

Thermal Studies on Boron-Based Initiator Formulation

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ABSTRACT

Boron-potassium nitrate pyrotechnic composition can be converted into a hot wire-sensitive initiator formulation by the addition of an extra fuel, viz. lead thiocyanate. The ignition temperature of this composition depends on the percentage of thiocyanate in the mix and follows a binomial fit. The kinetic parameters, viz. activation energy E and pre-exponential factor A of the charge have been calculated from TG and DSC curves using different approaches developed by Coats-Redfern and Kissinger. Ignition delays measured from isothermal TG runs were found to yield equally good values of E and A . A comparison of these values for the tricomponent system with those of the bicomponent systems as well as of the ingredients suggests that the starting reaction in this formulation is the reaction between lead thiocyanate and potassium nitrate which energises the main reaction between boron and potassium nitrate, leading to ignition.

NOMENCLATURE

A	Arrhenius pre-exponential factor
e	Base of natural logarithm
E	Activation energy
β	Linear heating rate
$g(\alpha)$	Function of α
α	Fractional decomposition/ reaction
k	Rate constant
n	Apparent order of reaction
R	Universal gas constant
t	Time
τ	Ignition delay
T	Temperature
T_i	Inception temperature of reaction
T_p	DSC/ DTG peak temperature
T_f	Temperature of completion of reaction

1. INTRODUCTION

Initiators find extensive application as first fire elements in all pyro/explosive-based systems and devices. Various prospective compositions are reported in literature for different applications. The selection of a formulation is dictated by its ability to meet the

specifications stipulated for a particular application. Thus, for launch vehicles these parameters are fixed in terms of no-fire, all-fire and recommended fire currents that decide thermal load for the flash charge.

Boron-potassium nitrate is a well known pyrotechnic formulation used extensively as booster/terminal charge in space ordnance. It is possible to convert this formulation into a hot wire sensitive initiatory charge by the addition of an extra fuel, lead thiocyanate. In this paper, an attempt has been made to understand the ignition behaviour of this charge *vis-a-vis* its components and the bicomponent systems through differential scanning calorimetric and thermogravimetric techniques.

2. EXPERIMENTAL DETAILS

2.1 Materials

Boron used in this study was procured from Riedel, Germany, having a purity of 98 per cent and average particle size of 3 μm . Lead thiocyanate with a purity of 99.5 per cent was obtained from Wilson Laboratories, Bombay and used after passing through a 400 mesh sieve (average particle size 12 μm). Potassium nitrate of over 99.5 per cent purity supplied by CDH was ground and

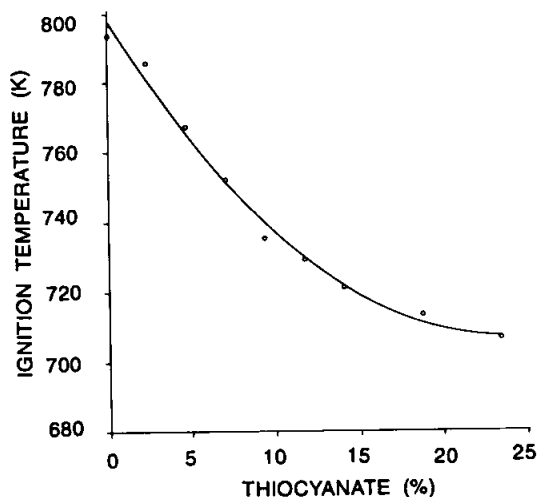


Figure 1. Dependence of ignition temperature of $B/Pb(SCN)_2/KNO_3$ initiator formulation on thiocyanate percentage.

sieved and the fraction passing through 350 mesh sieve was used.

2.2 Methods

Mix was made from accurately weighed out ingredients by sieving five times through a 150 mesh sieve. The lead thiocyanate percentage in the tri-component system boron-lead thiocyanate-potassium nitrate was varied by progressively replacing boron with equivalent quantities of lead thiocyanate (1:2.66).

Thermogravimetric (TG) and differential scanning calorimetric (DSC) measurements were performed using Perkin-Elmer thermal analyser, model TGA7 & DSC7, in flowing argon atmosphere at a flow rate of 30 cc/min for TG and 50 cc/min for DSC. Sample size was kept constant at about 1.5 mg. Ignition temperatures of the compositions were taken as the DSC peak temperature at a heating rate of 10 K/min. Dynamic TG runs for kinetic evaluations were made at a heating rate of 5 K/min.

3. RESULTS & DISCUSSION

3.1. Effect of Lead Thiocyanate Percentage on Ignition Temperature

Figure 1 shows the dependence of exothermic peak temperature of boron-lead thiocyanate-potassium nitrate formulation on thiocyanate percentage. As the percentage increases, initially the peak temperature decreases sharply till about 10 per cent thiocyanate.

Thus the formulation $B-Pb(SCN)_2-KNO_3$ (20:9.4:70.6) has an ignition temperature of 735 K against 794 K for $B-KNO_3$ (25:75). As the percentage is further increased, the effect becomes less pronounced and the dependence obeys a binomial fit. This effect can be attributed to the decreasing heat output as the more energetic fuel boron is successively replaced with thiocyanate. The dependence can be mathematically represented as,

$$T_{ig} = 0.165 [Pb(SCN)_2]^2 - 7.77 [Pb(SCN)_2] + 798 \quad (1)$$

where T_{ig} is the ignition temperature.

By suitably adjusting the percentage of thiocyanate it is possible to obtain a composition of desired ignition temperature to respond to hot wire ignition for a given current rating.

3.2 Weight Loss Studies

It was decided to investigate how the presence of thiocyanate causes a decrease in ignition temperature of the composition. For this purpose, kinetic investigations of ignition/decomposition reactions were carried out on ingredients as well as bicomponent and tricomponent systems applying DSC and TG techniques. Figure 2 shows the TG curves of ingredients and formulations and the results are tabulated in Table 1.

Table 1. TG results of various formulations

Sample	T_i (°C)	T_f (°C)	DTG peak (°C)	Wt. loss (%)
KNO_3	525	743	728	88
$Pb(SCN)_2$	220	338	325	24.3
$Pb(SCN)_2/$	220	320	298	14.4
KNO_3 (47/53)	320	339	335	2.9
	339	405	388	8.0
B/KNO_3 (25/75)	445	525	520	17.3
$B/Pb(SCN)_2/$	220	435	-	4.6
KNO_3 (22/5/73)	435	490	464	14.7

It can be seen that all the formulations have a lower decomposition/ignition temperature than that of KNO_3 , implying that in these formulations, reactions precede KNO_3 decomposition. On the contrary, lead thiocyanate decomposes exothermically at the low temperature range of 220 to 338 °C with a weight loss of 24.3 per cent. All

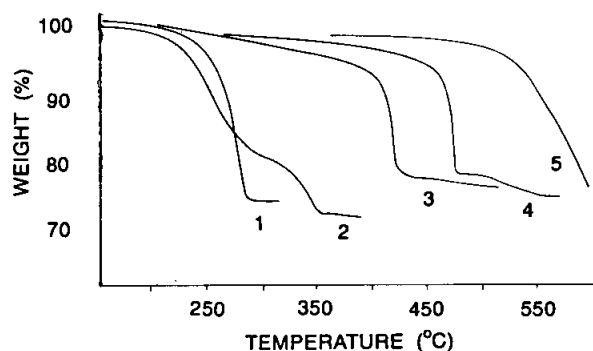


Figure 2. TG curves of different formulations. Heating rate 5 K/min; argon atmosphere [1. $Pb(SCN)_2$, 2. $Pb(SCN)_2/KNO_3$ (47/53), 3. $B/Pb(SCN)_2/KNO_3$ (22/5/73), 4. B/KNO_3 (25/75); 5. KNO_3 .]

thiocyanate compositions show weight loss starting from around 220 °C which is the inception temperature of thiocyanate decomposition. This means that in these formulations thiocyanate decomposition may be the starting reaction. Thus $Pb(SCN)_2/KNO_3$ combination shows weight loss in almost three stages, with the first stage accounting for a maximum of 14.4 per cent. This first stage decomposition ends by 320 °C, which is about 18 °C less than the T_f for thiocyanate decomposition. This is followed by a rapid weight loss of 2.9 per cent ending by 339 °C, which corresponds to T_f of thiocyanate. The weight loss in these stages comes to 17.3 per cent, whereas thiocyanate decomposition alone can lead to a weight loss of just 11.4 per cent only. This means that there is reaction between lead thiocyanate and potassium nitrate in this temperature range.

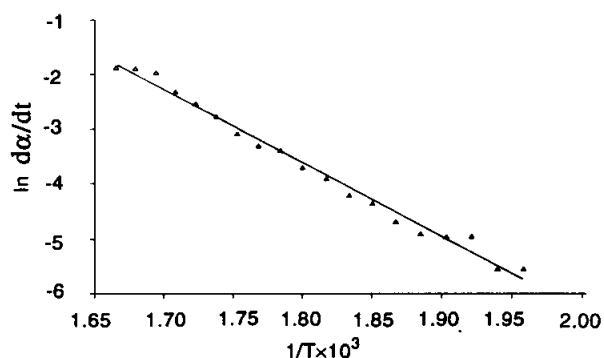


Figure 3. Plot of $\ln(d\alpha/dt)$ versus $1/T$ (K) for lead thiocyanate decomposition.

Boron-potassium nitrate reaction takes place in the temperature range of 445-525 °C. Boron-lead thiocyanate-potassium nitrate combination shows weight loss in two stages. From the above it can be inferred that the first stage from 220-435 °C corresponds to lead thiocyanate-potassium nitrate reaction and the second stage from 435-490 °C corresponds to boron-potassium nitrate reaction. These inferences have been checked by studying the kinetics of decomposition of all the formulations listed in Table 1.

3.3 Kinetic Studies

Kinetic parameters have been estimated by DSC and TG utilizing Coats-Redfern and Kissinger's methods.

3.3.1 Methods

3.3.1.1 Coats-Redfern Method¹

Table 2. Summary of kinetic parameters of various formulations [Heating rate 5 K/min, argon atmosphere]

Composition.	Method	Temp. range (°C)	α range	n	E (kJ/mol)	$\ln A$ (min^{-1})	r^2
KNO_3	Kissinger	525-743	0.05-0.95	1.0	153.2	16.3	0.7796
	Coats- Redfern				152.2	16.7	0.9843
$Pb(SCN)_2$	Coats-Redfern	220-340	0.007-0.99	0.0	107.9 ± 1.2	19.7	0.9977
	Zero-order: $\ln(d\alpha/dt)$ vs. $1/T$	220-340	0.007-0.76	0.0	107.2 ± 3.7	19.6	0.9784
$Pb(SCN)_2 / KNO_3$ (47/53)	Coats-Redfern	220-320	0.01-0.50	0.75	118.5 ± 1.5	22.4	0.9975
		338-405	0.69-0.77	1.0	20.9 ± 1.5		0.9789
B/ KNO_3 (25/75)	Kissinger	445-525	0.02-0.36	1.33	210.0 ± 3.4	30.2	0.9995
	Coats-Redfern				227.6 ± 7.6	32.4	0.9887
	Ignition Delay				226.9 ± 22.9	31.0	0.9702
$B/Pb(SCN)_2/KNO_3$ (22/5/73)	Kissinger	220-435	0.04-0.80	2.0	197.7 ± 10.1	30.0	0.9922
	Coats-Redfern				61.7 ± 1.1		0.9922
	Ignition Delay				198.4 ± 16.6	27.4	0.9794

According to this method

$$\log [g(\alpha)/T^2] = \log [AR/\beta E (1-2RT/E)] - E/2.303RT \quad (2)$$

where,

$$g(\alpha) = [1 - (1-\alpha)^{1-n}] / 1-n, \text{ when } n \neq 1 \text{ and}$$

$$g(\alpha) = -\log(1-\alpha) \text{ when } n = 1$$

The plots of L.H.S against $1/T$ will be linear with slope equal to $-E/2.303R$.

The fractional decomposition α for the respective temperature was first determined from the TG curves by the normal procedure. These values of α were substituted in Eqn (2) above and iterated for n ranging from 0.3 and the equation giving the highest value for the correlation coefficient was chosen as the correct form of $g(\alpha)$. Once the value of n is so determined, L.H.S of Eqn (2) is plotted against $1/T$ and from the slope and intercept E and A are calculated.

3.3.1.2 Kissinger's Method²

This is a multiple heating rate method applicable for reactions with the apparent order of reaction nearing 1. This is especially suitable for fast reactions where analysis of a single thermogram may yield abnormally high kinetic parameters.

$$d [\ln(\beta/T_p^2)] / d(1/T_p) = -E/R \quad (3)$$

with T_p being DSC or DTG peak temperatures. A plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ is linear and from the slope E is calculated. A is calculated from the equation,

$$A = \beta E e^{-E/RT_p} / RT_p^2 \quad (4)$$

3.3.2 Formulation Studies

3.3.2.1 Potassium Nitrate

The kinetics of KNO_3 decomposition has been analysed by Kissinger's method at heating rates of 5, 10, 15 and 20 K/min in TG and also by the Coats-Redfern method at the heating rate of 5 K/min. While both methods gave comparable E values of about 153 kJ/mol, the correlation coefficient was found to be better for the Coats-Redfern plot. The $\ln A$ values were also comparable at 16.3 min^{-1} and 16.7 min^{-1} respectively.

3.3.2.2 Lead Thiocyanate

Coats-Redfern equation gave a value of zero for n and it yielded an E value of 107.9 kJ/mol and $\ln A$ of 19.7 min^{-1} . Since the apparent order of reaction was

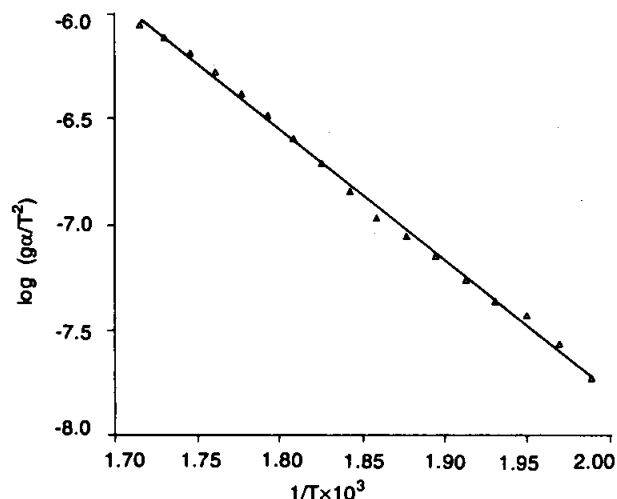


Figure 4. Coats-Redfern plot for $Pb(SCN)_2/KNO_3$ (47/53) reaction. $n = 0.75$.

found to be zero, the curve was analysed in a second way as well.

For a zero order reaction,

$$d\alpha/dt = k(1-\alpha)^0 = A e^{-E/RT} \quad (5)$$

$$\text{i.e., } \ln(d\alpha/dt) = \ln A - E/RT \quad (6)$$

Thus a plot of $\ln(d\alpha/dt)$ versus $1/T$ will be linear and from the slope and intercept E and A could be calculated. The $d\alpha/dt$ values for various temperatures have been computed using the DTG curve and plotted as mentioned above (Fig. 3). From the plot, a closely agreeing value of 107.2 kJ/mol was obtained for E and 19.6 min^{-1} for $\ln A$.

3.3.2.3 Lead Thiocyanate/Potassium Nitrate

The major peak (220-320 °C) of lead thiocyanate/potassium nitrate reaction has been analysed by Coats-Redfern method (Fig. 4). It yielded an activation energy of 118.5 kJ/mol for an n of 0.75. Similar treatment of the next major peak (338-405 °C) gave a low E value of 20.9 kJ/mol for n equals 1.

3.3.2.4 Boron/Potassium Nitrate

Kinetic parameters of this major composition have been determined by three different methods to confirm the validity of the results. Coats-Redfern analysis of the TG curve gave almost identical r value for n ranging from 1.0 to 1.5 with the E value varying between 222.6 kJ/mol and 230.2 kJ/mol. For $n = 1.33$, E was

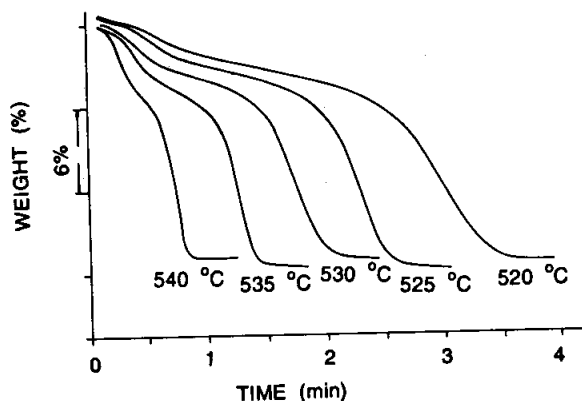


Figure 5. Isothermal TG curves for B/KNO_3 reaction at various temperatures (Argon atmosphere).

227.6 kJ/mol and $\ln A$ was 32.4 min^{-1} . However, Kissinger's method using DSC peak temperatures gave a value of 210 kJ/mol for E .

So, a third method based on ignition delay was also attempted. In this method, it is assumed that the major reaction leading to ignition of the charge starts from the extrapolated onset temperature. In an isothermal run it corresponds to the onset time. So the onset time of the reaction was determined at various isothermal runs using TG. Now, this time corresponds to the time interval during which sufficient reaction is built up to generate enough heat to lead to the main reaction. So, the magnitude of this interval can be counted as the ignition delay, τ and it is inversely proportional to the rate of reaction, and hence can be equated to $1/k$. So, it can be written that:

$$1/\tau = A e^{-E/RT} \quad (7)$$

From the plot of $\ln(1/\tau)$ versus $1/T$, E and A can be calculated. A similar approach has been used by Kishore *et al*³. in the estimation of activation energies of propellant ignition. Fig. 5 shows the isothermal TG curves of boron/potassium nitrate from 520-540 °C. From these plots, the extrapolated onset times were computed and plotted against the corresponding T values as in Fig. 6. It gave an E value of 226.9 kJ/mol, close to the value given by Coats-Redfern method. The intercept gave a value of 31 for $\ln A$. The relatively lower E value obtained by Kissinger's method must be partially due to the lower n value of 1 used in this calculation.

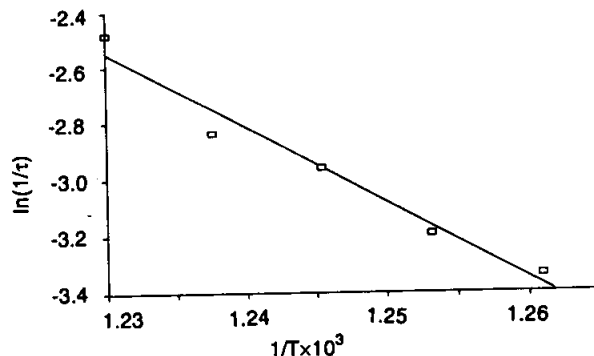


Figure 6. Plot of $\ln(\text{reciprocal ignition delay})$ against reciprocal temperature for B/KNO_3 (25/75).

3.3.2.5 Boron/Lead Thiocyanate/ Potassium Nitrate

As shown in Table 1, the tricomponent system decomposes in two major steps. The first step from 220-435 °C is a slow reaction showing a weight loss of 4.6 per cent. The second major reaction is in the range of 435-490 °C with a weight loss of 14.7 per cent. Since this decomposition is fast, Coats-Redfern method does not yield realistic E values. The first peak from 220-435 °C gave a low E value of 61.7 kJ/mol for $n = 2$. Figure 7 shows the DSC curves of this formulation at five different heating rates of 2, 4, 6, 8 and 10 K/min. Kissinger's plot of the peak temperatures are given in Fig. 8. From this plot an E value of 197.7 kJ/mol and $\ln A$ of 30.0 min^{-1} were calculated for this charge.

From isothermal TG runs at 460, 470, 475, 480 and 485 °C, the ignition delays were computed and E calculated as explained earlier. It yielded a close value of 198.4 kJ/mol for E and 27.4 min^{-1} for $\ln A$.

All the above results are summarised in Table 2. The activation energy of boron-potassium nitrate

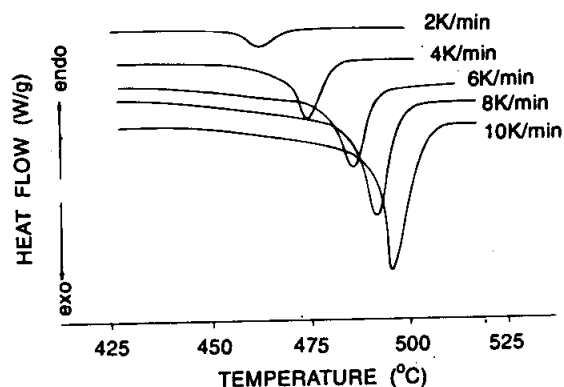


Figure 7. DSC curves of $B/Pb(SCN)_2/KNO_3$ (22/5/73) formulation at various heating rates.

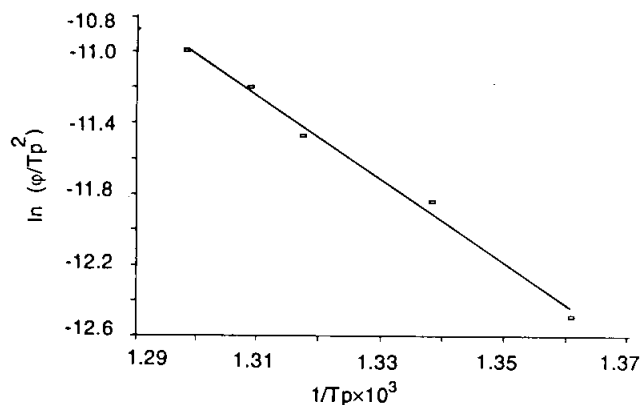


Figure 8. Kissinger's plot for $B/Pb(SCN)_2/KNO_3$ (22/5/73) formulation .

reaction is about 225 kJ/mol. This is brought down by the addition of lead thiocyanate. Thus a 5 per cent addition brings it down to around 198 kJ/mol. This lowering in activation energy must be attributed to the lower activation energy of lead thiocyanate/potassium nitrate reaction which is about 121 kJ/mol. Since the activation energy of lead thiocyanate decomposition is lower, viz. 108 kJ/mol and all the reactions start at the inception temperature of thiocyanate decomposition viz. 220 °C, it may be concluded that decomposition of lead thiocyanate followed by reaction with potassium nitrate is the starting reaction in boron/lead thiocyanate/potassium nitrate composition. This is followed by the more energetic reaction between boron and potassium nitrate.

4. CONCLUSIONS

1. The ignition temperature of the boron/potassium nitrate pyrotechnic formulation decreases as the percentage of lead thiocyanate addition is increased and the dependence follows a binomial fit.

2. Lead thiocyanate decomposition starts around 220 °C and is followed by the reaction with potassium

nitrate. The energy released by this pre-ignition reaction leads to the more energetic reaction between boron and potassium nitrate leading to charge ignition.

3. Activation energy values calculated by Kissinger method agree very well with the values derived by Coats-Redfern method when the value of apparent order of reaction is close to 1.

4. For reactive formulations, isothermal TG runs can be used to derive reliable kinetic values utilising ignition delay times measured up to extrapolated onset times of the major reaction stage.

5. Lead thiocyanate decomposition has an apparent zero order of reaction and the activation energy is about 108 kJ/mol, whereas lead thiocyanate-potassium nitrate formulation has an n value of 0.75 and an E value of about 118 kJ/mol.

6. A 5 per cent addition of lead thiocyanate to boron-potassium nitrate formulation brings down the activation energy of the latter from about 227 kJ/mol to about 198 kJ/mol. It is this decrease in activation energy brought about by the addition of lead thiocyanate that is responsible for the low temperature ignition of the tricomponent system, making it suitable as a hot wire-sensitive initiator charge.

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