

## **THERMAL IGNITION STUDIES ON METALLIZED FUEL-OXIDIZER SYSTEMS**

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The thermal ignition behaviour of various mixtures of organic fuels, magnesium and ammonium nitrate (AN) has been examined by differential thermal analysis technique. It has been observed that the thermal decomposition/ignition of organic fuel-AN mixtures is modified significantly in the presence of magnesium metal. The decomposition characteristics of the binary mixtures of AN with various metals indicate the specific action of magnesium and zinc in lowering the decomposition temperature. A possible explanation for the low temperature decomposition is given in terms of the solid state reaction causing the fusion of AN which further reacts with the metal resulting in a highly exothermic reaction.

The thermal characterization of various condensed fuel-oxidizer systems used in solid propellants and explosive compositions has been an important aspect of our earlier studies [1, 2]. Highly metallized fuel rich compositions have found application in solid-fuel ram jet propulsion systems. It is generally noticed, however, that the ignition of these systems becomes increasingly difficult with high loadings of metallic ingredients. The solid oxidizer, although used as a minor component, plays an important role in the ignition and sustenance of combustion. In a recent study [3] involving the hypergolicity of hybrid propellants, it has been observed that some solid organic fuels which by themselves are non-hypergolic, ignite readily with liquid oxidizers, such as nitric acid on mixing with metal powders. This synergistic ignition behaviour was explained in terms of the increased exothermicity of the system, primarily due to the exothermal reactions between the fuels and the oxidizer in the preignition stage. These results led us to study whether a similar effect could be observed with solid oxidizers, instead of nitric acid, on subjecting the mixture to controlled heating. If so, the decomposition/ignition of the metallized systems could take place at relatively low temperatures, thereby facilitating the ignition process.

In the present investigation the ignition behaviour of various magnesium containing fuels mixed with ammonium nitrate (AN) has been examined by differential thermal analysis (DTA) technique. Most of the organic fuels chosen in the present study, such as carbon, benzidine (BZ), thiocarbonylhydrazide (TCH), *p*-

dimethylaminobenzylideneaniline (PDBA) ignite synergistically with nitric acid on mixing with magnesium as reported earlier [3, 4]. The mixtures of anthracene, and bis *p*-hydroxybenzaldehydethiocarbonohydrazone (BTCH) with magnesium which do not show synergistic ignition with nitric acid have also been examined. Also, since in practical systems, the amount of the oxidizer used is very small, an attempt has been made to obtain ignitable compositions with maximum fuel content.

## Experimental

### *Materials*

Ammonium nitrate supplied by Merck Chemicals was used in the present investigation. Since it is a hygroscopic compound, maintaining the same particle size was found to be difficult. Magnesium powder with a particle size in the range 212–300  $\mu\text{m}$  was used. The carbon black used was finely powdered activated charcoal. Fine powders of zinc, nickel, iron, aluminium samples obtained from commercial sources were used as such. Thiocarbonylhydrazide, PDBA and BTCH were prepared as reported earlier [3, 5, 6].

The thermal curves were recorded using a DTA set-up described earlier [7]. In each experiment 100 mg of the sample was placed in the DTA cup and heated at a constant rate of 10 deg/min. For some of the samples the DTA curve was also recorded in a flowing nitrogen atmosphere (30 ml/min).

## Results and discussion

The DTA data of the ternary systems containing an organic fuel, magnesium and ammonium nitrate, are given in Table 1. A comparison of these data with those of the individual components, namely, the organic fuel, Mg and AN, shows that their thermal characteristics are drastically modified. Magnesium powder which is ignited only around 590° in air, when mixed with carbon and AN ignites completely around 130° itself immediately after the phase transformation of AN at 125° [8], as no DTA peak is seen beyond this temperature, when the composition contains up to about 25% Mg (Fig. 1). Beyond 25% Mg concentration the decomposition is not explosive and some Mg is left behind which is oxidized around 585°. The exothermic peak observed around 375° could be due to some reaction intermediate formed.

Mixtures of TCH, Mg and AN show the endothermic peak at 127°. The next small exothermic peak around 185° could be due to the decomposition of TCH [3].

**Table 1** DTA data of various fuel-oxidizer compositions

System	Composition, wt%	DTA peak temperature*, °C
C: Mg: AN	15:15:70	124(-) 126(+)
	25:25:50	124(-) 135(+)
	30:30:40	124(-) 146(+) 374(+) 584(+)
TCH: Mg: AN	20:20:60	123(-) 127(+) 185(+) 210(+)
	25:25:50	123(-) 127(+) 185(+) 213(+) 595(+)
	30:30:40	123(-) 127(+) 184(+) 209(+) 597(+)
BZ: Mg: AN	20:20:60	125(-) 239(+)
	25:25:50	125(-) 145(+) 244(+)
	30:30:40	125(-) 145(+) 244(+) 470(+)
	25:50:25	125(-) 150(+) 251(+) 455(+)
PDBA: Mg: AN	20:20:60	125(-) 128(+) 244(+) 390(+)
	25:25:50	125(-) 128(+) 244(+) 440(+)
	30:30:40	125(-) 128(+) 244(+) 480(+)
	35:35:30	125(-) 128(+) 244(+) 480(+) 535(+)
BTCH: Mg: AN	25:25:50	125(-) 144(+)
	30:30:40	125(-) 144(+)
	35:35:30	125(-) 144(+) 249(+) 470(+) 610(+)
Mg: AN	3:97	125(-) 140(+) 250(+) 390(-) 415(-)
	5:95	125(-) 135(+) 250(+) 398(-) 420(-)
	10:90	125(-) 135(+) 270(+) 385(-) 430(-) 599(+)
	25:75	125(-) 135(+) 380(-) 405(-) 540(+)
	50:50	125(-) 135(+) 380(-) 405(-) 540(+)
	60:40	125(-) 130(+) 380(-) 405(-) 436(+) 541(+)
	70:30	125(-) 130(+) 380(-) 405(-) 425(+) 537(+)
Zn: AN	20:80	125(-) 130(+) 210(-) 265(+) 296(+) 302(-)
	50:50	125(-) 130(+) 210(-) 244(+) 297(+) 300(-)
C: AN	5:95	125(-) 180(+) 252(+)
	10:90	125(-) 144(+) 166(+) 252(+)
	15:85	125(-) 135(+)
	20:80	125(-) 135(+)
	50:50	125(-) 135(+)
	70:30	125(-) 135(+)

\* (+) and (-) indicates exotherm and endotherm respectively.

The complete ignition of the mixture occurs around 210° when the Mg content is about 20% and the oxidizer concentration more than 60%. At lower concentration of the oxidizer Mg ignites only partially at 210°. The complete oxidation of Mg takes place around 600° as shown by the exothermic peak around this temperature.

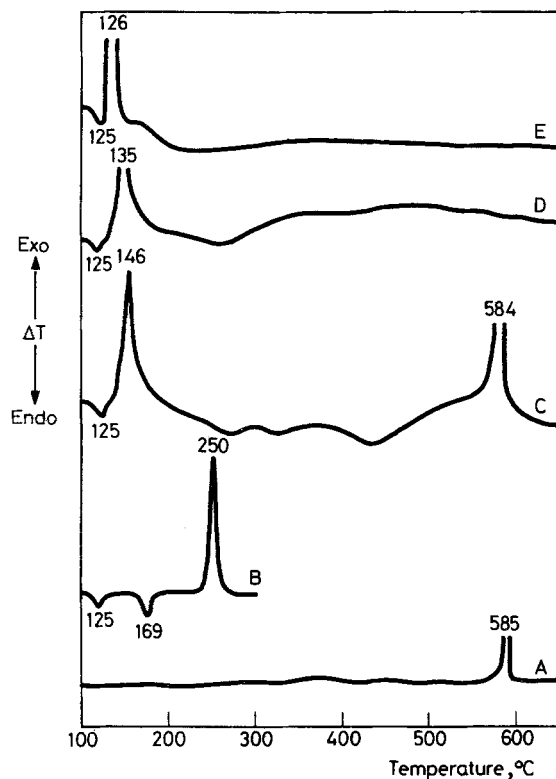


Fig. 1 DTA curves of (A) Mg (B) AN and mixtures of C-Mg-AN compositions, (C) 30:30:40, (D) 25:25:50, (E) 15:15:70

Unlike the systems containing C and TCH, the benzidine-Mg-AN system ignites around 240° (Fig. 2). No peak is observed above this temperature when the composition contains 20% Mg and 60% AN. Compositions with higher Mg content give an additional broad peak in the region around 450°. Compositions containing 25 to 50% of Mg have an additional small peak at 145°. The DTA curve of benzidine alone shows an endotherm at 123° due to melting and an exotherm around 315°. The latter peak is absent in the mixed compositions.

Compositions consisting of PDBA, Mg and AN show a sharp exotherm at 128° soon after the phase transition endotherm at 125° followed by another sharp exotherm at 244° indicating a two stage decomposition unlike other systems even at high loading of oxidizer. A complex thermal decomposition behaviour is seen beyond this temperature. A prominent broad exothermic peak is observed when the Mg concentration is above 20% in the sample. The sample containing 35% of Mg has a sharp peak around 540° which could be attributed to the ignition of the Mg

left over. *p*-dimethylaminobenzylideneaniline alone, on the other hand decomposes exothermally at 336° [3]. However, this peak is not seen in the DTA curves of the compositions.

A similar effect is seen for the BTCH–Mg–AN system (Fig. 3). In this case, mixtures containing up to 30% Mg could be ignited completely at 145°. The oxidizer concentration is 40% in this case, so it is clear that the composition containing 30% Mg is highly fuel rich. The mixtures with more than 30% Mg content decompose/ignite only partially and leave behind Mg partly as a metal, which is oxidized at 610°. An additional exotherm is observed at 249°, when the composition contains BTCH, Mg and AN in a ratio of 35:35:30. May be the decomposition takes place in two stages. Similarly, a mixture of anthracene, Mg and AN containing 25 to 30% of Mg ignites around 135°.

A common feature of these DTA curves is the presence of an exothermic peak around 130–145°. It is apparent from the data that the decomposition/ignition features of the ternary systems depend on the Mg and AN contents of the mixture and also on the nature of the fuel used.

In order to explain these results, binary mixtures of AN with Mg, C, the organic fuels used and other metals were examined. The DTA curves of Mg–AN mixtures

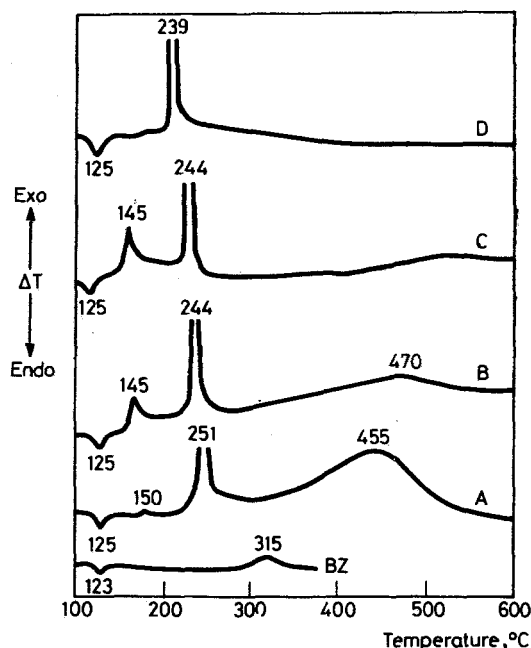


Fig. 2 DTA curves of benzidine and mixtures of BZ–Mg–AN compositions (A) 25:50:25, (B) 30:30:40, (C) 25:25:50, (D) 20:20:60

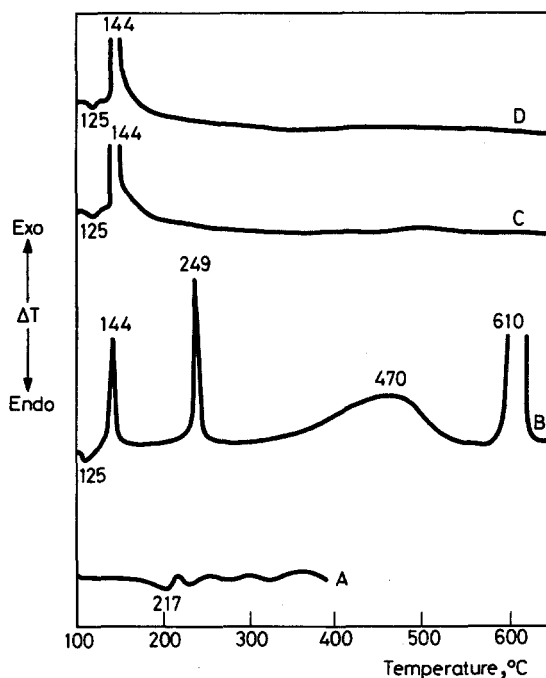


Fig. 3 DTA curves of (A) BTCH and mixtures of BTCH-Mg-AN compositions, (B) 35:35:30, (C) 30:30:40, (D) 25:25:50

(Fig. 4) show a sharp exothermic peak around 130–140°. This peak occurs soon after the phase transformation of AN from tetragonal to cubic at 125° well below the melting point of AN (169°), and is present in all compositions ranging from 3 to 70% Mg content. As a matter of fact the melting endotherm of AN is not at all observed in any of these compositions. These results indicate the occurrence of a solid–solid interaction causing an exothermic reaction between Mg and AN. At higher temperatures, modified decomposition/oxidation peaks of AN and Mg are seen depending on the composition of the mixture. However, it is worth noting that compositions containing over 5% of Mg show a separate peak in the region 500–600°, due to ignition of the Mg left over. In other words, compositions with more than 5% of Mg cannot be ignited fully at low temperatures with AN alone. On the other hand, as shown by the ternary systems, compositions with Mg content as high as 25% ignite at low temperatures (< 145°) when mixed with the appropriate organic fuels which by themselves are not ignitable with AN.

In order to understand the exotherm observed around 130–135°, many binary systems were examined. It was seen that besides Mg, Zn powder when mixed with AN had a similar effect on the thermal decomposition (Table 2). Here again,

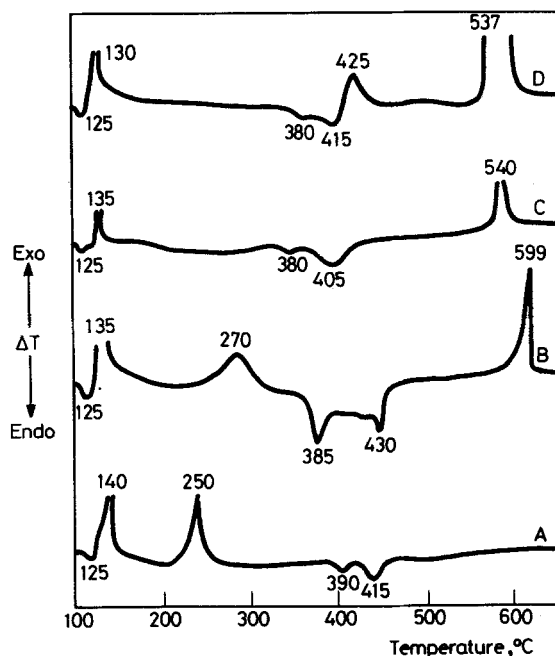


Fig. 4 DTA curves of mixtures of Mg-AN compositions (A) 3:97, (B) 10:90, (C) 25:75, (D) 70:30

Table 2 DTA data of various metal-ammonium nitrate mixtures

System	Composition, wt%	DTA peak temperature, °C
AN:Zn	50:50	125(-) 135(+) 210(-) 244(+) 297(+) 300(-)
AN:Al	50:50	125(-) 167(-) 220(-) 263(+)
AN:Ni	50:50	125(-) 164(-) 228(+)
AN:Fe	50:50	125(-) 169(-) 216(+)
AN:Sn	50:50	125(-) 162(-) 223(-) 256(+)
AN:Cu	50:50	125(-) 161(-) 185(+) 247(+)

individual decomposition patterns of AN and Zn are observed at high concentrations of either of the components (Fig. 5). It was also observed that the decomposition pattern of both binary systems containing Mg or Zn, remains unchanged with the variation of particle size of the metal and also of the sample size. Furthermore, the ignition characteristics remained unchanged when the DTA curve was taken in flowing nitrogen instead of air. However, other metals like Al, Ni, Fe, Sn, Cu etc. do not modify the decomposition significantly. In fact no exothermic peak is seen at 130°, and the decomposition occurs mainly in the region 215–260°, as expected for the decomposition of AN in these cases. The role of

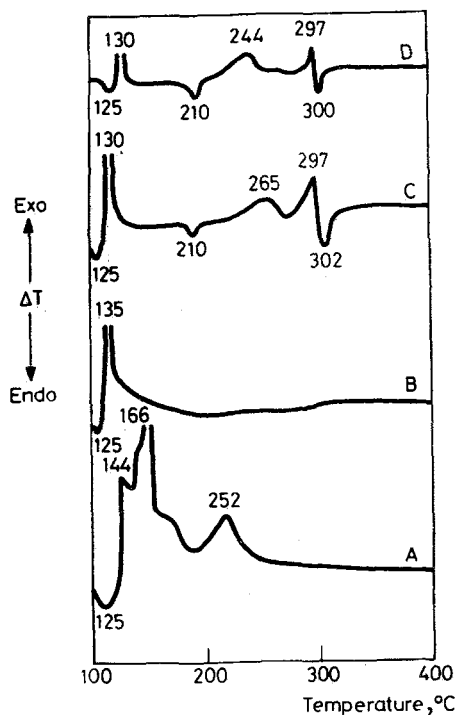


Fig. 5 DTA curves of mixtures of C-AN compositions (A) 10:90, (B) 15:85 and Zn-AN compositions, (C) 20:80, (D) 50:50

specificity of Mg and Zn metals is thus obvious since this effect is not seen with the other metals studied.

A hot stage microscopic study of the heterogeneous mixture of AN and Mg soon after the phase change of AN at 125°, shows some mobility of the individual components, just before the instant decomposition/ignition (130°), resulting in the fusion of the mixture. A similar change was noticed with mixtures of AN and Zn also around 130°. But in no case where the decomposition took place after melting of the AN, any mobility or the fusion of the component was observed around this temperature. This observation again suggests the specificity of Mg and Zn metals in causing the solid-solid interaction.

Although the specific interaction of these metals with AN in solid state has not been studied so far, there have been numerous studies on the dissolution of various metals in molten AN [9]. Zinc dissolves particularly rapidly in the fused salt evolving much heat and getting oxidized easily. It is therefore possible that the solid state interaction initiates the fusion on AN leading to dissolution and subsequent oxidation of zinc or magnesium. Once this occurs, the organic fuel if present



additionally, is also oxidized around this temperature. The oxidation of Mg could occur via formation of  $\text{Mg}(\text{NO}_3)_2$ . The nitrate formed, which was qualitatively identified appears as is indicated by the DTA curve by endothermic peaks of decomposition around  $390\text{--}420^\circ$ . In the case of Zn-AN mixtures, a similar reaction may be postulated. However, since  $\text{Zn}(\text{NO}_3)_2$  is unstable at high temperatures, the endotherm around  $300^\circ$  could be due to reaction products of ZnO and AN. This was confirmed by the DTA curve of the ZnO-AN system, which was found to give similar peaks around  $300^\circ$ .

Apart from Mg and Zn, when AN was mixed with carbon black the mixture was found to ignite around  $130^\circ$  when the C content exceeded 15% in the mixture (Fig. 5). Similar results were obtained by Glaskova et al. [10]. These authors, however, studied the decompositions of stoichiometric mixtures with lower than 15% C content, wherein the decomposition starts at the melting of AN and goes through a two stage decomposition mechanism. The ignition/explosion observed at  $130^\circ$  for the mixture with a carbon content of about 15% was, however, not explained. Apart from carbon, none of the other fuels used in the present study caused the ignition of the AN mixture around  $130^\circ$  (Table 3). The catalysed decomposition with carbon is thus apparently specific in character.

**Table 3** DTA data of various organic fuel-ammonium nitrate mixtures

System	Composition, wt%	DTA peak temperature, $^\circ\text{C}$
AN:C	50:50	125(-) 130(+)
AN:PDBA	50:50	120(-) 161(-) 222(+)
AN:BTCH	50:50	125(-) 167(-) 209(-) 250(+)
AN:Naphthalene	50:50	120(-) 163((-) 186(-) 236(+)
AN: Benzidine	50:50	125(-) 169(-) 189(+)
AN: Benzylidene-aniline	50:50	125(-) 163(-) 249(+)
AN: Anthracene	50:50	125(-) 165(-) 202(-) 266(+)
AN:TCH	50:50	125(-) 190(+)
		224(+)
		248(+)

It is thus seen that the decomposition/ignition of organic fuel-AN mixtures is modified drastically in the presence of magnesium metal. The ignition temperature of certain compositions is lowered drastically. It may, however, be pointed out that being highly specific in nature, the effect may not be the same as observed in the case of synergistic ignition of hybrid systems. For example, although the fuel mixtures used in the present study were the same which exhibited synergistic ignition with  $\text{HNO}_3$  in our earlier study, the ignition characteristics of the mixture in the present case, are not similar. Furthermore, although the anthracene-Mg- $\text{HNO}_3$  and the

BTCH–Mg–HNO<sub>3</sub> systems do not show synergistic ignition, the fuel mixture with AN, do show ignition characteristics similar to other systems dealt with in this study (Table 1). It may also be noted that whereas the synergistic ignition in hybrid systems was observed with a variety of metals, only Mg and Zn appear to be effective in lowering the ignition temperature in the present study.

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**Zusammenfassung** — Mittels DTA wurde das thermische Initiierungsverhalten verschiedener Gemische aus organischen Brennstoffen, Magnesium und Ammoniumnitrat (AN) untersucht. Es wurde festgestellt, daß die thermische Zersetzung/Initiierung von Gemischen aus organischen Brennstoffen und AN durch die Gegenwart von metallischem Magnesium bedeutsam beeinflußt wird. Die Zersetzungscharakteristiken binären Gemische aus AN und verschiedener Metalle zeigen eine spezielle Wirkung von Magnesium und Zink bei der Herabsetzung der Zersetzungstemperatur. Eine mögliche Erklärung für die Zersetzung bei niedrigerer Temperatur kann in Bezug auf die Festkörperreaktion gesehen werden, die das Schmelzen von AN verursacht, welches dann mit dem Metall stark exotherm reagiert.

**Резюме** — Методом дифференциального термического анализа изучено термическое воспламенение различных смесей органических топлив, магния и нитрата аммония (НА). Установлено, что термическое разложение/воспламенение смесей органическое топливо — НА значительно меняется в присутствии металлического магния. Характеристики разложения бинарных смесей НА с различными металлами показали специфическое влияние магния и цинка в понижении температуры разложения. Возможное объяснение такого низкотемпературного разложения дано, исходя из твердотельной реакции приводящей к плавлению нитрата аммония, вступающего затем в сильно экзотермическую реакцию с металлом.