3-硝基-1,2,4-三唑-5-酮铅金属盐快速热分解反应动力学研究

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摘要：利用温度快速跃升傅立叶变换红外原位分析技术对 3-硝基-1,2,4-三唑-5-酮铅盐的快速热分解反应动力学进行了研究。借助快速升温过程中 Pt 金属丝的控制电压变化曲线得到剧烈放热峰的诱导出现时间 t_x,利用 t_x 值计算得到了快速热分解过程的动力学参数。在 0.1 MPa 氩气气氛,230~270 ℃实验温度范围内,3-硝基-1,2,4-三唑-5-酮铅金属盐的活化能 E_a=94.0 kJ·mol^{-1},ln$A$ =20.5。同时得到了该化合物快速热分解过程的近似吉布斯自由能变,熵变和焓变。该方法借助温度快速跃升技术,在模拟材料实际使用情况下计算得到其动力学参数,可用于含能材料燃烧模型的建立。

关键词：3-硝基-1,2,4-三唑-5-酮；铅金属盐；动力学；温度快速跃升傅立叶变换红外光谱；快速热分解
中图分类号：O643.12；TQ134.3$^+$3　　文献标识码：A　　文章编号：1001-4861(2006)10-1819-04

Kinetics of Exothermic Decomposition Reaction of Flash Pyrolysis of Lead Salt of 3-Nitro-1,2,4-triazol-5-one

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Abstract: Flash pyrolysis of a thin film of lead salt of 3-nitro-1,2,4-triazol-5-one was studied by T-jump/FTIR spectroscopy. The kinetics of the exothermic decomposition reaction was determined by the time-to-exotherm (t_x) value derived from the control voltage traces of the Pt filament. The global Arrhenius activation energy E_a was 94.0 kJ·mol^{-1} and ln$A$ was 20.5 for the flash pyrolysis of this compound at 500~540 K under 0.1 MPa Ar atmosphere. The corresponding Gibbs energy, entropy and enthalpy of the hypothetical activated process of exothermic decomposition reaction for the flash pyrolysis were determined approximately. The values determined herein could be used in evaluation of the thermal stability under rapid heating conditions and could be incorporated into steady combustion modelling.

Key words: 3-nitro-1,2,4-triazol-5-one (NTO); lead salt; kinetics; *T*-jump/FTIR; flash pyrolysis

0　Introduction

NTO (3-nitro-1,2,4-triazol-5-one) can form salts with a large number of metals easily[1~3]. Recently these salts have received extensive attentions due to their potential properties[4~6]. Brill et al observed the formation of one or more volatile Pb(NCO)$_2$ isomers and lead cyanide when characterizing flash pyrolysis for the

lead salt of NTO (Pb(NTO)$_2$·2H$_2$O)[7]. These volatile metal compounds are able to form metal oxide particles that might be useful for controlling the stability of combustion by damping the acoustic modes in such combustion chamber as rocket motor. Kinetic parameters for the exothermic decomposition reaction of energetic materials are of great importance to understand such processes as ignition, combustion, and explosion.

However, relatively little is known about the chemistry at the surface of those processes owing to many parallel, multiphase reactions over a short linear dimension caused by the steep temperature gradient.

T-jump/FTIR spectroscopy [8~11] has been introduced to study flash pyrolysis of many energetic materials for measuring kinetics of the exothermic decomposition reactions[12~14] Thus, the Gibbs energy, entropy and enthalpy of the hypothetical activated process of the exothermic decomposition reaction of flash pyrolysis can be determined approximately. The aim of this work is to study the kinetics parameters, Gibbs energy, entropy and enthalpy of the exothermic decomposition reaction of flash pyrolysis of $Pb(NTO)_2 \cdot 2H_2O$. These data are quite useful in the evaluation of the thermal stability under rapid heating conditions and can be incorporated into models of steady and possibly unsteady combustion.

1 Experimental

1.1 T-jump/FTIR Spectroscopy

The NTO salt was prepared following procedures reported by Zhang Tong-lai[15]. The resulting crystal was dried in vacuum for 24 h and had the formula of $Pb(NTO)_2 \cdot 2H_2O$. Flash pyrolysis was conducted by using the T-jump/FTIR spectroscopy [7]. The IR cell was consisted of two antireflection-coated ZnSe windows with a 3.8 cm path length[16]. ZnSe was used for its good mid-IR throughput and high bursting pressure. The Pt filament was situated along the axis of the cell about 3 mm below the focal point of the IR beam. Approximately 300 μg of sample was thinly spread on the center of the Pt filament; the filament was inserted into the cell and connected to the CDS Analytical Pyroprobe. The cell was purged with Ar gas and pressurized at any desired pressure up to 7 MPa. The filament temperature was calibrated under each pressure using compounds with standard melting points. A pressure of 0.1 MPa was used in the present work. The power supply was set to heat the filament at a chosen rate of about 2 000 K·s⁻¹, but heat transfer effects limited the heating rate to about 800 K·s⁻¹.

The Pt filament was an element of very rapidly responding and sensitive circuit [17]. The difference control voltage trace for the Pt filament qualitatively indicates the sequential thermochemical events of the title compound. An upward deflection indicates an endotherm, whereas a downward deflection marks an exotherm. Under idealized conditions the trace profile could be used quantitatively[18], but normally it is better used as merely the mark of the qualitative occurrence of thermochemical changes.

Infrared spectra of the gas products were recorded simultaneously with the measurement of the filament control voltage. The relative percent concentrations of the gas products were obtained by a procedure based on Lambert-Beer Law and the effective width factors and absolute intensities of non-interfering absorbances[16,19,20]. Brill et al.[7] showed that $Pb(NTO)_2 \cdot 2H_2O$ appeared to produce one or more volatile $Pb(NCO)_2$ isomers and lead cyanide upon flash pyrolysis. $Pb(NTO)_2 \cdot 2H_2O$ violently exploded upon pyrolysis and, in fact, frequently exploded the filament. In addition to CO_2, HCN, NO and H_2O, a large amount of HNCO was formed, suggesting that volatile divalent metal complexes might not entirely possess isocyanate ligands.

1.2 Determination of kinetics of the exothermic decomposition reaction

An exotherm produces a sharp spike in the control voltage trace, which marks the time-to-exotherm (ignition, or explosion) value. The value can not only be employed to outline the chemistry that takes place within the simulated surface reaction zone, but also can be used to determine kinetics of flash pyrolysis of the compound.

$$\ln(1-\alpha) = k(T)t \qquad (1)$$

The rate expression is shown in Eq.**1**[21], where α is the amount of sample decomposed at time t, whose relationship to $k(T)$ is given by the heat balance Eq.**2**, where λ is the thermal diffusivity, C_p is the specific heat capacity; Q is the heat of reaction and can be derived from the DSC measurement.

$$-\lambda \nabla^2 T + \rho C_p(dT/dt) = \rho QA(1-\alpha)e^{-E_a/RT} \qquad (2)$$

It is known that $-\lambda \nabla^2 T = 0$ under adiabatic conditions[22,23]. The time-to-exotherm is equal to the time-to-explosion analyzed by Semenov for a thermal process. Eq.**3** can be used to determine apparent Arrhenius-like kinetics parameters, where t_x is the time-to-exotherm value at temperature T. Values of E_a and $\ln A$ are chosen to give the cumulative decomposition

rate. They do not refer to a specific reaction or event.

$$\ln t_x = E_a / RT - \ln A \tag{3}$$

1.3 Determination of the Gibbs energy, entropy and enthalpy

Substituting values of E_a and $\ln A$ mentioned above into the pyrolysis Eq.4 [24,25], we can have the linear regression rates k at various temperatures T.

$$\ln k = \ln A - \frac{E_a}{RT} \tag{4}$$

Eq.5[24,25] can be used to determine the Gibbs energy $\Delta G^{\neq}$, where R is the gas constant (R=8.314 J·mol⁻¹·K⁻¹), N is Avogadro constant (N=6.024 × 10²³ mol⁻¹), h is Plank constant (h=6.625 × 10⁻³⁴ J·s), k is the linear regression rate at temperature T.

$$\Delta G^{\neq} = RT \ln \frac{RT}{Nhk} \tag{5}$$

The enthalpy $\Delta H^{\neq}$ and entropy $\Delta S^{\neq}$ of the exothermic decomposition reaction can be determined according to Eyring Eq.6 [26], where k_B is Boltzmann constant (k_B=1.380 7 × 10⁻²⁷ J·K⁻¹).

$$\ln\left(\frac{kh}{k_B T}\right) = \frac{\Delta S^{\neq}}{R} - \frac{\Delta H^{\neq}}{RT} \tag{6}$$

2 Results and discussion

The difference control voltage traces of the Pt filament under 0.1 MPa Ar are shown in Fig.1, from which we can get the time-to-exotherm (t_x) values of the flash pyrolysis of Pb(NTO)$_2$·2H$_2$O in the 500~540 K range. The temperature range chosen is 20~60 K above the decomposition temperature measured by differential scanning calorimetry (DSC) and thermogravimetric (TGA)[15]. The t_x is the average value of five identical experiments, the relative standard deviation is not exceeding 1%. The experimental measurements of t_x are then plotted vs 1/T (shown in Fig. 2) to obtain the activation energy E_a and $\ln A$. E_a is 94.0 kJ·mol⁻¹ and $\ln A$ is 20.5 under 0.1 MPa Ar atmosphere, respectively, the correlation coefficient r is 0.993 and the standard deviation (SD) is 0.089.

The value E_a=94.0 kJ·mol⁻¹ determined experimentally here for the exothermic decomposition reaction of flash pyrolysis of Pb(NTO)$_2$·2H$_2$O under 0.1 MPa Ar is much smaller than E_a=270.1 kJ·mol⁻¹ given previ-
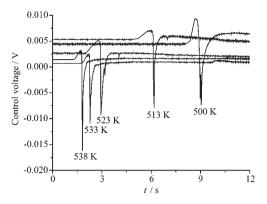

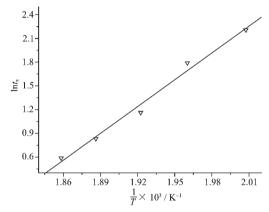Fig.1　Difference control voltage traces of the Pt filament of Pb(NTO)$_2$·2H$_2$O under 0.1 MPa Ar

Fig.2　Arrhenius-type plot for Pb(NTO)$_2$·2H$_2$O under 0.1 MPa Ar

ously by Zhang Tonglai based on Kissinger method[15]. Rate of diffusion, vaporization, nucleation, and reaction, together with the measurement and analysis methods all have their contributions to the Arrhenius kinetics parameters for the surface reaction zone, change in the heating rate can affect the relation between evaporation and decomposition; high heating rate reduces the "cooking" chemistry taken place at low heating rate. Additionally, sample amount of the explosive in the flash pyrolysis experiments is very small and, therefore, thermal explosion is very sensitive to heat losses. This is the main reason for the observed large diference from DSC data. Indeed, the values of E_a are usually small compared to the strength of the weakest bond in energetic molecules and the global Arrhenius kinetics parameters for decomposition of HMX and RDX derived from DSC, TGA and manometry.

The Gibbs energy $\Delta G^{\neq}$ of the hypothetical acti-

vated process of the exothermic decomposition reaction of flash pyrolysis is determined to be around 135 kJ·mol^{-1} in the temperature range. The $\ln(kh/k_B T)$ value plotted vs $1/T$ is shown in Fig.3. The enthalpy $\Delta H^{\neq}$ and entropy $\Delta S^{\neq}$ of the exothermic decomposition reaction are 89.6 kJ·mol^{-1} and 122.9 J·mol^{-1}·K^{-1}, respectively.

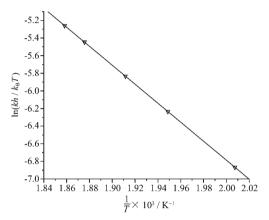
Fig.3　Plot of $\ln(kh/k_B T)$ to $1/T$ for Pb(NTO)$_2$·2H$_2$O under 0.1 MPa Ar

Recently spectroscopy has played an important role in gaining key information how the composition of an energetic material relates to its combustion characteristics. Although the importance that the heterogeneous reaction zone exists in the combustion and explosion for energetic material is recognized, the extremely complex conditions and the thin surface zone make studies very difficult to conduct under these conditions. The T-jump/FTIR spectroscopy enables studies to be conducted under conditions more closely representative of the surface of explosion reaction. By simultaneously recording the control voltage and the rapid-scanned IR spectra of the gas products near the surface zone, one learns considerable details about the chemical mechanism relevant to combustion of an energetic material. The time-to-exotherm (t_x) values derived from the control voltage traces of the Pt filament can be used to determine the global kinetics of the flash pyrolysis. The Gibbs energy, entropy and enthalpy can, thus, be determined. These pyrolysis results determined herein are quite useful in evaluation of the thermal stability under rapid heating conditions and can be incorporated into steady combustion modeling.

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