Investigation on the thermal stability of nitroguanidine by TG/DSC-MS-FTIR and multivariate non-linear regression

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Abstract Thermal behavior of nitroguanidine (NQ) has been investigated by TG/DSC-MS-FTIR simultaneous analysis performed under both isothermal and nonisothermal conditions. The isothermal test at 230 °C indicated that the release of gas products can be divided into several stages. The processing of the non-isothermal data, namely 5, 10, 15, and 20 K/min, was performed by using Netzsch Thermokinetics. The dependence of the activation energy evaluated by Friedman's isoconversional method on the conversion degree shows that the investigated process is complex one, and can be divided into three parts. The mechanism of the process and the corresponding kinetic parameters were determined by Multivariate Non-linear Regression Program. The kinetic results was used to simulate the thermal decomposition of NQ under isothermal condition at 210 °C. The simulated curve is in agreement with the tested curve. The obtained results were also used for prediction of the thermal lifetime of NQ corresponding to a certain temperature.

Keywords Explosives · Nitroguanidine · Thermal decomposition · Multivariate non-linear regression

Introduction

Nitroguanidine (NQ) is a white needle crystal, often used as propellants and explosives charge component [1–3]. At present, nitroguanidine as a gas producing component is widely applied to the air bag system in the motor vehicle or

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aircraft [4]. Several articles have been published about the mechanism of their decomposition [5–13] but some uncertainty still exists about the nature of reactions.

Because there is just one step on the TG curve for NQ decomposition, many investigators treat the reaction as one single reaction and calculate the kinetic parameters [5–8]. Our initial tests on the stability of NQ by isothermal method at 230 °C with a combined TG/DSC-QMS indicate one different and prominent observation: The release of gas products are not simultaneous, but can be divided into several parts.

In this article, the NQ will be studied under isothermal and nonisothermal methods by combined TG/DSC-QMS-FTIR, and the kinetic parameters will be calculated by multivariate non-linear regression. The object is to gain insight into the decomposition process as well as evaluate the thermal stability.

Experimental

Material

Nitroguanidine (NQ) was of analytical grade, made by Wuhan Huayuan Xin Technology Development Co., Ltd. The average particle size was 0.3–2 mm.

Thermal analysis method

All the tests were performed on a NETZSCH STA449C (DSC/TG), NETESCH-QMS403C, and NICOLET6700 FTIR coupling system. The thermal decomposition process was monitored by MS and FTIR on-line. This system can provide not only the thermal analysis data but also the information of the evolution of gases. The evolution of

gases could provide information on the chemical reactions occurring during thermal decomposition. The system provides outstanding performances: high detection sensitivity, high reproducibility and stability, and excellent resolution of closely overlapping decomposition steps.

All samples were placed in alumina crucibles. Experiments were performed using sample mass of 1 ± 0.2 mg. High-purity nitrogen was used as purge gas with a gas flow rate 20 mL/min. NETESCH-QMS403C conditions: ionizing electron energy of 70 eV, quartz capillary gas connector, pressure injection 1,000 mbar, and capillary temperature 200 °C. NICOLET6700 FTIR conditions: resolution of 4 cm^{-1}, the gas cell and the gas tube between the TG/DSC and the FTIR stay at 200 °C.

The tests were performed under isothermal conditions at 210 and 230 °C by TG/DSC-QMS, and non-isothermal conditions with constant heating rates of 5, 10, 15, and 20 K/min by TG/DSC-QMS-FTIR. Isothermal conditions: The sample was heated at a rate of 20 K/min from the starting temperature 30 to 200 °C, then heated at 5 K/min to 210 °C, and stayed at 210 °C for 30 min. The sample was heated at a rate of 20 K/min from the starting temperature 30 to 220 °C, then heated at 2 K/min to 230 °C, and stayed at 230 °C for 30 min. The solid residue under isothermal condition at 230 °C is detected by FTIR.

Processing of the experimental data

"Netzsch Thermokinetics-A Software Module for the Kinetic Analysis of Thermal Measurements" was used for processing of non-isothermal data. The basic concepts of this program have been given in [14].

The isoconversional differential method suggested by Friedman [15] (FR method) was applied for evaluation of the dependence of the activation energy on the conversion degree. The complex mechanism of the investigated process and the corresponding kinetic parameters were evaluated using "Multivariate Non-linear Regression" program.

The non-linear multivariate regression is an indispensable method to derive kinetic models. This technique is the only way to decide between different reaction models and get a global model which gives reliable results for the whole parameter range [16]. Multiple nonlinear regression has been wildly used to simulate the process of decomposition [17–23].

Thermal analysis results

Isothermal results

Figure 1 represents the mass spectra of the gas products of NQ under isothermal condition at 230 °C. It can be found
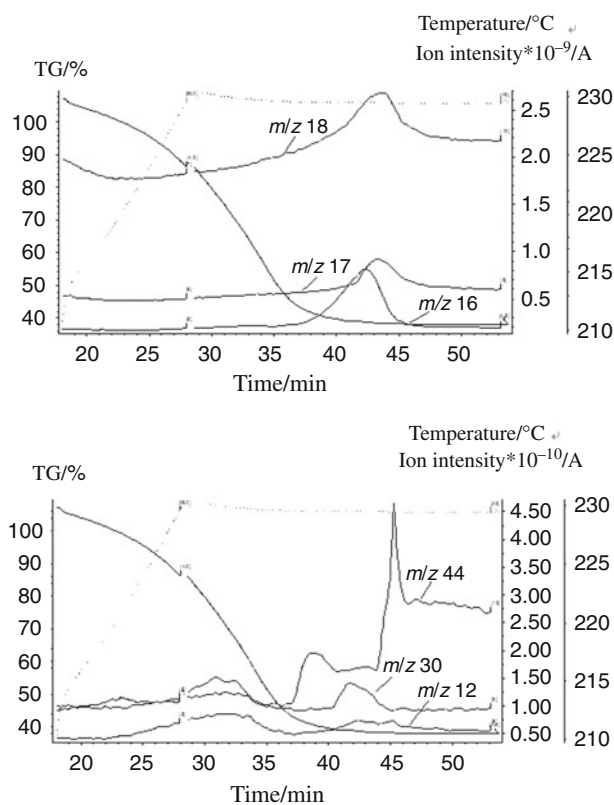

Fig. 1 The MS of the gas products of NQ (230 °C)

obviously that NQ decomposition is not one simple reaction, although there is just one step on the TG curve. The gas products are released into several stages. From 20 to 35 min, the gas products of m/z 12 (C^+), 18 (H_2O^+), 30 (NO^+), and 44 (CO_2^+, N_2O^+) are released first. After that m/z 12 (C^+), 16 (NH_2^+), and 18 (H_2O^+) are released between 35 and 45 min. The m/z 17 (NH_3^+) and 30 (NO^+) are released between 40 and 45 min. The m/z 44 (CO_2^+, N_2O^+) is released between 35 and 40 min, and between 45 and 47 min. The solid residue under isothermal condition at 230 °C is also detected by FTIR. The melamine is found in the solid residue. The ammeline, ammelide, and cyanuric acid are not found in the solid residue.

Nonisothermal results

Figure 2 represents TG/DSC curves of NQ at different heating rates (5, 10, 15 and 20 K/min). The curves show that the non-isothermal decomposition of NQ occurs in one step. The mass loss starts at about 240 °C and ends with mass loss of about 75%. The DSC curves show an endothermic peak for the melting and an exothermic peak for the decomposition.

From Fig. 2 it can be found that NQ decomposes slowly before melting at 5, 10, 15, and 20 K/min. With the increasing of the heating rate the initial temperature, peak
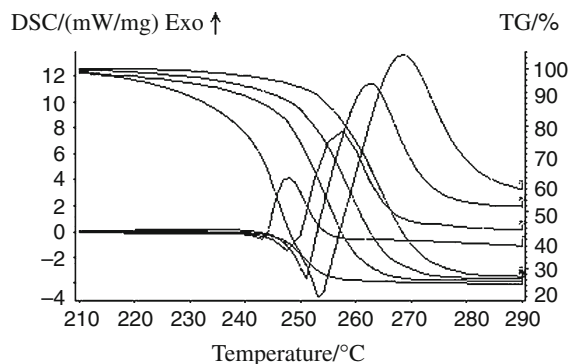
Fig. 2 TG-DSC curves of NQ at different heating rates (5, 10, 15 and 20 K/min)

temperature and the end temperature are shifted to the high temperature. The corresponding melting point, melting enthalpy, and decomposition enthalpy all increase. So in larger heating rate the decomposition reaction of NQ will be pushed into higher temperature zone at a faster reaction speed.

Figure 3 represents the mass spectra of the gas products of NQ at 10 K/min. It can be found that the m/z 12, 15, 16, 17, 18, 20, 27, 30, 44, and 46 are detected. Figure 4 represents the FTIR spectra of gas products of NQ at 10 K/min. Comparing the two figures, it is certain that there are N_2O (2,238 cm^{-1}) which is the main gas products, CO (2,176 cm^{-1}), CO_2 (2,368 cm^{-1}), NO_2 (1,658–1,549 cm^{-1}), and NH_3, and almost no NO (1,965–1,762 cm^{-1}). The content of NO_2 is seldom. The reason is the NO_2 reacts with other pyrolysis gas products. So NO_2 is seldom.

Kinetic calculation analysis

Multivariate non-linear regression

The model-free Friedman analysis was used to gain first insight into the reaction process. The nonisothermal data at 5, 10, 15, and 20 K/min were used to calculate the activation energy. The result is showed in Fig. 5. It yields strong variations of the apparent activation energy with the Conversion. The apparent activation energy shows three peaks with the conversion. The first peak is from 0 to 54%, the max value is 215 kJ/mol. The second peak is from 54 to 68%, the max value is 137 kJ/mol. The third peak is from 68% to the end, the max value is 146 kJ/mol.

The dependence of E on α shows that the process is complex one. In order to find the mechanism and the corresponding kinetic parameters, we have been used Netzsch Thermokinetics program. The non-isothermal data recorded at the four mentioned heating rates were
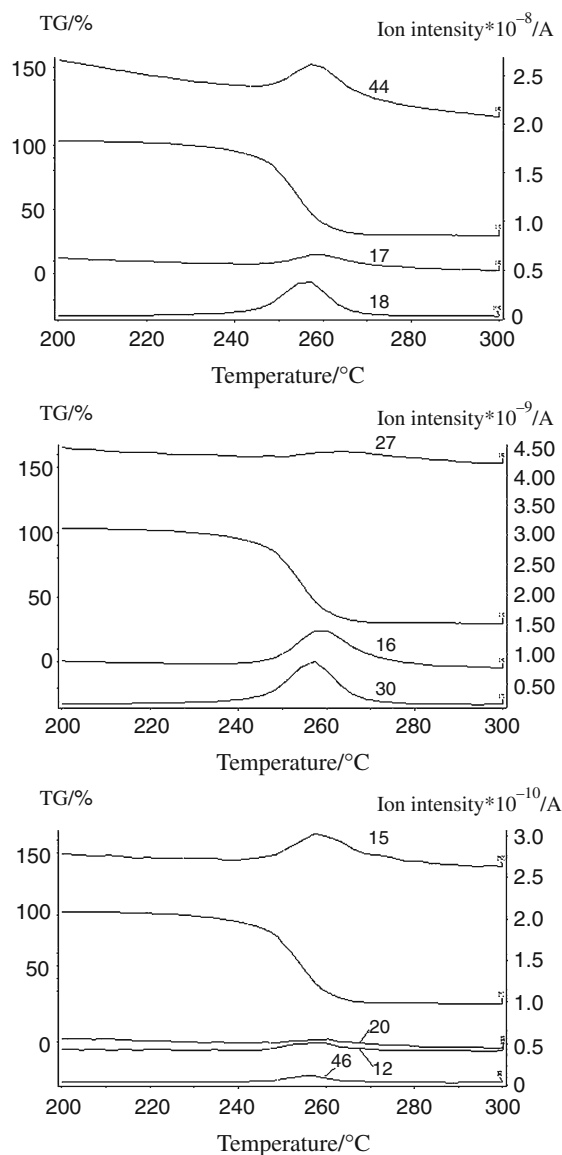

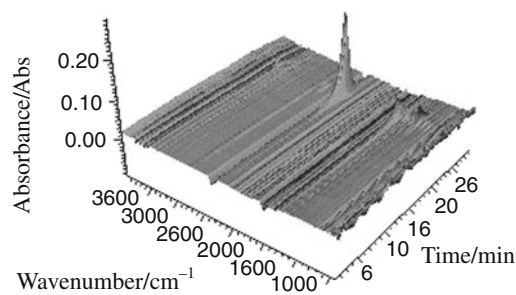**Fig. 3** The MS of the gas products of NQ (10 K/min)

Fig. 4 The FTIR spectra of gas products of NQ (10 K/min)

processed, and some statistical criteria, especially Correlation coefficient, were applied to decide whether the kinetic model can fit the data well.
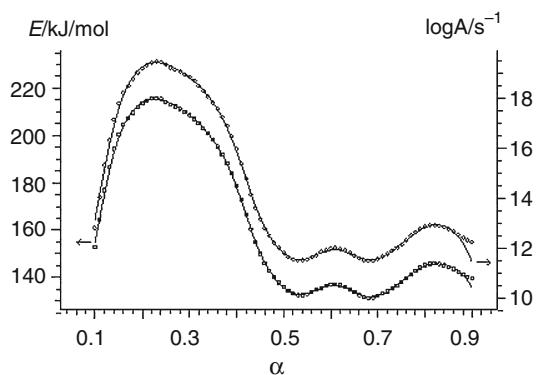
Fig. 5 The apparent activation energy at different extent of conversion of NQ calculated by model-free Friedman analysis
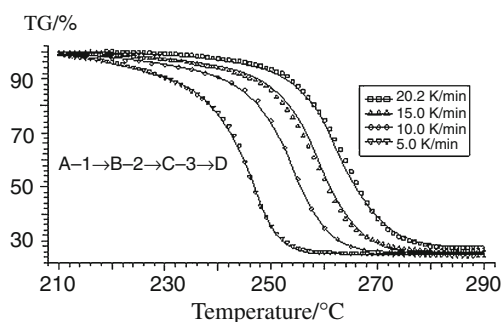

Fig. 6 Global model for the decomposition of NQ β = 5, 10, 15, and 20 °C/min

Since the gas release of NQ at 230 °C can be divided into three sections, and the dependence of E on α calculated by model-free Friedman analysis also shows three peaks. The model (mechanism) $A \xrightarrow{1} B \xrightarrow{2} C \xrightarrow{3} D$ was taken into account (A, B, C, D, and E are solid compounds; 1; 2; 3 denote the mechanism steps). For a single step, one of the following two differential conversion functions (kinetic models) was assumed:

- reaction order model, F_n: $f(\alpha) = (1 - \alpha)^n$ (n is the reaction order);
- nth-order reaction with autocatalysis, C_n: $f(\alpha) = ((1 - \alpha)^n (1 + K_{cat} * \alpha))$ (K_{cat} is the autocatalytic order) (The details is given in [24]).

The best fit is shown in Fig. 6, for the kinetic parameters see Table 1. The correlation coefficient here is 0.9996.

Figure 6 shows that the kinetic model fits the non-isothermal data well. There must be three consistent steps

during the process. The first reaction step F_n has activation energy 225 kJ/mol, log A_1 20.7, and a reaction order of 0.2. The second step F_n has activation energy 107 kJ/mol, log A_2 9, and a reaction order of 0.9. The third step C_n has activation energy 204 kJ/mol, log A_3 20, log K_{cat3} 0.6, and a reaction order of 0.6. This step is supposed to be accelerated by ammonia. The authors agree with Zukas [8] on this point.

In order to check the mechanism and corresponding kinetic parameters resulting from nonisothermal data, the prediction of the thermal stability of NQ at 210 was simulated under the kinetic model by "Netzsch Thermokinetics". The thermal analysis of NQ was also performed in isothermal program for $T = 210$ °C.

Thermal stability of NQ at low temperatures

The global kinetic model for decomposition from this study should allow a much more reliable prediction of the thermal stability of NQ at low temperatures. For testing the quality of fit results, the reaction of NQ under isothermal conditions at a temperature of 210 °C has been simulated with our model for a total exposition time of 30 min. At the same time the NQ sample was also tested at the same condition. The results were showed in Fig. 7. It can be found that, the simulated curve is basically consistent with the tested curve. So our kinetic model can describe the reaction well.

For the prediction of time-dependent stability of NQ at low temperatures, isothermal simulations of the total mass loss between 150 and 210 °C were performed. The results are shown in Fig. 8 for a total exposition time of 12 h. It
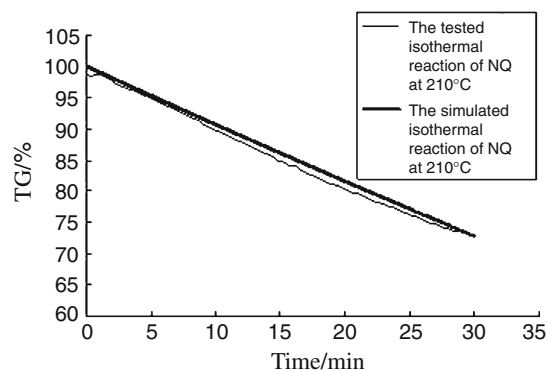

Fig. 7 The tested and simulated isothermal reaction of NQ at 210 °C

Table 1 Kinetic parameters of the decomposition of NQ calculated by multivariate non-linear regression

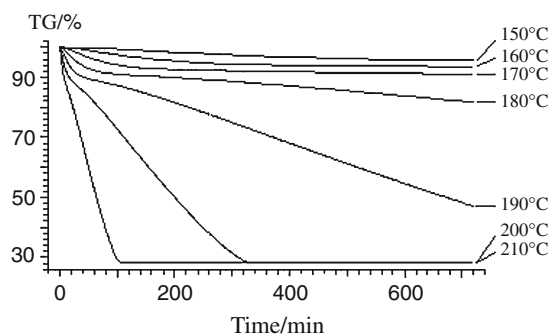| $A \xrightarrow{1} B$			$B \xrightarrow{2} C$			$C \xrightarrow{3} D$			
log A_1/S^{-1}	E_1/kJ/mol	n_1	log A_2/S^{-1}	E_2/kJ/mol	n_2	log A_3/S^{-1}	E_3/kJ/mol	n_3	log K_{cat3}
20.7	225	0.2	9	107	0.9	20	204	0.6	0.6

Fig. 8 The simulated total mass loss under isothermal condition

can be observed that before 170 °C the reaction just raises to 7%, after 170 °C it shifts rapidly to much more.

Conclusions

The stability of NQ by isothermal method at 230 °C indicates that: The release of gas products is not simultaneous, but can be divided into several stages. NQ heated at 5, 10, 15, and 20 K/min show that the main gas products of NQ are N_2O, CO, CO_2, NO_2, and NH_3, and almost no NO. The content of NO_2 is seldom.

The dependence of E calculated by Friedman method on α shows that the process is complex one. It can be divided into three stages. So a three consistent steps kinetic model was proposed to describe the process. This model was also used to simulate the isothermal reaction of NQ at 210 °C. The simulated curve is in agreement with the tested curve. So this kinetic model can describe both isothermal and non-isothermal data well.

The isothermal simulations of the total mass loss at temperatures between 150 and 210 °C were also performed for a total exposition time of 12 h. It can be observed that before 170 °C the reaction just raises to 7%, after 170 °C it shifts rapidly to much more.

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