Structural characterization and thermal decomposition mechanisms of alkaline earth metal (Mg, Ca, Sr, and Ba) salts of 3-nitro-1,2,4-triazol-5-one

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Abstract

Four alkaline earth metal salts of 3-nitro-1,2,4-triazol-5-one (NTO) have been prepared and characterized by using the presently available methods of infrared spectrometry, ^{13}C NMR, TG–DTG, elemental analysis, conductivity measurement and X-ray powder diffraction. The results obtained confirm that these salts are all hydrates of general formula $M(NTO)_2 \cdot nH_2O$, when M is Mg, Ca, Sr or Ba and n is 8, 4, 5 or 3, respectively. The far-infrared spectra of these salts show that M–N and M–O bonds are formed in the molecules. Under conditions of linear temperature increase, the thermal decomposition mechanisms and kinetic parameters of the salts have been studied. The thermal decomposition processes may be divided into three stages: dehydration, exothermic decomposition of the NTO ring and formation of metal oxide and/or carbonate. According to the values of the activation energy of the main exothermic peak, the thermal resistance of the salts increases in the sequence

$$Mg(NTO)_2 \cdot 8H_2O < Ca(NTO)_2 \cdot 4H_2O < Ba(NTO)_2 \cdot 3H_2O < Sr(NTO)_2 \cdot 5H_2O.$$
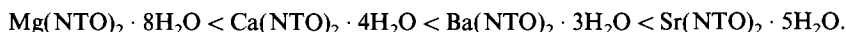
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1. Introduction

3-Nitro-1,2,4-triazol-5-one (NTO), as a newly developed high explosive, has received increasing attention [1–3]. Its amine salts and some metal salts have also been reported [4–6]. Those studies show that some of the salts of NTO have potential utility in the field of ammunition. In continuation of our studies on the metal salts of NTO, we now report the preparation, structural characterization and thermal decomposition mechanisms of some alkaline earth metal salts of NTO.

2. Experimental

2.1. Materials

The NTO used in these preparations was synthesized and recrystallized twice from distilled water. The metal carbonates $MgCO_3$, $CaCO_3$, $SrCO_3$ and $BaCO_3$ were all analytically pure.

2.2. Preparation of alkaline earth metal salts of NTO

A stoichiometric amount of NTO was placed in ten times its mass of distilled water, which was heated to 60°C with stirring. The equivalent amount of metal carbonate was then added in portions to the NTO solution, and carbon dioxide gas was evolved immediately. A little more carbonate was added when no more gas was released and the mixture was maintained at the same temperature for 30 min. The unreacted carbonate was removed by filtering the hot solution, and the clear yellow filtrate was allowed to cool to room temperature. Precipitation occurred except for the calcium salt, the solution of which required complete evaporation. The precipitate was recrystallized from distilled water to give a yellowish product (orange–red for the strontium salt).

2.3. Apparatus and conditions

The apparatus and conditions used in the experiments of elemental analysis, ^{13}C NMR, DSC, TG–DTG, and IR spectrometry were the same as described in our previous work [7], except that the contents of the metal elements were determined by using the TG–DTG technique and the far-IR spectra ($500-100$ cm^{-1}) of the metal salts of NTO were measured by using a nujol mull with a polyethylene film on a Perkin-Elmer 60 SXR FT-IR spectrophotometer (Nicolet Co., USA) at 10 cm^{-1} resolution. The molar conductivities were measured at 25°C at a salt concentration of $\approx 10^{-3}$ mol l^{-1} in twice distilled water by using a DDS-11A electrical conductivity apparatus (Shanghai Rici Instrumental Factory, China). X-ray powder diffraction (XRD) patterns were recorded on a Rikaku D/max-3C X-ray diffractometer using Cu Kα radiation.

Table 1
Analytical results and molar conductivity values of the salts

Salt	Contents/%					$\Lambda_M/S\ cm^2\ mol^{-1}$
		Metal	N	C	H	
Mg(NTO)$_2$ · 8H$_2$O	Calc.	5.70	26.27	11.26	4.25	145.9
	Found	5.46	26.36	10.69	4.24	
Ca(NTO)$_2$ · 4H$_2$O	Calc.	10.83	30.27	12.98	2.72	151.4
	Found	11.11	30.54	12.64	2.63	
Sr(NTO)$_2$ · 5H$_2$O	Calc.	20.11	25.71	11.02	2.78	145.0
	Found	19.87	26.28	11.26	2.78	
Ba(NTO)$_2$ · 3H$_2$O	Calc.	30.55	24.93	10.69	1.79	155.1
	Found	30.27	24.08	10.62	1.78	

3. Results and discussion

3.1. Elemental and conductivity analysis

The elemental analysis results and the molar conductivities of these salts are given in Table 1. The analytical results agree very well with the formulae proposed for these salts. All the formulae show the presence of water molecules. The molar conductivity values show all these salts to be 1:2 type electrolytes in aqueous solution, which confirms that one metal cation is associated with two NTO anions in these salts.

3.2. ^{13}C NMR results

The results of ^{13}C NMR analysis of NTO and its salts are summarized in Table 2. Comparing them, we find that the chemical shifts of the two carbon atoms of the metal salts appear at lower field than that of NTO, and the change of chemical

Table 2
Data of ^{13}C NMR chemical shifts of NTO and its salts

Compound	Chemical shift/ppm	
	>C=O	>C–NO$_2$
NTO	154.70	148.13
Mg(NTO)$_2$ · 8H$_2$O	165.04	159.77
Ca(NTO)$_2$ · 4H$_2$O	165.23	159.97
Sr(NTO)$_2$ · 5H$_2$O	165.04	159.25
Ba(NTO)$_2$ · 3H$_2$O	165.04	159.83

Table 3
Major absorption bands of IR spectra

Compound	$v(C=O)$	$v(C-N)$	$v_{as}(NO_2)$	$v_s(NO_2)$	$v(M-N)$	$v(M-O)$
NTO	1719	1474	1546	1357		
$Mg(NTO)_2 \cdot 8H_2O$	1687	1432, 1386	1546	1309	356	221
$Ca(NTO)_2 \cdot 4H_2O$	1699	1455, 1390	1526	1314	336	225
$Sr(NTO)_2 \cdot 5H_2O$	1654	1429, 1372	1507	1309	377	232
$Ba(NTO)_2 \cdot 3H_2O$	1650	1387, 1372	1504	1305	367	250

shifts for the carbon atoms are nearly the same for each salt, which indicates that when NTO is converted into its salts the influences on the carbon atoms are almost identical. Therefore we might infer that deprotonation has taken place in the position of N-4, which is between the two carbon atoms. The X-ray crystal structure analysis [8,9] confirmed this hypothesis.

3.3. IR spectral studies

The major absorption bands, together with the tentative assignments, in the IR spectra of NTO and its salts are summarized in Table 3. All the spectra show that, when NTO is converted into its alkaline earth metal salts, the absorption bands for the groups $>C=O$ and $-NO_2$, as well as for the bonds of C–N, C=N, C=O and N–H, are all shifted to lower wavenumbers. These results indicate that the negative charge on the NTO ring decreases when NTO coordinates with a metal cation. The far-IR spectrometric results confirm that the metal cations coordinate with nitrogen and oxygen atoms.

3.4. X-ray diffraction patterns

The X-ray powder diffractograms for NTO and its salts are very different, and it is difficult to confirm their crystalline parameters. The 2θ/deg values and relative intensities of three of the most intense peaks are summarized in Table 4. The results indicate that these substances are not the same as each other.

3.5. Thermal decomposition mechanism

The typical DSC curves and typical TG–DTG curves of these salts obtained under conditions of linear temperature increase are shown in Figs. 1 and 2, respectively. All the decomposition processes of these salts may be divided into three major stages: dehydration, exothermic decomposition of the NTO ring and formation of metal oxide and/or carbonate.

Decomposition mechanism of Mg(NTO)₂ · 8H₂O
In the first stage, the DSC curve of $Mg(NTO)_2 \cdot 8H_2O$ shows two endothermic peaks between 75°C and 180°C. The first peak is between 75°C and 125°C and the

Table 4
Data of the major XRD peaks for NTO and its salts

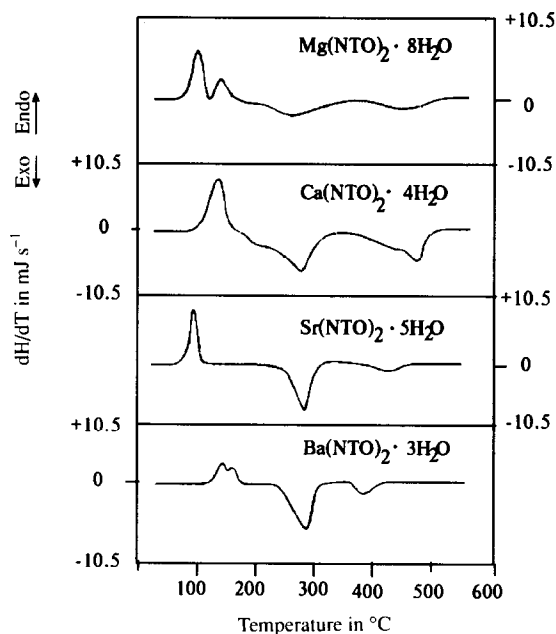| Compound	$2\theta/\mathrm{deg}$	$I \times I_0^{-1}/\%$
NTO	20.76	50
	27.04	100
	31.34	78
$Mg(NTO)_2 \cdot 8H_2O$	16.00	42
	27.52	100
	29.08	29
$Ca(NTO)_2 \cdot 4H_2O$	13.50	100
	26.80	13
	27.24	27
$Sr(NTO)_2 \cdot 5H_2O$	7.76	100
	8.16	56
	21.14	74
$Ba(NTO)_2 \cdot 3H_2O$	19.90	43
	26.24	100
	46.30	25

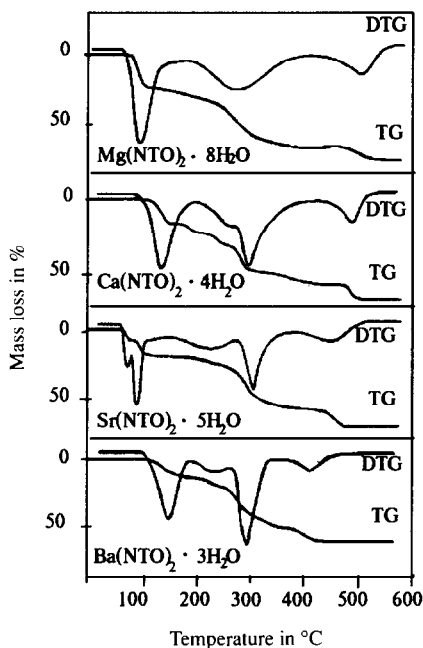Fig. 1. Typical DSC curves at a heating rate of 10°C min^{-1} for alkaline earth metal salts of NTO.

Fig. 2. Typical TG–DTG curves at a heating rate of 10°C min^{-1} for alkaline earth metal salts of NTO.

second is between 125°C and 180°C. Otherwise, the TG–DTG curves show only one mass loss process between 67°C and 186°C and the mass loss is 33.2%. This value almost coincides with the calculated loss of 33.8% which corresponds to the loss of a total of eight water molecules from $Mg(NTO)_2 \cdot 8H_2O$. By observation with a thermomicroscope, it could be confirmed that the second endothermic peak on the DSC curve is caused by a phase transition process. Because the dehydrated salt absorbs moisture very easily from air at room temperature, the IR spectra of the hydrate and anhydrous form of the salt are not very different. If detection is not performed in situ, it is impossible to distinguish between the two states by IR spectroscopy.

The second stage is a gradual exothermic decomposition process of the dehydrated salt $Mg(NTO)_2$, and the exothermic peak appears between 186°C and 395°C. The TG–DTG curves show that there is a pronounced mass loss process corresponding to this temperature range, and the mass loss is 38.8% between 186°C and 378°C. The IR spectrum of the decomposed residue at 380°C shows new absorption bands at 2245 and 1188 cm^{-1}, which may be assigned to the compound $Mg(OCN)_2$, and at 1457 and 852 cm^{-1} which may be assigned to magnesium carbonate. It could be concluded that the NTO ring ruptured, metal cyanate and metal carbonate were formed, and the residue from the decomposition is a mixture.

The third stage is the formation of a stable inorganic compound. The DSC curve shows only one exothermic peak. The IR absorption bands of the residue appear at 3450, 1473 and 429 cm^{-1}, coinciding closely with the standard spectrum [10] of

MgO. The TG–DTG curves indicate that the mass loss corresponding to the temperature range is 19.0% and the residue comprises 9.0%, which coincides very well with the calculated value of 9.4%. Therefore it could be concluded that the final residue from decomposition of $Mg(NTO)_2 \cdot 8H_2O$ is magnesium oxide.

Decomposition mechanism of $Ca(NTO)_2 \cdot 4H_2O$

The first stage in the decomposition of $Ca(NTO)_2 \cdot 4H_2O$ occurs as an endothermic process, and a sharp endothermic peak appears between 109°C and 172°C on the DSC curve. The TG–DTG curves corresponding to the temperature range show a mass loss of 19.7%, which agrees very well with the calculated value of 19.5%. Because the dehydrated salt absorbs moisture very easily from air at room temperature, the IR spectra of the hydrate and the anhydrous state of the salt are not very different. Without detection in situ it is impossible to distinguish the two states by IR spectroscopy.

The second stage is an exothermic decomposition process from 172°C to 356°C. The IR spectrum of the decomposed residue at 360°C shows absorption bands at 2194, 1180 and 649 cm^{-1} which may be assigned to the compound calcium cyanate, and at 1418 and 861 cm^{-1} which may be assigned to calcium carbonate. The absorption bands at 3384, 1636 and 1554 cm^{-1} show that some kind of polyamide exists in the residue. Therefore the residue of decomposition at this temperature is a mixture. The TG–DTG curves indicate that the mass loss between 186°C and 360°C is 36.0%. Because the residue is a mixture, it is difficult to predict the process stoichiometrically.

The third stage is a gradual exothermic process between 396°C and 556°C on the DSC curve, and the IR spectrum of the residue shows absorption bands only at 1432, 874 and 712 cm^{-1}, which coincide well with those in the standard spectrum [11] of $CaCO_3$. It can be concluded that the final residue is calcium carbonate. The TG–DTG curves indicate that the mass loss corresponding to this temperature range is 20.6% and the residual mass is 27.7%, which nearly coincides with the theoretical value of 27.0%. It is concluded that the final residue from decomposition of $Ca(NTO)_2 \cdot 4H_2O$ is calcium carbonate.

Decomposition mechanism of $Sr(NTO)_2 \cdot 5H_2O$

The first stage of the decomposition process of $Sr(NTO)_2 \cdot 5H_2O$ appears as an endothermic peak between 70°C and 153°C on the DSC curve. Otherwise, the TG–DTG curves show two mass loss processes. The first occurs between 64°C and 96°C and the mass loss is 9.0%, which corresponds to the loss of two water molecules from $Sr(NTO)_2 \cdot 5H_2O$ and agrees well with the calculated loss of 8.3%. The second stage occurs between 96°C and 160°C; the mass loss is 10.9%, which corresponds to losing three water molecules from $Sr(NTO)_2 \cdot 5H_2O$ and shows reasonable accord with the calculated value of 12.4%. Therefore it could be inferred that the dehydration processes of $Sr(NTO)_2 \cdot 5H_2O$ might be divided into two steps, the first involving loss of two water molecules and the second corresponding to the loss of the remaining water. Because the dehydrated salt absorbs moisture very easily from air at room temperature, the IR spectra of the hydrate and the

anhydrous form of the salt are not very different. Unless detection takes place in situ, it is impossible to distinguish between the two states by IR spectroscopy.

The second stage of the decomposition process of $Sr(NTO)_2 \cdot 5H_2O$ appears as a relatively sharp peak between 218°C and 350°C on the DSC curve, and the mass loss corresponding to the temperature range is 37.3%, as obtained from TG–DTG analyses. The IR spectrum of the residue at 380°C shows absorption bands at 2184 and 1178 cm^{-1} which may be assigned to the compound $Sr(OCN)_2$, and at 1466 and 866 cm^{-1} which may be assigned to $SrCO_3$. The absorption bands at 3406, 1634 and 1554 cm^{-1} show that some kind of polyamide exists in the residue, and the residue from decompoition is therefore a mixture.

The third stage of decomposition of $Sr(NTO)_2 \cdot 5H_2O$ shows a gradual exothermic peak between 422°C and 506°C. The IR spectrum of the residue shows absorption bands only at 1457, 859 and 701 cm^{-1}, which coincide very well with those in the standard spectrum [12] of $SrCO_3$. The TG–DTG curves indicate that the mass loss corresponding to the temperature range is 11.2% and the residue comprises 33.5%, which agrees well with the theoretical value of 33.9%. It could be concluded that the final decomposition residue of $Sr(NTO)_2 \cdot 5H_2O$ is strontium carbonate.

Decomposition mechanism of $Ba(NTO)_2 \cdot 3H_2O$

The first stage of the decomposition process of $Ba(NTO)_2 \cdot 3H_2O$ appears as two continuous endothermic peaks between 127°C and 176°C on the DSC curve. Otherwise, the TG–DTG curves show only one mass loss process and the mass loss is 12.0% which agrees well with the calculated loss of 11.8%. By observation through a thermomicroscope, it could be confirmed that the second endothermic peak on the DSC curve is caused by a phase transition process. Because the dehydrated salt absorbs moisture very easily from air at room temperature, the IR spectra of the hydrate and the anhydrous form of the salt are not very different. Without detection in situ it is impossible to distinguish between the two states by IR spectroscopy.

The second stage is the decomposition process of anhydrous $Ba(NTO)_2$. The DSC curve show a gradual exothermic peak between 209°C and 336°C, and the TG–DTG curves indicate that the mass loss is 27.0% corresponding to this temperature range. The IR spectrum of the decomposed residue at 340°C shows absorption bands at 2170 and 1174 cm^{-1} which may be assigned to the compound $Ba(OCN)_2$, and at 1446 and 869 cm^{-1} which may be assigned to $BaCO_3$. The absorption bands at 3376, 1625 and 1538 cm^{-1} show that polyamides of some kind exist in the residue. Therefore the residue from decomposition at these temperatures is also a mixture. Because the residue at the end of this stage is a mixture, it is impossible to determine every component quantitatively.

The third stage of the decomposition of $Ba(NTO)_2 \cdot 3H_2O$ shows a slowly developing exothermic peak between 391°C and 460°C on the DSC curve. The IR spectrum of the residue shows absorption bands only at 1426, 858 and 693 cm^{-1}, which coincide well with those in the standard spectrum [13] of $BaCO_3$. The TG–DTG curves indicate that the mass loss corresponding to this temperature range is 11.0% and the residue amounts to 43.5%, which agrees well with the theoretical
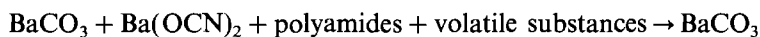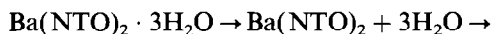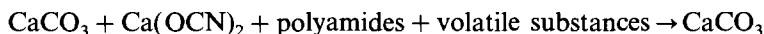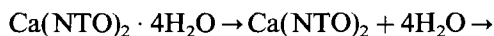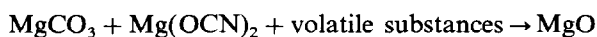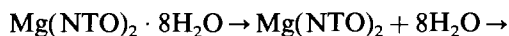
value of 43.9%. It could be concluded that the final residue from the decomposition of $Ba(NTO)_2 \cdot 3H_2O$ is strontium carbonate.

The apparent activation energies for the dehydration processes of these salts calculated by the Kissinger method [14] are 161.3, 263.2, 226.3, and 183.0 kJ mol^{-1} for $Mg(NTO)_2 \cdot 8H_2O$, $Ca(NTO)_2 \cdot 4H_2O$, $Sr(NTO)_2 \cdot 5H_2O$ and $Ba(NTO)_2 \cdot 3H_2O$ respectively. The order of ease of dehydration of these salts can be concluded as being: $Mg(NTO)_2 \cdot 8H_2O > Ba(NTO)_2 \cdot 3H_2O > Sr(NTO)_2 \cdot 5H_2O > Ca(NTO)_2 \cdot 4H_2O$.

The apparent activation energies for the anhydrous salts calculated by the Kissinger method for the main exothermic processes (the second stage) are 136.5, 156.0, 197.4 and 156.7 kJ mol^{-1} for $Mg(NTO)_2$, $Ca(NTO)_2$, $Sr(NTO)_2$ and $Ba(NTO)_2$, respectively. The ease of the exothermic decomposition of these salts might be concluded as following the order: $Mg(NTO)_2 > Ca(NTO)_2 > Ba(NTO)_2 > Sr(NTO)_2$. Thus the most stable anhydrous salt of the four is strontium carbonate.

4. Conclusions

The experimental results confirm that the thermal decomposition mechanisms of these salts can be expressed as

$$Mg(NTO)_2 \cdot 8H_2O \rightarrow Mg(NTO)_2 + 8H_2O \rightarrow$$

$$MgCO_3 + Mg(OCN)_2 + \text{volatile substances} \rightarrow MgO$$

$$Ca(NTO)_2 \cdot 4H_2O \rightarrow Ca(NTO)_2 + 4H_2O \rightarrow$$

$$CaCO_3 + Ca(OCN)_2 + \text{polyamides} + \text{volatile substances} \rightarrow CaCO_3$$

$$Sr(NTO)_2 \cdot 5H_2O \rightarrow Sr(NTO)_2 \cdot 3H_2O + 2H_2O \rightarrow Sr(NTO)_2 + 3H_2O \rightarrow$$

$$SrCO_3 + Sr(OCN)_2 + \text{polyamides} + \text{volatile substances} \rightarrow SrCO_3$$

$$Ba(NTO)_2 \cdot 3H_2O \rightarrow Ba(NTO)_2 + 3H_2O \rightarrow$$

$$BaCO_3 + Ba(OCN)_2 + \text{polyamides} + \text{volatile substances} \rightarrow BaCO_3$$

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