Studies on energetic compounds
Part 16. Chemistry and decomposition mechanisms of 5-nitro-2, 4-dihydro-3H-1,2,4-triazole-3-one (NTO)

Gurdip Singh[*], Inder Pal Singh Kapoor, Sunil Kumar Tiwari, Prem S. Felix

Chemistry Department, DDU Gorakhpur University, Gorakhpur 273009, India

Abstract

The present review deals with the chemistry and thermolysis of NTO and plausible decomposition pathways have been described. The decomposition of 5-nitro-2,4-dihydro-3H-1,2,4-triazole-3-one (NTO) induced by X-ray, UV, laser, photochemical irradiation has also been discussed. High-speed photographic studies of the impact responses of NTO are also included. The thermal decomposition of labelled NTO has also been described here. Methods of detection as well as safe disposal of NTO have also been mentioned. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: High energetic compounds; Thermolysis; Heterocyclic nitro compounds; Decomposition; Thermoanalytical techniques

1. Introduction

The common explosives RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) and TNT (trinitro toluene) were considered adequate for all weapons applications uptill now. Due to the many catastrophic explosions resulting from unintentional initiation of either impact, friction or shock, aboard ships, ammunition trains and aircraft carriers, these explosives have become less attractive. TATB (1,3,5-triamino-2,4,6-trinitro benzene) is noted for its insensitivity and is currently employed as an IHE (insensitive high explosive) in few applications. Unfortunately, TATB does not have the energetic performance of either RDX or HMX. Therefore, there

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[*] Corresponding author. Tel.: +91-551-200-745; fax: +91-551-340-459.
E-mail address: mss2@nde.vsnl.net.in (G. Singh).

was the dire need to develop an explosive that is powerful yet resistant to accidental and sympathetic initiation. This review describes a potential candidate, NTO (5-nitro-2,4-dihydro-3H-1,2,4-triazole-3-one) with high energy and low sensitivity [1–8]. Other commonly used names for this compound are 3-nitro-1,2,4-triazole-5-one, 5-nitro-1,2,4-triazole-3-one and 2,4-dihydro-5-nitro-3H-1,2,4-triazole-3-one. NTO has several desirable features, viz. high heat of formation [9,10] and high density [11].

NTO is unique among military high explosives in that it does not fall in the traditional classes, viz. nitrates, nitramines or nitrobenzenes. Though NTO possesses a $C–NO_2$ linkage, the presence of the $>C=N–$ prevents it from being classed as a nitro alkane. In the cyclic NTO, the two nitrogens, i.e. 2 and 4 contain lone electron pairs, which suggest that it is possibly aromatic in character. The salt derivatives of NTO with amines and metals are also very useful and interesting. Detailed studies regarding characterisation, crystal structure, thermal, photochemical and laser induced decomposition of NTO reported by various workers [12–26] have been summarised here. The mechanisms of decomposition of NTO have also been discussed.

Controversy still exists regarding the decomposition mechanism of NTO. Nevertheless, one school of thought have suggested that the first step in the thermal decomposition of NTO is scission of $C–NO_2$ bond either by direct thermal activation [27,28] or catalysed by H atom transfer and loss of HONO. The other school of thought has reported [14,19] that first decomposition products are CO_2 and N_2O. Recently, some workers have also reported CO_2 and N_2 as gaseous products while others detected NO_2 and HONO in small amount [25] or not at all [23]. Since NTO may potentially be used in the future, simple methods of detection of the compound, developed by various workers [29,30] have been described briefly. Various methods for NTO waste disposal have also been [31–33] presented here.

2. Superiority of NTO over traditional oxidisers such as AP, AN, RDX, HMX etc

NTO is a new energetic material with the attractive characteristics and high performance [1]. It has high heat of reaction ($>77\, kcal\, mol^{-1}$) [27] and showed autocatalytic behaviour during thermal decomposition [17,25]. From the results of small-scale screening tests of NTO and RDX [1], it has been observed that NTO is less sensitive and more stable than RDX in all tests (Table 1). Detonation properties of NTO, RDX and TATB are tabulated

Table 1
Physical and explosive properties

Parameters	NTO	RDX
Crystal density (g/cm^3)	1.93	1.806
DTA exotherm (°C)	>236	210
Heat of formation ($kcal\, mol^{-1}$)	−14.30	+14.71
Henkin critical temperature (°C)	237	219.6
Impact sensitivity (cm)	>280	22
Spark sensitivity (J)		
3 mil	0.91	0.22
10 mil	3.40	0.55
Vacuum stability ($ml\, g^{-1}$ per 48 h at 120°C)	0.3	0.12–0.9

Table 2
Detonation properties

| HEM	Charge density	Charge diameter (cm)	P_{CJ} (k bar)
NTO	1.93 (100% TMD)	–	–
	1.781 (92.2% TMD)	4.13	278
	1.853 (96% TMD)	4.13	260
	1.782 (92.3% TMD)	2.54	240
	1.855 (96.1% TMD)	2.54	–
	1.759 (91.1% TMD)	1.27	250
	1.824 (94.5% TMD)	1.27	–
RDX	1.767 (97.8% TMD)	4.12	388
TATB	1.87 (96.5% TMD)	4.12	277

in Table 2. Further studies are being carried out extensively on various aspects of NTO based explosive formulations [34,35]. NTO based high performance melt castable, general purpose and insensitive high explosive formulations are reported [36]. NTO is also being explored in pressed plastic bonded explosives (PBXs) [37].

Ammonium perchlorate (AP) and ammonium nitrate (AN) are the well known and widely used oxidisers for composite solid propellants. Now, interest is growing in oxidisers that might replace AP and AN generally used for solid propellants. AP liberates [28] HCl, N_2, O_2 and H_2O on combustion, and HCl is environmentally unsafe. Unfortunately, AN based propellants give low surface temperatures and low burn rates. Although these problems are somewhat overcome by formulating AN with a reactive metal (viz. Mg) but this metal is highly reactive with moist air or water. NTO is growing as better substitute for AP or AN since it neither liberates undesirable products like HCl nor it has low burn rate. Indeed, NTO has quite high burn rate in solid propellants.

RDX and HMX are being used as high energy additives to improve specific impulse (I_{sp}) in composite solid propellants and NTO has succeeded in replacing them [1]. Further, NTO as well as its transition metal salts [M(NTO)$_2$, M = Mn, Fe, Co, Ni, Cu and Zn] have also proved their worth as potential burn rate modifiers [38,39] for HTPB-AP propellants. NTO has also become a promising candidate to improve the performance of gun propellants. Thermodynamic data for energy output such as flame temperature, mean molecular weight, heat of explosion and specific energy of NTO have been reported by Volk and Bathelt [40]. Fouche and Schalkyk [41] reported that the incorporation of NTO and/or fine RDX in TNT showed significant improvements in sensitivity, mechanical properties and structural integrity of explosive columns. Thus 40:60 NTO–TNT and 25:25:50 RDX–NTO–TNT can be considered safe and reliable charges for various caliber artillery shells. NTO is highly useful in non-azide inflating propellant compositions for automobile air bags also [42,43].

3. Preparation, characterisation and crystal structure of NTO

NTO can be prepared [44] by the reaction of semicarbazide hydrochloride (SC) with formic acid followed by nitration with 70% nitric acid (Scheme 1).
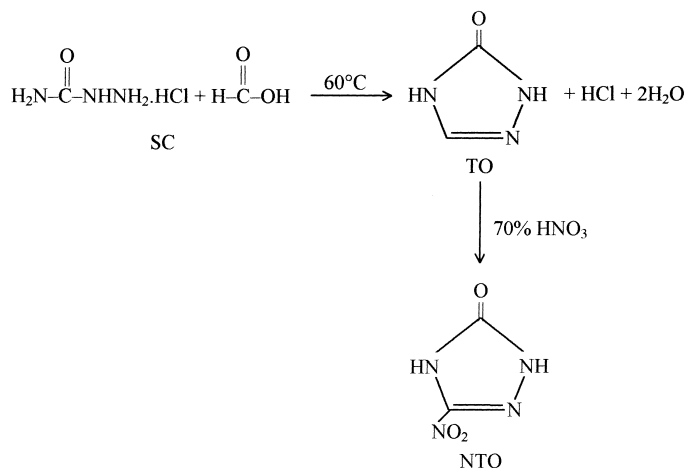
Scheme 1.

Li [45] describes an one-pot synthesis of NTO by cyclocondensation of semicarbazide with formic acid and then nitrating the product formed having an yield of 76.8%.

Crystal packing and molecular dynamics of NTO was thoroughly investigated by Lee and Gilardi [11] and Sorescu and Thompson [15]. It is known that NTO shows tautomerism and crystalline NTO exists in two phases, α (most stable) and β. It belongs to the triclinic space group P1 and contains eight molecules in the unit cell. However, attempts to determine the coordinates of individual atoms for this structure have not been successful due to 'some kind of twinning about the crystal needle axis' [11]. The β-phase has been resolved by X-ray diffraction measurements. The unit cell is monoclinic with four molecules in the unit cell and has the space group $P2_1/C$.

Two methods were used to calculate the crystal packing of β-NTO crystal [15]. The first one is 'molecular packing calculations' and the other is 'molecular dynamics calculations' at normal pressure and temperature (NPT).

Two values are reported for enthalpies of formation of NTO in both gas and solid phases [9,10,33]. The values for enthalpies of formation of NTO in gas phase are ΔH_f (g) $= -3.2$ and $-5.7\,\mathrm{kcal\,mol^{-1}}$ and in solid phase are ΔH_f (s) $= -30.927\,\mathrm{kcal\,mol^{-1}}$. Therefore enthalpy of sublimation of NTO was calculated using both the values and from these data, the lattice energy of NTO becomes -110.46 or $-121.02\,\mathrm{kJ\,mol^{-1}}$.

Lier [47] studied the effect of solvent in the crystallisation process of NTO. Heijden [48] gives a description of the solubility, nucleation and crystal growth mechanisms of NTO. Koo et al. [49] describes the production of NTO crystals of desired particle size and morphology by using various recrystallisation techniques.
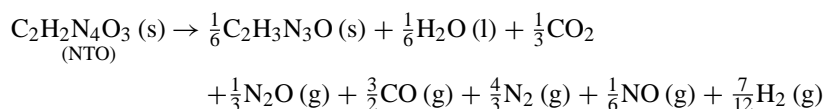
4. Decomposition of NTO using various techniques

Thermal, photochemical and laser induced decomposition studies on NTO have been carried out by various workers [13,14,17–26]. Since the decomposition reaction steps

depend upon temperature, pressure and possible phases, studies carried out under different experimental conditions have led to strong disagreement about the initial pathways. The reported values of the global kinetic parameters obtained from thermal heating experiments [14,17,21,50] differ considerably. According to Williams and Brill [20] NTO may decompose via sublimation and the sublimation and decomposition process were not always carefully isolated in the different experiments. Proton transfer has been suggested as the rate-determining step [17,21]. Though $C-NO_2$ is the weakest bond and thus would cleavage but NO_2 has never been detected as an early evolved gas. Nitro-nitrite rearrangement followed by loss of NO has also been observed. Botcher et al. [51] did not observe NO in their thin-film studies. The energy required to break the N–O bond in the nitro group is greater than $83\,kcal\,mol^{-1}$ and hence nitroso-TO ($m/z = 114$) seems to be a product of a bimolecular rather than unimolecular reaction [24]. Various techniques have been used to understand the mechanism of decomposition of NTO which are described here.

4.1. Thermoanalytical techniques

In case of high energetic compounds, the early thermal decomposition reactions are very important from the viewpoint of understanding the mechanism of explosion. The thermal decomposition of NTO was studied using DSC, TGA-MS and ARC by Rothgery et al. [27] and the major gaseous products were identified. They have observed that the stability of NTO is sensitive to aging of the sample. Kinetic analysis suggested an auto-catalytic mechanism. The decomposition mechanism changed abruptly at $212°C$ where an ignition occurred. Under identical conditions, the onset temperature for an NTO thermal runway was approximately $28°C$ higher than that found for RDX and its ignition temperature was approximately $12°C$ higher [52]. The decomposition products are as follows:

$$C_2H_2N_4O_3\,(s) \rightarrow \tfrac{1}{6}C_2H_3N_3O\,(s) + \tfrac{1}{6}H_2O\,(l) + \tfrac{1}{3}CO_2$$
$$\text{(NTO)}$$
$$+ \tfrac{1}{3}N_2O\,(g) + \tfrac{3}{2}CO\,(g) + \tfrac{4}{3}N_2\,(g) + \tfrac{1}{6}NO\,(g) + \tfrac{7}{12}H_2\,(g)$$

Prabhakaran et al. [14] have studied the decomposition of NTO using TGA, DTA, IR, DSC, XRD and hot stage microscopy. They have reported that the NTO crystal belongs to the tetragonal system with a *c/a* ratio of 0.329. The kinetics of the isothermal decomposition was studied in the temperature range $229–246°C$ under static air atmosphere. Out of the 18 equations tried, the best linearity, with a correlation coefficient of 0.9937 was obtained with Avrami–Erofeev equation for an α range of 0–83%, which gave an activation energy of $186.0\,kJ\,mol^{-1}$.

During NTO decomposition, the evolved gases were analysed by IR. At around $244°C$, carbon dioxide and nitrous oxide were detected as early gases. The bands due to CO_2, NO_2 and N_2O were prominent in the spectra. Formation of ${}^\bullet NO_2$ radical by $C-NO_2$ cleavage, with rupture of the adjacent C–N bond appears to be the probable mechanism in the thermal decomposition of NTO. The oxidative attack of the NO_2 group on the ring fragment accounts for the formation of gaseous products such as CO_2, NO and N_2O (Scheme 2).

Oxley and coworkers [21] reported that thermal decomposition proceed through C–N homolysis either by direct homolysis of $C-NO_2$ (important at higher temperature) or by
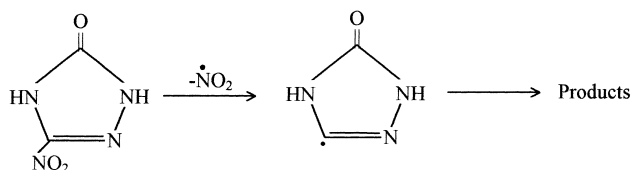
Scheme 2.

initial transfer of hydrogen and subsequent C–NO$_2$ cleavage. The autocatalytic nature of the NTO decomposition is attributed due to the generation of $^{\bullet}$NO$_2$ free radical. Decomposition in solution or in open thermolysis tubes is strictly of the first order. Analysis indicated the presence of C$_2$H$_2$N$_3$O, a formula consistent with 'polymerised TO' (1,2,4-triazole-5-one). TO is not a direct intermediate in the formation of this residue. Independent decomposition of TO resulted in a residue of somewhat different elemental composition [C$_{4.5}$H$_5$N$_{7.7}$O] as reported in Scheme 3.

William and Brill [20] have reported the decomposition and sublimation kinetics of NTO. The T-jump/FTIR experiment [53] was employed to determine the kinetic constants for decomposition of flash-heated NTO. Two dominant processes occurring in NTO at elevated temperatures are sublimation and decomposition. By optimising the conditions that are preferential to sublimation (i.e. low pressure, moderate temperature), the rate constants especially for sublimation were determined for the first time. The formation of sublimed
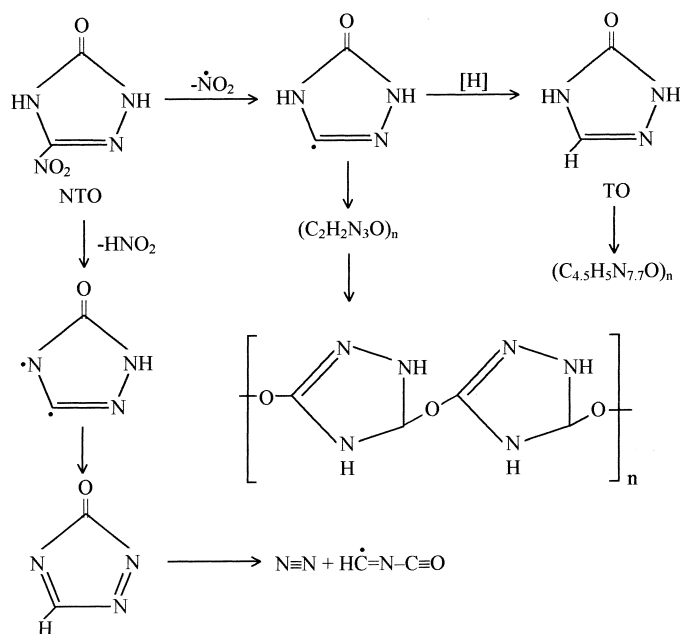
Scheme 3.

Table 3
Calculated and observed compensation parameters

Compound	a (kcal mol^{-1})		b (ln k s^{-1})
	Calculated ($1/RT$)	Observed	
HMX	0.96 ± 0.04	0.94	-5.4
RDX	0.96 ± 0.04	0.92	-1.1
NTO	0.96 ± 0.04	1.03	-13.0

NTO without detectable solid or gaseous decomposition products were analysed by IR. It is noteworthy that two ranges of E_a values emerged: 45–52 and 78–87 kcal mol^{-1}. The kinetic constants for decomposition that yield $E_a = 45$–52 kcal mol^{-1} almost entirely represent sublimation of NTO in the lower temperature range and a mixture of decomposition and sublimation at higher temperatures. It is evident that considerable care must be exercised when determining and interpreting the kinetic constants for decomposition of energetic compounds. In the unconfined state, the kinetic constants may be a mixture of the rates of sublimation and decomposition, the balance of which shifts with changes in two dominating processes may be separated and independently investigated. If the thermal decomposition rate of NTO is desired, then the kinetics which yield activation energies in the vicinity of 78–87 kcal mol^{-1} rather than 45–52 kcal mol^{-1} should be used.

The kinetic compensation effects in energetic materials like HMX, RDX, NTO were also studied by Brill and coworkers [22]. A linear relationship exists between the pre-exponential factor, $\ln A$ and the apparent activation energy (E_a) that are determined for a process from the Arrhenius equation (Eq. (1)) [54,55]

$$\ln k = \ln A - \frac{E_a}{RT} \tag{1}$$

$\ln A$ and E_a for a solid or melt-phase process do not necessarily have the same meaning as $\ln A$ and E_a from homogeneous kinetics [56]. When $\ln A$ and E_a are linearly related, the compensation parameters a and b are defined by Eq. (2) for all measurements [54,55,57].

$$\ln A = aE_a + b \tag{2}$$

For any compound exhibiting the compensation effect, a plot of $\ln A$ versus E_a yields a set of compensation parameters a, b, and $1/RT$ from Eqs. (1) and (2) which are reported in Table 3 for various compounds.

With a few exceptions, the rates of thermal decomposition of HMX, RDX and NTO exhibit a single compensation effect. Global kinetic measurements of thermal decomposition of these compounds are strongly affected by sample characteristics [46,58–62] such as sample mass, particle size, sample configuration, heating rate, self-heating of the sample, surrounding atmosphere, shape and material of construction of the sample holder.

4.2. X-ray and UV radiations

NTO, RDX, HMX and TATB were subjected to X-ray and UV radiation [63]. X-ray photoelectron spectroscopy (XPS) was used to detect chemical changes. RDX was the

most sensitive molecule to both the X-ray and UV radiation while HMX was only slightly less sensitive. NTO was found to be 1.5–3.0 times more sensitive to X-ray and UV damages than (1,3,5-triamino-2,4,6-trinitrobenzene) TATB. It was found interesting to identify decomposition products, which were consistent with the observed XPS data. The direct loss of NO_2 to produce TO is one possible mode of decomposition of NTO. Another product could be urazole resulting from elimination of NO via a cyclic intermediate reduction of nitro to nitroso is also a possible decomposition mechanism as observed in RDX. It appears unlikely that the presence of decomposition products in damaged NTO will increase the sensitivity. Thus it seems that NTO is therefore unique among commonly used energetic materials in that it may not be sensitised by molecular degradation.
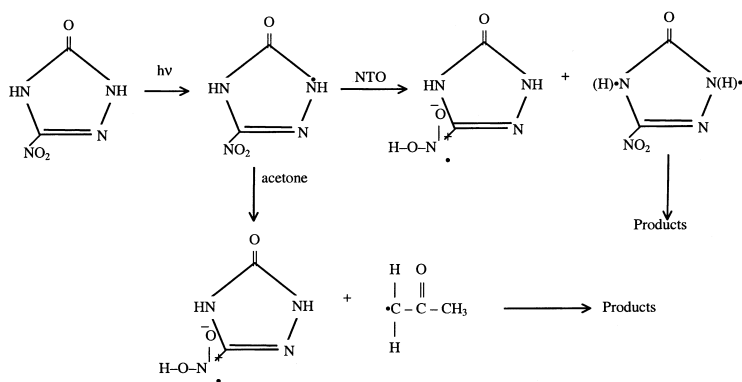
4.3. Laser irradiation

The initial decomposition products of NTO were characterised [19] using laser-induced decomposition of a solid sample. NTO was heated photothermally using laser irradiation of a solid sample. The relative yields of products with $m/z = 114, 101, 85$ and 83 were measured as a function of temperature. The product yields were normalised by the velocity-weighted, integrated ion signal from the parent NTO molecule. The early reaction pathways were characterised by analysis of temperature dependence of the relative products by net loss of an oxygen atom from NTO. This was consistent with earlier observation of evolution of CO_2 as an early product. Fragments produced by loss of NO and by scission of the C–NO_2 bond were early but not initial products.

### 4.4. Photochemical and thermochemical methods

EPR (electron paramagnetic resonance) and HPLC (high performance liquid chromatography) techniques have been used to monitor the decompositions of NTO and per deuterio NTO (NTO-d_2) under the thermochemical and photochemical conditions [17]. The global kinetic studies conducted between 498 and 518 K show that the loss of NTO (NTO-d_2) during neat thermochemical decomposition involves a solid-phase global autocatalytic reaction scheme. The KDIE (kinetic deuterium isotope effect) of the order of 1.67 (2.44 at 298 K) observed in the decomposition, suggested that a normal primary isotope effect was present for which N–H bond rupture took place along a main decomposition path leading to the loss of NTO. The KDIE also implied that N–H bond rupture took place on or before a mechanistic rate-limiting step governing the overall decomposition process.

The room temperature EPR photochemical decomposition experiments on NTO (NTO-d_2)/acetone (acetone-d_6) selections yield EPR spectra that can be identified as I, II and III radical species. The observation of identical EPR spectra in the NTO/acetone, NTO-d_2/acetone and NTO/acetone-d_6, decomposition corresponding to radicals I and II, implies that two different mechanistic reaction pathways are operative leading to the formation of radicals I–III. One reaction pathway involves an intermolecular reaction between

two NTO molecules, and the other involves a solvolysis reaction pathway between NTO and acetone.

I

II

III

The low temperature (370 K) EPR thermochemical decomposition performed on the NTO (NTO-d_2)/TNT (TNT-d_5) mixtures yield EPR spectra of radical intermediates which can be assigned as IV, V, VI and VII species.

IV

Hydroxy 3, 5–dinitro–4–methylphenyl nitroxide

V

Hydroxy 3, 5–dinitro–4–methylphenyl –d_5 nitroxide

VI

Hydroxy–d 3, 5 dinitro–4– methylphenyl–d_5 nitroxide

VII

2, 4, 6–trinitrobenzyl 3, 5–dinitro–4–methylphenyl nitroxide

These mechanistic pathways given in Scheme 4 appear to involve reactions by which the NO_2 group on NTO abstracts hydrogen atoms from other NTO species and/or from acetone.

4.5. Mass spectroscopy (MS)

According to Ostmark et al. [13], the mass spectrum consists of three characteristics parts: the molecular ion (*m/z* 130), the groups at *m/z* 83, 84 and 85 (the azole ring) and the azole ring fragment groups at *m/z* 41, 42, 43 and 44. The fact that the molecular ion (*m/z* 130) was found in relatively large amount in the electron impact (EI) spectrum (70 eV) indicates that the NTO molecule is very stable compared with HMX, RDX and TNT. The chemical ionisation (CI) spectrum of NTO showed two peaks at *m/z* 131 and *m/z* 261 (2M + 1); 261 peak is probably a cluster ion (adduct). The mass spectrum for TO (EI 70 eV) consisted

Scheme 4.

of only two peaks, at m/z 42 and 85. The proposed mass spectral fragmentation of NTO is shown in Scheme 5. Hence, the probable decomposition mechanism is an elimination of NO_2 followed by a breakdown of the azole ring.

McMillan and coworkers [24], for the first time, obtained real time photoionisation mass spectra of NTO causing surface analysis by laser ionisation (SALI) apparatus. Using vacuum UV single-photon ionisation, the shear induced NTO spectra were obtained with a spring-driven shearing device installed in a SALI chamber directly beneath the mass spectrometer sampling region. The shear induced spectra were dominated by a peak at m/z 99, which is not seen in the thermal or laser desorption spectra. This peak was assigned to the closed-shell triazole-diketone produced by a nitro-nitrite rearrangement, followed by NO loss and then by rapid bimolecular H-atom removal. The stability of the cyclic diketone intermediate thus generated could help to explain the shock insensitivity of NTO.

Scheme 5.
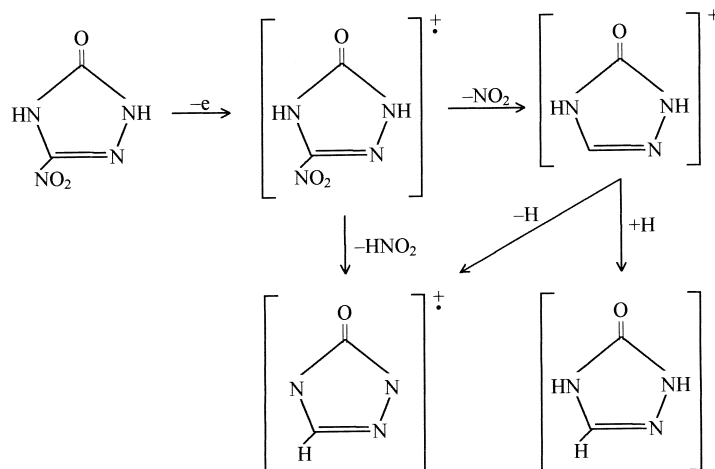
Laser-desorption spectra were also obtained both on fresh NTO samples and samples that have been recovered from marginally sub-critical drop weight impact tests. M-16, M-30, M-45, M-46 and M-59 dominated the sequence of thermally generated fragments. This series suggests several decomposition pathways, dominated by the same nitro-nitrate rearrangement and NO loss as the shear induced decomposition. However, under the thermal or laser-desorption conditions, subsequent bimolecular H-atom removal to produce the closed-shell diketone is evidently slower than unimolecular ring opening adjacent to the carbonyl group. It was shown how this sequence satisfactorily explains the following.

1. The initial formation of CO_2 that has been previously reported.
2. The result of nitrogen double-labelling experiments.
3. The fact that neither NO_2 nor HONO have been seen as substantial initial products of NTO decomposition.

4.6. Chemiluminescence (CL)

The thermal stability of NTO was studied by a chemiluminescence (CL) method [13,25] which is useful for determining the kinetic parameters of high explosive at low temperatures. Equipment using the chemiluminescence reaction between nitric oxide and ozone has been built. It is primarily used for studying NO development from explosives at different temperatures. The high sensitivity of the NO analysis makes determination of NO production from propellants during short periods (within minutes) even at room temperature. Assuming zero order Arrhenius kinetics, one can estimate the frequency factor and activation energy. From CL measurements the activation energy for NTO was calculated as $140 \, \text{kJ mol}^{-1}$ and the frequency factor as $5 \times 10^6 \, \text{s}^{-1}$ (temperature range = 100–140°C).

4.7. Critical temperature (T_c) for thermal explosion of NTO

The critical temperature for thermal explosion of NTO has been obtained [2] using various methods. Out of these, one method is based on experimental measurement while others are based on calculations. The calculated values were obtained using Frank-Kamenetskii's [64] (247.8°C), Zinn–Mader–Roger's equations [65,66] (256.6°C) and non-isothermal DSC method [67] (255.2°C) which are agreeable to each other within 5% error. These methods indicate that the heat resistant ability of NTO was higher than RDX but lower than HMX (i.e. HMX > NTO > RDX). Lee et al. [1] reported that the critical temperature of thermal explosion for NTO is 273°C, which is higher than that for RDX (219.6°C).

## 4.8. High-speed photographic study of the impact response of NTO

Aggrawal et al. [68] have studied the impact initiation of hexanitro-hexaaza-isowurtzitane (CL-20) and NTO by drop-weight impact using a high-speed photographic method. CL-20 was found to be slightly more sensitive and NTO less sensitive than β-HMX. The effect of additives on the impact initiation of NTO was also carried out in the same experimental set-up. It has been found that NTO was found to be sensitised by both hard high-melting point grits (60 μm borosilicate or pyrex glass) and brittle polymers.

5. ^{15}N-labelled NTO: preparation and thermal decomposition

Although NTO has a high melting point (268°C), free radicals from NTO are formed below 100°C in mixture of NTO and TNT [17]. Mechanistic studies on thermal decomposition of NTO are hampered by self-heating and autocatalytic reactions that make it difficult to control sample temperatures and to trap reaction intermediates. Thus, experiments with ^{15}N-labelled NTO can provide important mechanistic information that is not easily obtained otherwise.

Fan et al. [69] have reported the synthesis, spectral studies and thermal decomposition of NTO-1,2-^{15}N$_2$. Solid and gaseous thermal decomposition products of NTO-1,2-^{15}N$_2$ were detected by NMR spectroscopy and mass spectrometry respectively. For the first time, for any energetic material, ammonia has been reported as a product. The production of ammonia as a thermal decomposition product from NTO is surprising which was detected as ammonium ion, and it was believed that the major counter anion is the conjugate base of NTO. This assumption seems true since NTO was present in excess and has a low pK_a value (3.67). It was found that the yield of ammonia varies from 5 to 10%. The yield of ammonium ion is probably limited by the availability of water for hydrolysis of the C–N group (Scheme 6). A stepwise mechanism involving the homolysis of C–N bond followed by ring closure to form ^{14}N–^{15}N bond is most probable mechanism.

Isotopically labelled NTO was used to determine the origin of nitrogen atoms in its decomposition gases by Oxley and coworkers [18]. They have prepared and characterised NTO labelled with ^{15}N at positions 1, 2, 4 and 6 [70]. Thermolysis of NTO yields a brown insoluble residue and the nitrogen containing gases dinitrogen, nitrous oxide, nitric oxide
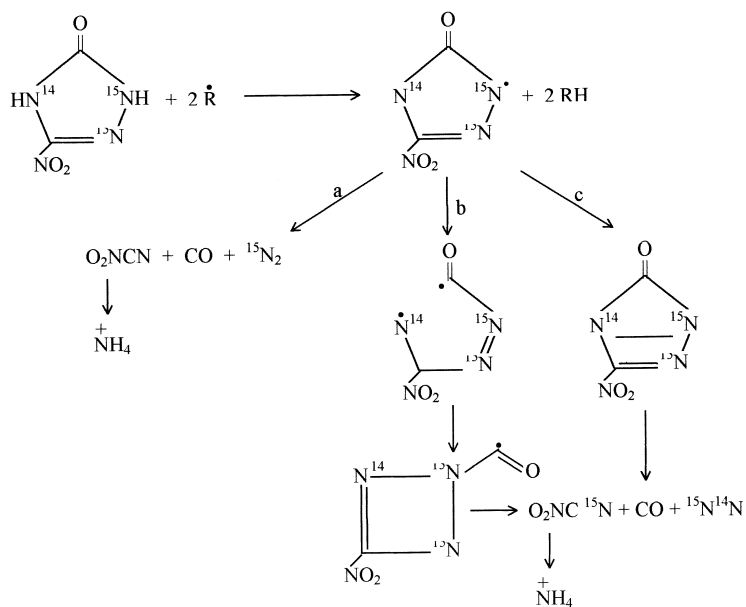
Scheme 6.
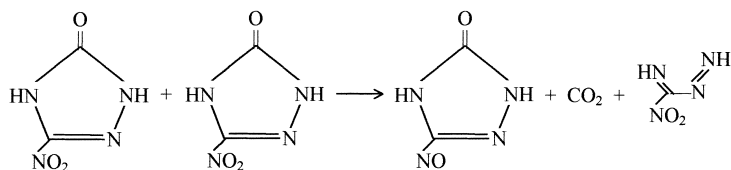
Scheme 7.

and hydrogen cyanide. The isotopic distribution of nitrogen atoms in the decomposition gases of NTO samples labelled with ^{15}N atoms at 1 and 2 where R may be NO_2, TO radical or other radical positions, 4 position and 6 position were determined at 10, 24 and 100% decomposition of NTO. Thermal decomposition of ^{15}N-labelled NTO samples were conducted at 250 and 270°C. A stoichiometric relationship for NTO decomposition in terms of the observed gaseous products was obtained assuming the production of a polymer precursor (CN_2) and water by three separate routes, which are presented in Scheme 7.

It was observed that in the dinitrogen gas, about 54% of the nitrogen atoms are from 1 and 2 positions, about 25% nitrogen atoms are from positions 4 and 6, 14% are from interaction of 1 or 2 position with 6 position of NTO and 6% involve exclusively nitrogen atoms from 6 position of NTO. From nitrous oxide, most of the nitrogen atoms (about 76%) are the result of interaction between nitrogen atoms at 1 or 2 position of NTO and those at 6 position and approximately 17% are exclusive from 6 position. Small contributors to nitrous oxide are, N (1, 2, 4) and N (4, 6) interactions.

6. Detection of NTO and its safe disposal

Since NTO has attracted wide interest for possible ingredient in various military propellants and explosive formulations, it is essential to develop methods for its easy detection and analysis. Thus Stuart et al. [29] have conducted studies on NTO compounds as well as fourteen other nitramines and nitro aromatic explosives and shown that these compounds can be analysed by capillary electrophoresis using a technique known as MECC (miscellar electrokinetic capillary chromatogram). A borate/boric acid buffer with sodium dodecyl-sulfate (SDS) was used in conjection with direct UV-detection at 185 nm. Campion et al. [30] described a direct, rapid and sensitive method for separating and quantifying NTO and its degradation product, 5-amino-1,2,4-triazole-3-one (ATO) in water and soil by reversed phase HPLC. A mixture of NTO, ATO, urazole and TO was separated by HPLC on a Hypercamb column packed with porous graphite C, or by capillary electrophoresis. Both methods are suitable to detect such compounds in environment and monitor their biological and chemical degradation.

Photochemical decomposition of energetic materials in alkaline solution has been considered for environmentally safe disposal of these materials. This method is already utilised for nitramines [71]. Pace et al. [31] investigated the photochemistry of NTO in strong alkaline solution. The results of this study show that NTO is not decomposed by alkaline solution and the >C–NO_2 bond remains intact (which was expected to homolyse to give $^\bullet NO_2$ free radical.

Campion et al. [33] have reported a method for eliminating a nitrogenated heterocyclic or aromatic compound comprising at least one nitro group, in an effluent by converting nitro group into an amino group with a reducing agent. The reducing agent can be H_2 in the presence of Pd/C or a microorganism. Thus NTO can be converted into ATO with 80% yield using a *Bacillus licheniformis* strain, and can be degraded further by the ring cleavage of ATO. Nitro group reduction of NTO was found to be completed in 24 h, while the degradation of ATO requires 2 weeks of incubation [32]. Campion et al. have also synthesised C^{14} labelled NTO and studied its hepatic metabolism by dexamethasome-induced murine hepatic microsomes [71].

7. Concluding remarks

NTO is a potential energetic compound, which could be a candidate for future weapons applications. Initial small scale sensitivity tests of NTO indicate that it is much less sensitive than RDX and TNT in all respects, but somewhat more sensitive than TATB. NTO could be produced on large scale in high yield economically. NTO is growing as better substitute for traditional oxidisers, viz. AP, AN etc. for composite solid propellants. There is a strong controversy about the initial decomposition pathways for NTO. Some authors reported that NO_2 is the initial product as a result of $C–NO_2$ cleavage, while others support the formation of CO_2 and NO as initial products. After a perusal of all these studies, one can conclude that the most plausible initial product is CO_2. These studies [51] have proved that the initial step is bimolecular in nature rather than unimolecular and carbonyl group can be converted to CO_2 by oxygenation of the former (Scheme 7).

Decomposition of ^{15}N labelled NTO at positions N (1), N (2), N (4) and N (6) is analogous to NTO.

Acknowledgements

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