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## Decomposition of TNT by Heat and Shock

Martin Kouba, Svatopluk Zeman, Eva Zemanová

(Department of Theory & Technology of Explosives, University of Pardubice, CZ-532 10 Pardubice, Czech Republic)

**Abstract:** Samples of technical TNT exposed to heat or to shock have been analyzed by means of high performance liquid chromatography (HPLC). It was found that the main decomposition products are identical in the two cases. It has been stated that the chemical micro-mechanism of the primary fragmentations of shocked TNT molecules should be the same as in the case of their low-temperature thermal decomposition.

**Key words:** analytical chemistry; TNT; shock; thermal decomposition; HPLC

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### 1 Introduction

On the basis of deuterium kinetic isotope effect (DKIE) it was proved<sup>[1,2]</sup> that the rate-limiting step for the thermal decomposition of 2, 4, 6-trinitrotoluene (TNT) in the condensed state and that for the initiation of its detonation are identical. This common rate-limiting step of thermal and detonation decomposition of TNT<sup>[1,2]</sup> made us presume the identity of the main products of incomplete thermal and detonation decomposition of the said explosive. The present paper deals with confirming this presumption using samples of shock- and heat-exposed TNT and liquid chromatography as the detection method.

### 2 Experimental

The exposition of TNT to a shock wave was realized by means of the small-scale gap test<sup>[3,4]</sup>. The donor charges (PETN with 10% wt. wax and RDX with 5% wt. wax) were separated from the acceptor TNT charge by a PMMA barrier of such a thickness that the intensity of the resulting shock wave were at the limit of initiation ability of TNT. The set prepared in this way was put into a round paper box serving for catching the TNT residues after its detonation. Then these residues were transferred in a crystallization dish, and 300 ml distilled water was added thereto. After the extraction, the solid explosion residua were removed by filtration, and the filtrate was subject to

analytical detection by means of HPLC.

The thermal exposition of TNT sample was realized by means of a self-developed<sup>[5]</sup> apparatus for differential thermal analysis DTA 550-Rez. At first, the measurement was carried out with the amount of 200 mg TNT, the heating being interrupted at 318 °C by taking the test tube with TNT out of the apparatus. Then the second exposition was carried out with an amount of 500 mg TNT, the sample being taken out of the apparatus at the temperature of 315 °C. An abrupt cooling of the exposed samples was achieved in a crystallization dish with 150 ml or 300 ml distilled water respectively. The subsequent extraction was carried out in dark overnight. The aqueous extract was analyzed by means of liquid chromatography.

The choice of water as the extraction agent for residues of exposed TNT samples was not random. It represents an application of a new efficient procedure for collecting after-explosion residua in criminology<sup>[6,7]</sup>. Water, which was used as the solvent, does not form any peak in the resulting chromatogram, which simplifies the determination of the TNT decomposition products (acetone produces a large response in the chromatogram which can overlap some important peaks).

The liquid chromatography was realized on an older computerized apparatus LCD 2040 (Laboratorní pístroje, Prague). As it was not possible to measure separately the UV spectra of each compound, the wavelength of 225 nm was chosen for the detection, which was previously evaluated as a versatile wavelength for analyses of the most

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common explosives. A mixture of acetonitrile and water 1 : 1 (v/v) was used as the mobile phase, its flow rate being adjusted at  $1.2 \text{ ml} \cdot \text{min}^{-1}$ . The measurements adopted a Biospher C18 column PSI 200, grain size  $7 \mu\text{m}$ . The pressure at the column was 10 MPa, the air humidity was about 40% and room temperature was  $25 \text{ }^\circ\text{C}$ . The resulting chromatograms are presented in Figs. 1 and 2.

The resulting values of retention time on chromatogram were compared with those of standards, see 2,4- and 2,6-dinitrotoluenes (DNT), 4,6-dinitroanthranil (DNAt), 2,4,6-trinitrobenzaldehyde (TNBz), 2,4,6-trinitrobenzoic acid (TNBA), TNT and 1,3,5-trinitrobenzene (TNB).

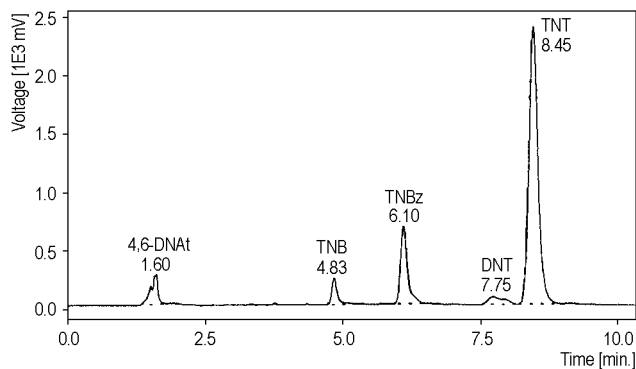


Fig. 1 A chromatogram (Biospher C18 column, PSI 200) of thermally exposed TNT

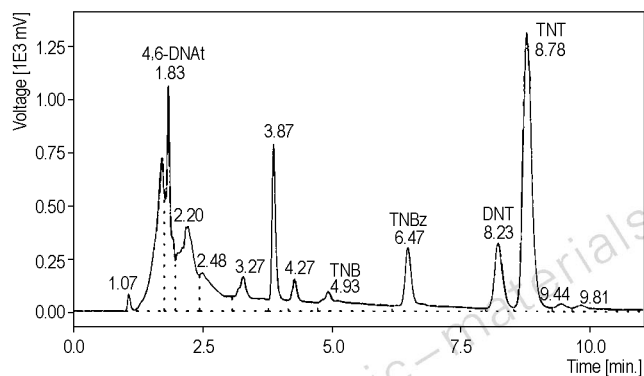


Fig. 2 A chromatogram (Biospher C18 column, PSI 200) of shock-exposed TNT

### 3 Results and discussion

Dacons et al.<sup>[8]</sup> analyzed a TNT sample that was exposed to  $200 \text{ }^\circ\text{C}$  16 h, and found that beside polymeric decomposition products it contained 4,6-dinitroanthranil (DNAt), TNBz and 2,4,6-trinitrobenzyl alcohol (TNBoI). The content of DNAt predominated. Rogers found also TNB and TNBA<sup>[9]</sup> in non-isothermally exposed TNT. At

our experimental conditions of thermal exposition of technical TNT and subsequent chromatographic analysis we have so far safely identified TNBz, TNB and DNAt (see Fig. 1). DNT was already present in the starting TNT. DNAt is a TNT thermolysis product formed by the so-called trinitrotoluene mechanism<sup>[10,11]</sup>. TNBz and TNB are products of oxidation of methyl group in TNT by nitrogen oxides<sup>[11]</sup>.

Shock-exposed TNT has not yet been described analytically. The chromatographic record is shown in Fig. 2. It can be seen that the substances present in Fig. 1 are also present in Fig. 2. It must be pointed out that amount of DNAt is higher in Fig. 2 than in Fig. 1. In near future we are going to deal with identification of the remaining peaks (they can come from residues of donor charges, too).

DNAt, TNBz and TNB in Fig. 1 are products of thermal decomposition of TNT. However, in the case of shock-wave-exposed TNT their formation cannot be interpreted as resulting from action of heat. The ideas about fragmentation of energetic materials by shock can be presented as follows<sup>[11,12]</sup>: The influence of shock on energetic materials results in adiabatic compression of the molecular layer struck. According to Klimenko and Dremmin<sup>[13-16]</sup>, the kinetic energy of the shock in this compression is accumulated, through translational-vibrational relaxation processes, by translational and vibrational modes of molecular crystals of the material within  $10^{-13}$  to  $10^{-12}$  seconds. This causes a considerable quasi-overheating ( $20\ 000$  to  $40\ 000 \text{ K}$ <sup>[15,16]</sup>) especially of vibrational modes. A non-equilibrium state is established with concomitant primary fission of the energetic material into ions and radicals. Chemical reactions of these active particles cause the shock front to spread and evoke a second equilibrium stage of detonation behind the front. This or similar ideas of transformation of low-frequency vibrations of crystal lattice (acoustic phonons) into high-frequency vibrations (vibrons), with subsequent spontaneous localization of vibrational energy in the explosivesophore groupings<sup>[17,18]</sup>, have been applied by a number of authors in their studies of shock reactivity of energetic materials (see Refs.<sup>[17,18]</sup>). The production of primary fragments after a weak stimulus (shock) is insufficient for formation

of a second equilibrium stage and the detonation goes out. These fragments are then stabilized by producing stable products identical with those of low-temperature thermal decomposition of energetic materials. In other words (see Introduction): chemical micro-mechanism of the primary fragmentations of shock-exposed explosive molecules should be the same as in the case of their low-temperature thermal decomposition.

#### 4 Conclusion

The main intermediates of the decomposition of TNT by shock and heat are identical. This finding excellently agrees with the experimental results obtained by Bulusu et al.<sup>[1,2]</sup> 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 micro-mechanism of the primary fragmentations of shock-exposed TNT molecules should be the same as in the case of their low-temperature thermal decomposition.

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## 受热、受冲击 TNT 的分解

**摘要:** 用高效液相色谱法 (HPLC) 分析了受热、受冲击工业 TNT 试样, 发现两种情况下的主要分解产物是相同的, 表明受冲击 TNT 分子初始分裂的化学微观机理与低温热分解情况下的机理相同。

**关键词:** 分析化学; TNT; 冲击; 热分解; HPLC

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