Synthesis of 1, 5, 6, 10 – Tetranitrodecahydro - [1, 4] Diazepino [2, 3-b] Diazepine and Its Thermal Property Research

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Abstract. 1, 5, 6, 10 - tetranitrodecahydro- [1, 4] diazepino [2, 3-b] diazepine (TNDP) was synthesized using tetranitroglycerol as the starting material by hydrolysis reaction and condensation. The thermo stability of TNDP was studied by DSC and TG-DTA methods, and the thermodynamic parameters were calculated by Kissinger method and related formulas. The results showed that TNDP was thermal stable and the peak temperature of DSC was 311.76 ℃. The apparent activation energy was 162.70 kJ/mol. In general, TNDP is a kind of good performance energetic materials.

1. Introduction
The major goal of high energy density materials is to develop explosives with outstanding comprehensive performance. Heterocyclic explosives containing N-NO₂ groups are attractive with high formation heat, high density and excellent oxygen balance [1]. The well-known 1, 3, 4, 6-tetranitroglycerol (TNGU) (1) is a powerful explosive with a density of 2.01g/cm³ and heat of formation of 50 kJ/mol⁻¹ [2]. But the applications of most nitrourea derivatives are limited by their hydrolytic unstable due to the electron-withdrawing nitro group resulting in the carbon atom of carbonyl attacked by water easily. As the hydrolysis product of 1, 1, 2, 2-tetranitraminoethane (TNAE) (2) was first published in 1980 by Peng et al. in China [3]. After the excellent acid-based reactivity of 2 was reported in 1991 [4], special attraction had been focused on the synthesis of novel heterocyclic explosives from 2 as a building block. As a kind of high oxygen enriched explosive, 2 has a certain stability [5-6]. 2 can also be used as an oxygen enriched intermediate. On account of this feature, Zheng Yuanyang and his colleagues synthesized 1, 5, 6, 10-tetranitrodecahydro-[1, 4]diazepino[2, 3-b]diazepine (TNDP) (3) in 1988 in China [7]. But its complete characterization and performance has not been studied until now.

Thermal decomposition kinetics is one of the most important content in the study of material thermal decomposition behavior. [8]. In this paper, 2 was prepared by direct hydrolysis reaction of 1 under the condition of acid. 3 was synthesized using 2 by condensation and paraformaldehyde in concentrated sulfuric acid. The thermal properties and decomposition kinetics of 3 were studied by thermo gravimetric analysis (TG) and differential scanning calorimetry (DSC). The kinetic parameters were calculated using two equations of Kissinger and Ozawa. The significance of this paper is to gain insight into the thermal decomposition kinetic process of TNDP.
2. Experiment

2.1. Methods and materials
Melting point was determined using an open capillary tube. The IR spectra were recorded by Perkin Elmer FT-IR based Fourier infrared spectrometer employing KBr pellet. 1H NMR and 13C NMR spectra were recorded with Bruker-500 type (500 MHZ) superconducting NMR instrument. Elemental analysis were performed on Vario EL-Ⅲ Elemental analyzer. Differential scanning calorimetry (DSC) and thermo gravimetric (TG) were carried out in a platinum sample container using Shimadzu DSC-60 and NSK-6300 analyzers. The density was measured by Micromeritics Accupyc Ⅱ 1340 type gas pycnometer. Urea (homemade), fuming nitric acid, acetic anhydride, magnesium oxide, sodium hydroxide, concentrated sulfuric acid, trioxymethylene are all analytically pure, Beijing Chemical Factory.

2.2. Synthesis of TNAE
Tetranitroglycoluril (10g, 0.03mol) was added slowly to the NaOH solution (0.32mol NaOH, 100ml H2O) at 0~5 ℃ and stirred for 1-2h. After that the pH value was adjusted to pH<1 with 20% sulfuric acid carefully. The precipitate was filtered off and the filtrate was extracted with ether. The ether was concentrated to a small volume in vacuum and 50ml dichloromethane was added to get white solid precipitated. At last, the yield of TNAE was 55%. IR (KBr, ν/cm⁻¹): 3245, 3008, 1579, 1452, 1347, 1234, 1163, 1096, 1064, 776, 602.

2.3. Synthesis of TNDP
TNAE (5g, 0.02mol) and trioxymethylene (11g, 0.12mol) were added to the concentrated sulfuric acid, kept stirring and the reaction temperature at -5-0 ℃ for 17h. Then the suspension was directly poured into 500ml ice water and the white product which precipitated from the liquid was filtered immediately, washed to neutral by using water, then washed with ether, ethanol, after vacuum drying, the target product was achieved and its structural formula was confirmed by X-ray diffraction. (Yield 75%). IR (KBr, ν/cm⁻¹): 3425, 3008, 1579, 1452, 1347, 1234, 1163, 1096, 1064, 776, 602.

2.4. Synthesis of TNGU
TNGU (5g, 0.02mol) and fuming nitric acid (11g, 0.12mol) were added to the concentrated sulfuric acid, kept stirring and the reaction temperature at -5-0 ℃ for 17h. Then the suspension was directly poured into 500ml ice water and the white product which precipitated from the liquid was filtered immediately, washed to neutral by using water, then washed with ether, ethanol, after vacuum drying, the target product was achieved and its structural formula was confirmed by X-ray diffraction. (Yield 75%). IR (KBr, ν/cm⁻¹): 3425, 3008, 1579, 1452, 1347, 1234, 1163, 1096, 1064, 776, 602.

Figure 1. Structures of high explosives TNGU, TNAE and TNDP

Figure 2. Synthetic route of TNAE
Figure 3. Synthetic route of TNDP

3. Results and Discussion

According to the characteristics of thermal decomposition of explosives, the thermal decomposition behavior of explosives can be studied by the method of measuring heat, weight loss and so on. In this paper, the thermal performance of the product was analyzed by differential scanning calorimetry (DSC) and thermogravimetry (TG).

Test condition: the aluminum cell sample, the reference material for the empty aluminum pool sample, the sample weight was 1.2mg, the temperature range 50~400 ℃. The heating rate was 10K/min, and the atmosphere was nitrogen, the flow rate was 50 mL/min.

As shown in Fig. 3, TNDP exhibited a thermal decomposition peak at 311.7 ℃. Respectively, the TG curve showed that TNDP had the stage of a mass loss in the decomposition process from 235.1 ℃ to 322.6 ℃, and a 1.13% residue at 322.6 ℃. These data showed that TNDP was thermal stability and had a very excellent thermal performance.

Figure 4. DSC and TG curve of TNDP at a heating rate of 10 K·min⁻¹

Figure 5. DSC curves of SHM at different heating rates
Figure 5 showed that the DSC curves of TNDP at different heating rates of 10 K/min, 15 K/min, 20 K/min and 25 K/min. Data of these curves were used to calculate the apparent activation energy E and pre-exponential factor A. Though Kissinger and Flynn-Wall-Ozawa method [9-10], the following equations (1) and (2), we got the linear fitting curves (Figure 5) of the product.

Kissinger method:

\[
\ln \left( \frac{\beta}{T_p^2} \right) = \ln \left( \frac{A_k R}{E_k} \right) - \frac{E_k}{R T_p}
\]  

Fly-Wall-Ozawa method:

\[
\lg \beta = C - \frac{0.4567 E_o}{R T_p}
\]

As is shown above, \( A_k \) is pre-exponential factor, \( \beta \) is the heating rate, \( E_k \) is apparent activation energy of Kissinger, \( E_o \) is apparent activation energy of Ozawa, \( T_p \) is the peak temperature of DNTP curve, R and C is the constant.

![Figure 6. Linear fitting curve of Ln (\( \beta / T_p^2 \)) vs. 1000/T_p relation](image)

The data of the kinetic parameters obtained by Kissinger (1) and Ozawa (2) methods were summarized in Table 1. The value of \( E_k \) calculated by Kissger method was similar with \( E_o \) calculated by Ozawa method. On the other hand, both of the linear correlation coefficients are very close to 1. It indicated that the data were credible.

| Heating rate (K/min) | \( T_0 \) (K) | \( T_p \) (K) | \( E_k \) (kJ/mol) | \( \lg (A_k/s-1) \) | \( R_k \) | \( E_o \) (kJ/mol) | \( R_o \) |
|---------------------|---------------|---------------|---------------------|----------------------|--------|----------------------|--------|
| 5                   | 573.4         |               |                     |                      |        |                      |        |
| 10                  | 584.9         |               |                     |                      |        |                      |        |
| 15                  | 553.26        | 589.1         | 162.13              | 32.83                | 0.9815 | 163.48               | 0.9836 |
| 20                  | 594.1         |               |                     |                      |        |                      |        |
| 25                  | 601.2         |               |                     |                      |        |                      |        |
4. Conclusion
The thermal decomposition of TNDP presented a sharp exothermic peak at 311.76 °C and a mass loss of 96.4% from 235.1 °C to 322.6 °C. The data of the kinetic parameters obtained by Kissinger and Ozawa methods showed that TNDP was thermal stability and had very excellent thermal performance.

Acknowledgments
I would like to express my gratitude to professor Zi-hui Meng who helped me during the writing of this thesis.

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