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Thermal behavior and thermal safety of 6b-nitrohexahydro-2H-1,3,5-trioxacyclopenta[cd]-pentalene-2,4,6-triyltrinitrate

Jiao-Qiang Zhang,  ^a Rui Liu, ^a Tie-Zheng Ji, ^a Jing-Chen Ren, ^b Qi Guo, ^b Bo-Zhou Wang^c and Rong-Zu Hu^c

6b-Nitrohexahydro-2H-1,3,5-trioxacyclopenta[cd]-pentalene-2,4,6-triyltrinitrate (NHTPN) is an energetic compound with interesting properties. Its thermal and kinetic behaviors were studied by differential scanning calorimetry (DSC), and its specific heat capacity (C_p) was determined by a continuous C_p mode of microcalorimetry (Micro-DSC III). In order to evaluate its thermal safety, the values (T_{e0} and T_{p0}) of T_e and T_p corresponding to $\beta \rightarrow 0$, critical temperature of thermal explosion (T_{be} and T_{bp}), adiabatic time-to-explosion ($t_{T_{ad}}$), 50% drop height (H_{50}) of impact sensitivity, critical temperature of hot-spot initiation (T_{cr}), thermal sensitivity probability density function [$S(T)$] vs. temperature (T) relation curves for NHTPN with radius of 1 m surrounded with ambient of 340 K, the peak temperature corresponding to the maximum value of $S(T)$ vs. T relation curve ($T_{S(T)_{max}}$), safety degree (SD) and critical ambient temperature (T_{acr}) of thermal explosion of NHTPN were calculated respectively, by means of the onset temperature (T_e) and maximum peak temperature (T_p) from the non-isothermal DSC curves of NHTPN at different heating rates (β), the apparent activation energy (E_a and E_0) and pre-exponential constant (A_K) of thermal decomposition reaction obtained by Kissinger's method and Ozawa's method, C_p , density (ρ) and thermal conductivity (λ), the decomposition heat (Q_d , taking half-explosion heat), Zhang–Hu–Xie–Li's formula, Smith's equation, Friedman's formula, Bruckman–Guillet's formula, Frank–Kamenetskii formula and Wang–Du's formulas.

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1 Introduction

Nitric acid esters have long been recognized as one class of useful and promising functional group in the design and synthesis of energetic plasticizer, such as 1,2,3-propanetriol trinitrate (nitroglycerin), nitrocellulose, and pentaerythritol tetranitrate (PETN), which are used in propellants, explosives, and pyrotechnics.^{1–5} 6b-Nitrohexahydro-2H-1,3,5-trioxacyclopenta[cd]-pentalene-2,4,6-triyltrinitrate (NHTPN) is a new explosive with interesting properties. Its density is higher than 1.8 g cm^{–3} because of its symmetrical molecular structure. The detonation velocity of NHTPN is up to 8.0 km s^{–1} at maximal working density. It melts at *ca.* 115 °C and begins to decompose at *ca.* 150 °C with a linear heating rate of 10 K min^{–1}. The apparent activation energy (E_a) of NHTPN is *ca.* 155 kJ mol^{–1}, which is close to that of conventional explosives. Its oxygen balance and oxygen quotient are –12.97% and 82.35%,

respectively. Moreover, NHTPN is an explosive sensitive to mechanical stimuli (2 J, 50 N).⁶

In this paper, using the original data of differential scanning calorimetry (DSC) and microcalorimetry, the self-accelerating decomposition temperature (T_{SADT}), the critical temperature of thermal explosion (T_b) and the adiabatic time-to-explosion ($t_{T_{ad}}$) were estimated. The 50% drop height of impact sensitivity (H_{50}), the critical temperature of hot-spot initiation caused by impact (T_{cr}), the safety degree (SD), the critical thermal explosion ambient temperature (T_{acr}) and thermal explosion probability (P_{TE}) were obtained. Thus the thermal safety of NHTPN was evaluated which is useful for the evaluation on the process of the explosion from the thermal decomposition.

2 Experimental

2.1 Materials

The title compound (NHTPN) (structure see Fig. 1) used in this work was prepared and purified according to the literature method.⁶ The sample was kept in a vacuum desiccators before use. The structure of NHTPN was characterized by ¹H and ¹³C NMR spectroscopy. ¹H NMR (CD₃OD, 500 MHz): δ = 5.72 ppm (s, 3H, H_{2a}, H_{4a}, H_{6a}); 6.70 ppm (s, 3H, H₂, H₄ and H₆). ¹³C

^aKey Laboratory of Space Applied Physics and Chemistry of Ministry of Education, Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an 710129, China. E-mail: zhangjq@nwpu.edu.cn; Tel: +86-29-88431616

^bXi'an Aerospace Chemical Propulsion Factory, Xi'an 710025, China

^cXi'an Modern Chemistry Institute, Xi'an, 710065, China



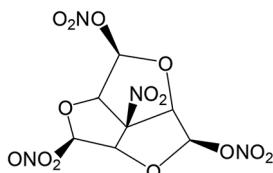


Fig. 1 Structure of NHTPN.

NMR (CD_3OD , 125 MHz): $\delta = 91.9$ ppm (C2a, C4a, C6a); 105.7 ppm (C6b); 107.6 ppm (C2, C4, C6).

2.2 Thermal decomposition conditions

The DSC experiments for the title compound were performed using a Model TA 910S differential scanning calorimeter. The heating rates used were 2, 5, 10, 15 and $20\text{ }^\circ\text{C min}^{-1}$ from ambient temperature to $500\text{ }^\circ\text{C}$ under a nitrogen atmosphere at a flow rate of 60 mL min^{-1} . DSC curves obtained under the same conditions overlapped with each other, indicating that the reproducibility of the tests was satisfactory.

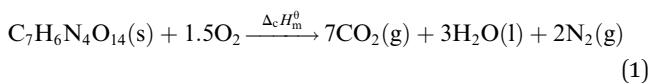
2.3 Determination of the specific heat capacity

The specific heat capacity of the title compound was determined by a continuous C_p mode within $283\text{--}353\text{ K}$ at a heating rate of 0.15 K min^{-1} on a Micro-DSC III apparatus (Seteram, France) with the sample mass of 450 mg. The Micro-calorimeter was calibrated with $\alpha\text{-Al}_2\text{O}_3$ (calcined), its math expression was $C_p/\text{J g}^{-1}\text{ K}^{-1} = 0.1839 + 1.9966 \times 10^{-3}T$ within $283\text{--}353\text{ K}$ and the standard molar heat capacity $C_{p,m}^\ominus$ ($\alpha\text{-Al}_2\text{O}_3$) at 298.15 K was determined as $79.44\text{ J mol}^{-1}\text{ K}^{-1}$ which is in an excellent agreement with the value of $79.02\text{ J mol}^{-1}\text{ K}^{-1}$ reported in the literature.⁷

3 Results and discussion

3.1 Standard enthalpy of combustion

The standard enthalpy of combustion of NHTPN, $\Delta_c H_m^\ominus$ (NHTPN, s, 298.15 K), is referred to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 100 kPa .



The standard enthalpy of combustion of NHTPN $\Delta_c H_m^\ominus$ is calculated by the following equations:

$$\Delta_c H_m^\ominus(\text{NHTPN, s, } 298.15\text{ K}) = \Delta_c U(\text{NHTPN, s, } 298.15\text{ K}) + \Delta n RT \quad (2)$$

$$\Delta n = n_{\text{g}}(\text{products}) - n_{\text{g}}(\text{reactants}) \quad (3)$$

where $\Delta_c U = -(Q_c) = -(2992.61 \pm 111.04)\text{ kJ mol}^{-1}$,⁶ n_{g} is the total amount in mole of gases present as products or as reactants, $\Delta n = 7 + 2 - 1.5 = 7.5$, $R = 8.314\text{ J K}^{-1}\text{ mol}^{-1}$, $T = 298.15\text{ K}$. The result is $-(2974.02 \pm 111.04)\text{ kJ mol}^{-1}$.

3.2 Standard enthalpy of formation

The standard enthalpy of formation of NHTPN, $\Delta_f H_m^\ominus$ (NHTPN, s, and 298.15 K), is calculated by Hess's law according to thermochemical eqn (4).

$$\begin{aligned} \Delta_f H_m^\ominus(\text{NHTPN, s, } 298.15\text{ K}) &= 7\Delta_f H_m^\ominus(\text{CO}_2, \text{g, } 298.15\text{ K}) \\ &+ 3\Delta_f H_m^\ominus(\text{H}_2\text{O, l, } 298.15\text{ K}) \\ &- \Delta_c H_m^\ominus(\text{NHTPN, s, } 298.15\text{ K}) \end{aligned} \quad (4)$$

when $\Delta_f H_m^\ominus(\text{CO}_2, \text{g, } 298.15\text{ K}) = (-393.51 \pm 0.13)\text{ kJ mol}^{-1}$, $\Delta_f H_m^\ominus(\text{H}_2\text{O, l, } 298.15\text{ K}) = (-285.83 \pm 0.042)\text{ kJ mol}^{-1}$, the result obtained is $-(638.04 \pm 111.04)\text{ kJ mol}^{-1}$.

3.3 Explosion properties

By substituting the values of a , b , c and d in $C_a\text{H}_b\text{N}_c\text{O}_d = \text{C}_7\text{H}_6\text{N}_4\text{O}_{14}$, $\rho = 1.884\text{ g cm}^{-3}$, $\Delta_f H_m^\ominus = -638.04\text{ kJ mol}^{-1}$ into Kamlet-Jacobs eqn (5)–(9),⁸ the values of D of 8.720 km s^{-1} , P of 34.65 GPa , N of 0.0284 mol g^{-1} , M_g of 33.53 g mol^{-1} , Q of 6086.2 J g^{-1} are obtained, showing that NHTPN has explosion performance level approaching that of PETN ($\rho = 1.780\text{ g cm}^{-3}$, $\Delta_f H_m^\ominus = -538.48\text{ kJ mol}^{-1}$. $\text{C}_5\text{H}_8\text{N}_4\text{O}_{12} \rightarrow 2\text{N}_2 + 4\text{H}_2\text{O} + 4\text{CO}_2 + \text{C}$, $D = 8.461\text{ km s}^{-1}$, $P = 32.06\text{ GPa}$ from eqn (5) and (6), $D = 8.708\text{ km s}^{-1}$, $P = 33.25\text{ GPa}$ from eqn (11) and (12)).

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (5)$$

$$P = 1.558NM^{1/2}Q^{1/2}\rho^2 \quad (6)$$

$$N = \frac{b + 2d + 2c}{4M} \quad (7)$$

$$M = \frac{4M}{b + 2c + 2d} \quad (8)$$

$$Q = 4.184 \times \left(\frac{28.9b + 94.05a + 0.239\Delta_f H^\ominus}{M} \right) \times 10^{-3} \quad (9)$$

where D is detonation velocity (km s^{-1}), P detonation pressure (GPa), N moles of gases detonation products per gram of explosive, M average molecular weight of gaseous products, Q chemical energy of detonation (J g^{-1}), ρ density of explosives (g cm^{-3}), and $\Delta_f H^\ominus$ standard enthalpy of formation.

By substituting the values of $x_{\text{N}_2} = 2$, $x_{\text{H}_2\text{O}} = 3$, $x_{\text{CO}_2} = 5$, $x_{\text{CO}} = 1$, $x_{\text{H}_2} = 0$, $x_{\text{O}_2} = 0$, $x_{\text{C}} = 1$, $M = 370.143\text{ g mol}^{-1}$ from reaction formula (10) and $\rho = 1.884\text{ g cm}^{-3}$ into empirical nitrogen equivalent eqn (11) and (12) (ref. 9) for predicting the D and P of C–H–N–O explosives, the values of D of 8.859 km s^{-1} , P of 35.45 GPa are obtained.



$$D = \frac{100}{M} (695 + 1150\rho)(1.00x_{\text{N}_2} + 0.64x_{\text{H}_2\text{O}} + 1.34x_{\text{CO}_2} + 0.72x_{\text{CO}} + 0.18x_{\text{H}_2} + 0.50x_{\text{O}_2} + 0.12x_{\text{C}}) \quad (11)$$

where 695 and 1150 are constants; 1.00, 0.64, 1.34, 0.72, 0.18, 0.50, 0.12 are the nitrogen equivalent coefficient of gaseous detonation products N_2 , H_2O , CO_2 , CO , H_2 , O_2 , C of explosive.



And

$$P = 1.060 \left[\rho \frac{100}{M} (1.000x_{N_2} + 0.64x_{H_2O} + 1.34x_{CO_2} + 0.72x_{CO} + 0.18x_{H_2} + 0.50x_{O_2} + 0.12x_C) \right]^2 - 0.619 \quad (12)$$

where 1.060 and 0.619 are constants.

3.4 The thermal behavior of NHTPN

A typical DSC curves at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ for NHTPN is shown in Fig. 2. DSC curve consists of one endothermic peak and one exothermic peak. The endothermic peak at $114.55\text{ }^{\circ}\text{C}$ is the phase change from solid to liquid. The exothermic peak is the decomposition reaction of NHTPN, and the peak temperature is $185.50\text{ }^{\circ}\text{C}$ and the onset temperature is $165.12\text{ }^{\circ}\text{C}$.

3.5 Heat-temperature quotient for the exothermic decomposition process of NHTPN

The exothermic peak in Fig. 2 is caused by the decomposition reaction. Heat-temperature quotient of the process equals to

$$\Delta S_d = \frac{Q_d}{T_{p0}} = \frac{-H_d}{T_{p0}} = \frac{-(1126.4)\text{kJ} \times \text{mol}^{-1}}{439.95\text{ K}} = 2.560\text{ kJ(K} \times \text{mol})^{-1}$$

where the heat of decomposition reaction Q_d is defined as $Q_d = 0.5 Q$, i.e. Q_d , taking half-chemical energy (heat) of detonation. For NHTPN, $Q_d = 0.5Q = 3043.1\text{ J g}^{-1}$. T_{p0} is the peak temperature T_p corresponding to $\beta \rightarrow 0$.

3.6 Analysis of kinetic data for the exothermic main decomposition reaction of NHTPN

To obtain the kinetic parameters (the apparent activation energy (E_a) and pre-exponential constant (A)) of the exothermic main decomposition reaction for the title compound, two isoconversional methods [eqn (13) and (14)] are employed.

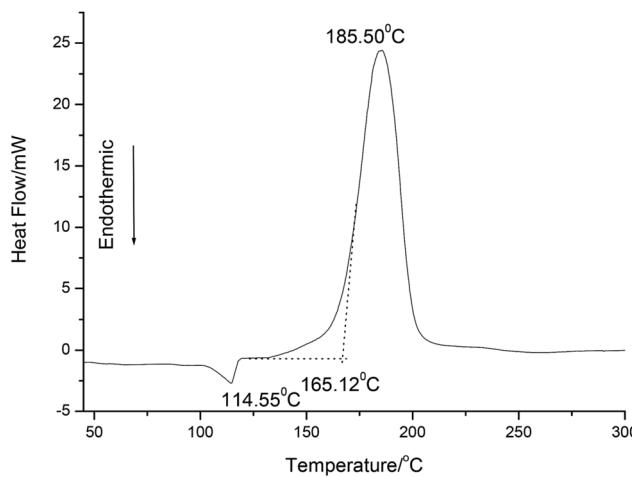


Fig. 2 DSC curve for NHTPN at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

Differential methods. Kissinger equation¹⁰

$$\ln \left(\frac{\beta_i}{T_{pi}^2} \right) = \ln \frac{A_k R}{E_k} - \frac{E_k}{R} \frac{1}{T_{pi}} \quad (13)$$

Integral methods. Ozawa equation¹¹

$$\lg \beta_i = \lg \left[\frac{AE_{oe(\text{or op})}}{RG(\alpha)} \right] - 2.315 - 0.4567 \frac{E_{oe(\text{or op})}}{RT_{o(\text{or p})i}} \quad (14)$$

where α is the conversion degree, T the absolute temperature, E the apparent activation energy, β the heating rate, R the gas constant, T_p the peak temperature of DSC curve, A the pre-exponential factor.

From the original data in Table 1, E_k obtained by Kissinger's method¹⁰ is determined to be $199.48\text{ kJ mol}^{-1}$. The pre-exponential constant (A) is $10^{20.95}\text{ s}^{-1}$. The linear correlation coefficient (r_k) is 0.9965. The value of E_o obtained by Ozawa's method¹¹ is $196.90\text{ kJ mol}^{-1}$. The value of r_0 is 0.9968. The value of E_{eo} obtained by T_{ei} vs. β_i relation is $197.02\text{ kJ mol}^{-1}$. The value of r_{eo} is 0.9816.

By substituting the experimental data, β_i , T_i and α_i , $i = 1, 2, \dots, n$, listed in Table 2 from DSC curves in Fig. 2 into eqn (15) which is known as Arrhenius-type's integral isoconversional non-linear method (NL-INT method) of solving E_α , the values of E_α satisfying the minimum value of eqn (15) for any given value of α are obtained and shown in Table 2 and Fig. 3. The average value of E_α in the α range of 0.20 to 0.80 in Fig. 2 is in good agreement with the calculated values obtained by Kissinger's method and Ozawa's method. The E values calculated using eqn (15) are used to check the validity of activation energy by the other methods.

$$Q_{11}(E_\alpha) = \min \left| \sum_{i=1}^n \sum_{j \neq i}^n \frac{\beta_j \cdot I(E_\alpha, T_{\alpha,i})}{\beta_i \cdot I(E_\alpha, T_{\alpha,j})} - n(n-1) \right| \quad (15)$$

where, $I(E_\alpha, T_\alpha)$ integral is obtained taking Senum-Yang approximation calculation for approximation of 3rd degree: $I_{SY-3}(E, T) = \left[T e^{-u} \left(\frac{u^2 + 10u + 18}{u^3 + 12u^2 + 36u + 24} \right) \right]$, where, $u = E/RT$.

The data (β , T_i , α_i , $i = 1, 2, \dots$) in the range of $\alpha = 0.20\text{--}0.80$ and 41 kinetic model functions¹² were input to eqn (16) to obtain the values of E and A from a single non-isothermal DSC curve.

$$\ln \left[\frac{G(\alpha)}{T^2 \left(1 - \frac{2RT}{E} \right)} \right] = \ln \frac{AR}{\beta E} - \frac{E}{RT} \quad (16)$$

Table 1 Maximum peak temperature (T_p) and onset temperature (T_e) of the exothermic decomposition reaction for NHTPN determined by the DSC curves at various heating rates (β)

$\beta/(K\text{ min}^{-1})$	2	5	10	15	20
T_p/K	446.31	454.40	458.65	462.79	466.05
T_e/K	426.44	429.93	438.27	439.94	442.47



Table 2 Data of NHTPN determined by DSC at different heating rates and apparent activation energies (E_a) of thermal decomposition obtained by NL-INT method

α (%)	T_d /°C					E_a /kJ mol ⁻¹	min
	2 °C min ⁻¹	5 °C min ⁻¹	10 °C min ⁻¹	15 °C min ⁻¹	20 °C min ⁻¹		
0.000	398.95	401.15	404.48	406.15	414.82	178.20	
0.025	421.54	426.23	428.8	429.09	433.23	310.53	0.9906
0.050	426.32	432.36	436.04	437.13	441.08	249.62	0.3722
0.075	429.08	435.57	439.9	441.45	445.28	228.32	0.2098
0.100	431.04	437.74	442.43	444.3	447.96	219.08	0.1330
0.125	432.6	439.38	444.3	446.4	449.95	214.16	0.09445
0.150	433.9	440.72	445.81	448.08	451.53	211.18	0.07032
0.175	435.03	441.86	447.09	449.48	452.88	209.05	0.05740
0.200	436.04	442.87	448.21	450.71	454.06	207.51	0.04780
0.225	436.95	443.78	449.22	451.79	455.13	206.19	0.04368
0.250	437.78	444.62	450.14	452.77	456.1	205.11	0.04057
0.275	438.56	445.4	450.98	453.67	456.99	204.37	0.03831
0.300	439.29	446.13	451.77	454.51	457.83	203.64	0.03720
0.325	439.98	446.83	452.51	455.31	458.63	202.93	0.03616
0.350	440.64	447.5	453.22	456.07	459.39	202.32	0.03540
0.375	441.28	448.15	453.89	456.79	460.11	201.96	0.03488
0.400	441.9	448.78	454.55	457.49	460.82	201.50	0.03512
0.425	442.49	449.39	455.18	458.17	461.5	201.01	0.03453
0.450	443.08	449.99	455.81	458.84	462.16	200.67	0.03365
0.475	443.66	450.58	456.43	459.48	462.81	200.41	0.03401
0.500	444.22	451.16	457.04	460.12	463.46	199.93	0.03412
0.525	444.78	451.73	457.65	460.75	464.1	199.53	0.03452
0.550	445.34	452.31	458.25	461.38	464.73	199.25	0.03406
0.575	445.9	452.88	458.86	462	465.36	198.97	0.03441
0.600	446.46	453.45	459.46	462.63	465.99	198.66	0.03436
0.625	447.02	454.03	460.08	463.26	466.63	198.30	0.03439
0.650	447.59	454.61	460.7	463.89	467.28	197.96	0.03542
0.675	448.16	455.19	461.33	464.54	467.94	197.46	0.03599
0.700	448.75	455.79	461.97	465.2	468.61	197.11	0.03658
0.725	449.35	456.41	462.64	465.89	469.31	196.56	0.03683
0.750	449.96	457.04	463.33	466.61	470.03	195.87	0.03670
0.775	450.6	457.69	464.05	467.37	470.8	195.00	0.03786
0.800	451.28	458.37	464.81	468.18	471.62	194.03	0.03985
0.825	451.99	459.08	465.64	469.07	472.51	192.60	0.04211
0.850	452.76	459.85	466.55	470.09	473.53	190.51	0.04616
0.875	453.6	460.69	467.6	471.28	474.72	187.45	0.05297
0.900	454.55	461.63	468.87	472.8	476.22	182.45	0.06698
0.925	455.69	462.75	470.59	475.07	478.4	173.03	0.10284
0.950	457.2	464.2	473.63	480.02	482.83	149.07	0.26368
0.975	459.71	466.53	483.54	494.25	495.87	97.70	0.80034
1.000	483.75	486.65	520.82	527.15	541.48	65.97	1.79787

where $G(\alpha)$ is the integral model function, T the temperature (K) at time t , α the conversion degree, R the gas constant.

The kinetic parameters obtained by the logical choice method¹³ were presented in Table 3. Their values of E are very close to each other. The values of E_a and A obtained from a single non-isothermal DSC curves are in good agreement with the calculated values obtained by Kissinger's method and Ozawa's method. Therefore, we conclude that the reaction mechanism of exothermic main decomposition process of the compound is classified as $G(\alpha) = -\ln(1 - \alpha)$, $f(\alpha) = 1 - \alpha$. Substituting $f(\alpha)$ with $1 - \alpha$, E with 199.12 kJ mol⁻¹ and A with $10^{18.89}$ s⁻¹ in eqn (17):

$$\frac{d\alpha}{dt} = Af(\alpha)\exp(-E/RT) \quad (17)$$

the kinetic equation of exothermic decomposition reaction for NHTPN may be described as

$$d\alpha/dt = 10^{18.89}(1 - \alpha)e^{-2.3950 \times 10^4/T} \quad (18)$$

3.7 Self-accelerating decomposition temperature T_{SADT}

Setting T_e as the onset temperature and T_p as the peak temperature, and defining T_{e0} or p_0 as the value of $T_{(e0 \text{ or } p0)i}$ corresponding to $\beta \rightarrow 0$ and T_{e0} as the self-accelerating decomposition temperature T_{SADT} , we have

$$T_e \text{ or } p = T_{e0} \text{ or } p_0 + b\beta_i + c\beta_i^2 + d\beta_i^3, i = 1, 2, \dots, L \quad (19)$$

and



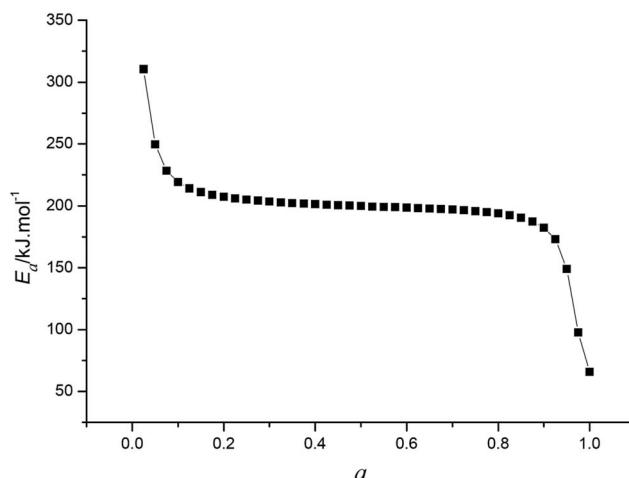


Fig. 3 The $E_d \sim \alpha$ curve obtained by Qzawa's method.

$$T_{e0} = T_{SADT} \quad (20)$$

Submitting the original data: $\beta_i, T_{ei}, T_{pi}, i = 1, 2, \dots, 5$ in Table 1 into eqn (19), the values of T_{e0} of 422.06 K and T_{p0} of 439.95 K are obtained. The value of T_{SADT} of 422.06 K is obtained by eqn (20).

3.8 The critical temperature of thermal explosion (T_b)

The critical temperature of thermal explosion (T_b) is an important parameter of evaluating the safety and elucidating transition tendency from thermal decomposition to thermal explosion for small-scale energetic materials (EMs).

For NHTPN, the values of T_b obtained by Zhang-Hu-Xie-Li equation [eqn (21)] taken from¹⁴ using the values of T_{e0} (=422.06 K) and T_{p0} (=439.95 K) and the value of E_{oe} (=197.02 kJ mol⁻¹) and E_{op} (=196.90 kJ mol⁻¹) are 429.86 and 448.44 K, respectively:

$$T_{be0(\text{or } bp0)} = \frac{E_{oe \text{ or } op} - \sqrt{E_{oe \text{ or } op}^2 - 4E_{oe \text{ or } op}RT_{e0(\text{or } p0)}}}{2R} \quad (21)$$

The values of T_b obtained by eqn (23) (ref. 15) based on Berthelot's equation using the values of b_{e0} (=0.1338) and b_{p0} (=0.1213) obtained by eqn (22) and T_{e0} (=422.06 K), and T_{p0}

(=439.95 K) obtained by eqn (19) via data in Table 1 are 429.53 and 448.19 K, respectively.

$$\ln \beta_i = \ln \left[\frac{A_0}{b_{e0(\text{or } p0)} G(\alpha)} \right] + b_{e0(\text{or } p0)} T_{e(\text{or } p)i} \quad (22)$$

$$T_{be0(\text{or } bp0)} = T_{e0(\text{or } p0)} + \frac{1}{b_{e0(\text{or } p0)}} \quad (23)$$

In comparison with PETN with $T_{bp} = 459.29$ K, lower value of T_b shows that the transition from thermal decomposition to thermal explosion is easy to take place.

3.9 Thermodynamic parameters of activation reaction

The entropy of activation (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger), and Gibbs free energy of activation (ΔG^\ddagger) corresponding to $T = T_{p0} = 439.95$ K, $E = E_k = 199\ 480$ J mol⁻¹, $A = A_k = 10^{20.95}$ s⁻¹ obtained by eqn (24)–(26) are 144.60 J mol⁻¹ K⁻¹, 195.82 kJ mol⁻¹ and 132.20 kJ mol⁻¹, respectively. The positive value of ΔG^\ddagger indicates that the exothermic decomposition reaction for NHTPN must proceed under the heating condition.

$$Ae^{-E/RT} = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} \quad (24)$$

$$\Delta H^\ddagger = E - RT \quad (25)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (26)$$

where k_B is the Boltzmann constant (1.3807×10^{-23} J K⁻¹) and h is the Planck constant (6.626×10^{-34} J s).

3.10 The specific heat capacity of NHTPN

Fig. 4 shows the determination results of NHTPN using a continuous specific heat capacity mode of the Micro-DSC III apparatus. We can see that specific heat capacity of NHTPN presents a good linear equation relationship with temperature in the determining temperature range. Specific heat capacity equation is shown as:

$$C_p(\text{NHTPN J g}^{-1} \text{ K}^{-1}) = -6.918054 \times 10^{-2} + 3.676170 \times 10^{-3}T \quad (28.1 \text{ K} < T < 323.2 \text{ K}) \quad (27)$$

Table 3 Kinetic parameters obtained for thermal decomposition process of the NHTPN^a

Method	β /(K min ⁻¹)	E /(kJ mol ⁻¹)	$\lg(A_0/s^{-1})$	r_{icc}	Q_v
Ordinary-integral	2	205.00	21.57	0.9993	0.0185
	5	207.77	21.91	0.9991	0.0215
	10	198.92	20.86	0.9990	0.0242
	15	190.92	19.95	0.9993	0.0168
	20	192.99	20.15	0.9991	0.0215
Mean		199.12	18.89		
Kissinger		199.48	20.95	0.9965	
Flynn-Wall Ozawa		196.90		0.9968	

^a Note: r_{icc} is the linear correlation coefficient; Q_v is the variance.

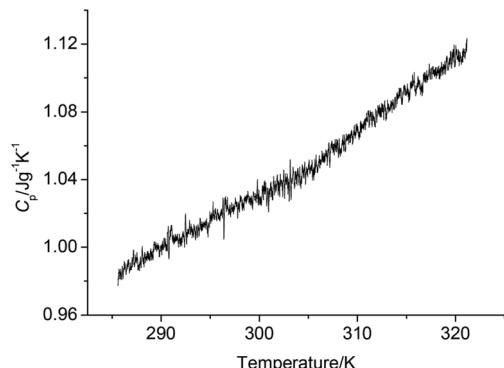


Fig. 4 Determination results of the continuous specific heat capacity C_p of NHTPN.

The specific heat capacity of NHTPN is $1.027 \text{ J g}^{-1} \text{ K}^{-1}$ at 298.15 K. The standard molar heat capacity of NHTPN is $380.14 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298.15 K.

3.11 Thermodynamic functions of NHTPN

The enthalpy change, the entropy change and the Gibbs free energy change for NHTPN are calculated by eqn (28) to (30) within 283 K and 353 K, taking 298.15 K as the benchmark. The results are listed in Table 4.

$$H_T - H_{298.15} = \int_{298.15}^T C_p dT \quad (28)$$

$$S_T - S_{298.15} = \int_{298.15}^T C_p T^{-1} dT \quad (29)$$

$$G_T - G_{298.15} = \int_{298.15}^T C_p dT - T \int_{298.15}^T C_p T^{-1} dT \quad (30)$$

where C_p as eqn (27) expressed.

Table 4 The enthalpy change, the entropy change and the Gibbs free energy change for NHTPN within 283 K and 353 K, taking 298.15 K

T/K	$H_T - H_{298.15} \text{ kJ/mol}$ (J g^{-1})	$S_T - S_{298.15} \text{ kJ/mol}$ ($\text{J K}^{-1} \text{ g}^{-1}$)	$G_T - G_{298.15} \text{ kJ/mol}$ (J g^{-1})
283.15	-14.99	-0.052	10.14
288.15	-10.09	-0.034	6.85
293.15	-5.09	-0.017	3.47
298.15			
303.15	5.189	0.017	-3.55
308.15	10.459	0.034	-7.19
313.15	15.82	0.052	-10.92
318.15	21.27	0.069	-14.73
323.15	26.82	0.086	-18.63
328.15	32.46	0.104	-22.61
333.15	38.19	0.121	-26.68
338.15	44.02	0.138	-30.84
343.15	49.93124	0.156	-35.08
348.15	55.93868	0.173	-39.41
353.15	62.03802	0.190	-43.83

3.12 The determination of the adiabatic time-to-explosion

The adiabatic time-to-explosion (t_{Tiad} , s) of energetic materials is the time of energetic material thermal decomposition transiting to explosion under the adiabatic conditions, and is an important parameter for assessing the thermal stability and the safety of energetic materials. The estimation formulae of calculating the adiabatic time-to explosion (t) of energetic materials used are Smith's eqn (31)–(33) taken from ref. 16.

$$C_p \frac{dT}{dt} = QA \exp(-E/RT) f(\alpha) \quad (31)$$

$$\alpha = \int_{T_0}^T \frac{C_p}{Q} dT \quad (32)$$

$$t = \frac{1}{QA} \int_{T_0}^T \frac{C_p \exp(E/RT)}{f(\alpha)} dT \quad (33)$$

where C_p is the specific heat capacity ($\text{J g}^{-1} \text{ K}^{-1}$); $f(\alpha)$ is the differential mechanism function; E is the apparent activation energy; A is the pre-exponential constant; Q is the heat of decomposition; R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and α is the conversion degree.

By substituting the original data of $C_p = 1.027 \text{ J g}^{-1} \text{ K}^{-1}$, $f(\alpha) = 1 - \alpha$, $E = 199480 \text{ J mol}^{-1}$, $A = 10^{20.95} \text{ s}^{-1}$, $Q_d = 3043.1 \text{ J g}^{-1}$, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, the integral upper limit $T = T_b = 448.44 \text{ K}$ and the lower limit $T_0 = T_{\text{eo}} = 422.06 \text{ K}$ into eqn (33), the value of t of 13.80 s is obtained.

3.13 The critical temperature of hot-spot initiation (T_{cr})

The inner of EMs can create a local hot-spot when the EMs accepted energy and the EMs will explore from thermal decomposition when the hot-spot temperature reaches to the explosive temperature. The critical temperature of hot-spot initiation (T_{cr}) is an important parameter for evaluating the thermal safety of EMs.

By submitting the density $\rho = 1.884 \text{ g cm}^{-3}$ of NHTPN, specific heat capacity $C_p = 1.027 \text{ J g}^{-1} \text{ K}^{-1}$. Thermal conductivity $\lambda = 22.50 \times 10^{-4} \text{ J cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$, heat of decomposition $Q_d = 3043.1 \text{ J g}^{-1}$, kinetic parameters $E = 199480 \text{ J mol}^{-1}$ and $A = 10^{20.95} \text{ s}^{-1}$, $T_{\text{room}} = 293.15 \text{ K}$, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, hot-spot critical radius $a = 10^{-3} \text{ cm}$ and time interval $t - t_0 = 10^{-4} \text{ s}$ (ref. 15) to Bruckman-Guillett's first-order estimation equation [eqn (34)],^{17,18} the value of $T_{\text{cr,hot spot}}$ of $314.18 \text{ }^{\circ}\text{C}$ is obtained.

$$\begin{aligned} & \left(\frac{4}{3} \pi a^3 \right) \rho Q_d \left\{ 1 - \exp \left[-(t - t_0) A e^{-E/RT_{\text{cr}}} \right] \right\} \\ &= \int_a^\infty 4\pi r^2 \rho c_p \left[\frac{d\theta_0}{r} \operatorname{erfc} \left[\frac{r - a}{2\sqrt{Bt}} \right] \right] dr \\ &= \int_a^\infty 4\pi r^2 \rho c_p \left[\frac{a(T_{\text{cr,hot spot}} - T_{\text{room}})}{r} \operatorname{erfc} \left[\frac{r - a}{2\sqrt{\frac{\lambda}{\rho c_p} t}} \right] \right] dr \quad (34) \end{aligned}$$



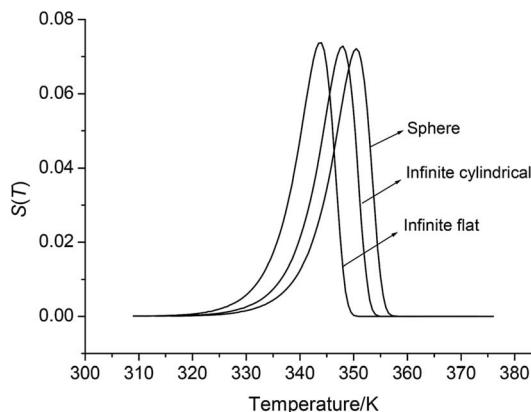


Fig. 5 $S(T)$ vs. T relation curves for spheroidal, infinite cylindrical and infinite platelike NHTPN.

3.14 50% drop height (H_{50}) of impact sensitivity

The impact sensitivity is an important parameter for evaluating the security and reliability of EMs and can be characterized by 50% drop height (H_{50}). Using data of $\lambda = 22.50 \times 10^{-4} \text{ J cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$, $\rho = 1.884 \text{ g cm}^{-3}$, $Q_d = 3043.1 \text{ J g}^{-1}$, $E = 199 480 \text{ J mol}^{-1}$, and $A = 10^{20.95} \text{ s}^{-1}$, the H_{50} of NHTPN was estimated as 13.13 cm by Friedman's formula (eqn (35)).^{19,20} This value shows that it has impact sensitivity level approaching those of PETN (16 cm) and tetryl (17 cm)

$$0.282312 \lg(H_{50}) + \lg \sqrt{\frac{\lambda}{ApQ_d}} - 0.347174 + \frac{0.02612E}{T_1 + 33.8765H_{50}^{0.564623}} = 0 \quad (35)$$

3.15 Critical thermal explosion ambient temperature T_{acr} , thermal sensitivity probability density function $S(T)$, safety degree SD and thermal explosion probability P_{TE}

To explore the heat-resistance ability of NHTPN, the values of T_{acr} , $S(T)$ vs. T relation, SD and P_{TE} are calculated by Frank-Kamenetskii formula (36) (ref. 21) and Wang-Du's formulas (36)–(42).^{22,23} In formulas (36)–(40), T_{acr} is the critical thermal explosion ambient temperature in K; E is the activation energy in J mol^{-1} ; A is the pre-exponential constant in s^{-1} ; R is the gas constant in $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$; λ is the thermal conductivity in $\text{W m}^{-1} \text{ K}^{-1}$; δ is the Frank-Kamenetskii parameter (FK); δ_{cr} is the criticality of thermal explosion of exothermic

system; r is the characteristic measurement of reactant in m; Q_d is the decomposition heat in J kg^{-1} ; ρ is the density in kg m^{-3} ; μ_T is the average value of temperature, K; σ_δ is the standard deviation of FK parameter; σ_T is the standard deviation of ambient temperature; T is the surrounding temperature; $S(T)$ is the thermal sensitivity probability density function; SD is the safety degree; P_{TE} is the thermal explosion probability.

By substituting the values of $r = 1 \text{ m}$, $Q_d = 3043.1 \times 10^3 \text{ J kg}^{-1}$, $E = 199 480 \text{ J mol}^{-1}$, $A = 10^{20.95} \text{ s}^{-1}$, $\rho = 1.884 \times 10^3 \text{ kg m}^{-3}$, $\lambda = 0.2250 \text{ W m}^{-1} \text{ K}^{-1}$, ambient temperature $T_a = 340 \text{ K}$, $\sigma_\delta = 10 \text{ K}$ into eqn (36)–(42), the $S(T)$ vs. T relation curves for infinite plate, infinite cylindrical and spheroidal NHTPN in Fig. 5 and determination results of the thermal sensitivity of the NHTPN in Table 5 are obtained, showing that the accelerating tendency from adiabatic decomposition to explosion of large scale NHTPN and the thermal safety of NHTPN with different shape decreases in the order of sphere > infinite cylinder > infinite plate.

$$T_{acr} = \frac{-E_K}{2R \text{ Lambert } W_{-1} \left[-\frac{1}{2} \sqrt{\frac{\lambda E_K \delta_{cr}}{r^2 Q_d \rho A_K R}} \right]} \quad (36)$$

$$S(T) = \frac{W(E_K - 2RT)}{\sqrt{2\pi\sigma_\delta RT^4}} \times \exp \left\{ - \left[W \frac{\exp \left(-\frac{E_K}{RT} \right)}{T^2} - \delta_{cr} \right]^2 \right\} \left/ 2\sigma_\delta^2 - \frac{E_K}{RT} \right\} \quad (37)$$

where

$$\frac{r^2 Q_d E_K \rho A_K}{\lambda R} = W \quad (38)$$

$$\sigma_\delta = W \left(\frac{E_K - 2R\mu_T}{R\mu_T^4} \right) \exp \left(-\frac{E_K}{R\mu_T} \right) \sigma_T \quad (39)$$

$$\mu_T = \frac{-E_K}{2R \text{ Lambert } W_{-1} \left(-\frac{1}{2} \sqrt{\frac{\lambda E_K \delta_{cr}}{r^2 Q_d \rho A_K R}} \right)} \quad (40)$$

SD is obtained by eqn (41)

Table 5 Determination results of the thermal sensitivity of the NHTPN^a

Shape types of reactant	W/K^2	T_{acr}/K	σ_T/K	$T_{S(T)\text{max}}/\text{K}$	$S(T)_{\text{TP}}$	SD/%	$P_{TE}/\%$
1	5.45×10^{35}	345.76	6.47	350.49	0.07214	52.53	47.46
2	5.45×10^{35}	343.17	3.96	347.89	0.07280	47.10	52.90
3	5.45×10^{35}	339.06	1.78	343.76	0.07388	37.27	62.73

^a 1 is the sphere; 2 is the infinite cylindrical; 3 is the infinite flat.



$$SD = \int_0^{+\infty} \int_0^{+\infty} \frac{W(E_K - 2RT)}{2\pi\sigma_\delta\sigma_T RT^4} \times \exp\left\{ - \left[W \frac{\exp\left(-\frac{E_K}{RT}\right)}{T^2} - \delta_{cr} \right]^2 \right\} \frac{1}{2\sigma_\delta^2} dT dY \quad (41)$$

$$- \frac{E_K}{RT} - \frac{(Y - T + \mu_T)^2}{2\sigma_T^2} \right\} dT dY$$

The thermal explosion probability (P_{TE}) is expressed as eqn (42)

$$P_{TE} = 1 - SD \quad (42)$$

4 Conclusions

(1) Using T_{bp} as criterions, the heat-resistance abilities and the transition resistance from thermal decomposition to thermal explosion of NHTPN and PETN decrease in the order of PETN > NHTPN.

(2) The value of Gibbs free energy of activation ($\Delta G^\#$) of 132.20 kJ mol⁻¹ of NHTPN corresponding to $T = T_{p0} = 439.95$ K, $E = E_k = 199.480$ J mol⁻¹, $A = A_k = 10^{20.95}$ s⁻¹ is close to the one of $\Delta G^\#$ of 134.11 kJ mol⁻¹ of PETN corresponding to $T = T_{p0} = 443.93$ K, $E = E_k = 112.300$ J mol⁻¹, $A = A_k = 10^{10.40}$ s⁻¹.

(3) NHTPN is sensitive to impact and shock, and has impact sensitivity level approaching those of PETN and tetryl.

(4) The thermal safety of large scale NHTPN with different shape decreases in the order of sphere > infinite cylinder > infinite plate.

(5) NHTPN has explosion performance level approaching that of PETN and can be used as a main ingredient of composite explosive.

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