Computational Methods in Organic Chemistry. 3. Correction of Computed Enthalpies for Multiple Conformations

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The first explicitly calculated G3(MP2) enthalpies and Gibbs energies of formation for undecane through eicosane are presented. These values, when corrected for the presence of multiple conformations, are found to be within 4 and often 2 kJ/mol of the experimental values. The derivation of the corrections for the enthalpies, which differ from those of the Gibbs energies published earlier, is presented and also applied to the first 10 homologues of the alkene, alkyne, alcohol, and thiol families.

Introduction

It has been demonstrated that Gaussian 3 theory[1] and other similar high level model chemistries such as CBS-QB3[2] or Wn methods[3] have the ability to compute very accurate enthalpies of formation. These workers have demonstrated that inclusion of extensive polarization functions is required to achieve an accuracy within 8 kJ/mol; however, the use of these functions renders the measurement of thermodynamic properties computationally expensive and limits the available molecules for study to those having a limited number of heavy atoms. As an alternate, numerous workers have employed smaller basis sets with fewer polarization functions, choosing to supplement or augment the computation with corrections that negate the deficiency of the method. Whether they are adjustments to the atom enthalpy of formation,[4−6] atomic energy corrections,[5] conversion to formal steric enthalpies,[7] or bond additivity corrections (BAC),[8−12] the effect is the same as the parametrization of the semiempirical methods. In some instances, bond additivity corrections have been applied to computations from high level model chemistries.[13,14] For the chemist who would like an enthalpy of formation not found in the standard databases, the choice appears to be limited to those small molecules that can be accommodated by the high level model chemistries or a less accurate but patched up result from one or more corrections which the nonspecialist may find confusing.

There is one fundamental difference between an experimental energy and one derived by computation. The former is a value that is a composite of the formation energies of all conformers having populations at standard conditions whereas the latter is the energy of one and only one of the conformers (usually the most stable). The effect will depend upon which thermodynamic property is sought. In the case of the enthalpies of formation, the computed enthalpy will be somewhat lower and can be computed according to eq 1; however, this requires computation of all conformers that might be expected to have statistically significant populations at standard conditions. Normally, this effect is quite small.

$$\Delta H^\circ_{\text{tot}} = \sum_i^k \chi_i \, \Delta H^\circ_i \qquad (1)$$

Although the Gibbs energies are available directly from the output (they are next to the enthalpies), it is important to remember that the underlying computation includes the determination of the entropy, and this entropy is also affected by the presence of higher energy conformers. The effect of these multiple conformations will be much larger on the Gibbs energy than on the enthalpy because the equation for calculation includes a term for the entropy of mixing (eq 2). As a result, a Gibbs energy that is computed will be higher than the experimental Gibbs energy, and computation of all conformers will have the effect of lowering the energy.

$$\Delta S^\circ_{\text{tot}} = \sum_i^k \chi_i \, \Delta S^\circ_i - R \sum_i^k \chi_i \ln \chi_i \qquad (2)$$

A considerable amount of work has been done on computational enthalpies that is only partly summarized in our introduction. However, even if one has computed enthalpies for all reasonable conformers of a molecule, it is still not possible to use eq 1 to calculate a composite enthalpy because the mole fractions can only be determined by knowing the Gibbs energies, and these have received scant attention. This problem of multiple conformations is further complicated by the fact that large molecules, those of most interest to organic chemists, are those that have many more conformations needing computation, and where it is already expensive to calculate one of these conformers, it is much more so to calculate all of them.

Recently, we examined computational methodologies for obtaining enthalpies and Gibbs energies of formation. In our first paper, we examined cyclic and acyclic aliphatic alkanes, alkenes, and alkynes having up to 10 carbon atoms.[15] In the case of both properties, we noted that the errors became larger as the length of the chain increased. In the case of the enthalpy, the errors for decane and decene were less than the 4 kJ/mol that was our standard for ideal. The enthalpy computed for 1-decyne was only slightly larger than this, so we let it go.

For the Gibbs energies, the errors approached our limit for ideality beginning with pentane and exceeded it with heptane.

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TABLE 1: Comparison of Straight Chain Enthalpies[a] of Formation Computed Explicitly (Ref 15) and by Increments (Ref 17)

			G3 enthalpy		G3(MP2) enthalpy	
compound	source[b]	experiment	Bond[c]	Redfern et al.	Bond[c]	Redfern et al.
methane	CC	−74.6	−76.0	−75.9	−74.8	−74.7
ethane	CC	−84.0	−85.5	−85.3	−84.4	−84.1
propane	CC	−104.7	−104.7	−106.0	−104.8	−104.9
butane	CC	−125.8	−126.0	−127.2	−124.8	−126.3
pentane	CC	−146.8	−147.2	−148.4	−147.1	−147.4
hexane	CC	−166.9	−168.5	−169.6	−168.3	−168.7
heptane	DH	−187.7	−189.9	−190.9	−189.5	−190.0
octane	WB	−208.4	−211.1	−212.3	−210.7	−211.0
nonane	DH	−228.2	−232.7	−233.6	−232.0	−232.6
decane	WB	−249.7		−254.9	−253.1	−253.9
undecane	WB	−270.3		−276.2	−274.6	−276.1
dodecane	WB	−290.9		−297.6	−295.8	−296.4
tridecane	WB	−311.5		−318.9	−317.1	−317.6
tetradecane	WB	−332.1		−340.2	−338.3	−339.0
pentadecane	WB	−354.8		−361.5	−359.6	−360.2
hexadecane	DH	−374.8		−382.8	−380.9	−381.5
heptadecane	DH	−393.9			−402.2	
octadecane	DH	−414.6			−423.5	
nonadecane	DH	−435.1			−444.7	
eicosane	DH	−455.8			−466.0	

[a] In kJ/mol. [b] CC = ref 20; WB = ref 24; DH = ref 25. [c] Our values for methane through decane are taken from ref 15; those for undecane through eicosane were computed for this work.

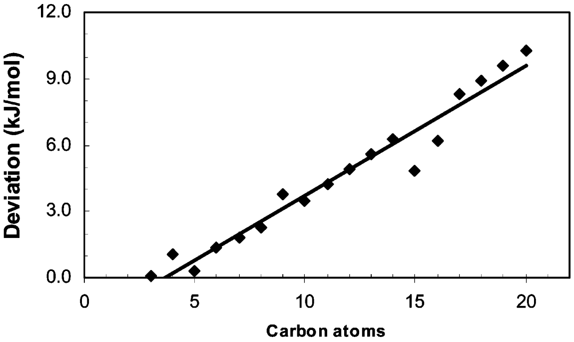

Figure 1. Plot of the deviation between computed and experimental enthalpies of formation vs the number of carbon atoms.

Similar results were noted with the alkenes and alkynes. To compensate, we corrected the computed Gibbs energy by 1.2 kJ/mol per rotatable bond. In those instances where we compared the Gibbs energy derived by explicit computation of all conformers, the agreement with experiment was excellent. In a subsequent work, we extended these methods to common functional derivatives of organic compounds, finding that correction of the Gibbs energies affords values that are comparable to those derived from experiment.[16] In that work, we also noted that the higher homologues of those series of compounds that were examined tended to have enthalpies that deviated from experiment by values in excess of our ideal threshold of 4 kJ/mol.

In this paper, we propose a parallel set of corrections to be applied to enthalpies in order to correct for multiple conformations and back test it to other families of organic compounds. In order to do this, we have extended our previous work to include enthalpies and Gibbs energies of formation for undecane through eicosane. Only two reports of computational determination of the enthalpies of formation of these compounds are found in the literature. Redfern et al. reported gas-phase enthalpies of the straight chain alkanes through hexadecane; however, only methane through octane were explicitly calculated.[17] Higher homologues were estimated using incremental energy values based on pentane through heptane. Liu et al. also examined the first 16 members of the straight chain alkane series of compounds, computing not only the formation energies but also the atomization and Gibbs energies.[18] They used B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) for the calculations[19] and obtained results that are distinctly inferior to those that are reported in ref 17. However, when the data were subjected to a least-squares analysis of a three-parameter equation having one constant and two variables that are a function of the number carbon and hydrogen atoms, the resulting enthalpies had a lower mean average deviation than those reported by Redfern et al.

Methods

We have used the CCCBDB library of computational results for those compounds having one through six carbon atoms.[20] The remainder were computed using the Gaussian 98[21] series of programs which was employed for calculations used in the early stages of this project and Gaussian 03[22] in the latter part. The absolute energies obtained by these calculations were converted into enthalpies or Gibbs energies of formation using isodesmic bond separation methods.[23]

Literature values were obtained primarily from the NIST databases, either the Webbook[24] or the previously mentioned CCCBDB library. We have also used the work by Domalski and Hearing[25] which, although primarily a compendium of group additivity values, nevertheless, has extensive references to experimental data for comparison. To the extent possible, we took both enthalpies and entropies of formation from the same source.

Results and Discussion

At the outset, we determined to test the suitability of the assumption made by Redfern et al. on the additivity of the G3 and G3(MP2) calculations. They determined the incremental quantity between three pairs of compounds: octane/heptane, heptane/hexane, and hexane/pentane according to eq 3 and averaged the results. These increments were then used to compute absolute enthalpies for nonane through hexadecane and, from these, enthalpies of formation.

$$E_{\mathrm{inc}} = E(C_{n+1}H_{2(n+1)+2}) - E(C_nH_{2n+2}) \qquad (3)$$

TABLE 2: G3 or G3(MP2) Enthalpies and Gibbs Energies of Formation[a] for the Straight Chain Alkanes

		enthalpies of formation			Gibbs energies of formation		
compound	source	literature	corrected	uncorrected	literature	corrected	uncorrected
propane	CC	−104.7	−104.7	−104.7	−24.4	−24.6	−24.6
butane	CC	−125.8	−125.4	−126.0	−16.6	−16.3	−15.1
pentane	CC	−146.8	−146.0	−147.2	−8.8	−7.9	−5.5
hexane	CC	−166.9	−166.7	−168.5	0.1	0.3	3.9
heptane	DH	−187.7	−187.5	−189.9	8.3	8.5	13.3
octane	WB	−208.4	−208.1	−211.1	16.6	16.9	22.9
nonane	DH	−228.2	−229.1	−232.7	25.9	24.9	32.1
decane	WB	−249.7	−248.9	−253.1	33.1	34.1	42.5
undecane	WB	−270.3	−269.8	−274.6	41.9	42.1	51.7
dodecane	WB	−290.9	−290.4	−295.8	50.4	50.5	61.3
tridecane	WB	−311.5	−311.1	−317.1	58.8	58.8	70.8
tetradecane	WB	−332.1	−331.7	−338.3	67.2	67.1	80.3
pentadecane	WB	−354.8	−352.4	−359.6	73.7	75.3	89.7
hexadecane	DH	−374.8	−373.1	−380.9	82.7	83.6	99.2
heptadecane	DH	−393.9	−393.8	−402.2	92.6	92.0	108.8
octadecane	DH	−414.6	−414.5	−423.5	101.0	100.5	118.5
nonadecane	DH	−435.1	−435.1	−444.7	109.4	108.8	128.0
eicosane	DH	−455.8	−455.8	−466.0	117.8	117.1	137.5
mean absolute deviation			0.6	4.7		0.5	10.3

[a] In kJ/mol. Propane through nonane are G3 values; decane and above are G3(MP2). [b] CC = ref 20; WB = ref 24; DH = ref 25.

The comparison is shown in Table 1. Those values which Redfern et al. computed by increments tend to be about 0.6−0.8 kJ/mol lower than our results which were explicitly computed. The one exception is undecane where the difference is nearly doubled. Hence, it appears that adding incremental values to the results of high level computations on smaller molecules is a reasonable way of avoiding long calculations.

Using the data in Table 1, we have plotted the difference between our G3(MP2) enthalpies and experiment vs the carbon count in Figure 1. Two points are well off the trend line: those of pentadecane and hexadecane. Examination of the experimental data reveals that the values given for these two compounds do not follow the normal Benson equivalents[26] and hence may be erroneous. We have excluded these two values from the computation of the slope of the line, although the exclusion only changes the value by ∼0.03 kJ/carbon. With these exclusions, the slope of the line is 0.6 ± 0.1 kJ/mol, which is the error per rotatable bond.

We propose that this value of 0.6 kJ/mol per rotatable bond be added to the computed enthalpy to compensate for carbon−carbon bond rotation. By rotatable bond, we mean those bonds whose rotation affords a different conformer. The computed increment per methylene unit is −21.3 kJ/mol. When we add the correction, we obtain a value of −20.7 kJ/mol, which is very close to the Benson methylene group value. In Table 2, we present the G3(MP2) enthalpies and Gibbs energies of formation for the first 20 straight chain alkanes. Those of methane through decane were first reported in ref 15 along with corrections to the Gibbs energies. What is added here are the enthalpy corrections for those first 10 members of the series along with complete data for the next 10.

After correction, both mean absolute deviations are 0.6 kJ/mol, well within experimental error, and confirm that computation errors at this level of theory for the hydrocarbons can be attributed to the presence of additional conformers having significant populations at standard conditions. Table 2 also shows that the Gibbs energy correction of 1.2 kJ/mol per rotatable bond proposed in our initial paper[15] in this series affords excellent results in the longer chain compounds as well.

In our initial work we did not count bonds to quaternary carbon atoms as rotatable because rotation around these bonds generated high-energy conformers having an insignificant population. Similarly, we did not count those bonds between two tertiary atoms that were separated by one or two bonds.[27] Examination of the branched chain alkanes for which we have data suggests that all bonds whose rotation will afford a different conformer should be counted when correcting the enthalpies. In Table 3, we summarize the mean absolute deviations of all branch chain alkanes computed by the two methods.[28]

TABLE 3: Comparison of the Mean Absolute Deviation[a] for Branch Chain Hydrocarbons Calculated by Counting All Rotatable Bonds vs Omission of Bonds to Quaternary and Vicinal Tertiary Atoms

group	no. in sample	all rotatables mean absolute deviation	restricted rotatables mean absolute deviation
monosubstituted alkanes	18	0.8	0.8
disubstituted alkanes	32	1.7	1.9
polysubstituted alkanes	16	2.3	3.1

[a] In kJ/mol.

The mean deviations for the monosubstituted alkanes are the same by either method because the number of rotatable bonds is the same. It is in those compounds having two or more alkyl groups that we find a difference, and it is clear that counting all bonds affords better results. The best improvement is seen with the polysubstituted alkanes although these compounds have more significant errors which were noted in our first paper.

In Table 4, we extend the analysis to straight chain functionalized molecules that were originally examined in our second paper in this series.[16] The enthalpies for the 3−10-carbon straight chain alkenes, alkynes, alcohols, and thiols are corrected for the effects of multiple conformations. For the alkene Gibbs energy corrections, we separated the rotatable bonds into two groups: those adjacent to the π-bond and all others. The former required a correction that was just over double that normally applied to bonds not proximate to a functional group. Examination of the enthalpy increase resulting from explicit calculations of all conformers resulting from rotation adjacent to the double bond as well as the mean absolute deviation of the values in the table suggests that the bond adjacent to the double bond can be ignored in correcting computed enthalpies. The correction computed in Table 4 results from counting only the carbon sp^3−carbon sp^3 bonds whose rotation affords a different conformer.

TABLE 4: Comparison of Corrected vs Uncorrected Enthalpies[a] for Selected Functional Groups

	alkenes			alkynes			alcohols			thiols		
carbon atoms	lit.	cor	uncor	lit.	cor	uncor	lit.	cor	uncor	lit.	cor	uncor
3	19.7	20.7	20.7	185.4	184.1	184.1	−255.2	−254.3	−255.5	−68.6	−69.0	−70.2
4	−0.5	2.1	2.1	165.2	165.3	165.3	−275.3	−274.7	−276.6	−88.1	−89.5	−91.3
5	−21.5	−19.9	−20.5	146.0	144.1	143.5	−295.6	−295.4	−297.9	−110.8	−110.2	−112.7
6	−41.5	−40.6	−41.8	122.3	123.8	122.5	−314.7	−316.1	−319.1	−129.0	−130.9	−133.9
7	−62.7	−61.3	−63.1	103.8	102.9	101.1	−339.7	−336.7	−340.4	−150.0	−151.6	−155.2
8	−82.9	−81.9	−84.4	80.7	82.3	79.9	−355.6	−357.4	−361.6	−170.2	−172.3	−176.5
9	−103.5	−102.6	−105.6	62.3	61.7	58.6	−375.5	−378.0	−382.9	−190.8	−192.9	−197.8
10	−123.3	−123.2	−126.9	41.9	41.0	37.4	−396.6	−398.4	−403.8	−211.5	−213.4	−218.9
mean absolute deviation		1.2	1.5		1.1	2.0		1.5	3.7		1.5	4.7

[a] In kJ/mol.

Even uncorrected, the errors between experiment and computed enthalpy remain less than 2 kJ/mol through 1-octene, partly because the double bond introduces a segment of rigidity which reduces the number of possible conformers.

Correction affords modest improvement For 1-decene, the error is less than the 4 kJ/mol that we have defined as our ideal; however, in all cases, correction affords an improved result. The alkynes have a similar segment of rigidity in the chain, but more dramatic improvement is found in the mean deviations after correction. Decyne has a 4.5 kJ/mol deviation from experiment before correction and less than 1 kJ/mol after. All of the alkynes are within 2 kJ/mol after correction.

More significant improvement is found for the alcohols and thiols. The mean deviation drops by over 2 kJ/mol for the former and more than 3 kJ/mol for the latter. In computing the corrections for these compounds, we have counted all bonds whose rotation results in a new conformer, including the X−H. These were treated separately in computing corrections for the Gibbs energies, the alcohols requiring a value of 2.5 kJ/mol and the thiols just 0.5 kJ/mol; however, for correcting the enthalpies, we find no evidence based upon explicit calculation of all conformers resulting from rotation about the CC−XH bond to treat rotation of this bond any differently than the other carbon−carbon bonds in the molecule. Nevertheless, the errors for the larger members of the series have errors which are larger than in the hydrocarbon series. In one case, 1-heptanol, we noted in our previous paper that there appear to be some issues with the experimental value. Still, there are only two alcohols and one thiol whose corrected computed enthalpy of formation differs from experiment by more than 2 kJ/mol.

Conclusion

Computed enthalpies have two inherent weaknesses: (1) limitation of the basis sets to adequately describe the molecule being computed and (2) the value obtained is only for a single conformer, whereas an experimental sample is a composite of many. The latter causes serious problems in computing Gibbs energies of formation and less significant errors in the enthalpies. Hence, our enthalpies have two corrections. The first is the high level correction which is inherent in the final absolute value for the enthalpy and Gibbs energy obtained by many of the packaged model chemistries such as G3 and G3(MP2) which we have employed in this series of papers and is transparent to the chemist or physicist performing the computation. The second is based upon the number of bonds whose rotation affords a new conformation. We proposed a series of corrections in earlier papers for the Gibbs energies noting that problems with enthalpy values arise only when the molecules become quite large. The alkane hydrocarbon enthalpies of formation for undecane through eicosane presented in this paper differed from experiment by more than our 4 kJ/mol ideal standard, and we have used these values to develop a series of corrections to compensate for these multiple conformers. The corrections proposed by other workers in the field and which we have cited in our introduction were often an attempt to provide additional compensation for basis set deficiencies beyond those of the higher level corrections but may have inadvertently also compensated for multiple conformations.

Incorporation of the 0.6 kJ/mol/CC bond brings the computed enthalpy of these compounds within 2 kJ/mol in most cases. The combination of the correction value with the computational methylene increment of 21.3 kJ/mol affords a result that is nearly identical to the Benson methylene equivalent. Application of these values across several other families of organic compounds also makes substantial improvements, bringing the results within our ideal standard of 4 and often 2 kJ/mol. They are simpler to apply than the corrections for the Gibbs energies in that there is just the single value.

We have also extended our Gibbs energy corrections to the C_{11} through C_{20} alkanes and demonstrate that these provide agreement with the literature that is within 1 kJ/mol in all cases except two. These two are pentadecane and hexadecane, for which we have noted possible problems with the literature values.

Finally, we have refuted the conventional wisdom that high level computation of thermodynamic properties is limited to small molecules. It is true that we needed to employ computers with 64-bit processors for the last four members of the alkane series, but until this time no G3(MP2) computation on 20 heavy atoms has been reported.

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Supporting Information Available: Full citations for refs 21 and 22, standard state element entropies, experimental and computed energies of inorganic substances used in the computation of the formation energies and Cartesian coordinates for all compounds reported here and not available from ref 2; G3 and G3(MP2) absolute energies for all organic substances computed for this paper. This information may be obtained free of charge via the Internet at http://pubs.acs.org.

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

(28) The full list of compounds, experimental data, and corrected enthalpies are shown in Table S1 of the Supporting Information.