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Thermal characteristics of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate in contact with nitrocellulose/nitroglycerine under continuous heat flow



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Abstract Dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50) and nitrocellulose/ nitroglycerine (NC/NG) possess good energy properties, which were widely used in propellants, explosives and pyrotechnics. They are easy to contact with each other during their application and storage. However, their thermal characteristics under continuous heat flow have not been reported yet. Therefore, it is of great practical significance to study the thermal properties of TKX-50/NC/NG (mixture of TKX-50 and NC/NG). In this paper, the thermal characteristics and pressure behaviors of TKX-50/NC/NG, TKX-50 and NC/NG were characterized by high pressure differential scanning calorimetry (HPDSC) and adiabatic scanning calorimetry (ASC). The results showed that TKX-50 and NC/NG can promote each other to decompose under continuous heat flow, especially the thermal decomposition which affected by gases generation and heat feedback was more violent in the confined space. The decomposition peak temperature of TKX-50/NC/NG shifted to low temperature when the heat loss was ignored and the removal of decomposition gas was suppressed. The possible decomposition mechanism of TKX-50/NC/NG was speculated. It was considered that the intermediate products of TKX-50 and NC/NG decomposition under thermal stimulation would react with each other, which promoted TKX-50/NC/NG decomposition in one step at lower temperature. Thus, TKX-50 has

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1878-5352 © 2021 The Author(s). Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/). high reactivity and high potential risk after contact with NC/NG under continuous heat flow. TKX-50 is not suitable for application with NC/NG. This study provides a reference for the structural design of nitrogen rich explosives and further broadens the researchers' understanding of the application of TKX-50.

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1. Introduction

The dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50), as a newly synthesized explosive, has widely attracted researcher's attention (Fischer et al., 2012). As one of the most valuable high energy insensitive explosives, it is considered to replace the conventional energetic materials such as cyclotrimethylene trinitramine (RDX), cyclotetramethylenete tranitramine (HMX), and hexanitrohexaazaisowurtzitane (CL-20) in explosives and propellants owing to its low sensitivity, high detonation velocity, high strength, low toxicity, high density and relatively low cost (Gan et al., 2020; Chen et al., 2019; Talawar et al., 2018; Badgujar et al., 2017; Xiong et al., 2016).

At present, most of the research on TKX-50 are on synthesis (Fischer et al., 2012; Lee and Kwon, 2019; Golenko et al., 2017), stability (Li et al., 2019a; Niu et al., 2017a; Li et al., 2015; Dreger et al., 2015; Meng et al., 2016), sensitivity (Deng et al., 2020; Lu et al., 2017a; Zhou et al., 2019; An et al., 2015), energy performance (Xing et al., 2019; Yu et al., 2017; Badgujar and Talawar, 2017; Klapötke et al., 2016; Gottfried et al., 2017), reaction mechanism (Li et al., 2019b; Tidey et al., 2017; Lu and Zhang, 2017b), preparation and properties of composite materials (Ma et al., 2016; Yu et al., 2016; Xiao et al., 2019; Dong et al., 2019a; Dong et al., 2019b). The thermal risk evaluation (Zhao et al., 2019a; Niu et al., 2017b; Wang et al., 2017; Huang et al., 2015a) or the interaction mechanism (Tao et al., 2020; Xiong et al., 2017) of TKX-50 with some materials was also reported. The thermal characteristics (Xu et al., 2020; Zhu et al., 2019; Huang et al., 2015b; Wang et al., 2018a) and the decomposition mechanism (Zhao et al., 2019b; Zhao et al., 2019d; Wang et al., 2018b; Yuan et al., 2015) of TKX-50 under different conditions were also studied. It is well known that energetic materials are rarely used pure, and the thermal properties between the energetic material and the other components may alter the thermal stability of the energetic material itself, leading to high potential risks. NC/NG is aliphatic nitrate ester compounds that is used in a wide range of both civilian and military applications, for example, as gas generators in airbags (Ing and Phys, 1993), as a component of combustible cartridge case (Yang et al., 2017; Shedge et al., 2008), as fuels in rocket motors (Kalaycioglu et al., 2010; Wu et al., 2017) or to shoot projectiles in guns (Yi et al., 2009; Zhang et al., 2018; Wang et al., 2018). It is possible that TKX-50 will be exposed to NC/NG during application, storage or transportation, which are usually in confined spaces. The decomposition of TKX-50 has been investigated by different methods (Zhao et al., 2019c; Jia et al., 2017; Lu et al., 2017b; Xiao et al., 2016; An et al., 2014), however, there have not been reported on the thermal properties and pressure behaviors of the mixture (TKX-50/NC/NG) in confined space with continuous heat flow in detail. The safety or potential risks of the mixture in

confined spaces are not known. The study of the thermal characteristics of TKX-50/NC/NG is of great importance and urgency, which will contribute to the development of emergency measures in the application, storage and transportation of TKX-50. It is also an important basis for the study of potential risks and physicochemical stability of TKX-50.

Here, the thermal characteristics of TKX-50/NC/NG was studied, while the thermal decomposition of TKX-50 and NC/NG was compared. We focus on the thermal decomposition of TKX-50/NC/NG, TKX-50 and NC/NG characterized by various methods. The thermal decomposition experiment under atmospheric pressure was carried out by the DSC equipment. The decomposition with different pressures (0.5 MPa, 1.5 MPa and 2.5 MPa) under continuous heat flow was carried out by HPDSC test. Moreover, the thermal characteristics and pressure behaviors under adiabatic conditions with the constant power were studied by ASC test. The results showed that TKX-50 and NC/NG can promote each other's decomposition under certain conditions. The possible decomposition mechanism of TKX-50/NC/NG was speculated. The interesting research provides reference information for the theoretical research and practical application of TKX-50.

2. Experimental

2.1. Materials

Dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50) (\geq 99.5%) was purchased from Gansu Yinguang Chemical Industry Group. Co. LTD.; nitrocellulose (NC, 13.0% for nitrogen percent) and nitroglycerine (NG) (\geq 99.5%) were provided by Sichuan Nitrocell Co., Ltd. (Sichuan, China); ethanol



Fig. 1 Chemical structures of (a) TKX-50, $C_2H_8N_{10}O_4$, (b) NG, $C_3H_5N_3O_9$ and (c) NC, $(C_6H_7N_3O_{11})_n$ (Atoms colouring are: C (grey), H (white), O (red), N (blue).

 $(\geq 99.7\%)$ and acetone $(\geq 99.7\%)$ were purchased from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). The chemical structures of TKX-50, NG and NC are presented in Fig. 1. Fig. 1c shows part of the structure of the linear polymer NC.

2.2. Characterization

At 25 °C, 0.50 g TKX-50 and 0.50 g NC/NG were kneaded with solvent (0.5 mL ethanol and 0.50 mL acetone) for 0.5 h in a square crucible to make them in close contact. And the sample (TKX-50/NC/NG) was dried in a drying vacuum oven at 50 °C for 48 h to remove the solvent. Then the response of TKX-50/NC/NG to heating was studied at 100 °C. Meanwhile, the same operation was also performed for 0.50 g pure TKX-50 and 0.50 g NC/NG respectively. A schematic diagram of their heating process is shown in Fig. 2.

Thermal decomposition of the samples was performed by high pressure differential scanning calorimetry (DSC, Mettler Toledo, HPDSC827), recording with 20 mL·min⁻¹ argon at 10 °C·min⁻¹ from 50 °C to 350 °C. Thermal properties in confined space with different pressures (0.5 MPa, 1.5 MPa and 2.5 MPa) were tested by HPDSC in the temperature range of 50–350 °C and the heating rate was 10 °C·min⁻¹. The samples were in the static high-pressure environment, and the pressures of the confined space were regulated by high-purity argon. All samples (1 \pm 0.02 mg) were placed in alumina crucibles.

Adiabatic scanning calorimetry (ASC) measurements were conducted on an instrument (MMC274) supplied by NETZSCH Company. As shown in Fig. 3, the ASC is designed to maintain the accurate temperature by surrounding the sample vessel with guard heaters. The sample vessel was connected with a pressure transducer to measure the pressure inside the vessel as a function of time and temperature.

In this paper, the constant power mode was used. The samples were heated on a constant power (200 mW) in this mode.



Fig. 2 TKX-50 in contact with NC/NG under continuous heat flow.



Fig. 3 Schematic diagram of adiabatic scanning calorimetry for samples.

The vessel with a volume of 2.6 mL and a wall thickness of 0.51 mm was used to measure 40.0 mg of samples. The vessel is made of titanium alloy, so it can withstand high pressure (pressure range: 0-10 MPa).

ASC can form an approximately adiabatic system, and all the heat generated in the decomposition process is used to increase the temperature of the system. In addition, the vessel was sealed in air and the confined space allows the releasing gases to participate in the decomposition reaction, which could simulate the circumstance of application, storage or transportation.

3. Results and discussion

3.1. The response of TKX-50-NC/NG to thermal stimulation

As shown in Fig. 4a, the white block in the square crucible is TKX-50/NC/NG before heating. It was found that the color of sample around the square crucible was light green after heating at 50 °C for 24 h (Fig. 4b) and then it turned dark green after heating at 50 °C for 48 h (Fig. 4c). It was implied that the physical and chemical properties of TKX-50/NC/NG have changed and the sample has been decomposed. When the temperature was raised to 100 °C, the sample exploded horribly after 1 h later (Fig. 4d). By comparison, the pure TKX-50 (Fig. 4e, f, g, h) and NC/NG (Fig. 4i, j, k, l) did the same operation and no abnormal phenomenon was found. This phenomenon has aroused our interest, and further research on the decomposition of TKX- 50/NC/NG has been done in this research.

3.2. Thermal decomposition of TKX-50/NC/NG

In order to better understand the thermal decomposition of TKX-50/NC/NG, TKX-50 and NC/NG, we measured their decomposition process under continuous heat flow by DSC test. The decomposition of TKX-50 has two stages with exothermic peaks of 241.5 °C and 274.5 °C, as shown in Fig. 5. There was only one decomposition exothermic peak (206.7 °C) for NC/NG. There were three exothermic peaks (170.9 °C, 205.7 °C and 259.4 °C) for the decomposition of



Fig. 4 Photos of TKX-50/NC/NG (a, b, c, d), TKX-50 (e, f, g, h) and NC/NG (i, j, k, l): (a, e, i) before heating, (b, f, j) and (c, g, k) heating at 50 °C for 24 h and 48 h, (d, h, l) heating at 100 °C for 1 h.

TKX-50/NC/NG in the presence of purge gas. For the decomposition of TKX-50/NC/NG, it was guessed that the decomposition of most NG in the gas phase after evaporation (Matečić Mušanić et al., 2010) was the cause of the first exothermic peak (170.9 °C). The decomposition of remaining NG, NC and the first decomposition stage of TKX-50 caused the appearance of the second exothermic peak (205.7 °C). The last exothermic peak was generated by the second decomposition stage of TKX-50 (259.4 °C). The exothermic peaks of TKX-50 and NC/NG have shifted, indicating that they may be promote each other in the decomposition of TKX-50/NC/NG.

The purge gas of DSC test could take away part of the decomposition gas, which may affect the decomposition of TKX-50 and NC/NG. Thus, it is necessary to study the thermal decomposition of TKX-50/NC/NG without loss of decomposition gas, so as to eliminate the influence of gas removal on decomposition.

3.3. Thermal properties of TKX-50/NC/NG without loss of decomposition gas

HPDSC can keep the sample in a confined space, so it can suppress the removal of gas which produced during the test. The thermal characteristics of TKX-50/NC/NG, TKX-50 and NC/NG under 0.5 MPa were observed by HPDSC curves. As shown in Fig. 6a, compared with the results of DSC test, the thermal decomposition of TKX-50/NC/NG has only one sharp exothermal peak (152.4 °C) under 0.5 MPa. The exothermic peak (240.6 °C) of the first decomposition stage of TKX-50 has little change, while the exothermic peak (292.1 °C) of the second decomposition stage obviously shifts to high temperature. For the NC/NG sample, the exothermic peak (197.2 °C) shifts to low temperature. In order to prove that the decomposition gas in the confined space has a great influence on the decomposition of TKX-50/NC/NG, rather



Fig. 5 DSC curves of the thermal decomposition of TKX-50/NC/NG, TKX-50 and NC/NG using high-purity argon as purge gas with flowing rate of 20 mL·min⁻¹.

than the pressure. The samples decomposed under 1.5 MPa and 2.5 MPa, and the results were shown in Fig. 6b and 6c. TKX-50/NC/NG has only one exothermic peak under 1.5 MPa (152.7 °C) and 2.5 MPa (154.5 °C). The first decomposition stage of TKX-50 has an exothermic peak of 242.4 °C under 1.5 MPa and 241.5 °C under 2.5 MPa. Compared with the peak (240.6 °C) under 0.5 MPa, the shift of these peaks changes little. The exothermic peaks of the second stage decomposition of TKX-50 under 1.5 MPa and 2.5 MPa shifted

to 297.2 °C and 298.7 °C, respectively. Significant increase in the chemical stability of TKX-50 with pressure was attributed to a suppression of hydrogen-transfer (Dreger et al., 2017). For the decomposition of NC/NG, the exothermic peaks under 1.5 MPa and 2.5 MPa are 194.1 °C and 193.5 °C.

By comparing the decomposition of samples under different pressures (0.5 MPa, 1.5 MPa and 2.5 MPa), it was considered that the pressure in the confined space caused the position of the peak to shift, not the number of peaks. The pressure could inhibite or promote the decomposition of samples, not the reason for the exothermic peak of TKX-50/NC/NG around 153 °C. Accordingly, it was believed that the one-step decomposition of TKX-50/NC/NG around 153 °C was caused by the inability to remove the decomposition gas.

Meanwhile, the time required to complete the whole decomposition of the sample (t_{total}) under different pressures was analyzed. On the one hand, t_{total} can indicate the chemical stability of the sample. On the other hand, it reflected the decomposition reaction rate. It can be seen from Fig. 6d that with the increase of pressure, the t_{total} of TKX-50 was prolonged. For the NC/NG sample, t_{total} was slightly shorter with the increase of pressure. Surprisingly, the thermal decomposition of TKX-50/NC/NG was completed in a short time, only about 2 min, which was shorter than that of TKX-50 and NC/NG. It showed that the thermal stability of TKX-50 in contact with NC/NG under continuous heat flow was greatly reduced. The failure to remove the decomposition gases made TKX-50/NC/NG has a high potential risk. Simultaneously, there were still a lot of heat losses in HPDSC, which could not be fed back to the thermal decomposition reaction of samples, and may also have a great impact on the decomposition.



Fig. 6 Thermal decomposition of TKX-50/NC/NG, TKX-50 and NC/NG under (a) 0.5 MPa, (b) 1.5 MPa and (c) 2.5 MPa). (d) is the time required to complete the whole decomposition of the samples.

3.4. Thermal characteristics of TKX-50/NC/NG without removal of decomposition gas and heat loss

We further studied the thermal decomposition characteristics of TKX-50/NC/NG without removal of decomposition gas and heat loss by means of an instrument. ASC is a good choice, which can provide adiabatic environment when sample decomposes. As shown in Fig. 7, the temperature and temperature rise rate during the thermal decomposition of TKX-50/NC/NG (20.0 mg TKX-50 and 20.0 mg NC/NG), TKX-50 (40.0 mg) and NC/NG (40.0 mg) were measured by ASC under 200 mW. TKX-50/NC/NG ignited at 132.7 °C and decomposed rapidly, but TKX-50 and NC/NG ignited at 225.0 °C and 171.8 °C, respectively. The ignition temperature of TKX-50/NC/NG is 92.3 °C lower than that of TKX-50 and 39.1 °C lower than that of NC/NG. The maximum temperature rise rates of TKX-50/NC/NG, TKX-50 and NC/NG reached 127.1 °C min⁻¹, 141.6 °C min⁻¹, and 123.5 °C min⁻¹ at 135.8 °C, 228.4 °C, and 174.7 °C, respectively. In addition, they completed the decomposition at 141.1 °C, 233.5 °C and 179.6 °C. The temperature of the whole thermal decomposition process of TKX-50/NC/NG, TKX-50 and NC/NG increased by 8.5 °C, 8.5 °C and 7.8 °C. The detailed parameters of the decomposition of TKX-50/NC/NG, TKX-50 and NC/NG under 200 mW were listed in Table 1.

Controllable thermal power input technology can be used to directly measure exothermic or absorptive enthalpy without knowing the heat capacity of the sample in advance, and the curve similar to DSC can be obtained. In this paper, the heat balance equation can be expressed by equation (1).

$$P_i = HR \cdot C_t + q_S \tag{1}$$

where P_i is defined as the input power, C_t as the total heat capacity of the sample and the container, HR as the measured temperature rise rate, q_s as the heat absorption and exothermic power of the sample.

According to the equation (1), before and after heat absorption and heat release:

$$q_s = 0 \tag{2}$$

$$P_i = HR \cdot C_t \tag{3}$$

Based on the above equations, C_t can be measured in real time.

Further, the total heat capacity of the heat absorption and heat release effect interval can be calculated by interpolation. The q_s can be measured in real time according to Eq. (1). Then the heat of reaction Q can be calculated by integration. The calculated heat of reaction Q and the ASC curves of TKX-50/NC/NG, TKX-50 and NC/NG were shown in Fig. 8. The ASC curve of TKX-50/NC/NG had only one exothermic peaks of 134.0 °C, and the heat released Q_1 was 1963 J·g⁻¹. The exothermic peaks of TKX-50 and NC/NG by ASC test were 226.5 °C and 173.0 °C, as well as the heat released Q_2 and Q_3 were 1620.3 J·g⁻¹ and 1600.1 J·g⁻¹, respectively. TKX-50/NC/NG decomposed extremely fast around 133 °C due to gases generated by decomposition and the self-heating of heat accumulation in an adiabatic environment.



Fig. 7 Temperature and temperature rise rate of the decomposition of (a) TKX-50/NC/NG, (b) TKX-50 and (c) NC/NG under 200 mW.

The temperature of exothermic peak of ASC curve for TKX-50/NC/NG was lower than that of HPDSC, which indicated that thermal feedback promoted the thermal decomposition of TKX-50/NC/NG.

Table 1 The detailed parameters of the temperature during decomposition under 200 mw.						
Samples	T _{ignition} (°C)	T _{final} (°C)	ΔT (°C)	T _{HRmax} (°C)	HR _{max} (°C·min ⁻¹)	
TKX-50/NC/NG	132.7	141.1	8.5	135.8	127.1	
TKX-50	225.0	233.5	8.5	228.4	141.6	
NC/NG	171.8	179.6	7.8	174.7	123.5	

Note: $T_{ignition}$ is the ignition temperature; T_{final} stands for the temperature after decomposition in the vessel; ΔT is T_{final} minus $T_{ignition}$; T_{HRmax} and HR_{max} are the temperature and the maximum temperature rise rate during the decomposition, respectively.

3.5. Pressure behaviors of TKX-50/NC/NG without removal of decomposition gas and heat loss

In the process of heating, the safety of the warhead and closed storage containers was affected not only by the exothermicity of the energetic materials decomposition but also the fast pressure rise during the energetic materials decomposition. For this reason, it is necessary to continuously and directly monitor the pressure change during the decomposition process. To obtain the pressure behaviors of TKX-50/NC/NG, TKX-50, and NC/NG decomposition, the decomposition processes of them had been recorded under 200 mW.

The pressure and temperature of initial decomposition of sample in a closed container is key parameter to describe the decomposition process and the safety performance of the energetic materials (Wang et al., 2019). As shown in Fig. 9 and Table 2, TKX-50/NC/NG, TKX-50 and NC/NG began to decompose at 125.9 °C, 205.2 °C and 149.0 °C respectively, meanwhile, the pressures P_{initial} were 0.13 MPa, 0.14 MPa and 0.14 MPa. The pressures were 0.15 MPa, 0.21 MPa and 0.21 MPa when TKX-50/NC/NG, TKX-50 and NC/NG were ignited. At the beginning of the rapid decomposition, as shown in Fig. 9, the rapid rise of pressure started at T_{ignition} , which is the same as the temperature rise, indicating that the heat release of TKX-50/NC/NG, TKX-50 and NC/NG were almost



Fig. 8 ASC curves of the thermal decomposition of TKX-50/NC/NG, TKX-50 and NC/NG. The shaded areas below the curves represent the heat of reaction of TKX-50/NC/NG (Q_1), TKX-50 (Q_2) and NC/NG (Q_3).



Fig. 9 Plots of pressure versus temperature of TKX-50/NC/NG, TKX-50 and NC/NG under 200 mW.

Table 2 The detailed parameters of the pressure duringdecomposition under 200 mW.

Samples	TKX-50/NC/NG	TKX-50	NC/NG
P _{initial} (MPa)	0.13	0.14	0.14
Pignition (MPa)	0.15	0.21	0.21
P _{max} (MPa)	1.23	1.50	1.08
P _{final} (MPa)	1.16	1.47	1.03
ΔP (MPa)	1.10	1.36	0.94
dP/dt _{max}	28.40	34.50	22.90
$(MPa \cdot min^{-1})$			
T _{initial} (°C)	125.9	205.2	149.0
T _{Pmax} (°C)	133.0	226.6	172.1
T _{dP/dtmax} (°C)	132.7	255.0	171.8

Note: The ignition pressure $P_{ignition}$ means the pressure at the ignition temperature $T_{ignition}.$ T_{Pmax} is the temperature at $P_{max}.$ ΔP is P_{max} minus $P_{initial}$. The value of $T_{dP/dtmax}$ is the temperature at $dP/dt_{max}.$

synchronous with the gas released by the process of decomposition.

The vulnerability of the ammunition and closed container was affected by the decomposition process of the energetic materials. Therefore, the time-dependent pressure and the related pressure rise rate in a closed container were important parameters to describe the decomposition process and the safety performance of the energetic materials. With the increase of pressure, the strain rate of the shell increases. Thus, it is easier to form shear crack at the final pressure (Hoggatt



Fig. 10 The pressure and pressure rise rate of (a) TKX-50/NC/NG, (b) TKX-50 and (c) NC/NG under 200 mW.

and Recht, 1968; Levy et al., 2012). Hence, a larger value of the pressure rise rate and lower initial decomposition temperature indicated that the energetic materials would be more dangerous to the closed container and the surroundings. On the contrary, a lower value of the pressure rise rate and a higher initial decomposition temperature exhibited a good safety performance and low vulnerability of the ammunition.

The pressure and pressure rise rates of TKX-50/NC/NG, TKX-50 and NC/NG as a function of time were displayed in Fig. 10 and Table 2. The maximum pressures P_{max} during the decomposition of TKX-50/NC/NG, TKX-50 and NC/NG reached 1.23 MPa, 1.50 MPa and 1.08 MPa at 133.0 °C, 226.6 °C and 172.1 °C, and the pressures increased by 1.10 MPa, 1.36 MPa and 0.94 MPa respectively. The stable pressures P_{final} in the vessel after decomposition were 1.16 MPa, 1.47 MPa and 1.03 MPa. The decomposition was finished at P_{final} . The maximum pressure rise rates dP/dt_{max} TKX-50/NC/NG, TKX-50 and NC/NG of were 28.40 MPa min⁻¹, 34.50 MPa min⁻¹ and 22.90 MPa min⁻¹ at 132.7 °C, 225.0 °C and 171.8 °C, respectively. The pressure and maximum pressure rise rate of TKX-50/NC/NG were between those of TKX-50 and NC/NG. However, according to the ideal gas law, pressure is proportional to temperature. Thus, the maximum pressure value reached bv TKX-50/NC/NG was the highest among them. Moreover, the ignition temperature of TKX-50/NC/NG was the lowest of them. As a result, TKX-50/NC/NG was considered the most dangerous, followed by NC/NG and TKX-50. It can be seen from the pressure that TKX-50 and NC/NG promote the decomposition of each other after mixing, which indicates that TKX-50/NC/NG has a strong chemical reaction and high potential risk when heated.

3.6. Chemical mechanism of thermal decomposition of TKX-50 in contact with NC/NG under continuous heat flow

Having obtained above data, we were able to propose the chemical mechanism of TKX-50 in contact with NC/NG under continuous heat flow (Fig. 11). It should be clearly emphasized here that these reaction steps are not elementary. At present, it is not possible to provide a complete description of all physical and chemical processes in the solid-state decomposition of the energetic materials at the microscopic level by using the available macroscopic thermoanalytical techniques.

The thermal decomposition mechanism of TKX-50 was shown in Fig. 11a. The first stage commences with dissociation of the TKX-50 salt to the corresponding acid and base, viz., hydroxylamine (NH₂OH) and 1,1'-bistetrazolediol (BTO), accompanied H-transfer. Both compounds are less stable than the original salt, and NH₂OH has the least stability. Then the decomposition of NH₂OH to form H₂O, NH₃, N₂ and N₂O, and that NH₃ combines with BTO to form diammonium 5,5'-bistetrazole-1,1'-diolate (ABTOX). When the temperature continues to rise, ABTOX eventually breaks down into small molecular gaseous products such as N₂O, CO₂, N₂, etc., which was the secondary decomposition of TKX-50. Similar conclusions have been reported by some researchers (Jia et al., 2017; Muravyev et al., 2017; Sinditskii et al., 2015; Jia et al., 2019). It has been reported that NC/NG could decompose slowly below 100 °C (Matečić Mušanić et al., 2010). NC/NG, as one of the nitric acid ester compounds, NO2 is bonded to carbon by oxygen atoms. It is prone to fracture and decomposition for O-NO2. The decomposition of NC/NG is initiated by the hydrogen bond between ·NO2 and NC/NG. Because ·NO2 and nitro have the same spatial configuration and similar physicochemical properties, the close proximity between them will produce a greater repulsive force. Thus, NO₂ could



Fig. 11 Chemical mechanism of thermal decomposition of (a) TKX-50, (b) R-CH₂-O-NO₂ (R of R-CH₂-O-NO₂ is represented by yellow), the nitric acid ester compounds (NC/NG), and (c) TKX-50/NC/NG.

gradually approach NC/NG from the side far away from the nitro group, and capture the hydrogen bonded on the carbon atom to promote the fracture of O-NO₂, then realize the catalytic decomposition of NC/NG. The intermediate products may be \cdot HNO₂, \cdot NO₂, R-CHO \cdot and so on, and they will further participate in the decomposition reaction. The decomposition mechanism of NC/NG is shown in Fig. 11b. Similar results (Ding et al., 2017) have also been reported.

Nevertheless, the thermal decomposition mechanism of TKX-50/NC/NG (Fig. 11c) is different from that of TKX-50 and NC/NG. It is known that TKX-50 is a hydroxylamine salt, and NH₂OH is alkaline. Most of the intermediate products of NC/NG decomposition are acidic, such as HNO₂. HNO₂ and NH₂OH, would undergo redox reaction to form H₂O and N₂O. As a nucleophilic reagent, NH₂OH reacts with carbonyl group of R-CHO by nucleophilic addition reaction. The product of nucleophilic addition reaction is R-CH = N-OH, which may undergo Beckmann rearrangement, forming amide to participate in decomposition. Under thermal stimulation, the consumption of NH₂OH promoted the hydrogen transfer, which accelerates the primary decomposition of TKX-50. Then the BTO was broken down into simple gas products, such as N_2O , NO, CO_2 , CO, N_2 , H_2O , etc. It is reasonable that BTO occurs in one-step decomposition instead of producing ABTOX as soon as the structure was destroyed.

Hence, it is inferred that the intermediate products of TKX-50 and NC/NG decomposition were fully contact with each other and difficult to escape in confined space, which promoted the one-step thermal decomposition of the mixture and react violently.

4. Conclusion

This work investigated the thermal stability between TKX-50 and NC/NG under continuous heat flow. It was found that the presence of NC/NG significantly decreases the decomposition peak temperature of TKX-50. Consequently, the mixture of TKX-50 and NC/NG has a high potential risk. By studying the thermal characteristics and pressure behaviors of the TKX-50/NC/NG, TKX-50 and NC/NG, the following conclusions can be drawn:

- TKX-50 can react with NC/NG and the color of the mixture turn green, and then deflagrate under continuous heat flow, which is dangerous.
- (2) The intermediate products of the decomposition of TKX-50 and NC/NG would undergo chemical reaction, thus promoting the one-step decomposition of TKX-50/ NC/NG. By analyzing the results of HPDSC and DSC test, the decomposition of the mixture was more intense than TKX-50 and NC/NG because the removal of the decomposed gas was suppressed in the confined space. The characterizations of ASC and HPDSC showed that the ignition temperature of the mixture was lower and the potential danger was greater under adiabatic condition due to the increase of decomposition heat feedback of energetic materials and the suppression of decomposition gas removal.
- (3) The contact between TKX-50 and NC/NG should be avoided during their application, storage and transportation. Our work presented here will be useful for

developing thermomechanical and thermochemical models to describe the unreacted and reacted response of TKX-50.

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Authors' Contributions

Y. Fu. conceived of the study, designed the study; X. Wang collected ASC data; Y. Zhu collected HPDSC data; B. Xu contributed to analysis and interpretation of ASC data; Z. Liu contributed to analysis and interpretation of DSC and HPDSC data; L. Chen collected DSC data; X. Liao. critically revised the manuscript. All authors gave final approval for publication and agree to be held accountable for the work performed therein.

Competing Interests

We have no competing interests.

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