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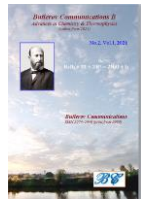

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Study of thermal (phase and chemical) conversions of 1-[2,2-bis(methoxy-NNO-azoxy)ethyl]-3-nitropyrazoleby DSC, TG and mass spectrometry

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Abstract

Thermal (phase and chemical) transformations of two polymorphic modifications (α and β) of 1-[2,2-bis(methoxy-NNO-azoxy)ethyl]-3-nitropyrazole (**I**) under non-isothermal conditions have been studied using the methods of thermal analysis, IR spectroscopy, and mass spectrometry. Compound **I** is of practical interest as a prototype and model for a wide class of high-energy pyrazole-based compounds. The Kissinger equation was used to determine the kinetic parameters (activation energy and preexponential factor) of the thermal decomposition of **I**. The heat of the α-**I**→β-**I** polymorphic transition, the heat of β-**I** melting, and the heat of thermal decomposition of **I** are, respectively, -1.5±0.3, -26.1±1.9, and 332.6±43.0 kJ/mol. N_2O, H_2O, NO_2, NO, N_2, CH_3OH, and 3-nitropyrazole have been found among the products. Based on the data of IR spectroscopy of condensed rest after thermal decomposition of **I**, it was concluded that the main condensed products of the reaction are 3-nitropyrazole and an amorphous polymer containing a polyconjugated system of bonds formed by carbon and nitrogen atoms. From the DSC and TG data, the effective values of the activation energy of the decomposition process were determined to be equal to 127.2 ± 2.5 and 135.2 ± 8.5 kJ/mol, respectively. It was confirmed that the first stage of the reaction involves the elimination of the methoxydiazenoxide group through a five-membered cyclic transition state. The proposed reaction scheme assumes that the reaction proceeds sequentially and includes the decomposition of the resulting intermediate (with the formation of 3-nitropyrazole) and its polymerization with the opening of the C=C double bond.

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