

Thermal Stability of Dinitrotriazolopyridines and Dinitrobenzotriazoles: Interplay of Thermal Analysis and Computational Chemistry

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Understanding the thermal stability of novel hazardous materials is of a great importance for storage and safety issues. The objects of present study are recently synthesized heterocyclic derivatives of pyridine and benzene, viz., 6,8-dinitrotriazolopyridine (DTP), 2-amino-6,8-dinitrotriazolopyridine (ADTP) [1], 5,7-dinitrobenzotriazole (DBT), and 4-amino-5,7-dinitrobenzotriazole (ADBT) [2]. These compounds exhibit high decomposition onset temperatures (>290°C) [1,2], however, the nature of their thermal stability is poorly studied. Therefore, we studied the mechanism and kinetics of thermal decomposition for the title compounds. The thermal stability of DTP and ADTP in the condensed phase was studied using differential scanning calorimetry at elevated pressures (2.0 MPa). Thermokinetic analysis was performed using the isoconversional and model-fitting analysis. The thermolysis of DTP occurs in the melt with the kinetic parameters $E_a=135.1\pm 0.4$ kJ/mol and $\log(A, s^{-1})=10.37\pm 0.03$. The thermal decomposition of ADTP as low (0.13-2 K/min) and high (5-20 K/min) heating rates is described by very high kinetic parameters. The obtained results indicate that thermolysis of ADTP is complicated by parallel physical processes, most importantly, melting. The experimental kinetics was complemented with theoretical mechanistic insights obtained at a modern reliable level of theory (DLPNO-CCSD(T)/aVQZ). In all cases, the nitro-nitrite rearrangement and C-NO₂ bond cleavage are the most important initial decomposition channels. The nitro-nitrite rearrangement is the energetically preferred reaction with the activation energy ~240 kJ/mol (DTP, ADTP) and ~270 kJ/mol (DBT, ADBT). However, due to higher preexponential factors, the C-NO₂ bond cleavage is a dominant decomposition reaction at the high temperatures (>230°C) with activation barriers ~280 kJ/mol (DTP, ADTP) and 300 kJ/mol (DBT, ADBT).

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[1] A.M. Starosotnikov et al. *ChemistrySelect* **2019**, *4*, pp. 1510–1515.

[2] D. Ehlers, et al. *Chem. Eur. J.* **2015**, *21*, pp. 16073–16082.