Thermal safety study of bistetrazolohydrazine

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Abstract

The thermal decomposition behavior of HBT was studied by TG-DSC thermal analysis method. The decomposition products of HBT were analyzed. TGA curves and differential thermal curves of HBT were measured in different heating rates. The activation energy and pre-exponential factor of HBT was separately calculated by Ozawa equation and Kissinger equation. Thermal decomposition Mechanism of HBT were derived by Ozawa equation and its possible mechanism function was got. The differential thermal curves of HBT prepared by different dispersants were measured and the kinetic parameters were obtained. These kinetic parameters are in good agreement. The test values of the HBT dispersed with acetone have a higher accuracy, so the activation energy calculated is more meaningful.

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Keywords: nitrogen-rich compound; bistetrazolohydrazine; thermal analysis

1. Introduction

There are a large amount of N-N and C-N bonds in the molecular of nitrogen-rich compound. It is a new energetic material for its high positive heat of formation, high density, good thermal stability and a series of excellent properties[1-4]. The nitrogen-rich compound is mainly used in high energy explosive, solid fuel propulsion system, smokeless pyrotechnic potion, flameless cryogenic extinguishant, military chemistry and explosion safety fields in recent years[5,6].

Bistetrazolohydrazine (HBT), its nitrogen content is 83.3%, density is 1.841 g·cm⁻³, detonation pressure is 27.7 GPa, detonation velocity is 8523 m/s, the shock sensitivity is greater than 30 J, the friction sensitivity is greater...

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than 108 J, the electrostatic spark sensitivity is not sensitive, and the thermal decomposition products are mainly nitrogen. Therefore, it has a good application prospect in gas generating agent and propellant field[7]. HBT was prepared by Thiele et al[8] with N, N′-bistetrazolohydrazine salt as raw material and magnesium powder as reduction for the first time. In 2007, the method of Thiele was optimized by Klapötke et al[7], the yield of HBT increased to 63%, and the application of HBT is studied. In 2008, large-scale study of synthetic experiment was carried out by Klapötke et al[9]. In 2010, the synthetic technology was optimized by Meng Lingqiao et al[10], the best process condition was gained, and the highest yield was 91.53%. At the same time the structure of HBT was characterized. However, there is no related report about thermal stability of HBT.

In this paper, the thermal behavior of HBT was studied by TG-DSC and TG-DTA techniques. The kinetic parameters were calculated by Ozawa method and Kissinger method.

2. Experimental

2.1. The experimental method

2.1.1. Thermogravimetry

Thermogravimetry is a kind of technology to measure the change of the quality of the samples with the temperature under the process temperature control. The molecular structure of energetic material can keep relatively stable in the general case. It can be volatile, sublimation and broken down to the gas phase products only at higher temperature or other special conditions. This makes the weight of the sample change. The thermal weight loss is closely related to material performance. The thermal decomposition endanger the safety when using and storage. TG-DTA test conditions of HBT are shown in Table 1.

| serial number | dispersant | quality (mg) | heating rate (°C·min⁻¹) | N₂ rate(mL·min⁻¹) |
|---------------|------------|--------------|--------------------------|-------------------|
| M-1           | methanol   | 3.5          | 2                        | 50                |
| M-2           |            | 3.1          | 5                        | 50                |
| M-3           |            | 3.9          | 10                       | 50                |
| M-4           |            | 4.0          | 15                       | 50                |
| M-5           |            | 3.9          | 20                       | 50                |
| A-1           | acetone    | 3.5          | 2                        | 50                |
| A-2           |            | 3.5          | 5                        | 50                |
| A-3           |            | 3.5          | 10                       | 50                |
| A-4           |            | 3.6          | 15                       | 50                |
| A-5           |            | 3.5          | 20                       | 50                |
| W-1           | water      | 3.9          | 2                        | 50                |
| W-2           |            | 4.0          | 5                        | 50                |
| W-3           |            | 3.7          | 10                       | 50                |
| W-4           |            | 3.8          | 15                       | 50                |
| W-5           |            | 3.2          | 20                       | 50                |

2.1.2. Differential scanning calorimetry

Differential scanning calorimetry is a kind of technology to measure the change of energy difference in per unit time between sample and reference substance with the temperature under program temperature. The reference substance is α-Al2O3. DSC test conditions of HBT are shown in Table 2.
Table 2. DSC test conditions of HBT.

| quality (mg) | heating rate (°C·min⁻¹) | atmosphere | rate (mL·min⁻¹) |
|-------------|--------------------------|------------|----------------|
| 3.5920      | 5                        | N₂         | 100            |

2.1.3. Adiabatic scanning calorimetry

Adiabatic scanning calorimeter (ARC), is a calorimetric apparatus to simulate the sample thermal behavior in the adiabatic environment. It can keep a minimum heat exchange between sample and instrument, and be controlled by computer automatically. The thermal stability parameters and the relationship between parameters of the test system prepared by samples and sample room can be gained from the acquisition of data: the temperature-time, pressure-time, the initial exothermal temperature (T₀), the adiabatic temperature (ΔTₐd), the largest since the acceleration rate temperature, temperature rise rate-temperature and so on.

2.2. Experimental apparatus and reagents

The experimental apparatus and reagents are listed in Table 3 and Table 4 separately.

Table 3. Experimental apparatus.

| apparatus  | type     | manufacturer                                    |
|------------|----------|-------------------------------------------------|
| TG-DTA     | HCT-1    | Beijing permanent scientific instrument factory |
| DSC        | Q600SDT  | American Thermal Analysis company               |
| ARC        | CSI-ARC  | Columbia company of science and industry        |

Table 4. Reagents.

| reagents        | class | manufacturer                        |
|-----------------|-------|-------------------------------------|
| Anhydrous ethanol | AR    | Beijing chemical factory            |
| acetone         | AR    | Beijing chemical factory            |
| Anhydrous methanol | AR    | Beijing chemical factory            |

3. Results and discussion

3.1. Thermo gravimetric analysis of HBT

3.1.1. DSC-TG of HBT

Seen from Fig. 1, HBT had obvious exothermic decomposition weightlessness peak in the heating process. It began to decompose when the temperature is about 210 °C, and decompose violently at 233.28 °C. The peak temperature in DSC was 233.58 °C, and the enthalpy change was 632.1 J·g⁻¹. HBT had a very narrow range of weightlessness, almost completely weightless in the range 233.28-233.50 °C, weight loss rate 93.92%, the final residue is 0.2180 mg, accounting for 6.08% of the original sample weight. HBT molecule contains only three kinds of organic elements C, H, N, and carbon accounts for 14.29%. When filling nitrogen gas, the atmosphere was oxygen-free environment, so it can be speculated that the gas phase products are mainly nitrogen and a small amount of HCN, NH₃. Carbon element may formed other organic matters beside HCN and CH₄. In addition, there is a sharp peak at 233.28 °C in the TG curve. It was caused by a lot of gas produced by the intense decomposition of HBT. The probable thermal decomposition mechanism of HBT is shown in Fig. 2.

The EI-MS spectrum of the decomposition products of HBT is shown in Fig. 3. m/z=126 was the fragmentation peak of melamine. m/z=44 was the fragmentation ion of NH₄CN. m/z=27 was the fragmentation ion of HCN.
Fig. 1. DSC-TGA curves of HBT.

2N₂ + 2NH₂CN → 2N₂ + 2NH₃ + 2HCN

4NH₂CN → 4/3NH₃ + 4HCN + 6/3N₂

2NH₂CN + NH₂CN → 2N₂ + 2NH₃ + 2HCN

m/z = 126

m/z = 111

Fig. 2. The probable thermal decomposition mechanism of HBT.

3.1.2 Thermo ravimetric analysis of HBT

The thermo-gravimetric curves can be obtained at different heating rates. The temperature with the same conversion is got according to the thermo-gravimetric curves. The activation energy and pre-exponential factor at different decomposition temperature can be obtained by Ozawa equation[11].

\[
\lg \beta = \lg \left[ \frac{AE_0}{RG(\alpha)} \right] - 2.315 - 0.4567 \frac{E_0}{RT_m}
\]

where \( \alpha \) is the conversion rate; \( A \) is the pre-exponential factor, \( s^{-1} \); \( E_0 \) is the activation energy, kJ mol\(^{-1} \); \( T_m \) is the temperature, K; \( \beta \) is the heating rate, °C min\(^{-1} \); \( R \) is the ideal gas constant, J min\(^{-1} \) K\(^{-1} \); \( G(\alpha) \) is the mechanism function in integral form. (\( \beta_i, T_i \)) are substituted into Ozawa equation at the same conversion rate \( \alpha \). The slope of the line was obtained by \( 1/T_i \) after linear simulation with \( \lg \beta_i \). Activation energy can be calculated by the slope of the line. The slope of the line can also solve the thermal decomposition mechanism functions.

It can be obtained by the transformation of Ozawa equation.
\[ \lg G(\alpha) = \lg \left[ \frac{AE_0}{R\beta} \right] - 2.315 - 0.4567 \frac{E_0}{RT} \]  

(2)

For any reaction mechanism function, there is a linear relationship between \( \lg G(\alpha) \) and \( 1/T_i \). For a hypothetical reaction mechanism function, activation energy and linearly dependent coefficient are calculated by Ozawa equation, and then the thermal decomposition mechanism functions can be gained.

TGA curve of HBT prepared by dispersant water at different heating rates are shown in Fig. 4. The maximum weight loss temperature of HBT moved to higher temperature with the increase of heating rate. The maximum weight loss temperature was from 220 to 233 °C with heating rate from 2 to 20 °C·min\(^{-1}\). The termination temperature was from 224 to 235 °C with heating rate from 2 to 20 °C·min\(^{-1}\). Weight loss rates were 98.4%, 96.94%, 98.44%, 99.82% and 99.87%. The thermal decomposition of HBT is intense, a large amount of gas was generated in the decomposition, and almost all of the weight loss occurred in a short reaction time. HBT has almost no quality change under 200 °C. Slow exothermic reactions take place at about 220 °C. Once its temperature reaches about 230 °C, the decomposition is violent. That is to say HBT is relatively safe under 200 °C. The gas products are large and mainly nitrogen, and the weight loss are more than 95%. Therefore, it has potential application in gas generating agent. The decomposition at different heating rates and conversion rates are shown in Table 5.

![Fig. 3. The EI-MS spectrum of the decomposition products of HBT.](image)

![Fig. 4. TGA curve of HBT prepared by dispersant water at different heating rates.](image)
Table 5. The decomposition at different heating rates and conversion rates.

| β (°C min⁻¹) | α=0.01 | α=0.05 | α=0.1 | α=0.5 | α=0.9 |
|--------------|--------|--------|--------|--------|--------|
| 2            | 209.12 | 216.75 | 220.56 | 222.62 | 222.84 |
| 5            | 215.11 | 222.66 | 226.11 | 226.19 | 227.67 |
| 10           | 221.29 | 227.52 | 228.42 | 229.62 | 230.20 |
| 15           | 222.94 | 229.75 | 230.86 | 231.15 | 232.02 |
| 20           | 224.96 | 233.38 | 233.40 | 233.80 | 234.04 |

The thermal analysis kinetic parameters of HBT gained from Ozawa equation are shown in Table 6.

Table 6. The thermal analysis kinetic parameters of HBT gained from Ozawa equation.

| lgβ | α=0.01 | α=0.05 | α=0.1 | α=0.5 | α=0.9 |
|-----|--------|--------|--------|--------|--------|
|     | 1/T×10³ | 1/T×10³ | 1/T×10³ | 1/T×10³ | 1/T×10³ |
| 0.3010 | 2.0735 | 2.0412 | 2.0255 | 2.0171 | 2.0163 |
| 0.6990 | 2.0481 | 2.0169 | 2.0030 | 2.0026 | 1.9968 |
| 1.0000 | 2.0225 | 1.9973 | 1.9937 | 1.9890 | 1.9868 |
| 1.1761 | 2.0158 | 1.9885 | 1.9841 | 1.9829 | 1.9796 |
| 1.3010 | 2.0076 | 1.9742 | 1.9741 | 1.9726 | 1.9717 |

(β, T) were substituted into Ozawa equation with the same conversion rate α. The slope of the line was obtained by 1/Ti after linear simulation with lgβi. The line is shown in Fig. 5.

Activation energy E0 can be calculated by the slope of the line. The activation energy and the linear correlation coefficient of HBT calculated by Ozawa equation are shown in Table 7.

For the hypothetical mechanism function, the linear relation of lgG(α) and 1/Ti can be obtained by formula (2). Thermal decomposition reaction mechanism function can be obtained by the linear correlation coefficient. Common integral form of mechanism functions are shown in Table 8.

The correlation coefficient comparisons of different mechanism function linear fitting are shown in Table 9. Seen from Table 9, the mechanism function G(α)=[1/(1+α)1/3-1]² has the largest correlation coefficient at different reaction depth. Therefore, we can speculate that the thermal decomposition mechanism function of HBT is G(α)=[1/(1+α)1/3-1]².
3.2. Differential scanning calorimetry analysis of HBT

3.2.1. The influence of heating rate on decomposition temperature of HBT

Fig. 5. Activation energy fitting line at different reaction depth.

Table 7. The activation energy of HBT calculated by Ozawa equation.

| heating rate (°C·min⁻¹) | activation energy $E_o$(kJ mol⁻¹) | correlation coefficient $r_o$ |
|-------------------------|-----------------------------------|------------------------------|
| 0.01                    | 269.73                            | -0.99627                     |
| 0.05                    | 279.28                            | -0.99627                     |
| 0.1                     | 369.85                            | -0.99266                     |
| 0.5                     | 418.42                            | -0.99306                     |
| 0.9                     | 423.21                            | -0.99644                     |

DTA curves of HBT prepared by dispersant water at different heating rates are shown in Fig. 6. The DTA results of HBT prepared by dispersant water are shown in Table 10.
Table 8. Common integral form of mechanism functions.

| serial number | integral form of mechanism functions $G(\alpha)$ |
|---------------|-----------------------------------------------|
| 1             | $\alpha^2$                                |
| 2             | $\alpha^2(1-\alpha)\ln(1-\alpha)$              |
| 3             | $(1-2\alpha/3)(1-\alpha)^2/3$                   |
| 4–5           | $[1-(1-\alpha)^{1/n}](n=2,1/2)$                 |
| 6             | $[1-(1-\alpha)^{1/2}]^{1/2}$                    |
| 7             | $[1/(1+\alpha)^{1/3}].1^2$                      |
| 8             | $-(\ln(1-\alpha)$                              |
| 9             | $[-\ln(1-\alpha)]n(n=2,1/3,3,1/4,4,2,3)$         |
| 10–16         | $[1-(1-\alpha)n](n=1/2,3,2,4,1/3,1/4)$           |
| 17–22         | $\alpha n(n=1,3/2,1/2,1/3,1/4)$                 |
| 23–27         | $n(1-\alpha)^{1/2}$                            |
| 28            | $(1-\alpha)^{1/2}$                             |
| 29            | $(1-\alpha)^2$                                 |
| 30            | $a^2, a^2n$                                    |

Table 9. The correlation coefficient comparisons of different mechanism function linear fitting.

| mechanism function | $\alpha=0.01$ | $\alpha=0.05$ | $\alpha=0.10$ | $\alpha=0.50$ | $\alpha=0.90$ |
|--------------------|---------------|---------------|---------------|---------------|---------------|
| $\alpha^2, \alpha n$ | 0.96074 | 0.97934 | 0.98591 | 0.97979 | 0.98112 |
| $(1-2\alpha/3)(1-\alpha)^2/3$ | 0.95338 | 0.97678 | 0.98287 | 0.97874 | 0.97668 |
| $[1-(1-\alpha)^{1/2}]n$ | 0.94848 | 0.97469 | 0.98048 | 0.9775 | 0.97345 |
| $[1/(1+\alpha)^{1/3}].1^2$ | 0.95208 | 0.97628 | 0.98228 | 0.97847 | 0.97587 |
| $[1/(1+\alpha)^{1/3}].1^2$ | 0.9649 | 0.98106 | 0.98789 | 0.98063 | 0.9388 |
| $[-\ln(1-\alpha)]n$ | 0.9686 | 0.98232 | 0.98941 | 0.98099 | 0.98619 |
| $[-\ln(1-\alpha)]n$ | 0.9408 | 0.97048 | 0.97582 | 0.97457 | 0.96765 |
| $(1-\alpha)^{1/2}$ | 0.90671 | 0.94966 | 0.95355 | 0.95753 | 0.94188 |

Fig. 6. DTA curves of HBT prepared by dispersant water at different heating rates.
Table 10. The DTA results of HBT prepared by dispersant water.

| β (°C min⁻¹) | Initial temperature (°C) | Peak temperature (°C) | Final temperature (°C) | ΔH_d (J g⁻¹) |
|--------------|--------------------------|-----------------------|------------------------|--------------|
| 2            | 204.67                   | 225.00                | 229.46                 | 662.91       |
| 5            | 214.34                   | 230.53                | 240.76                 | 576.45       |
| 10           | 222.87                   | 236.45                | 248.77                 | -            |
| 15           | 226.56                   | 241.98                | 260.29                 | -            |
| 20           | 230.40                   | 246.19                | 269.46                 | -            |

Seem from Table 10, Initial temperature, peak temperature and final temperature of HBT decomposition are shifted to higher temperature with the increase of heating rate. However, the increase of heating rate lead to the decrease of decomposition enthalpy. The reason may be that the decomposition reaction is very severe and the gas which produced in short time carried away some heat. The decomposition enthalpy of HBT is 662.91 J g⁻¹ when the heating rate is 2 °C·min⁻¹. The decomposition enthalpy of HBT is 576.45 J g⁻¹ when the heating rate is 5 °C·min⁻¹. It also suggests that the decomposition of HBT is relatively stable when the heating rate is low.

DTA curves of HBT prepared by dispersant methanol at different heating rates are shown in Fig. 7. The DTA results of HBT prepared by dispersant methanol are shown in Table 11.

![Fig. 7. DTA curves of HBT prepared by dispersant methanol at different heating rates.](image)

Table 11. The DTA results of HBT prepared by dispersant methanol.

| β (°C min⁻¹) | Initial temperature (°C) | Peak temperature (°C) | Final temperature (°C) | ΔH_d (J g⁻¹) |
|--------------|--------------------------|-----------------------|------------------------|--------------|
| 2            | 201.53                   | 224.48                | 226.98                 | 672.92       |
| 5            | 214.24                   | 234.67                | 244.78                 | 651.45       |
| 10           | 227.87                   | 240.19                | 254.45                 | -            |
| 15           | 228.98                   | 240.55                | 256.35                 | -            |
| 20           | 230.16                   | 244.76                | 268.24                 | -            |

Seem from Fig. 7 and Table 11, Initial temperature, peak temperature and final temperature of HBT decomposition are shifted to higher temperature with the increase of heating rate. The decomposition enthalpy of HBT is 668.73 J g⁻¹ when the heating rate is 2 °C·min⁻¹. The decomposition enthalpy of HBT is 596.40 J g⁻¹ when the heating rate is 5 °C·min⁻¹. The difference between decomposition enthalpy is smaller.

DTA curves of HBT prepared by dispersant acetone at different heating rates are shown in Fig. 8. The DTA results of HBT prepared by dispersant acetone are shown in Table 12.
3.2.2. The influence of dispersant on decomposition temperature of HBT

The experiment condition is: heating rate 2 °C·min⁻¹, 3.0–3.5 mg sample, N₂ atmosphere, gas rate 50 mL·min⁻¹. DTA curves of HBT prepared by different dispersant are shown in Fig. 9.

Seen from Fig. 9, Initial temperature, peak temperature and final temperature of HBT with three kinds of dispersant were nearly identical. The peak temperature of HBT with methanol and acetone as the dispersant are lower than that with water as the dispersant. The peak temperature are 224.91 °C, 224.96 °C and 223.02 °C respectively. The decomposition enthalpies are roughly similar when the maximum decomposition temperature is reached. The decomposition enthalpies are 72.92 J·g⁻¹, 668.73 J·g⁻¹ and 662.91 J·g⁻¹ respectively.

Fig. 8. DTA curves of HBT prepared by dispersant acetone at different heating rates.

Table 12. The DTA results of HBT prepared by dispersant acetone.

| β (°C min⁻¹) | Initial temperature (°C) | Peak temperature (°C) | Final temperature (°C) | ΔH₀(J g⁻¹) |
|-------------|--------------------------|-----------------------|------------------------|------------|
| 2           | 204.68                   | 224.96                | 231.60                 | 668.73     |
| 5           | 218.09                   | 234.26                | 249.63                 | 596.40     |
| 10          | 223.04                   | 240.29                | 252.49                 | -          |
| 15          | 225.23                   | 242.96                | 258.85                 | -          |
| 20          | 226.67                   | 245.80                | 266.29                 | -          |

Fig. 9. DTA curves of HBT prepared by different dispersant.

a: acetone; b: methanol; c: water
3.2.3. The calculation of activation energy of HBT

The decomposition peak temperature can be got at different peaking rates. The activation energy can be gained with Kissinger equation.

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{A_k R}{E_k}\right) - \frac{E_k}{R T_p}, \quad i = 1, 2, \ldots, n$$  (3)

where $\beta$ is the heating rate, K min$^{-1}$; $T_p$ is the peak temperature, K; $A_k$ is the pre-exponential factor, s$^{-1}$; $E_k$ is the activation energy, kJ·mol$^{-1}$; $R$ is the gas constant, J min$^{-1}$ K$^{-1}$. Lines are drawn using $\ln(\beta/T_p^2)$ and $1/T_p$. The slope $E_k$, intercept $A_k$ and appropriate mechanism function can be calculated. Kinetic parameters of HBT are shown in Table 13.

### Table 13. Kinetic parameters of HBT calculated by Kissinger equation.

| dispersant | $\beta$ (°C min$^{-1}$) | $T_i$ (°C) | $T_p$ (K) | $1/T_p \times 10^3$ | $\ln(\beta/T_p^2)$ |
|------------|--------------------------|------------|---------|------------------|------------------|
| methanol   | 2                        | 224.48     | 497.48 | 2.0101           | -11.7260         |
|            | 5                        | 234.67     | 507.67 | 1.9698           | -10.8502         |
|            | 10                       | 240.19     | 513.19 | 1.9486           | -10.1787         |
|            | 15                       | 240.55     | 513.55 | 1.9472           | -9.7746          |
|            | 20                       | 244.76     | 517.76 | 1.9314           | -9.5033          |
| acetone    | 2                        | 224.96     | 497.96 | 2.0082           | -11.7279         |
|            | 5                        | 234.26     | 507.26 | 1.9714           | -10.8486         |
|            | 10                       | 240.29     | 513.29 | 1.9482           | -10.1791         |
|            | 15                       | 242.96     | 515.96 | 1.9381           | -9.7840          |
|            | 20                       | 245.80     | 518.8  | 1.9275           | -9.5073          |
| water      | 2                        | 225.00     | 498.00 | 2.0080           | -11.7281         |
|            | 5                        | 230.53     | 503.53 | 1.9860           | -10.8338         |
|            | 10                       | 236.45     | 509.45 | 1.9629           | -10.1641         |
|            | 15                       | 241.98     | 514.98 | 1.9418           | -9.7802          |
|            | 20                       | 246.19     | 519.19 | 1.9261           | -9.5088          |

Fig. 10 is drawn with $\ln(\beta/T_p^2)$ as $Y$ and $1/T_p$ as $X$. The slope of the line could be calculated respectively by three figures, and then the pre-exponential factor and the correlation coefficient can be got, which are listed in Table 14.

### Table 14. The activation energy of HBT prepared with different dispersants.

| dispersant | $E$ (kJ·mol$^{-1}$) | pre-exponential factor ($A$) | correlation coefficient ($r_0$) |
|------------|----------------------|------------------------------|---------------------------------|
| water      | 221.40               | $4.26 \times 10^{21}$        | 0.98383                         |
| methanol   | 240.96               | $3.20 \times 10^{24}$        | 0.98324                         |
| acetone    | 230.79               | $3.43 \times 10^{23}$        | 0.99706                         |

The activation energy of HBT prepared with different dispersants are roughly similar. The correlation coefficient of HBT prepared with acetone as the dispersant is the best. The activation energy is 230.79 kJ·mol$^{-1}$, the pre-exponential factor is $3.43 \times 10^{23}$ s$^{-1}$, linear equation is $y = 43.96 - 27.76x$, correlation coefficient $r_0$ is 0.99706. The activation energy of HBT prepared with different dispersants are shown in Table 14.
3.3. ARC results

The kinetic parameters of HBT were measured by ARC. The heating rate and temperature curve is shown in Fig. 11(a). The temperature and time curve is shown in Fig. 11(b).

Seen from Fig. 11, there was no exothermic phenomenon when the temperature was below 140 °C. After the circulation of “heat-wait-seek”, the heat release was explored by the calorimeter at 150.74 °C. The rate of heat release was 0.1078 °C·min⁻¹ at this time. The heating rate continued to increase. The highest heating rate was 110.02 °C·min⁻¹ at 185.79 °C. After that the effect of reactant consumed on the reaction rate of the sample had exceeded the effect of temperature on the reaction rate. The heating rate declined and the system temperature raised. The highest system temperature was 202.04 °C at the end of the exothermic.
4. Conclusions

The thermal decomposition behavior of HBT was studied in this work. The main results are as follows.

(1) The highest weightlessness temperature of HBT was 230 °C, the weight loss ratio was 93.92%, peak temperature was 233.58 °C, the enthalpy change was 632.1 J·g⁻¹. The decomposition products of HBT were amine substance: melamine, NH₄CN and HCN.

(2) The activation energy and pre-exponential factor of HBT were calculated by Ozawa equation and Kissinger equation. The possible mechanism function was \( G(\alpha) = \frac{1}{(1+\alpha)^{1/3} - 1} \). The differential thermal curves test values of the HBT dispersed with acetone have a higher accuracy than that of water and methanol.

References

[1] Singh R P, Verma R D, Meshri D T, et al. Energetic nitrogen-rich salts and ionic liquids. Angewandte Chemie, 2006, 45(22): 3584-3601.
[2] CHAI Yu-ping, ZHANG Tong-lai, YAO Jun. Synthesis and characterization of bitetrazole salts. Journal of Solid Rocket Technology, 2007, 30 (3): 248-252.
[3] ZHU Ya-hong, SHENG Di-lun, CHEN Li-kui, et al. Synthesis and characterization of energetic intermediate 5-Hydrazinotetrazole. Chinese Journal of Explosives and Propellants, 2008, 31 (6): 39-41.
[4] HE Chun-lin, DU Zhi-ming, CONG Xiao-min, et al. Study on characterization and performance of guanidinium azotetrazolate. Chemical Propellants and Polymeric Materials, 2009, 7(6): 31-34.
[5] Karaghiosoff K, Klapötke T M, Sabate C M. Nitrogen-rich compounds in pyrotechnics: alkaline earth metal salts of 5, 5'-Hydrazine-1, 2-diylbis (1Htetrazole). European Journal of Inorganic Chemistry, 2009(2): 238-250.
[6] WANG Hong-she, DU Zhi-ming. Progress in synthesis and properties of nitrogen-rich compound. Chinese Journal of Energetic Materials, 2005, 13 (3): 196-199.
[7] Klapotke T M, Sabate C M. 5, 5'-Hydrazinebi-tetrazole: an oxidation-stable nitrogen-rich comound and starting material for the synthesis of 5, 5'-azobistetrazoles. Zeitschrift fuer Anorganische und Allgemeine Chemie, 2007, 633(15): 2671-2677.
[8] Hammerl A, Holl G, Kaiser M, et al. Nitrogen rich materials: salts of N, N'-bistetrazolatohydrozine. Zeitschrift fuer Anorganische und Allgemeine Chemie, 2003, 629(12): 2117-2121.
[9] Klapotke T M, Sabate C M. Bistetrazoles: nitrogen rich, high-performing. Insensitive energetic compounds. Chemistry of Materials, 2008, 20 (11): 3629-3637.
[10] Meng Lingqiao, Du Zhiming, He ChunLin, Zhao Linshuang, Cong Xiaomin, Fang Li. Structural Characterization and Process Optimization of Bistetrazolohydrazine. Chinese Journal of Explosives & Propellants, 2010, 33(5): 15-18.
[11] Ozawa T. A new method of analyzing thermogravimetric data. Bull. Chem. Soc. Jpn., 1965, 38(11): 1702-1706.