

Decomposition of some polynitro arenes initiated by heat and shock Part II: Several *N*-(2,4,6-trinitrophenyl)-substituted amino derivatives

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Abstract

Samples of 2,4,6-trinitroaniline (PAM), 2,4,6-trinitro-*N*-(2,4,6-trinitrophenyl)aniline (DPA), *N,N'*-bis(2,4,6-trinitrophenyl)-3,5-dinitropyridine-2,6-diamine (PYX) and *N,N',N''*-tris(2,4,6-trinitrophenyl)-1,3,5-triazine-2,4,6-triamine (TPM) were exposed to heat or to shock and then analysed chromatographically (LC–UV and LC/MS). It was found that the main identified decomposition products of these two incomplete initiations are identical for each of the compounds studied. It has been stated that the chemical micro-mechanism of the primary fragmentations of their low-temperature decomposition should be the same as in the case of their initiation by shock, including fragmentation during their detonation transformation.

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Keywords: Chromatography; Initiation; Shock; Thermal decomposition; *N,N'*-Bis(2,4,6-trinitrophenyl)-3,5-dinitropyridine-2,6-diamine; 4,6-Dinitrobenzofurazane; 2,4,6-Trinitroaniline; 2,4,6-Trinitro-*N*-(2,4,6-trinitrophenyl)aniline; *N,N',N''*-Tris(2,4,6-trinitrophenyl)-1,3,5-triazine-2,4,6-triamine; 2,4,6-Trinitrophenol

1. Introduction

The intermediates of initiation of 2,4,6-trinitrotoluene (TNT) were dealt with in the first part [1] of this series. Attention was given to the initiation by heat, shock, and also to the residua of detonation of TNT charge. It was found that the main identified decomposition intermediates are identical in all the three cases [1]. It was stated that this finding excellently corresponds to the experimental results obtained by Bulusu et al. [2,3] from the study of the TNT initiation by means of deuterium kinetic isotope effect (DKIE).

TNT is a polynitro arene having a hydrogen atom at γ -position with respect to the nitro group. Transfer of the hydrogen atom to oxygen atom of *ortho*-standing nitro group is a start of the TNT decomposition in its initiation. The primary fission should concern the N–OH bond homolysis in the molecule of its *aci*-form (so called “trinitrotoluene mechanism”—for general scheme see Ref. [1]) [4–6]. Polyamino derivatives of 1,3,5-trinitrobenzene fall into the same category of com-

pounds, too. Also in these compounds, a mutual similarity of chemical micro-mechanism of the primary fragmentations of their molecules by shock and by heat can be found. Thus the presence of benzofuroxanes and benzofurazanes in the XPS spectrum of 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) exposed to shock [7–9] corresponds to the fact that the pyrolysis of *ortho*-nitroanilines is a method of synthesis of benzofurazane [10], and in the case of 2,4-diamino-1,3,5-trinitrobenzene (DATB) this reaction leads to 5,7-dinitro-benzofurazane-4-amine [11]. 4,6-Dinitrobenzofurazane-5,7-diamine and 7-nitrobenzodifurazane-8-amine were specified as intermediates of the thermal decomposition of TATB [12]. It would be very interesting to extend knowledge in this area by a study of initiation of some other polynitro arenes with amino groups in their molecule.

In this part, attention is paid to decomposition intermediates from the point of view of influence of the instrumentation arrangement of heat and shock on 2,4,6-trinitroaniline (PAM), 2,4,6-trinitro-*N*-(2,4,6-trinitrophenyl)aniline (DPA), *N,N'*-bis(2,4,6-trinitrophenyl)-3,5-dinitropyridine-2,6-diamine (PYX) and *N,N',N''*-tris(2,4,6-trinitrophenyl)-1,3,5-triazine-2,4,6-triamine (TPM). For this purpose, forensic methods of analysis were applied.

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2. Experimental

2.1. Substances investigated

2,4,6-Trinitroaniline was obtained by ammonolysis of 2-chloro-1,3,5-trinitrobenzene (CTB) in methyl alcohol. It was crystallized from an acetone–methyl alcohol mixture. 2,4,6-Trinitro-*N*-(2,4,6-trinitrophenyl)aniline was obtained by nitration of *N*-(2,4-dinitrophenyl)aniline with an HNO₃–H₂SO₄ mixture [13]; it was not crystallized. *N,N',N''*-Tris(2,4,6-trinitrophenyl)-1,3,5-triazine-2,4,6-triamine was a product of nitration of *N,N',N''*-triphenyl-1,3,5-triazine-2,4,6-triamine with an HNO₃–H₂SO₄ mixture [14]; it was purified by crystallization from acetone–methyl alcohol mixture. *N,N'*-Bis(2,4,6-Trinitrophenyl)-3,5-dinitropyridine-2,6-diamine resulted from nitration of *N,N'*-bis(2,4,6-trinitrophenyl)pyridine-2,6-diamine with nitric acid [15]; it was not crystallized.

2.2. Collecting of samples

The exposition of samples of explosives to a shock wave was realized by means of the small-scale gap test [1,16] and with the donor charges (pentaerythritol tetranitrate, i.e. PETN, with 10 wt.% wax, and 1,3,5-trinitro-1,3,5-triazinane, i.e. RDX, with 5% wax) were separated from the acceptor charges by a poly(methyl methacrylate) (PMMA) barrier. The technique of the residues collection is described in the first part of this study [1].

We used a DTA 550-Rez apparatus [1,17] (specially developed at our Institute for the purpose of differential thermal analysis of explosives) for thermal exposition of PAM, DPA, PYX and TPM. The measurements were carried out with the amounts of 50 mg, the heating being interrupted at 350, 253, 367 and 310 °C, respectively, by taking the test tube with PAM, DPA, PYX and TPM 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.

For the decomposition products of PAM, DPA, PYX and TPM an acetonitrile–water mixture was used as the mobile phase, and that is why the samples were transferred from the methanol to the distilled water for attaining compatibility. These samples were obtained by evaporation of the methanolic extracts until dry, and immediate addition of distilled water (ca. 2 ml). The filtered aqueous extracts of these samples were submitted to the LC–UV and LC/MS analyses. Moreover, this transfer of the residua from methanol into water was connected with lowering of interference from the huge concentration of the original analyte (particularly in the cases of PYX and TPM, which are almost insoluble in water) and with purification of the extracts from contaminants and other undesirable products extracted during the original extraction with organic solvents.

2.3. LC–UV analysis of organic extracts

The liquid chromatography was carried out with an LC-10AS Shimadzu Liquid Chromatograph coupled with SPD-10A

UV–vis detector [1]. As it was impossible to measure separately the UV spectra of each compound, the wavelength chosen for the detection was that previously evaluated as a versatile wavelength for analyses of the investigated decomposition products (255 nm for PAM, DPA, PYX and TPM). In the cases of decomposition products of PAM, DPA, PYX and TPM, a mixture of acetonitrile and water (1:1) was used, its flow rate being adjusted at 1 ml/min. The measurements were performed in a column LiChrospher 100 RP-18, 250 mm; grain size 5 μm.

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. 2-chloro-1,3,5-trinitrobenzene, 2,4,6-trinitrophenol (PA), 2,4,6-trinitroaniline, 2,4,6-trinitro-*N*-(2,4,6-trinitrophenyl)aniline, *N,N'*-2,6-bis(2,4,6-trinitrophenyl)-3,5-dinitropyridine-2,6-diamine, *N,N',N''*-tris(2,4,6-trinitrophenyl)-1,3,5-triazine-2,4,6-triamine, 4,6-dinitrobenzofuroxane (DNBF), 4,6-dinitrobenzofurazane (DNBFz),

2.4. 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 [1]. The used chromatographic and mass spectrometric conditions are shown below.

Chromatographic conditions;

Column: LiChrospher 100 RP-18, 250 mm, grain size 5 μm;
mobile phases: acetonitrile/water; 50:50 (v/v), with addition of ammonium chloride and formic acid;
flow rate: 1 ml/min;
injection volume: 20 μl.

Mass spectrometric conditions:

Ionization source: APCI-mode: scan and SIM; ionization polarity: negative;
capillary voltage: 3000 V; pressure in nebulizer: 60 psi; vaporizer temperature: 300 °C;
drying gas flow and temperature: 5 l/min, 330 °C;
fragmentor voltage: 30 V.

The stock solutions of individual explosives (CTB, PA, PAM, DPA, DNBF and DNBFz) were prepared in distilled water. 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 [1]. Because of the very low solubility of PYX and TPM in water, the mass spectra of these analytes were measured with the use of methanol/water mobile phase (1:1). Then, the selected ion monitoring (SIM) method for decomposition products of PAM, DPA, PYX and TPM was used. In the SIM mode, at least three dominant ions of each substance were measured.

The following ions (*m/z*) were considered in SIM analysis of the PAM, DPA, PYX and TPM decomposition products: PAM

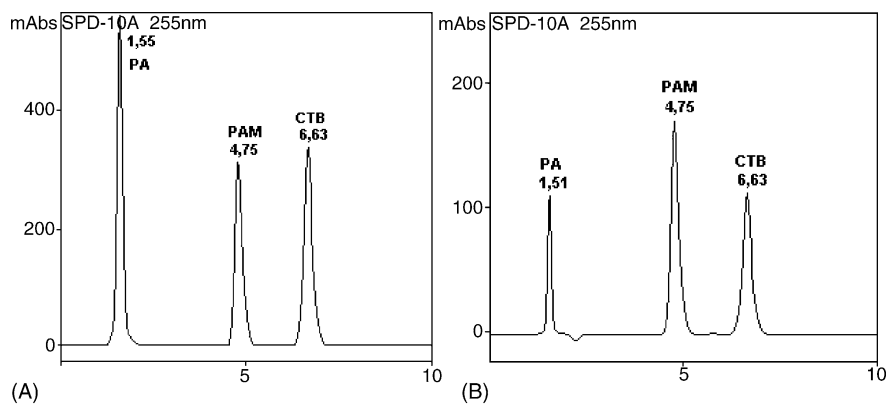


Fig. 1. LC–UV chromatograms of thermally exposed PAM at 350 °C (A) and of shock-exposed PAM (B).

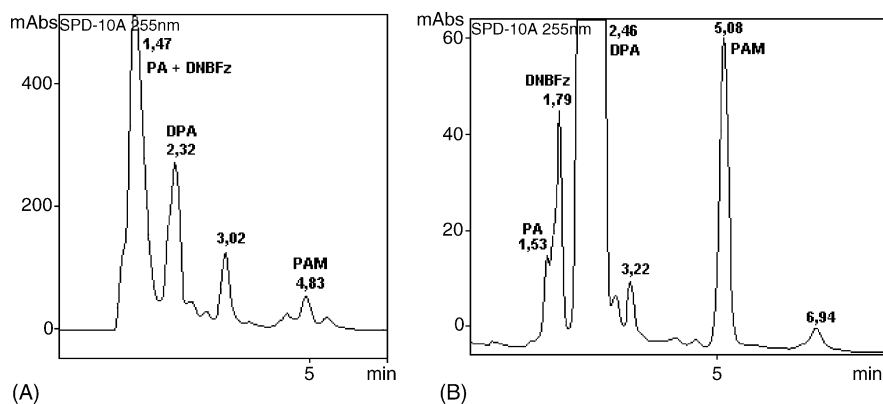


Fig. 2. LC–UV chromatograms of thermally exposed DPA at 253 °C (A) and of shock-exposed DPA (B).

227 and 228; PA 228 and 229; CTB 228 and 229; DPA 438 and 439; DNBF and DNBFz 210, 211, 226, 359 and 435. The identification consisted in comparing the retention times and characteristic mass spectra of unknown components with those of standards.

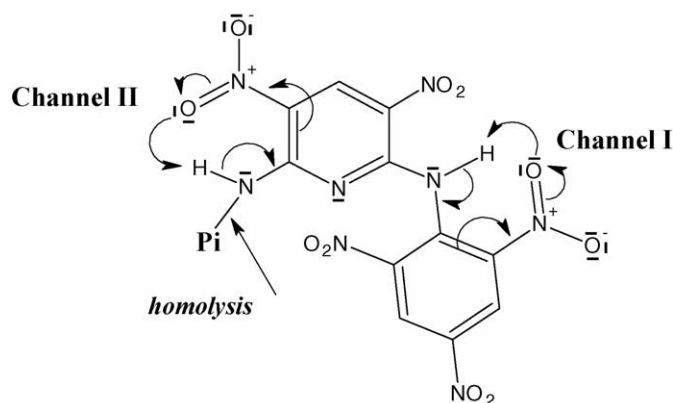
3. Results and discussion

The stable intermediate of initiation decomposition of PAM should be DNBFz [7,8]. However, the LC–UV chromatogram of thermally exposed PAM (see Fig. 1A) lacks any marked presence of this intermediate (it could be overlapped by the PA peak). The presence of PA is logical: it can be a product of action of nitrogen oxides upon the starting PAM (which is an analogy of secondary reactivity of methyl group in heat- or shock-exposed 2,4,6-trinitrotoluene [1]). Practically the same can be stated in the case of the shock-exposed PAM (see the chromatogram in Fig. 1B). The peaks of CTB in Fig. 1A and B are connected with the contamination of original PAM with traces of this basic component in its synthesis.

In the case of heat-exposed DPA (Fig. 2A), the DNBFz peak is obviously overlapped by the PA peak. The presence of PAM in this sample signals a possibility of another, not yet specified, mechanism of secondary decomposition of DPA. The same can be said also about the result of the LC–UV analysis of the shock-exposed DPA sample (Fig. 2B); here we can emphasise

the obvious indication of separation of PA peak from DNBFz peak.

The PYX molecule contains two potential reaction centres of primary decomposition [18] documented in Scheme 1 [19]. On the basis of investigation of the impact reactivity [18,19] and, subsequently, by means of quantum–chemical analysis [19] it was found that the probability of participation of these cen-



Scheme 1. Presumed reaction mechanisms (centers) of primary fission of the *N,N'*-bis(2,4,6-trinitrophenyl)3,5-dinitropyridine-2,6-diamine (PYX) molecule in initiation processes (taken from Ref. [19]); here Pi- is 2,4,6-trinitrophenyl whose breakaway (a secondary process) as a radical and subsequent reaction with other fragments of the PYX molecule gives DPA.

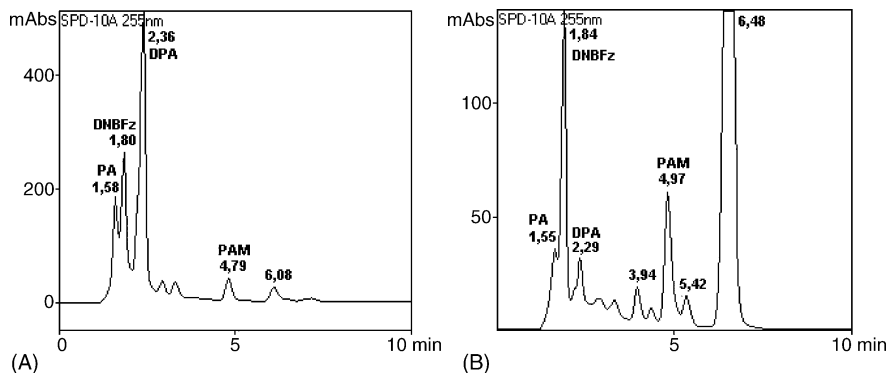


Fig. 3. LC-UV chromatograms of thermally exposed PYX at 367 °C (A) and of shock-exposed PYX (B).

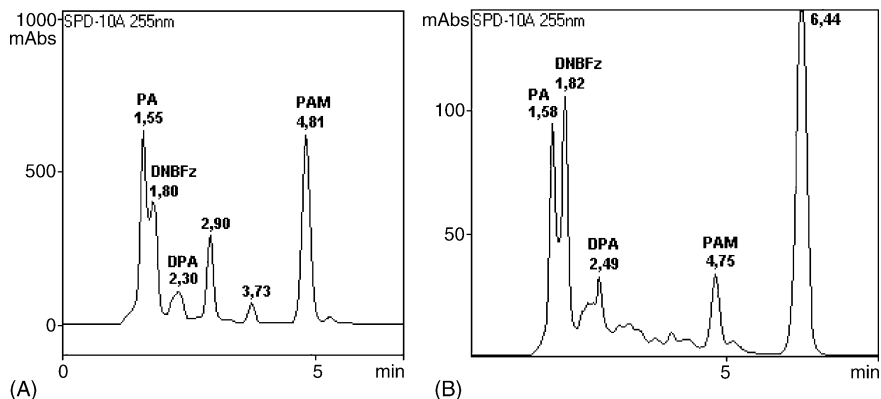


Fig. 4. LC-UV chromatograms of thermally exposed TPM pri 310 °C (A) and of shock-exposed TPM (B).

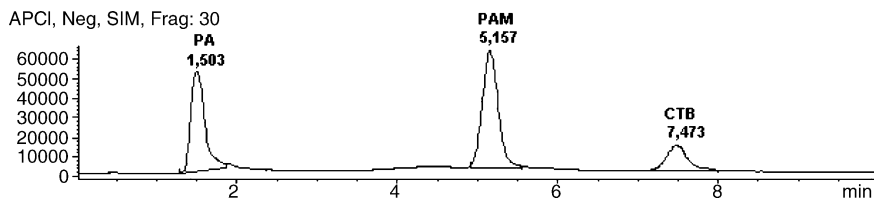


Fig. 5. LC/MS chromatogram of thermally exposed PAM at 350 °C.

tures in the initiation processes could be approximately the same [18,19].

Considering the above-mentioned finding obtained from initiation splitting of DPA, we can denote the results obtained from analysis of the heat- and shock-exposed PYX (Fig. 3A and B) as expected. In this case, the PA peak is distinctly separated from the DNBfz peak. The presence of DPA in the decomposition products of PYX can be connected with the secondary formation of 2,4,6-trinitrophenyl radicals (see Scheme 1) and their subsequent reactions with the decomposing PYX molecule.

From what has been said so far it can be concluded that the presence of the monitored compounds in the chromatograms of heat- and shock-exposed TPM (Fig. 4A and B) corresponds the expectation.

The results of LC-UV analyses are supported also by results obtained with the LC/MS technique (see Figs. 5–12). The cause for the absence of DNBfz from the LC/MS chromatograms of heat- and shock-wave-exposed PAM (Figs. 5 and 6), DPA (Figs. 7 and 8), PYX (Figs. 9 and 10), and TPM (Figs. 11 and 12) most likely lies in the decomposition of this component

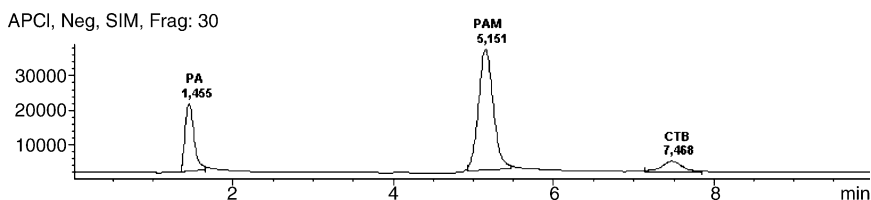


Fig. 6. LC/MS chromatogram of shock-exposed PAM.

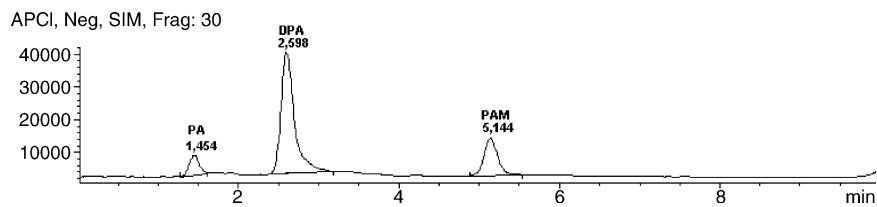


Fig. 7. LC/MS chromatogram of thermally exposed DPA at 253 °C.

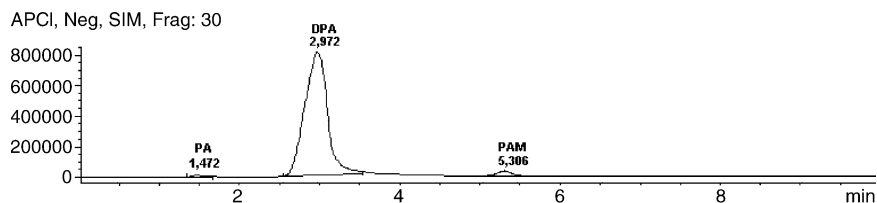


Fig. 8. LC/MS chromatogram of shock-exposed DPA.

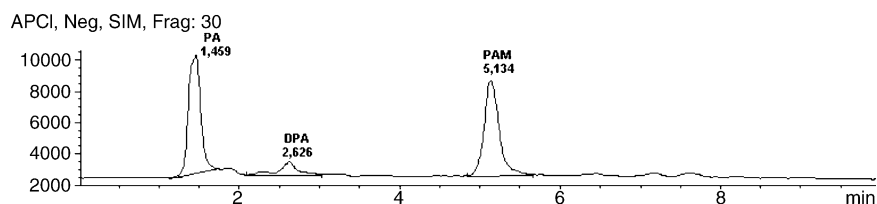


Fig. 9. LC/MS chromatogram of thermally exposed PYX at 367 °C.

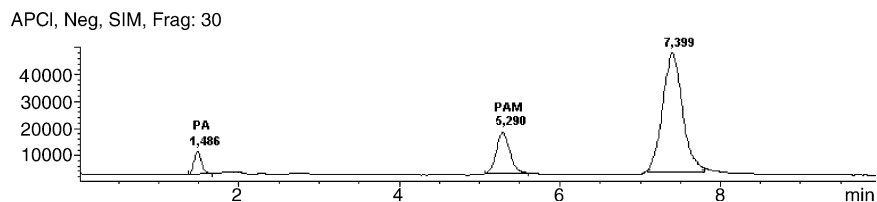


Fig. 10. LC/MS chromatogram of shock-exposed PYX.

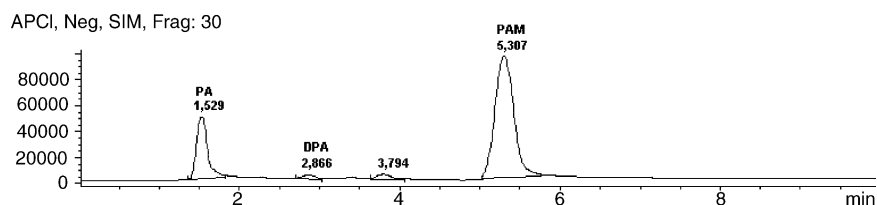


Fig. 11. LC/MS chromatogram of thermally exposed TPM at 310 °C.

at the high ionization temperature used (300 °C). This is a close analogy of the problem of detection of 4,6-dinitro-2,1-benzisoxazole by this technique in the 2,4,6-trinitrotoluene exposed to heat and shock [1]. *N*-Oxide of DNBfz, i.e. 4,6-

dinitro-benzofuroxane, is subject to decomposition at temperatures as low as 140–170 °C [20]. This reactivity can cause its absence from the decomposition intermediates of all the poly nitro arenes studied.

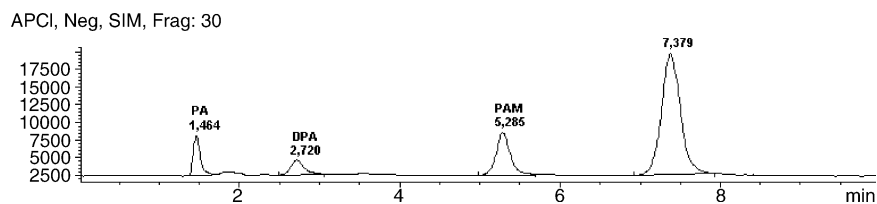
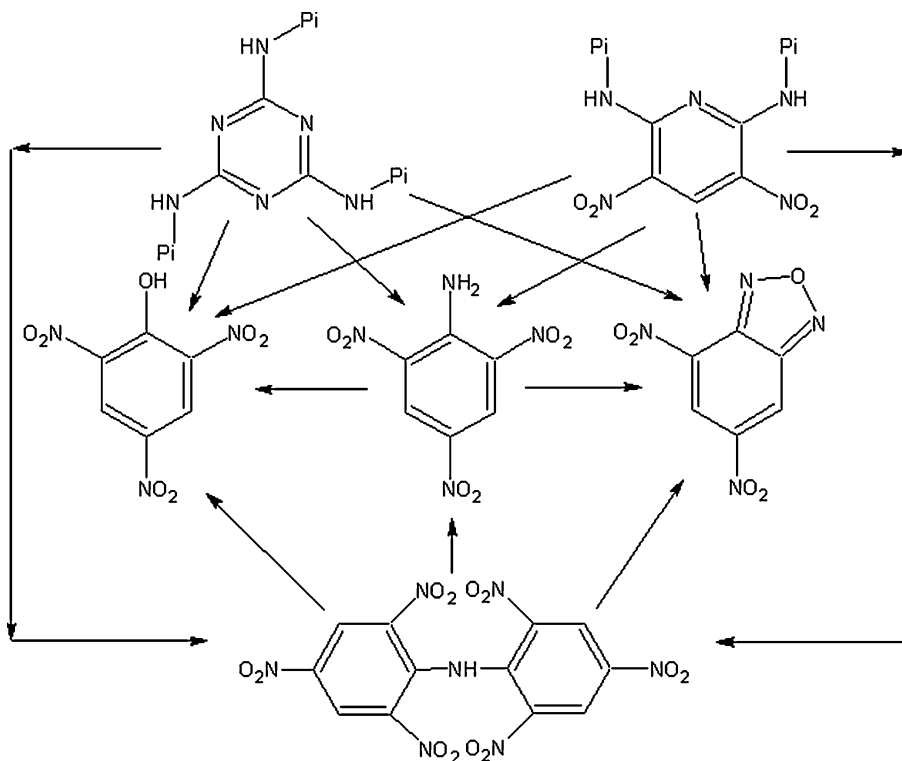


Fig. 12. LC/MS chromatogram of shock-exposed TPM.



Scheme 2. Mutual relation of main products of incomplete initiation of PAM, DAP, PYX and TPM by heat and shock; here Pi- is 2,4,6-trinitrophenyl.

A partial difference between the incomplete initiations by heat and by shock can be seen in the products of secondary decomposition of PYX and TPM. In this case, the LC–UV and LC/MS analyses of the shock-wave-exposed PYX (Figs. 3B and 10) and TPM (Figs. 4B and 12) revealed the same decomposition intermediate with the ions at m/z 226 and 227, which is, however, absent from those of their heat initiation (Figs. 3A and 9 for PYX; Figs. 4A and 11 for TPM). This means that the influence of both stimuli brings about the same primary fragmentation, but the subsequent extinguishing detonation (in the case of shock) or the incomplete thermal decomposition (in initiation by heat) are different, first of all, in the pressure during the secondary termination reactions. It need not be stressed that it is impossible to compare the secondary reactions of these extinguishing processes with the secondary reactions in the induction period and in the reaction zone of detonation wave.

On the basis of the results obtained in this work, it is possible to present the mutual relationship of main stable products from incomplete initiation of PAM, DPA, PYX and TPM by heat and shock in Scheme 2.

4. Conclusion

The main identified products of incomplete initiation of 2,4,6-trinitroaniline, 2,4,6-trinitro-*N*-(2,4,6-trinitrophenyl)aniline, *N,N'*-bis(2,4,6-trinitrophenyl)-3,5-dinitropyridine-2,6-diamine and *N,N',N''*-tris(2,4,6-trinitrophenyl)-1,3,5-triazine-2,4,6-triamine by heat and shock are identical for each from these compounds. This finding also corresponds with the comparison of older results of influence of shock [7–9] and heat [11,12]

upon the polyamino derivatives of 1,3,5-trinitrobenzene. It is also perfectly congruent with the results obtained by us in analogous studies of 2,4,6-trinitrotoluene [1]. Taking into account also the older results of studies of chemical micro-mechanism of initiation of energetic materials [1–3,18,19], we can state that these our results signalize again identity of the chemical micro-mechanism of their low-temperature thermal primary decomposition with their primary fragmentations by shock, including primary fragmentations in their detonation transformation.

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