

Nonisothermal decomposition kinetics, specific heat capacity, and adiabatic time-to-explosion of $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$

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Abstract A new energetic zinc-FOX-7 complex, $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ (FOX-7 = 1,1-diamino-2,2-dinitroethylene), was first synthesized. Thermal decomposition behavior and nonisothermal decomposition kinetics of $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ were studied with DSC and TG/DTG methods. The kinetic equation obtained is $\frac{d\alpha}{dT} = \frac{10^{13.99}}{\beta} 4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4} \exp(-1.448 \times 10^5/RT)$. The self-accelerating decomposition temperature (T_{SADT}) and critical temperature of thermal explosion (T_b) are 183.2 and 195.8 °C, respectively. The specific-heat capacity of $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ was determined with a micro-DSC method, and the molar-heat capacity is $454.6 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298.15 K. Adiabatic time-to-explosion was also estimated to be about 20 s. The thermal stability of $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ is good and higher than that of analogous $\text{Cu}(\text{NH}_3)_2(\text{FOX-7})_2$.

Keywords 1,1-Diamino-2,2-dinitroethylene (FOX-7) · Zinc complex · Nonisothermal decomposition kinetics · Specific-heat capacity · Adiabatic time-to-explosion

Introduction

1,1-Diamino-2,2-dinitroethylene (FOX-7) is a novel high-energy material with high-thermal stability and low sensitivity to impact and friction. Since first synthesized in 1999 [1, 2], FOX-7 has been considered as an important research field of energetic materials and will be used in insensitive ammunition or solid propellant [3–14]. FOX-7 is a representative “push-pull” nitro-enamine compound, 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 [15, 16]. So, FOX-7 can react with strong alkalis to prepare some energetic salts, such as potassium salt, rubidium salt, cesium salt, and guanidine salt [8, 17–19]. Other salts and metal complexes of FOX-7 also can be synthesized through replacement reaction. Garg et al. [20, 21] and Vo et al. [22] have reported $\text{Ag}(\text{amine})(\text{FOX-7})$ [amine: ammonia, methylamine and propylamine], $\text{Cu}(\text{amine})_2(\text{FOX-7})_2$ [amine: ammonia, methylamine, propylamine and dimethylamine, ethylenediamine and 1,3-propane diamine], and other copper (nickel) bipyridyl (phenanthroline) FOX-7 complexes. He et al. [23] also reported two copper complexes containing other anions [$\text{Cu}(\text{phen})_2(\text{FOX-7})(\text{phen})\text{NO}_3 \cdot 4\text{H}_2\text{O}$ and $[\text{Cu}(\text{phen})_2(\text{FOX-7})\text{Cl} \cdot 3\text{H}_2\text{O}]$]. The syntheses, crystal structures, theoretical calculations, and properties of these complexes have been discussed. Despite those studies, the reactivity of FOX-7 is still an unresolved issue. We hope to explore the structure-property relationship through largely synthesizing series of FOX-7 complexes. The synthesis and crystal structure of a new zinc-FOX-7 complex [$\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$] is just reported by our group [24]. In this article, we will first report the nonisothermal decomposition kinetics, specific-heat capacity, and adiabatic time-to-explosion of $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ to evaluate its thermal stability.

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Experimental

Synthesis

K(FOX-7)·H₂O was prepared according to Ref. [18].

K(FOX-7)·H₂O (0.01 mol) was put into excess ammonia water (15 mL) to clear, and then zinc nitrate (0.005 mol) was added to it. After reaction at room temperature for 20 min, the resulting mixture was stored at room temperature. Then, many yellow crystals of Zn(NH₃)₂(FOX-7)₂ were formed, which were filtered, washed with water, and dried under vacuum, yielding 0.83 g (42 %). Anal. Calcd.(%) for C₄H₁₂N₁₀O₈Zn: C 12.20, H 3.073, N 35.58; found: C 12.11, H 3.11, N 35.36. IR (KBr): 3407, 3326, 2737, 2505, 1645, 1613, 1508, 1467, 1357, 1232, 1128, 802, 758 cm⁻¹. The powder XRD result and the theoretical result of single-crystal diffraction are shown in Fig. 1. We can see that they are consistent with each other and all have big diffraction peaks at 107, 15.3, 19.4, 21.2, 29.5, and 34.5 degree, respectively. The molecular structure of Zn(NH₃)₂(FOX-7)₂ is shown in Fig. 2. The crystal belongs to monoclinic, space group *C2/c* with crystal parameters of *a* = 18.468(2) Å, *b* = 6.454(1) Å, *c* = 12.979(2) Å, *β* = 117.11°, *V* = 1377.1(3) Å³, *Z* = 4, *μ* = 0.185 mm⁻¹, *F*(000) = 800, *D_c* = 1.898 g cm⁻³, *R*₁ = 0.0252, and *wR*₂ = 0.0594 [24]. The crystal data of Zn(NH₃)₂(FOX-7)₂ have been deposited in the Cambridge Data Center with the number of 873109.

Experimental equipments and conditions

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 crucible is a standard

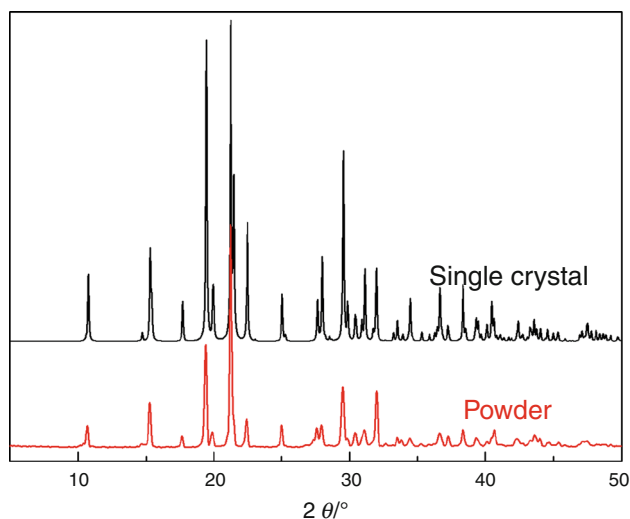


Fig. 1 XRD result of Zn(NH₃)₂(FOX-7)₂

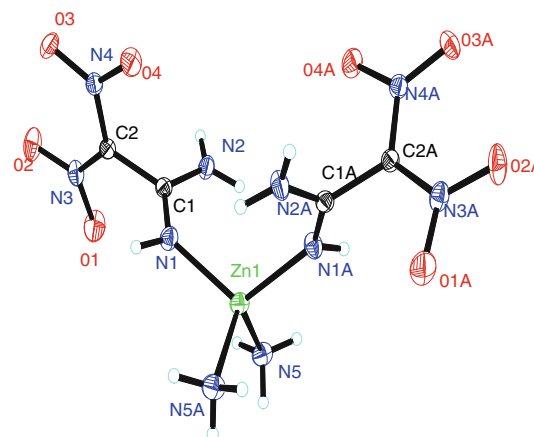


Fig. 2 Molecular structure of Zn(NH₃)₂(FOX-7)₂

aluminum product, and the condition of crucible is open. The heating rates were 5.0, 7.5, 10.0, 12.5, and 15.0 °C min⁻¹ from ambient temperature to 350 °C, 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 crucible is a standard aluminum product, and the condition of crucible is open. The heating rate was 10.0 °C min⁻¹ from ambient temperature to 500 °C.

The specific-heat capacity was determined using a Micro-DSCIII apparatus (SETARAM, France). The heating rate used was 0.15 °C min⁻¹ from 10 to 80 °C. The sample cell is a standard sealed cell of apparatus. The sample mass used was 302.59 mg.

Results and discussion

Thermal decomposition behavior

Typical DSC and TG-DTG curves (Figs. 3, 4) indicate that the thermal decomposition of Zn(NH₃)₂(FOX-7)₂ can be divided into two continuous exothermic decomposition processes. The first is an intense exothermic decomposition process which occurs at 180–235 °C with a mass loss of about 37.5 %. The extrapolated onset temperature and peak temperature are 198.1 and 204.4 °C, respectively, at the heating rate of 10.0 °C min⁻¹. The second is a slow exothermic decomposition process with a mass loss of about 28.1 % at the temperature range of 235–330 °C, and the peak temperature is 279.3 °C at a heating rate of 10.0 °C min⁻¹. The decomposition heat of the two continuous processes is 2,072 ± 71 J g⁻¹. The final residue at 500 °C is about 28 %. Comparing with the thermal behavior of similar Cu(NH₃)₂(FOX-7)₂, we can see that they have the same thermal decomposition behavior, but

Fig. 3 DSC curve of $Zn(NH_3)_2(FOX-7)_2$

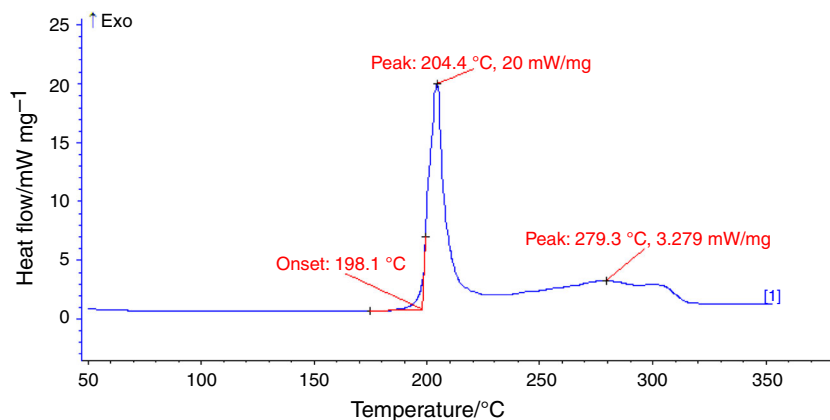
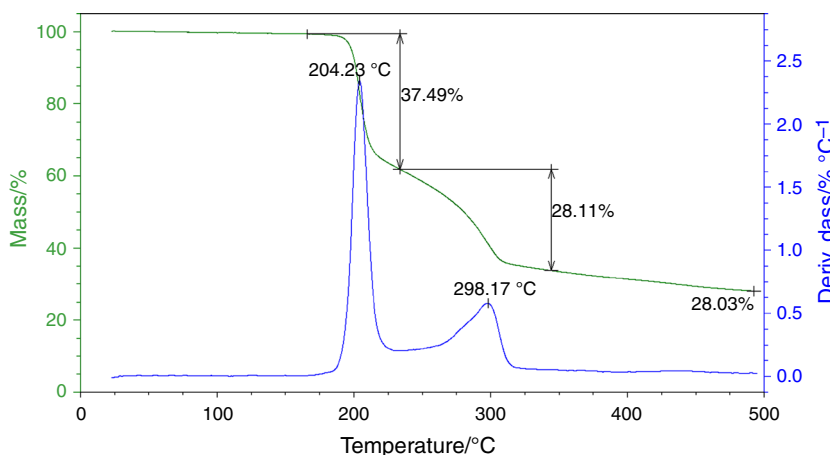


Fig. 4 TG/DTG curves of $Zn(NH_3)_2(FOX-7)_2$



$Zn(NH_3)_2(FOX-7)_2$ has much higher thermal stability than $Cu(NH_3)_2(FOX-7)_2$, the extrapolated onset temperature of which and peak temperature of the first decomposition process are 165.1 and 167.3 °C at a heating rate of 10.0 °C min⁻¹, respectively [21, 25, 26].

Nonisothermal decomposition kinetics

In order to obtain the kinetic parameters [the apparent activation energy (E) and preexponential constant (A)] of the first exothermic decomposition process, the multiple heating method (Kissinger method [27] and Ozawa method [28]) was employed. The determined values of the beginning temperature (T_0), extrapolated onset temperature (T_c) and the peak temperature (T_p) at the different heating rates are listed in Table 1. The values of T_{00} and T_{c0} corresponding to $\beta \rightarrow 0$ obtained by Eq. (1) are also listed in Table 1 [29].

$$T_{0i \text{ or } ei} = T_{00 \text{ or } e0} + n\beta_i + m\beta_i, \quad i = 1 - 5, \quad (1)$$

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 by Ozawa method. The linear correlation coefficients (r) are all close to 1. So, the results are credible. Moreover, the apparent activation energy of the exothermic decomposition process is low, indicating that $Zn(NH_3)_2(FOX-7)_2$ easily decompose at temperature above 170 °C.

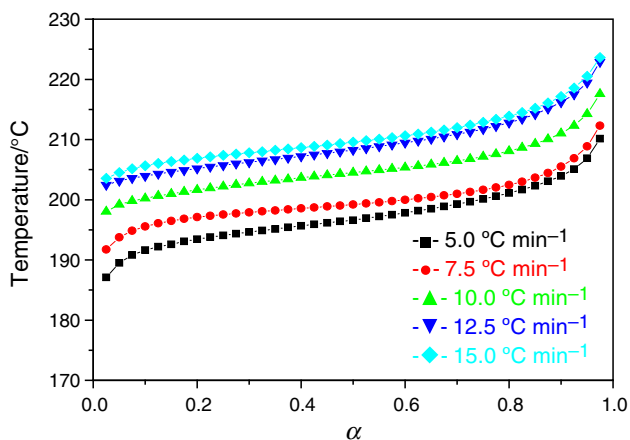
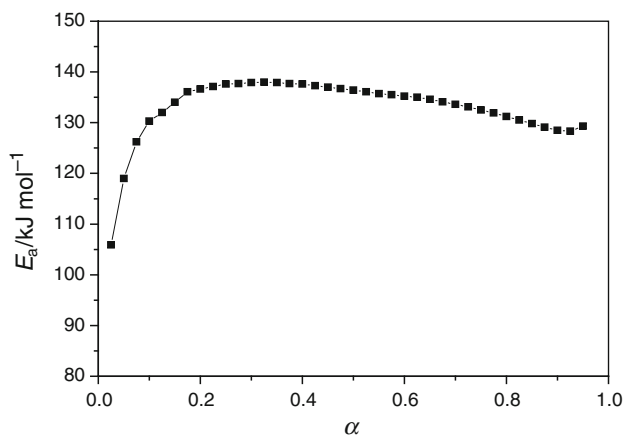
T versus α (the conversion degree) curves at different heating rates (thermal decomposition data from DSC curves) were shown in Fig. 5. By substituting corresponding data (β_i , T_i and α_i , $i = 1, 2, 3, \dots$) into Ozawa equation, the values of E_a for any given value of α were obtained and shown in Fig. 6. The values of E steadily distribute from 130 to 138 kJ mol⁻¹ in the α range of 0.15–0.85, and the average value of E is 135.3 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.

Five 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

Table 1 The values of T_0 , T_e , T_p , T_{00} , and T_{e0} and the kinetic parameters of the first exothermic decomposition process for $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ determined from the DSC curves

$\beta/^\circ\text{C min}^{-1}$	$T_0/^\circ\text{C}$	$T_e/^\circ\text{C}$	$T_p/^\circ\text{C}$	$T_{00}/^\circ\text{C}$	$T_{e0}/^\circ\text{C}$	$E_k/\text{kJ mol}^{-1}$	$\log(A/\text{s}^{-1})$	r_k	$E_o/\text{kJ mol}^{-1}$	r_o
5.0	175.6	189.7	195.7							
7.5	178.7	195.6	198.4							
10.0	183.8	198.1	204.4	169.7	183.2	144.8	13.99	0.9795	145.2	0.9815
12.5	187.1	201.4	206.3							
15.0	192.4	203.5	207.8							

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

**Fig. 5** T versus α curves for the decomposition reaction of $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ at different heat rates**Fig. 6** E_a versus α curve for the decomposition reaction by Ozawa method

[29, 30]. Forty-one types of kinetic model functions taken from Ref. [29] and experimental data from each DSC curve were put into the above five integral equations for calculating, respectively. The kinetic parameters (E and A), probable kinetic model function and linear correlation coefficient (r), standard mean square deviation (Q), and

believable factor [d , where $d = (1-r)Q$] are listed in Table 2. We can see that the values of E and $\log A$ obtained by the five equations agree with each other, and the mean value is much close to that by Kissinger method and Ozawa method and that by equal conversion-degree method. So, the most probable kinetic model function is classified as:

$$f(\alpha) = 4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}, \quad (2)$$

(No. 10, Avrami–Erofeev equation, assumes random nucleation and its subsequent growth, $n = 1/4$, $m = 4$),

$$G(\alpha) = [- \ln(1 - \alpha)]^{1/4}, \quad (3)$$

according to the unanimity rule of calculation results from each model equation [29]. The kinetic equation of the first exothermic decomposition process for $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ can be described as:

$$\frac{d\alpha}{dT} = \frac{10^{13.99}}{\beta} 4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4} \exp(-1.448 \times 10^5/RT) \quad (4)$$

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. T_{SADT} and T_b can be obtained by Eqs. (5) and (6) [29, 31], respectively.

$$T_{\text{SADT}} = T_{e0}, \quad (5)$$

$$T_b = \frac{E_o - \sqrt{E_o^2 - 4E_oRT_{e0}}}{2R}, \quad (6)$$

where E_o is the apparent activation energy obtained by Ozawa method.

T_{SADT} and T_b for $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ are 183.2 and 195.8 $^\circ\text{C}$, respectively, which all are much higher than those of analogous $\text{Cu}(\text{NH}_3)_2(\text{FOX-7})_2$ as 142.1 and 152.9 $^\circ\text{C}$ [26], also indicating $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ has higher thermal stability than $\text{Cu}(\text{NH}_3)_2(\text{FOX-7})_2$.

Table 2 Calculated values of kinetic parameters of the decomposition reaction

$\beta/^\circ\text{C min}^{-1}$	Eq.	No.	$E/\text{kJ mol}^{-1}$	$\log(A/\text{s}^{-1})$	r	Q	d
5.0	The general integral equation	10	123.99	11.37	0.9852	1.16×10^{-2}	1.72×10^{-4}
	The universal integral equation	10	122.48	10.08	0.9849	1.16×10^{-2}	1.72×10^{-4}
	MacCallum–Tanner equation	10	124.02	11.31	0.9871	2.19×10^{-3}	2.84×10^{-5}
	Šatava–Šesták equation	10	125.83	11.58	0.9871	2.19×10^{-3}	2.84×10^{-5}
	Agrawal equation	10	123.99	11.37	0.9852	1.16×10^{-2}	1.72×10^{-4}
7.5	The general integral equation	10	163.92	16.27	0.9809	1.56×10^{-2}	2.97×10^{-4}
	The universal integral equation	10	162.46	14.82	0.9806	1.56×10^{-2}	3.02×10^{-4}
	MacCallum–Tanner equation	10	164.41	16.28	0.9825	2.94×10^{-3}	5.14×10^{-5}
	Šatava–Šesták equation	10	162.86	16.14	0.9825	2.94×10^{-3}	5.14×10^{-5}
	Agrawal equation	10	163.92	16.27	0.9809	1.56×10^{-2}	2.97×10^{-4}
10.0	The general integral equation	10	147.02	14.17	0.9914	6.98×10^{-3}	6.02×10^{-5}
	The universal integral equation	10	145.69	12.80	0.9912	6.97×10^{-3}	6.10×10^{-5}
	MacCallum–Tanner equation	10	147.41	14.15	0.9922	1.31×10^{-3}	1.02×10^{-5}
	Šatava–Šesták equation	10	147.36	14.19	0.9922	1.31×10^{-3}	1.02×10^{-5}
	Agrawal equation	10	147.02	14.16	0.9914	6.98×10^{-3}	6.02×10^{-5}
12.5	The general integral equation	10	130.33	12.15	0.9834	1.31×10^{-2}	2.18×10^{-4}
	The universal integral equation	10	129.09	10.87	0.9831	1.31×10^{-2}	2.21×10^{-4}
	MacCallum–Tanner equation	10	130.59	12.12	0.9854	2.47×10^{-3}	3.61×10^{-5}
	Šatava–Šesták equation	10	132.04	12.34	0.9854	2.47×10^{-3}	3.61×10^{-5}
	Agrawal equation	10	130.33	12.15	0.9834	1.31×10^{-2}	2.18×10^{-4}
15.0	The general integral equation	10	133.24	12.63	0.9770	1.83×10^{-2}	4.22×10^{-4}
	The universal integral equation	10	132.03	11.31	0.9766	1.83×10^{-2}	4.28×10^{-4}
	MacCallum–Tanner equation	10	133.62	12.61	0.9795	3.46×10^{-3}	7.09×10^{-5}
	Šatava–Šesták equation	10	134.34	12.74	0.9795	3.46×10^{-3}	7.09×10^{-5}
	Agrawal equation	10	133.24	12.63	0.9770	1.83×10^{-2}	4.22×10^{-4}
Mean			139.6	13.06			

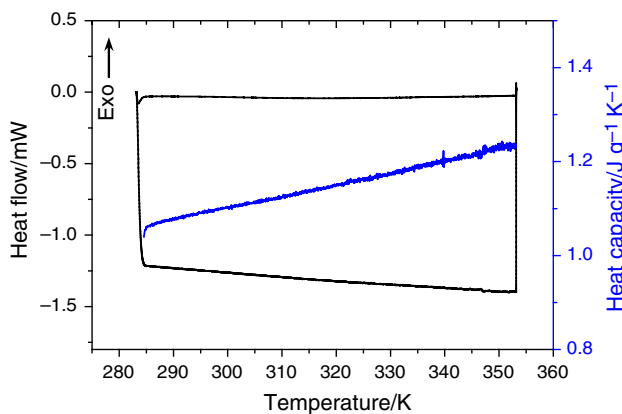


Fig. 7 Determination results of the continuous specific-heat capacity of $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$

Specific-heat capacity

Figure 7 shows the determination result of $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$, using a continuous specific-heat capacity mode of Micro-DSCIII. In determined temperature range, specific-heat

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

Equations	Rate order	Model	Time/s
11	$n = 1$	$f(\alpha) = 1$	5.4
	$n = 2$	$f(\alpha) = 2\alpha^{1/2}$	17.6
	$n = 3$	$f(\alpha) = 3\alpha^{2/3}$	21.9
	$n = 4$	$f(\alpha) = 4\alpha^{3/4}$	22.4
12	$n = 0$	$f(\alpha) = 1$	5.4
	$n = 1$	$f(\alpha) = 1 - \alpha$	5.5
	$n = 2$	$f(\alpha) = (1 - \alpha)^2$	5.7
13	$n = 1$	$f(\alpha) = 1 - \alpha$	5.5
	$n = 2$	$f(\alpha) = 2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	17.9
	$n = 3$	$f(\alpha) = 3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	22.2
	$n = 4$	$f(\alpha) = 4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$ #1	22.8

#1 The above obtained most probable kinetic model function

capacity presents a good linear relationship with temperature. Specific-heat capacity equation of $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ is:

$$C_p(\text{J g}^{-1} \text{K}^{-1}) = 0.3727 + 2.6240 \times 10^{-3} T (285.0 \text{ K} < T < 350.0 \text{ K}) \quad (7)$$

The molar-heat capacity of $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ is $454.6 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298.15 K .

Estimating of 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 Eqs. (8) and (9) [29, 32–35].

$$C_p \frac{dT}{dt} = Q A \exp(-E/RT) f(\alpha), \quad (8)$$

$$\alpha = \int_{T_0}^T \frac{C_p}{Q} dT, \quad (9)$$

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

After integrating of Eq. (8), the adiabatic time-to-explosion equation can be obtained as:

$$t = \int_0^t dt = \int_{T_0}^T \frac{C_p \exp(E/RT)}{Q A f(\alpha)} dT, \quad (10)$$

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

In fact, the conversion degree (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, we separately used Power-law model [Eq. (11)], Reaction-order model [Eq. (12)], Avrami–Erofeev model [Eq. (13)], and the above obtained kinetic model function to estimate the adiabatic time-to-explosion and supposed different rate orders (n) [29, 30]. The calculation results are listed in Table 3.

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

$$f(\alpha) = (1 - \alpha)^n \quad (12)$$

$$f(\alpha) = n(1 - \alpha)[- \ln(1 - \alpha)]^{(n-1)/n} \quad (13)$$

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. From the whole results, we believe the adiabatic time-to-explosion of $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ should be about 20 s. It is a relatively short time, and the result can be

proved credible according to the intense change of DSC curves in the first exothermic decomposition process.

Conclusions

$\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ was first synthesized and structurally characterized. The thermal decomposition behavior of $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ presents two continuous exothermic decomposition processes. The nonisothermal kinetic equation of the first decomposition process is obtained. The self-accelerating decomposition temperature (T_{SADT}) and critical temperature of thermal explosion (T_b) are 183.2 and 195.8 °C, respectively.

Specific-heat capacity equation of $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ is $C_p(\text{J g}^{-1} \text{K}^{-1}) = 0.3727 + 2.6240 \times 10^{-3} T (283.0 \text{ K} < T < 353.0 \text{ K})$, and the molar-heat capacity is $454.6 \text{ J mol}^{-1} \text{K}^{-1}$ at 298.15 K . Adiabatic time-to-explosion of $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ was estimated to be about 20 s. The thermal stability of $\text{Zn}(\text{NH}_3)_2(\text{FOX-7})_2$ is good and higher than that of analogous $\text{Cu}(\text{NH}_3)_2(\text{FOX-7})_2$.

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References

- Latypov NV, Bergman J, Langlet A, Wellmar U, Bemm U. Synthesis and reactions of 1,1-diamino-2,2-dinitroethylene. *Tetrahedron*. 1998;54:11525–36.
- Bemm U, Östmark H. 1,1-Diamino-2,2-dinitroethylene: a novel energetic material with infinite layers in two dimensions. *Acta Crystallogr C*. 1998;54:1997–9.
- Ji GF, Xiao HM, Dong HS, Gong XD, Li JS, Wang ZY. The theoretical study on structure and property of diaminodinitroethylene. *Acta Chim Sinica*. 2001;59:39–47.
- Cai HQ, Shu YJ, Huang H, Cheng BB, Li JS. Study on reactions of 2-(dinitromethylene)-4,5-imidazolidinedione. *J Org Chem*. 2004;69:4369–74.
- Cai HQ, Shu YJ, Yu WF, Li JS, Cheng BB. Study on synthesis of FOX-7 and its reaction mechanism. *Acta Chim Sinica*. 2004; 62:295–301.
- Sorescu DC, Boatz JA, Thompson DL. First-principles calculations of the adsorption of nitromethane and 1,1-diamino-2,2-dinitroethylene (FOX-7) molecules on the $r\text{-Al}_2\text{O}_3(0001)$ surface. *J Phys Chem B*. 2005;109:1451–63.
- Trzciński WA, Cudzilo S, Chylek Z, Szymańczyk L. Detonation properties of 1,1-diamino-2,2-dinitroethene (DADNE). *J Hazard Mater*. 2006;157:605–12.
- Anniyappan M, Talawar MB, Gore GM, Venugopalan S, Gandhe BR. Syntheses, characterization and thermolysis of 1,1-diamino-2,2-dinitroethylene (FOX-7) and its salts. *J Hazard Mater*. 2006; 137:812–9.
- Evers J, Klapotke TM, Mayer P, Oehlinger G, Welch J. α and β -FOX-7, polymorphs of a high energy density material, studied by X-ray single crystal and powder investigations in the temperature range from 200 to 423 K. *Inorg Chem*. 2006;45:4996–5007.

- Gao HX, Zhao FQ, Hu RZ, Pan Q, Wang BZ, Yang XW, Gao Y, Gao SL, Shi QZ. Thermochemical properties, thermal behavior and decomposition mechanism of 1,1-diamino-2,2-dinitroethylene (DADE). *Chin J Chem*. 2006;24:177–81.
- Fan XZ, Li JZ, Liu ZR. Thermal behavior of 1,1-diamino-2,2-dinitroethylene. *J Phys Chem A*. 2007;111:13291–4.
- Xu KZ, Song JR, Zhao FQ, Cao ZH, Ma HX, Hu RZ, Gao HX, Huang J. Specific heat capacity, thermodynamic properties and adiabatic time-to-explosion of FOX-7. *Acta Chim Sinica*. 2007;65:2827–31.
- Buszewski B, Michel M, Cudzilo S, Chylek Z. High performance liquid chromatography of 1,1-diamino-2,2-dinitroethene and some intermediate products of its synthesis. *J Hazard Mater*. 2009;164:1051–8.
- Ahn JH, Kim JK, Kim HS, Kim EJ, Koo KK. Solubility of 1,1-diamino-2,2-dinitroethylene in *N,N*-dimethylformamide, dimethyl sulfoxide, and *N*-methyl-2-pyrrolidone. *J Chem Eng Data*. 2009;54:3259–60.
- Rajappa S. Nitroamines preparation, structure and synthetic potential. *Tetrahedron*. 1981;37:1453–80.
- Hervé G, Jacob G, Latypov N. Novel illustrations of the specific reactivity of 1,1-diamino-2,2-dinitroethylene (DADNE) leading to new unexpected compounds. *Tetrahedron*. 2007;63:953–9.
- Xu KZ, Song JR, Zhao FQ, Ma HX, Gao HX, Chang CR, Ren YH, Hu RZ. Thermal behavior, specific heat capacity and adiabatic time-to-explosion of G(FOX-7). *J Hazard Mater*. 2008;158:333–9.
- Xu KZ, Zuo XG, Song JR, Wang F, Huang J, Chang CR. Preparation, crystal structure and thermal behavior of K(FOX-7)·H₂O. *Chem J Chin Uni*. 2010;31:638–43.
- Luo JA, Xu KZ, Wang M, Song JR, Ren XL, Chen YS, Zhao FQ. Syntheses and thermal behaviors of Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O. *Bull Korean Chem Soc*. 2010;31:2867–71.
- Garg S, Gao HX, Joo YH, Parrish DA, Huang Y, Shreeve JM. Taming of the silver FOX. *J Am Chem Soc*. 2010;132:8888–90.
- Garg S, Gao HX, Parrish DA, Shreeve JM. FOX-7 (1,1-diamino-2,2-dinitroethene): trapped by copper and amines. *Inorg Chem*. 2011;50:390–5.
- Vo TT, Parrish DA, Shreeve JM. 1,1-Diamino-2,2-dinitroethene (FOX-7) in copper and nickel diamine complexes and copper FOX-7. *Inorg Chem*. 2012;51:1963–8.
- He F, Xu KZ, Zhang H, Qiu QQ, Song JR, Zhao FQ. Two new copper-FOX-7 complexes: synthesis, crystal structure, and thermal behavior. *J Coord Chem*. 2013;66:845–55.
- Gao Z, Huang J, Xu KZ, Zhang WT, Song JR, Zhao FQ. Synthesis, structural characterization and thermal properties of a new energetic zinc-FOX-7 complex. *J Coord Chem*. 2013;66:3572–80.
- Chen YS, Xu KZ, Wang M, Ma HX, Zhao FQ. Crystal structure and thermal behavior of Cu(NH₃)₂(FOX-7)₂[J]. *Chin J Explos Propell*. 2011;34(4):5–9 (in Chinese).
- Qiu QQ, Gao Z, Chen YS, Xu KZ, Zhao FQ. Non-isothermal decomposition kinetics of Cu(NH₃)₂(FOX-7)₂. *Chin J Energy Mater*. 2013 (accepted).
- Kissinger HE. Reaction kinetics in differential thermal analysis. *Anal Chem*. 1957;29:1702–6.
- Ozawa T. A new method of analyzing thermogravimetric data. *Bull Chem Soc Jpn*. 1965;38:1881–6.
- Hu RZ, Gao SL, Zhao FQ, Shi QZ, Zhang TL, Zhang JJ. Thermal analysis kinetics. 2nd ed. Beijing: Science Press; 2008 (in Chinese).
- Vyzovkin S, Burnham AK, Criado JM, Maqueda LA, Popescu C, Sbirrazzuoli N. ICTAC kinetics committee recommendation for performing kinetic computations on thermal analysis data. *Thermochim Acta*. 2011;520:1–19.
- Zhang TL, Hu RZ, Xie Y, Li FP. The estimation of critical temperatures of thermal explosion for energetic materials using non-isothermal DSC. *Thermochim Acta*. 1994;244:171–6.
- Smith LC. An approximate solution of the adiabatic explosion problem. *Thermochim Acta*. 1975;13:1–6.
- Ma HX, Yan B, Li ZN, Song JR, Hu RZ. Synthesis, molecular structure, non-isothermal decomposition kinetics and adiabatic time to explosion of 3,3-dinitroazetidinium 3,5-dinitrosalicylate. *J Therm Anal Calorim*. 2009;95:437–44.
- Xu KZ, Chen YS, Wan M, Luo JA, Song JR, Zhao FQ, Hu RZ. Synthesis and thermal behavior of 4,5-dihydroxyl-2-(dinitromethylene)-imidazolidine (DDNI). *J Therm Anal Calorim*. 2011;105:293–300.
- Xu KZ, Zuo XG, Zhang H, Yan B, Huang J, Ma HX, Wang BZ, Zhao FQ. Synthesis and thermal behavior of a new high-energy organic potassium salt: K(AHDNE). *J Therm Anal Calorim*. 2012;110:585–91.