

Studies on energetic compounds

25. An overview of preparation, thermolysis and applications of the salts of 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO)

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Abstract

The research work reported on the preparation, characterisation and applications of more than 50 salts of NTO has been reviewed thoroughly. A broad classification and sub classification of all these compounds has been given on the basis of nature of the compounds with which NTO forms salts. Attempt has been made to discuss the structure of these salts by summarising analytical data reported from ^{13}C NMR. The structure as determined by IR spectroscopy as well as XRD has also been discussed briefly. A generalised mechanism for the thermolysis of the metal salts has also been given and any deviation from this has been narrated in particular cases. The kinetic details, thermodynamical and thermochemical data as well as performance parameters have also been reviewed. Thus, the futuristic potentials of these salts are analysed critically and further studies have been suggested. © 2002 Published by Elsevier Science B.V.

Keywords: NTO; Thermal behaviour; Critical temperature (T_c); Performance parameters; Futuristic potentials

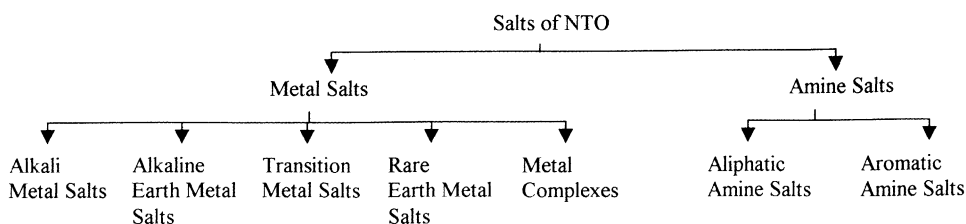
1. Introduction

Chemically and thermally stable explosive compounds are needed for military applications. The research in the field of high energetic materials, nowadays is directed towards the synthesis of simple molecules with high energy, high density, high heat resistance and low sensitivity. NTO is just, such an energetic compound with performance properties comparable to that of RDX, while its sensitivity is close to that of 1,3,5-triamino-2,4,6-trinitro benzene (TATB). NTO was first reported in the year 1905 [1] from nitration of 1,2,4-triazol-3-one

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(TO) (the authors have incorrectly attributed NTO to be its hydroxy tautomer). There was renewed interest in NTO in the mid-late 1960s [2–5], but none of these studies appear to be directed to explosives. However, it was Lee et al. [6], who had first published the study of NTO as an explosive. And subsequently the compound attracted the attention of many researchers worldwide and research on various aspects of NTO has been appeared in a large number of papers in different journals. We have recently reviewed [7,8] the various facets of work done on NTO.

Owing to the acidic nature of NTO (pK_a 3.67) [6], it forms salts with a large number of metals as well as aromatic and aliphatic amines. The salts of NTO reported in literature can be broadly classified into metal salts and amine salts, on the basis of nature of the compounds with which they are formed. They can also be sub-classified as follows: A compilation of all



the salts which we have encountered in literature is given in Table 1. Since these salts are also insensitive and high energetic in nature, these have also been a subject of research interest. A number of papers on preparation, characterisation, thermal and explosive behaviour of the NTO salts have been published. But the data in this field is highly scattered and the research on the application seems to be directionless. Additionally there are contradictory reports in literature about the ionisation of NTO, i.e. the proton leaves from which nitrogen, and whether there is partial (NTO^+) or complete (NTO^{2+}) ionisation possible etc. Hence it is thought appropriate to review the research reports on salts of NTO. Efforts were made to compile some of the important analytical parameters reported in literature of representative salts. We feel that this effort would make this review a single source of reference for a wide range of NTO salts.


2. Preparation of salts of NTO

Preparation of salts of NTO is very easy in most cases, since it only involves simple acid–base reaction. Manchot and Noll [1] who were first to prepare NTO in the year 1905, also prepared a potassium ($\text{KNTO}\cdot\text{H}_2\text{O}$) and a mercuric [$\text{Hg}(\text{NTO})_2$] salt. Both of the salts were characterised only by elemental analysis. They have also mentioned about the preparation of lithium, barium, sodium and silver salts. Thus the preparation of salts had been reported as long back as the preparation of NTO. However their potential as high energetic materials has been revealed recently only.

A group of scientists [9–13] from the Peoples Republic of China reported the preparation and characterisation of a number of metal salts given in Table 1. The method of preparation of different categories of NTO salts are discussed briefly.

Table 1
A compilation of salts of NTO reported in literature

Metal salts					Amine salts	
Alkali	Alkaline earth	Transition	Rare earth	Complexes	Aliphatic amine	Aromatic amine
Li(NTO)·2H ₂ O	Mg(NTO) ₂ ·8H ₂ O	Mn(NTO) ₂ ·8H ₂ O	Ce(NTO) ₃ ·7H ₂ O	[Sr(NTO) ₂ (H ₂ O) ₄]·2H ₂ O	NH ₄ NTO	RSANTO ^a
Na(NTO)·H ₂ O	Ca(NTO) ₂ ·4H ₂ O	Fe(NTO) ₂	Pr(NTO) ₃ ·7H ₂ O	[Yb(NTO) ₃ (H ₂ O) ₄]·6H ₂ O	H ₂ NCH ₂ CH ₂ NH ₂ (NTO) ₂	
K(NTO)·H ₂ O	Sr(NTO) ₂ ·5H ₂ O Ba(NTO) ₂ ·3H ₂ O	Fe(NTO) ₃ ·2H ₂ O	Nd(NTO) ₃ ·8H ₂ O	[Cd(NTO) ₄ ·Cd(H ₂ O) ₆]·4H ₂ O	H ₂ NNH ₂ (NTO) ₂	
		Co(NTO) ₂ ·8H ₂ O	Nd(NTO) ₃ ·7H ₂ O	[Co(H ₂ O) ₆ (NTO) ₂]·2H ₂ O	(NH ₂) ₂ -C=NH(NTO)	
	Ni(NTO) ₂	Sm(NTO) ₃ ·7H ₂ O	[Dy(NTO) ₂ (H ₂ O) ₆]·NTO·4H ₂ O	H ₂ NCNHNH ₂ (NTO)		
	Cu(NTO) ₂	Eu(NTO) ₃ ·7H ₂ O	H[Pr(NTO) ₄ (H ₂ O) ₄]·2H ₂ O			
	Cu(NTO) ₂ ·2H ₂ O	Gd(NTO) ₃ ·7H ₂ O	[Y(NTO) ₂ NO ₃ (H ₂ O) ₅]·2H ₂ O			
	Cu(NTO) ₂ ·4H ₂ O	Tb(NTO) ₃ ·5H ₂ O				
	Zn(NTO) ₂	Dy(NTO) ₃ ·5H ₂ O				
	Ag(NTO)·1H ₂ O	Yb(NTO) ₃ ·6H ₂ O				
	Cd(NTO) ₂ ·2H ₂ O	Y(NTO) ₃ ·6H ₂ O				
	Hg(NTO) ₂ ·2H ₂ O	La(NTO) ₃ ·7H ₂ O				
	Pb(NTO) ₂					
	Pb(NTO) ₂ ·H ₂ O					
	Cr(NTO) ₃ ·8H ₂ O					

^a RSANTO:  NH₃⁺ NTO⁻, where R = H, 2-CH₃, 3-CH₃, 4-CH₃, 2-Cl, 3-Cl, 4-COOH, 2-NO₂, 3-NO₂, 4-NO₂, 2-OCH₃, 3-OCH₃, 4-OCH₃, 2-OC₂H₅ or 4-OC₂H₅.

2.1. Alkali metal salts

The alkali metal (Li, Na, K) salts were prepared [14,15] by mixing the hot aqueous solution of NTO with the aqueous solution of corresponding metal hydroxides, and thus salt hydrates were obtained.

2.2. Alkaline earth metal salts

The alkaline earth metal salt hydrates of NTO have been prepared [16] by the addition of corresponding metal carbonate to the hot aqueous solution of NTO with the evolution of CO₂.

2.3. Transition metal salts

Transition metal salts of NTO (Table 1) have been reported to be prepared [9,17] by the double decomposition of NaNTO/KNTO/LiNTO/NH₄NTO with a suitable salt of the corresponding transition metal in hot aqueous solutions.

2.4. Rare earth metal salts

Some of the rare earth metal salts of NTO (Table 1) have been prepared [18] by treating the corresponding metal hydroxide with hot aqueous solutions of NTO. The preparation by the treatment of aqueous solution of LiNTO with aqueous solutions of corresponding metal nitrates have also been reported [19].

2.5. Metal complexes

[Dy(NTO)₂(H₂O)₆].NTO.4H₂O was prepared [20] by treating the hot aqueous solution of LiNTO and dilute nitric acid solution of dysprosium oxide. [Yb(NTO₃(H₂O)₄].6H₂O and [Sr(NTO)₂(H₂O)₄].2H₂O were prepared [21] by treating hot aqueous solution of NTO with a solution of Yb-oxide/Sr-carbonate. [Cd(NTO)₄.4Cd(H₂O)].4H₂O has been prepared [22] by mixing aqueous solution of NTO and cadmium carbonate in excess. Crystals of [Co(H₂O)₆](NTO)₂.2H₂O were grown [23] from aqueous solution containing Co(NO₃)₂, NTO and LiOH. The metal complex of Pr, H[Pr(NTO)₄(H₂O)₄].2H₂O was prepared [24] by mixing the aqueous solution of LiNTO and the dilute nitric acid solution of Pr₆O₁₁, whereas [Y(NTO)₂NO₃(H₂O)₅].2H₂O [25] was made from the mixture of aqueous solution of LiNTO and dilute nitric acid solution of yttrium oxide.

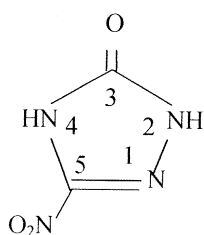
2.6. Aliphatic and aromatic amine salts

The amine salts of NTO have got a pretty long history as Chipen et al. [3] reported the preparation of some amine salts along with the preparation of NTO and its metal salts. But detailed study of preparation, characterisation and application started with the joint efforts of US department of the army and the US department of energy. The preparation of the amine salts of NTO were accomplished by mixing the hot aqueous solution of NTO with

the solution of corresponding base. Lee and co-workers [26,27] have prepared seven amino salts of NTO (hydrazine (HNTO), ammonia (ANTO), ethylenediamine (ENTO), guanidine (GuNTO), aminoguanidine (AGuNTO), diaminoguanidine (DAGuNTO), triaminoguanidine (TAGuNTO)), and characterised them using ^{13}C NMR spectroscopy. Singh et al. [28] have also prepared fifteen ring substituted arylammonium salts of NTO.

3. Characterisation and structure of the salts of NTO

Almost all of the reported salts of NTO have been well characterised by ^{13}C NMR, IR, microanalysis and XRD [14–28]. Thermal behaviour and energetic parameters have also been assessed in most cases. Earlier workers have not studied the structural properties in detail and the molecular formulae have been identified simply from elemental analysis. The structure of NTO is reported [6–8] to be as given below: There are two ionisable hydrogen



sites in NTO molecule at positions N(2) and N(4). Redman and Spear [14] argued that both the positions are easily ionisable and thus NTO form salts of the type $M^{n+}[\text{NTO-H}]^-$ or $M^{n+}[\text{NTO-2H}]_{n/2}^{2-}$ (e.g. $\text{Hg}(\text{NTO-H})_2$, $\text{Hg}(\text{NTO-2H})$). Both acidic and normal salts of NTO have been reported with the same metal. But their observations have been contradicted later on, by the Chinese research workers [16] who have done some commendable job in bringing out the real structure of NTO salts using spectral and XRD studies.

3.1. ^{13}C NMR studies on salts of NTO

^{13}C NMR is a powerful tool to characterise NTO as well as its salts. The values of chemical shift (δ , ppm) from ^{13}C NMR of NTO and its salts has been summarised in Table 2. ^{13}C NMR was used [29] to determine the site from which the proton leaves when NTO is converted into some of its salts. The spectrum of NTO gives two values for chemical shifts, approximately at 148 and 154 ppm, respectively, which are reported [6] to be corresponding $>\text{C}-\text{NO}_2$ and $>\text{C}=\text{O}$. Comparing the ^{13}C NMR spectrum of NTO with some of its salts, it has been observed [29] that the chemical shifts of both the carbon atoms in the NTO salts are to the downfield and that the amount of shifting is almost the same. This indicates that the attraction is equal to both the carbon atoms and for this the proton might leave from position N(4) which is in between the two carbon atoms. However our compilation in Table 2, shows that this observation could be extended to almost all other salts of NTO with very few exceptions (rare earth metal salts). It is also notable that some metal salts of NTO like CuNTO does not show any peak in ^{13}C NMR spectrum due to paramagnetism [29].

Table 2
 ^{13}C NMR data of NTO and its salts

Sl. No.	Compound	Solvent	Chemical shift, δ (ppm)		Reference
			>C–NO ₂	>C=O	
1	NTO	DMSO- <i>d</i> ₆	148.00	154.40	[6]
		CDCl ₃	148.13	154.70	[29]
2	ANTO	DMSO- <i>d</i> ₆	159.40	164.60	[27]
3	ENTO	DMSO- <i>d</i> ₆	158.10	164.40	[27]
4	HNTO	DMSO- <i>d</i> ₆	159.40	164.86	[27]
5	GuNTO	DMSO- <i>d</i> ₆	159.12	164.86	[27]
6	AGuNTO	DMSO- <i>d</i> ₆	159.33	164.86	[27]
9	DAGuNTO	DMSO- <i>d</i> ₆	159.30	164.96	[27]
10	TAGuNTO	DMSO- <i>d</i> ₆	160.00	165.00	[27]
11	KNTO·H ₂ O	CDCl ₃	159.97	165.17	[29]
12	Mg(NTO) ₂ ·8H ₂ O	DMSO- <i>d</i> ₆	159.77	165.04	[16]
13	Ca(NTO) ₂ ·4H ₂ O	DMSO- <i>d</i> ₆	159.97	165.23	[16]
14	Sr(NTO) ₂ ·5H ₂ O	DMSO- <i>d</i> ₆	159.25	165.04	[16]
15	Ba(NTO) ₂ ·3H ₂ O	DMSO- <i>d</i> ₆	159.83	165.04	[16]
16	PbNTO	DMSO- <i>d</i> ₆	159.19	164.52	[29]
17	Pr(NTO) ₃ ·9H ₂ O	DMSO- <i>d</i> ₆	146.51	172.74	[18]
18	Nd(NTO) ₃ ·9H ₂ O	DMSO- <i>d</i> ₆	145.46	166.36	[18]
19	Sm(NTO) ₃ ·8H ₂ O	DMSO- <i>d</i> ₆	150.73	156.00	[18]

3.2. X-ray diffraction studies on salts of NTO

Single crystals were grown and structure has been determined using XRD in many cases. The crystal structures of ENTO [30] and DAGuNTO [31] were resolved by X-ray crystallography. Crystals of ANTO [32] were grown by slow evaporation from aqueous solution and the structure is orthorhombic with space group P_{222} . The geometrical structure of ANTO has also been investigated using semi-empirical AM1 MO calculations [33], which revealed that there are four distinguished H-bondings in the ANTO molecular or ionic system. This structural determination has also indicated that the N(4) proton is more acidic than the one at N(2) and thus deprotonation is easier from N(4), and this result is in agreement with the results reported by Ritchie [34]. The deprotonation of N(4) is also confirmed by X-ray analysis of some crystalline metal salts [11,35–38]. The crystal structures of all the metal complexes [20–23,25] given in Table 1 is monoclinic except that of $\text{H}[\text{Pr}(\text{NTO})_4(\text{H}_2\text{O})_4]2\text{H}_2\text{O}$ [24], which is triclinic.

3.3. IR spectral studies on salts of NTO

In the case of alkaline earth metal salts of NTO, IR spectra shows that, when NTO is converted into its salts, the absorption frequencies for >C=O and –NO₂ groups as well as for the frequencies of C–N, C=N, C=O and N–H are all shifted to lower wave numbers. These results indicates that the negative charge on the NTO ring decreases when NTO co-ordinates with a metal cation. The far IR spectrometric results confirm that the metal cation co-ordinates with both nitrogen and oxygen atoms [16].

Table 3
Data from thermal analysis and kinetic parameters for NTO and its salts^a

Sl. No.	Compound	Peak temperature (°C)		<i>E</i> (kJ mol ⁻¹)		log <i>A</i>		Reference
		Endothermic	Exothermic	<i>E</i> _I	<i>E</i> _{II}	I	II	
1	NTO		275	520.30		48.10		[29]
2	KNTO·H ₂ O		230, 257	192.40	118.00	17.10	8.70	[29]
3	Mg(NTO) ₂ ·8H ₂ O	118, 164	263					[42]
4	Ca(NTO) ₂ ·4H ₂ O	93, 175	231					[42]
5	Sr(NTO) ₂ ·5H ₂ O	92	302					[42]
6	Ba(NTO) ₂ ·3H ₂ O	142, 232	243, 314					[42]
7	Mn(NTO) ₂	80, 127	186, 251					[17]
8	Fe(NTO) ₂	91	367					[17]
9	Fe(NTO) ₃ ·2H ₂ O	60	175	115.70	76.77	3.94	2.19	[43]
10	Co(NTO) ₂		280					[43]
11	Ni(NTO) ₂		312					[17]
12	Cu(NTO) ₂		355					[17]
13	Cu(NTO) ₂ ·4H ₂ O		285, 353	115.50	87.10	8.12	6.98	[29]
14	Zn(NTO) ₂		346					[17]
15	Ag(NTO)·H ₂ O	130	150, 238, 280	200.60	51.06	6.35	1.11	[43]
16	Cd(NTO) ₂ ·2H ₂ O	50	257	66.30	41.81	1.91	0.65	[43]
17	Hg(NTO) ₂ ·2H ₂ O	55, 116	198	129.20	36.67	4.55	0.77	[43]
18	Cr(NTO) ₃ ·8H ₂ O	68	246	119.00	26.73	4.25	2.19	[43]
19	Pr(NTO) ₃ ·9H ₂ O		263	153.90		13.10		[18]
20	Nd(NTO) ₃ ·7H ₂ O		255	130.50		10.90		[18]
21	Sm(NTO) ₃ ·8H ₂ O		259	148.80		12.70		[18]

^a *E*_I and *E*_{II} correspond to the two exothermic decomposition processes in [29]; *E*_I correspond to endothermic dehydration and *E*_{II} correspond to exothermic decomposition process in [43]. The peak temperature values in [42,43] are from DTA and all other peak values are from DSC. The DSC as well as DTA experiment were carried out in static air atmosphere and heating rate was 10 °C min⁻¹ except in [42] where it was 15 °C min⁻¹.

4. Thermal behaviour of NTO salts

Thermal behaviour is perhaps one of the most studied aspects of the salts of NTO, yet it seems to be insufficient in detail as compared to that of pure NTO. One Ph.D. thesis [39] has been known to be produced on this aspect of NTO salts. The thermolysis of salts of NTO have usually been undertaken using TG, TG–DTG, DSC/DTA, etc. and the mechanistic pathways have been suggested by following the reaction by analysing the intermediate products and residues by using IR and/or XRD. Data from the thermal analysis of some of the metal salts has been summarised in Table 3. In the case of hydrated metal salts, the general mechanism of thermolysis may be represented as shown in Scheme 1, where M is metal. For alkali and alkaline earth metal salts the corresponding metal carbonate is the final product of thermolysis.



Scheme 1.

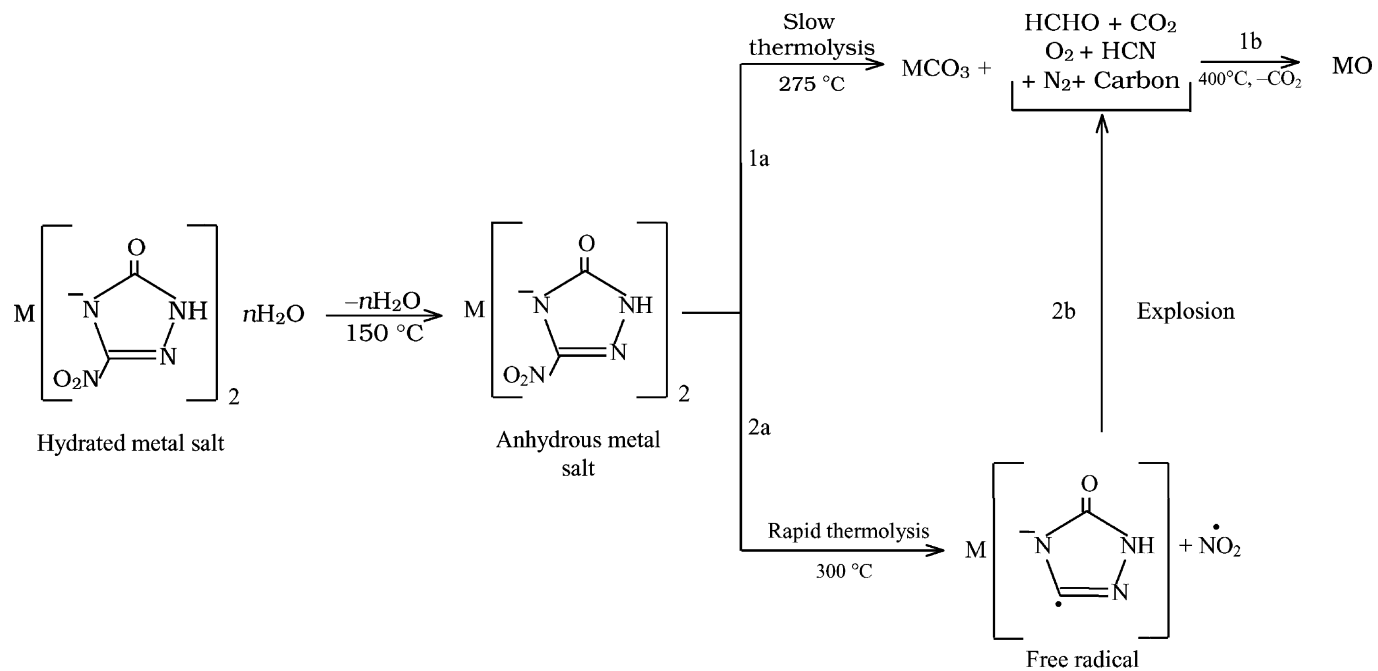
The dehydration may take place in a single step or multi-steps. In the case of alkali metal salts [15] of NTO, the LiNTO directly gives lithium carbonate as the final product of thermolysis, whereas sodium and potassium salts do so via the intermediate formation of corresponding metal cyanate and cyanide, respectively. However, Brill et al. [40] have carried out flash pyrolysis study using T-jump/FTIR spectroscopy and concluded that the intermediate product formed during the pyrolysis of all the alkali metal salts of NTO is metal isocyanate (MNCO) rather than metal cyanate (MCNO).

Among the alkaline earth metal salts MgNTO gives MgO as the end product of thermolysis, whereas all the other three salts namely Ca, Sr and Ba forms the corresponding metal carbonates. All the four salts after dehydration undergoes NTO ring cleavage to form a mixture of the corresponding metal carbonate, polyamides and volatile substances [16]. However, the above said conclusions were drawn from TG and DSC studies in different atmospheres (i.e. TG was run under N₂ atmosphere whereas DSC under static air atmosphere) yet the data from both techniques is corroborative. Singh et al. [41] undertook thermal studies on the above said alkaline earth metal salts using TG and DTA (both under static air atmosphere) and found that the final product in all cases is metal oxide. They have conducted explosion delay studies (rapid thermolysis) also on these compounds and suggested the mechanism for thermolysis as given in Scheme 2.

The thermolysis of transition metal salts of NTO has been studied [17,29,43] in detail and the general mechanism of thermolysis is almost same as shown in Scheme 1. In the case of salts which do not contain water of crystallisation, the first endothermic dehydration process is absent, and thus they undergo denitrification along with NTO ring cleavage and finally metal oxide is formed. The silver salt ultimately gives metallic silver [28] due to the instability of its metal oxide.

The Cu and Pb salts of NTO are reported [29] to be having two stage exothermic decomposition process. In the first stage, denitrification takes place along with NTO ring cleavage and thus a mixture containing corresponding metal carbonate is formed. The residue on further heating gives metal oxide which is indicated by a second exothermic peak in DSC. Flash pyrolysis studies [40] were also conducted on Cu and Pb salts of NTO. It shows that the lead salt liberates one or more volatile metal complexes, which may include one or more Pb(NCO)₂ isomers and lead cyanide. The presence of co-ordinated water in the gaseous metal salts and polynuclear species also being suspected. But the Cu salt exploded violently and showed the presence of only a small amount of volatile isocyanate like complexes. The primary metal containing species were solid copper oxides. The thermal decomposition of rare earth metal salts [9,18] as well as the metal complexes [20–25] also takes place according to the Scheme 1.

The ethylene diamine salts of NTO has only one exothermic peak in DSC, which is similar to that of NTO, but the peak temperature is lower than that of NTO [29]. However, ANTO has a unique mechanism of thermolysis and is autocatalytic in nature [29]. In a flowing air atmosphere, dehydration is the first process for ANTO followed by deamination and thus NTO is formed. And in the third stage, the residue formed after deamination, goes on decomposing as does NTO. Under a static air atmosphere, the gaseous NH₃ formed by the decomposition of ANTO, catalyses the decomposition of NTO. In the case of RSANTOates [44] thermolysis of some of the salts in static air atmosphere take place in a single exothermic step. But in rest of the salts, the thermal decomposition proceeds via proton transfer (N–H



Scheme 2. Schematic representation of thermolysis of alkaline earth metal salts of NTO, where $n = 3-8$.

5. Kinetics of thermolysis of NTO salts

Kinetics of thermolysis is also usually presented along with mechanistic aspects for many salts of NTO and the values of activation energy (E) and pre-exponential factor ($\log A$) are summarised in Table 3. However, these data are inadequate in the sense that an isothermal kinetic analysis is seldom reported. The kinetic parameters reported are usually evaluated by using non-isothermal methods of Ozawa [45], Kissinger [46], Coats and Redfern [47], etc. The values of apparent activation energy (E) for the thermolysis of NTO, determined by the same method differ considerably (365.8 [29], 520.3 kJ mol⁻¹ [48]). However, the values of E for the salts are more consistent. A direct comparison of thermal stability of the entire range of NTO salts on the basis of values of E summarised in Table 3 is not possible. This is because the kinetic parameters may suffer from the complexities imposed by the conditions under which the values were obtained. However, a legitimate comparison is possible as far as the conditions are same. Thus on the basis of E , the thermal stability of NTO and its salts follows the order NTO \gg PbNTO $>$ ENT0 $>$ KNTO $>$ CuNTO [29] and NTO $>$ FeNTO $>$ AgNTO $>$ CdNTO $>$ HgNTO $>$ CrNTO [43]. Thus it can be seen that the thermal stability of NTO is lowered when it gets converted into its salts. This may be due to the catalytic effect of the metals on the thermolysis of NTO, in their corresponding metal salts.

6. Thermodynamical, thermochemical and performance parameters of salts of NTO

Thermodynamical and thermochemical parameters such as heat of formation (ΔH_f), lattice energy, lattice enthalpy, etc. are of great importance for any energetic compound. Performance parameters such as impetus, flame temperature, sensitivity to impact, friction, spark, etc. and critical temperature for thermal explosion (T_c) are also important from the application point of view. The details of these parameters for the salts of NTO are briefly discussed below.

6.1. Thermodynamical and thermochemical properties

The standard enthalpies of formation of silver, ammonium, sodium and potassium salts of NTO has been determined by Finch et al. [49,50]. Later on the Chinese scientists [51,52] have determined standard enthalpies of formation ($-\Delta_f H_m^\theta$) of KNTO·H₂O, Ba(NTO)₂·3H₂O, LiNTO·2H₂O, Ca(NTO)₂·4H₂O and Gd(NTO)₃·7H₂O from the measurements of enthalpy of solution in water using a Calvet micro-calorimeter. From measurements of enthalpy of precipitation of KNTO·H₂O crystal with Pb(NO₃)_{2(aq)}, CuSO_{4(aq)} and Zn(NO₃)_{2(aq)}, the standard enthalpy of formation of Pb(NTO)₂·H₂O, Cu(NTO)₂·2H₂O and Zn(NTO)₂·H₂O were also determined and the values are summarised in Table 4. The standard enthalpy of formation of fourteen other metal salt hydrates are also reported [53] to be calculated from their respective enthalpies of dissolution in water and the data is given in Table 4. With the help of all above mentioned data, literature data and Kapustinskii's equation [52], the lattice energies (ΔU_1^θ) and lattice enthalpies (ΔH_1^θ) of 20 metal salts of NTO were

Table 4

The standard enthalpy of formation, lattice enthalpy, lattice energy and standard enthalpy of dehydration for metal salts of NTO

Compound	$-\Delta_f H_m^\theta$ (kJ mol ⁻¹)	$-\Delta H_1^\theta$ (kJ mol ⁻¹)	$-\Delta U_1^\theta$ (kJ mol ⁻¹)	ΔH_d^θ (kJ mol ⁻¹)
Li(NTO)·2H ₂ O	966.6 ± 2.2	788.13	778.21	6.21
Na(NTO)·H ₂ O	650.6 ± 2.4	643.36	635.92	2.17
K(NTO)·H ₂ O	676.9 ± 2.6	574.98	567.54	5.97
Mg(NTO) ₂ ·8H ₂ O	3002.6 ± 4.5	2667.74	2640.46	269.86
Ca(NTO) ₂ ·4H ₂ O	1905.5 ± 4.4	2115.32	2097.96	70.48
Mn(NTO) ₂ ·8H ₂ O	2759.7 ± 4.7	2595.54	2568.26	279.66
Co(NTO) ₂ ·8H ₂ O	2594.7 ± 4.5	2752.94	2725.66	211.06
Cu(NTO) ₂ ·2H ₂ O	712.1 ± 5.4	2533.66	2521.26	438.84
Zn(NTO) ₂ ·2H ₂ O	628.8 ± 5.7	2420.88	2410.96	381.07
Y(NTO) ₃ ·6H ₂ O	2755.2 ± 6.7	4395.08	4370.28	340.32
La(NTO) ₃ ·7H ₂ O	3031.8 ± 6.6	4120.36	4093.08	145.59
Ce(NTO) ₃ ·7H ₂ O	3020.9 ± 6.5	4168.86	4141.58	169.09
Pr(NTO) ₃ ·7H ₂ O	3025.6 ± 6.7	4211.66	4184.38	192.89
Nd(NTO) ₃ ·8H ₂ O	3304.9 ± 6.7	4288.44	4258.68	208.66
Sm(NTO) ₃ ·7H ₂ O	3025.0 ± 6.5	4304.36	4277.08	238.59
Eu(NTO) ₃ ·7H ₂ O	2936.8 ± 6.6	4352.06	4324.78	271.99
Gd(NTO) ₃ ·7H ₂ O	3020.1 ± 6.4	4370.06	4342.78	278.99
Tb(NTO) ₃ ·5H ₂ O	2437.0 ± 6.5	4302.00	4289.68	283.95
Dy(NTO) ₃ ·5H ₂ O	2452.2 ± 6.5	4326.80	4314.48	293.75
Yb(NTO) ₃ ·6H ₂ O	2708.6 ± 6.6	4516.38	4491.58	389.62

determined. The lattice energies, lattice enthalpies and standard enthalpies of dehydration (ΔH_d^θ) were also estimated for the above twenty metal salts and are given Table 4. The above said thermodynamical as well as thermochemical parameters are reported [20–25] for the metal complexes of NTO also.

The ΔH_f of ENTO, ANTO, HNTO, GuNTO, AGuNTO, DAGuNTO and TAGuNTO are calculated from the values of heat of combustion measured using a parr bomb calorimeter. Based on the measured ΔH_f , values for impetus and flame temperature of these salts as monopropellants were also calculated [27]. A more positive value for ΔH_f was obtained as the nitrogen content of the guanidium homolog salt increases.

6.2. Explosive properties of salts of NTO

Extensive measurements of explosion delay on NTO as well as the metal salts [17,42,43] and RSANTOates [44] have been reported. The activation energy for thermal explosion has also been determined and it shows that the metal salts are thermally less stable than NTO, whereas the RSANTOates showed almost similar thermal stability as that of NTO.

Redman and Spear [14] after their studies on salts of NTO using ‘ball and disc’ method, concluded that the response of the materials is typical of sensitive high explosives. However, Singh [54] has assessed the impact as well as friction sensitivity of 10 transition metal salts of NTO and found that all these salts may be classified as insensitive high explosives. The spark sensitivity has also been measured and were found to be insensitive up to 5 J of electrical energy. The small scale sensitivity studies on the amine salts [27] of NTO show

Table 5

Experimental and theoretical values of critical temperature of thermal explosion (T_c) for NTO and its salts^a

Method	NTO	ENTO	KNT0	PbNTO	CuNTO	HMX	RDX	PETN	Tetryl
T_c (K)	513.0	497.0	491.0	472.0	463.0	529.0	488.0	478.0	473.0
$T_{c(F-K)}$ (K)	520.8	488.8	495.2	454.0	475.2	–	–	–	–
$T_{c(Z-M-R)}$ (K)	529.6	517.5	495.6	479.6	–	–	–	–	–
$T_{c(DSC)}$ (K)	528.2	493.3	488.3	464.3	445.3	–	–	–	–

^a $T_{c(F-K)}$, $T_{c(Z-M-R)}$ and $T_{c(DSC)}$ are the values of T_c obtained by Frank-Kamenetskii's method, Zinn and co-workers method and non-isothermal DSC method, respectively.

that the compounds are significantly less sensitive to impact and spark than the common propellant ingredients, such as RDX, triamino guanidium nitrate (TAGuN), etc.

The value of T_c for NTO has been reported by Lee et al. [6]. Later on T_c for NTO and its salts (ANTO, ENTO, CuNTO and PbNTO) has been determined by the Chinese scientists [48] using four different methods and the values are summarised in Table 5. The T_c values were experimentally obtained and the values obtained are compared with that obtained from three other theoretical methods (Frank-Kamenetski method [55], Zinn and co-workers method [56,57] and a calculation formula under non-isothermal DSC condition [58]). The values of T_c obtained using all the four methods are found to be within the limit of experimental error. The thermal stability of NTO as well as its salts have been compared with that of RDX, HMX, tetryl and PETN on the basis of values of T_c and the order is as follows:



7. Applications and futuristic studies on salts of NTO

Safety aspects of high energy materials are one of the major concerns of research activities in this field. The military services worldwide are also adopting policies to make their munitions insensitive (invulnerable) to accidental hazardous stimuli. Thus, compounds with high energy combined with less sensitivity are sought for. Fortunately, NTO is such a compound with performance properties comparable to that of RDX and insensitivity comparable to that of TATB. NTO is now widely used in explosive formulations, plastic bonded explosives (PBX), gas generator for automobile inflatable air bags systems, etc. The salt derivatives of NTO are also insensitive than popular explosives like RDX, PETN, TAGuN, etc. and thus are attractive. Since NTO is acidic and thus the ease of formation of salts offer the chance of making a large variety of compounds which can be tailored for a wide spectrum of applications. However, although the preparation and properties of a large number of NTO salts are available in open literature, the reports on the applications of these materials are either hidden in classified reports or meagerly available.

Initially ANTO and ethyleneaminoguanidine salts were considered for explosives. However these studies [59] concluded that neither these salts nor those from similar non-energetic amines are likely to show any properties of primary explosives and the potential use of such

materials is in low melting eutectic explosives with ammonium nitrate (AN) [60]. ANTO has also been considered [61,62] as one of the ingredients of composite explosives and found to be having more advantages than AN and ammonium perchlorate (AP). Redman and Spear [14] wanted to use their prepared metal salts as primary explosives, but their screening showed that they have no application as primary explosives.

Later, studies on the NTO salts have focused attentions towards the applications in propellants. Lee and Stincipher [27,63] have assessed the applicability of seven amine salts of NTO as gun propellant ingredients. Their study shows that the compounds have less flame temperature than TAGuN, but with lesser impetus also, when considered as mono-propellants. However, the mixtures of these salts can be well tailored with HMX, so that to achieve considerably lower flame temperature than pure HMX, with a small compromise with impetus. ANTO has got higher heat of formation ($-276.56 \text{ kJ mol}^{-1}$) than the conventional solid propellant ingredients like AP ($-296.0 \text{ kJ mol}^{-1}$) and AN ($-365.04 \text{ kJ mol}^{-1}$). Given the facts that its combustion is environment friendly than AP and its thermolysis is autocatalytic in nature, it can be considered as a replacement for AP in solid rocket propellants.

The metal salts of NTO have also been suggested to be potential high energetic ballistic modifiers for solid propellants [64]. Willims et al. [65] after their pyrolysis studies concluded that NTO forms a polymeric azine-like residue when it is decomposed below about 280°C . This residue can accumulate transiently on the burning surface and retard the mass transfer from condensed phase to gas phase and affect the heat transfer from gas phase to condensed phase. Thus they have hypothetically suggested that NTO can be used as a potential additive in solid propellants for suppressing the burn rate and enhance the combustion stability. Later on the pyrolytic characteristics of NTO and some of its salts have been used as a criterion to evaluate the catalytic activity, when these compounds are used as ballistic modifiers [66]. Singh et al. [67] have also studied the catalytic activity of NTO and its salts as burning rate catalysts for hydroxyl terminated polybutadiene (HTPB) and AP composite solid propellants and found that transition metal salts of NTO have a high potential for this application.

The metal salts of NTO needs particular attention as high energetic ballistic modifiers for solid propellants. These compounds have a lot of added advantages than the conventional transition metal oxides (TMO), for the use as burning rate catalysts. TMO are non-energetic and hence, the increase of their percentage in propellant formulations reduce total energy of the propellants. The metal salts of NTO can be formulated to be used at higher amounts than that for TMO with little compromise in energy. The higher catalytic activity of the high energetic salts may also be attributed to the fact that the 'active metal oxides' are formed in situ in the system. Brill et al. [40] have shown that the metal salts of NTO forms volatile metal compounds which may be further converted to metal oxides in the gas phase. They have hypothetically suggested the tailoring of these salts so as to dampen the high frequency acoustic modes inside the combustor [68] and thus, avoid unsteady combustion. This is also an added advantage of metal salts of NTO over the conventional TMO as ballistic modifiers.

However, much work is needed to be carried out on the effect of these salts on the processing parameters as well as ageing of solid propellants, before its actual usage. The hypothetical suggestions also need further experimental support. The energy computations

also need experimental assessment to verify the effect of these catalysts on the total energy as well as specific impulse of the propellants. The extension of these studies to composite modified double base propellants (CMDB), and environment friendly propellants with AN may also be considered.

8. Conclusions

NTO forms salts with a wide range of compounds and the salts formed may be generally classified as metal salts and amine salts. The proton leaves from position N(4) when NTO is converted to its salts. Generally the metal salt hydrates of NTO during their thermolysis first undergo dehydration. Then the dehydrated salt on further heating undergo exothermic decomposition ultimately yielding metal oxides. The thermal stability of almost all the metal salts are lower than that of NTO, on account of values of E for thermolysis. All salts of NTO are also rather insensitive like the parent compound. The metal salts of NTO are potential energetic ballistic additives for solid propellants, but further studies are required.

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