Mechanism and Kinetics of Thermal Decomposition of CL-20: Ab inito molecular dynamics study

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CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) is a high-energy nitramine explosive. To improve atomistic understanding of its thermal decomposition in gas and solid phases, we performed a series of ab initio molecular dynamics simulations.

Unlike the case of the other nitramines (e.g. RDX/HMX), we found only one distinct initial reaction channel (homolysis of $N–NO_2$ bond) during unimolecular decomposition. We did not observe any HONO elimination reaction under investigated conditions. However, we did find ring breaking followed by NO_2 fission. Therefore, in spite of limited sampling that provided a mostly *qualitative* picture, we proposed a scheme of unimolecular decomposition of CL-20. The averaged products population over all trajectories was estimated at 4 HCN, 2-4 NO_2, 2-4 NO, ~1 CO, and ~1 OH molecules per one CL-20.

These simulations provide a detailed description of the chemical processes in the initial stages of thermal decomposition of condensed CL-20. We elucidated key features of this process: composition of primary reaction products, reaction timing, Arrhenius behavior of the system, etc. They clearly indicate that the primary reactions leading to NO_2, NO, N_2O and N_2 occur at very early stages. We also estimated the activation barrier for the formation of NO_2 which essentially determines overall decomposition kinetics and effective rate constants for NO_2 and N_2. Calculated solid phase decomposition pathways correlate with available condensed phase experimental data. Unfortunately, a comparison of the predicted gas phase mechanism was not possible.