Ab initio quantum chemical predictions of enthalpies of formation, heat capacities, and entropies of gas-phase energetic compounds

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Abstract

This paper presents the thermochemical properties of 42 energetic materials commonly used in explosives and/or propellants. The standard enthalpies of formation at 298.15 K and heat capacities and entropies in the temperature range of 300–5000 K have been computed by means of the density functional theory in quantum chemistry along with a protocol developed for these energetic compounds. The resulting data, currently not available in the literature, are critical for modeling reaction mechanisms and combustion-wave structures of these materials.
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1. Introduction

The combustion of solid propellants is a complex phenomenon involving many intricate physiochemical processes in the gas-phase, near-surface, and sub-surface regions [1–4]. Despite the extensive efforts made over the past 5 decades, the thermochemical properties of many propellant ingredients and related molecules and radicals in the reaction pathways are not available [1,5]. Even for such nitramine compounds as RDX and HMX, whose gas-phase reaction mechanisms have been reasonably well established by Yetter et al. [2], Melius [6], and Manaa et al. [7], thermochemical data for many participating species

are still lacking. The situation becomes more severe when a new energetic material is formulated and its combustion needs to be characterized. The lack of data hampers the development of detailed chemical kinetic models for the decomposition and subsequent combustion chemistry of the new compound. Experimental measurements are always preferred, but the amount of data needed is so vast that validated theoretical tools must be employed to make available the required information. The purpose of this paper is to provide such fundamental thermochemical properties as standard enthalpies of formation, heat capacities, and entropies for selected energetic compounds in the gas phase. It is not certain whether all the molecules considered below exist in the gas phase near the burning surface of a given energetic material. Many of them, including RDX [8], Keto-RDX [8],

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and TNAZ [9], however, have been observed both experimentally and theoretically due to evaporation or ejection from the condensed phase. The subsequent thermal decomposition and reactions then lead to ignition and combustion in the gas phase.

2. Computational method

The energetic materials under consideration have large molecules containing one or several nitro, nitrate, or amino groups. The most reliable existing ab initio methods, G2 and G3, are computationally too expensive [10] to be of interest for the present work. Moreover, these methods have been benchmarked only for relatively small molecules, and their validity for large molecules remains to be demonstrated. Density functional methods (such as the B3LYP/6-311G(d,p) method) using a conventional atomization approach have been shown [11] to provide a reasonable treatment of naphthalene ($C_{10}H_8$), quite a large molecule. The molecules investigated in the present study, however, are even larger. For this reason, a method with a smaller basis set is desired. Rice et al. [12] used a B3LYP/6-31G(d)//B3LYP/6-31G(d) method based on the atomization approach and atomic corrections to predict enthalpies of formation of several energetic materials. A total of seven atomic corrections were defined, four for C, H, N, and O atoms involved in single bonds and three for C, N, and O atoms involved in multiple bonds. Unfortunately, this method was not validated because all of the 35 gaseous species considered [12] were used to determine atomic corrections. It should be noted, however, that validation for those energetic materials poses practical challenges because of the scarcity of experimental data. Wilcox and Russo [13] proposed a B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) method for C, H, and N compounds with parametric corrections for these atoms. The method, derived with 35 compounds, was not validated in a strict sense. Moreover, it is of limited use for the energetic materials considered here because calculations with O atoms are not feasible, although it is expected to be slightly more accurate than the B3LYP/6-31G(d)//B3LYP/6-31G(d) method employed by Rice et al. [12]. A comparative study of several existing approaches, including the semiempirical PM3 method, indicates that the B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) technique appears to offer the best compromise between numerical accuracy and expense.

The model employed in this paper includes zero-point energies and several new atomic corrections. Rice et al. [12] considered only two classes of atoms involved in either single or multiple bonds. We introduce a distinction between nitrogen atoms in a 'normal' environment (trivalent according to the octet rule) and nitrogen atoms in a hypervalent state (pentavalent), such as those in nitro and nitrate groups. Many energetic materials are fluorinated and an atomic correction for F atoms is required. A total of nine atomic corrections are derived in the present work: two for H and F atoms, three for C, N, and O atoms involved in single bonds, three for C, N, and O atoms involved in multiple bonds, and one for hypervalent N atoms.

The gas-phase standard enthalpy of formation of molecule j at 298.15 K can be determined from the equation

$$\Delta_f H^0_{298.15K(g)}$$
$$= 627.51 \times \left(E_j + ZPE_j \right.$$
$$\left. + \text{thermal corrections} + \sum_i \alpha_i c_i^* \right),$$

where α_i is the number of atoms i in molecule j and c_i^* is the atomic correction for atom i. E_j and ZPE_j denote, respectively, the absolute electronic energy and zero-point energy, calculated using the Gaussian 98W [14] and Gaussian 03 [15] software packages. The units are Hartree molecule^{-1} for E_j, ZPE_j, and thermal corrections and Hartree atom^{-1} for c_i^*, whereas $\Delta_f H^0_{298.15K(g)}$ is in kcal mol^{-1}. The method employed in the present study is based on 28 energetic and nonenergetic compounds having well-calibrated enthalpies of formation with uncertainty less than 1 kcal mol^{-1}. The atomic corrections c_i^* are determined by least-square fitting of the 28 selected experimental gas-phase standard enthalpies of formation at 298.15 K. Table 1 reports the comparison between experimental and computed standard enthalpies of formation at 298.15 K for some of the 28 compounds considered. Table 2 gives the atomic corrections. The work of Rice et al. [12] was recently refined [16] with the introduction of group-based corrections and modification of the values of the atom-based corrections. Such refinements allow computation of the gas-phase enthalpies of formation of molecules containing all types of N atoms described above.

3. Validation of model

The ab initio method developed here was validated for 16 nitro or nitrate compounds, including RDX. Table 3 shows the measured and calculated gas-phase enthalpies of formation. The corresponding statistical analysis is given in Table 4. Good agreement is obtained with experimental data, indicating that the predicted results are sufficiently accurate. It is usually recognized that the level of accuracy required