A DSC Analysis of Inverse Salt-pair Explosive Composition

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Abstract

Alkali nitrates are used as an ingredient in low explosive compositions and pyrotechnics. It has been suggested that alkali nitrates can form inverse salt-pair explosives with the addition of ammonium chloride. Therefore, the thermal behavior of low explosive compositions containing potassium nitrate mixed with ammonium chloride has been studied using Differential Scanning Calorimetry (DSC). Results provide information about the ion exchange reaction between these two chemical substances and the temperature region at which the formation of a cloud of salt particles of potassium chloride takes place. Furthermore, the addition of ammonium chloride quenches the flame of deflagrating compositions and causes the mixture to undergo explosive decomposition at relatively low temperatures.

Keywords: Alkali Nitrates, Inverse Salt-pair Explosives, Explosive Decomposition, Deflagrating Composition, Thermal Behavior.

1 Introduction

Determination of thermal behavior is an important part of explosive chemistry. It provides information on the type of physical and energy changes, which occur when a material undergoes an explosive decomposition. The thermal behavior of high explosives such as RDX, PETN and HMX [1–3] has been studied by using differential scanning calorimetry, thermogravimetry and differential thermal analysis techniques. Studies have also been carried out on alkali nitrates when mixed with fuel oil, [4] high explosives, [1, 3] and metals having a higher value of heat of combustion [7]. Thermal characteristics of inverse salt-pair explosives, formed on addition of ammonium chloride with alkali nitrate, [5] have not been investigated so far. In such type of explosives, the long-lasting deflagration process is changed into a short lived explosive decomposition, thus suppressing the ignition of methane-air and coal dust-air mixtures in mines and other industrial applications. The commonly used low explosive composition that contains alkali nitrate may act as an inverse salt-pair explosive. This phenomenon prompted us to study ion-exchange behavior of low explosive mixtures containing potassium nitrate by using differential scanning calorimetry.

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2 Methods and Materials

2.1 Materials

Potassium nitrate (Purified, Merck), Ammonium chloride (GR, Merck), Sulphur (Loba Chemie) and Charcoal (Activated, Merck) were used as supplied.

2.2 Operating Conditions

Differential scanning thermograms were recorded at a heating rate of 20 °C/min using a Perkin Elmer Pyris 1 DSC with zero air (IOLAR-2) as purge gas flowing at the rate of 20 ml/min. The temperature calibration of the instrument was referenced to the melting points of two standard samples, viz. Indium (156.6 °C), and Zinc (419.47 °C).

2.3 Sample Preparation

Homogeneous samples of required composition were prepared by grinding the components with mortar and pestle (Table 1). All the samples were accurately weighed and sealed in aluminum pans using a crimping device.

3 Results and Discussion

The recorded exothermic and endothermic peak temperatures of all eight samples are given in Table 2.

The DSC thermograms of potassium nitrate, ammonium chloride and sulphur are shown in Figures 1, 2 and 3

Table 1. Samples and their Mixtures

Composition	Ratio (w/w)
Potassium nitrate	Neat
Ammonium chloride	Neat
Sulphur	Neat
Potassium nitrate and ammonium chloride	1 : 1
Potassium nitrate and sulphur	9 : 1
Potassium nitrate, ammonium chloride and sulphur	4.5 : 4.5 : 1
Potassium nitrate, charcoal and sulphur	7.5 : 1.5 : 1
Potassium nitrate, ammonium chloride, charcoal and sulphur	3.75 : 3.75 : 1.5 : 1

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Table 2. Exothermic and endothermic peak values

Composition	Endothermic peak values (°C)	Exothermic peak values (°C)
Potassium nitrate	134, 338	–
Ammonium chloride	194, 302	300
Sulphur	108, 115,121, 180	306, 341
Potassium nitrate and ammonium chloride	133, 188, 292, 362	–
Potassium nitrate and sulphur	110, 116, 121, 134, 182, 336	328, 349
Potassium nitrate, ammonium chloride and sulphur	116, 120, 133, 189	274, 328
Potassium nitrate, charcoal and sulphur	116, 122, 135	307, 347
Potassium nitrate, ammonium chloride, charcoal and sulphur	115, 121, 132, 189, 334	281

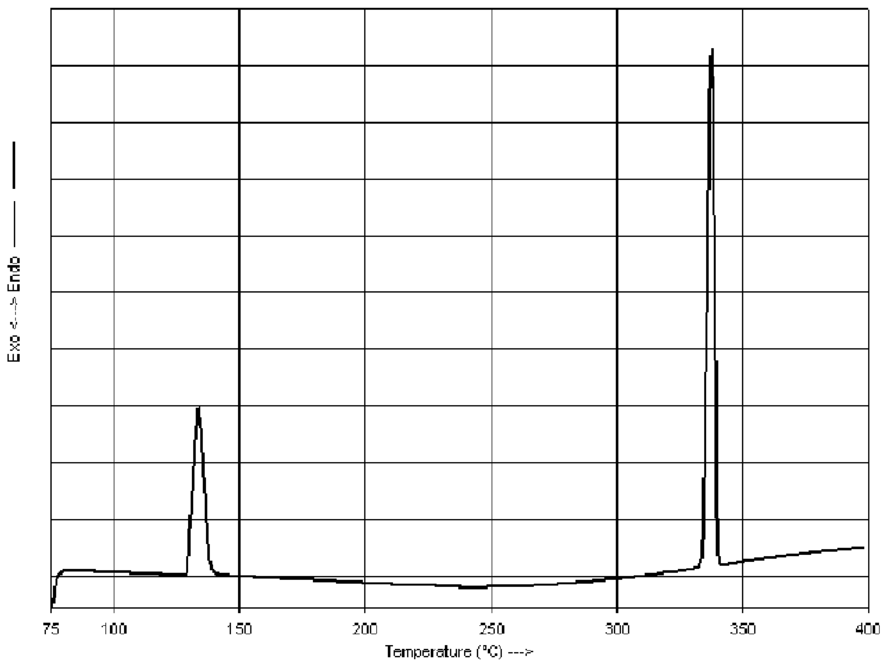

Figure 1. DSC thermogram for potassium nitrate

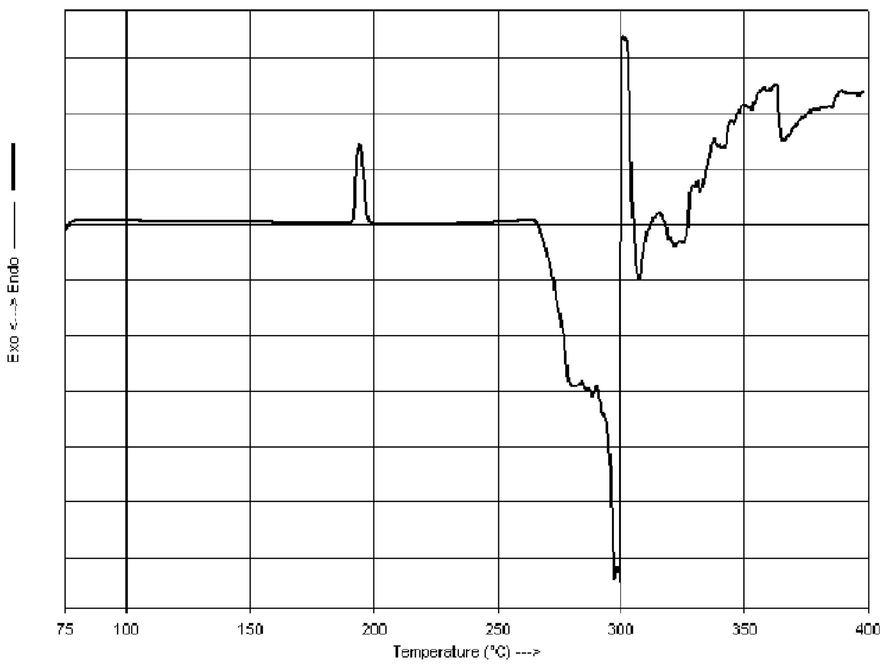

Figure 2. DSC thermogram for ammonium chloride

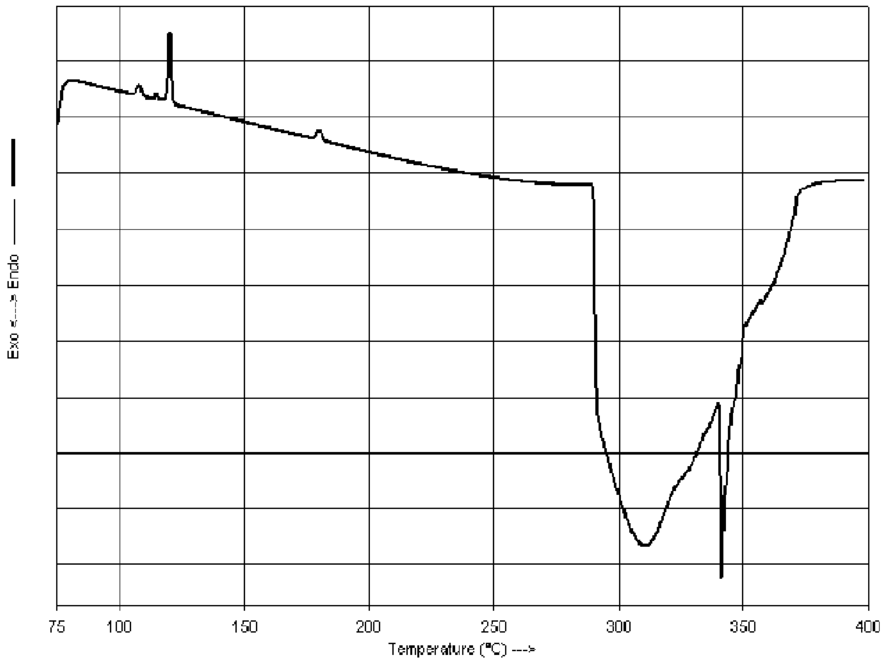

Figure 3. DSC thermogram for sulphur

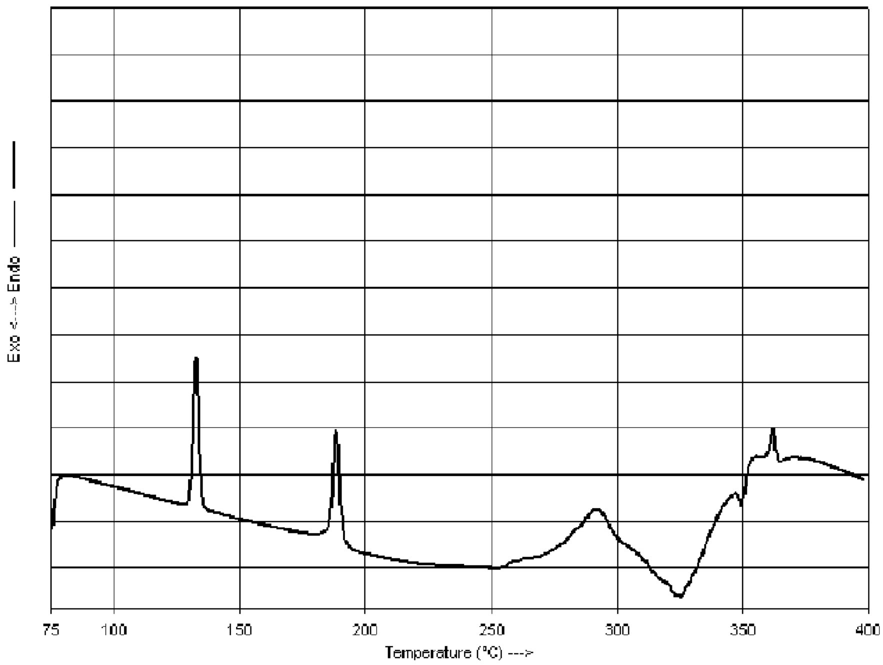

Figure 4. DSC thermogram for the mixture of potassium nitrate and ammonium chloride

respectively. Potassium nitrate exhibits two endothermic peaks owing to its transition from rhombic to trigonal form, and its melting [3]. Ammonium chloride shows two endothermic peaks in addition to one strong and broad exothermic peak with onset at 290 °C and peak at 300 °C, which could be due to its thermal decomposition. Sulphur exhibits four endothermic peaks due to its various structural transformations between rhombic and monoclinic forms [6]. It also shows one broad humplike exothermic peak with onset temperature at 290 °C followed by a secondary sharp exothermic peak at 341 °C. The broad hump shows that there was a long-lasting exothermic reaction due to the deflagration of sulphur.

The DSC thermogram of potassium nitrate and ammonium chloride mixture (see Figure 4) in the ratio (w/w) of 1 : 1 has characteristic endothermic peaks of its components. The strong exothermic peak at 300 °C as observed in neat ammonium chloride is missing in the thermogram of the

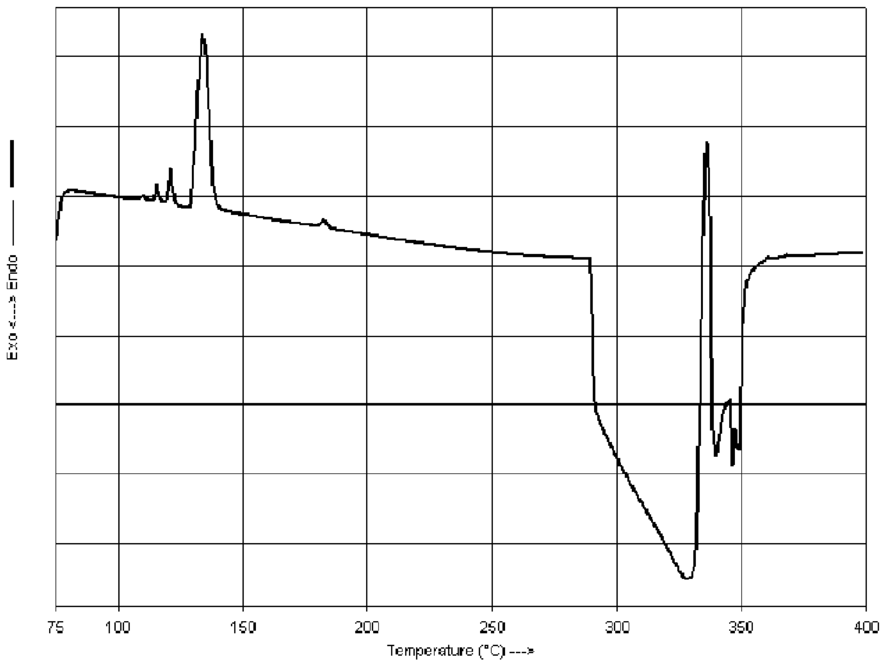

Figure 5. DSC thermogram for the mixture of potassium nitrate and sulphur

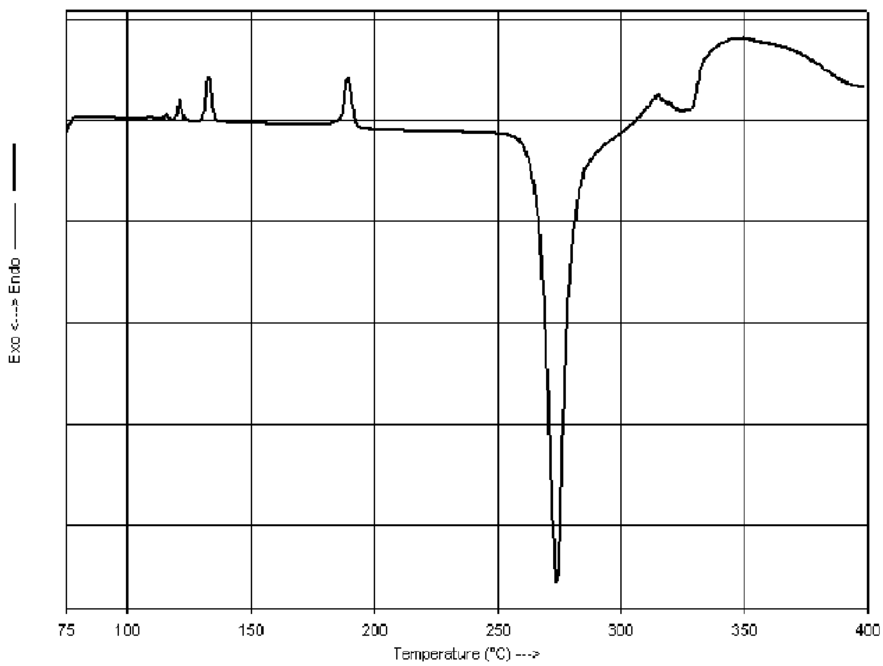

Figure 6. DSC thermogram for the mixture of potassium nitrate, ammonium chloride and sulphur

mixture. An interesting phenomenon is noticed in the temperature region from ≈270 °C to ≈325 °C where a broad hump occurs due to an endothermic reaction. This could be attributed to the formation of the flame extinguishing fine salt particles of potassium chloride thus formed in the reaction. The reaction can be represented by the following equation:

$$NH_4Cl + KNO_3 \longrightarrow N_2 + 2H_2O + ½\ O_2 + KCl$$

It can be seen from Figure 5 that the thermogram of potassium nitrate and sulphur mixture has five endothermic peaks in the region from 75 °C to 200 °C (Table 2). These peaks are characteristic for the melting of sulphur and structural changes of potassium nitrate. An endothermic peak with onset at 334 °C, which immediately follows the first exothermic peak, denotes the melting of residual potassium nitrate. It is interesting to note that even though the onset of the first exothermic peak due to deflagration of

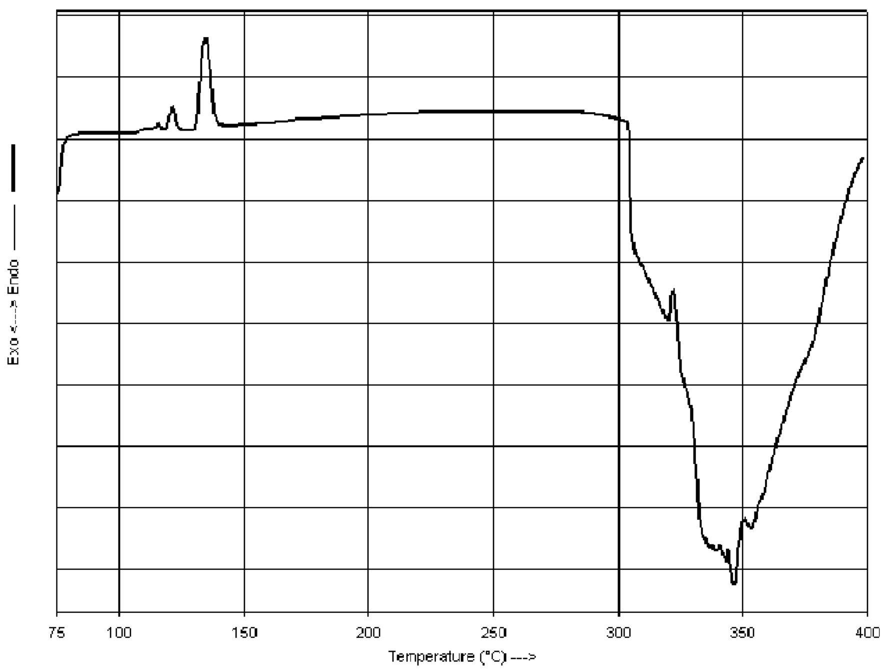

Figure 7. DSC thermogram for the mixture of potassium nitrate, charcoal and sulphur

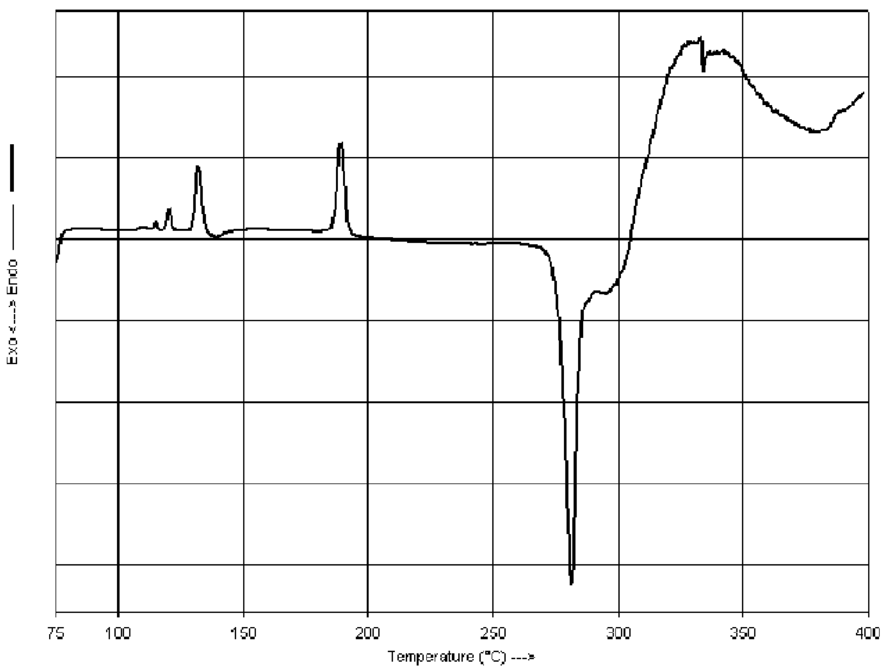

Figure 8. DSC thermogram for the mixture of potassium nitrate, ammonium chloride, charcoal and sulphur

sulphur occurs at 290 °C, which is in accordance with that of neat sulphur, the exothermic peak temperature of the combination is at 328 °C. This indicates a shift of 22 °C towards the higher side of the temperature region when compared with the peak temperature of 306 °C of neat sulphur.

The DSC thermogram of the mixture of potassium nitrate, ammonium chloride, and sulphur (see Figure 6) shows two exothermic peaks in addition to four endothermic peaks due to the structural transformation of its constituents as described earlier. It is to be noted that the first exothermic peak is very sharp and strong when compared to the one in the potassium nitrate and sulphur mixture. Moreover, in the potassium nitrate and sulphur mixture the first exothermic peak was at 328 °C whereas in the potassium nitrate, sulphur and ammonium chloride mixture, the first exothermic peak was observed at 274 °C indicating a marked downward temperature shift of 54 °C. This clearly indicates that it is an explosive decomposition rather than deflagration.

Figure 7 shows the DSC thermogram of the mixture of potassium nitrate, charcoal and sulphur in the ratio (w/w) of 7.5 : 1.5 : 1. There is no endothermic peak due to the melting of residual potassium nitrate at 336 °C, which is otherwise present in the mixture of potassium nitrate and sulphur. This indicates that the addition of charcoal to the mixture of potassium nitrate and sulphur ensures complete explosive decomposition of potassium nitrate.

The DSC thermogram of potassium nitrate, charcoal, sulphur and ammonium chloride mixture in the ratio (w/w) of 3.75 : 3.75 : 1.5 : 1 is shown in Figure 8. The mixture shows an exothermic peak at 281 °C. This shows a marked downward temperature shift of 66 °C when compared to the exothermic peak observed at 347 °C in the potassium nitrate, charcoal and sulphur mixture. This clearly indicates that the mixture undergoes explosive decomposition at a comparatively lower temperature with the addition of ammonium chloride.

4 Conclusion

Potassium nitrate, sulphur and charcoal mixture can be made to act as an ion-exchanged explosive when mixed with ammonium chloride.

Addition of ammonium chloride with potassium nitrate causes the formation of a cloud of fine salt particles of potassium chloride at the temperature region from ≈270 °C to ≈325 °C, which extinguishes the flame of deflagrating composition.

Addition of ammonium chloride lowered the explosion temperature of low explosive composition remarkably and thus changes the long-lasting deflagration reaction into short-lived explosive decomposition.

5 References

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