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Thermal Behaviour and Detonation Characterization of N-Benzoyl-3,3-dinitroazetidine

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ABSTRACT

N-benzoyl-3,3-dinitroazetidine(BDNAZ) is a derivative of 3,3-dinitroazetidine (DNAZ). Its thermal behaviour was studied by DSC methods. The results show that there are one melting process and two exothermic decomposition processes. The kinetic parameters of the intense exothermic decomposition process were obtained from the analysis of the DSC curves. The apparent activation energy, pre-exponential factor and the mechanism function are 170.77 kJ mol^{-1}, $10^{14.12}$ s^{-1} and $f(\alpha) = (1–a)^{-1}/2$, respectively. The specific heat capacity of BDNAZ was determined with a continuous C_p mode of a micro-calorimeter. The standard mole specific heat capacity of BDNAZ was 286.31 J mol^{1} K^{-1} at 298.15 K. Using the relationship between C_p and T with the thermal decomposition parameters, the time of the thermal decomposition from initialization to thermal explosion (adiabatic time-to-explosion, t_{TIAD}), the self-accelerating decomposition temperature (T_{SADT}), thermal ignition temperature (T_{TIT}), critical temperatures of thermal explosion (T_b) and period of validity ($t_{0.9}$) were obtained to evaluate its thermal safety. The detonation velocity (D) and pressure (P) of BDNAZ were estimated by using the nitrogen equivalent equation according to the experimental density.

KEYWORDS

N-benzoyl-3,3-dinitroazetidine(BDNAZ), thermal behaviour, non-isothermal kinetics, thermal safety, detonation characterization.

1. Introduction

Dinitro- and trinitro-derivatives of azetidine are of interest because they contain strained ring systems during decomposition. This makes them good candidates for energetic materials (propellants or explosives). Initial reports concentrate on the synthesis of 1,3,3-trinitroazetidine (TNAZ) and 3,3-dinitroazetidine (DNAZ).[1,2] As one of the important derivatives of TNAZ, DNAZ[2,3] can be used to prepare a variety of solid energetic materials with a high oxygen–balance.[3–12] N-benzoyl-3,3-dinitroazetidine (BDNAZ, Fig. 1) is a novel insensitive high energy explosive. Presently, there are no reports about the thermal behaviour and detonation characterization of BDNAZ. In this paper, the thermal behaviour, non-isothermal decomposition reaction kinetics and thermal safety of BDNAZ were studied by DSC and TG/DTG methods. The detonation velocity and pressure were also calculated to estimate its detonation properties.

2. Experimental

A single crystal of BDNAZ was prepared by a reported method.[12] The thermal behaviour of BDNAZ was studied by using a Q2000 DSC (TA, USA) by the DSC method under atmospheric pressure. The sample mass was about 2.742 mg at the heating rates of 3.0, 5.0, 10.0 and 15.0 K min^{-1} with nitrogen as the purge gas and a flow rate of 50 mL min^{-1}. The temperature and heat were calibrated by using pure indium and tin particles.

The specific heat capacity of BDNAZ 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-DSCIII (Seteram, France) instrument with a sample mass of 330.60 mg under atmospheric pressure.

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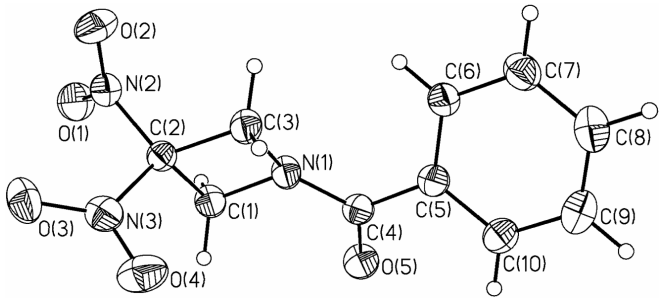

Figure 1 Molecular structure of BDNAZ.

3. Results and Discussion

3.1. Thermal Behaviour

The DSC heat flow curve for BDNAZ at the heating rate of 10 K min^{-1} by DSC is shown in Fig. 2. It indicates that the thermal decomposition of BDNAZ can be divided into three stages. The first stage is a melting process, the extrapolated onset temperature (T_e) and peak temperature (T_p) at a heating rate of 10 K min^{-1} are 423.27 K and 424.31 K, respectively. The second stage is a feeble exothermic decomposition process where T_e and T_p are 432.28 K and 446.23 K, respectively. The third stage is an intense exothermic decomposition process, where T_e and T_p are 518.41 K and 543.28 K, respectively. The basic data for the intense exothermic decomposition process are listed in Table 1.

3.2. Non-isothermal Reaction Kinetics

To explore the reaction mechanism of the intense exothermic decomposition process of BDNAZ and obtain the corresponding

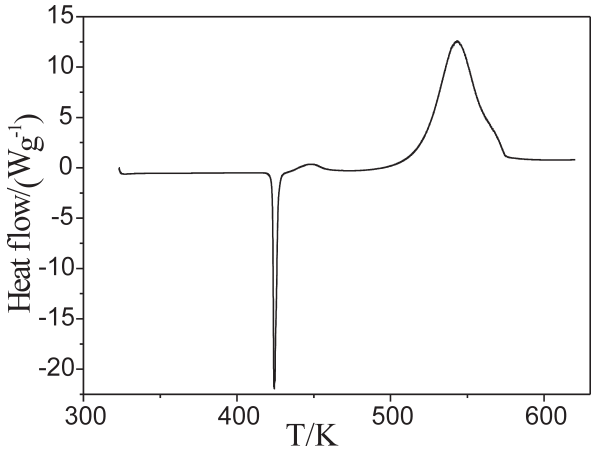

Figure 2 DSC curve of BDNAZ obtained at a heating rate of 10 K min^{-1}.

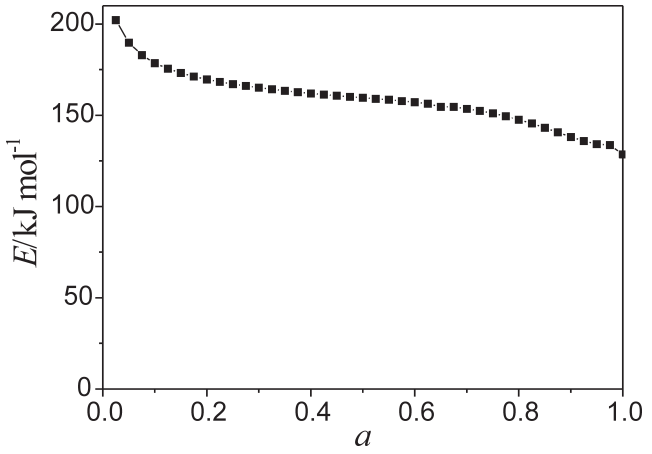

Figure 3 E_a *vs.* α curve of BDNAZ by Flynn-Wall-Ozawa's method.

Table 1 Basic data for the intense exothermic decomposition process of BDNAZ.

β/K min^{-1}	T_e/K	T_p/K	ΔH/J g^{-1}
3	505.71	528.19	680.4
5	511.92	534.51	671.4
10	518.41	543.28	704.5
15	525.58	551.03	747.4

Note: T_e is the onset temperature for the intense exothermal decomposition reaction in the DSC curve and T_p is the peak temperature; ΔH is the decomposition heat.

kinetic parameters [apparent activation energy (E_a/kJ mol^{-1}), pre-exponential constant (A/s^{-1})] and the most probable kinetic model functions, the DSC curves at the heating rates of 3.0, 5.0, 10.0 and 15.0 K min^{-1} were dealt with by mathematic means, and the temperature data corresponding to the conversion degrees (α) were found. Six integral methods (MacCallum-Tanner, Šatava-Šesták, Agrawal, General integral, Universal integral, Flynn-Wall-Ozawa) and one differential method (Kissinger) were employed.[4–7,13] The values of E_a were obtained by Ozawa's method from the iso-conversional DSC curves at the heating rates of 3.0, 5.0, 10.0 and 15.0 K min^{-1}, and the E_a–α relation is shown in Fig. 3. From Fig. 3, one can see that the activation energy slightly changes in the section of 0.10–0.60 (α), and the ranges were selected to calculate the non-isothermal reaction kinetics.

Forty-one types of kinetic model functions and the basic data were put into the integral and differential equations for calculation. The kinetic parameters and the probable kinetic model function were selected by the logical choice method and satisfying the ordinary range of the thermal decomposition kinetic parameters for energetic materials (E_a = 80–250 kJ mol^{-1}, log A = 7–30 s^{-1}). These data together with their appropriate values of linear correlation coefficient (r), standard mean square deviation (Q) and believable factor (d, where $d = (1–r)Q$), are presented in Table 2. The values of E_a and log A obtained from a single non-isothermal DSC curve is in good agreement with the calculated values obtained by Kissinger's method and Ozawa's method. Therefore, we conclude that the reaction mechanism of the intense exothermic decomposition process of BDNAZ is classified as Reaction order $G(\alpha) = 1–(1–\alpha)^2$, $f(\alpha) = (1–a)^{-1}/2$. Substituting $f(\alpha)$ with $(1–a)^{-1}/2$, E with 170.77 kJ mol^{-1} and A with $10^{14.12}$ s^{-1} in Eq. (1),

$$d\alpha/dT = Af(\alpha)\exp(–E/RT)/\beta \quad (1)$$

the kinetic equation of the intense exothermic decomposition reaction may be described as $d\alpha/dT = 10^{13.82}(1–a)^{-1}\exp(–2.05 \times 10^4/T)/\beta$.

3.3. Specific Heat Capacity

Figure 4 shows the results obtained for the specific heat capacity of BDNAZ by using the continuous specific heat capacity mode of a Micro-DSCIII apparatus. The specific heat capacity of BDNAZ presents a good cubic equation relationship with temperature in the temperature range studied. The specific heat capacity equation is shown as:

$$C_p\,(\text{J g}^{-1}\,\text{K}^{-1}) = 11.0657 – 1.0546 \times 10^{-1}T \;\; 3.5884 \times 10^{-4}T^2 – 3.9165 \times 10^{-7}T^3 \;(283\ \text{K} < T < 354\ \text{K}) \quad (2)$$

The standard molar specific heat capacity of BDNAZ is 286.31 J mol^{-1} K^{-1} at 298.15 K.

3.4. Thermal Safety Studies

The values (T_{e0} and T_{p0}) of the onset temperature (T_e) and peak temperature (T_p) corresponding to $\beta \to 0$ were obtained by Eq. (3), and the self-accelerating decomposition temperature (T_{SADT}) was obtained by Eq. (4).[4–7,13] The values (T_{SADT} and T_{p0}) are 489.13 K and 513.44 K. respectively.

$$T_{e(\text{or p})} = T_{e0(\text{or p0})} + a\beta_i + b\beta_i^2 + c\beta_i^3 \qquad i = 1\sim4 \quad (3)$$

where a, b and c are coefficients.

$$T_{SADT} = T_{e0} \quad (4)$$

The thermal ignition temperature (T_{be0} or T_{TIT}) was obtained

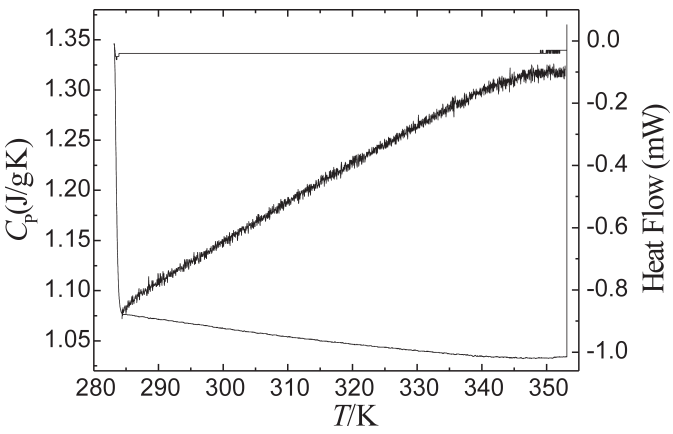

Figure 4 Results of the continuous C_p of BDNAZ.

Table 2 Kinetic parameters for the intense exothermic decomposition process of BDNAZ.

Method	β/K min^{-1}	E_a/kJ mol^{-1}	log(A s^{-1})	r	S	d
MacCallum-Tanner	3	182.17	15.50	0.9883	1.66×10^{-2}	1.94×10^{-4}
	5	181.98	15.48	0.9887	1.60×10^{-2}	1.80×10^{-4}
	10	162.90	13.56	0.9897	1.46×10^{-2}	1.50×10^{-4}
	15	160.90	13.33	0.9898	1.44×10^{-2}	1.47×10^{-4}
Šatava-Šesták	3	180.18	15.32	0.9883	1.66×10^{-2}	1.94×10^{-4}
	5	180.00	15.31	0.9887	1.60×10^{-2}	1.80×10^{-4}
	10	161.99	13.50	0.9897	1.46×10^{-2}	1.50×10^{-4}
	15	160.10	13.28	0.9898	1.44×10^{-2}	1.47×10^{-4}
Agrawal	3	180.80	15.40	0.9871	8.82×10^{-2}	1.14×10^{-3}
	5	180.51	15.37	0.9876	8.49×10^{-2}	1.05×10^{-3}
	10	161.42	13.46	0.9885	7.76×10^{-2}	8.91×10^{-4}
	15	159.32	13.22	0.9886	7.68×10^{-2}	8.76×10^{-4}
General integral	3	180.80	15.40	0.9871	8.82×10^{-2}	1.14×10^{-3}
	5	180.51	15.37	0.9876	8.49×10^{-2}	1.05×10^{-3}
	10	161.42	13.46	0.9885	7.76×10^{-2}	8.91×10^{-4}
	15	159.32	13.22	0.9886	7.68×10^{-2}	8.76×10^{-4}
Universal integral	3	180.37	14.04	0.9871	8.79×10^{-2}	1.13×10^{-3}
	5	180.20	14.02	0.9876	8.46×10^{-2}	1.05×10^{-3}
	10	161.26	12.17	0.9885	$7.72 \times 10^{->2}$	8.85×10^{-4}
	15	159.27	11.94	0.9886	7.65×10^{-2}	8.70×10^{-4}
Mean		170.77	14.12			
Flynn-Wall-Ozawa		175.19(E_{eo})		0.9939	3.53×10^{-3}	2.15×10^{-5}
		164.30(E_{po})		0.9966	1.94×10^{-3}	6.53×10^{-6}
Kissinger		163.80(E_K)	13.76	0.9962	1.04×10^{-3}	3.90×10^{-5}
Mean(E_{eO},E_{pO}, E_K)		167.76				

Note: E with the subscript of eO and pO is the apparent activation energy obtained from the onset temperature (T_e) and the peak temperature (T_p) by Ozawa's method, E with the subscript of K is the apparent activation energy obtained from the peak temperature (T_p) by Kissinger's method.

by substituting E_{eo} and T_{e0} into the equation of Zhang *et al.* [Eq. (5)],[14] and the critical temperatures of thermal explosion (T_{bp0} or T_b) were obtained by substituting E_{po} and T_{p0} into equation (5). The values (T_{TIT} and T_b) are 501.04 K and 527.52 K, respectively.

$$T_{be0(or\ bp0)} = \frac{E_o - \sqrt{E_o^2 - 4E_oRT_{e0(or\ po)}}}{2R} \quad (5)$$

The entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$) and Gibbs energy of activation ($\Delta G^{\neq}$) of the main exothermic decomposition reaction of BDNAZ corresponding to $T = T_{po}$, $E_a = E_k$ and $A = A_k$ were obtained from Eqs (6) – (8),[4–7] and are 13.99 J mol^{-1} K^{-1}, 163.80 kJ mol^{-1} and 156.62 kJ mol^{-1}, respectively. The positive value of ($\Delta G^{\neq}$), indicates that the exothermic decomposition reaction of BDNAZ must proceed under the heating condition.

$$A = \frac{k_B T}{h} e^{\Delta S^{\neq}/R} \quad (6)$$

$$A\exp(-E_a/RT) = \frac{k_B T}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(\frac{-\Delta H^{\neq}}{RT}\right) \quad (7)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (8)$$

where k_B is the Boltzman constant and h is the Plank constant.

After the kinetic parameters (E_a and A) were obtained, the rate constant (k) for the decomposition reaction could be calculated by the following equation:

$$\ln k = \ln A - E_a/RT \quad (9)$$

The period of validity of the BDNAZ could be determined by the equation:

$$T_{0.9} = G(\alpha)/k \quad (10)$$

where k was the rate constant and could be obtained by Eq. (9), where α is 0.1 and $G(\alpha)$ is the decomposition reaction mechanism function. For the temperature of 298.15 K and using the values of the activation energies (E_a) and frequency factors (A) obtained in the above, Eq. (10) could be solved. The period of validity for BDNAZ is 38.04 million years, which indicates that BDNAZ is very stable at 298.15 K.

The adiabatic time-to-explosion (t_{TIAD}) of energetic materials is the time of decomposition transiting to explosion under the adiabatic conditions and is an important parameter for assessing the thermal stability and the safety of energetic materials.

$$t_{TIAD} = \frac{1}{Q_d A}\int_{Te0}^{T_{bp0}} \frac{C_p \exp(E/RT)}{f(\alpha)} dT \quad (11)$$

$$\alpha = \int_{Te0}^{T_{bp0}} \frac{C_p}{Q_d} dT \quad (12)$$

where Q_d decomposition heat, 700.9 J g^{-1}. A, pre-exponential constant, $A = 10^{14.12}$ s^{-1}; C_p as Eq. (2) expressed, J g^{-1} K^{-1}, E, activation energy, 170.77 kJ mol^{-1}; R, the gas constant, 8.314 J mol^{-1} K^{-1}; $f(\alpha)$, differential mechanism function $f(\alpha) = (1–a)^{-1}/2$.

Substituting the corresponding data into the Smith equation [Eqs (11) and (12)],[15–16] the value of t_{TIAD} is 550.97 s, which is longer than that of DNAZ·HClO$_4$ (3,3-dinitroazetidinium perchloric acid),[4] DNAZ·PA (3,3-dinitroazetidinium picrate),[5]

Table 3 Nitrogen equivalents of different detonation products.

Detonation product	N_2	H_2O	CO	CO_2	O_2	C	H_2
Nitrogen equivalent index	1	0.54	0.78	1.35	0.5	0.15	0.290

DNAZ DNS (3,3-dinitroazetidinium 3,5-dinitrosalicylate),[6] NTO DNAZ (3-nitro-1,2,4-triazol-5-one 3,3-dinitroazetidinium)[7] and TNAZ[17]. In the calculation process of adiabatic time-to-explosion, a little change in the activation energy located in the integral equation with exponential form can make a great difference in the result, and a small increase of the activation energy can induce t_{TIAD} to rise greatly.

3.5. Characterization of Detonation Velocity and Pressure

Detonation velocity (D) and detonation pressure (P) are the most important targets of scaling the detonation characteristics of energetic materials. The detonation velocity and pressure of an explosive can be predicted with the nitrogen equivalent equation (NE equation) shown as formulas (13)–(15).[18]

$$V_D = (690 + 1160\,\rho_0)\,\Sigma N \quad (13)$$

$$P = 1.092(\rho_0 \Sigma N)^2 - 0.574 \quad (14)$$

$$\Sigma N = 100 \Sigma x_i N_i / M \quad (15)$$

in which V_D represents detonation velocity of an explosive, ρ_0 represents density of an explosive, ΣN represents nitrogen equivalent of the detonation products, N_i is the nitrogen equivalent index of certain detonation products, x_i is the mole number of certain detonation products produced by a mole of explosive.

The detonation products produced by general explosives together with their nitrogen equivalent indices are listed in Table 3. According to the order of H_2O–CO–CO_2 in forming detonation products, the detonation products of BDNAZ are calculated as follows:

$$C_{10}H_9N_3O_5 = (4.5)H_2O + (0.5)CO + (9.5)C + (1.5)N_2.$$

According to Eq. (15), in which $M = 251.20$ g mol^{-1}, $\rho = 1.504$ g cm^{-3},[12] total nitrogen equivalents of BDNAZ are obtained through the nitrogen equivalent indices of the detonation products in Table 3:

$$\Sigma N = 100 \times (4.5 \times 0.54 + 0.5 \times 0.78 + 9.5 \times 0.15 + 1.5 \times 1)/251.2 = 2.287$$

According to Eqs (13) and (14), the calculated detonation velocity and pressure of BDNAZ are 5568.08 m s^{-1} and 12.34 GPa, respectively.

4. Conclusions

The thermal behaviour of BDNAZ under non-isothermal conditions by DSC methods was studied. The apparent activation energy and pre-exponential factor of the intense exothermic decomposition reaction are 170.77 kJ mol^{-1} and $10^{14.12}$ s^{-1}, respectively. The reaction mechanism of the intense exothermic decomposition process of BDNAZ is classified as Reaction order $G(\alpha) = 1–(1–a)^2$, $f(\alpha) = (1–a)^{-1}/2$. The specific heat capacity was determined with a Micro-DSC method. The specific heat capacity equation is C_p(J g^{-1} K^{-}) = $11.0657 - 1.0546 \times 10^{-1}T + 3.5884 \times 10^{-4}T^2 - 3.9165 \times 10^{-7}T^3$ (283 K < T < 353 K) and the standard molar specific heat capacity is 286.31 J mol^{-1}K^{-1} at 298.15 K. The self-accelerating decomposition temperature, the thermal ignition temperature and the critical temperatures of thermal explosion are 489.13 K, 501.04 K and 527.52 K, respectively. The values of ($\Delta S^{\neq}$), ($\Delta H^{\neq}$) and ($\Delta G^{\neq}$) of this reaction are 13.99 J mol^{-1} K^{-1}, 163.80 kJ mol^{-1} and 156.62 kJ mol^{-1}, respectively. The period of validity is 38.04 million years. The adiabatic time-to-explosion was calculated to be 550.97 s. The detonation velocity and pressure are 5568.08 m s^{-1} and 12.34 GPa, respectively.

Acknowledgements

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