

Explosive performance of HMX/NTO co-crystal

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Abstract. A new co-crystal explosive of 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) and 3-nitro-1, 2, 4-triazol-5-one (NTO) in a molar ratio of 1:1 has been prepared by solvent/anti-solvent method. The SEM photographs show that HMX/NTO co-crystals are distinctly different from HMX and NTO crystals. The co-crystals are prisms with well formed crystal surfaces. Thermal analysis results indicate the melting point of the co-crystal is 29.3 °C higher than that of NTO. Moreover, the co-crystal exhibits a modified mechanical sensitivity. The characteristic height (H_{50}) of impact sensitivity increases 14.8 cm, and the explosion percentage (P) of friction sensitivity decreases by 40% compared with HMX. The HMX/NTO co-crystals possess good thermal property and low sensitivity, which mean huge advantages in blasting engineering.

1. Introduction

The combination of high performance and low sensitivity has become a main challenge for further application and development of explosives. In the past, various approaches to modify the properties of explosives including crystallizing with solvents and coating with polymers have been adopted. Unfortunately, these traditional methods hardly produced remarkable improvements on the performances of existing explosives [1]. Aim of the co-crystallization technique is to include two or more different molecules in a single crystal lattice. This approach has been widely used in pharmaceutical field to improve the solubility and/or stability of either component of the co-crystal. In the area of energetic materials, co-crystallization is emerging as a new technology for modifying or enhancing the properties of existing energetic substances [2]. Therefore co-crystallisation would potentially provide a way to achieve the combination of high energy and low sensitivity on the molecular level [3].

1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX, 1, figure 1) is one of the most important energetic ingredients used in various propellants and explosives. HMX-based systems have many advantages, i.e. high melting point, high density, potentially high specific impulse, high detonation velocity, little smoke produced and, as compared to ammonium perchlorate, lower toxicity and lower corrosiveness [4]. However, its applications could potentially be enhanced by further decreasing its sensitivity. In an effort to reduce the sensitivity of highly energetic materials, Matzger and co-workers prepared a novel HMX/CL-20 co-crystal [5] and seven HMX co-crystals containing non-energetic materials [6]. In addition to these HMX co-crystals, HMX/*N*-methyl-2-pyrrolidone (NMP), HMX/*N*-*N*



dimethylformamide (DMF) and HMX/2,4-dinitro-2,4-diazapentane co-crystals were reported [7]. Unfortunately, all these co-crystals possess low densities or high sensitivities.

The compound 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO, **2**, figure 1) is a less sensitive energetic material. In previous studies [8], NTO is proposed to co-crystallize with HMX. The binding energies, heat of formations (HOFs), thermodynamic properties, atoms in molecules, and natural bond orbital analysis of four HMX/NTO complexes have been calculated using density functional theory methods. The calculation results show that HMX/NTO complexes are thermally stable and meet the thermal requirement of high energy density material [8].

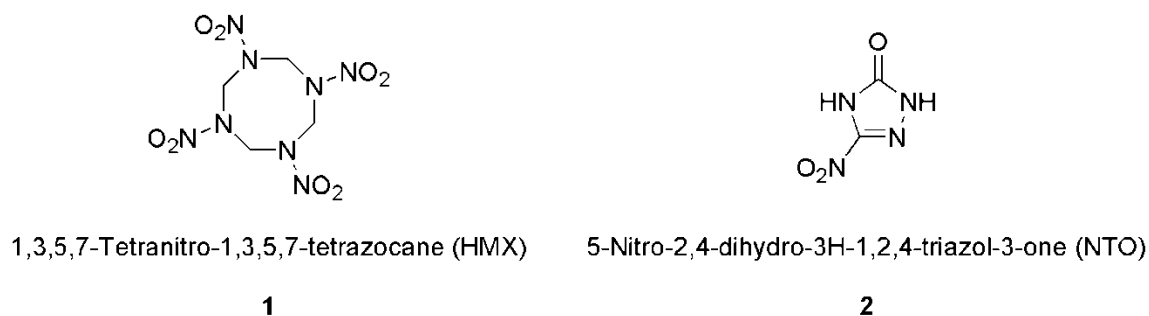


Figure 1. Chemical Structures of HMX (**1**) and NTO (**2**).

Herein, we prepared a HMX/NTO co-crystal in a 1:1 molar ratio by treatment with an appropriate mixture of solvent/anti-solvent. Scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and mechanical sensitivity analyzer were employed to characterize of the samples.

2. Experimental

2.1. Material

β -HMX, E grade; HMX and NTO were obtained from North University of China. Acetone and trichloromethane were reagent grade and obtained from Guangdong Guanghua Chemical Reagent Chemical Technology Company.

2.2. Preparation method

A 1:1 molar ratio of HMX (1.48g) and NTO (0.65g) was dissolved into acetone (70ml) at 56 °C temperature, stir the solution. Then anti-solvent trichloromethane (50ml) was slowly dropped into the solution and filtered. The new co-crystal of HMX/NTO was formed.

2.3. Scanning electron microscopy (SEM)

Scanning electron microscopy of the samples were taken under the S-4700 SEM, Japan Hitachi.

2.4. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was carried out with a DSC-131 instrument, France Setaram. The sample (0.7 \pm 0.1) mg was heated from room temperature to 400 °C at a heating rate of 5 °C/min in a nitrogen flow.

2.5. Impact sensitivity test

The impact sensitivity was conducted according to the GJB772A-97 standard method 601.2 [9]. The test conditions are: drop weight, 5 kg; sample mass, 50 mg; trial quantity, 20 samples. For the varying of the impact energy in each trial, the ultimate impact energy is determined statistically with 50% probability of ignition.

2.6. Friction sensitivity test

The determination of the friction sensitivity was performed referring to the method of GJB772A-97 standard method 601.1 [9]. Sample amount is 20 mg, pendulum quality is 5 kg, the swing angle is 90° and gauge pressure is 3.92 MPa. The fraction sensitivity of each test sample was expressed by explosion probability (P).

3. Results and Discussion

3.1. Morphology

The crystal morphology of HMX, NTO and HMX / NTO co-crystal explosive is shown in figure 2.

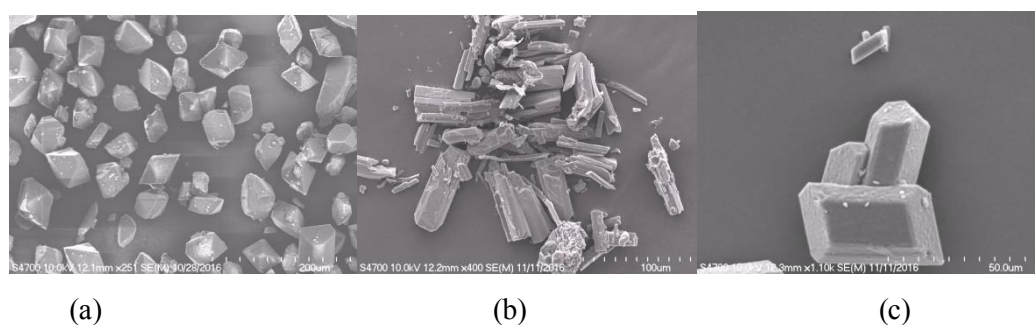


Figure 2. Microscope images of HMX (a), NTO (b) and HMX / NTO co-crystal (c).

The SEM photographs show that HMX/NTO co-crystals are distinctly different from HMX and NTO crystals. HMX crystals have regular shape with smooth surface and uniform size. NTO with a rod-like morphology is easily agglomerated. The HMX/NTO co-crystals are prisms with well formed crystal surfaces.

The crystal structure of HMX/NTO co-crystal has been predicted using compass force field in Monte Carlo simulations, which are widely used to predict the molecular packing (crystal structure) of energetic materials. The HMX/NTO co-crystal is most likely to crystallize in triclinic system with $P-1$ space group, due to its lowest lattice energy [8].

3.2. Thermal analysis (DSC)

Differential Scanning Calorimeter (DSC) is helpful in studies on the thermal behaviour of the co-crystal, and the DSC curves of HMX/NTO co-crystal, HMX and NTO are depicted in figure 3.

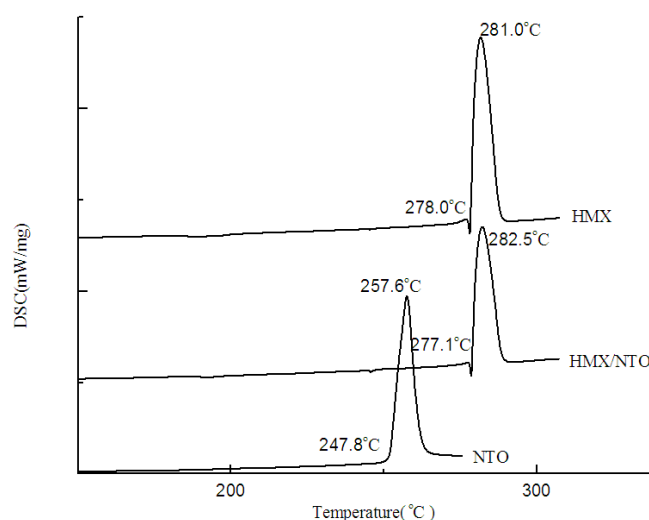


Figure 3. The DSC curves of HMX, NTO and HMX / NTO co-crystal.

It was evident from the curves that the thermal behavior of co-crystal differs from the crystals of their individual components, and the differences in thermal stability of these substances suggest the formation of a new crystal aggregate. The HMX/NTO co-crystal DSC curve shows a sharp and narrow endothermic peak at the temperature of 277.1 °C, corresponding to the melting point of the co-crystal which is 29.3 °C higher than that of NTO (247.8 °C). Besides, the co-crystal exhibits a strong exothermic peak in the temperature of 282.5 °C which is 1.5 °C higher than that of HMX (281.0 °C). The shift may be caused by the change of lattice energy and crystal packing.

3.3. Sensitivity

To analyze the safety profile of these co-crystals, their impact and friction sensitivity were studied. The mechanical sensitivity tests of the HMX/NTO co-crystal, HMX and NTO were expressed by the drop height of 50% explosion probability (H_{50}) for impact sensitivity and explosion percentage (P) for the friction sensitivity. The results are presented in table 1.

Table 1. The results of mechanical sensitivity for HMX, NTO and HMX / NTO co-crystal.

	H_{50}/cm	$P/\%$
HMX	22.4	100
NTO	57.5	32
HMX/NTO	37.2	60

The co-crystal exhibits a modified mechanical sensitivity. The characteristic height (H_{50}) of impact sensitivity increases 14.8 cm from 22.4 cm (HMX) to 37.2 cm (co-crystal). The explosion percentage (P) of friction sensitivity is 60%, which is 40% lower than HMX (100%). The HMX/NTO co-crystal shows a satisfactory safety than that of HMX. This phenomenon indicates that the formation of co-crystal can significantly increase the safety of the sensitive explosive. The intermolecular interactions between HMX and NTO molecules in the co-crystal structure make the molecules pack closer and decrease the volume and number of cavities which leads to a lower sensitivity of co-crystal than the mixture. Besides, the stability of co-crystal is also improved by hydrogen bond interactions.

4. Conclusion

A 1:1 molar ratio of HMX /NTO co-crystal explosive is prepared by treatment with a mixture of solvent/anti-solvent using acetone as the solvent and trichloromethane as the anti-solvent. The SEM photographs show that HMX/NTO co-crystals are distinctly different from HMX and NTO crystals. The co-crystals are prisms with well formed crystal surfaces. The HMX/NTO co-crystal is most likely to crystallize in triclinic crystal system with $P-1$ space group. Thermal analysis results indicate the HMX/NTO co-crystal shows good thermal property. The melting point of the co-crystal is 29.3 °C higher than that of NTO, and the exothermic peak temperature is 282.5 °C which is 1.5 °C higher than that of HMX (281.0 °C). Moreover, the co-crystal exhibits a modified mechanical sensitivity. The characteristic height (H_{50}) of impact sensitivity increases 14.8 cm, and the explosion percentage (P) of friction sensitivity decreases by 40% compared with HMX alone. The HMX/NTO co-crystals possess low sensitivity and good thermal property, which mean huge advantages in blasting engineering. Some other investigation on the properties of HMX/NTO co-crystal and researches on other co-crystal explosives are still ongoing.

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