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Research on the thermal behavior of novel heat resistance explosive 5,5′-bis (2,4,6-trinitrophenyl)-2,2′-bi(1,3,4-oxadiazole)

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ABSTRACT

5,5′-bis(2,4,6-trinitrophenyl)-2,2′-bi(1,3,4-oxadiazole) (TKX-55) was synthesized through an oxidation-chloridization-condensation-cyclization sequence. Thermal decomposition behavior and non-isothermal decomposition reaction kinetics of TKX-55 were investigated by the differential scanning calorimetry and thermogravimetric analysis (DSC-TG) methods The research of decomposition mechanism of the molecule was further carried out through in-situ FTIR spectroscopy technologies. The experiment results showed that the enlarged conjugated system has a marked effect on the thermal stability and the picryl moiety is much more stable than the 1,3,4-oxadiazole moiety during the heat-up process, indicating that the decomposition process is mostly likely to initiate from the ring-opening reaction of 1,3,4-oxadiazole moiety which is supported by the computational scanning result of potential energy surface.

1. Introduction

Thermal stability is one of the most important characteristics of high-energy materials to ensure the safety in handling, especially when they are applied in the area of deep sea oil, gas exploitation and space exploration [1–4]. Developing molecules with high thermal stability and figure out their decomposition behavior is always an urgent problem to be solved in the research of energetic materials [5]. Some aromatic nitro molecules have been recognized for their high thermal stability. For example, 2,2′,4,4′,6,6′-Hexanitrostilbene (HNS) and 2,2′,4,4′,6,6′-hexanitroazobenzene (HNAB) (Fig. 1) are typical thermal stable energetic molecules with conjugated aromatic structures which find wide application on space ship for stage separation [6,7]. Furthermore, the increase of the conjugation between aromatic rings has been found to be able to improve thermal stability impressively [8].

5,5′-Bis(2,4,6-trinitrophenyl)-2,2′-bi(1,3,4-oxadiazole) (TKX-55) is a recent developed energetic molecule with low sensitivity to friction and impact [9]. (Fig. 1) The structure of TKX-55 is similar with the structure of 2,5-dipicryl-1,3,4-oxadiazole (DPO), a novel heat-resistant explosive [10,11]. Both of the molecules contain 2,4,6-trinitrophenyl groups which are connected by 1,3,4-oxadiazole bridge. Compared with DPO, the conjugated system of TKX-55 is larger and its density, enthalpy of formation, nitrogen content, detonation velocity, and detonation pressure values are higher than most of the currently used heat resistance explosives. The good detonation performance and insensitive properties makes TKX-55 a potential candidate for thermally stable explosive. However, its detailed thermal decomposition behavior and the compatibilities with typical explosives are still unclear which hinders the application research severely.

Herein, we reported the research on the real-time thermal decomposition behavior of TKX-55. The thermal decomposition of TKX-55 was studied by DSC-TG method [12–14] and the intermediates formed during the pyrolysis process were characterized through in-situ FTIR spectroscopy technologies [15,16]. The deep research on the thermal behavior of TKX-55 will promote the studies of the intrinsic decomposition mechanism of conjugation aromatic system in explosives as well as their stabilizing effect.

2. Experiment

2.1. Reagents and sample preparation

TNT (99.0%) was supplied by Xi'an Modern Chemistry Research Institute. Potassium dichromate (99%), thionyl chloride (99.0%), Oxalyldihydrazide (98.0%) and Oleum (20%) were purchased from the Aladdin Chemistry Co. Ltd. (Shanghai, China).

The sample of TKX-55 was synthesized through an oxidation-chloridization-condensation-cyclization [9] sequence (Scheme 1) and characterized by ^{1}H NMR, ^{13}C NMR, FTIR and elemental analysis.

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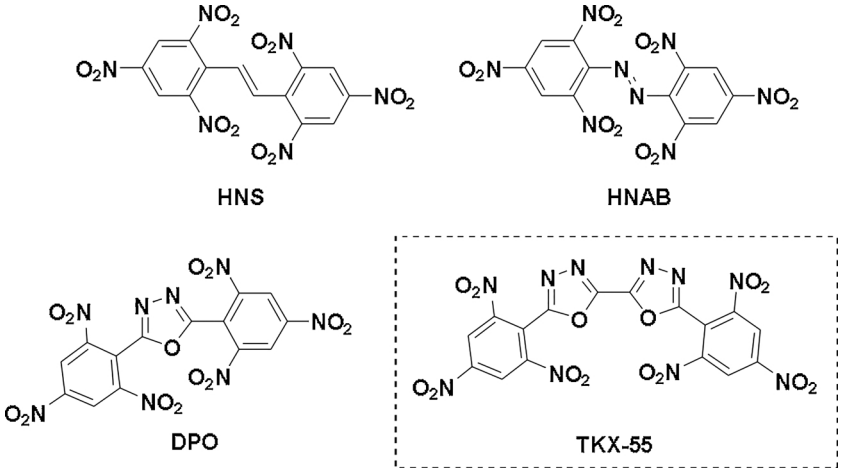
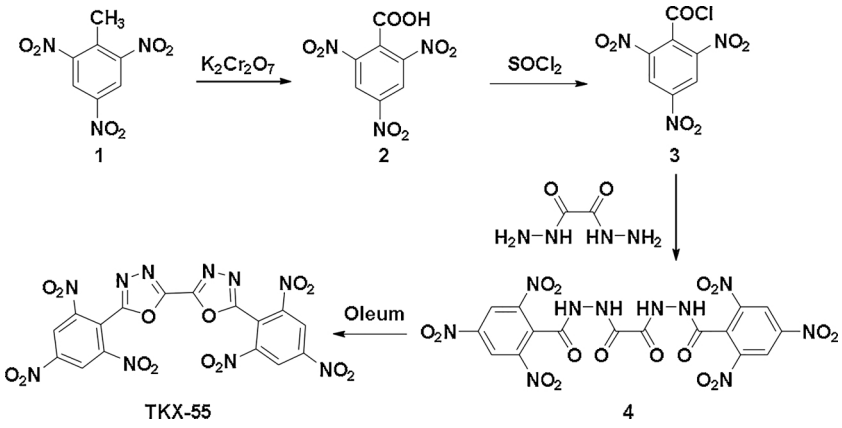
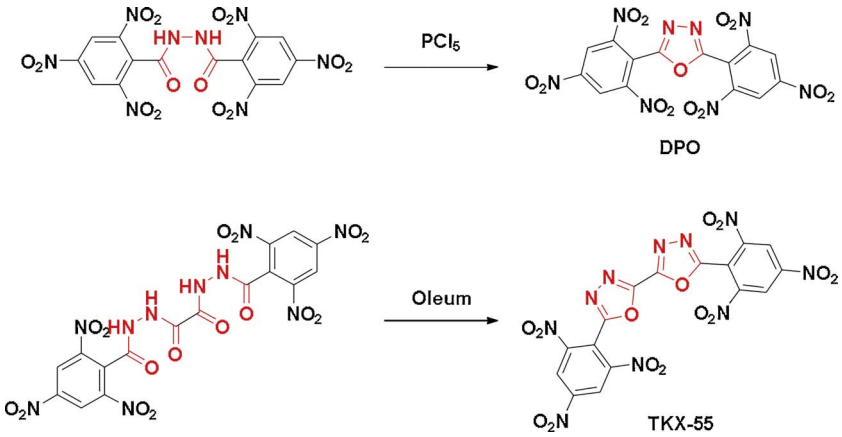


Fig. 1. Structures of HNS, HNAB, DPO and TKX-55.



Scheme 1. Synthetic route of TKX-55.



Scheme 2. Synthesis of 1,3,4-oxadiazolemoiety by dehydration cyclization.

2.2. Apparatus and measurements

The thermal analysis experiments was performed with a model TG-DSC STA 449C instrument (NETZSCH, Germany). Operation conditions: sample mass, 0.6 mg; atmosphere, dynamic nitrogen; aluminum cell. The IR spectra were recorded on a Nicolet 60SX FTIR spectrometer employing an HgCdTe detector. The in-situ FTIR spectroscopy was carried out with Nicolet 60 SXR FTIR spectrometer. Operation conditions: sample mass, 0.6 mg; heating rate, 10 °C·min^{-1}; resolution, 4 cm^{-1}; spectral acquisition rate, 17.8 file·min^{-1}, 16 scans·file^{-1}; temperature range, 20 °C ~ 450 °C.

2.3. Computational methods

The optimized geometries and harmonic frequencies were calculated using the B3LYP [17,18] method and 6–31G(d) [19] basis set. TKX-55 and its dissociative products have true minima on their potential energy surfaces without any imaginary frequencies, and the two correlative transition states have only one imaginary frequency. The xyz coordinates of optimized geometries are presented in ESI. The electronic structure calculations were carried out using the Gaussian 09 program package [20].