

Decomposition Kinetics of Pyrotechnic Mixture from Sound-Producing Fire Crackers

A. Jeya Rajendran,^{a*} T. Lekshmana Thanulingam,^b A. Meisudar² and U. Manikandan^b

^a Department of Chemistry, Loyola College, Nungambakkam, Chennai-600034, India.
Email: jeyarajendran@yahoo.com

^b Fireworks Research and Development Centre, Petroleum and Explosives Safety Organisation, Anayoor village, Sivakasi -626124, India. Email: tlthanulingam@yahoo.co.in

Abstract: *Dynamic, non-isothermal analysis of the pyrotechnic mixture of a sound-producing fire cracker, $KNO_3/Al/S/H_3BO_3$, was carried out under N_2 atmosphere by using a simultaneous thermogravimetric and differential thermal analyser. Intermediates and the residue formed in each stage of thermal decomposition of the pyrotechnic mixture were characterised by X-ray diffraction analysis and the most probable reaction pathway was proposed. Thermogravimetric (TG) and differential thermogravimetric data (DTA) were used for the interpretation of the mechanisms and kinetics of decomposition by means of a model-fitting method, the Coats–Redfern equation, and model-free methods, the Arrhenius and Kissinger methods. The values of activation energy (E) were calculated as 11–16 $kJ\ mol^{-1}$, 24–53 $kJ\ mol^{-1}$ and 15–56 $kJ\ mol^{-1}$ for stages I, II and III respectively by the model-fitting method, with the Avrami–Erofe’ev model (A2), two-dimensional model, nucleation and growth mechanism. The pre-exponential factor ($\ln A$) of each stage of thermal decomposition at various linear heating rates was calculated and the probable decomposition mechanism was proposed for the first decomposition step as the expulsion of sulphur, and the second and third decomposition steps as the conversion of aluminium to alumina are obtained. Similarly, the reaction was also found to be first order.*

Keywords: *pyrotechnics, fireworks, thermal analysis, activation energy, Coats–Redfern equation.*

Introduction

Pyrotechnic compositions are mixtures of reducing and oxidising chemicals that are capable of undergoing self-sustained combustion. The reducing agent is often referred to as fuel. In general, the composition of fireworks is a mixture of sulphur or phosphorus, perchlorate or nitrate and pure aluminium powder.¹ The pyrotechnic mixtures are sensitive to impact, friction, electrostatic thermal energy and auto-ignition temperature. The composition of fireworks should possess high sensitiveness to flame and low sensitiveness to other factors like impact, friction and electrostatic energy.

A pyrochemical reaction characteristically produces heat energy which may be useful

directly as thermal energy or more usually as light, sound and kinetic energy to achieve a desired effect. This reaction must not begin to proceed as soon as the pyrotechnic composition is mixed and the spontaneity is prevented by the characteristic property of pyrotechnic compositions, the ‘activation energy’ barrier. An externally applied flame can initiate the ignition process by supplying the activation energy to the composition. If the activation energy barrier is low, accidental ignition will be more likely because a small amount of mechanical or electrostatic energy can cause ignition of the composition. Different oxidizers are used in the pyrotechnic mixture in order to get the desired effect of the fireworks and the parameter, energy of activation, can be used to check which oxidizer in the pyrotechnic mixture can be

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effective for a particular type of fireworks.

Potassium permanganate and phosphorus have low activation energy and therefore could not be used in the composition of pyrotechnics in the firework industry. Activation energy is not only affected by the nature of the oxidizers and the igniter but the same materials in different combinations may also lead to low activation energy creating a significant hazard. Accidental ignition during processing or spontaneous ignition during storage is the major problem in the fireworks industry which is the main focus of our work. The mechanism involved in the combustion and explosion reaction of pyrotechnic mixture in a firework is entirely different compared to the spontaneous ignition reaction of pyrotechnic mixture during storage.

In the firework industry, after mixing the ingredients, the pyrotechnic mixture is used to fill contrivances. Cardboard boxes are used for cake bombs and atom bombs; tubes are used for Chinese crackers and cones are used for flower pots and the combustion reaction is carried out in a confined way in the fire crackers. Differential Scanning Calorimetry (DSC) and Accelerating Rate Calorimetry (ARC) are suitable techniques for calculating thermodynamic parameters in a closed system as well as to interpret the mechanism. Simultaneous thermal analysis (TA), thermogravimetric (TG) and differential thermal analysis (DTA) can be used for studying the decomposition kinetics of the pyrotechnic mixture for ignition or explosion during storage.

The parameters that influence the thermal behaviour are particle size distribution, purity and moisture content of the chemicals etc. Decrease in particle size of KNO_3 had an adverse effect on sensitivity to both impact and friction to a greater extent than the particle size of Al,² and set the lowest onset temperature for the exothermic activity. The heat content from the exothermic activity was also found to vary with particle size.³ Decreasing the particle size from micro-size to nano-size pyrotechnic mixture was found to produce sound effectively and it was reported that a smaller amount of pyrotechnic mixture is required to produce the allowed sound level of 120–125 dB(A) as prescribed by the Govt. of India⁴ on using a nano pyrotechnic mixture.⁵ Although it is expected that the particle sizes create large interfacial areas and increased number of atoms at the particle interface which on ignition lead to a higher heat of reaction, the various physical and chemical processes occurring concomitantly and competitively may affect the process.

The effect of particle size of the pyrotechnic mixture on the heat of reaction was carried out using DSC⁵ and ARC.³ Many studies have been carried out on the factors affecting the sound level produced from the fire crackers⁵ and especially on particle size^{6–8} which played a key role in producing the sound level from the fire crackers. Kinetic parameters for all the stages of decomposition have not been reported so far. In the present work, thermal analysis was carried out to deduce the decomposition pattern of the pyrotechnic mixture under well controlled conditions by TGA and DTA techniques. Kinetic parameters for different decomposition stages are derived from the results and the conclusions drawn from them are presented. Importance is given to calculating the kinetic parameters, energy of activation (E) and pre-exponential factor ($\ln A$) by following model-fitting methods, the Coats–Redfern equation, and model-free methods, the Arrhenius and Kissinger methods. Data for energy of activation related to different proportions of pyrotechnic composition and for commonly used mixtures of oxidizers and igniter have not been reported in the literature. An attempt is made to calculate the energy of activation for pyrotechnic mixtures with different oxidizers in varying compositions.

The present work focuses on the most commonly used oxidizer in sound producing fire crackers, KNO_3 with sulphur, aluminium and boric acid.

Experimental

Chemicals and materials

The chemicals used for the preparation of fire cracker were obtained from a firework manufacturing company situated in Tamilnadu, India. The purity and assay of the chemicals are: KNO_3 – 97.6%, Sulphur (S) – 99.9%, Aluminium (Al) – 99.8% and boric acid (H_3BO_3) – 99%. Aluminium powders were of grade 999 (200 mesh, 75 microns), KNO_3 of 120 mesh and 125 microns, S of 100 mesh and 150 microns and H_3BO_3 of 100 mesh and 150 micron sizes were used. All these chemicals were sieved through a 100 mesh brass sieve. The samples were stored away from light and moisture. All these samples were mixed in the ratio of KNO_3 : Al : S : H_3BO_3 as 57.5/20/22/0.5 %.

Instruments

Thermal analyser

Thermal analysis (TA), thermogravimetric (TG) and differential thermal analysis (DTA) were carried out using a Perkin-Elmer, Pyris diamond

model thermal analyser with a heating rate of 1, 10 and 20 °C min⁻¹, and a temperature range of the standard system of room temperature to 900 °C.

X-Ray diffraction analyser

The pyrotechnic mixture and its intermediate products on decomposition were analysed by X-ray analysis by employing a Siemens 800 X-ray diffractometer (XRD) with Cu K α radiation with a view to characterising the intermediate products of decomposition. Thermal runs of the pyrotechnic mixture were interrupted in the TGA-DTA system (heating rate 10 K min⁻¹, cooling rate 60 K min⁻¹) and the intermediates in the range of temperatures, 280–300 °C and 950–980 °C were collected and the collected residues were analysed by XRD. Adequate care was taken to avoid moisture pick up before XRD analysis.

Results and discussion

Figure 1 shows the simultaneous TGA, DTG and DTA curves of pyrotechnic mixture obtained at a heating rate of 10 K min⁻¹ under N₂ atmosphere. The decomposition patterns obtained under other heating rates are similar and the increase in heating rate leads to an increase in the characteristic peak temperature (T_p) which can be seen in the thermograms

(Figure 2).

DTG analysis showed that decomposition occurred in three stages: the first stage ranges from 150 to 250 °C, the second stage is in the range from 580 to 680 °C and the third stage ranges from 750 to 850 °C (Table 1).

Decomposition occurred only in three stages by increasing the heating rate. In TG analysis, the second and third stages are not clearly differentiated. Pyrotechnic mixture before decomposition and residues after the first and third stages of decomposition were collected and were analysed by XRD analysis (Figure 3). Powder diffraction patterns are typically plotted as the intensity of the diffracted X-rays *versus* the angle 2θ . Peaks will appear in the diffraction pattern at 2θ values when constructive interference is at a maximum. By measuring the 2θ values for each diffraction peak, the d -spacing (the distance between the diffracting planes) can be calculated automatically by the data analysis software for all of the peaks in the diffraction pattern. The 2θ values obtained from the XRD pattern were compared with standard JCPDS (Joint Committee on Powder Diffraction Standards) data and marked in the XRD pattern in Figures 3–5.

The sharp mass loss at 150–250 °C is assigned to the removal of sulphur making a weight loss of

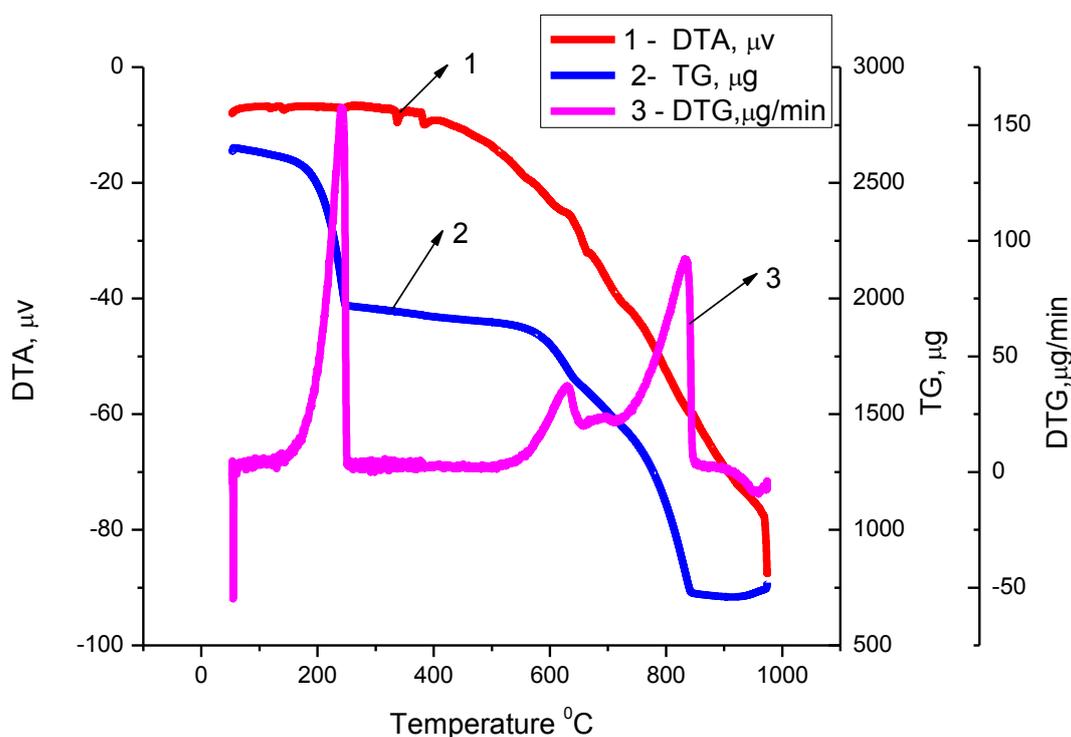


Figure 1. TG, DTA and DTG curves of KNO₃/S/Al/H₃BO₃ in N₂ atmosphere; heating rate: 10 K min⁻¹.

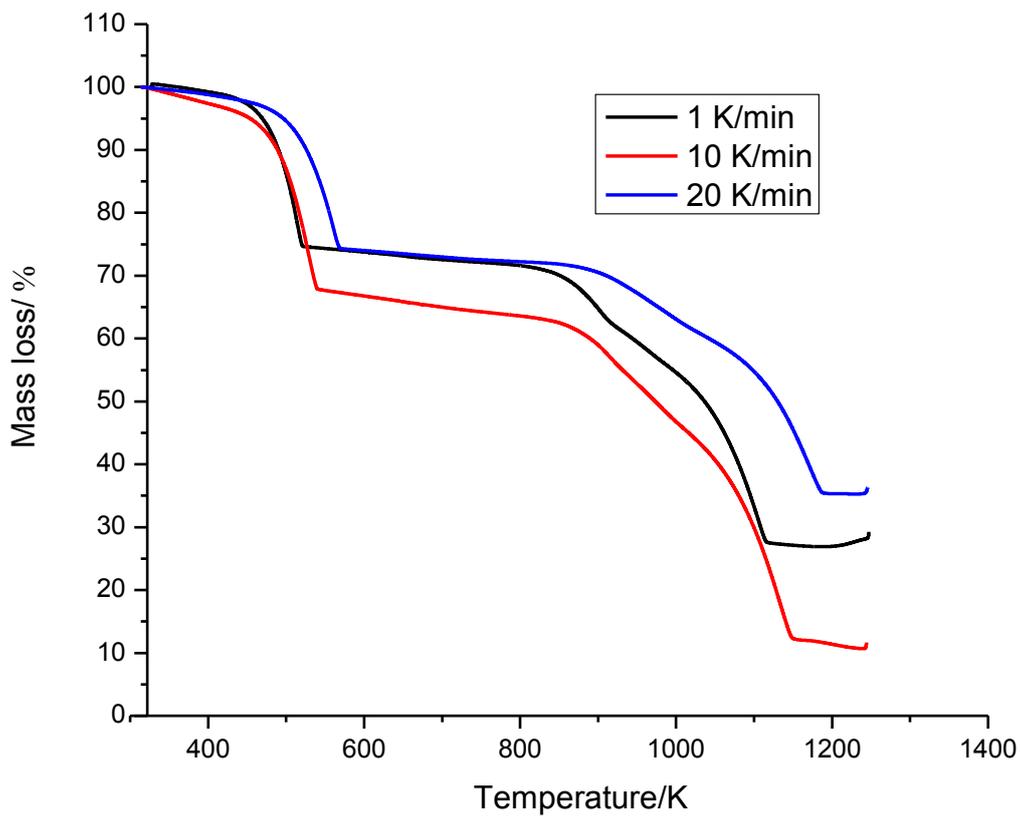


Figure 2. TG analysis of $KNO_3/S/Al/H_3BO_3$ in N_2 atmosphere; at three different β : 1, 10, 20 K.

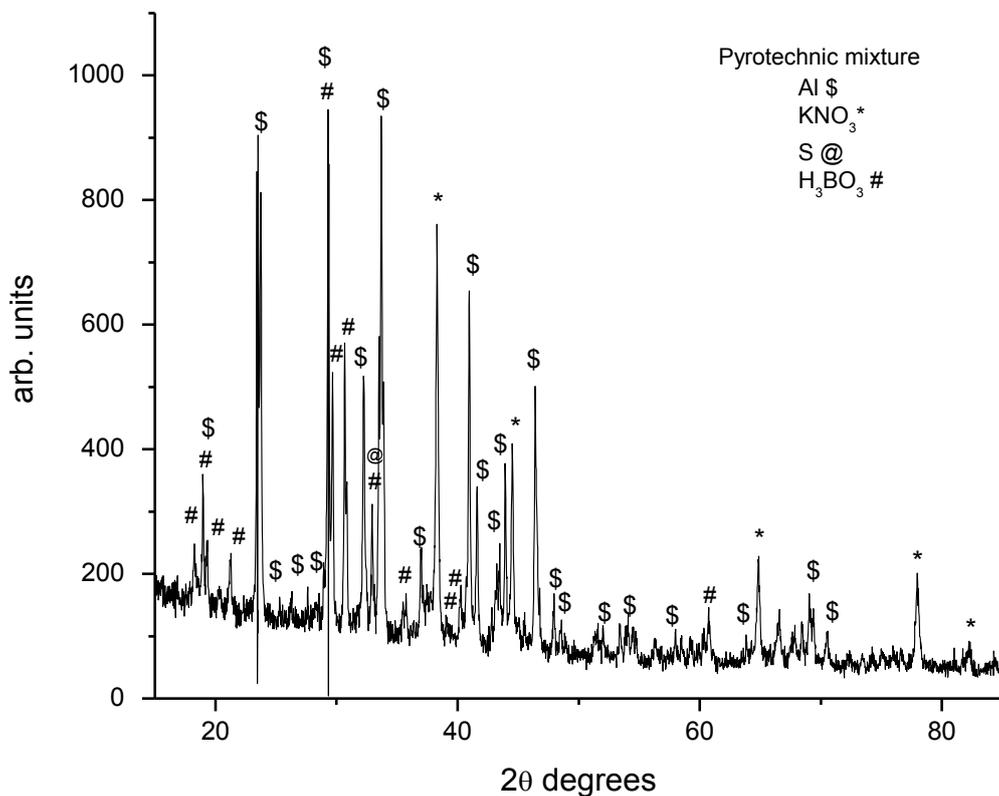


Figure 3. XRD pattern of pyrotechnic mixture, $KNO_3/S/Al/H_3BO_3$, before decomposition.

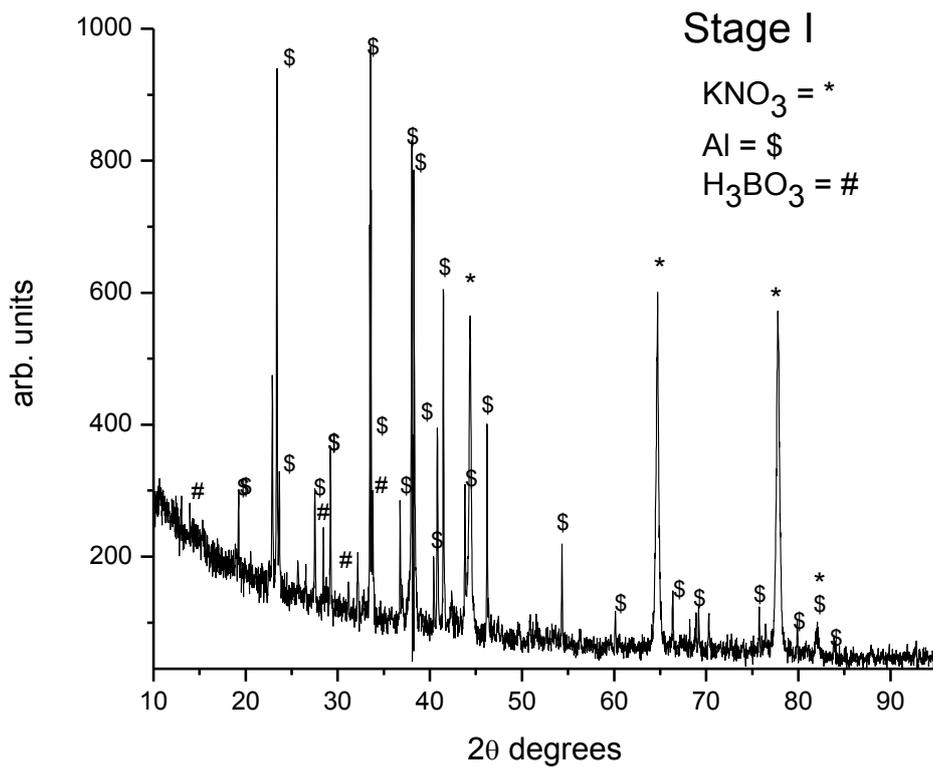


Figure 4. XRD pattern of the residue after decomposition between 280 and 300 °C.

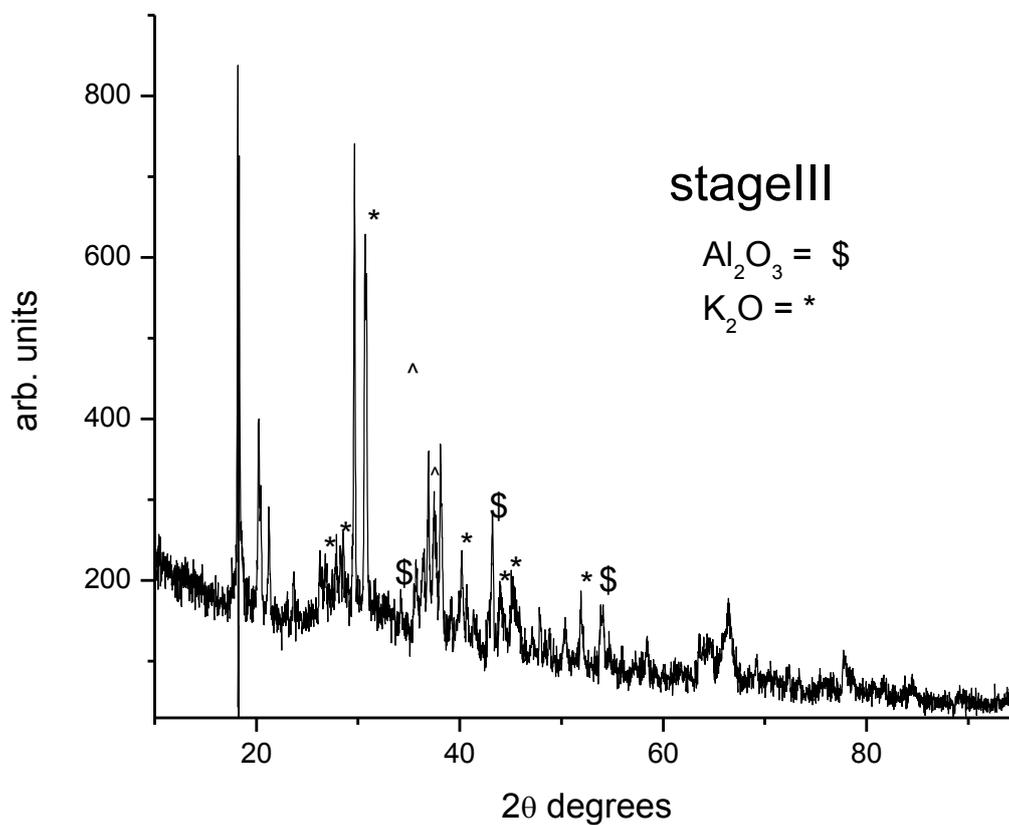


Figure 5. XRD pattern of the residue after decomposition between 950 and 980 °C.

Table 1 Comparison of the expected and the observed mass loss for the decomposition of $KNO_3/Al/S/H_3BO_3$ at 10 K min^{-1} under nitrogen atmosphere

Stages	Temperature	Assumed reactions	Weight loss (TG data) (%)	
			Observed	Expected
I	150–250 °C	$S \rightarrow S(l) \rightarrow S(g)$	24	22
II	580–680 °C	$2KNO_3 \rightarrow 2KNO_2 + O_2(g)$	15	15.84
III	750–850 °C	$4Al + 3O_2(g) \rightarrow 2Al_2O_3$ $4KNO_2 \rightarrow 2K_2O + 4NO(g) + O_2(g)$	35	35.29

24% by exothermic reaction. The exothermic reaction indicated the conversion of sulphur into molten melt by melting or fusion and is a physical process that results in the phase transition of a substance from a solid to a liquid, at which the ordering of ionic or molecular entities in the solid breaks down to a less ordered state and the solid liquefies. Substances in the molten state generally have reduced viscosity with elevated temperature; an exception is the element sulphur, whose viscosity increases to a point due to polymerization and then decreases with higher temperatures in its molten state. Sulphur is not removed by sublimation which is an endothermic phase transition of a substance directly from the solid phase to the gas phase without passing through an intermediate phase and requires additional energy.

In the fire crackers, it is assumed that all the sulphur taken in the pyrotechnic mixture is converted to sulphur dioxide and the reaction is highly exothermic providing energy to initiate the reaction of the pyrotechnic mixture. The absence of peaks due to sulphur (Figure 4) confirms the removal of sulphur in the first stage as shown in the XRD of the residue at stage I.

The second stage of mass loss which occurred between 580–680 °C is assigned to decomposition of oxidizer, KNO_3 , liberating oxygen. Liberation of oxygen from the oxidizer causes 15% weight loss and the reaction is exothermic. The third stage of decomposition occurred immediately after stage II of decomposition between 750–850 °C with 35% mass loss corresponding to the expulsion of NO gas and as the heating rate increases, the

temperature difference between these two stages is narrowed down. Complete exothermic reaction of pyrotechnic mixture occurred at stage III leaving only Al_2O_3 and K_2O as residue which were collected for XRD analysis. The XRD pattern (Figure 5) supported the suggested mechanism and confirmed the final residue obtained from the fire cracker is only potassium oxide and aluminium oxide (Table 1).

Based on the observations of weight loss from TG data of pyrotechnic mixture by three stages, the mechanism given in Table 1 is assumed to take place. There is good agreement between the expected theoretical mass loss and the observed mass loss for all the stages of decomposition of pyrotechnic mixture of $KNO_3 : Al : S : H_3BO_3$ in the ratio of 57.5/20/22/0.5 % shown in Table 1.

The kinetics of the thermal decomposition of sound producing pyrotechnic mixture, $KNO_3/S/Al/H_3BO_3$ under N_2 atmosphere at different heating rates, were studied by model-dependent and model-free methods for each stage separately.

Determination of energy of activation, E_a : model-free methods

The transformation rate during a reaction is the product of two functions, one depending solely on the temperature, T , and the other depending solely on the fraction transformed, α :

$$d\alpha/dt = f(\alpha).k(T) \quad (1)$$

where $d\alpha/dt$ is the derivative of the fraction converted with respect to time. It was calculated for every 10% mass loss of the mixture for all

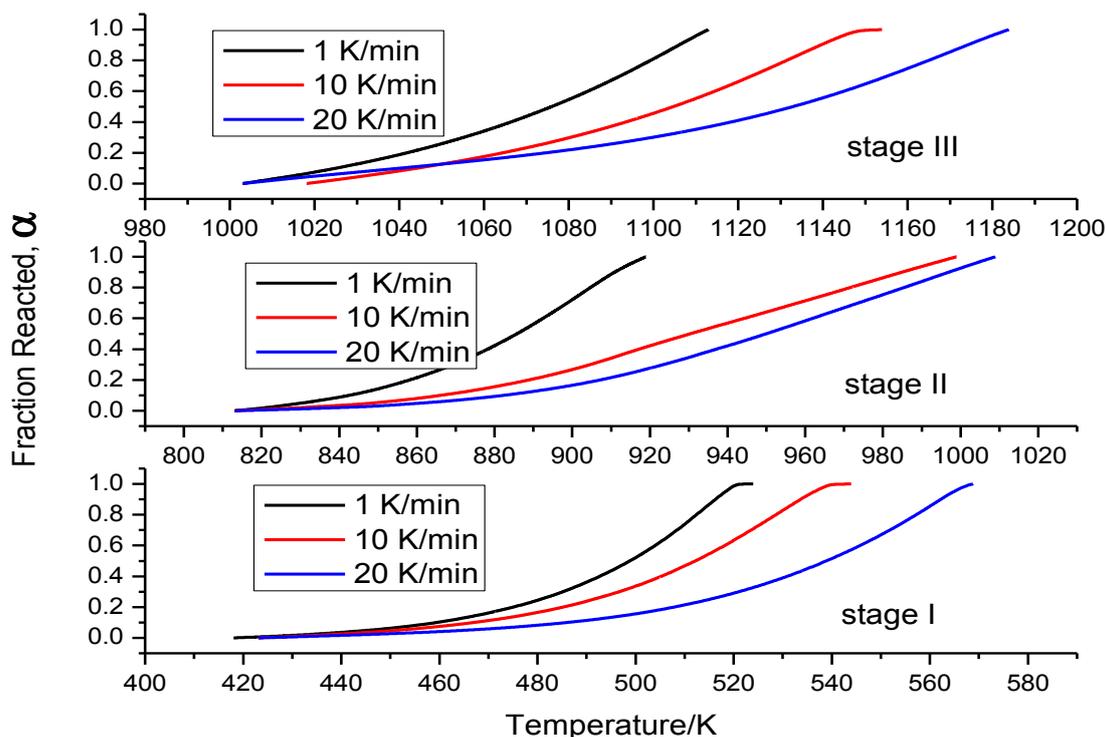


Figure 6. Fraction reacted, α , versus temperature for stages I, II and III at three different heating rates.

the three stages of decomposition in the temperature range of 150–250 °C, 580–680 °C and 750–850 °C respectively at different heating rates. α is defined by the expression as

$$\alpha = (\%w_t - \%w_i) / (\%w_f - \%w_i) \quad (2)$$

where $\%w_t$ is the mass percent at any time t and $\%w_i$ and $\%w_f$ are the initial and final mass percent sample,^{9–15} respectively. A typical plot of α versus temperature for stages I, II and III is shown in Figure 6.

The temperature dependent function is generally assumed to follow an Arrhenius type^{9–13} dependency:

$$\ln k = \ln A - E_a/RT \quad (3)$$

Thus, to describe the progress of the reaction for non-isothermal experiments at all temperatures and for all temperature–time programmes, the reaction rate at all times depends on both $f(\alpha)$ and $k(T)$, and hence the determination of $f(\alpha)$, $\ln A$ and E (the so-called kinetic triplet) are needed. The non-isothermal DTG data (Figure 7) were used to calculate the kinetic parameters using Arrhenius method. The linear Arrhenius plots of $\ln k$ versus $1/T$ for the first stage of decomposition of pyrotechnic mixture at various

heating rates were plotted and similar type plots were obtained for other stages also (Figure 8).

From the slope, the activation energy (E_a)¹⁶ for the decomposition of the pyrotechnic mixture was calculated (Table 2). The activation energy values obtained are 30.7 ± 3.4 , 58.23 ± 4.2 , 58.83 ± 4.6 kJ mol⁻¹ for stages I, II and III respectively.

The activation energy for the non-isothermal decomposition of pyrotechnic mixture was also calculated from the TG data using Kissinger expression:¹⁷

$$\ln(\beta/T_m^2) = \ln[n(1 - \alpha_m)^{n-1}AR/E_a] - E_a/RT_m \quad (4)$$

where β is the heating rate, A is the pre-exponential factor, E_a is the energy of activation, T_m and α_m are the absolute temperature and mass loss at the maximum mass loss rate $(d\alpha/dt)_m$, and R is the gas constant. This method yielded values of 29.9 ± 2.0 , 45.1 ± 2.0 and 108.1 ± 2.0 kJ mol⁻¹ for stages I, II and III, respectively (Table 2) from the slope of $\ln(\beta/T_m^2)$ as a function of $1/T_m$ at the maximum mass loss rate (Figure 9).

The fraction reacted, α , 0.10–0.9, was also used for the kinetic analysis using the Flynn–Wall method¹⁸ at different heating rates β using the expression:

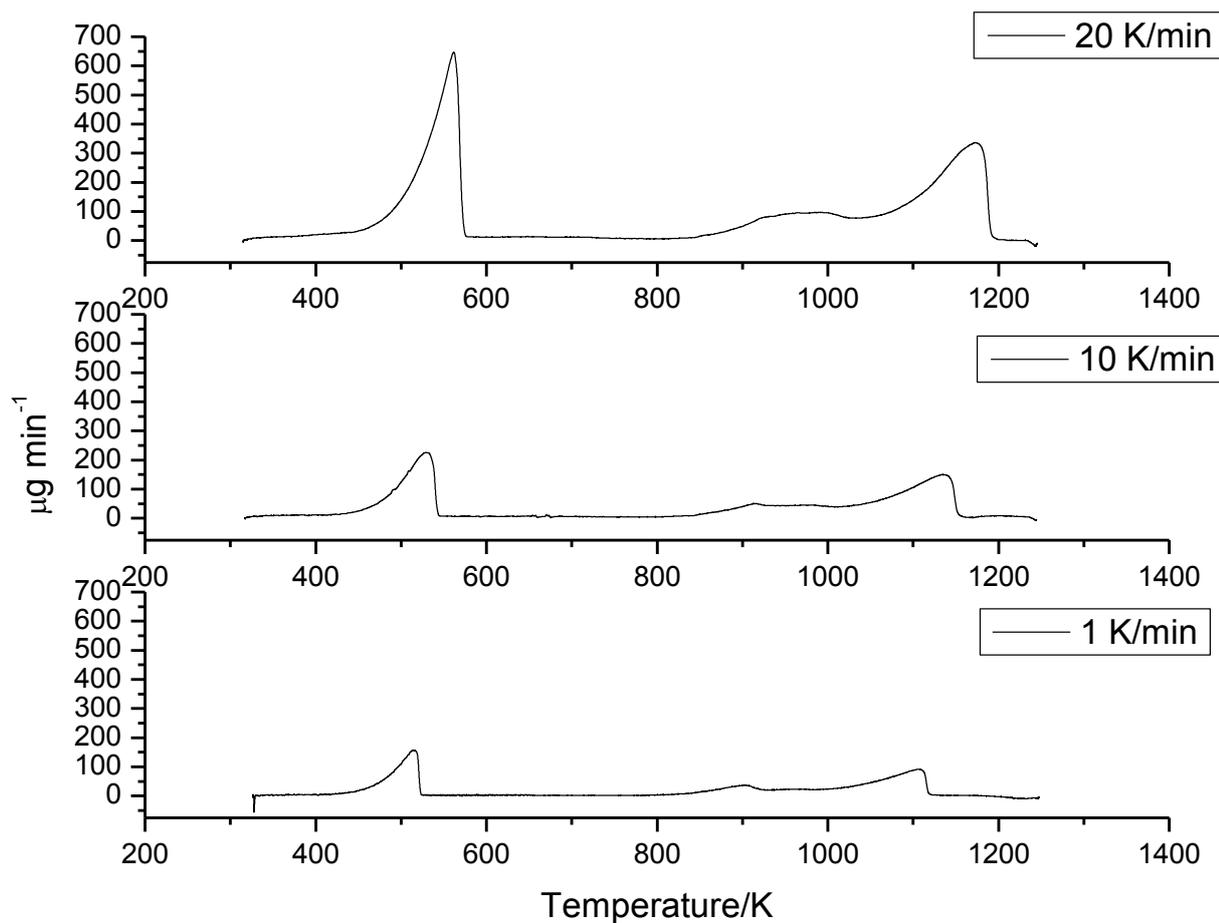


Figure 7. DTG analysis of $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$ in N_2 atmosphere at three different heating rates.

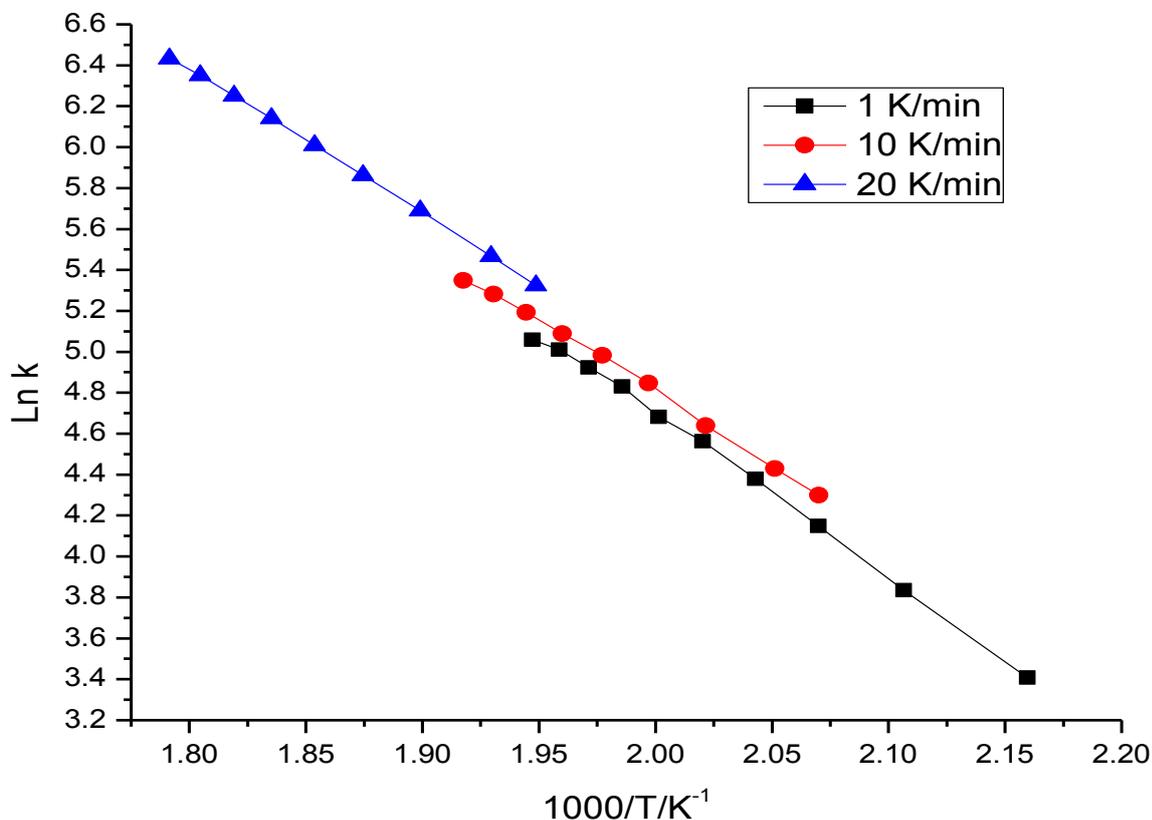


Figure 8. Arrhenius plot of $\ln k$ versus temperature for non-isothermal decomposition of $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$ in N_2 atmosphere; heating rate: 1, 10 and 20 K min^{-1} .

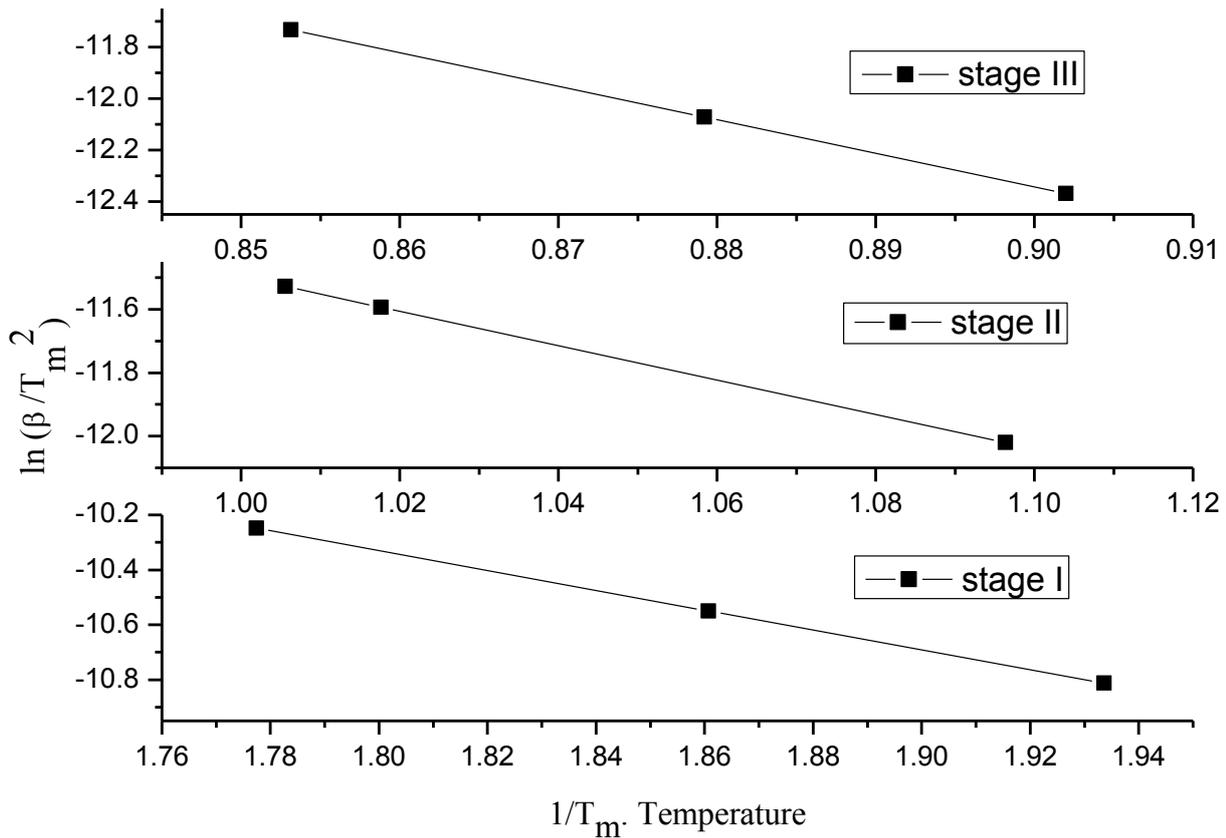


Figure 9. Kissinger plot for stages I, II and III in N_2 atmosphere for the non-isothermal decomposition of $KNO_3/S/Al/H_3BO_3$ using TG data.

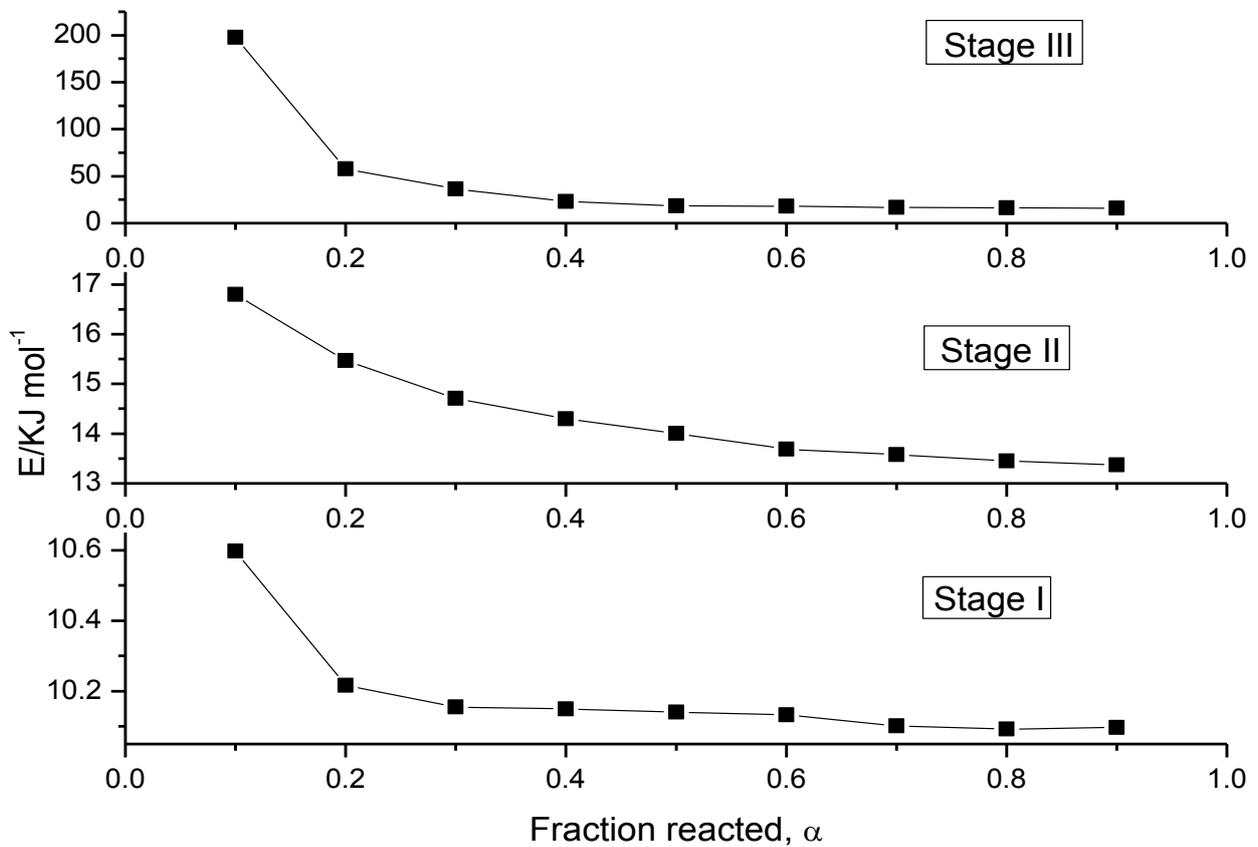


Figure 10. Apparent activation energy versus α , fraction reacted, for stages I, II and III in N_2 atmosphere for non-isothermal decomposition of $KNO_3/S/Al/H_3BO_3$.

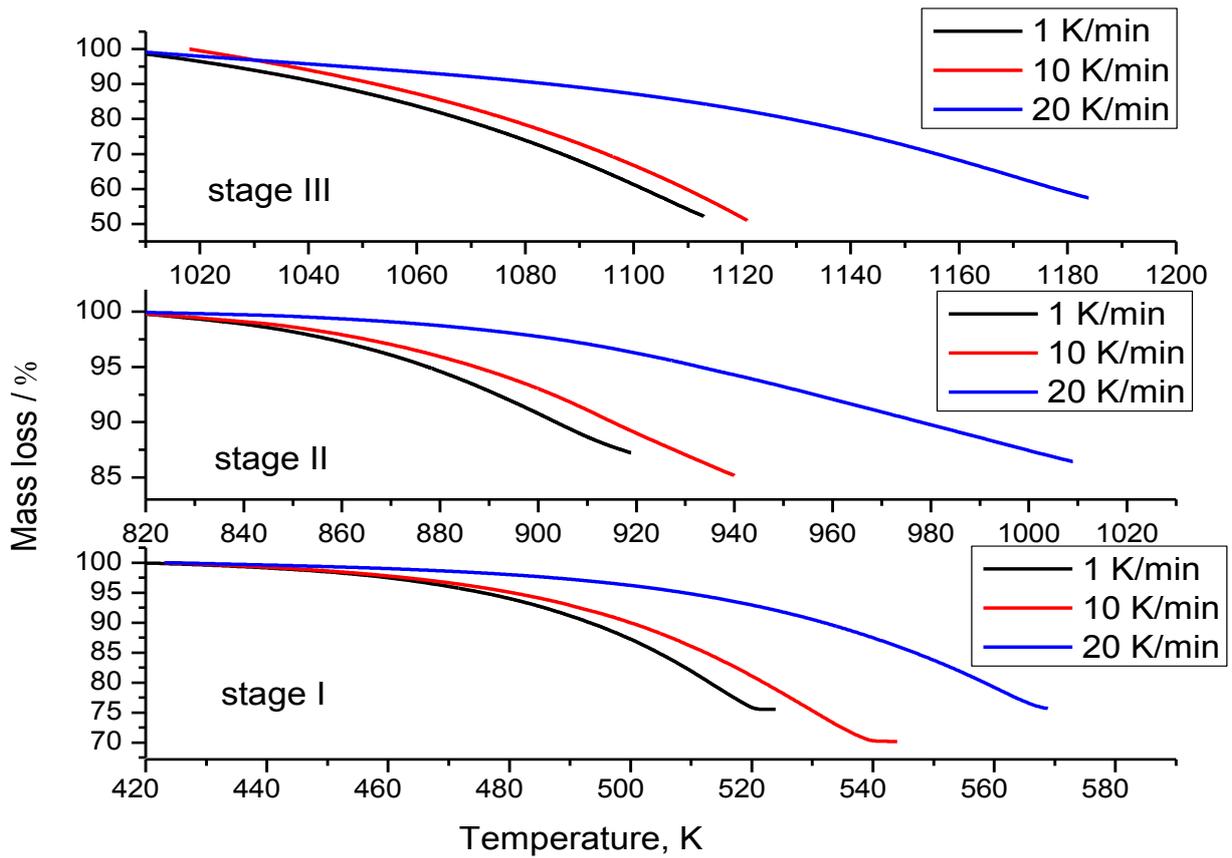


Figure 11. Mass loss (%) for stages I, II and III versus temperature for the decomposition of $KNO_3/S/Al/H_3BO_3$ at different β .

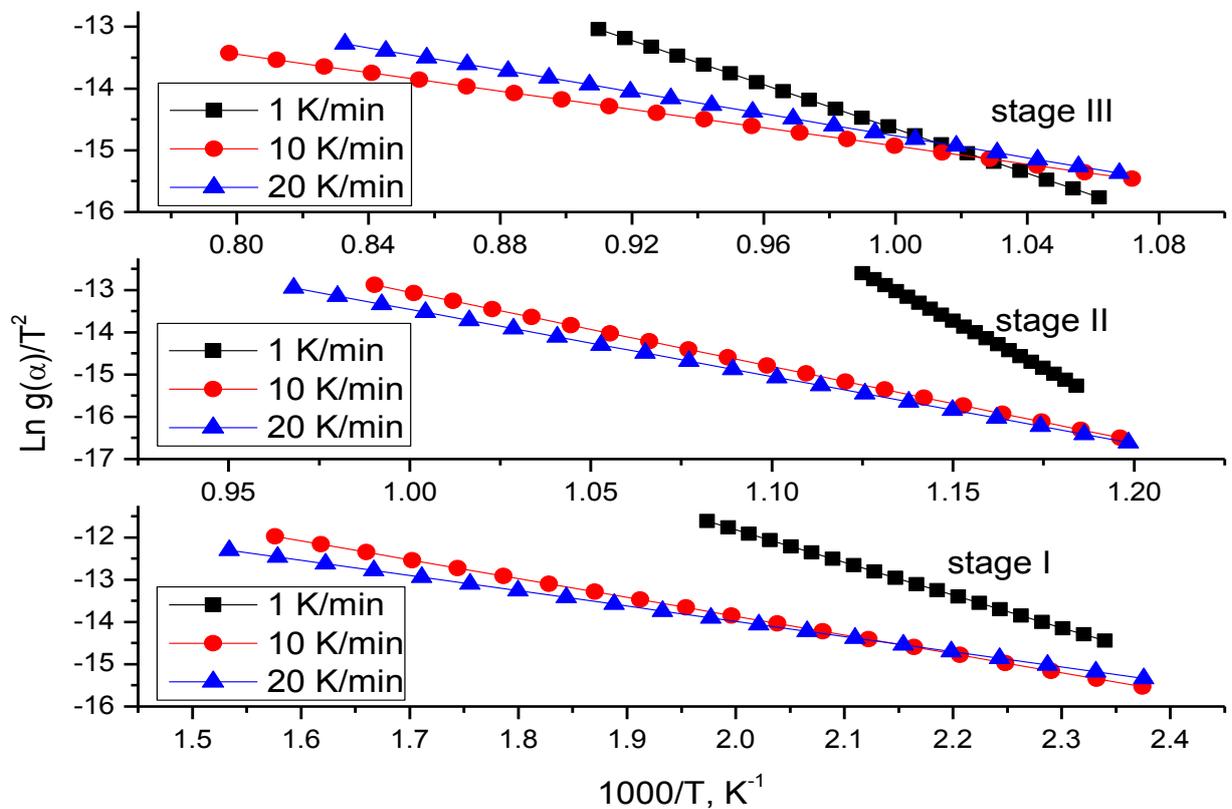


Figure 12. A2-mechanistic plot of $\ln g(\alpha)/T^2$ versus $1000/T$ for $KNO_3/Al/S/H_3BO_3$ in N_2 atmosphere at different β .

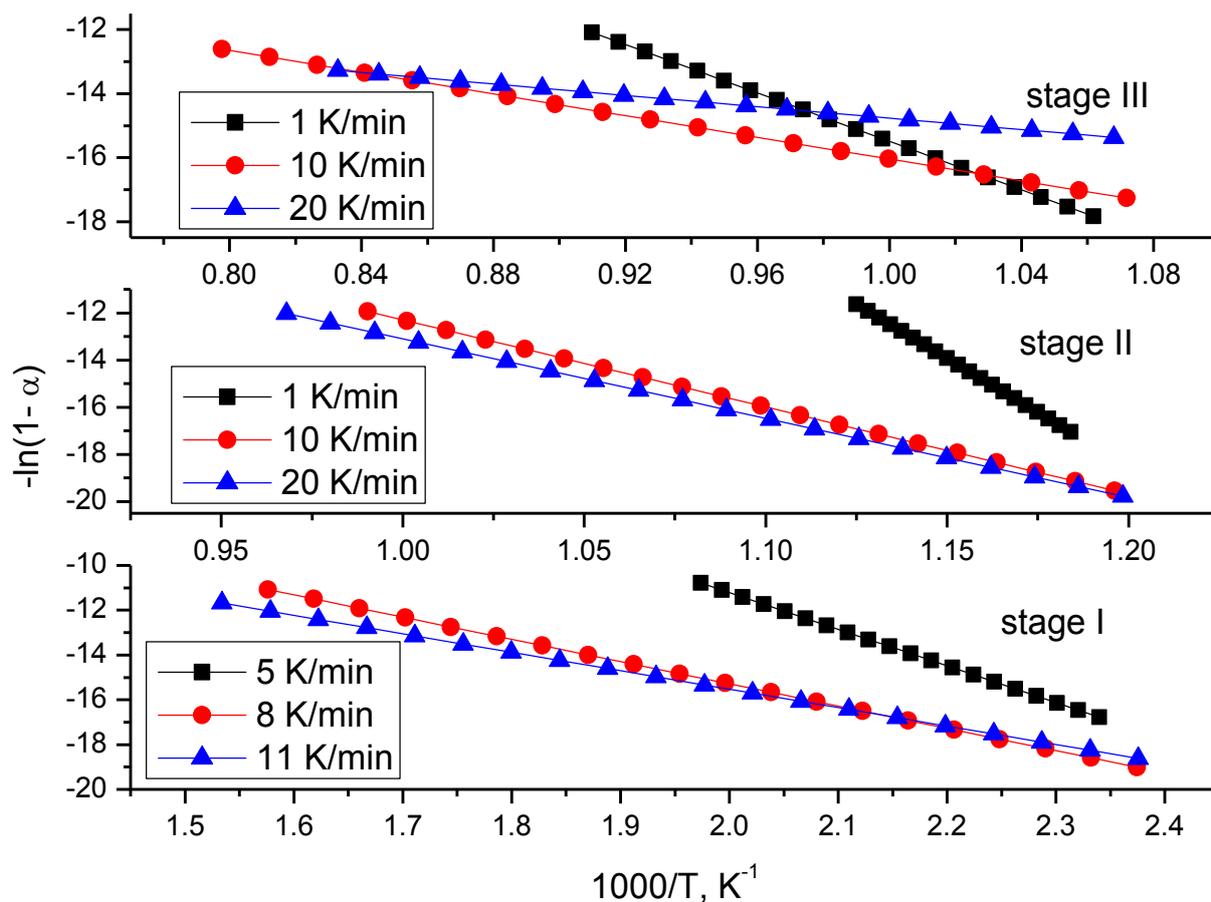


Figure 13. *F1 plot of $[-\ln(1 - \alpha)]$ versus $1000/T$ by $KNO_3/Al/S/H_3BO_3$ in N_2 atmosphere at different β .*

Table 2 *Activation energy for the decomposition of $KNO_3/Al/S/H_3BO_3$*

Methods	Stages	$E/kJ\ mol^{-1}$	Correlation coefficient (r)
Kissinger	I	29.9 ± 5	-0.96452
	II	45.1 ± 5	-0.97819
	III	106.0 ± 2	-0.98159
Arrhenius	I	30.7 ± 4	-0.89253
	II	58.2 ± 6	-0.92733
	III	58.93 ± 6	-0.9157
iso-conversional	I	10.6 ± 4	-0.95209
	II	17.0 ± 6	-0.82797
	III	60 ± 10	-0.92403

Table 3 List of solid-state rate equations used in the present study

Description	Equation
Rate controlling mechanism	$g(\alpha)$
P1 power law	$\alpha^{1/n}$
E1 exponential law	$\ln \alpha$
A2 Avrami–Erofe'ev equation 1 .	$[-\ln(1-\alpha)]^{1/2}$
A3 Avrami–Erofe'ev equation 2	$[-\ln(1-\alpha)]^{1/3}$
A4 Avrami–Erofe'ev equation 3	$[-\ln(1-\alpha)]^{1/4}$
B1 Prout–Tompkins	$\ln[\alpha/(1-\alpha)]$
R2 contracting area	$1 - (1 - \alpha)^{1/2}$
R3 contracting volume	$1 - (1 - \alpha)^{1/3}$
D1 one-dimensional diffusion	α^2
D2 two-dimensional diffusion	$(1 - \alpha)\ln(1 - \alpha) + \alpha$
D3 three-dimensional diffusion, Jander's	$[1 - (1 - \alpha)^{1/3}]^2$
D4 three-dimensional diffusion, Ginstling Brounshtein	$(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$
F1 first order	$-\ln(1 - \alpha)$
F2 second order	$1/(1 - \alpha)$
F3 third order	$[1/(1 - \alpha)]^2$

$$\ln \beta = \ln (AE_a/R) - \ln [F(\alpha)] - E_a/RT \quad (5)$$

The activation energy for each conversion point (E_a , α) was calculated from the slope of the linear plot of the Flynn–Wall method at different heating rates β . The plots of E_a versus α , fraction reacted for stage I, II, III (Figure 10) show that E_a decreases with the extent of conversion (α), $0.2 < \alpha < 0.9$ and the activation energy is high at the initial fraction reacted which indicates that the decomposed products are in equilibrium with the gaseous reactants. The decreasing of E_a with increasing extent of conversion indicates that porous type solids decomposed more easily. The results reveal that the dependence of apparent activation energy (E_a) on the extent of conversion helps not only to disclose the

complexity of a decomposition process, but to identify its kinetic scheme as well.

The E_a value is lower for stage I and II (10.444 and 15.88 kJ mol⁻¹) compared to the E_a value of the third stage of decomposition (50.25 kJ mol⁻¹).

Dissociation mechanism – model-fitting method

Kinetic analysis by model-fitting of the thermal data obtained for all the three stages of decomposition was done in order to arrive at the mechanism of the dissociation processes and to deduce the kinetic parameters. The rate of the reaction under non-isothermal conditions can be expressed by the following relation:

Table 4 Kinetic parameters and possible rate controlling processes of decomposition of $KNO_3/Al/S/H_3BO_3$

Stage	Mechanism	$\beta/K \text{ min}^{-1}$	TG data		Correlation coefficient (r)
			$E/kJ \text{ mol}^{-1}$	$\ln A/\text{min}$	
Stage I	A2	1	16.054	3.662	-0.96027
		10	12.771	-4.950	-0.97311
		20	11.916	-6.778	-0.97636
Stage II	A2	1	53.316	38.02	-0.88901
		10	25.884	4.518	-0.92033
		20	24.195	2.423	-0.90682
Stage III	A2	1	56.222	3.253	-0.94685
		10	15.729	-7.516	-0.7897
		20	17.212	5.868	-0.90674

$$d\alpha/dT = K(T)/\beta - f(\alpha) \quad (6)$$

where α is the fraction reacted at temperature T . $f(\alpha)$ is the conversion function which is dependent on the mechanism of the reaction. β is the rate of heating employed in the experiment and $k(T)$ is the rate constant as a function of temperature. Equation (6) can be represented by its integral form as follows:

$$\ln[g(\alpha)/T^2] = \ln[(AR/\beta E)(1 - 2RT/E)] - E/RT \quad (7)$$

The algebraic expression of the integral $g(\alpha)$ functions that are tested in this work are listed in Table 3. A plot of $\ln g(\alpha)/T^2$ versus $1/T$ gives a straight line when the correct $g(\alpha)$ function is used in the equation. The $g(\alpha)$ function describes the mechanism of the reaction. Straight lines with a high correlation coefficient and low standard deviation were selected to represent the possible controlling mechanism. The plot of mass loss for the stages I, II and III with respect to the temperature is given in Figure 11. The fraction reacted, α , was evaluated as a function of temperature.

The kinetics of all the three stages of the thermal decomposition of sound producing pyrotechnic mixture, $KNO_3/S/Al/H_3BO_3$ in N_2 atmosphere at different heating rates was followed by employing the Coats-Redfern¹⁹ approximation (Table 3) which gives the expression.

A plot of $\ln g(\alpha)/T^2$ versus $1/T$ gives a straight

line when the correct $g(\alpha)$ function is used in the equation. The $g(\alpha)$ function describes the mechanism of the reaction. Straight lines with high correlation coefficient and low standard deviation were selected to represent the possible controlling mechanism. The corresponding kinetic parameters were then calculated and are shown in Table 4. The model-fitting method is performed in the conversion region where the apparent activation energy is approximately constant and where a single model may fit.

The non-isothermal kinetic data of mixture in the limit of $0.2 < \alpha < 0.9$ are fitted to each of the thirteen reaction models which are indicated in Table 3. The values of activation energy (E_a), pre-exponential factor ($\ln A$) and the coefficient of linear correlation (r) for various kinetic models at three different heating rates are presented in Table 4. The Arrhenius parameters (E_a , $\ln A$) are highly variable, exhibiting a strong dependence on the reaction model chosen. On the other hand, more than one model, namely A2 and A3, gave fairly good coefficients of linear equations. However by comparing the E_a value with the model-free method, the A2 mechanism (Figure 11) was accepted.

The corresponding kinetic parameters were then calculated and are shown in Table 4. The best fit for the first decomposition step of expulsion of sulphur, and the second and third decomposition steps of converting aluminium to alumina are obtained using A2, the two-dimensional Avrami

Table 5 Kinetic parameters and order for $KNO_3/Al/S/H_3BO_3$

Stage	Order	$\beta/K \text{ min}^{-1}$	TG data		Correlation coefficient (<i>r</i>)
			$E/kJ \text{ mol}^{-1}$	$\ln A/\text{min}$	
Stage I	F1	1	24.72276	21.60864	-0.96452
		10	18.25368	4.58985	-0.97819
		20	16.55692	0.9595	-0.98159
Stage II	F1	1	100.05091	91.57722	-0.89253
		10	45.28849	24.68004	-0.92733
		20	41.92852	20.51068	-0.9157
Stage III	F1	1	46.16195	22.35522	-0.95209
		10	25.29485	0.93511	-0.82797
		20	28.22128	4.19184	-0.92403

–Erofe'ev model which corresponds to nucleation and growth mechanism. Similarly, the order of the reaction was also found to obey F1 (Figure 12), a first order reaction and the calculated kinetic parameters are given in Table 5.

Conclusions

Thermal analysis of pyrotechnic mixture, $KNO_3/Al/S/H_3BO_3$, from sound producing fire crackers was carried out at three different heating rates, 1, 10 and 20 $K \text{ min}^{-1}$. The thermal decomposition of the pyrotechnic mixture occurred in three stages. The pathway of the decomposition was predicted by analysing the XRD pattern of the residue at stages I and III as sulphur in the mixture is first decomposed exothermically, and the liberated heat energy is used to initiate further exothermic reactions in the mixture leaving K_2O and Al_2O_3 as final residue. The kinetics of thermal decomposition were studied for all three stages and the energy of activation, E_a , was calculated as 10–30 kJ mol^{-1} , 20–58 kJ mol^{-1} and 56–70 kJ mol^{-1} for stages I, II and III respectively by the model-free methods, Arrhenius, Kissinger and isoconversional methods which are in good agreement with the energy of activation, E_a , calculated as 11–16 kJ mol^{-1} , 24–53 kJ mol^{-1} and 15–56 kJ mol^{-1} for stages I, II and III respectively by the model-fitting method A2, a two-dimensional model, nucleation and growth mechanism. The dependence of effective activation energy on extent of conversion shows that the process is

kinetically complex. The order of the reactions obeys first order with the energy of activation, E_a , as 16–24 kJ mol^{-1} , 41–53 kJ mol^{-1} and 25–46 kJ mol^{-1} for stages I, II and III respectively. It is our duty to identify some chemicals which can be added to the pyrotechnic mixture so as to increase the E_a value to prevent autoignition of pyrotechnic mixtures while in storage in the fireworks industry. The calculation of the kinetic factor E_a will help to identify the best composition of pyrotechnic mixture for storage.

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