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2,2,2-三硝基乙基-*N*-硝基甲胺的热安全性

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摘要: 为评价2,2,2-三硝基乙基-*N*-硝基甲胺(TNMA)的热安全性, 得到计算TNMA热安全性参数用的基本数据, 用经验式估算了TNMA的比热容(C_p)和热导率(λ). 用键能贡献于生成热 Q_f 的加和法, 估算了TNMA的标准生成焓 $\Delta_f H_m^\ominus$ (TNMA, s, 298.15 K). 用热力学公式计算了TNMA的标准燃烧焓 $\Delta_c H_m^\ominus$ (TNMA, s, 298.15 K)和标准燃烧能 $\Delta U_m^\ominus$ (TNMA, s, 298.15 K). 用Kamlet-Jacobs公式估算了爆速、爆压和爆热. 用经验式估算了解热(Q_d). 通过差示扫描量热(DSC)曲线和高灵敏度布鲁顿玻璃薄膜压力计测得的逸出气体标准体积(V_H)–时间(t)曲线, 得到了TNMA放热分解反应的动力学参数. 用上述基本数据得到了评价TNMA的热安全性参数: 自加速分解温度(T_{SADT}), 热爆炸临界温度(T_{be0} 和 T_{bp0}), 绝热至爆时间(t_{Tiad}), 撞击感度50%落高(H_{50}), 热点起爆临界温度(T_{cr}), 被300 K环境包围的半厚和半径为1 m的无限大平板、无限长圆柱和球形TNMA的热感度概率密度函数 $S(T)$, 相应于 $S(T)$ – T 关系曲线最大值的峰温($T_{S(T)max}$), 安全度(SD), 临界热爆炸环境温度(T_{acr})和热爆炸概率(P_{TE}). 结果表明: (1) TNMA有较好的热安全性和对热抵抗能力, 与环三亚甲基三硝胺(RDX)相比, TNMA易从热分解过渡到热爆炸; (2) 不同形状大药量TNMA热安全性降低的次序为: 球>无限长圆柱>无限大平板; (3) TNMA有高的燃烧能、高的爆轰化学能(爆热)和接近环四亚甲基四硝胺(HMX)的爆炸性能, 其对冲击敏感, 冲击感度与季戊四醇四硝酸酯(PETN)和特屈尔接近, 可用作混合炸药主组分.

关键词: TNMA; 热分解; 热安全性; 热爆炸

中图分类号: O641; O643

Thermal Safety of 2,2,2-Trinitroethyl-*N*-nitromethyl Amine

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Abstract: To evaluate the thermal safety of 2,2,2-trinitroethyl-*N*-nitromethyl amine (TNMA), basic data, including specific heat capacity (C_p) and thermal conductivity (λ), were estimated using empirical formulae. The standard enthalpy of formation of TNMA, $\Delta_f H_m^\ominus$ (TNMA, s, 298.15 K), was calculated by an additive method of contributing bond energy to heat of formation Q_f , and the standard combustion enthalpy $\Delta_c H_m^\ominus$ (TNMA, s, 298.15 K) and standard combustion energy $\Delta U_m^\ominus$ (TNMA, s, 298.15 K) were calculated by thermodynamic formulae. The detonation velocity, detonation pressure, and heat of detonation were estimated using the Kamlet-Jacobs equation. The heat of decomposition reaction (Q_d) of TNMA was estimated by an empirical formula, and the thermal behavior of TNMA was studied by differential scanning

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calorimetry (DSC). The kinetic parameters of the exothermic decomposition reaction of TNMA were obtained from analysis of DSC curves and standard volume of gas evolved (V_H) vs time (t) curves determined using a highly sensitive Bourdon glass membrane manometer. The parameters used to evaluate the thermal safety of TNMA, such as the self-accelerating decomposition temperature (T_{SADT}), critical temperature of thermal explosion (T_{be0} and T_{bp0}), adiabatic time-to-explosion (t_{Tlad}), 50% drop height (H_{50}) of impact sensitivity, critical temperature of hot-spot initiation (T_{cr}), thermal sensitivity probability density function $S(T)$ for infinite plate-like, infinite cylindrical and spheroidal TNMA with half-thickness and radius of 1 m at 300 K, peak temperature corresponding to the maximum value of the $S(T)$ vs T curve ($T_{S(T)max}$), safety degree (SD), critical thermal explosion ambient temperature (T_{acr}), and thermal explosion probability (P_{TE}), were obtained from the abovementioned basic data. Results show that (1) TNMA has better thermal safety and heat-resistant ability than cyclotrimethylenetrinitramine (RDX), and that in TNMA, the transition from thermal decomposition to thermal explosion occurs readily; (2) the thermal safety of large amounts of TNMA of different shapes decreases in the order: sphere>infinite cylinder > infinite plate; (3) TNMA has high standard combustion energy and high chemical energy (heat) of detonation, with an explosion performance level approaching that of cyclotetramethylenetetranitramine (HMX). It is sensitive to shock, and has an impact sensitivity level approaching those of pentaerythritol tetranitrate (PETN) and tetryl, so TNMA can be used as a main ingredient in composite explosives.

Key Words: TNMA; Thermal decomposition; Thermal safety; Thermal explosion

1 Introduction

The nitramines with *N*-trinitroethyl groups have good explosion properties.¹ 2,2,2-Trinitro ethyl-*N*-nitro methyl amine (TNMA), which contains one nitramine and one trinitroethyl group, is well known as a powerful nitramine which is structurally shown in Scheme 1. TNMA was widely studied in the 1960s. Its crystal density is $1.80 \text{ g} \cdot \text{cm}^{-3}$. The detonation velocity (D) corresponding to the density of composite explosive with TNMA, $\rho=1.787 \text{ g} \cdot \text{cm}^{-3}$ is about $8.732 \text{ km} \cdot \text{s}^{-1}$, approaching explosion performance level of cyclotrimethylenetrinitramine (RDX) ($\rho=1.770 \text{ g} \cdot \text{cm}^{-3}$, $D=8.700 \text{ km} \cdot \text{s}^{-1}$). Its chemical structure is the most simple in this kind of nitramines. It has wide raw material sources, simple synthesis process, and good plasticity, and is used as a main ingredient of composite explosive. Thermal behavior and thermal safety are two of the most important aspects of TNMA. There are a few reports on the thermal behaviors of TNMA, such as its explosion properties and thermal and kinetic behaviors under isothermal and non-isothermal conditions,²⁻⁶ and properties stored for 35 years.⁷ However thermal safety for TNMA has not yet been reported. The aim of this work is to study the thermal behavior, heat-resistance ability, and thermal safety of small-scale TNMA by differential scanning calorimetry (DSC) and highly-sensitive Bourdon glass membrane manometer and calculation method and the thermal safety of large scale TNMA with different shapes by numerical calculation method. This is quite useful in the evaluation of its heat-resistance ability and thermal safety under non-isothermal condition and in the better understanding of its phenomenon, mechanism, and process from thermal

decomposition to thermal explosion.

2 Experimental

2.1 Material

TNMA was prepared in Xi'an Modern Chemistry Research Institute. The compound was purified by recrystallization from nitromethane with analytical purity. m.p. >84.5 °C; ¹H NMR (90 MHz, CDCl₃) δ : 3.62(s, 3H, CH₃), 5.94(s, 2H, CH₂); IR (KBr) ν/cm^{-1} : 1638, 1300(N—NO₂), 1550, 1360(C—NO₂), 870 (C—N), 820(N—O), 2975(CH₃), 2925(CH₂); MS m/z : 239 (M^+). The theoretical value of elemental analysis for C₃H₅N₅O₈ (%): C 15.07, H 2.11, N 29.29; measured value (%): C 14.94, H 2.20, N 28.95. Its purity was more than 99.5%. The sample was kept in a vacuum desiccator before use.

2.2 Apparatus and experimental conditions

DSC apparatus, highly-sensitive Bourdon glass membrane manometer, and their operating procedure and conditions used in experiment, the principal and method of collecting, analyzing and treating the data from DSC curves, and pressure (p)–time (t) curves were the same as those in references.^{2,4,7-10}

3 Results and discussion

3.1 Establishment of basic data

3.1.1 Thermodynamic parameter: specific heat capacity

Assuming that the relation between specific heat capacity at constant pressure (C_p) and specific heat capacity at constant volume (C_v) as $C_p=0.8C_v$ and substituting the relative molecular weight (M) of 239.07 of TNMA and the values of a , b , c , and d in Eq.(1) into Eq.(2),

$$\text{C}_3\text{H}_5\text{N}_5\text{O}_8 = \text{C}_3\text{H}_5\text{O}_8\text{N}_5 \quad (1)$$

$$C_v = \left\{ \frac{3}{2} \frac{R(a+b+c+d)}{M} \right\} \left[1 + \frac{2c^2}{(4a+b)(a+b+c+d)} \right] -$$

Scheme 1 Structure of TNMA

$$\left. \frac{2ac^2}{(4a+b)(a+b+c+d)^2} \right\} \quad (2)$$

we obtain $C_p=0.8C_v=1.15 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$.

3.1.2 Thermophysical property parameter: thermal conductivity (λ)

By substituting the values of C_p of $1.15 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$, ρ of $1.80 \text{ g} \cdot \text{cm}^{-3}$, T_m (melting point) of 358 K , and M of 239.07 into Eq. (3)¹¹

$$\lambda = \frac{3.7287 \times 10^{-5} C_p^{3.0116} \rho^{0.9279}}{T_m^{-0.7652} M^{0.2158}} \quad (3)$$

the value of λ of $0.2705 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ is obtained.

3.1.3 Thermochemical parameter: standard enthalpy of formation ($\Delta_f H_m^\ominus$)

The standard enthalpy of formation of TNMA, $\Delta_f H_m^\ominus$ (TNMA, s, 298.15 K), is calculated by an additive method of contributing bond energy to heat of formation (Q_i) according to the Eq. (4):

$$\begin{aligned} \Delta_f H_m^\ominus(\text{TNMA, s, } 298.15 \text{ K}) &= -Q_i(\text{TNMA, s, } 298.15 \text{ K}) \\ &= -[5Q_i(\text{C-H}) + Q_i(\text{C-C}) + 3Q_i(\text{C-NO}_2) + Q_i(\text{N-NO}_2) + \\ &\quad Q_i[\text{C-(NO}_2)_3] + 2Q_i(\text{C-N})] \end{aligned} \quad (4)$$

where $Q_i(\text{C-H})=16.74 \text{ kJ} \cdot \text{mol}^{-1}$, $Q_i(\text{C-C})=-9.80 \text{ kJ} \cdot \text{mol}^{-1}$, $Q_i(\text{C-NO}_2)=76.15 \text{ kJ} \cdot \text{mol}^{-1}$, $Q_i(\text{N-NO}_2)=43.96 \text{ kJ} \cdot \text{mol}^{-1}$, $Q_i[\text{C-(NO}_2)_3]=-207.24 \text{ kJ} \cdot \text{mol}^{-1}$, $Q_i(\text{C-N})=-44.80 \text{ kJ} \cdot \text{mol}^{-1}$. The result is $-49.45 \text{ kJ} \cdot \text{mol}^{-1}$.

3.1.4 Thermochemical parameter: standard combustion enthalpy ($\Delta_c H_m^\ominus$)

The standard combustion enthalpy of TNMA, $\Delta_c H_m^\ominus$ (TNMA, s, 298.15 K), is referred to the combustion enthalpy change of the following ideal combustion reaction (5) at 298.15 K and 100 kPa .

and calculated by Hess's law according to the thermochemical equation (6):

$$\begin{aligned} \Delta_c H_m^\ominus(\text{TNMA, s, } 298.15 \text{ K}) &= 3\Delta_f H_m^\ominus(\text{CO}_2, \text{g, } 298.15 \text{ K}) + \\ &\quad 2.5\Delta_f H_m^\ominus(\text{H}_2\text{O, l, } 298.15 \text{ K}) - \Delta_f H_m^\ominus(\text{TNMA, s, } 298.15 \text{ K}) \end{aligned} \quad (6)$$

when $\Delta_f H_m^\ominus(\text{CO}_2, \text{g, } 298.15 \text{ K})=(-393.51 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^\ominus(\text{H}_2\text{O, l, } 298.15 \text{ K})=(-285.83 \pm 0.04) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^\ominus(\text{TNMA, s, } 298.15 \text{ K})=-49.45 \text{ kJ} \cdot \text{mol}^{-1}$, the result obtained is $-(1844.58 \pm 0.40) \text{ kJ} \cdot \text{mol}^{-1}$.

3.1.5 Thermochemical parameter: standard combustion energy ($\Delta U_m^\ominus$)

The standard combustion energy of TNMA, $\Delta U_m^\ominus$ (TNMA, s, 298.15 K), is calculated by the following equations:

$$\begin{aligned} \Delta_c H_m^\ominus(\text{TNMA, s, } 298.15 \text{ K}) &= \Delta U_m^\ominus(\text{TNMA, s, } 298.15 \text{ K}) + \\ &\quad \Delta nRT \end{aligned} \quad (7)$$

$$\Delta n = n_g(\text{products}) - n_g(\text{reactants}) \quad (8)$$

where $\Delta_c H_m^\ominus=-(1844.58 \pm 0.40) \text{ kJ} \cdot \text{mol}^{-1}$, n_g is the total amount in mole of gases present as products or as reactants, $\Delta n=3+2.5-0.25=5.25$, $R=8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $T=298.15 \text{ K}$. The result is $-(1857.59 \pm 0.40) \text{ kJ} \cdot \text{mol}^{-1}$.

3.1.6 Explosion properties

By substituting the values of a , b , c , and d in $\text{C}_a\text{H}_b\text{N}_c\text{O}_d=$

$\text{C}_3\text{H}_5\text{N}_5\text{O}_8$, $M=239.07$, $\rho=1.80 \text{ g} \cdot \text{cm}^{-3}$, $\Delta_f H_m^\ominus=-49.45 \text{ kJ} \cdot \text{mol}^{-1}$ into Kamlet-Jacobs Eqs.(9)–(13)

$$D = 1.01(NM_g^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (9)$$

$$p = 1.558NM_g^{1/2}Q^{1/2}\rho^2 \quad (10)$$

$$N = \frac{b + 2d + 2c}{4M} \quad (11)$$

$$M_g = \frac{4M}{b + 2c + 2d} \quad (12)$$

$$Q = 4.184 \times \left(\frac{28.9b + 94.05a + 0.239\Delta_f H^\ominus}{M} \right) \times 10^{-3} \quad (13)$$

where p is detonation pressure (GPa), N is moles of gases detonation products per gram of explosive, M_g is average molecular weight of gaseous products, Q is chemical energy (heat) of detonation ($\text{J} \cdot \text{g}^{-1}$).

The values of D of $9.075 \text{ km} \cdot \text{s}^{-1}$, p of 36.54 GPa , N of $0.0324 \text{ mol} \cdot \text{g}^{-1}$, M_g of $30.45 \text{ g} \cdot \text{mol}^{-1}$, Q of $6849.2 \text{ J} \cdot \text{g}^{-1}$ are obtained, showing that TNMA has explosion performance level approaching that of cyclotetramethylenetetramine (HMX) ($\rho=1.89 \text{ g} \cdot \text{cm}^{-3}$, $D=9.11 \text{ km} \cdot \text{s}^{-1}$).

3.1.7 Heat of decomposition reaction

The heat of decomposition reaction (Q_d) is defined as $Q_d=0.5Q$, i.e. Q_d , taking half-chemical energy (heat) of detonation. For TNMA, $Q_d=0.5Q=3424.6 \text{ J} \cdot \text{g}^{-1}$.

3.1.8 Thermal behavior

A typical DSC curves for TNMA is shown in Fig.1. DSC curve consists of one endothermic peak and one exothermic peak. The endothermic peak at 85.0°C is the phase change from solid to liquid, while the exothermic peak at 197°C is caused by the decomposition reaction.

3.1.9 Non-isothermal kinetic parameters based on peak temperatures and onset temperatures at different heating rates

In order to obtain the kinetic parameters (the apparent activation energy (E) and pre-exponential constant (A)) of the exothermic decomposition reaction of TNMA, a multiple heating method—Kissinger's method¹² [Eq.(14)] is employed. From the original data in Table 1, the value of E_k is determined to be $122.62 \text{ kJ} \cdot \text{mol}^{-1}$. The value of A_k is $10^{12.09} \text{ s}^{-1}$. The linear correlation coefficient r_k is 0.9660 . The values of E_{op} and E_{oc} obtained by Ozawa's method¹³ [Eq.(15)] are 123.73 and 122.64

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

Table 1 Original data of TNMA determined by non-isothermal DSC and kinetic parameters of thermal decomposition reaction obtained by Kissinger's method, Ozawa's method, and Eqs.(16)–(20)

β (K·min ⁻¹)	Initial data ^a			Calculated values ^c																
	T_0 /K	T_i /K	T_p /K	Kissinger's method						Ozawa's method				Eq.(16)		Eq.(17)		Eq.(18)	Eq.(19)	Eq.(20)
				T_{00} /K ^b	T_{01} /K ^b	T_{p0} /K ^b	E_K (kJ·mol ⁻¹)	$\lg(A_k/s^{-1})$	r_K	E_{Op} (kJ·mol ⁻¹)	r_{Op}	E_{Oc} (kJ·mol ⁻¹)	r_{Oc}	b_{e0} ^d	b_{p0} ^d	a_{e0} ^e	a_{p0} ^e	b^f	a^g	E^h (kJ·mol ⁻¹)
2.051	401.15	419.15	437.15	397.05	413.80	430.99	122.62	12.09	0.9660	123.73	0.9696	122.64	0.9701	0.0831	0.0770	34.91	33.71	0.0813	35.12	126.10
5.271	409.15	428.15	447.15											0.9698*	0.9694*	0.9700*	0.9695*	0.9694*	0.9695*	0.9694*
10.71	423.15	442.15	462.15																	
22.27	425.15	444.15	464.15																	

^a T_0 : the initial decomposition temperature, at which the DSC curve deviates from the baseline; T_i : the onset temperature; T_p : the peak temperature. ^b T_{00} or p_0 : the value of T_{e0} or p_0 corresponding to $\beta \rightarrow 0$. ^c E : apparent activation energy; A : pre-exponential constant; subscript K: data obtained by Kissinger's method;¹² subscript O: data obtained by Ozawa's method.¹³ ^dThe value of b_{e0} or p_0 is from $\ln \beta_i$ vs T_{e0} or p_0 relation in Eq.(16). ^eThe value of a_{e0} or p_0 is from $\ln \beta_i$ vs $\ln T_{e0}$ or p_0 relation in Eq.(17). ^fThe value of b is from $\ln[\beta_i/(T_{e0}-T_{0i})]$ vs T_{e0} relation in Eq.(18). ^gThe value of a is from $\ln[\beta_i/(T_{e0}-T_{0i})]$ vs $\ln T_{e0}$ relation in Eq.(19). ^hThe value of E is from $\ln[\beta_i/(T_{e0}-T_{0i})]$ vs $1/T_{e0}$ relation in Eq.(20).

*the linear correlation coefficient

kJ·mol⁻¹, respectively. The values of r_{Op} and r_{Oc} are 0.9696 and 0.9701, respectively. The values of b_{e0} , b_{p0} , a_{e0} , and a_{p0} obtained by Eqs.(16) and (17) and the values of b , a , and E obtained by Eqs.(18), (19), and (20) are shown in Table 1.

$$\ln\left(\frac{\beta_i}{T_{pi}^2}\right) = \ln\left(\frac{A_K R}{E_K}\right) - \frac{E_K}{R} \frac{1}{T_{pi}} \quad (14)$$

$$\lg \beta_i = \lg\left[\frac{A_K E_{Oc}(\text{or } Op)}{R G(\alpha)}\right] - 2.315 - 0.4567 \frac{E_{Oc}(\text{or } Op)}{R T_{e0}(\text{or } p_0)} \quad (15)$$

$$\ln \beta_i = \ln\left[\frac{A_0}{b_{e0}(\text{or } p_0) G(\alpha)}\right] + b_{e0}(\text{or } p_0) T_{e0}(\text{or } p_0) \quad (16)$$

$$\ln \beta_i = \ln\left[\frac{A_0}{(a_{e0}(\text{or } p_0) + 1) G(\alpha)}\right] + (a_{e0}(\text{or } p_0) + 1) \ln T_{e0}(\text{or } p_0) \quad (17)$$

$$\ln\left(\frac{\beta_i}{T_{ci} - T_{0i}}\right) = \ln\left[\frac{A_0}{G(\alpha)}\right] + b T_{ci} \quad (18)$$

$$\ln\left(\frac{\beta_i}{T_{ci} - T_{0i}}\right) = \ln\left[\frac{A_0}{G(\alpha)}\right] + a \ln T_{ci} \quad (19)$$

$$\ln\left(\frac{\beta_i}{T_{ci} - T_{0i}}\right) = \ln\left[\frac{A_0}{G(\alpha)}\right] - \frac{E}{R T_{ci}} \quad (20)$$

where β is the constant heating rate, R in Eqs.(14), (15), and (20) is the gas constant; A_0 , b_{e0} , b_{p0} , a_{e0} , a_{p0} , b , and a in Eqs. (16)–(20) are non-Arrhenius kinetic parameters; $G(\alpha)$ is the in-

tegral mechanism function.

3.1.10 Isothermal kinetic parameters of decomposition reaction at the temperature range 130–150 °C

To verify the reliability of the values of E_K , E_{Op} , and E_{Oc} , we measured the thermal decomposition processes of TNMA under the conditions of vacuum and low loading density at 130, 135, 140, 145, and 150 °C, using a highly sensitive Bourdon glass membrane manometer and calculated the characteristic data, half decomposition period ($t_{1/2}$), initial decomposition rate (W_0), and maximum decomposition rate (W_M) at different temperatures from the obtained standard volume of gas evolved (V_H) and decomposition rate (dV_H/dt) vs time (t) curves shown in Figs.2 and 3 and the values of apparent activation energy (E_a , α is conversion), obtained by differential and integral iso-conversional non-linear Eqs.(21)–(23) tabulated in Table 2. These E values are greater than those of E_K , E_{Op} , and E_{Oc} of TNMA with negative oxygen balance obtained by Kissinger's method and Ozawa's method under the condition of static air, indicating that oxygen gas in static air is principal factor affecting the apparent activation energy of decomposition reaction of TNMA.

$$\Omega_{\text{isol}/t_{1/2}}(E_a) = \min \left| \sum_{i=1}^n \sum_{j=1, j \neq i}^n \frac{t_{1/2,i}}{t_{1/2,j}} e^{\frac{-E_a}{RT_{a,i}}} - n(n-1) \right| \quad (21)$$

Fig.2 Curves of change in gas formation with time during the thermal decomposition of TNMA with the loading density of $1 \times 10^{-3} \text{ g} \cdot \text{mL}^{-1}$ at various temperatures

Fig.3 Curves of change in rate with time during the thermal decomposition of TNMA at various temperatures

Table 2 Apparent activation energy obtained by characteristic data of the thermal decomposition reaction of TNMA at different temperatures^a

$T/^\circ\text{C}$	$t_{1/2}/\text{min}$	$E_d/(\text{kJ}\cdot\text{mol}^{-1})^b$	$W_0/(\text{mL}\cdot\text{g}^{-1}\cdot\text{min}^{-1})$	$E_d/(\text{kJ}\cdot\text{mol}^{-1})^b$	$W_{50}/(\text{mL}\cdot\text{g}^{-1}\cdot\text{min}^{-1})$	$E_d/(\text{kJ}\cdot\text{mol}^{-1})^b$
130	189	160.22	0.302	159.27	1.095	174.61
135	174		0.37		2.89	
140	89					
145	65		1.40		6.30	
150	28		2.60		16.12	

^a $t_{1/2}$: the half decomposition period; W_0 : the initial decomposition rate; W_{50} : the maximum decomposition rate. ^b The data are obtained by differential and integral isoconversional non-linear methods.^{14,15}

$$\mathcal{Q}_{\text{isoD}/W_0}(E_a) = \min \left| \sum_{i=1}^n \sum_{j=1}^n \frac{W_{0i} e^{-E_a/RT_{a,i}}}{W_{0j} e^{-E_a/RT_{a,j}}} - n(n-1) \right| \quad (22)$$

$$\mathcal{Q}_{\text{isoD}/W_M}(E_a) = \min \left| \sum_{i=1}^n \sum_{j=1}^n \frac{W_{Mi} e^{E_a/RT_{a,i}}}{W_{Mj} e^{E_a/RT_{a,j}}} - n(n-1) \right| \quad (23)$$

where $\mathcal{Q}(E_a)$ stands for the evaluation function; subscript isoI stands for the integral isoconversional non-linear method; subscript isoD stands for the differential isoconversional non-linear method.

3.2 Thermal safety description

3.2.1 Self-accelerating decomposition temperature (T_{SADT})

Defining T_{00} or e_0 or p_0 as the value of $T_{(0 \text{ or } e \text{ or } p)}$ corresponding to $\beta \rightarrow 0$ and T_{e0} as the self-accelerating decomposition temperature T_{SADT} , we have

$$T_{0 \text{ or } e \text{ or } p} = T_{00 \text{ or } e_0 \text{ or } p_0} + b\beta_i + c\beta_i^2 + d\beta_i^3, i = 1, 2, \dots, L \quad (24)$$

and

$$T_{e0} = T_{\text{SADT}} \quad (25)$$

The values of T_{00} , T_{e0} , and T_{p0} obtained by using linear regression of T_{0i} , T_{ei} , and T_{pi} against β_i as described in Eq.(24) are all listed in Table 1. The value of T_{SADT} of 413.80 K is obtained by the value of T_{e0} in Table 1 and Eq.(25). This value is less than that of T_{SADT} of 440.73 K of *N,N'*-bis[*N*-(2,2,2-trinitroethyl)-*N*-nitro]ethylene diamine (BTNEDA)¹⁶ and greater than those of T_{SADT} of 374.75 K of bis(2,2,2-trinitroethyl)-nitramine (BTNNA)¹⁷ and of T_{SADT} of 410.92 K of 2,2,2-trinitroethyl-4,4,4-trinitrobutyrate (TNETB), indicating that the heat-resistance abilities of four trinitromethyl explosives decrease in the order BTNEDA>TNMA≈TNETB>BTNNA. This shows that TNMA has better thermal safety and heat-resistant ability.

3.2.2 Critical temperature of thermal explosion (T_b)

The 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 TNMA, the values of T_b obtained by Zhang-Hu-Xie-Li equation [Eq.(26)] taken from literature¹⁸ using the values of T_{e0} and T_{p0} , E_{Oe} and E_{Op} listed in Table 1 are 426.11 and 444.25 K, respectively.

$$T_{\text{be0(or bp0)}} = \frac{E_{\text{Oe or Op}} - \sqrt{E_{\text{Oe or Op}}^2 - 4E_{\text{Oe or Op}}RT_{e0(or p0)}}}{2R} \quad (26)$$

The values of T_b obtained by Hu-Yang-Liang-Xie equation [Eq.(27)] taken from literature^{19,20} using the values of T_{00} , T_{e0} or

T_{p0} , E_{Op} (or E_{Oe}) listed in Table 1 are 423.31 and 442.12 K, respectively.

$$\frac{E_{\text{Oe(or Op)}}(T_{\text{be0(or bp0)}} - T_{00}) + 2RT_{\text{be0(or bp0)}}T_{00}}{RT_{\text{be0(or bp0)}}^2 + E_{\text{Oe(or Op)}}(T_{\text{be0(or bp0)}} - T_{00})} = 1 \quad (27)$$

The values of T_b obtained by Eq.(28)^{21,22} based on Berthelot's equation using the values of b_{e0} and T_{e0} , b_{p0} and T_{p0} listed in Table 1 are 425.83 and 443.98 K, respectively.

$$T_{\text{be0(or bp0)}} = T_{e0(or p0)} + \frac{1}{b_{e0(or p0)}} \quad (28)$$

The values of T_b obtained by Eq.(29)^{21,23} based on Harcourt-Esson's equation using the values of a_{e0} and T_{e0} , a_{p0} and T_{p0} listed in Table 1 are 426.01 and 444.16 K, respectively.

$$T_{\text{be0(or bp0)}} = \frac{a_{e0(or p0)}}{a_{e0(or p0)} - 1} T_{e0(or p0)} \quad (29)$$

The value of T_b obtained by Eq.(30)^{21,24} based on Berthelot's equation using the values of b and T_{e0} , T_{00} listed in Table 1 is 412.14 K.

$$b(T_b - T_{e0}) \left[1 + \frac{1}{1 + (T_b - T_{00})b} \right] = 1 \quad (30)$$

The value of T_b obtained by Eq.(31)^{21,25} based on Harcourt-Esson's equation using the values of a , and T_{e0} and T_{00} listed in Table 1 is 408.31 K.

$$(T_b - T_{e0}) \left[\frac{a}{T_b} + \frac{\frac{a}{T_b} - \frac{a}{T_b^2}(T_b - T_{00})}{1 + (T_b - T_{00})\frac{a}{T_b}} \right] = 1 \quad (31)$$

It can be seen from the above-mentioned results that the calculated values of $T_{\text{be0(or bp0)}}$ obtained by the six different formulae agree well to each other, demonstrating that: (1) for TNMA, the values of T_{be0} of 420.28 K and T_{bp0} of 443.63 K are acceptable; (2) Eqs.(26)–(31) are suitable for estimating the values of T_b for small-scale EMs; (3) in comparison with RDX with $T_b=454.08$ K,³ lower value of T_b for TNMA shows that the transition from thermal decomposition to thermal explosion is easy to take place.

This value of T_b of 426.11 K is less than that of T_b of 449.88 K of BTNEDA¹⁶ and greater than those of T_b of 387.11 K of BTNNA¹⁷ and 426.05 K of TNETB, indicating that the thermal safety and heat-resistance abilities of four trinitromethyl explosives decrease in the order of BTNEDA>TNMA≈TNETB>

BTNNA. TNMA has better thermal safety and heat-resistant ability.

3.2.3 Adiabatic time-to-explosion (t_{Tlad})

The t_{Tlad} of EMs is the time of EM decomposition transiting to explosion under the adiabatic conditions and is an important parameter for assessing the thermal stability and the safety of EMs. In order to acquire the value of t_{Tlad} of TNMA, substituting the following data: $C_p=1.15 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$, $Q_d=3424.6 \text{ J} \cdot \text{g}^{-1}$, $A_K=10^{12.09} \text{ s}^{-1}$, $E=E_K=122620 \text{ J} \cdot \text{mol}^{-1}$, $R=8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $f(\alpha)=(1-\alpha)^n$, $T_0=T_{e0}=413.80 \text{ K}$, $T=T_b=444.25 \text{ K}$ into Eqs.(32)–(34)^{21,26}

$$C_p \frac{dT}{dt} = Q_d A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (32)$$

$$t_{\text{Tlad}} = \int_0^t dt = \frac{1}{Q_d A} \int_{T_0}^T \frac{C_p \exp(E/RT)}{f(\alpha)} dT \quad (33)$$

$$\alpha = \frac{1}{Q_d A} \int_{T_0}^T \frac{C_p}{Q_d} dT \quad (34)$$

the values of t_{Tlad} of 9.12 s ($n=0$), 9.21 s ($n=1$), and 9.31 s ($n=2$) are obtained. In comparison with BTNNA with $t_{\text{Tlad}}=2.24 \text{ s}$ ($n=0$), 2.25 s ($n=1$), and 2.26 s ($n=2$),¹⁷ the values of t_{Tlad} for TNMA increase approximately by a factor of 4, meaning that TNMA has a relative better heat-resistance ability.

3.2.4 Critical temperature of hot-spot initiation ($T_{\text{cr, hot-spot}}$)

In order to obtain the $T_{\text{cr, hot-spot}}$ of TNMA, assuming that $T_{\text{cr, hot-spot}}$ is a function of the size and duration of the hot-spot and of the physical and chemical properties of the explosive, the equation^{27,28} for calculating the value of $T_{\text{cr, hot-spot}}$ may be expressed as

$$\begin{aligned} & \left(\frac{4}{3} \pi a^3 \right) \rho Q_d \left\{ 1 - \exp\left[-(t-t_0)Ae^{-E/RT_{\text{cr}}}\right] \right\} \\ &= \int_a^\infty 4\pi r^2 \rho C_p \left[\frac{a\theta_0}{r} \operatorname{erfc}\left(\frac{r-a}{2\sqrt{Bt}}\right) \right] dr \\ &= \int_a^\infty 4\pi r^2 \rho C_p \left[\frac{a(T_{\text{cr, hot-spot}} - T_{\text{room}})}{r} \operatorname{erfc}\left(\frac{r-a}{2\sqrt{\frac{\lambda}{\rho C_p} t}}\right) \right] dr \end{aligned} \quad (35)$$

where a is the radius of the hot-spot in cm; $t-t_0$ is the time interval in s; T_{room} is the ambient temperature in K.

By substituting the following data of TNMA: $a=10^{-3} \text{ cm}$, $\rho=1.80 \text{ g} \cdot \text{cm}^{-3}$, $Q_d=3424.6 \text{ J} \cdot \text{g}^{-1}$, $t-t_0=10^{-4} \text{ s}$, $A=A_K=10^{12.09} \text{ s}^{-1}$, $E=E_K=122620 \text{ J} \cdot \text{mol}^{-1}$, $R=8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $C_p=1.15 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$,

$T_{\text{room}}=293.15 \text{ K}$, $\lambda=27.05 \times 10^{-4} \text{ J} \cdot \text{cm}^{-1} \cdot \text{s}^{-1} \cdot \text{K}^{-1}$ into Eq.(35), the value of $T_{\text{cr, hot-spot}}$ of 467.73 °C is obtained. In comparison with BTNEDA with $T_{\text{cr, hot-spot}}=333.86 \text{ °C}$, BTNNA with $T_{\text{cr, hot-spot}}=446.41 \text{ °C}$, and TNETB with $T_{\text{cr, hot-spot}}=638.14 \text{ °C}$, the thermal safety of four trinitroethyl explosives decreases in the order of TNETB>TNMA≈BTNNA>BTNEDA, indicating that TNMA has a better thermal safety.

3.2.5 Characteristic drop height of impact sensitivity (H_{50})

To obtain the H_{50} of TNMA, by substituting the values of λ , ρ , A , Q_d , and E of eight explosives with known 50% drop height listed in Table 3 into Eq.(36),^{29,30} the corresponding values of n of 0.564623, and D_2 of 33.8765, and D_3 of -0.347174 are obtained. By substituting the values of λ , ρ , A , Q_d , and E of TNMA listed in Table 3 and the values of n , D_2 , and D_3 into Eq. (36), the corresponding value of H_{50} of TNMA is obtained (data shown in Table 7), showing that it has impact sensitivity level approaching those of PETN and tetryl.

$$\frac{1}{2} n \lg H_{50} + \lg \sqrt{\frac{\lambda}{A \rho Q_d}} + D_3 + \frac{0.02612E}{T_1 + D_2 H_{50}^n} = 0 \quad (36)$$

where n , D_2 , and D_3 are parameters of the correlation.

3.2.6 Critical thermal explosion ambient temperature

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

In order to explore the heat-resistance ability of TNMA, the values of T_{acr} , $S(T)$ vs T relation, SD, and P_{TE} are calculated by Frank-Kamenetskii (FK) formula (37)³¹ and Wang-Du's formulas (38)–(41)^{32,33}.

$$T_{\text{acr}} = \frac{-E_K}{2RLambertW_{-1}\left[-\frac{1}{2}\sqrt{\frac{\lambda E_K \delta_{\text{cr}}}{r^2 Q_d \rho A_K R}}\right]} \quad (37)$$

$$\begin{aligned} S(T) &= \frac{W(E_K - 2RT)}{\sqrt{2\pi} \sigma_\delta RT^4} \exp\left\{-\left[\frac{\exp(-\frac{E_K}{RT})}{T^2} - \delta_{\text{cr}}\right]^2\right\} \\ &2\sigma_\delta^2 - \frac{E_K}{RT} \end{aligned} \quad (38)$$

$$\frac{r^2 Q_d E_K \rho A_K}{\lambda R} = W \quad (39)$$

$$\sigma_\delta = W\left(\frac{E_K - 2R\mu_T}{R\mu_T^4}\right) \exp\left(-\frac{E_K}{R\mu_T}\right) \sigma_T \quad (40)$$

Table 3 Explosive parameters and comparison of experimental and predicted 50% drop heights

No.	Acronym	$10^4 \lambda^a$	ρ	$\lg(A/\text{s}^{-1})^b$	Q_d^c	E^b	H_{50}/cm		n	D_2	D_3
		($\text{J} \cdot \text{cm}^{-1} \cdot \text{s}^{-1} \cdot \text{K}^{-1}$)	($\text{g} \cdot \text{cm}^{-3}$)				Exp.	predicted			
1	HMX	34.43	1.79	33.80	2764	373700	32 ^a	33.4	0.564623	33.8765	-0.347174
2	RDX	10.58	1.66	12.50	2810	140000	26 ^a	20.1			
3	TNT	21.30	1.57	11.10	1506	155017	59 ^a	56.4			
4	PETN	25.10	1.68	10.40	3263	112300	16 ^a	15.60			
5	BTF	20.92	1.81	22.81	2949	255000	28 ^a	30.0			
6	HNS	8.53	1.65	22.63	1389	289000	54 ^a	50.1			
7	Tetryl	18.74	1.67	16.90	1904	172500	17 ^d	17.6			
8	NG	12.55	1.60	16.09	2092	150122	7 ^d	9.4			
9	TNMA	27.05	1.80	12.09	3424.6	122620	–	12.51			

^acited from Ref. 1; ^bcited from Ref. 2; ^c Q_d taking a half of the explosion heat; ^dcited from Ref. 29; $T_{\text{room}}=300 \text{ K}$

Table 4 Calculated values of $T_{S(T)max}$, SD, T_{act} , and P_{TE} for TNMA

Explosive name	T/K	r/m	Infinite cylinder				Sphere				Infinite plate			
			$T_{S(T)max}/K$	T_{act}/K	$P_{TE}/\%$	SD/%	$T_{S(T)max}/K$	T_{act}/K	$P_{TE}/\%$	SD/%	$T_{S(T)max}/K$	T_{act}/K	$P_{TE}/\%$	SD/%
TNMA	300	1.0	299.55	299.85	59.14	40.86	299.55	303.11	51.12	48.88	299.55	294.71	72.33	27.67
TNETB	300	1.0	311.5	306.59	42.89	57.31	315.00	310.28	36.26	63.75	305.50	300.78	56.26	43.74
BTNNA	310	1.0	308.5	303.82	74.43	25.57	312.00	307.02	66.33	33.67	303.50	298.77	85.43	14.57
BTNEDA	350	1.0	354.5	349.73	60.69	39.31	357.00	352.42	54.19	45.81	350.00	345.47	71.45	28.55

$$\mu_T = \frac{-E_K}{2RLambertW_{-1}\left(-\frac{1}{2}\sqrt{\frac{\lambda E_K \delta_{cr}}{r^2 Q_d \rho A_K R}}\right)} \quad (41)$$

SD was obtained by Eq.(42)

$$SD = \int_0^{+\infty} \int_0^{+\infty} \frac{W(E_K - 2RT)}{2\pi\sigma_\delta \sigma_T R T^4} \exp\left\{-\left[\frac{\exp(-\frac{E_K}{RT})}{T^2} - \delta_{cr}\right]^2\right\} \left[2\sigma_\delta^2 - \frac{E_K}{RT} - \frac{(Y - T + \mu_T)^2}{2\sigma_T^2}\right] dT dY \quad (42)$$

The P_{TE} was expressed as Eq.(43)

$$P_{TE} = 1 - SD \quad (43)$$

where, δ is the Frank-Kamenetskii (FK) parameter; δ_{cr} is the criticality of thermal explosion of exothermic system; r is characteristic measurement of reactant; μ_T is the average value of temperature T ; σ_δ is the standard deviation of FK parameter; σ_T is the standard deviation of the measured surrounding temperature; T is the surrounding temperature;

Substituting E with $122620 \text{ J} \cdot \text{mol}^{-1}$, A with $10^{12.09} \text{ s}^{-1}$, ρ with $1.80 \times 10^{-3} \text{ kg} \cdot \text{m}^{-3}$, λ with $0.2705 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, Q_d with $3.4246 \times 10^6 \text{ J} \cdot \text{kg}^{-1}$, r with 1.0 m , T with 300 K , σ_T with 10 K in Eqs. (37)–(43), $S(T)$ vs T relation curves for infinite plate, infinite cylindrical and spheroidic TNMA in Fig.4 and the maximum value of $S(T)$ vs T relation curve ($T_{S(T)max}$), SD, T_{act} and P_{TE} of TNMA in Table 4 are obtained, showing that the accelerating tendency from adiabatic decomposition to explosion of large scale TNMA and the thermal safety of TNMA with different shapes decreases in the order: sphere>infinite cylinder>infinite plate. For comparison with the other trinitromethyl explosives the literature values of $T_{S(T)max}$, SD, T_{act} and P_{TE} for BTNEDA¹⁶, BTNNA¹⁷ and 2,2,2-trinitroethyl-4,4,4-trinitrobutyrate (TNETB) are also listed in Table 4. It can be seen in Table 4 that the critical thermal explosion ambient temperature T_{act} of four trinitro-

Fig.4 $S(T)$ vs T relation curves for infinite platelike, infinite cylindrical, and spheroidic TNMA

methyl explosives decreases in the order of BTNEDA>TNETB>BTNNA>TNMA.

4 Conclusions

(1) Using T_{SADT} and T_b as criterions, the heat-resistance abilities and the transition resistance from thermal decomposition to thermal explosion of four trinitroethyl explosives decrease in the order of BTNEDA>TNMA≈TNETB>BTNNA, showing that TNMA has better thermal safety and heat-resistant ability.

(2) Using $T_{cr, hot-spot}$ as criterion, the thermal safety of four trinitroethyl explosives decreases in the order of TNETB>TNMA≈BTNNA>BTNEDA.

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

(4) The thermal safety of large scale TNMA with different shapes decreases in the order: sphere>infinite cylinder>infinite plate. Using $T_{S(T)max}$ and T_{act} as criterions, the thermal safety of large scale TNMA is poorer than those of large scale BTNNA, TNETB and BTNEDA.

(5) TNMA has high standard combustion energy and high chemical energy (heat) of detonation, and explosion performance level approaching that of HMX. It can be used as a main ingredient of composite explosive.

References

- (1) Dong, H. S.; Zhou, F. F. *Properties of High Explosives and Related Materials*; Science Press: Beijing, 1989. [董海山, 周芬芬. 高能炸药及相关物性能. 北京: 科学出版社, 1989.]
- (2) Chen, S. P.; Hu, R. Z.; Song, J. R.; Yang, D. S.; Gao, S. L.; Zhao, H. A.; Shi, Q. Z. *Chin. J. Chem.* **2003**, *21* (11), 1419.
- (3) Dong, H. S.; Hu, R. Z.; Yao, P.; Zhang, X. Y. *Collection of Thermospectrum of Energetic Materials*; National Defense Industry Press: Beijing, 2002. [董海山, 胡荣祖, 姚朴, 张孝仪. 含能材料热谱集. 北京: 国防工业出版社, 2002.]
- (4) Song, Q. C.; Hu, R. Z.; Zhao, F. Q.; Gao, H. X.; Dong, H. S. *Chin. J. Energ. Mater.* **2007**, *15* (3), 193. [松全才, 胡荣祖, 赵凤起, 高红旭, 董海山. 含能材料, **2007**, *15* (3), 193.]
- (5) Hu, R. Z.; Song, Q. C.; Dong, H. S.; Zhao, F. Q.; Gao, H. X.; Zhao, H. A.; Ma, H. X. *Chin. J. Explos. Propell.* **2009**, *32* (6), 62. [胡荣祖, 松全才, 董海山, 赵凤起, 高红旭, 赵宏安, 马海霞. 火炸药学报, **2009**, *32* (6), 62.]
- (6) Hu, R. Z.; Gao, H. X.; Zhao, F. Q.; Zhang, H.; Gou, M.; Zhao, H. A.; Wang, X. J.; Ma, H. X. *Chin. J. Energ. Mater.* **2009**, *17* (2), 127. [胡荣祖, 高红旭, 赵凤起, 张海, 勾明, 赵宏安, 王喜军, 马海霞. 含能材料, **2009**, *17* (2), 127.]

- (7) Bai, J. N.; Jin, S. H.; Song, Q. C. *Chin. J. Energ. Mater.* **2000**, *8* (4), 168. [白景瑞, 金韶华, 松全才. 含能材料, **2000**, *8* (4), 168.]
- (8) Hu, R. Z. *Explosive Materials* **1966**, *9* (4), 54. [胡荣祖. 爆炸器材, **1966**, *9* (4), 54.]
- (9) Hu, R. Z.; Lu, X. S.; Fang, Y. G. *J. Energ. Mater.* **1993**, *11* (3), 219. doi: 10.1080/07370659308227812
- (10) Hu, R. Z.; Xie, J. J. Investigation of the Ingredients Compatibility and Available Life of the Plastic Bonded Explosives (PBX). In *The Joint Symposium Entitled Compatibility of Plastics/ Materials with Explosives Processing Explosives*, Blacksburg, Virginia USA. Oct 14–16, 1980; Bartron, L. R. Ed.; American Defense Preparedness Association, Arlington, 1980; pp 335–348.
- (11) Hu, R. Z.; Zhao, F. Q.; Gao, H. X.; Song, J. R. *Fundamentals and Application of Calorimetry*; Science Press: Beijing, 2011. [胡荣祖, 赵凤起, 高红旭, 宋纪蓉. 量热学基础与应用. 北京: 科学出版社, 2011.]
- (12) Kissinger, H. E. *Anal. Chem.* **1957**, *29* (11), 1702. doi: 10.1021/ac60131a045
- (13) Ozawa, T. *Bull. Chem. Soc. Jpn.* **1965**, *38* (1), 1881. doi: 10.1246/bcsj.38.1881
- (14) Hu, R. Z.; Zhao, F. Q.; Gao, H. X.; Zhang, H.; Song, Q. C. *Chin. J. Energ. Mater.* **2007**, *15* (2), 97. [胡荣祖, 赵凤起, 高红旭, 张 海, 松全才. 含能材料, **2007**, *15* (2), 97.]
- (15) Hu, R. Z.; Shi, Q. Z. *Thermal Analysis Kinetics*; Science Press: Beijing, 2001. [胡荣祖, 史启桢. 热分析动力学, 北京: 科学出版社, 2001.]
- (16) Hu, R. Z.; Zhao, F. Q.; Gao, H. X.; Ma, H. X.; Zhang, H.; Zhao, H. A.; Xu, K. Z.; Yao, E. G. *Chin. J. Energ. Mater.* **2012**, *20* (5), 505.
- (17) Hu, R. Z.; Zhao, F. Q.; Gao, H. X.; Ma, H. X.; Zhang, H.; Zhao, H. A.; Xu, K. Z.; Yao, E. G. *Chin. J. Explos. Propell.* **2013**, *36* (1), 9.
- (18) Zhang, T. L.; Hu, R. Z.; Xie, Y.; Li, F. P. *Thermochim. Acta* **1994**, *244* (2), 171.
- (19) Hu, R. Z.; Gao, S. L.; Zhao, F. Q.; Shi, Q. Z.; Zhang, T. L.; Zhang, J. J. *Thermal Analysis Kinetics*; Science Press: Beijing, 2008. [胡荣祖, 高胜利, 赵凤起, 史启桢, 张同来, 张建军. 热分析动力学. 北京: 科学出版社, 2008.]
- (20) Xie, Y.; Hu, R. Z.; Yang, C. Q.; Feng, G. F.; Zhou, J. H. *Propellants Explos. Pyrotech.* **1992**, *17* (6), 298.
- (21) Hu, R. Z.; Ma, H. X.; Yan, B.; Zhang, H.; Han, L.; Gao, H. X.; Zhao, F. Q.; Yao, E. G.; Zhao, H. A. *Chin. J. Energ. Mater.* **2013**, *21* (2), 180. [胡荣祖, 马海霞, 严 彪, 张 海, 韩 路, 高红旭, 赵凤起, 姚二岗, 赵宏安. 含能材料, **2013**, *21* (2), 180.]
- (22) Xue, L.; Zhao, F. Q.; Hu, R. Z.; Gao, H. X. *J. Energ. Mater.* **2010**, *28* (1), 17. doi: 10.1080/07370650903124518
- (23) Zhao, F. Q.; Hu, R. Z.; Gao, H. X. *Chin. J. Chem.* **2009**, *27* (6), 1067. doi: 10.1002/cjoc.v27:6
- (24) Zhao, F. Q.; Hu, R. Z.; Zhang, H.; Gao, H. X.; Zhao, H. A.; Ma, H. X. *Chem. Res. Chin. Univ.* **2010**, *26* (5), 829.
- (25) Zhang, H.; Hu, J. Y.; Hu, R. Z.; Zhao, F. Q.; Gao, H. X. *Journal of Shanghai Jiaotong University* **2011**, *16* (2), 247. doi: 10.1007/s12204-011-1131-6
- (26) Smith, L. C. *Thermochim. Acta* **1975**, *13* (1), 1. doi: 10.1016/0040-6031(75)80060-8
- (27) Friedman, M. H. *Trans. Faraday Soc.* **1963**, *59* (8), 1865.
- (28) Bruckman, H. J.; Guillet, J. E. *Can. J. Chem.* **1968**, *46* (20), 3221. doi: 10.1139/v68-534
- (29) Friedman, M. H. A Correlation of Impact Sensitivities by Means of the Hot Model. In: 9th Symposium (International) on Combustion, Cornell University, Ithaca, Aug 27–Sept 1, 1962; Berl, W. G. Ed.; Academic Press Inc. Led.: New York, 1963; pp 294–302.
- (30) Hu, R. Z.; Zhao, F. Q.; Gao, H. X.; Zhang, H.; Zhao, H. A.; Wang, X. J.; Zhang, X. L.; Feng, Y.; Ma, H. X. *Chin. J. Energ. Mater.* **2009**, *17* (3), 251. [胡荣祖, 赵凤起, 高红旭, 张 海, 赵宏安, 王喜军, 张晓亮, 冯 煜, 马海霞. 含能材料, **2009**, *17* (3), 251.]
- (31) Frank-Kamenetskii, D. A.; Frank-Kamenetskii, O. A. *J. Phys. Chem. (USSR)* **1939**, *13* (6), 738.
- (32) Wang, P. Study on Thermal Safety and Ignition Reliability of Exothermic System. Ph. D. Dissertation, Beijing Institute of Technology, Beijing, 2008. [王 鹏. 放热系统热安全性和点火可靠性研究[D]. 北京: 北京理工大学, 2008.]
- (33) Wang, P.; Du, Z. M. *Energ. Mater.* **2007**, *15* (6), 633. [王 鹏, 杜志明. 含能材料, **2007**, *15* (6), 633.]