



Thermodynamic properties, detonation characterisation and free radical of N-acetyl-3,3-dinitroazetidine



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ARTICLE INFO

Article history:

Received 1 July 2015

Received in revised form 1 August 2015

Accepted 4 August 2015

Available online 8 August 2015

Keywords:

N-acetyl-3,3-dinitroazetidine (ADNAZ)

Thermal behaviour

Thermodynamics

Detonation characterisation

Free radicals

ABSTRACT

N-acetyl-3,3-dinitroazetidine (ADNAZ) is an important precursor for synthesizing new multinitroazetidine energetic compounds. Its thermal behaviour was studied under a non-isothermal condition by DSC and TG/DTG methods, the results show that there are one melting process and one endothermic decomposition process. The specific molar heat capacity ($C_{p,m}$) of ADNAZ was determined by a continuous C_p mode of micro-calorimeter and theoretical calculation, and the $C_{p,m}$ of ADNAZ was $240.37 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ at $T = 298.15 \text{ K}$. The detonation velocity (D) and detonation pressure (P) of ADNAZ were estimated using the nitrogen equivalent equation according to the experimental density, the value of D and P are $(6685.83 \pm 3.12) \text{ m} \cdot \text{s}^{-1}$ and $(18.36 \pm 0.02) \text{ GPa}$, respectively. The free radical signals of ADNAZ were detected by electron spin resonance (ESR) technique, which is used to estimate its sensitivity.

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1. Introduction

Dinitro- and trinitro- derivatives of azetidine contain a strained ring systems, and this structural feature makes them good candidates for energetic materials (propellants or explosives), among them, 1,3,3-trinitroazetidine (TNAZ) is one of the most promising energetic materials. N-acetyl-3,3-dinitroazetidine (ADNAZ, shown in figure 1) is not only useful in itself but also used as an intermediate to prepare TNAZ [1] and 3,3-dinitroazetidine (DNAZ) [2], DNAZ is the basis for the preparation of a variety of solid energetic materials with a high oxygen-balance [2–11]. ADNAZ is insensitive [1] and its crystal density is $1.549 \text{ g} \cdot \text{cm}^{-3}$ [3], therefore, it is suitable as an ingredient in energetic materials, either by itself or with other compounds. ADNAZ has an additional advantage, it can form a eutectic with TNAZ, the composition of eutectic is about 34% (M/M) ADNAZ/TNAZ, its melting point is $T = 351.75 \text{ K}$ [1]. This is a relatively low melting point for an energetic material and is in the range where it can be melt cast into articles. Meanwhile, the eutectic of low melting point can be used as an energetic carrier for energetic materials of higher melting point, such as HMX and the like.

In this paper, the thermal behaviour of ADNAZ was studied by differential scanning calorimetric (DSC) and thermogravimetric/dif-

ferential thermogravimetric (TG/DTG) techniques. The specific molar heat capacity ($C_{p,m}$) of ADNAZ was determined by continuous C_p mode of micro-calorimeter and theoretical calculation. The detonation velocity (D) and pressure (P) were also calculated to estimate its detonation properties.

Free radicals (FR) are molecules, atoms or ions with unpaired electrons, the greater presence of FR yields the higher reactivity, so they play an important role in the sensitivity and energization of energetic materials. The initial and propagation of detonation is usually related with the formation and torrent diffusion of FR. Therefore, the electron spin resonance (ESR) technique was used to determine the FR signals for estimating the sensitivity of energetic materials.

2. Experimental

2.1. Materials and methods

ADNAZ was synthesized and purified by a reported method, and the colourless single crystal of ADNAZ (CCDC 907765) was obtained by recrystallization from dichloromethane [3]. The mass fraction purity of the single crystal of ADNAZ was measured by high performance liquid chromatography (HPLC type Shimadzu LC-10AT, infusion pump type LC-10ATvp, detector type SPD-10Avp, the mobile phase is acetone) and found to be above 0.999 (table 1). The DSC and TG/DTG analyses of ADNAZ were conducted

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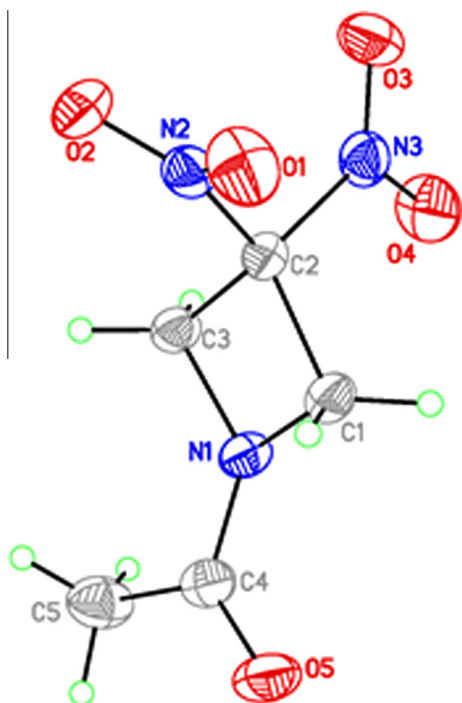
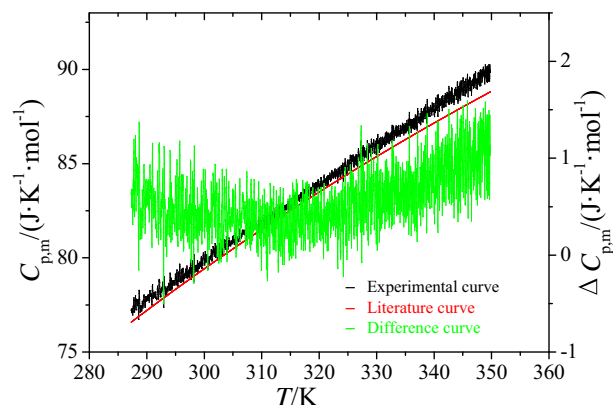


FIGURE 1. Molecular structure of ADNAX.

using a Q600SDT (TA, USA) instrument under atmospheric pressure. The sample mass was about 1.467 mg at the heating rate was $10.0 \text{ K} \cdot \text{min}^{-1}$ with nitrogen as the purge and the flow rate is $100 \text{ cm}^3 \cdot \text{min}^{-1}$. The temperature and heat were calibrated using pure indium and tin particles by onset temperatures under a nitrogen atmosphere at the same conditions. The melting point (onset temperatures) of In (429.76 K) [12] and Sn (505.04 K) [13] are $(429.71 \pm 0.27) \text{ K}$ and $(505.10 \pm 0.33) \text{ K}$, respectively. The melting enthalpy of In ($28.4 \text{ J} \cdot \text{g}^{-1}$) [12] and Sn ($60.6 \text{ J} \cdot \text{g}^{-1}$) [13] are $(28.6 \pm 0.2) \text{ J} \cdot \text{g}^{-1}$ and $(60.8 \pm 0.3) \text{ J} \cdot \text{g}^{-1}$, respectively. All the results indicate that the accuracy of tests is satisfactory.

The $C_{p,m}$ of ADNAX was determined by a continuous C_p mode from $T = (283.15 \text{ to } 353.15) \text{ K}$ at a heating rate of $0.15 \text{ K} \cdot \text{min}^{-1}$ on a Micro-DSCIII (Setaram, France) instrument with the sample mass of 318.94 mg under atmospheric pressure. The micro-calorimeter was calibrated with $\alpha\text{-Al}_2\text{O}_3$ (calcined), its mathematical expression was $C_p/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 18.82369 + 2.033349 \cdot 10^{-1} (T/\text{K})$, the recommended equation is $C_p/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = -1.32506 \cdot 10^8 (T/\text{K})^{-3} + 4.54238 \cdot 10^6 (T/\text{K})^{-2} - 5.475599 \cdot 10^4 (T/\text{K})^{-1} + 2.574076 \cdot 10^2 - 1.715032 \cdot 10^{-1} (T/\text{K}) + 1.2897189 \cdot 10^{-4} (T/\text{K})^2 - 4.60768 \cdot 10^{-8} (T/\text{K})^3 + 6.31755 \cdot 10^{-12} (T/\text{K})^4$ from $T = (273.15 \text{ to } 2250) \text{ K}$ [14,15] (figure 2). The difference between the experimental and recommended value are $(-0.5 \text{ to } 1.59) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ from $T = (283.15 \text{ to } 353.15) \text{ K}$, the standard uncertainty is $\pm 0.63 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

The FR experiment was performed on an ESR equipment EMX-10/12 (Bruker, Germany) with illumination frequency and energy

FIGURE 2. Experimental/literature/difference curves of the $C_{p,m}$ of $\alpha\text{-Al}_2\text{O}_3$.

of 9.780 GHz and 19.971 mW, respectively, and within the magnetic flux density rang (B) from $(0.2980 \text{ to } 0.4000)T$ in 30 min.

2.2. Quantum chemical calculations

Single crystal structural data of ADNAX were used in the theoretical calculations [3]. The density functional theory (DFT) calculation was performed with the program package DMol³ in Materials Studio (version 8.0) of Accelrys Inc. on a personal computer [16,17]. The generalised gradient approximation (GGA) with the RPBE functional [18] and double-numerical quality basis set with polarisation functions (DNP) were used for all the atoms. A thermal smearing of $2.0 \cdot 10^{-3}$ hartree (Ha, 1Ha = 27.2114 eV) and a real-space cutoff of 0.40 nm were adopted. For the numerical integration, the fine quality mesh size of the program was used. A $3 \cdot 3 \cdot 3$ k -point sampling was applied in geometry optimisation [19–22]. The convergences of energy, gradient and maximal displacement were set as 10^{-5} Ha, $2.0 \cdot 10^5 \text{ Ha} \cdot \text{cm}^{-1}$ ($2.0 \cdot 10^{-2} \text{ Ha} \cdot \text{nm}^{-1}$) and $5.0 \cdot 10^{-4} \text{ nm}$, respectively. In addition, the frequency analysis [19–21] was performed to check if the stationary point was a potential minimum and to obtain thermodynamic properties at different temperatures under atmospheric pressure. The crystal data, input coordinates, final coordinates, vibrational frequencies and standard thermodynamic quantities for ADNAX are listed in tables S1–S5.

3. Results and discussion

3.1. Thermal behaviour

Typical DSC and TG/DTG curves for ADNAX are shown in figures 3 and 4. The DSC curve indicates that the thermal decomposition of ADNAX can be divided into two stages. The first stage is a melting process ($121.1 \pm 2.5) \text{ J} \cdot \text{g}^{-1}$, the extrapolated onset temperature (T_e , melting point) and peak temperature (T_p) obtained at a heating rate of $10.0 \text{ K} \cdot \text{min}^{-1}$ are $(385.77 \pm 0.65) \text{ K}$ and $(387.64 \pm 0.53) \text{ K}$, respectively. This melting point falls within the temperature range of $(384.15 \text{ to } 387.95) \text{ K}$ values reported in the literature [1,23,24],

TABLE 1

Provenance and mass fraction purity of the materials used in this study. ADNAX is N-acetyl-3,3-dinitroazetidine, HPLC is the high performance liquid chromatography.

Compound	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
ADNAX	Synthesis		Recrystallization	>0.999	HPLC
Nitrogen	Xi'an Xin Xiang Electric Co., Ltd.	>0.99999			
Indium	TA	>0.9999			
Tin	TA	>0.9999			

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