Thermogravimetric Study on Decomposition Rate of Ammonium Nitrate Under Effect of Chromium Containing Catalysts

M. Pandey[1,*], S. Jha[1], A. Jha[1] and R.R. Jha[2]

[1]Sikkim Manipal Institute of Technology, Majitar-737 132, India
[2]Department of Chemistry, Ranchi University, Ranchi-834 008, India

*Corresponding author: E-mail: mrpandey1@rediffmail.com; ajeya61@yahoo.com

The catalytic influence of chromium based catalyst on thermal degradation of pure ammonium nitrate has been analyzed through thermogravimetric analyses in a temperature range from ambient to 350 ℃. The TGA results reveal that all the additives alter the degradation rate and activation energy. The TGA thermograms show that in case of chromium oxide (CrO_3), ammonium dichromate and potassium dichromate catalyzed ammonium nitrate system degradation start at earlier temperature with respect of pure ammonium nitrate degradation where as in case of lead chromate and copper chromate, initially degradation is get delayed but in all cases it completed at lower temperature. Delay in degradation is correlated with the ionic size of cation and melting point of each catalyst. Further activation energy of various ammonium nitrate-additive systems have also been found to alter significantly in comparison to pure ammonium nitrate (31.31 kcal/mol) where lower value in all systems except with copper chromate-ammonium nitrate system (31.909 kcal/mol). There appears to be a clear link between the ionic radii of cations of chromate/dichromate additives and their efficacy in enhancing the decomposition process of ammonium nitrate. A plausible mechanism has been proposed.

Key Words: Thermogravimetry, Decomposition, Ammonium nitrate, Chromium.

INTRODUCTION

Thermal decomposition behaviour of ammonium nitrate as an oxidizer for propellant, plays an important role in understanding the detail of events taking place during the combustion in condensed phase and developing mathematical description of the reaction kinetics in surface layer. The condensed phase reactions are now well known to play an important role in initial stage of combustion particularly in catalyzed propellant. However, the differentiation in the gas phase and condensed phase is difficult to distinguish under practical conditions. It is obvious that the different reaction regimes would contribute differently with variation in temperature and pressure.

The thermal behaviour of ammonium nitrate has been studied by various researchers[1-9] indicating that decomposition process is temperature and pressure sensitive. It is reported that balance of ionic and radical reactions shift towards radical's mode at higher temperature and reaction rate is affected by the gases that contact the sample. It is interesting to note that surface temperature of the burning ammonium nitrate remains in the range of 300-350 ℃. Minor concentration of additives in propellant formulations is helpful in bringing about the

desired changes in ballistic properties and at the same time also influences the behaviour of ammonium nitrate thermal decomposition. The main additives considered include, metal such as Mg and Zn, first row transition metal oxides, various other metal cations, ammonium halides, sodium chloride, carbon and some of chromium and cobalt salts[10-16].

Majority of these studies have been focusing on phase stabilization and hygroscopicity control aspects on ammonium nitrate. However, catalytic decomposition behaviour deserves significant importance from propellant performance viewpoint. We expect our study to reveal that some chromium containing salts considerably influences the slow thermal decomposition process of ammonium nitrate. Similar observations have also been made in past to understand the mode of thermal decomposition under the effect of chromium ion[17]. The ammonium nitrate samples containing varying amount of Cr^+ cations were prepared by dissolving $Cr(NO_3)_3 \cdot 9H_2O$ and NH_4NO_3 in distilled water.

Thermo analytical study of energetic material is important not only for understanding the kinetics of their thermal decomposition but also for assessing the effect of their decomposition on the potential hazards in their handling, processing and storage. Kinetic studies also provide useful information on

thermal stability and life expectancy under different thermal environment during storage. Various researchers have analyzed the thermal behaviour of ammonium nitrate and other energetic compounds with instruments like differential scanning calorimeter (DSC), differential thermal analyzer (DTA) or thermogravimetric analyzer (TGA). However, their data related to decomposition varies from person to person, owing to variation of amount of ammonium nitrate sample taken for analysis or other factors like degree of purity of ammonium nitrate sample, moisture content or even due to change in set of instruments.

The slow decomposition behaviour of ammonium nitrate with and without catalysts in this temperature range of practical importance has not been studied so much and thus such thermal response kinetic data would be of immense use in understanding initial combustion mechanism, condensed phase combustion of ammonium nitrate propellant and individual role of the catalyst during decomposition reaction and their involvement in enhancing the decomposition energy. Thus, to standardize our data, we used ammonium nitrate with similarly processed and analyzed samples with different chromium catalysts to understand the catalytic effect on decomposition behaviour. Effort has also been made to understand role of each catalyst on the alteration of the decomposition behaviour of ammonium nitrate under slow heating rate with respect of their individual thermal properties like melting point/decomposition temperature.

EXPERIMENTAL

The five chromium oxide based catalysts were selected for study of their effects on ammonium nitrate degradation. All the catalysts, chromium oxide (BDH Lab, Bombay), copper chromate (Nadia Chemical Work, Calcutta), ammonium dichromate (BDH Lab, Bombay), potassium dichromate (BDH Lab, India) and lead chromate (Burgoyne Burbidges & Co. India) were individually incorporated at a fixed concentration level of 3 g/100 g of ammonium nitrate procured from M/S E Merk, Darmsteadt Germany in pure crystal form.

The TGA experiment for samples of ammonium nitrate with and without catalyst were conducted on Parkin Elmer (model TGS-2) USA. Each sample of 10 mg weight was taken in a silver crucible and heated slowly maintaining rise of temperature at rate of 10 °C/min with help of temperature program controller and heater control unit connected with thermocouple of furnace. During heat up process, dry N_2 gas was purged throughout the experiment at the rate of 45 cc/min. The weight loss in sample with temperature rise was plotted as TG curve *i.e.*, weight loss *versus* temperature rise through recorder with the help of signal absorbed send by first derivative computer.

Kinetic modeling: The thermal analysis of catalyzed or uncatalyzed ammonium nitrate samples have been carried out under non isothermal condition, in which a sample is heated at a constant rate. The weight loss *verses* temperature data so obtained for each sample is recorded though program. Activation energy and exponential factors have been derived using Coats and Redfern equation[18].

$$\ln\left[-\ln\left(\frac{1-\alpha}{T^2}\right)\right] = \ln\left[\frac{AR}{\phi E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad (1)$$

where,

$$\alpha = \frac{(W_0 - W_t)}{(W_0 - W_f)} = \text{per cent conversion (reaction progress)} \quad (2)$$

W_0 = initial weight of the sample, W_t = sample weight at time 't', W_f = final weight and t = time.

$$\beta = \frac{dT}{dt} = \text{the rate of weight loss} \qquad (3)$$

As the thermal decomposition of ammonium nitrate is of first order[19] (*i.e.*, n = 1), the solution of this eqn. 1 permits graphical evaluation of E in the coordinates

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2}\right] \text{ versus } \frac{1}{T} \qquad (n=1) \qquad (4)$$

the term (1-2RT/E) is << 1 and is neglected during calculation of Arrhenius factors (A) for the temperature ranges over which reaction generally occurs. The plot of ln [-ln (1-α)/T^2] *versus* 1/T gives a straight line and from which the value of the E and A have been computed from the slope and intercept, respectively.

RESULTS AND DISCUSSION

Thermogravimetric results (Fig. 1) reveals that degradation of ammonium nitrate starts at 171 °C and in first phase degrades slowly up to 21 % with the rise of temperature 246.4 °C. Later on 99.4 % weight loss is recorded with the rise of temperature of 284 °C with a faster rate degradation. The graph also reflects that degradation process is being completed in three phases, first at very slow up to 10 % weight loss, second little faster rate up to nearly 25 % and third phase with still faster rate. Whereas in case of ammonium nitrate catalyzed with copper chromate and lead chromate degradation gets started at earlier temperature and is completed also at much earlier temperature compared to ammonium nitrate degradation. The initiation and completion of degradation of ammonium nitrate are recorded at 160.0 and 244.5 °C with copper chromate system and 151 and 228 °C with lead chromate system. However in both catalyzed system, in first slow decomposition zone degradation rate become slower than of pure ammonium nitrate degradation as may be observed in the curve. Less amount of ammonium nitrate is degraded up to 15 % in case of copper chromate
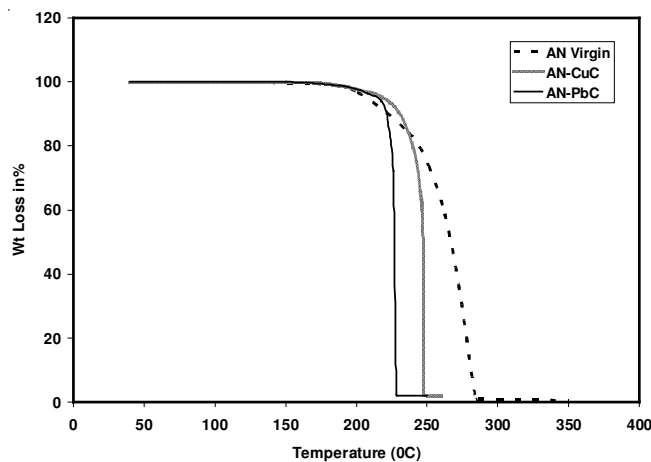

Fig. 1. TGA curves of pure ammonium nitrate and along with 3 % copper chromate and lead chromate as catalyst

catalyzed system and 10 % in case of lead chromate system. Thus in the Fig. 1, results reflect that in the presence of these two catalyst the degradation first become slower and after rise of temperature become faster than ammonium nitrate degradation.

In Fig. 2 where degradation of ammonium nitrate is recorded along with catalyst like chromium oxide (CrO_3), ammonium dichromate and potassium dichromate, TGA results reflect that degradation of ammonium nitrate get catalyzed from initial and degradation get completed at much earlier temperature. In case of potassium dichromate catalyzed ammonium nitrate sharp effect is observed up to 5.5 % and later-on it gets accelerated to achieve the complete degradation at 216 °C. In the case of chromium oxide (CrO_3), ammonium nitrate degradation gets accelerated at much faster rate and degraded completely at 189.0 and 206.3 °C, respectively. In case of chromium oxide catalyzed system, it is seen that degradation gets accelerated even at first slow zone, however, such acceleration in this zone is not seen so much with ammonium dichromate system.
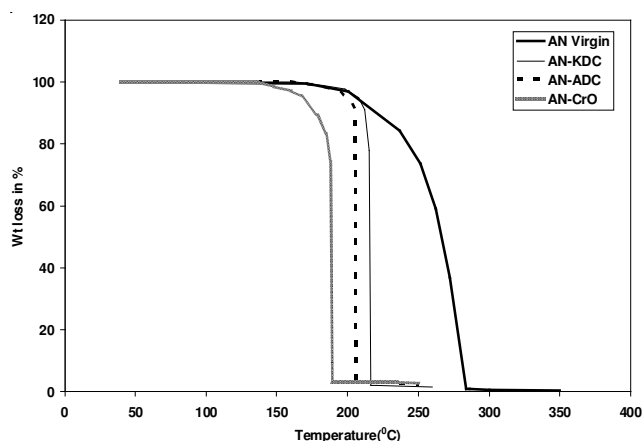

Fig. 2.   TGA curves of ammonium nitrate with 3 % potassium dichromate, ammonium dichromate and CrO_3 under slow heating rate

The thermogravimetric data obtained for percentage weight loss with the change of temperature for pure ammonium nitrate and catalyzed system are summarized in Table-1. On the verifying the data, it is clearly reflected that in all the catalyzed systems, degradation above 20 % wt. loss is recorded at lower temperature compared to pure ammonium nitrate. Only in two cases, where ammonium nitrate was catalyzed with copper chromate and lead chromate degradation gets delayed in the region of slow degradation *i.e.*, within 15 and 10 % wt loss. This suggest that delay may be due to a marginal suppression of escaping of decomposition products by absorption or by some sort of complex formation. Since after 20 % wt loss, degradation rate becomes faster in all catalyzed systems, so it is necessary to examine the catalytic efficiency of each individual catalyst on decomposition reaction of ammonium nitrate. Therefore, the rate of change of wt loss (Δm) with change of temperature (ΔT) for each sample is summarized in Table-2 and result reflects that $\Delta m/\Delta T$ ratio is higher in all the catalyst containing ammonium nitrate degradation compared to pure ammonium nitrate after 10 % wt loss. Even in the case of copper chromate catalyzed sample below 10 % weight loss degradation rate was slower but above 20 % this catalyst acts

effectively. Especially for range of weight range of 50-100 %, $\Delta m/\Delta T$ value is second largest after ammonium dichromate catalyzed system. From this table, effectiveness of catalysts can be summarized as in order of ammonium dichromate > copper chromate > CrO_3 > potassium dichromate > lead chromate, which supports that copper chromate is the second most effective catalyst after ammonium dichromate, to alter the degradation rate of ammonium nitrate and develop an expectation that decomposition process of ammonium nitrate with copper chromate must be exothermic. However, it was earlier reported that decomposition of ammonium nitrate catalyzed with copper chromate is endothermic[20] in nature where as more exothermic decomposition with ammonium dichromate, potassium dichromate and CrO_3 catalyzed system compared to lead chromate catalyzed system. Again a question arises that when all the catalysts contain the chromium oxide, then why the decomposition is endothermic in these cases of catalyzed ammonium nitrate and low exothermic in the case of lead chromate catalyzed ammonium nitrate? Also, why is there a delay in the initial phase of degradation?

TABLE-1 COMPARATIVE VIEW OF WEIGHT LOSS OF PURE AND CATALYZED AMMONIUM NITRATE						
Weight loss (%)	Temperature (°C) for the system					
	AN	AN-CuC	AN-PbC	AN-KDC	AN-ADC	AN-CrO_3
10	230.0	230.0	221.3	212.0	205.30	180.0
20	245.0	239.4	224.0	214.5	205.45	187.2
30	254.0	243.6	226.3	215.1	205.55	188.1
50	266.4	244.0	227.3	215.5	205.70	188.4
100	284.0	244.5	228.0	216.3	206.00	189.0
AN: Ammonium nitrate, CuC: cupper chromate, PbC: Lead chromate, KDC: potassium dichromate, ADC: ammonium dichromate.						

The expected reason may be complex formation or because it follows some different path of catalysis as against to ammonium dichromate, potassium dichromate and CrO_3. Thus mechanism of the working of the catalysts needs to be studied in detail.

Kinetic parameters like activation energy (E) and Arrhenius factors (A) for ammonium nitrate and catalyzed system have been evaluated and tabulated in Table-3 with the help of the Coats and Redfern model. The increased activation energy is observed for degradation of ammonium nitrate-copper chromate system. With lead chromate, ammonium dichromate, potassium dichromate and CrO_3. On the other hand, the activation energy drops sharply to its lowest value 23.47. These data underline the catalytic activity of these catalysts and the decomposition mechanism of ammonium nitrate.

The decomposition chemistry of pure ammonium nitrate has extensively been studied and an in-depth review[7] is available. The thermal decomposition is believed to be initiated by an endothermic proton transfer reaction and the balance of reactions shifts from ionic to radical mode at higher temperature.
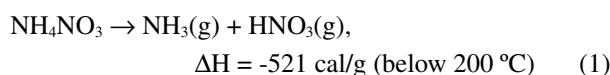
$$NH_4NO_3 \rightarrow NH_3(g) + HNO_3(g),$$

$$\Delta H = -521 \text{ cal/g (below 200 °C)} \qquad (1)$$

TABLE-2
DEGRADATION RATE OF AMMONIUM NITRATE WITH
AND WITHOUT CATALYST IN TERM OF Δm/ΔT

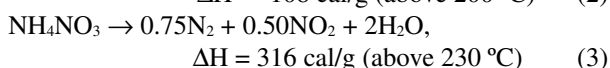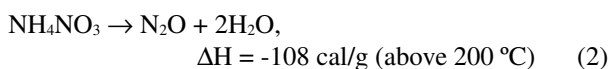| System	Weight range (Δm) (% form)	Temperature range (ΔT) (°C)	Δm/ΔT
AN	10-100	230-284	1.667
	20-100	245.2-284	2.067
	30-100	254-284	2.333
	50-100	266.4-284	2.941
AN-CuC	10-100	236-244.5	6.207
	20-100	239.4-244.5	15.686
	30-100	243.6-244.5	77.778
	50-100	244.0-244.5	100.000
AN-PbC	10-100	221.3-228	13.433
	20-100	224-228	20.000
	30-100	226.3-228	41.173
	50-100	227.2-228	62.500
AN-KDC	10-100	212-216.3	20.930
	20-100	214-216.3	44.444
	30-100	215.1-216.3	58.333
	50-100	215.5-216.3	62.500
AN-ADC	10-100	205.3-206	128.571
	20-100	205.45-206	145.450
	30-100	205.55-206	155.550
	50-100	205.7-206	166.667
AN-CrO₃	10-100	180-189	9.000
	20-100	187.2-189	44.444
	30-100	188.1-189	77.777
	50-100	188.4-189	83.333

AN: Ammonium nitrate, CuC: cupper chromate, PbC: Lead chromate, KDC: potassium dichromate, ADC: ammonium dichromate.

TABLE-3
KINETIC PARAMETERS E AND log A CALCULATED FOR
NH_4NO_3 WITH AND WITHOUT CATALYST FOR THE
WEIGHT LOSS OF RANGE OF FROM 3-97 %

System	Activation energy (E) (kcal/mol)	log A
NH_4NO_3	31.310	14.535
NH_4NO_3 + CuC	31.909	17.270
NH_4NO_3 + PbC	30.036	37.363
NH_4NO_3 + KDC	28.750	101.693
NH_4NO_3 + ADC	28.750	185.740
NH_4NO_3 + CrO₃	23.470	26.950

CuC: cupper chromate, PbC: Lead chromate, KDC: potassium dichromate, ADC: ammonium dichromate.

$$NH_4NO_3 \rightarrow N_2O + 2H_2O,$$
$$\Delta H = -108 \text{ cal/g (above 200 °C)} \quad (2)$$
$$NH_4NO_3 \rightarrow 0.75N_2 + 0.50NO_2 + 2H_2O,$$
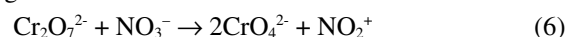$$\Delta H = 316 \text{ cal/g (above 230 °C)} \quad (3)$$

Later on, different pathways are suggested for detonation and explosion reactions of ammonium nitrate at higher temperatures. However, realistic dissociation products of HNO_3 may be

$$2HNO_3 \Leftrightarrow 2NO_2 + H_2O + 0.50O_2 \quad (4)$$
$$\text{or} \quad HNO_3 \Leftrightarrow H^+ + NO_3^- \quad (5)$$
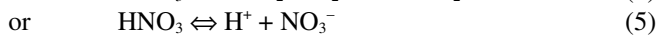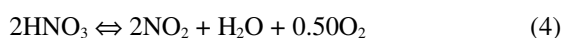
As it was reported that surface temperature of burning ammonium nitrate remains in the range of 300-350 °C, so the slow decomposition behaviour of ammonium nitrate in this temperature range has a practical importance from propellant

combustion viewpoint. Under slow decomposition, below the 200 °C, just after melting ammonium nitrate gives NH_3 (a base) and HNO_3 (acid).

The chromium salts on decomposition gives acid base type of products and the effects of chromium ion containing catalyst is found to vary with variation of size of cation and their cationic activities. It is noteworthy that though chromium cations are known to transform the ammonium nitrate decomposition from endothermic to exothermic at very low concentrations[17] (1:3000 mol of ammonium nitrate), the detailed studies on the subject are very few. The general agreement on the probable role of dichromates in ammonium nitrate decomposition suggest their involvement in catalytic cycles in acidic melt *via* Lux- type acid base displacement in a typical reaction scheme given below:

$$Cr_2O_7^{2-} + NO_3^- \rightarrow 2CrO_4^{2-} + NO_2^+ \quad (6)$$
$$CrO_4^{2-} + H^+ \rightarrow HCrO_4^- \quad (7)$$
$$2HCrO_4^- \rightarrow Cr_2O_7^{2-} + H_2O \quad (8)$$

According to a previous finding[21], the catalytic action of chromium is mainly due to $Cr_2O_7^{2-}$ ions and the cycle stops when the nitrate ions are exhausted, probably *via* the reaction

$$Cr_2O_7^{2-} + 2H^+ \rightarrow Cr_2O_3 + H_2O + 3/2O_2 \quad (9)$$
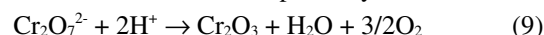
Present thermogram results indicate the degradation of ammonium nitrate catalyzed with CrO_3 is achieved at faster rate just after the melting temperature (m.p. 169 °C) whereas in other catalyzed system it was at higher temperature. The CrO_3, (m.p. 198 °C) is a highly acidic and powerful oxidizing agent, decomposes above 200 °C into a basic Cr_2O_3 and active oxygen. The TGA indicates the degradation starts just after the melting temperature (m.p. 169 °C). It indicates that the melted ammonium nitrate and its primary products easily get oxidized whereas CrO_3 gets reduced with primary product of ammonium nitrate and finally yields $H_2Cr_2O_7$ and H_2CrO_4. This accelerates the total decomposition reaction of ammonium nitrate following the above described reaction path with a continuous acid-base reaction.

Among the ammonium dichromate, potassium dichromate, lead chromate and copper chromate catalyzed system, ammonium nitrate degradation starts at earlier phase with ammonium dichromate and potassium dichromate systems, although a delay is noticed in lead chromate and copper chromate catalyzed system in the initial state. The difference can be explained on the basis of the fact that how easily these compounds are ionized to give the chromate ion. This is directly related to how strongly their ions bind together. Chromate ions are common in all cases whereas only size of cation (NH_4^+: 1.48 Å, K^+: 1.33 Å, Pb^{2+}: 1.21 Å and Cu^{2+}: 0.77 Å) varies in each system. With the increase in the size of cation, binding strength decreases which ultimately makes easy availability of the $Cr_2O_7^{2-}$ and CrO_4^{2-} for the catalytic reaction. In ammonium dichromate and potassium dichromate system degradation starts just after melting of ammonium nitrate *via* nitration reaction and is completed much earlier than it gets completed with lead chromate and copper chromate.

The slow down of catalytic action can be explained with above argument but it fails to explain why is the initial degradation of lead chromate and copper chromate catalyzed ammonium nitrate is even slower than pure ammonium nitrate

(Fig. 1). One possible explanation could be that such ion exchange reaction that results in a more stable and less reactive products slows down the evaporation of primary products. This could be explained by the solid-solid interaction chemistry of ammonium nitrate with lead chromate and copper chromate at melting phase. Lead chromate is insoluble in ammonia and shows high affinity with acid, so the possible reaction is: $PbCrO_4 + HNO_3 \rightarrow PbNO_3 + HCr_2O_4$. On further heating of $PbNO_3$ decomposes exothermically into lead oxide and NO_2. However both $PbNO_3$ (m.p. 270 °C) and $PbCr_2O_7$ (m.p. 844 °C), require the high temperature to accelerate the degradation reaction. This slows down the evaporation of possible products from HNO_3 reaction during initial stage and ultimately delays the initial degradation.

Here also our TGA graph confirms that rate of degradation is even low-within the range of 15 % wt loss compared to the degradation of pure ammonium nitrate. It also exhibits higher observed value of activation energy (Table-3). This supports our view-point.

It may be inferred that chromium containing additive would prove to be more promising in ammonium nitrate based composite propellants as they would not only accelerate the rate of oxidizer decomposition reaction leading to shorter ignition time but also increase the rate of gasification in condensed phase subsurface reactions. This will ultimately increase burn rate as well. The additives bring down the complete degradation temperature of ammonium nitrate by lowering the activation energy and accelerating the rate of degradation. This subsequently signify their participation in ammonium nitrate decomposition process right from the inception and more vigorously after melting of ammonium nitrate. The effectiveness of catalysts is found to be in following order at atmospheric pressure:

CrO_3 > ammonium dichromate > potassium dichromate > lead chromate > copper chromate

The results reveal a clear link between the ionic radii of cations of chromate/dichromate additives and their efficacy in enhancing the degradation process of ammonium nitrate. Formation of CrO_3 during the ammonium nitrate-dichromate/chromate condensed phase reactions is seen to be the first step for subsequent degradation.

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