J Therm Anal Calorim (2011) 105:293–300
DOI 10.1007/s10973-010-1244-4

Synthesis and thermal behavior of 4,5-dihydroxyl-2-(dinitromethylene)-imidazolidine (DDNI)

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Received: 15 November 2010 / Accepted: 2 December 2010 / Published online: 24 December 2010

Abstract A novel energetic material, 4,5-dihydroxyl-2-(dinitromethylene)-imidazolidine (DDNI), was synthesized by the reaction of FOX-7 and glyoxal in water at 70 °C. Thermal behavior of DDNI was studied with DSC and TG-DTG methods, and presents only an intense exothermic decomposition process. The apparent activation energy and pre-exponential factor of the decomposition reaction were 286.0 kJ mol^{-1} and $10^{31.16}$ s^{-1}, respectively. The critical temperature of thermal explosion of DDNI is 183.78 °C. Specific heat capacity of DDNI was studied with micro-DSC method and theoretical calculation method, and the molar heat capacity is 217.76 J mol^{-1} K^{-1} at 298.15 K. The adiabatic time-to-explosion was also calculated to be a certain value between 14.54 and 16.34 s. DDNI presents lower thermal stability, for its two ortho-hydroxyl groups, and its thermal decomposition process becomes quite intense.

Keywords 4,5-Dihydroxyl-2-(dinitromethylene)-imidazolidine (DDNI) · 1,1-Diamino-2,2-dinitroethylene (FOX-7) · 2-(Dinitromethylene)-1,3-diazacyclopentane (DNDZ) · Synthesis · Thermal behavior

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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 and has been considered as an important preferred component of propellant in future. Many researches have been carried out on the synthesis [2–9], mechanism [2–4], molecule structure [10, 11], theoretical calculation [12–19], thermal behavior [20–22], explosive performance [23], and application of FOX-7 [24–27].

FOX-7 is a nitro-enamine belonging to the group of compounds known as “push–pull” alkenes [28], and possesses a highly polarized carbon–carbon double bond with positive and negative charges being stabilized by the two amino groups and the two nitro groups, respectively. So, FOX-7 can react with some nucleophiles to substitute one or two amino groups, and then synthesize new high-energy compounds [2, 5–7]. Our interest mainly consisted in modifying molecular structure of FOX-7 in order to obtain some new high-energy compounds and study their structure–property relationship. We have prepared a series of mucleophilic substitution derivatives of FOX-7 [29–35].

However, we found that FOX-7 can also react with some strong electrophilic reagents to obtain another kind of energetic derivatives of FOX-7, because of the lone pair electrons of two amino nitrogen atoms. We have papered 4,5-dihydroxyl-2-(dinitromethylene)-imidazolidine (DDNI), with the reaction of FOX-7 and glyoxal, and found that DDNI is a good intermediate, for its two ortho-hydroxyl groups, to synthesize other new valuable energetic compounds.

In this article, we mainly reported the preparation and thermal behavior of DDNI, determined its specific heat capacity with micro-DSC method and theoretical calculation method, calculated its adiabatic time-to-explosion for further estimating thermal stability and compared the above results with that of FOX-7 and 2-(dinitromethylene)-1,3-diazacyclopentane (DNDZ) (Scheme 1).

Experimental section

Sample

4,5-Dihydroxyl-2-(dinitromethylene)-imidazolidine used in this research was prepared according to the following method: Glyoxal (0.04 mol, 2.32 g) was suspended in 20 mL of water and to it a solution of KOH (1.12 g in 5 mL of water) was added dropwise until glyoxal was neutralized to pH 7–8. After that, FOX-7 (0.02 mol, 2.96 g) was also added. The mixture was heated to 70 °C. After reaction for 5 h, the resulting mixture was slowly cooled to ambient temperature. The faint yellow precipitate of DDNI was filtered, washed with water and ethanol, and dried under vacuum, yielding 2.33 g (78%). Anal. Calcd.(%) for $C_4H_6N_4O_6$: C 23.31, H 2.93, N 26.71; found: C 23.22, H 2.75, N 26.59. IR (KBr) v: 3431, 3363, 3308, 1563, 1519, 1448, 1349, 1189, 1048, 929, 815 cm^{-1}.

Single crystal suitable for X-ray measurement was obtained by slow evaporation of DDNI methanol solution. Crystal data for DDNI are monoclinic, space group $P2_1/c$, $a = 11.560(2)$ Å, $b = 7.5553(15)$ Å, $c = 17.164(3)$ Å, $\beta = 98.587°$, $F(000) = 848$, $V = 1482.3(5)$ Å^3, $Z = 8$, $\mu = 0.145$ mm^{-1}, $D_c = 1.847$ g cm^{-3}, $R_1 = 0.0454$ and $wR_2 = 0.1716$. Crystallographic data for DDNI have been deposited in the Cambridge Crystallographic Data Center as supplementary publications (CCDC number 776466). The molecular structure is shown in Fig. 1.

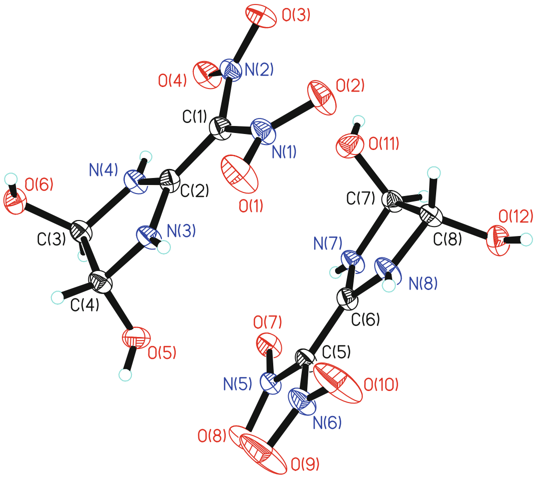


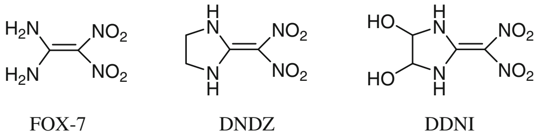
Fig. 1 Molecular structure of DDNI in a min-asymmetry unit

Experimental equipments and conditions

The DSC experiments for DDNI 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 1.5 mg. The heating rates used were 2.5, 5.0, 10.0 and 15.0 °C min^{-1} from ambient temperature to 350.0 °C, respectively.

The TG experiment for DDNI 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 1.5 mg. The heating rate used was 5.0 °C min^{-1} from ambient temperature to 500.0 °C.

The specific heat capacity (C_p) of DDNI was determined using a micro-DSC III apparatus (SETARAM, France), the amounts of used samples was 372.95 mg. The heating rate used was 0.15 °C min^{-1} (2.5×10^{-3} K s^{-1}) from 10.0 to 80.0 °C.



Scheme 1 Structural formulas of FOX-7, DNDZ, and DDNI

Theoretical calculation of specific heat capacity

According to the crystal structure, a single molecule or a min-asymmetry unit of DDNI was selected as the initial structure, while DFT-B3LYP method with 6-311+G or 6-311++G* basis set in Gaussian 03 package [36] was used to optimize the structure and compute frequencies at different temperatures. We can get a series of thermodynamic data of DDNI based on the statistic thermodynamic theory. At the same time, vibration analysis showed that the optimized structure is in accord with the minimum points on the potential energy planes, which means no virtual frequencies, proving that the optimized structure is stable and our calculation results is reliable. All the convergent precisions are the system default values, and all the calculations were carried out on the Lenovo T280 server.

Results and discussion

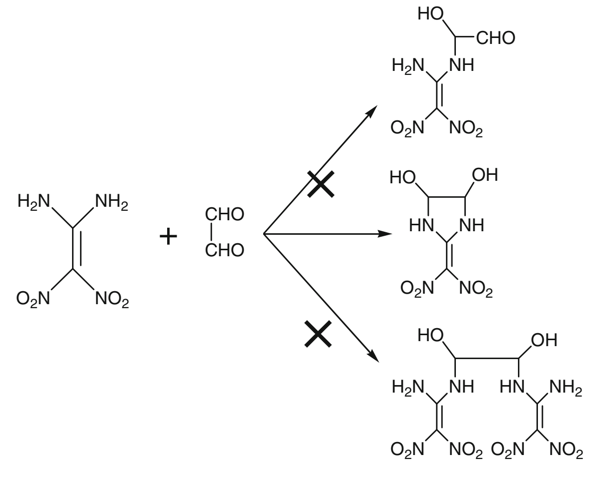
Synthesis

In the synthesis of DDNI, pH value of reacting solution is the most important factor and must be controlled strictly in 7–8. The pH value greater than 8 can result in a sharp decrease in the yield. But, if the pH value was not adjusted with strong base (KOH), the reaction cannot occur for the inert reactivity of FOX-7 in acid solution.

In addition, the five-number ring has lower energy and is more stable than corresponding long chain compounds, so DDNI has stronger advantage in competition to be synthesized than other possible products in given reacting conditions. We synthesize only one product DDNI, and did not synthesize another two theoretically possible products, despite in using different molar proportions of FOX-7 and glyoxal in our experiments (Scheme 2).

Thermal behavior

From the typical DSC and TG-DTG curves of DDNI (Figs. 2, 3), we can see that the thermal behavior of DDNI has only one intense exothermic decomposition process with a mass loss of about 59%. The extrapolated onset temperature, peak temperature and enthalpy of the exothermic decomposition reaction are 184.21, 184.33, and 940.1 J g^{-1} at the heating rate of 5.0 °C min^{-1}, respectively. The final residua mass percent is about 24% at 500 °C. All are quiet different from that of FOX-7 whose thermal behavior presents two obvious exothermic decomposition processes, and the peak temperatures of the two processes are 230.1 and 295.5 °C at the heating rate of 10.0 °C min^{-1} [20, 21]. After close-ring reacting with glyoxal, the result compound becomes easy to decompose and presents lower thermal stability than FOX-7. Comparing the result with that of another nucleophilic close-ring derivative of FOX-7, 2-(dinitromethylene)-1,3-diazacyclopentane (DNDZ) [29], we can see that they all have only one intense exothermic decomposition process, but DNDZ has much higher thermal decomposition temperature and decomposition heat, whose extrapolated onset temperature and peak temperature of thermal decomposition are 254.56 and 262.92 °C at the heating rate of 5.0 °C min^{-1}, respectively. Two ortho-hydroxyl groups should be the reason for DDNI having lower thermal decomposition temperature and decomposition heat than FOX-7 and DNDZ.



Scheme 2 Synthetic route

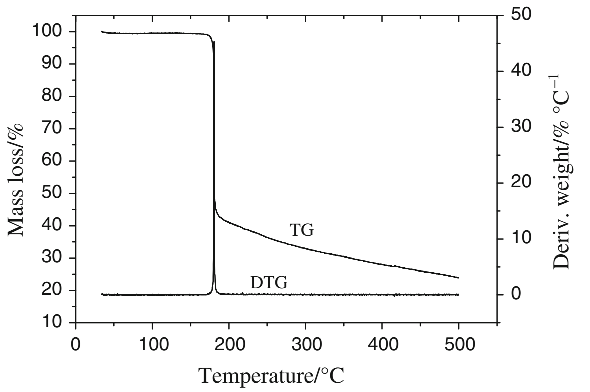


Fig. 3 TG-DTG curves of DDNI at a heating rate of 5.0 °C min^{-1}

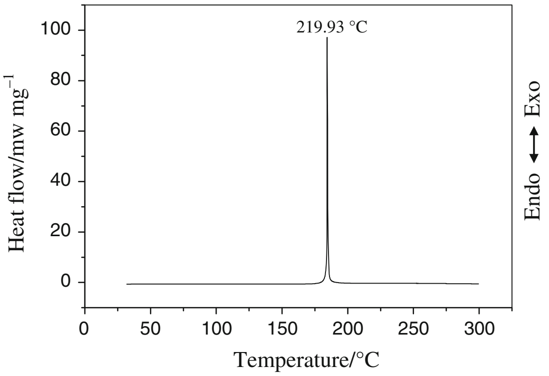


Fig. 2 DSC curve of DDNI at a heating rate of 5.0 °C min^{-1}

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

$$\ln\left(\frac{\beta}{T_{\mathrm{p}}^{2}}\right) = \ln\frac{AR}{E} - \frac{E}{R}\frac{1}{T_{\mathrm{p}}} \quad (1)$$

$$\log\beta + \frac{0.4567E}{RT_{\mathrm{p}}} = C \quad (2)$$

where T_{p} is the peak temperature (K), β is the linear heating rate (K 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 decomposition reaction for DDNI were listed in Table 1. The values of T_{00}, T_{e0}, and

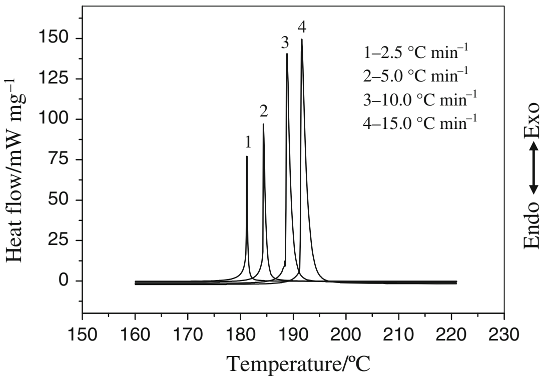


Fig. 4 DSC curves of DDNI at various heating rates

T_{p0} corresponding to $\beta \to 0$ obtained by Eq. 3 were also listed in Table 1 [39].

$$T_{(0,\mathrm{e}\ \mathrm{or}\ \mathrm{p})i} = T_{(00,\ \mathrm{e}0\ \mathrm{or}\ \mathrm{p}0)} + n\beta_i + m\beta_i^2, \quad i = 1 - 4 \tag{3}$$

where n and m are coefficients.

The kinetic parameters obtained by the data in Table 1 were listed in Table 2. We can see that the apparent activation energies (E) obtained by Kissinger method agrees well with that obtained by Ozawa method. Moreover, the linear correlation coefficients (r) are all very close to 1. So, the result is credible.

The critical temperatures of thermal explosion (T_b) of DDNI obtained by Eq. 4 was 183.78 °C [39], which is lower than that of FOX-7 and DNDZ as 207.08 and 261.04 °C [20, 29], indicating that DDNI presents lower thermal stability than FOX-7 and DNDZ.

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

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

The entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$) and free energy of activation ($\Delta G^{\neq}$) of the thermal decomposition process corresponding to $T = T_{p0}$, $A = A_k$, and $E = E_k$ obtained by Eqs. 5–7 taken from Ref. [39] for DDNI are 348.2 J mol^{-1} K^{-1}, 289.5 and 132.5 kJ mol^{-1}, respectively.

Table 2 The kinetic parameters obtained by the data in Table 1[a]

E_k/ kJ mol^{-1}	Log(A)/ s^{-1}	r_k	E_O/ kJ mol^{-1}	r_O	$\bar{E}$/kJ mol^{-1}
289.5	31.16	0.9959	282.5	0.9962	286.0

[a] Subscript k, data obtained by Kissinger's method; subscript o, data obtained by Ozawa's method

$$A = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \tag{5}$$

$$A \exp\left(-\frac{E}{RT}\right) = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \tag{6}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{7}$$

where k_B is the Boltzman constant, and h is the Plank constant.

Specific heat capacity

Figure 5 shows the determination result of DDNI, 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 DDNI is:

$$C_p\ (\mathrm{J g^{-1} K^{-1}}) = 17.9833 \times 10^{-3} + 3.4828 \times 10^{-3}\, T\ (283.0\,\mathrm{K} < T < 353.0\,\mathrm{K}) \tag{8}$$

The molar heat capacity of DDNI is 217.76 J mol^{-1} K^{-1} at 298.15 K.

Comparing the result with the specific heat capacities of FOX-7 and DNDZ (Fig. 6), we can see the specific heat capacity of FOX-7 is equivalent to that of DNDZ, but they are all greater than that of DDNI. The sequence for the three compounds in determined temperature range is: C_p(FOX-7) > C_p(DNDZ) > C_p(DDNI) [22, 40]. Only amino ring-closure hardly affects the specific heat capacity, but reincreasing two ortho-hydroxyl groups can lead to the obvious decline of specific heat capacity.

Table 3 shows the results of specific heat capacity by the theoretical calculation and experimental determination and their relative deviations at different temperatures. We can see that the calculation results by 6-311+G basis set are

Table 1 The values of T_0, T_e, T_p, ΔH_d, T_{00}, T_{e0}, and T_{p0} of the thermal decomposition by DSC curves at various heating rates (β)

β/°C min^{-1}	T_0/°C	T_e/°C	T_p/°C	ΔH_d/kJ mol^{-1}	T_{00}/°C	T_{e0}/°C	T_{p0}/°C
2.5	170.44	181.04	181.19	−193.8 ± 4.4	166.84	177.64	177.79
5.0	175.66	184.21	184.33				
10.0	179.45	188.55	188.81				
15.0	183.68	191.29	191.64				

greater than that by 6-311++G* basis set to a single molecule of DDNI, but the influence of basis set to calculation result of specific heat capacity is small. To a min-asymmetry unit (two molecules of DDNI), the calculation results are greater than that of a single molecule. However, all calculation results are less than the experimental results, and the relative deviations (the calculation results by 6-311+G for DDNI in a min-asymmetry unit and the experimental results) are from 1.46% to 6.67%. At the same time, we can see the relative deviations enlarge with the rising of temperature. The reason for the result is that only gas phase molecule was used in theoretical calculation process, which is clearly different from the actual solid phase molecule.

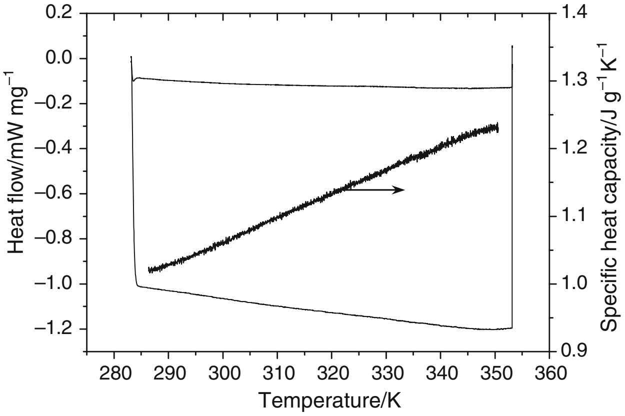


Fig. 5 Determination results of the continuous specific heat capacity of DDNI

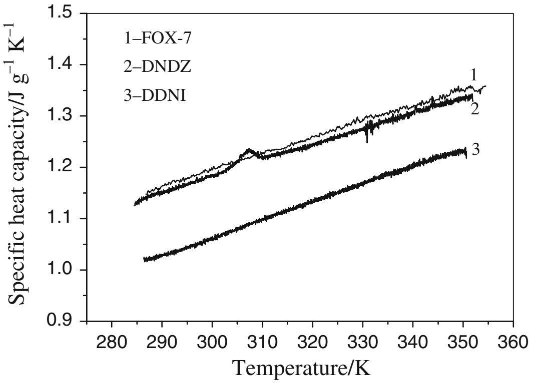


Fig. 6 Comparison of specific heat capacity of FOX-7, DNDZ, and DDNI

Thermodynamic properties

The enthalpy changes, entropy changes and Gibbs free energy changes of DDNI were calculated by Eqs. 9–11 at 283–353 K, taking 298.15 K as the benchmark. The results were listed in Table 4.

$$H_T - H_{298.15} = \int_{298.15}^{T} C_{\mathrm{p}} \mathrm{d}T \tag{9}$$

$$S_T - S_{298.15} = \int_{298.15}^{T} C_{\mathrm{p}} \cdot T^{-1} \mathrm{d}T \tag{10}$$

$$G_T - G_{298.15} = \int_{298.15}^{T} C_{\mathrm{p}} \mathrm{d}T - T \int_{298.15}^{T} C_{\mathrm{p}} \cdot T^{-1} \mathrm{d}T \tag{11}$$

The enthalpy (*H*) and entropy (*S*) of calculation by 6-311+G for DDNI in a min-asymmetry unit are 389.89 kJ mol^{-1} and 380.41 J mol^{-1} K^{-1} at 298.15 K, respectively. Corresponding enthalpy changes and entropy

Table 3 Results of specific heat capacity by the theoretical calculation and experimental determination and their relative deviation at different temperatures

Temperature/K	Heat capacity/J mol^{-1} K^{-1}				RD/%
	Theoretical calculation values			Experimental values	
	I	II	III		
283.0	194.96	193.49	203.86	206.87	1.46
293.0	200.20	199.24	209.19	214.05	2.27
298.15	202.87	201.83	211.97	217.76	2.66
303.0	205.37	204.25	214.54	221.23	3.02
313.0	210.29	208.89	219.81	228.41	3.77
323.0	215.54	214.11	224.70	235.59	4.62
333.0	220.35	218.87	229.89	242.77	5.31
343.0	225.38	223.70	234.91	249.95	6.02
353.0	230.23	228.39	239.98	257.13	6.67

I—obtained by 6-311+G for a single DDNI molecule, II—obtained by 6-311++G* for a single DDNI molecule, III—obtained by 6-311+G for DDNI in a min-asymmetry unit

Table 4 Thermodynamic function data of DDNI

Temperature/K	$H_T - H_{298.15}$/kJ mol^{-1}		$S_T - S_{298.15}$/J mol^{-1} K^{-1}		$G_T - G_{298.15}$/kJ mol^{-1}
	Experimental values	Theoretical calculation values	Experimental values	Theoretical calculation values	
283.0	−3.22	−3.02	−11.07	−10.32	−0.08
293.0	−1.11	−1.01	−3.76	−3.66	−0.01
303.0	1.06	0.99	3.54	3.48	−0.01
313.0	3.31	3.16	10.84	10.38	−0.08
323.0	5.63	5.34	18.14	17.22	−0.23
333.0	8.02	7.43	25.43	24.02	−0.44
343.0	10.49	9.72	32.72	30.89	−0.73
353.0	13.02	11.95	40.00	37.73	−1.10

changes at 283–353 K, taking 298.15 K as the benchmark, were also listed in Table 4. We can see the calculated results are all less than the experimental results and the deviations of the two results are very small, which is consistent with the results of specific heat capacity.

Estimation of adiabatic time-to-explosion

Energetic materials need a time from the beginning thermal decomposition to thermal explosion in adiabatic condition. We called the time as the adiabatic time-to-explosion [22, 39–46]. Ordinarily, we use heating rate ($\mathrm{d}T/\mathrm{d}t$) and critical heating rate $(\mathrm{d}T/\mathrm{d}t)_{T_\mathrm{b}}$ in thermal decomposition process to evaluate the thermal stability of energetic materials. However, we can calculate the adiabatic time-to-explosion (t) by the following Eqs. 12 and 13 [22, 39, 40, 42–46] when we have obtained a series of experimental data. Thereby, as an important parameter, it is easy and intuitionistic to evaluate the thermal stability of energetic materials according to the length of the adiabatic time-to-explosion.

$$C_\mathrm{p}\frac{\mathrm{d}T}{\mathrm{d}t} = QA\exp(-E/RT)f(\alpha) \tag{12}$$

$$\alpha = \int_{T_0}^{T} \frac{C_\mathrm{p}}{Q}\mathrm{d}T \tag{13}$$

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 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 fraction of conversion.

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

$$C_\mathrm{p} = a + bT \tag{14}$$

where a and b are coefficients.

In fact, the conversion degree (α) of energetic materials from the beginning thermal decomposition to thermal explosion in the adiabatic conditions is very small, the most probable kinetic model function [$f(\alpha)$] at this beginning decomposition process is unimportant and almost has no influence on the result of the estimation of the adiabatic time-to-explosion. So, we used Eq. 15 and supposed that the rate order of the mechanism function (n) of DDNI in the decomposition process equaled 0, 1, and 2 [22, 39, 42].

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

The combination of Eqs. 12–15 gives the following adiabatic time-to-explosion equation:

$$\begin{aligned} t &= \int_0^t \mathrm{d}t = \int_{T_0}^{T} \frac{C_\mathrm{p}\exp(E/RT)}{QAf(\alpha)}\,\mathrm{d}T \\ &= \frac{1}{QA}\int_{T_0}^{T} \frac{(a+bT)\exp(E/RT)}{(1-\alpha)^n}\,\mathrm{d}T \\ &= \frac{1}{QA\left\{1-\frac{1}{Q}\left[a(T_\mathrm{b}-T_{00})+\frac{b}{2}(T_\mathrm{b}^2-T_{00}^2)\right]\right\}^n} \\ &\quad \times \int_{T_0}^{T} (a+bT)\exp(E/RT)\,\mathrm{d}T \end{aligned} \tag{16}$$

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

We can directly get $t_0 = 14.54$ s, $t_1 = 15.41$ s, $t_2 = 16.34$ s from Eq. 16, according to the above obtained data. As a rule, the rate order (n) of energetic materials ranges from 0 to 2, so the adiabatic time-to-explosion should be a certain value between 14.54 and 16.34 s. It is a short time, and can be proved credible according to the intense change of DSC curves in the exothermic decomposition. The time is much shorter than that of FOX-7 and DNDZ as 78.94–88.93 and 263.94–289.58 s [22, 40], further indicating that DDNI has much lower thermal stability than FOX-7 and DNDZ.

Conclusions

4,5-Dihydroxyl-2-(dinitromethylene)-imidazolidine (DDNI) was synthesized by the reaction of FOX-7 and glyoxal. The thermal behavior of DDNI was studied with DSC and TG/DTG methods, and presents only one intense exothermic decomposition process. The apparent activation energy and pre-exponential factor of the decomposition reaction were obtained as 286.0 kJ mol^{-1} and $10^{31.16}$ s^{-1}, respectively. The critical temperature of thermal explosion of DDNI is 183.78 °C.

Specific heat capacity equation of DDNI is C_p (J g^{-1} K^{-1}) $= 17.9833 \times 10^{-3} + 3.4828 \times 10^{-3}$ T (283.0 K $< T <$ 353.0 K), and the molar heat capacity is 217.76 J mol^{-1} K^{-1} at 298.15 K. The adiabatic time-to-explosion was also calculated to be a certain value between 14.54 and 16.34 s. DDNI presents lower thermal stability, for its two ortho-hydroxyl groups, and its thermal decomposition process becomes quiet intense.

Acknowledgements This investigation received financial assistance from the National Natural Science Foundation of China (No. 20803058), Basal Science Foundation of National Defense (No. B0920110005), and Education Committee Foundation of Shaanxi Province (No. 2010JK881).

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