Organic Thermochemistry at High ab Initio Levels. 1. A G2(MP2) and G2 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 G2 methods, 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 G2(MP2) and G2 levels through both atomization reactions and bond separation isodesmic reactions, and comparison with experimental values has been made. A linear relationship between the differences between experimental and calculated (from atomization reactions) heats of formation and the number of formal double bonds is obtained.

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, $\Delta_f H^\circ_m$(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, $\Delta_f H^\circ_m$(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 $\Delta_f H^\circ_m$(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] (notably G2(MP2)[7] and G2[5] itself) 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.[1,12,13]

It is thus tempting to explore the scope of these computational methods as a potentially valuable tool for organic chemists. So far, most of the studies have dealt with small molecules, both organic and inorganic. In this series of papers, we examine a variety of organic molecules and explore in particular various compounds of substantial size (up to 10 carbon atoms) as well as the possible influence of strain, unsaturation, and unusual (very short or very long) bonds. The present paper reports our studies on the influence of strain and unsaturation of cyclic hydrocarbons on the reliability of the computational $\Delta_f H^\circ_m$(M, g) values.

Computational Details

1. G2 Techniques. Standard ab initio molecular orbital calculations[14] were performed with the Gaussian94 series of programs.[15]Energies were obtained at the G2[5] and G2(MP2)[7] levels of theory. The two methods differ in their implementation of additivity approximations, but each corresponds effectively to calculations at the QCISD(T)/6-311+G(3df,2p) level on MP2(full)/6-31G(d) optimized geometries, incorporating scaled HF/6-31G(d) zero-point vibrational energies and a so-called higher-level correction to accommodate remaining deficiencies.

Treatment of electron correlation in G2 theory is by Møller−Plesset (MP) perturbation theory at the MP2 and MP4 levels, and quadratic configuration interaction (QCI). G2(MP2) theory is based on reduced order of Møller−Plesset perturbation

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Table 1. G2(MP2) and G2 Total Energies at 0 K and Enthalpies at 298 K of the Studied Compounds and Other Atoms and Molecules Used in This Study[a]

	G2(MP2)		G2	
compd	E_0	H_{298}	E_0	H_{298}
cyclopropane, **1**	−117.628 85[b]	−117.624 48[b]	−117.631 15[b]	−117.626 78[b]
cyclopropene, **2**	−116.379 07[b]	−116.374 79[b]	−116.381 29[b]	−116.377 02[b]
cyclobutane, **3**	−156.855 42[b]	−156.850 23[b]	−156.858 60[b]	−156.853 41[b]
cyclobutene, **4**	−155.640 77[b]	−155.635 95[b]	−155.643 88[b]	−155.639 06[b]
bicyclo[1.1.0]butane, **5**	−155.617 67[b]	−155.612 95[b]	−155.620 45[b]	−155.615 73[b]
cyclopentane, **6**	−196.110 22[c]	−196.103 88[c]	−196.114 24	−196.107 93
cyclopentene, **7**	−194.904 72[c]	−194.899 01[c]	−194.908 56	−194.902 85
1,3-cyclopentadiene, **8**	−193.703 70[c]	−193.698 52[c]	−193.707 34	−193.702 15
bicyclo[2.1.0]pentane, **9**	−194.859 28[c]	−194.853 84[c]	−194.863 03	−194.857 60
spiropentane, **10**	−194.848 79	−194.842 84	−194.852 52	−194.846 56
cyclohexane, **11**	−235.344 38[d]	−235.337 49[d]	−235.349 22	−235.342 33
cyclohexene, **12**	−234.136 17[d]	−234.129 56[d]	−234.140 81	−234.134 19
1,3-cyclohexadiene, **13**	−232.930 75[d]	−232.924 48[d]	−232.935 15	−232.928 88
1,4-cyclohexadiene, **14**	−232.929 91[d]	−232.923 59[d]	−232.934 27	−232.927 95
benzene, **15**	−231.776 25[d]	−231.770 80[d]	−231.780 53	−231.775 08
cycloheptane, **16**	−274.558 94	−274.550 70	−274.564 65	−274.556 42
cycloheptene, **17**	−273.355 04	−273.347 17	−273.360 07	−273.352 21
1,3-cycloheptadiene, **18**	−272.151 74	−272.144 18	−272.156 96	−272.149 39
1,3,5-cycloheptatriene, **19**	−270.954 49	−270.947 61	−270.959 57	−270.952 69
1,3,5,7-cyclooctatetraene, **20**	−308.965 03[e]	−308.957 28[e]	−308.970 60[e]	−308.962 86[e]
naphthalene, **21**			−385.134 80[f]	−385.126 80[f]
H	−0.500 00	−0.497 64	−0.500 00	−0.497 64
C	−37.783 89	−37.781 53	−37.784 30	−37.781 94
CH_4	−40.409 66	−40.405 84	−40.410 88	−40.407 06
CH_3CH_3	−79.628 93	−79.624 45	−79.630 90	−79.626 42
$CH_2{=}CH_2$	−78.414 30	−78.410 30	−78.415 93	−78.411 93

(a) All values in hartrees. 1 hartree = 627.5 kcal mol^{-1}. (b) Value taken from ref 16. (c) Value taken from ref 17. (d) Value taken from ref 18. (e) Value taken from ref 19. (f) Value taken from ref 20.

theory and has larger deviations, but saves computational time and disk space.

G2(MP2)- and G2-calculated energies, at 0 K, for all the species involved in the calculations are given in Table 1. All of these structures are minima on 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.[21] The thermal correction in G2 theory is made using scaled (0.8929) HF/6-31G(d) frequencies for the vibrations in the harmonic approximation for vibrational energy,[22] 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).

G2(MP2) and G2 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 G2 theory, theoretical enthalpies of formation at 0 K are calculated through atomization reactions.

Consider the cyclic hydrocarbon molecule C_mH_n in the gas phase. $\Delta_f H°_m$ (0 K) for this compound is calculated from the G2 [or G2(MP2)] energies at 0 K for the atomization reaction 1, $\Delta H°_a$, and the experimental heats of formation of C(g) and H(g).

$$C_mH_n(g) \rightarrow mC(g) + nH(g) \quad \Delta H°_a \tag{1}$$

Combining the next two equations

$$\Delta H°_a = m\mathrm{G2}(\mathrm{C, 0\ K}) + n\mathrm{G2}(\mathrm{H, 0\ K}) - \mathrm{G2}(C_mH_n, 0\ \mathrm{K}) \tag{2}$$

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

the heat of formation of C_mH_n is given by

$$\Delta_f H°_m(C_mH_n, 0\ \mathrm{K}) = \mathrm{G2}(C_mH_n, 0\ \mathrm{K}) - m\mathrm{G2}(\mathrm{C, 0\ K}) - n\mathrm{G2}(\mathrm{H, 0\ K}) + m\Delta_f H°_{m,\mathrm{exp}}(\mathrm{C, 0\ K}) + n\Delta_f H°_{m,\mathrm{exp}}(\mathrm{H, 0\ K}) \tag{4}$$

where G2(0 K) are the G2 total energies at 0 K and $\Delta_f H°_{m,\mathrm{exp}}$ are the enthalpies of formation, at 0 K, of the isolated atoms. We have used the NIST-JANAF values[22] 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]

$$\Delta_f H°_m(C_mH_n, 298\ \mathrm{K}) = \Delta_f H°_m(C_mH_n, 0\ \mathrm{K}) + \Delta H_T^{\mathrm{calc}}(C_mH_n) - m\Delta H_T^{\mathrm{exp}}[\mathrm{C(s)}] - {}^n/_2\Delta H_T^{\mathrm{exp}}[\mathrm{H_2(g)}] \tag{5}$$

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 23, 0.25 kcal mol^{-1} for C(s) and 2.02 kcal mol^{-1} for H_2(g).

G2(MP2) and G2-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.[1,3,12,13] Glukhovtsev and Laiter[12] have shown that

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[22] 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)- and G2-Calculated (from Both Atomization and Bond Separation Isodesmic Reactions) Heats of Formation, at 298 K, of the Studied Compounds[a,b]

	G2(MP2)		G2		
compd	atomization	bond separation	atomization	bond separation	exptl[c]
cyclopropane, **1**	14.2 (−1.5)	13.3 (−0.6)	13.6 (−0.9)	13.2 (−0.5)	12.7 ± 0.1
cyclopropene, **2**	69.7 (−3.5)	68.1 (−1.9)	69.1 (−2.9)	67.9 (−1.7)	66.2 ± 0.6
cyclobutane, **3**	7.9 (−1.3)	6.6 (0.0)	7.0 (−0.4)	6.5 (0.1)	6.6 ± 0.3
cyclobutene, **4**	41.1 (−3.6)	39.3 (−1.8)	40.2 (−2.7)	39.0 (−1.5)	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)	51.9 ± 0.2
cyclopentane, **6**	−15.9 (−2.4)	−17.5 (−0.8)	−17.1 (−1.2)	−17.7 (−0.6)	−18.3 ± 0.2
cyclopentene, **7**	11.4 (−3.3)	9.3 (−1.2)	10.3 (−2.2)	9.0 (−0.9)	8.1 ± 0.3
1,3-cyclopentadiene, **8**	36.0 (−3.9)	33.3 (−1.2)	35.0 (−2.9)	32.9 (−0.8)	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)	37.7[d]
spiropentane, **10**	46.7 (−2.4)	44.6 (−0.3)	45.6 (−1.3)	44.3 (0.0)	44.3 ± 0.2
cyclohexane, **11**	−27.1 (−2.4)	−29.1 (−0.4)	−28.6 (−0.9)	−29.3 (−0.2)	−29.5 ± 0.2
cyclohexene, **12**	2.1 (−3.1)	−0.4 (−0.6)	0.8 (−1.8)	−0.7 (−0.3)	−1.0 ± 0.2[e]
1,3-cyclohexadiene, **13**	29.6 (−4.2)	26.5 (−1.1)	28.4 (−3.0)	26.2 (−0.8)	25.4 ± 0.2
1,4-cyclohexadiene, **14**	30.1 (−4.0)	27.1 (−1.0)	29.0 (−2.9)	26.7 (−0.6)	26.1[d,f]
benzene, **15**	24.8 (−5.1)	21.2 (−1.5)	23.6 (−3.9)	20.7 (−1.0)	19.7 ± 0.2
cycloheptane, **16**	−25.5 (−2.7)	−27.8 (−0.4)	−27.3 (−0.9)	−28.1 (−0.1)	−28.2 ± 0.2
cycloheptene, **17**	0.9 (−3.1)	−1.9 (−0.3)	−0.4 (−1.8)	−2.0 (−0.2)	−2.2 ± 0.3
1,3-cycloheptadiene, **18**	27.1 (−4.6)	23.7 (−1.2)	25.6 (−3.1)	23.3 (−0.8)	22.5 ± 0.3
1,3,5-cycloheptatriene, **19**	49.2 (−4.6)	45.2 (−0.6)	47.8 (−3.2)	44.7 (−0.1)	44.6[g,h]
1,3,5,7-cyclooctatetraene, **20**	77.2 (−6.1)	72.0 (−0.9)	75.8 (−4.7)	71.4 (−0.3)	71.1 ± 0.3[i]
naphthalene, **21**	(−7.2)[j]	(−0.3)[j]	41.7 (−5.8)	35.9 (0.0)	35.9 ± 0.3

[a] Values in parentheses are the differences between experimental and calculated values. [b] All values in kcal mol^{-1}. [c] Values taken from ref 24, unless noted otherwise. [d] Value taken from ref 25. [e] Value taken from ref 26, extremely close to that reported in ref 24 (−1.2 ± 0.1 kcal mol^{-1}). [f] Reference 24 reports an experimental value of 24.0 ± 0.7 kcal mol^{-1}. [g] Value taken from ref 27. [h] Reference 24 reports an experimental value of 43.2 ± 0.5 kcal mol^{-1}. [i] Value calculated in ref 19 from experimental data. [j] Value taken from ref 4.

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",[14] 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 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

$$C_mH_{2m}(g) + mCH_4(g) \rightarrow mCH_3CH_3(g) \quad \Delta H^\circ_{BS} \qquad (6)$$

The bond separation reaction energies are then evaluated at G2, or G2(MP2), levels of theory

$$\Delta H^\circ_{BS} = mG2(CH_3CH_3, 298\ K) - mG2(CH_4, 298\ K) - G2(C_mH_{2m}, 298\ K) \qquad (7)$$

and using the experimentally known heats of formation for the reference molecules, as given in ref 28:[29]

$$\Delta_f H^\circ_m(C_mH_{2m}, 298\ K) = G2(C_mH_{2m}, 298\ K) + mG2(CH_4, 298\ K) - mG2(CH_3CH_3, 298\ K) - m\Delta_f H^\circ_{m,exp}(CH_4, 298\ K) + m\Delta_f H^\circ_{m,exp}(CH_3CH_3, 298\ K) \qquad (8)$$

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.

$$C_mH_{2m-2}(g) + mCH_4(g) \rightarrow (m-1)CH_3CH_3(g) + CH_2{=}CH_2(g) \qquad (9)$$

$$C_mH_{2m-4}(g) + mCH_4(g) \rightarrow (m-2)CH_3CH_3(g) + 2CH_2{=}CH_2(g) \qquad (10)$$

G2(MP2)- and G2-calculated heats of formation using bond separation reactions are collected in Table 2.

Discussion

The differences between experimental and calculated heats of formation are shown in Table 2. As can be seen, the enthalpies of formation calculated at the G2(MP2) level through atomization reactions are higher than the experimental ones, and in most cases, the differences are beyond the so-called "chemical accuracy" (0.1 eV ~ 2.4 kcal mol^{-1}) of the G2 methods.

There seems to be no definite relationship between the size of the molecule and the difference between the

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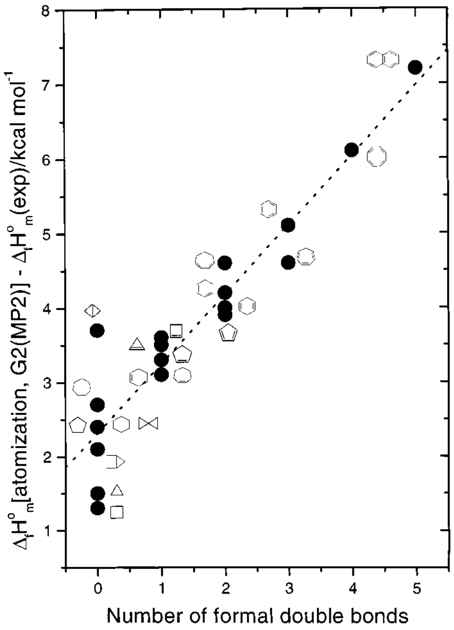

Figure 1. Plot of the difference between $\Delta_fH°_m$ values calculated at G2(MP2) level using atomization reactions and the experimental $\Delta_fH°_m$ values versus the number of formal double bonds in the molecule.

experimental and calculated $\Delta_fH°_m$ values. But if we plot these differences, Δ, versus the number, *N*, of formal double bonds in the molecule, there is a clear linear relationship, Δ increasing with the number of formal double bonds (see Figure 1).

The correlation equation, for all the studied compounds, is

$$\Delta = (2.32 \pm 0.15) + (0.932 \pm 0.076)N \qquad (11)$$

$$n = 21; \quad R = 0.942; \quad \mathrm{sd} = 0.50 \text{ kcal mol}^{-1}$$

This expression shows that for saturated cyclic hydrocarbons, the estimated error of the calculated $\Delta_fH°_m$ values is of some 2.3 kcal mol^{-1}, whereas for unsaturated cyclic hydrocarbons, the estimated error regularly increases by 0.9 kcal mol^{-1} for each formal double bond.

A similar pattern is displayed by the G2 results. Again, for the same set of compounds

$$\Delta = (1.25 \pm 0.17) + (0.866 \pm 0.085)N \qquad (12)$$

$$n = 21; \quad R = 0.919; \quad \mathrm{sd} = 0.56 \text{ kcal mol}^{-1}$$

In this case, the estimated error of the calculated $\Delta_fH°_m$ values for saturated cyclic hydrocarbons is ca. 1.3 kcal mol^{-1}, and the estimated error increases by 0.9 kcal mol^{-1} for each formal double bond, in the case of unsaturated cyclic hydrocarbons. This suggests the existence of a systematic effect in the quantitative treatment of the C=C bond by these methods.

Again (see Table 2), the enthalpies of formation computed at both theoretical levels using bond separation isodesmic reactions, agree remarkably well with the experimental data. This remarkably good agreement, particularly in the case of molecules containing formal double bonds, confirms the fact that the G2 and G2(MP2) methods tend to systematically underestimate the stability of these bonds by about 1 kcal mol^{-1} per double bond. In the case of the bond separation technique, as implemented through equations such as (9) and (10), this contribution is very efficiently canceled.

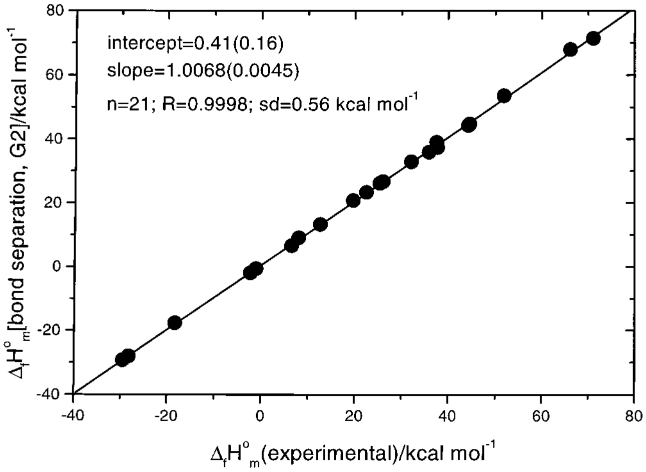

Figure 2. Plot of the $\Delta_fH°_m$ values calculated at G2 level using bond separation isodesmic reactions versus the experimental $\Delta_fH°_m$ values.

We present in Figure 2 the correlation between the experimental and calculated (G2, bond separation) 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 0.56 kcal mol^{-1}, while $R^2 = 0.9996$.

Also important are the following:

1. This fit has a very small intercept (0.41 ± 0.16) and a slope extremely close to unity (1.0068 ± 0.0045). This indicates a rewarding closeness to "perfect match". Indeed, direct comparison of the experimental and computed data displays an unsigned average difference of 0.60 kcal mol^{-1}. This difference as well as the standard deviation of fit are somewhat larger than the uncertainty limits reported for some of the molecules studied in this work. However, it is a fact that, 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).
2. The direct determination by the atomization method leads to systematic errors that increase with the number of double bonds. These errors are essentially removed by means of the bond separation technique.
3. The results at the G2(MP2) level, using the bond separation isodesmic reaction, are slightly worse (average difference of 0.86 kcal mol^{-1}) but are still quite valuable for large molecules or as a tool for exploratory work.
4. No significant systematic errors related to structural features are detected when using the G2 methods combined with the bonds separation technique.

Conclusion

The study of simple cyclic, saturated, unsaturated and aromatic molecules reveals that the combination of the G2 methodology with the bond separation technique provides standard heats of formation of hydrocarbons (cyclic saturated and unsaturated as well as aromatic) of "nearly experimental" quality.

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