CATALYTIC EFFECTS FOR ANIONS IN MOLECULAR CRYSTALS OF 3-NITRO-4,5-DIHYDRO-1,2,4-TRIAZOL-5-ONE SALTS IN THERMAL DECOMPOSITION PROCESS

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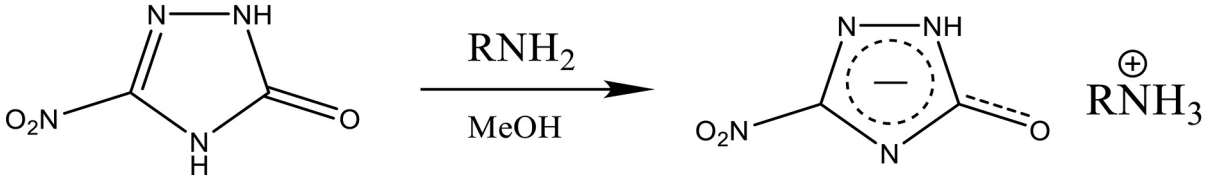
High-energetic compounds that are used in various compositions of explosives for defense technologies in a number of countries include 3-nitro-4,5-dihydro-1,2,4-triazol-5-one (NTO) [1, 2]. This substance has high values of heat of formation, density, and low sensitivity to external influences [2]. At the same time, NTO has disadvantages that hinder its widespread use, such as a reduced level of energetic characteristics (87% of RDX) and chemical resistance, in particular, an increased level of acidity of the compound itself and solutions based on it. Due to the low pKa = 3,67 [2], metal-containing NTO salts may form during storage and processing of NTO, which belong to the high hazard class 1.1A [3]. In addition, the catalytic effect of water on NTO during storage and transportation was shown by the authors of [4] using theoretical methods of quantum chemistry. One of the ways to increase the chemical stability of NTO, with a possible increase in the rate of its explosive transformation, is to create salts containing two or more ions in the unit cell volume of a crystalline solid, which are different in structure and do not contain metal and water ions. Thus, a low pH level generally does not interfere with the use of NTO and even allows the creation of more energetic-intensive salts, ion-molecular complexes, and co-crystals [5].

In this work the structures of 3-nitro-4,5-dihydro-1,2,4-triazol-5-one (NTO) salts with ammonia, hydrazine, and hydroxylamine have been studied using a combination of powder x-ray diffraction data, elemental analysis, and IR-Fourier spectroscopy. For the first time, the data obtained from the Raman spectra of NTO **2a-c** (scheme 1) salts should be used for rapid assessment of the chemical composition of substances based on NTO, as well as for the compilation of phonon spectra. The analysis of structural fragments of **2a-c** salts revealed the relationship between thermal stability and chemical activity. Combined methods of thermal analysis, IR Fourier spectroscopy, and mass spectrometry have established the mechanisms of activation and decomposition of NTO salts. **2a-c**. The values of the catalytic effects of anions in crystals of NTO salts are obtained (table 1).



R = NH2 (**a**), OH (**b**), H (**c**)

Scheme 1. Synthesis of NTO salt samples

Table 1

Catalytic effects found for thermal decomposition of salts **2a-c** regarding the NTO **1**

Name	The structural fragment is a catalyst for crystal decomposition	The catalytic effect	
		%	kJ/mol
HNTO **2a**	$^{+}NH_3NH_2$	39.0	136.1
HANTO **2b**	$^{+}NH_3OH$	44.6	155.6
ANTO **2c**	H_2O, $^{+}[H_4N]$	58.4	203.7

It has been shown that under thermal action, NTO **2a-c** salts undergo a restructuring of crystal structures and gradually, in several stages, decompose with the release of weakly bound compounds in the lattice.

The nature of the decomposition of salts **2a-c** depends on the rate of thermal action. The salt 3-nitro-5-oxo-4,5-dihydro-1,2,4-ammonium triazolide monohydrate (ANTO, **2c**) decomposes under slow thermal action at speeds of no more than 0.25 s-1 to form the initial NTO 1. At higher exposure rates, the catalytic effects of ammonium ions on the decomposition of NTO are observed. The salt 3-nitro-5-oxo-4,5-dihydro-1,2,4-hydroxylammonium triazolide (HANTO, **2b**) decomposes to release hydroxylamine, which is a catalyst for the decomposition of NTO. The salt 3-nitro-5-oxo-4,5-dihydro-1,2,4-triazolide of hydrazinium (HNTO, **2a**) is thermally stable at the level of RDX, has a similar density and sensitivity to mechanical influences, but at the same time has a higher detonation rate. The processes end with the decomposition of NTO, the end products of which are nitrogen and water. It has been established that the resistance of NTO to thermal effects is due to its crystalline structure, not its molecular structure.

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