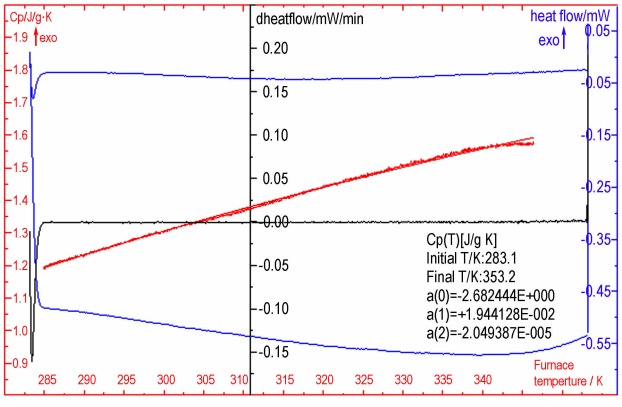

Fig. 5 Determination results of the continuous specific heat capacity of $Cu(pn)_2(FOX\text{-}7)_2$

3.5 Adiabatic Time-to-explosion

The adiabatic time-to-explosion[24, 28] is also an important parameter for evaluating the thermal stability of energetic materials and can be calculated by Eqs. (6) and (7).

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

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

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

The adiabatic time-to-explosion equation is:

$$t=\frac{1}{QA}\int_{T_0}^{T}\frac{c_p\exp(E/RT)}{f(\alpha)}\mathrm{d}T \quad (8)$$

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

In fact, the value of α of energetic materials from the beginning thermal decomposition to thermal explosion in the adiabatic conditions is very small, and it is very difficult to obtain the most probable kinetic model function [$f(\alpha)$] at the process. So, Power-low model [Eq. (9)], Reaction-order model [Eq. (10)] and Avrami-Erofeev model [Eq. (11)] were separately used to estimate the adiabatic time-to-explosion [24, 29]. The calculation results are listed in Table 3.

$$f(\alpha)=n\alpha^{(n-1)/n} \quad (9)$$

$$f(\alpha)=(1-\alpha)^n \quad (10)$$

$$f(\alpha)=n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n} \quad (11)$$

Table 3 The calculation results of adiabatic time-to-explosion

equation	rate order	model	time/s
Eq. 9	$n=1$	$f(\alpha)=1$	25.55
	$n=2$	$f(\alpha)=2\alpha^{1/2}$	66.86
	$n=3$	$f(\alpha)=3\alpha^{2/3}$	77.39
	$n=4$	$f(\alpha)=4\alpha^{3/4}$	76.48
Eq.10	$n=0$	$f(\alpha)=1$	25.55
	$n=1$	$f(\alpha)=1-\alpha$	26.51
	$n=2$	$f(\alpha)=(1-\alpha)^2$	27.52
Eq.11	$n=1$	$f(\alpha)=1-\alpha$	26.51
	$n=2$	$f(\alpha)=2(1-\alpha)[-\ln(1-\alpha)]1/2$	68.74
	$n=3$	$f(\alpha)=3(1-\alpha)[-\ln(1-\alpha)]2/3$	79.31
	$n=4$	$f(\alpha)=4(1-\alpha)[-\ln(1-\alpha)]3/4$	78.26

From Table 3, we can see that the calculation results exhibit some deviation and the decomposition model has big influence on the estimating result of adiabatic time-to-explosion. Form the results, the adiabatic time-to-explosion of Cu(pn)$_2$(FOX-7)$_2$ is calculated to about 77 s. The time can be proved credible according to the change of DSC curves in the exothermic decomposition process.

3.6 Sensitivity

The experimental results indicate that the characteristic drop height (H_{50}) of Cu(pn)$_2$(FOX-7)$_2$ is 71 cm (about >14 J). Explosion probability for friction sensitivity is 40 % (25 time experiments). So, Cu(pn)$_2$(FOX-7)$_2$ is relatively less sensitive. Moreover, the impact sensitivity of Cu(pn)$_2$(FOX-7)$_2$ is lower than that of RDX (>7.5 J), but higher than that of FOX-7 (>24.7 J) [30].

4 Conclusions

(1) The thermal decomposition of Cu(pn)$_2$(FOX-7)$_2$ exhibits two exothermic processes. The non-isothermal decomposition kinetic equation of the first process is $\mathrm{d}\alpha/\mathrm{d}T = (10^{17.83}/\beta)3\alpha^{2/3}\exp(-1.635\times10^5/RT)$. The self-accelerating decomposition temperature and critical temperature of thermal explosion are 145.6 and 146.7 ℃, respectively.

(2) Specific heat capacity equation of Cu(pn)$_2$(FOX-7)$_2$ is $c_p=-2.6824+1.9441\times10^{-2}T-2.0494\times10^{-5}T^2$ (285.0 K<T<350.0 K), and the molar heat capacity is 653.79 J·mol^{-1}·K^{-1} at 298.15 K. Adiabatic time-to-explosion of Cu(pn)$_2$(FOX-7)$_2$ is about 77 s. Cu(pn)$_2$(FOX-7)$_2$ is relatively less sensitive (>14 J) (RDX>7.5 J).

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Cu(pn)$_2$(FOX-7)$_2$的非等温分解动力学、比热容与绝热至爆时间

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摘 要: 通过K(FOX-7)·H$_2$O和Cu(NO$_3$)$_2$·3H$_2$O在1,3-丙二胺溶液中的反应制得含能配合物Cu(pn)$_2$(FOX-7)$_2$(pn=1,3-丙二胺)。用差示扫描量热法(DSC)和热重/微商热重法(TG/DTG)研究了Cu(pn)$_2$(FOX-7)$_2$的热分解行为,采用微量热DSC法测定了比热容,也研究了绝热至爆时间和撞击感度。结果表明,第一放热分解过程的非等温动力学方程为: $d\alpha/dT=(10^{17.83}/\beta)3\alpha^{2/3}\exp(-1.635\times10^5/RT)$。自加速分解温度和热爆炸临界温度分别为145.6 ℃和146.74 ℃。298.15 K时摩尔比热容为653.79 J·mol^{-1}·K^{-1}。绝热至爆时间约为77 s,Cu(pn)$_2$(FOX-7)$_2$的特性落高(H_{50})是71 cm (>14 J)(RDX>7.5 J), Cu(pn)$_2$(FOX-7)$_2$是相对不敏感的。

关键词: 1,1-二氨基-2,2-二硝基乙烯(FOX-7); 铜配合物; 1,3-丙二胺(pn); 非等温分解动力学; 绝热至爆时间
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