

Enthalpies of formation of small free radicals and stable intermediates: Interplay of experimental and theoretical values[☆]

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Dedicated in honour of Professor Jean Demaison

Abstract

A set of small radicals $\cdot\text{SiF}$, $\cdot\text{SiCl}$, $\text{F}\cdot\text{C}=\text{O}$, $\text{C}=\text{N}\cdot\text{O}$, $\cdot\text{O}_3\text{H}$, $\cdot\text{NO}_3$, $\cdot\text{CH}_2\text{NC}$, $\text{CF}_3\text{O}\cdot$, and O_3 exhibit pronounced discrepancies between different experimental as well as experimental and calculated values of the respective enthalpies of formation $\Delta_f H^\circ(298.15)$. For stable molecules, this quantity is well established and reliable values are available. However, for free radicals and other short-lived intermediates, the situation is not nearly as favorable. Consequently, critical evaluation of thermodynamic properties of free radicals is necessary, both originating from experiment and computation. Calculated enthalpies of formation for the above systems are based on the ab initio methods G3MP2B3 and CCSD(T)–CBS (W1U) for which mean absolute deviations are known.

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1. Introduction

The knowledge of accurate thermodynamic properties of free radicals or other reactive species is of paramount importance in many areas of chemistry, e.g. combustion or atmospheric chemistry. Frequently quite substantial uncertainties are associated with experimental data of such species. Thus, computational methods have become increasingly important in the determination of accurate enthalpies of formation $\Delta_f H^\circ$. We have previously reported for a set of 32 free radicals with well established thermochemistry, a mean absolute deviation (MAD) of 3.9 kJ mol^{-1} between reliable experimental and calculated $\Delta_f H^\circ(298.15)$ values using the G3MP2B3 procedure [1]. For a different set of 60 less well characterized radicals, larger

discrepancies occur between experimental and calculated values [2]. Some of these discrepancies are, at least partly, due to the inclusion of computationally demanding systems. Since, for the original set of radicals, the MAD could be further reduced to 2.3 kJ mol^{-1} with the aid of the CCSD(T)–CBS (W1U) procedure, we thought it worthwhile to recalculate those radicals showing the largest deviation between calculated and experimental $\Delta_f H^\circ$ values. These are fluoro- and chlorosilylydyne ($\cdot\text{SiF}$, $\cdot\text{SiCl}$), carbonyl-fluoride $\cdot\text{CFO}$, nitrosomethylidyne $\text{CNO}\cdot$, hydrotrioxyl $\cdot\text{O}_3\text{H}$, nitrogen trioxide $\cdot\text{NO}_3$, isocyanomethyl $\cdot\text{CH}_2\text{NC}$, trifluoromethoxyl $\text{CF}_3\text{O}\cdot$, and ozone O_3 . Moreover, for most of these species the experimental results show either rather large error bars or are even questionable. Thus, the results obtained for these radicals will be used to illustrate the interplay between theory and experiment for deriving accurate thermodynamic data.

2. Computational methods

Gaussian-3 (G3) theory is a procedure for calculating total energies of atoms and molecules containing atoms for $Z \leq 18$ (hydrogen to argon) based on ab initio calculations as well as empirically based molecule-independent corrections [3].

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G3 theory was assessed on a total of roughly 300 energies from which enthalpies of formation as well as reaction enthalpies, ionization energies, and electron affinities were obtained. Meanwhile, different modifications of G3 theory have been developed, which require less computational time and can be applied to larger systems with more than 150 electrons (20 heavy atoms out of the range between carbon and chlorine) without significant loss of accuracy. The variation, referred to as G3MP2B3, is described in the following [4].

First, the geometries as well as the complete set of vibrational wave numbers are calculated at the B3LYP/6-31G(d) level. The zero-point energies (ZPE) are scaled by 0.96. The B3LYP density functional [5] used for the calculation of the geometries and ZPE is a linear combination of Hartree-Fock exchange, 1988 Becke exchange, and Lee, Yang, Parr correlation functional [6]. Second, a single-point quadratic configuration interaction calculation is performed in the frozen core approximation for the correlation calculation, QCISD(T,FC)/6-31G(d). Third, second-order Møller–Plesset perturbation theory, MP2(FC), is performed with the basis sets 6-31G(d) and 6-311+G(2df,2p) on Li–Ne, and 6-311+G(3d2f,2p) on Na–Ar, summarized as G3MP2large. Fourth, a spin-orbit (SO) corrections is included for atomic species. Fifth, the higher level correction (HLC) takes into account remaining deficiencies in the energy calculations. The HLC is simply a linear function of the number of valence electrons with α and β spin, $-An_{\beta} - B(n_{\alpha} - n_{\beta})$, with $n_{\alpha} \geq n_{\beta}$. The values of A and B are 10.041 and 4.995 mE_h , respectively, for molecules, and 10.188 and 2.323 mE_h , respectively, for atoms; $1 mE_h = 2.625500 \text{ kJ mol}^{-1}$ [4]. In summary, the G3MP2B3 total energy E_0 results to be

$$\begin{aligned}
 E_0[\text{G3MP2B3}] &= E[\text{QCISD}(T)/6-31\text{G}(d)] \\
 &+ E[\text{MP2}/\text{G3MP2 large}] - E[\text{MP2}/6-31\text{G}(d)] \\
 &+ \Delta E(\text{ZPE}) + \Delta E(\text{SO}) + \Delta E(\text{HLC}) \quad (1)
 \end{aligned}$$

A more accurate but also more expensive method, restricted to small systems, is based on the CCSD(T) electron correlation method (Coupled Cluster with all Single and Double substitutions followed by a perturbative estimate of the effect of connected Triple excitations) [7]. Different series of calculations are used to achieve CBS (Complete Basis Set) results by means of extrapolation schemes. We follow the strategy of Martin and de Oliveira [8] who abbreviate their CCSD(T)–CBS arrangement of methods by W1. This series of methods is modified for radicals where UCCSD (Unrestricted open shell) instead of ROCCSD (Restricted Open shell) is applied. The protocol for the various steps of W1U is described in the following.

(1) The geometry as well as the complete set of harmonic vibrational wave numbers are calculated at the B3LYP/VTZ

level (cc-pVTZ, or VTZ for short, if only first-row atoms are present). The zero-point energy (ZPE) is scaled for the total energy as well as for thermochemical properties by 0.985. (2) The following single-point calculations are carried out: CCSD(T)/AVDZ, CCSD(T)/AVTZ, and CCSD/AVQZ. (2a) The SCF component of total energy is extrapolated by $A + B/C^l$ from the above SCF components ($l = 2, 3$, and 4, respectively). (2b) The CCSD valence correlation component is obtained from applying $A + B/l^\beta$ to CCSD/AVTZ and CCSD/AVQZ valence correlation energies ($l = 3$ and 4, respectively; $\beta = 3.22$). (2c) The (T) valence correlation component is obtained from applying $A + B/l^\beta$ to CCSD(T)/AVDZ and CCSD(T)/AVTZ values for the (T) contribution. (3) Core correlation contributions are obtained from CCSD(T)/MTsmall. (4) Scalar relativistic corrections are calculated with the previous step [9]. (5) Spin-orbit coupling effects are considered manually from experimental values [10]. SO splittings (cm^{-1}): C (16.4), O (158.3), F (404.1), Si (77.1), Cl (882.4); energy corrections (cm^{-1}): C (−29.6), O (−79.2), F (−134.7), Si (−149.7), Cl (−294.1); $1 \text{ kJ mol}^{-1} = 83.5935 \text{ cm}^{-1}$. In summary, the W1U total energy E_0 results to be

$$\begin{aligned}
 E_0[\text{CCSD}(T) - \text{CBS}(W1U)] &= E[\text{SCF} - \text{CBS}] + \Delta E_{\text{val.-correl}}[\text{CCSD} - \text{CBS}] \\
 &+ \Delta E_{\text{val.-correl.}}[\text{CCSD}(T) - \text{CBS}] \\
 &+ \Delta E_{\text{core-correl.}}[\text{CCSD}(T)/\text{MTsmall}] \\
 &+ \Delta E_{\text{relativ.}}[\text{CCSD}(T)/\text{MTsmall}] + \Delta E(\text{ZPE}) \\
 &+ \Delta E_{\text{exp.}}[\text{SO}] \quad (2)
 \end{aligned}$$

All calculations have been performed using the GAUSSIAN03 computer program [11].

The above-mentioned B3LYP/cc-pVTZ (for W1U) and B3LYP/6-31G(d) (for G3MP2B3) calculations for the energy minimum structures and vibrational wave numbers are the basis for the thermochemical corrections to the electronic total energy E_0 . These corrections were calculated at specified states T , p by using standard rigid-rotor harmonic oscillator (RRHO) partition function expressions. In addition to complete sets of structural parameters and vibrational wave numbers $\tilde{\nu}$, principal moments of inertia I_A , I_B , and I_C , heat capacities $C_p^0(T)$, entropies $S^0(T)$, and thermal energy contents $H^0(T) - H^0(0)$ are available upon request.

The spin contamination, described by the expectation value $\langle S^{*2} \rangle$, of the different free radicals is as follows. B3LYP/6-31G(d) (for G3MP2B3): $\cdot\text{SiF}$ (0.7528), $\cdot\text{SiCl}$ (0.7530), $\text{F}-\cdot\text{C}=\text{O}$ (0.7533), $\text{C}=\text{N}-\text{O}\cdot$ (0.7571), $\cdot\text{O}_3\text{H}$ (0.7563), $\cdot\text{NO}_3$ (0.7984), $\cdot\text{CH}_2\text{NC}$ (0.7618), $\text{CF}_3\text{O}\cdot$ (0.7524). B3LYP/VTZ (for CCSD(T)–CBS (W1U)): $\cdot\text{SiF}$ (0.7553), $\cdot\text{SiCl}$ (0.7552), $\text{F}-\cdot\text{C}=\text{O}$ (0.7537), $\text{C}=\text{N}-\text{O}\cdot$ (0.7574), $\cdot\text{O}_3\text{H}$ (0.7571), $\cdot\text{NO}_3$ (0.7557), $\cdot\text{CH}_2\text{NC}$ (0.7611), $\text{CF}_3\text{O}\cdot$ (0.7527).

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