Thermal decomposition and combustion of azo and azoxy derivatives of azoles

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Relevance of the research topic. Azoles constitute a promising class of energetic materials due to a combination of high enthalpy of formation, high density, and a favorable oxygen balance. To enhance the energetic properties of an energetic material (EM), azo and azoxy groups are frequently incorporated into the molecule, as this leads to a significant increase in the enthalpy of formation. In addition to its enthalpic contribution, the azoxy group introduces an extra atom of "active" oxygen capable of participating in redox reactions with the combustible fragments of the molecule, thereby increasing the heat release during decomposition.

Researchers at the N.D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences (ZIOC RAS) have recently developed a strategy for synthesizing (dinitropyrazolyl)azoxyfurazans. These compounds are of interest not only as powerful explosives but also as effective energetic fillers for solid rocket propellants, offering a higher specific impulse than similar formulations based on well-known compounds such as RDX, HMX, and even CL-20.

An even more promising option in terms of energetic performance is the introduction of an azoxy group between a nitro group and the heterocycle. Among the high-energy nitro-NNO-azoxy compounds synthesized at ZIOC RAS, 1,1’-azo-bis[3-(nitro-NNO-azoxy)-1H-1,2,4-triazole] (ANAzTr) stands out; it is proposed as a high-energy filler for high-impulse composite solid rocket propellants and as a component of powerful explosive formulations.

Previously, most research focused on introducing an azo bridge between two carbon atoms; however, linking the azo group to nitrogen atoms is not only energetically more favorable but also resolves the issue of the acidic N–H proton characteristic of nitropyrazole molecules. Such compounds—specifically 1,2-bis(3,4-dinitro-1H-pyrazol-1-yl)diazene (3,4-DNPAz) and 1,2-bis(3,5-dinitro-1H-pyrazol-1-yl)diazene (3,5-DNPAz)—were synthesized via the oxidation of N-aminodinitropyrazoles. These compounds possess excellent energetic properties and can serve as effective energetic additives that enhance key performance parameters of advanced solid rocket propellants.

The practical application of new energetic materials (EMs) is determined by the combination of their properties. In addition to energetic characteristics, chemical stability and combustion behavior play pivotal roles. Understanding the combustion behavior of EMs is critical for the design of rocket motors, weapon systems, pyrotechnic devices, gas generators, and other systems relying on combustion processes. Establishing structure-property relationships

requires more than just data on burning rates; a detailed study of the combustion mechanism—which is inextricably linked to the thermal decomposition mechanism of the EM—is essential.

Current state of research on the topic. The thermal stability of the azo- and azoxy-derivatives of azoles under consideration has previously been studied exclusively under non-isothermal conditions, necessitating further research for a comprehensive assessment of their stability. Furthermore, data on the burning rates of compounds in this class are lacking, even though such information is critical for both establishing safe handling procedures and identifying optimal practical applications.

The aim of this work: Investigation of the thermal stability and combustion characteristics of new heterocyclic energetic compounds containing azo and azoxy groups.

The objectives of this work: a) study of the thermal stability of new energetic materials under non-isothermal and isothermal conditions; b) study of the combustion characteristics of new energetic materials over a wide pressure range; c) study of the temperature distribution within the combustion wave using thin tungsten-rhenium thermocouples; d) determination of the composition of decomposition products using infrared (IR) spectroscopy, high-performance liquid chromatography, and mass spectrometry; e) elucidation of the decomposition and combustion mechanisms of new energetic materials.

Scientific novelty. A detailed study of the thermal decomposition of dinitropyrazoles linked to furazan derivatives via azoxy bridges was conducted for the first time using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), isothermal TGA, and manometry. It was established that the decomposition process of the azoxy compounds is initiated by the cleavage of the bond between the N(O) nitrogen atom of the azoxy moiety and the substituent. The activation energies obtained for the elimination of N_2O from the azoxy compounds range from 129 to 146 kJ/mol, which is consistent with the kinetics of the trans-to-cis isomerization of azoxy compounds calculated via quantum-mechanical methods. It was found that the initial stage of azoxy compound decomposition, under conditions where reaction products are removed, can proceed either without heat release or with a heat release that does not form a distinct peak on the thermogram. This negligible thermal effect complicates the determination of true kinetic parameters by DSC, as the recorded thermal signal is largely attributable to the decomposition of intermediate products. However, under closed conditions, a significant increase in decomposition rate constants—by a factor of 10 or more—is observed.

The thermal decomposition of two isomeric 1,1'-azobis(dinitropyrazoles) was investigated under both non-isothermal and isothermal conditions. It was demonstrated that, over a wide temperature range, their activation energies (143.5 and 134.6 kJ/mol for 3,4-DNPAz and

3,5-DNPAz, respectively) are also determined by the isomerization of the azo groups from the trans form to the less stable cis form, rather than by unimolecular N–N bond cleavage.

The thermal decomposition of 1,1’-azo-bis[3-(nitro-NNO-azoxy)-1H-1,2,4-triazole] (ANAzTr) was investigated for the first time under both non-isothermal and isothermal conditions. It was found that the activation energy for the decomposition of ANAzTr in the liquid phase (157.2 kJ/mol) is close to the calculated energy required to break the $N\text{-}NO_2$ bond.

Based on an analysis of decomposition products using high-performance liquid chromatography–mass spectrometry, a decomposition mechanism was proposed for all the compounds studied.

The combustion characteristics of isomeric 1,1'-azo-bis(dinitropyrazoles) and the nitroazoxytriazole ANAzTr were investigated for the first time. Thermocouple measurements revealed that the unusually large difference in the burning rates of the isomeric azo compounds is attributable to a difference in surface temperatures. The high surface temperatures observed for 3,4-DNPAz indicate that its burning rate is governed by the kinetics of heat release in the condensed phase. In the case of 3,5-DNPAz, surface temperatures are lower, and the fraction of substance decomposed in the melt is negligible (less than 1%); this, combined with a steep temperature gradient above the burning surface, points to a gas-phase combustion mechanism. It is suggested that the lower surface temperature during the combustion of 3,5-DNPAz is determined not by the boiling point of the starting material, but by the boiling point of an intermediate decomposition product—3,3',5,5'-tetranitro-1,1'-bipyrazole.

The compound ANAzTr proved to be a fast-burning substance that outperforms tetracene—a well-known component of igniter compositions—in terms of stability, density, detonation velocity and pressure, and combustion temperature. Despite the extremely short residence time of ANAzTr in the condensed phase, its combustion process is governed by the decomposition reaction occurring at the boiling (surface) temperature. A relationship estimating the dependence of the ANAzTr surface temperature on pressure was derived. For substances whose burning rate is determined by reactions in the melt at the surface temperature, it was established that kinetic parameters obtained from combustion thermocouple data are consistent with the kinetics of thermal decomposition in the liquid phase.

Theoretical and practical significance of the work. Data obtained on the decomposition kinetics of (dinitropyrazolyl)azoxyfurazans, isomeric 1,1'-azobis(dinitropyrazoles), and the nitroazoxytriazole ANAzTr made it possible to determine storage conditions for the compounds under study.

The research revealed that 3,5-DNPAz and the nitroazoxytriazole ANAzTr are fast-burning substances; this allows 3,5-DNPAz to be considered as a burning-rate modifier for

rocket propellants and gunpowders, and ANAzTr as an energetic replacement for the sensitizer tetracene. Thermocouple measurements provided the thermal diffusivity and the temperature dependence of vapor pressure—data essential for the practical application of the substances investigated.

Research methodology and methods. The primary research methods employed in the thesis were differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and isothermal gravimetry (iso-TG); a manometric method for studying thermal decomposition kinetics; IR spectroscopy, high-performance liquid chromatography, and mass spectrometry for analyzing decomposition products; a method for determining the pressure dependence of the burning rate using a constant-pressure apparatus; and a thermocouple technique for obtaining temperature profiles within the combustion wave. The research methodology encompassed the determination of decomposition kinetic parameters for novel energetic compounds, as well as the patterns and mechanisms of their combustion.

Propositions submitted for defense:

Experimental data on the decomposition kinetics of (dinitropyrazolyl)azoxyfurazans, isomeric 1,1'-azobis(dinitropyrazoles), and the nitroazoxytriazole ANAzTr; combustion characteristics of 1,1'-azobis(dinitropyrazoles) and the nitroazoxytriazole ANAzTr; data from thermocouple studies of their combustion waves; and the interpretation of the obtained results.