Synthesis and Properties of Hydrazine Picrate

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Abstract: Picric acid was reacted with liquid propellant anhydrous hydrazine to synthesize anhydrous hydrazine picrate. Its structure was characterized by elemental analysis, infrared spectrum analysis, nuclear magnetic resonance, and its thermal decomposition performance was analyzed by TG-DTG and DSC. The thermal decomposition of anhydrous hydrazine picrate was studied by using Kissinger method and its activation energy was calculated. The critical temperature of thermal explosion was calculated by using the characteristic data of non-isothermal DSC curve. The results show that the thermal decomposition of anhydrous hydrazine is mainly between 179.8~200.9°C, the decomposition process is exothermic reaction, the melting point is about 140°C, the non-isothermal kinetic equation is ln(β/TP)=−17652 (1/TP)+28.009, the activation energy of thermal decomposition is E=146.76kJ/mol, pre-exponential factor lnA=30.34, and the critical temperature of thermal explosion Tc=175.3°C. Anhydrous hydrazine picrate has the characteristics of simple synthesis, rapid reaction and good thermal stability. It provides a new way for the disposal and reuse of anhydrous hydrazine.

1. Introduction
Picric acid, also known as 2, 4, 6-trinitrophenyl phenol (PA), is a nitrophenol compound with strong acidity. It can react with metals (copper, potassium, lead and barium, etc.) to produce metal salts of picric acid[1-3], and react with organic base compounds to produce corresponding salts[4-7]. Picric acid energy-containing ionic salts, as a new type of energy-containing materials, have important applications in the field of explosives due to their good thermal stability, high density and energy, low vulnerability and other advantages[8-13].

In order to solve the problem of treatment and reuse of useless liquid propellant hydrazine, picric acid was synthesized by reaction of picric acid and hydrazine. Its composition and structure were analyzed and characterized by elemental analyzer, infrared spectrometer, nuclear magnetic resonance spectrometer, etc., and its thermal behavior was analyzed and studied by DSC analyzer and TGA thermogravimetric analyzer, etc., laying a foundation for the subsequent research on the application of hydrazine picrate in the field of explosives.

2. Experiment
2.1 Instruments and reagents
Vario ELIII element Analyzer, Elementar, Germany; Vertex70 Fourier Transform infrared spectrometer, Bruker, Germany; Sdt-q600 TG/DSC Analyzer, TA, USA.

Picric acid, analytically pure, Taishan Chemical Plant Chemical Reagent Co., LTD.; Anhydrous hydrazine, purity ≥97%, Dawn Chemical Research Institute; Anhydrous ethanol, analytically pure, Xi'an Miura Chemical Reagent Co. LTD.

2.2 preparation
With anhydrous ethanol as solvent and anhydrous hydrazine and picric acid carried out in accordance with the mole ratio of 1:1 mixing, stirring at room temperature, the solution was crystal precipitation, instantly become cloudy and gradually when the solution was neutral, stop stirring, product to filter and anhydrous ethanol washing, 2 h under 100℃ oven temperature dry, yellow crystal, the yield was about 86%. The synthesis reaction equation of anhydrous hydrazine picrate was:

2.3 Structural characterization and performance analysis
The structures were characterized by IR, 1H-NMR, TG and DSC. The products were analyzed by 1H-NMR using DMSO as solvent and tetramethylsilane (TMS) as internal standard. Elemental analysis: Experimental value: C is 27.6%, N is 26.4%, H is 2.6%; The measured value is 27.4% for C, 26.7% for N and 2.6% for H.

3. Results and discussion
3.1 Structural Characterization
Infrared spectra and 1H-NMR spectra of the products are shown in Figure 1.
It can be seen from Figure.1 (a) that 3453.00 cm$^{-1}$ is the stretching vibration peak of N-H bond. 3050.40 cm$^{-1}$ is the stretching vibration peak of C-H bond in the benzene ring; 1616.50 cm$^{-1}$, 1571.40 cm$^{-1}$, 1542.17 cm$^{-1}$, 1501.56 cm$^{-1}$ is the stretching vibration peak of C=C in the benzene ring skeleton. 1428.39 cm$^{-1}$ is the deformation vibration peak of C-H bond in -CH$_3$; 1365.37 cm$^{-1}$ is the stretching vibration peak of -NO$_2$; 1264.27 cm$^{-1}$ is the deformation vibration peak of NH$_3^+$. 1080.98 cm$^{-1}$ is the stretching vibration peak of C-O; 957.43 cm$^{-1}$, 789.11 cm$^{-1}$ is the C-H deformation vibration peak in the benzene ring. From Figure.1 (b), $\delta=8.61$ is the H on the benzene ring, $\delta=3.34$ is the H on -NH$_3^+$, and $\delta=2.65$ is the H on -NH$_2$.

3.2 TG-DTG and DSC curves of anhydrous hydrazine picrate

TG-DTG and DSC were used to analyze and characterize the thermal stability of anhydrous hydrazine picrate. The results are shown in Figure.2 (a).
By TG curve in Figure 2 (a) it can be seen that with the increase of temperature, the thermal decomposition of anhydrous hydrazine picrate is only a process of weightlessness, the extrapolation starting point temperature of 177.4℃, the DTG curve shows that at 184.6℃, the sample mass loss rate is highest, up to 198.1℃, the weightlessness curve begins to flatten out, the whole process of thermal decomposition of the sample mass loss of about 60.4% in total; As can be seen from Figure 2 (b), dynamic DSC scanning was carried out on the product at a heating rate of 10K/min. With the increase of temperature, the DSC curve of anhydrous hydrazine picrate presented two peak positions. The first peak is sunken downward, which can be judged as an endothermic peak. Its starting point temperature ($T_0$) is 136.9℃, and its peak endothermic temperature ($T_p$) is 140.2℃. The second peak protrudes upward and can be judged to be an exothermic peak. Its starting point temperature ($T_0$) is 179.8℃, and its peak exothermic temperature ($T_p$) is 191.4℃. Thus, DSC curve can preliminarily infer that the first
heat absorption peak is the temperature of sample melting, so a small heat absorption peak will appear at 140.2°C, while the appearance of the second exothermic peak indicates that the thermal decomposition of anhydrous hydrazine picrate is an exothermic process.

3.3 Calculation of kinetic parameters of thermal decomposition of hydrazine picrate without water

Figure 3 shows the DSC curve of anhydrous hydrazine picrate at different heating rates (=5,7.5,10,15°C/min)[14]. As can be seen from Figure 3, with the increase of temperature, the DSC curve of anhydrous hydrazine picrate has two peaks, and with the increase of the heating rate, the peak decomposition temperature $T_p$ also increases. The thermal decomposition characteristic data of DSC curve under different temperature rising rates are shown in Table 1.

![DSC curves of anhydrous hydrazine picrate at different heating rates](image)

**Table 1** Thermal decomposition characteristic data of non-isothermal DSC curves of anhydrous hydrazine picrate

| $\beta$/(K·min$^{-1}$) | $T_0$/°C | $T_p$/°C | $T_e$/°C |
|------------------------|-----------|-----------|----------|
| 5                      | 169.8     | 183.1     | 195.4    |
| 7.5                    | 173.2     | 189.2     | 197.6    |
| 10                     | 179.8     | 191.4     | 200.9    |
| 15                     | 181.6     | 195.8     | 207.7    |

Note: $\beta$ is the heating rate; $T_0$ is the initial decomposition temperature; $T_p$ is the peak temperature; $T_e$ is the termination decomposition temperature;

Under the Kissinger method[14], the thermal decomposition kinetic equation is obtained as follows:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{RA}{E}\right) - \frac{E}{RT_p}$$  (1)

Where: $A$ refers to the former factor; $E$ is the apparent activation energy, kJ/mol; $R$ is the molar gas constant, 8.314J·K$^{-1}$·mol$^{-1}$; $T_p$ is the peak temperature, K; $\beta$ is the heating rate at K/min.
Figure 4 The linear relationship between $\ln(\beta/T_p^2)$ and $1/T_p$

Using the peak temperature data $\beta$ of the product at different temperature rates, a straight line can be obtained by plotting $\ln(\beta/T_p^2) - 1/T_p$. The results are shown in Figure 4. The thermal decomposition kinetic parameters $E$ and $A$ of the anhydrous hydrazide picrate can be obtained from the slope and intercept of the straight line.

After calculating $E$ and $A$, the temperature characteristics of the activation entropy $\Delta S^\neq$ indicates, activation enthalpy $\Delta H^\neq$ indicates and activation free energy $\Delta G^\neq$ indicates $A$ value through thermodynamics equation\(^{15}\) (2), (3), (4) is obtained:

\[
\begin{align*}
A \exp(-E/RT) &= v \exp(-\Delta G^*/RT) = k_B T/h \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad (2) \\
\Delta H^\neq &= E - RT \\
\Delta G^\neq &= \Delta H^* - T \Delta S^* 
\end{align*}
\]

Where, $T$ is the characteristic temperature (K); $h$ and $k_B$ are Planck's constant and Boltzmann's constant respectively. In 469 K anhydrous hydrazine picrate peak temperature in DSC curve of thermodynamics function value is: the apparent activation energy $E$ is 146.76 kJ/mol, $\ln A$, refers to the former factor is 30.34, activation entropy $\Delta S^\neq$ indicates is -175.89 J/(mol·K), the activation enthalpy $\Delta H^\neq$ indicates is 142.90 kJ/mol, activation free energy $\Delta G^\neq$ indicates is 224.61 kJ/mol.

### 3.4 Critical temperature of thermal explosion

For the estimation method of critical temperature $T_b$ of thermal explosion under non-isothermal conditions, it can be calculated by formula\(^{16,17}\) (5) and (6).

\[
\begin{align*}
T_i &= T_{e0} + b \beta_i + c \beta_i^2 + d \beta_i^3 \\
T_b &= E - \sqrt{E^2 - 4ERT_{e0}} / 2R
\end{align*}
\]

Where $T_{e0}$ is the temperature at the starting point of the extrapolation, and its value can be obtained from the non-isothermal DSC curve according to the characteristic temperature data of different temperature rising rates. When $\beta=0$, $T_{e0}$ is the extrapolation starting point temperature. After fitting formula (5) by using the least square approximation method, the equation is obtained as follows:

\[
T_{e0} = 163.9 - 2.03 \beta_i + 0.658 \beta_i^2 - 0.0296 \beta_i^3
\]
Therefore, when $\beta=0$, $T_{s0}=163.9^\circ C$, substitute the required data into (6), and the critical temperature of $T_s$ for thermal explosion of methyl hydrazine picrate can be calculated as $175.3^\circ C$.

4. Conclusion

(1) Anhydrous hydrazine picrate was synthesized from anhydrous hydrazine and picric acid. The thermal analysis of TG-DTG and DSC show that the thermal decomposition process of anhydrous hydrazine picrate mainly occurs between 179.8-200.9$^\circ C$. The decomposition process is an exothermic reaction, and the melting point is about 140$^\circ C$.

(2) The kinetics of thermal decomposition of hydrazine picrate without water was studied by using non-isothermal DSC curves at different temperature rising rates. The activation energy $E$ is 146.76kJ/mol and the pre-finger factor $lnA$ is $30.34/s^{-1}$ calculated by the Equation of Kissinger. The critical thermal explosion temperature $T_s$ value is $175.3^\circ C$.

(3) As a new energy-containing ionic salt, anhydrous hydrazine picrate has the advantages of simple synthesis process, rapid reaction and high yield. Its synthesis not only provides a new research direction for solving the problem of waste treatment and reuse of anhydrous hydrazine, but also lays a certain foundation for its application in the field of explosives.

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