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

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6b-Nitrohexahydro-2H-1,3,5-trioxacyclopenta[cd]-pentalene-2,4,6-triylnitritrate (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 (Cp) was determined by a continuous Cp mode of microcalorimetry (Micro-DSC III). In order to evaluate its thermal safety, the values (Tc0 and Tp0) of Tc and Tp corresponding to β → 0, critical temperature of thermal explosion (Tb and Tbp), adiabatic time-to-explosion (tad), 50% drop height (HD50) of impact sensitivity, critical temperature of hot-spot initiation (Tcr), thermal sensitivity probability density function (5(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 5(T) vs. T relation curve (Tad), safety degree (SD) and critical ambient temperature (Tad) of thermal explosion of NHTPN were calculated respectively, by means of the onset temperature (To), the maximum peak temperature (Tp) from the non-isothermal DSC curves of NHTPN at different heating rates (β), the apparent activation energy (Ea and E0) and pre-exponential constant (A0) of thermal decomposition reaction obtained by Kissinger’s method and Ozawa’s method, Cp, density (ρ) and thermal conductivity (λ), the decomposition heat (Qd), 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.

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-triylnitritrate (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 (Ea) 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 (Tad), the critical temperature of thermal explosion (Tb) and the adiabatic time-to-explosion (tad) were estimated. The 50% drop height of impact sensitivity (HD50), the critical temperature of hot-spot initiation caused by impact (Tcr), the safety degree (SD), the critical thermal explosion ambient temperature (Tad) and thermal explosion probability (PTE) 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, H2a, H4a, H6a); 6.70 ppm (s, 3H, H2, H4 and H6). 13C
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 °C min⁻¹ from ambient temperature to 500 °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 283–353 K at a heating rate of 0.15 K min⁻¹ on a Micro-DSC III apparatus (Setaram, France) with the sample mass of 450 mg. The Micro-calorimeter was calibrated with α-Al₂O₃ (calcined), its math expression was $C_p(J^{-1}K^{-1}) = 0.1839 + 1.9966 	imes 10^{-3}T$ within 283 K–353 K and the standard molar heat capacity $C^{o}_{p,m} (\alpha-Al_2O_3)$ at 298.15 K was determined as 79.44 J mol⁻¹ K⁻¹ which is in an excellent agreement with the value of 79.02 J mol⁻¹ K⁻¹ reported in the literature.

3 Results and discussion

3.1 Standard enthalpy of combustion

The standard enthalpy of combustion of NHTPN, $\Delta_{c}H_{m}^{\circ}$ (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.

$$\text{C}_7\text{H}_6\text{N}_4\text{O}_{14}(s) + 1.5\text{O}_2 \xrightarrow{\Delta_{c}H_{m}^{\circ}} 7\text{CO}_2(g) + 3\text{H}_2\text{O}(l) + 2\text{N}_2(g)$$

The standard enthalpy of combustion of NHTPN $\Delta_{c}H_{m}^{\circ}$ is calculated by the following equations:

$$\Delta_{c}H_{m}^{\circ} (\text{NHTPN}, \text{s}, 298.15 \text{ K}) = \Delta_{c}U (\text{NHTPN, s, 298.15 K}) + \Delta nRT$$

$$\Delta n = n_g \text{ (products)} - n_g \text{ (reactants)}$$

where $\Delta_{c}U = -(Q_o) = -(2992.61 \pm 111.04) \text{kJ mol}^{-1}$, $n_g$ 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, $\Delta_{f}H_{m}^{\circ}$ (NHTPN, s, and 298.15 K), is calculated by Hess’s law according to thermochemical eqn (4).

$$\Delta_{f}H_{m}^{\circ} (\text{NHTPN, s, 298.15 K}) = 7\Delta_{f}H_{m}^{\circ} (\text{CO}_2, \text{g, 298.15 K}) + 3\Delta_{f}H_{m}^{\circ} (\text{H}_2\text{O, l, 298.15 K}) - \Delta_{f}H_{m}^{\circ} (\text{NHTPN, s, 298.15 K})$$

when $\Delta_{f}H_{m}^{\circ} (\text{CO}_2, \text{g, 298.15 K}) = -(393.51 \pm 0.13) \text{kJ mol}^{-1}$, $\Delta_{f}H_{m}^{\circ} (\text{H}_2\text{O, l, 298.15 K}) = -(285.83 \pm 0.042) \text{kJ mol}^{-1}$, 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 $C_nH_{2n}O_d = C_7H_6N_4O_{14}$, $\rho = 1.884 \text{ g cm}^{-3}$, $\Delta_{f}H_{m}^{\circ} = -638.04 \text{kJ mol}^{-1}$ into Kamlet–Jacobs eqn (5)–(9),\(^*\) the values of $D$ of 8.720 km s⁻¹, $P$ of 34.65 GPa, $N$ of 0.0284 mol⁻¹ g⁻¹, $M$ 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 ($\rho = 1.780 \text{ g cm}^{-3}$).

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

$$P = 1.558NM^{1/2}Q^{1/2}\rho^2$$

$$N = b + 2d + 2c$$

$$M = 4M$$

$$Q = 4.184 \times \left(\frac{28.9b + 94.05a + 0.239\Delta_H^{\circ}}{M}\right) \times 10^{-3}$$

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), $\rho$ density of explosives (g cm⁻³), and $\Delta_H^{\circ}$ standard enthalpy of formation.

By substituting the values of $x_N = 2$, $x_{H_2O} = 3$, $x_{CO_2} = 5$, $x_{CO} = 1$, $x_H = 0$, $x_O = 0$, $x_C = 1$, $M = 370.143$ 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.

$$\text{C}_7\text{H}_6\text{N}_4\text{O}_{14}(s) \rightarrow 5\text{CO}_2 + 3\text{H}_2\text{O} + 2\text{N}_2 + \text{CO} + \text{C}$$

$$D = \frac{100}{M} \left[(695 + 1150\rho)\{1.00x_N + 0.64x_{H_2O} + 1.34x_{CO_2} + 0.72x_CO + 0.18x_H + 0.50x_O + 0.12x_C\}\right]$$

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
\[
P = 1.060 \left[ 100 \frac{\rho}{M} (1.000x_{N_2} + 0.64x_{H_2}O + 1.34x_{CO_2} + 0.72x_{CO}) + 0.18x_{H_2} + 0.50x_{O_2} + 0.12x_{C} \right]^2 - 0.619 \tag{12}
\]
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 °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 °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 °C and the onset temperature is 165.12 °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
\[
\Delta S_d = \frac{Q_d}{T_{P0}} = -\frac{H_d}{T_{P0}} = -\frac{(-1126.4) \text{kJ} \times \text{mol}^{-1}}{439.95 \text{K}} = 2.560 \text{ kJ} (\text{K} \times \text{mol}^{-1})
\]
where the heat of decomposition reaction \(Q_d\) is defined as \(Q_d = 0.5 Q_i\), 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 \(\beta \to 0\).

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

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

Differential methods. Kissinger equation\(^{10}\)
\[
\ln \left( \frac{\beta}{T_p^2} \right) = \ln \frac{A_R R}{E_x} - \frac{E_x}{R} \frac{1}{T_p} \tag{13}
\]

Integral methods. Ozawa equation\(^{11}\)
\[
\lg \beta = \lg \left[ \frac{AE_{E(x, \alpha)} op}{RG(\alpha)} \right] - 2.315 - 0.4567 \frac{E_{E(x, \alpha)} op}{RT_i (\alpha, p)} \tag{14}
\]
where \(\alpha\) is the conversion degree, \(T\) the absolute temperature, \(E\) the apparent activation energy, \(\beta\) 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, \(E_x\) obtained by Kissinger’s method\(^{10}\) is determined to be 199.48 kJ mol\(^{-1}\). The pre-exponential constant \((A)\) is \(10^{20.95} \text{ s}^{-1}\). The linear correlation coefficient \((R)\) is 0.9965. The value of \(E_v\) obtained by Ozawa’s method\(^{11}\) is 196.90 kJ mol\(^{-1}\). The value of \(r_0\) is 0.9968. The value of \(E_v\) obtained by \(T_{oi} \) vs. \(\beta\) relation is 197.02 kJ mol\(^{-1}\). The value of \(r_0\) is 0.9816.

By substituting the experimental data, \(\beta_i\), \(T_i\) and \(\alpha_i\), \(i = 1, 2, \ldots, n\), 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 \(E_v\), the values of \(E_v\) satisfying the minimum value of eqn (15) for any given value of \(\alpha\) are obtained and shown in Table 2 and Fig. 3. The average value of \(E_v\) in the \(\alpha\) 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.

\[
\Omega_{11}(E_v) = \min \left[ \sum_{i=1}^{n} \sum_{j=1}^{n} \beta_i \cdot I(E_v, T_{oi}) - n(n-1) \right] \tag{15}
\]
where, \(I(E_v, T_{oi})\) integral is obtained taking Senum-Yang approximation calculation for approximation of 3rd degree:
\[
I_{SY-3}(E, T) = \left[ T e^{-u} \left( \frac{u^2 + 10u + 18}{u^3 + 12u^2 + 36u + 24} \right) \right], \text{ where, } u = E/RT
\]

The data (\(\beta_i, T_i, \alpha_i\), \(i = 1, 2, \ldots\)) in the range of \(\alpha = 0.20–0.80\) and 41 kinetic model functions\(^{12}\) were input to eqn (16) to obtain the values of \(E\) and \(A\) from a single non-isothermal DSC curve.

\[
\ln \left[ \frac{G(\alpha)}{T^2 (1 - 2RT/E)} \right] = \ln \frac{AR}{E} \cdot \frac{E}{RT} \tag{16}
\]

| Table 1 | Maximum peak temperature \((T_p)\) and onsets temperature \((T_o)\) of the exothermic decomposition reaction for NHTPN determined by DSC curves at various heating rates \((\beta)\) |
|---------|----------------------------------|---------|----------|----------|----------|----------|
| \(\beta (\text{K min}^{-1})\) | 2 | 5 | 10 | 15 | 20 |
| \(T_p/\text{K}\) | 446.31 | 454.40 | 458.65 | 462.79 | 466.05 |
| \(T_o/\text{K}\) | 426.44 | 429.93 | 438.27 | 439.94 | 442.47 |
Substituting $f_{1018.89 \text{ s}^{-1}}$ by NL-INT method, the compound is classified as exothermic main decomposition process of the wa’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):

$$\frac{d\alpha}{dt} = Af(\alpha)\exp(-E/RT)$$  \hspace{1cm} (17)

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

$$\frac{d\alpha}{dt} = 10^{18.89}(1 - \alpha)e^{-2.3950 \times 10^{18.89}T^{-1}}$$  \hspace{1cm} (18)

3.7 Self-accelerating decomposition temperature $T_{\text{SADT}}$

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 $T_{e0}$ or $p_0$ corresponding to $\beta \to 0$ and $T_{e0}$ as the self-accelerating decomposition temperature $T_{\text{SADT}}$, we have

$$T_{e or p} = T_{e0 or p0} + b\beta_i^2 + c\beta_i^4 + d\beta_i^3 + \ldots, i = 1,2, \ldots L$$  \hspace{1cm} (19)

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

The kinetic parameters obtained by the logical choice method$^{13}$ 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):
Fig. 3 The $E_a \sim a$ curve obtained by Ozawa’s method.

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

Submitting the original data: $\theta_n, T_{en}, T_{pi} , i = 1, 2, \ldots , 5$ 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 (EMSs).

For NHTPN, the values of $T_b$ obtained by Zhang–Hu–Xie–Li equation [eqn (21)] taken from(4) using the values of $T_{e0}$ (=422.06 K) and $T_{p0}$ (=439.95 K) and the value of $E_{oc}$ (=197.02 kJ mol$^{-1}$) and $E_{op}$ (=196.90 kJ mol$^{-1}$) are 429.86 and 448.44 K, respectively:

$$T_{b0(\text{or } p0)} = \frac{E_{oc \text{ or } op}}{2R} \sqrt{E_{oc \text{ or } op}^2 - 4E_{oc \text{ or } op}RT_{e0(\text{or } p0)}}$$ (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.

$$\ln \beta_i = \ln \left[ \frac{A_0}{b_{e0(\text{or } p0)}G(\alpha)} \right] + \frac{1}{b_{e0(\text{or } p0)}}$$ (22)

$$T_{b0(\text{or } p0)} = T_{e0(\text{or } p0)} + \frac{1}{b_{e0(\text{or } p0)}}$$ (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 ($\Delta S^\ddagger$), enthalpy of activation ($\Delta H^\ddagger$), and Gibbs free energy of activation ($\Delta G^\ddagger$) corresponding to $T = T_{p0}$ = 439.95 K, $E = E_b$ = 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 $\Delta G^\ddagger$ indicates that the exothermic decomposition reaction for NHTPN must proceed under the heating condition.

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

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

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

where $k_b$ is the Boltzmann constant (1.3807 × 10$^{-23}$ J K$^{-1}$) and $h$ is the Planck constant (6.626 × 10$^{-14}$ 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:

$$C_p(\text{NHTPN } J \text{ g}^{-1} \text{ K}^{-1}) = -6.918054 \times 10^{-2} + 3.676170 \times 10^{-3}T(283.1 \text{ K} < T < 323.2 \text{ K})$$ (27)

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

| Method          | $\beta/(K \text{ min}^{-1})$ | $E/(kJ \text{ mol}^{-1})$ | $\log(A_0/\text{s}^{-1})$ | $r_{c0c}$ | $Q_\times$ |
|----------------|-------------------------------|---------------------------|---------------------------|-----------|------------|
| 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            |                               |                           |                           |           |            |
| Kissinginger    | 199.12                        | 18.89                     |                           |           |            |
| Flynn-Wall Ozawa| 199.48                        | 20.95                     | 0.9965                    |           |            |
|                 | 196.90                        |                           | 0.9968                    |           |            |

$^a$ Note: $r_{c0c}$ is the linear correlation coefficient; $Q_\times$ is the variance.
The specific heat capacity of NHTPN is 1.027 J g⁻¹ K⁻¹ at 298.15 K. The standard molar heat capacity of NHTPN is 380.14 J mol⁻¹ 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.

\[
\begin{align*}
H_T - H_{298.15} &= \int_{298.15}^{T} C_p dT \\
S_T - S_{298.15} &= \int_{298.15}^{T} C_p T^{-1} dT \\
G_T - G_{298.15} &= \int_{298.15}^{T} C_p dT - \int_{298.15}^{T} C_p T^{-1} dT
\end{align*}
\]

where \( C_p \) as eqn (27) expressed.

### 3.12 The determination of the adiabatic time-to-explosion

The adiabatic time-to-explosion \( t_{\text{Trad}} \) 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.

\[
C_p \frac{dT}{dt} = \frac{Q_A \exp(-E/RT)}{f(\alpha)}
\]

\[
\alpha = \int_{T_0}^{T} \frac{C_p dT}{Q/\alpha}
\]

\[
t = \frac{1}{Q_A} \int_{T_0}^{T} \frac{C_p \exp(E/RT)}{f(\alpha)} dT
\]

where \( C_p \) is the specific heat capacity (J g⁻¹ 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 \( \alpha \) is the conversion degree.

By substituting the original data of \( C_p = 1.027 \text{ J g}^{-1} \text{ K}^{-1} \), \( f(\alpha) = 1 - \alpha \), \( E = 199480 \text{ J mol}^{-1} \), \( A = 10^{20.05} \text{ s}^{-1} \), \( Q_\text{d} = 3043.1 \text{ J g}^{-1} \), \( R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \), the integral upper limit \( T = T_\text{b} = 448.44 \text{ K} \) and the lower limit \( T_0 = T_\text{b} = 422.06 \text{ K} \) into eqn (33), the value of \( t \) of 13.80 s is obtained.

### 3.13 The critical temperature of hot-spot initiation \( (T_c) \)

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 \( (T_c) \) 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 \( Q_\text{d} = 3043.1 \text{ J g}^{-1} \), kinetic parameters \( E = 199480 \text{ J mol}^{-1} \) and \( A = 10^{20.05} \text{ s}^{-1} \), \( T_\text{room} = 293.15 \text{ K} \), \( R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \), hot-spot critical radius \( a = 10^{-3} \text{ cm} \) and time interval \( t - t_0 = 10^{-4} \text{ s} \) (ref. 15) to Bruckman–Guillet’s first-order estimation equation [eqn (34)]\(^{18,19}\) the value of \( T_{c, \text{hot-spot}} \) of 314.18 °C is obtained.

\[
\left(\frac{4}{3}\pi a^3\right)\rho Q_\text{d}\{1 - \exp\left[-(t - t_0)Ae^{-E/RT_a}\right]\}
\]

\[
= \int_{0}^{a} 4\pi r^2 \rho c_p \left[ \frac{a d_0}{r} \right] \text{erfc} \left[ \frac{r - a}{2\sqrt{Br}} \right] \text{dr}
\]

\[
= \int_{0}^{a} 4\pi r^2 \rho c_p \left[ a(T_{c, \text{hot-spot}} - T_{\text{room}}) \right] \text{erfc} \left[ \frac{r - a}{2\sqrt{\lambda \rho c_p t}} \right] \text{dr}
\]
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 $\lambda = 22.50 \times 10^{-4}$ J cm$^{-1}$ s$^{-1}$ K$^{-1}$, $\rho = 1.884$ g cm$^{-3}$, $Q_0 = 3043.1$ J g$^{-1}$, $E = 199480$ J mol$^{-1}$, and $A = 10^{20.95}$ s$^{-1}$, the $H_{50}$ of NHTPN was estimated as 13.13 cm by Friedman’s formula (eqn (35)). This value shows that it has impact sensitivity level approaching those of PETN (16 cm) and tetryl (17 cm)

$$0.282312 \log(H_{50}) + \log\left(\frac{\lambda}{4\rho Q_0} - 0.347174\right) + \frac{0.02612E}{T_1 + 33.8765H_{50}^{0.064424}} = 0$$

(35)

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

To explore the heat-resistance ability of NHTPN, the values of $T_{\text{acr}}$, $S(T)$ vs. $T$ relation, SD and $P_{\text{TE}}$ are calculated by Frank-Kamenetskii formula (36) (ref. 21) and Wang–Du’s formulas (36)–(42). In formulas (36)–(40), $T_{\text{acr}}$ 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 J K$^{-1}$ mol$^{-1}$; $\lambda$ is the thermal conductivity in W m$^{-1}$ K$^{-1}$; $\sigma$ is the Frank-Kamenetskii parameter (FK); $\delta_{\text{acr}}$ 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$^{-1}$; $\rho$ is the density in kg m$^{-3}$; $\mu_T$ is the average value of temperature; $K$; $\sigma_\delta$ is the standard deviation of FK parameter; $\sigma_T$ 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; $P_{\text{TE}}$ is the thermal explosion probability.

By substituting the values of $r = 1$ m, $Q_0 = 3043.1 \times 10^3$ J kg$^{-1}$, $E = 199480$ J mol$^{-1}$, $A = 10^{20.95}$ s$^{-1}$, $\lambda = 1.884 \times 10^4$ kg m$^{-3}$, $\mu_T = 0.2250$ W m$^{-1}$ K$^{-1}$, ambient temperature $T_a = 340$ K, $\sigma_\delta = 10$ K into eqn (36)–(42), the $S(T)$ vs. $T$ relation curves for infinite plate, infinite cylindrical and spheroidical 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 flat.

$$T_{\text{acr}} = \frac{-E_k}{2R \text{ Lambert \ } W^{-1} \left( \frac{1}{2} \sqrt{\frac{\lambda E_k \delta_{\text{acr}}}{r^2 Q_d \rho A_k R}} \right)}$$

(36)

$$S(T) = \frac{W(E_k - 2RT)}{\sqrt{2\pi \sigma_\delta RT^4}}$$

$$\times \exp \left\{ -W \left( \frac{E_k}{RT^2} - \delta_{\text{acr}} \right)^2 \right\} \frac{2\sigma_\delta^2 - E_k}{RT}$$

(37)

where

$$\frac{r^2 Q_d E_k \rho A_k}{\lambda R} = W$$

(38)

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

(39)

$$\mu_T = \frac{-E_k}{2R \text{ Lambert \ } W^{-1} \left( \frac{1}{2} \sqrt{\frac{\lambda E_k \delta_{\text{acr}}}{r^2 Q_d \rho A_k R}} \right)}$$

(40)

SD is obtained by eqn (41).

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

* 1 is the sphere; 2 is the infinite cylindrical; 3 is the infinite flat.
Infinite cylinder to the one of C0

4 Conclusions

1. Using \( T_{bp} \) as criteria, 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 \( (\Delta G^a) \) of NHTPN corresponding to \( T = T_{po} = 439.95 \text{ K} \), \( E = E_k = 199480 \text{ J mol}^{-1} \), \( A = A_k = 10^{20.95} \text{ s}^{-1} \) is close to the one of \( \Delta G^a \) of 134.11 kJ mol\(^{-1} \) of PETN corresponding to \( T = T_{po} = 443.93 \text{ K} \), \( E = E_k = 112300 \text{ J mol}^{-1} \), \( A = A_k = 10^{10.40} \text{ s}^{-1} \).

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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