Improved Synthesis and Characterization of 2-(Dinitromethylene)-1-nitro-1,3-diazacyclopentane

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A new approach is described to synthesize 2-(dinitromethylene)-1-nitro-1,3-diazacyclopentane (4). 2-(Dinitromethylene)-1,3-diazacyclopentane (1) was synthesized first by the nucleophilic substitution of ethylenediamine and 1,1-diamino-2,2-dinitroethylene (FOX-7) catalyzed by Mg(OAc)$_2$, then 1 was transformed to 4 through nitration, reduction and hydrolysis. The crystal morphology of 4 was investigated by scanning electron microscopy (SEM). Compound 4 was also characterized by IR, NMR, MS and elemental analysis, and by thermogravimetry (TG) and differential scanning calorimetry (DSC), which revealed that 4 decomposes at 126 $^\circ$C. The explosive performance of 4 was calculated using the VLW equation. The crystal density of 4 was determined as 1.79 g cm$^{-3}$. The experimental results indicate that 4 is sensitive towards impact and spark stimuli, but insensitive to friction.

Key words: 2-(Dinitromethylene)-1,3-diazacyclopentane, Thermal Stability, Energetic Material

Introduction

As a well-known high energy insensitive explosive with a simple structure but very unusual properties, 2,2-dinitroethene-1,1-diamine (FOX-7) was synthesized in 1998 [1]. One part of this molecule contains two geminal electron-withdrawing nitro groups as a strong oxidation center and the other part contains two electron-donating amino groups. The combination of these property-opposite parts in FOX-7 creates the so-called electron “push-pull” effect [2 – 4]. The unbalanced electron distribution enables the typical intramolecular electron transfer reactions of energetic materials. Recently, due to the increasing need for new energetic materials with both higher energy and lower sensitivity [5 – 9], some insensitive energetic materials have been modified to further reduce the sensitivity and increase the energy. FOX-7 has been considered as an ideal candidate for further transformation because nucleophilic substitution reactions can take place on its two amino-connected carbon atoms [10 – 13], and many derivatives of FOX-7 have been reported [14 – 24]. Among these derivatives, 2-(dinitromethylene)-1-nitro-1,3-diazacyclopentane (4), synthesized by Baum \textit{et al.} in 1992 [2], has recently been used as an important precursor to synthesize nitrogen-rich energetic ionic liquids [25], however its properties have not been investigated systematically. Herein we report an improved procedure to synthesize 4 in which a cheap catalyst and nitration agent were used. The thermal stability and sensitivity of 4 were investigated experimentally, and its detonation performance has been predicted.

Results and Discussion

Synthesis of 2-(dinitromethylene)-1-nitro-1,3-diazacyclopentane (4)

According to the literature [2], compound 1 was nitrated using nitric acid and trifluoroacetic anhydride in
methylene chloride to produce 2. Then 2 was denitridated by potassium iodide to form the corresponding nitronate salt 3. After being acidified with concentrated HCl, compound 3 was finally transformed into the target compound 4 (Scheme 1). However, in order to synthesize 1 which is the crucial starting material for 4, FOX-7 has to be heated in the presence of an excessive amount of diamine for a long time due to its very low reactivity. Therefore, a low-cost and efficient synthetic method of 1 is needed in order to synthesize 4 more efficiently.

In our previous work, we found that magnesium salts could catalyze the nucleophilic substitution reaction between FOX-7 and 1,2-diaminoethane, and that freshly prepared Mg(OAc)$_2$ is to be preferred [26]. As the alkaline earth metal with the largest ratio of charge to radius after beryllium, magnesium has the highest tendency to form strong bonds with high coordination numbers (up to 6) [27]. The high Lewis acidity, oxyphilicity and coordination ability of Mg$^{2+}$ [28] results in its wide applications in organic synthesis as catalyst [29–37]. Herein, 1 was synthesized using this method in a yield of 83.9 % with very high purity (99 %) under the optimized conditions, which was a significant increase from the literature yield of 61 %. Furthermore, the required reaction time was also reduced from 48 h to 5.5 h. The synthesis of 2 was improved as well. A more economic nitration system, using acetic anhydride and 98 % HNO$_3$, has been shown to give almost the same result as that with trifluoroacetic anhydride and 90 % HNO$_3$ (Scheme 1).

**Thermal and structure analysis**

The thermal stability of 4 was studied by using DSC with a heating rate of 5 °C min$^{-1}$ (Fig. 1). Exothermic decomposition occurred with $T_{\text{max}}$ at 126.01 °C without melting, and the decomposition heat was 1.135 kJ·g$^{-1}$. The thermogram of 4 (Fig. 2) revealed that most of weight loss (73 %) occurred at...
130.21 °C, indicating that 4 is unstable at high temperature.

The SEM image of 4 showed its cuboid-type crystal morphology (Fig. 3). The column-like crystals were arranged loosely with large cavities.

Explosive performance

Theoretical explosive performance

The explosive performance of 4 was predicted by the VLW equation (an equation of state of detonation products as proposed by Wu based on the virial theory [38]) as shown in Table 1. The calculated velocity of detonation (VOD), pressure of detonation (\(P\)), and explosive temperature (ET) of 4 were superior as compared to those of HNS, TACOT and RDX.

Experimental explosive performance

Density is one of the most important properties of an energetic compound because it directly affects the main detonation performance according to the Kamlet-Jacobs equations [39–41], in which the detonation pressure is dependent on the square of the density and the detonation velocity is proportional to the density. The incorporation of nitro groups in 4 could increase the energy as well as the density of the molecule compared to those of its parent compounds, whereas the sensitivity usually is increased due to a better oxygen balance. However, the density of 4 measured by a gas pycnometer was 1.79 g·cm\(^{-3}\), lower than the crystal value (1.83 g·cm\(^{-3}\)). Experimental results in Table 2 indicate that 4 was friction insensitive, but impact and spark sensitive compared to other nitramine explosives, such as RDX and HMX.

Conclusion

A FOX-7 derivative, 2-(dinitromethylene)-1-nitro-1,3-diazacyclopentane (4), was synthesized in a more efficient way using Mg(OAc)\(_2\) as catalyst and a modified nitration method. The crystal density was experimentally determined as 1.79 g·cm\(^{-3}\), lower than the crystal value (1.83 g·cm\(^{-3}\)). The experimental results indicated that 4 was sensitive towards impact and spark stimuli, but insensitive to friction. These results complement the existing data of 4, but also give an insight into its possible thermal decomposition mechanism. This study could warrant the further in-depth studies on performance parameters of 4, which is now a popular precursor for nitrogen-rich energetic compounds.
Experimental Section

Materials and instruments

FOX-7 was provided by Xi’an Modern Chemistry Research Institute with a purity of 98%, and magnesium acetate (Mg(OAc)₂) was prepared as reported [43]. The other reagents were purchased with AR grade and used directly. The reaction was monitored by TLC and the purity of the product was confirmed by HPLC (Shimadzu LC-20AT) with a C18 column (4.6 mm x 250 mm, 5 µm, Agela). The melting point of 4 was measured on an X-5 microscope melting point apparatus. IR spectra were recorded on a Thermo Nicolet FTIR-Nexus 870 spectrophotometer with KBr pellets. Mass spectra were obtained from a HP5989B mass spectrometer. NMR spectra were obtained from a 500 MHz Bruker AV500 spectrometer with tetramethylsilane (TMS) as an internal standard. Elemental analysis was carried out on an Elementar Vario EL III instrument. DSC experiments were performed on a Perkin-Elmer DSC-7 with a heating rate of 5 °C min⁻¹, and the baseline corrected and indium and zinc used as standards for calibration. The thermogravimetric (TG) study on FOX-7 was provided by Xi'an Modern Chemistry Re- search Institute with a purity of 98%, and magnesium ac- etate (Mg(OAc)₂) was prepared as reported [43]. The other

Synthesis of 3-nitro-2-(trinitromethyl)-1,3-diazacyclo- pentane (2)

Nitric acid (98%, 100.0 mL) was added to a mixture of acetic anhydride (50.0 mL) and methylene chloride (300.0 mL) at 0 °C. After the mixture was stirred for 5 min, 1 (10.0 g) was dropped into the solution over 10 min, and the mixture was stirred for another 1 h at 0 °C. Then ice water (100 mL) was added to the solution slowly in order to keep the temperature at 5–10 °C. The organic layer was washed with water (3 × 70 mL) and brine (50 mL) and dried with anhydrous MgSO₄. The solvent was removed under vacuum, and the residue was recrystallized from methylene chloride-hexane to give 10.9 g (yield 70%) of 2 as a colorless solid. M. p. 112 °C. – IR (KBr): ν = 2877 (CH₂), 1617 (C=O), 1553 (NO₂), 1275 cm⁻¹ (NO₂). – ¹H NMR (500 MHz, CDCl₃), δ = 4.32 ~ 4.52 (m, 4 H, CH₂₋O). – ¹³C NMR (125 MHz, CDCl₃), δ = 50.10, 54.08, 120.07, 143.61. – C₂H₄N₃O₅K (264.11): calcd. C 18.19, H 1.53, N 31.82; found C 18.05, H 1.60, N 31.41. – MS (+)-ESI: m/z = 268 [M+H]⁺.

Synthesis of the potassium salt of 2-(dinitromethyl)-3-nitro-1,3-diazacyclopentane-1-ene (3)

A mixture of 2 (4.0 g, 15.2 mol), potassium iodide (8.0 g, 48 mmol) and 18-crown-6 (4.0 g) in 200 mL of dry tetrahydrofuran was stirred at room temperature for 16 h. The solid product was isolated by filtration, washed with tetrahydrofuran, and recrystallized from water-methanol to give 2.82 g (yield 73%) of 3 as a colorless solid. M. p. 205 °C. – IR (KBr): ν = 2957 (CH₂), 1643 (C=O), 1496 (NO₂), 1265 cm⁻¹ (NO₂). – ¹H NMR (500 MHz, [D₆]DMSO): δ = 3.94 ~ 4.20 (m, 4 H, CH₂₋O). – ¹³C NMR (125 MHz, [D₆]DMSO): δ = 47.97, 51.41, 125.44, 148.14. – C₂H₄N₃O₅K (258.21): calcd.C 18.61, H 1.95, N 27.12; found C 18.45, H 1.58, N 28.41. – MS (+)-ESI: m/z = 259 [M+H]⁺.

Synthesis of 2-(dinitromethylene)-1-nitro-1,3-diazacyclopentane (4)

An aqueous solution of 3 (3.25 g, 12.6 mmol) in 150 mL water was cooled to 0 °C, and conc. HCl (35.0 mL) was added dropwise. After 15 min the precipitate was washed with water and recrystallized from acetone-hexane to produce 1.87 g of 4 (yield 69%) as a bright-yellow solid. M. p. 121 °C. – IR (KBr): ν = 3300 (NH), 1619 (C=O), 1574, 1520 (NO₂), 1265 cm⁻¹ (NO₂). – ¹H NMR (500 MHz, [D₆]DMSO): δ = 3.97 (t, 2 H), 4.37 (t, 2 H), 10.01 (br s, 1
H). \(^{13}\)C NMR (125 MHz, [D\(_6\)]DMSO): \(\delta = 48.57, 49.34, 128.20, 150.29\). – C\(_2\)H\(_4\)N\(_2\)O\(_6\) (219.11): calcd. C 21.93, H 2.30, N 31.96; found C 22.30, H 2.36, N 31.86. – MS (ESI): \(m/z = 218\) [M–H]–.

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