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«Thermal decomposition and combustion of hybrid heterocyclic compounds»

Abstract

Relevance of the theme. There is a great interest in the synthesis of hybrid compounds containing various heterocyclic systems all over the world nowadays. Nitrogen-rich heterocycles and their derivatives are of considerable interest due to their multiple applications as environmentally friendly high-energetic materials, such as explosives, rocket propellants, and pyrotechnic components. Researchers consider that the various heterocyclic fragments combination in one molecule could lead to the appearance of new properties or give an option of effective regulation of existing properties.

At present time at the N.D. Zelinskiy Institute of Organic Chemistry RAS a series of compounds containing covalently bonded pyrazole and tetrazole rings was synthesized. The tetrazole cycle has high nitrogen content, a large positive enthalpy of formation, and its derivatives usually have a high burning rate. At the same time, the pyrazole cycle can bring complementary properties - an increase in thermal stability and a decrease in sensitivity to mechanical stimuli. Moreover, pyrazoles are unique in their ability to form stable N-nitro derivatives at the endocyclic nitrogen atom among other NH-azoles. These N-nitro (as well as N-amino) pyrazole derivatives don’t contain acidic NH protons and have excellent enthalpies of formation. Pyrazole-tetrazole combinations containing nitro groups demonstrate good theoretical detonation parameters, but experimental data on other properties (thermal stability, combustion behavior) are either limited or absent.

Of interest from an energetic point of view are hybrid molecules in which acyclic nitramines are combined with a furazan or tetrazole ring. The furazan cycle is characterized by a positive enthalpy of formation, high density, and acceptable

thermal stability. Nitramines are a source of active oxygen and increase the energetic characteristics of the compound.

The possibility of new energetic materials to find a practical use depends on the complex of their properties: energetic characteristics, chemical stability and combustion behavior. Fundamental studies of the mechanisms of chemical processes by which energic materials release the energy stored in them are extremely important.

The aim of the work was to study the thermal stability and combustion behavior of new hybrid compounds.

Tasks: a) to study the thermal stability of new energetic compounds under isothermal and non-isothermal conditions; b) to study the combustion behavior of new EMs in a wide range of pressures; c) to study the temperature distribution in the combustion wave using thin tungsten-rhenium thermocouples; d) to determine the composition of decomposition and combustion products using spectroscopic, chromatographic and mass spectrometric methods of analysis; e) to establish the mechanisms of decomposition and combustion of new EMs.

Scientific novelty.

For the first time, thermal decomposition under nonisothermal and isothermal conditions of new hybrid compounds containing pyrazole and tetrazole rings, as well as acyclic nitramines fused with a furazan or tetrazole ring was studied in detail. Beyond that, the thermal decomposition of pyrazole N-nitro derivatives was studied to understand the processes occurring in a thermal wave. It has been shown that N-(nitropyrazolyl)tetrazoles thermal decomposition begins with azido-tetrazole isomerization followed by elimination of a nitrogen molecule from the azidoimine fragment, and their stability decreases with increasing of the nitropyrazole fragment electronegativity. The activation energies of liquid-phase decomposition are 116-127 kJ mol^{-1} for N-(pyrazolyl)tetrazoles compared to 140.2 kJ mol^{-1} for C-(pyrazolyl)tetrazole, which is in reasonable agreement with theoretical calculations. The kinetics of decomposition in the solid phase of N-(pyrazolyl)tetrazoles strongly depends on the effect of sub-melting and the

occurrence of azido-tetrazole isomerization. A characteristic feature of N-nitropyrazoles thermal decomposition is that the decomposition rate is determined by the kinetics of the preliminary [1,5]-sigmatropic shift of the NO_2 group, rather than the kinetics of N-NO_2 bond cleavage. A study of the thermal stability of hybrid compounds based on acyclic nitramines fused with a furazan or tetrazole ring showed that the heterocyclic ring reduces the thermal stability of azacyclic nitramines by weakening the N-NO_2 bond. The influence of the structure on the thermal stability of the studied compounds is analyzed. A mechanism for their decomposition is proposed.

Combustion behavior of N-(nitropyrazolyl)tetrazoles and hybrid compounds based on acyclic nitramines fused with a furazan or tetrazole rings was studied for the first time. The thermocouple studies were carried out, and it was found that the leading combustion reaction is located in the condensed phase. The kinetics of thermal decomposition in the liquid phase is in good agreement with the kinetic parameters determined from the combustion wave. A specific effect of heterocycles on the burning rate of acyclic nitramines has been found. On the one hand, according to thermocouple measurements, the introduction of heterocycles into the nitramine molecule increases its volatility and reduces the combustion surface temperature, which should lead to combustion rate decrease. On the other hand, thermal stability is decreased and the rate of heat release in the melt is increased. As a result, the burning rate increases rather than decreases. During the combustion of 1,4,5,8-tetranitrodifurazano[3,4-c][3,4-h]tetraazadecalin, a rare phenomenon was found - the combustion surface temperature is determined by the boiling temperature of the intermediately formed stable decomposition product, rather than the boiling temperature of the initial substance.

Practical relevance

Kinetic data on the decomposition of a series of N-(nitropyrazolyl)tetrazoles and hybrid compounds based on acyclic nitramines fused with a furazan or tetrazole ring have been obtained. The obtained correlation between substituent electronegativity and thermal stability allows a targeted approach to the synthesis

of promising compounds. Based on the obtained data, conditions for the use and storage of new compounds are proposed. The accuracy of the previously found correlation between the length of $N\text{-}NO_2$ bonds and the decomposition constants of cyclic nitramines has been increased, which makes it possible to predict the stability of new hypothetical compounds of this class.

As a result of the research, it was found that N-pyrazolyltetrazoles are fast-burning compounds with burning rates of 70-80 mm s^{-1} at 10 MPa, which allows them to be considered as combustion modifiers for rocket propellants and gunpowder.

Based on thermocouple studies, such physicochemical parameters as thermal diffusivity and vapor pressure of the studied substances were determined.

Statements submitted for defense:

-experimental data on the decomposition kinetics of N-(nitropyrazolyl)tetrazoles, hybrid compounds based on acyclic nitramines fused with a furazan or tetrazole ring, as well as pyrazole N-nitro derivatives,

- combustion behavior of these compounds,

- data from thermocouple studies of their combustion wave

- interpretation of the obtained results.