Review

Studies on energetic compounds
Part XI: Preparation and thermolysis of polynitro organic compounds

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Abstract

The thermolysis of high energetic polynitro organic compounds has been reviewed in the present communication. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The chemistry of polynitro compounds have been described in a good number of publications [1–3]. Kamlet [4], Kamlet and Adolph [5] and Bliss et al. [6] have investigated the relationship between structure of organic compounds with impact sensitivity. The early thermal decomposition reactions are very important from the view point of understanding the mechanism of explosion. Thus, the thermolysis of polynitro compounds have been undertaken using TG/DTA/DTG/DSC techniques in the last decade and most of the work is scattered and, hence, it was thought to review these studies. Further, the data on density, oxygen balance (OB), velocity of detonation (VOD) and impact sensitivity ($h_{50\%}$ cm applying 2 kg weight) are also available in literature for some cases and this has also been included in the manuscript. The

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preparation and mechanistic aspects of thermolysis of polynitro compounds have been described critically in the present review.
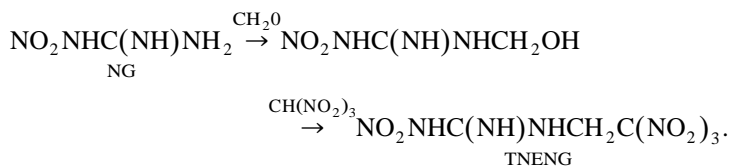
2. Aliphatic nitro compounds

Aliphatic nitro compounds with nearly zero or even positive OB having high melting points are desirable explosives and useful oxidizers for solid propellants. New processes have been discovered to prepare polynitro aliphatic derivatives, in which an additional electronegative moiety has been incorporated into the molecule at the methyl group. This class of compounds have the general formula: $RC(NO_2)_2X$, where $X = NO_2$ (trinitromethyl), F (fluorodinitromethyl, Ref. [7]), CN (cyanodinitromethyl) and N_3 (azidonitromethyl, Ref. [8]). The incorporation of an azide group has obvious energy benefits, because of its high energy content (80 kcal/mol). Lower polynitro aliphatic compounds may be obtained by direct vapour phase nitration of aliphatic hydrocarbons either with HNO_3 vapour or with NO_2 and they form powerful explosive mixtures with combustible substances.

2.1. Nitroguanidines

Nitroguanidine (NG) is an important ingredient of flashless propellants and a potential insensitive explosive having two crystalline modifications called α- and β-forms both belong to the orthorhombic crystal system. Spectroscopic investigations on the structures of NG and its derivatives exhibit their existence in nitramine form. The most important method of preparing NG is the addition of guanidine nitrate to concentrated sulphuric acid.

During thermal decomposition of NG, besides the simple decomposition products like N_2O, NH_3, CO_2, HCN, urea, cyanogen, cyanamide, cyanic acid, polymeric products like melamine, ammeline, ammelide, cyanuric acid, melem, melam, melon and para cyanogen were also identified [9,10]. NG is made up of two amino groups, one nitramine group and one carbon atom, which may be easily availed as an ideal element to form a desired explosive molecule [11]. The reaction between NG with formaldehyde or urotropine form a number of polynitro heterocyclic explosives and its derivatives, which are valuable intermediates for preparing some high explosives [12].

The more energetic derivative of NG is *N*-nitro-*N*-(2,2,2-trinitroethyl) guanidine (TNENG) and is a potential burn rate accelerator, two to three times higher than HMX [13]. TNENG mainly exists in nitramine form and is prepared by reacting NG with formaline to produce methylolnitroguanidine, followed by the reaction of trinitromethane.

$$NO_2NHC(NH)NH_2 \xrightarrow{CH_2O} NO_2NHC(NH)NHCH_2OH$$
$$\text{NG}$$

$$\xrightarrow{CH(NO_2)_3} NO_2NHC(NH)NHCH_2C(NO_2)_3.$$
$$\text{TNENG}$$

Thermolysis of TNENG liberate NO_2, NO, N_2O, CO_2, CO, H_2O, HCN and HNCO and show slight sublimation of the parent molecule. Impact sensitivity of NG is very less than that of TNENG, since the hydrogen bonding present in the NG crystal lattice would absorb impact energy and thereby desensitise it [14].

3. Aromatic nitro compounds

Aromatic nitro compounds are obtained mostly either by the nitration of corresponding aromatic compound or by the oxidation of corresponding amines. Presence of even one nitro group is sufficient to increase the thermal decomposition of aromatic compounds. Nevertheless, aromatic compounds which have two or more nitro groups, exhibit distinctly marked explosive properties. Zeman et al. [15] and Zeman [16] have correlated the thermal decomposition kinetics of polynitro aromatic explosives at lower temperatures with molecular structure, heat of explosion, detonation characteristics and thermal stability.

Several polynitro aromatic compounds undergo thermal decomposition by simple bond scission or rearrangements of the substituents on the ring [17]. Mostly, $C–NO_2$ homolysis to form NO_2 and an aromatic radical, is a dominant decomposition channel and it appears to be a major early thermal decomposition reaction at higher temperatures. $NO_2(g)$ was rarely detected as a decomposition product and the evolution of large quantity of NO has been reported [17]. The next stage of thermal decomposition is propagation reactions, which involve exothermic oxidation and reduction that lead to lower molecular weight and thermodynamically stable products.

3.1. Nitrobenzenes

m-Dinitrobenzene (DNB) can be prepared [18] either by the nitration of benzene or by the oxidation of nitroaniline. The explosive decomposition products of DNB are CO_2, CO, H_2, N_2, CH_4, HCN, C_2H_2, NH_4HCO_3 and C and its VOD is 6100 m/s. Among the various isomers of trinitrobenzene, 1,3,5-trinitrobenzene (TNB) is chemically most stable one. It has high stability, great explosive power and less sensitivity towards impact and friction. TNB can be obtained by nitrating DNB by a mixture of HNO_3 and oleum. 1,2,4,6-Tetranitrobenzene is an impact sensitive explosive, readily decomposes to picric acid in presence of moisture. Hexanitrobenzene can be prepared [19] by oxidising the amino group of pentanitroaniline with H_2O_2 in H_2SO_4. Tetra- and pentanitrobenzene can also be obtained [20] by the oxidation of their corresponding nitroanilines using peroxydisulphuric acid.
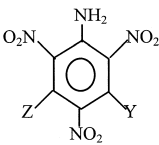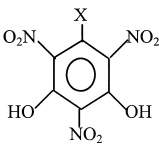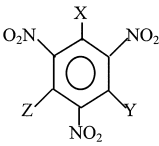
3.2. Trinitrobenzene derivatives

Trinitrobenzene derivatives [21] have long been important for technological applications. Their physical parameters and $h_{50\%}$ data are compiled in Table 1. 1-Amino-2,4,6-trinitrobenzene (MATB) (Compound no. **1**), is prepared by the successive nitration of aniline or by heating picric acid with urea. 1,3-Diammino-2,4,6-trinitrobenzene (DATB)

($\mathbf{2}$) is mainly prepared [22] from stiphnic acid and is used in high explosive compositions. 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) ($\mathbf{3}$) can be readily obtained [23] from aniline and it has qualified as heat resistant explosive. The unique structure of TATB confers properties which include high density and extremely insensitive to impact and shock. Moreover, the introduction of amino groups to these molecules, adds sufficient energy to the crystal lattice and increase the melting point [24]. The initial decomposition mechanism of MATB, DATB and TATB below 500°C is more complicated, since a $-NH_2$ group *ortho* to $-NO_2$, in an aromatic ring, will cyclize on heating to form furazan and furoxan derivatives [17]. Their explosive sensitivity [25,26] was

Table 1
Structure, melting point, density and impact sensitivity data of trinitrobenzene derivatives

Structure	Compound No.	Substituents	m.p. (°C)	Density (g/cm³)	$h_{50\%}$ (cm)
1	2	3	4	5	6
(structure 1)	1	Y, Z = H	188	1.760	177
	2	Y = NH₂; Z = H	286	1.837	260
	3	Y,Z = NH₂	350	1.938	490
(structure 2)	4	Y, Z = H	129	1.710	-
	5	Y = NH₂; Z = H	188(d)	-	-
	6	Y,Z = NH₂	186(d)	-	-
(structure 3)	7	Y, Z = F	82	2.00	-
	8	Y = F; Z = NH₂	118	1.939	62
	9	Y, Z = NH2	223	1.946	176
	10	Y = F; Z = NHCHO	179	-	-
	11	Y, Z = NHCHO	238	-	-
	12	Y=F;Z=NHCONH₂	164	-	-
(structure 4)	13	X = NHCHO	229	1.83	226
	14	X = NHCONH₂	> 350	1.90	320
	15	X=NHC(NH₂)=N-NO₂	184	1.65	466
	16	X=NH(CH₂)₂NH₂	305	1.80	189

Table 1 (continued)

1	2	3	4	5	6
(structure: benzene ring with NH₂ top, O₂N and NO₂ at 2,6 positions, NO₂ bottom, Z and Y substituents)	17	Y = CN; Z= NH₂	221	1.83	184
	18	Y, Z = CN	179	1.76	93
	19	Y = CONH₂; Z = NH₂	290	1.88	221
	20	Y, Z = CONH₂	> 340	1.85	168
	21	Y = COOH; Z = NH₂	240	1.86	> 320
(structure: benzene ring with X top, O₂N and NO₂ at 2,6 positions, NO₂ bottom, HO and OH substituents)	22	X = NH₂	234	1.88	324
	23	X = NHCHO	174	1.71	74
	24	X = NHCONH₂	164	1.81	36
(structure: benzene ring with X top, O₂N and NO₂ at 2,6 positions, NO₂ bottom, Z and Y substituents)	25	X = OCH₂CF(NO₂)₂; Y,Z = NH₂	190	1.82	568
	26	X,Y = OCH₂CF(NO₂)₂; Z = NH₂	140	1.79	300
	27	X,Y,Z=OCH₂CF(NO₂)₂	170	1.77	149
	28	X=NHCH₂CF(NO₂)₂; Y,Z=NH₂	198	1.82	493
	29	X,Y=NHCH₂CF(NO₂)₂; Z=NH₂	145	1.81	212
	30	X,Y,Z=NHCH₂CF(NO₂)₂	182	1.75	220
	31	X=N₃; Y,Z = H	83	-	-

found to be in the order: MATB > DATB > TATB. However, the desensitising influence of $-NH_2$ group is due to its electron donating and/or hydrogen bonding characteristics. 2,4,6-(Trinitrophenyl) methylnitramine (Tetryl) (**4**), 3-aminotetryl (3AT) (**5**) and 3,5-diaminotetryl (3,5 DAT) (**6**) are practical explosives. Recently Luper and Cooper [27] have reported the low and high order detonation in Tetryl. Tetryl (**4**) can be prepared [28] by the nitration of *N*-methylaniline. Hutchinson et al. [29] have prepared (**5**) and (**6**) from their corresponding chlorotetryl by the displacement of halogen by ammonia. Their explosive sensitiveness is in the order: (**6**) > (**5**) > (**4**). 1,3,5-Trifluoro-trinitrobenzene (TFTNB) (**7**) have been prepared by the direct nitration of 1,3,5-trifluorobenzene. Difloropicramide (DFP) (**8**) and fluorodiamino-trinitrobenzene (FDATB) (**9**) have been prepared from compound (**7**). The compounds (**7**), (**8**) and (**9**) are very good precursors to synthesize a large number of TNB derivatives [30]. TFTNB reacted with formamide, in presence of tetrahydrofuran (THF) to give the formamide derivatives (**10**)
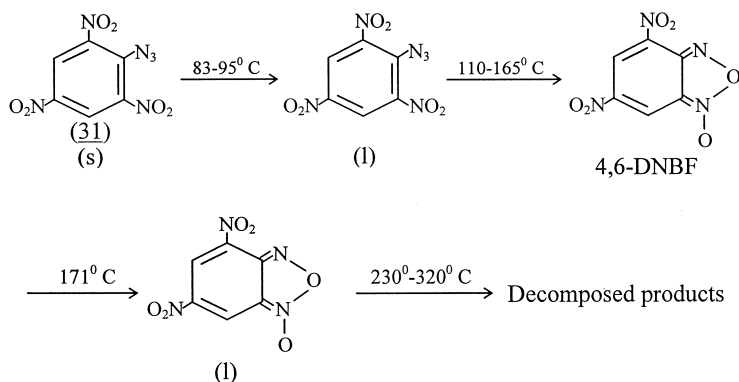
Scheme 1.

and (11) and with urea to give ureido derivative (12). TFTNB on refluxing with formamide in *p*-dioxane gave (13). The compounds (14), (15) and (16) can be obtained from FDATB by the direct displacement of fluorine. The aromatic nitriles (17) and (18) were hydrolysed by conc. H_2SO_4 to the corresponding amides (19) and (20), respectively, and 70% aqueous H_2SO_4 converted them to the carboxylic acid (21).

The compounds (8), (10) and (11) were hydrolysed to the substituted styphnic acids (22), (23) and (24), respectively. The starting materials (7), (8) and (9) reacted with fluorodinitroethanol [31] to give the fluorodinitroethoxy derivatives (25), (26) and (27) and reacted with fluorodinitroethylamine to give the fluorodinitroethylamino derivatives (28), (29) and (30), respectively. Reddy et al. [32] have undertaken studies on the kinetics of decomposition of picryl azide (31) by DTA, DSC and isothermal TG techniques. It was found to melt at 83–93°C and looses $N_2(g)$ to yield 4,6-dinitrobenzo-furagan oxide (4,6-DNBF), which decomposes to give gaseous products along with carbonaceous residue. The N–O bond cleavage is reported as the rate-controlling step (Scheme 1).

The replacement of a nitro group in a polynitro compound by fluoroxano groups can result in the increase of density and VOD. Accordingly, N,N'-bis(2,4-dinitrobenzo-furoxan)-1,3,5-trinitro-2,6-diaminobenzene as an explosive with high density (1.92 g/cm³) and high VOD (8574 m/s) by taking 1,3-diaminobenzene and 1,3-dichloro-TNB as the starting materials.

In polynitroaromatics [5], the initiation step is presumably a scission of the C–NO₂ bond. But those having C–H bond alpha to the polynitroaromatic ring, decompose by C–H bond scission (Scheme 2).

3.3. Nitrotoluenes

The specific feature of nitration of toluene, is the presence of methyl group which greatly facilitates the nitration as compared to benzene. Out of the various nitro derivatives of toluene, 2,4,6-trinitrotoluene (TNT) achieves its special position, because of its low hygroscopicity, high compatibility, low melting point, relatively low sensitiv-
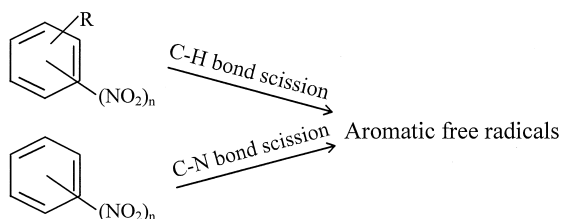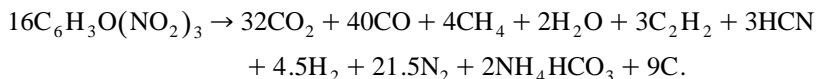
Scheme 2.

ity to impact and friction, good thermal stability and high power during explosion. TNT is normally prepared by the nitration of toluene by successive introduction of nitro groups. Its decomposition products are CO, CO_2, H_2, H_2O, N_2, NH_3, HCN, CH_4, C_2H_2, C_2N_2 and C. The evaporation of TNT starts above 200°C and exothermic decomposition occurs at 300°C with the involvement of some partly oxidised polymeric radicals as heat sensitizers [33]. Below 770°C, the initiation chemistry is dominated by oxidation reactions of the methyl group and above 770°C, $C-NO_2$ homolysis dominates the initiation process [34]. Tetranitrotoluene is more resistant to hydrolytic action of water and cannot be obtained by the direct nitration of trinitrotoluene. Recently, Nielsen et al. [35] and Atkins and Wilson [36] have developed new synthetic routes, which involve peroxydisulphuric acid oxidation of trinitrotoluidines and hypophosphorous acid reduction of diazonium salts derived from tetranitrotoluidine.

3.4. Nitrophenols

Among the three isomers of mononitrophenol, *ortho* and *para* are readily formed, when phenol is nitrated with dil. HNO_3. The *meta* isomer is usually prepared by diazotization of *m*-nitroaniline. Out of the six isomers (2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-) of dinitrophenol, 2,4- and 2,6-isomers may be obtained by the nitration of phenol and all other isomers are prepared by indirect methods. 2,4,6-Trinitrophenol (picric acid) is of the greatest importance and is prepared by the nitration of 2,4-dinitrophenol. Its thermal decomposition [3] can be represented as follows:

$$16C_6H_3O(NO_2)_3 \rightarrow 32CO_2 + 40CO + 4CH_4 + 2H_2O + 3C_2H_2 + 3HCN$$
$$+ 4.5H_2 + 21.5N_2 + 2NH_4HCO_3 + 9C.$$

The impact and friction sensitivities of picric acid are higher than that of TNT and its VOD was reported to be in the range 4020–7504 m/s. 2,3,4,6-Tetranitrophenol was obtained by reacting hydroxylamine with dinitroresorcinol. It is more sensitive to impact than tetryl.

3.5. Nitrostilbenes and nitrobibenzyls

4,4′-Dinitrostilbene was prepared by warming *p*-nitrotoluene in alkaline alcoholic solution. All the three possible isomers of 2,4,4′-trinitrostilbene can be obtained by heating *o*-, *m*- or *p*-nitrobenzaldehyde with 2,4-dinitrotoluene, 2,2′, 4,4′, 6,6′-

hexanitrostilbene (HNS) [37] is a heat resistant explosive [38], used as a crystal modifying additive and also in explosive boosters. The thermolysis of HNS and its derivatives have been studied [39] by isothermal DSC. Zene-guo et al. [40] described the synthesis of 3,3′-bis (HNS) based on the Ullmann reaction by reacting 3-chloro HNS with hydrazine. Synthesis of 3,3′-disubstituted polynitrostilbenes having substituents with increasing electron donating ability (MeNH > MeO > Cl) have also been described [41]. Tetranitrobibenzyl and 2,2′, 4,4′, 6,6′-hexanitrobibenzyl can be prepared [42] by treating nitrobenzyl halogenide with TNT.

4. Homocyclic nitro compounds

There is a considerable current interest in the synthesis [43–47] and thermolysis of polynitrohomocyclic (''cage'') compounds [48]. These are relatively highly strained molecules, that contain several $-NO_2$ substituents, and emerging as high-density energetic materials [49]. Recently, Eaton et al. [50] have developed a systematic methodology for the syntheses of 1,3,5-trinitrocubane and 1,3,5,7-tetranitrocubane as superior high energy shock insensitive explosives. The thermal behaviour and detonation properties of D3-hexanitrotrishomocubane [51] have been investigated and the explosive output calculations show that it is substantially more powerful explosive than TNT. Dave [52] have prepared 4,4′-dinitroadamentane-2,6-dione as an intermediate to make high energetic compounds. 1,4,6,9-Tetranitrodiadamentane and 1,3,5,7-tetranitrodiadamentane can be obtained [53] by the oxidation of their corresponding tetraaminodiadamentane and adamentane by $KMnO_4$. These compounds have an OB of -121.7 and are useful as solid rocket fuel. 1,3,5,7-Tetranitroxyadamentane (TNODA) has been prepared [54] by the nitration of 1,3,5,7-tetrahydroxyadamantane and it has an excellent thermal and impact stability.

5. Heterocyclic nitro compounds

Heterocyclic nitro compounds may be aliphatic or aromatic in character, depending upon the electronic constitution. These compounds represent explosives of higher performance compared with analogous aromatic systems, regarding their elemental composition, OB, density, standard heat of formation and VOD. Reactions of a polyatomic substituents with an *ortho* $-NO_2$ group in an aromatic ring are now widely used to synthesise many heterobicyclic molecules [55–57]. In general, the reactions between $-NO_2$ and *ortho*-related substituents profoundly affect the thermal decomposition chemistry and explosive properties of polynitroaromatic explosives [58–60]. The proton transfer from $O-CH_3$ to $-NO_2$ is energetically favourable. Normally, decomposition of *ortho*-substituted aromatic nitro compounds at lower temperatures favours cyclization reactions whereas, higher temperatures favour homolysis of the $C-NO_2$ bond.

5.1. Four-membered ring compounds

Nitro-substituted four-membered ring compounds possess high strain energy and are expected to have excellent explosive performance. It is more difficult to prepare these

compounds by the direct cyclization of straight-chain intermediates. Azetidine based explosives such as 3,3-dinitroazetidine (DNAZ) and 1,3,3-trinitroazetidine (TNAZ) have occupied a significant place [61].

(DNAZ)   (TNAZ)
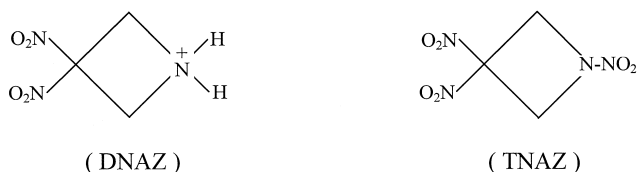
DNAZ has been prepared from 1-*t*-butyl-3,3-dinitroazetine. The basicity of DNAZ allows the preparation of a large variety of salts, by introducing energetic anions like nitrate (DNAZ-Nitrate), dinitramidate (DNAZ-DN) and five-membered heterocyclic aromatic ring namely, 2,4-dinitroimidazolate (DNAZ-DNI); 4,4′, 5,5′-tetranitro-2,2′-bi-imidazolate (2DNAZ-N4BIM), 5-nitro-2,4-dihydro-3*H*-1,2,4-triazole-3-onate (DNAZ-NTO); 3,5-dinitro-1,2,4-triazolate (DNAZ-DNT). These DNAZ salts were prepared by either mixing the free base with the appropriate acid or by metathesis of 3,3-dinitroa-zetidinium trifluromethanesulfonate with the ammonium salt of the acid [62]. The density, thermal and $h_{50\%}$ data of these DNAZ salts are summarized in Table 2.

5.2. Five-membered ring compounds

The C-nitro derivatives of five-membered *N*- and *N,O*-heterocycles are of interesting energetic compounds [63]. 2,5-Dipicryl-1,3,4-oxadiazole (DPO) was prepared [64] as a thermally stable explosive by the cyclization of *N,N′*-bis(2,4,6-trinitrobenzyl) hydrazine. Polynitroimidazoles are generally obtained by the nitration of polyiodoimidazoles [65]. 1,3-Dinitroimidazolidine can be obtained by treating ethylene-dinitramine with formaldehyde. The synthesis of 3-picrylamino-1,2,4-triazole involves the condensation reaction of tetryl with aminotriazole [66]. It yields stable explosives on nitration. 1,1′-dinitro-3,3′-azo-1,2,4-triazole may be obtained [67] from 3-amino-1,2,4-triazole by oxidation and reduction followed by nitration. It has more impact sensitivity and finds application as high energy propellant.

Table 2
Density, thermal and impact sensitivity data of 3,3-dinitroazetinide (DNAZ) salts

Compound name	Density (g/cm^3)	ΔH_f (kcal/mol)	DTA (exotherm) (°C)	Impact sensitivity $h_{50\%}$ (cm)
DNAZ-Nitrate	1.764	-64 ± 2	150	32
DNAZ-DN	1.791	-8 ± 4	140	14
DNAZ-DNI	1.652	-18 ± 12	160	54
2DNAZ-N4BIM	1.782	$+5 \pm 15$	150	71
DNAZ-NTO	1.757	-48 ± 1	160	42
DNAZ-DNT	1.694	$+20 \pm 2$	150	37

Among nitroazole explosives, 5-nitro-2,4-dihydro-3H-1,2,4-triazole-3-one (NTO) is emerging as a new candidate having high performance than RDX and HMX. The preparation [68–70] of NTO mainly involves the condensation reaction of semicarbazide hydrochloride and formic acid to form 1,2,4-triazole-3-one (TO) followed by nitration with 70% HNO_3.

Crystal packing and molecular dynamics of NTO were studied by Lee and Gilardi [71] and Sorescu and Thompson [72]. Crystalline NTO exists in α and β phases, out of these the first one is most stable.
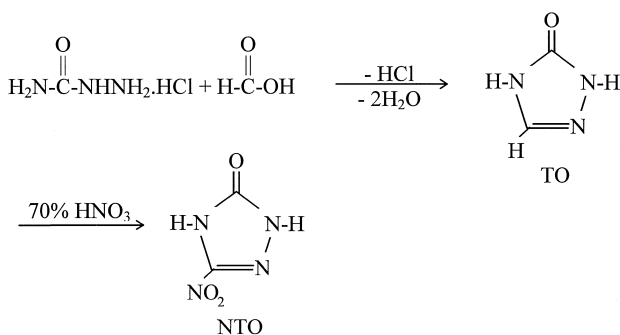
NTO is widely investigated for its thermal, impact, friction and shock sensitivities [73–75]. Mass spectrometric studies [76], quantum mechanical studies [77,78] and isotopic effect of deuterium on the kinetics [73] of NTO have also been investigated. Prabhakaran et al. [79] have evaluated the kinetic parameters of NTO using various kinetic models. The C–NO_2 bond cleavage, with rupture of the adjacent C–N bond has been suggested as the rate-determining step. The oxidative attack of the NO_2 group on the ring fragments, accounts for the formation of products like CO_2, NO and N_2O. Recently, Oxley et al. [80] have proposed a decomposition pathway for NTO (Scheme 3) which is initiated by loss of HONO or NO_2.
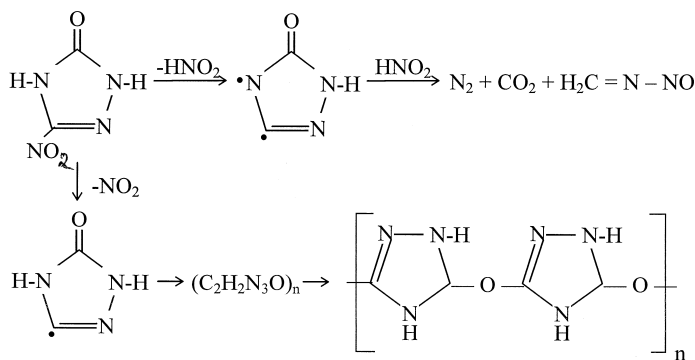
Scheme 3.
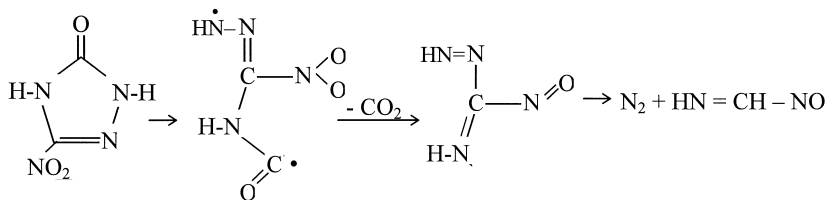
Scheme 4.

Botcher et al. [81] have proposed Scheme 4 for NTO decomposition based on products such as N_2, CO_2 and nitroso isocyanide which were detected by IR.

Very recently, Oxley et al. [82] have also reported Scheme 5 where NO_2 migration take place to form less thermodynamically stable $N-NO_2$ from $C-NO_2$.

Decomposition of NTO [83] has also been shown to involve the formation of a hypothetical polymer precursor CN_2 as follows (Scheme 6).

These three decomposition pathways have been postulated based on the compositional analysis of the gaseous products. The percentages express the extent to which each route contribute to the thermal decomposition of NTO. Garland et al. [84] suggested that CO_2 is an early product of decomposition of NTO. Botcher et al. [81] reported that during thermal decomposition, the initial step is bimolecular in nature in which oxygenation of the carbonyl group to CO_2 takes place with the $-NO_2$ functional group on a neighbouring molecule (Scheme 7).

Amine salts [85] of NTO have been synthesised by mixing an aqueous solution of NTO with the corresponding bases namely, ammonium (ANTO), hydrazine (HNTO), ethylenediamine (ENTO), guanidinium (GNTO), aminoguanidinium (AGNTO), di-aminoguanidinium (DAGNTO), triamino guanidinium (TAGNTO). Their thermal and $h_{50\%}$ data are listed in Table 3.

5-Amino-3-nitro-1,2,4-triazole (ANTA) has received a fair attention as a new insensitive high explosive. Its preparation [86] involves a four step process initiating from
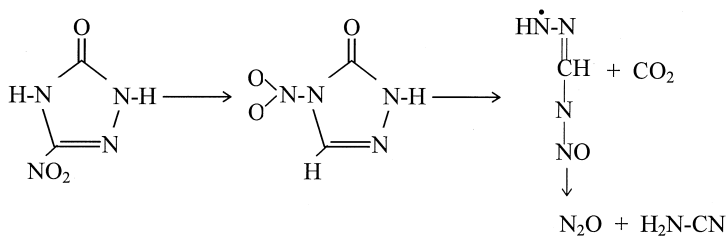
Scheme 5.
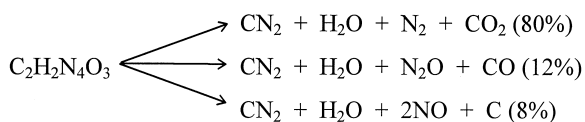
Scheme 6.

Scheme 7.

3,5-diamino-1,2,4-triazole. Fast thermolysis studies [87] on ANTA and NTO exhibit the formation of polymeric melone like cyclic azine residues. Thermal investigations by Gao et al. [88] on six related nitramino-1,2,4-triazole and nitraminotetrazoles, reveal that the nitramine position of the molecule initiates the degradation. Ring-substituted arylammonium salts of NTO (RSA NTOates, having el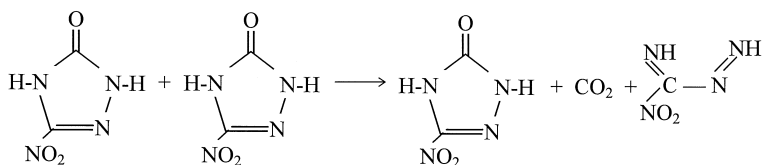ectron donating or attracting substituents) have been prepared, characterised and their thermolysis was also investigated in our laboratory [89,90]. These salts were prepared by treating hot aqueous solution of NTO with the solution of corresponding base. Thermolysis of RSA NTOates reveals that these salts undergo proton transfer to form amine and NTO prior to explosion (Scheme 8).

5.3. Six-membered ring compounds

The most important ring system of this class is pyridine, which also show explosive nature, depending upon its substituents. Trinitropyridine and its derivatives [91] namely: trinitropyridine-1-oxide (TNPyOx), 2,6-diazo-4-nitropyridine-1-oxide (DAzNPyOx), 2-methylnitramino-3,5-dinitropyridine (2-MNP), 4-methylnitramino-3,5-dinitropyridine (4-MNP), 2,6-bis(methylnitramino)-3,5-dinitropyridine (2,6-BMNP), dinitrodipicrylpyridine (PYX). Their density, OB and thermal data are compiled [92,93] in Table 4.

The synthesis and initial thermal characterisation of nitroderivatives of 3,5-dinitro-2,6-diaminopyridine have been carried out by Naixing et al. [94]. 2,6-Bis(picrylamino)-3,5-dinitropyrimidine (2,6-BPNP) has been synthesised [95] from 2,6-diaminopyridine and 2,4-dinitrofluorobenzene in isopropanol solution by heating at 50°C for 30 min and at 80°C for 3.5 h. To increase the density of 2,6-BPNP, replacement of nitro groups by benzofuroxano groups has also been suggested [96,97], since the introduction of aminoheterocycles in explosive molecule can result in increase of density and VOD and decrease of impact sensitivity. 1,3,5,5-Tetranitrohexahydropyrimidine (TNHHP) has

Table 3
Molecular weight, thermal and impact sensitivity data of NTO and its amine salts

NTO and its amine salts	Molecular weight	ΔH_f (kcal/mol)	DTA exotherm (°C)	Impact sensitivity $h_{50\%}$ (cm)
NTO	130	-14.3	236	280
ANTO	147	-66.1 ± 3.6	190	–
HNTO	162	-38 ± 5	170	92
ENTO	320	-112 ± 1.4	250	–
GNTO	189	-73 ± 3	260	–
AGNTO	204	$+42.5 \pm 2.3$	200	–
DAGNTO	219	-21 ± 2	190	252
TAGNTO	234	$+14 \pm 4$	170	103

RSA NTOate   Activated complex

Scheme 8.
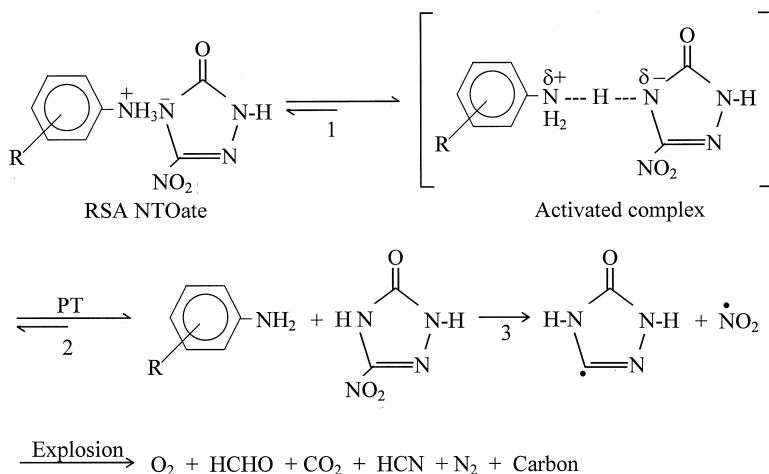
been prepared [98,99] as an oxygen rich energetic compound by the direct nitrolysis of 1,3-diisopropyl-5,5′-dinitrohexahydropyrimidine (I):
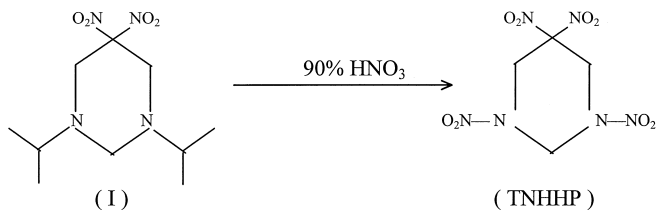
(I)   (TNHHP)

The thermolysis of TNHHP has been recently investigated by Brill et al. [100]. Ritter and Licht [101] have synthesised 1,3,5-trinitrohexahydropyrimidine (TNHP) by triple

Table 4
Density, OB and thermal data of six-membered, eight-membered and heterocyclic polynitro compounds

Compound	Density (g/cm^3)	OB	VOD	DTA exotherm (°C)	ΔH_f
TNPy	1.77	−37.4	8161	–	–
TNPyOx	1.86	−27.8	8369	–	–
DAzNOyOx	–	−57.6	8532	–	–
2-MNP	1.71	−55.9	7585	190	–
4-MNP	1.71	−55.9	7500	210	–
2,6-BMNP	1.73	−47.9	7700	190	–
TNHHP	1.80	–	8360	–	17.5
TNHP	1.78	−39.8	8020	155	–
NMHP	1.79	−27.0	8210	190	–
RDX	1.80	−21.6	8783	–	60.2
HND	1.88	−16.3	8800	–	−17.0
HMX	1.91	−21.6	9124	–	60.5

aminoalkylation of nitromethane with formaldehyde and *tert*-butylamine. TNHP on hydroxymethylation and subsequent nitration converted it to 5-nitroxymethyl-1,1′,3,5-tri-nitrohexahydropyrimidine (NMHP). TNHHP, TNHP and NMHP possess pronounced explosive properties (Table 4). The cleavage of N–N bond appears to be the thermolysis of TNHP [102]. After the initial cleavage of one of the nitramino group, the ring opens with the formation of $N=CH_2$ at one end and CH_2-CHO at the other (Scheme 9).

The most thoroughly studied system of triazine group is hexahydro-1,3,5-trinitro-1,3,5-triazine, which is commonly called RDX or cyclonite, which is a valuable high explosive (Table 4). RDX is obtained from hexamethylenetetramine by nitration with N_2O_5 in 100% HNO_3 at $-20°C$. It is a binary energetic molecule, in which more than one energy-rich sites exist [103–105].

Early studies [106–113] suggested that decomposition of RDX begins with N–N bond cleavage [114]. However, a mass spectrometric study has indicated the possibility of C–N bond scission mechanism. The recent studies [115–120] provide convincing evidence for N–N bond scission by the detection of N_2O_4 (dimer of NO_2) and the following mechanism has been proposed (Scheme 10).

Out of the three NO_2 groups in RDX molecule, one group is released as $NO_2(g)$ and other groups are converted into NO and N_2O. Maeros et al. [121] have studied the

Scheme 9.

NO_2

(RDX) $\longrightarrow$ (A) $\cdot NO_2$

(A) $\longrightarrow$ $\cdot CH_2$ — N ... N–NO + OH + HCN   (B)

(B) + OH $\longrightarrow$ N_2O + H_2O + HCN + NO + CH_2O
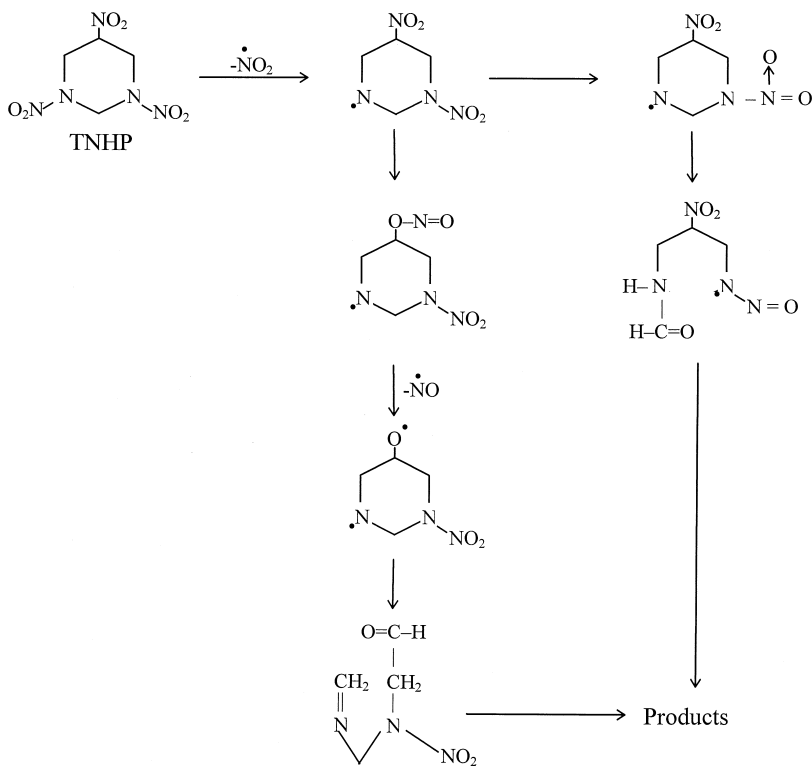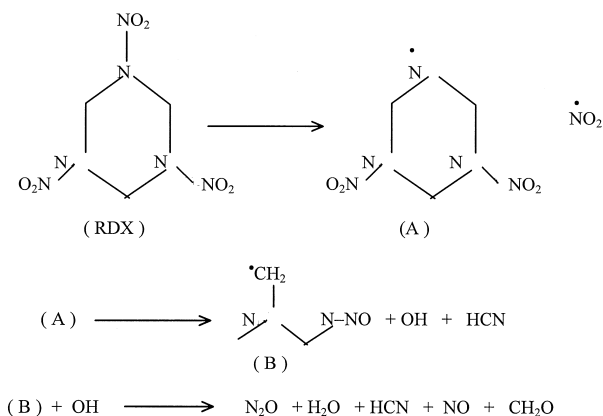
Scheme 10.

thermolysis of nitrosole and nitrosamine [122] derivatives of RDX. Ostmark et al. [123] have proposed the decomposition paths of two closely related compounds RDX and keto RDX (Schemes 11 and 12).

5.4. Eight-membered ring compounds

In recent years, a number of cyclooctane compounds containing two hetero (N) atoms (diazocines) have been synthesised as energetic oxidizers. Cichra and Adolph [124] have synthesised a series of polynitro and nitronitroso perhydro-1,5-diazocines. Franke et al. [125] have synthesised 1,3,3',5,7,7'-hexanitrooctahydro-1,5-diazocine (HND) and characterised by thermal techniques (Table 4). The replacement of N–NO_2 by N–NO decreases their impact sensitivity.

NO_2

RDX $\xrightarrow{-\dot{N}O_2}$ O_2N–N ... N–NO_2

+ HONO

+ $\dot{N}O_2$

$3CH_2 = N - NO_2$ $\nearrow$ H_2CO + N_2O $\searrow$ HCN + HONO
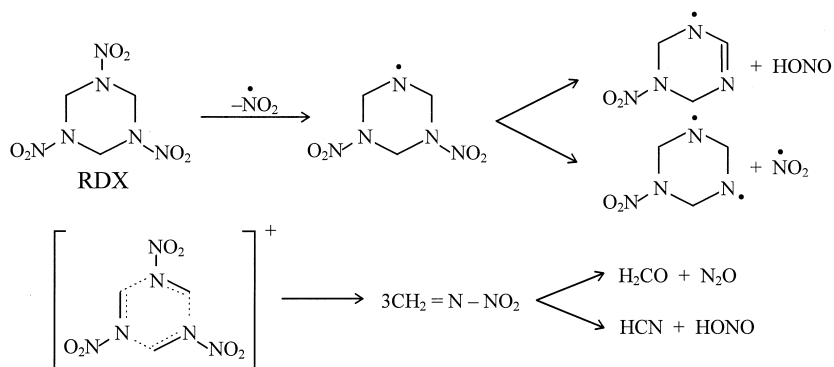
Scheme 11.

Scheme 12.
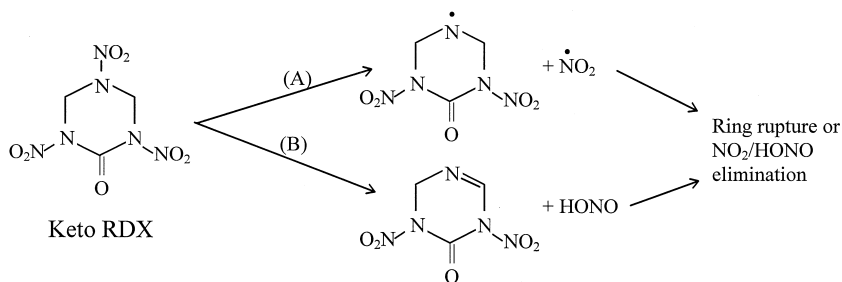
1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane commonly known as HMX (Table 4) has recently occupied a key position in the field of military high-energy propellants and explosives. At present, it is used as the major ingredient of smokeless double-base propellants. Zeman and Dimun [126,127] and Zeman et al. [128,129] have suggested a number of methods to synthesise HMX from 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetra-azacyclooctane by nitrolysis. The thermal behaviour of HMX has been investigated extensively. The early works indicated that the thermal degradation of HMX proceeds by the predominant breakage of C–N bonds and NO_2 is eliminated. Recent investigations [130–132] have shown that major part of the decomposition reactions of HMX occur in gas phase, which involves N–N bond rupture. However, the formation of NO_2 can be hardly detected, since NO_2 react quite rapidly with formaldehyde, which has been recognised as the major product of HMX decomposition. Kiumra and Kubota [133] suggested that HMX produces predominantly hydroxymethyl formamide as a non volatile product in homogeneous liquid phase decomposition (Scheme 13).

Oyumi and Brill [134] and Palopoli and Brill [135] revealed that CH_2O and N_2O are the main decomposition products at lower temperatures and HCN and NO_2 are formed at higher temperatures. Frankel and Woolery [136] have obtained 1-azidomethyl-3,5,7-trinitro-1,3,5,7-tetraazacyclooctane (AZTC) by replacing one NO_2 group of HMX by an azidomethyl (CH_2N_3) group. Thermal decomposition [137] of AZTC involves C–N bond cleavage with the formation of N_2O and CH_2O. Thermal decomposition pathways in RDX, HMX and other closely related cyclic nitramines has recently been reported [138].

6. Metal salts of nitro compounds

Metal salts of nitro compounds have long been of interest as energetic additives and/or as burning rate modifiers in composite solid rocket propellants and in explosive compositions. Recently, Rao et al. [139] have prepared Cu(II), Ag(I), Pb(II) salts of 2,4,N-trinitroanilinoacetic acid (2,4,N-TNAAA) and 2,4,6-trinitroanilino acetic acid (2,4,6-TNAAA). The order of thermal stability of salts of 2,4,N-TNAAA is reported to be Ag > Pb > Cu, while for salts of 2,4,6-TNAAA, it is Cu > Ag > Pb.

Metal salts of NTO [140] is currently receiving a fair attention. Yi et al. [141] have reported K, Cu and Pb salts of NTO and compared their heat resistance ability with the

HMX

$\downarrow$

$+ \ \overset{\bullet}{N}O_2 \ \cdots\cdots\rightarrow \ NO$

$O_2N-\overset{\bullet}{N}-CH_2-NH-CHO$
$+ \ NH + H_2CO$

$O = N \rightarrow O$

$H_2C = N$

$NNO \ + \ HO-\overset{\bullet}{C}-NH-C=O$
$\qquad\qquad\qquad | \qquad\quad |$
$\qquad\qquad\qquad H \qquad\quad H$

$H_2\overset{\bullet}{C} = O \ + \ NNO$

$\qquad\qquad H$
$\qquad\qquad |$
$HO-C-NH-C=O$
$\qquad | \qquad\qquad |$
$\qquad H \qquad\qquad H$
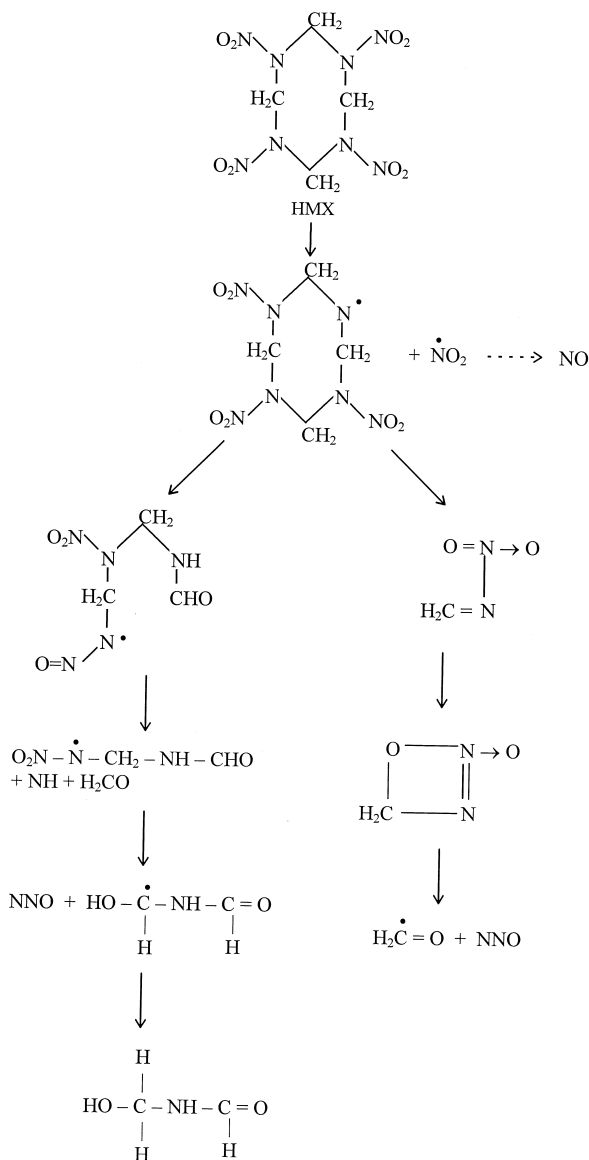
Scheme 13.

standard explosives in the order: HMX > NTO > KNTO > RDX > PETN > PbNTO > CuNTO. The alkali metal [142] (Li, Na and K) salt hydrates of NTO can be obtained by adding the corresponding metal hydroxide with aqueous solution of NTO at 40–60°C. The thermal stability of alkali metal salts of NTO has been found to be in the order. Li $(NTO) \cdot 2H_2O$ > $Na(NTO) \cdot H_2O$ > $K(NTO) \cdot H_2O$. Alkaline earth metal (Mg,Ca,Sr,Ba) and rare-earth metal (Pr,Nd,Sm) salts of NTO have also been prepared and characterised
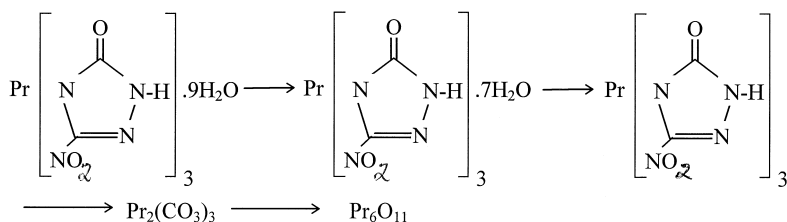
Scheme 14.

[143,144]. Alkaline earth metal salts can be prepared by the reaction of aqueous NTO and corresponding metal carbonate. The rare earth metal salts of NTO were prepared by the reaction of NTO with corresponding metal hydroxide. Thermal decomposition of these salt hydrates involve three steps: dehydration, exothermic decomposition of NTO ring and formation of metal oxide/carbonate. For instance, $Pr(NTO)_3 \cdot 9H_2O$ decomposes in the following manner (Scheme 14).

The transition metal salts of NTO $[M(NTO)_2$, M=Mn,Fe,Co,Ni,Cu or Zn] have proved to be better burning rate catalysts for AP/HTPB propellants [145]. These salts also catalyse the thermal decomposition of ammonium perchlorate (AP) and ammonium nitrate (AN) to greater extent.

Table 5
Decomposition temperature (T_d), impact ($h_{50\%}$), friction sensitivities, VOD, activation energy for explosion (E^*) and explosion temperature (ET) of nitrophenates of transition metals. MNP = Mononitrophenate, DNP = Dinitrophenate, TNP = Trinitrophenate.
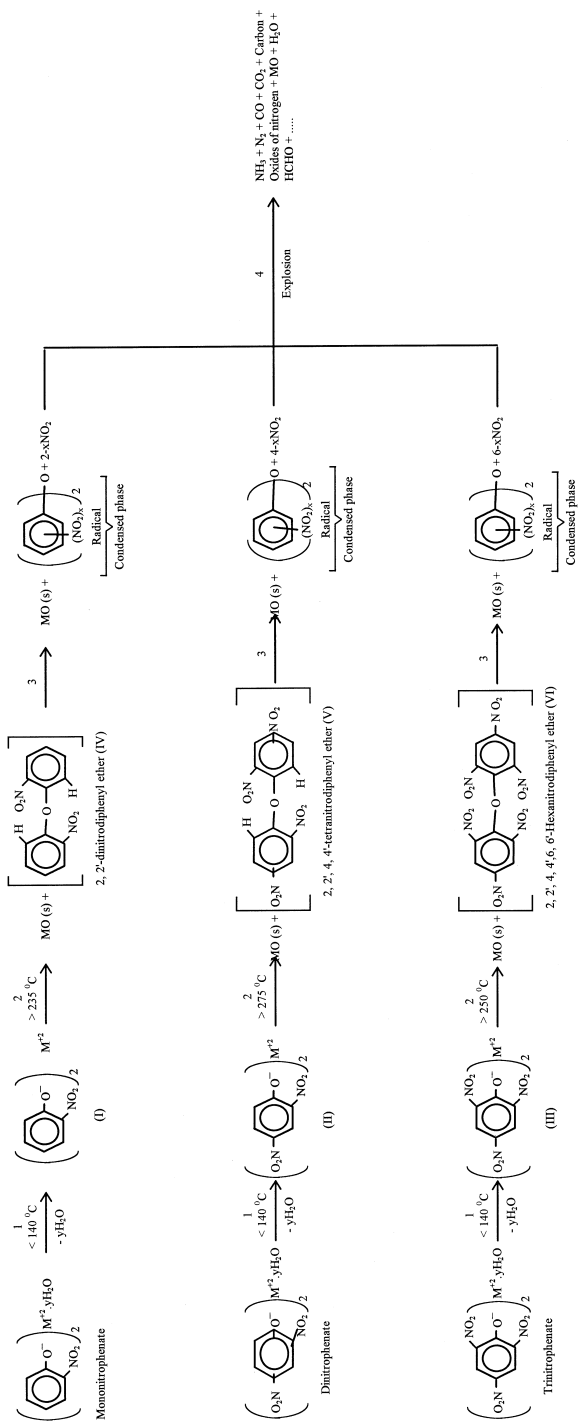
Compound	DTA peak temperature T_d (°C)	$h_{50\%}$ (cm)	Friction insensitive limit (kg)	VOD (ms^{-1})	Activation energy for explosion (E^*) (kJ mol^{-1})	ET for D_E of 10 s
Mn-MNP	331	180	36.0	4959	31.9	630
Mn-DNP	264	175	36.0	6399	28.7	594
Mn-TNP	295	145	25.2	7259	28.3	546
Fe-MNP	326	180	36.0	5001	31.8	645
Fe-DNP	292	176	36.0	6403	31.1	603
Fe-TNP	285	54	12.0	7313	30.9	561
Co-MNP	345	153	36.0	5032	32.0	648
Co-DNP	304	140	36.0	6418	30.7	618
Co-TNP	297	135	25.2	7320	29.3	580
Ni-MNP	341	130	36.0	5059	31.6	651
Ni-DNP	279	110	36.0	6416	25.1	609
Ni-TNP	291	85	28.8	7320	24.8	567
Cu-MNP	327	180	36.0	5080	31.8	666
Cu-DNP	298	158	36.0	6442	28.9	630
Cu-TNP	294	122	25.2	7331	27.0	591
Zn-MNP	334	162	36.0	5101	36.9	634
Zn-DNP	294	173	36.0	6452	34.1	600
Zn-TNP	324	180	36.0	7336	30.8	561

$NH_3 + N_2 + CO + CO_2 + Carbon + Oxides of nitrogen + MO + H_2O + HCHO + ...$

4
Explosion

Mononitrophenate

$\left(\begin{array}{c} O^- \\ NO_2 \end{array} \right) M^{+2} \cdot yH_2O \xrightarrow[-yH_2O]{1 \quad <140\ ^0C} \left(\begin{array}{c} O^- \\ NO_2 \end{array} \right)_2 M^{+2}$ (I) $\xrightarrow[>235\ ^0C]{2} MO\ (s) + \left[\begin{array}{c} H \quad O_2N \\ O \\ NO_2 \quad H \end{array} \right]$ 2, 2'-dinitrodiphenyl ether (IV)

$\xrightarrow{3} MO\ (s) + \left[\left(\begin{array}{c} (NO_2)_x \end{array} \right) O + 2 \times NO_2 \right]_2$ Radical Condensed phase

Dinitrophenate

$\left(\begin{array}{c} O^- \\ O_2N \quad NO_2 \end{array} \right) M^{+2} \cdot yH_2O \xrightarrow[-yH_2O]{1 \quad <140\ ^0C} \left(\begin{array}{c} O_2N \quad O^- \\ NO_2 \end{array} \right)_2 M^{+2}$ (II) $\xrightarrow[>275\ ^0C]{2} MO\ (s) + O_2N \left[\begin{array}{c} H \quad O_2N \\ O \\ NO_2 \quad H \end{array} \right]$ NO$_2$ 2, 2', 4, 4'-tetranitrodiphenyl ether (V)

$\xrightarrow{3} MO\ (s) + \left[\left(\begin{array}{c} (NO_2)_x \end{array} \right) O + 4 \times NO_2 \right]_2$ Radical Condensed phase

Trinitrophenate

$\left(\begin{array}{c} NO_2 \\ O_2N \quad O^- \\ NO_2 \end{array} \right) M^{+2} \cdot yH_2O \xrightarrow[-yH_2O]{1 \quad <140\ ^0C} \left(\begin{array}{c} NO_2 \\ O_2N \quad O^- \\ NO_2 \end{array} \right)_2 M^{+2}$ (III) $\xrightarrow[>250\ ^0C]{2} MO\ (s) + O_2N \left[\begin{array}{c} NO_2 \quad O_2N \\ O \\ NO_2 \quad NO_2 \end{array} \right]$ NO$_2$ 2, 2', 4, 4'6, 6'-Hexanitrodiphenyl ether (VI)

$\xrightarrow{3} MO\ (s) + \left[\left(\begin{array}{c} (NO_2)_x \end{array} \right) O + 6 \times NO_2 \right]_2$ Radical Condensed phase

x = 0-6
y = Number of water of crystallisation
s = solid

Scheme 15.

Metal picramates can be easily precipitated by adding a solution of sodium picramate to a solution of salt of the metals. Many workers [146–149] have studied the thermolysis of picramates of Fe, Co, Ni, Cu, Ag, Zn, Cd, Hg, Ti, Zr and Th. Explosive studies on benzylidene picramates of Fe, Co and Ni reveal that the thermal stability of these salts increases as the atomic radius of the metal decreases.

Metal salts of picric acid [Trinitrophenate (TNP)] may be formed by the action of picric acid on metals, their oxides, carbonates or hydroxides. The explosive properties of picrates of Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Ag, Cd, Ba, Hg, Tl and Pb have been examined by several authors [146–150]. Di- and mononitrophenols can also form metallic dinitrophenate (DNP) and mononitrophenate (MNP), respectively.

Recently, Singh et al. [151–153] have prepared mono-, di- and trinitrophenates of transition metals and followed their thermolysis by isothermal and non-isothermal TG, DTA, impact, friction measurements (Table 5). Explosion temperature (ET), activation energy for explosion (E^*) and $h_{50\%}$ have been found to be in the order: trinitro < dinitro < mononitrophenates of transition metals. Only trinitrophenates have been found to be friction sensitive. It has also been observed that all the nitrophenates undergo complete dehydration below 140° C (Scheme 15) to form anhydrous species I, II and III (confirmed by TG). The anhydrous species undergo transitory states IV, V and VI prior to explosion and gaseous products are formed.

7. Concluding remarks

The thermolysis of energetic compounds is a very complex process. The thermal decomposition of several polynitro organic compounds involve simple bond scission prior to explosion. A notable feature of these reactions is the fact that the aromatic ring remains intact. The next stage of thermolysis involves propagation reaction which involve exothermic oxidation/reduction reactions leading to the formation of low molecular weight and thermodynamically stable gaseous products. It has also been proved that dissociation of ring does not occur until most of the attached substituents are removed.
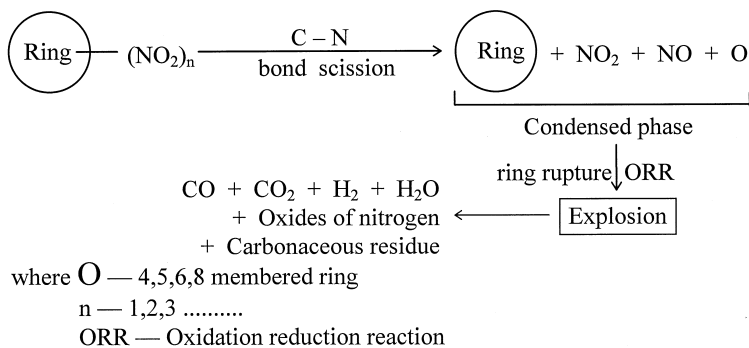
Scheme 16.

Generally, the thermolysis of polynitro aromatic compounds begins with one or more endothermic initiation steps. These steps involve C–NO$_2$ homolysis and NO$_2$ or NO are formed which attack the aromatic ring producing CO and CO$_2$. Thus, the overall unified thermolysis mechanism can be suggested in (Scheme 16).

The energy released during propagation reactions seems to cause explosion and gaseous products are formed.

Although much research on the thermolysis of polynitro organic compounds has been undertaken still a large void exists in several crucial areas such as:

(i) the kinetics and mechanism of specific reactions are extremely difficult to evaluate;

(ii) the thermolysis reactions are generally induced by thermal energy and role of pressure has not been investigated;

(iii) the isomerisation of –NO$_2$ to –ONO in condensed phase reactions is poorly understood.

Acknowledgements

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