Assessment of Gaussian-3 and Density Functional Theories for Enthalpies of Formation of C_1-C_{16} Alkanes[†]

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We have examined the performance of Gaussian-3 (G3) theory and six related methods for the calculation of enthalpies of formation of *n*-alkanes of up to 16 carbons and isoalkanes of up to 10 carbons. We have also examined the accuracy of the B3LYP density functional theory for the *n*-alkanes. The G3 enthalpies of formation of the *n*-alkanes have errors of less than 2 kcal/mol compared to experiment. There is a small accumulation of error (0.04 kcal/mol per bond) that increases the deviation with chain length. The effects of conformational averaging on the G3 enthalpies of the *n*-alkanes are estimated to be small, but are in the direction to reduce the error. The branched alkanes have errors of less than 1 kcal/mol. Four of the variations of G3 theory [G3(MP3), G3(MP2), G3(MP2)//B3LYP, and G3(MP2,CCSD)//B3LYP] also have errors similar to or smaller than G3 theory while two of the variations [G3(CCSD) and G3(MP2,CCSD)] have maximum errors for the *n*-alkanes of about 2.5 kcal/mol. The B3LYP method does very poorly for the calculation of enthalpies of formation of the larger *n*-alkanes with an error of over 30 kcal/mol for hexadecane. This suggests that B3LYP has a significant problem with accumulation of errors as the molecular size increases. Several schemes for correcting systematic errors in B3LYP calculations for large molecules are also explored.

1. Introduction

Fossil fuels, which are mixtures of hydrocarbons, will continue to be a principal source of energy worldwide for years to come. A complete understanding of alkane combustion reactions is of enormous practical importance in reducing emissions and improving efficiency of internal combustion engines. The combustion of a fossil fuel involves many chemical species and chemical reactions. For example, gasoline used in motor fuel is a complex mixture of hundreds of different hydrocarbons, most being saturated and containing 4−12 carbon atoms per molecule.[1] Diesel fuels are made up of hydrocarbons containing up to about 18 carbons. Many of the important chemical species involved in these reactions are short-lived and cannot be studied in the laboratory. Quantum chemical methods can potentially be used to calculate the important thermochemical properties and reaction rates of gasoline and diesel fuel chemistry, but it is necessary to assess the reliability of the different methods.

There are numerous quantum chemical approaches for making thermochemical predictions. Some of these methods are very accurate,[2,3] but with present computational capabilities they can only be applied to relatively small molecules. The Gaussian-*n* (G*n*)[4,5] and CBS[6,7] methods, which use moderate-sized basis sets and molecule-independent empirical parameters, can be applied to large molecules. However, these methods (e.g., G2 theory, G3 theory, CBS-QB3) are "parametrized" using a test set of relatively small molecules. Actual combustion reactions in fossil fuel burning engines may involve large alkanes containing up to 20 or more carbons, so it is important to determine how various theoretical methods fare on these larger molecules. This is also true for the widely used B3LYP[8,9] density functional theory that was parametrized using a set of small molecules.

In this paper we assess G3 theory and six variations of G3 theory [G3(MP3), G3(MP2), G3(CCSD), G3(MP2,CCSD), G3(MP2)//B3LYP, and G3(MP2,CCSD)//B3LYP] for the calculation of enthalpies of formation of large alkanes such as are involved in combustion reactions. We have assessed these methods on *n*- and isoalkanes (C_nH_{2n+2}) of up to 16 carbons that have accurate experimental data. In addition, the B3LYP density functional method is assessed on these species. The methods are described in section 2. Results are given in section 3 and conclusions are drawn in section 4.

2. Theoretical Methods

Gaussian-3 (G3) theory[5] is a procedure for calculating energies of molecules in the spirit of G2 theory,[4] but is more accurate. G3 theory uses geometries from second-order perturbation theory [MP2/6-31G(d)] and scaled zero-point energies from Hartree−Fock theory [HF/6-31G(d)] followed by a series of single-point energy calculations including electron correlation effects. In addition, corrections for spin−orbit effects and core-correlation are included. Details are given in ref 5. G3 theory was assessed on a total of 299 energies (enthalpies of formation, ionization energies, electron affinities, and proton affinities) from the G2/97 test set.[10,11] The average absolute deviation from experiment of G3 theory for the 299 energies is 1.01 kcal/mol compared to 1.59 kcal/mol for G2 theory.

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TABLE 1: Deviations of Theory from Experimental Enthalpies of Formation (in kcal/mol) of Straight-Chain Alkanes[a]

	$\Delta H_f°(298)$		deviation, kcal/mol							
atomic species	expt[b]	G3	G3	G3 (MP3)	G3 (MP2)	G3 (CCSD)	G3(MP2, CCSD)	G3(MP2, CCSD), est.	G3(MP2)// B3LYP	G3(MP2,CCSD)// B3LYP
CH_4 (methane)	−17.90 ± 0.1	−18.15	0.25[c]	0.47	−0.05	0.31	0.02		−0.30	−0.29
C_2H_6 (ethane)	−20.08 ± 0.04	−20.39	0.31[c]	0.57	0.03	0.42	0.15		−0.23	−0.18
C_3H_8 (propane)	−25.00 ± 0.1	−25.33	0.33[c]	0.58	0.08	0.48	0.26		−0.19	−0.13
C_4H_{10} (butane)	−30.00 ± 0.2	−30.40	0.40[c]	0.63	0.18	0.60	0.40		−0.11	−0.03
C_5H_{12} (pentane)	−35.11 ± 0.2	−35.46	0.35[d]	0.54	0.12	0.59	0.40		−0.20	−0.11
C_6H_{14} (hexane)	−39.94 ± 0.2	−40.54	0.60[d]	0.75	0.37	0.88	0.70		0.04	0.15
C_7H_{16} (heptane)	−44.86 ± 0.3	−45.63	0.77[d]	0.89	0.54	1.10	0.91		0.15	0.27
C_8H_{18} (octane)	−49.86 ± 0.3	−50.74	0.88[d]	0.96	0.63	1.25	1.06		0.24	0.38
C_9H_{20} (nonane)	−54.54 ± 0.2	(−55.83)	(1.29)	(1.33)	1.05	(1.71)	1.53	(1.51)	(0.63)	(0.78)
$C_{10}H_{22}$ (decane)	−59.63 ± 0.3	(−60.93)	(1.30)	(1.30)	1.06	(1.75)	1.59	(1.56)	(0.60)	(0.77)
$C_{11}H_{24}$ (undecane)	−64.75 ± 0.6	(−66.02)	(1.27)	(1.23)	(1.00)	(1.77)	1.62	(1.57)	(0.55)	(0.73)
$C_{12}H_{26}$ (dodecane)	−69.24 ± 0.5	(−71.12)	(1.88)	(1.80)	(1.59)	(2.42)	2.28	(2.22)	(1.12)	(1.32)
$C_{13}H_{28}$ (tridecane)	−74.45 ± 0.4	(−76.21)	(1.76)	(1.64)	(1.47)	(2.34)	2.23	(2.14)	(0.98)	(1.19)
$C_{14}H_{30}$ (tetradecane)	−79.38 ± 0.4	(−81.31)	(1.93)	(1.77)	(1.63)	(2.55)	2.45	(2.35)	(1.11)	(1.34)
$C_{15}H_{32}$ (pentadecane)	−84.81 ± 0.5	(−86.40)	(1.59)	(1.39)	(1.28)	(2.26)	(2.06)	(2.06)	(0.75)	(0.99)
$C_{16}H_{34}$ (hexadecane)	−89.58 ± 0.5	(−91.49)	(1.91)	(1.68)	(1.60)	(2.62)	(2.42)	(2.42)	(1.04)	(1.30)

[a] Values in parentheses are estimated from smaller alkanes (average of hexane, heptane, and octane) in the series as described in the text. [b] Reference 23. [c] Reference 5. [d] Reference 28.

Six variations of G3 theory are also assessed in this study. G3(MP2) theory[12] is a modification of G3 theory, similar in spirit to G2(MP2) and G2(MP2,SVP) theories,[13,14] that eliminates the fourth-order perturbation calculations and has an average absolute deviation of 1.30 kcal/mol for the 299 energies. G3(MP3) theory[15] is a modification of G3 theory that replaces the fourth-order perturbation calculations by third-order perturbation calculations and has an average absolute deviation of 1.22 kcal/mol for the 299 energies. The G3(MP2) and G3(MP3) methods take less computational time than G3 theory. Two G3 methods, G3(CCSD)[16] and G3(MP2,CCSD),[16] that are based on coupled cluster energies [CCSD(T)] instead of quadratic configuration interaction energies [QCISD(T)] are also assessed in this study. Finally, two G3 methods, G3(MP2)//B3LYP[17] and G3(MP2,CCSD)//B3LYP,[16] that are based on B3LYP/6-31G(d) geometries and zero-point energies, are assessed. The B3LYP density functional[8,9] calculations reported in this paper use the 6-311+G(3df,2p) basis set. Two sets of geometries, MP2/6-31G(d) and B3LYP/6-31G(d), were used in the assessment of the B3LYP functional.

The enthalpies of formation at 298 K were calculated using the procedure outlined in ref 10. The calculations in this paper were done with the Gaussian94[18] and NWCHEM[19] computer programs.

For very large molecules, e.g., hexadecane, it is difficult to calculate the G3 energy directly because of the large amount of computational time required, but the G3 energies can be estimated based on energy differences between smaller molecules in the series. We have used an estimation procedure for those systems for which the calculation is difficult computationally. In the series of *n*-alkanes, *n*-pentane is the first molecule with a true interior carbon. Thus, the energy difference between *n*-pentane and *n*-hexane can be used to estimate the energy of *n*-heptane by adding this difference to the energy of *n*-hexane.

$$E(n\text{-heptane}) = E(n\text{-hexane}) + [E(n\text{-hexane}) - E(n\text{-pentane})] \quad (1)$$

Multiples of this energy difference can be added to the energy of *n*-hexane in order to estimate the energies of larger molecules in the series. In order to reduce any error from taking the energy difference between any one pair, we have used an average of three pairs (pentane/hexane, hexane/heptane, and heptane/octane). The energy that is used in (1) can be the total energy or an enthalpy. We have found little dependence on which quantity is used and have used the enthalpies at 298 K to make the estimation. A similar procedure is also used for isoalkanes.

We also use an isodesmic scheme based on a combination of theoretical and experimental data to determine the enthalpies of formation of the hydrocarbons. This approach eliminates systematic errors in the methods and improves the results. We have used the isodesmic bond separation scheme[20] that has all formal bonds between non-hydrogen atoms of the subject molecule separated into the simplest parent molecules containing these same linkages. The bond separation reaction energy is then evaluated at a certain level of theory and combined with the experimental enthalpies of formation for the reference molecules in the reaction to derive an enthalpy of formation for the molecule in question. Such a scheme has been used recently by Raghavachari et al.[21] for the related G2 method to get substantial improvement in the calculated results. The set of reference molecules (CH_4, C_2H_6) used in this study is taken from the set of Raghavachari et al. Finally, for the B3LYP method where the errors with the isodesmic bond separation scheme are still large, we also use a homodesmotic scheme[22] for calculating improved heats of formation.

3. Results and Discussion

a. G3 Theory and Modified G3 Theories. The G3 enthalpies of formation calculated for the *n*-alkanes C_nH_{2n+2}, $n = 1-16$, and the deviations from experiment are given in Table 1. The experimental values used to compare with theory are taken from the compilation of Pedley et al.[23] and have quoted uncertainties of less than 0.6 kcal/mol. Table 1 also includes the deviations of the six modified G3 theories from the experimental enthalpies of formation for the *n*-alkane series. The deviations for G3 and some of the methods are plotted in Figure 1 as a function of hydrocarbon size. The results in Table 1 include estimated values for the enthalpies derived as discussed in section 2. Estimated and calculated errors in the G3(MP2,CCSD) enthalpies are given in Table 1 for $n = 9$ to $n = 14$. The results indicate that the estimated values differ by less than 0.1 kcal/mol from the actual calculated values.

The deviations in the G3 enthalpies range from 0.25 to 1.93 kcal/mol with the deviation increasing with chain length. The other G3 methods have similar ranges of errors, but with different maximum deviations as shown in Figure 1. The

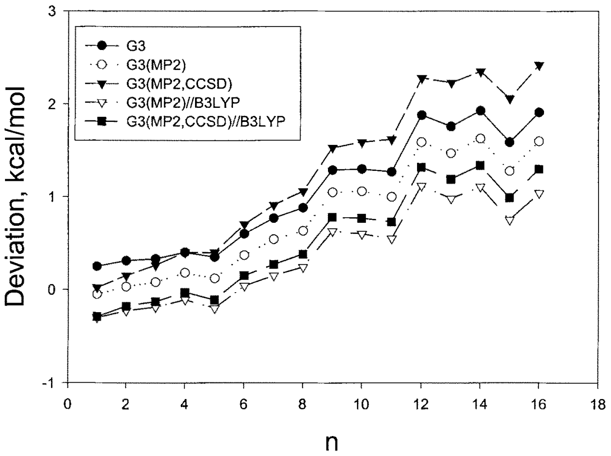

Figure 1. Deviations from experiment in calculated enthalpies of formation for *n*-alkanes.

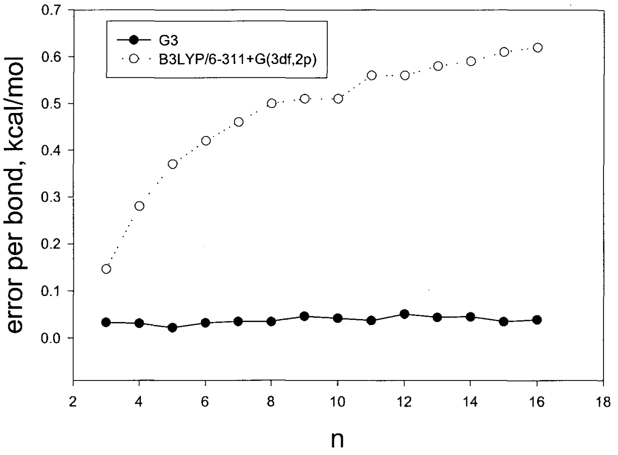

Figure 2. Error per bond in calculated enthalpies of formation for *n*-alkanes.

smallest maximum deviations occur for the B3LYP-based methods: G3(MP2)//B3LYP (1.04 kcal/mol) and G3(MP2, CCSD)//B3LYP (1.30 kcal/mol). The largest occur for the CCSD(T)-based methods with MP2 geometries, G3(CCSD) (2.62 kca/mol) and G3(CCSD,MP2) (2.42 kcal/mol). The reason for the larger errors with the CCSD(T)-based methods is not clear.

The average error per bond is very small and stays remarkably constant for the whole series of alkanes. This is illustrated by a plot of error per bond as a function of alkane chain length in Figure 2. The G3 error per bond is 0.035 kcal/mol in propane and 0.039 kcal/mol in hexadecane. Hence, the higher level correction (HLC) in G3 theory accounts for much of the systematic deficiencies in the method such as neglect of scalar relativistic effects and low-frequency torsional modes. Scalar relativistic effects are large, but very systematic.[24] For example, for the enthalpy of formation of hexadecane this effect is estimated to be about 3.6 kcal/mol on the basis of calculations of the relativistic effect on the enthalpy of formation of methane, butane and propane.[24]

TABLE 2: Deviations from Experimental Enthalpies of Formation of Straight-Chain Alkanes Using the Isodesmic Scheme[a]

	deviation, kcal/mol			
species	G3	G3(MP2)	G3(CCSD)	G3(MP2, CCSD)
C_3H_8 (propane)	−0.03	−0.02	−0.04	−0.03
C_4H_{10} (butane)	−0.01	−0.01	−0.03	−0.02
C_5H_{12} (pentane)	−0.12	−0.14	−0.14	−0.16
C_6H_{14} (hexane)	0.08	0.03	0.05	0.00
C_7H_{16} (heptane)	0.20	0.12	0.17	0.08
C_8H_{18} (octane)	0.26	0.14	0.21	0.09
C_9H_{20} (nonane)	(0.62)	0.47	(0.56)	0.42
$C_{10}H_{22}$ (decane)	(0.57)	0.41	(0.51)	0.35
$C_{11}H_{24}$ (undecane)	(0.49)	(0.26)	(0.42)	0.24
$C_{12}H_{26}$ (dodecane)	(1.04)	(0.78)	(0.96)	0.77
$C_{13}H_{28}$ (tridecane)	(0.87)	(0.58)	(0.79)	0.58
$C_{14}H_{30}$ (tetradecane)	(0.99)	(0.66)	(0.89)	0.66
$C_{15}H_{32}$ (pentadecane)	(0.60)	(0.23)	(0.49)	(0.13)
$C_{16}H_{34}$ (hexadecane)	(0.87)	(0.47)	(0.76)	(0.36)

[a] Values in parentheses are estimated from smaller alkanes in the series (see text).

Another source of error in the calculations is the increasing number of gauche conformers that become available with increasing chain length. As a result the experimental enthalpies of formation will reflect a Boltzmann distribution of conformers that will make the enthalpies of formation more positive than if there is only the trans conformation present. A correction for the theoretical enthalpy of formation can be estimated from the conformational energy differences based on Boltzmann averaging. There have been several theoretical studies,[25−27] of the energy differences for the conformers of *n*-butane, *n*-pentane, and *n*-hexane. We have calculated the G3(MP2) energies of all of the low-energy conformers of butane and pentane. The gauche (g) conformer of butane is 0.64 kcal/mol above the trans (t) conformer at 298 K. The gt, g+g+, and g−g+ conformers of pentane are 0.57, 0.92, and 2.33 kcal/mol less stable than the tt conformer of pentane. We estimated energy corrections to the G3 enthalpies of formation using ensemble averages over Boltzmann distributions. The corrections for *n*-butane and *n*-pentane are 0.26 and 0.46 kcal/mol, respectively. In both cases the correction is in the right direction to improve agreement with experiment. The g+g+g+ conformer of hexane is only 1.18 kcal/mol higher in energy than the ttt conformer due to a cooperative effect noted by Frey et al.[26] Because of the many conformers that are possible for the longer chains, it would be difficult to calculate the energy correction for them. However, a rough estimate based on conformer energies of *n*-butane, *n*-pentane, and *n*-hexane indicates that the conformer distribution correction for *n*-hexadecane would be about 1 kcal/mol. Conformational averaging is a small effect, but tends to correct the error toward too negative enthalpies in all of the G3 methods and is not taken into account by the higher level correction. A more detailed theoretical study is needed to assess this effect in the longer chains quantitatively.

The application of the isodesmic bond separation scheme to the alkyl series further eliminates systematic errors in the G3 methods that are not corrected by the HLC. The resulting enthalpies of formation for several of the G3 methods are listed in Table 2. The maximum deviations are reduced by a about a factor of 2. For example the maximum deviation in the G3 enthalpy for the series is reduced from 1.93 kcal/mol to 1.04 kcal/mol, while the maximum error of G3(MP2) is reduced from 1.60 to 0.78 kcal/mol. This reduction in error is similar to what has been found in other investigations using this isodesmic scheme.[21] The magnitude and direction of the errors in the isodesmic enthalpies in Table 2 are such that the conformational averaging corrections noted above will improve agreement with experiment. The remaining error of 0.87 kcal/mol in the G3 isodesmic enthalpy of hexadecane is nearly the same as the estimated conformational averaging correction of about 1 kcal/mol.

Table 3 gives the deviations of various G3 theories from experimental enthalpies of formation for the isoalkane series. Comparing molecules from butane to decane, the isoalkane

TABLE 3: Deviations from Experimental Enthalpies of Formation of Branched Alkanes[a]

		deviation, kcal/mol					
species	$\Delta H_f°(298)$ expt[b]	G3	G3(MP3)	G3(MP2)	G3(CCSD)	G3(MP2,CCSD)	G3(MP2,CCSD), est
C_4H_{10} (isobutane)	−32.07 ± 0.2	0.25	0.41	0.03	0.44	0.26	
C_5H_{12} (isopentane)	−36.74 ± 0.2	0.13	0.23	−0.06	0.37	0.21	
C_6H_{14} (isohexane)	−41.78 ± 0.2	0.19	0.24	−0.02	0.47	0.31	
C_7H_{16} (isoheptane)	−46.51 ± 0.2	(0.55)	(0.56)	0.38	(0.87)	0.75	(0.71)
C_8H_{18} (2−methylheptane)	−51.48 ± 0.4	(0.68)	(0.65)	0.51	(1.04)	0.93	(0.88)
$C_{10}H_{22}$ (isodecane)	−62.12 ± 0.6	(0.23)	(0.11)	(−0.01)	(0.67)	0.59	(0.50)

[a] Values in parentheses are estimated from smaller alkanes (isopentane, isohexane) in the series (see text). [b] Reference 23.

TABLE 4: Deviations from Experimental Enthalpies of Formation of Straight-Chain Alkanes Using the B3LYP Methods[a]

	$\Delta H_f°(298$ K)		deviations, kcal/mol			
species	expt	B3LYP	B3LYP	B3LYP//B3LYP[b]	B3LYP (isodesmic)	B3LYP (homodesmotic)
CH_4 (methane)	−17.90	−19.52	1.62	1.11		
C_2H_6 (ethane)	−20.08	−20.68	0.60	−0.06		
C_3H_8 (propane)	−25.00	−23.54	−1.46	−2.24	−1.04	
C_4H_{10} (butane)	−30.00	−26.31	−3.69	−4.62	−2.25	−0.17
C_5H_{12} (pentane)	−35.11	−29.12	−5.99	−7.09	−3.54	−0.41
C_6H_{14} (hexane)	−39.94	−31.86	−8.07	−9.31	−4.60	−0.43
C_7H_{16} (heptane)	−44.86	−34.61	−10.25	−11.66	−5.76	−0.55
C_8H_{18} (octane)	−49.86	−37.36	−12.50	−14.04	−6.99	−0.74
C_9H_{20} (nonane)	−54.54	−40.10	−14.44	−16.20	−7.92	−0.62
$C_{10}H_{22}$ (decane)	−59.63	−42.85	−16.78	−18.65	−9.24	−0.90
$C_{11}H_{24}$ (undecane)	−64.75	−45.59	−19.16	−21.23	−10.60	−1.22
$C_{12}H_{26}$ (dodecane)	−69.24	−48.34	−20.90	−23.09	−11.31	−0.90
$C_{13}H_{28}$ (tridecane)	−74.45	−51.09	−23.36	−25.76	−12.76	−1.30
$C_{14}H_{30}$ (tetradecane)	−79.38	−53.83	−25.55	−28.03	−13.93	−1.43
$C_{15}H_{32}$ (pentadecane)	−84.81	−56.57	−28.24	−30.95	−15.60	−2.06
$C_{16}H_{34}$ (hexadecane)	−89.58	−59.32	−30.26	−33.05	−16.60	−2.02

[a] B3LYP/6-311+G(3df,2p) at MP2/6-31G* geometries and using HF/6-31G* zero-point energies with 0.8929 scale factor unless noted. These are the same geometries and zero-point energies that are used in G3 theory. [b] B3LYP/6-311+G(3df,2p) at B3LYP/6-31G* geometries and using B3LYP/6-31G* zero-point energies with a scale factor of 0.96. (Note that use of a scale factor of 0.98 increases the deviations from experiment. For example, for hexadecane it is −39.03 kcal/mol.)

series exhibits a smaller range of deviations than the *n*-alkane series and also smaller maximum deviations. The deviations for G3 theory range from 0.13 kcal/mol for isopentane to 0.68 kcal/mol for 2-methylheptane. Isodecane has a deviation of only 0.23 kcal/mol with G3 theory. The G3(MP2,CCSD) method has a maximum deviation of 0.93 kcal/mol for this series and only 0.59 kcal/mol for isodecane, significantly less than for *n*-hexane (1.59 kcal/mol).

b. Density Functional Methods. Table 4 shows the deviations of the B3LYP/6-311+G(3df,2p) results from experimental enthalpies of formation for the *n*-alkane series. There is increasing error in the B3LYP results with increasing chain length. The maximum deviation from experiment is −30.26 kcal/mol for hexadecane. This is due to an accumulation of error in the B3LYP enthalpies of formation. The results in Table 4 indicate that each CH_2 group decreases the experimental enthalpy of formation by about 5 kcal/mol compared to about 3 kcal/mol from B3LYP. Thus, the error per added CH_2 group is about 2 kcal/mol, or about 0.67 kcal/mol per bond since addition of a CH_2 group adds three bonds. The error per bond (or electron pair) for the $n = 1$ to $n = 16$ alkanes from the deviations in Table 4 is plotted in Figure 2 and increases from 0.15 kcal/mol in propane to 0.62 kcal/mol in hexadecane, approaching a limit at the longer alkanes. From extrapolation to longer alkanes this limit is about 0.67 kcal/mol, the same value that is obtained from the CH_2 group energy differences. In contrast, the error per bond remains constant at about 0.04 kcal/mol for G3 theory as shown in Figure 2.

If a higher level correction per electron pair (optimized to give minimal deviation with experiment for this series) is added to the B3LYP energies for the C_nH_{2n+2} series, the maximum deviation is reduced significantly to 4.78 kcal/mol. Although addition of a higher level correction to B3LYP improves the calculated values for this series, it does not work for B3LYP over a broad range of molecules. We have found little improvement in the mean absolute deviation when a higher level correction is added to B3LYP for the G2/97 test set.[28]

Table 4 also lists the errors in the calculated heats of formation for the B3LYP method using the isodesmic bond separation scheme. As seen previously by Raghavachari et al.,[29] there is significant improvement in the B3LYP results. However, the factor of 2 improvement still leaves a maximum deviation of −16.6 kcal/mol. The results in Table 4, however, show that the increase in error is still systematic and roughly linear with system size. In order to induce further cancellation of systematic errors, we have now investigated a homodesmotic[22] scheme for calculating the heats of formation of *n*-alkanes. We use the homodesmotic reactions $C_nH_{2n+2} + (n - 3)C_2H_6 = (n - 2)$-$C_3H_8$. In addition to being isodesmic, this homodesmotic reaction has equal numbers of CH_2 and CH_3 groups in the reactants and the products. The experimental heats of formation of the reference molecules C_2H_6 and C_3H_8 are used along with the homodesmotic reaction energy to derive the heats of formation of the larger *n*-alkanes. The results are listed in the last column of Table 4. There is a dramatic improvement with the maximum error falling to a reasonable value of −2.1 kcal/mol. Similar schemes may be useful for improving the accuracy of B3LYP results for other large molecules.

4. Conclusions

In this paper we have examined Gaussian-3 theory and six variations for the calculation of enthalpies of formation of *n*-alkanes of up to 16 carbons and isoalkanes of up to 10 carbons. We have also examined the accuracy of the density functional theory B3LYP for the *n*-alkanes. The following conclusions can be drawn:

1. The G3 enthalpies of formation of the *n*-alkanes deviate with experiment by less than 2 kcal/mol. There is evidence of a small accumulation of error (about 0.04 kcal/mol per bond) that increases the deviation with chain length. The effects of conformational averaging on the G3 enthalpies of the *n*-alkanes are estimated to be small, but are in the direction to reduce the error. The branched alkanes have errors of less than 1 kcal/mol.

2. Four of the variations of G3 theory [G3(MP3), G3(MP2), G3(MP2)//B3LYP, and G3(MP2,CCSD)//B3LYP] also have deviations similar to or smaller than G3 theory. Two of the variations [G3(CCSD) and G3(MP2,CCSD)] have maximum deviations for the *n*-alkanes of about 2.5 kcal/mol.

3. The B3LYP method does very poorly for the calculation of enthalpies of formation of the larger *n*-alkanes. While the B3LYP enthalpy of formation for propane deviates from experiment by only −1.46 kcal/mol, the deviation for hexadecane is −30.3 kcal/mol. This suggests that B3LYP has a significant problem with accumulation of errors in large molecules. Several schemes for correcting systematic errors improve the B3LYP calculations for large molecules.

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