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Crystal Structure and Thermal Behavior of GDN

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Abstract: Guanidine dinitramide ($[(NH_2)_2C{=}NH_2]^+N(NO_2)_2^-$, GDN) was prepared by mixing ammonium dinitramide (ADN) and guanidine hydrochloride in water, and its structure was firstly determined by single-crystal X-ray diffraction. The crystal is triclinic, space group *P*-1 with crystal parameters of $a = 0.8332(5)$ nm, $b = 0.9306(6)$ nm, $c = 0.9878(6)$ nm, $\alpha = 84.659(11)°$, $\beta = 69.213(12)°$, $\gamma = 67.451(12)°$, $V = 0.6605(7)$ nm^3, $Z = 4$, $\mu = 0.159$ mm^{-1}, $F(000) = 344$, and $D_{calc} = 1.671$ g·cm^{-3}. The thermal behavior of GDN was studied with DSC and TG/DTG methods, and its thermal decomposition process can be divided into four stages, and the third stage is an intense exothermic decomposition process. The apparent activation energy and pre-exponential constant of the exothermic decomposition reaction are 118.75 kJ·mol^{-1} and $10^{10.86}$ s^{-1}, respectively. The critical temperature of thermal explosion is 164.09 ℃. GDN presents higher thermal stability than ammonium dinitramide (ADN).

Key words: physical chemistry; ammonium dinitramide (ADN); guanidine dinitramide (GDN); crystal structure; thermal behavior

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1 Introduction

Since the synthesis of the nitrogen oxy-anion dinitramide, many researches have been carried out on dinitramide compounds, and the most well known is ammonium dinitramide(ADN), a powerful environmental-friendly oxidizer developed in 1990s for its usage in composite solid rocket propellants[1-2]. A number of metal and organic ion salts of dinitramide have also been studied[3-6]. However, most of these salts are water soluble and highly hygroscopic, which is a big restrictive factor for their abroad application. In this paper, we describe a new organic dinitramide salt($[(NH_2)_2C{=}NH_2]^+N(NO_2)_2^-$, GDN), and firstly report its crystal structure and thermal behavior.

GDN is neither soluble in cold water nor hygroscopic, and has much lower sensitivity than ADN[7]. To some degree, GDN also presents superior thermal stability and explosive performance to those of ADN. In addition, the very valuable point for GDN is its high content of nitrogen, more than 50%, which has been proved to produce more clean gas in thermal decomposition process, and is expected to be used as a safe gas-generator or additive in the applications of propellant and car safety airbag.

2 Experimental

2.1 Synthesis

GDN used in this work was prepared according to the following method: an appropriate amount of ADN was put into water under stirring and the same equimolar of guanidine hydrochloride aqueous solution was added dropwise. After reacting at 40 ℃ for 30 min, the resulting mixture was cooled to room temperature. After two days, bright crystals of GDN were formed, which were filtered, washed with ethanol and dried under vacuum, yielding 78%. Anal. Calcd. (%) for $CH_6N_6O_4$: C 7.23, N 50.59, H 3.64; found (%): C 7.29, N 50.23, H 3.71; IR (KBr) ν: 3461, 3360, 1657, 1510, 1421, 1187, 1011 cm^{-1}.

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2.2 Determination of the single crystal structure

Single crystals suitable for X-ray measurement were obtained by slow evaporation from reaction filtrate at room temperature. A crystal with dimensions of 0.38 mm × 0.25 mm × 0.12 mm was chosen for X-ray determination. X-ray intensities were collected at 293(2) K on a Bruker SMART CCD X-ray diffractometer equipped with a graphite monochromatized MoK_α radiation (λ = 0.071073 nm). Data were collected in the range of $2.21° < \theta < 27.46°$, $-7 < h < 10$, $-11 < k < 12$, $-12 < l < 12$, and 3924 independent reflections were got. The crystal structure was found to be triclinic with space group *P*-1. The compound could be expressed in the formula of $CH_6N_6O_4$ with unit-cell parameters a = 0.8332(5) nm, b = 0.9306(6) nm, c = 0.9878(6) nm, α = 84.659(11)°, β = 69.213(12)°, γ = 67.451(12)°, V = 0.6605(7) nm^3, Z = 4, μ = 0.159 mm^{-1}, $F(000)$ = 344, and D_{calc} = 1.671 g · cm^{-3}. The crystal structure was solved by direct methods and expanded by using Fourier differential techniques with SHELXL – 97. All non-hydrogen atoms were located with successive difference Fourier syntheses. The structure was refined by a full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were added according to the theoretical models. A full-matrix least-squares refinement gave the final R = 0.0702 and wR = 0.1670, $w = 1/[s^2(F_o^2) + (0.0680P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$. The crystal data have been deposited in the Cambridge Crystallographic Data Center with the number of 675017.

2.3 Thermal decomposition conditions

The DSC and TG/DTG experiments for GDN were performed using an SDT-Q600 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 100 mL · min^{-1}. The sample mass was about 1 mg. The heating rates were 2.5, 5.0, 10.0 and 15.0 ℃ · min^{-1} from ambient temperature to 400 ℃.

3 Results and discussion

3.1 Crystal structure

The molecular structure and atom labeling are shown in Fig. 1, 3D framework of GDN is illustrated in Fig. 2. The selected bond lengths and bond angles are summarized in Table 1.

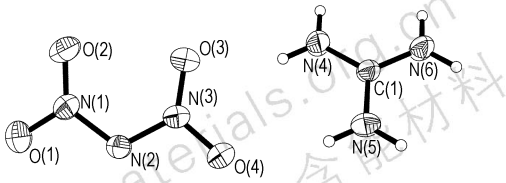

Fig. 1 Molecular structure of GDN

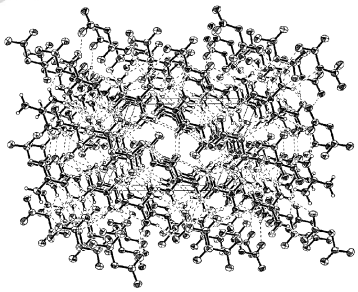

Fig. 2 3D framework of GDN

Table 1 Selected bond lengths and bond angles of GDN

bond	bond length /nm	bond	bond angle /(°)
N(1)—O(1)	0.1244(4)	O(1)—N(1)—O(2)	122.6(5)
N(1)—O(2)	0.1224(4)	O(1)—N(1)—N(2)	111.3(4)
N(1)—N(2)	0.1386(5)	O(2)—N(1)—N(2)	126.1(4)
N(2)—N(3)	0.1368(5)	N(1)—N(2)—N(3)	115.4(4)
N(3)—O(3)	0.1227(4)	N(2)—N(3)—O(3)	125.9(5)
N(3)—O(4)	0.1231(4)	N(2)—N(3)—O(4)	111.5(4)
C(1)—N(4)	0.1304(5)	O(3)—N(3)—O(4)	122.6(5)
C(1)—N(5)	0.1309(5)	N(4)—C(1)—N(5)	120.3(5)
C(1)—N(6)	0.1310(5)	N(5)—C(1)—N(6)	119.5(5)
		N(4)—C(1)—N(6)	120.3(4)

Table 2 Hydrogen bonds of GDN

D—H...A	d(D—H) /nm	d(H...A) /nm	d(D...A) /nm	∠DHA /(°)
N(4)—H—N(2)	0.086	0.222	0.305	163.0
N(4)—H—O(3)	0.086	0.212	0.297	168.1
N(5)—H—N(2)	0.086	0.255	0.312	124.4
N(5)—H—O(4)	0.086	0.256	0.309	121.5
N(6)—H—O(4)	0.086	0.219	0.303	165.4
N(6)—H—O(2)	0.086	0.221	0.304	163.5

The analytical results indicate that the compound molecule is made up of a cation of $[(NH_2)_2C{=}NH_2]^+ \cdots G^+$, and an anion of $N(NO_2)_2^- \cdots DN^-$. The bonding of which is strengthened by lots of N—H···O and N—H···N hydrogen bond interactions (Table 2), because of the special structure of the cation and anion of GDN, that is to say, there are many N—H bonds of amidogen in the cation and N—O bonds of nitryl in the anion, respectively, which all are fit for forming hydrogen bond. It is these

classical and no-classical hydrogen bonding interactions that lead to the formation of 3D framework, as shown in Fig. 2, which may be an important reason for GDN having higher thermal stability.

From Table 1, we can see that the bond lengths of three C—N bonds (0.1304, 0.1309 and 0.1310 nm) in the G^+ are obviously shorter than usual C—N single bond (0.147 – 0.150 nm), showing that the theoretical C—N double bonds in guanidine is conjugated and averaged with the two adjacent C—N single bonds. The dihedral angle of N(4)—C(3)—N(5)—N(6) is 179.20°, and the above four atoms are almost in one plane. So the structure formula of the cation in GDN can be expressed as $[C(NH_2)_3]^+$. But from the band angles of N(4)—C(1)—N(5), N(4)—C(1)—N(6) and N(5)—C(1)—N(6), C(1)—N(4) still has some double bond vestige.

3.2 Thermal behavior

From the typical DSC and TG/DTG curves (Fig. 3 and Fig. 4), we can see that the thermal behavior of GDN can be divided into four stages, which is basically similar to that of ADN[8]. The first stage is a phase transition process, and the extrapolated onset temperature (T_e), peak temperature (T_p) and enthalpy of the phase transition obtained at a heating rate of 10 ℃ · min^{-1} are 101.36 ℃, 104.61 ℃ and 12.63 J · g^{-1}, respectively. The second stage is a melting process, and the extrapolated onset temperature (T_e) and peak temperature (T_p) obtained at the heating rate of 10 ℃ · min^{-1} are 141.40 ℃, 144.47 ℃ and 67.30 J · g^{-1}, respectively. The third stage is an intense exothermic decomposition process with a mass loss of about 48.34%, ranging from 160 ℃ to 225 ℃. The extrapolated onset temperature (T_e), peak temperature and enthalpy of the exothermic decomposition reaction at a heating rate of 10 ℃ · min^{-1} are 175.72 ℃, 204.02 ℃ and 954 J · g^{-1}, respectively. Comparing the thermal behavior of GDN with that of ADN whose melting point is about 92 ℃ and the beginning decomposition temperature is 145 ℃[8], we can draw the conclusion that GDN presents higher thermal stability than ADN.

In order to obtain the kinetic parameters (the apparent activation energy (E) and pre-exponential constant (A)) of the exothermic decomposition reaction for GDN, a multiple heating method (Kissinger's method[9] and Ozawa's method[10]) was employed.

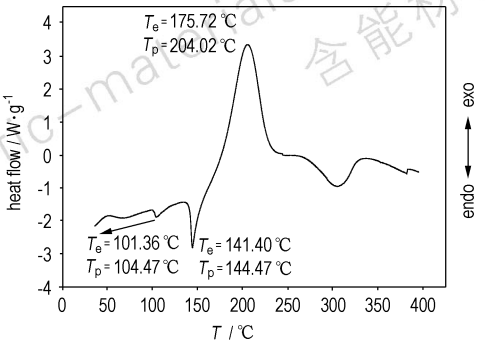

Fig. 3　DSC curve of GDN

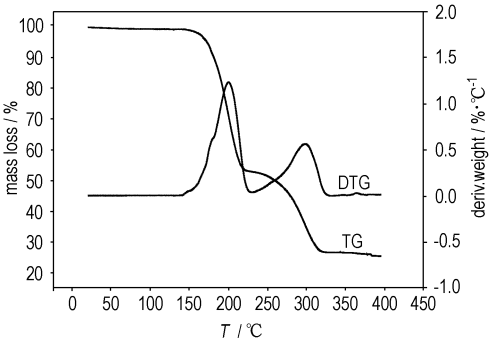

Fig. 4　TG-DTG curves of GDN

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_k}\right) - \frac{E_k}{R}\frac{1}{T_p} \quad (1)$$

$$\log\beta + \frac{0.4567E_O}{RT_p} = C \quad (2)$$

From the original data in Table 3, the above-mentioned values were determined by Kissinger's method and Ozawa's method, which are also listed in Table 3. From the results, we can see that the apparent activation energy obtained from Kissinger's method is in good consistence with that of Ozawa's method. The linear correlation coefficients are all very close to 1, so the results are credible. Moreover, we can see that the apparent activation energy of the exothermic decomposition reaction of GDN was very low, indicating that this reaction easily took place at the temperature range of 150 – 255 ℃.

The values of T_{e0} corresponding to $\beta \to 0$ was obtained by Eq. (3) is 150.8 ℃[11].

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

where b and c are coefficients.

The critical temperature of thermal explosion (T_b)

obtained by Eq. (4) is 164.09 ℃[11-12].

$$T_b = \frac{E_O - \sqrt{E_O^2 - 4E_O R T_{e0}}}{2R} \quad (4)$$

where E_O is the value of E obtained by Ozawa's method.

Table 3 The values of T_e, T_p and the kinetic parameters for GDN determined from the DSC curves at various heating rates

β/℃ · min^{-1}	T_e/℃	T_p/℃	E_k/kJ · mol^{-1}	log(A /s^{-1})	r_k	E_o/kJ · mol^{-1}	r_o	$\overline{E}$/kJ · mol^{-1}
2.5	159.23	186.14	117.9	10.86	0.9984	119.6	0.9986	118.75
5.0	168.30	196.09						
10.0	175.72	205.31						
15.0	179.08	213.02						

Note: Subscript k, data obtained by Kissinger's method; subscript o, data obtained by Ozawa's method.

4 Conclusions

The compound GDN was synthesized and structurally determined. GDN is an ionic compound made up of a cation G^+ and an anion DN^-. The thermal behavior of GDN can be divided into four stages and the third stage is an intense exothermic decomposition process. The apparent activation energy and pre-exponential constant of the exothermic decomposition reaction are 118.75 kJ · mol^{-1} and $10^{10.86}$ s^{-1}, respectively. The critical temperature of thermal explosion is 164.09 ℃. GDN presents higher thermal stability than ADN.

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二硝酰胺胍(GDN)的晶体结构和热行为

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摘要: 利用二硝酰胺铵(ADN)和盐酸胍在水溶液中合成了二硝酰胺胍([$(NH_2)_2C{=}NH_2$]$^+$N$(NO_2)_2^-$, GDN),首次培养出了用于X射线衍射的无色透明单晶。GDN属三斜晶系,空间群为P-1,晶体结构参数为: a = 0.8332(5) nm, b = 0.9306(6) nm, c = 0.9878(6) nm, α = 84.659(11)°, β = 69.213(12)°, γ = 67.451(12)°, V = 0.6605(7) nm^3, Z = 4, μ = 0.159 mm^{-1}, $F(000)$ = 344, D_{calc} = 1.671 g · cm^{-3}。通过DSC和TG/DTG法研究了GDN的热行为,其中第三阶段为强烈的放热分解过程,分解反应的表观活化能和指前因子分别为118.75 kJ · mol^{-1}和$10^{10.86}$ s^{-1}。GDN热爆炸的临界温度为164.09 ℃。GDN比ADN有更好的热稳定性。

关键词: 物理化学; 二硝酰胺铵(ADN); 二硝酰胺胍(GDN); 晶体结构; 热行为

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