Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

International Journal of Thermal Sciences 45 (2006) 814–818

International Journal of Thermal Sciences

www.elsevier.com/locate/ijts

Decomposition kinetics of manganese tris (carbohydrazide) perchlorate (MnCP) derived from the filament control voltage of the T-jump/FTIR spectroscopy

Yuan-Hua Sun, Tong-Lai Zhang *, Jian-Guo Zhang, Li Yang, Xiao-Jing Qiao

State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China

Received 27 May 2005; received in revised form 26 October 2005; accepted 26 October 2005

Abstract

By using T-jump/FTIR spectroscopy, a "snapshot" simulation of the surface reaction zone is captured by a thin film of material heated rapidly to temperatures characteristic of the burning surface. Additionally, the Pt filament is highly sensitive to the heat changes and thermochemical reactions of the material, the time-to-exotherm (t_x) kinetics method derived from the control voltage trace of the Pt filament is introduced to determine kinetics of the exothermic decomposition reaction of energetic materials. It yields kinetic parameters of flash pyrolysis of manganese tris (carbohydrazide) perchlorate (MnCP) in the 343–388 °C range at 0.1 MPa Ar atmosphere: $E_s = 87.05\ \mathrm{kJ\,mol^{-1}}$, $\ln A_s = 15.03$. Value of the activation energy determined herein is smaller than that of Kissinger and Ozawa–Doyle method, the T-jump/FTIR spectroscopy might be more representative of the surface of explosion reaction and enable the pyrolysis surface to be incorporated into models of steady and possibly unsteady combustion. The kinetics can also be profitably of great importance to the understanding of the behavior of energetic material in practical combustion problems. Performance study shows that MnCP warrants further in-depth trials for the adoption in detonators and chemically compatible primary explosives.

Keywords: Manganese perchlorate; Carbohydrazide; Kinetics; Thermal decomposition; T-jump/FTIR; Flash pyrolysis

---

1. Introduction

Kinetic parameters for the rapid thermal decomposition of solid energetic materials are of great importance to the understanding of many processes such as ignition, combustion, and explosion. The rates of decomposition are frequently known only in a temperature range where the rates are relatively slow [1–3]. The kinetics is frequently not applicable to the high-temperature regime that exists during combustion and explosion. Consequently, we attempt to measure the kinetic processes of decomposition reaction of energetic materials in the temperature range that more closely resembles surface of the explosives during explosion. The strategy has been to use flash pyrolysis of a thin film of material at a relatively controlled high temperature as a snapshot simulation of the burning surface [4,5]. A reasonably well-defined method for the purpose is T-jump/FTIR spectroscopy, which was described previously in details [6].

One method to determine the kinetics of flash pyrolysis is to measure the rate of liberation of individual gas products by using rapid-scan FTIR spectroscopy. This approach has been applied to flash pyrolysis of nonenergetic polymers by T-jump/FTIR spectroscopy [7,8]. For energetic materials, this kinetics method can also be employed [4], but the concentration fluctuation of the gas products makes it difficult to measure the liberation rate accurately. Additionally, characteristics of the control voltage trace of the Pt filament, which highly senses the thermochemical changes of the condensed phase, might be used to determine the kinetics. For example, the time-to-exotherm (t_x) values of the film involving the heat release from the condensed phase could be used in conjunction with the theory of thermal explosion to determine global kinetics and this method was recently applied to several energetic materials [9,10], terms of "activation energy", "pre-exponential factor" are retained but

---

* Corresponding author. Tel.: +86 10 68913818; fax: +86 10 68912158.
E-mail address: ztlbit@bit.edu.cn (T.-L. Zhang).

1290-0729/$ – see front matter © 2005 Elsevier SAS. All rights reserved.
doi:10.1016/j.ijthermalsci.2005.10.008

Nomenclature

CHZ	$NH_2NHCONHNH_2$, N,N′-diaminourea
MnCP	manganese tris (carbohydrazide) perchlorate
T-jump/FTIR	temperature jump/Fourier transform infrared spectrum
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

do not necessarily have the same meaning as in homogeneous phase kinetics [4,11]. The rate of heat transfer between the sample and the filament appears to be fast enough to allow the heat release of sample to be extracted from the change of the control voltage of the Pt filament in T-jump/FTIR spectroscopy. In addition, casting a thin film of sample onto the filament increases the heat transfer coefficient, thus enhances the success of the kinetics experiment.

Manganese tris (carbohydrazide) perchlorate (MnCP) is an energetic material, which decomposes at rapid but controllable rate. Flash pyrolysis of MnCP liberates 12 IR-active gas products, which has been characterized [12] previously. Herein, the time-to-exotherm (t_x) kinetics method is applied to determine kinetics of flash pyrolysis of MnCP, which enables comparisons to be made among the nonisothermal DSC kinetics methods and T-jump/FTIR spectroscopy.

2. Experimental

2.1. Sample preparation

MnCP was synthesized by mixing the aqueous solution of carbohydrazide and manganese perchlorate [13]. The obtained crystal was purified with distilled water and dried in vacuum at 60 °C for 6 h prior to use.

2.2. T-jump/FTIR spectroscopy

The theory and practice of T-jump/FTIR spectroscopy have been given in details previously [6]. Approximately 200 mg of MnCP is thinly spread on the center of the Pt ribbon filament and inserted into the spectroscopy cell. The cell is purged with Ar gas and pressurized at any desired pressure up to 7 MPa. A pressure of 0.1 MPa was used in present work. Heating occurs at a chosen rate of about $2000\,^{\circ}\mathrm{C\,s^{-1}}$ to a chosen temperature by using the CDS analytical. Although the filament is heated at $2000\,^{\circ}\mathrm{C\,s^{-1}}$, MnCP sample is able to heat approximately $800\,^{\circ}\mathrm{C\,s^{-1}}$ to the set temperature (T_f) actually because of the heat capacity of sample and heat transfer limitations between the sample and filament [14]. T_f can be maintained while the gas products are analyzed by rapid-scan FTIR spectroscopy. The fact that T_f is adjustable enables the products to be determined at selected temperatures including the expected burning surface temperature.

The IR beam was focused about 3 mm above the Pt filament. IR spectra of the gas products were recorded at $4\ \mathrm{cm^{-1}}$ resolution, 0.25 s intervals on a Nicolet 20SXB FTIR spectrometer with an MCT detector.

The Pt filament is an element of a very rapidly responding and sensitive bridge circuit. The control voltage of the circuit linearly responds to the Pt resistance during the programmed heating step and maintains a constant resistance once T_f is reached. The temperature of the filament is calibrated and is determined by the resistance as in a Pt thermometer. The control voltage increases or decreases very rapidly to maintain T_f in response to endothermic or exothermic events of the sample. Therefore, monitoring the control voltage as a function of time uncovers these sequential events.

2.3. Determination of the kinetic parameters

$$k(T) = A_s e^{-E_s/RT} \tag{1}$$

Flash pyrolysis leads to amounts of gas, volatile and nonvolatile intermediate products, followed by many time-dependent chemical and physical processes in the condensed phase. Despite the complications, major temperature segments of the decomposition regime follow Arrhenius behavior, Eq. (1). E_s, is the surface activation energy, A_s is the frequency factor, and k is linear regression rates at various surface temperatures T:

$$\ln(1-\alpha) = k(T)t \tag{2}$$

It is widely agreed that the overall process is modeled by a first-order rate expression [15,16] (Eq. (2)), where α is the amount of sample decomposed at time t. Attempts to measure $k(T)$ are usually made under adiabatic or isothermal conditions whose relationship to $k(T)$ for a first-order process is given by the heat balance Eq. (3) [17]. λ is the thermal diffusivity, C_p is the specific heat capacity, Q is the heat of reaction and can be derived from DSC measurement. The first term of Eq. (3) accounts for heat loss to the surroundings, the second term is the heat accumulated by the explosive. The sum of these two terms equals the heat generated by the thermal decomposition:

$$-\lambda\nabla^2 T + \rho C_p(\mathrm{d}T/\mathrm{d}t) = \rho Q A(1-\alpha)e^{-E_a/RT} \tag{3}$$

Eq. (3) cannot be solved under nonisothermal, nonadiabatic conditions. Under adiabatic conditions ($\lambda\nabla^2 T = 0$), such as time-to-explosion or time-to-exotherm experiments [15,18], the activation energy can be calculated from Eq. (4), where t_x is the time-to-exotherm value at temperature T. Under isothermal conditions ($\mathrm{d}T/\mathrm{d}t = 0$ in Eq. (3)), such as is achieved by evolved gas products and DSC methods, Arrhenius constants are obtained from Eq. (1). The intercept, γ, is not the conventional Arrhenius preexponential factor A, but is assumed to be about $-\ln A_s$ [19]. Values of E_s and $\ln A_s$ are chosen to give the cumulative decomposition rate. They do not refer to a specific reaction or event:

$$\ln t_x = (E_s/RT_s) + \gamma \tag{4}$$

2.4. Sensitivity characterization

The impact sensitivity was determined on impact machine using drop weight test method (0.8 kg drop weight) according to Bruceton Staircase approach. The results were reported in terms of height of 50% probability of explosion ($h_{50\%}$). The friction sensitivity was determined on CGY-1 type friction machine (made in China); the load was increased in increments till there was no explosion/ignition in five consecutive experiments.

2.5. Performance evaluation

350 mg MnCP was placed in the standard detonator No. 27 tube and pressed at 7 MPa with dwell time of 45 s gently. 20 cm length safety fuse was inserted into the tubular detonator touching the MnCP layer and crimped softly. The humidity (RH $< 55\%$) was ensured in the process room throughout filling operation. The MnCP-filled tubular detonator was vertically held on a 3 mm lead plate and the safety fuse was initiated by the safety match.

3. Results and discussion

Fig. 1 shows IR spectra of the gas products when MnCP is heated at 0.1 MPa Ar to the temperature given, these IR modes are assigned to the corresponding molecules based on close match of the frequencies. It can be seen that CO_2 and H_2O are the two major gas products, content of other gas products such as CO, HCN and so on is slightish. MnCP appears to produce volatile metal carbonate upon flash pyrolysis in view of 1200–1000 cm^{-1} absorption peak, occurrence of volatile metal-containing compounds raises the possibility that subsequent reactions in the gas phase might produce small particles, which dampen high-frequency acoustic oscillations in the combustor. It suggests that MnCP may be used for detonator applications. Additionally, both temperature and pressure have effect on flash pyrolysis of most energetic materials, so the species and concentration-time change curves of the gas products change under different experimental conditions to a certain extent [12].

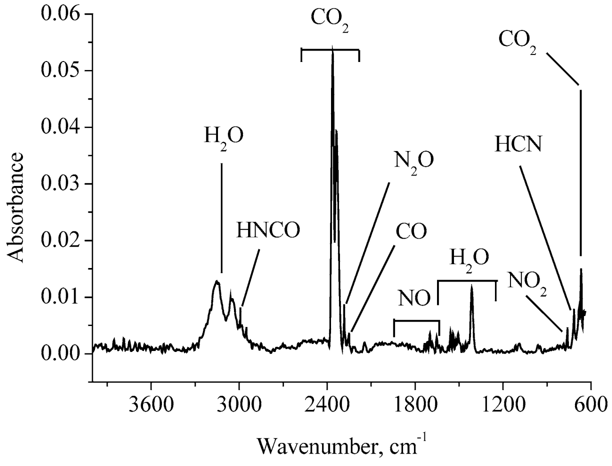

Fig. 1. IR spectrum of the gas products from flash heating of MnCP to 358 °C under 0.1 MPa Ar.

Typical control voltage traces of the Pt filament under 0.1 MPa Ar are shown in Fig. 2. The temperature 343–388 °C range chosen is about 60–100 °C above the decomposition temperature measured by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) methods [13]. The time before detection of the release of heat is determined primarily by the rate of heat buildup in the sample as opposed to the rate of heat transfer to the filament sensor. An exotherm process produces a sharp spike in the control voltage trace, which marks the time-to-exotherm (runaway reaction, ignition, or explosion), thus we can get the t_x values (t_x is the time to the maximum of the spike) of flash pyrolysis of MnCP at different temperatures. t_x is the average value of five identical experiments, the relative error is not exceeding 1.0%.

The experimental measurements of t_x were then plotted versus $1/T$ (shown in Fig. 3) to obtain the surface activation energy E_s and $\ln A_s$, which yield $E_s = 87.05\ \text{kJ mol}^{-1}$ and $\ln A_s = 15.03$ respectively, the correlation coefficient R is 0.994 and the root-mean-square deviation SD is 0.057.

$E_s = 87.05\ \text{kJ mol}^{-1}$ determined experimentally here for the exothermic decomposition reaction of flash pyrolysis of

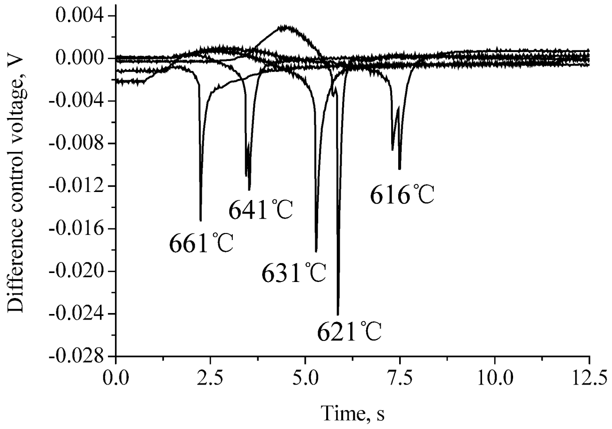

Fig. 2. Difference control voltage traces of the Pt filament of flash pyrolysis of MnCP under 0.1 MPa Ar.

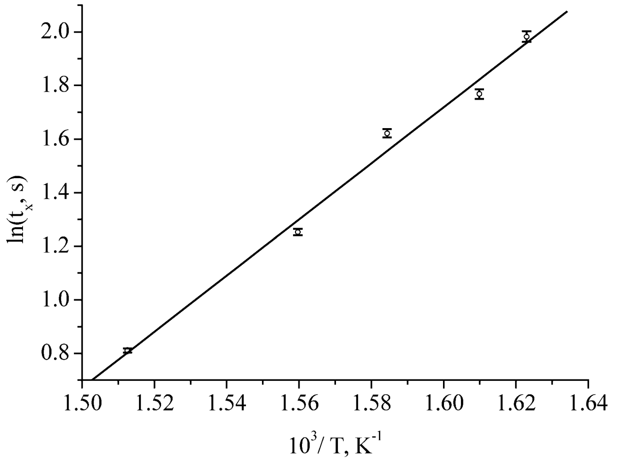

Fig. 3. The Arrhenius surface activation energy E_s determined by the t_x values.

MnCP under 0.1 MPa Ar by using T-jump/FTIR spectroscopy is much smaller than $E_a = 180.4\ \text{kJ mol}^{-1}$ given previously by Kissinger method [13] ($E_a = 180.2\ \text{kJ mol}^{-1}$ given by Ozawa–Doyle method [13]). This trend is also observed with many other energetic materials such as HMX and RDX [20]. Rate of diffusion, vaporization, nucleation, and reaction, together with the measurement and analysis methods all contribute to the Arrhenius parameters for the surface reaction zone [11]. Change in the heating rate can affect the relation between evaporation and decomposition, high heating rate reduces the "cooking" chemistry that takes place at low heating rate. Additionally, sample of the explosive in the flash pyrolysis experiments is very small and, therefore, the thermal explosion is very sensitive to heat losses. This is the main reason for the observed strong difference from data of DSC experiments. The kinetics determined in this article should enable the surface pyrolysis to be incorporated into steady combustion modelling.

In fact, starting with Merzhanov and Dubovitskii [21], a number of authors [22,23] have shown that r^2 is related to the Arrhenius parameters of bulk-phase chemical decomposition. Eq. (5) shows this relationship for many propellants, where T_0, d and C_p are the initial temperature, thermal diffusivity, and specific heat of the propellant, respectively. Q is the heat released in the surface layer. According to Eq. (1) and (5), $E_s < E_a$:

$$r^2 = \frac{\mathrm{d}RT_s^2 A e^{-E_a/RT_s}}{E_a(T_s - T_0 - Q/2C_p)} \tag{5}$$

Indeed, the values of E_s are usually small compared to the strength of the weakest bond in energetic molecules and the global Arrhenius parameters for decomposition of HMX and RDX [23] that are derived from DSC, TGA and manometry. $\ln A_s = 15.05$ determined herein by using T-jump/FTIR spectroscopy is almost of the same value with that $\ln A = 15.21$ reported for MnCP derived from DSC method [12].

Sensitivity results show that MnCP is friction insensitive up to 1 kg. Impact sensitivity test data reveal $h_{50\%}$ of the low value of 28 cm. It suggests the overall safe nature of MnCP for the detonator applications compared with such energetic materials as HMX and lead azide [24]. The initiation of explosives by the impact and friction stimuli is a complex phenomenon, and depends on the molecular structure, crystal hardness, shape and size as well as on thermal conductivity.

The performance evaluation of the filled detonators bring out that the extent of damage is comparable to the damage caused by the standard detonator containing azide, styphynate and aluminium metal composition. The occurrence of volatile metal-containing compounds raises the possibility that subsequent reactions in the gas phase might produce small particles, which dampen high-frequency acoustic oscillations in the combustor; it suggests that MnCP may be used for detonator applications. Additionally, flash pyrolysis of MnCP produces large amounts of CO_2 and H_2O, only a small amount of toxic and oxidative-reductive gas products produces, it warrants further in-depth trials for the adoption in detonators and chemically compatible primary explosives.

4. Conclusions

By simultaneously recording the control voltage trace and the rapid-scan IR spectra of the gas products near the surface zone, one learns considerable detail about the chemical mechanism relevant to combustion of energetic material by using T-jump/FTIR spectroscopy. MnCP appears to produce volatile metal carbonate and large amounts of CO_2 and H_2O upon flash pyrolysis. Kinetic parameters can also be obtained from the time-to-exotherm (t_x) values of the control voltage trace of T-jump/FTIR spectroscopy. The resultant surface activation energy of $E_s = 87.05\ \text{kJ mol}^{-1}$ herein is smaller than that given previously by DSC method.

T-jump/FTIR spectroscopy is the most promising approach to gaining key information about how the composition of an energetic material relates to its combustion characteristics. This can, thus, be used profitably to understand the behavior of bulk energetic materials in practical combustion problems, such as energy production, propulsion, and explosion. The kinetics determined by using T-jump/FTIR spectroscopy should enable the surface flash pyrolysis to be incorporated into models of steady and possibly unsteady combustion.

Acknowledgements

We greatly acknowledge the Nature Science foundations of China (NSFC 20471008) and our university basic research foundations (BIT-UBF- 200302B01) for their financial supports on this work.

References

[1] W.N. Zhang, Y.H. Yuan, L.Q. Li, D.H. Cheng, A description of thermal decomposition kinetics of dehydration of zinc oxalate dihydrate, Acta Phys. – Chim. Sin. 20 (2004) 33–37.

[2] F. Xu, L.X. Sun, Z.C. Tan, J.G. Liang, D.H. Zhou, Y.Y. Di, X.Z. Lan, T. Zhang, Studies on thermal decomposition mechanism and kinetics of Aspirin, Acta Phys. – Chim. Sin. 20 (2004) 50–54.

[3] R.Z. Hu, J.R. Song, F.Q. Zhao, B.Z. Wang, S.L. Gao, C.H. Zhu, P. Chen, Y. Luo, B.K. Ning, S.P. Chen, Q.Z. Shi, Kinetic study on the exothermic decomposition reaction of 2,4,6,8-tetranitro-2,4,6,8-tetraazabicyclo[3,3,1]onan-3,7-dione, Chin. J. Chem. 22 (2004) 1083–1086.

[4] T.B. Brill, H. Arisawa, P.J. Brush, P.E. Gongwer, G.K. Williams, Surface chemistry of burning explosives and propellants, J. Phys. Chem. 99 (1995) 1384–1392.

[5] T.B. Brill, K.J. James, Kinetics and mechanisms of thermal decomposition of nitroaromatic explosives, Chem. Rev. 93 (1993) 2667–2692.

[6] T.B. Brill, P.J. Brush, J.E. Shepherd, K.J. Pfeiffer, T-jump/FT-IR spectroscopy: A new entry into the rapid, isothermal pyrolysis chemistry of solids and liquids, Appl. Spectrosc. 46 (1992) 900–911.

[7] P.E. Gongwer, H. Arisawa, T.B. Brill, Kinetics and products from flash pyrolysis of cellulose acetate butyrate (CAB) at 460–600 °C, Combust. Flame 109 (1997) 370–381.

[8] H. Arisawa, T.B. Brill, Thermal decomposition of energetic materials 71: Structure decomposition and kinetic relationships in flash pyrolysis of glycidyl azide polymer (GAP), Combust. Flame 112 (1998) 533–544.

[9] G.K. Williams, T.B. Brill, Thermal decomposition of energetic materials 68. Decomposition and sublimation kinetics of NTO and evaluation of prior kinetic data, J. Phys. Chem. 99 (1995) 12536–12539.

[10] G.K. Williams, T.B. Brill, Thermal decomposition of energetic materials 67. Hydrazinium nitroformate (HNF) rates and pathways under combustion like conditions, Combust. Flame 102 (1995) 418–426.

[11] J.K. Chen, T.B. Brill, Thermal decomposition of energetic materials 50. Kinetics and mechanism of nitrate ester polymers at high heating rates by SMATCH/FTIR spectroscopy, Combust. Flame 85 (1991) 479–488.

[12] Y.H. Sun, T.L. Zhang, J.G. Zhang, The Flash Pyrolysis of $[Mn(CHZ)_3](ClO_4)_2$ (MnCP),$[Ni(CHZ)_3](ClO_4)_2$ (NiCP) and $[Pb(CHZ)_3](ClO_4)_2$ (PbCP) by T-jump/FTIR Spectroscopy, Chin. J. Inorg. Chem. 21 (2005) 113–116.

[13] C.H. Lu, Researches on Energetic Coordination Compounds with Carbohydrazide Ligand [D], Beijing Institute of Technology, Beijing, 2000.

[14] O.K. Rice, R. Ginell, The theory of the burning of double-base rocket powders, J. Phys. Colloid Chem. 54 (1950) 885–917.

[15] A.J.B. Robertson, The decomposition, boiling and explosion of trinitrotoluene at high temperatures, Trans. Faraday Soc. 48 (1948) 977–1002.

[16] R.M. Guidry, L.P. Davis, Thermochim. Acta 32 (1979) 1–10.

[17] J. Zinn, C.L. Mader, Thermal initiation of explosives, J. Appl. Phys. 31 (1960) 323–332.

[18] J. Zinn, R.N. Rogers, Thermal initiation of explosives, J. Phys. Chem. 66 (1962) 2646–2654.

[19] S.T. Thynell, D.G. Gongwer, T.B. Brill, Condensed phase kinetics of cyclotrimethylenetrini tramine by modeling the T-jump/infrared spectroscopy experiment, J. Propul. Power 12 (1996) 93–98.

[20] T.B. Brill, P.E. Gongwer, G.K. Williams, Thermal decomposition of energetic materials 66. Kinetic compensation effects in HMX, RDX, and NTO, J. Phys. Chem. 98 (1994) 12242–12247.

[21] A.G. Merzhanov, F.I. Dubovitskii, On the theory of steady state monopropellant combustion, Proc. USSR Acad. Sci. 129 (1959) 153–156.

[22] N. Kubota, Combustion mechanisms of nitramines composite propellants, Prog. Astronaut. Aeronaut. 90 (1984) 1–52.

[23] G. Lengelle, Thermal degradation kinetics and surface pyrolysis of vinyl polymers, AIAA J. 8 (1970) 1989–1996.

[24] Y.L. Lao, Chemistry and Technology of Primary Explosive, Beijing Institute of Technology, Beijing, 1997.