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Journal of Hazardous Materials A132 (2006) 165–170

Journal of Hazardous Materials

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Decomposition of some polynitro arenes initiated by heat and shock
Part I. 2,4,6-Trinitrotoluene

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Received 12 July 2005; received in revised form 11 August 2005; accepted 12 August 2005
Available online 28 November 2005

Abstract

Samples of 2,4,6-trinitrotoluene (TNT) exposed to heat or to shock and residues after their detonation have been analyzed chromatographically (LC-UV and LC/MS). It was found that the main identified decomposition intermediates are identical in all the three cases. 4,6-Dinitro-2,1-benzoisoxazole and 2,4,6-trinitrobenzaldehyde are the most reactive from them. It has been stated that the chemical micro-mechanism of the primary fragmentations of shock-exposed TNT molecules and/or its detonation transformation should be the same as in the case of its low-temperature thermal decomposition.

Keywords: Chromatography; Detonation; 4,6-Dinitro-2,1-benzoisoxazole; Initiation; Thermal decomposition; 2,4,6-Trinitrotoluene

1. Introduction

The homolytic fragmentations or reactions of the C–NO_2, N–NO_2, N–NO and O–NO_2 groupings, or other bearers of explosiveness (i.e. explosophores), are common primary fission processes of energetic materials under thermal, impact, shock and electric spark stimuli (for all, see Refs. [1,2] and references herein). Therefore, it is natural that there are relationships between characteristics of low-temperature thermal decomposition and impact or electric spark sensitivities and also detonation characteristics of polynitro compounds (Refs. [1,2] and references herein).

From what has been said so far it follows that chemical micro-mechanism of the primary fragmentations of explosive molecules in all the above-mentioned stimuli should be the same as in the case of their low-temperature thermal decomposition. This similarity or identity is dealt with in numerous papers (Refs. [1,2] and references herein). In the case of initiation of detonation, the said identity is confirmed by some striking pieces of experimental evidence [1,2]. On the basis of deuterium kinetic isotope effect (DKIE) it was proved [3,4] that the rate-limiting step of the thermal decomposition of 2,4,6-trinitrotoluene (TNT) in the condensed state and that of the initiation of its detonation are identical. Recently, it has been found that the main identified intermediates of both the TNT decompositions by heat and shock are identical [5]. The identity is also reflected in a relationship between the kinetics of the low-temperature thermal decomposition of the energetic materials and reaction rates in the reaction zone of their detonation [6,7].

The above-mentioned listing is by far not complete, also polyamino-trinitrobenzenes are an exquisite example of the said identity (see Refs. [1,8] and references herein), but their case will be dealt with in another part of this series. In this part, attention is paid again to not only the TNT decomposition intermediates from the point of view of influence of the instrumentation arrangement of heat and shock on it, but also to main condensed products of its detonation (with the exception of carbon particles). For this purpose, forensic methods of analysis were applied.

2. Experimental

2.1. Collecting of samples

The exposition of TNT to a shock wave was realized by means of the small-scale gap test [9]. The donor charges (pentaerythritol tetranitrate, i.e. PETN, with 10 wt.% wax and 1,3,5-trinitro-

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doi:10.1016/j.jhazmat.2005.08.048

1,3,5-triazinane, i.e. RDX with 5% wax) were separated from the acceptor TNT charge by a polymethylmethacrylate (PMMA) barrier of such a thickness that the intensity of the resulting shock wave was at the limit, or below and above, of initiation ability of TNT samples. The system in such arrangement was placed on a reference plate made of stainless steel, its thickness being 2 mm and dimensions 12 cm × 12 cm. After firing, the residues of explosive remained trapped upon this plate. They were collected by rinsing the plate in a crystallization dish with 100 ml methanol. The extractions were carried out in dark overnight. After the extraction, soot and other mechanical impurities were removed by filtration, and the filtrates were concentrated in a stream of nitrogen to a volume of ca. 5 ml and investigated by means of the LC-UV and LC/MS techniques.

We used a DTA 550-Rez apparatus [10] (specially developed at our Institute for the purpose of differential thermal analysis of explosives) for thermal exposition of TNT. The measurement was carried out with the amount of 50 mg TNT, the heating being interrupted at 290, 300 and 316 °C by taking the test tube with TNT out of the apparatus. An abrupt cooling of the exposed sample was achieved by immersion in a beaker with water performed in such a way as to avoid a contact of the sample with the cooling water. After that, the samples were extracted with methanol (25 ml). The extracts were filtered and concentrated to a volume of ca. 2 ml and submitted to the LC-UV and LC/MS analyses.

Methanol was chosen for effective extraction of TNT residues with regard to their good solubility in it. This extraction agent is also well compatible with the mobile phase (methanol–water) used in the LC-UV and LC/MS analyses. Although the solubility of the monitored analytes in methanol is lower than that in acetone (which is considered an universal solvent for organic explosives [11]), it nevertheless is connected with more selective extraction [12,13].

2.2. LC-UV analysis of organic extracts

The liquid chromatography was realized by means of the LC-10AS Shimadzu Liquid Chromatograph coupled with the SPD-10A UV–vis detector. As it was impossible to measure separately the UV spectra of each compound, the wavelength of 226 nm was chosen for the detection, which was previously evaluated as a versatile wavelength for analyses of the investigated decomposition products. A mixture of methanol and water (1:1) was used as the mobile phase, its flow rate being adjusted at 0.6 ml/min. The measurements were performed in a column LiChrospher 100 RP-18, 250 mm; grain size 5 μm. The LC-UV chromatograms of thermally and shock-exposed TNT are shown in Figs. 1 and 2. The results of trace analysis of the residues after detonation of TNT are presented in Fig. 3.

The qualitative analysis by means of LC-UV consisted in comparison of the retention times of the components of mixtures being separated with those of the chosen standards, i.e. 1,3,5-trinitrobenzene (TNB), 2,4,6-trinitrobenzyl alcohol (TNBAlc), 2,4,6-trinitrobenzaldehyde (TNBAld), 2,4,6-trinitrobenzoic acid (TNBA), 4,6-dinitro-2,1-benzoisoxazole (4,6-dinitroanthranil, DNAt) and 2,4,6-trinitrotoluene.

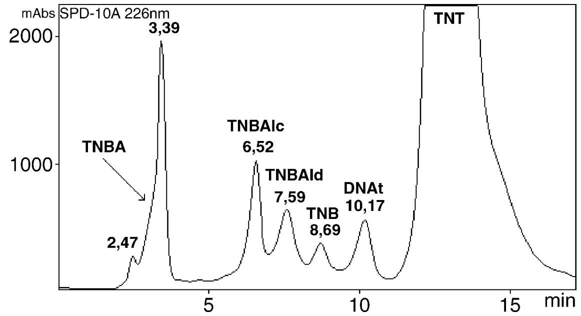


Fig. 1. LC-UV chromatogram of thermally exposed TNT at 316 °C.

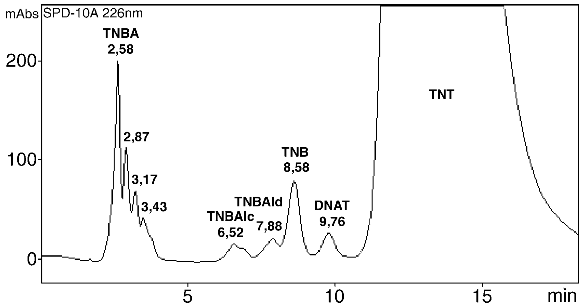


Fig. 2. LC-UV chromatogram of shock-exposed TNT at the limit of its initiation ability.

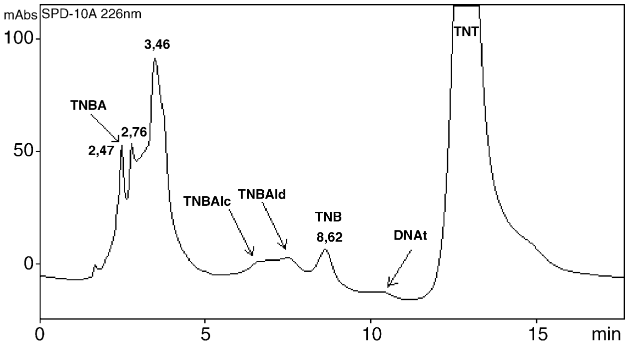


Fig. 3. LC-UV chromatogram of residues after the TNT detonation.

Chromatographic conditions:

Column	LiChrospher 100 RP-18, 250 mm, grain size 5 μm
Mobile phase	Methanol/water(50:50 (v/v) with addition of ammonium chloride and formic acid
Flow rate	0.6 ml/min
Injection volume	20 μl

2.3. LC/MS analysis of organic extracts

All the analyses were performed by means of Agilent 1100 series LC–MSD system with the atmospheric pressure chemical ionization (APCI) source, in the negative-ion mode. The used chromatographic and mass spectrometric conditions are shown below.

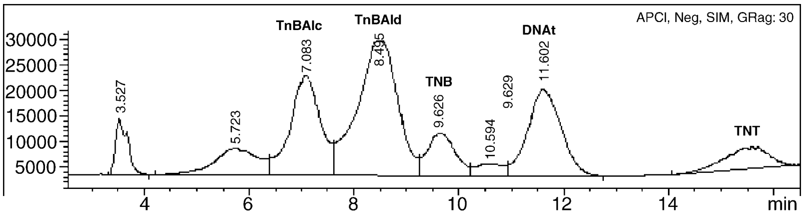


Fig. 4. LC-APCI/MS chromatogram of thermally exposed TNT at 316 °C.

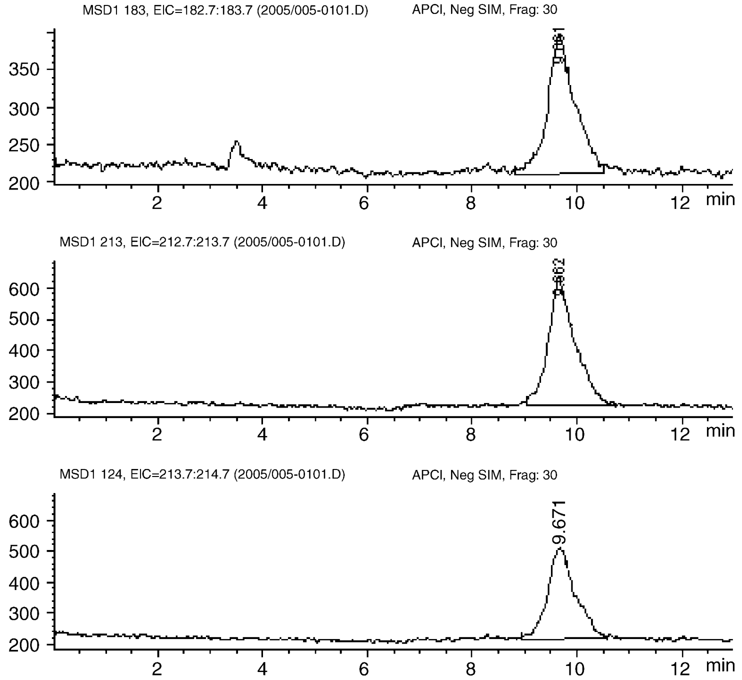


Fig. 5. The major ions of TNB at *m*/*z* 183, 213 and 214 in shock-exposed TNT at its limit of initiation ability.

MS conditions:

Source: APCI
Mode: SCAN and SIM
Ionization polarity: negative
Capillary voltage: 3000 V
Nebulizer: 60 psi

Vaporizer temperature: 300 °C
Dry gas flow: 5 l/min
Drying gas temperature: 330 °C
Fragmentor: 30 V

The stock solutions of individual explosives (TNB, TNBAld, TNBA, TNBAlc, DNAt and TNT) were prepared also in methanol p.a. Standard mixtures were prepared by diluting the stock solution to a final concentration as necessary.

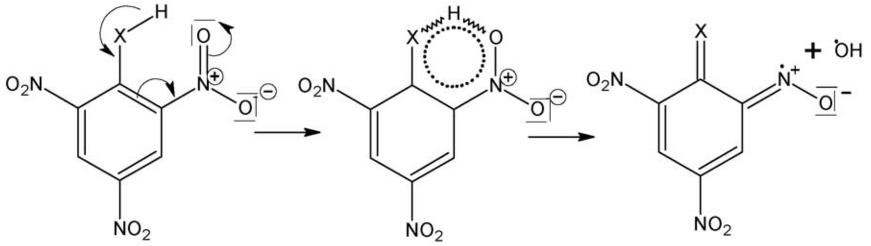
First the scan negative-ion APCI mass spectra of all explosives were measured in order to find out their major ions. Then, the selected ion monitoring (SIM) method for decomposition products of TNT was used. In the SIM mode, at least three dominant ions of each substance were measured. The corresponding chromatograms are presented in Figs. 4 and 5.

The following ions (*m*/*z*) were considered in SIM analysis of the TNT decomposition products: DNAt 164, 209 and 388; TNB 183, 213 and 214; TNBAld 183, 200, 211, 214 and 241; TNBA 183, 213, 214, 425 and 426; TNBAlc 183, 213 and 214; TNT 197, 226 and 227. The identification consisted in comparing the retention times and characteristic mass spectra of unknown components with those of standards. The absence of TNBA from the record (Fig. 4) can be interpreted by its decarboxylation giving TNB [14] due to the high temperature of ionization (300 °C) and, at the same time, due to the low concentration of TNBA in the residue. The fragmentations of TNB, TNBAld, TNBAlc and TNBA are practically identical, which is why these analytes have common ions at 183, 213 and 214.

The LC–APCI/MS analysis of the TNT decomposition induced by shock wave only proved TNB reliably (Fig. 5); other components were not recorded due to their low concentrations in the residues and, at the same time, due to the detection limits of this analysis. The analytes investigated did not form any adduct ions with the mobile phase added; the mass spectra of these compounds mainly contained the molecular and fragment ions.

3. Results and discussion

Dacons et al. [15] analyzed a TNT sample that was exposed to 200 °C for the duration of 16 h, and found that beside polymeric decomposition products it contained 4,6-dinitro-2,1-benzoisoxazole (4,6-dinitroanthranil, DNAt), 2,4,6-



Scheme 1. Trinitrotoluene mechanism of thermal decomposition of polynitro arenes with hydrogen atom in γ – position towards the nitro group – here *X* can be CH, CH_2, O, N or S; in the case of TNT, the last fragment forms 4,6-dinitro-2,1-benzoisoxazole and other decomposition products.

trinitrobenzaldehyde (TNAld) and 2,4,6-trinitrobenzyl alcohol (TNBAlc). The content of DNAt predominated. Rogers found also 1,3,5-trinitrobenzene (TNB) and 2,4,6-trintrobenzoic acid (TNBA) [16] in non-isothermally exposed TNT. At experimental conditions of thermal exposition of technical TNT, and subsequent chromatographic analysis described in paper [5], the presence of TNBAld, TNB and DNAt was reliably proved. DNAt is a TNT thermolysis intermediate formed by the so-called trinitrotoluene mechanism [17–19] (in general, see Scheme 1). TNAld, TNBAlc, TNBA and TNB are products of subsequent reactions of methyl group in TNT with hydroxyl radicals and/or with nitrogen oxides [8] (with decarboxylation of TNBA to TNB).

For the first time, a shock-exposed TNT was analytically described in paper [5]. The corresponding chromatographic record incorporated the same main characteristic peaks as in the case of thermally exposed TNT [5] (i.e. DNAt, TNBAld, TNB and TNT); only the DNAt content was higher here.

Our new analytical results of thermally exposed TNT (see Fig. 1) agree with findings by Rogers [16]. However, the peak of TNBA in Fig. 1 is considerably overlapped by a peak of unidentified product of TNT decomposition. Therefore, it was impossible to estimate the content of this acid in the extract of residue.

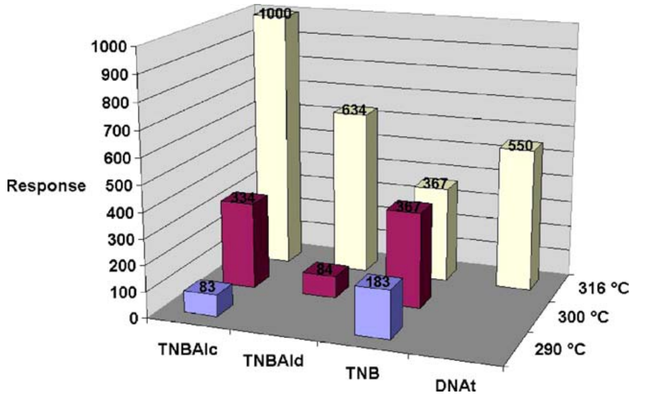
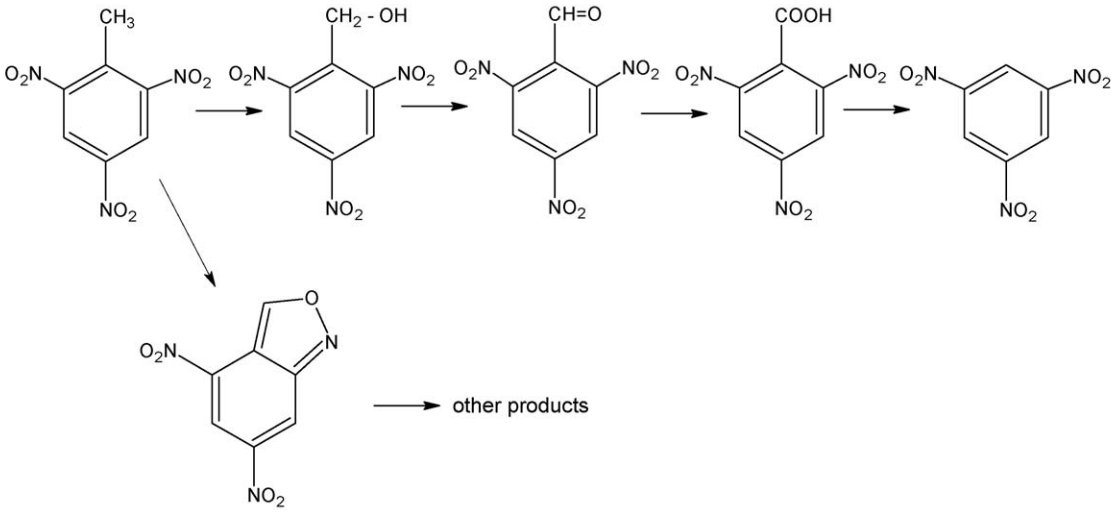


Fig. 6. Comparison of products of the thermal decomposition of TNT at various temperatures.

An interesting finding concerns the development of content of intermediates of thermal decomposition in thermally exposed TNT depending on the temperature of this decomposition (see Fig. 6, here TNAB is missing, which is due to the already mentioned overlapping of TNBA peak in Fig. 1). The primary intermediate, i.e. DNAt, can be analytically proved in decomposition residues only at the decomposition temperatures above 300 °C. It was observed that DNAt has a strong catalytic effect upon the thermal decomposition of TNT [20]. With regard to the reactivity order of methyl group in the sense of Scheme 2, it follows from Fig. 6 that DNAt and TNBAld are the most reactive intermediates of thermal decomposition of TNT. Up to the temperatures of 300 °C, the reaction rate of formation of these intermediates should not exceed the reaction rate of their consumption in subsequent reactions. The temperature



Scheme 2. The sequence of intermediates corresponding to methyl group reactivity in the thermal decomposition of TNT.

of 316 °C turned out to be the limit at the given experimental conditions—at this temperature the investigated TNT sample underwent explosive decomposition.

Fig. 2 represents the LC-UV chromatogram of the shock wave-exposed TNT (at the limit of its initiation ability). It need not be stressed that this chromatogram is similar to that of thermally exposed TNT (i.e. Fig. 1) as far as the peaks of main analytes are concerned. All the analytes identified were also present in the TNT samples exposed to lower initiation pressures.

The analysis of TNT detonation residues (after complete detonation of its charge) gave the LC-UV chromatogram presented in Fig. 3. This method of forensic analysis highly reliably proved the presence of TNT, TNB and TNBA, and it also distinctly indicated the presence of DNAt, TNBAlc and TNBAld in the residues mentioned.

Inspection of Figs. 1–3 also reveals significant variation in the proportion of the various products depending on the method adopted to start decomposition. It is logical because the fragments of the primary homolysis and/or products of subsequent reactions, can attack the neighboring unchanged molecules (intermolecular redox processes in thermal decomposition of polynitro arenes were documented by means of the ESR spectroscopy [21]), and can enter into various reactions with each other; such chemical interactions depend very strongly upon temperature and pressure.

DNAt and other intermediates in Fig. 1 are products of thermal decomposition of TNT. However, in the case of shock wave-exposed TNT or its detonation, their formation cannot be interpreted as resulting from the action of heat. Many recent papers have dealt with this and related problems in energetic materials (for example, [22–30]). An idea about the initiation of detonation reads as follows: the excitation of crystal lattice vibration (phonons) after receiving impact or shock [23,27,28] is converted into bond stretching frequencies (vibrons) with subsequent spontaneous localization of vibrational energy in the nitro (explosophore) groupings [23,24]. Similar, but more detailed, description of this initiation is presented in another idea about electronic excitations facilitated by edge dislocations in explosive solids, which was obtained from application of physics of the solid state aspect to the study of pre-explosion state of heavy metal azides [29,30] and 1,3,5-trinitro-1,3,5-triazinane (RDX; see Ref. [29] and references herein).

The results of this paper thus mean that the primary fission processes in low-temperature thermal decomposition (i.e. in the range up to 600 K) of TNT and polynitro compounds in general, should be identical with those in the detonation initiation and transformation of these compounds. This statement, accompanied by quite a number of other pieces of evidence, is also dealt with in our recent or new papers [1,2,5,8,31,32] and excellently corresponds to the experimental results obtained by Bulusu et al. [3,4].

From the point of view of a practice of the forensic science, a mutual comparison of chromatograms of the Figs. 2 and 3 type might be interesting for evaluation of deflagration or full detonation of TNT charges from residues after their explosion transformation.

4. Conclusion

The main identified intermediates of the decomposition of TNT by shock and heat are identical. 4,6-Dinitro-2,1-benzoisoxazole and 2,4,6-trinitrobenzaldehyde are the most reactive from them. The first finding excellently agrees with the experimental results obtained by Bulusu et al. [3,4] in the field of application of DKIE to study of initiation of TNT. Our results as well as those by Bulusu signalize that the chemical micromechanism of the primary fragmentations of shock-exposed TNT molecules and/or its detonation transformation should be the same as in the case of their low-temperature thermal decomposition.

Acknowledgements

The authors express their gratitude to the management of the Institute of Criminology of Police Forces of the Slovak Republic in Bratislava for enabling and supporting of realization of the analytic part of this study in the Institute.

The work was carried out under the auspices of the Ministry of Education, Youth & Sports of the Czech Republic as a part of its Research project no. MSM 0021627501.

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