

# Synthesis and thermal behavior of a new high-energy organic potassium salt

## K(AHDNE)

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**Abstract** A new high-energy organic potassium salt, 1-amino-1-hydrazino-2,2-dinitroethylene potassium salt [K(AHDNE)], was synthesized by reacting of 1-amino-1-hydrazino-2,2-dinitroethylene (AHDNE) and potassium hydroxide in methanol aqueous solution. The thermal behavior of K(AHDNE) was studied using DSC and TG/DTG methods and can be divided into three obvious exothermic decomposition processes. The decomposition enthalpy, apparent activation energy and pre-exponential factor of the first decomposition process were  $-2662.5 \text{ J g}^{-1}$ ,  $185.2 \text{ kJ mol}^{-1}$  and  $10^{19.63} \text{ s}^{-1}$ , respectively. The critical temperature of thermal explosion of K(AHDNE) is  $171.38 \text{ }^\circ\text{C}$ . The specific heat capacity of K(AHDNE) was determined using a micro-DSC method, and the molar heat capacity is  $208.57 \text{ J mol}^{-1} \text{ K}^{-1}$  at  $298.15 \text{ K}$ . Adiabatic time-to-explosion of K(AHDNE) was also calculated. K(AHDNE) presents higher thermal stability than AHDNE.

**Keywords** 1,1-Diamino-2,2-dinitroethylene (FOX-7) ·  
1-Amino-1-hydrazino-2,2-dinitroethylene (AHDNE) ·  
Potassium salt · Synthesis · Thermal behavior

## 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 [2–9], mechanism [2–4], molecule structure [10, 11], thermal behavior [12–20], explosive performance [21] and application of FOX-7 [22–27].

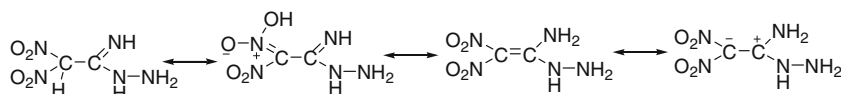
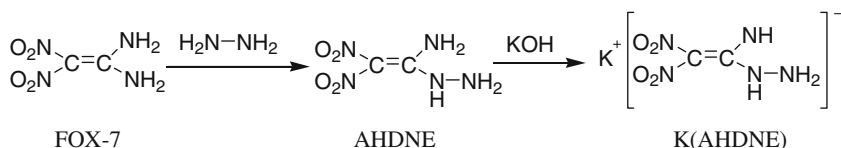
“Push–pull” nitro-enamine is a kind of compound with special construction [28], which possesses a highly polarized carbon–carbon double bond with positive and negative charges being stabilized by the amino group and nitro group, respectively, and exists in manifold tautomers and resonances [2, 5]. FOX-7 is a representative “push–pull” nitro-enamine compound, presents certain acidic properties and can react with some nucleophiles to synthesize new high-energy derivatives [2, 5, 7]. 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 [29–36].

We prepared a derivative of FOX-7, 1-amino-1-hydrazino-2,2-dinitroethylene (AHDNE), and found that 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) [30, 31]. It can also react with strong alkalis (KOH), and we have used it to prepare a new high-energy organic potassium salt, 1-amino-1-hydrazino-2,2-dinitroethylene potassium salt K(AHDNE) (Scheme 2), which will be used as flame suppressor in solid propellant to substitute inorganic potassium salt (KCl,  $\text{K}_2\text{SO}_4$ ,  $\text{KNO}_3$  and  $\text{K}_3\text{AlF}_6$ ) to generate much more energy and clean gas. Furthermore,

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**Scheme 1** Tautomers and resonances of AHNDE**Scheme 2** Synthesis of K(AHDNE)

K(AHDNE) can raise the combustion rate of propellant, according to its intense thermal decomposition.

In this paper, we reported the synthesis of K(AHDNE), studied its thermal behavior under non-isothermal conditions by DSC, TG/DTG methods, determined specific heat capacity using a micro-DSC method and calculated adiabatic time-to-explosion for further estimating the thermal stability of K(AHDNE).

## Experimental section

### Sample

AHDNE was prepared according to [30, 31].

K(AHDNE) was prepared as follows: AHDNE (0.01 mol, 1.63 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, 40 mL of methanol was also added drop wise, and the resulting mixture was slowly cooled to 0 °C. Many brown sediments of K(AHDNE) were formed, which were filtered, washed with methanol and dried under vacuum, yielding 1.24 g (62%). Anal. Calcd. (%) for  $C_2H_4N_5O_4K$ : C 11.94, H 2.00, N 34.81; found: C 11.82, H 2.15, N 33.98. IR (KBr): 3434 ( $\nu_{N-H}^{as}$ ), 3343 ( $\nu_{N-H}^s$ ), 3104, 1658 ( $\nu_{C=C}$ ), 1581 ( $\nu_{NO_2}^{as}$ ), 1489, 1388 ( $\nu_{NO_2}^s$ ), 1329, 1246, 1115 ( $\nu_{C-NH_2}$ ), 885 ( $\nu_{C-NO_2}$ )  $cm^{-1}$ .

### Experimental equipments and conditions

The DSC experiments for K(AHDNE) 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 0.6 mg. The heating rates used were 2.5, 5.0, 7.5, 10.0 and 20.0  $^{\circ}C\ min^{-1}$  from ambient temperature to 500.0 °C.

The TG/DTG experiment for K(AHDNE) 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 0.6345 mg. The heating rate

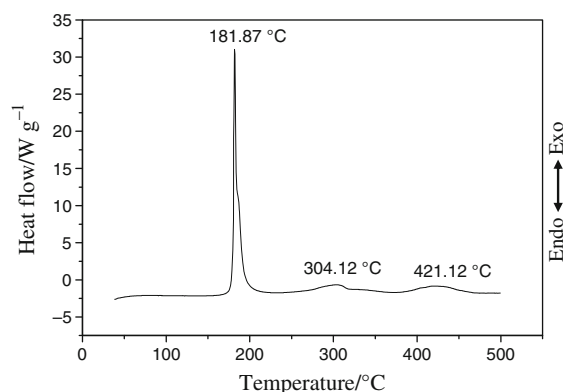
used was 10.0  $^{\circ}C\ min^{-1}$  from ambient temperature to 500.0 °C.

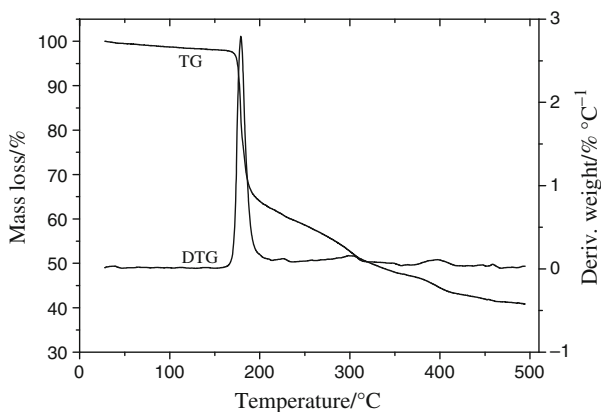
The specific heat capacity ( $C_p$ ) of K(AHDNE) was determined using a Micro-DSCIII apparatus (SETARAM, France). The amount of used sample was 309.18 mg. The heating rate used was 0.15  $^{\circ}C\ min^{-1}$  ( $2.5 \times 10^{-3}\ K\ s^{-1}$ ) from 10.0 to 80.0 °C.

## Results and discussion

### Thermal behavior

The typical DSC and TG/DTG curves (Figs. 1, 2) indicate that the thermal behavior of K(AHDNE) can be divided into three obvious exothermic decomposition stages. The first stage is an intense decomposition, occurs at 160–230 °C with a mass loss of about 39%, and the extrapolated onset temperature, peak temperature and decomposition enthalpy are 179.80 °C, 181.87 °C and  $-2662.5\ J\ g^{-1}$  at the heating rate of 10.0  $^{\circ}C\ min^{-1}$ , respectively. The second stage occurs at 250–370 °C with a mass loss of about 13%, and the extrapolated onset temperature, peak temperature and enthalpy are 264.91 °C, 304.12 °C and  $-558.9\ J\ g^{-1}$  at the heating rate of 10.0  $^{\circ}C\ min^{-1}$ , respectively. The third stage occurs at 380–470 °C with a mass loss of about 7%, and the

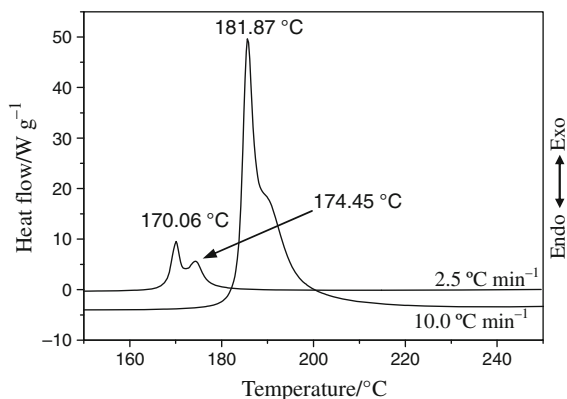
**Fig. 1** DSC curve of K(AHDNE) at a heating rate of 10.0  $^{\circ}C\ min^{-1}$



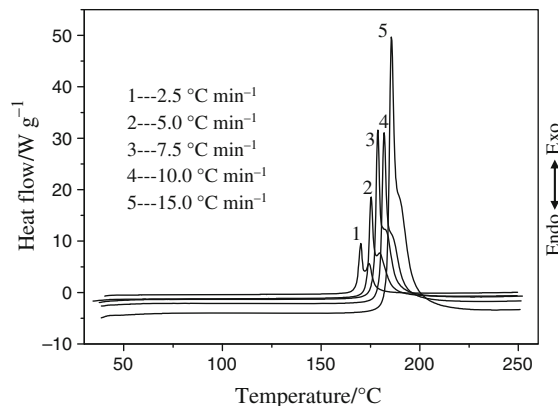
**Fig. 2** TG/DTG curves of K(AHDNE) at a heating rate of 10.0 °C min<sup>-1</sup>

extrapolated onset temperature, peak temperature and enthalpy are 386.50 °C, 421.12 °C and -470.4 J g<sup>-1</sup> at the heating rate of 10.0 °C min<sup>-1</sup>, respectively. The final residua mass percent is about 41%. However, the first decomposition stage should be two continuous decomposition processes, and the peak temperatures are 170.06 and 174.45 °C at the heating rate of 2.5 °C min<sup>-1</sup>, respectively. But, the two continuous decomposition processes easily become a decomposition process with the addition of heating rate (Fig. 3). All are different from that of AHDNE whose thermal behavior only presents two continuous decomposition processes, and the peak temperatures are 112.95 and 133.73 °C at the heating rate of 5.0 °C min<sup>-1</sup> [30], respectively. K(AHDNE) has higher thermal stability than AHDNE.

In order to obtain the kinetic parameters (the apparent activation energy (*E*) and pre-exponential constant (*A*)) of the first exothermic decomposition process for K(AHDNE), a multiple heating method (Kissinger method [37] and Ozawa method [38]) was employed (Fig. 4). The Kissinger and Ozawa equations are as follows:



**Fig. 3** DSC curves of K(AHDNE) at a heating rates of 2.5 and 10.0 °C min<sup>-1</sup>



**Fig. 4** DSC curves of K(AHDNE) at various heating rates

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

$$\log \beta + \frac{0.4567E}{RT_p} = C \tag{2}$$

where *T<sub>p</sub>* is the peak temperature (K), *β* is the linear heating rate (K min<sup>-1</sup>), *E* is the apparent activation energy (kJ mol<sup>-1</sup>), *A* is the pre-exponential constant (s<sup>-1</sup>), *R* is the gas constant (J mol<sup>-1</sup> K<sup>-1</sup>) and *C* is a constant.

The measured values of the beginning temperature (*T<sub>0</sub>*), extrapolated onset temperature (*T<sub>e</sub>*), peak temperature (*T<sub>p</sub>*) and decomposition enthalpy (*ΔH<sub>d</sub>*) of the first exothermic decomposition at different heating rates were listed in Table 1. The values of *T<sub>00</sub>*, *T<sub>e0</sub>* and *T<sub>p0</sub>* in the stage corresponding to *β* → 0 obtained by Eq. 3 were also listed in Table 1 [39].

$$T_{(0, \text{corp})i} = T_{(00, \text{e0orp}0)} + n\beta_i + m\beta_i^2 \quad i = 1 - 4 \tag{3}$$

where *n* and *m* are coefficients.

The above-mentioned values (*E* and *A*) obtained by Kissinger method and Ozawa method and their linear correlation coefficients (*r*) were listed in Table 2. We can see that the apparent activation energy obtained by Kissinger method agrees well with that obtained by Ozawa method, and the linear correlation coefficients are all very close to 1. So, the result is credible. Moreover, the apparent activation energy is lower, indicating that K(AHDNE) is easy to decompose at temperature above 150 °C.

*T* versus *α* (the conversion degree) curves at different heating rates were shown in Fig. 5. By substituting corresponding data (*β<sub>i</sub>*, *T<sub>i</sub>* and *α<sub>i</sub>*, *i* = 1, 2, 3, ...) into Eq. 2, the values of apparent activation energy for any given value of conversion degree were obtained and shown in Fig. 6. We can see that the values of the apparent activation energy to the equal conversion degree steadily distribute from 165 to 182 kJ mol<sup>-1</sup> in the range of 0.05 to 0.85, and the average value of apparent activation energy is 177.9 kJ mol<sup>-1</sup>. It is

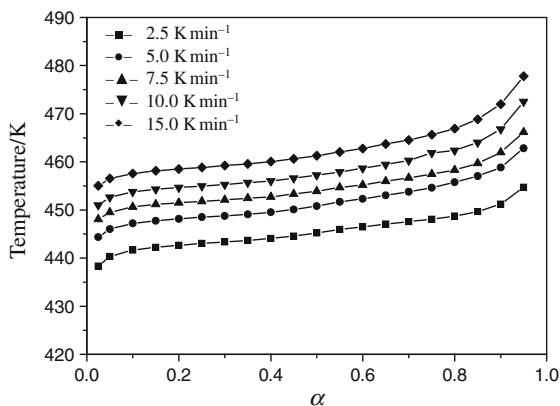
**Table 1** The values of  $T_0$ ,  $T_c$ ,  $T_p$ ,  $\Delta H_d$ ,  $T_{00}$ ,  $T_{e0}$  and  $T_{p0}$  of the first exothermic decomposition stages for K(AHDNE) determined from the DSC curves at various heating rates ( $\beta$ )

$\beta/^\circ\text{C min}^{-1}$	$T_0/^\circ\text{C}$	$T_c/^\circ\text{C}$	$T_p/^\circ\text{C}$	$\Delta H_d/\text{J g}^{-1}$	$T_{00}/^\circ\text{C}$	$T_{e0}/^\circ\text{C}$	$T_{p0}/^\circ\text{C}$
2.5	154.31	167.98	170.06	$-2662.5 \pm 95.4$	147.53	162.46	164.61
5.0	161.16	173.42	175.40				
7.5	165.81	176.89	178.81				
10.0	167.37	179.80	181.87				
15.0	171.11	183.50	185.61				

**Table 2** The kinetic parameters obtained by the data in Table 1

$E_k/$ $\text{kJ mol}^{-1}$	$\text{Log}(A)/$ $\text{s}^{-1}$	$r_k$	$E_o/$ $\text{kJ mol}^{-1}$	$r_o$	$\bar{E}/$ $\text{kJ mol}^{-1}$
186.2	19.63	0.9985	184.2	0.9986	185.2

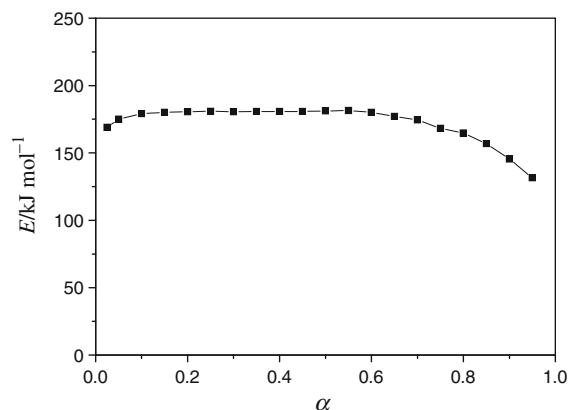
Subscript k, data obtained by Kissinger method; subscript o, data obtained by Ozawa method

**Fig. 5**  $T$  versus  $\alpha$  curves for the decomposition reaction of K(AHDNE) at different heating rates

in agreement with that obtained by Kissinger method and Ozawa method from only peak temperature values, which also indicates that the result is credible. In addition, the values of apparent activation energy become less at the conversion degree above 0.65. The reason for the result should be that the first decomposition of K(AHDNE) consists of two decomposition processes.

The entropy of activation ( $\Delta S^\ddagger$ ), enthalpy of activation ( $\Delta H^\ddagger$ ) and free energy of activation ( $\Delta G^\ddagger$ ) of the first thermal decomposition process corresponding to  $T = T_{p0}$ ,  $A = A_k$  and  $E = E_k$  obtained by Eqs. 4–5 taken from [39] are  $127.7 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $186.2 \text{ kJ mol}^{-1}$  and  $130.3 \text{ kJ mol}^{-1}$ , respectively.

$$A = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (4)$$

**Fig. 6**  $E$  versus  $\alpha$  curve for the decomposition reaction of K(AHDNE) by Ozawa method

$$A \exp\left(-\frac{E}{RT}\right) = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (5)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (6)$$

where  $k_B$  is the Boltzmann constant, and  $h$  is the Plank constant.

#### Critical explosion temperature

The critical temperature of thermal explosion ( $T_b$ ) is an important parameter required to insure safe storage and process operations for the energetic materials and then to evaluate the thermal stability and can be obtained by Eq. 7 [39]. So, the critical temperature of thermal explosion ( $T_b$ ) of K(AHDNE) was  $171.38 \text{ }^\circ\text{C}$ , which is much higher than that of AHDNE as  $98.16 \text{ }^\circ\text{C}$  [30].

$$T_b = \frac{E_o - \sqrt{E_o^2 - 4E_o RT_{e0}}}{2R} \quad (7)$$

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

Specific heat capacity

Figure 7 shows the determination results of K(AHDNE), using a continuous specific heat capacity mode of Micro-DSCIII. In determined temperature range, specific heat capacity presents a good linear relationship with temperature. Specific heat capacity equation of K(AHDNE) is:

$$C_p (\text{J g}^{-1} \text{K}^{-1}) = 0.4278 + 2.0311 \times 10^{-3} T (283.0 < T < 353.0 \text{ K}) \quad (8)$$

The molar heat capacity of K(AHDNE) is 208.57 J mol<sup>-1</sup> K<sup>-1</sup> at 298.15 K. Although only 70 K range was taken in the determining process, the specific heat capacity equation is a stable and continuous equation, which can provide a reference and some help for the wide temperature applications.

Thermodynamic properties

The enthalpy changes, entropy changes and Gibbs free energy changes in K(AHDNE) were calculated by Eqs. 9–11 at 283–353 K, taking 298.15 K as the benchmark. The results were listed in Table 3.

$$H_T - H_{298.15} = \int_{298.15}^T C_p dT \quad (9)$$

$$S_T - S_{298.15} = \int_{298.15}^T C_p \cdot T^{-1} dT \quad (10)$$

$$G_T - G_{298.15} = \int_{298.15}^T C_p dT - T \int_{298.15}^T C_p \cdot T^{-1} dT \quad (11)$$

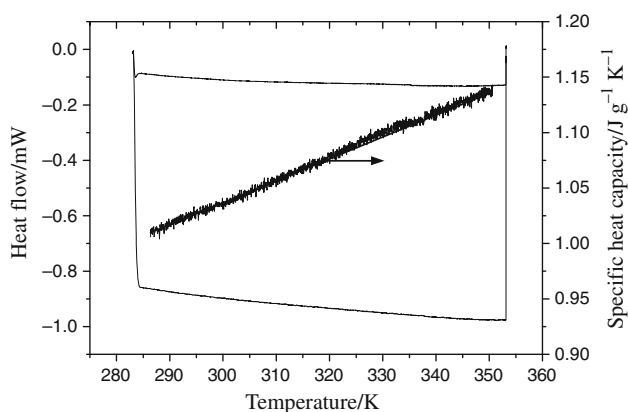


Fig. 7 Determination results of the continuous specific heat capacity of K(AHDNE)

Table 3 Thermodynamic functions of K(AHDNE)

Temperature/ K	$H_T - H_{298.15}/$ kJ mol <sup>-1</sup>	$S_T - S_{298.15}/$ J mol <sup>-1</sup> K <sup>-1</sup>	$G_T - G_{298.15}/$ kJ mol <sup>-1</sup>
283.0	-3.1030	-10.6799	-0.0806
293.0	-1.0653	-3.6043	-0.0093
303.0	1.0132	3.3709	-0.0082
313.0	3.1326	10.2523	-0.0764
323.0	5.2929	17.0458	-0.2129
333.0	7.4940	23.7568	-0.4170
343.0	9.7360	30.3901	-0.6878
353.0	12.0188	36.9502	-1.0246

Estimation of adiabatic time-to-explosion

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 [31, 39–45]. Ordinarily, the heating rate (dT/dt) and critical heating rate (dT/dt)<sub>T<sub>b</sub></sub> were used to evaluate the thermal stability of energetic materials in adiabatic decomposition process. However, the adiabatic time-to-explosion (t) can be calculated by the following Eqs. 12–13 [31, 39, 40, 42–45], after obtaining a series of experimental data. Thereby, as an important parameter, it is easy to directly evaluate the thermal stability of energetic materials according to the length of the adiabatic time-to-explosion.

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

$$\alpha = \int_{T_0}^T \frac{C_p}{Q} dT \quad (13)$$

where C<sub>p</sub> is the specific heat capacity (J mol<sup>-1</sup> K<sup>-1</sup>), T is the absolute temperature (K), t is the adiabatic time-to-explosion (s), Q is the exothermic values (J mol<sup>-1</sup>), A is the pre-exponential factor (s<sup>-1</sup>), E is the apparent activation energy of the thermal decomposition reaction (J mol<sup>-1</sup>), R is the gas constant (J mol<sup>-1</sup> K<sup>-1</sup>), f(α) is the most probable kinetic model function and α is the conversion degree.

According to the above determining results of specific heat capacity, we use:

$$C_p = a + bT \quad (14)$$

where a and b are coefficients.

The combination of Eqs. 12–14 gives the following adiabatic time-to-explosion equation:

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

$$= \frac{1}{QA} \int_{T_0}^T \frac{(a + bT) \exp(E/RT)}{f(\alpha)} dT \quad (16)$$

The limit of the temperature integral in Eq. 16 is from  $T_{00}$  to  $T_b$ .

In fact, the conversion degree ( $\alpha$ ) of energetic materials from the beginning thermal decomposition to thermal explosion in the adiabatic conditions is very small, and the most probable kinetic model function [ $f(\alpha)$ ] at the process is very difficult to be got. So, we separately used Power-low model (Eq. 15), Reaction-order model (Eq. 16) and Avrami–Erofeev model (Eq. 17) to estimate the adiabatic time-to-explosion and supposed different rate orders ( $n$ ) [39, 46]. The calculation results were listed in Table 4.

$$f(\alpha) = n\alpha^{(n-1)/n} \quad (15)$$

$$f(\alpha) = (1 - \alpha)^n \quad (16)$$

$$f(\alpha) = n(1 - \alpha)[-\ln(1 - \alpha)]^{(n-1)/n} \quad (17)$$

From Table 4, we can see that the calculation results exist in some deviation and the decomposition model has big influence on the adiabatic time-to-explosion. From the whole results, we think the adiabatic time-to-explosion of K(AHDNE) should be a certain value between 50 and 90 s. It is a relatively short time and can be proved credible according to the intense change of DSC curves in the exothermic decomposition.

**Table 4** The calculation results of adiabatic time-to-explosion

Equation	Rate order	Model	Time/s
Eq. 15	$n = 1$	$f(\alpha) = 1$	11.59
	$n = 2$	$f(\alpha) = 2\alpha^{1/2}$	53.55
	$n = 3$	$f(\alpha) = 3\alpha^{2/3}$	74.93
	$n = 4$	$f(\alpha) = 4\alpha^{3/4}$	81.41
Eq. 16	$n = 0$	$f(\alpha) = 1$	11.59
	$n = 1$	$f(\alpha) = 1 - \alpha$	11.72
	$n = 2$	$f(\alpha) = (1 - \alpha)^2$	11.86
Eq. 17	$n = 1$	$f(\alpha) = 1 - \alpha$	11.72
	$n = 2$	$f(\alpha) = 2(1 - \alpha)[-\ln(1 - \alpha)]^{1/2}$	54.03
	$n = 3$	$f(\alpha) = 3(1 - \alpha)[-\ln(1 - \alpha)]^{2/3}$	75.52
	$n = 4$	$f(\alpha) = 4(1 - \alpha)[-\ln(1 - \alpha)]^{3/4}$	82.01

## Conclusions

K(AHDNE) was synthesized by reacting of AHDNE and potassium hydroxide in methanol aqueous solution. The thermal behavior of K(AHDNE) can be divided into three obvious exothermic decomposition processes. The decomposition enthalpy, apparent activation energy and pre-exponential factor of the first decomposition process were  $-2662.5 \text{ J g}^{-1}$ ,  $185.2 \text{ kJ mol}^{-1}$  and  $10^{19.63} \text{ s}^{-1}$ , respectively. The critical temperature of thermal explosion is  $171.38 \text{ }^\circ\text{C}$ . K(AHDNE) is easy to decompose at temperature above  $150 \text{ }^\circ\text{C}$ .

Specific heat capacity equation of K(AHDNE) is  $C_p(\text{J g}^{-1} \text{ K}^{-1}) = 0.4278 + 2.0311 \times 10^{-3}T$  ( $283.0 < T < 353.0 \text{ K}$ ), and the molar heat capacity is  $208.57 \text{ J mol}^{-1} \text{ K}^{-1}$  at  $298.15 \text{ K}$ . The adiabatic time-to-explosion of K(AHDNE) was also calculated. K(AHDNE) has higher thermal stability than AHDNE.

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