

# Effect of Energetic Materials on Thermal Decomposition of Phase-Stabilised Ammonium Nitrate – An Eco-Friendly Oxidiser

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## ABSTRACT

Phase-stabilised ammonium nitrate (PSAN) was prepared by incorporating copper (II) diamine nitrate in the ammonium nitrate (AN) crystal lattice, thereby avoiding the abrupt volume change within the useful temperature range. The effect of RDX on the thermal decomposition of PSAN has been investigated. Decomposition temperatures of PSAN and RDX are almost in the same temperature range. The synergetic effect of the interaction between PSAN and RDX resulted in a net exothermic reaction of PSAN. The kinetic and thermodynamic parameters of the exothermic decomposition have been computed. Two well-known equations based on variable programme heating rate method, viz., Kissinger and Ozawa equations were employed for the kinetic evaluation. The approximate activation energy obtained from Ozawa method was refined by an iteration procedure using the two-term approximation for Arrhenius temperature integral,  $p(x)$  and the refinement was found to be unwarranted for the reaction. There is a close agreement between the values of kinetic parameters of the exothermic reaction of PSAN and RDX obtained from the Kissinger and Ozawa methods.

## 1. INTRODUCTION

Composite propellants based on ammonium perchlorate (AP) as oxidiser are state-of-the-art. However, global environmental impact restricts AP-based propellants because of their *HCl* exhaust. Therefore, efforts are on to innovate propellants with clean exhaust. Ammonium nitrate (AN) has, thus, regained importance in the field of propellants and explosives, more specifically in insensitive formulations, because of its clean burning and low hazard. However, the stumbling block for the application of AN – as solid propellant oxidiser – has been its dimensional instability caused by polymorphic transitions near the propellant processing and storage temperatures and its

extreme hygroscopicity. The transitions occurring at these temperatures cause destruction of AN crystal, which results in increase of volume and concomitant porosity of the propellant grain, as a result of non-alignment of the crystallographic axes of micro-crystallites in AN particles undergoing recrystallisation. This can be overcome by the use of phase-stabilised ammonium nitrate<sup>1-4</sup> (PSAN). The typical ones are the preparation of metal-diamine dinitrate complex formed by the reaction of molten AN and nickel or copper oxide.

The PSAN is prepared by incorporating copper (II) diamine nitrate in the AN crystal lattice, thereby avoiding the abrupt volume change within the useful temperature range. The permanent

volume change due to growth of AN when it is thermally cycled, is undesirable because of loss in density and mechanical properties, unstable combustion, thermal expansion and structural instability.

The energetics of the PSAN-based propellant is not that encouraging and therefore warrant incorporation of high energy materials like RDX or HMX for improved ballistic performance. As a preliminary evaluation to assess the effect of an energetic material, a study was undertaken on the thermal behaviour of PSAN with RDX (cyclo-1,3,5-trimethylene-2,4,6-trinitramine) as an additive using thermogravimetry (TG) and differential scanning calorimetry (DSC). The study also encompasses the kinetic evaluation of thermal decomposition of PSAN-RDX using the DSC peak temperature-programme rate relationship by Ozawa<sup>5</sup>. The Kissinger<sup>6</sup> method and an iteration procedure<sup>7</sup> were used for the evaluation of activation parameters for comparison.

## 2. EXPERIMENTAL METHOD

The PSAN was prepared by incorporating copper (II) diamine nitrate in the AN crystal lattice, by a melt process of stoichiometric quantities of AN and copper oxide. The PSAN thus prepared was sieved and used for investigation. The PSAN and RDX (1:1) samples were prepared by careful mixing of the two components in a 5 cm diameter polished-porcelain container with a polished glass rod. Care was taken to avoid contact with moisture during storage.

### 2.1 Instrumental Setup

The DSC and TG curves were recorded by a Mettler TA-3000 thermal analysis system in conjunction with DSC-20 standard cell, TG-50 thermobalance and TC10A TA processor. The heat flow and temperature calibration of DSC were done using Indium standard, as per procedure, recommended by the manufacturer. The experiments were carried out in static air. The DSC curves were recorded at five heating rates, namely, 2, 5, 7, 10 and 15 °C min<sup>-1</sup>. Almost constant sample

mass of 3 ± 0.1 mg (PSAN:RDX - 1:1) was used in all the experiments. The samples were placed in an aluminium pan (40 µl) sealed with a pierced lid.

## 3. RESULTS & DISCUSSION

AN exhibits four enantiotropic changes, one endothermic melting peak followed by endothermic decomposition peak. The PSAN sample is temperature-programmed through completion of all polymorphic transformations and thermal decomposition. The peak temperatures corresponding to the phase changes and decomposition are given in Table 1. The presence of moisture below 0.2 per cent results in the appearance of phase III. The transition temperature IV→III, however, does not drop below 50 °C. This observation distinguishes PSAN from pure AN, whose transition temperature IV→III drops remarkably below 50 °C at these moisture levels<sup>8</sup>. Therefore, the presence of diamine complex in AN crystal lattice as a solid solution is effective<sup>9</sup>. It restricts the occurrence of phase III partially and keeps the transition temperature above 50 °C, avoiding caking and also preserving free flow of the material<sup>8</sup>. The TG curve of PSAN shows a single-stage mass loss. Though the inception temperature of PSAN:RDX mixture is same as that of pure PSAN, the reaction interval ( $T_f - T_i$ ) is shortened, showing the synergetic effect of RDX on the decomposition of PSAN.

**Table 1. Phenomenological data and enthalpy of PSAN ( $\phi = 5\text{ }^\circ\text{C min}^{-1}$ )**

Peak	$T_m$ (°C)	$\Delta H$ (J g <sup>-1</sup> )	Process
Endotherm	54	20	IV→II
Endotherm	86.7	3	III→II
Endotherm	125	46	II→I
Endotherm	168	58	Melting
Endotherm	229	1540	Decomposition

The DSC trace of pure RDX shows one sharp endotherm ( $T_m = 204\text{ }^\circ\text{C}$ ) corresponding to its melting, followed by an exothermic peak indicating decomposition of RDX ( $T_m = 235\text{ }^\circ\text{C}$ ). The enthalpy of the exothermic decomposition of RDX at different heating rates and the corresponding peak

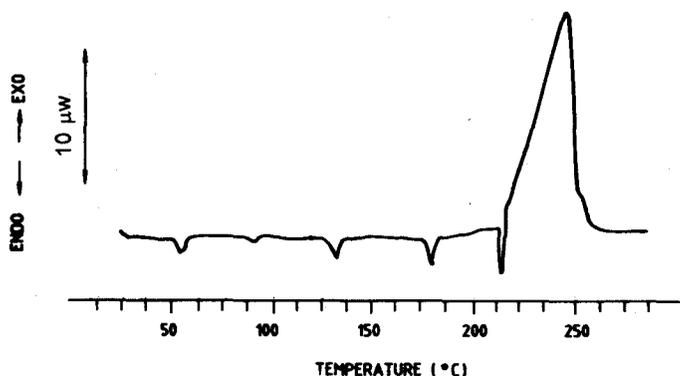


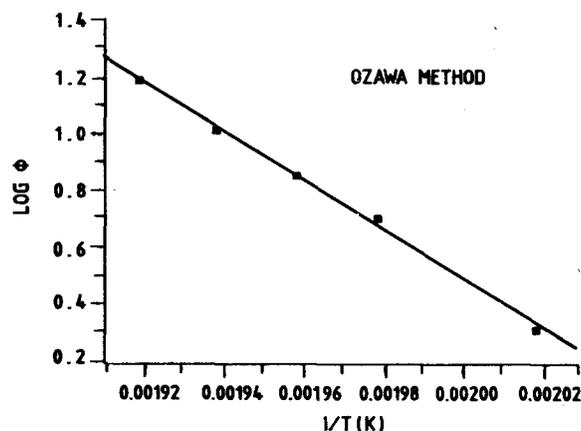
Figure 1. DSC curve of PSAN and RDX

temperatures are shown in Table 2. With increase in the heating rate, there is a natural shift in the peak maximum of the exothermic peak.

Table 2. Enthalpy and peak temperature of exothermic decomposition of RDX

Heating rate (°C min <sup>-1</sup> )	ΔH (J g <sup>-1</sup> )	T <sub>m</sub> (°C)
2	2304	222.6
5	2016	234.0
7	2198	238.3
10	2031	241.3
15	2049	245.0

The DSC trace of PSAN:RDX mixture shows five endothermic peaks above room temperature, due to three enantiotropic changes of PSAN, the melting of PSAN and the melting of RDX, followed by a sharp exotherm, as shown in Fig 1. The DSC trace shows that the endothermic decomposition of PSAN is suppressed by high exothermic decomposition of RDX occurring at almost the same temperature range. It is interesting to calculate the net enthalpy change at a particular experimental condition ( $\phi = 5$  °C min<sup>-1</sup>). The enthalpy change of PSAN decomposition is approximately 1540 J g<sup>-1</sup> (endo), while that of RDX is 2010 J g<sup>-1</sup> (exo). A 1:1 mixture of these two should therefore result in a net enthalpy change of 235 J g<sup>-1</sup> (exo). However, the observed higher value of 1390 J g<sup>-1</sup> (exo) clearly indicates gas phase oxidation reaction (combustion) among the decomposition products of PSAN and RDX,


 Figure 2. Plot of  $\log \phi$  vs  $1/T$  (K) of exothermic reaction of PSAN:RDX (1:1).

analogous to the gas phase reactions during propellant combustion.

### 3.1 Kinetic Analysis using DSC Data

The kinetic parameters for thermal decomposition of PSAN:RDX (1:1) mixture were evaluated using DSC data. The Ozawa method was employed for carrying out DSC experiments at a series of heating rates between 2 and 15 °C min<sup>-1</sup>. The variation of peak temperature  $T_m$  with heating rate and the enthalpy change involved in the exothermic reaction of PSAN-RDX mixture is shown in Table 3.

Table 3. Enthalpy and peak temperature of exothermic decomposition of PSAN:RDX (1:1)

Heating rate (°C min <sup>-1</sup> )	ΔH (J g <sup>-1</sup> )	T <sub>m</sub> (°C)
2	1144	222.4
5	1391	232.0
7	1287	238.0
10	1216	242.8
15	1194	248.3

### 3.2 Ozawa Method

The popularly used Ozawa method is based on plotting of  $\log(\text{heating rate})$ ,  $\phi$ , vs reciprocal of DSC peak temperature in absolute ( $1/T_m$ ). The slope of the straight line plot is used for calculating approximate value of activation energy ( $E$ ). The DSC data used for Ozawa kinetic plot are given in

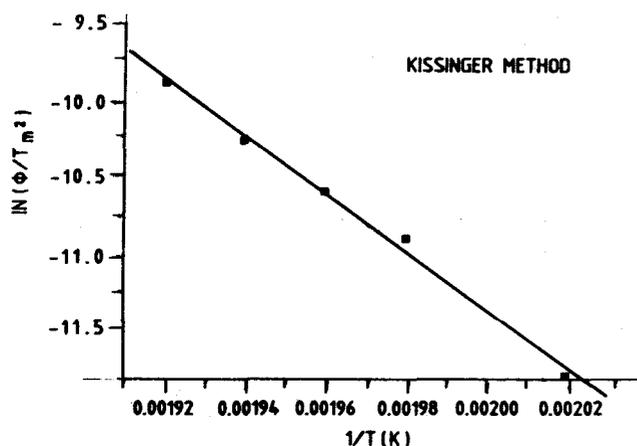


Figure 3: Plot of  $\log \phi/T_m^2$  vs  $1/T$  (K) of exothermic reaction of PSAN:RDX (1:1).

Table 3 and the corresponding plot is shown in Fig. 2.

The equations for the calculation of  $E$  and  $A$  are:

$$E = 2.19Rd[\log \phi / d(1/T_m)] \quad (1)$$

where  $d[\log \phi / d(1/T_m)]$  is the slope of the curve

$$A = (\phi E \exp E / RT_m) / RT_m^2 \quad (2)$$

### 3.2.1 Refinement of Activation Energy from Ozawa Method

The  $E$  value obtained from the Ozawa method is approximate and therefore requires refinement<sup>10</sup>. This is done by a series of iterations using the relationship,  $g(\alpha) = (AE/\phi R) p(x)$  where  $p(x)$  is Arrhenius temperature integral, derived by a two-term approximation<sup>7</sup>. The value of the refined activation energy of the exothermic reaction obtained by the iteration method is very close to the approximate  $E$  value obtained by the Ozawa method, showing that the refinement is unwarranted for this reaction.

### 3.4 Kissinger Method

The Kissinger method is basically the plot of  $\log(\phi/T_m^2)$  vs  $1/T_m$ .  $E$  is calculated from the slope of the above plot (Fig. 3). The equations is:

$$E = Rd[\log(\phi/T_m^2)]/[d(1/T_m)] \quad (3)$$

where  $d[\log(\phi/T_m^2)/d(1/T_m)]$  is the slope.

The data used to evaluate  $E$  from the Kissinger plot are given in Table 4. The pre-exponential factor ( $A$ ) was also calculated for five heating rates using Eqn (2). The  $E$  and the computed average values of  $A$  for Ozawa and Kissinger methods are given in Table 4. The kinetic parameters computed by both the methods are comparable.

Table 4. Kinetic parameters for exothermic reaction of P and RDX using Ozawa and Kissinger methods

Method	$E$ (kJ mol <sup>-1</sup> )	$A$ (s <sup>-1</sup> )
Ozawa *	158.63	$1.4248 \times 10^{14}$
Ozawa **	158.55	$1.3973 \times 10^{14}$
Kissinger	158.20	$1.2367 \times 10^{14}$

\* Ozawa method (without refinement)

\*\* Ozawa method (with refinement)

## 4. CONCLUSIONS

The thermal decomposition of PSAN and RDX occurring at nearly the same temperature range is modified because of the interaction between their decomposition products, resulting in a net exothermic gain for the reaction. The Arrhenius activation parameters computed for this reaction with the Ozawa and Kissinger methods show good agreement. The value of  $E$  from Ozawa method is not altered by the standard refinement using a two-term approximation for the Arrhenius temperature integral. Investigations on the synergetic effect of RDX and HMX in various proportions on the thermal decomposition of PSAN are in progress.

## ACKNOWLEDGEMENTS

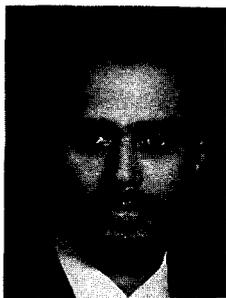
The authors are thankful to the Director, Vikram Sarabhai Space Centre, Thiruvananthapuram, for his kind permission to publish this work.

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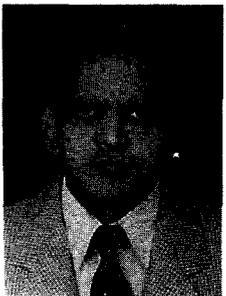
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#### Contributors



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