Studies on energetic compounds (Part 18): Preparation and kinetics of thermolysis of alkaline earth metal salts of 5-nitro-2,4-dihydro-3H-1,2,4-triazole-3-one (NTO)

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Four alkaline earth metal (Mg, Ca, Sr, Ba) salts of 5-nitro-2,4-dihydro-3H-1,2,4-triazole-3-one (NTO) have been prepared and characterised. The thermal and explosive behaviour of these hydrated salts were studied by TG, DTA and explosion delay measurements. The activation energy for the explosion is found in the range 28-34 kJ mol⁻¹. A suitable pathway involving slow thermolysis (decomposition) and rapid thermolysis (explosion) have been suggested. The oxidation reduction reactions near the surface of thermolysing material [M(NTO)₂₉₂₀] seems to be responsible for the decomposition and explosion.

NTO¹⁻⁴ is a powerful oxidiser/catalyst for composite solid rocket propellants. Earlier⁵⁻⁷ the preparation, characterisation and thermal decomposition studies on 15 ring substituted arylammonium salts and six transition metal salts of NTO have been undertaken, out of which the latter proved to be potential burning rate catalysts for HTPB-AP (HTPB - hydroxyl terminated polybutadiene, AP - ammonium perchlorate) propellants.⁸ Rongzu et al.⁹,¹⁰ has also done a lot of work on the salts of NTO. As a programme of research on energetic materials¹¹⁻¹⁴, alkaline earth metal (Mg, Ca, Sr and Ba) salts of NTO have been prepared and characterised. The thermolysis of these salts have also been investigated using thermoanalytical techniques.

Experimental Procedure
Materials—5-Nitro-2,4-dihydro-3H-1,2,4-triazole-3-one (NTO) was prepared in the laboratory by the reported procedure¹⁻¹⁵. Magnesium carbonate, calcium carbonate, strontium carbonate and barium carbonate (Qualigens) were used as received.

Preparation of M(NTO)₂₉₂₀—A weighed amount of NTO was placed in about ten times its mass of double distilled water, which was heated to 60 °C with constant stirring. The equivalent amount of corresponding metal carbonate was then added in instalments to the NTO solution till CO₂ gas evolution stops (Scheme 1). The solution was maintained at the same temperature for 30 min. The unreacted metal carbonate was removed by filtering the hot solution and the clear yellow filtrate was allowed to cool at room temperature. The yellow (orange for Ba) coloured salt hydrates were obtained in good yields. The precipitates were recrystallised from double distilled hot water.

where M = Mg, Ca, Sr or Ba and n = 8, 4, 5 and 3 respectively

Characterisation of M(NTO)₂₉₂₀—All the salts were characterised by UV, gravimetric estimation, TLC and pH measurements. Physical parameters and analytical data are reported in Tables 1 and 2. The purity of all these salts was checked by TLC using a mixture of n-butanol and dioxane [3:3.5] as mobile phase. All the salts were self-locating (yellow spot) and Rf values for each salt are presented in Table 1.

UV spectra—UV spectra of NTO and M(NTO)₂₉₂₀ were taken in 0.005M aqueous solution on UV/Visible spectrophotometer model U-2000 (Hitachi, Japan). The λmax value for cyclic >C=O in all four metal salt was [λmax 341=1.11], higher than the NTO [λmax=324(1.85)].

Gravimetric estimation—The metal contents (%) in all these salt hydrates was estimated gravimetrically.
Table 1—Physical and analytical parameters for NTO and M(NTO)$_2\cdot n$H$_2$O

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Weight</th>
<th>Crystal shape</th>
<th>Colour</th>
<th>Melting point (°C)</th>
<th>Percent metal content</th>
<th>TLC Rf*</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTO</td>
<td>130.00</td>
<td>Crystalline</td>
<td>White</td>
<td>d268</td>
<td>—</td>
<td>0.65</td>
<td>2.96</td>
</tr>
<tr>
<td>Mg(NTO)$_2\cdot$8H$_2$O</td>
<td>426.30</td>
<td>Crystalline</td>
<td>Yellow</td>
<td>d228</td>
<td>5.70</td>
<td>0.55</td>
<td>7.94</td>
</tr>
<tr>
<td>Ca(NTO)$_2\cdot$4H$_2$O</td>
<td>370.08</td>
<td>Amorphous</td>
<td>Yellow</td>
<td>d234</td>
<td>10.82</td>
<td>0.67</td>
<td>7.40</td>
</tr>
<tr>
<td>Sr(NTO)$_2\cdot$5H$_2$O</td>
<td>435.62</td>
<td>Amorphous</td>
<td>Yellow</td>
<td>d236</td>
<td>20.11</td>
<td>0.63</td>
<td>7.56</td>
</tr>
<tr>
<td>Ba(NTO)$_2\cdot$3H$_2$O</td>
<td>449.33</td>
<td>Amorphous</td>
<td>Orange</td>
<td>d226</td>
<td>30.56</td>
<td>0.77</td>
<td>7.75</td>
</tr>
</tbody>
</table>

* mobile phase = n-butanol: dioxane (3 : 3.5)

Table 2—TG and DTA studies (slow thermolysis) of NTO and M(NTO)$_2\cdot n$H$_2$O

<table>
<thead>
<tr>
<th>Compound</th>
<th>std fdt</th>
<th>Temp range</th>
<th>Modes of thermolysis</th>
<th>Mass loss (%)</th>
<th>Endo (°C)</th>
<th>Exo (°C)</th>
<th>OB (m s$^{-1}$)</th>
<th>VOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTO</td>
<td>132 447</td>
<td>50 - 145</td>
<td>(I)</td>
<td>34.0 33.0</td>
<td>118 164</td>
<td>263</td>
<td>-18.18</td>
<td>7965</td>
</tr>
<tr>
<td>Mg(NTO)$_2\cdot$8H$_2$O</td>
<td>50 410</td>
<td>95 - 140</td>
<td>(II)</td>
<td>19.0 19.4</td>
<td>93 175</td>
<td>231</td>
<td>-9.09</td>
<td>8271</td>
</tr>
<tr>
<td>Ca(NTO)$_2\cdot$4H$_2$O</td>
<td>95 400</td>
<td>58 - 125</td>
<td>(II)</td>
<td>20.0 20.0</td>
<td>92 302</td>
<td>-8.33</td>
<td>8297</td>
<td></td>
</tr>
<tr>
<td>Sr(NTO)$_2\cdot$5H$_2$O</td>
<td>58 430</td>
<td>104 - 150</td>
<td>(I)</td>
<td>12.0 12.0</td>
<td>142 232</td>
<td>243, 314</td>
<td>-10.00</td>
<td></td>
</tr>
<tr>
<td>Ba(NTO)$_2\cdot$3H$_2$O</td>
<td>104 398</td>
<td>104 - 150</td>
<td>(II)</td>
<td>57.0 56.0</td>
<td>142 232</td>
<td>243, 314</td>
<td>-10.00</td>
<td></td>
</tr>
</tbody>
</table>

(I) = dehydration  [II] = Metal carbonate formation  [III] = Metal oxide formation

**Slow thermolysis of M(NTO)$_2\cdot n$H$_2$O**

**TG studies**—Dynamic TG studies were undertaken on indigenously fabricated TG apparatus. The sample (10 mg, 100 - 200 mesh) was taken in a platinum crucible and TG data were undertaken in static air at heating rate of 5°C min$^{-1}$. The percent decomposed (α) values are plotted against temperature, °C (Fig. 1) and the std (starting decomposition temperature) and fdt (final decomposition temperature) are reported in Table 2.

**DTA studies**—DTA (Table 2) studies were taken by Rigaku 8150 thermal analysis system at a heating rate of 15°C min$^{-1}$ in static air. The thermograms are presented in Fig 2, and DTA peak temperatures (endo/exo) are given in Table 2.

**Rapid thermolysis of M(NTO)$_2\cdot n$H$_2$O**

**Explosion delay (D$_E$) studies**—Explosion delay studies on M(NTO)$_2\cdot n$H$_2$O were undertaken by tube furnace (TF) technique. The sample (weight =
20 mg, 100–200 mesh) was taken in an ignition tube (4 cm length and 0.4 cm diameter) and the time interval between the insertion of the tube into the TF and the moment of an audible explosion noted with the help of stopwatch, gave the value of $D_E$. The ignition tube loaded with the sample and clamped in a bent wire, was inserted manually into the TF up to a fixed depth (8 cm) just above the probe of temperature indicator cum controller (Decibel DT

Fig. 2—DTA thermograms for $M(\text{NTO})_2 \cdot n\text{H}_2\text{O}$

Fig. 3—Plots of log $D_E$ versus $1/T$ ($^\circ$K) for $M(\text{NTO})_2 \cdot n\text{H}_2\text{O}$

Fig. 4—Plots of (a) $E^*$ versus $ET$, (b) $E^*$ versus first IP and (c) $E^*$ versus ionic radii.
The time taken for insertion of the ignition tube was also kept constant throughout the measurement. The accuracy of TF was ± 1°C. Each reading was repeated three times and mean of the $D_E$ values have been reported in Table 3. The $D_E$ data were found to fit in the following $^{24-26}$ equation [Eq. (1)].

$$D_E = A e^{E^* / RT} \quad \ldots \quad (1)$$

where $E^*$ is the activation energy for explosion and $T$ is the absolute temperature. The plots of $\log D_E$ versus $1/T$ have been given in Fig. 3.

**Results and Discussion**

TG taken in air up to 450 °C show that each sample undergoes appreciable mass loss and nature of thermograms (Fig. 1) are totally different from that of NTO$^6$. Plateau obtained in Fig. 1 clearly suggest that dehydration, formation of corresponding metal carbonates and oxides are involved during thermolysis (Table 2). The decomposition of the salt hydrates appears to proceed through two routes, slow and rapid. It seems that the first step is the dehydration (Scheme II) involving removal of total number of water molecules up to 150°C (Fig. 1 A → B). The dehydrated salts have been found to be stable between 150 - 250°C (Fig. 1 B → C). Mass losses (%) in various temperature ranges under non-isothermal conditions are given in Table 2. The anhydrous salts (I) undergo exothermic decomposition (Step 1a) at 275°C by NTO ring rupture to yield corresponding metal carbonates (II) (Fig. 1, C→D). Then the metal carbonates release a molecule of carbon dioxide (step 1b)

**Scheme II** – Schematic representation of thermolysis of alkaline earth metal salts of NTO

$$\begin{align*}
\text{Hydrated metal salt} & \Rightarrow \text{MNH}_2\text{O}_2\text{N} \quad n\text{H}_2\text{O} \quad -n\text{H}_2\text{O}, \quad 150^\circ\text{C} \\
\text{Anhydrous metal salt} & \Rightarrow \text{MNH}_2\text{O}_2\text{N} \quad 275^\circ\text{C} \\
\text{HCHO + CO}_2 & \Rightarrow \text{MCO}_3 \quad (\text{II}) \\
\text{HCHO + CO}_2 + \text{HCN} & \Rightarrow \text{MO} \quad (\text{III}) \\
\end{align*}$$

where $n = 3 - 8$

![Fig. 5](image-url) - Plots of (a) $ET$ versus $VOD$ and (b) $ET$ versus $OB$
Table 3—Explosion delay (D_E), explosion temperature (ET) and activation energy for explosion (E*) of alkaline earth metal salts of NTO

<table>
<thead>
<tr>
<th>Compound</th>
<th>D_E (s) at various temperatures (°C)</th>
<th>ET(°C) for DE 40 s</th>
<th>E* (kJ mole⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTO#</td>
<td>-</td>
<td>300</td>
<td>401 (for 15 s)</td>
</tr>
<tr>
<td>Mg(NTO)₂.8H₂O</td>
<td>165.3±4</td>
<td>300</td>
<td>477</td>
</tr>
<tr>
<td>Ca(NTO)₂.4H₂O</td>
<td>DNE</td>
<td>325</td>
<td>500</td>
</tr>
<tr>
<td>Sr(NTO)₂.5H₂O</td>
<td>DNE</td>
<td>350</td>
<td>565</td>
</tr>
<tr>
<td>Ba(NTO)₂.3H₂O</td>
<td>107.0±3</td>
<td>375</td>
<td>400</td>
</tr>
</tbody>
</table>

Data taken from Ref 6.

DNE—did not explode

at higher temperature (400°C) to give finally metal oxides (III) (Fig. 1 D→E) and other gaseous and carbonaceous products. The first endothermic peak in case of each metal salts (Fig. 2, Table 2) seems to be due to dehydration and second endotherm due to phase transition (except Sr salt, which does not show phase transition). The exothermic peaks are on account of decomposition for both NTO and its metal salts.

Although M(NTO)₂.nH₂O are stable at room temperature, they explode when subjected to sudden high temperatures. The explosion delay data were taken (Table 3) in the range 300–600°C. Salts of Ca and Sr have been found to explode at 350°C. The higher value of explosion delay (D_E), explosion temperature (ET) and activation energy for explosion (E*) suggest the stable nature of Sr(NTO)₂.5H₂O. However, the value of explosion delay and explosion temperature are lower for Ba(NTO)₂.3H₂O. For Mg, Ca and Sr salts, as the value of E* increases the ET also increases (Fig. 4a). Moreover, E* have also been found to be related with first ionisation potential (IP) and ionic radii (M⁺²) (Fig. 4b and c). However, Sr salts does not show any relationship with either first IP or ionic radii. The rapid thermolysis (Scheme II) involves the formation of NO₂ free radical (IV) from anhydrous salts at 300°C (Step 2a) which seems to react rapidly with the heterocyclic backbone by oxidation—reduction reactions leading to gaseous products of carbon and nitrogen (Step 2b). The formation of NO₂ as free radical has been reported earlier.²³,⁶

The energy released during explosion is obtained mainly from the oxidation of carbon and hydrogen by oxygen and the percentage oxygen excess or deficient will play a major role during thermolysis of these compounds. Thus, oxygen balance (OB) per mole (Table 2) was calculated using Eq. (2)

\[ \text{OB} = \{ \{ \frac{Z-2X-Y}{2} \} \} \cdot n \]  

(2)

where X, Y and Z are the numbers of carbon, hydrogen and oxygen atoms respectively and n is the total number of atoms in the molecule.

Mg(NTO)₂.8H₂O having the highest OB (−6.66) is more sensitive towards explosion. Further, the velocity of detonation (VOD), reported in Table 2, has been calculated by Eq. (3) suggested by Martin and Yallop.²⁷

\[ \text{VOD} = 8578 + 33.74 \times (\text{OB}) \]  

(3)

VOD and OB for salts also showed linear relationship with ET (Figs 5a & b) and E* (Fig. 6). However,
Mg salt (Figs 5a & b) and Sr salt (Figs 6a & b) were found to deviate from linearity. The reason for which is not clear.

It was reported\(^{28,29}\) that explosion products of C-H-N-O explosives are primarily water, nitrogen, carbon dioxide and simple organic molecules like formaldehyde. Cleavage of C-NO\(_2\) bond has also been reported earlier\(^{30}\).

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**References**