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Thermal Decomposition Processes and Non-isothermal Kinetics of KDNBF

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Abstract: The thermal decomposition process of potassium 4,6-dinitro-7-hydroxy-7-hydrobenzofuroxanate (KDNBF) is studied by using DSC, TG-DTG and FT-IR techniques. The results show that the solid residue at 230 °C are RCOOK, KNCO, RNO₂ and KNO₃, and at 306 °C are KNC, RCOOK and KNO₃, respectively. The Arrhenius parameters of the decomposition reaction are calculated using Kissinger's and Ozawa-Doyle's method, indicating that the results obtained by the two methods agree well with each other and the Arrhenius equation of this reaction can be expressed by $\ln k = 45.2 - 192600/RT$.

Key words: physical chemistry; KDNBF; thermal decomposition process; non-isothermal analysis

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1 Introduction

Mercury fulminate, lead azide, lead styphnate and tetrazene etc. are those primary explosives of which are being used widely since they were synthesized. However, all of them have their own shortages that are not suitable for either military or civilian applications. For example, mercury fulminate is instable and easily being pressed "dead", and lead styphnate is too sensitive to static electricity. What's more, the heavy metal pollutions after detonation or combustion have aroused more and more concerns. Therefore, efforts should be done to develop heavy metal free and good property primary explosives. Potassium salt of 4,6-dinitrobenzofuroxan, i. e. potassium 4,6-dinitro-7-hydroxy-7-hydrobenzofuroxanate (KDNBF) is one of such primary explosives that has been used in initiating compositions since the early 1950's^[1].

As an environmental-friendly primary explosive, KDNBF is very sensitive to flame. Its mechanical sensitivity is between mercury fulminate and lead azide. It can be used in many military and commercial applications to

replace the heavy-metal primary explosives, such as mercury fulminate, lead azide and lead styphnate^[2].

As a highly sensitive material, the thermal hazard studies on KDNBF are both practical and fundamental. A better understanding of the thermal hazards of KDNBF should improve safety in manufacture and handling operations. On the thermal studies of KDNBF, Jones et al^[3] has done considerable work on the gaseous products of KDNBF, but little is known on the composition of the solid residues of which will influence the igniting ability and the environmental properties. the study on the thermal decomposition process of KDNBF in this area is continue and complemented.

For a reaction in the expression: $A(s) \rightarrow B(s) + C(g)$, the Kissinger's and Ozawa-Doyle's method can be used to obtain the activation energy, E_a and the pre-exponential factor, A , which are used to give the Arrhenius equation, without consideration of the kinetics mechanism function. Therefore, the Kissinger's method and Ozawa-Doyle's method to calculate and analyze E_a and A will also be described in this paper.

2 Experimental

2.1 Materials

KDNBF was prepared according to the method reported by Piechowics^[4], but using a different crystal modifier, by replacement of sodium ion with potassium ion in

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sodium salt of 4,6-dinitrobenzofuroxan (NaDNBF). The preparation of spherical KDNBF was illustrated in detail elsewhere^[5]. Quantitative analysis of KDNBF was conducted by spectrophotometry. Its purity was more than 99%. Antistatic precautions were used when manipulating KDNBF. Conductive tablemats, samples containers, goggles and wrist straps were used in consideration of safety. The relative humidity in the room was kept above 50%.

2.2 DSC

A Perkin-Elmer Pyris 1 DSC analyzer was used for DSC measurements. Dry, oxygen-free nitrogen was used to purge the DSC at $20 \text{ mL} \cdot \text{min}^{-1}$. Heating rate analyzing the thermal decomposition process was $10 \text{ K} \cdot \text{min}^{-1}$. For non-isothermal analysis, the heating rates were 2, 5, 10 and $20 \text{ K} \cdot \text{min}^{-1}$ respectively. Sample mass is about 0.5 mg, contained in sealed aluminum pans.

2.3 TGA

A Perkin-Elmer Pyris 1 TG analyzer was used for TG-DTG measurements. About 0.5 mg of sample was held in a platinum pan, with a flow of dry, oxygen-free nitrogen at $20 \text{ mL} \cdot \text{min}^{-1}$. The heating rate was $10 \text{ K} \cdot \text{min}^{-1}$.

2.4 FT-IR

A Bruker Equinox 55 FT-IR spectrometer (KBr pellet) with the resolution of 4 cm^{-1} was used to record the infrared spectra of solid residue for decomposition study of KDNBF at various temperature.

All of the equipments have been calibrated before use.

3 Results and discussion

3.1 Thermal decomposition processes

The DSC and TG-DTG curves are shown in Fig. 1 and Fig. 2 to demonstrate the thermal decomposition processes of KDNBF. As shown in Fig. 1, there are two exothermic peaks in the DSC curve, one strong initial peak, with another much weaker subsequent peak. The first exothermic peak starts at $197 \text{ }^\circ\text{C}$ and ends at $226 \text{ }^\circ\text{C}$, with peak temperature at $216 \text{ }^\circ\text{C}$. The IR spectrum of solid residue at $230 \text{ }^\circ\text{C}$ was performed using FT-IR (see Fig. 3). The absorption at 2193 cm^{-1} indicates the existence of $-\text{N}=\text{C}=\text{O}$ ^[6], which is the asymmetric stretch vibration $\nu_{\text{as}}(-\text{N}=\text{C}=\text{O})$. At the same time, the very strong absorption at 1628 cm^{-1} may be attributed to the asymmetric stretch vibration of $\nu_{\text{as}}(\text{RCO}_2^-)$. The

existence of NO_3^- and NO_2^- can also be detected, which is at 1388 cm^{-1} and 1264 cm^{-1} , respectively.

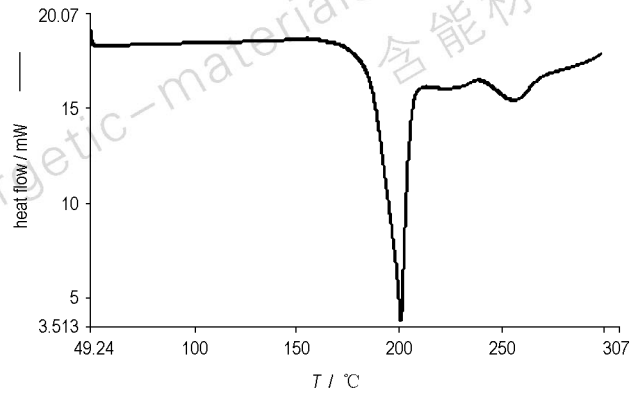


Fig. 1 DSC curve of KDNBF

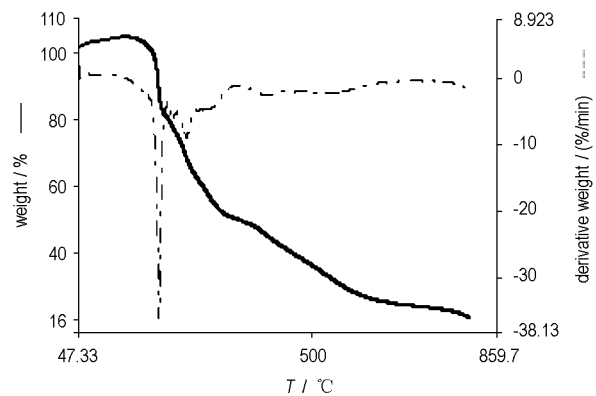


Fig. 2 TG-DTG curves of KDNBF; solid line, TG curve; dotted-dash line, DTG curve

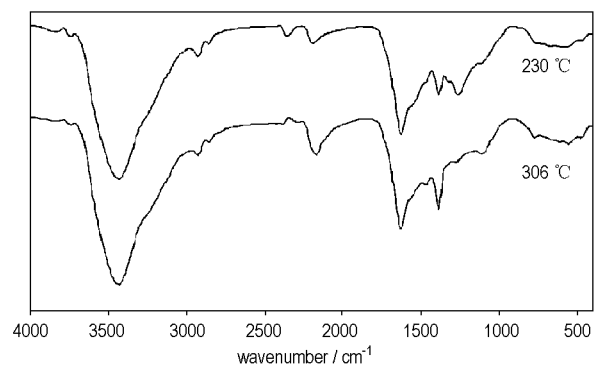


Fig. 3 IR spectra of the solid residues of KDNBF

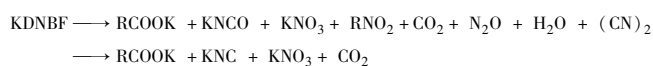
The second exothermic peak starts at $239 \text{ }^\circ\text{C}$ and ends at $265 \text{ }^\circ\text{C}$. The IR spectrum of residue at $306 \text{ }^\circ\text{C}$ was also performed using FT-IR (see Fig. 3). The absorption at 2193 cm^{-1} is replaced by the absorption at

2171 cm^{-1} which indicates the existence of —N=C and the disappearance of —N=C=O . The very strong absorption at 1628 cm^{-1} of $\nu_{\text{as}}(\text{RCO}_2^-)$ and the strong absorption at 1388 cm^{-1} of $\nu_{\text{s}}(\text{NO}_3^-)$ still exists but the strong absorption at 1264 cm^{-1} of $\nu_{\text{s}}(\text{NO}_2^-)$ disappears.

A third exothermic peak, with peak temperature at 374 $^{\circ}\text{C}$ also appears in static air but disappears with nitrogen or helium as purge gas. This indicates that the third exothermic peak is the oxidization process of the solid residues.

According to Fig. 2, there was still 22% residue left at 800 $^{\circ}\text{C}$, which is a substantial solid residue comparing with the decomposition of $\text{K}(\text{NTO})(\text{H}_2\text{O})$ ^[7], KPA ^[7], $\text{K}_2(\text{TNR})(\text{H}_2\text{O})$ ^[8] and $\text{KH}(\text{TNR})(\text{H}_2\text{O})$ ^[9]. For example, in our previous work^[8,9], it was found the residues of $\text{K}_2(\text{TNR})(\text{H}_2\text{O})$ and $\text{KH}(\text{TNR})(\text{H}_2\text{O})$ were very little, which were 11% and 2.9%, respectively.

In a word, the thermal decomposition processes of KDNBF can be displayed with the following illustration according to our above work and the work reported by Jones et al^[3], who paid much more attention on the determination of its gaseous products:



It is obvious that the thermal decomposition of KDNBF is a complex process according to the DSC, TG-DTG and the FT-IR analysis. There are no N—C—O bonds in KDNBF, therefore the form of KNCO requires the breaking and forming of several chemical bonds. Similarly, there are no C—O bonds on the original molecule, so the formation of RCO_2K should be a multi-step process.

It can be seen no endothermic peaks from the DSC curve, which usually owing to the melting, thawing of the sample or dehydration of the sample. This in fact is one of the differences between primary explosives and high explosives^[2]. Usually, the thermal decompositions of primary explosives contain no endothermic stage but the exothermic peak is very sharp. However, it is may be the mask from the initial exotherm that causes no endothermic peak, as Jones, et al^[3] and Spear and Norris^[1] had mentioned.

3.2 Kinetics parameters of non-isothermal decomposition reaction

As mentioned above on the basis of DSC data, kinetics parameters for thermal decompositions of KDNBF could be obtained by Kissinger's^[10] and Ozawa-Doyle's method^[11,12]. The kinetic analysis that follows was based on the first exothermic peak.

Arrhenius parameters for the thermal decomposition of KDNBF, from this study and elsewhere are shown in table 1.

Table 1 E_a and $\ln A$ for first-step thermal decomposition of KDNBF

method	$E_a/\text{kJ} \cdot \text{mol}^{-1}$	$\ln(A/\text{s}^{-1})$
Kissinger(this work)	208	48.3
Ozawa-Doyle(this work)	205	—
ASTM E698 ^[3]	181 ± 10	42.7 ± 0.1
ASTM E1641 ^[13]	190 ± 6	46.6 ± 0.3
DSC dynamic ^[14]	179	43

The values about E_a and $\ln A$ through this work are a little higher than these in literature [3, 13, 14]. This can be attributed to the different test conditions and the physical properties such as granularity etc. of KDNBF obtained in different laboratory.

Therefore, the Arrhenius equation can be expressed with unweighted average of E_a and $\ln A$ obtained from this work and others^[3,13,14], as follows:

$$\ln k = 45.2 - 192600/RT$$

4 Conclusion

(1) The thermal decomposition process of KDNBF results in the formation of RCOOK, KNCO, RNO_2 , KNO_3 at 230 $^{\circ}\text{C}$ and KNC, RCOOK and KNO_3 at 306 $^{\circ}\text{C}$.

(2) The Arrhenius equation can be expressed as $\ln k = 45.2 - 192600/RT$, using Kissinger's and Ozawa-Doyle's method.

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KDNBF 的热分解过程及非等温反应动力学

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摘要: 利用 DSC, TG-DTG 及 FT-IR 技术对 4,6-二硝基-7-羟基-7-氢化苯并氧化呋咱钾 (KDNBF) 的热分解过程进行了研究。结果表明, 230 °C 时, 固体残渣中含有 RCOOK, KNCO, RNO_2 , KNO_3 , 而在 306 °C 时则含有 KNC, RCOOK 及 KNO_3 。利用 Kissinger 法与 Ozawa-Doyle 法对 KDNBF 的热分解过程进行了动力学计算。两种方法所得结果互相吻合, 结合本文及文献结果, Arrhenius 方程可表达为: $\ln k = 45.2 - 192600/RT$ 。

关键词: 物理化学; KDNBF; 热分解机理; 非等温分析法

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