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# Synthesis and Thermal Properties of 1,1'-Dioxide-5,5'-azotetrazole Dipotassium Salt

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**Abstract:** 1,1'-Dioxide-5,5'-azotetrazole dipotassium salt was synthesized via two-step reactions of azido-cyclization and oxidation-coupling using cyanogen bromide, sodium azide and 50% solution of hydroxylamine as raw materials. The yields of two-step reactions were 78% and 82%, respectively. The structure of 1,1'-dioxide-5,5'-azotetrazole dipotassium salt was characterized by infrared spectrum (IR), nuclear magnetic resonance (NMR), elemental analysis and thermal properties were studied by differential scanning calorimetry (DSC) and thermogravimetry-derivative thermogravimetry (TG-DTG). Results show that there were two thermal decomposition peaks at 271.0 °C and 328.0 °C under heating condition, respectively, while possess a total mass loss of 37.5% before 320 °C for 1,1'-dioxide-5,5'-azotetrazole dipotassium salt.

**Key words:** 1,1'-dioxide-5,5'-azotetrazole dipotassium salt; energetic materials; properties

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## 1 Introduction

Recently, attractive strategies in the design of new high-performing energetic materials have fallen into a major category, ring- or cage-shaped compound with high heats of formation<sup>[1-3]</sup>. For energetic materials based on this strategy<sup>[4-10]</sup>, the tetrazole-*N*-oxides has been found to occupy the ideal middle properties including high explosive performance and superior stabilities at the same time. Therefore, the tetrazole-*N*-oxide unit can be used as precursor for the preparation of novel energetic materials which possess high density releasing plenty of energy and gasses upon decomposition or explosion<sup>[11-16]</sup>. For example, the recent work from Niko Fischer<sup>[16]</sup>, tetrazole-*N*-oxides have been used to prepare dihydroxylammonium bistetrazolate-1,1'-dioxide (TKX-50), a useful explosive compound with performance exceeding that of HMX. Furthermore, Dennis Fischer et al<sup>[17]</sup> reported the synthesis and properties of 1,1'-dioxide-5,5'-azotetrazole dipotassium salt, which possessed superior calculated detonation properties and presents superior stability towards thermal and mechanical stimulation. In this work, we reported the synthesis and characterization of 1,1'-dioxide-5,5'-azotetrazole dipotassium salt and the reaction mechanism was hypothesized for the first time in nation, as well as the thermal performance was studied by

DSC and TG-DTG in this article.

## 2 Synthesis and Characterization

### 2.1 Materials and Instruments

All chemicals were of reagent-grade quality obtained from commercial sources and used without further purification.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker AV-800 spectrometer. FT-IR (KBr) spectra were recorded on a PerkinElmer FT-IR spectrometer, and mass spectra were collected on a HP5989B mass spectrometer. Decomposition points were determined by differential scanning calorimetry (DSC) on a Linseis DSC-PT10 at a heating rate of 5 °C · min<sup>-1</sup>. Thermogravimetry-derivative thermogravimetry (TG-DTG) were carried out on PerkinElmer Pyris-1 thermogravimetric analyzer with a heating rate of 5 °C · min<sup>-1</sup> from 50 °C to 500 °C under N<sub>2</sub> atmosphere.

### 2.2 Synthesis and Characterization

1,1'-Dioxide-5,5'-azotetrazole dipotassium salt was synthesized via two-step reactions of azido-oximes-cyclization and oxidation-coupling using cyanogen bromide, sodium azide and 50% solution of hydroxylamine as raw materials (Scheme 1). As depicted, the cyanogen azide intermediate generated by the reaction of cyanogen bromide and sodium azide, could be followed by azido-oxime-cyclization reaction with excess of aqueous hydroxylamine yielding 1-hydroxy-5-aminotetrazole hydroxylammonium salt. Whereafter, the —NH<sub>2</sub> group of above hydroxylammonium salt was completed oxidation-coupling by reaction of potassium permanganate at

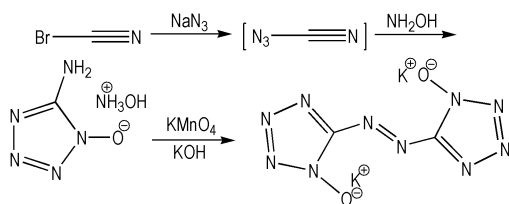
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the present of potassium hydroxide, yielding 1, 1'-dioxide-5, 5'-azotetrazole dipotassium salt.



**Scheme 1** Synthesis of 1,1'-dioxide-5,5'-azotetrazole dipotassium salt

### 2.2.1 1-Hydroxy-5-aminotetrazole Hydroxylammonium Salt

Cyanogen bromide (6.36 g, 60 mmol) was dissolved in acetonitrile (300 mL). The solution was cooled to 0 °C and the sodium azide (4.20 g, 64.5 mmol) was added. After stirring for 4 h in ice bath, the suspension was filtered and washed with MeCN (30 mL). Then, the filtrate was cooled to -20 °C and a 50% solution of hydroxylamine (13.2 g, 200 mmol) in MeCN (60 mL) was added dropwise in order to keep the temperature under 0 °C. The resulting suspension was stirred for 1 h at room temperature and then filtered. The white solid was washed with Et<sub>2</sub>O (50 mL) and dried in air to afford pure compound (6.27 g, 78% yield).

IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2469 (m), 1744 (w), 1645 (w), 1561 (m), 1536 (m), 1451 (w), 1308 (m), 1266 (w), 1258 (w), 1204 (w), 1165 (w), 1143 (w), 1125 (w), 1102 (m), 1006 (m), 860 (s), 805 (w);

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>)  $\delta$ : 8.73, 8.25.

<sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>)  $\delta$ : 148.65.

Anal. Calcd. for CH<sub>6</sub>N<sub>6</sub>O<sub>2</sub> (%): C 8.96, H 4.51, N 62.67; Found: C 9.43, H 4.36, N 62.41.

### 2.2.2 1,1'-Dioxide-5,5'-azotetrazole Dipotassium Salt

1-Hydroxy-5-aminotetrazole hydroxylammonium salt (2.69 g, 20 mmol) was dissolved in water (80 mL) and 2 M KOH (15 mL) was added. The solution was heated to 75 °C and a solution of KMnO<sub>4</sub> (3.178 g, 20 mmol) in hot water (70–80 °C) was added dropwise. After stirring for 1 h at 75 °C, MeOH (25 mL) was added in one portion and the mixture was stirred for a further 30 min at 75 °C. The resulting suspension was filtered and the filtrate was concentrated until the red solid product started to precipitate. The solid-liquid mixture was left to precipitate completely by adding of EtOH. The precipitate was filtered and washed with EtOH and Et<sub>2</sub>O to afford orange-red solid (2.25 g, 82% yield).

IR (KBr,  $\nu/\text{cm}^{-1}$ ): 1744 (w), 1418 (m), 1367 (w), 1247 (w), 1219 (m), 1135 (m), 1062 (w), 785 (vs), 715 (w).

<sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>)  $\delta$ : 168.71.

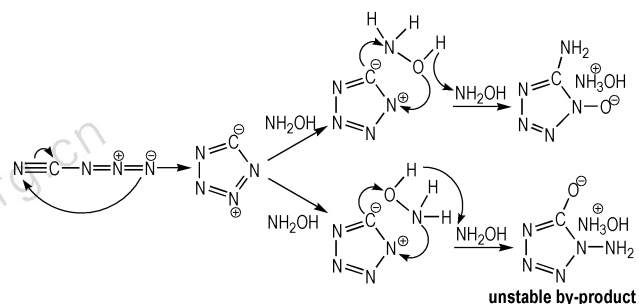
Anal. Calcd. for K<sub>2</sub>C<sub>2</sub>N<sub>10</sub>O<sub>2</sub> (%): C 8.76, N 51.07;

Found: C 9.01, N 51.59.

## 3 Results and Discussions

### 3.1 Synthesis

According to the literature<sup>[17]</sup>, 1-hydroxy-5-aminotetrazole could be readily prepared by the reaction of the cyanogen azide intermediate (generated by the reaction of cyanogen bromide and sodium azide) with excess of hydroxylammonium, as depicted in Scheme 1. It is found obviously that if one equivalent of hydroxylamine is applied in the reaction, 1-hydroxy-5-aminotetrazole hydroxylammonium salt in a low yield (<10%) from the MeCN solution. The yield can be increased about 90% when using two equivalent of hydroxylammonium. Because the reaction is quite exothermic which leads to a temperature rise of about 20 °C and an yellow unstable by-product always formed during the reaction, it was useful to cool the reaction medium down to -20 °C before the addition of hydroxylammonium as well as the speed of droprise should be controlled slowly. The above mentioned yellow unstable by-product always decomposes to gaseous products slowly while the quantity of white main-product increased at room temperature. This unstable by-product is probably another addition product because hydroxylammonium can also attack through the oxygen atom resulting corresponding *N*-amino tetrazole derivative (Scheme 2).



**Scheme 2** Reaction mechanism of cyanogen zaide and hydroxylammonium

Because hydroxylamine can be destroyed in hot basic medium, the 1, 1'-dioxide-5, 5'-azotetrazole dipotassium salt can be prepared directly by coupling reaction of -NH<sub>2</sub> group in 1-hydroxy-5-aminotetrazole hydroxylammonium salt using excess of potassium permanganate as oxidizer. The any excess potassium permanganate in oxidation state is destroyed by the addition of MeOH after complete coupling. Therefore, the pure 1, 1'-dioxide-5, 5'-azotetrazole dipotassium salt can be isolated after the removal of dioxide manganese.

### 3.2 Thermal Performance

The DSC and TG-DTG analysis was carried out at a heating rate of  $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  from  $50\text{ }^{\circ}\text{C}$  to  $500\text{ }^{\circ}\text{C}$  under  $\text{N}_2$  atmosphere. The DSC curve showed in Fig. 1 reveals that the 1,1'-dioxide-5,5'-azotetrazole dipotassium salt is thermally stable up to  $270\text{ }^{\circ}\text{C}$  and has no melting point, but exists two thermal decomposition peaks at  $271.0\text{ }^{\circ}\text{C}$  and  $328.0\text{ }^{\circ}\text{C}$ , respectively. The TG-DTG curves showed in Fig. 2 exhibits that 1,1'-dioxide-5,5'-azotetrazole dipotassium salt possess two-stage decomposition process with a mass loss of 28.60% before  $300\text{ }^{\circ}\text{C}$  in the first stage decomposition and a total mass of 37.5% before  $320\text{ }^{\circ}\text{C}$  in the second stage decomposition.

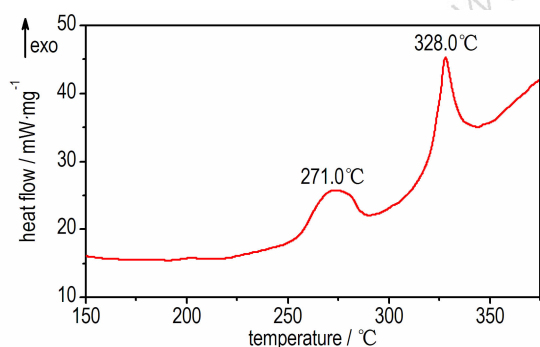


Fig. 1 DSC curve of 1,1'-dioxide-5,5'-azotetrazole dipotassium salt

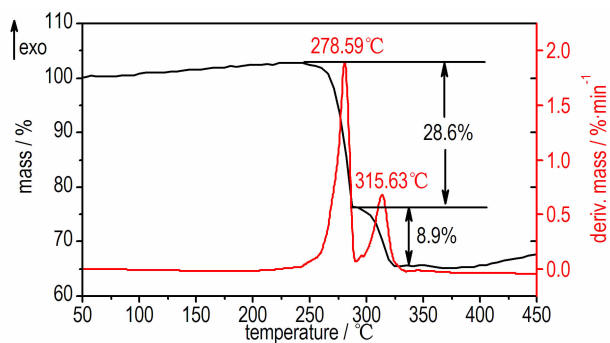


Fig. 2 TG-DTG curve of 1,1'-dioxide-5,5'-azotetrazole dipotassium salt

### 4 Conclusions

1,1'-Dioxide-5,5'-azotetrazole dipotassium salt was synthesized using cyanogen bromide, sodium azide and 50% solution of hydroxylamine as raw materials via two-step reactions of azido-oximes-cyclization and oxidation-coupling. DSC and TG-DTG curves indicates that 1,1'-dioxide-5,5'-azotetrazole dipotassium salt possess two thermal decomposition peaks at  $271.0\text{ }^{\circ}\text{C}$  and  $328.0\text{ }^{\circ}\text{C}$  under heating condition, respectively, while possess two-stage decomposition process with a mass loss of 28.60% before  $300\text{ }^{\circ}\text{C}$  in the first stage decomposition

and a total mass of 37.5% before  $320\text{ }^{\circ}\text{C}$  in the second stage decomposition.

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## 1,1'-二氧化-5,5'-偶氮四唑二钾盐的合成与热性能

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**摘 要:** 以溴化氰、叠氮化钠和 50% 羟胺水溶液为原料, 经叠氮化-环化和氧化偶联两步反应合成出了 1,1'-二氧化-5,5'-偶氮四唑二钾盐, 两步反应的收率分别为 78% 和 82%。用红外光谱、核磁共振和元素分析表征了其结构。以差示扫描热分析 (DSC) 和热重分析 (TG-DTG) 研究了热性能。结果表明, 1,1'-二氧化-5,5'-偶氮四唑二钾盐在 271.0 °C 和 328.0 °C 处分别有两个热分解峰, 320 °C 时总热失重量为 37.5%。

**关键词:** 1,1'-二氧化-5,5'-偶氮四唑二钾盐; 含能材料; 性能  
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