Thermal Behaviors of 1-Amino-2-nitroguanidine

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Abstract：To evaluate the thermal stability of 1-amino-2-nitroguanidine（ANQ）and investigate the potential application value of ANQ as energetic material, thermal behaviors, specific heat capacity and adiabatic time-to-explosion of ANQ were studied by DSC, micro-DSC and TG/DTG methods. Results show that thermal behavior of ANQ can be divided into two coterminous intense exothermic decomposition processes. The peak temperatures of the two decomposition processes at the heating rate of 5 ℃·min^{-1} are 192.5 ℃ and 196.2 ℃, respectively, and the whole decomposition enthalpy is −2075 J·g^{-1}. The apparent activation energy and pre-exponential constant of the first decomposition process are 224.3 kJ·mol^{-1} and 10$^{23.15}$ s^{-1}, respectively. The self-accelerating decomposition temperature and critical temperature of thermal explosion for ANQ are 184.5 ℃ and 192.7 ℃, respectively. The molar heat capacity of ANQ is 145.5 J·mol^{-1}·K^{-1} at 298.15 K. Adiabatic time-to-explosion was estimated to be about 60 s. The thermal stability of ANQ is good.

Key words：energetic material；1-amino-2-nitroguanidine（ANQ）；thermal behavior；specific heat capacity；adiabatic time-to-explosion

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1 Introduction

Guanidine compounds are a kind of important nitrogen-rich energetic materials, and have evolved into an extremely wide-ranging field of application. Various high-nitrogen-content energetic salts including full series of amination products of the guanidinium cation（amino-, diamino-, triamino-guanidinium and nitroguanidine cation）have been investigated[1-3]. As a known guanidine derivative containing both an amine and a nitro substituent, 1-Amino-2-nitroguanidine（ANQ）is also an important concerned object for its good detonation properties[4]. ANQ was first synthesized in 1920 s[5-7], while it was not considered as energetic material at that time. In recent years, Klapötke T M started to research the potential properties of ANQ as energetic material, and found that ANQ is a promising energetic compound to replace RDX[8-10]. The density, detonation velocity and detonation pressure of ANQ are 1.767 g·cm^{-3}, 8977 m·s^{-1} and 32.3 GPa, respectively[8], which are close to that of RDX and better than guanidine and its derivatives, but its sensibility and production cost are lower than those of RDX.

It is predicted that the ANQ-based energetic salts may have potentially broad application in the fields of explosives. For example, ANQ can be used as an intermediate for the synthesis of 5-nitriminotetrazole[11] and bis-nitraminotriazoles[12]. In addition, Klapötke reported a series of derivatives of ANQ, including halides（Cl^{-}, Br^{-} and I^{-}）of ANQ[13], some transition metal complexes[14], and other energetic salts[4]. 1-Amino-2-nitroguanidinium nitrate（ANGN）was synthesized by Jin X H[15], and it has been found that ANGN possesses excellent energetic properties compared to those of RDX and HMX. Moreover, other ionic energetic materials of ANQ have been also developed recently[16-19]. Unfortunately, for a majority of these derivatives of ANQ, their decomposition temperatures are much lower than that ANQ, which is a great shortage for these derivatives.

In this paper, we mainly reported the thermal behavior, specific heat capacity and adiabatic time-to-explosion of ANQ for further estimating its thermal stability.

2 Experimental

2.1 Synthesis

ANQ was prepared according to reference [20] and recrystallized in hot water. ^{13}C NMR（DMSO-d_6, 800 MHz）：162；^{1}H NMR（DMSO-d_6, 800 MHz）：9.32, 8.27, 7.55, 4.67；IR（KBr, ν/cm^{-1}）：3357, 3280, 1667, 1615, 1579, 1515, 1497, 1410, 1261, 1146, 846, 745, 687. Anal. Calcd. for $CH_5N_5O_2$（%）：C 10.09, H 4.23, N 58.81；Found：C 10.22, H 4.32, N 58.78.

2.2 Physical Measurements

Differential scanning calorimetry (DSC) experiments were performed using a DSC200F3 apparatus (Germany, NETZSCH). The heating rates were 2.5, 5.0, 7.5, 10.0 ℃·min^{-1} from ambient temperature to 300 ℃, respectively. The thermogravimetry/differential thermogravimetry (TG/DTG) experiment was performed using a SDT-Q600 apparatus (TA, USA). The heating rate used was 5.0 ℃·min^{-1} from ambient temperature to 400 ℃. The specific heat capacity (c_p) was determined using a Micro-DSCIII apparatus (SETARAM, France), and the sample mass was 215.00 mg. The heating rate was 0.2 K·min^{-1} from 10 ℃ to 80 ℃.

3 Results and Discussion

3.1 Thermal Decomposition Behavior

Typical DSC in Fig.1 indicates that the thermal behavior of ANQ presents two coterminous intense exothermic decomposition processes. The two decompositions occur in a narrow range of temperature from 185 ℃ to 205 ℃ at the heating rate of 5 ℃·min^{-1}. The extrapolated onset temperatures and peak temperatures of the two decomposition processes are 191.4 ℃ and 192.7 ℃ for the first, and 196.1 ℃ and 196.2 ℃ for the second, respectively. The whole decomposition enthalpy is −2075 J·g^{-1}. TG/DTG curves at the heating rate of 5 ℃·min^{-1} in Fig.2 also indicate the two decomposition processes are overlapped, but

there is obvious transition at 195.21 ℃. The two exothermic decompositions are very intense, and can produce certain jet power to make thermobalance shake up and down. Meanwhile, the two decompositions are very complete, and there is almost no residuum in crucible (0.06%) at 300 ℃. Moreover, we also can find that the thermal decomposition process of ANQ becomes more and more intense with the rise of heating rate, even the tumble of common Al crucible can be found at the heating rate of 10 ℃·min^{-1}, DSC curve changes up and down as shown in Fig.3. The decomposition of ANQ presents a distinguishing feature of temperature-high and process-intense.

The apparent activation energy (E) and pre-exponential constant (A) of the first exothermic decomposition process for ANQ was obtained by a multiple heating method (Kissinger method[21] and Ozawa method[22]). DSC curves are shown in Fig.4. The determined values of the beginning temperature (T_0), extrapolated onset temperature (T_e) and peak temperature (T_p) at the different heating rates are listed in Table 1. The values of T_{00} and T_{e0} corresponding to $\beta \rightarrow 0$ obtained by Eq.(1) are 167.7 and 184.5 ℃[23].

$$T_{(0 \text{ or } e)i} = T_{(00 \text{ or } e0)} + n\beta_i + m\beta_i^2 \qquad i=1-3 \qquad (1)$$

where n and m are coefficients.

From the calculated values of E and $\lg A$ in Table 1, E obtained by Kissinger method agrees well with that by Ozawa method, and the linear correlation coefficients (r) are close to 1. So the result is credible. Moreover, E of the process was low, indicating that ANQ easily decompose above 180 ℃.
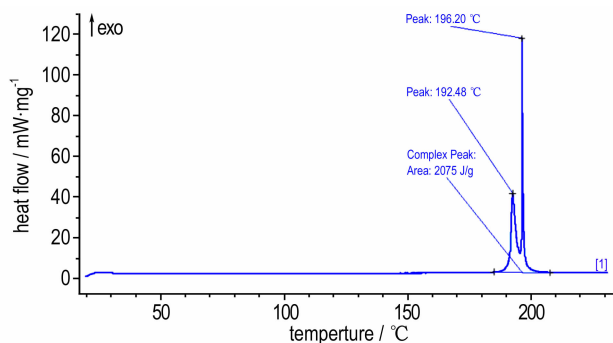

Fig.1 DSC curve of ANQ at 5 ℃·min^{-1}
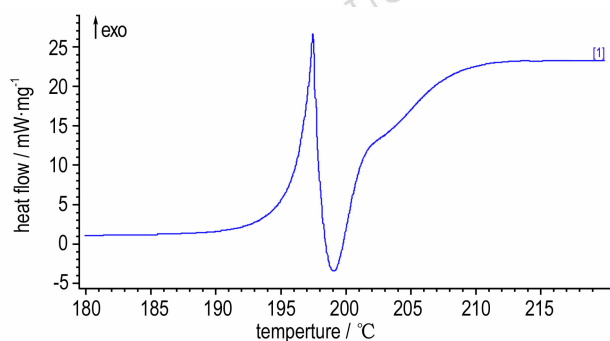

Fig.2 TG/DTG curves of ANQ at 5 ℃·min^{-1}

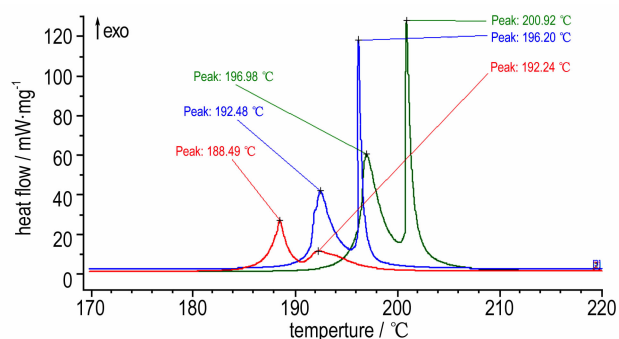**Fig.3** DSC curve of ANQ at 10 ℃·min^{-1}

Fig.4 DSC curves of ANQ at different heat rates

Table 1　The values of T_0, T_e, T_p and kinetic parameters of the first decomposition process for ANQ

β/ ℃·min⁻¹	T_0/℃	T_e/℃	T_p/℃	E_K/kJ·mol⁻¹	lg(A/s^{-1})	r_K	E_O/kJ·mol⁻¹	r_O
2.5	176.9	187.6	188.5					
5.0	183.7	191.5	192.5	224.3	23.15	0.983	220.6	0.984
7.5	188.1	196.2	197.0					

Note：Subscript K, data obtained by Kissinger method；subscript O, data obtained by Ozawa method.

The self-accelerating decomposition temperature (T_{SADT}) and critical temperature of thermal explosion (T_b) are two important parameters required to ensure safe storage and process operations for energetic materials and then to evaluate the thermal stability. T_{SADT} and T_b can be obtained by Eqs. (2) and (3)[23-24]. T_{SADT} and T_b for ANQ are 184.5 ℃ and 192.7 ℃, respectively, indicating that the thermal stability of ANQ is high.

$$T_{SADT} = T_{e0} \tag{2}$$

$$T_b = \frac{E_O - \sqrt{E_O^2 - 4E_O R T_{e0}}}{2R} \tag{3}$$

The entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$) and free energy of activation ($\Delta G^{\neq}$) of the thermal decomposition process for ANQ corresponding to $T = T_{p0} = 458.15$ K, $A = A_K = 10^{23.15}$ s⁻¹ and $E = E_K = 224.3$ kJ·mol⁻¹ can be calculated as 186.38 J·mol⁻¹·K⁻¹, 220.49 kJ·mol⁻¹ and 135.10 kJ·mol⁻¹[25], respectively. 194.7 J·mol⁻¹·K⁻¹, 224.3 kJ·mol⁻¹ and 135.1 kJ·mol⁻¹[25], respectively.

3.2　Specific Heat Capacity

Fig. 5 shows the determination result of c_p for ANQ, using a continuous specific heat capacity mode of apparatus. c_p presents a good linear relationship with temperature in determined temperature range. Specific heat capacity equation is shown as：

$$c_p(\text{J·g}^{-1}\text{·K}^{-1}) = 0.3632 + 2.8810 \times 10^{-3} T$$
$$(283.0 \text{ K} < T < 353.0 \text{ K}) \tag{4}$$

where c_p is the specific heat capacity in J·g⁻¹·K⁻¹

The specific heat capacity and molar heat capacity of ANQ are 1.222 J·g⁻¹·K⁻¹ and 145.5 J·mol⁻¹·K⁻¹ at 298.15 K, respectively.
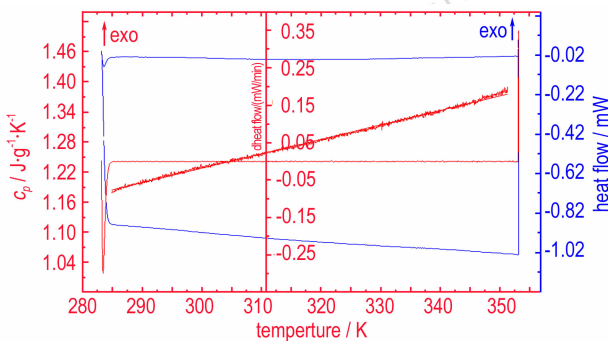

Fig. 5　Determination results of the continuous specific heat capacity for ANQ

3.3　Adiabatic Time-to-explosion

The adiabatic time-to-explosion is also an important parameter for evaluating the thermal stability of energetic materials and can be calculated by Eqs. (5), (6) and (7)[23, 25-28].

$$c_p \frac{dT}{dt} = QA\exp(-E/RT)f(\alpha) \tag{5}$$

$$\alpha = \int_{T_0}^{T} \frac{c_p}{Q} dT \tag{6}$$

$$t = \int_0^t dt = \int_{T_0}^{T} \frac{c_p \exp(E/RT)}{QAf(\alpha)} dT \tag{7}$$

Where c_p is the specific heat capacity, J·mol⁻¹·K⁻¹; T is the absolute temperature, K; t is the adiabatic time-to-explosion, s; Q is the exothermic values, J·mol⁻¹; A is the pre-exponential factor, s⁻¹; E is the apparent activation energy of the thermal decomposition reaction, J·mol⁻¹; R is the gas constant, J·mol⁻¹·K⁻¹; $f(\alpha)$ is the most probable kinetic model function; α is the conversion degree and the limit of temperature integration is from T_{00} to T_b.

In fact, the conversion degree (α) of energetic materials from the beginning decomposition to explosion in the adiabatic condition is very small, and it is very difficult to obtain the most probable kinetic model function $f(\alpha)$. So, we separately used Power-low model, Reaction-order model, Avrami-Erofeev model and the above obtained kinetic model function to estimate the adiabatic time-to-explosion and supposed different rate orders (n)[23, 29]. The calculation results are listed in Table 2.

Table 2　The calculation results of adiabatic time-to-explosion

model	rate order	equation	time/s
power-low model	$n=1$	$f(\alpha)=1$	15.2
	$n=2$	$f(\alpha)=2\alpha^{1/2}$	53.6
	$n=3$	$f(\alpha)=3\alpha^{2/3}$	68.6
	$n=4$	$f(\alpha)=4\alpha^{3/4}$	71.2
reaction-order model	$n=0$	$f(\alpha)=1$	15.2
	$n=1$	$f(\alpha)=1-\alpha$	15.5
	$n=2$	$f(\alpha)=(1-\alpha)^2$	15.8
avrami-erofeev model	$n=1$	$f(\alpha)=1-\alpha$	15.5
	$n=2$	$f(\alpha)=2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	54.4
	$n=3$	$f(\alpha)=3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	69.5
	$n=4$	$f(\alpha)=4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	72.1

The calculated result indicates that there are some deviations, and the decomposition model has big influence on the estimate of adiabatic time-to-explosion. From the whole estimated result, the adiabatic time-to-explosion of ANQ should be about 60 s. Though the decomposition of ANQ is very intense, certain time of heat accumulation from the beginning decomposition to thermal explosion is necessary, which can be certified by DSC curve of low heating rate. The time also indicates that ANQ has good thermal stability.

4 Conclusions

(1) The thermal behavior of ANQ can be divided into two coterminous intense exothermic decomposition processes. The peak temperatures of the two decomposition processes at the heating rate of 5 ℃·min^{-1} are 192.5 and 196.2 ℃, and the whole decomposition enthalpy is −2075 J·g^{-1}. The self-accelerating decomposition temperature and critical temperature of thermal explosion are 184.5 ℃ and 192.7 ℃, respectively.

(2) Specific heat capacity equation of ANQ is c_p(J·g^{-1}·K^{-1}) = 0.3628+2.8810×10^{-3} T (283.0 K<T<353.0 K), and the molar heat capacity is 145.5 J·mol^{-1}·K^{-1} at 298.15 K. Adiabatic time-to-explosion of ANQ is about 60 s. The thermal stability of ANQ is good.

References：

[1] Wang R, Xu H, Shreeve J M, et al. Bis[3-(5-nitroimino-1,2,4-triazolate)]-based energetic salts：Synthesis and promising properties of a new family of high-density insensitive materials[J]. *Journal of the American Chemical Society*, 2010, 132：11904−11905.

[2] Huang Y G, Zhang Y Q, Shreeve J M. Nitrogen-rich salts based on energetic nitroaminodiazido[1,3,5]triazine and guanazine [J]. *Chemistry-A European Journal*, 2011, 17：1538−1546.

[3] Jin X H, Hu B C, Liu Z L. Synthesis and properties of two energetic salts based on 1-amino-2-nitroguanidine[J]. *Journal of the Brazilian Chemical Society*, 2015, 26：124−130.

[4] Fischer N, Klapötke T M, Stierstorfer J. 1-Amino-3-nitroguanidine (ANQ) in high-performance ionic energetic materials[J]. *Zeitschrift für Naturforschung B*, 2012, 67：573−588.

[5] Phillips R, Williams J F. Nitro-aminoguanidine[J]. *Journal of the American Chemical Society*, 1928, 5：2465−2470.

[6] Henry R A, Makosky R C, Smith G B L. Preparation of nitroaminoguanidine[J]. *Journal of the American Chemical Society*, 1951, 73：474.

[7] McKay A F. Nitroguanidines[J]. *Chemical Review*, 1952, 51：301−346.

[8] Klapötke T M, Stierstorfer J. Current advances in RDX replacements[C] // Proceedings of the 27th Army Science conference. Orlando, FL, USA, 2010, November 29-December 2.

[9] Klapötke T M, Stierstorfer J. Potential replacements of RDX with low sensivities[C] // Insensitive Munitions Energetic Materials Technology Symposium. Munchen Marriott Hotel Munich, Germany, 2010, October 11-October 14.

[10] Zhang G Q, Liu X B, Huang M. Review on energetic nitroguanidine derivatives[J]. *Chinese Journal of Energetic Materials(Hanneng Cailiao)*, 2013, 21(5)：668−674.

[11] O′Connor T E, Fleming G, Reilly J. Diazotization of nitroaminoguanidine[J]. *Journal of the Society of Chemical Industry*, 1949, 68：309−310.

[12] Metelkina E L, Novikova T A, Berdonosova S N, et al. 2-Nitroguanidine derivatives：IX. Reaction of 1-amino-2-nitroguanidine with oxalic acid as a method of synthesis of 3(5)-nitroamino-1,2,4-triazole-5(3)-carboxylic acid and 5,5′-bi(3-nitroamino-1,2,4-triazole) salts[J]. *Russian Journal of Organic Chemistry*, 2005, 41：440−443.

[13] Fischer N, Klapötke T M, Lux K, et al. Inorganic amino-nitroguanidinium derivatives[J]. *Crystals*, 2012(2)：675−689

[14] Fischer N, Joas M, Klapötke T M, et al. Transition metal complexes of 3-amino-1-nitroguanidine as laser ignitible primary explosives：Structures and Properties [J]. *Inorganic Chemistry*, 2013, 52：13791−13802.

[15] Jin X H, Hu B C, Liu Z L, et al. Structure and properties of 1-amino-2-nitroguanidinium nitrate[J]. *RSC Advance*, 2014(4)：23898−23903.

[16] Whitemore W F, Revukas A J. Nitroguanylhydrazones of some common aldehydes and ketone [J]. *Journal of the American Chemical Society*, 1935, 57：706−708.

[17] Lieber E, Sherman E, Henry R A, et al. The reaction of nitrous acid with nitroaminoguanidine [J]. *Journal of the American Chemical Society*, 1951, 73：2327−2329.

[18] Gao H X, Shreeve J M. Azole-based energetic salts[J]. *Chemical Review*, 2011, 111：7377−7436.

[19] Wu B, Yang H W, Tang Y X, et al. New energetic derivatives of 1-amino-3-nitroguanidine [J]. *Journal of Energetic Materials*, 2015, 33：180−190

[20] Castillo-Meléndez J A, Golding B T. Optimization of the synthesis of guanidine from amines via nitroguanidines using 3,5-dimethyl-N-nitro-1H-pyrazole-1-carboxamidine [J]. *Synthesis*, 2010, 10：1655−1663.

[21] Kissinger H E. Reaction kinetics in differential thermal analysis [J]. *Analytical Chemistry*, 1957, 29：1702−1706.

[22] Ozawa T. A method of analyzing thermogravimetric data[J]. *Bulletin of the Chemical Society of Japan*, 1965, 38：1881−1886.

[23] Hu R Z, Gao S L, Zhao F Q, et al. Thermal Analysis Kinetics (2th)[M]. Beijing：Science Press, 2008.

[24] Zhang T L, Hu R Z, Xie Y, et al. The estimation of critical temperatures of thermal explosion for energetic materials using non-isothermal DSC[J]. *Thermochimica Acta*, 1994, 244：171−176.

[25] Xu K Z, Chen Y S, Wang M, et al. Synthesis and thermal behavior of 4,5-dihydroxyl-2-(dinitromethylene)-imidazolidine (DDNI)[J]. *Journal of Thermal Analysis and Calorimetry*, 2011, 105：293−300.

[26] Smith L C. An approximate solution of the adiabatic explosion problem[J]. *Thermochimica Acta*, 1975, 13：1−6.

[27] Xu K Z, Song J R, Zhao F Q, et al. Thermal behavior, specific heat capacity and adiabatic time-to-explosion of G(FOX-7)[J]. *Journal of Hazardous Materials*, 2008, 158: 333–339.

[28] Xu K Z, Qiu Q Q, Ma H X, et al. Thermal properties of 1-amino-1-hydrazino-2,2-dinitroethylene cesium salt[J]. *Journal of*

Energetic Materials, 2013, 31: 273–286.

[29] Vyzovkin S, Burnham A K, Criado J M, et al. ICTKA kinetics committee recommendations for performing kinetic computations on thermal analysis data[J]. *Thermochimica Acta*, 2011, 520: 1–19.

1-氨基-2-硝基胍的热行为

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摘　要： 用差示扫描量热法(DSC)，微量热仪和热重-微分热重分析(TG/DTG)研究了1-氨基-2-硝基胍(ANQ)的热分解行为、比热容和绝热至爆时间。结果表明，ANQ 的热行为分为相连的两个剧烈放热分解过程。5 ℃·min^{-1} 下两个分解过程的峰温分别为 192.5 ℃和 196.2 ℃，总共的分解焓为 −2075 J·g^{-1}。第一分解阶段的表观活化能和指前因子分别为 224.3 kJ·mol^{-1} 和 10$^{23.15}$ s^{-1}。自加速分解温度和热爆炸临界温度分别为 184.5 ℃和 192.7 ℃。298.15 K 时摩尔比热容为 145.5 J·mol^{-1}·K^{-1}。估算的绝热至爆时间约为 60 s，表明 ANQ 的热稳定性良好。

关键词： 含能材料；1-氨基-2-硝基胍(ANQ)；热行为；比热容；绝热至爆时间

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