文章编号：1006-9941(2005)06-0371-04

Synthesis, Structural Analysis and Sensitivity Properties of RbDNBF

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Abstract: The RbDNBF (rubidium 7-hydroxy-4, 6-dinitro-5,7-dihydrobenzofuroxanide) is synthesized by reacting sodium salt of DNBF and rubidium nitrate solution. The molecule structure is characterized by IR and the thermal decomposition process is studied by DSC and TG-DTG. The sensitivity properties of RbDNBF are tested by various sensitivity apparatus. The results demonstrate that the bulk density of RbDNBF is higher than that of KDNBF (Potassium 7-hydroxy-4,6-dinitro-5,7-dihydrobenzofuroxanide) and the free-flowing property is also better than that of KDNBF. From 189 ℃ to 236 ℃, the thermal decomposition process occurs with the peak temperature at 210 ℃. The mass percent of solid residue is up to 25%. The sensitivity results show that the sensitivity properties of RbDNBF are equivalent with that of KDNBF.

Key words: applied chemistry; RbDNBF; synthesize; sensitivity property

CLC number: TJ55; O69 **Document code**: A

1 Introduction

Primary explosive is a kind of substance that is sensitive to the external stimulus and enable to be fired with little simply initial energy. The common primary explosives are $Pb(N_3)_2$, tetrazene and so on. The $Pb(N_3)_2$ is of lower flame sensitivity and can not consistent with copper, the tetrazene is of bad thermal stability and the weak explosion capacity. With the development of modern ammunitions technology and consciousness of environmental protection, the common primary explosives can not satisfied with the need of modern ammunitions. Thus new primary explosives harmless to environment are needed to cater to the development of ammunitions.

Potassium energetic materials are emphasized for no heavy metal pollution and their explosion capacity is corresponding or prior to the common primary explosives. More work were taken up with the potassium 7-hydroxy-4, 6-dinitro-5, 7-dihydrobenzofuroxanide (KDNBF). KDNBF was first synthesized in 1899 by Drost[1]. In 1965, three different groups made sure that the structure of KDNBF was Meisenheimer complex[2-4]. In 1983, Norris tested the sensitivity of KDNBF and analyzed its molecule structure with IR and NMR[5]. Jones[6] et al did research on the thermochemical characteristic of KDNBF in details and obtained the thermal decomposition mechanism.

Because the atom weight of K in the KDNBF is small, it is difficult to get good crystal shape and free-flowing property, it can not satisfy with the requirement of industrial bulk loading. According to the fact that elements in the same main group have the similar characteristic, the DNBF salt of the big atom weight alkaline metal Rb is studied. There is no report of RbDNBF in literature[7], so the present work studied its preparation, structural characteristics and sensitivity properties.

2 Experimental

2.1 Instrument

Bruker EQUINOX55 FT-IR spectrometers (KBr pellet), a Perkin-Elmer Pyris1 DSC analyzer (the conditions of DSC were aluminum crucible, dry, oxygen-free nitrogen at 20 ml · min^{-1}, heating rate with 10 ℃ · min^{-1}), a Perkin-Elmer Pyris1 TG analyzer (the conditions of TG were dry, oxygen-free nitrogen at 20 ml · min^{-1}, heating rate with 10 ℃ · min^{-1}) and apparatus of determining the friction sensitivity, impact sensitivity, flame sensitivity and static sensitivity are used to characterize the compound, thermal behaviors and sensitivity properties, respectively.

2.2 Reagent

4,6-dinitro-5,7-dihydrobenzofuroxanide (DNBF)

Received Date: 2005-04-21; **Revised Date**: 2005-07-05

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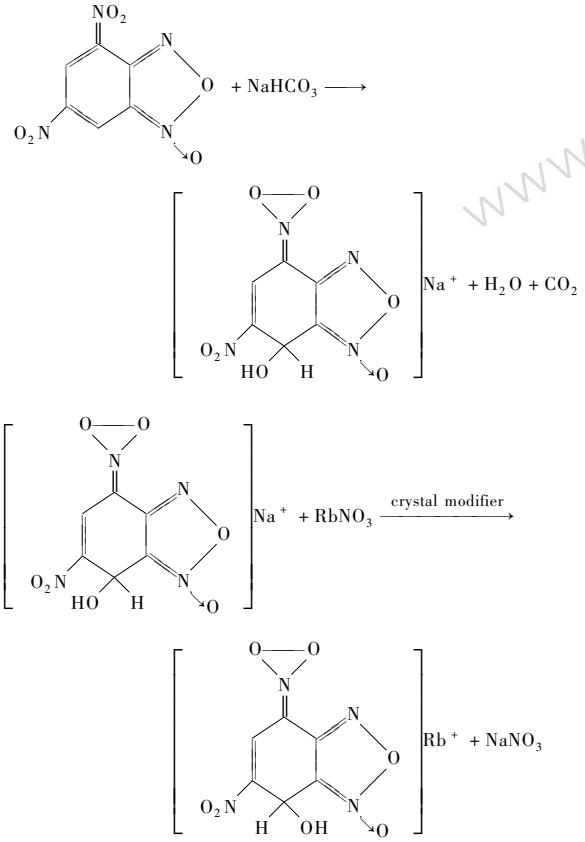
was synthesized and purified in our laboratory; $NaHCO_3$ and $RbNO_3$ was A. R. grade from Beijing Chemical Reagents Company.

2.3 Synthesis of RbDNBF

The reaction equations are as follows:



To a 500 mL beaker, DNBF (4.52 g, 0.02 mol) was transferred carefully and 120 mL distilled water was also added to it. After this, $NaHCO_3$ (0.021 mol) was added gradually at with continuous swirling till evolution of CO_2 ceased. The reaction mixture was kept at 60 ℃ for about 20 minutes. Then, the pH value of the solution was adjusted to acidity, the color of mixture is red-brown. Filtrated and adjusted the volume of the solution to 160 mL.

The NaDNBF was carefully transferred into a synthesis instrument and warmed to 49 ℃. At this stage, $RbNO_3$ (3.32 g) dissolved in 30 mL of distilled water and crystal modifier was added slowly. Then, the reaction mixture was kept at 49 ℃ for about 15 minutes and cool at ambient temperature. The precipitate, thus obtained, was filtered and washed thoroughly with distilled water and finally with ethanol.

With the microscope, the crystal shape of RbDNBF is oblong or tomato shape with high bulk density and better free-flowing property. The average bulk density is 0.8 g · cm^{-3} and the highest is 1.1 g · cm^{-3}.

3 Characterization of molecular structure and thermal decomposition

3.1 IR analysis

The IR spectrum of RbDNBF was determined by a Bruker EQUINOX55 FT-IR analyzer. The IR spectrum is shown in Fig. 1.

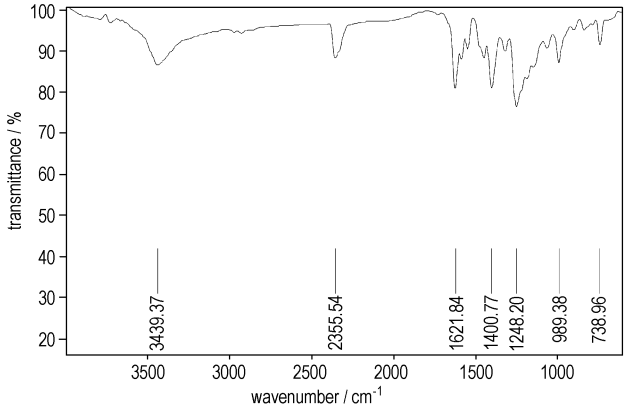


Fig. 1 IR spectrum of RbDNBF

The IR absorption peak is identified as follows: the absorption at 3439 cm^{-1} shows the stretch vibration of —O—H, the absorption at 1619 cm^{-1} may be attribute to the stretch vibration of furoxan ring; the absorption at 1409 cm^{-1} shows the stretch vibration of $—NO_2$, which is the symmetric stretch vibration; the strong absorption at 1248 cm^{-1} show the stretch vibration of N—oxide; the strong absorption at 989 cm^{-1} shows the stretch vibration of C—H band existing in the C═C; the strong absorption at 739 cm^{-1} shows the bend vibration of C—N band which link with $—NO_2$.

3.2 Thermal decomposition process of RbDNBF

The DSC and TG-DTG curves are shown in Fig. 2 and Fig. 3 to demonstrate the thermal decomposition process of RbDNBF.

As shown in Fig. 2, there is a strong exothermic peak in the DSC curve. The exothermic peak starts at 189 ℃ and ends at 236 ℃ with the peak temperature at 210 ℃, which demonstrates that a fast exothermic

decomposition process takes place between 189 ℃ and 236 ℃. Corre-sponding to TG-DTG curve (shown in Fig. 3), between 189 ℃ and 236 ℃, there is a obvious mass loss process of which the mass loss is up to 25%. With increasing temperature, the mass loss process was going on. At 530 ℃, the solid residue is up to 25% of total mass of RbDNBF.

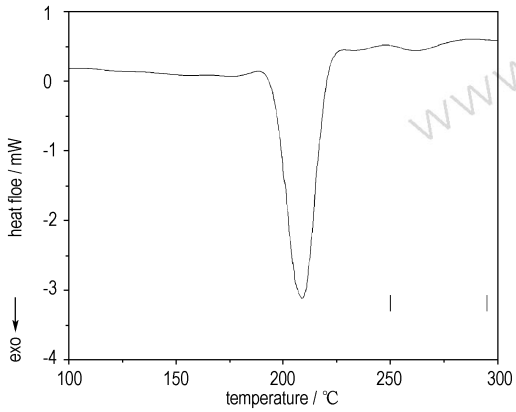


Fig. 2　DSC curve of RbDNBF

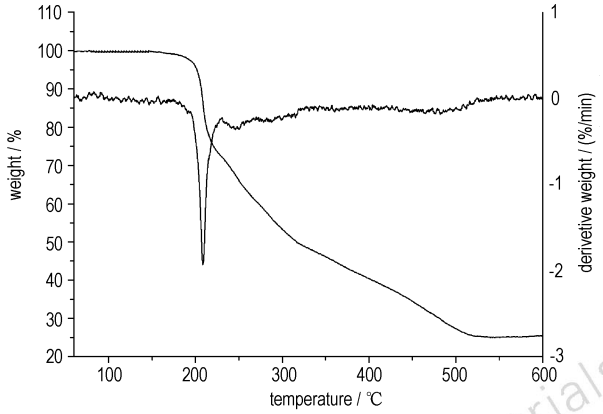


Fig. 3　TG-DTG curve of RbDNBF

3.3　Kinetic parameters of non-isothermal decomposition reaction

From the DSC data mentioned above, kinetic parameters for thermal decomposition of RbDNBF could be obtained by Kissinger's and Ozawa-Dolye's Method[9]. The heating rate (β) selected is 2 ℃ · min^{-1}, 5 ℃ · min^{-1}, 10 ℃ · min^{-1} and 15 ℃ · min^{-1}, respectively.

Maximum peak temperature (T_p) and Arrhenius parameters for the thermal decomposition of RbDNBF are shown in Table 1.

Therefore, the Arrhenius equation can be expressed with average of E_a and ln$A$ from this work.

$$\ln k = 33.61 - 325900/RT$$

Table 1　E_a and ln$A$ for thermal decomposition of RbDNBF

β	T_p	Kissinger Method		Ozawa-Doyle Method
/℃ · min^{-1}	/℃	E_a/kJ · mol^{-1}	ln(A/s^{-1})	E_a/kJ · mol^{-1}
2	202.2			
5	206.7	325.9	33.61	317.5
10	209.7			
15	214.1			

4　Sensitivity properties

4.1　Friction sensitivity

According to the WJ 1871-89, the friction sensitivity of RbDNBF was tested by a model MGY-1 switch angle friction sensitivity apparatus. The testing condition is that the switch angle is 50° and the pressure is 0.64 MPa. Twenty-five samples were tested and calculated the firing percent for two groups. The testing result is 84% and 80%, respectively. The average result is 82%.

The result shows that the friction sensitivity of RbDNBF is higher that of KDNBF[8] (at the same testing condition, the result is 16%) which is usually used.

4.2　Impact sensitivity

According to WJ 1870-89, the impact sensitivity of RbDNBF was tested by a model CGY-1 mechanical impact sensitivity apparatus. The testing condition is that the weight of dropping hammer is 0.8 kg and quantity of RbDNBF is (20 ± 2) mg and pressure 39.2 MPa.

According to the testing regulation, the height for 50% probability of ignition (H_{50}) and the deviation were determined as 8.7 cm and 2.2 cm.

The result shows that the impact sensitivity of RbDNBF is lower than that of $Pb(N_3)_2$ (10.3 cm)[8], which shows that the impact sensitivity of RbDNBF is high.

4.3　Flame sensitivity

According to WJ 1872-89, the flame sensitivity of RbDNBF was tested by a model HGY-1 flame sensitivity apparatus. The testing condition is that quantity of RbDNBF is (20 ± 2) mg and pressure 39.2 MPa.

The result is that the height for 50% probability of ignition H_{50} is 48.7 cm and the deviation is 4 cm.

The result shows that the flame sensitivity of RbDNBF is similar to that of KDNBF(48.9 cm)[8].

4.4 Static sensitivity

According to WJ 1869-89, the static sensitivity of RbDNBF was tested by a model JGY-50 static sensitivity apparatus. The testing condition is that quantity of RbDNBF is (20 ± 2) mg and capacitance is 500 pf and the voltage is positive.

The result is that V_{50} is 2 kV, s = 0.32 kV, the firing energy of 50% probability of ignition is 1.03 mJ.

The result shows that the static sensitivity of RbDNBF is higher than that of KDNBF(1.62 mJ)[8].

The static sensitivity of RbDNBF and the common primary explosives[8] are shown in Table 2.

Table 2 Static sensitivity of RbDNBF and the common primary explosives

product	E_{50}/mJ
KDNBF	1.62
RbDNBF	1.03
LTNR[1)]	0.342
$Pb(N_3)_2$(powder)	0.664

Note: 1) lend trinitroresorcinate

5 Conclusions

(1) RbDNBF with good free-flowing property is prepared with DNBF, $NaHCO_3$, $RbNO_3$ and the crystal modifier, the average bulk density is 0.8 g·cm^{-3} and the highest is up to 1.1 g·cm^{-3}.

(2) A fast exothermic decomposition process takes place from 189 ℃ to 236 ℃ with the peak temperature at 210 ℃. There is a obvious mass loss process between 189 ℃ and 236 ℃.

(3) The sensitivity properties of RbDNBF are similar to that of KDNBF.

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RbDNBF 的制备、结构表征和感度性能研究

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摘要: 硝酸铷与 DNBF(4,6-二硝基-5,7-二氢化苯并氧化呋咱)的钠盐反应,制得了标题化合物 RbDNBF(7-羟基-4,6-二硝基-5,7-二氢化苯并氧化呋咱铷盐)。通过 IR 对其分子结构进行了表征,利用 DSC 和 TG-DTG 研究了其热分解过程,并对其感度性质进行了测试。研究表明: RbDNBF 的假密度高于 DNBF 的钾盐(KDNBF),流散性好;在 189 ~ 236 ℃范围内发生热分解,峰顶温度为 210 ℃,固相残渣含量为 25%;它的感度性能与 KDNBF 相当。

关键词: 应用化学; RbDNBF; 制备; 感度性能

中图分类号: TJ55; O69 **文献标识码:** A