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ESTIMATION OF THE CRITICAL TEMPERATURE OF THERMAL EXPLOSION FOR THE HIGHLY NITRATED NITROCELLULOSE USING NON-ISOTHERMAL DSC

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Abstract

Two methods for estimating the critical temperature (T_b) of thermal explosion for the highly nitrated nitrocellulose (HNNC) are derived from the Semenov's thermal explosion theory and two non-isothermal kinetic equations, $d\alpha/dt=Af(\alpha)e^{-E/RT}$ and $d\alpha/dt=Af(\alpha)[1+E/(RT)(1-T_o/T)]e^{-E/RT}$, using reasonable hypotheses. We can easily obtain the values of the thermal decomposition activation energy (E), the onset temperature (T_e) and the initial temperature (T_o) at which DSC curve deviates from the baseline of the non-isothermal DSC curve of HNNC, and then calculate the critical temperature (T_b) of thermal explosion by the two derived formulae. The results obtained with the two methods for HNNC are in agreement to each other.

Keywords: critical temperature, DSC, HNNC, non-isothermal

Introduction

HNNC containing 14.14% of nitrogen has the potential use as an energetic ingredient of propellants. Its critical temperature (T_b) of thermal explosion has never been reported so far. The aim of this work is to present two methods for estimating the value of T_b. The data needed for the two methods can be obtained by the non-isothermal DSC measurement alone.

Theoretical

The enthalpy (q_1) of thermal decomposition reaction per unit time for HNNC can be expressed by the equation

$$q_1 = Q\frac{VD}{M}\frac{d\alpha}{dt} \tag{1}$$

where Q is the enthalpy of the thermal decomposition reaction in J mol^{-1}, V is the volume of HNNC loaded in cm^3, d is the loading density in g cm^{-3}, M is the mole

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mass of HNNC in g mol^{-1} and dα/dt is the reaction rate. According to previous papers [1, 2], the reaction rate may be expressed as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=Af(\alpha)\left[1+\frac{E}{RT}\left(1-\frac{T_{\mathrm{oo}}}{T}\right)\right]\mathrm{e}^{-\mathrm{E/RT}} \tag{2}$$

where α stands for the conversion degree, T for the temperature (K), $f(\alpha)$ for the differential mechanism functions, t for the time, R for the gas constant, A for the pre-exponential factor, and E for the activation energy. T_{oo} is the initial temperature at which the DSC curve deviates from the baseline when the heating rate tends to zero in K.

In the general case $f(\alpha)=(1-\alpha)^{\mathrm{n}}$, where n stands for the reaction order. Since the transition from thermal decomposition to combustion starts in the range of low conversion degree, i.e., $f(\alpha)\approx 1$, the enthalpy of decomposition reaction in unit time for one mole HNNC may be expressed as

$$q_1=QA\left[1+\frac{E}{RT}\left(1-\frac{T_{\mathrm{oo}}}{T}\right)\right]\mathrm{e}^{-\mathrm{E/RT}} \tag{3}$$

At the same time, the amount of heat (q_2) transferred by the wall of the reactor to surrounding medium in unit time is

$$q_2=k'(T-T_{\mathrm{c}})S \tag{4}$$

where S is the external surface of the loaded sample in cm^2, k' is an overall heat transfer coefficient in J cm^{-2} K^{-1} s^{-1}, T_{c} is the temperature of the reaction wall and surroundings according to the linear relationship $T_{\mathrm{c}}=T_{\mathrm{o}}+\beta t$, where β is the heating rate in K min^{-1}. When the thermal explosion starts, Eq. (4) becomes

$$q_2=k'(T_{\mathrm{b}}-T_{\mathrm{eo}})S \tag{5}$$

where T_{b} is the thermal explosion temperature of HNNC in K (Fig. 1); T_{eo} is the onset temperature in the DSC curve under linear temperature increase condition when β tends to zero (Fig. 2).

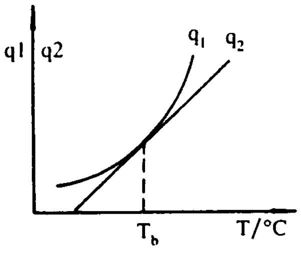

Fig. 1 q_1–q_2 relation

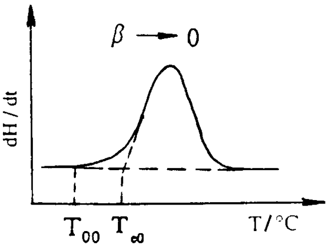

Fig. 2 Schematic diagrams of typical DSC curves of thermal decomposition for energetic materials

According to the Semenov's thermal explosion theory [3] the sufficient and essential conditions from thermal decomposition to thermal explosion are as follows:

$$(q_1)_{\mathrm{T_b}} = (q_2)_{\mathrm{T_b}} \tag{6}$$

$$\left(\frac{\mathrm{d}q_1}{\mathrm{T}}\right)_{\mathrm{T_b}} = \left(\frac{\mathrm{d}q_2}{\mathrm{T}}\right)_{\mathrm{T_b}} \tag{7}$$

When the thermal explosion starts, Eq. (3) becomes

$$q_1 = QA\left[1 + \frac{E}{RT_{\mathrm{b}}}\left(1 - \frac{T_{\mathrm{oo}}}{T_{\mathrm{b}}}\right)\right]\mathrm{e}^{-\mathrm{E/RT_b}} \tag{8}$$

Differentiation of Eq. (3) with respect to t gives

$$\frac{\mathrm{d}q_1}{\mathrm{d}t}\Big|_{\mathrm{T=T_b}} = QA\mathrm{e}^{-\mathrm{E/RT_b}}\frac{E}{RT_{\mathrm{b}}^2}\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\mathrm{b}}\left[\frac{2T_{\mathrm{oo}}}{T_{\mathrm{b}}} + \frac{E}{RT_{\mathrm{b}}}\left(1 - \frac{T_{\mathrm{oo}}}{T_{\mathrm{b}}}\right)\right] \tag{9}$$

Differentiation of Eq. (4) with respect to t gives

$$\frac{\mathrm{d}q_2}{\mathrm{d}t}\Big|_{\mathrm{T=T_b}} = k'S\left[\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\mathrm{b}} - \beta\right] \tag{10}$$

Combining Eqs (5), (6) and (8), we have

$$QA\left[1 + \frac{E}{RT_{\mathrm{b}}}\left(1 - \frac{T_{\mathrm{oo}}}{T_{\mathrm{b}}}\right)\right]\mathrm{e}^{-\mathrm{E/RT_b}} = k'S(T_{\mathrm{b}} - T_{\mathrm{eo}}) \tag{11}$$

Combining Eqs (7), (9) and (10), we have

$$k'S\left[\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\mathrm{b}} - \beta\right] = QA\mathrm{e}^{-\mathrm{E/RT_b}}\frac{E}{RT_{\mathrm{b}}^2}\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\mathrm{b}}\left[\frac{2T_{\mathrm{oo}}}{T_{\mathrm{b}}} + \frac{E}{RT_{\mathrm{b}}}\left(1 - \frac{T_{\mathrm{oo}}}{T_{\mathrm{b}}}\right)\right] \tag{12}$$

Mutiplying both sides of Eq. (12) by (T_{b}–T_{eo}), we obtain

$$k'S\left[\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\mathrm{b}}-\beta\right](T_{\mathrm{b}}-T_{\mathrm{eo}})= \tag{13}$$
$$=QA\mathrm{e}^{-E/RT_{\mathrm{b}}}\frac{E}{RT_{\mathrm{b}}^{2}}\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\mathrm{b}}\left[\frac{2T_{\mathrm{oo}}}{T_{\mathrm{b}}}+\frac{E}{RT_{\mathrm{b}}}\left(1-\frac{T_{\mathrm{oo}}}{T_{\mathrm{b}}}\right)\right](T_{\mathrm{b}}-T_{\mathrm{eo}})$$

Substituting Eq. (11) into Eq. (13), we obtain

$$\frac{\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\mathrm{b}}-\beta}{\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\mathrm{b}}}=\frac{\frac{E}{RT_{\mathrm{b}}^{2}}\left[\frac{2T_{\mathrm{oo}}}{T_{\mathrm{b}}}+\frac{E}{RT_{\mathrm{b}}}\left(1-\frac{T_{\mathrm{oo}}}{T_{\mathrm{b}}}\right)\right](T_{\mathrm{b}}-T_{\mathrm{eo}})}{1+\frac{E}{RT_{\mathrm{b}}}\left(1-\frac{T_{\mathrm{oo}}}{T_{\mathrm{b}}}\right)} \tag{14}$$

As the thermal explosion starts, $(\mathrm{d}T/\mathrm{d}t)_{\mathrm{b}}>>\beta$, and Eq. (14) may be simplified to the form

$$\frac{E(T_{\mathrm{b}}-T_{\mathrm{oo}})+2RT_{\mathrm{b}}T_{\mathrm{oo}}}{RT_{\mathrm{b}}^{2}+E(T_{\mathrm{b}}-T_{\mathrm{oo}})}\,\frac{E}{RT_{\mathrm{b}}^{2}}(T_{\mathrm{b}}-T_{\mathrm{eo}})=1 \tag{15}$$

or

$$R^{2}T_{\mathrm{b}}^{4}+RET_{\mathrm{b}}^{3}-(3RET_{\mathrm{oo}}+E^{2})T_{\mathrm{b}}^{2}+ \tag{16}$$
$$(E^{2}T_{\mathrm{eo}}+E^{2}T_{\mathrm{oo}}+2RET_{\mathrm{eo}}T_{\mathrm{oo}})T_{\mathrm{b}}-E^{2}T_{\mathrm{eo}}T_{\mathrm{oo}}=0$$

Equation (16) is the relation formula for estimating the critical temperature of thermal explosion of HNNC under linear temperature increase conditions.

Similarly, the following equation can be obtained if $\mathrm{d}\alpha/\mathrm{d}t=A\mathrm{e}^{-E/RT}f(\alpha)$.

$$\frac{E}{RT_{\mathrm{b}}^{2}}(T_{\mathrm{b}}-T_{\mathrm{eo}})=1 \tag{17}$$

Substituting the measured values of T_{oo}, T_{eo} and E or the values of T_{eo} and E, respectively, into Eq. (16) or Eq. (17), the value of T_{b} is obtained.

Experimental

Materials

HNNC (14.14% N) used in this work was prepared and purified at our institute.

Instrument and conditions

In the present experiments, the initial data needed for calculating all the kinetic parameters were obtained using a CDR-1 differential scanning calorimeter (Shanghai Tianping Instrument Factory, China) with an aluminium cell. The conditions of the DSC analyses were: sample mass, about 0.7 mg; heating rates, 1, 2, 5, 10 and 20 K $\min^{-1}$, respectively; calorimetric sensitivities, ±20.92 and ±41.84 mJ s^{-1}; atmosphere, static air; reference sample, $\alpha-Al_2O_3$; the precision of temperature was 0.25 K; the temperature and heat were calibrated using pure indium and tin powders.

Results and discussion

The measured values of β, T_{oi} and T_{ei} (i=1,2,···,5), the calculated value of E_{ke} by the Kissinger's method and the obtained values of T_{oo} and T_{eo} when β tends to zero, together with the reasonable values of T_b obtained by substituting the above-mentioned values into Eqs (16) and (17), are shown in Table 1. It can be seen that the calculated values of T_b obtained by the two different methods agree well to each other, clearly demonstrating that Eqs (16) and (17) are suitable for estimating the values of T_b for HNNC.

Table 1 The calculated values of the critical temperature of thermal explosion for HNNC (14.14% N)

β/ K $\min^{-1}$	T_o/ K	T_e/ K	E_{ke}/ kJ mol^{-1}	T_{oo}/ K	T_{eo}/ K	T_b/K Eq. (16)	T_b/K Eq. (17)
21.386	455.9	481.7	171.4				
10.770	448.9	473.4					
5.202	443.9	465.7					
2.211	443.4	457.9					
1.059	440.9	451.2					
$\beta \to 0$				440.9	446.3	453.3	456.4

β – heating rate; T_o – initial temperature at which the DSC curve deviates from the baseline; T_e – onset temperature in the DSC curve; E_{ke} – apparent activation energy obtained by Kissinger's method [4]

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