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Aliphatic nitroalkanes: Evaluation of thermochemical data with complementary experimental and computational methods

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ABSTRACT

Thermochemical properties of aliphatic nitroalkanes available in the literature are scarce and inconsistent. New standard molar enthalpies of vaporization and sublimation of 2-nitropropane, 2-methyl-2-nitropropane, and 2,3-dimethyl-2,3-dinitrobutane were derived from the vapor pressure temperature dependence measured by the transpiration method. Thermodynamic data on linear and branched aliphatic mono- and di-nitroalkanes available in the literature were combined with own experimental results and evaluated with help of empirical and theoretical methods aiming at recommendation of the sets of vaporization and formation enthalpies for aliphatic nitroalkanes as the reliable benchmark properties for further thermochemical calculations. Gas phase standard molar enthalpies of formation of aliphatic nitro-compounds derived by high-level quantum-chemical method G4 were found in a good agreement with the evaluated and recommended experimental data. Group-additivity procedure for calculation of vaporization and formation enthalpies have been developed and tested.

1. Introduction

Design and synthesis of new formulations of advanced propellants and explosives is a challenging task. Last decade, a computer aided screening of suitable hypothetical energetic materials is a popular endeavor [1–7]. However, it is reasonable to expend resources only on those molecules that show promise to provide enhanced performance, reduced sensitivity, or reduced environmental hazards. In order to assess potential performance of an energetic compound in explosive or propellant cases, the standard molar enthalpy of formation $\Delta_f H_m^\circ$, standard molar enthalpy of sublimation $\Delta_{cr}^g H_m^\circ$, standard molar enthalpy of vaporization $\Delta_l^g H_m^\circ$, and standard molar enthalpy of fusion $\Delta_{cr}^l H_m^\circ$, are considered as an important property [3,4,7]. They are used for the calculation of explosive and propellant properties such as detonation pressure, detonation velocity and specific impulse to investigate characteristics of energetic materials. The prediction of thermochemical properties of explosives to within 'chemical accuracy' (usually defined as theoretical values with mean absolute deviation within 4–5 kJ mol^{-1} from experimental data) using selected high-level methods from the G* family seems to be practicable [5] and these methods can be used to reduce experimental efforts to prepare promising compounds exhibiting required enhanced performance. However, the triumph of the modern quantum-chemical methods is aggravated with several issues thwarting a proper interpretation of the computational results. First of all converting of the enthalpic values H_{298} (directly available from the Gaussian output) to the standard molar enthalpy of formation is ambiguous. The conventionally used atomization and isodesmic reactions provide too different results even for simple compounds. For example, the most accurate Gaussian-4 (G4) method provides the $\Delta_f H_m^\circ$(g) values calculated from the atomization reactions by 13 kJ mol^{-1} underestimated in comparison to the common isodesmic reaction procedure including 5–26 isodesmic reactions with different reference species that were constructed for each compound [8]. The second issue is that the thermochemical properties of reference species used for the construction of the isodesmic reactions are mostly of ill-defined quality. As a matter of fact, the most combustion experiments for simple aliphatic mono- and di-nitroalkanes were performed over 50 years ago [9–12] and at those times the methods for the purity attestation of the samples were not always sensitive enough. Moreover, in many cases the combustion results measured in different labs were significantly different [9–14] or for many nitro-alkanes only a single enthalpy of formation value was available. Experimental results on vaporization and sublimation enthalpies, required for calculation of $\Delta_f H_m^\circ$(g), are practically absent in the literature in spite of the sufficient

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