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Comparison of G3 and G4 Theories for Radical Addition and Abstraction Reactions

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A test set of 21 radical addition and 28 hydrogen abstraction reactions has been studied at the W1, G4, G3X, G3X(MP2), and G3X(MP2)-RAD levels of theory with a view to establishing whether the recently introduced G4 theory offers improved performance over the G3 methods. All methods tested approximated the benchmark W1 values to within a mean absolute deviation (MAD) of 4 kJ mol⁻¹ or less, although maximum absolute deviations for problematic reactions (such as radical addition to thiocarbonyl compounds) can be as much as 10 kJ mol⁻¹ for the G3 methods. The new noncanceling higher-level correction (HLC) term in G4 was found to be capable of mitigating these errors in radical addition, but it introduced a systematic error to the reaction energies of the abstraction reactions, and its format may therefore require re-examination. G3 methods were shown to offer “chemical accuracy” even for these problematic cases, provided they were corrected to the W1 level of theory via an ONIOM-based approach.

Introduction

The Gaussian-*n* (*Gn*; *n* = 1, 2, 3, 4)¹ methods were introduced by Curtiss, Pople, and co-workers as a cost-effective strategy to obtain chemically accurate thermochemical calculations. Their basic principle is to approximate coupled cluster single–double excitation (with triples) [CCSD(T)] or quadratic configuration interaction single–double excitation (with triples) [QCISD(T)] calculations with a large basis set using a series of additivity corrections, carried out by use of Møller–Plesset perturbation theory. The methods also include spin orbit corrections for atoms and an empirical higher-level correction (HLC) term. A number of variants of these methods exist, according to the exact nature of basis set correction, the level of theory used for the geometry optimizations and frequency calculations, and whether CCSD(T) or QCISD(T) is used as the highest level of theory. A series of “RAD” variants of the *Gn* methods also exist in which open-shell species are treated with restricted open-shell rather than unrestricted wave functions.²

In G3 theory, the HLC term is given by either eq 1 or eq 2 depending on whether the species is a molecule or an atom:

$$\text{HLC (molecules)} = -An_{\beta} - B(n_{\alpha} - n_{\beta}) \quad (1)$$

$$\text{HLC (atoms)} = -Cn_{\beta} - D(n_{\alpha} - n_{\beta}) \quad (2)$$

In these equations, *n*_α and *n*_β are the numbers of α and β valence electrons respectively, and the parameters *A*, *B*, *C*, and *D* are obtained by fitting to a large test of experimental data. It is important to note that since it only depends on the number of α and β valence electrons, the HLC cancels entirely from most reaction energies, except when the reactions involve a mixture of atoms and molecules (as in heats of formation and bond dissociation energies) and/or when spin is not conserved. In other words, for most types of chemical reaction, the G3 family of methods contains no empirical correction terms and can thus be viewed as truly ab initio in nature.

Recently, G4 theory was introduced as a successor to G3.^{1f} Among other improvements, G4 includes a revised HLC in which the open- and closed-shell molecules are now treated separately. Thus, for closed-shell molecules, the HLC is calculated via eq 3, while for open-shell molecules, eq 4 is used:

$$\text{HLC (closed-shell molecules)} = -An_{\beta} \quad (3)$$

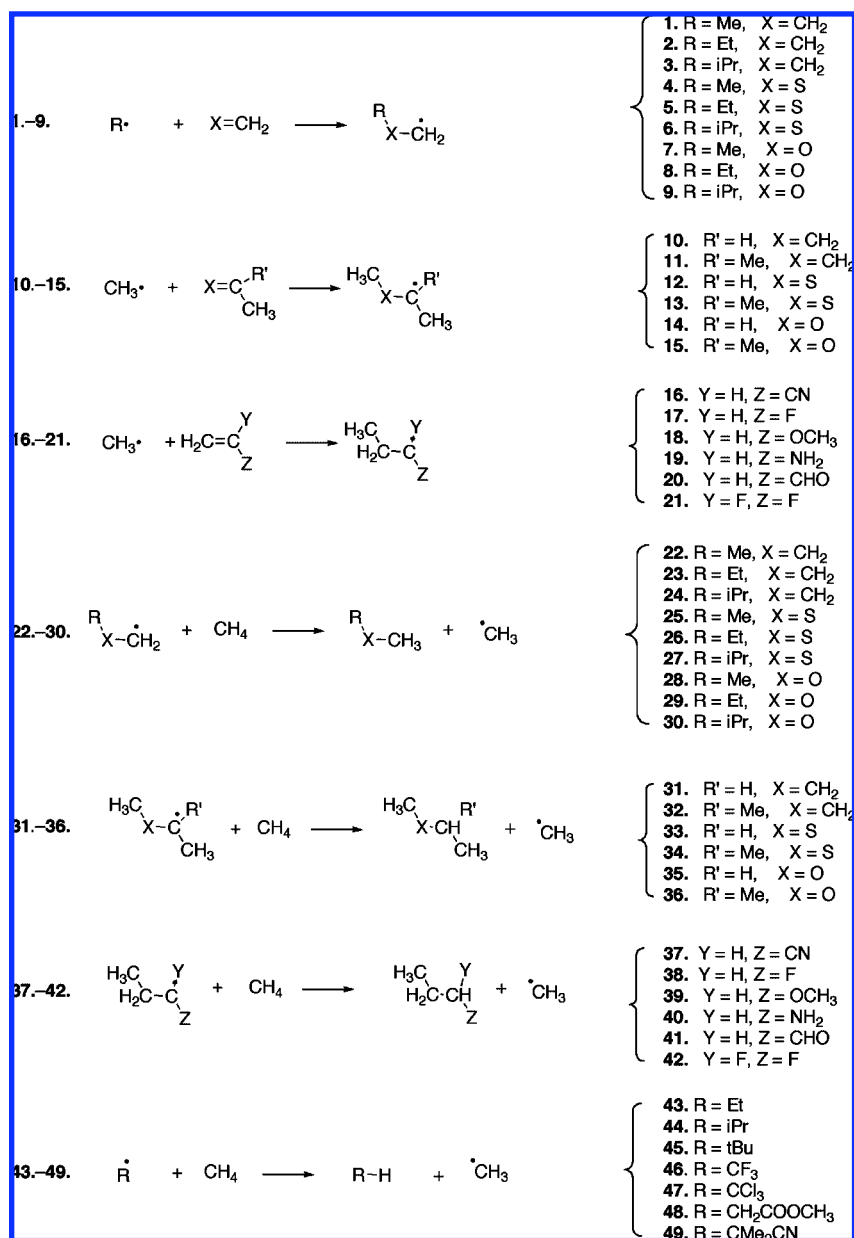
$$\text{HLC (open-shell molecules)} = -A'n_{\beta} - B(n_{\alpha} - n_{\beta}) \quad (4)$$

As in G3 theory, *A*, *B*, and *A'* are empirical parameters, obtained by fitting to a large test set of gas-phase experimental thermochemical data. Importantly, because the values of *A* and *A'* are not equal, this term no longer cancels from reaction energies for radical reactions (such as addition and transfer) in which the number of electrons on the radical and nonradical species change. Indeed, in such cases, the HLC can potentially make a significant contribution to the reaction energies (>2 kcal for reactions such as CH₃CH₂• + CH₂=CHCOOCH₃).

G3 methods, which have been widely adopted for thermochemical calculations, have been shown to deliver “chemical accuracy” (ca. 1 kcal mol⁻¹) in testing against a large test set of gas-phase experimental heats of formation, electron affinities, ionization energies, and proton affinities.^{1,2} While this excellent performance is in part due to the fitted HLC term, good performance has also been observed in reaction energies where this term cancels entirely. Thus, for example, methods from the G3 family have been generally found to reproduce the energies of radical reactions such as addition and transfer to within kilocalorie accuracy, when assessed against experiment and/or higher levels of theory such as W1.³ Nonetheless, there are some systems for which deviations between G3 methods and experiment are larger than 2 kcal mol⁻¹; among which are included methyl radical addition to C=S bonds⁴ and the stabilization energies of certain radicals.⁵ It is of interest to examine whether G4 theory (and in particular its new noncanceling HLC term) can offer improved performance in these problematic cases.

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SCHEME 1: Test Set of Reactions Studied



In the present work we compare the performance of G4 against the equivalent G3 method (G3X) for a series of radical addition and transfer reactions (see Scheme 1), with a view to establishing whether the noncanceling empirical correction term in G4 leads to improved performance. We also examine whether the other changes between G3X and G4 theory have a significant effect on reaction energies. In particular, G4 introduces an extrapolation to the infinite basis set limit, carried out at the Hartree–Fock (HF) level. This can increase the computational cost of the calculations by more than 50% and it is of interest to examine whether this additional cost is justifiable. Curtiss et al.^{1f} have shown that infinite basis set extrapolation greatly improves the accuracy of G4 (compared with the equivalent G3 theory) when calculating the heats of formation of the subset of “nonhydrogen” species in the G3/05 test set, a subset that is heavily laden with pseudohypervalent second-row species for which HF basis set convergence is known to be slow. However, the improvements in accuracy for the rest of the heats of formation in the G3/05 test set were found to be more modest. Moreover, in chemical reactions where more bonds are con-

served, one might expect the basis set convergence errors to be further reduced by systematic error cancellation, and the HF extrapolation term to become unnecessary. As part of this work, we also examine the performance of the lower-cost variants of G3 theory, G3X(MP2) and G3X(MP2)-RAD, in order to determine whether these methods are sufficiently accurate.

Theoretical Procedures

Standard ab initio molecular orbital theory and density functional theory calculations were carried out with GAUSSIAN 03.⁶ Geometries of all species were optimized at the B3LYP/6-31G(2df,p) level of theory, and frequencies were also calculated at this level of theory and scaled by the recommended scale factor (0.9854).^{1e} This level of theory was chosen as it is recommended for use with the G4, G3X, G3X(MP2), and G3X(MP2)-RAD methods studied herein; it was also used in the present work for the W1 calculations so that any differences in the results obtained could be attributed solely to the energy calculations. The frequency calculations were used to confirm

the nature of the stationary points, calculate the zero-point vibrational energies, and calculate the thermal corrections required for correcting 298 K experimental data to 0 K for comparison with theory. Where relevant, complete systematic conformational searching (at 120° resolution) was carried out to ensure that all species were studied in their global minimum energy conformations.

Improved energy calculations were then carried out at the G4 level of theory^{1f} and three variants of G3 theory: G3X,^{1e} G3X(MP2),^{1e} and G3X(MP2)-RAD.² Additional calculations were also performed with W1 theory⁷ as a benchmark. Full details of these methods are available in the original references; the principal differences between the methods are as follows. G3X theory approximates QCISD(T) calculations with a large triple- ζ basis set via a series of additivity approximations, carried out at the MP4, MP2, and HF levels of theory; an empirical HLC term and spin orbit corrections for atoms are also included. G4 theory is very similar to G3X but uses CCSD(T) in place of QCISD(T) and uses an improved basis set correction that makes use of a larger triple- ζ basis set at the MP2 level of theory and an extrapolation to the infinite basis set limit at the HF level of theory. As noted in the Introduction, the HLC term is also different in this method and, in contrast to the various G3 methods, does not cancel from the reaction energies studied herein. G3X(MP2) is similar to G3X but uses a lower-cost basis set correction that omits the MP4 calculations; G3X(MP2)-RAD is similar to G3X(MP2) but uses CCSD(T) calculations in place of QCISD(T) and uses restricted-open-shell wave functions in place of unrestricted wave functions when studying open-shell species. W1 theory is a very high level of theory in which CCSD(T) calculations are extrapolated to the infinite basis set limit and can generally predict the thermodynamics of normal ground-state chemical reactions with subkilocalorie accuracy.⁷ Where possible, we use both W1 calculations and experimental data as benchmark.

Results and Discussion

The test set of reactions chosen for the present work is shown in Scheme 1 and includes 21 radical addition reactions and 28 hydrogen atom abstraction reactions. In this study we use high-level W1 calculations as our primary benchmark level of theory. As a result, this limits the size of any molecules involved in the reactions to no more than 5 non-hydrogen atoms. Within this constraint, we chose reactions that would maximize any potential differences between G3X and G4; we also included reactions (such as radical addition to thiocarbonyl compounds) where earlier studies had found significant errors in G3 theory, in order to examine whether the changes included in G4 theory led to improved performance. Optimized geometries of all species are provided in the Supporting Information. Enthalpies (in kilojoules per mole; 0 K) for the radical addition and abstraction reactions at the various levels of theory are provided in Tables 1 and 2, respectively.

When first the W1 values are compared against the available experimental data,⁸ wide scatter is seen in the experimental data (more than 10 kJ mol⁻¹ in several cases), which reflects the difficulty in obtaining accurate thermochemical data for radical species. Not surprisingly then, the W1 values (and indeed the other levels of theory tested) generally fall within this scatter, particularly when the associated error bars of the experimental values are taken into account. However, it is clear that the uncertainty in the experimental values themselves is too large to allow for discrimination between the alternative levels of theory tested.

It is for this reason that in the present work we use W1 theory as our primary benchmark. As noted above, this very high level of theory has been shown in previous studies to deliver kilojoule accuracy in testing against reliable gas-phase experimental thermochemical data, without recourse to use of an empirical HLC term.⁷ Unfortunately, its computational cost limits its application to relatively small molecules and it is therefore desirable to identify whether any the lower-cost *Gn* methods can provide a reasonable approximation to it for use on larger and more practical systems.

The mean absolute deviations (MADs) from W1 of the various *Gn* methods tested are provided in Tables 1 and 2. On average, the deviations of all the tested methods are relatively small, comparable to the “kilocalorie accuracy” expected for this family of methods. For the overall test set, the MADs at the G3X and G4 levels of theory are very similar to one another at 2.6 and 2.8 kJ mol⁻¹, respectively; those for the lower-cost G3 methods, G3X(MP2) and G3X(MP2)-RAD, are slightly larger at 3.2 and 4.0 kJ mol⁻¹ respectively. For use in reliable thermochemical calculations, it is also important that the maximum absolute deviations of the tested methods fall within a reasonable range. When these are examined, some important differences in the performance of the various methods emerge. In particular, the maximum absolute deviations for the various G3 methods range from 8.2 kJ mol⁻¹ (for G3X) to 9.7 kJ mol⁻¹ [for G3X(MP2)-RAD]; in contrast, G4 shows greatly improved performance, having an maximum absolute deviation of just 5.6 kJ mol⁻¹. Thus, on the basis of these results, it would appear that G4 can offer “kilocalorie accuracy”, even for the more problematic radical reactions examined.

To identify the origin of this improved performance, the contribution of the various differences between G3X and G4 theory were analyzed. As noted above, the principal differences between G3X and G4 theory are G4 theory's use of CCSD(T) in place of QCISD(T), an extrapolation to infinite basis set at the HF level of theory, and a new noncanceling HLC term. Figure 1 shows the effect of these individual contributions on the mean and mean absolute deviations of G3X from G4 theory for addition, abstraction, and overall test sets; the data used to construct these plots are provided in the Supporting Information. From Figure 1, it is clear that the principal difference between G3X and G4 is the noncanceling HLC term. Indeed, when G4 is calculated without its HLC term, it yields very similar results to G3X (see Tables 1 and 2). This is encouraging, as it implies that the expensive HF extrapolation in G4 theory may not be necessary in chemical reactions such as these, for which significant systematic error cancelation is expected. However, the results also imply that the success of G4 is dependent on an empirical correction term, and therefore this method should be used cautiously.

This is further highlighted when the addition and abstraction test sets are examined separately. Figure 2 shows a plot of the G3X and G4 reaction energies as a function of the corresponding W1 benchmark values; data for the radical addition and abstraction reactions are plotted separately. From Figure 2 it is clear that while G4 outperforms G3X for the radical addition reactions, for the hydrogen atom abstraction reactions the HLC actually introduces a small but significant systematic error. This is also evident in the mean and maximum absolute deviations for these methods for the separate test sets. For the addition reactions, G4 theory has an MAD of just 1.9 kJ mol⁻¹, which is small compared with 4.1 kJ mol⁻¹ for G3X and 3.7 kJ mol⁻¹ for the non-HLC-corrected G4 results. However, for the abstraction reactions,

TABLE 1: Evaluation of Theoretical Procedures for Enthalpies^a of Radical Addition Reactions

reaction	G3X(MP2)-RAD	G3X(MP2)	G3X	G4 no HLC	G4	W1-ONIOM ^b	W1	experiment ⁸
1	-87.1	-87.1	-88.7	-88.7	-91.5	-92.8	-92.8	-93.80 ± 3.0 -98.00 ± 5.1 -98.40 ± 9.3 -92.60 ± 3.0
2	-86.3	-86.3	-87.7	-87.5	-90.4	-92.0	-89.1	-88.67 ± 2.37 -87.37 ± 10.77 -90.77 ± 2.37 -84.47 ± 4.47
3	-84.8	-84.7	-86.0	-85.8	-88.6	-90.4	-85.2	-88.27 ± 8.19
4	-114.2	-114.6	-115.1	-117.2	-120.0	-123.9	-123.9	-123.03 ± 16.70 -139.23 ± 21.30 -135.83 ± 13.30
5	-116.2	-116.7	-117.3	-118.5	-121.4	-126.0	-123.6	
6	-116.9	-117.3	-118.1	-118.6	-121.5	-126.6	-122.7	
7	-23.5	-24.4	-25.8	-25.7	-28.5	-30.0	-30.0	-24.03 ± 0.9 -26.53 ± 0.9 -37.03 ± 0.9 -27.43 ± 0.9 -21.13 ± 0.9 -42.30 ± 2.37
8	-35.8	-36.6	-38.2	-37.2	-40.0	-42.2	-39.9	
9	-42.8	-43.5	-45.6	-43.8	-46.6	-49.1	-44.2	
10	-87.4	-87.5	-89.1	-89.3	-93.6	-93.2	-93.4	-94.64 ± 3.27 -91.14 ± 2.77 -93.24 ± 3.17 -94.44 ± 3.17 -98.24 ± 5.27 -95.13 ± 2.09 -112.13 ± 10.49 -92.13 ± 6.29 -108.53 ± 2.09 -93.93 ± 2.09
11	-84.7	-85.0	-86.5	-87.1	-92.8	-90.7	-90.0	
12	-98.1	-98.4	-98.4	-100.4	-104.7	-107.7	-107.5	
13	-85.2	-85.5	-85.1	-86.7	-92.4	-94.8	-94.9	
14	-9.7	-10.5	-11.2	-11.2	-15.5	-16.1	-14.4	-15.53 ± 2.57 -20.93 ± 4.27 -5.13 ± 4.97
15	7.1	6.3	6.0	5.9	0.2	0.7	4.8	
16	-117.6	-118.1	-119.6	-118.4	-123.1	-123.8	-123.2	
17	-86.8	-87.8	-88.8	-88.9	-93.2	-93.5	-92.4	
18	-87.5	-88.5	-89.8	-90.4	-96.1	-94.2	-93.3	
19	-93.9	-94.7	-95.7	-95.8	-100.1	-100.4	-99.8	
20	-115.1	-116.4	-117.8	-117.2	-122.4	-122.1	-121.3	
21	-103.5	-105.4	-105.6	-106.0	-111.7	-111.1	-108.7	
Absolute Values								
MAD	5.5	4.9	4.1	3.7	1.9	1.7	(0)	
max	9.7	9.4	9.8	8.2	4.6	5.3	(0)	
Relative Values ^c								
MAD	1.8	2.1	2.1	1.6	2.4		(0)	
max	5.3	5.2	5.7	4.7	5.9		(0)	

^a Enthalpies at 0 K, given in kilojoules per mole. ^b ONIOM values were calculated by use of reaction 1 as the core reaction for all additions to C=C bonds; reaction 4 is used as the reference for additions to C=S bonds, and reaction 7 was used for addition to C=O bonds. The W1 ONIOM value was calculated as the sum of the W1 value for the core reaction and a correction for the remaining substituent effects, as calculated at the G3X(MP2)-RAD level of theory. In calculating the MADs of the ONIOM values, deviations for reactions that had zero error by construction (i.e., reactions 1, 4, and 7 in this case) were omitted. ^c For all radical addition reactions (1–21), relative values were calculated as the difference between reaction energy for the given reaction and the corresponding value for reaction 1, irrespective of the substrate. In calculating the MADs of the relative values, deviations for reactions that had zero error by construction (i.e., reaction 1 in this case) were omitted.

the mean and maximum errors in the various G3 methods are all much smaller, consistent with the greater systematic error cancelation expected for these isodesmic reactions. In contrast, for G4 theory the MAD for the abstraction test (3.4 kJ mol⁻¹) is actually larger than for the addition test set and improves significantly (to 1 kJ mol⁻¹) when the HLC is omitted from this method. In other words, for these isodesmic reactions, the HLC term in G4 appears to be introducing additional errors to the calculated reaction energies. While

these errors are relatively small for the present test set, it should be noted that the HLC term scales with the number of valence electrons and can make a potentially large contribution to the reaction energy. For example, the HLC term of G4 would contribute 12.8 kJ mol⁻¹ to the enthalpy of the relatively small reaction H-CF₂CF₂CF₃ + •CH₃ → •CF₂CF₂CF₃ + CH₄; for corresponding reaction of H-CF₂CF₂CF₂CF₃, this would grow to 17.1 kJ mol⁻¹. Although it is not possible as yet to perform W1 calculations

TABLE 2: Evaluation of Theoretical Procedures for Enthalpies^a of Hydrogen Atom Abstraction

reaction	G3X(MP2)-RAD	G3X(MP2)	G3X	G4 no HLC	G4	W1-ONIOM ^b	W1	experiment ⁸
22	13.0	13.1	13.4	13.6	16.4	14.2	14.2	17.6 ± 2.5 21.8 ± 4.6 22.2 ± 8.8 16.4 ± 2.5
23	13.2	13.3	13.5	13.7	18.0	14.4	14.3	18.4 ± 0.4 17.1 ± 8.8 20.5 ± 0.4 14.2 ± 2.5
24	14.5	14.7	15.0	15.2	20.9	15.7	15.3	20.3 ± 4.6
25	41.8	42.6	43.5	43.7	46.5	43.0	44.0	47.1 ± 6.3 58.6 ± 10.9 55.2 ± 2.9
26	42.8	43.6	44.4	44.7	49.0	44.0	45.9	
27	42.5	43.3	44.2	44.4	50.1	43.7	47.5	
28	31.8	33.0	33.2	33.5	36.4	33.0	34.5	36.9 ± 0.4 39.4 ± 0.4 49.9 ± 0.4 40.3 ± 0.4 34.0 ± 0.4 49.8 ± 0.4
29	31.7	33.0	33.2	33.5	37.7	32.9	34.9	
30	35.2	36.5	36.7	37.1	42.8	36.4	37.5	
31	23.3	23.6	24.0	24.5	28.8	24.5	25.5	29.0 ± 2.6 25.5 ± 2.1 27.6 ± 2.5 28.8 ± 2.5 32.6 ± 4.6 39.6 ± 0.4 56.6 ± 8.8 36.6 ± 4.6 53.0 ± 0.4 38.4 ± 0.4
32	29.4	29.8	30.7	31.6	37.3	30.6	32.2	
33	46.8	47.4	48.2	48.9	53.2	48.0	50.3	
34	46.6	47.3	48.2	49.1	54.8	47.8	52.5	
35	37.0	38.3	38.5	39.0	43.3	38.2	40.1	50.3 ± 0.4 55.7 ± 2.1 39.9 ± 2.8
36	36.6	37.9	38.2	38.8	44.5	37.8	39.5	
37	44.4	45.0	46.0	45.0	49.8	45.6	46.0	45.8 ± 13.0 63.4 ± 10.0 62.5 ± 8.8 42.0 ± 0.4 51.9 ± 0.4 28.3 ± 8.8 32.1 ± 8.8 22.3 ± 0.4 50.2 ± 0.4 55.6 ± 2.1 39.8 ± 2.8 58.3 ± 8.8 49.5 ± 8.8 54.5 ± 0.4
38	17.6	18.9	18.6	19.2	23.4	18.8	20.1	22.6 ± 4.6 19.5 ± 1.7 19.5 ± 2.5 18.3 ± 3.3 17.4 ± 2.1
39	35.3	36.7	36.9	37.6	43.3	36.5	38.6	29.8 ± 3.3 26.5 ± 2.9 27.8 ± 2.1 31.1 ± 2.5 32.8 ± 4.6
40	48.9	50.0	50.7	51.0	55.3	50.1	52.2	40.2 ± 3.3 40.6 ± 3.3 43.1 ± 0.4 41.0 ± 3.3 41.0 ± 1.7
41	53.7	55.2	55.8	55.4	60.6	54.9	56.2	−6.6 ± 3.3 −5.6 ± 0.4 −7.8 ± 4.6 −10.8 ± 0.4 −17.0 ± 0.4
42	10.3	12.2	11.7	13.2	18.9	11.5	14.1	46.2 ± 2.9 37.9 ± 4.6 40.4 ± 0.4 41.6 ± 8.8 71.6 ± 0.4
43	14.4	14.5	14.7	15.2	16.6	15.6	16.1	31.3 ± 10.9 44.7 ± 0.4 33.6 ± 0.4 55.3 ± 0.4 77.9 ± 8.8 67.6 ± 0.4
44	24.5	24.7	25.1	25.9	28.8	25.7	26.7	
45	30.3	30.7	31.5	32.5	36.8	31.5	33.7	
46	−13.1	−11.0	−12.0	−10.4	−6.2	−11.9	−10.1	
47	42.6	43.8	44.0	45.5	49.8	43.8	46.2	
48	21.7	22.9	23.2	22.8	28.0	22.9	24.2	
49	59.2	60.2	61.4	60.8	65.5	60.4	62.1	

TABLE 2A: Continued

reaction	G3X(MP2)-RAD	G3X(MP2)	G3X	G4 no HLC	G4	W1-ONIOM ^b	W1	experiment ^s
Absolute Values								
MAD	2.8	1.9	1.5	1.0	3.4	1.7	(0)	
max	5.9	5.2	4.3	3.4	5.6	4.7	(0)	
Relative Values ^c								
MAD	1.7	0.9	0.9	0.6	1.4	—	(0)	
max	4.7	4.2	3.5	2.8	3.3	—	(0)	
Overall (reactions 1–49) Absolute Values								
MAD	4.0	3.2	2.6	2.2	2.8	1.7	(0)	
max	9.7	9.4	9.8	8.2	4.6	5.3	(0)	
Overall (reactions 1–49) Relative Values ^c								
MAD	1.7	1.4	1.4	1.0	1.9	—	(0)	
max	5.3	5.2	5.7	4.7	5.9	—	(0)	

^a Enthalpies at 0 K, given in kilojoules per mole. ^b ONIOM values were calculated with reaction 22 as the core reaction for all hydrogen atom abstraction reactions. The W1 ONIOM value was calculated as sum of the W1 value for the core reaction and a correction for the remaining substituent effects, as calculated at the G3X(MP2)-RAD level of theory. In calculating the MADs of the relative values, deviations for reactions that had zero error by construction (i.e., reaction 22 in this case) were omitted. ^c For abstraction reactions (22–49), relative values were calculated as the difference between the reaction energy for the given reaction and the corresponding value for reaction 22. In calculating the MADs of the relative values, deviations for reactions that had zero error by construction (i.e., reaction 22) were omitted.

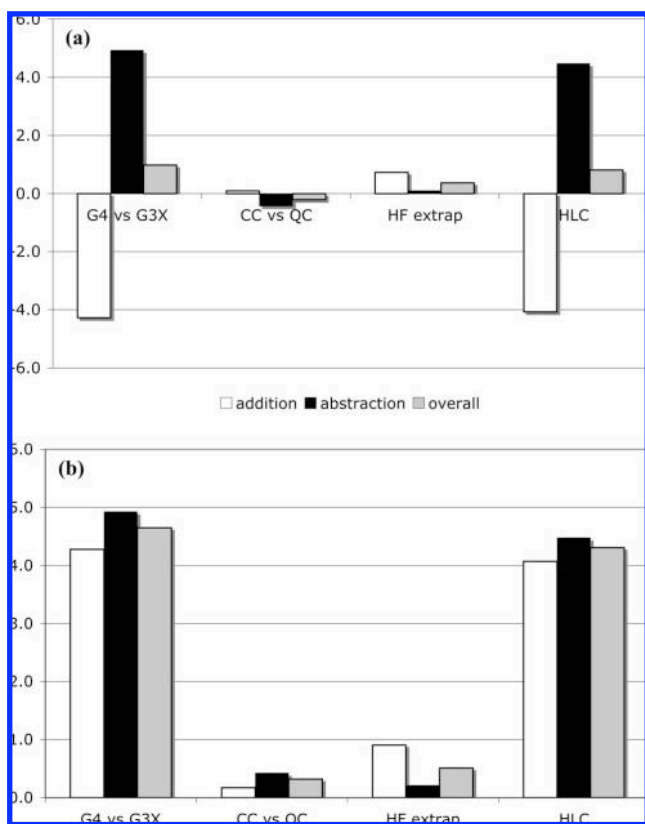


Figure 1. Analysis of contributions to (a) mean and (b) mean absolute deviations between G4 and G3X for the addition, abstraction, and overall test sets (in kilojoules per mole).

in such cases, it seems likely that the large HLC term in G4 could potentially introduce significant errors in larger chemical reactions.

This raises a problem. For radical addition reactions, particularly those involving thiocarbonyl reactions, there are significant errors (ca. 8–10 kJ mol⁻¹) at the G3 level of theory and the HLC term of G4 appears to be correcting for these. However, given the problems of this HLC term for the abstraction test set, it would be unwise to rely upon it for larger chemical reactions, particularly as it has the potential to grow rapidly with the size of the system. One possible solution would be to further modify the HLC term of G4. For example, the present results suggest that it is not

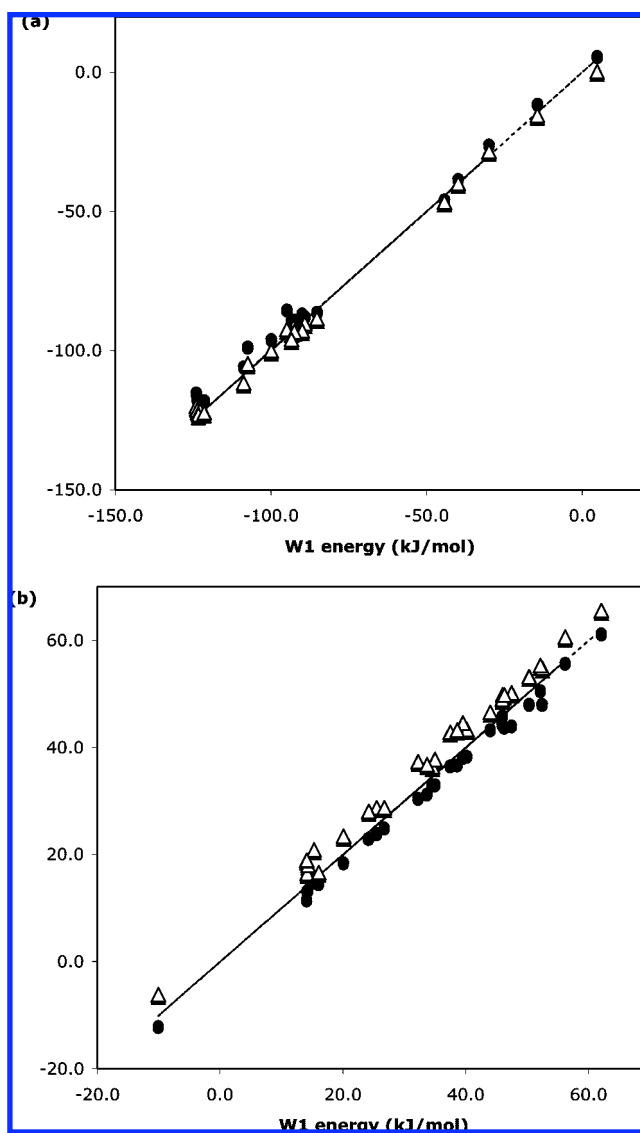


Figure 2. Comparison of the performance of G3X (●) and G4 (Δ) methods against W1 theory for (a) addition reactions and (b) abstraction reactions in the test set.

the open-shell species that are being treated incorrectly at the G3 level of theory but rather the unsaturated compounds

in the radical addition reactions. Hence an HLC term based on the number of π bonds, lone pairs, and unpaired electrons present in a compound, similar to that adopted in the KMLYP functional,⁹ might be more appropriate. Designed appropriately, such an HLC term would cancel from the abstraction energies but not the addition energies; it would also not cancel from heats of formation, bond dissociation energies, and other problematic reactions where the HLC terms of the G_n methods have been shown to be valuable.

An alternative approach to correcting the errors at G3 theory, adopted successfully in our studies of RAFT polymerization,¹⁰ is to use an ONIOM-based approach in which W1 calculations are performed for a small model reaction (the “core”) that includes the principal forming and breaking bonds. The energies for the full system are then obtained by correcting the energies of the core for the remaining substituent effects, as calculated at a lower level of theory such as G3. For larger systems, an additional “ONIOM layer” can be added in which remote substituent effects are treated at a lower level of theory, such as RMP2/6-311+G(3df,2p).^{3e} The success of this type of approach rests upon the lower level of theory in question modeling substituent effects (i.e., relative values of reaction energies) accurately, even if the absolute values are subject to error. Using our new test set of W1 energies, we are now in a position to determine whether G3 methods can provide an accurate approximation to W1.

Mean and maximum absolute deviations of the *relative* values of the reaction energies (measured relative to reaction 1 for radical addition and relative to reaction 22 for abstraction) are included in Tables 1 and 2. From these data it is clear that all of the G3 methods tested do an excellent job of modeling the relative reaction energies, with MADs from W1 of around 2 kJ mol⁻¹ and maximum deviations of around 5 kJ mol⁻¹. Importantly, for the problematic subset of five thiocarbonyl reactions (reactions 4–6, 12, and 13) the MADs decrease from around 8 kJ mol⁻¹ (for the absolute reaction energies) to less than 2 kJ mol⁻¹ (for the relative values) when the simplest thiocarbonyl addition, reaction 4, is taken as the reference reaction. This indicates that accurate values are possible by use of a lower-cost G3 method, provided these are then corrected to the W1 level of theory by using the difference of W1 and G3 for the core of the reaction. This is illustrated in Tables 1 and 2 where ONIOM values are calculated from the G3X(MP2)-RAD data using W1 values for the smallest practical reaction cores; namely, reactions 1, 4, and 7 for radical addition to alkenes, thiocarbonyls, and carbonyls, respectively; and reaction 22 for the hydrogen atom abstraction reactions. This ONIOM approach greatly reduces the errors at the G3X(MP2)-RAD level of theory and results in overall mean and maximum absolute deviations of just 1.7 and 5.3 kJ mol⁻¹, respectively. Hence “chemical accuracy” does appear to be possible for these problematic reactions, without recourse to an empirical HLC term, provided an ONIOM-based approach is used in which the reaction core is studied at W1.

Conclusion

This study, which presents some of the most computationally expensive W1 calculations so far published, further validates the use of G_n theory methods for calculating the energies of radical reactions. All methods tested can approximate the benchmark W1 values to within a mean absolute deviation (MAD) of 4 kJ mol⁻¹ or less, although maximum absolute deviations for problematic reactions (such as radical addition

to thiocarbonyl compounds) can be as much as 10 kJ mol⁻¹ for the G3 methods. While the new noncanceling HLC term in G4 was found to be capable of mitigating these errors in radical addition, it introduced a systematic error to the reaction energies of the abstraction reactions, and its format may therefore require re-examination. In the meantime, G3 methods can offer “chemical accuracy” even for these problematic cases, provided they are corrected to the W1 level of theory via an ONIOM-based approach.

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Supporting Information Available: B3LYP/6-31G(d) optimized geometries in the form of GAUSSIAN archive entries; corresponding total energies; available experimental data for the individual reactants and products and their calculated temperature corrections. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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