Non-isothermal Decomposition Kinetics of a New High-energy Organic Potassium Salt: K(DNDZ)

Kangzhen Xu,* Fengqi Zhao,*,· Jirong Song,‡ Xiaolei Ren, Hongxu Gao,* Siyu Xu,† and Rongzu Hu†

*Department of Chemical Engineering, Northwest University, Xi'an 710069 P. R. China. *E-mail: xukz@nwu.edu.cn*
·Xi'an Modern Chemistry Research Institute, Xi'an 710065. P. R. China. ·E-mail: zhaofqi@163.com
‡Conservation Technology Department, the Palace Museum, Beijing 100009, P. R. China

A new high-energy organic potassium salt, 2-(dinitromethylene)-1,3-diazepentane potassium salt K(DNDZ), was synthesized by reacting of 2-(dinitromethylene)-1,3-diazepentane (DNDZ) and potassium hydroxide. The thermal behavior and non-isothermal decomposition kinetics of K(DNDZ) were studied with DSC, TG/DTG methods. The kinetic equation is $\dfrac{d\alpha}{dT} = \dfrac{10^{13.92}}{\beta} 3(1 - \alpha)[-\ln(1 - \alpha)]^{\frac{2}{3}} \exp(-1.52 \times 10^5 / RT)$. The critical temperature of thermal explosion of K(DNDZ) is 208.63 °C. The specific heat capacity of K(DNDZ) was determined with a micro-DSC method, and the molar heat capacity is 224.63 J mol^{-1} K^{-1} at 298.15 K. Adiabatic time-to-explosion of K(DNDZ) obtained is 157.96 s.

Key Words: 1,1-Diamino-2.2-dinitroethylene (FOX-7). 2-(Dinitromethylene)-1.3-diazepentane (DNDZ), Non-isothermal 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. When first synthesized in 1998,[1] FOX-7 received much attention. Many researches have been carried out on the synthesis. mechanism, molecular structure. thermal behavior. explosive performance and application of FOX-7.[2-17]

"Push-pull" nitro-enamine is a kind of compound with special construction. 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 exists in manifold tautomers and resonances.[18] FOX-7 is a representative "push-pull" nitro-enamine compound. FOX-7 presents certain acidic properties and can react with some nucleophiles to syn-

thesize new high-energy derivatives.[5, 10-12] Our interest mainly consisted in modifying molecular structure of FOX-7 in order to obtain some new high-energy compounds and research their structure-property relationship.[19-22]

We prepared a derivative of FOX-7.2-(dinitromethylene)-1.3-diazepentane (DNDZ). and found it still belongs to "push-pull" nitro-enamine compound, has the same characteristics to FOX-7 and exists in many manifold tautomers and resonances (Scheme 1).[19] It can also react with strong alkalis (KOH). and we have used it to prepare a new high-energy organic potassium salt (Scheme 2). which will be used as flame suppressor in propellant to substitute inorganic potassium salt (KCl, K₂SO₄, KNO₃ and K₃AlF₆) to generate much more energy and clean gas.

In this paper. we studied the decomposition kinetic behavior of K(DNDZ) under non-isothermal conditions by DSC. TG/
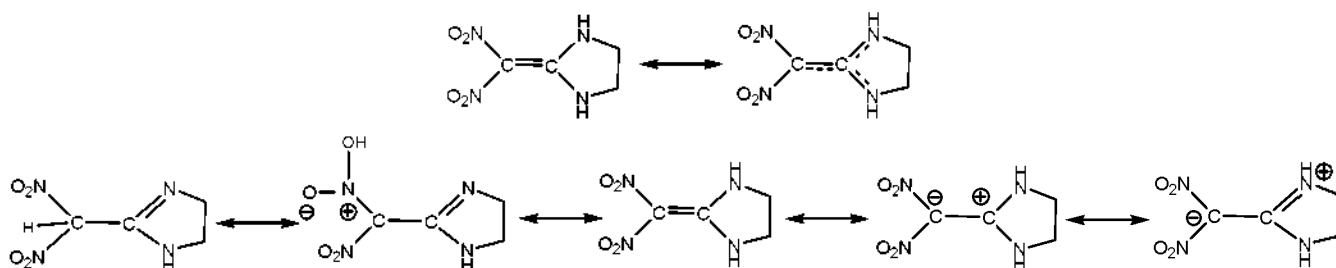
Scheme 1. Tautomers and resonances of DNDZ.
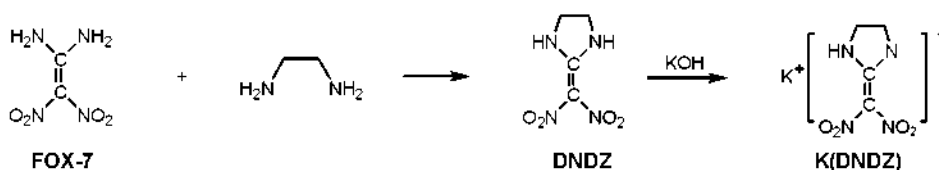
Scheme 2. Synthesis of K(DNDZ).

DTG methods, determined the specific heat capacity with a micro-DSC method and calculated the adiabatic time-to-explosion for further estimating the thermal stability of K(DNDZ).

Experimental

Sample. K(DNDZ) was prepared as follows: DNDZ (1.74 g) was suspended in 10 mL of water and to it a solution of KOH (1.12 g in 4 mL of water) was added drop wise. After reaction at room temperature for 20 min, 25 mL of methanol were also
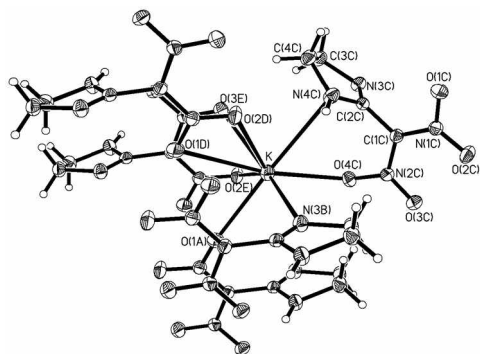
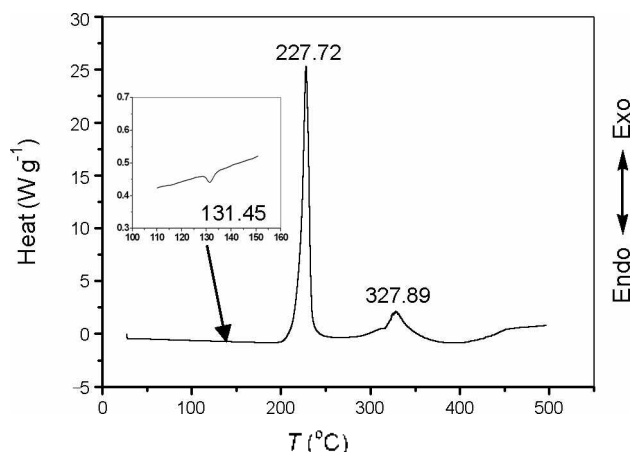**Figure 1.** Crystal structure of K(DNDZ).
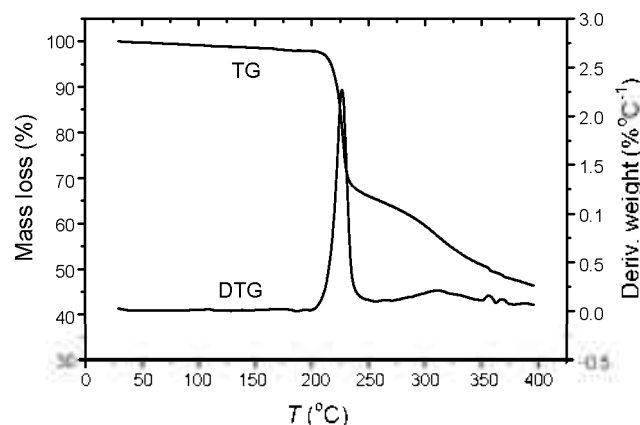
Figure 2. DSC curve of K(DNDZ).

Figure 3. TG/DTG curves of K(DNDZ) at a heating rate of 10.0 °C min⁻¹.

added drop wise, and the resulting mixture was slowly cooled to 0 °C. Many bright yellow crystals of K(DNDZ) were formed, which were filtered, washed with methanol and dried under vacuum, yielding 1.51 g (71%). Anal. Calcd.(%) for $C_4H_5N_4O_4K$: C 17.39, H 4.39, N 47.33; found: C 17.46, H 4.38, N 46.63. The characteristic peaks of IR (KBr) are: 3317, 2972, 2866, 1622, 1511, 1475, 1438, 1361, 1278, 1226, 1097 cm⁻¹. The molecular structure is shown in Figure 1.

Experimental Equipments and Conditions. The DSC experiments for K(DNDZ) were performed using a DSC-Q200 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 50 mL min⁻¹ and the amount of used sample was about 1 mg. The heating rates used were 2.0, 5.0, 10.0 and 20.0 °C min⁻¹ from ambient temperature to 500.0 °C.

The TG/DTG experiment for K(DNDZ) was performed using a SDT-Q600 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 100 mL min⁻¹. The amount of used sample was about 1 mg. The heating rate used was 10.0 °C min⁻¹ from ambient temperature to 400.0 °C.

The specific heat capacity (C_p) of K(DNDZ) was determined using a Micro-DSC III apparatus (SETARAM, France), the amount of used sample was 393.73 mg. The heating rate used was 0.15 °C min⁻¹ from 10.0 to 80.0 °C.

Results and Discussion

Thermal Behavior. The typical DSC and TG/DTG curves (Figures 2 and 3) indicate that K(DNDZ) has no melting point, and its thermal behavior can be divided into two obvious exothermic decomposition stages. The first stage occurs at 180 ~ 240 °C with a mass loss of about 35%, and the extrapolated onset temperature, peak temperature and decomposition enthalpy are 220.43 °C, 227.72 °C and 1832.5 J g⁻¹ at the heating rate of 10.0 °C min⁻¹, respectively. The second stage occurs at 240 ~ 360 °C with a mass loss of about 18%, and the extrapolated onset temperature, peak temperature and enthalpy are 316.83 °C, 327.89 °C and 637.13 J g⁻¹ at the heating rate of 10.0 °C min⁻¹, respectively. But, there is still a very unconspicuous crystal phase transition process. The peak temperature and enthalpy of the crystal phase transition are 131.45 °C and 1.923 J g⁻¹ at the heating rate of 2.5 °C min⁻¹. All are very different from that of DNDZ whose thermal behavior has only one intense exothermic decomposition process, and the extrapolated onset temperature and peak temperature are 256.64 and 267.60 °C at the heating rate of 10.0 °C min⁻¹.[15] K(DNDZ) has lower thermal stability than DNDZ.

Non-isothermal Decomposition Kinetics. In order to obtain the kinetic parameters (the apparent activation energy (E) and pre-exponential constant (A)) of the two exothermic decomposition reactions for K(DNDZ), a multiple heating method (Kissinger method[23] and Ozawa method[24]) was employed (Figure 4). The Kissinger and Ozawa equations are as follows:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\frac{AR}{E} - \frac{E}{R}\frac{1}{T_p} \qquad (1)$$

$$\log\beta + \frac{0.4567E}{RT_p} = C \qquad (2)$$

where T_p is the peak temperature (K). β is the linear heating rate (°C min⁻¹). E is the apparent activation energy (kJ mol⁻¹). A is the pre-exponential constant (s⁻¹). R is the gas constant (J mol⁻¹ K⁻¹) and C is a constant.

The measured values of the beginning temperature (T_0). extrapolated onset temperature (T_e). peak temperature (T_p) and enthalpy (ΔH_d) of the two exothermic decomposition reactions were listed in Table 1. The above-mentioned values (E and A) determined by Kissinger method and Ozawa method and the linear correlation coefficients (r) are listed in Table 2.

From Table 2. we can see that the apparent activation energy obtained by Kissinger method agrees well with that obtained by Ozawa method. moreover. the linear correlation coefficients are all very close to 1. So. the result is credible. Moreover. the apparent activation energy of the first exothermic decomposition reaction was low. indicating that K(DNDZ) is easy to decompose at temperature above 180 °C.

T versus α (the conversion degree) curves at different heating rates [Thermal decomposition data of K(DNDZ) by DSC curves] were shown in Figure 5. By substituting corresponding data (β_i. T_i and α_i, $i = 1, 2, 3, \cdots$) into Eq. (2). the values of E for any given value of α were obtained and shown in Figure 6. We can see that the values of E steadily distribute from 139 to 150 kJ mol⁻¹ in the α range of 0.0125 ~ 0.95. and the average value of E is 142.78 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.

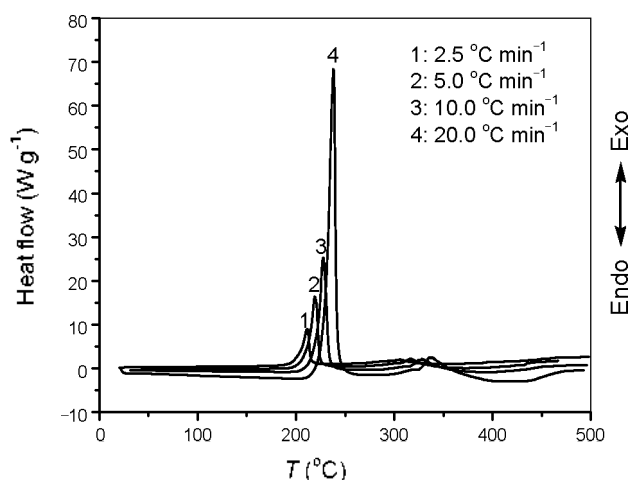The integral Eqs. (3)-(7) are cited to obtained the values of

E, A and the most probable kinetic model function ($f(\alpha)$) from each single DSC curve.[25]

The general integral equation[26]:

$$\ln\left[\frac{G(\alpha)}{T^2\left(1 - \frac{2RT}{E}\right)}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \tag{3}$$

The universal integral equation[27]:

$$\ln\left[\frac{G(\alpha)}{T - T_0}\right] = \ln\frac{A}{\beta} - \frac{E}{RT} \tag{4}$$

MacCallum-Tanner equation[28]:

$$\log[G(\alpha)] = \log\left[\frac{AE}{\beta R}\right] - 0.4828E^{0.4357}$$
$$- \frac{0.449 + 0.217E}{0.001} \frac{1}{T} \tag{5}$$

Šatava-Šesták equation[29]:

$$\log[G(\alpha)] = \log\left[\frac{AE}{\beta R}\right] - 2.315 - 0.4567\frac{E}{RT} \tag{6}$$

Agrawal equation[30]:

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln\left\{\frac{AR}{\beta E}\left[\frac{1 - 2\left(\frac{RT}{E}\right)}{1 - 5\left(\frac{RT}{E}\right)}\right]\right\} - \frac{E}{RT} \tag{7}$$

where $G(\alpha)$ is the integral model function. T is the absolute temperature (K). E is the activation energy (kJ mol⁻¹). β is the linear heating rate (K min⁻¹). R is the gas constant (J mol⁻¹ K⁻¹).

Figure 4. DSC curves of K(DNDZ) at various heating rates.

Table 2. Kinetic parameters obtained by the data in Table 1.

	E_k (kJ mol⁻¹)	$\log A_k$ (A_k,s⁻¹)	r_k	E_o (kJ mol⁻¹)	r_o
The first stage	152.0	13.92	0.9985	152.4	0.9987
The second stage	181.5	13.80	0.9993	182.0	0.9994

*Subscript k is data obtained by Kissinger's method. Subscript O is data obtained by Ozawa's method.

Table 1. The measured values of T_0, T_e, T_p and ΔH_d of the two exothermic decomposition stages for K(DNDZ) from the DSC curves at various heating rates (β).

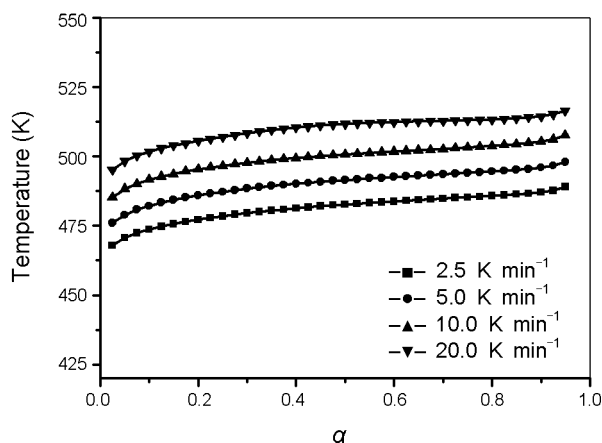| β (°C min⁻¹)	The first stage				The second stage		
	T_0 (°C)	T_e (°C)	T_p (°C)	ΔH_d (kJ mol⁻¹)	T_e (°C)	T_p (°C)	ΔH_d (kJ mol⁻¹)
2.5	182.39	203.13	211.39		292.14	306.10	
5.0	189.21	211.76	219.26	388.89	304.01	316.44	135.21
10.0	194.51	220.43	227.72		316.83	327.89	
20.0	205.19	229.31	238.17		324.50	337.76	

Figure 5. T *vs* α curves for the decomposition reaction of K(DNDZ) at different heat rates.
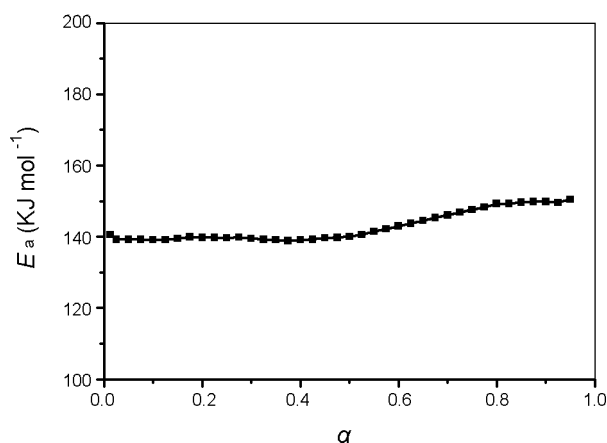

Figure 6. E_a *vs* α curve for the decomposition reaction of K(DNDZ) by Ozawa's method.

and α is the conversion degree.

Forty-one types of kinetic model functions in Ref. [25] and corresponding experimental data form DSC curves at different heating rates were put into Eqs. (3)-(7) for calculating, respectively. The kinetic parameters (E and A), probable kinetic model function and linear correlation coefficient (r) are presented in Table 3. We can see that their values of E and $\log A$ obtained by the five equations agree well with each other, especially to small heating rates, and the mean value is close to that obtained by Kissinger method and Ozawa method. So, we can conclude that the most probable kinetic model function of the first exothermic decomposition reaction of K(DNDZ) is classified as $f(\alpha) = 3(1-\alpha)[-\ln(1-\alpha)]^{\frac{2}{3}}$, Avrami-Erofeev equation (No. 11), and $G(\alpha) = [-\ln(1-\alpha)]^{\frac{1}{3}}$, according to the unanimity rule of calculation results to each model equation. So, the kinetic equation of the exothermic decomposition reaction can be described as [25]:

$$\frac{d\alpha}{dT} = \frac{10^{13.92}}{\beta} 3(1-\alpha)[-\ln(1-\alpha)]^{\frac{2}{3}}$$
$$\times \exp(-1.52 \times 10^5/RT) \tag{8}$$

Table 3. Calculated values of kinetic parameters of decomposition reaction for K(DNDZ).

β (K min^{-1})	Eq.	No.	E (kJ mol^{-1})	$\log A$ (A, s^{-1})	r
2.5	4	11	137.70	12.36	0.9982
	5	11	141.67	11.23	0.9983
	6	11	138.03	12.33	0.9984
	7	11	138.50	12.43	0.9983
	8	11	137.69	12.36	0.9982
5.0	4	11	137.15	12.32	0.9977
	5	11	141.19	11.20	0.9978
	6	11	137.61	12.31	0.9979
	7	11	138.11	12.41	0.9979
	8	11	137.15	12.32	0.9977
10.0	4	11	142.90	12.95	0.9979
	5	11	147.03	11.82	0.9980
	6	11	143.57	12.96	0.9981
	7	11	143.73	13.03	0.9981
	8	11	142.90	12.94	0.9979
20.0	4	11	149.27	13.60	0.9858
	5	11	153.47	12.46	0.9866
	6	11	150.14	13.64	0.9873
	7	11	149.94	13.66	0.9872
	8	11	149.27	13.60	0.9858
mean			142.85	12.60	

The values of T_{00}, T_{e0} and T_{p0} in the first exothermic decomposition stage corresponding to $\beta \to 0$ obtained by Eq. (9) are 178.36, 195.95 and 204.87 °C.[25]

$$T_{(0, e \text{ or } p)i} = T_{(00, e0 \text{ or } p0)i} + n\beta_i + m\beta_i^2 \quad i = 1\sim 4 \tag{9}$$

where n and m are coefficients.

The critical temperature of thermal explosion (T_b) obtained by Eq. (10) was 208.63 °C,[25, 31] which is lower than that of DNDZ as 261.04 °C.[19]

$$T_b = \frac{E_0 - \sqrt{E_0^2 - 4E_0 R T_{e0}}}{2R} \tag{10}$$

where E_0 is the apparent activation energy obtained by Ozawa's method.

Specific Heat Capacity of K(DNDZ). Figure 7 shows the determination results of K(DNDZ), using 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 K (DNDZ) is:

$$C_p(\text{J g}^{-1}\text{K}^{-1}) = -0.7957 + 9.4028 \times 10^{-3} T$$
$$-1.0679 \times 10^{-5} T^2 (283.0 \text{ K} < T < 353.0 \text{ K}) \tag{11}$$

The molar heat capacity of K(DNDZ) is 224.63 J mol^{-1} K^{-1} at 298.15 K. Although only 70 K range was taken in the determi-
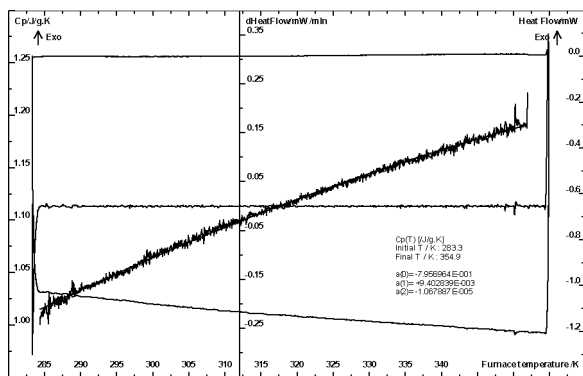
Figure 7. Determination results of the continuous specific heat capacity of K(DNDZ).

ning process. the specific heat capacity equation obtained is a stable and continuous equation. which can provide a reference and some help for the wide temperature applications.

Adiabatic Time-to-explosion of K(DNDZ). Energetic materials need a time from the beginning thermal decomposition to thermal explosion in the adiabatic condition. We called the time as the adiabatic time-to-explosion.[25,32-35] Ordinarily. the heating rate (dT/dt) and critical heating rate (dT/dt)$_{Tb}$ were used to evaluate the thermal stability of energetic materials in adiabatic decomposition process. However, we can calculate the adiabatic time-to-explosion (t) by the following Eqs.(12) - (13) when we have obtained a series of experimental data.[22,25,33-35] Thereby, as an important parameter. it is very easy and intuitive to directly evaluate the thermal stability of energetic materials according to the length of the adiabatic time-to-explosion.

$$C_p \frac{dT}{dt} = QA \exp(-E/RT) f(\alpha) \tag{12}$$

$$\alpha = \int_{T_0}^{T} \frac{C_p}{Q} dT \tag{13}$$

where C_p is the specific heat capacity (J mol^{-1} 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 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.

The combination of Eqs. (12) - (13) gives the following equation:

$$t = \int_0^t dt = \int_{T_i}^{T} \frac{C_p \exp(E/RT)}{QAf(\alpha)} dT \tag{14}$$

The limit of the temperature integration in Eq. (14) is from T_{00} to T_b. So. we can directly get t = 157.96 s from Eq. (14). according to the above experimental results. This is a short time. and can be proved credible according to the change of DSC curve in the first exothermic decomposition stage. The time is also shorter than that of DNDZ as a certain value between 263 ~ 290 s. In another aspect. it further proves the lower thermal stability of K(DNDZ) than that of DNDZ.

Conclusion

(1) The thermal decomposition reaction kinetics of K(DNDZ) was studied under the non-isothermal conditions by DSC and TG/DTG methods. and the kinetic equation of the exothermic obtained is $\frac{d\alpha}{dT} = \frac{10^{13.92}}{\beta} 3(1 - \alpha)[-\ln(1 - \alpha)]^{\frac{2}{3}} \exp(-1.52 \times 10^5 / RT)$. The critical temperature of thermal explosion is 208.63 °C.

(2) Specific heat capacity equation of K(DNDZ) is C_p(J g^{-1} K^{-1}) = $-0.7957 + 9.4028 \times 10^{-3} T - 1.0679 \times 10^{-5} \times T^2$ (283.0 K < T < 353.0 K). and the molar heat capacity is 224.63 J mol^{-1} K^{-1} at 298.15 K. The adiabatic time-to-explosion of K(DNDZ) was calculated to be 157.96 s. K(DNDZ) is easy to decompose at temperature above 180 °C.

Appendix A. Supplementary Material. Crystallo-graphic data for K(DNDZ) have been deposited in the Cambridge Crystallographic Data Center as supplementary publications (CCDC number 675360).

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