



Thermal Decomposition and Kinetics Studies of AN, KDN and Their Mixtures with and without Catalysts

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Abstract: Potassium dinitramide (KDN) was incorporated in ammonium nitrate (AN) crystals in AN/KDN ratio of 90/10, 75/25 and 50/50 by a co-crystallization method. These mixtures were subjected to thermal decomposition studies (DSC-TG) using a Simultaneous Thermal Analyzer (STA). The catalysts used for the present studies were: i) cupric(II) oxide (CuO) and, ii) copper-cobalt based metal oxide (Cu-Co^{*}). For all catalytic samples, 2% by weight percent of catalyst was added to the total weight of the samples. Thermal decomposition studies were carried out for all the oxidizer samples prepared. Thermal decomposition studies were carried out at three different heating rates, *i.e.* 3 K/min, 5 K/min and 10 K/min, and the kinetic parameters were computed using the model free Flynn-Wall-Ozawa equation. It has been observed that 50% KDN addition resulted in complete suppression of endothermicity indicating total suppression of the phase changes of AN in this temperature range. Further, it was noticed that CuO acts as a better phase stabilizer for AN as compared to Cu-Co^{*}. However, Cu-Co^{*} considerably increased the net exothermic decomposition heat release (J/g) of AN.

Keywords: green oxidizers, phase stabilization, thermal decomposition, thermo-kinetics, catalysts

1 Introduction

Composite solid propellants (CSPs) are extensively used in rockets, missiles and satellite launch vehicles. CSPs are heterogeneous in nature and composed of oxidizer crystals held in the matrix of a fuel binder. Other ingredients such as plasticizer, cross-linking agent, metallic fuel and catalysts are also added to achieve the desired mechanical, visco-elastic and ballistic properties. Among oxidizers, ammonium perchlorate (AP) is a workhorse in today's CSPs because of its excellent burning characteristics, low shock and friction sensitivity, easy

availability, and cost effectiveness. The disadvantages of AP-based CSPs are chlorine compounds in the exhaust and their toxicity. The chlorine compounds in the exhaust include hydrochloric acid (HCl), chlorine itself, and chlorine oxides (ClO_x). All these gases are highly noxious/toxic and have detrimental effects on the ozone layer and on the global environment.

Ammonium nitrate (AN) is one of the possible alternatives for AP as an oxidizer in CSP's for its clean burning. It is a cheap and readily available solid oxidizer. It is widely used in gas generators, explosives, and automotive air bags [1, 2]. However, the application of AN in rocket motors is limited because of its crystallographic phase changes near to room temperature, high hygroscopicity, low energetics, low burning rate, and inability to burn metallic fuels. The existence of four phase transitions in the temperature range $-17\text{ }^\circ\text{C}$ to $+125\text{ }^\circ\text{C}$ strongly hinders the use of AN in energetic formulations [3]. It has been observed that AN-based composite propellants crack during storage at room temperature ($32\text{ }^\circ\text{C}$) due to the $\text{IV} \rightarrow \text{III}$ phase transition (which has a volume change of 4%) and consequently the density also increases. This density increase results in the formation of cracks over the propellant surface which can lead to catastrophic solid rocket motor failure.

The problem of this abrupt volume change in AN crystals can be resolved by the use of various phase stabilizers. Metal halides [4, 5], potassium-based compounds [6, 7], copper-based compounds [8, 9], organic compounds [10, 11], and ammonium sulfate and chlorides [12] are reported to stabilize AN phase transitions. Out of all the compounds, potassium-based compounds are the most effective at phase stabilizing AN.

The reasons that potassium-based compounds are an effective phase stabilizer and energy enhancer for AN are:

- a) At and above ambient room temperature, the ammonium cation (NH_4^+) undergoes free rotation in the AN crystal lattice and has the property of a single-atom cation with an effective radius of 1.48 \AA . If AN is doped with a cation of nearly the same ionic radius, a solid solution will form which results in the suppression of phase transitions. The potassium cation (K^+) has an ionic radius of 1.33 \AA , and the addition of K^+ results in a reduction in the $\text{IV} \rightarrow \text{III}$ transition, and raises the $\text{III} \rightarrow \text{II}$ temperature range [13].
- b) KDN is a member of the dinitramide anion $[\text{DA}, \text{N}(\text{NO}_2)_2]^-$ family with the molecular formula $[\text{K}^+][\text{N}(\text{NO}_2)_2]^-$. The presence of dinitramide anions imparts a high heat of formation, density, and oxygen balance [14]. There are numerous other synthesized DA-based energetic compounds with many possible applications [15].

Cupric(II) oxide $[\text{CuO}]$ acts both as a decomposition catalyst as well as

a phase stabilizer for AN. CuO forms a solid solution of copper(II) diammine nitrate in the AN crystal lattice when heated. The reaction proceeds as:



When this complex cools down to room temperature, it slowly converts to the tetramine complex which stabilizes AN [8, 9].

In the present investigation, attempts were made to study the effects of KDN as a phase stabilizer and as an energy enhancer for AN/KDN based oxidizer samples. Along with KDN, two catalysts [cupric oxide (CuO)], and copper-cobalt based metal oxide (Cu-Co*) were also added as 2% of the total weight of prepared oxidizer samples so as to study their catalytic effects. KDN was added to AN crystals by a *co-crystallization method* in the ratio of 10/90, 25/75, and 50/50, while catalysts were added by a *evaporative crystallization method*.

2 Experimental

2.1 KDN synthesis

The steps adopted to synthesize KDN were followed as described by Gołofit *et al.* [16]. For obtaining KDN, the first step is the nitration of potassium sulfamate ($\text{K}[\text{NH}_2\text{SO}_3]$) using mixed nitric and sulfuric acids in the volumetric ratio of 4:1. Nitric acid (100% conc.) was supplied by Merck (Germany) and sulphuric acid (95% conc.) was supplied by Acros (Belgium) and used in the present work. The nitrating mixture was kept at -40°C in an ultra low immersion chiller. Potassium sulfamate was added in small increments while vigorously stirring the nitrating mixture. The reaction proceeds via the formation of the dinitramide anion $[\text{N}^-(\text{NO}_2)_2]$ and potassium bisulfate (KHSO_4). The reaction mixtures were immediately poured onto a finely crushed mixture of ice and water after 30 min. Afterwards, a cold solution of potassium hydroxide (50%) solution was gradually added while maintaining the temperature in the range of -10°C to 0°C . At the neutralization point, the mixture turned a characteristic green-yellow color. At this point, a white precipitate formed which slowly settled down in the solution. This precipitate was a mixture of potassium dinitramide ($\text{KN}(\text{NO}_2)_2$, KDN), potassium nitrate (KNO_3 , KN), and potassium bisulfate (KHSO_4). As only KDN is soluble in acetone while other two salts are insoluble, the salt mixtures obtained were washed vigorously with acetone until the whole KDN was dissolved in acetone, leaving behind the other two salts in insoluble form.

Acetone was collected in a clean beaker, and then a rotary evaporator was used for obtaining the slightly viscous yellowish white colored KDN crystals. The KDN crystals obtained were again vacuum-dried in an oven and finally pure dried KDN crystals were obtained.

2.1.1 Characterization of synthesised KDN

UV-Spectroscopy (Perkin Elmer, Lambda 25, USA)

UV-spectroscopy is one of the best and simplest methods for KDN characterization since KDN is a water soluble salt. The UV-spectrum of KDN in water shows two absorbance maxima coefficient peaks at 212 nm and at 286 nm as shown in Figure 1. The observed result is in agreement with a previous report, in which absorbance peaks were observed at 214 nm and 285 nm [16]. The peak at 284 nm to 286 nm is the characteristic absorption peak of the dinitamide anion. The plot is of absorbance (A , cm) versus wavelength (λ , nm).

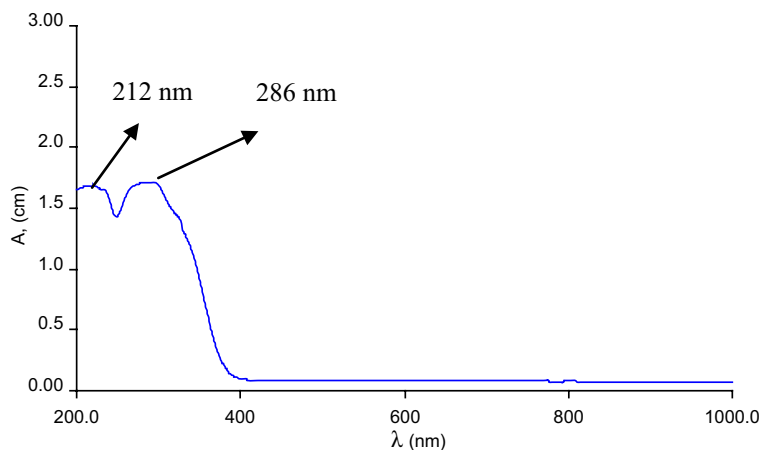


Figure 1. UV spectrum of KDN

DSC (TA instruments, Universal V4.2E, USA)

DSC characterization of the synthesized KDN was carried out at a heating rate of 10 K/min, with N_2 as a purge gas. The sample mass was about 6 mg, and the sealed cell used for placing the sample in the machine was made of sealed aluminum with a hole pierced in it. The DSC curve of synthesized KDN shows one endothermic melting peak at 130 °C, and one exothermic decomposition peak at 202 °C. The decomposition temperature range lay between 190 °C and 210 °C. The melting and decomposition peaks of KDN, and their associated

enthalpy values varied greatly sample to sample. Such variations in the thermal profile of KDN depends on many factors, which are discussed briefly in the results and discussion sections. The observed values are in agreement with previous reports [17]. The DSC curve obtained is shown in Figure 2.

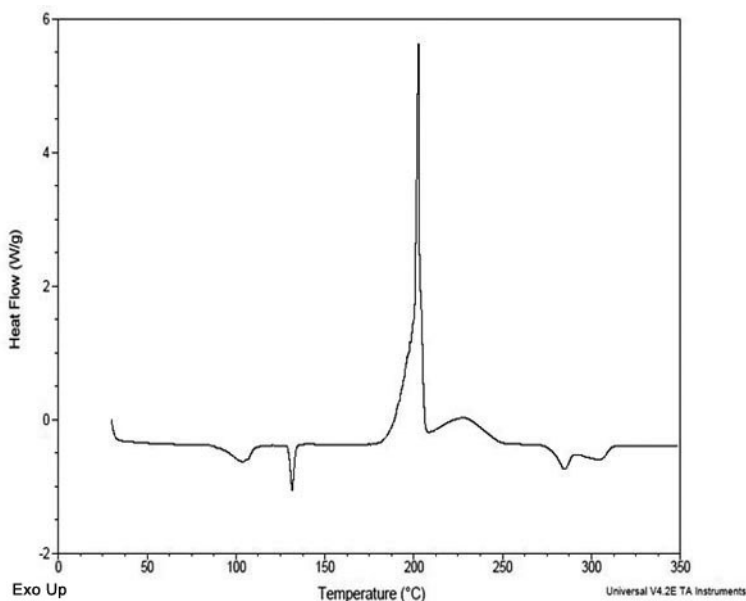


Figure 2. DSC curve of KDN

2.2 Copper-cobalt based mixed metal oxide (Cu-Co^{*}) preparation

The *citric acid sol-gel method* was used to synthesize copper-cobalt based metaloxides (Cu-Co^{*}). Citric acid acts both as a chelating agent as well as a carbon source in the *citric acid sol-gel method*. This method was previously used for synthesizing other mixed metal oxides [18, 19].

The starting materials for synthesizing Cu-Co^{*} are copper(II) nitrate trihydrate [Cu(NO₃)₂·3H₂O], cobalt(ous) nitrate hexahydrate [Co(NO₃)₂·6H₂O], and citric acid (C₆H₈O₇·H₂O). All the chemicals used were of analytical grade and were purchased from CDH, India. At first, 0.6 g of copper nitrate, 0.72 g of cobalt nitrate, and 3.15 g of citric acid were placed in a cleaned porcelain china dish. These chemicals were further mixed with 25 mL of distilled water and stirred continuously until all the chemicals were completely dissolved.

For obtaining dried Cu-Co^{*}, heating of the solution was performed in 3 stages. In the 1st stage, the homogeneous solution was heated at 90 °C for 3-4 h to evaporate the water solvent to produce viscous-gels of the mixtures. In

the 2nd stage, the gel so obtained was heated at 165 °C for 2 h to obtain a bubbly light violet color dried gel. In the 3rd stage, the dried gel was heated at 550 °C for 3 h to obtain the final black Cu-Co*.

Before using Cu-Co* as a catalyst in oxidizer samples, it was crushed and then mixed homogeneously in the prepared oxidizer samples. The same catalyst was used with AP-HTPB based propellants [29], and in AN/KDN-HTPB based propellants [30] for enhancing the burning rate of propellant samples.

2.3 Samples

KDN and Cu-Co* were prepared in our lab as discussed in Sections 2.1 and 2.2. Ammonium nitrate (AN) of purity 99.9% (CDH, India) and cupric(II) oxide of particle size less than 10 µm (Sigma Aldrich, USA) were used as received without any further purification or modification.

AN/KDN samples were prepared by incorporating KDN in the AN crystals using a *co-crystallization method*. As for preparing AN/KDN (50/50), two separate solutions of AN and KDN each of 100 mg were prepared by dissolving them in 2 mL of distilled water. Both solutions were then mixed together and well-stirred until the solution became homogeneous. The solutions were then kept in a vacuum oven at 50 °C until dry crystals were obtained. Before using the samples for thermal analysis the crystals were further dried in a vacuum oven. The same methodology was used for the preparation of two other samples of AN/KDN in the ratio of 90/10 and 75/25.

In another set of experiments, 2% by mass CuO and Cu-Co* were mixed thoroughly into AN and AN/KDN (50/50) for studying their effectiveness in the thermal decomposition of these oxidizers. The AN + CuO, AN + Cu-Co*, AN/KDN (50/50)+CuO, and AN/KDN (50/50) + Cu-Co* samples were prepared by a *evaporative crystallization method* [9]. For preparing samples, such as AN + CuO or AN + Cu-Co*, 100 mg of AN was dissolved in 2 mL of distilled water with continuous stirring. After complete dissolution, 2% by weight of CuO or Cu-Co* were added to the AN solution. After 10 min of stirring, the AN + CuO solution was kept at 100 °C on a hot plate with continuous stirring till dried crystals were obtained.

2.4 Instrumentation

A Simultaneous Thermal Analyzer (STA Model 409 PG luxx of NETZSCH, Germany) was used to obtain DSC-TG thermograms for each sample. Nitrogen at a flow rate of 60 mL/min was used as a purge gas. An alumina crucible with a lid having a small perforation in it was used to place the samples in the STA sample carrier. The sample weight used for each analysis was 5 ± 0.5 mg. The

experiments were carried out at three different heating rates, *i.e.* 3 K/min, 5 K/min and 10 K/min. The kinetic analysis was carried out using a model-free method based on the *Ozawa-Flynn-Wall equation*.

3 Results and Discussion

3.1 DSC and TG-DTG of AN and KDN

The DSC curve for pure AN at a heating rate of 5 K/min is shown in Figure 3a, and the corresponding TG-DTG curve is shown in Figure 3b. The DSC curve shows 4 endothermic peaks at 56.4 °C, 131.2 °C, 169.3 °C and 288.5 °C. The TG-DTG curve shows one-step decomposition in the temperature range 179-300 °C with a mass loss of 98.8%. It has been reported that AN when heated undergoes four enantiotropic phase changes, melting, and subsequently decomposition. However the DSC curve obtained in the present investigation shows two enantiotropic phase changes at 56.4 °C and 131.2 °C respectively, one solid to liquid phase change at 169.3 °C, and one decomposition peak at 288.5 °C. The reason that AN shows such behavior by AN was given by Bowen [20]. He noted that, excessively dried AN shows no phase transitions at 32 °C (IV→III) or at 82 °C (III→II), but shows only one transition near 50 °C to 55 °C and is in a metastable state between forms IV and II and therefore eliminates form III.

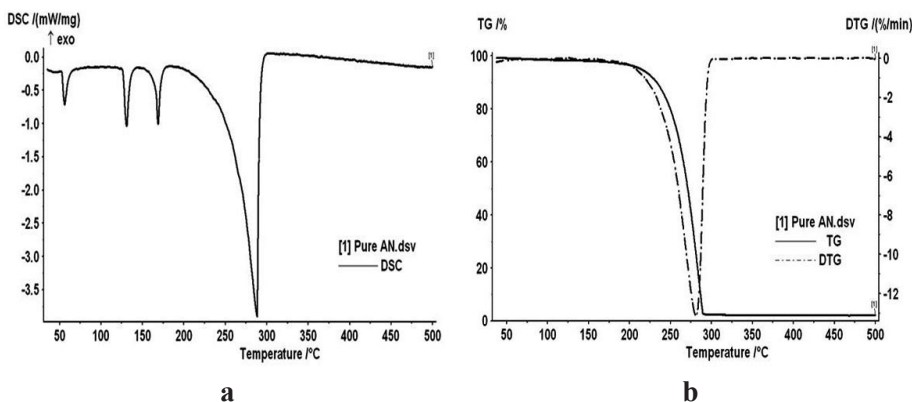


Figure 3. (a) DSC of pure AN and (b) TG-DTG of pure AN

KDN samples (which were used to examine thermal decomposition) were synthesized and stored in a vacuum desiccator. The DSC thermogram of stored KDN at a 5 K/min heating rate is presented in Figure 4a, and the corresponding TG-DTG curve is shown in Figure 4b. Stored KDN was used in an attempt to

understand the effect of storage conditions and of time on the thermal properties of KDN, and on stabilization of AN through the DSC/TG method. A comparison of DSC curves between fresh KDN (Figure 2) and of stored KDN (Figure 4a) depicts many observable differences, which are discussed in the next paragraph.

During storage, KDN slowly decomposes to form potassium nitrate, KNO_3 (KN). KN forms a eutectic mixture with KDN and a eutectic melting point (m.p.) was observed at 106.5°C (Figure 4a) for stored KDN as compared to 129°C for freshly prepared KDN (Figure 2). The value of the eutectic m.p. varied from sample to sample as it depends upon the percentage of KN present in the KDN to form an eutectic mixture [21-23]. KDN melting was followed by two exothermic decomposition peaks at 172°C and 220°C , while fresh KDN shows only one exothermic decomposition at 202°C .

The TG-DTG curve (Figure 4b) shows three-step decomposition for stored KDN. The first DTG peak was at 210°C , which corresponds to decomposition of KDN [$\text{KN}(\text{NO}_2)_2 \rightarrow \text{KNO}_3 + \text{N}_2\text{O}$] [24]. KNO_3 is quite stable up to 600°C , hence these second major decomposition starts from 600°C onwards. When KNO_3 was heated above 600°C , it released oxygen and formed potassium nitrite (KNO_2). KNO_2 decomposition started above 700°C and formed K_2O and O_2 [25]. The DTG curve (Figure 4b) shows two decomposition peaks in the temperature range $600\text{--}850^\circ\text{C}$, first at 684°C for KNO_3 , and second at 712°C for KNO_2 .

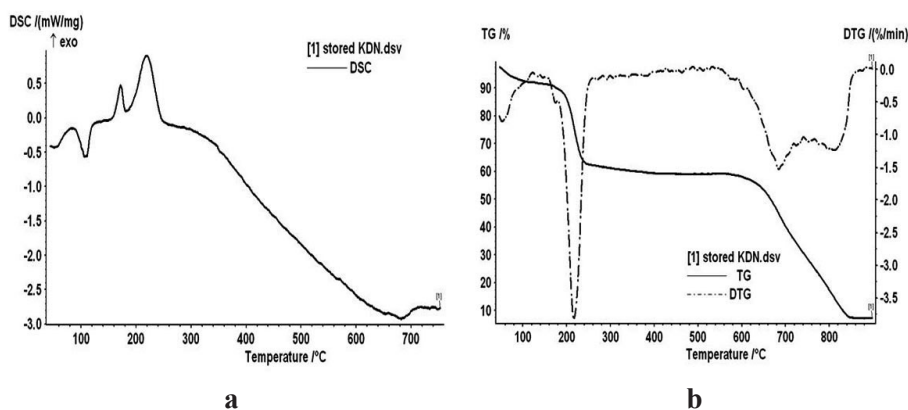


Figure 4. (a) DSC of stored KDN and (b) TG-DTG of stored KDN

3.2 DSC and TG of AN-KDN mixtures

For stabilizing AN, stored KDN was used as the phase stabilizing material as well as to increase the net decomposition heat release of AN. The DSC curves for AN/KDN in the ratio of 90/10, 75/25, and 50/50 at a heating rate of 5 K/min are shown in Figure 5a, and the corresponding TG curves are presented in Figure 5b.

The DSC curves show that AN is phase-stabilized by the addition of 10% KDN, as the first phase transition was observed above 100 °C. In AN/KDN (90/10), two phase transition peaks were observed at 112.7 °C and 130.1 °C, and a melting peak was seen at 146.8 °C. Our results are in agreement with a previous study [23]. Addition of 10% KDN induces the following effects: i) it increased the IV→III/ II transition from 56.4 °C to 112.7 °C, ii) it had virtually no effects on the II→I transition, and iii) it decreased the melting point of AN from 169 °C to 146.8 °C. Similarly, better phase-stabilized ammonium nitrate (PSAN) was produced with the addition of 25% and 50% KDN. In AN/KDN (75/25), only one phase transition peak and one melting peak were observed at 118.6 °C and at 147.3 °C respectively, while in AN/KDN (50/50) neither a phase transition nor a melting peak were observed, but only two exothermic decomposition peaks were observed at 201.5 °C and at 220 °C.

From the TG curve analysis (Figure 5b), it can be observed that with increasing KDN percentage, the one step decomposition process gradually changes into two steps decomposition with reduction in the onset decomposition temperature. It shows that as we increase the percentage of KDN, sufficient heat is generated during KDN decomposition to make AN decompose simultaneously with KDN.

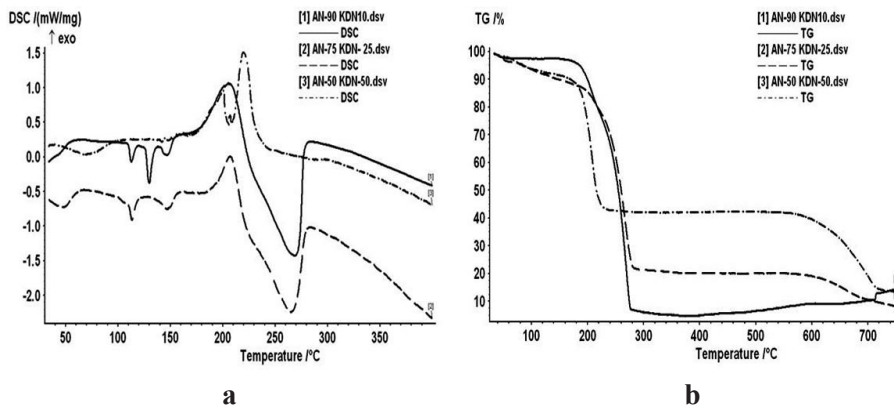


Figure 5. (a) DSC of AN/KDN mixtures and (b) TG of AN/KDN mixtures

3.3 DSC and TG-DTG of AN and AN/KDN (50/50) in the presence of 2% CuO and Cu-Co*

In the third set of experiments, an attempt was made to analyze the effectiveness of CuO and Cu-Co* on the thermal decomposition of AN and AN/KDN (50/50) mixtures. CuO was chosen for study because it is a well known decomposition catalyst, it acts as a phase stabilizer for AN, and it enhances the low pressure

deflagration limit (LPDL) of dinitramide-based propellants such as ammonium dinitramide (ADN) and AN-based propellants [26, 27]. The DSC curves for [AN, AN+CuO, and AN+Cu-Co*], and of [AN/KDN (50/50), AN/KDN (50/50)+CuO, and AN/KDN (50/50)+Cu-Co*] are presented in Figures 6a, and 7a, while the corresponding TG curves are presented in Figures 6b and 7b.

3.3.1 DSC and TG of AN, AN+CuO and AN+Cu-Co*

From DSC (Figure 6a), it is clear that the first phase transition and decomposition peaks occur at 88.1 °C and at 265.7 °C in the presence of CuO, while in the presence of Cu-Co* the same peaks are at 54.7 °C and at 274.3 °C. It shows that, CuO is a better phase stabilizer and decomposition catalyst for AN as compared to Cu-Co*. The second phase transition and melting peaks are nearly the same for all three samples. After decomposition, one exothermic peak is observed in the temperature range 342-387 °C in the presence of both catalysts. This sharp peak may be due to faster oxidation reaction between NH₃ and the decomposition products of HNO₃. NO₂ reacts with NH₃ to form N₂O and H₂O. This reaction happens instantaneously in the presence of a catalyst and hence one exothermic peak was observed just after decomposition.

The TG curves (Figure 6b) show two-steps decomposition for all three samples. The first major decomposition was observed in the temperature range 200-300 °C. Between 200 °C and 300 °C, AN decomposes into NH₃ and HNO₃, and HNO₃ further breaks down into N₂, NO₂ and H₂O. In the temperature range 342-387 °C, NO₂ reacts with NH₃ to form N₂O and H₂O. This reaction happened instantaneously in the presence of catalyst and hence one exothermic peak was observed in the DSC curves just after decomposition.

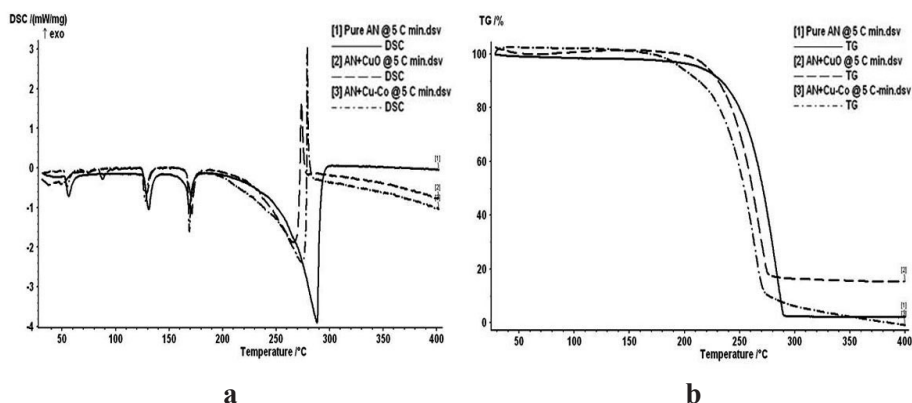


Figure 6. (a) DSC of AN, AN+CuO, and AN+Cu-Co*; (b) TG of AN, AN+CuO, and AN+Cu-Co*

3.3.2 DSC and TG of AN/KDN (50/50), AN/KDN (50/50)+CuO, and AN/KDN (50/50)+Cu-Co*

From DSC traces (Figure 7a), it can be observed that in the presence of 50% KDN there was a complete absence of any kind of phase transition peaks, melting peak or endothermic decomposition peak for AN. For all three samples, one dominant and major exothermic decomposition peak was observed in the temperature range 150 °C to 250 °C, *i.e.* both KDN and AN decomposed simultaneously within this temperature range. In the presence of CuO, in addition to one major exothermic peak there is also one minor exothermic peak at 261.6 °C, which might be due to the gas phase reaction product.

Thermal decomposition of AN/KDN (50/50) in the presence of catalyst was completed in three steps while that of AN/KDN (50/50) was completed in only two steps as shown in Figure 7b. With the increase in percentage of KDN, the total percentage mass loss for the first two decompositions decreased while the percentage mass loss for the third decomposition increased. This is because more KNO₃ comes into the picture as the decomposition product of KDN. The onset temperature for decomposition in the presence of catalyst is less than that of AN/KDN (50/50) without catalyst. The DSC and TG data for all nine oxidizer samples are given in Tables 1 and 2, respectively.

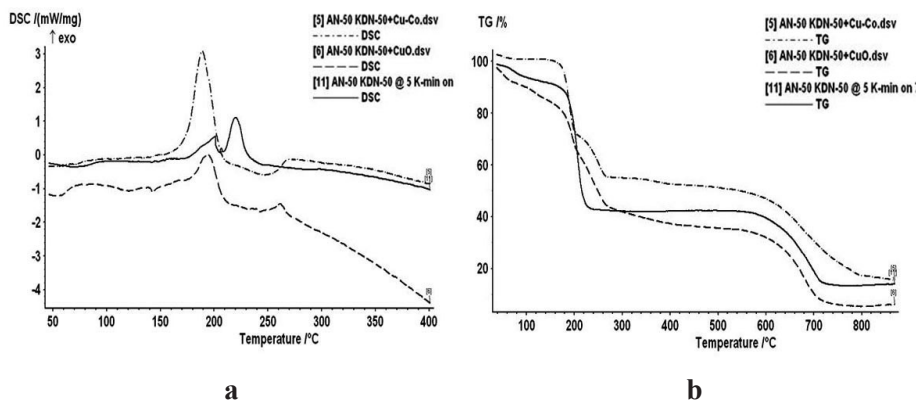


Figure 7. (a) DSC of AN/KDN (50/50), AN/KDN (50/50) + CuO AN/KDN (50/50)+Cu-Co*; (b) TG of AN/KDN (50/50), AN/KDN (50/50) + CuO AN/KDN (50/50) + Cu-Co*

Table 1. DSC data for all samples

| Sample | Phase Transitions [°C] | Enthalpy [J·g ⁻¹] | Melting [°C] | Enthalpy [J·g ⁻¹] | Decomposition [°C] | Enthalpy [J·g ⁻¹] | Net enthalpy [J·g ⁻¹] |
|----------------------------|------------------------|-------------------------------|--------------|-------------------------------|--------------------|-------------------------------|-----------------------------------|
| AN | 56.40 131.2 | -27.89 -60.31 | 169.3 | -68.09 | 288.5 | -1299 | -1455.29 |
| KDN (stored) | - | - | 106.5 | -86.68 | 172 220 | 53.4 340.2 | 306.92 |
| AN/KDN (90/10) | 112.7 130.1 | -14.4 -31.72 | 146.8 | -18.83 | 269.1 205.7 | -588.3 313.8 | -339.45 |
| AN/KDN (75/25) | 113.6 | -14.01 | 147.3 | -28.22 | 265.1 207.5 | -431 196 | -277.23 |
| AN/KDN (50/50) | - | - | - | - | 201.5 220 | 75.34 148.8 | 224.14 |
| AN + CuO | 88.1 129.3 | -14.99 -54.04 | 171.5 | -75.15 | 265.7 | -622 | -766.18 |
| AN+Cu-Co* | 54.7 127.9 | -20.79 -45.96 | 169.1 | -60.96 | 274.3 279.5 | -156.0 111.92 | -171.79 |
| AN/KDN (50/50) + CuO | - | - | 143.1 | -5.61 | 194.1 261.1 | 321.8 43.38 | 359.99 |
| AN/KDN (50/50) + Cu-Co* | - | - | - | - | 189.2 247.6 | 753.2 -129 | 624.20 |

Table 2. TG-DTG data for all samples

| Sample | 1 st Temp range [°C] | Mass loss [%] | 2 nd Temp range [°C] | Mass loss [%] | 3 rd Temp range [°C] | Mass loss [%] | 4 th Temp range [°C] | Mass loss [%] | 5 th Temp range [°C] | Mass loss [%] |
|---------------------------|--|---------------------|--|---------------------|--|---------------------|--|---------------------|--|---------------------|
| AN | 179-300 | 98.80 | - | - | - | - | - | - | - | - |
| KDN (stored) | 031-106 | 06.73 | 154-183 | 02.00 | 182-259 | 27.27 | 553-739 | 22.72 | 722-856 | 28.25 |
| AN/KDN (90/10) | 166-224 | 20.08 | 224-287 | 69.81 | - | - | - | - | - | - |
| AN/KDN (75/25) | 038-182 | 11.12 | 182-221 | 08.59 | 221-296 | 57.15 | 543-705 | 09.68 | 708-825 | 04.91 |
| AN/KDN (50/50) | 036-104 | 05.44 | 147-243 | 48.78 | 551-783 | 28.14 | - | - | - | - |
| AN+CuO | 032-080 | 03.06 | 150-284 | 84.63 | - | - | - | - | - | - |
| AN+Cu-Co* | 035-075 | 02.45 | 150-270 | 87.55 | - | - | - | - | - | - |
| AN/KDN (50/50) +CuO | 40-190 | 19.21 | 190-280 | 36.27 | 280-570 | 12.86 | 570-710 | 31.87 | - | - |
| AN/KDN (50/50) +Cu-Co* | 032-70 | 1.26 | 190-260 | 42.37 | 260-600 | 4.57 | 600-800 | 31.26 | - | - |

3.4 Decomposition kinetics

Non-isothermal or iso-conversional method for TG analysis is a great tool for predicting the decomposition kinetics for solid decomposition. The rate constant for solid state decomposition was assumed to follow the Arrhenius rate law. The rate of conversion, for TG experiments at constant heating rate, $\beta = \frac{dx}{dT}$, is expressed as:

$$\frac{dx}{dt} = \beta \frac{dx}{dT} = K(T)f(x) \quad (1)$$

where, x is the degree of conversion, $K(T)$ and $f(x)$ are functions of temperature and conversion, respectively. $K(T)$, the temperature dependence of the rate of weight loss, can be expressed using the Arrhenius equation:

$$K(T) = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where, E is the activation energy, A is the pre-exponential factor, and R is the gas constant.

Various expressions for estimating the activation energy and pre-exponential factor have been developed based on the above rate equations and the *Ozawa-Flynn-Wall* (OFW) method is one of them [28]. In the present work the OFW model was used for evaluation of the activation energy and pre-exponential factor.

OFW is an iso-conversional integral method for calculating the activation energy and is more accurate than the Friedman method. This method does not require any assumptions for the form of kinetic equation other than the Arrhenius type temperature dependence. This method is derived from the integral iso-conversional method. First the Arrhenius rate law (*i.e.* Eq. 2) was integrated and then Doyle's approximation was used to obtain the following equation.

$$\ln \beta = \ln \left(\frac{AE}{Rg(x)} \right) - 5.331 - 1.052 E/RT \quad (3)$$

where, $g(x)$ is the integral form of kinetic model, *i.e.* $g(x) = kt$.

The plot of $\ln \beta$ vs. $1/T$ gives a straight line with slope $1.052 E/R$. This slope can be used to evaluate the apparent activation energy.

In the present investigation, we computed the activation energy (E_a) and the Arrhenius constant (A) only for the first major decomposition steps for all 8 prepared samples in the temperature range 100-300 °C, while for AN the

temperature range was 150 °C to 300 °C. The values obtained for E_a and A using the Flynn-Wall-Ozawa method at three heating rates are presented in Table 3.

Table 3. Kinetic parameters of all samples

| Samples | E_a [kJ·mol ⁻¹] | log A [s ⁻¹] | Temperature Range [°C] |
|-------------------------|-------------------------------|----------------------------|------------------------|
| AN | 124.04 ± 20.48 | 08.98 | 150-300 |
| KDN (stored) | 128.83 ± 67.12 | 14.32 | 100-300 |
| AN/KDN (90/10) | 104.58 ± 51.76 | 07.11 | 100-300 |
| AN/KDN (75/25) | 76.92 ± 43.95 | 04.71 | 100-300 |
| AN/KDN (50/50) | 82.83 ± 27.76 | 06.44 | 100-300 |
| AN + CuO | 115.03 ± 29.57 | 08.53 | 100-300 |
| AN+Cu-Co* | 105.29 ± 27.92 | 07.89 | 100-300 |
| AN/KDN (50/50) + CuO | 70.14 ± 56.27 | 05.62 | 100-300 |
| AN/KDN (50/50) + Cu-Co* | 63.56 ± 31.73 | 05.47 | 100-300 |

4 Conclusions

The science of stabilizing AN for obtaining PSAN is now a well matured science. Currently, the majority of research throughout the world in the energetic materials community is on the energy enhancement of pure AN, and its use as a green energetic material (GEM) and as a possible replacement for AP. Many energetic binders, nitramines, nano catalysts, newly synthesized catalysts and various other energetic materials are being added to AN crystals to increase its combustion enthalpy and to make it viable as a future green energy source and for green propulsion. The present study is an attempt in this direction. Some of the important conclusions that can be drawn from the present studies are:

1. Phase stabilization of ammonium nitrate was observed at 112.2 °C by the addition of 10% KDN. As the percentage KDN is increased in AN crystals, the net exothermicity increases with complete suppression of any endothermic peaks.
2. With storage time, KDN slowly decomposes to form potassium nitrate (KN). KN changes the melting point and phase transition temperature of KDN by forming a eutectic mixture with KDN.
3. CuO serves both as a decomposition catalyst and phase stabilizer for AN. The activation energy has a lower value for AN+CuO compared to pure AN, and the first phase transition was observed at 87.8 °C for AN crystallized with CuO, where for AN alone it is 56.4 °C.
4. Cu-Co* is not a better phase stabilizer as compared to CuO since the first phase transition was observed at 54.7 °C. Although, Cu-Co* is an effective

- decompositional and energy enhancer catalyst for AN and AN/KDN (50/50).
5. With increasing percentage of KDN, early decomposition was observed for all AN/KDN based oxidizer samples. This is because of the low decomposition temperature of KDN with net high exothermic decomposition reaction of dinitramide salts.
 6. The lowest activation energy, much early initiation of decomposition and highest net enthalpy was observed for AN/KDN (50/50) + Cu-Co* as compared to other compositions investigated in the present work. The reason for better catalytic activity of Cu-Co* is because of the method adopted for its synthesis, *i.e.* the citric acid sol-gel method. It is an effective method for preparing metal complexes with fine particle size. A fine particle size of Cu-Co* results in better mixing, which makes Cu-Co* a better decomposition and probably better burning rate catalyst for AN/KDN (50/50) + Cu-Co* based propellant samples.

Acknowledgement

Authors are thankful to Dr. Usha Jha and Dr. Ashok Sharon, Department of Applied Chemistry, Birla Institute of Technology, for their help during the experimentation. The authors are also grateful to the Birla Institute of Technology for funding in the form of an institute fellowship.

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