

# Thermal Decomposition of Dinitropyrazoles: New Insights from Predictive Electronic Structure Theory and Thermal Analysis

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Nitrogen-rich heterocycles and their derivatives are promising environmental-friendly energetic compounds. In present work, we studied most important safety concerns, thermal decomposition, of 3,5-dinitropyrazole (3,5-DNP), and 5-amino-3,4-dinitropyrazole (5-ADP) using a complementary combination of thermal analysis and quantum chemical calculations. Differential scanning calorimetry (DSC) measurements were performed at atmospheric and elevated pressures (up to 5 MPa) under different heating rates (0.5 - 20 K/min). The increase of the external pressure renders the decomposition kinetics to be dominant rather than vaporization process. The experimental data were processed using isoconversional and formal kinetic approaches to derive the kinetic models. The experiment was complemented by the highly accurate CCSD(T)-F12 and DLPNO-CCSD(T) quantum chemical calculations to justify the use of particular reaction models and to compare the kinetic parameters for the dominating primary thermolysis reactions. Among the reaction pathways, conventional reactions, namely, radical reaction of C-NO<sub>2</sub> bond scission, the intramolecular oxidation, hydrogen transfer, and nitro-nitrite rearrangement were considered. The most energetically favorable channels for 3,5-DNP we identified new decomposition channel that commences from sigmatropic [1,5] H-shift followed by the pyrazole ring opening yielding a molecular nitrogen and a nitro radical as simple primary products. The limiting stage is the first hydrogen transfer with the effective activation energy  $E_a = 60.7$  kcal/mol. For 5-ADP the decomposition starts with a [1,2] sigmatropic hydrogen shift, followed by another [2,3] hydrogen shift leading to 5-amino-3,4-dinitro-3H-pyrazole, which can then decompose via several pathways. The limiting stage of the process is the second hydrogen transfer with an effective activation energy is 52 kcal/mol. To understand the autocatalytic nature of 5ADP decomposition, we also considered the secondary thermolysis reactions. Among those reactions we identified the one that can be responsible for the autocatalytic nature of 5ADP decomposition: viz., the primary radical product can be easily accessed from the reactants and then NO<sub>2</sub> is promptly eliminated.

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