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Thermal Decomposition of Nitropyrazoles

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Abstract

Fully nitrated five-membered heterocycles (pyrazoles), polynitropyrazoles in particular, have been actively studied as promising high-energy materials. Polynitropyrazoles have high density and high enthalpy of formation combined with reduced sensitivity to external stimuli. We have studied non-equilibrium processes of thermal decomposition of the first members of high-energy polynitropyrazoles row, i.e., 3,4-dinitropyrazole, 3,5-dinitropyrazole, and 3,4,5-trinitropyrazole, under atmospheric and increased pressures. The use of increased pressure allowed to reduce the influence of evaporation process of 3,5-dinitropyrazole and to determine the temperature and heat effect of its decomposition, which was found to exceed this value for HMX. For the first time evolved gas products were identified for each stage of decomposition. As a result the probable thermal decomposition pathway for the investigated materials was suggested.

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Nomenclature

T_m	melting temperature
Q_m	heat of fusion
T_o	onset temperature for heat release
Q_d	heat release at decomposition

1. Introduction

Among new high-energy materials with higher performance and/or lower sensitivity fully nitrated five-membered heterocycles (pyrazoles) have high enthalpy of formation and high density. Recently synthesized 3,4,5-trinitropyrazole (TNP) has impact sensitivity value close to TNT, and detonation velocity close to ones of RDX and HMX [1-2]. 3,4-dinitropyrazole (DNP-1) could be used as a melt cast matrix, alternatively to TNT [4]. The aim of the present study is to investigate thermal stability both in atmospheric and high pressures for three polynitropyrazoles: 3,4-dinitropyrazole, 3,5-dinitropyrazole, and 3,4,5-trinitropyrazole (Fig. 1).

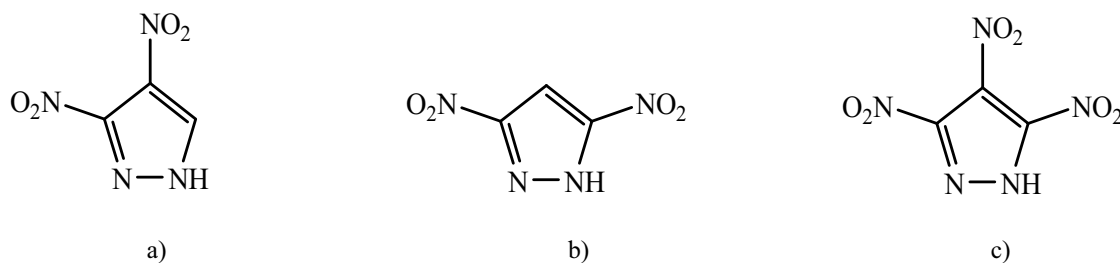


Fig. 1 Synthesized monocyclic polynitropyrazoles: a) - DNP-1 (3,4-dinitropyrazole), b) - DNP-2 (3,5-dinitropyrazole), c) - TNP (3,4,5-trinitropyrazole).

2. Experimental study and results*2.1. Physical measurements*

The samples of the synthesized compounds were investigated by simultaneous thermal analysis DSC/TG at a scanning rate of 10 K/min using STA 449 F3 (Netzsch) apparatus. Samples of mass about 2 mg were placed into closed alumina pans with pierced lids and then heated in dynamic argon atmosphere 70 ml/min. In order to estimate the thermal stability under elevated pressure DSC 204 HP (Netzsch) was used. The scanning rate and the sample mass were the same. Samples were placed into the aluminum crucibles, covered with a pierced lids, sealed, and heated in dynamic nitrogen atmosphere (flow rate 100 ml/min) under 50 bar pressure. The temperature range for both DSC/TG and DSC HP was from 30 to 600°C.

Simultaneously with DSC/TG analysis, FTIR-spectroscopy via coupling Bruker ALPHA FTIR device was used to study the gas phase products. As a result a full set of FTIR spectra for the whole range of time (temperature) was obtained. The most intense peaks were selected, analyzed, and identified. Some of the peaks, however, were impossible to identify using NIST database. In order to identify these spectra and, probably, to attribute them to the vapors of investigated materials, IR spectra of initial compounds in chloroform solution were obtained. The matching of these peaks allowed indicating the evaporation of the initial materials. Concentration curves for the main gas products were calculated in relation to CO₂ [5]. For main products the relative concentration was plotted in the same scale, unlike the curves of the evaporated initial materials. message, with clear lines of thought and validation of the techniques described.

2.2. Results

The comparative results of the experiments are presented in Figure 3 and Table 1. It is evident that three materials firstly melt with further significant mass loss. For DNP-1 and TNP such mass loss is accompanied by a series of overlapping exothermal peaks, for DNP-2 however it is accompanied by an endothermic peak, which could indicate the evaporation process. The FTIR spectroscopy showed that the only gas product detected is DNP-2 vapor itself, which proves the hypothesis of 3,5-dinitropyrazole evaporation at elevated temperature. For DNP-1 and TNP the concentration curves reveal the start of mass loss to be accompanied with NO₂ evolution. Latter decomposition products include CO₂, HCN, and the evaporated compound DNP-1 itself. Concentration peaks for gas products match the peak values of DSC curve.

When higher pressure was applied, the evaporation process of DNP-2 was suppressed and the onset decomposition temperature has been found to be 321°C with heat effect of 4.3 kJ/g. The heat effect measured for HMX decomposition under the same conditions is much less, *i.e.*, 2.6 kJ/g. Unlike DNP-1, which decomposition does not change significantly under elevated pressure, the decomposition process for TNP proceeds in one stage with intense self-heating, which suggests autocatalytic character of thermolysis. The results of the conducted experiments are summarized in Table 1.

Table 1. Parameters of melting and decomposition of monocyclic nitropyrazoles at 1 and 50 bar.

Sample	P, bar	Melting			Decomposition		
		T_m , °C	Q_m , J/g	T_o , °C (TG)	T_o , °C (DSC)	Q_d , J/g	DSC peaks, T_{max} , °C
DNP-1	1	87	-104	297	306	2360	338; 376; 404
	50	87	-100	275	310	3710	346;359;404
DNP-2	1	169	-151	(evaporation)	-	- 240	-
	50	170	-151		321	4230	345
TNP	1	186	-138	254	261	997	278; 359
	50	186	-140		259	1890	270

3. Discussion

Relocating the nitro group in DNP-1 from position 4 to position 5 (in DNP-2) leads to increase of melting temperature from 87°C to 169°C. Introducing the third nitro group leads to the further increase of melting temperature up to 186°C. The melting temperature increase in the row DNP-1, DNP-2, TNP correlates with the crystal lattice energy growth for these compounds [3]. Based on the obtained data for di- and trinitropyrazoles the first stage of decomposition assumed to be the radical C-NO₂ bond breaking with NO₂ emission, probably proceeding by radical mechanism. The next stages of decomposition is rather complex and consists of several stages. We assume it is breakdown of the pyrazole ring, which is evident from CO₂ and HCN appearing in gas phase products.

Using high pressure allowed obtaining new data and comparing three substances, revealing that the thermal stability is increasing in the flowing order: TNP, DNP-1, DNP-2, which is connected with amount of nitro groups and their location in the pyrazole ring. Apparently the highest thermostability of 3,5-dinitropyrazole (DNP-2) is caused by the lack of steric strains in the molecule, which in turn is a result of the both nitro groups location complanarly to the pyrazole ring plain. For DNP-1, nitro group in position 3 and for TNP one in position 4 are both located almost orthogonally to the pyrazole ring plain, forming dihedral angles of 70°-80°. This leads to the C-NO₂ bond weakening because of the lack of conjugation, and as a result, to the reduced thermal stability for DNP-1, and especially for TNP. However, it should be noted that still bi- and trinitropyrazoles are more thermostable and have higher enthalpy of formation than their isomeric analogues - nitroimidazoles [6-8].

Moreover the heat effect of both DNP-1 and DNP-2 decomposition at 50 bar pressure is higher than the same of HMX, which proves the importance of further research and good potential for the future use of these compounds.

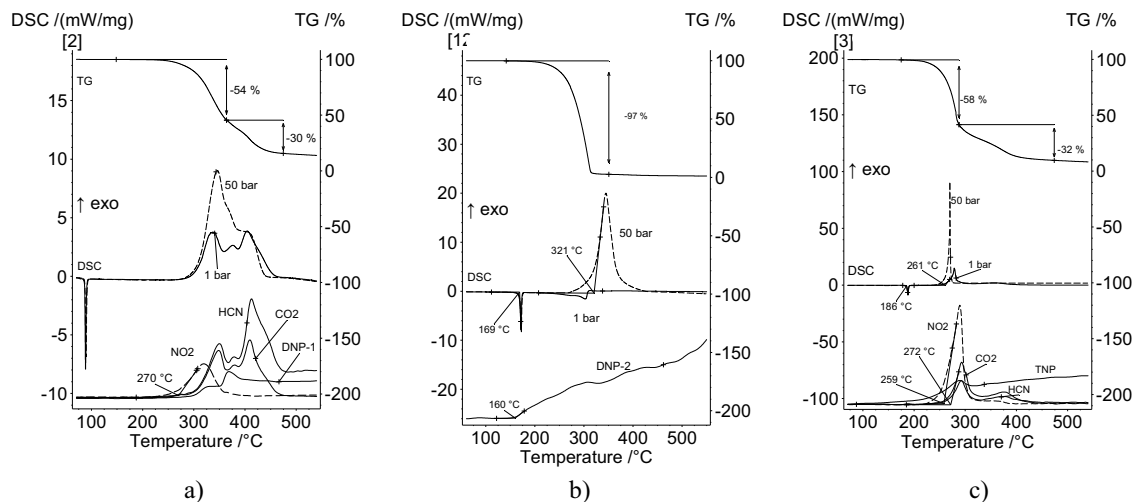


Fig. 2 TG-curves at 1 bar (top curves), combined with DSC signals at 1 (solid line in the middle) and 50 bar (dashed line) pressure and with concentration curves (at the bottom) for a) DNP-1 (3,4-dinitropyrazole), b) DNP-2 (3,5-dinitropyrazole), c) TNP (3,4,5-trinitropyrazole).

4. Summary

New promising high energy compounds – monocyclic nitropyrazoles – were synthesized and investigated. The gas phase decomposition products were analyzed, and possible decomposition pathway was proposed. The thermal stability, melting and decomposition were studied both at atmospheric and higher pressures. For the first time parameters of thermal behavior under high pressure were obtained, revealing the heat effect of 3,5-dinitropyrazole decomposition to be higher than that one of HMX.

Acknowledgements

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