doi:10.3969/j.issn.1001-8352.2018.04.001

Thermal Decomposition and Stability of Red Phosphorus Smoke Agent with Different Oxidants*

SHAN Congming, LIU Jie, ZHU Shunguan, ZHANG Lin
School of Chemical Engineering, Nanjing University of Science and Technology (Jiangsu Nanjing, 210094)

[**ABSTRACT**] Thermal behaviors of red phosphorus (RP) and its mixtures with oxidants, such as KNO_3, $Ba(NO_3)_2$, MnO_2, Fe_2O_3, and $KMnO_4$, were studied experimentally using differential thermal analysis (DTA) and thermogravimetry (TG) methods in air atmosphere. Oxidation temperature of RP and decomposition temperatures of oxidants mentioned above were obtained. For the KNO_3 + RP + Teflon, $Ba(NO_3)_2$ + RP + Teflon, MnO_2 + RP + Teflon, Fe_2O_3 + RP + Teflon, and $KMnO_4$ + RP + Teflon pyrotechnic systems, chemical reaction happen within the range of 399.5-469.8 ℃, 445.7-471.6 ℃, 409.8-479.3 ℃, 419.8-466.5 ℃ and 396.2-467.4 ℃, respectively. Self-accelerating decomposition temperature (T_{e0}), critical ignition temperature (T_b), apparent activation energy (E), $\triangle S^{\#}$, $\triangle H^{\#}$, and $\triangle G^{\#}$ of the pyrotechnic mixtures were measured according to DTA-TG experiments. Furthermore, friction sensitivity and property of hygroscopicity of pyrotechnic mixtures were examined. Based on these data, appropriate oxidants in red phosphorus smoke agent, which are $Ba(NO_3)_2$, MnO_2 and Fe_2O_3, can be selected.

[**KEYWORDS**] red phosphorus smoke agent; ignition temperature; kinetic parameters; red phosphorus
[**CLASSIFICATION CODE**] TQ567

赤磷基发烟剂的热分解及稳定性研究

单聪明 刘 杰 朱顺官 张 琳
南京理工大学化工学院(江苏南京,210094)

[**摘 要**] 采用热重-差热(TG-DTA)分析方法在空气气氛中对赤磷(RP)、硝酸钾 KNO_3、硝酸钡 $Ba(NO_3)_2$、二氧化锰 MnO_2、氧化铁 Fe_2O_3、高锰酸钾 $KMnO_4$ 及其混合物的热分解行为进行研究。所得结果如下:赤磷与 KNO_3、$Ba(NO_3)_2$、MnO_2、Fe_2O_3、$KMnO_4$ 构成混合物的反应温度区间分别为 399.5~469.8 ℃、445.7~471.6 ℃、409.8~479.3 ℃、419.8~466.5 ℃、396.2~467.4 ℃。同时,根据不同升温速率下赤磷与不同氧化剂组成的混合物的热分析结果,计算得到各混合物的自加速分解温度(T_{e0}),临界点火温度(T_b)、活化能(E)、活化熵($\triangle S^{\#}$)、活化焓($\triangle H^{\#}$)以及活化吉布斯自由能($\triangle G^{\#}$)等重要参数。另外,对赤磷与不同氧化剂组成混合物的摩擦感度和吸湿性也进行了研究,根据这些结果发现最适合与赤磷组配的氧化剂为 $Ba(NO_3)_2$、MnO_2 和 Fe_2O_3。

[**关键词**] 赤磷发烟剂;点火温度;动力学参数;赤磷

Introduction

As an important ingredient for the manufacture of pyrotechnic smokes, red phosphorus (RP) has been widely used in screening applications where obscuration is achieved in various portions of the electromagnetic spectrum, including the visible range and in several IR bands. It is likely to be in service for many years [1].

In spite of the extensive use of pyrotechnic smokes, delays, signals, incendiaries, only in the last two decades some attentions have been paid to understand and apply the laws of thermodynamics and the principles of solid state chemistry to explain the vagaries of pyrotechnic systems [2-3]. Recent investigations into the parameters affecting the pyrotechnic reactions

* 收稿日期:2018-01-24
作者简介:单聪明(1988-),男,硕士,主要从事火工药剂的性能研究。E-mail:13097363230@163.com
通信作者:朱顺官(1962-),男,研究员,主要从事火工药剂技术和新型爆破器材研究。E-mail:zhusg@mial.njust.edu.cn

showed that the complicated chemical behavior of these reactions in solid state could be attributed to various factors, including the nature of oxidants and fuels, particle size, impurities, and oxidation layers on the surface of fuels[4-6]. However, there is a need for development of appropriate models to take these parameters into account.

However, the thermal stability of RP-based pyrotechnic mixtures is less reported, and also the evaluation methods. In this paper, differential thermal analysis (DTA) coupled with thermogravimetry (TG) method were used to analysis the reaction process and evaluate the stability of pyrothchnic mixture. Thermal analysis is a well-established technique for studying the thermochemical and thermophysical properties of energetic materials in reasonable way[7-8]. This method can reveal the relation between ignition temperature and thermal behavior, which governs the safety of a pyrotechnic mixture . Such thermal analysis methods are useful for substances exhibiting exothermic or endothermic changes when temperature is varied[9-11]. Such studies of pyrotechnic compositions are important not only for understanding the kinetics of their thermal decomposition, but also for assessing the effect of their exothermic decomposition and ignition temperature on potential hazards during handling, usage, and storage. Therefore, to provide information on the sensitivity of igniter compositions to various accidental factors.

In this paper, the thermal behavior and ignition temperature of the following pyrotechnic mixtures were measured: KNO_3 + RP + Teflon, $Ba(NO_3)_2$ + RP + Teflon, MnO_2 + RP + Teflon, Fe_2O_3 + RP + Teflon, and $KMnO_4$ + RP + Teflon. Non-isothermal kinetic analysis was used to estimate Arrhenius parameters of the combustion reactions[12]. This study was focused on the thermoanalytical properties of the individual reactants and the binary pyrotechnic mixtures. Their thermal behavior has been compared for future applications as conventional pyrotechnic mixtures.

Furthermore, friction sensitivity and hygroscopicity of pyrotechnic mixtures, which are important factors to evaluate the stability of pyrotechnic mixtures, were measured. The three parameters (ignition temperature, friction sensitivity and hygroscopicity) are the most important factors for the pyrotechnic mixtures to evaluate the potential hazards during handling, usage, and it storage. And it has the guiding siginificance for the practical application.

1 Experiment

1.1 Materials

Red phosphorus powder with a particle size of about 80-100 mesh was provided by Shanghai Zhanyun Chemical Co., Ltd. (China). KNO_3, $Ba(NO_3)_2$ and Fe_2O_3 were purchased from Sinopharm Chemical Reagent Co., Ltd. with particle size of 120 mesh. MnO_2 (120 mesh) was provided by Shantou Xilong Chemical Factory. $KMnO_4$ (120 mesh) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Teflon with a particle size of 5 μm was purchased from Shanghai 3F New Materials Co., Ltd. All of them were of analytic reagent grade.

1.2 Procedure

1.2.1 Preparation of the ternary mixtures

All chemicals were stored in a vacuum oven at 60 ℃ before being mixed. The ternary mixtures (oxidizer/combustibles/binders) which the total mass of the compositions were 3 g were initially prepared by wet mixing in acetone based on the ratio presented in Tab. 1. After evaporation of the solvent, small quantities of the pyrotechnic mixtures were carefully sieved through a sieve slightly coarser than the particles.

1.2.2 Thermal analysis of the samples

A thermal analysis instrument of HCT-2 was used for TG/DTA studies. Pure compounds and mixtures were separately studied under similar conditions (the heating rate and sample's weight were 10 ℃/min and 2.0 mg, respectively) using TG/DTA thermal analysis instrument in air atmosphere. Thermochemical behavior of pure RP, KNO_3, $Ba(NO_3)_2$, MnO_2, Fe_2O_3, $KMnO_4$ and mixtures of them were characterized according to Tab. 1. The mixtures had the same oxygen balance (OB: −90 g oxygen/100 g sample) except $KMnO_4$ + RP + Teflon pyrotechnic mixture (OB: −108 g oxygen/100 g sample), because it is easy to be ignited. The mass fraction of $KMnO_4$ is 12%, which is much less than the others . DTA experiments were run at the heating rates of 10, 12, 14, and 16 ℃/min from 25 ℃ to 700 ℃ with sample's weight of 2.0 mg

Tab. 1 Summary of experimental results for DTA/TG of pure components and mixtures

No.	Components	Mass fraction/%	Transition temperature[a)]/℃		
			Fusion[b)]	Ignition or decomposition	T^*
1#	RP	100		364.3	364.3-423.3(increase)
2#	KNO_3	100	336.8	500.0	500.0-800.0(decrease)
3#	$Ba(NO_3)_2$	100	598.0	594.2	594.2-695.1(decrease)
4#	MnO_2	100	548.3	537.0	537.0-560.9(decrease)
5#	Fe_2O_3	100	1 565.0		
6#	$KMnO_4$	100		224.3	224.3-298.0(decrease)
7#	KNO_3 + RP + Teflon	20.0,77.0,3.0	354.3	331.2,399.5	331.2-378.3(decrease) 399.5-469.8(increase)
8#	$Ba(NO_3)_2$ + RP + Teflon	21.5,75.5,3.0		445.7	445.7-471.6(increase)
9#	MnO_2 + RP + Teflon	20.5,76.5,3.0		409.8	409.8-479.3(increase)
10#	Fe2O$_3$ + RP + Teflon	22.1,74.9,3.0		419.8	419.8-466.5(increase)
11#	$KMnO_4$ + RP + Teflon	12.0,85.0,3.0		200.0,396.0	200.0-350.0(decrease) 396.2-467.4(increase)

a) Peak temperatures at maximum heat flux. b) Fusion temperatures for the mixtures are given for fuel and oxidants, respectively. T^* is temperature range associated with a variation of sample's weight.

in air atmosphere. All the samples were dried before testing, and the measurements were repeated three times.

1.2.3 Test for friction sensitivity

The combine falling angle swing hammer method was used to measure the friction sensitivity of the pyrotechnic mixtures. There were six different falling angles, 90°, 80°, 70°, 60°, 50°, and 40°, respectively and the corresponding to the pressures were 4.50, 3.50, 2.80, 2.10, 1.50 MPa, and 1.00 MPa. Each combination needed to be tested 20 times. The equation of average ignition ratio was $\bar{P}_i = n_i/20 \times 100\%$, and the cumulative ignition ratio was $P = \sum n/120 \times 100\%$.

1.2.4 Test of hygroscopicity

Five grams RP or pyrotechnic mixtures were placed in a thermo-hygrostatic chamber kept at a constant temperature of 25 ℃ and a relative humidity of 95%. The resulting test sample was weighed to calculate the percentage of increasing weight after 7 days. Relative hygroscopic rate (%) = hygroscopic rate of pyrotechnic mixture/hygroscopic rate of RP ×100%.

2 Results and discussion

2.1 Thermal properties of pure compounds

Fig. 1(a) shows TG and DTA curves for pure compounds. Pure RP powder shows a sharp exothermic peak in 411.6 ℃. At this temperature, the compound reacts with oxygen and TG curves shows considerable increasing in the sample weight (approximately 109.5% in the experimental value and 103.2% in the theoretical value) in temperature range between 364.3-423.3 ℃ because of the produced P_2O_3 and P_2O_5.

$$4P(s) + 4O_2(g) \longrightarrow P_2O_3(s) + P_2O_5(s)。$$

Fig. 1(b) shows the TG/DTA curves of KNO_3 sample used in this study. In alignment with recent reports by Koch[13] and Freeman[14], the endothermic peaks at 139.5 ℃ and 336.8 ℃ correspond to phase transition of rhombic crystalline solid to trigonal structure and melting of KNO_3, respectively. The molten KNO_3 is stable up to 500 ℃ and then decomposition reaction starts at above this temperature, and finishes at about 1 000 ℃, resulting in no solid residue [15]. The result of theoretical mass loss is 53.5%, and the experimental mass loss is 30.2% because of incomplete reaction.

$$4KNO_3(l) \longrightarrow 2K_2O(l) + 6NO(g) + 3O_2(g)。$$

Thermal analysis (DTA/TG) of pure $Ba(NO_3)_2$ indicats that the melting of $Ba(NO_3)_2$ with a strong endothermic peak at 598.0 ℃ [Tab. 1 and Fig. 1(c)], which subsequently decomposed at 652.0 ℃. After complete decomposition of the sample, oxygen, nitrous oxide and barium oxide are produced [16]:

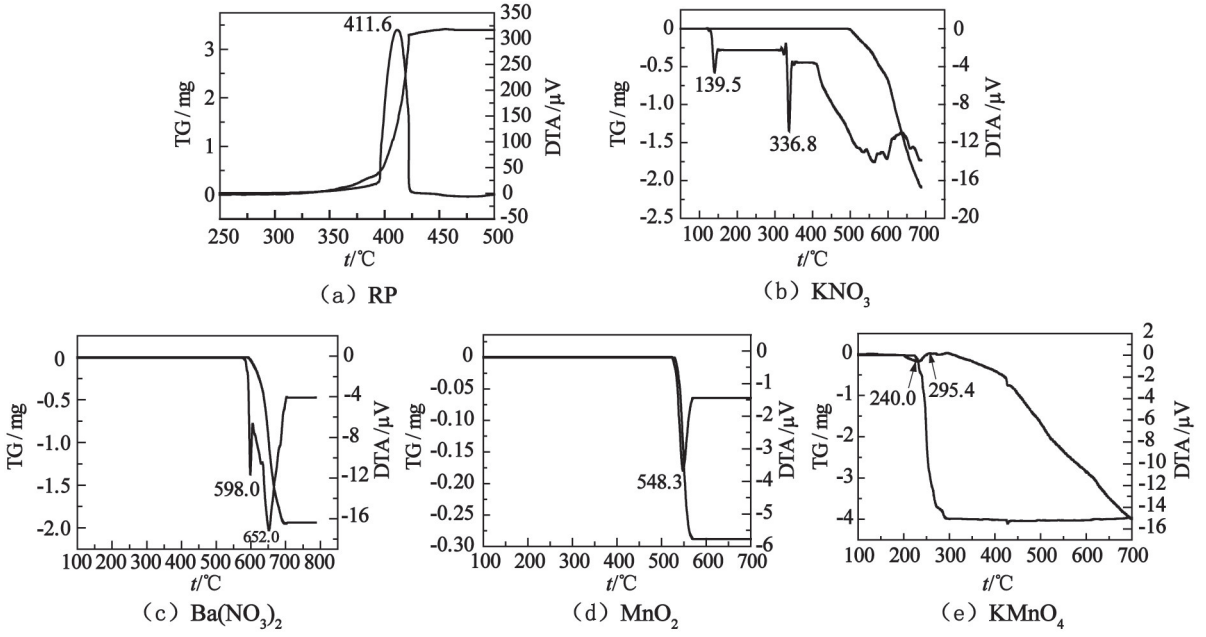

Fig. 1　TG and DTA curves

$$2Ba(NO_3)_2(s) \longrightarrow 2BaO(s) + 4NO(g) + 3O_2(g)。$$

As shown in Fig. 1(d), an endothermic peak at 548.3 ℃ is observed, corresponding to decomposition of MnO_2. The TG curve confirms this result by decreasing 8.7% weight of sample. After complete decomposition of the sample, O_2 and MnO are produced:

$$2MnO_2(s) \longrightarrow 2MnO(s) + O_2(g)。$$

As shown in Fig. 1(e), an endothermic peak at 240 ℃ is observed, corresponding to decomposition of $KMnO_4$. The TG curve confirms this result by decreasing 98.85% weight of sample. After complete decomposition of the sample, O_2, K_2O and MnO_2 are produced:

$$4KMnO_4(s) \longrightarrow 4MnO_2(g) + 2K_2O(g) + 3O_2(g)。$$

2.2　Thermal properties of mixtures

DTA and TG curves of RP and KNO_3 mixture are shown in Fig. 2(a). The DTA curve reveals a weak exothermic peak at 354.3 ℃ with about 3.0% mass loss, which is the decomposition of KNO_3. Up to the decomposition point the DTA curve reveals two exothermic peaks at 436.5℃ and 466.0℃ with about 92.6% mass increase. This is due to the oxidation of RP. And the exothermic peak at 436.5 ℃ is corresponds to the pre-oxidation of RP. As the heating rate increased, the two exothermic peaks combined into an exothermic peak. According to the decomposition reaction equation of KNO_3 and the mass gain (92.6%) of the sample, the complex solid state reaction could be represented as follows:

$$34P(s) + 10KNO_3(s) + 23O_2(g) \longrightarrow 5K_2O(s) + 5P_2O_5(s) + 12P_2O_3(s) + 10NO(g)。$$

Fig. 2(b) shows the DTA and TG curves for the sample containing RP and $Ba(NO_3)_2$. A sharp exothermic phenomenon was observed at 471.2 ℃ with about 102.4% mass increase, which is corresponding to the oxidation of RP by nitrate and air. According to the decomposition reaction equation of $Ba(NO_3)_2$ and the mass gain (102.4%) of the sample, the following reaction equation could represent the complex solid state reaction.

$$84P(s) + 20Ba(NO_3)_2(s) + 53O_2(g) \longrightarrow 20BaO(s) + 20P_2O_5(s) + 22P_2O_3(s) + 40NO(g)。$$

Fig. 2(c) shows DTA and TG curves for the mixture of RP and MnO_2. There are two exothermic peaks (436.3 ℃ and 476.1 ℃) in the DTA curve with about 111.0% mass increase, which is due to the oxidation of RP. The weak exothermic peak at 436.3 ℃ may be the pre-oxidation of RP. As the heating rates increased, the two exothermic peaks combined into an exothermic peak, which can be demonstrated by Fig. 3(e). According to the decomposition reaction equation of MnO_2 and the mass gain (111.0%) of the sample, the reaction is as follows:

$$12P(s) + 4MnO_2(s) + 11O_2(g) \longrightarrow$$

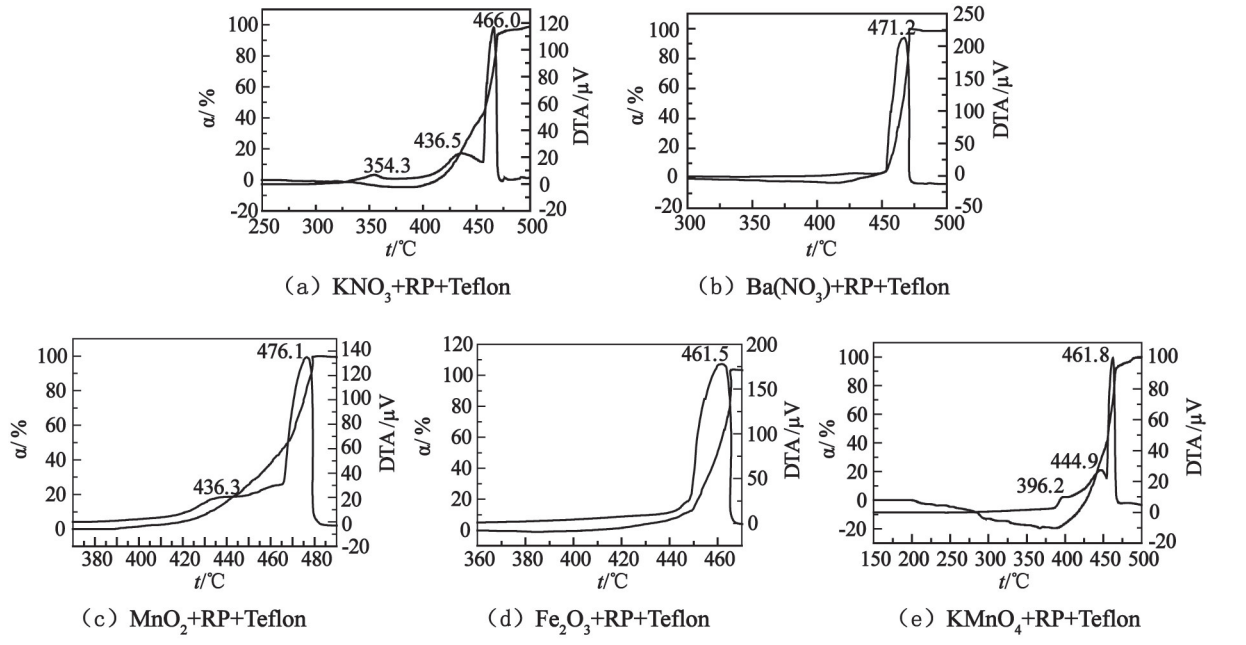

Fig. 2 TG and DTA curves for mixtures

$4P_2O_5(s) + 2P_2O_3(s) + 4MnO(s)$。

Fig. 2(d) shows DTA and TG curves for the mixture of RP and Fe_2O_3. DTA curve of RP/Fe_2O_3 mixture shows a sharp exothermic peak around 461.5 ℃ with 98.9% mass increase due to oxidation of RP. The temperature of exothermic peak for the mixture of RP and Fe_2O_3 is higher than the neat RP, which is due to the Fe_2O_3 makes the oxidation rate of RP slows down. The melting point of Fe_2O_3 is 1 565 ℃, which is so high that the Fe_2O_3 is solid state when the RP is oxidized. And the RP is surrounded by the solid state Fe_2O_3 which slow down the oxidation reaction. According to the mass gain (98.9%) of the mixture, the reaction equation is as follows:

$24P(s) + 23O_2(g) \longrightarrow 5P_2O_5(s) + 7P_2O_3(s)$。

Fig. 2(e) shows the DTA and TG curves for the mixture of RP and $KMnO_4$. In the TG curve, the weight loss (12.4%) at 200-360 ℃ with a slow slope that is corresponds to the releasing of oxygen during decomposition process of $KMnO_4$. After decomposition, the mixtures undergo a sharp exothermic peak around 461.8 ℃ with two week exothermic peaks 396.2 ℃ and 444.9 ℃. And the TG curve shows 80.5% mass increase with the temperature range 396.2-461.8 ℃, which is due to the oxidation of the RP by the permanganate and air. According to the decomposition reaction equation of $KMnO_4$ and the mass gain (80.5%) of the mixture, the reaction equation is as follows:

$$2KMnO_4(s) + 34P(s) + 25O_2(g) \longrightarrow K_2O(s) + P_2O_5(s) + 2MnO_2(s) + 16P_2O_3(s)。$$

2.3 Effect of heating rate

Fig. 3 shows DSC curves for the oxidation of mixtures at several heating rates. The curves demonstrate that as the heating rate increases, the oxidation peaks of mixtures shift to higher temperatures. On the other hand, as shown in Fig. 3, there is an increase in the ignition temperature of each mixture as the heating rate increases.

2.4 Kinetics of thermal ignition

Potential hazards associated with the thermal behavior of energetic materials require that stability evaluation and ignition kinetics were carried out to assure their safe processing, handling, and storage [12, 17]. In this study, kinetic parameters were determined using Ozawa and Kissinger approach [18-19]. The equations are as follows:

Ozawa

$$\lg\beta = \lg\frac{AE}{Rg(\alpha)} - 2.315\,0 - 0.456\,7\frac{E}{RT_i},\quad i = 1,2,3,\cdots,n。 \tag{1}$$

Kissinger

$$\ln\frac{\beta}{T_p^2} = \ln\frac{AR}{E} - \frac{E}{RT_p}。 \tag{2}$$

In the equations: β, heating rate, K/min; A, pre-

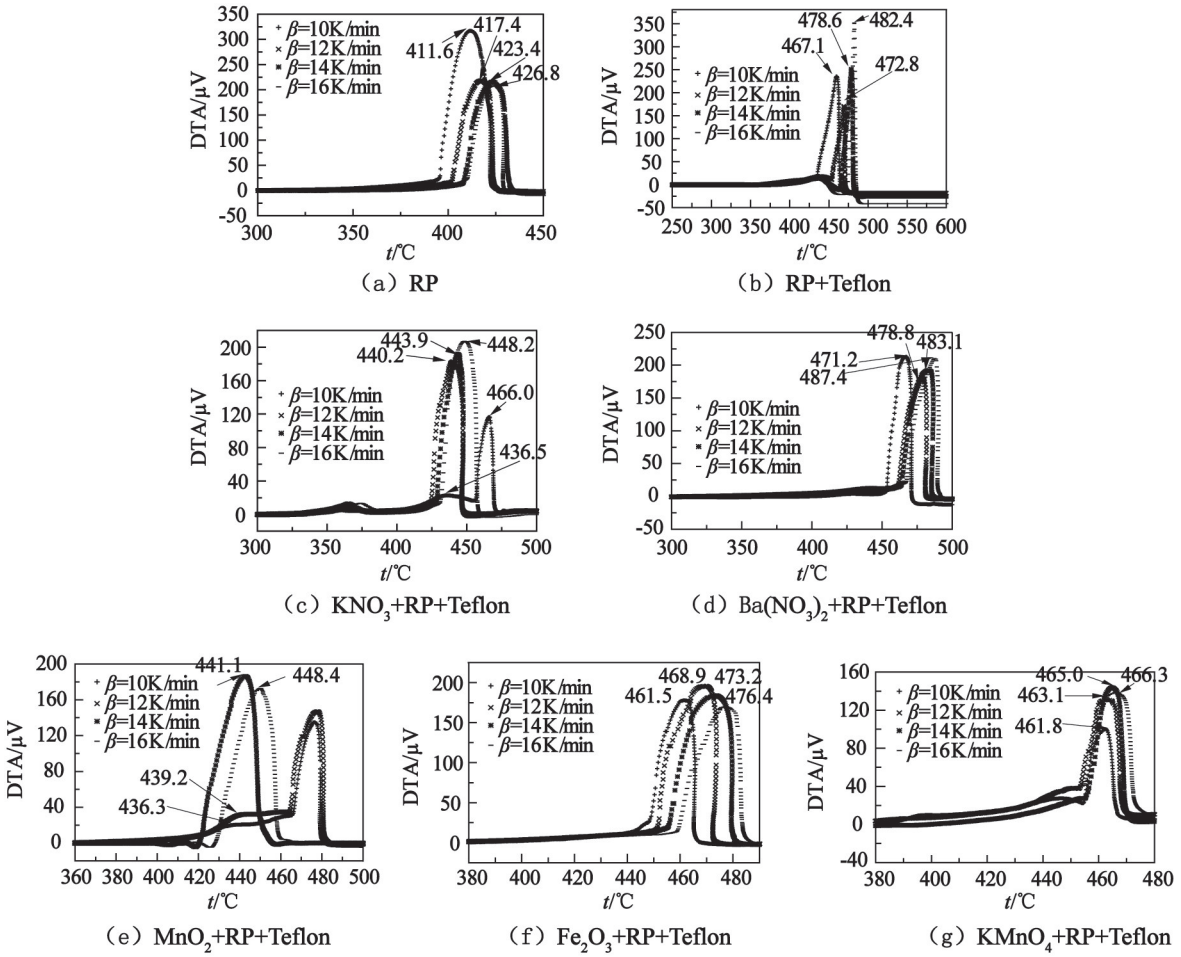

Fig. 3　Effect of heating rate on the DTA curves of thermal ignition

exponential or Arrhenius frequency factor, s^{-1}; E, activation energy, kJ/mol; R, the gas constant, J/(mol·K); T, temperature of the sample, K; α, the degree of conversion.

Based on Ozawa and Kissinger methods, the apparent activation energy (E) could be obtained as the slope of a plot of $\lg\beta$ vs. $1/T_i$ and $\ln(\beta/T_p^2)$ vs. $1/T_p$, in which β and T_p are heating rate and temperature of max peaks of DTA curve, respectively.

On the other hand, the Arrhenius frequency factor (A) was found for all pyrotechnic mixtures from the following relation [20-21]:

$$A = \frac{\beta E e^{\frac{E}{RT_p}}}{RT_p^2}。 \tag{3}$$

The computed activation parameter for all mixtures are given in Tab. 2.

The entropy of activation ($\triangle S^{\#}$), enthalpy of activation ($\triangle H^{\#}$) and free energy of activation ($\triangle G^{\#}$) corresponding to the each mixture obtained by Equation (4)-Equation (6) [22-23]. All resulted data are summarized in Tab. 2.

$$A = \frac{k_B T_{p0}}{h} e^{\frac{\triangle S^{\#}}{R}}; \tag{4}$$

$$\triangle H^{\#} = E_0 - RT_{p0}; \tag{5}$$

$$\triangle G^{\#} = \triangle H^{\#} - T_{p0}\triangle S^{\#}。 \tag{6}$$

In these equations: A, obtained by Equation (3); k_B, Boltzmann constant, $1.380\ 7 \times 10^{-23}$ J/K; h, Plank constant, 6.626×10^{-34} J/s; T_{p0}, the onset temperature corresponding to $\beta \to 0$.

2.5　Critical ignition temperature

The critical ignition temperature (T_b) is an important parameter required to insure safe storage and process operations involving explosives, propellants, and pyrotechnics. It is defined as the highest temperature to which a specific charge may be heated without undergoing thermal runaway [24]. T_b may be calculated from inflammation theory and appropriate thermokinetic parameters namely the activation energy, pre-exponential factor, and heat of reaction. In order to obtain the critical temperature of thermal ignition (T_b)

Tab. 2 Kinetic and thermodynamic parameters of thermal decomposition for pyrotechnic mixtures

Samples	E/(kJ · mol^{-1})				A/	$\triangle G^{\#}$/	$\triangle H^{\#}$/	$\triangle S^{\#}$/
	Ozawa (E_a)	R^2	Kissinger (E_k)	R^2	s^{-1}	(kJ · mol^{-1})	(kJ · mol^{-1})	(J · mol^{-1} · K^{-1})
RP	114.1	0.992 7	108.4	0.991 1	8.7×10^{8}	163.2	106.5	−98.3
KNO_3 + RP + Teflon	162.6	0.985 1	159.1	0.982 8	2.7×10^{11}	176.0	155.7	−32.4
$Ba(NO_3)_2$ + RP + Teflon	130.5	0.986 5	121.5	0.978 0	1.9×10^{8}	183.0	120.4	−93.2
MnO_2 + RP + Teflon	270.2	0.995 3	265.0	0.991 6	3.2×10^{19}	187.3	262.5	122.5
Fe_2O_3 + RP + Teflon	135.5	0.974 6	130.1	0.969 8	1.4×10^{9}	179.9	127.4	−80.8
$KMnO_4$ + RP + Teflon	438.5	0.982 9	443.8	0.982 0	1.9×10^{34}	226.5	434.2	407.0

for the pyrotechnic mixtures, Equation(7) and Equation(8) were used [25].

$$T_e = T_{e0} + a\beta_i + b\beta_i^2 + c\beta_i^3; \quad (7)$$

$$T_b = \frac{E - \sqrt{E^2 - 4ERT_{e0}}}{2R}。 \quad (8)$$

In these Equations: a, b and c coefficients; R is the gas constant; E is the value of average activation energy obtained by Ozawa and Kissinger methods.

The value of the onset temperature (T_{e0}) corresponding to $\beta\rightarrow0$ and critical temperature of thermal ignition (T_b) obtained by Equation(7) and Equation(8) for all pyrotechnic mixtures are in Tab. 3.

Tab. 3 Critical ignition temperature calculated for pyrotechnic mixtures

Samples	Onset temperature T_{e0}/℃	Critical ignition temperature T_b/℃
RP	303.3	330.5
KNO_3 + RP + Teflon	356.5	378.4
$Ba(NO_3)_2$ + RP + Teflon	389.3	421.1
MnO_2 + RP + Teflon	340.8	353.0
Fe_2O_3 + RP + Teflon	377.3	406.1
$KMnO_4$ + RP + Teflon	237.2	242.6

For the mixture of $KMnO_4$ + RP + Teflon, as seen in Tab. 3, critical ignition temperature is 242.6 ℃, which is less than the critical ignition temperature of RP itself, indicating that the mixture of $KMnO_4$ + RP + Teflon was more reactive than RP itself. On the other hand, by replacing $KMnO_4$ with MnO_2 and KNO_3 powder, the thermal sensitivity of the mixture decreases and ignition temperature of MnO_2 + RP + Teflon and KNO_3 + RP + Teflon systems reach to 353.0 ℃ and 378.4 ℃. Finally, the replacement of $KMnO_4$ with Fe_2O_3 and $Ba(NO_3)_2$ raises the thermal stability of the mixture and ignition shifts toward the higher temperature up to 406.1 ℃ and 421.1 ℃. $Ba(NO_3)_2$ + RP + Teflon mixture with ignition temperature about 178 ℃ higher than that most reactive mixture has the highest stability among the investigated mixtures.

2.6 Friction sensitivity

Friction sensitivity of pyrotechnic mixtures is essential to characterize their stability. In this regard, combine falling angle swing hammer method was used to test friction sensitivity. The results are shown in Tab. 4.

In Tab. 4, the pyrotechnic mixtures are sensitive when the oxidants are KNO_3 and $KMnO_4$, and the cumulative rate of ignition are 81.7 % and 66.7 %, respectively. When the oxidant is $Ba(NO_3)_2$, the pyrotechnic mixture is less sensitive with the cumulative

Tab. 4 Friction sensitivity of pyrotechnic mixtures

%

Samples	90°, 4.5 MPa	80°, 3.5 MPa	70°, 2.8 MPa	60°, 2.1 MPa	50°, 1.5 MPa	40°, 1.0 MPa	Cumulative rate of ignition
KNO_3 + RP + Teflon	100	100	100	100	70	10	81.7
$Ba(NO_3)_2$ + RP + Teflon	100	100	100	55	20	0	61.7
MnO_2 + RP + Teflon	90	20	0	0	0	0	18.3
Fe_2O_3 + RP + Teflon	80	10	0	0	0	0	15.0
$KMnO_4$ + RP + Teflon	100	100	100	80	20	0	66.7

rate of ignition 61.7 %. When the oxidants are Fe_2O_3 and MnO_2, the pyrotechnic mixtures are insensitive with the cumulative rate of ignition 18.3 % and 15.0 %, respectively. Mass fraction of $KMnO_4$ is 12.0 %, which is much less than that of the others. Hence, the most sensitive of pyrotechnic mixture to friction is $KMnO_4$ as oxidant.

2.7 Hygroscopicity of pyrotechnic mixtures

The property of hygroscopicity about pyrotechnic mixtures are exhibited in Tab. 5.

Tab. 5 Hygroscopicity of pyrotechnic mixtures

Samples	Relative hygroscopic rate/%
KNO_3 + RP + Teflon	83.2
$Ba(NO_3)_2$ + RP + Teflon	55.4
MnO_2 + RP + Teflon	13.9
Fe_2O_3 + RP + Teflon	6.4
$KMnO_4$ + RP + Teflon	14.5

In Tab. 5, hygroscopic rate of pyrotechnic mixtures decrease compared to RP, this is because Teflon, which is hydrophobic material, is coated on the surface of RP to prevent the uptake of water by the RP. On the other hand, the oxidizers have an important effect on the hygroscopicity of pyrotechnic mixtures. When the oxidizers are easier to absorb moisture, the pyrotechnic mixtures have higher relative hygroscopic rate, such as the oxidants are KNO_3 and $Ba(NO_3)_2$. When the oxidizers are not easier to absorb moisture, the pyrotechnic mixtures have lower relative hygroscopic rate, such as MnO_2, Fe_2O_3 and $KMnO_4$.

3 Conclusions

Thermal behavior of pyrotechnic mixtures were studied by TG and DTA methods. The results show that the mixture of $KMnO_4$ + RP + Teflon and KNO_3 + RP + Teflon have a low ignition temperature. Also, TG-DTA analysis of the mixture indicates that the decomposition temperature of $KMnO_4$ and KNO_3 are 240.0 ℃ and 336.8 ℃. Furthermore, the mixtures have high sensitivity to friction. The relative hygroscopic rate of KNO_3 + RP + Teflon is 83.2% which is the highest in all pyrotechnic mixtures. This is why the $KMnO_4$ + RP + Teflon and KNO_3 + RP + Teflon mixtures are not appropriate pyrotechnic mixtures.

On the other hand, when the oxidants are $Ba(NO_3)_2$, Fe_2O_3 and MnO_2, the pyrotechnic mixtures show high stability, high ignition temperature, low sensitivity to friction and low relative hygroscopic rate. So the three oxidants are appropriate for pyrotechnic mixture.

It was observed that heating rate is an important factor in the thermal decomposition of pyrotechnic mixtures. As the heating rate was increased, the melting points and ignition temperatures of mixtures was enhanced. Finally, the values of the kinetic parameters were obtained for each mixture. Also, $\triangle G^{\#}$, $\triangle H^{\#}$ and $\triangle S^{\#}$ for the decomposition reaction of pyrotechnic mixtures were computed.

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