

Thermal Characterization And Kinetic Modeling Of A Pyrotechnic Flash Composition Under Adiabatic Conditions

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Abstract: *A pyrotechnic flash composition consisting of 53% KNO₃, 30% Al and 17% S is subjected to Accelerating Rate Calorimetry (ARC) studies. The onset point for thermal explosion is 191 °C resulting in the generation of a considerable quantity of gaseous products. The mixture is vulnerable to thermal hazards. There is good agreement between the predicted and experimental self-heat rates determined using adiabatic thermo kinetics.*

Keywords: *Flash composition, ARC, fireworks, adiabatic thermo kinetics, thermal characterization*

Introduction

In recent years, frequent accidents during processing, storage and transportation have been reported in the fireworks industry.¹ This is of great concern because large quantities of different types of fireworks are manufactured in India and demand for them is steadily increasing. Generally, the composition of fireworks is a mixture of oxidizer, fuel, igniter, binder and color enhancing chemicals. These mixtures have high sensitivity to temperature, impact, friction and electrostatic stimuli. A thorough knowledge of thermal stability, auto-ignition temperature, impact sensitivity, frictional sensitivity and electrostatic sensitivity of these mixtures is imperative to assess the hazard potential.² Also, it should lead to a suitable plan for safety during processing, storage and transportation.

Chemical reactions of pyrotechnics produce large amounts of heat when confined to a closed system and result in thermal explosion. Although there are numerous thermal measurement techniques available to characterize the hazardous nature of pyrotechnic mixtures, Accelerating Rate Calorimetry (ARC) is the only adiabatic and versatile calorimetry that produces reliable data. Because ARC measurements are conducted adiabatically (*i.e.* no heat losses), the result can be

effectively correlated with the behavior of energetic materials in bulk. The information obtained from ARC experiments relates to the onset temperature, self-heat rates and pressure activation energy for an exothermic reaction. The ARC data can be used to set ceiling temperatures and pressures for safe operation, storage and transportation.

In the past, researchers have studied the thermal stability and kinetics of pyrotechnic mixtures using Differential Scanning Calorimetry (DSC).³ The thermal data obtained from DSC could not be used for determining safe operating temperatures due to the uncertainties associated with the very small quantity of samples (2–5 mg) used in the experiments and poor reproducibility of results and non-adiabatic experimental conditions. Subjecting flash composition mixtures to ARC studies would throw light on the behavior of these samples under adiabatic conditions; *i.e.*, under conditions of bulk storage, handling and transportation. Such a study has not been attempted, except for a theoretical paper detailing the suitability of ARC for studying the thermal decomposition of pyrotechnic mixtures.⁴ In the present study the thermal data from ARC and the thermo kinetics of a pyrotechnic flash mixture consisting of potassium nitrate (KNO₃), sulphur (S), and aluminum (Al) have been studied.

Experimental

Materials: Preparation of flash composition mixture

The chemicals used in this study were of commercial grade and obtained from a fireworks chemical manufacturing company situated in southern Tamilnadu, India. The purity and assay of the chemicals were KNO₃: 91.6%, S: 99.84% and Al: 99.1%. The flash composition consisting of potassium nitrate, sulphur and aluminum in the ratio of 53 : 17 : 30 was mixed using a wooden spatula in a non-flammable container, and each time a sample size of 1 g was prepared. The sample was then stored in an airtight container and kept away from light and moisture sources.

Method: Accelerating Rate Calorimeter (ARC) experiments

The ARC used in this study was an ARC 1000 supplied by CSI of Austin, TX. The working principle, design description, and operational details of ARC are well cited in the literature.⁶ ARC measurements were made using a titanium sample vessel in heat–wait–search mode. Before loading of the sample, the bomb was flushed with inert nitrogen gas and precautions were taken not to allow air to enter during the sample loading as well as during attachment of the sample vessel to the instrument. After connection, the sample vessel was pressurized to 2500 psi nitrogen gas to ensure that there was no leak and that the air in the assembly was replaced. The instrument was switched to step mode at an initial temperature of 80 °C, and a wait time of 15 min was set prior to entering the search mode. About 1 g of sample was loaded into the titanium bomb of the calorimeter, and its temperature was raised incrementally by 5 °C min⁻¹ in heat–wait–search mode, until a measurable rate of exothermic activity was detected (0.02 °C min⁻¹) or the final temperature was attained without any positive thermal input. The self-heat rate, time, temperature, and pressure data were obtained as ARC output.

Overview of adiabatic thermo kinetics⁶

The first assumption in the interpretation of ARC experimental data is the representation of concentration in terms of temperature differences. The equivalence of temperature and concentration for a simple well-defined chemical reaction is

established using the ratio:

$$\frac{C}{C_0} = \frac{T_F - T}{T_F - T_0} = \frac{T_F - T}{\Delta T} \quad (1)$$

where C is the concentration of the reacting substance and T is the temperature. The subscript 0 indicates some initial condition, and F a final state in which the substance has been consumed. Then $\Delta T = T_F - T_0$ is the temperature rise for the reaction. It is also equal to the ratio of enthalpy to average specific heat. In this relation the disappearance of the reacting species produces a proportionate increase in the heat energy. The heat of reaction, ΔH can be calculated from

$$\Delta H = m\bar{C}_P\Delta T$$

where \bar{C}_P is the average heat capacity, and m is the mass of the sample.

The heat generated in an exothermic reaction is used in three ways *viz.*, to heat the material, the container or bomb and the surroundings. The heat being used up in heating the sample mass depends on the specific heat. The proportion of heat used in heating the container is called thermal inertia (ϕ), which is expressed as $\phi = [\text{heat capacity of sample (S) and container or bomb (B)}]/[\text{heat capacity of sample}]$.

$$\phi = \frac{m_s \bar{C}_{ps} + m_B \bar{C}_{pB}}{m_s \bar{C}_{ps}}$$

$$\phi = 1 + \frac{m_b \bar{C}_{pB}}{m_s \bar{C}_{ps}} \quad (2)$$

Incorporating the effects of thermal inertia (ϕ), the corrected heat of reaction ΔH_r is calculated using equation (3):

$$\Delta H_r = \phi m \bar{C}_P \Delta T \quad (3)$$

The question that is basic to the study of the relationship of time to explosion is the measurement and extrapolation of data. Extrapolation must involve a concept of concentration since no material can continue to self-heat forever. The time dependence of concentration for an N th order reaction rate is expressed as follows:

$$\frac{-dC}{dt} = kC^N \quad (4)$$

where C is the concentration, k is the rate coefficient and t is the time. When equations (1) and (4) are used, additional temperature dependence appears.

$$\frac{dC}{dt} = C_0 \frac{d}{dt} \left(\frac{T_F - T}{\Delta T} \right) = \frac{-C_0}{\Delta T} \cdot \frac{dT}{dt}$$

$$m_T = \frac{dT}{dt} = k \left(\frac{T_F - T}{\Delta T} \right)^N \cdot C_0^{N-1} \cdot \Delta T \quad (5)$$

Here m_T is defined as the rate of temperature increase (or slope of the graph of T vs. t), *i.e.* the self-heat rate. To remove this extra temperature dependence, a modified rate is defined as the pseudo rate constant, k^* . It is defined in such a way that its dimensions for any order reaction are reciprocal of time.

$$k^* = k \cdot C_0^{N-1} = \frac{m_T}{\Delta T} \cdot \left(\frac{\Delta T}{T_F - T} \right)^N \quad (6)$$

In practice, k^* is evaluated from experimental data using the right hand side of the expression. With the proper choice of N , k^* has the same temperature dependence as k and yields a straight-line graph.

The Arrhenius relationship for determining the rate coefficients is

$$k = A e^{\left(\frac{-\Delta E}{RT} \right)} \quad (7)$$

where T is the absolute temperature in Kelvin, E is the activation energy, R is the universal gas constant and A is the pre-exponential factor. The $\ln k^*$ vs. $1/T$ plot yields a straight line with the proper choice of N . The activation energy and the pre-exponential factor are calculated by the following expressions:

$$\Delta E = \frac{RT_1 T_2}{T_2 - T_1} \ln \frac{k_2^*}{k_1^*} \quad (8)$$

$$\ln A = \ln \frac{k_1^*}{60} + \frac{\Delta E}{RT} \quad (9)$$

Results and Discussion

Flash composition under adiabatic conditions

The self-heat rate plot for thermal decomposition of flash composition consisting of potassium nitrate, sulfur, aluminum in the ratio of 53 : 17 : 30 is shown in Figure 1 and the results are summarized in Table 1. The onset for reaction occurred at 191 °C and extended until 450 °C. A maximum self-heating rate of 2.625 °C min⁻¹ occurred at 302 °C. The adiabatic temperature rise for the process was 259 °C. Under adiabatic conditions flash compositions decomposed slowly until 1700 min (250 °C) (Figure 2) and beyond this the rise in temperature was sudden and sharp as indicated in Figures 1 and 2. The reaction process was also accompanied by a considerable pressure rise (Figure 3); the peak pressure observed was 34 psi (2.312 bar) at 450 °C. As per equation (3), the heat of reaction was calculated as 1.311 × 10³ J g⁻¹, which is found to be more than the value of 409 J g⁻¹ obtained under isothermal conditions.³ The ARC data showed that the pyrotechnic decomposition process under adiabatic condition was vigorous and therefore dangerous.

Thermo kinetics of flash composition

First order model (*i.e.* $N = 1$) kinetics were assumed for the decomposition of pyrotechnic flash composition. For $N = 1$ equation (6) becomes

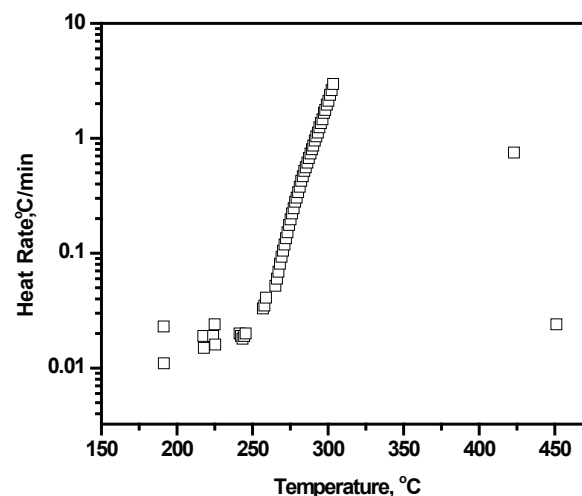


Figure 1 Self-heat rate vs. temperature plot for thermal decomposition of flash composition ($KNO_3 : S : Al; 53 : 17 : 30$).

Table 1 Summary of ARC data of flash composition.

Thermal inertia (Φ)	Onset Temperature T_o ($^{\circ}\text{C}$)	Final Temperature T_f ($^{\circ}\text{C}$)	Adiabatic temperature rise ΔT ($^{\circ}\text{C}$)	Absolute temperature rise ΔT_{ab} ($^{\circ}\text{C}$)	Heat of reaction ΔH_r (J g^{-1})
4.84	191	450	259	1253.6	1.311×10^3

$$k^* = k = m_d / (T_f - T) \quad (10)$$

Pseudo rate constants (k^*) were calculated using equation (10). Then $\ln k^*$ versus the inverse of temperature was plotted and the plot obtained is shown Figure 4. The straight line obtained confirms the assumption that the flash composition

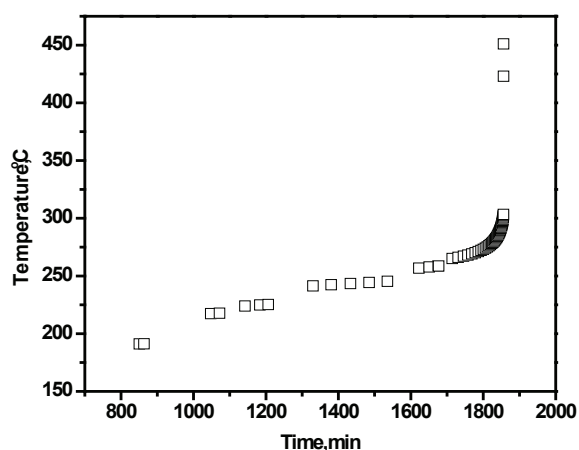


Figure 2 Time vs. temperature plot for thermal decomposition of flash composition ($\text{KNO}_3 : \text{S} : \text{Al} ; 53 : 17 : 30$).

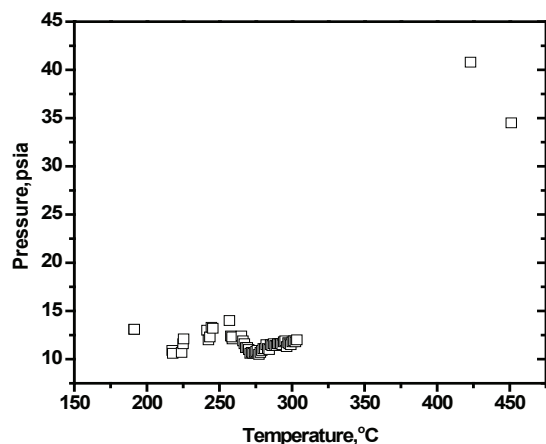


Figure 3 Temperature vs. pressure plot for thermal decomposition of flash composition ($\text{KNO}_3 : \text{S} : \text{Al} ; 53 : 17 : 30$).

mixture follows first order kinetics.

The slope of the plot is equal to $\Delta E/R$. As per equation (8), the activation energy was calculated as $63.99 \text{ kcal mol}^{-1}$ (268 kJ mol^{-1}). It is seen that the activation energy obtained under adiabatic conditions is close to those found under isothermal conditions ($199.7 \text{ kJ mol}^{-1}$) reported by us elsewhere.³ This shows decomposition under isothermal and adiabatic condition operates on the same mechanism. Using equation (9), the pre-exponential factor was evaluated as 6.13×10^{20} . Thus the Arrhenius rate law for thermal decomposition of flash composition can be given as

$$k = 6.13 \times 10^{20} \exp\left(\frac{-268}{RT}\right) \quad (11)$$

Thermo kinetics

The heat rates determined using equation (11) have been compared with the experimentally observed heat rates and the results are shown in Figure 5. A

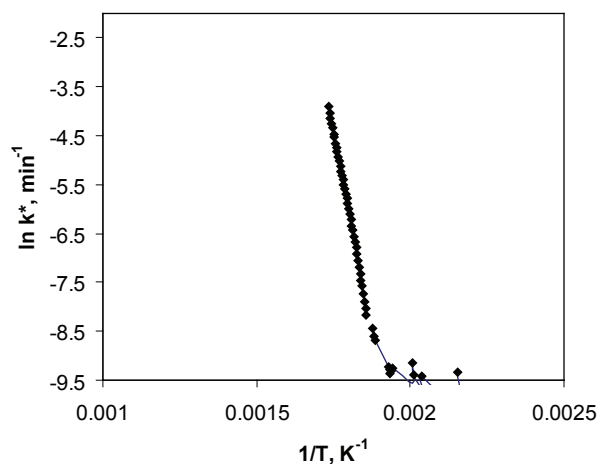


Figure 4 Pseudo rate constant plot for the adiabatic thermal decomposition of flash composition ($\text{KNO}_3 : \text{S} : \text{Al} ; 53 : 17 : 30$).

close examination of Figure 5 indicates that there is good agreement between the experimental and predicted values. It can be observed now that the kinetics obtained in this study are highly reliable.

Process safety

Pyrotechnic mixtures are vulnerable to thermal hazards. ARC data are used for determining the ceiling temperature for processing, handling and transportation of hazardous materials. Accordingly the practice adopted is that the process/handling temperature should be 100 °C below the onset temperature observed in ARC.^{7,8} This rule has been in practice in the process chemical industry for the safe and successful operation of process plants, storage systems and transportation. On these considerations, in the case of flash composition the ceiling temperature should never exceed 91 °C. Although there is no possibility of reaching this temperature during normal mixing⁹ and packing processes of flash composition, this temperature can be achieved under situations like heat radiation from a neighboring area or ignition from unknown sources. During such abnormal situations the flash composition mixture is vulnerable to hazard.

Further, impact and friction sensitivities can also lead to triggering of explosive decompositions. There is no direct correlation available between thermal, impact and frictional sensitiveness, either to predict one from the other or to predict which of these forces can come together to trigger a thermal explosion. We hypothesize that an impact or frictional stimulus brings about a thermal stimulus

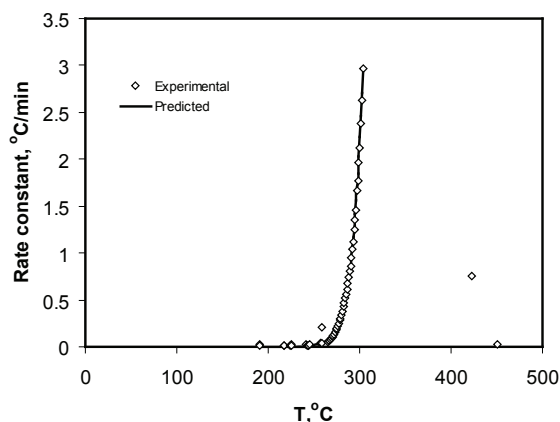


Figure 5 Kinetic modeling for the adiabatic thermal decomposition of flash composition (KNO_3 : S : Al; 53 : 17 : 30).

for the flash composition to undergo thermal explosion. Under severe impact or friction stimuli, thermal stimuli can occur immediately, and this can lead to a catastrophic thermal explosion. Irrespective of the nature of the stimulus, explosion occurs through a thermal mechanism only. This means that, for the current flash composition, an impact or any other stimulus can only initiate the thermal mechanism by providing the minimum threshold energy needed/necessary to raise the reaction temperature of 191 °C as this has been observed experimentally as the onset point for thermal explosion in ARC. Therefore it is possible to relate the mechanical form of energy to the threshold energy (ΔE) observed in the ARC. This provides a means of suggesting a predictive correlation in such explosive systems. The degree of explosivity also depends on the other factors such as chemical components, percentages of those components, compactness, particle size and shape and other environmental conditions.

Conclusions

The ARC studies of the flash composition mixture confirm that the mixture is vulnerable to thermal hazard if exposed above 191 °C. This temperature can be achieved under situations like direct heat radiation from neighboring areas or ignition from unknown sources or through other ignition stimuli like impact or friction. For the first time, a lower onset temperature of 191 °C for thermal decomposition is recorded in this study. It was shown that the observed onset temperature can be achieved through ignition stimuli like friction or impact. Thus this study can offer a better explanation for the accident triggering mechanism in fireworks factory during the summer months in southern India. The kinetic study reveals that there is good agreement between the experimental and predicted heat rate values. The Arrhenius kinetic constants reported in this study are reliable.

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