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SPECTROSCOPIC AND THERMAL STUDIES ON 2,4,6-TRINITRO TOLUENE (TNT)

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Abstract

The kinetics and mechanism of the initial stage of thermal decomposition of 2,4,6-trinitro toluene (TNT), a widely used high explosive, have been studied, together with its morphology and evolved gaseous products using thermogravimetry (TG), differential thermal analysis (DTA), infrared spectroscopy (IR) and hot-stage microscopy. The kinetics of the thermolysis has been followed by IR after suppressing volatilisation by matrixing and by isothermal TG without suppressing volatilisation to simulate actual user conditions. The best linearity was obtained for Avrami-Erofeev equation for $n=1$ in isothermal IR and also in isothermal TG. The activation energy was found to be 135 kJ mol^{-1}, with log$A$ (in s^{-1}) 12.5 by IR. The effect of additives on the initial thermolysis of TNT has also been studied. Evolved gas analysis by IR showed that CO_2, NO_2, NO and H_2O are more dominant than N_2O, HCN and CO. The decomposition involves the initial rupture of the C–NO_2 bond, weakened by hydrogen bonding with the labile hydrogen atom of the adjacent CH_3 group, followed by the abstraction of the hydrogen atom of the methyl group by NO_2, generated in the initial step.

Keywords: IRS, kinetics, mechanism, nitro aromatic, TA

Introduction

2,4,6-trinitro toluene (TNT) owing to its good castability, high power and safety in handling is a widely used high explosive. Study of its thermal stability is important as regards its storage, safety and end use. Thermal decomposition of TNT has been studied by manometric measurement of evolved gas [1], time to explosion [2, 3], DTA and isothermal differential scanning calorimetry [4] and ESR [5]. Many discrete species have been identified as products of decomposition using column chromatography [6, 7].

In the decomposition of nitro compounds, in general, the influence of different types of nitro group has been found to depend primarily upon the energy of the bond linking the nitro group to the parent molecule and the reactivity of the products formed. The bond energy of different types of nitro groups determine

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the thermal stability of the respective nitro compounds. In addition, when the molecules are in the condensed phase in the presence of like molecules there arise more important reactions than in gas phase studies of individual molecules which make the determination of mechanism of decomposition, an extremely difficult task in the case of polynitro aromatics in heterogeneous condensed phase. Therefore the decomposition of C-nitro compounds is complex [8].

In the thermal analysis of TNT volatilisation sets in prior to decomposition making thermal decomposition kinetic study still more difficult. Recent studies have shown that volatilisation can be almost completely eliminated before the beginning of the decomposition by coating the TNT sample with fine grained alumina [9]. We have found that pelletisation of TNT in KBr matrix also suppresses volatilisation and thus make it possible to study the decomposition kinetics devoid of evaporation effect by TG and high temperature IR. This has in addition the advantage of minimising the intermolecular associations [10] operative in the bulk TNT complicating the decomposition pathways.

Also as a precise study of the kinetics of thermal decomposition is possible with respect to specific functional group in a molecule, by following the variation in the IR band intensity with time, high temperature IR spectroscopy [11, 12] has been used in conjuction with pyrolysis gas analysis, hot stage microscopy and iso TG, and also to detemine the structural changes in the thermal decomposition [13, 14] of TNT in the present study.

Experimental

Crude TNT to specification IND/ME/451 was obtained from Indian Ordnance Factory. It was purified by recrystallization from acetone solution. Crystals of TNT were grown by solvent evaporation technique. Elemental analysis was carried out using Perkin-Elmer 240C. TG-DTA and isothermal TG were carried out on a Netzsch STA 409 thermal analyser. The kinetics of decomposition was followed by isothermal mass change determination [12] using about 10 mg of sample in the temperature range 185 to 203°C in static air atmosphere. The stability of the temperature was within ±1°C. The temperature was so selected that the initial decomposition before reaching the desired temperature is negligible.

For kinetics [12, 15] by IR a ratio recording IR spectrophotometer Perkin-Elmer model 683, was used. The high temperature IR cell was fabricated in the Laboratory [12] and temperature programming was done using a Stanton-Redcroft universal temperature programmer having chromel-alumel thermocouple. The temperature remained constant during the experiment within ±1°C of the set temperature.

Spectroscopic grade KBr was used as the matrix material. Spectra of the sample in KBr were recorded in the frequency range 4000 to 200 cm^{-1} at the desired temperature at regular time intervals using medium speed of scanning. It was verified that the peak intensity of the band at 1350 cm^{-1} corresponding to NO_2

symmetric stretching vibration of C–NO_2 bond varied linearly with the amount of sample in the concentration range of 0.1 to 0.75% TNT in the KBr matrix.

A specially designed experimental set up and IR gas cell (14, 15) made of pyrex glass with KBr windows were used to study the gaseous phase composition during the thermal decomposition of TNT.

A Leitz-Orthoplan polarising microscope with hot stage attachment was used under dynamic heating conditions to observe the morphological sequence of the decomposition.

Results

Figure 1 shows simultaneous TG-DTA-DTG curves of TNT recorded at a heating rate of 10°C min^{-1} in nitrogen atmosphere. The reaction is a two stage process. It shows melting at 81°C and volatilisation before exothermic thermal decomposition. In thermogravimetry TNT decomposes in two clearcut stages. The first stage decomposition from 153 to 286°C is very steep and amounts to about 67% mass loss. This is followed by a sluggish second stage involving about 20% mass loss.

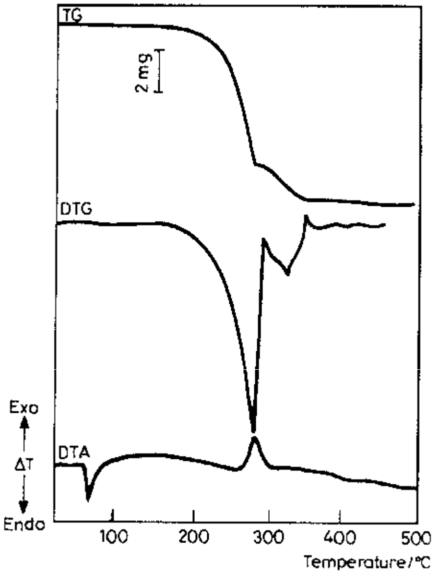


Fig. 1 TG-DTA-DTG curves of TNT. Sample: 10 mg; Reference: calcined alumina

Kinetics by IR spectroscopy

IR spectra of TNT in KBr matrix at room temperature and at desired elevated temperatures at regular intervals were recorded. Figure 2 represents the variation of band intensity for different groups with time at 208.5°C with progressive de-

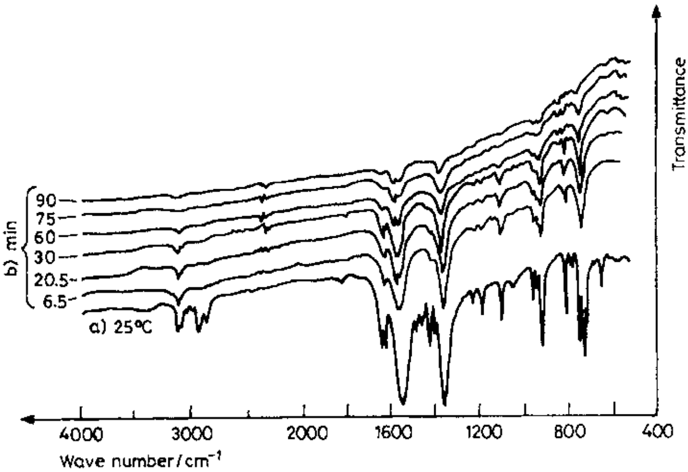


Fig. 2 IR spectra of TNT. a – at 25°C; b – at 208.5°C as a function of time

composition. Preferential loss in intensity of C–N band (1085 cm^{-1}), aliphatic –CH at 2840–2910 cm^{-1} and –NO$_2$ (1350 and 1530 cm^{-1}) during thermolysis are significant.

In IR the variation in intensity of –NO$_2$ symmetric stretching vibration at 1350 cm^{-1} was used to monitor the decomposition by KBr pellet method. For calculating the fraction of TNT decomposed, the peak absorbance after attaining the selected isothermal temperature was taken as the initial concentration. The value of α *vs.* t, thus obtained (Fig. 3) was analysed using various kinetic expressions [16–19]. α–t curves are characterised by long induction period at lower temperatures and are sigmoidal in nature. Long induction period also indicated that the volatilisation has been effectively suppressed. The induction period was how-

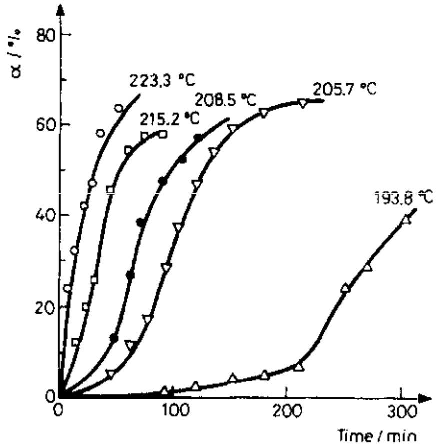


Fig. 3 α-t plot for the thermal decomposition of TNT(IR)

ever not that prominent at higher temperatures, which is characteristic of some metastable systems. α–t curve was found to fit the Prout-Tomkins' autocatalytic equation better at 193.8°C (Table 1). However, at higher temperatures the obedience to *A–E* equation, n=1, similar to pseudo first-order behaviour as reported by earlier workers was better. This type of kinetic obedience was interestingly also noted for nitromethane decomposition [20]. Table 1 gives the seven rate expressions which gave better correlation. The decomposition of TNT was found to be best described by Avram-Erofeev equation for n=1 in the first stage.

Kinetics by isothermal TG

Kinetics of decomposition of TNT without suppressing the volatilisation, which is de facto the condition under which it is actually used as a high explosive, have also been studied using isothermal thermogravimetry (Fig. 4). The basic difference in the α–t curve obtained after matrixing in IR where volatilisation is suppressed and in isoTG is the dominant induction period leading to sigmoidal α-t curve in IR method and the near absence of the induction stage in isoTG where volatilisation is not suppressed. Comparison of the DTA-TG data obtained where in volatilisation is not suppressed and the DTA-TG data reported after coating with Al_2O_3, by which volatilisation is suppressed, shows that the two stage thermal decomposition is common for both but for the slight loss due to volatilisation prior to decomposition in the TG of pure TNT without matrixing. Kinetics were obtained for the first stage from the isoTG data using the computerised method for various kinetic expressions as in IR method. Table 2 gives the seven rate equations which gave better correlation coefficient along with the rate parameters obtained.

A–E equation for n=1 gave the best fit. It is significant to note that these rate parameters are comparable to those obtained under conditions wherein volatilisation is suppressed. It is widely agreed that the overall process [2, 5] in the liquid phase is governed by a pseudo first-order rate expression, but autocatalysis and self-heating complicate the process.

Isothermal mass loss method was also used to study the thermal decomposition kinetics of TNT after matrixing in KBr to suppress evaporation. As the dilu-

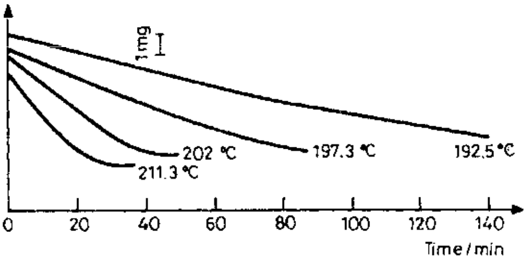


Fig. 4 Iso-TG curves for the thermal decomposition of TNT

Table 1 Correlation coefficient 'R' obtained for various $F(\alpha)$ and rate parameters by isothermal IR

No.	$F(\alpha)$	'R' isothermal temperature/°C					E/kJ mol^{-1}	log$A$/s^{-1}
		193.8	205.7	208.5	215.2	223.3		
1	$1-(1-\alpha)^{1/2}$	0.8297	0.9926	0.9746	0.9829	0.9833	121	10.6
2	$1-(1-\alpha)^{1/3}$	0.8276	0.9925	0.9781	0.9831	0.9839	125	11.0
3	$[-\ln(1-\alpha)]$	0.8235	0.9909	0.9841	0.9828	0.9836	135	12.5
4	$[-\ln(1-\alpha)]^{3/2}$	0.8636	0.9931	0.9669	0.9843	0.9832	105	9.3
5	$[-\ln(1-\alpha)]^{1/2}$	0.8857	0.9900	0.9544	0.9821	0.9806	90	7.6
6	$[-\ln(1-\alpha)]^{1/3}$	0.9082	0.9839	0.9393	0.9775	0.8439	74	5.7
7	$\ln[\alpha/(1-\alpha)]$	0.9438	0.9756	0.9225	0.9708	0.9734	52	4.2

tion required to efffectively suppress volatilisation was more than two hundred times the mass of the sample i.e. for about 10 mg of TNT the mass of the KBr pellet was of about 2 g automatic isothermal microthermogravimetry could not be used for the thermal decomposition study. Isothermal mass loss obtained by periodic weighing showed induction period as in the IR method. Detailed kinetics, however, was not attempted by this method because of its inherent limitations.

Effect of additives

Effect of additives on the kinetics of thermal decomposition of TNT, was studied using IR spectroscopy. IR spectra of pure TNT and TNT mixed with 10% additives in KBr matrix were recorded at 208.5°C at regular time intervals. The variation in intensity of $-NO_2$ symmetric stretching vibration at 1350 cm^{-1} was used to monitor the decomposition. α–t plots of pure TNT and TNT mixed with 10% carbamite, calcium carbonate and magnesium oxide at 208.5°C show that there is an accelerating effect by magnesium oxide on the initial stage of thermal decomposition of TNT, while carbamite and calcium carbonate show retarding effect on the accelerating and decay period of decomposition of TNT respectively. Similar results were obtained from the dynamic TG-DTA studies too on the effect of additives.

Analysis of evolved gas and solid residue by IR

It was difficult to study gaseous species evolved when TNT was decomposed at controlled heating rate of 5°C min^{-1} due to volatilisation of TNT. Therefore to suppress the volatilisation of TNT, alumina was mixed with TNT. Gaseous species evolved when TNT mixed with alumina was decomposed at controlled heating rate of 10°C min^{-1} were identified using IR spectroscopy, Fig. 5. From 180°C onwards gaseous species evolved were collected. It is seen from Fig. 5 that IR absorption bands due to CO_2 (2330–40 cm^{-1}), NO_2 (1630 cm^{-1}) and H_2O (1595 cm^{-1}) are no-

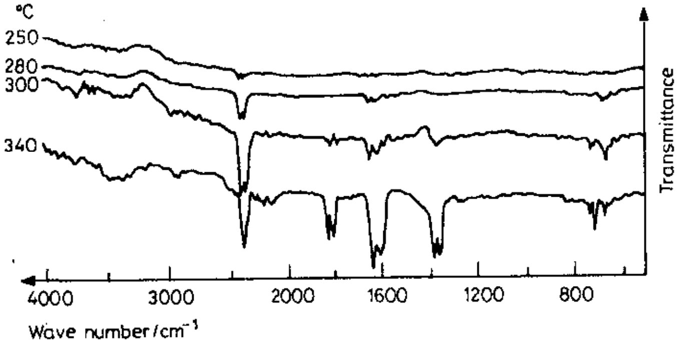


Fig. 5 IR spectra of the gaseous products formed in the decomposition of TNT as a function of temperature

Table 2 Correlation coefficient '*R*' obtained for various $F(\alpha)$ and rate parameters by isothermal TG

No.	$F(\alpha)$	'*R*' isothermal temperature/°C				E/kJ mol^{-1}	log$A$/s^{-1}
		192.5	197.3	202	211.3		
1	$1-(1-\alpha)^{1/2}$	0.9916	0.9968	0.9972	0.9833	154	14.8
2	$1-(1-\alpha)^{1/3}$	0.9952	0.9976	0.9962	0.9867	153	14.5
3	$[-\ln(1-\alpha)]$	0.9985	0.9967	0.9918	0.9916	150	14.8
4	$[-\ln(1-\alpha)]^{3/2}$	0.9857	0.9928	0.9976	0.9765	154	15.1
5	$[-\ln(1-\alpha)]^{1/2}$	0.9677	0.9798	0.9914	0.9613	155	15.2
6	$[-\ln(1-\alpha)]^{1/3}$	0.9402	0.9576	0.9781	0.9400	156	15.2
7	$\ln[\alpha/(1-\alpha)]$	0.9028	0.9196	0.9560	0.9110	154	15.8

ticed in the initial stage which increase in intensity at higher temperatures (280–340°C) and bands due N_2O (2220 and 1250 cm^{-1}), HCN (710 cm^{-1}) and CO (2100 cm^{-1}) are noticed in trace amounts even at higher temperatures i.e. (300–330°C). At higher temperature HCHO/NO (near 1800 cm^{-1}) has been noticed. Gas analysis was also carried out at the heating rate of 10°C min^{-1} and at isothermal temperatures, 232 and 312°C as a function of time. Results were found to be mutually corroborative.

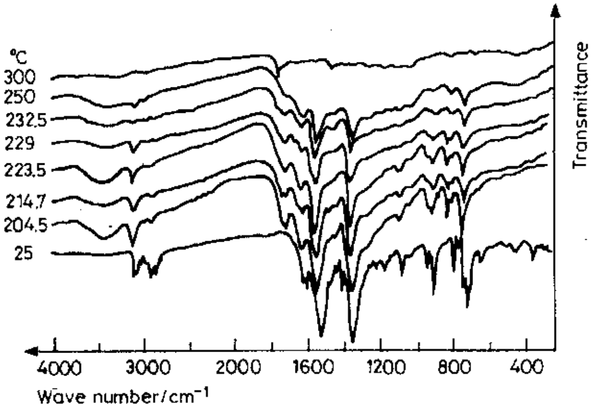


Fig. 6 IR spectra of the solid residue obtained in the thermolysis of TNT at different temperatures

IR spectra of the solid residues obtained in the thermal decomposition of TNT were recorded in KBr matrix to unravel the additional bands developed during the thermolysis and these are given in Fig. 6. Residues at 204–250°C showed additional bands at 3440 cm^{-1} (O–H), 1710 cm^{-1} (acid C=O), 1260 cm^{-1} (C–O) and 805 and 725 cm^{-1} (C–H out of plane deformation and benzene ring substitution). Residue at 300°C in addition also showed a band at 1740 cm^{-1} (aldehyde C=O). These additional bands were not conspicuous in the spectra recorded for the kinetic study by IR for the concentration of residue left behind in the pellet matrix was marginal.

Microscopic studies

Microscopic studies on the thermal decomposition of TNT under dynamic heating conditions (Fig. 7) reveal that TNT crystals gradually loose their transparency from outer surface to inner surface layer by layer. At about 80°C, melting sets in and rapid crystal movements are observed. After melting evolution of gases sets in and increases in intensity at localised points. Some of these points develop into pipe holes through which gaseous products bubble out. The number of these holes gradually increases when the whole crystal is consumed, a black charred residue is left behind.

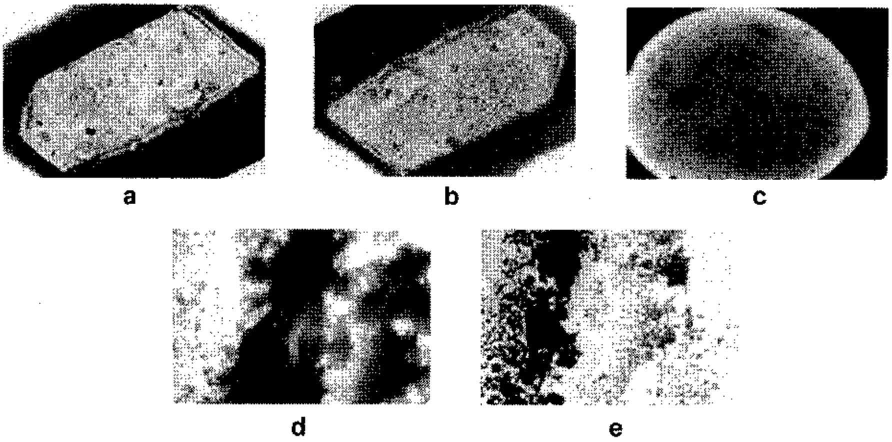


Fig. 7 Photomicrograph of TNT as a function of temperature. a – at 25°C; b – at 60°C; c – at 85°C; d – at 150°C; e – at 250°C

Discussion

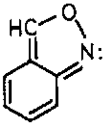
In TNT, three NO_2 and one CH_3 contributes to about 67% of the molecular weight. It is interesting to note here, that the first stage loss in TG, is also about 67%. The second stage involves about 20%. This means that the gaseous products are the main and constitute about 87%. Only the rest constitutes the condensed products.

Many compounds especially ones which can generate H· and other radicals were found to accelerate the rate of decomposition of TNT [2, 5, 6, 21–24]. TNT and most of its decomposition products produce radicals when heated and several of these products were found to catalyse the decomposition of TNT including elemental carbon. These facts suggest that TNT probably undergoes thermolysis through a free radical mechanism.

Intermolecular association and atom transfer have been proposed by Maksimov to be responsible for the accelerated rate of decomposition of TNT in the melt phase expressed as a first-order rate constant than in the gas phase or solution as against the converse observed in most energetic molecules like RDX, HMX [10].

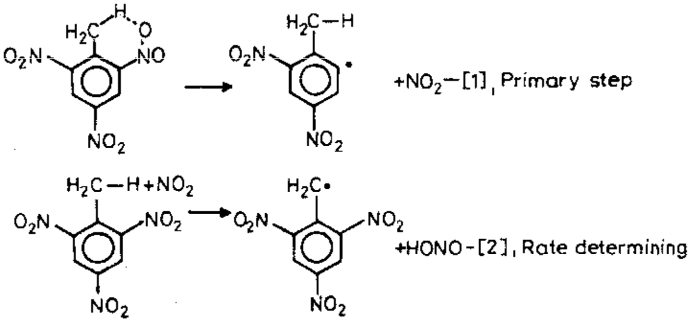
The hydrogen bonded network contributes to the relative weakening of the C–N bond as also observed in TATB [14] and thus makes the scission of the C–NO_2 bond more facile. The interaction of the nitro group and the labile α-hydrogen atom of the CH3 group through hydrogen bonding in TNT is postulated [6, 7, 22–28].

The trace level formation of 4,6-dinitroanthranil with the grouping



in the induction period, which was experimentally found to catalyse the TNT decomposition also substantiates such an initial interaction between $-CH_3$ and the closeby, NO_2 groups [7, 23].

Therefore we propose the following mode of decomposition.

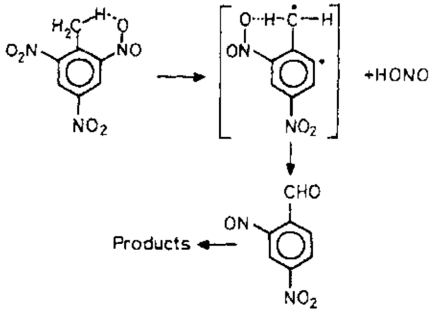


As NO_2 has marked affinity for the weakly bonded α-labile hydrogen atom in the CH_3 group than the ring hydrogen atom, reaction (2) is favoured. The formation of 2,4,6-trinitrobenzyl radical and protonated TNT radical wherein para nitro group picks up the hydrogen atom [28, 29] as immediate intermediate products is in conformity with the proposed reaction step (2). The primary step involves essentially the homolysis of the $C-NO_2$ bond. The known activation energy for this step is 250–280 kJ mol^{-1} when hydrogen bonding is not involved. The second step involving the abstraction of the hydrogen atom of the methyl group by the NO_2 generated in the primary step is expected to have an activation energy of 135 kJ mol^{-1}. The activation energy obtained experimentally is 135 kJ mol^{-1} and this suggests that step 2 would be the rate determining. Kinetic isotope effect [23] also indicates that step (2) is rate-determining. C–H bond rupture is also indicated by electron spin resonance investigations [22, 27].

It may be noted that 2–2', 4–4, 6–6' hexanitrobibenzyl (HNBB) which is related in its molecular structure to TNT, rupturing of the benzylic C–H bond has been found to be the rate controlling step [30]. After the initial scission of the weakest bond, the bond dissocation energy for the other bonds are considerably lower leading to additional radical disproportionation reaction [31]. A number of competitive and consecutive reactions are thus feasible leading to a variety of intermediate decomposition products which have been isolated in the thermolysis of TNT [6, 7, 23, 28, 29] like 2,4,6-trinitro benzaldehyde, 2,4,6-trinitrobenzoic acid, 4,6-dinitroanthranil, 2,4,6-trinitrobenzyl alcohol, dimeric reduction product of TNT containing bridging azo and azoxy linkage and 2,4-dintirotoluene (DNT).

These findings and the extra bands observed in the IR study of the residues at various temperatures (Fig. 6) are also consistent with the mode of decomposition proposed for TNT. The formation of polymeric residue in the decomposition and the fact that carbamite, a known chain breaker retarded the decomposition, supports the free radical chain mechanism as observed in other polynitroaromatic compounds.

Alternative initial reaction mechanism can be a five centered HONO elimination [32] as shown below:



This explains the formation of NO as well as aldehyde in the decomposition. Such a mechanism is more favoured in the vapour phase and becomes important when the decomposition occurs along with volatilisation as in the normal decomposition of TNT where volatilisation is not suppressed.

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