Modern Predictive Quantum Chemical Calculations for Thermochemistry and Decomposition Kinetics of Energetic Materials

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Highly accurate theoretical values of bond energies and activation barriers of primary decomposition reactions are crucial for reliable predictions of thermal decomposition and detonation-related phenomena of energetic materials (EM). However, due to the prohibitive computational cost, high-level ab initio calculations had been impractical for a large number of important EMs of medium size, including, e.g., CL-20. The widely used DFT calculations very often could not provide the uniform "chemical accuracy" (~1 kcal/mol) and, ultimately, the convincing mechanistic evidence on the decomposition pathways of important EMs.

Here we report on the advantages in the theoretical thermochemistry and kinetics of EM achieved with the use novel local modifications of the coupled cluster (DLPNO-CCSD(T)). These render feasible high-accuracy calculations on caged polynitroamino and polynitro EMs, e.g., CL-20 and octanitrocubane (ONC). For all important species studied, the obtained values of bond energies are at least 10 kcal/mol more accurate than those reported in the literature so far. We also studied in detail the gas-phase thermochemistry of novel high-energy polynitro derivatives of 5/6/5 heterocyclic frameworks comprised of fused tetrazine and two triazole or pyrazole rings. To this end, we proposed and benchmarked a "bottom-up" approach. First, highly accurate multi-level procedures W2-F12 and/or W1-F12 in conjunction with the atomization energy approach were utilized for smaller species. In turn, for medium-sized species (up to 24 non-H atoms), these values were complemented with the enthalpies of isodesmic reactions calculated using DLPNO-CCSD(T)/aVQZ. In a more general sense, the latter approach is a viable step beyond the commonly used DFT procedures and represents a new level of predictive computational thermochemistry and kinetics for important EMs.

We also proposed a new approach for the determination of standard (solid) state enthalpy of formation of EM based on complementary high-level quantum chemical calculations (W1-F12 and W2-F12) of the gas-phase values and advanced thermal analysis techniques yielding sublimation enthalpies. We performed a massive benchmarking of the proposed procedure on a large set of EMs.