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Structure and Properties of 3,7-Bis(nitroimino)-2,4,6,8-tetraazabicyclo[3.3.0]octane

JIN Xing-hui, HU Bing-cheng, GAO Si-jing, WANG Chang-ying, LIU Zu-liang, Lü Chun-xu

(*School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing* 210094, *China*)

Abstract: The thermal properties, electronic structure and detonation performances of 3,7-bis(nitroimino)-2,4,6,8-tetraazabicyclo[3.3.0]octane were investigated by the TG-DTG-DSC method and density functional theory, respectively. Results show that the thermal decomposition of title compoud is a two-stage process and has an evident exothermic peak at around 320 ℃, and the activation energy and pre-exponential factor of thermal decomposition are 225.80 kJ·mol^{-1} and $10^{17.71}$ s^{-1}, respectively. The critical temperature of thermal explosion is 600.25 K, and entropy of activation 80.81 J·mol^{-1}·k^{-1}, enthalpy of activation 220.92 kJ·mol^{-1}, free energy of activation 173.87 kJ·mol^{-1}, detonation pressure 34.34 GPa, detonation velocity 8.70 km·s^{-1}, indicating that it can be used as a potential candidate of high-energy and stable energetic material.

Key words: 3,7-bis(nitroimino)-2,4,6,8-tetraazabicyclo[3.3.0]octane; thermal properties; electronic structure; detonation performances

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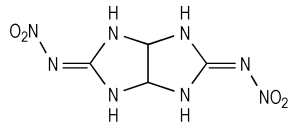
1 Introduction

Over the past decades, considerable efforts have been focused on the development of nitrogen-rich high energy density materials (HEDM) with high performance and decreased sensitivity as well as environmental compatibility[1-3]. One of the most exciting developments in the field of HEDMs is N-heterocyclic energetic compounds with high nitrogen content. Because there are lots of energetic C—N or N—N bonds to enhance the heat of formation and energetic properties. Meanwhile, a mountain of nitrogen were released during the decomposition process which makes them have a wide use in gas generating agent, low characteristic signal propellant, high energy yet low sensitivity materials[4-6]. 3,7-Bis(nitroimino)-2,4,6,8-tetraazabicyclo[3.3.0]octane (BNITABO) is a homothetic energetic compound of this type containing two nitroimino groups and a large number of C—N or N—N bonds in the molecule. Though, BNITABO has been synthesized, little research was found on its thermal behavior, electronic structure and energetic properties (heats of formation, detonation velocity and detonation pressure)[7]. In the presented paper, the thermal properties, electronic structure and detonation performances of 3,7-bis(nitroimino)-2,4,6,8-tetraazabicyclo[3.3.0]octane were fully investigated.

2 Experiments

2.1 Material

According to Ref [8], 3,7-bis(nitroimino)-2,4,6,8-tetraazabicyclo[3.3.0]octane (Scheme 1, $C_4H_6O_4N_8$) was prepared though addition, condensation and nitration reactions. Yield 58%, m.p. 326 ℃, ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 9.53 (s, 4H), 5.84 (s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 161.9, 69.6; IR (KBr, ν/cm^{-1}): 3190, 1504, 1558, 1435, 1270, 1200, 1071, 1045, 1017, 952, 884, 780, 753, 637; m/z (%): 229 (M^-, 100); ρ, 1.87 g·cm^{-3}.



Scheme 1 Structure of 3,7-bis(nitroimino)-2,4,6,8-tetraazabicyclo[3.3.0]octane

2.2 Experimental equipments and computational methods

^{1}H NMR, ^{13}C NMR, IR, MS spectrum and computations were performed on the Bruker Avance III 500 MHz, Thermo Nicolte IS10 IR instrument, Finnigan TSQ Quantum Mass Spectrometer and Gaussian 03 program with the B3LYP/6-31G(d,p) basis set[9-10], respectively. TG-DTG-DSC curves were also performed on a NETZSCH STA 409 PC/PG coupling system with an initial mass of about 3.0 mg placed in alumina crucibles (nitrogen atmosphere with the flow rate of 30 mL·min^{-1}).

3 Results andDiscussion

3.1 Thermal properties

Fig.1 shows the TG-DTG-DSC curves of BNITABO at the heating rate of 5 K·min^{-1}. From the Fig.1, it is seen that the decomposition of the title compound is a two-steps process. The first step starts from 280 ℃ to 320 ℃ with 60% mass loss and the second step starts from 320 ℃ to 650 ℃ with about 40% mass loss. Correspondingly, there is an evident sharp peak at about 320 ℃ and a faint peak at around 550 ℃ in the DTG curve.

Fig.2 shows the TG-DSC curves of the decomposition process of BNITABO at different heating rates of 5, 10, 15 K·min^{-1} and 20 K·min^{-1}. It was found that the decomposition temperatures and the exothermic peaks shifted to higher temperatures as the heating rate increased. This may be attributed to the "thermal hysteresis" of the heat transfer effect at different

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Biography: JIN Xing-hui(1986-), male, Ph.D. student. engaged in in synthesis of energetic materisls. e-mail: jingetiema0000@126.com

Corresponding Author: HU Bing-cheng(1969-), male, professor, engaged in in synthesis of energetic materisls. e-mail: hubingcheng210094@163.com

heating rates.

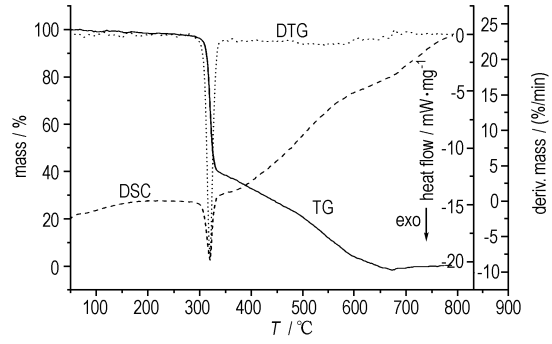


Fig. 1 TG-DTG-DSC curves of BNITABO at 5 K · min^{-1}

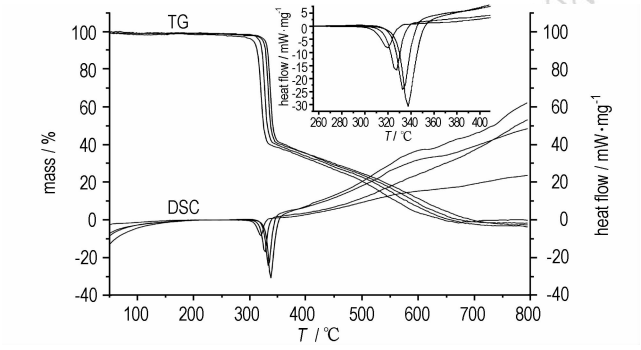


Fig. 2 TG-DSC curves of BNITABO at different heating rates

3.2 Non-isothermal decomposition kinetics

The relative kinetic parameters such as activation energy (E_a), pre-exponential factor (A), entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), free energy of activation ($\Delta G^{\neq}$) and the critical ignition temperature (T_b) were obtained based on the following methods.

(1) Kissinger equation[11]:

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

(2) Ozawa-Flynn-Wall equation[12]:

$$\lg\beta=C-0.4567\frac{E_O}{RT} \quad (2)$$

where, β is the heating rate, K; T_{pi} is the maximum peak temperature which can be obtained from the DSC curves, K; R is the gas constant, E_K and E_O are the activation energy calculated by the Kissinger and Ozawa's methods, kJ · mol^{-1}, respectively; A is the pre-exponential factor, C is the constant.

β, T_{pi} and the kinetic parameters obtained by Kissinger and Ozawa methods were summarized in Table 1. It is obviously seen that the values of T_{pi} of the exothermic peak shifted to higher temperatures due to the "thermal hysteresis" of the heat transfer effect. On the other hand, the values of E calculated by Kissinger method (E_K = 225.80 kJ · mol^{-1}) very similar with that obtained by Ozawa's method (E_O = 224.24 kJ · mol^{-1}). Besides, both of the linear correlation coefficients (r_K = 0.9945 and r_O = 0.9949) are very close to 1. All the above-obtained data indicates that the results are credible.

Table 1 Calculated values of the kinetic parameters of title compound

β/ K · min^{-1}	T_{pi} /℃	Kissinger method		Ozawa method		
		E_K /kJ · mol^{-1}	A	r_K	E_O /kJ · mol^{-1}	r_O
5	320.0					
10	327.0	225.80	$10^{17.71}$	0.9945	224.24	0.9949
15	333.3					
20	337.5					

Then, the values of $\Delta S^{\neq}$, $\Delta H^{\neq}$, $\Delta G^{\neq}$ and T_b can be obtained based on the following equations combined with the calculated E_K and A[13].

$$A\exp\left(-\frac{E}{RT}\right)=\frac{k_B T}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \quad (3)$$

$$\Delta H^{\neq}=E_a-RT \quad (4)$$

$$\Delta G^{\neq}=\Delta H^{\neq}-T\Delta S^{\neq} \quad (5)$$

Where, $T=T_{p0}$, the peak temperature (T_{pi}) corresponding to $\beta\to 0$; $E_a=E_K$, calculated by Kissinger's method; $A=A_K$, calculated by Kissinger's method; $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ are the entropy of activation, the enthalpy of activation and the free energy of activation, respectively; k_B is the Boltzmann constant, 1.3807×10^{-23} J · K^{-1}; h is the Plank constant, 6.626×10^{-34} J · s.

T_{p0} could be calculated by Eq. (6).

$$T_{pi}=T_{p0}+b\beta_i+c\beta_i^2+d\beta_i^3 \quad (6)$$

Where, b, c and d are coefficients.

Based on the above-described equations, the value of T_{p0}, $\Delta S^{\neq}$, $\Delta H^{\neq}$, and $\Delta G^{\neq}$ were calculated as 586.85 K, 80.18 J · mol^{-1} · K^{-1}, 220.92 kJ · mol^{-1} and 173.87 kJ · mol^{-1}, respectively.

The critical temperature of thermal explosion, as an important parameter during the storage or usage of an energetic material, was calculated by Eq. (7).

$$T_b=\frac{E_O-\sqrt{E_O^2-4E_O RT_{p0}}}{2R} \quad (7)$$

Where, T_b is the critical temperature of thermal explosion; E_O is the apparent activation energy obtained by Ozawa's method; R is the gas constant; T_{p0} is the peak temperature corresponding to $\beta\to 0$.

The calculated value of T_b is 600.25 K, which indicates that BNITABO satisfy the meets of the safety.

3.3 Electronic structure

Molecular orbital and the electronic structure of BNITABO were investigated based on the B3LYP/6-31G(d,p) level-optimized structure. The calculated energy gap value of BNITABO is 5.58 eV, indicating it may have a lower reactivity. Fig. 3 illustrates the 3D plots of the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and the molecular electrostatic potentials (MEP) of BNITABO. There exists 59 the highest occupied molecular orbital and 60 the lowest unoccupied molecular orbital in the mole-

cule. It is also obviously seen that most of the HOMO and LUMO levels are 2-fold degenerate indicating that the removal of an electronic from the HOMO level or addition of an electronic to the LUMO level could weaken the skeleton framework. In view of the MEP, the negative potentials appear to be distributed mostly on the oxygen atoms of the $—NO_2$ groups while the positive potentials appear to be at the center of the skeleton. It may attribute to the stabilization of the molecular structure according to the law proposed by Klapotke et al[14].

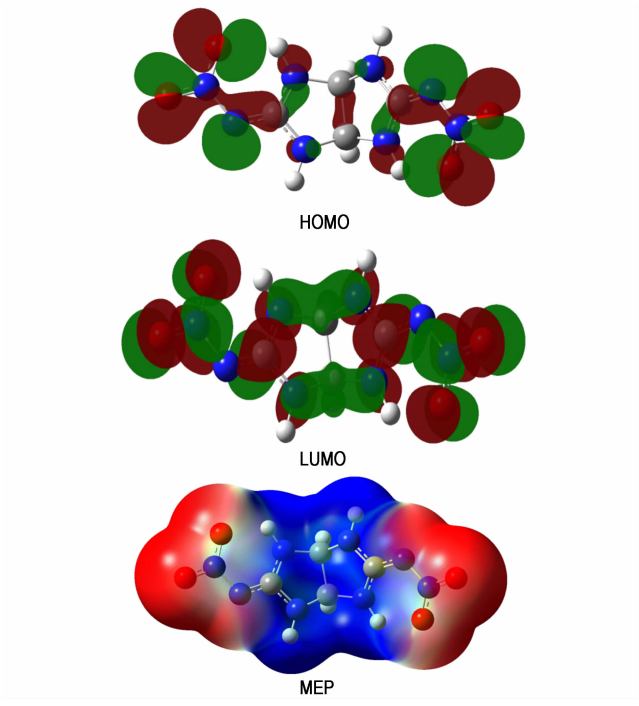


Fig. 3 HOMO, LUMO and MEP of 3,7-bis(nitroimino)-2,4,6,8-tetraazabicyclo[3.3.0]octane

3.4 Heat of formation and detonation performances

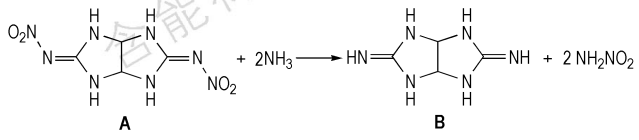
Detonation performances are of great importance parameter for an energetic material and could be obtained according to Kamlet-Jacobs equations[15].

$$D=1.01\ (N\bar{M}^{0.5}Q^{0.5})^{0.5}(1+1.3\rho) \quad (8)$$

$$P=1.558\rho^2 N\bar{M}^{0.5}Q^{0.5} \quad (9)$$

Where, ρ is the crystal density of the explosive, g·cm^{-3}; D is the detonation velocity, km·s^{-1}; p is the detonation pressure, GPa; N is the number of moles of detonation gases per-gram explosive, mol·g^{-1}; $\bar{M}$ is the average molecular weight of these gases, g·mol^{-1}; and Q is the heat of detonation, J·g^{-1}.

The accurate heat of formation of BNITABO can be calculated using the isodesmic reaction[16].



Scheme 2 Isodesmic reaction designed for the title compound

Based on the above-described equations, the accurate heat of formation of BNITABO was obtained as 514.8 kJ·mol^{-1}. In view of the detonation velocities (8.70 km·s^{-1}, ρ=1.87 g·cm^{-3}) and detonation pressure (34.34 GPa), its detonation performances are superior to those of TNT (D=6.8 km·s^{-1}; p=19.5 GPa)[17], and similar with those of RDX (D=8.75 km·s^{-1}; p=34.0 GPa)[18], indicating that BNITABO can be used as a potential candidate of high-energy and stable energetic material.

4 Conclusions

(1) The thermaldecomposition of 3,7-bis(nitroimino)-2,4,6,8-tetraazabicyclo[3.3.0]octane presents a two-stage process with the mass loss of 100% and a single sharp exothermic peak were observed at around 320 ℃.

(2) The calculated E_a via Kissinger and Ozawa methods are 225.80 and 224.24 kJ·mol^{-1}, respectively. Thermodynamic parameters such as $\Delta S^{\neq}$, $\Delta H^{\neq}$, $G^{\neq}$ and T_b were calculated as 80.81 J·mol^{-1}·k^{-1}, 220.92 kJ·mol^{-1}, 173.87 kJ·mol^{-1} and 600.25 K, respectively.

(3) The electron structure of 3,7-bis(nitroimino)-2,4,6,8-tetraazabicyclo[3.3.0]octane shows that the negative potentials appear to be distributed $—NO_2$ groups and the positive potentials appear to be at the center of the skeleton which attribute to the stabilization of the molecular structure.

(4) The calculated values of detonation velocity (D = 8.70 km·s^{-1}) and detonation pressure (p = 34.34 GPa) involve that 3,7-bis(nitroimino)-2,4,6,8-tetraazabicyclo[3.3.0]octane has the potential to be used as high-energy and stable energetic material.

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3,7-二硝亚氨基-2,4,6,8-四氮杂双环[3.3.0]辛烷的结构和性能

金兴辉, 胡炳成, 高思静, 王长英, 刘祖亮, 吕春绪
(南京理工大学化工学院, 江苏 南京 210094)

摘　要: 用 TG-DTG-DSC 方法研究富氮含能化合物 3,7-二硝亚氨基-2,4,6,8-四氮杂双环[3.3.0]辛烷的热性能,用量子化学方法研究其电子结构及爆轰性能。结果表明,3,7-二硝亚氨基-2,4,6,8-四氮杂双环[3.3.0]辛烷热分解是一个二阶段过程,在 320 ℃左右有一个剧烈的放热峰。其热分解活化能和指前因子分别为 225.80 kJ·mol^{-1} 和 $10^{17.71}$ s^{-1}。考虑到其热爆炸临界温度为 600.25 K,活化熵为 80.18 J·mol^{-1}·k^{-1},活化焓为 220.92 kJ·mol^{-1},吉布斯自由能为 173.87 kJ·mol^{-1}。利用 K-J 公式得到其爆速为 8.70 km·s^{-1}, 爆压为 34.34 GPa,表明 3,7-二硝亚氨基-2,4,6,8-四氮杂双环[3.3.0]辛烷可用作潜在的高能、稳定的含能材料的候选物。

关键词: 3,7-二硝亚氨基-2,4,6,8-四氮杂双环[3.3.0]辛烷;热性能;电子结构;爆轰性能
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《含能材料》固体推进剂专栏征稿

高能量、低特征信号、低易损、低成本、低污染、灵活能量管理和高可靠性成为当前固体推进剂面临的紧迫课题,为促进其研究,本刊将于 2015 年开设推进剂研究专栏,以专题报道固体推进剂研究的最新研究进展。欢迎广大学者投稿,来稿时请选择对应的专栏。

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