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Organic Thermochemistry at High ab Initio Levels. 3. A G3 Study of Cyclic Saturated and Unsaturated Hydrocarbons (Including Aromatics)

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With the purpose of exploring the reliability of the enthalpies of formation calculated using the G3 method, we have examined a series of saturated and unsaturated alicyclic hydrocarbons varying the size and the number of formal double bonds in the molecule. Heats of formation have been calculated at the G3 level through both atomization reactions and bond separation isodesmic reactions, and comparisons with experimental values and with values previously calculated at the G2(MP2) and G2 levels have been made. The quality of the G3-calculated enthalpies of formation using atomization reactions is comparable to that obtained at the G2 level using bond separation reactions, whereas G3 calculations are two to three times faster than G2 calculations.

Introduction

In formal terms, the possible evolution of a chemical system is determined by the standard Gibbs energies of reagents and products. In the absence of solvent, the standard molar enthalpy of formation in the gas phase of a species M, $\Delta_f H°_m$(M, g) (standard heat of formation in the gas phase), is one of the two contributors (often the largest in absolute value) to this thermodynamic parameter. In the case of organic molecules, $\Delta_f H°_m$(M, g) is also valuable because it is a key piece of information for the quantitative study of structural effects (e.g., strain) on reactivity.

The experimental determination of $\Delta_f H°_m$(M, g) by standard thermochemical techniques requires the use of extremely pure materials. Worse yet is the fact that these techniques are necessarily destructive.

It has been reported[1−4] that the G2 family of computational methods[5−11] allows the reliable estimation of the standard enthalpies of formation in the gas phase of a variety of compounds. In many cases, the computed values agree with the experimental data within about 1.8 kcal mol^{-1}.[3] Some exceptions, however, are also known.[1,12−16]

In the first paper in this series,[17] we explored the scope of these methods (G2(MP2) and G2) as a potentially valuable tool for organic chemists. We examined a series of saturated and unsaturated alicyclic hydrocarbons varying the size (up to 10 carbon atoms) and the number of formal double bonds in the molecule.

Very recently, Curtiss et al.[18] have presented a new procedure within the Gaussian-*n* series of model chemistries, the so-called Gaussian-3 (G3) theory, which achieves significantly improved accuracy relative to G2 theory. G3 theory was assessed on a total of 148 enthalpies of formation from the G2/97 test set.[3,19] The average absolute deviation from experiment of G3 theory for the 148 enthalpies of formation is 0.94 kcal mol^{-1}, a significant improvement over G2 theory which has an average absolute deviation of 1.56 kcal mol^{-1} for this set. G3 theory is also about two to three times faster than G2 theory for typical calculations.[20]

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We have applied successfully the new G3 method to the calculation of the enthalpies of formation of dithianes and a series of related compounds,[21] and there are other recent successful applications of the G3 theory to the calculation of enthalpies of formation,[22−25] among them a study of the enthalpies of formation of bi-, tri-, and tetracyclic C_7 hydrocarbons carried out by Rogers and McLafferty[24] at the G3(MP2) level.[26]

This has prompted us to apply the G3 method to the same set of molecules studied in ref 17, to compare this new method with the previous G2(MP2) and G2 methods.

Computational Details

1. G3 Method. Standard ab initio molecular orbital calculations[27] were performed with the Gaussian98 series of programs.[28] Energies were obtained at the recently proposed G3[18] level of theory.

Gaussian-3 (G3) theory[18] is a new procedure for calculating energies of molecules containing atoms of the first and second row of the periodic chart based on ab initio molecular orbital theory. G3 theory uses geometries from second-order perturbation theory [MP2(full)/6-31G(d)] and scaled zero-point energies from Hartree−Fock theory [HF/6-31G(d)] followed by a series of single-point energy calculations at the second-order Møller−Plesset (MP2), fourth-order Møller−Plesset (MP4), and quadratic configuration interaction [QCISD(T)] levels of theory. The MP4 calculations are carried out with the 6-31G(d) basis set and several basis set extensions. The QCISD(T) calculation is done with the 6-31G(d) basis set. The MP2 calculation is performed with a new basis set, referred to as G3large, and includes core correlation. The other single-point energy calculations are done with a frozen core approximation. G3 theory is effectively at the QCISD(T,full)/G3large level, making certain assumptions about the additivity of the calculations. It also includes a spin−orbit correction for atomic species only. A higher-level empirical correction, HLC, is added to take into account remaining deficiencies in the energy calculations. The HLC is now different for atoms and for molecules. It depends on the number of α and β valence electrons and includes some empirical parameters whose values were chosen to give the smallest average absolute deviation from experiment for the G2/97 test set.[19]

More recently, variations of the G3 theory using reduced Møller−Plesset order (MP2[26] or MP3[20]), density functional geometries and zero-point energies,[29] coupled cluster energies,[30] and multiplicative scale factors[31] have been presented.

Table 1. G3 Total Energies at 0 K, and Enthalpies at 298 K, of the Studied Compounds and Other Atoms and Molecules Used in This Work[a]

compd	G3	
	E_0	H_{298}
cyclopropane, **1**	−117.767 61[b]	−117.763 24[b]
cyclopropene, **2**	−116.516 48[b]	−116.512 21[b]
cyclobutane, **3**	−157.040 52[b]	−157.035 32[b]
cyclobutene, **4**	−155.824 64[b]	−155.819 82[b]
bicyclo[1.1.0]butane, **5**	−155.800 66[b]	−155.795 93[b]
cyclopentane, **6**	−196.342 37	−196.336 06
cyclopentene, **7**	−195.135 81	−195.130 10
1,3-cyclopentadiene, **8**	−193.933 77	−193.928 58
bicyclo[2.1.0]pentane, **9**	−195.089 03	−195.083 60
spiropentane, **10**	−195.079 12[b]	−195.073 16[b]
cyclohexane, **11**	−235.622 87	−235.615 98
cyclohexene, **12**	−234.413 73	−234.407 11
1,3-cyclohexadiene, **13**	−233.207 00	−233.200 73
1,4-cyclohexadiene, **14**	−233.206 75	−233.200 42
benzene, **15**	−232.052 21[b]	−232.046 76[b]
cycloheptane, **16**	−274.883 76	−274.875 52
cycloheptene, **17**	−273.678 54	−273.670 68
1,3-cycloheptadiene, **18**	−272.474 58	−272.467 02
1,3,5-cycloheptatriene, **19**	−271.275 89	−271.269 01
1,3,5,7-cyclooctatetraene, **20**	−309.331 76	−309.324 01
naphthalene, **21**	−385.586 58	−385. 578 58
H	−0.501 00[b]	−0.498 64
C	−37.827 72[b]	−37.825 36
CH_4	−40.457 62[b]	−40.453 81[b]
CH_3CH_3	−79.723 40[b]	−79.718 91[b]
$CH_2{=}CH_2$	−78.507 42[b]	−78.503 42[b]

[a] All values in hartrees (E_h). 1 E_h = 627.5 kcal mol^{-1}. [b] Value taken from ref 18.

G3-calculated energies, at 0 K, for all the species involved in the calculations are given in Table 1. The harmonic vibrational frequencies, determined at the HF/6-31G(d) level in the framework of the G3 theory, confirm that all of these structures correspond to real minima of the potential energy surface.

To calculate enthalpy values at 298 K, the difference between the enthalpy at temperature T and 0 K can be evaluated according to standard thermodynamics.[32] The thermal correction in G3 theory is made using scaled (0.8929) HF/6-31G(d) frequencies for the vibrations in the harmonic approximation for vibrational energy,[33] the classical approximation for translation ($^3/_2RT$) and rotation ($^3/_2RT$ for nonlinear molecules, and RT for linear molecules), and an additional RT for converting energy to enthalpy (the PV term).

G3-calculated enthalpies at 298 K are also collected in Table 1.

2. Standard Heats of Formation in the Gas Phase. (a) From Atomization Reactions. In standard Gaussian-*n* theories, theoretical enthalpies of formation at 0 K are calculated through atomization reactions.

Consider the cyclic hydrocarbon molecule C_mH_n in the gas phase. $\Delta_fH°_m$ (0 K) for this compound is calculated from the G3 energies at 0 K for the atomization reaction 1, $\Delta H°_a$, and the experimental heats of formation of C(g) and H(g).

$$C_mH_n(g) \rightarrow mC(g) + nH(g)\ \Delta H°_a \qquad (1)$$

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(33) Each normal mode contributes $Nh\nu/((e^{h\nu/kT})^{-1})$ to thermal correction, where N is Avogadro's constant, h is Planck's constant, ν is the frequency, k is Boltzmann's constant, and T is the temperature.

Table 2. G2(MP2)-, G2-, and G3-Calculated (from Both Atomization and Bond Separation Isodesmic Reactions) Heats of Formation, at 298 K, of the Studied Compounds[a] (Values in Parentheses Are the Differences between Experimental and Calculated Values)

	G2(MP2)[b]		G2[b]		G3					
					atomization		bond separation			
compd	atomization	bond separation	atomization	bond separation	(c)	(d)	(c)	(d)	GA[e]	exptl[f]
cyclopropane, **1**	14.2 (−1.5)	13.3 (−0.6)	13.6 (−0.9)	13.2 (−0.5)	13.4 (−0.7)	13.4 (−0.7)	13.7 (−1.0)	13.7 (−1.0)	12.7	12.7 ± 0.1
cyclopropene, **2**	69.7 (−3.5)	68.1 (−1.9)	69.1 (−2.9)	67.9 (−1.7)	68.5 (−2.3)	68.5 (−2.3)	68.6 (−2.4)	68.6 (−2.4)	66.5	66.2 ± 0.6
cyclobutane, **3**	7.9 (−1.3)	6.6 (0.0)	7.0 (−0.4)	6.5 (0.1)	6.8 (−0.2)	6.7 (−0.1)	7.2 (−0.6)	7.1 (−0.5)	6.8	6.6 ± 0.3
cyclobutene, **4**	41.1 (−3.6)	39.3 (−1.8)	40.2 (−2.7)	39.0 (−1.5)	39.5 (−2.0)	39.5 (−2.0)	39.8 (−2.3)	39.8 (−2.3)	37.4	37.5 ± 0.4
bicyclo[1.1.0] butane, **5**	55.6 (−3.7)	53.8 (−1.9)	54.9 (−3.0)	53.6 (−1.7)	54.5 (−2.6)	54.5 (−2.6)	54.7 (−2.8)	54.7 (−2.8)	52.2	51.9 ± 0.2
cyclopentane, **6**	−15.9 (−2.4)	−17.5 (−0.8)	−17.1 (−1.2)	−17.7 (−0.6)	−17.8 (−0.5)	−18.1 (−0.2)	−17.3 (−1.0)	−17.6 (−0.7)	−17.9	−18.3 ± 0.2
cyclopentene, **7**	11.4 (−3.3)	9.3 (−1.2)	10.3 (−2.2)	9.0 (−0.9)	9.0 (−0.9)	8.8 (−0.7)	9.3 (−1.2)	9.2 (−1.1)	8.5	8.1 ± 0.3
1,3-cyclo pentadiene, **8**	36.0 (−3.9)	33.3 (−1.2)	35.0 (−2.9)	32.9 (−0.8)	32.9 (−0.8)	32.9 (−0.8)	33.1 (−1.0)	33.1 (−1.0)	32.2	32.1 ± 0.4
bicyclo[2.1.0] pentane, **9**	39.8 (−2.1)	37.7 (0.0)	38.7 (−1.0)	37.4 (0.3)	38.2 (−0.5)	38.2 (−0.5)	38.4 (−0.7)	38.4 (−0.7)	–	37.7[g]
spiropentane, **10**	46.7 (−2.4)	44.6 (−0.3)	45.6 (−1.3)	44.3 (0.0)	44.7 (−0.4)	44.7 (−0.4)	45.0 (−0.7)	45.0 (−0.7)	44.3	44.3 ± 0.2
cyclohexane, **11**	−27.1 (−2.4)	−29.1 (−0.4)	−28.6 (−0.9)	−29.3 (−0.2)	−29.3 (−0.2)	−29.4 (−0.1)	−28.8 (−0.7)	−28.8 (−0.7)	−29.3	−29.5 ± 0.2
cyclohexene, **12**	2.1 (−3.1)	−0.4 (−0.6)	0.8 (−1.8)	−0.7 (−0.3)	−0.7 (−0.3)	−0.8 (−0.2)	−0.3 (−0.7)	−0.4 (−0.6)	−1.9	−1.0 ± 0.2[h]
1,3-cyclo hexadiene, **13**	29.6 (−4.2)	26.5 (−1.1)	28.4 (−3.0)	26.2 (−0.8)	26.3 (−0.9)	26.2 (−0.8)	26.5 (−1.1)	26.4 (−1.0)	25.2	25.4 ± 0.2
1,4-cyclo hexadiene, **14**	30.1 (−4.0)	27.1 (−1.0)	29.0 (−2.9)	26.7 (−0.6)	26.5 (−0.4)	26.3 (−0.2)	26.7 (−0.6)	26.6 (−0.5)	22.8	26.1[g,i]
benzene, **15**	24.8 (−5.1)	21.2 (−1.5)	23.6 (−3.9)	20.7 (−1.0)	20.4 (−0.7)	20.4 (−0.7)	20.5 (−0.8)	20.5 (−0.8)	19.8	19.7 ± 0.2
cycloheptane, **16**	−25.5 (−2.7)	−27.8 (−0.4)	−27.3 (−0.9)	−28.1 (−0.1)	−28.1 (−0.1)	−28.3 (0.1)	−27.4 (−0.8)	−27.6 (−0.6)	−28.2	−28.2 ± 0.2
cycloheptene, **17**	0.9 (−3.1)	−1.9 (−0.3)	−0.4 (−1.8)	−2.0 (−0.2)	−2.0 (−0.2)	−2.2 (0.0)	−1.5 (−0.7)	−1.7 (−0.5)	−2.0	−2.2 ± 0.3
1,3-cyclo heptadiene, **18**	27.1 (−4.6)	23.7 (−1.2)	25.6 (−3.1)	23.3 (−0.8)	23.3 (−0.8)	23.0 (−0.5)	23.6 (−1.1)	23.3 (−0.8)	22.7	22.5 ± 0.3
1,3,5-cyclo heptatriene, **19**	49.2 (−4.6)	45.2 (−0.6)	47.8 (−3.2)	44.7 (−0.1)	45.1 (−0.5)	45.0 (−0.4)	45.3 (−0.7)	45.2 (−0.6)	43.5	44.6[j,k]
1,3,5,7-cyclo octatetraene, **20**	77.2 (−6.1)	72.0 (−0.9)	75.8 (−4.7)	71.4 (−0.3)	72.2 (−1.1)	72.0 (−0.9)	72.3 (−1.2)	72.1 (−1.0)	70.9	71.1 ± 0.3[l]
naphthalene, **21**	43.1 (−7.2)[m]	36.2 (−0.3)[m]	41.7 (−5.8)	35.9 (0.0)	35.7 (0.2)	35.5 (0.4)	35.7 (0.2)	35.5 (0.4)	35.8	35.9 ± 0.3
|dev|[n]	3.6 (3.6)	0.9 (0.7)	2.6 (2.3)	0.6 (0.4)	0.8 (0.5)	0.7 (0.3)	1.1 (0.8)	1.0 (0.7)		

[a] All values in kcal mol^{-1}. [b] Values taken from ref 17. [c] Calculated $\Delta_f H°$ values using the harmonic oscillator approximation in the evaluation of thermal corrections at 298 K (See text). [d] Calculated $\Delta_f H°$ values using the free rotor approximation in the evaluation of thermal corrections at 298 K (See text). [e] Estimated $\Delta_f H°$ values using group additivities. Values taken from ref 35. [f] Values taken from ref 36, unless noted otherwise. [g] Value taken from ref 37. [h] Value taken from ref 38, extremely close to that reported in ref 36 (−1.2 ± 0.1 kcal mol^{-1}). [i] Reference 36 reports an experimental value of 24.0 ± 0.7 kcal mol^{-1}. [j] Value taken from ref 39. [k] Reference 36 reports an experimental value of 43.2 ± 0.5 kcal mol^{-1}. [l] Value calculated in ref 40 from experimental data. [m] Value taken from ref 4. [n] Average absolute deviations, in kcal mol^{-1}; values in parentheses have been calculated without taking into account the compounds **2**, **4**, and **5**.

Combining the next two equations

$$\Delta H°_a = m\mathrm{G3}\,(\mathrm{C}, 0\ \mathrm{K}) + n\mathrm{G3}\,(\mathrm{H}, 0\ \mathrm{K}) - \mathrm{G3}(\mathrm{C}_m\mathrm{H}_n, 0\ \mathrm{K}) \quad (2)$$

$$\Delta H°_a = m\Delta_f H°_{m,\mathrm{exp}}\,(\mathrm{C}, 0\ \mathrm{K}) + n\Delta_f H°_{m,\mathrm{exp}}\,(\mathrm{H}, 0\ \mathrm{K}) - \Delta_f H°_m(\mathrm{C}_m\mathrm{H}_n, 0\ \mathrm{K}) \quad (3)$$

the heat of formation of C_mH_n is given by

$$\Delta_f H°_m\,(\mathrm{C}_m\mathrm{H}_n, 0\ \mathrm{K}) = \mathrm{G3}\,(\mathrm{C}_m\mathrm{H}_n, 0\ \mathrm{K}) - m\mathrm{G3}\,(\mathrm{C}, 0\ \mathrm{K}) - n\mathrm{G3}\,(\mathrm{H}, 0\ \mathrm{K}) + m\Delta_f H°_{m,\mathrm{exp}}\,(\mathrm{C}, 0\ \mathrm{K}) + n\Delta_f H°_{m,\mathrm{exp}}\,(\mathrm{H}, 0\ \mathrm{K}) \quad (4)$$

where G3 (0 K) are the G3 total energies at 0 K and $\Delta_f H°_{m,\mathrm{exp}}$ are the experimental enthalpies of formation, at 0 K, of the isolated atoms. We have used the NIST-JANAF values[34] for the enthalpies of formation of C(g) and H(g), 169.98 and 51.63 kcal mol^{-1}, respectively.

The theoretical enthalpy of formation at 298 K is calculated by correcting $\Delta_f H°_m$ (0 K) as follows:[2]

$$\Delta_f H°_m\,(\mathrm{C}_m\mathrm{H}_n, 298\ \mathrm{K}) = \Delta_f H°_m\,(\mathrm{C}_m\mathrm{H}_n, 0\ \mathrm{K}) + \Delta H_T^{\mathrm{calc}}\,(\mathrm{C}_m\mathrm{H}_n) - m\Delta H_T^{\mathrm{exp}}\,[\mathrm{C(s)}] - {}^{n}\!/_{2}\Delta H_T^{\mathrm{exp}}\,[\mathrm{H_2(g)}] \quad (5)$$

where $\Delta H_T^{\mathrm{calc}}$ (C_mH_n), the difference between the enthalphy at temperature T and 0 K, is evaluated as indicated above, and $\Delta H_T^{\mathrm{exp}}$ for the elements refers to their standard states at 298 K and are taken from ref 34, 0.25 kcal mol^{-1} for C(s) and 2.02 kcal mol^{-1} for H_2(g).

G3-calculated heats of formation at 298 K of the studied compounds are given in Table 2.

(b) From Bond Separation Isodesmic Reactions. As indicated above, there is some evidence that there is an accumulation of errors in the application of G2 theory to larger molecules.[1,3,12,15] Glukhovtsev and Laiter[12] have shown that more accurate heats of formation for benzene and 1,3-butadiene can be derived using isodesmic or homodesmotic reactions rather than atomization energies as in standard G2 theory. The cancellation of errors for such cases involving similar chemical bonds obviously improves the agreement with experiment. More recently, Nicolaides and Radom[1] have shown that the heats of formation for benzene and other hydrocarbons can be improved significantly by the use of isodesmic and isogyric reactions involving these species.

As Raghavachari et al.[4] have pointed out, one of the deficiencies of the isodesmic reaction approach is that many different isodesmic reactions can be set up for the same molecule yielding different results. These authors have very recently proposed to use simpler, but better defined reactions to assess the performance of theoretical methods in a more systematic manner. A standard set of isodesmic reactions is "bond separation reactions",[27] where all formal bonds between non-hydrogen atoms are separated into the simplest parent molecules containing these same kinds of linkages. They demonstrated[4] that the combination of such bond separation reactions with G2 theory generally leads to a significant

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(34) Chase, M. W., Jr. NIST-JANAF Thermochemical Tables, *J. Phys. Chem. Ref. Data*, Monograph 9, **1998**, 1−1951.

improvement in the accuracy of theoretically evaluated heats of formation.

In the case of saturated cyclic hydrocarbons, the bond separation reaction using its effective valence bond structure is:

$$C_mH_{2m}(g) + mCH_4(g) \rightarrow mCH_3{-}CH_3(g)\ \Delta H^\circ_{BS} \quad (6)$$

The bond separation reaction energies are then evaluated at G3 level of theory:

$$\Delta H^\circ_{BS} = m\mathrm{G3}\ (CH_3{-}CH_3,\ 298\ \mathrm{K}) - m\mathrm{G3}\ (CH_4,\ 298\ \mathrm{K}) - \mathrm{G3}\ (C_mH_{2m},\ 298\ \mathrm{K}) \quad (7)$$

and using the experimentally known heats of formation for the reference molecules, as given in ref 41:[42]

$$\Delta_f H^\circ_m\ (C_mH_{2m},\ 298\ \mathrm{K}) = \mathrm{G3}\ (C_mH_{2m},\ 298\ \mathrm{K}) + m\mathrm{G3}\ (CH_4,\ 298\ \mathrm{K}) - m\mathrm{G3}\ (CH_3{-}CH_3,\ 298\ \mathrm{K}) - m\Delta_f H^\circ_{m,exp}(CH_4,\ 298\ \mathrm{K}) + m\Delta_f H^\circ_{m,exp}(CH_3{-}CH_3,\ 298\ \mathrm{K}) \quad (8)$$

In the cases of unsaturated cyclic hydrocarbons, the process is similar, using the corresponding bond separation reactions: reaction 9 in the case of hydrocarbons with one double bond, reaction 10 in the case of hydrocarbons with two double bonds, and so on.

$$C_mH_{2m-2}(g) + mCH_4(g) \rightarrow (m-1)\ CH_3{-}CH_3(g) + CH_2{=}CH_2(g) \quad (9)$$

$$C_mH_{2m-4}(g) + mCH_4(g) \rightarrow (m-2)CH_3{-}CH_3(g) + 2CH_2{=}CH_2(g) \quad (0)$$

G3-calculated heats of formation using bond separation reactions are collected in Table 2.

Discussion

The differences between experimental and calculated, from both atomization and bond separation reactions, heats of formation are shown in Table 2. Also in Table 2, and for comparison purposes, the enthalpies of formation calculated at the G2(MP2) and G2 levels, taken from our previous work,[17] are shown.

As can be seen, there is a very dramatic improvement in the calculated heats of formation through atomization reactions from the G2(MP2) and G2 to the G3 level. The average absolute deviations decrease from 3.6 kcal mol^{-1} (at the G2(MP2) level) and 2.6 kcal mol^{-1} (at the G2 level) to only 0.8 kcal mol^{-1} when the G3 method is used. The enthalpies of formation calculated at the G3 level are in very good agreement with the experimental values except in three cases (compounds **2**, **4**, and **5**), the differences Δ between experimental and calculated values being less than 1.1 kcal mol^{-1}.

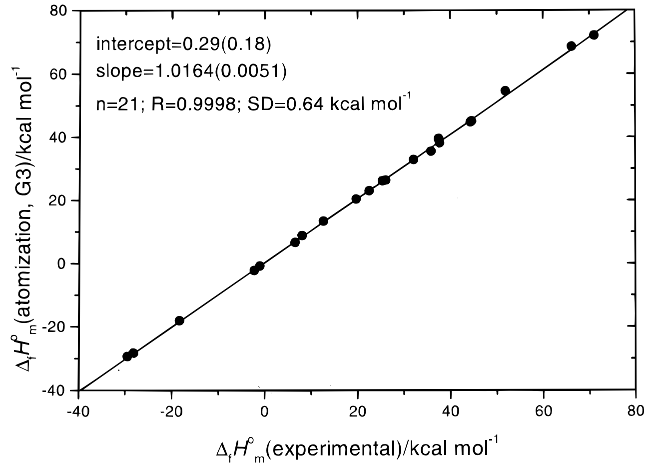

Figure 1. Plot of the $\Delta_f H^\circ_m$ values calculated at the G3 level, using atomization reactions and the free rotor approximation (see text), versus the experimental $\Delta_f H^\circ_m$ values.

As Radom and co-workers[2] have pointed out the harmonic oscillator model fails to describe internal rotors adequately when the barrier to rotation is close to or below the thermal energy. In the limit of heigh temperatures or low frequencies, a harmonic oscillator contributes RT but a free rotor only contributes 1/2RT.[32] Since many very low frequencies are rotational in nature, it is often more appropriate to calculate the thermal component of enthalpy associated with very low frequencies using a free rotor approximation. Radom and co-workers[2,44] recommend treating internal rotations with frequencies below 260 cm^{-1} (291 cm^{-1} at the HF/6-31G(d) level, before the application of the 0.8929 scaling factor) as free rotors ($^1/_2RT$) rather than as harmonic oscillators in the evaluation of ΔH_T at 298 K.

Several of the compounds studied here have one or more calculated frequencies below 291 cm^{-1}. The application of free rotor approximation to the calculation of ΔH_T at 298 K yields to small but not negligible effects in the $\Delta_f H^\circ$ values, the higher corrections being 0.3 kcal mol^{-1} in the case of cyclopentane and 1,3-cycloheptadiene. The corresponding $\Delta_f H^\circ$ values evaluated using the free rotor approximation are collected in Table 2. As can be seen in Table 2, these values are now closer to the experimental ones. The average absolute deviation is now 0.7 kcal mol^{-1} (0.3 kcal mol^{-1} excluding the compounds **2**, **4**, and **5**; the differences Δ between experimental and calculated values being less than 0.9 kcal mol^{-1}).

We present in Figure 1 the correlation between the experimental and calculated (G3, atomization, free rotor) heats of formation for all the species examined in this work. The correlation spans a range of 100 kcal mol^{-1} and the standard deviation of fit is 0.64 kcal mol^{-1} while $R = 0.9998$. This fit has a very small intercept (0.29 ± 0.18) and a slope extremely close to unity (1.0164 ± 0.0051). This indicates a rewarding closeness to “perfect match”. The standard deviation of fit is somewhat larger than the uncertainty limits reported for some of the molecules studied in this work. However, it is a fact that,

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(35) Cohen, N. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1411−1481.

(36) Pedley, J. B. *The Thermochemical Data and Structures of Organic Compounds*; Vol. I, TRC Data Series; TRC: Texas, 1994.

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(41) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. *Neutral Thermochemical Data*. In NIST Chemistry WebBook, NIST Standard Reference Database Number 69; Mallard, W. G., Linstrom, P. J., Eds.; February 2000, National Institute of Standards and Technology, Gaithersburg, MD, 20899 (http://webbook.nist.gov).

(42) These values are −17.90, −20.04, and 12.54 kcal mol^{-1} for methane,[34] ethane,[43] and ethylene,[34] respectively.

(43) Pittam, D. A.; Pilcher, G. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 2224−2229.

(44) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513.

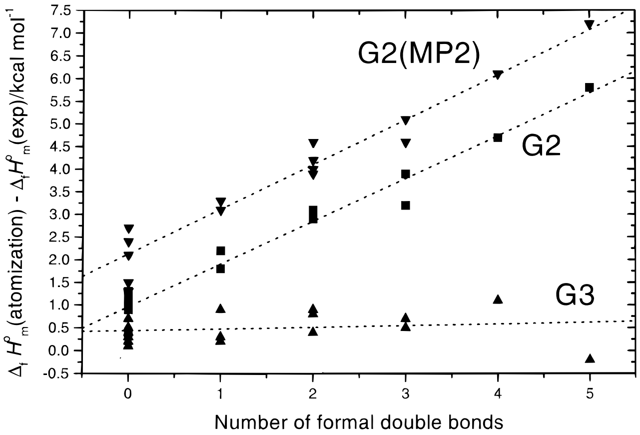

Figure 2. Plot of the difference between $\Delta_f H^\circ_m$ values calculated at the G2(MP2)(▼), G2(■) and G3(▲) levels, using atomization reactions, and the experimental $\Delta_f H^\circ_m$ values versus the number of formal double bonds in the molecule.

very often, the experimental accuracy assessed by comparison of data obtained in different laboratories is quite comparable to these figures (see, e.g., footnotes to Table 2).

In our previous work,[17] we observed a linear relationship between the Δ differences, computed at the G2(MP2) and G2 levels, and the number of formal double bonds in the molecule, Δ increasing with the number of formal double bonds. This fact is not observed now when the Δ differences are computed at the G3 level, as shown in Figure 2. This suggests that the G3 method does not tend to underestimate the stability of C=C bonds as it is the case of the G2 and G2(MP2) methods.

Contrary to the G2(MP2) and G2 methods, the enthalpies of formation calculated at the G3 level using bond separation reactions are worse than those calculated using atomization reactions (average absolute deviation of 1.0 kcal mol^{-1} instead of 0.7 kcal mol^{-1}) and those obtained at the G2(MP2) and G2 levels using the same method.

Raghavachari et al.[4] have pointed out that bond separation reactions bring out cancellation of the HLC so that this empirical factor does not appear in the final result. They refer to the bond separation method as "nonempirical" because of HLC cancellation, but the scheme is not a pure ab initio method because of the error cancellation that motivates all isodesmic reaction schemes and because the infusion of empirical heats of formation values for the reference molecules.[24]

As Rogers and McLafferty[24] point out, it is likely that a reason for the accuracy of bond separation method relative to the original atomization method in G2 calculations is that they involve only molecular orbital results while the atomization method mixes approximate atomic orbital and molecular orbital results. In the new G3 procedure the atomization method is modified by including an HLC for atoms as well as for molecules to take into account deficiencies in the energy calculations (see Computational Details). From our data, it is clear that the new parametrization in the G3 method works adequately and the atomization method gives very satisfactory results. In the bond separation method, the systematic errors[45] related to the coefficients of methane, ethane, and ethylene in eqs 6, 9, and 10, yield to worse results.

Finally, it is interesting to compare our calculated $\Delta_f H^\circ$ values at the G3 level with the values estimated using the empirical group additivities developed by Benson and co-workers.[46−48] Group additivity (GA) is currently the most widely used method for estimating thermochemical data for molecules and radicals in either ideal gas or liquid state.[48] The $\Delta_f H^\circ$ values for the hydrocarbons studied in this work obtained from revised GA values recently published[35] are given in Table 2. As can be seen, excluding compounds **2**, **4**, and **5**, there is generally a good agreement between our G3-calculated values and the GA-estimated ones. The only cases with serious discrepancies are those of 1,4-cyclohexadiene and 1,3,5-cycloheptatriene. In both cases, there are different experimental values (see footnotes to Table 2), and the G3-calculated ones compare very well with values different of those recopilated by Pedley,[36] that were the values used[35] to estimate the ring strain corrections (RSC) in the GA method. This result seems to suggest that a new reevaluation of RSC values for 1,4-cyclohexadiene and 1,3,5-cycloheptatriene rings would be necessary.

Conclusions

The study of simple cyclic, saturated, unsaturated and aromatic molecules reveals that the combination of the G3 methodology with the atomization reaction method provides standard heats of formation of hydrocarbons of "nearly experimental" quality.

The use of bond separation reaction method yields to worse results than the atomization reaction method.

The quality of the G3-calculated enthalpies of formation using atomization reactions is comparable to that obtained at the G2 level using bond separation reactions, whereas G3 calculations are two to three times faster than G2 calculations.

A useful practical conclusion derived from this paper is the fact that the recently proposed G3 method is appropriate to obtain the heats of formation of simple cyclic, saturated and unsaturated hydrocarbons and its use is highly recommended.

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