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LETTERS TO THE EDITOR

Thermolysis of 1-Ethyl-3-nitro-1,2,4-triazole in the Melt

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Kinetic studies of gas-phase thermal decomposition have shown that ethyl-3-nitro-1,2,4-triazole decomposes primarily via the monomolecular homolytic rupture of the C–NO_2 bond, and it is characterized by the following activation parameters: E_a = 272.6± 10.5 kJ mol^{-1} and log A = 16.81±0.84 [1]. The question arises: whether this mechanism is unique, or it varies depending on the 1-ethyl-3-nitro-1,2,4-triazole aggregate state?

Therefore we studied the thermal decomposition of 1-ethyl-3-nitro-1,2,4-triazole in the melt under argon at a pressure of the inert gas 200–220 mm Hg and the reaction vessel surface to volume ratio (S/V) 1.2–1.5 cm^{-1}. At the ratio below this value the decomposition rate constant remains unchanged. The kinetic investigation was carried out under static conditions in a glass manometer of Bourdon type [2]. Before argon inflow to the reaction vessel containing a molten substance, a manometer was evacuated to a pressure of 10^{-2}–10^{-1} mm Hg at the alternate heating (up to melting) and cooling (up to hardening) to remove volatile impurities in the studied material. This operation was repeated 3–4 times.

The thermolysis of the molten 1-ethyl-3-nitro-1,2,4-triazole proceeds at 230–270°C as a first-order reaction. The rate constant calculation was performed by the Guggenheim method [3]. The temperature dependence of the thermolysis is described by the equation: $k = 10^{13.73}\exp(-175000/RT)$.

Thermal decomposition of *o*- and *p*-dinitrotoluene has been shown to occur in the liquid phase via the redox-mechanism involving the methyl and nitro functions. It is not excluded that in our case the thermal decomposition of 1-ethyl-3-nitro-1,2,4-triazole proceeds through a similar mechanism. By the chromatography, the qualitative composition of the major gaseous products at 93–95% conversion at 250ºC was shown to contain N_2, NO, CO and CO_2. In the infrared spectrum of the condensed residue was found a broad absorption band of NH-group in the range of 3360–3400 cm^{-1}. Its appearance combined with the composition of gaseous decomposition products can serve as an argument in favor of intermolecular redox-mechanism between methyl and nitro groups in the thermal decomposition of 1-ethyl-3-nitro-1,2,4-triazole.

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