J Therm Anal Calorim (2011) 104:671–678
DOI 10.1007/s10973-010-1062-8

Improving safety performance of lactose-fueled binary pyrotechnic systems of smoke dyes

Abbas Eslami · Seyed Ghorban Hosseini

Received: 11 July 2010 / Accepted: 16 September 2010 / Published online: 7 October 2010

Abstract The lactose/$KClO_3$ is a widely used pyrotechnic mixture to vaporize organic materials, such as smoke dyes. However, because of low ignition temperature of this mixture, serious precaution should be taken into account to prevent its accidental self-ignition. In order to find a safe and efficient alternative of this conventional mixture, $KClO_3$ has been replaced by common oxidizing agents including $KMnO_4$, KNO_3, $KClO_4$, $Ba(NO_3)_2$, PbO_2 and NH_4ClO_4. TG and DTA analysis have been used to obtain thermal characteristic of the mixtures. Based on ignition temperature of the pyrotechnic mixtures we can divide them into four categories as follows: (1) the mixture igniting at low temperature, i.e., at about 200 °C. (2) Moderate temperature igniting mixture, in which ignition occurs at 300–400 °C. (3) High temperature igniting mixture with ignition temperature higher than 400 °C .(4) Not igniting mixtures. Also, the apparent activation energy (E), $\Delta G^{\#}$, $\Delta H^{\#}$, $\Delta S^{\#}$ and critical ignition temperature (T_b) of the ignition processes of low and moderate temperature igniting mixtures were obtained from the DSC experiments. Finally, among the investigated mixtures, lactose/KNO_3 can be considered as a safe and efficient pyrotechnic composition for vaporization of organic materials, such as smoke dyes, due to its moderate safe ignition temperature.

Keywords Smoke dye composition · TG/DTA analysis · Safety · Critical ignition temperature (T_b) · Kinetic parameters

A. Eslami (✉) · S. G. Hosseini
Faculty of Chemistry, University of Mazandaran,
P.O. Box 47416-95447, Babolsar, Iran
e-mail: eslami@umz.ac.ir

Introduction

Pyrotechnic compositions are typically composed of finely divided mixtures of metallic or non-metallic elements as reducing agent with inorganic oxidizing agents to chemically generate heat, light, or color and used in smoke dye, emergency signaling, fireworks, air bag inflators, and special effects devices for the entertainment industry [1–3].

Pyrotechnic smoke dyes are widely exploited for military purposes to screen and obscure objects, to signal friendly forces and to mark positions. These are made of an oxidizer, frequently potassium chlorate, a fuel such as lactose, and an organic dye such as 1,4-dihydroxy anthraquinone (orange), 1-(*p*-tolylamino)-4-hydroxy anthraquinone (violet), 1-methylamino anthraquinone (red), and 4,4′-methylidyne-bis-3-methyl-1-phenyl-2-pyrazolin-5-one (yellow), and some additives which facilitate burning and improve the processing characteristics of the composition [4, 5].

Some simple sugars are used as fuels in various pyrotechnic mixtures and their burning results in a colorless flame and liberate less heat per gram than less-oxidized organic fuels. Simple sugars such as lactose can be obtained in high purity at moderate cost, and so can be considered as proper fuel for pyrotechnic applications. Also, toxicity problems tend to be minimal with these fuels [6, 7].

Lactose has two forms α, β in crystalline structure, its moisture contents is about 5% and increase to about 7% at high humidity. Its ignition temperature with oxidants such as, potassium chlorate is somewhat higher than that of sucrose but lower than that of starch. It reacts with common inorganic oxidizers at moderate temperatures [8, 9]. Therefore, lactose is among the most exploited fuel in colored smoke compositions.

Thermal analysis methods are well-established techniques for studying the thermal properties of energetic

materials in reasonable ways [10–14]. A detailed knowledge of the thermal behavior of each component of a mixture or the mixture itself is necessary, both for safety and also to predict the thermal behavior of new energetic formulations. However, understanding the thermolysis of energetic materials is not a trivial task. Typically, the mechanisms of ignition phenomena are very complex and dependent not only on the physico-chemical properties of the reactive samples, but also on the conditions of their occurrence [15–17].

In this work, the lactose/oxidant binary compositions with different types of oxidant powders such as $KClO_3$, $KMnO_4$, KNO_3, $KClO_4$, $Ba(NO_3)_2$, PbO_2 and NH_4ClO_4 were initially prepared, then the thermal properties and kinetic parameters of lactose/oxidant compositions were investigated using thermal analysis techniques. Although, the thermal behavior of potassium chlorate in the mixture with lactose powder have previously been reported [5, 6], but there is no report on the effect of the other oxidants. The conventional lactose/chlorate smoke pyrotechnic mixture suffers from low thermal stability which may lead to safety problems through its accidental self-ignition [5, 18]. The aim of this investigation is to overcome this disadvantage by combination of lactose with some other oxidants in smoke dye pyrotechnic mixture. Among them, a novel lactose/KNO_3 composition has been found to show desirable safe ignition properties.

Experimental

Materials

Potassium chlorate, potassium permanganate, potassium nitrate, potassium perchlorate, barium nitrate, lead dioxide, ammonium perchlorate (mesh 300) and lactose monohydrate powders (10 μm) were purchased from Merck (Tehran, Iran).

Apparatus

A thermobalance (Stanton, Model TR-01, with a sensitivity of 0.1 mg, with a Stanton 780 differential thermal analysis (DTA) attachment) was used to investigate thermal property (DTA/TG) of pure and binary pyrotechnic mixtures.

A differential scanning calorimetry, DSC, technique with a Dupont DSC model 910 was used to kinetic investigation of mixtures.

Procedure

Preparation of samples

Seven pyrotechnic mixtures containing, lactose/$KClO_3$, lactose/$KMnO_4$, lactose/KNO_3, lactose/$KClO_4$, lactose/$Ba(NO_3)_2$, lactose/PbO_2 and lactose/NH_4ClO_4 were initially prepared based on their reaction stoichiometric ratio (as presented in Table 1) through wet mixing in acetone. After evaporation of the solvent, small quantities of the pyrotechnic mixtures were carefully sieved through a slightly coarser sieve than the particles [14].

Thermal analysis of samples

Approximately, 3.0 mg of sample and reference (Pt foil) were placed in alumina pans and heated 10 °C min^{-1} from 30 to 1000 °C. In this study, nitrogen atmosphere was used for pure compounds and air atmosphere for binary mixtures. DTA baseline and temperature calibrations were performed prior to the experiments. Before testing, all samples were stored in a vacuum oven at 65 °C for at least 3 h.

DSC experiments were run at the heating rates of 5, 10, 15, 20 °C min^{-1} from 50 °C up to the end of the reaction. DSC measurements were conducted by placing 3.0 mg of each mixture in a sample pan with a perforated cover under air atmosphere (40 ml min^{-1}).

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

No	Component	Composition/%	Transition temperature[a]/°C		
			Fusion[b]	T^c_{max}	ΔT^d
1	Lactose	100	216	358, 497	135–580
2	$KClO_3$	100	356	472	470–550
3	KNO_3	100	337	700	500–1000
4	$KMnO_4$	100	–	290, 630	240–650
5	$Ba(NO_3)_2$	100	588	685	575–778
6	$KClO_4$	100	590	592	590–605
7	Lactose/$KClO_3$	26.9/73.1	–	206.9	140–360
8	Lactose/KNO_3	18.2/81.8	218, 327	335.7	140–392
9	Lactose/$KMnO_4$	12.5/87.5	219, –	393	140–600
10	Lactose/$Ba(NO_3)_2$	14.7/85.3	221, –	446.2	140–620
11	Lactose/$KClO_4$	30.15/69.85	219, –	476	140–550

[a] Peak temperatures at maximum heat flux

[b] Fusion temperatures for the mixtures are given for fuel and oxidant, respectively

[c] T_{max} is maximum temperature of decomposition (no 1–6) and ignition phenomenon (no 7–11)

[d] ΔT is Temperature range associated with a sample's mass loss

Results and discussion

Thermal behavior of pure compounds

Lactose

Lactose monohydrate was examined in nitrogen atmosphere by using simultaneous DTA/TG to access its thermal characteristics. As shown in Fig. 1a, three successive thermal events were found to occur at above 140 °C in which the first two ones are endothermic and the last one is exothermic process. The first phenomenon, occurring at about 149 °C, can be attributed to dehydration process of lactose. The small amount of mass loss during the process (about 5%), determined from TG curve, confirms the dehydration reaction. No mass change has been observed in the next stage of heating, so that the sharp endothermic peak of DTA curve at 216 °C could be assigned to lactose melting. After the melting process, a large and broad exothermic peak appeared in DTA, starting at about 218 °C and continuing to 580 °C. This broad peak corresponds to the decomposition of molten lactose. This result agrees with the TG curve of the entire process that shows 98% total mass loses [6]. After complete decomposition of the sample, water, and carbon may be produced:

$$C_{12}H_{22}O_{11} \cdot H_2O(l) \rightarrow 12C(g) + 12H_2O(g)$$

$KClO_3$

The DTA and TG curves for pure potassium chlorate are shown in Fig. 1b. No thermal event was observed prior to 356 °C, when the DTA curve exhibits a sharp endothermic peak due to melting phenomenon. After this, as seen in the DTA curve in Fig. 1b, a relatively great temperature elevation should be attained before its first rapid exothermic decomposition at 472 °C. The decomposition process is accompanied by 40% mass loss. In agreement with previous report, the results show that pure potassium chlorate is kinetically stable over a wide temperature range higher than its melting point [19]. After complete decomposition of the sample, oxygen and potassium chloride (KCl) are produced [20, 21]:

$$KClO_3(l) \rightarrow KCl(s) + \frac{3}{2}O_2(g)$$

KNO_3

Figure 1c shows the results of DTA and TG analysis of the KNO_3 sample used in this study. In alignment with recent reports by Koch [22] and by us [23], the endothermic peaks at 130 °C and 337 °C correspond to phase transition of rhombic crystalline solid to trigonal structure and melting of KNO_3, respectively. The molten KNO_3 is said to be stable up to 500 °C, since no thermal event was observed at this temperature interval. However, an endothermic pyrolysis gasification reaction starts at just a little above this temperature, and finishes at about 1000 °C, resulting in no solid residue. Accordingly, the reaction processes of KNO_3 are suggested as follows:

$$2KNO_3(l) \rightarrow K_2O(l) + 2NO(g) + \frac{3}{2}O_2(g)$$

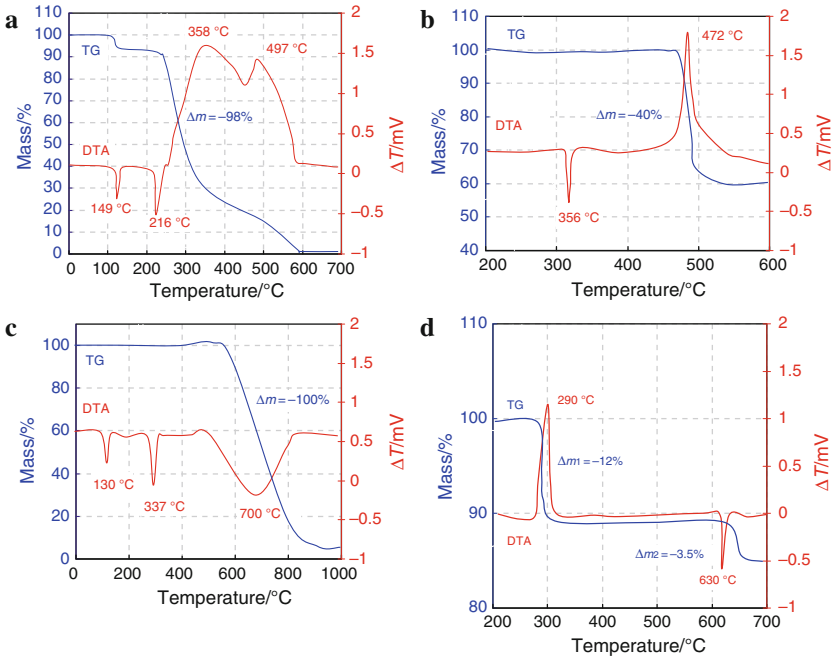

Fig. 1 TG and DTA curves for pure powder of **a** lactose, **b** potassium chlorate, **c** potassium nitrate, and **d** potassium permanganate (sample mass 3.0 mg; heating rate 10 °C min^{-1}; nitrogen atmosphere)

$KMnO_4$

As shown in Fig. 1d, decomposition of potassium permanganate occurs in two discrete stages. A sharp exothermic DTA peak was observed at about 290 °C and an endothermic one at 630 °C. The former stage is accompanied with a rapid mass loss of about $\Delta m_1 = 12\%$ of the initial mass, but for the last stage of decomposition is about $\Delta m_2 = 3.5\%$ of the original mass. The results are in agreement with the previous thermal and chemical analysis, reported by Herbstein et al. [24] who proposed based on a mass loss of 12.1% that the stoichiometry of the first stage of decomposition is as:

$$10KMnO_4(s) \rightarrow 2.65K_2MnO_4(s) + (2.35K_2O \cdot 7.35MnO_{2.05})(s) + 6O_2(g)$$

while the second stage was represented as:

$$10K_2MnO_4(s) \rightarrow 5.7K_3MnO_4(s) + 0.5(2.9K_2O \cdot 8.6MnO_{2.1})(s) + 3.4O_2(g)$$

and was found to be reversible in air.

$Ba(NO_3)_2$

Thermal analysis (DTA/TG) of pure barium nitrate (Table 1) indicated that $Ba(NO_3)_2$ melts at 588 °C with a strong endothermic peak, which subsequently decomposed at 685 °C [23]. This result agrees with the TG curve that shows barium nitrate decomposes at 575–778 °C temperature range with 42% mass loss. After complete decomposition of the sample, oxygen, nitric oxide and barium oxide are produced:

$$Ba(NO_3)_2(l) \rightarrow BaO(s) + NO(g) + NO_2(g) + O_2(g)$$

$KClO_4$

Thermal analysis (DTA/TG) of pure potassium perchlorate is also presented in Table 1. Beside decomposition and melting, potassium perchlorate undergoes a rhombic–cubic endothermic phase transition around 300 °C. At higher temperature, (~590 °C), it decomposes rapidly during the melting process [19]. After complete decomposition of potassium perchlorate, oxygen and potassium chloride (KCl) are produced. It is confirmed by a 46% mass loss in the TG curve [5].

$$KClO_4(l) \rightarrow KCl(s) + 2O_2(g)$$

Thermal properties of binary mixtures

Lactose/$KClO_3$

Figure 2a shows DTA and TG curves for lactose/$KClO_3$ pyrotechnic mixture. First thermal event occurs at 142 °C together with 7% mass loss and can be related to the endothermic dehydration of the lactose. Subsequently, the mixture ignites at 206.9 °C, while both fuel and oxidant were unmelted. The ignition reaction between fuel and oxidizer is a complete reaction, accompanied with 60% total mass loss as follows [5, 6].

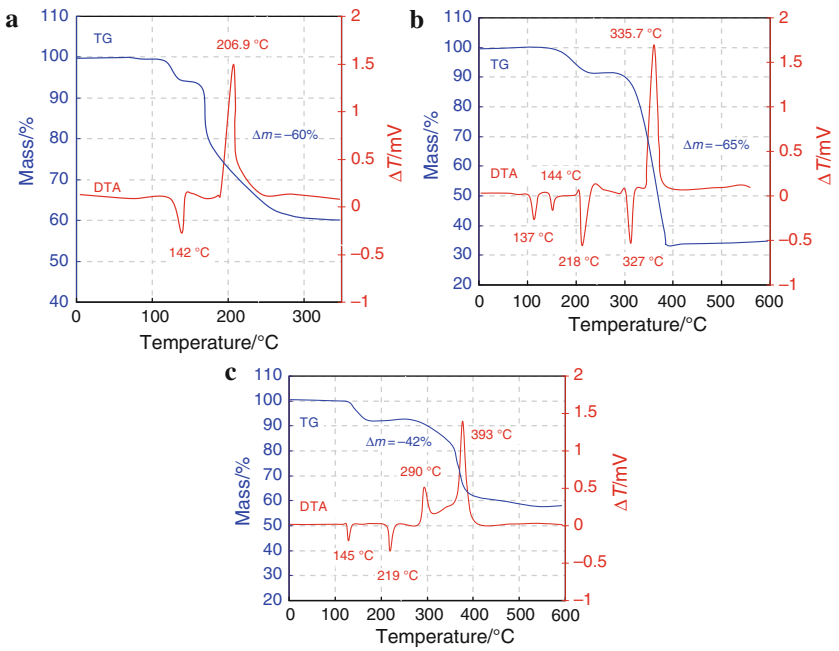

Fig. 2 TG and DTA curves for mixture of lactose powder with **a** potassium chlorate, **b** potassium nitrate, and **c** potassium permanganate (sample mass 3.0 mg; heating rate 10 °C min^{-1}; air atmosphere)

$$C_{12}H_{22}O_{11} \cdot H_2O(s) + 8KClO_3(s) \rightarrow 8KCl(s) + 12CO_2(g) + 12H_2O(g)$$

Lactose/KNO_3

As shown in Fig. 2b, an endothermic peak at 137 °C is observed, corresponding to a phase transition of oxidant without any decrease in the mixture's mass. Subsequent peak at 144 °C can be attributed to the lactose dehydration with 5.5% mass loss. The organic fuel and the oxidant melt at 218 and 327 °C, respectively. Following these endothermic events, a rapid ignition occurs at 335.7 °C. The following stoichiometry has been assigned to the overall reaction and is confirmed by a 65% total mass loss in the TG curve.

$$C_{12}H_{22}O_{11} \cdot H_2O(l) + 16KNO_3(l) \rightarrow 8K_2O(l) + 16NO(g) + 12CO_2(g) + 12H_2O(g)$$

Lactose/$KMnO_4$

Figure 2c shows four thermal events for lactose/$KMnO_4$ mixture, of which two first processes are endothermic and the two other ones are exothermic. The first detectable thermal phenomenon, occurred at 145 °C with 6% mass loss, is associated with water loss from lactose. The next sharp peak at 219 °C is due to the fuel fusion. As mentioned above, first exothermic peak (~290 °C) can be related to the first decomposition stage of $KMnO_4$ and is followed by the mixture ignition, occurring exothermally at about 393 °C. The TG results shows continuous mass loss (total 42%) in a long period of temperature range (140–600 °C) and the amount of mass loss lead us to presume following stoichiometry for the overall process:

$$C_{12}H_{22}O_{11} \cdot H_2O(l) + 16KMnO_4(s) \rightarrow 8K_2O(s) + 16MnO_2(s) + 12CO_2(g) + 12H_2O(g)$$

Lactose/$Ba(NO_3)_2$

The DTA and TG curves of lactose/$Ba(NO_3)_2$ mixture that summarized in Table 1, show two endothermic peaks at 147 and 221 °C which correspond to the dehydration and the melting of lactose in the mixture, respectively. High thermal stability of the oxidant causes a delay, with respect to the above mixtures, in next thermal event up to near 446.2 °C at which the ignition happens exothermally with about 55% mass loss. The overall reaction between the fuel and this oxidizer is as follows:

$$C_{12}H_{22}O_{11} \cdot H_2O(l) + 8Ba(NO_3)_2(s) \rightarrow 8BaO(s) + 16NO(g) + 12CO_2(g) + 12H_2O(g)$$

Lactose/$KClO_4$

The results of DTA and TG for the mixture of potassium perchlorate and lactose are summarized in Table 1. The DTA and TG curves of this mixture reveal an endothermic peak about 147.2 °C, which is related to dehydration of fuel. After this, two other endothermic peaks with no mass loss were observed at 219 and ~302 °C, and were assigned to the melting of the fuel and rhombic-cubic phase transition of the oxidant, respectively. Similar to previous mixture, a delayed but rapid ignition occurs at 476 °C together with a ~65% sample's mass fall. The presumed reaction between fuel and oxidizer is as follows:

$$C_{12}H_{22}O_{11} \cdot H_2O(l) + 6KClO_4(s) \rightarrow 6KCl(s) + 12CO_2(g) + 12H_2O(g)$$

Among the investigated mixtures, the lactose/NH_4ClO_4 and lactose/PbO_2 mixtures were not thermally ignited, and therefore have no merit for pyrotechnic purposes.

Comparison of ignition temperatures

Ignition temperature is one of the main characteristics determining efficiency of the pyrotechnic mixtures for smoke dye. Low temperature igniting pyrotechnics may raise hazardous issues such as uncontrollable and accidental self-ignition, on other hand high temperature ones may result in decomposition of dye component at ignition temperature. So the pyrotechnic mixtures with moderate ignition temperatures have desirable characteristics for smoke dye applications [8, 14]. Diversity of ignition temperatures of the above pyrotechnic mixtures leads us to divide them into four categories as follows: (1) Low temperature igniting mixture: the mixture of lactose with $KClO_3$, igniting at about 200 °C, belongs to this category. The relatively low ignition temperature of the mixture makes it as a suitable mixture for smoke generator system. Due to the high reactivity of $KClO_3$, the ignition occurs at a temperature that is much lower than its decomposition temperature. In fact, the mixture is so reactive as to ignite at a temperature at which both components are solid. (2) Moderate temperature igniting mixture: this category includes the mixture of lactose with KNO_3 or $KMnO_4$ igniting at 300–400 °C. The replacement of $KClO_3$ with KNO_3 raises the thermal stability of the mixture and ignition shifts toward the higher temperature up to around 335.7 °C. On the other hand, using $KMnO_4$ as oxidizer a further increase in thermal stability of the pyrotechnic mixture has been observed so that ignition temperature of the lactose/$KMnO_4$ mixture increases up to 393 °C. (3) High temperature igniting mixtures, fabricated with $KClO_4$ or $Ba(NO_3)_2$ as oxidizing agent, that ignite at higher than

400 °C. As the results of Table 1 shown, by replacing $KClO_3$ with $Ba(NO_3)_2$, thermal stability of the mixture increased. Table 1 shows that the mixtures of lactose/$Ba(NO_3)_2$ and lactose/$KClO_4$ ignite at 446.2 and 476 °C, respectively. (4) Not igniting mixtures: besides above mentioned oxidants which show diverse ignition reactivity upon mixing with lactose, some other well known oxidants, such as PbO_2 and NH_4ClO_4, form not igniting mixtures with lactose. A comparison of ignition temperature of reactive mixtures is also summarized in Table 1.

On the other hand, since the organic dyes compounds that used in pyrotechnic smoke composition, usually decompose at relatively lower than 400 °C [7, 14], thus the ignition temperature of smoke dye pyrotechnic mixture is an important parameter and should not exceed their decomposition temperature. Therefore, among the investigated pyrotechnic mixtures, only low and moderate temperature igniting mixtures can potentially be considered for vaporization of organic dye compounds.

Kinetics of thermal ignition

Potential hazards associated with the thermal behavior of energetic materials require that stability evaluation and ignition kinetics be carried out to assure their safe processing, handling and storage. Kinetic characteristics of ignition processes of low and moderate temperature igniting mixtures have been explored through DSC measurement at several heating rate. Figure 3 shows DSC curves for the ignition reaction of lactose/$KClO_3$ pyrotechnic mixtures at several heating rates. The curves show that as the heating rate was increased, the onset ignition temperature (T_e) and ignition peaks of mixture were shifted to higher temperatures. This trend was also observed for all other mixtures (Table 2).

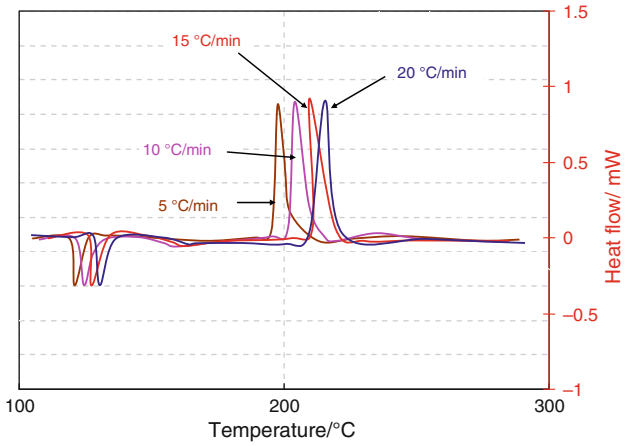

Fig. 3 The effect of heating rate on the DSC curves of thermal ignition of lactose/$KClO_3$ mixture

In this study, kinetic parameters were determined using Kissinger approach [25–27].

Based on Kissinger method, the apparent activation energy (E) could be obtain as slope of a plot of $\ln(\phi/T_m^2)$ versus $1/T_m$, in which ϕ and T_m are heating rate and temperature of max/min peaks of DSC curve, respectively [28].

On the other hand, the Arrhenius frequency factor (A) was found for all mixtures from the following relation [29, 30]:

$$A = [\varphi E \exp(E/RT_m)]/RT_m^2 \quad (1)$$

The calculated activation parameters for all mixtures are given in Table 3.

The entropy of activation ($\Delta S^{\#}$), enthalpy of activation ($\Delta H^{\#}$) and free energy of activation ($\Delta G^{\#}$) corresponding to the each mixture were obtained [31, 32]. Table 3 gives the calculated kinetics parameters for the studied pyrotechnic systems.

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 lowest temperature to which a specific charge may be heated without undergoing thermal runaway [33]. 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) for the pyrotechnic mixtures, Eqs. 2 and 3 were used. [34].

Table 2 Effect of heating rate on the onset and peak ignition temperature of lactose with $KClO_3$, KNO_3, and $KMnO_4$ pyrotechnic mixtures

Mixture	Lactose/$KClO_3$		Lactose/KNO_3		Lactose/$KMnO_4$	
Heating rate/°C min^{-1}	Onset temperature/°C	Peak temperature/°C	Onset temperature/°C	Peak temperature/°C	Onset temperature/°C	Peak temperature/°C
5	192	198	318.3	327.8	378.5	386
10	198.9	206.9	321.5	335.7	386	393
15	207	212.1	331	342	390	397.8
20	210	217.8	342	348	394.6	402.5

Table 3 Kinetic parameters of thermal ignition of lactose with $KClO_3$, KNO_3, and $KMnO_4$ pyrotechnic mixtures

Mixture	E/kJ mol^{-1}	Frequency factor log A/s^{-1}	r	$\Delta G^{\#}$/kJ mol^{-1}	$\Delta H^{\#}$/kJ mol^{-1}	$\Delta S^{\#}$/J mol^{-1} K^{-1}
Lactose/$KClO_3$	129	13.9	0.9965	121.1	125	8
Lactose/KNO_3	203.7	17.3	0.9910	164.6	199.7	73
Lactose/$KMnO_4$	303.25	23.7	0.9952	205.2	299	196

r linear regression coefficient

$\Delta G^{\#}$, $\Delta H^{\#}$, and $\Delta S^{\#}$ are given at ignition temperature of most reactive mixture, i.e., lactose/$KClO_3$

$$T_e = T_{e0} + b\phi_i + c\phi_i^2, \quad i = 1 - 4 \tag{2}$$

$$T_b = \frac{E - \sqrt{E^2 - 4ERT_{e0}}}{2R} \tag{3}$$

where b and c are coefficients, R is the gas constant, and E is the value of activation energy obtained by kinetic method.

The value (T_{e0}) of the onset temperature (T_e) corresponding to $\phi \rightarrow 0$ obtained by Eq. 2 is 181.6, 317.8, and 370.6 °C for lactose/$KClO_3$, lactose/KNO_3, and lactose/$KMnO_4$ mixture, respectively.

The critical temperature of thermal ignition (T_b) obtained from Eq. 3 is 195.8, 332.8 and 382.4 °C for lactose/$KClO_3$, lactose/KNO_3 and lactose/$KMnO_4$ mixture, respectively.

Conclusions

In order to improve safety issues of lactose/$KClO_3$ pyrotechnic mixture which has been widely used in smoke dye formulation, several common oxidizing agents, including $KMnO_4$, KNO_3, $KClO_4$, $Ba(NO_3)_2$, PbO_2 and NH_4ClO_4, have been examined as alternative oxidant for this application. DTA/TG and DSC techniques have been employed to evaluate thermal behavior of the pyrotechnic mixtures. The results showed that lactose/$KClO_3$ has lowest apparent activation energy (E) and critical ignition temperature (T_b) in comparison with other mixtures. Although these characteristics seem to make this mixture useful for smoke generator formulations that need low temperature reactions, but cause it to suffer potentially from self-ignition during mixing and storage. Among alternative mixtures, lactose/PbO_2 and lactose/NH_4ClO_4 form not igniting mixtures and therefore are unsuitable for above mentioned application. Also, kinetic parameters and ignition temperatures revealed the following order for their thermal reactivity:

$$\text{Lactose/KClO}_3 > \text{lactose/KNO}_3 > \text{lactose/KMnO}_4 > \text{lactose/Ba(NO}_3)_2 > \text{lactose/KClO}_4$$

Efficient pyrotechnic mixture for smoke dye application should have moderate ignition temperature and release its energy within limited temperature range, since high temperature igniting mixtures cause dye decomposition and low temperature ones result in hazardous issues. In this view, lactose/$Ba(NO_3)_2$ and lactose/$KClO_4$ mixtures, which ignite at higher than the decomposition temperature of common organic dyes (~400 °C) [35, 36], are not proper alternative for hazardous lactose/$KClO_3$ mixture. Although, ignition of lactose/$KMnO_4$ starts from moderate temperature, but occurs at a wide temperature range (240–650 °C). So this mixture does not provide the proper characteristics for smoke dye application. But lactose/KNO_3 ignites at 336 °C and its critical ignition temperature (T_b) is 332.8 °C and its ignition process does not exceed 400 °C. So, this pyrotechnic mixture not only have proper ignition temperature to vaporized many stable organic dyes, such as 1-methylamino anthraquinone (red dye), but also can be used as safe pyrotechnic mixture in smoke dyes system [36]. Finally, the result of this investigation shown that, lactose/KNO_3 mixture can be used instead of very famous lactose/$KClO_3$ mixture that used as conventional mixture in smoke dye system. The advantage of the new system is its higher apparent activation energy (E) and critical ignition temperature (T_b) that prevents accidental self-ignition during mixing or storage period.

References

1. Berger B. Parameters influencing the pyrotechnic reaction. Propellants Explos Pyrotech. 2005;30:27–35.
2. Brown ME. Some thermal studies on pyrotechnic compositions. Therm Anal Calorim. 2001;65:323–34.
3. Qian XM, Wang Y, Feng CG. Investigation of thermal decomposition of $KClO_3$/CuO/S/Mg-Al/C_6Cl_6 system by accelerating rate calorimeter. Acta Phys-Chim Sin. 2001;17:70–3.
4. Hemmila M, Hihkio M, Linnainmaa K. Evaluation of the acute toxicity and genotoxicity of orange, red, violet and yellow pyrotechnic smokes in vitro. Propellant Explos Pyrot. 2007;32:415–22.
5. Fathollahi M, Pourmortazavi SM, Hosseini SG. The effect of the particle size of potassium chlorate in pyrotechnic compositions. Combust Flame. 2004;138:304–6.
6. Hosseini SG, Pourmortazavi SM, Hajimirsadeghi SS. Thermal decomposition of pyrotechnic mixtures containing sucrose with

either potassium chlorate or potassium perchlorate. Combust Flame. 2005;14:322–6.
7. Ellern H. Military and civilian pyrotechnic. New York: Chemical Publishing Company Inc.; 1968.
8. McLain JH. Pyrotechnics from the viewpoint of solid state chemistry. Philadelphia: The Franklin Institute Press; 1980.
9. Akhavan J. The chemistry of explosives. 2nd ed. London: The Royal Society of Chemistry; 2004.
10. Eslami A, Hosseini SG, Pourmortazavi SM. Thermoanalytical investigation on some boron-fuelled binary pyrotechnic systems. Fuel. 2008;87:3339–43.
11. Roduit B, Borgeat C, Berger B, Folly P, Andres H, Schädeli U, Vogelsanger B. UP-scaling of DSC DATA of high energetic materials, simulation of cook-off experiments. J Therm Anal Calorim. 2006;85:195–202.
12. Berger B, Brammer AJ, Charsley EL, Rooney JJ, Warrington SB. Thermal analysis studies on the boron–potassium perchlorate–nitrocellulose pyrotechnic system. J Therm Anal Calorim. 1997; 49:1327–55.
13. Gunawan R, Zhang D. Thermal stability and kinetics of decomposition of ammonium nitrate in the presence of pyrite. J Hazard Mater. 2009;165:751–8.
14. Charsley EL, Laye PG, Brown ME. Handbook of thermal analysis and calorimetry: pyrotechnics. 1st ed. Amsterdam: Elsevier; 2003. p. 777–815.
15. Pineda EAG, Ferrarezi ADM, Ferrarezi JG, Hechenleitner AAW. Thermal decomposition of enalapril maleate studied by dynamic isoconversional method. J Therm Anal Calorim. 2005;79:259–62.
16. Ramos LA, Cavalheriro ETG, Chierice GO. Preparation, characterization and thermal decomposition of ammonium salts of dithiocarbamic acids. J Therm Anal Calorim. 2005;79:349–53.
17. Brown SD, Charsley EL, Goodall SJ, Laye PG, Rooney JJ, Griffiths TT. Studies on the ageing of a magnesium–potassium nitrate pyrotechnic composition using isothermal heat flow calorimetry and thermal analysis techniques. Thermochim Acta. 2003;401:53–61.
18. Scans FS. Thermal analysis of pyrotechnic compositions containing potassium chlorate and lactose. Combust Flame. 1974;23: 363–71.
19. Markowitz MM, Boryta DA. The differential thermal analysis of perchlorate. J Phys Chem. 1964;68:2282–9.
20. Pourmortazavi SM, Hajimirsadeghi SS, Hosseini SG. Characterization of the aluminum/potassium chlorate mixtures by simultaneous TG-DTA. J Therm Anal Calorim. 2006;84:557–61.
21. Wendlandt WW. Thermal methods of analysis. 2nd ed. New York: Wiley; 1974.
22. Koch EC, Clement D. Special materials in pyrotechnics: VI. Silicon—an old fuel with new perspectives. Propellants Explos Pyrotech. 2007;32:205–12.
23. Hosseini SG, Eslami A. Thermoanalytical investigation of relative reactivity of some nitrate oxidants in tin-fueled pyrotechnic systems. J Therm Anal Calorim. 2010;101:1111–19.
24. Herbstein FH, Kapon M, Weissman A. Old and new studies of the thermal decomposition of potassium permanganate. J Therm Anal Calorim. 1991;41:303–22.
25. Kissinger HE. Reaction kinetics in differential thermal analysis. Anal Chem. 1957;29:1702–6.
26. Lehmann B, Karger-Kocsis J. Isothermal and non-isothermal crystallisation kinetics of pCBT and PBT. J Therm Anal Calorim. 2009;95:221–6.
27. Hatakeyama T, Quinn FX. Thermal analysis, fundamentals and applications to polymer science fundamentals and applications to polymer science. New York: Wiley; 1994.
28. ASTM E698-05. Standard test method for Arrhenius kinetic constants for thermally unstable materials. doi:10.1520/E0698-05.
29. Criado JM, Perez-Maqueda LA, Sanchez-Jimenez PE. Dependence of the preexponential factor on temperature. J Therm Anal Calorim. 2005;82:671–5.
30. Hosseini SG, Eslami A. Orthogonal array design method for optimization experiments of sodium azide microencapsulation with stearic acid. Prog Org Coat. 2010;68:313–8.
31. Eslami A, Hosseini SG, Asadi V. The effect of microencapsulation with nitrocellulose on thermal properties of sodium azide particles. Prog Org Coat. 2009;65:269–74.
32. Guo S, Wang Q, Sun J, Liao X, Wang Z-S. Study on the influence of moisture content on thermal stability of propellant. J Hazard Mater. 2009;168:536–41.
33. Wang T, Lu YX, Zhu ML, Zhang JS, Ji SJ. DSC research on critical temperature in thermal explosion synthesis reaction $Ti_3 + Al \rightarrow TiAl^3$. J Therm Anal Calorim. 2002;67:605–11.
34. Zhang TL, Hu RZ, Xie Y, Li FP. The estimation of critical temperatures of thermal explosion for energetic materials using non-isothermal DSC. Thermochim Acta. 1994;244:171–6.
35. Tabak A. Structural analysis of reactive dye species retained by the basic alumina surface. J Therm Anal Calorim. 2009;95:31–6.
36. Bayer KH. AMCP 706-185. Military pyrotechnics series, Part 1, theory and application. United State Army Material Command, Washington; 1967.