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Thermal behavior of 1,3,3-trinitroazetidine

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Abstract

The thermodynamic parameters of the melting process, the kinetic parameters of the exothermic decomposition and the critical temperature of thermal explosion for 1,3,3-trinitroazetidine (TNAZ) were measured by using a microcalorimeter, a differential scanning calorimeter and a time-to-explosion testing apparatus. Information was obtained on its thermal behavior.

Keywords: DSC; Kinetic and thermodynamic parameters; Microcalorimetry Thermal behavior; TNAZ

1. Introduction

1,3,3,-trinitroazetidine (TNAZ), which contains one nitramine and one geminal-dinitroalkyl group is a main ingredient of cast explosives. Thermal behavior is one of the most important aspects of TNAZ. There are a few reports on the thermal behavior of TNAZ, such as its initial dissociation mechanism [1] and rapid thermal decomposition process [2–4]. The thermal behavior of TNAZ under non-isothermal TG conditions has also been studied in [2]. However, determination of the thermodynamic parameters of the melting process, the kinetic parameters of exothermic decomposition reaction and the critical temperature of thermal explosion for TNAZ has not yet been reported. The aim of this work is to study these parameters of TNAZ with a microcalorimeter, a differential scanning calorimeter and a time-to-explosion testing apparatus.

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2. Experimental

2.1. Materials

TNAZ was prepared and purified according to a reported method [5]. The structure of TNAZ was characterized by elemental analysis, molecular weight measurements, IR spectrometry, mass spectrometry and nuclear magnetic resonance spectrometry. Its purity was more than 99.4%.

2.2. Experimental equipment and conditions

The heat flow curves of the melting process of TNAZ were measured with a Calvet microcalorimeter, type E (SETARAM, France), which had a sensitivity of 66.5 $\mu V\ mW^{-1}$ and was equipped with two 15 ml vessels. The microcalorimeter was calibrated via the Joule effect. The precision of the enthalpy measurements was 2%. The amount of TNAZ used was about 20 mg.

DSC experiments were carried out with a MODEL CDR-1 thermal analyzer made in the Shanghai Balance Instrument Factory, using a Ni/Cr-Ni/Si thermocouple plate and working under static air conditions with five different heating rates ranging from 1 to 25 K min^{-1}. α-Al_2O_3 was used as reference material. The DSC curves of the exothermic decomposition of TNAZ were obtained with a sealed cell of stainless steel. The amount of TNAZ used was about 0.5 mg.

The time-to-explosion experiments for the determination of the critical temperature (T_b) of thermal explosion were carried out in measuring equipment for small-scale solid explosives, using empty aluminium blasting cap shells (approximately 7.0 mm O.D. × 6.1 mm I.D. and 50 mm long). The explosive sample of 40 mg was placed in the shell, which was confined with an aluminium plug and a pressed shim of stainless steel. The sample and confining shell and plug with shim were pressed with an oil press in a suitable die body to a pressure of 4.2 MPa. The above-mentioned assembly was dropped into a preheated Wood's-metal bath, and the time to explosion was measured automatically using a sound responder relay.

3. Results and data analysis

3.1. Thermodynamic data for the melting process of TNAZ

A typical heat flow curve of the melting process of TNAZ is shown in Fig. 1. The extrapolated onset temperature (T_e), peak temperature (T_m), melting enthalpy (ΔH_m) and melting entropy (ΔS_m) obtained by five measurements are 99.0 ± 0.1°C, 102.5± 0.1°C, 30.31 ± 0.30 kJ mol^{-1}, and 80.7 ± 0.3 J K^{-1} mol^{-1}, respectively. The final temperature of melting (T_f) is obtained by the calculated formula presented in Fig. 1. The average value of five measurements is 99.7 ± 0.1°C. Thus, the temperature range of melting for TNAZ, $T_e \sim T_f$ is from 99.0°C to 99.7°C.

3.2. The kinetic parameters of thermal decomposition of TNAZ

In order to obtain the kinetic parameters (the apparent activation energy (E) and pre-exponential constant

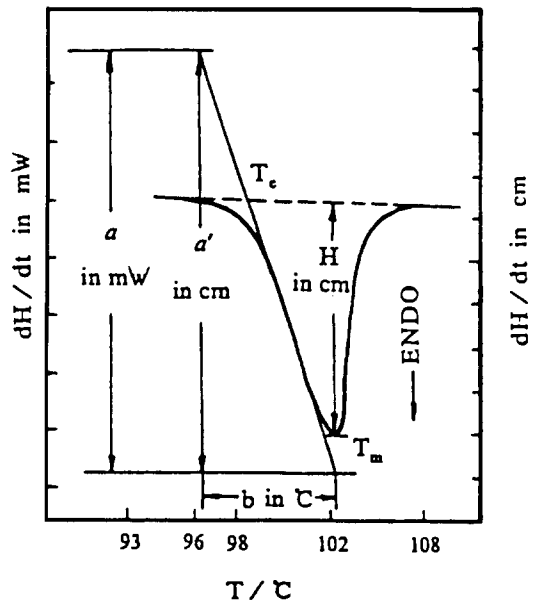

Fig. 1. Typical thermogram of the melting process of TNAZ at a heating rate of 7°C h^{-1}. $T_f=T_m-T_{td}=T_m-SHR_0=T_m-(H\cdot b)/a'$, where $T_{td}=SHR_0=(H\cdot b)/a'$, thermal delay temperature, in °C; $S=a/a'$, sensitivity, in mw cm^{-1}; H, peak height, in cm; $R_0=b/a$, thermal resistance, in °C w^{-1}.

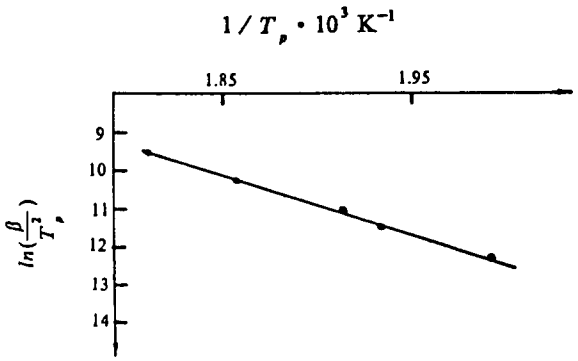

Fig. 2. Kissinger's plot of the exothermic peak temperature obtained by DSC experiments.

(A) of the exothermic decomposition of TNAZ, a multiple heating rate method (Kissinger's method [6]), was employed. As shown in Fig. 2, the relationship between $\ln(\beta/T_p^2)$ and T_p^{-1} was a straight line, where β is the heating rate and T_p is the maximum peak temperature of the exothermic decomposition in the DSC curves. From the original data in Table 1, the apparent activation energy (E_K) obtained by Kissin-

Table 1
The values of T_e, T_{e0}, T_p, E_K and T_b for TNAZ, HMX and RDX determined from the DSC curves at various heating rates

Sample	β_i/K min^{-1}	T_e/K	T_{e0}/K	T_p/K	E_K/kJ mol^{-1}	T_b/K
TNAZ	1.03	—		501.7	129.0	511
	2.07	497.7	494.7	512.2		
	5.28	504.7		522.1		
	10.5	518.4		538.5		
	21.7	528.4		552.7		
HMX*	1	537	534.2	538	380.9	541
	5	545		548		
	11	550		551		
	23	557		558		
RDX*	2	473	468.1	485	134.7	482
	5	480		497		
	10	490		508		
	23	499		521		

*Cited from [8].

ger's method is determined to be 129.0 kJ mol^{-1}. The pre-exponential constant is $10^{10.4}$ s^{-1}. The linear correlation coefficient is 0.99. The value of the apparent activation energy (E_0) obtained by Ozawa's method [7] is 130.6 kJ mol^{-1}. The linear correlation coefficient is 0.99. The value (T_{e0}) of the extrapolated onset (T_e) corresponding to $\beta \rightarrow 0$ obtained by Eq. (1) taken from [8] is 494.7 K.

$$T_{ei} = T_{e0} + b\beta_i + c\beta_i^2 + d\beta_i^3, \quad i = 1,2,3,4 \tag{1}$$

where b, c and d are coefficients.

The critical temperature of thermal explosion (T_b) obtained from Eq. (2) taken from [8] is 511 K.

$$T_b = \frac{E_K - \sqrt{E_K^2 - 4E_K RT_{e0}}}{2R} \tag{2}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}).

For comparing the heat-resistance ability of TNAZ with common simple explosives, the values of T_{e0} and T_b of HMX and RDX are also listed in Table 1. This shows that the heat-resistance ability of TNAZ is higher than RDX and lower than HMX.

In order to obtain the values of E and A from a single non-isothermal DSC curve, the integral Eq. (3), differential Eq. (4) and exothermic rate Eq. (5) were employed

$$\ln\left[\frac{g(\alpha_i)}{T_i - T_0}\right] = \ln\left[\frac{A}{\beta}\right] - \frac{E}{RT_i} \tag{3}$$

$$\ln\left[\frac{(d\alpha/dT)_i}{f(\alpha_i)[E(T_i - T_0)/RT_i^2 + 1]}\right] = \ln\left[\frac{A}{\beta}\right] - \frac{E}{RT_i} \tag{4}$$

$$\ln\left[\frac{dH_t}{dt}\right]_i = \ln\left\{AH_0 f(\alpha_i)\left[1 + \frac{E}{RT_i}\left(1 - \frac{T_0}{T_i}\right)\right]\right\} - \frac{E}{RT_i} \tag{5}$$

where $g(\alpha)$ is the integral mechanism function, T_i is the temperature (K) at time t; T_0 is the initial point at which DSC curve deviates from the baseline; R is the gas constant; α is the conversion degree; $f(\alpha)$ is differential mechanism function; dH_t/dt is the exothermic rate at time t; H_0 is total exothermicity of the substance (corresponding to the global area under the DSC curve); H_t is the reaction heat in a certain time (corresponding to the partial area under the DSC curve).

The original data tabulated in Table 2 were fitted to the integral, differential and exothermic rate Eqs. (3)–(5) by linear least-squares, iterative, combined dichotomous and least-squares methods [9]. The calculated results of E and A are shown in Table 3. The values of E and A obtained from a single non-isothermal DSC curve are in good agreement with the calculated values

Table 2
Data of TNAZ determined by DSC with the sealed cell of stainless steel

Data point	T_i/K	α_i	$(dH_i/dt)_i$/mJ s^{-1}	$(d\alpha/dT)_i \times 10^4$/K^{-1}
1	484.40	0.0093	0.0975	2.582
2	487.65	0.0174	0.1389	3.680
3	490.90	0.0314	0.1481	3.923
4	494.90	0.0453	0.1519	4.023
5	497.65	0.0587	0.1544	4.090
6	501.65	0.0749	0.1736	4.600
7	505.90	0.0935	0.1833	4.855
8	510.15	0.1133	0.2155	5.708
9	514.15	0.1365	0.2711	7.182
10	518.40	0.1688	0.3644	9.654
11	521.15	0.2069	0.5130	13.59
12	525.40	0.2667	0.7004	18.55
13	530.15	0.3608	1.0598	28.07
14	534.90	0.4828	1.4548	38.54
15	538.40	0.6403	1.8067	47.86

$T_0 = 479.65$ K; $H_0 = 2160$ mJ; $\beta = 0.1748$°C s^{-1}.

Table 3
Calculated values of kinetic parameters of thermal decomposition for TNAZ

Eq. (3)		Eq. (4)		Eq. (5)	
E/kJ mol^{-1}	log A/s^{-1}	E/kJ mol^{-1}	log A/s^{-1}	E/kJ mol^{-1}	log A/s^{-1}
132	9.9	139	9.7	135	9.1

obtained by the methods of Kissinger and Ozawa. Thus, the values of E of 133 kJ mol^{-1} and A of $10^{9.8}$ s^{-1} are believed to be for the thermal decomposition of TNAZ.

3.3. *The critical temperature of thermal explosion of TNAZ*

The relationship between the thermal explosion temperature (T_b) and the determined explosion induction time (t_{exp}) obtained using the critical temperature measured for thermal explosion of small-scale solid explosives is shown in Fig. 3.

The value of critical temperature of thermal explosion (T_b), i.e. the value of T_1 corresponding to $t_{exp} = 1000\,s$ obtained from Fig. 3 is 523 K, which is agreement with the value of T_b of 511 K obtained using Eq. (2) for estimating the critical temperature of thermal explosion under non-isothermal DSC conditions. The error between the experimental and calculated values is estimated to be 2.3%.

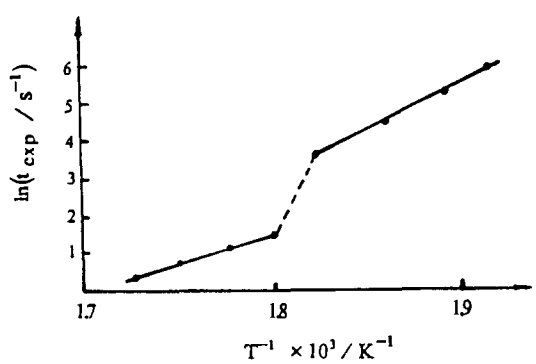

Fig. 3. Explosion time of TNAZ.

4. Conclusions

1. The extrapolated onset temperature, peak temperature, melting enthalpy and melting entropy of the melting process of TNAZ are 99.0 ± 0.1°C, 102.3 ± 0.1°C, 30.31 ± 0.30 kJ mol^{-1} and 80.7± 0.3 J K^{-1} mol^{-1}, respectively. The melting temperature range is from 99.0°C to 99.7°C.

2. The apparent activation energy and pre-exponential constant of the exothermic decomposition of TNAZ are 133 kJ mol^{-1} and $10^{9.8}$ s^{-1}, respectively.
3. The values of critical temperature of thermal explosion of TNAZ obtained by using a time-to-explosion testing apparatus and the non-isothermal DSC are 523 and 511 K, respectively.
4. The heat-resistance ability of TNAZ is higher than RDX and lower than HMX.

Acknowledgements

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