The Assessment of the Accuracy of Experimental Enthalpies of Formation of High-Nitrogen Compounds by Quantum Chemical Calculations

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Numerous high-nitrogen compounds have explosive properties and attract great attention in the modeling of new high energy materials with projected properties. Important characteristics of explosives and propellants can be calculated from the enthalpy of formation, which is closely related to the stability and sensitivity of these compounds. The experimental enthalpies of formation for many important high-nitrogen compounds are often unknown or determined with relatively large uncertainties. Today quantum chemical calculations can be used successfully for prediction of thermochemical properties or analyzing of experimental data.

The Gaussian-n family methods (G4 and G4(MP2)) combined with atomization reaction were tested in their possibilities to quantitatively estimate the values of enthalpy of formation. To get the accurate gas-phase enthalpies of formation, the quantum chemical calculations combined with isodesmic reaction scheme were used in this study. A set of internally consistent values of enthalpies of formation of nitrogen-containing compounds has been obtained. Among these are nitro compounds, nitramines, amines, heterocycles, and azides with different architecture and functional groups.

The experimental condensed phase enthalpies of formation and enthalpies of sublimation/vaporization were analyzed based on recommended values of the gas phase enthalpy of formation. In some cases a possible inaccuracy of the experimental values has been suggested. The enthalpies of sublimation or vaporization were estimated by quantum chemical calculations for compounds for which no experimental data are available.