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Computational Methods in Organic Thermochemistry. 1. Hydrocarbon Enthalpies and Free Energies of Formation

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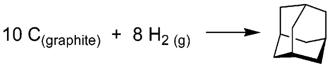

Standard state enthalpies and free energies of formation can be computed with reasonable accuracy (usually within 4 and often 2 kJ/mol) using high level model chemistries. A comparison set of nearly 300 organic compounds ranging from 1 to 10 carbon atoms having a variety of functional groups for which enthalpy and free energy literature values are available has been examined using G2, G2MP2, G3, G3MP2, G3B3, G3MP2B3, CBS-QB3, and density functional (B3LYP/6-311+G(3df,2p)) model chemistries. G3 gives an average mean absolute deviation of 3.0 and 13.4 kJ/mol for the enthalpies and free energies, respectively, using the atomization method and 3.1 and 3.7 kJ/mol when bond separation reactions are employed. G3 and G3B3 are the most accurate overall; the related G3MP2 and G3MP2B3 are nearly as accurate and can compute larger molecules. CBS-QB3 was also found to be accurate but is more limited in the size of molecules that can be computed. The density functional energies were found to have large deviations from the literature values using either the atomization or the bond separation method. Regardless of the model employed, the free energies are increasingly underestimated by computation as the size of the molecule increases. A series of corrections applied to the aliphatic hydrocarbons is presented, which usually reduces the deviations to less than 4 kJ/mol regardless of the size of the molecule.

Introduction

The enthalpy and free energy of formation are the critical thermodynamic properties of a compound allowing a chemist to determine the energy changes of a chemical reaction. The most extensive compilations within easy reach of the chemist, the NIST Webbook (WB)[1] or Computational Chemistry Comparison and Benchmark Database (CC)[2] have both enthalpies and entropies for all of the acyclic alkanes having six carbon atoms or less. The former has enthalpies for all of the seven- and eight-carbon isomers, but entropies are not always available. Data is available for only a few of the larger molecules. As we incorporate rings, π bonds, or heteroatoms onto a carbon skeleton, complete data can be found for the smallest molecules, but as the molecule becomes larger (even at five carbon atoms), first the free energies disappear and then the enthalpies. Because of this dearth of data, organic chemists often rely on bond energies to estimate the enthalpy changes of a reaction, and for radical reactions where bond dissociation energies are employed, this affords good results. For polar reactions, average bond energies must be used;[3] at best these may apply to the molecules at hand and in the worst case will be a range of values from which the chemist is ill prepared to make a choice.[4]

As an alternate to experimental enthalpies, the Benson[5] and Sussex[6] groups have worked on the development of group additivities in which each structural component of a molecule has an inherent enthalpy that can be summed to afford a total

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[2] *NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101 Release 11*; Johnson, R. D., III, Ed.; National Institute of Standards and Technology: Gaithersburg, MD, May 2005 (http://srdata.nist.gov/cccbdb).

[3] For a discussion of methods used to determine bond energies, see: Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Harper Collins Row: NewYork, 1983.

[4] For examples widely used by organic chemists, see: (a) Smith, M. B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 5th ed.; Wiley: New York, 2000; p 24. (b) Luo, Y.-R. *Comprehensive Handbook of Chemical Energies*; Taylor and Francis: Oxford, 2006.

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enthalpy of formation for the compound.[7] A complete table of enthalpies, entropies, free energies, and heat capacities based on the Benson methods are available for the alkanes[8] (up to 10 carbon atoms) and the alkenes and alkynes (up to eight carbon atoms).[9] Building on this concept, Damalski and Hearing have developed a system of group additivities for determining both enthalpies and entropies having a variety of functional groups.[10] Nevertheless, values computed using group additivities may still be missing or inaccurate owing partly to a paucity of data for one or more groups of the reference molecule and also because the whole may be more than the sum of its parts. In the aldol condensation, for example, hydrogen bonding between the carbonyl and newly neighboring hydroxyl group will not be reflected in an enthalpy or entropy change computed by summing the groups of the product molecule. The only solution to this problem lies in computations that evaluate a molecule from first principles.[11]

Several reports have appeared in the literature in recent years exploring this possibility. A system of group additivities derived from ab initio calculations for hydrocarbons was devised by Wiberg[12] and a similar scheme for a broader range of functionality by Ibrahim and Schleyer.[13] More recently, Sabbe et al. have used ab initio calculations to determine a revised set of Benson values.[14] The Pople group used the Gaussian-2 procedure (G2) to compute atomization energies[15] and from which enthalpies can be derived. Initially, they computed the heats of formation of hypovalent radicals and cations derived from methanol[16] and then extendied it to the G2 test set.[17] Enthalpies of formation have also been derived from absolute energies by hydrogenation reactions[18] and bond separation methods,[19] and the methodology has been reviewed.[20] Extending the absolute energies at 0 K to the standard state requires the use of scaled vibrational frequencies, usually the weak link in the calculation. While many of the reports of computational enthalpies have been directed at a small number of compounds, several have focused on an extensive number of examples from common organic families such as aromatic nitro compounds,[21] hydrocarbons,[22,23] fluorohydrocarbons,[24] and fluorinated ethers.[25] None have examined the range of families that an organic chemist routinely encounters, and the application of computational methods to the free energies of formation has received scant attention despite the fact that the energies for 298 K enthalpies and free energies are adjacent to each other in the output. Nevertheless, it is from the $\Delta G°$ that we calculate the value of the equilibrium constant. In this paper, we will examine the ability of common model chemistries to predict the enthalpies and free energies of formation for a broad range of compounds commonly used by the organic chemist and then discuss the results obtained for the aliphatic hydrocarbons. In a subsequent paper, we will examine the results obtained with molecules having one or more heteroatom functional groups.

Methods

We have made extensive use of the CCCBDB library of computational results.[2] The Gaussian 98[26] series of programs was employed for all other calculations used in this work. We endeavored to examine as many of the off-the-shelf model chemistries that could reasonably be employed by a chemist who does not specialize in computational chemistry including the G2, G3, and associated methods,[27] the CBS methods,[28] and density functional techniques.[29] The Wn models[30] have been examined for a few small molecules; however, this model chemistry is computationally very expensive and is beyond the capability of common computational systems for molecules having more than one heavy atom.

Calculations employing G2 theory are at the QCISD(T)/6-311+G(3df,2p)//MP2(FU)/6-31G* level with a higher level correction (HLC) to correct for basis set deficiencies.[15] The final energies are corrected for zero point energies and with additional corrections from the thermochemistry package also provide enthalpies and free energies at 298 K. In practice, after optimization, a QCISD(T)/6-311G(d,p) calculation is performed for a base energy, which is then augmented by additional calculations employing diffuse functions and polarization corrections. Stepwise calculation affords the final result in less time and with less disk storage space than a single calculation at the full basis set. In a truncated version of G2, called G2MP2,[31] the diffuse and polarization functions are calculated at the MP2/6-311+G(3df,2p) level. While some accuracy may be lost by this procedure, it is less demanding both of CPU time and disk space. The other model chemistries, G3, and the CBS methods use comparable stepwise procedures and are described in the references cited.

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A variation of G3, G3B3,[32] employs a B3LYP/6-31G(d) geometry optimization/frequency analysis instead of the Hartree/Fock procedure. A truncation of both methods, G3MP2 and G3MP2B3,[33] provides for shorter CPU times and reduced disk demands at a modest cost of accuracy. There are a variety of CBS methods of which we examined two extensively: CBS-Q[28b] and CBS-QB3.[28c] We found CBS-Q much less accurate and somewhat problematic, especially for aromatic compounds, and are reporting only the results of CBS-QB3 in this paper. Although CBS-Q is computationally somewhat faster than CBS-QB3, the storage requirements are comparable; hence the range of molecules that are accessible is the same for both models. The time saved by using the former model is more than offset by the lack of accuracy. The highly accurate CBS-APNO[34] was not examined because of computational cost and lack of parameters for second row elements.

Curtiss et al.[17,35] have compared G2 results with those obtained from seven density functional models. They found the best results using the B3LYP model employing the 6-311+G(3df,2p) basis set. The results in this paper were computed by this method; however, we have also done extensive testing with the 6-311+G(d,p) basis and in some cases with the 6-31(d) basis.

The absolute energies obtained by these calculations were converted into enthalpies or free energies of formation using both the atomization and bond separation methods. The atomization energy is the energy of the following reaction and may be calculated from both experiment and computed energies (eqs 1 and 2, respectively).

$$\mathrm{M}_m\mathrm{N}_n \rightarrow m\mathrm{M} + n\mathrm{N}$$

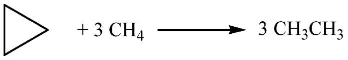
$$\Delta H_{\mathrm{atom}} = [(m\Delta H_{\mathrm{f}}(\mathrm{M})) + n\Delta H_{\mathrm{f}}(\mathrm{N})] - \Delta H_{\mathrm{f}}(\mathrm{M}_m\mathrm{N}_n) \qquad (1)$$

$$\Delta H_{\mathrm{atom}} = [mE(\mathrm{M}) + nE(\mathrm{N})] - E(\mathrm{M}_m\mathrm{N}_n) \qquad (2)$$

Since the atomization energy is the same either way, we can combine the right-hand sides of eqs 1 and 2 and solve for ΔH_{f}($\mathrm{M}_m\mathrm{N}_n$) (eq 3). The formation energies of the elements M and N are available from reference 1 and the energies (*E*) can be computed. A similar procedure affords the free energies of formation from the appropriate data.

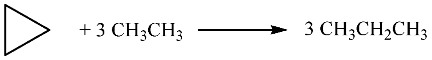
$$\Delta H_{\mathrm{f}}(\mathrm{M}_m\mathrm{N}_n) = [m\Delta H_{\mathrm{f}}(\mathrm{M}) + n\Delta H_{\mathrm{f}}(\mathrm{N})] + E(\mathrm{M}_m\mathrm{N}_n) - [m\Delta H_{\mathrm{f}}(\mathrm{M}) + n\Delta H_{\mathrm{f}}(\mathrm{N})] \quad (3)$$

The bond separation method requires a balanced chemical reaction using (primarily) molecular species. There are two ways to achieve this. In addition to being balanced in a material sense, an isodesmic reaction[36] has the same number and type of bonds on each side of the arrow. Ideally, any other substances in the equation would have no more than two heavy atoms.[37] An example using cyclopropane is shown in eq 4.



$$+ 3\,\mathrm{CH_4} \longrightarrow 3\,\mathrm{CH_3CH_3} \qquad (4)$$

The three carbon−carbon bonds of cyclopropane are balanced by the carbon−carbon bond in each of three ethane molecules. In addition to there being 18 hydrogen atoms on each side of the reaction arrow, there are also 18 carbon−hydrogen bonds. Note, however, that the hydrogen atoms are in different environments: -CH_2-, -CH_3, and CH_4. A homodesmotic equation[38] is one in which all hydrogen atoms are in the same environment, e.g., the same number of methylenes on both sides of the arrow, and is illustrated in eq 5. In the example shown below, the number of methyl and methylene groups has been conserved.



$$+ 3\,\mathrm{CH_3CH_3} \longrightarrow 3\,\mathrm{CH_3CH_2CH_3} \qquad (5)$$

The energy of the above transformations can be determined from readily available enthalpies in the literature and from computed energies. By combining the two and solving for the energy of the desired species, cyclopropane in this case, we obtain a result similar to eq 3. Because of the greater simplicity of the isodesmic equations, we have employed these throughout this work.

Results and Discussion

At the outset of this work, we intended to obtain literature values for comparison from either the NIST websites[1,2] or the work of Domalski and Hearing.[10] In all cases, references to the original sources are available. Recently, Cioslowski et al.[39] published a set of standard enthalpies for 600 organic and inorganic compounds to be used in comparisons with results from electronic structure methods. The Cioslowski 600 have been collected from the original literature and critically reviewed, and we have used this compilation as a final check against the others. In some instances, it was necessary to use values outside of these sources for comparison. These situations will be discussed.

When the results do not agree, which value, literature or computed, is correct? It is important to remember that enthalpies and free energies in the literature may well be derived or estimated from other data rather than a result of a direct thermochemical measurement. Because we have examined most of the compounds having comparison data in the literature rather than just representative samples, it is reasonable to presume that a deviation from the literature value by only one member of a group may imply an incorrect value in the literature. When we believe that computation has provided a better value, we will provide reasoning to support our hypothesis.

When the Gaussian model chemistries were first introduced, the goal was a deviation of no more than 8 kJ/mol from experiment, as this was generally the margin of error in most thermochemical measurements. Examination of ref 39, however, shows that the potential error for many organic compounds is less than 4 kJ/mol; consequently, we consider acceptable any deviation that is less than 8 kJ/mol, but we have set as our ideal an accuracy of 4 kJ/mol or less.

The demands of these high level computations have played a significant role in the types and sizes of molecules that have been examined. There are few constraints in a 64-bit computer system other than time; however, in a 32-bit system there is a practical limit of six heavy atoms for G2 calculations because

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(37) There are actually a number of potential bond separation equations that can be written for many of the compounds that we have examined, some of these employing more than two heavy atoms. What is critical is that the molecules selected have well-defined experimental energies.

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TABLE 1. Summary of the Mean Absolute Deviations[a] between Computed and Literature Standard State Enthalpies/Free Energies of Formation for All Compounds in the Comparison Set

	G2		G2MP2		G3		G3MP2		G3B3		G3MP2B3		CBS-QB3		DFT[b]	
	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG
Atomization																
overall	6.8	13.4	9.0	12.1	3.0	13.4	5.6	17.3	2.6	12.5	3.5	15.1	8.1	13.1	40.5	29.9
halogenated	12.0	20.5	14.7	23.2	5.6	13.9	5.8	14.1	4.5	11.5	5.3	13.7	18.2	26.5	21.8	16.3
aromatic	10.0	12.1	12.6	10.9	2.3	22.6	6.7	28.9	1.6	22.1	7.6	29.9	6.4	22.2	38.5	16.9
all others	4.9	11.5	6.9	9.1	2.5	12.4	5.5	17.0	2.3	11.8	2.8	14.2	5.3	8.1	45.1	34.2
Bond Separation																
overall	3.5	3.8	3.7	4.2	3.1	3.7	3.2	4.1	2.9	3.8	3.2	4.3	4.5	5.6	16.4	18.4
halogenated	5.2	4.6	4.9	4.6	5.2	5.2	4.3	4.6	4.3	4.7	3.7	4.2	7.6	8.4	11.2	12.7
aromatic	4.2	5.0	4.9	4.7	3.3	4.5	4.5	4.1	4.0	3.8	7.7	5.8	7.9	9.8	4.5	6.2
all others	2.9	3.4	3.2	4.1	2.6	3.3	2.9	4.0	2.4	3.5	2.7	4.2	3.3	4.3	18.7	20.9

[a] In kJ/mol. [b] B3LYP 6/311+G(3df,2p).

of the method of allocating disk space.[40] Molecules with seven heavy atoms can be computed by the G2 method if C_s symmetry is present, and higher symmetry allows computation of eight. The use of G2MP2 decreases the computation time; however, the size of the scratch files is not reduced enough to permit calculation of larger molecules in most cases. These same limitations apply to the CBS models. G3 (and G3B3) allow the computation of molecules having seven heavy atoms and no symmetry. In some cases, eight heavy atoms are possible with C_s symmetry and we report nonane (C_2v symmetry). The importance of the role of symmetry can be seen with decalin. G3 successfully computes absolute energies for *trans*-decalin (C_{2h} symmetry) but fails in an attempt to calculate *cis*-decalin (C_2 symmetry). G3MP2 and G3MP2B3 permit the calculation of decane (C_{2h} symmetry) and molecules of this size or larger can be computed with the latter two methods even when symmetry is not present.

Both G3 and CBS-QB3 are capable of computing aromatic molecules of up to eight heavy atoms with C_1 symmetry. We have done larger molecules with G3: naphthalene ($C_{10}H_8$, D_{2h} symmetry) and anthracene ($C_{14}H_{10}$, also D_{2h} symmetry); however, phenanthrene ($C_{14}H_{10}$, C_{2v}) was successful only with G3MP2. Questions of speed and storage requirements are less problematic for density functional theory calculations and consequently numerous reports are found in the computational literature examining the application of these methods to the determination of thermodynamic properties.

Comparison of Models. Statistical summaries for our results using the atomization and bond separation methods are recorded in Tables 1 and 2. In Table 1, we show the mean absolute deviations by model for both atomization and bond separation. It became clear as the data for this project accumulated that two classes of compounds, aromatic and halogenated aliphatic, deviated farther from experiment than the other families of compounds that we examined. In Table 1, we have reported the means for these compounds on a separate line and the mean for the remaining compounds is shown in the final line, “all others.”

Looking first at the enthalpies and free energies determined by atomization, we note that regardless of compound type or model chemistry employed, free energies are normally less accurate than enthalpies by 5−10 kJ/mol. Excepting the halogenated compounds, the G3 methods are able to give enthalpies that lie in our ideal range. The free energies are, on average, outside even our acceptable range. G2 enthalpies are within the acceptable range, but CBS-QB3 values are not unless the aromatic and aliphatic halocarbons are excluded. In both cases, the free energies are worse. For those values determined by Density Functional Theory, the results deviate from the mean by an amount (>20 kJ/mol) that we have defined as unacceptable.

Considerable improvement is found in the mean absolute deviations of the enthalpies and free energies determined by bond separation. All of the ab initio enthalpies are in our ideal range as are the free energies for the G2, G3, and G3B3 methods. Free energies for the G2MP2, G3MP2, and G3MP2B3 and CBS-QB3 methods lie well into our acceptable range. Aliphatic halocarbon and aromatic compounds have larger deviations. When these are excluded, all ab initio mean absolute deviations fall into the ideal category. Density functional results are also much improved by using bond separation with the mean absolute deviation dropping from 38.8 to 11.9 kJ/mol. As large as these are (they fall outside our acceptable range) they are better than those obtained with the smaller basis sets.[41]

That our deviations are larger than those reported by Raghavachari[35] is a consequence of the design of the respective test sets. The G2 test set has a sample of representative compounds, both organic and inorganic, of which only benzene has more than five heavy atoms. We have examined a much broader range of molecules, many having 7−10 heavy atoms. Thus, we have calculated decane for which the best result deviates from experiment by 36.0 kJ/mol. There is a general trend of increasing error as the chain length increases. As we will demonstrate later in this section of the paper, the deviations in the ab initio results can be explained by including the effects of higher energy conformers having significant populations at standard conditions. This is particularly true of the free energies. Nevertheless, the errors from the density functional enthalpies and free energies go well beyond what we can rationalize by including these conformers.

The density functional results are so divergent that comment is required. They were not unexpected. Jursic[42] has examined

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(40) The NIST Compuational Chemistry Comparison and Benchmark DataBase (see ref 2) has a significant number of compounds that are included in our study. The NIST adheres to the six heavy atom limit with the exception of some aromatic compounds.

(41) Calculations at the higher level are time-consuming. Taking a mid-sized molecule such as hexane as an example, a smaller basis set (6-311+G-(d,p)) requires under 3 h for computation. Using 3df,2p polarization functions requires in excess of 18 h, whereas a G3 calculation will be completed in just over 6 h and give much better results. Only in the size of the scratch files is the density functional more economical. The G3 scratch files are 5.6 GB, whereas those for the large density functional are only 101 MB.

TABLE 2. Count of Mean Absolute Deviations[a] by Error Range and Percentages Falling into Ideal or Acceptable Ranges

	G2		G2MP2		G3		G3MP2		G3B3		G3MP2B3		CBS-QB3		DFT[b]	
	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG
All Compounds																
atomization																
error < 4	95	18	69	64	209	19	192	24	212	24	197	18	91	46	16	37
4 < error < 8	80	40	64	37	36	26	83	26	37	37	73	29	86	59	14	25
8 < error < 12	43	69	57	46	12	71	21	55	8	70	15	63	42	48	21	27
12 < error < 20	27	78	51	61	6	103	8	122	4	90	8	113	23	50	35	31
error > 20	10	50	19	52	0	44	2	79	0	40	1	71	14	53	214	180
% < 8 kJ/mol error	69	23	51	39	93	17	90	16	95	23	92	16	69	41	10	21
% < 4 kJ/mol error	37	7	27	25	79	7	63	8	81	9	67	6	36	18	5	12
bond separation																
error < 4	153	144	150	135	172	152	201	162	181	145	193	138	173	125	49	44
4 < error < 8	57	64	68	74	50	66	66	87	43	71	51	89	35	70	51	39
8 < error < 12	14	15	13	21	13	15	12	28	8	16	15	34	12	21	31	39
12 < error < 20	7	8	5	5	2	5	4	7	3	3	6	3	10	13	60	43
error > 20	0	0	1	2	2	1	1	0	0	0	0	1	5	6	82	108
% < 8 kJ/mol error	91	90	92	88	93	91	94	88	95	92	92	86	89	83	37	30
% < 4 kJ/mol error	66	62	63	57	72	64	71	57	77	62	73	52	74	53	18	16
Excluding Halogenated and Aromatic Compounds																
atomization																
error < 4	83	14	60	57	170	19	169	22	171	20	173	16	81	45	10	22
4 < error < 8	67	38	55	34	27	17	64	19	27	26	54	20	65	57	11	18
8 < error < 12	29	57	43	39	7	60	11	47	3	59	6	56	33	39	11	17
12 < error < 20	5	52	28	38	0	82	2	103	1	73	2	96	6	33	25	19
error > 20	0	23	3	21	0	26	1	56	0	24	0	47	0	11	172	153
% < 8 kJ/mol error	82	28	61	48	97	18	94	17	98	23	97	15	79	55	9	17
% < 4 kJ/mol error	45	8	32	30	83	9	68	9	85	10	74	7	44	24	4	10
bond separation																
error < 4	122	111	119	102	145	127	174	135	149	117	165	111	142	101	34	31
4 < error < 8	32	41	42	47	30	42	44	62	25	49	35	71	18	48	30	20
8 < error < 12	8	7	6	16	5	10	5	24	2	10	5	24	2	10	21	26
12 < error < 20	2	5	2	3	1	3	3	6	2	2	3	1	2	7	46	34
error > 20	0	0	1	2	1	0	1	0	0	0	0	1	4	2	75	95
% < 8 kJ/mol error	94	93	95	88	96	93	96	87	98	93	96	88	95	89	31	25
% < 4 kJ/mol error	74	68	70	60	80	70	77	59	84	66	79	53	85	60	17	15

[a] In kJ/mol. [b] B3LYP 6/311+G(3df,2p).

several hydrocarbon and heterocyclic compounds with two dozen combinations of functionals and basis sets, finding that the results can vary by as much as 80 kJ/mol and with no assurance at the outset which method will agree best with experiment. Williams and Whitehead,[43] Ball,[44] Pan et al.,[45] and Chen et al.[21] also noted similar results. Izgorodina et al.[46] have shown that DFT overestimates the stabilizing effect of larger alkyl groups on bond dissociation energies. Grimme[47] has demonstrated that current implementations of DFT do not predict the correct relative energies of a series of hydrocarbon isomers and that this is primarily due to an inability to account for electron correlation. Delley has examined a variety of functionals and basis sets using the 577 compounds from the ref 2 database.[48] They report larger deviations than we do for the G2 and G3 models; however, it must be kept in mind that many of the compounds are inorganic compounds that are poorly described by ab initio methods. Nevertheless, the best performing density functional model in their paper has deviations comparable to those that we report in Table 1, and the worst has mean deviations that are nearly double ours.

Attempts to patch the results with semiempirical corrections[49] or revised experimental heats of formation[23] for carbon and hydrogen have not always provided acceptable results. The empirical atomic correction terms employed by Politzer et al.[50] give better results, but these still differ from experiment by an average of 10.9 kJ/mol. Liu et al.[51] performed B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) calculations on the straight chain hydrocarbons through hexadecane and found mean errors of 81.2 kJ/mol for the enthalpies and 70.4 kJ/mol for the free energies. Application of a 3-parameter modification equation improved these values to 1.1 and 1.9 kJ/mol, respectively. The former value for the enthalpy compares favorably with the 2.3 kJ/mol mean deviation reported by Redfern et al.[52] for G3 calculations; however, it should be noted that the latter group did not explicitly calculate the energies of the alkanes having more than eight carbon atoms. The energies of the larger homologs were determined by adding the incremental energy of the CH_2 group determined from the energies of pentane, hexane, and heptane.

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TABLE 3. Error[a] in the TΔS Term for Straight Chain and Cyclic Alkanes

carbon atoms	straight chain G3	straight chain G3MP2	cyclic G3	cyclic G3MP2
3	−0.3	−0.3	−4.8	−4.8
4	1.7	2.0	−0.6	−4.0
5	3.6	3.6	−6.9	−8.2
6	5.4	5.5	−1.6	−1.6
7	7.2	7.2	−1.5	−1.5
8	8.9	8.9		−0.2
9	10.7	10.7		
10		12.5		

[a] In kJ/mol.

An alternate approach was employed by Sebbar et al.[53] to obtain reliable enthalpies of formation for unsaturated oxygenated compounds. Where we have broken each compound into the smallest molecule having the reference bonds, they used larger compounds having well-defined experimental enthalpies. Thus, 2-formyl-3-butenal was broken into ethane, methanal, carbon monoxide, and 1-pentene. Using this approach, they found that B3LYP/6-311G(d,p) gave results consistent with G3MP2B3. Check and Gilbert[54] found that density functional theory consistently underestimated reaction enthalpies in cyclization energies and homolytic bond breaking reactions. They attributed this to a consistent underestimation of the carbon−carbon bond energy by B3LYP. The results reported by Sebbar just described may have avoided this problem by minimizing the number of such bonds in the computation.

Table 2 shows the number of compounds having mean absolute deviations in the ideal, acceptable, two categories of less acceptable, and completely unacceptable for each model chemistry examined. Identical analysis is shown for results of enthalpies and free energies of formation computed by the atomization and bond separation methods. The bottom two lines of each section show the percent of entries that fall into the acceptable and ideal ranges. The results show again that bond separation affords better enthalpies and free energies, but note that even by the less accurate atomization method the G3 models give enthalpies that fall into our acceptable range over 90% of the time and ideal between 71% and 77%. Unfortunately, the free energies are mostly in the less and unacceptable ranges for all models. Consequently, atomization is not an acceptable method for computation of free energies.

Examining the overall bond separation results, we see that the ab initio enthalpies fall into the acceptable range for more than 90% of the compounds examined. The G3 methods were able to attain values in the ideal range for 75−85% of the compounds. Percentages of free energies are lower for all methods, with ideal results obtained in more than half of the examples and acceptable in almost 90%.

In assessing the source of potential errors, we note that these formation energies are based on the lowest energy conformer. For many of these compounds alternate conformers exist that are low enough in energy to have a significant population at 298.15 K. How many of these errors can be attributed to neglect of these higher energy conformers? The enthalpy of a mixture of "k" conformers is given by

$$\Delta H^\circ_{\mathrm{Tot}} = \sum_i^k \chi_i \Delta H^\circ_i \tag{6}$$

The consequence of mixing in higher energy conformers is to raise the value of $\Delta H^\circ_{\mathrm{tot}}$. Examination of the straight chain alkane enthalpies that comprises part of the data in Table 2 shows that indeed our computed enthalpies are lower than experiment but the deviation is less than 4 kJ/mol in all cases.

The determination of the overall entropy for multiple conformers is similar, but there is a second term added to account for the entropy of mixing.

$$\Delta S^\circ_{\mathrm{Tot}} = \sum_i^k \chi_i \Delta S^\circ_i - R \sum_i^k \chi_i \ln \chi_i \tag{7}$$

Whereas the first term will increase the free energy from the computed value, the second will lower it. In those cases where the second term becomes larger than the first, the experimental entropy will be at lower energy than that of any single conformer. That this is so and that the difference can be attributed to conformational mobility can be seen in Table 3. The error in the $T\Delta S$ term for the straight chain alkanes is positive (i.e., the calculated free energy is higher than the experimental value) beginning with butane and increases regularly as the number of carbon atoms increases. In contrast, there is no regular pattern with the cyclic compounds and with the exceptions of cyclopropane and cyclopentane, these are quite small. Similar results are seen in other families of compounds.

We have employed two strategies to improve the free energies. First, we have computed the energies of all possible gauche conformers for those alkanes having multiple conformers and for representative samples from other families.[55] The second is simpler but less rigorous. As a step toward estimation of the free energy of binding in a ligand−protein complex, Böhm developed a scoring function that used the contact surface, number of hydrogen bonding and ionic interactions, and the number of rotatable bonds.[56] They used a value of 1.4 kJ/mol per rotatable bond; however, we have employed the smaller value, 1.2 kJ per rotatable bond, which gives a lower corrected mean. Further computational work has shown that these values do not hold for all bond types.

The discussion that follows will be by major classes of compounds: saturated and unsaturated, acyclic and cyclic hydrocarbons. Compounds having group 15 through group 17 heteroatoms were examined in our evaluation of the model chemistries reported in this section. A thorough discussion of these results as well as techniques for correcting the computed free energies will be reported in a future paper. In each we will examine the performance of the G3 and G3MP2 models listing all hydrocarbons that formed the basis for the discussion above as well as additional compounds commonly employed by the chemist for which partial or no data can be found in the literature. At the end of each table is a summary of the average mean absolute deviations for the entire table and for each subgroup. The models chosen provide access to rigorous computation for a limited number of heavy atoms and a less rigorous but still very accurate calculation for chemical systems

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TABLE 4. Experimental Enthalpies, Free Energies of Formation,[a] and Deviations for Representative Alkanes Determined by G3 and G3MP2 Model Chemistries Using the Bond Separation Method

		enthalpies of formation			free energies of formation				
molecule	source[b]	literature	G3	G3MP2	literature	G3	G3MP2	corrected[c]	full calc[d]
propane	CC	−104.7	−104.7	−104.8	−24.4	−24.6	−24.7		
butane	CC	−125.8	−126.0	−124.8	−16.6	−15.1	−13.6	−16.3	−17.2
2-methylpropane	CC	−135.0	−134.0	−134.0	−21.5	−20.8	−20.9		
pentane	CC	−146.8	−147.2	−147.1	−8.8	−5.5	−5.5	−7.9	−8.8
2-methanebutane	CC	−153.7	−153.1	−153.1	−13.9	−11.9	−11.9	−13.1	−13.9
2,2-dimethylpropane	CC	−167.9	−168.9	−168.7	−16.9	−19.0	−18.8		
hexane	CC	−166.9	−168.5	−168.3	0.1	3.9	4.2	0.3	−0.5
2-methylpentane	CC	−174.6	−174.5	−174.4	−5.3	−2.5	−2.4	−4.9	−4.9
3-methylpentane	CC	−172.0	−171.7	−171.7	−3.3	−0.2	−0.1	−2.2	−2.7
2,2-dimethylbutane	CC	−184.0	−185.5	−185.2	−7.9	−10.8	−10.6	−10.8	
2,3-dimethylbutane	CC	−175.9	−177.0	−177.1	−2.1	−3.8	−2.1	−3.8	−6.0
heptane	DH	−187.7	−189.9	−189.5	8.3	13.3	13.7	8.5	7.3
2-methylhexane	WB	−195.0	−196.0	−195.7	3.3	6.8	7.0	3.2	
3-methylhexane	DH	−191.3	−193.1	−192.9	5.8	9.1	9.3	5.5	
2,2-dimethylpentane	WB	−206.2	−206.9	−206.4	0.2	−1.4	−1.0	−1.4	
2,3-dimethylpentane	DH[e]	−198.9	−193.7	−193.6	1.2	9.8	9.8	8.6	
2,4-dimethylpentane	WB	−202.1	−203.4	−203.1	3.2	3.4	2.0	3.4	
3,3-dimethylpentane	WB	−201.5	−201.0	−200.5	3.4	5.2	3.9	5.2	
2,2,3-trimethylbutane	DH	−204.5	−206.1	−205.8	4.7	−2.1	−1.8		
3-ethylpentane	WB	−189.7	−190.3	−190.0	11.2	14.3	14.5	10.7	
octane	WB	−208.4	−211.1	−210.7	16.6	22.9	23.3	16.9	16.3[f]
2-methylheptane	WB	−215.5		−217.0	11.7		16.5	11.7	
3-methylheptane	WB	−212.6		−214.3	12.7		18.7	13.9	
4-methylheptane	DH	−212.0		−214.2	17.1		18.8	14.0	
2,2-dimethylhexane	DH	−224.6		−227.9	11.1		8.2	8.2	
2,3-dimethylhexane	DH[g]	−213.8		−217.2	18.1		16.8	14.4	
2,4-dimethylhexane	DH	−219.2		−222.0	12.1		13.7	12.5	
2,5-dimethylhexane	DH[h]	−222.5		−222.7	10.8		11.3	7.7	
3,3-dimethylhexane	DH	−220.0		−221.7	13.6		13.0	13.0	
3,4-dimethylhexane	DH	−212.8		−210.8	17.7		25.9	23.5	
2,2,3-trimethylpentane	DH	−220.0		−222.7	17.5		15.3	14.1	
2,3,3-trimethylpentane	DH	−216.3		−220.1	19.3		19.7	19.7	
2,2,4-trimethylpentane	DH	−224.0		−224.7	14.0		14.5	14.5	
2,3,4-trimethylpentane	WB	−217.4		−219.5	19.5		17.9	17.9	
3-ethyl-2-methylpentane	DH	−211.0		−213.0	21.7		24.7	22.3	
2,2,3,3-tetramethylbutane	WB	−225.9		−230.4	22.3		13.8	13.8	
nonane	DH	−228.2	−232.7	−232.0	25.9	32.1	32.8	24.9	26.9[f]
2,2-dimethylheptane	DH	−246.2		−249.3	18.0		17.7	16.5	
3,3-diethylpentane	DH	−232.3		−238.5	34.9		32.1	32.1	
2,2,3,3-tetramethylpentane	WB	−237.1		−243.9	34.7		32.8	32.8	
2,2,4,4-tetramethylpentane	WB	−241.5		−246.9	35.1		27.8	27.8	
decane	WB	−249.7		−253.1	33.1		42.5	34.1	36.0[f]
2,2-dimethyloctane	DH	−266.2		−270.6	27.0		27.2	24.8	
2,7-dimethyloctane	DH	−264.0		−264.4	27.8		31.7	24.5	
mean absolute deviations			1.3	2.2		2.7	3.2	2.1	

[a] In kJ/mol. [b] CC, ref 2; WB, ref 1; DH, literature cited in ref 10. [c] A constant value of 1.2 kJ/mol was substracted from the computed free energy for each carbon−carbon bond that can be rotated to afford different conformers. There are exceptions; see text for details. [d] Based on G3 (unless otherwise noted) computation of each gauche conformef. [e] Group additivity (ref 10) gives a value of −194.1 kJ/mol for the enthalpy and 5.8 kJ/mol for the free energy. [f] G3MP2 computation. [g] $\Delta H = -214.9$ kJ/mol; $\Delta G = 14.5$ kJ/mol. [h] $\Delta G = 9.8$ kJ/mol.

with many more heavy atoms.[57] The chemist who prefers optimization by density functional methods will do as well with either the G3B3 or G3MP2B3 models. With the exception previously noted, CBS-QB3 does as well as the aforementioned methods; however, owing to the disk storage requirements, there are more limitations on the size of the molecules that can be computed. In addition, we will include an adjusted value for the free energy based on the number of rotatable bonds.

Saturated Alkanes. In Table 4, we present the experimental and computed enthalpies and free energies of formation for the aliphatic hydrocarbons. The two columns at the far right of the table show the results obtained by correcting the free energies for the presence of higher energy conformers. The first shows the computed free energy adjusted by the product of the bond constant and the number rotatable bonds. In determining the number of rotatable bonds, we counted all carbon−carbon bonds whose rotation affords different conformers except those (a) adjacent to quaternary centers and (b) between tertiary centers that are separated by one or two bonds.[58] In addition, for the straight chain alkanes and a few others, we have shown the free energy obtained by explicit calculation of all possible conformers having a single gauche interaction. Where comparisons between the two methods can be made, the results are strikingly close.

As a rule, these compounds are accurately described by computation and afford enthalpies that are within our ideal range for all but seven of the 44 compounds. Twenty-seven of the remaining have deviations that are within 2 kJ/mol of experiment, and 13 of the 20 alkanes having seven and fewer carbon

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(57) Enthalpies and free energies of formation calculated by all other methods may be found in Supporting Information.

(58) For example, 2,2-dimethylhexane has two rotatable bonds and 2,4-dimethyl hexane has one.

TABLE 5. Comparison of Experimental, Corrected, and ab Initio Enthalpies[a] for the Straight Chain Alkanes

	chain length					
enthalpy	5	6	7	8	9	10
experimental	−146.8	−166.9	−187.7	−208.4	−228.2	−249.7
corrected[b]	−145.3	−166.3	−188.7	−209.6	−230.0	−251.2
ab initio[c]	−147.2	−168.5	−168.5	−211.1	−232.7	−253.1

[a] In kJ/mol. [b] Pentane and hexane were computed with the G3 model, all others with G3MP2. [c] G3 except for decane, which is G3MP2.

atoms are within 1 kJ/mol of experimental enthalpies. We noted in the previous section that the deviation of the enthalpies of the straight chain alkanes becomes larger as the chain length increases. Explicit calculation of the free energies for each gauche conformer of the straight chain alkanes permits calculation of the mole fractions for each of the conformers. From this data we are able to compute the corrected enthalpies shown in Table 5. All six had enthalpies within 4 kJ/mol as originally computed except for nonane. Correction brings them closer to experiment, and it is probable that the other octanes through decanes that we show in Table 4 would show smaller deviations if all conformations were explicitly computed. Nevertheless, most of these compounds have deviations that are less than 4 kJ/mol and are within or close to experimental error. The mean deviation for the G3 enthalpies is smaller than that for the G3MP2, although we note that when we compare only those compounds for which both methods have been employed (propane through octane), they are comparable at 1.2 and 1.1 kJ/mol for G3 and G3MP2, respectively.

Those compounds having deviations that are within ideal but larger than 2 kJ/mol tend to be longer chain alkanes having two or three methyl groups that are geminal or nearby. There is no pattern to this. Comparing the dimethylhexanes, we find that the 2,2 and 2,3 isomers have deviations larger than 2 kJ/mol, but the 3,3 and 3,4 isomers have deviations that are smaller. Steric congestion is also a common factor for those whose deviations are larger than 4 kJ/mol, and these are unlikely to be improved by inclusion of higher energy of conformers. In one case, 2,3-dimethylpentane, the enthalpies and free energies obtained by group additivity,[8] −194.1 and 6.0 kJ/mol, respectively, are closer to our results than are the experimental results. For the others, in particular the tri- and tetramethylpentanes, group additivity values and experiment match closely and the computed results differ from both.

The mean deviations for the free energies are more than double that of the enthalpies with G3 and G3MP2 giving comparable results. When the corrections are applied, the mean drops by just over 1 kJ and exclusion of four compounds from the list brings down further to 1.5 kJ/mol. The majority of compounds that we have examined have corrected free energies within 2 kJ/mol of experiment. There is no consistent pattern in the dozen that do not, but some of these include molecules whose enthalpies are problematic. In cases where group additivity values are closer to our computational results than the experimental enthalpies or free energies, we have indicated this in the footnotes to Table 4. In several cases, including some of the sterically congested tri- and tetramethylalkanes, the computed free energy without corrections is lower than the experimental value.

Saturated Alicyclic Hydrocarbons. The unsubstituted cycloalkanes for which we have comparison data have enthalpies and free energies that are within our ideal standard except for the cyclopentane free energy. Indeed most of the deviations are less than 2 kJ/mol. We noted earlier that the errors for the $T\Delta S$ terms of cyclopropane and cyclopentane were inconsistent with those of the other cycloalkanes. Although the enthalpies and free energies of these two compounds fall into or near the ideal range, the computed enthalpies in both cases are too high and the free energies are too low. The errors reinforce each other rather than cancel.

For the substituted cycloalkanes, the only compound that falls outside the ideal is 1,1-dimethylcyclohexane. For the compounds having side chains of two or more carbon atoms, we have included our corrections for the free energies, but note that these do not increase the accuracy of the results. Rotation of the ethyl side chain is severely restricted and even the propyl group has restrictions on its rotation. Hence, it appears that free energy corrections for side chains of three carbon atoms or less on rings of any size are unnecessary. If we make the assumption that the first two rotatable bonds from the ring can be excluded, then the butyl group would have only one such bond and the correction would be 1.4 instead of 4.8 kJ/mol. This affords values for butylcyclopentane and butylcyclohexane of 63.4 and 55.7 kJ/mol, respectively, which are well within our ideal range.

The polycyclic compounds also show acceptable agreement with experiment, although the mean absolute deviations tend to the high end of our ideal range. Dicyclopropyl and *cis*-decalin differ by 6−8 kJ/mol from experiment depending upon the method and lie outside the experimental error bar for the compound. Adamantane lies at the edge of our ideal standard, and *cis*-decalin is in the acceptable range.

Unsaturated Aliphatic Hydrocarbons. The mean absolute deviation for the G3 enthaplies is 2.0 kJ/mol, and that of the G3MP2 enthalpies is slightly larger at 2.7 kJ/mol. With few exceptions, the enthalpies fall into the ideal range and the handful that do not are within the acceptable range. This includes simple alkenes and the conjugated, cumulated, and isolated dienes. Exceptions tend to be sterically congested around the double bond. For example, (*E*)-3-methyl-2-pentene has a deviation that is just over 4 kJ/mol. The corresponding *Z* isomer is off by just 3 kJ/mol. It is worth noting that the experimental enthalpies for these two compounds are within 1 kJ of each other, as are the computed enthalpies, but experiment puts the *E* isomer at lower energy while our computations, both G3 and G3MP2, reverses the order. Also, both of the 2,3-dimethylbutenes show large deviations from experiment.

For G3 free energies, the uncorrected mean absolute deviation is larger at 3.4 kJ/mol, whereas that of the G3MP2 energies is more than 1 kJ larger at 4.6 kJ/mol. Correction for the presence of multilple conformers is done in two parts. The rotation about the standard carbon−carbon bond is the same 1.2 kJ per rotatable bond that we employed for the alkanes. In addition, it is necessary to account for the more facile rotation about the $C_{sp^2}-C_{sp^3}$ bond adjacent to the double bond. Explicit calculation of the energy lowering that occurs only upon rotation of the bond adjacent to the double bond shows that we can expect the free energy to drop by about 2.2 kJ/mol. Substitution at the adjacent carbon atom reduces this by about 0.5 kJ. Nevertheless, we have found that a larger value of 2.5 kJ/mol per adjacent bond minimizes the deviations over the test set which we have employed and other alkenes which are not part of this study. We have used this value regardless of the substitution at the double bond or adjacent atoms.

Why does the larger value give better results? There is a second source of error in the free energies that we are

TABLE 6. Experimental Enthalpies, Free Energies of Formation,[a] and Deviations for the Saturated Alicyclic Hydrocarbons Determined by the G3 and G3MP2 Model Chemistries Using the Bond Separation Method

		enthalpies of Formation			free energies of formation			
molecule	source[b]	literature	G3	G3MP2	literature	G3	G3MP2	corrected[c]
Cycloalkanes								
cyclopropane	CC	53.3	56.0	56.5	104.5	102.4	102.9	
cyclobutane	CC	28.4	28.3	28.7	112.2	111.5	108.5	
cyclopentane	CC	−77.1	−74.7	−74.1	38.9	34.4	33.7	
cyclohexane	CC	−123.1	−123.0	−122.2	32.1	30.7	31.5	
cycloheptane	DH	−118.1	−117.8	−117.2	64.5	63.3	63.8	
cyclooctane	DH	−124.4		−123.8	91.5		91.9	
cyclononane	DH	−132.8		−136.2			118.3	
cyclodecane	DH	−154.3		−153.6			129.1	
methylcyclopropane	WB[d]	23.2	26.2	27.0		103.7	104.4	
methylcyclobutane	DH[e]	3.3	−5.1	−4.4		106.1	106.8	
methylcyclopentane	DH	−106.0	−105.8	−104.9	36.6	36.1	37.0	
methylcyclohexane	DH	−154.8	−154.1	−154.3	27.4	27.4	26.8	
ethylcyclopropane	WB[d]	1.4	3.83	4.6		112.3	113.1	110.9
ethylcyclobutane	WB	−27.7	−24.36	−23.6		117.8	118.6	116.4
ethylcyclopentane	WB	−127.1	−127.1	−126.0	44.7	44.8	45.8	43.4
ethylcyclohexane	WB	−171.8		−173.3	39.4		38.6	37.2
propylcyclopentane	WB	−148.1		−147.6	53.6		55.4	52.6
propylcyclohexane	WB	−193.3		−194.8	47.4		47.9	45.1
butylcyclopentane	WB	−168.3		−169.1	62.3		64.8	60.6
butylcyclohexane	WB	−213.2		−216.3	56.3		57.1	52.9
1,1-dimethylcyclopropane	CC	−8.2	−9.7	−8.4	103.3	99.9	101.2	
1,1-dimethylcyclopentane	WB	−138.3	−140.8	−139.5	39.2	37.0	38.4	
1,1-dimethylcyclohexane	DH	−180.9	−185.6	−184.6	35.6	27.9	30.2	
Polycyclic Alkanes								
spiropentane	CC	185.2	185.3	187.8	265.4	265.0	267.4	
dicyclopropyl	WB	130.0	136.0	137.9		243.1	244.9	
adamantane	WB	−137.9[f]	−145.9	−141.9		84.5	88.6	
trans-hexahydroindane	DH	−131.6		−132.1			83.1	
cis-hexahydroindane	DH	−127.2		−129.6			85.9	
trans-decalin	WB	−182.2	−188.2	−185.8		65.4	67.7	
cis-decalin	WB	−169.2		−174.6			79.8	
mean absolute deviations			2.3	2.1		1.8	1.6	

[a] In kJ/mol. [b] CC, ref 2; WB, ref 1; DH, literature cited in ref 10. [c] A constant value of 1.2 kJ/mol was substracted from the computed free energy for each carbon−carbon bond that can be rotated to afford different conformers. [d] Computed from the liquid phase ΔH°_f and ΔH_{vap}; the latter estimated from the method of Chicos, J. S., Hyman, A. S., Ladon, L. H., Liebman, J. F. *J. Org. Chem.* **1981**, *46*, 4294. [e] The value is a group additivity estimate; a value of 18.3 kJ/mol is derived using a liquid-phase experimental value from reference 10 and the ΔH_{vap} estimated by the method of Chickos, et al. (see footnote d). Using the same ΔH_{vap} and the liquid-phase group additivity estimate in ref 10 gives a value of 1.1 kJ/mol. [f] Reference 39 gives a values of −133.1 kJ/mol.

reporting: the inability of the frequency calculation to properly account for anharmonic oscillations. These errors are particularly acute with those at low frequencies. We note that the lowest frequency for many of these molecules, occurring between 85 and 100 cm^{-1} is the rotational vibration around the $C_{sp^2}-C_{sp^3}$ bond. It is possible that this larger value is compensating not only for the multiple conformers but also for the errors in frequencies due to anharmonic oscillators as well.

Looking at the range of 1-alkenes from propene through 1-decene, we see that the free energies are within 2 kJ/mol of experiment in all cases. The free energies of the substituted alkenes are within 2 kJ/mol of the experimental value except for that same group of sterically crowded molecules that we discussed above. The cumulated dienes follow experiment within 2.5 kJ/mol for both enthalpies and free energies. Only 1,2-pentadiene has multiple conformations, and correction for this possibility affords an improved result. The conjugated dienes are also close to experiment and require no correction. Even the simplest member of the group, 1,3-butadiene, has an *s-cis* conformer (slightly nonplanar) that is high enough in energy that it is relatively unpopulated. Finally, the isolated dienes have enthalpies that are within 2 kJ/mol for all except (*Z*)-1,4-hexadiene, which is within 3 kJ/mol of experiment. Because of increased conformational mobility, the calculated free energies are probably too high, although only 1,4-pentadiene has an experimentally known value. Our computed result is about 6 kJ/mol too large; however, adjusting the value for the two rotatable bonds affords a value that is within 2 kJ/mol. Alternately, explicit computation of the other conformers gives a composite value that is about 1 kJ higher. The remaining isolated dienes in Table 5 have no experimental free energies; however, in each case we have explicitly computed the alternate conformer energies and obtained corrected values that are within 1 kJ of the value obtained from counting the rotatable bonds (these are shown in the footnotes to Table 5).

At 3.7 kJ/mol for G3 enthalpies, the alkyne mean absolute deviation is the largest that we have encountered. However, in this case as well, it is large deviations for a few compounds that inflate these averages. We report the results for the terminal alkynes from propyne through 1-decyne, finding only the latter to fall outside our ideal standard. The internal and substituted alkynes in our list also show similar precision. It is the conjugated compounds that give erroneous results. For example, the largest, 1,3-butadiyne, deviates by 16 kJ/mol, and the three enynes in Table 7 fall 6−8 kJ below the experimental values. Removal of these four compounds from the list brings the mean absolute deviation for the enthalpies to 2.0 kJ/mol, identical with that of the alkenes.

The alkyne free energies also have a large mean deviation. Removal of the most extreme member, 1,3-butadiyne, brings the average inside the ideal range. The other conjugated enynes whose enthalpies are problematic do not have experimental free energies and are not responsible for the large mean deviation. Correction of these alkyne free energies is simplified by the non-participation of the triple bond and the adjacent $C_{sp}-C_{sp^3}$ bonds in generating new conformers. Thus we count the remaining single bonds whose rotation generates a new conformer which affords a mean deviation of 1.8 kJ/mol. This improved result is misleading since so few of these compounds are large enough to be corrected, and among these is 2-pentyne whose deviation is outside our acceptable range. More accurate but still outside the ideal are 2-butyne and propyne. For 1-pentyne the corrected energy is farther from experiment than the uncorrected value. Correction of 1-hexyne affords a value just larger than experiment, and explicit computation of all conformers gives a value that is within 1 kJ of experiment and deviates by just over 1 kJ from the value resulting from rotational bond correction. The homologs through 1-decyne are all within the ideal range.

Unsaturated Alicyclic Hydrocarbons. At 4.8 and 6.1 kJ/mol for the enthalpies and free energies, the mean absolute deviations from experiment for the cycloalkenes are largest of those that we have encountered. Yet if just one deviation, that of 1-methylcyclohexene, is removed from the list, the mean drops to 2.7 and 4.0 kJ/mol. Four other compounds in Table 8 also have large deviations. Cyclopropene, cyclobutene, and 1.5-cyclooctadiene all have deviations outside our acceptable range. Within acceptability is methylenecyclopropane. The remaining compounds have relatively small errors.

We believe that the literature value for 1-methylcyclohexene is in error. Our argument is grounded in the basic concept of the group additivity schemes that we summarized in the

TABLE 7. Experimental Enthalpies, Free Energies of Formation,[a] and Deviations for the Unsaturated Aliphatic Hydrocarbons Determined by G3 and G3MP2 Model Chemistries Using the Bond Separation Method

		enthalpies of formation			free energies of formation			
molecule	source[b]	literature	G3	G3MP2	literature	G3	G3MP2	corrected[c]
				Alkenes				
propene	CC	19.7	20.5	20.7	62.1	63.0	63.2	
1-butene	CC	−0.5	0.7	2.1	70.3	73.9	74.7	71.4
(*E*)-2-butene	CC	−12.5	−10.2	−9.3	61.8	62.5	65.1	
(*Z*)-2-butene	CC	−7.8	−4.7	−4.4	65.0	68.5	68.8	
1-pentene	DH	−21.5	−21.0	−20.5	78.7	83.0	83.5	79.3
(*E*)-2-pentene	CC	−31.1	−30.4	−29.5	69.9	73.0	74.0	70.5
(*Z*)-2-pentene	CC	−26.3	−29.1	−24.3	73.4	75.2	78.0	72.7
1-hexene	DH	−41.5	−42.5	−41.8	87.8	92.3	93.0	87.4[d]
(*E*)-2-hexene	CC	−53.9	−52.3	−51.2	76.6	82.0	83.1	78.3
(*Z*)-2-hexene	GA	−48.5	−47.6	−47.0	80.7	86.1	86.7	82.4
(*E*)-3-hexene	CC	−54.4	−52.3	−51.2	77.8	82.0	83.1	77.1
2-methyl-1-propene	CC	−17.8	−16.0	−15.3	57.4	59.1	59.7	
2-methyl-1-butene	CC	−34.9	−34.3	−33.4	67.1	69.4	70.3	65.7
2-methyl-2-butene	CC	−40.8	−40.0	−39.0	61.5	62.5	63.5	62.5
3-methyl-1-butene	CC	−27.8	−28.3	−27.6	76.1	76.9	77.6	74.4
2-methyl-1-pentene	DH	−59.4	−56.1	−55.1	70.6	78.3	79.3	73.4
3-methyl-1-pentene	DH	−49.5	−50.6	−49.7	82.1	85.8	86.6	82.1
4-methyl-1-pentene	CC	−51.3	−51.1	−50.5	83.1	85.5	86.1	81.8
2-methyl-2-pentene	AG	−66.9	−60.5	−59.3	64.3	72.8	74.0	69.1
(*E*)-3-methyl-2-pentene	DH	−63.1	−58.7	−57.5	67.0	73.8	75.0	70.1
(*Z*)-3-methyl-2-pentene	DH	−62.3	−59.3	−58.1	68.8	74.5	75.6	70.1
(*E*)-4-methyl-2-pentene	DH	−61.5	−59.7	−58.3	72.6	75.7	77.1	71.3
(*Z*)-4-methyl-2-pentene	DH	−57.5	−54.0	−53.0	75.1	80.3	81.2	77.5
2,3-dimethyl-1-butene	DH	−66.3	−61.1	−59.8	68.6	74.3	75.6	74.3
3,3-dimethyl-1-butene	DH	−61.6	−60.6	−59.9	79.9	78.7	79.5	78.7
2,3-dimethyl-2-butene	DH	−69.8	−62.8	−61.6	65.4	68.5	69.8	68.5
2-ethyl-1-butene	DH	−56.0	−53.7	−52.5	75.6	82.3	83.5	77.3
1-heptene	DH	−62.7	−63.9	−63.1	95.6	101.8	102.5	95.7
1-octene	DH	−82.9		−84.4	104.4		112.0	104.7
1-nonene	DH	−103.5		−105.6	112.9		121.5	113.0
1-decene	DH	−123.3		−126.9	122.1		131.0	121.3
1,2-propadiene	CC	190.9	188.6	189.8	201.2	199.2	200.3	
1,2-butadiene	CC	162.3	161.6	163.2	198.7	198.2	199.9	
1,2-pentadiene	CC	140.7	139.6	141.3	205.2	207.4	209.1	204.9[e]
2,3-pentadiene	CC	133.1	133.8	136.1	199.3	201.9	204.2	
3-methyl-1,2-butadiene	CC	129.1	127.9	130.3	197.5	197.0	199.4	
1,3-butadiene	CC	109.2	111.7	112.4	149.7	152.0	152.7	
(*E*)-1,3-pentadiene	CC	75.8	76.5	80.3	146.0	146.9	149.1	
(*Z*)-1,3-pentadiene	CC	82.8	84.7	85.7	150.8	152.8	153.7	
2-methyl-1,3-butadiene	CC	75.8	76.5	77.5	146.3	146.9	147.9	
(2*E*,4*E*)-2,4-hexadiene	CC	44.4	47.2	49.1		147.8	149.7	
(2*E*,4*Z*)-2,4-hexadiene	CC	48.1	52.4	53.9		150.5	152.0	
(2*Z*,4*Z*)-2,4-hexadiene	CC	52.3	58.2	59.4		154.9	156.1	
(*E*)-1,3,5-hexatriene	CC	167.8	167.2	168.8		232.2	233.9	
(*Z*)-1,3,5-hexatriene	CC	172.0	174.1	175.4		240.5	241.9	
1,4-pentadiene	CC	105.7	106.2	107.2	170.4	176.1	177.1	171.1[f]
(*E*)-1,4-hexadiene	CC	74.1	74.5	76.0		172.9	174.5	167.9[g]
(*Z*)-1,4-hexadiene	CC	77.4	80.3	81.0		178.0	178.6	173.0[h]
1,5-hexadiene	CC	85.4	84.1	85.2		184.8	185.8	178.6[i]

TABLE 7. (Continued)

molecule	source[b]	enthalpies of formation			free energies of formation			
		literature	G3	G3MP2	literature	G3	G3MP2	corrected[c]
				Alkynes				
propyne	CC	185.4	183.5	184.1	194.3	189.7	190.2	
propyne	CC	185.4	183.5	184.1	194.3	189.7	190.2	
1-butyne	CC	165.2	164.7	165.3	202.3	201.4	202.1	
2-butyne	CC	145.2	145.2	146.4	184.4	180.1	181.3	
1-pentyne	GA	146.0	142.7	143.5	212.4	210.3	211.1	209.1
2-pentyne	DH	128.9	125.9	127.2	194.3	184.6	185.9	
3-methyl-1-butyne	DH	136.4	137.1	138.1	205.6	205.6	206.6	
1-hexyne	DH	122.3	121.8	122.5	217.3	220.1	220.9	217.7[j]
2-hexyne	CC/AG	107.7	103.9	107.8	201.7	194.5	200.1	193.3
3-hexyne	CC/AG	105.4	106.5	105.3	198.4	197.6	195.9	
1-heptyne	DH	103.8	100.2	101.1	227.3	229.2	230.2	225.6
1-octyne	DH	80.7		79.9	233.8		239.8	235.0
1-nonyne	DH	62.3		58.6	244.4		249.3	243.3
1-decyne	DH	41.9		37.4	253.1		258.8	251.6
3,3-dimethyl-1-butyne	CC/AG	107.0	103.3	104.8	213.0	207.6	209.1	
cyclopropylethyne	CC	292.0	294.6	296.5		330.5	332.5	
2-methyl-1-butene-3-yne	CC	258.6	251.3	253.3		283.5	285.5	
(*E*)-3-penten-1-yne	CC	259.0	252.8	254.7		284.4	286.4	
(*Z*)-3-penten-1-yne	CC	258.2	251.4	253.0		282.9	284.5	
1,3-butadiyne	DH	472.8	456.2	458.5	444.0	428.3	430.6	
1,5-hexadiyne	GA	416.1	414.5	416.0		442.2	443.8	441.0
overall mean absolute dev			2.5	2.7		3.6	4.6	1.5
alkenes			2.0	2.7		3.4	4.6	1.5
alkynes			3.7	2.8		4.7	4.5	1.5
propyne	CC	185.4	183.5	184.1	194.3	189.7	190.2	

[a] In kJ/mol. [b] CC, ref 2; WB, ref 1; DH, literature cited in ref 10; GA, values determined by group additivity method in ref 10; CC/AG enthalpies are from ref 2; entropies are from group additivities in ref 10. [c] A constant value of 2.5 kJ/mol was subtracted from the computed free energy for each carbon−carbon single bond adjacent to a double bond that can be rotated to afford different conformers and an additional 1.4 kJ/mol for each additional bond between saturated centers. [d] Full computation of all conformers = 87.5 kJ/mol. [e] Full computation = 205.1 kJ/mol. [f] Full computation = 172.6 kJ/mol. [g] Full computation = 168.9 kJ/mol. [h] Full computation = 174.5 kJ/mol. [i] Full computation = 180.4 kJ/mol. [j] Full computation = 216.5 kJ/mol.

TABLE 8. Experimental Enthalpies, Free Energies of Formation,[a] and Deviations for the Unsaturated Cyclic Alkenes Determined by G3 and G3MP2 Model Chemistries Using the Bond Separation Method

molecule	source[b]	enthalpies of formation			free energies of formation		
		literature	G3	G3MP2	literature	G3	G3MP2
cyclopropene	CC	277.0	285.7	286.6	287.4	294.5	295.4
cyclobutene	CC	156.7	164.7	165.3	202.2	208.1	208.7
cyclopentene	CC	33.9	36.7	37.5	111.4	113.5	114.3
cyclohexene	CC	−4.3	−4.0	−3.0	108.1	107.7	108.7
cycloheptene	DH	−9.2	−9.4	−8.5		134.6	135.5
1-methylcyclopropene	CC	243.6	241.4	243.3	290.4	279.4	281.3
1-methylcyclobutene			121.2	122.7		194.5	196.1
1-methylcyclopentene	DH	−3.8	−2.5	−0.8	103.9	105.0	106.7
1-methylcyclohexene	WB	−81.3	−41.9	−40.0		100.7	102.6
3-methylcyclopropene			254.8	256.2		294.1	295.4
3-methylcyclobutene			133.4	134.4		208.1	209.2
3-methylcyclopentene	DH	7.4	6.8	8.0	113.8	115.5	116.6
3-methylcyclohexene			−34.3	−33.1		109.1	110.3
methylenecyclopropane	CC	200.5	193.5	194.9	243.7	236.4	237.8
methylenecyclobutane	CC	121.5	123.0	124.4	197.2	196.9	198.4
methylenecyclopentane	WB	10.2	11.1	12.8		119.4	121.1
methylenecyclohexane	PNK	−25.2	−34.2	−32.2		110.6	112.5
1,3-cyclopentadiene	CC	134.3	136.4	137.4	177.9	177.9	178.9
1,3-cyclohexadiene	CC	106.2	108.5	109.9	181.8	183.2	184.5
1,4-cyclohexadiene	CC	109.0	109.3	110.5	186.7	183.4	184.5
1,3,5-cycloheptatriene	DH	183.7	186.4	188.6	257.3	258.7	260.9
1,5-cyclooctadiene	DH	101.0		112.8	269.5		252.1
1,3,5,7-cyclooctatetraene	DH	297.6	299.4	302.1	369.6	371.3	374.0
mean absolute deviation			4.8	6.1		3.2	4.8

[a] In kJ/mol. [b] CC, ref 2; WB, ref 1; DH, literature cited in ref 10; PNK, value from ref 6.

introduction, i.e., each structural subunit makes a specific contribution to the enthalpy of a compound. Thus the difference between any given substituted cyclobutene and cyclopropene or any other pair of cyclic compounds should be a constant. That this is nearly so is shown in Table 9.

There is insufficient data to compare across the complete series of compounds, but there is sufficient to see that where they do exist, the literature values for the cycloalkene series match our computations. It is also clear that the difference between the 1-methylcyclopentene and 1-methyl-cyclohexene

TABLE 9. Differences between the Enthalpies of Formation[a] for Substituted Cyclopropenes through Cyclohexenes

	cycloalkene	1-methyl cycloalkene	3-methyl cycloalkene
		G3 ab Initio	
Cyc3-Cyc4	121.0	120.2	121.4
Cyc4-Cyc5	128.0	123.7	126.5
Cyc5-Cyc6	40.7	39.4	41.2
		Literature	
Cyc3-Cyc4	120.3		
Cyc4-Cyc5	122.8		
Cyc5-Cyc6	38.2	77.4	

[a] In kJ/mol.

does not fit the pattern. Thus we believe that our enthalpy of −41.9 kJ/mol is within experimental error of the correct value. We believe that it is possible that our values for cyclopropene and cyclobutene are also within experimental error of the correct value. These are the other two contributors to the large mean absolute deviation with both outside the acceptable range; however, the data to support such an argument is equivocal. The difference between the literature and computational cyclopropene/cyclobutene values is nearly identical; however, the difference between the cyclobutene/cyclopentene literature values is smaller than the computational result. Unfortunately, this series is the least consistent across the table. Nevertheless, if the error for cyclopropene was a consequence of basis set inability to cope with the difficulties of a double bond in a small ring, then 1-methylcyclopropene should also be deviant, which it is not. It should also be noted that the major errors in the free energies also involve cyclopropane rings and further work is needed to clarify the picture with regard to these compounds. Finally, the errors associated with methylene cyclopropane and cyclohexene cannot be resolved readily. Our computations give values for both that are lower than the experimental energy. Further work is in progress to clarify these discrepancies.

We have examined several cyclopolyenes with good results. The one exception is (*Z*,*Z*)-1,5-cyclooctadiene for which our G3 value lies 11.8 kJ/mol higher than the literature value. In principle, the reduction of this compound to cyclooctane should have an enthalpy effect comparable to the reduction of 2 mol of (Z)-2-butene, which comes to −236 kJ/mol. Using this value and assuming that the experimental value for cyclooctane is correct, we estimate an enthalpy of formation for the diene of −111.2 kJ/mol, very close to our value. There is little conformational mobility in these compounds, and hence the computed free energies should match experiment which is normally the case.

Conclusions

Accurate enthalpies and free energies of formation have been computed for a wide variety of acyclic and cyclic alkanes, alkenes, and alkynes ranging in size from 3 to 10 carbon atoms. They vary from straight chain to highly branched and from single functional groups to polyunsaturated. Most deviate from experiment by no more than 4 kJ/mol, and a significant number are within 2 kJ/mol. This is true as well for the free energies when we correct for the presence of higher energy conformers that have a significant population at 298.15 K. When we have explicitly calculated the energies of these conformers, we find that the resulting energy is normally within 1 kJ of the value determined by our simple bond correction method. The G3 methods (G3/G3MP2 or G3B3/G3MP2B3) are the most versatile and accurate, with CBS-QB3 also quite accurate but limited to a smaller subset of compounds than the G3 methods because of computational requirements. Density functional B3LYP/6-311+G(3df,2p) does not make accurate predictions.

We have tried to maintain a balance when evaluating errors, giving favor neither to experiment nor computation unless we have been able to find evidence to support such a distinction. Difficulties include molecules that are sterically congested and alkynes that are conjugated to another double or triple bond. It is not possible to resolve these difficulties with the methodology reported in this paper, but work is under way to determine if accurate computational measurements can be made or whether the difficulty is in the experimental determination. Additional work is also in progress to apply the bond corrections to molecules having a variety of functional groups that are commonly employed by organic chemists. This will extend the ability to determine free energies for an extensive number of compounds for which no current method is capable of providing an answer.

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Supporting Information Available: Cartesian coordinates for all compounds reported here and not available from ref 2, energies computed with all model chemistries for the elements, inorganic compounds, and organic compounds that are required to compute our enthalpies and free energies, and all thermodynamic data computed with the atomization and bond separation methods for all molecules in our comparison set that is not included in the paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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