

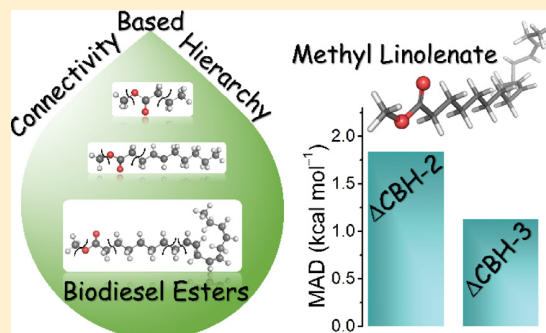
Eliminating Systematic Errors in DFT via Connectivity-Based Hierarchy: Accurate Bond Dissociation Energies of Biodiesel Methyl Esters

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Supporting Information

ABSTRACT: We present a computational study focusing on the determination of accurate bond dissociation energies (BDEs) involved in the combustion of biodiesel methyl esters. We have adapted our previously developed efficient error-cancellation protocols, based on the systematic “connectivity-based hierarchy” (CBH), to derive accurate BDEs of biodiesel molecules at a modest computational cost. Using DFT energies on the full biodiesel molecule in conjunction with accurate G4 energies on the small fragments involved in the CBH reaction schemes, systematic errors in the DFT methods can be cancelled efficiently. Herein, we apply our G4-corrected Δ CBH-2 and Δ CBH-3 schemes in conjunction with several popular DFT methods to determine accurate bond dissociation energies of different C–C, C–H, and C–O bonds in biodiesel surrogate molecules. We first evaluate the performance of different DFT methods using a test set of 21 reactions involving various bond dissociations in small to medium biodiesel surrogates (up to methyl decanoate, a C10-methyl ester) by calibration against accurate values calculated with multireference methods (MRACPF2), reported by Carter and co-workers. The CBH-2 corrections for all tested dispersion-corrected functionals yield mean absolute deviations (MADs) in a narrow range of 1.3–1.5 kcal/mol, the best performance being obtained for B97-D3 and ω B97X-D functionals (MAD = 1.3 kcal/mol). Further, significant improvement yielding a MAD of only 0.9 kcal/mol is obtained using the G4-corrected CBH-3 scheme. Finally, the protocol has been applied to derive accurate BDEs of eight different bonds in the larger biodiesel molecule, methyl linolenate, yielding a MAD of only 1.13 kcal/mol using the Δ CBH-3 error correction scheme. The results suggest that our protocol in conjunction with different DFT methods should be broadly applicable to yield accurate BDEs for a variety of large biodiesel molecules.



1. INTRODUCTION

Biodiesel, a clean, affordable, and renewable energy resource, is being increasingly harnessed as an alternative fuel for diesel engines.^{1–3} The steady increase in the percentage of biodiesel content in automobile fuel and its recent introduction in aviation have steeply enhanced its demands.⁴ The chemical composition of biodiesel is an inherent mixture of methyl esters of long, unsaturated fatty acids, such as oleic acid or linolenic acid, typically contain 16–18 carbon atoms with one to three C=C double bonds in the hydrocarbon chain. A complete study of the intrinsic thermodynamic parameters controlling the different bond strengths is a crucial factor in the search of more efficient biofuels.^{5–10}

Combustion of esters, even the modest-sized ones, involves multiple reaction pathways, generating numerous intermediates and products. Experimental isolation of all the elementary reaction products among the many different pyrolytic pathways of biofuel combustion is a herculean task¹¹ and often provides results with large uncertainties.^{12,13} As an alternative, computational modeling of combustion has become the go-to approach to obtain accurate thermochemical and kinetic parameters.^{14,15}

The recent surge in computational studies^{16–21} deriving and analyzing thermochemical properties of biodiesel esters demonstrates the active nature of the field.

Among the different combustion properties of biodiesel, bond dissociation enthalpies (BDEs) are the most significant and play a key role in the associated reaction mechanisms. In particular, comparison of the BDEs of the different chemical bonds provide insight into the preferred bond breakage processes to produce relatively more stable radicals.^{22,23} Thus, the knowledge of thermochemical properties of different radical reactions including hydrogen abstraction, addition of radicals to double bonds, and homolytic cleavage is pertinent in the assessment of the stability of the various radical intermediates. The calculated BDEs of the different underlying elementary reactions provide an assessment of the ease of breakage of different bonds leading to the prediction of feasible end products in the combustion process.

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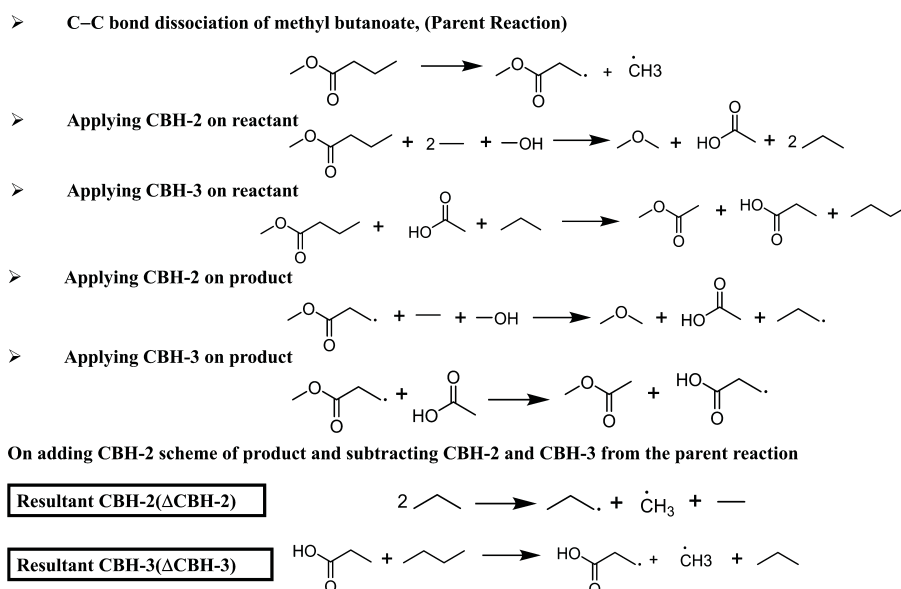


Figure 1. Δ CBH-2 and Δ CBH-3 schemes for a representative bond dissociation reaction for methyl butanoate.

While calculations for BDEs of all different C–C, C–O, and C–H bonds in small esters are widely prevalent in the literature,^{24–28} studies on larger biodiesel esters have been limited. The steep scaling of accurate quantum chemical methods, such as the “gold-standard” CCSD(T),²⁹ coupled with the need to examine multiple elementary combustion pathways of biodiesel esters have restricted many of these studies to smaller surrogate systems^{30,31} such as methyl butanoate ($\text{C}_3\text{H}_7\text{COOCH}_3$).^{32,33} Nevertheless, two groups have recently carried out significant studies on both small and large methyl esters. Carter and co-workers^{38,39} applied a multireference averaged coupled-pair functional method³⁴ (MRACPF) and an improved MRACPF2 model³⁵ to compute BDEs of the different bonds in C1–C4 methyl esters acting as surrogates of biodiesel esters.^{36,37} The calculated values were found to be in good agreement with multireference singles and doubles configuration interaction (MRSDCI) results. A local reduced-scaling variant developed by Carter and co-workers^{38,39} was then applied on C_{10} and C_{18} esters to derive their thermochemical properties.¹⁸ In general, the calculated BDEs were largely consistent with those obtained from the earlier calculations on ester surrogates.³⁶ In a later study, Li et al.¹⁹ evaluated the performance of over 50 DFT methods with respect to MRACPF2 results and with CCSD(T)/CBS energies obtained for some of the smaller systems. While the results varied widely across the different density functionals, some recommended functionals such as M08-HX performed very well and were subsequently used to study the BDEs in the larger methyl linolenate ($\text{C}_{19}\text{H}_{32}\text{O}_2$). However, the study shows that even the best functionals such as M08-HX, which worked very well for C–H and C–C bond dissociations, had significant deviations for some C–O bond dissociations.

As an alternative to brute force calculations, systematic error cancellation schemes can be highly effective for deriving accurate thermochemical properties of large organic molecules using computationally inexpensive methods such as density functional theory (DFT).^{40,41} We have developed a broadly applicable structure-based thermochemical scheme called connectivity-based hierarchy (CBH) to derive accurate enthalpies of formation of large organic molecules containing

a variety of heteroatoms and functional groups.⁴² Subsequent applications on amino acids and other biomolecules were performed to derive heats of formation with DFT methods that were consistent with the highly accurate G4 composite method.^{43,44} The method was extended to open-shell organic systems to derive thermochemical properties of organic radical species.⁴⁵ The hierarchy consists of error cancellation schemes using fragment molecules capturing the local environment of the system of interest. As we ascend up the rungs of the hierarchy, a larger chemical environment of the system of interest is preserved to obtain greater error cancellation. In particular, reaction schemes at the CBH-2 or CBH-3 rungs are usually sufficient to derive accurate thermochemical properties of large organic molecules. The CBH-2 scheme preserves the immediate chemical bonding environment of all heavy atoms in the molecule, while CBH-3 preserves the bonding environments of all the heavy-atom bonds. The hierarchy was later extended to obtain extrapolated CCSD(T) energies of large molecules⁴⁶ and to work effectively (with errors <1 kcal/mol) for both open- and closed-shell organic systems.^{46,47}

Very recently, we have developed a systematic protocol using CBH reaction schemes to derive accurate reaction enthalpies of complex organic reactions with DFT methods.⁴⁸ The approach starts with full calculations on the reaction involving large organic molecules using a given DFT method. For each rung of CBH- n ($n = 1, 2, 3, \dots$), the CBH reaction schemes are set up for the reactant and the product to identify the net change in the elementary model reactions. G4 and DFT calculations are performed on the small fragment molecules involved in the model reactions to calculate and correct the systematic DFT error in the large molecule reactions. We found that the mean absolute deviation of B3LYP calculated reaction energies significantly reduced from 12.9 to 1.7 kcal/mol using the CBH-2 correction schemes for a set of 25 organic reactions of significant complexity. More importantly, we observed a dramatic improvement on the performances of all density functionals with the use of our protocol. In particular, the calculated reaction energies with dispersion-corrected DFT methods had errors well within 1.5 kcal/mol relative to G4 results. Jensen et al.⁴⁹ have further

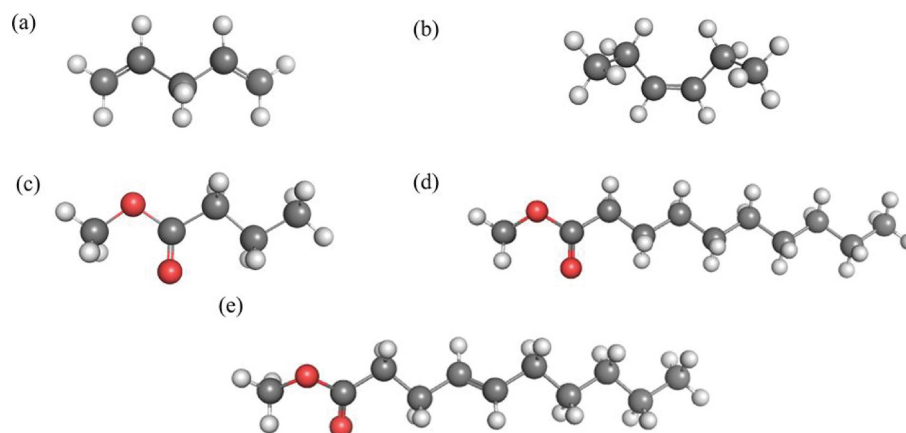


Figure 2. Surrogates of biodiesel methyl esters (a) 1,4-pentadiene, (b) 3-hexene, (c) methyl butanoate, (d) methyl decanoate, and (e) *trans*-4-methyl decanoate.

explored the performance of semiempirical and faster *ab initio* methods (such as HF-3c and PBEh-3c with minimal basis sets) in conjunction with our protocol on the same test set of chemical reactions.

The CBH protocol provides a route to obtain accurate reaction enthalpies that are relatively insensitive to the underlying exchange–correlation functional employed. Herein, we apply the protocol to derive accurate BDEs of various biodiesel esters. We assess the performance of five different popular DFT methods, with and without empirical dispersion corrections, in conjunction with the CBH protocol. The calibrations are performed by calculating the BDEs of several C–C, C–H, and C–O bonds in methyl esters and by comparing them with the MRACPF2 values.¹⁸ The protocol is then applied to derive the bond dissociation energies in a larger system, methyl linolenate.

2. COMPUTATIONAL DETAILS

2.1. Resultant CBH Schemes. Figure 1 illustrates a schematic representation of the application of CBH-2 and CBH-3 error correction schemes to derive accurate BDE of methyl butanoate.

The reaction energy for the parent reaction is first calculated with the current DFT method, and the calculated deviation from the reference energy (e.g., MRACPF2) is denoted as Dev-0. The CBH-2 schemes are then set up for both reactants and products to identify the net change in the elementary model reactions, referred to as resultant CBH-2 (Δ CBH-2) scheme. Fragment molecules common to both the reactant and product sides are cancelled in deriving the Δ CBH-2 scheme. Calculations are then carried out on the resultant reaction with the current DFT method and an accurate reference method (e.g., CCSD(T)/CBS or G4 theory as in this work) to calculate the associated corrections, $\text{Corr-2} = \Delta$ CBH-2(G4) – Δ CBH-2(method). The overall energy deviation after application of the correction is represented as $\text{Dev-2} = \text{Dev-0} - \text{Corr-2}$. Similarly, the correction Corr-3 can be obtained for the CBH-3 reaction scheme, leading to an overall deviation from MRACPF2, denoted as Dev-3.

The central idea in our scheme is that the error in the calculated parent reaction energy for a given functional is principally due to the propagation of the corresponding errors associated with the bonding changes in the underlying elementary model reactions representing the Δ CBH-2 scheme.

The errors in the elementary reactions can then be easily corrected by using an accurate level of theory such as G4. Note that the G4 calculations are only needed for the small CBH-2 or CBH-3 fragments that are independent of the size of the large biodiesel molecule. In addition, since the same fragments occur in the Δ CBH-2 schemes for many different parent biodiesel molecules, the G4 energies for repeating fragments can be obtained from a look-up data table containing the DFT and G4 energies.

2.2. Computational Methods. All the calculations were performed using the Gaussian 16 program suite.⁵⁰ Geometry optimizations on all the species were carried out at the B3LYP/6-31G(2df,p) level of theory (as in G4). All optimized structures were confirmed to be minima, and the harmonic frequencies were scaled by a factor of 0.9854 in calculating the zero-point energy and thermal corrections. Single-point calculations at these optimized geometries were then performed with a larger 6-311++G(3df,2p) basis set using five different density functionals such as B3LYP, B97, M06-2X, ω B97X, and B2PLYP with and without Grimme's empirical dispersion corrections.⁵¹ For the density functionals such as B3LYP, B97, M06-2X and B2PLYP, we have used Grimme's standard empirical GD3 corrections. For the range-separated ω B97X functional, we have used the independent ω B97X-D dispersion correction. Single-point energies were added to the zero-point and thermal energy corrections to calculate BDEs. G4 enthalpies for the fragments were used with the Δ CBH-*n* reaction schemes to obtain corrected BDEs for all the parent reactions (see Table S1). All the MRACPF2 results were taken from ref 18. The coordinates of all the structures are given in the Supporting Information.

3. RESULTS AND DISCUSSION

To illustrate the performance of our CBH protocol described above for the calculation of BDEs, we have considered a test set of five different biodiesel surrogates, as shown in Figure 2. The test set includes a range of small to large surrogates of biodiesel esters, for example, 1,4-pentadiene, 3-hexene, methyl butanoate, methyl decanoate, and *trans*-4-methyl decanoate. The reactions considered involve 21 single bonds, which are composed of 11 C–H bonds, 8 C–C bonds, and 2 C–O bonds. First, the accuracy of the CBH-2 protocol is tested for different bond dissociation energies computed with five different density functionals with and without empirical

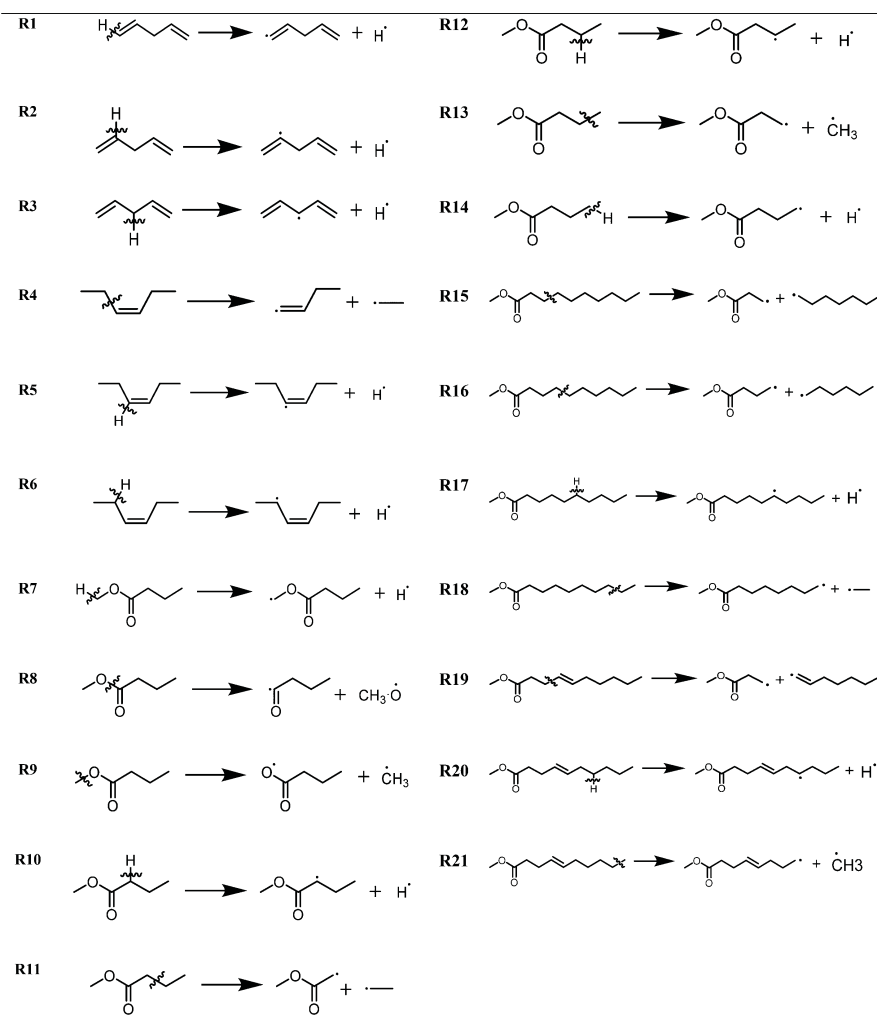


Figure 3. Test set of reactions R1–R21 involving various C–C, C–O, and C–H bond dissociations.

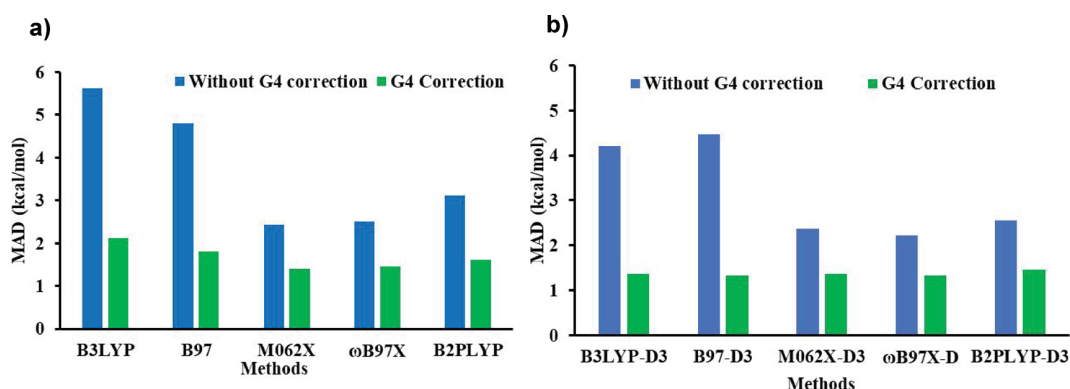


Figure 4. Graphical representations of the calculated mean absolute deviations (MADs) in BDEs of all the reactions with and without the inclusion of the G4 correction (Δ CBH-2 scheme) using (a) DFT and (b) DFT-D methods.

dispersion corrections. The BDEs representing the parent reactions, R1–R21, as illustrated in Figure 3, are first calculated by employing the 6-311++G(3df,2p) basis set using different DFT methods. The resultant reactions are then derived as described in the Computational Methods section to determine the CBH-2 corrected BDEs. The BDEs obtained for each reaction are then compared against the

results of MRACPF2 (multireference averaged coupled-pair functional) method.¹⁸ The next subsection presents the extension of our CBH protocol to one higher rung to derive the CBH-3 corrected BDEs.

3.1. DFT versus DFT-D. The bond dissociation reactions yield open-shell species in the form of organic radicals and hydrogen atoms. The performance of the different DFT and

DFT-D functionals were assessed with and without the inclusion of the G4 correction. This allows an assessment of the effect of dispersion-corrected DFT methods and the effect of G4 corrections. Figure 4 shows a graphical representation summarizing the mean absolute deviation (MAD) in BDEs with respect to MRACPF2 values of the 21 reactions shown in Figure 3.

The blue bars in Figure 4 represent the deviation in BDEs obtained for DFT methods with and without the inclusion of dispersion corrections. Overall, there is a small improvement in the range of 0.1–1.5 kcal/mol from the inclusion of dispersion corrections to the DFT methods in predicting the BDEs. For instance, upon inclusion of the dispersion correction (D3) in B97, the average deviation decreases slightly from 4.7 to 4.5 kcal/mol. A similar trend is observed using ω B97X-D and B2PLYP-D3, accounting for a reduction of 0.4 and 0.5 kcal/mol, respectively (see Figure 4). Among the DFT functionals considered, the most significant improvement is seen in the case of B3LYP with MAD dropping from 5.7 to 4.2 kcal/mol upon inclusion of the dispersion correction. Conversely, the least improvement is seen using M06-2X functional reducing the deviation from 2.4 to 2.3 kcal/mol upon inclusion of the dispersion correction. Overall, we recommend using dispersion-corrected DFT-D methods for determining bond dissociation energies for systems such as biodiesel surrogates; although, the improvement is only expected to be modest.

3.2. Δ CBH-2 Error Correction Scheme. In this section, we evaluate the performance of different DFT methods upon incorporation of Δ CBH-2 corrections. It is clearly evident from Figure 4 that although there is a substantial variation in the raw performance of different functionals (blue bars), consistent improvements are observed upon inclusion of G4 corrections using both DFT and DFT-D methods (green bars) with dramatic improvements in the performance of B3LYP and B97. For example, the deviation ranges from 2.4 to 5.7 kcal/mol without using the dispersion corrections (Figure 4a). However, the spread becomes significantly narrower with G4 corrections and the error ranging between 1.4 and 2.1 kcal/mol. Among all the different DFT methods with G4 corrections, the meta-hybrid M06-2X produces the smallest average deviation of 1.4 kcal/mol. As illustrated earlier (vide supra), after inclusion of dispersion corrections (Figure 4b), the MAD for the density functionals range from 2.1 to 4.5 kcal/mol. Most importantly, they all improve significantly upon inclusion of G4 corrections, and the MAD occurs in even a smaller range of 1.3–1.5 kcal/mol. Among the dispersion-corrected DFT methods with G4 corrections, the two methods (B97-D3 and ω B97X-D) gave the lowest MAD of only 1.3 kcal/mol. The MAD of 1.5 kcal/mol corresponds to the double-hybrid functional (B2PLYP-D3). The Minnesota functional (M06-2X-D3) and hybrid functional (B3LYP-D3) produce a MAD of 1.4 kcal/mol. Overall, the error cancellation strategy in the form of Δ CBH-2 correction term provides more accurate BDEs that are almost independent of the nature of underlying exchange–correlation functional. A similar observation was found in our previous study,⁴⁸ where almost any density functional can calculate accurate reaction enthalpies using the systematic Δ CBH-2 error cancellation scheme.

Finally, comparing the raw performance of most of the tested density functional methods shows a low deviation for the nonpolar C–C and C–H bonds, whereas a relatively large deviation was observed for the polar C–O bonds (see Table S2, in the Supporting Information). A similar performance

trend was reported by Li et al.¹⁹ However, we found that adding G4 correction on the top of raw BDEs resulted in a substantial decrease in the deviation, especially for C–O bonds. Overall, we suggest that such systematic error corrections provide a better strategy to obtain accurate BDEs, in strong contrast to the search for the “best functional” for the problem at hand, typically most DFT studies in the literature.

3.3. Δ CBH-3 Error Correction Scheme. The last part of this section analyzes the deviations obtained for the individual reactions (R1–R21) using ω B97X-D, one of the best performing functionals. Although, inclusion of Δ CBH-2 corrections on ω B97X-D resulted in an accurate deviation of 1.3 kcal/mol, 3 out of 21 reactions yield deviations >2.5 kcal/mol (see Table 1, boldface). Among these three reactions with

Table 1. Deviation Obtained for BDEs of All the Reactions (R1–R21) Calculated Using Best Performing DFT Methods (ω B97X-D) without and with G4 Corrections (Δ CBH-2 and Δ CBH-3)

reactions	without G4	CBH-2	CBH-3
R1	2.0	1.2	1.3
R2	3.7	2.1	1.6
R3	3.6	2.8	1.1
R4	0.5	0.4	0.3
R5	2.8	2.0	1.9
R6	4.0	1.9	1.7
R7	3.0	2.8	1.0
R8	0.7	0.2	0.4
R9	2.8	1.6	0.4
R10	3.2	2.1	1.0
R11	3.0	2.9	2.0
R12	0.4	0.4	0.2
R13	0.7	0.1	0.1
R14	2.4	1.8	1.6
R15	0.5	0.5	0.1
R16	3.9	1.6	1.3
R17	3.1	0.7	1.0
R18	0.7	0.1	0.1
R19	1.0	0.4	1.3
R20	2.4	1.9	0.2
R21	0.8	0.2	0.3
average deviation	2.15	1.32	0.91

large errors, two (R3 and R7) involve C–H bond dissociations, while the other (R11) involves a C–C bond dissociation at the β position to C=O. In the case of R3, the C–H bond dissociation generates a secondary radical center that participates in a more extended conjugation, resulting in a Δ CBH-2 deviation of 2.8 kcal/mol. Here, the Δ CBH-2 corrections derived from the model reaction is not sufficient to preserve the local environment of the radical product. However, incorporation of corrections from one higher rung (Δ CBH-3) decreases the deviation by 1.7 kcal/mol, as shown in Table 1. Similarly in R7, upon scission of the terminal C–H bond, the singly occupied carbon $2p_\pi$ orbital, which most likely undergoes hyperconjugation with the adjacent $2p_\pi$ oxygen lone pair, resulting in a π -resonance-stabilized primary fragment.³⁷ An improvement of 1.8 kcal/mol is observed upon going from CBH-2 to CBH-3. In addition, R11 involves dissociation of the C–C bond at the β position to C=O, which generates a primary radical participating in an extended

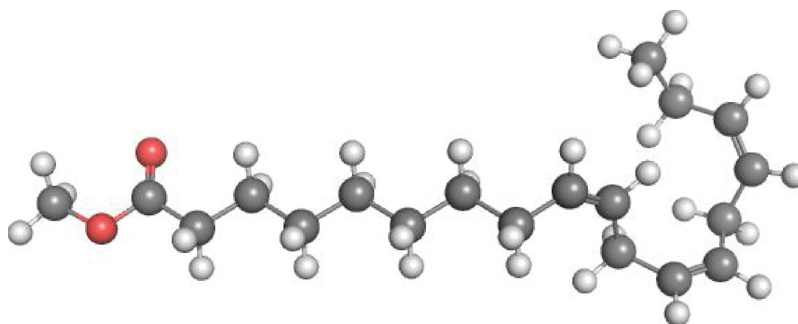


Figure 5. Methyl linolenate as large biodiesel component.

Table 2. Deviations in BDEs of Methyl Linolenate Calculated Using ω B97X-D Including Δ CBH-2 and Δ CBH-3 Corrections with Respect to MRACPF2 Calculated BDEs from Ref 18

	Δ CBH-2	Δ CBH-3	Ref
Rx1	0.9	1.1	86.0
Rx2	0.3	0.2	92.1
Rx3	2.9	1.4	81.6
Rx4	2.3	1.0	75.0
Rx5	3.0	2.1	86.9
Rx6	1.3	1.9	99.7
Rx7	2.3	1.2	109.1
Rx8	1.7	0.1	76.1
MAD	1.84	1.13	

conjugation with C=O. Consequently using CBH-2, this results in a large deviation of 2.9 kcal/mol. However, a noticeable reduction is observed using the Δ CBH-3 scheme, yielding a deviation of 2.0 kcal/mol. Overall, some of the larger deviations obtained using CBH-2 corresponds to an inadequate treatment of delocalized states, which is a well-known deficiency in DFT.^{52,53} But using the CBH-3 reaction scheme, a larger balance in the chemical environment is achieved, reducing the average deviation to only 0.9 kcal/mol for all reaction test sets.

3.4. Bond Dissociation Energies in the Larger Biodiesel Molecule, Methyl Linolenate. Finally, we apply CBH to determine BDEs of several bonds in a C18 methyl ester (methyl linolenate), an important constituent of biodiesel, to demonstrate the applicability of our method for larger systems. Methyl linolenate comprises an unsaturated methyl ester with three C=C bonds and an ester group. The present section focuses on the performance of both Δ CBH-2 and Δ CBH-3 schemes to determine the BDEs in the all *cis*-conformer of methyl linolenate (*cis* for all three C=C double bonds), as shown in Figure 5. In general, direct calculations with chemical accurate methods such as G4 on large systems, for examples, methyl linolenate are computationally expensive. Thus, the BDEs are more commonly estimated from individual BDEs of the fragments or small molecules based on the local structure of the parent molecule. However, our standard protocol is easily applicable for such larger molecules. This is due to the fact that only DFT calculations have to be performed on the full molecule, while the more expensive G4

calculations are only needed for the small fragment molecules involved in the CBH reaction schemes. Additionally, the Δ CBH-2 or Δ CBH-3 schemes for analogous bond dissociation of different methyl esters are similar, and hence, many of the G4 energies can be obtained from a look-up table containing stored data on the repeating systems. Table 2 shows the lists of the MAD in BDEs of eight different bonds in methyl linolenate calculated with Δ CBH-2 and Δ CBH-3 corrections using ω B97X-D, one of the best performing functionals seen in our benchmarking BDEs for smaller biodiesel surrogates seen earlier.

The calculated BDEs of eight different bonds, represented as reactions Rx1–Rx8, are compared with the MRACPF2 results reported by Carter and co-workers.^{38,39} The BDEs of methyl linolenate reported by them were computed by combining the dissociation energies of smaller surrogates, for example, methyl butanoate, 1,4-pentadiene, 3-hexene, and 1-pentene.¹⁸ The MAD obtained for both CBH-2 and CBH-3 schemes are within our target accuracy of 2 kcal/mol. Δ CBH-2 produces an average MAD of 1.84 kcal/mol. Nevertheless, a smaller average deviation of 1.14 kcal/mol is obtained using the Δ CBH-3 protocol. Among all the reactions, the largest deviation is observed for Rx5, that is, 3.0 kcal/mol using Δ CBH-2 corrections, and a smaller deviation of 2.1 kcal/mol is observed with the Δ CBH-3 protocol. This reaction corresponds to the cleavage of C11–H37 bond. For the same dissociation, Li et al.¹⁹ have observed a relatively larger average deviation of $\sim$ 4.5 kcal/mol using nine different DFT methods. Such a large deviation might be due to a larger structural difference between

methyl linolenate and the smaller surrogate (1-pentene) that was used as the reference BDE. Our error cancellation strategy performs relatively better, producing a smaller deviation of 2.1 kcal/mol. Significant improvements in the deviations are observed for most of the reactions upon going from CBH-2 to CBH-3. Overall, based on the performances of different rungs, we recommend CBH-3 as a cost-effective route to obtain accurate BDEs of different bonds in large organic systems such as biodiesel components.

4. CONCLUSIONS

In this study, we have benchmarked BDEs of 21 reactions involving smaller- to medium-sized biodiesel surrogate molecules. The results obtained have been compared with the accurate energies from the MRACPF2 method, computed previously by Carter and co-workers.^{38,39} The Δ CBH-2 corrections require DFT calculations on the full molecule, but G4 calculations are required only on the modest-sized fragments. Thus, after application of the Δ CBH corrections, G4 quality results are obtained at essentially the DFT cost for larger molecules. For the test set of 21 bond dissociation reactions, the performance of five different popular density functionals are assessed with or without the empirical dispersion corrections. The dispersion corrections improve the results slightly (0.1–1.5 kcal/mol). The G4 corrections improve the performance dramatically for all DFT functionals. The MAD for the five dispersion-corrected functionals occurs in a narrow range of 1.3–1.5 kcal/mol. Among the different functionals, B97-D3 and ω B97X-D show the best performance (MAD = 1.3 kcal/mol). Further improvements are obtained using the Δ CBH-3 corrections, yielding a MAD within 1 kcal/mol (0.91 kcal/mol for ω B97X-D). Finally, we have applied our CBH scheme to a larger biofuel component, methyl linolenate. For a set of eight different dissociation reactions studied in methyl linolenate, the calculated ω B97X-D BDEs with Δ CBH-2 and Δ CBH-3 corrections yield a MAD of 1.84 and 1.13 kcal/mol, respectively, relative to the MRACPF2 results. Overall, our cost-effective error cancellation approach can be used for predicting accurate BDEs of a range of large biodiesel components.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.9b01478.

Cartesian coordinates of all the structures, deviations in the bond dissociation energies for the different methods, and mean absolute deviations in the bond dissociation energies for the different bond types (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Dale, B. E.; Anderson, J. E.; Brown, R. C.; Csonka, S.; Dale, V. H.; Herwick, G.; Jackson, R. D.; Jordan, N.; Kaffka, S.; Kline, K. L.; et al. Take a Closer Look: Biofuels Can Support Environmental, Economic And Social Goals. *Environ. Sci. Technol.* **2014**, *48*, 7200–7203.
- (2) Escobar, J. C.; Lora, E. S.; Venturini, O. J.; Yáñez, E. E.; Castillo, E. F.; Almazan, O. Biofuels: Environment, Technology and Food Security. *Renewable Sustainable Energy Rev.* **2009**, *13*, 1275–1287.
- (3) Kohse-Höinghaus, K.; Oßwald, P.; Cool, T. A.; Kasper, T.; Hansen, N.; Qi, F.; Westbrook, C. K.; Westmoreland, P. R. Biofuel Combustion Chemistry: From Ethanol to Biodiesel. *Angew. Chem. Int. Ed.* **2010**, *49*, 3572–3597.
- (4) Fellet, M. Now boarding: Commercial Planes Take Flight With Biobased Jet Fuel. *Chem. Eng. News* **2016**, *94*, 16–18.
- (5) Lai, J. Y. W.; Lin, K. C.; Violi, A. Biodiesel combustion: Advances In Chemical Kinetic Modeling. *Prog. Energy Combust. Sci.* **2011**, *37*, 1–14.
- (6) Karton, A. A computational chemist's guide to accurate thermochemistry for organic molecules. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2016**, *6*, 292–310.
- (7) Goerigk, L.; Grimme, S. A thorough benchmark of density functional methods for general main group thermochemistry, kinetics, and noncovalent interactions. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6670–6688.
- (8) Liu, C.; Assary, R. S.; Curtiss, L. A. Investigation of Thermochemistry Associated with the Carbon–Carbon Coupling Reactions of Furan and Furfural Using Ab Initio Methods. *J. Phys. Chem. A* **2014**, *118*, 4392–4404.
- (9) Xie, Y.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. Highly Efficient Process for Production of Biofuel from Ethanol Catalyzed by Ruthenium Pincer Complexes. *J. Am. Chem. Soc.* **2016**, *138*, 9077–9080.
- (10) Dahmen, M.; Marquardt, W. Model-Based Design of Tailor-Made Biofuels. *Energy Fuels* **2016**, *30*, 1109–1134.
- (11) Lam, K.-Y.; Davidson, D. F.; Hanson, R. K. High-Temperature Measurements of the Reactions of OH with Small Methyl Esters: Methyl Formate, Methyl Acetate, Methyl Propanoate, and Methyl Butanoate. *J. Phys. Chem. A* **2012**, *116*, 12229–12241.
- (12) Berkowitz, J.; Ellison, G. B.; Gutman, D. Three Methods to Measure RH Bond Energies. *J. Phys. Chem.* **1994**, *98*, 2744–2765.
- (13) Widegren, J. A.; Bruno, T. J. Vapor Pressure Measurements On Saturated Biodiesel Fuel Esters by the Concatenated Gas Saturation Method. *Fuel* **2011**, *90*, 1833–1839.
- (14) Irikura, K. K.; Frurip, D. J., Eds.; *Computational Thermochemistry: Prediction and Estimation of Molecular Thermodynamics*; American Chemical Society: Washington, DC, 1998; Vol. 677, DOI: 10.1021/bk-1998-0677.
- (15) Tran, L. S.; Sirjean, B.; Glaude, P.-A.; Fournet, R.; Battin-Leclerc, F. Progress in Detailed Kinetic Modeling of the Combustion of Oxygenated Components of Biofuels. *Energy* **2012**, *4*, 1–18.
- (16) Zheng, J.; Meana-Pañeda, R.; Truhlar, D. G. Prediction of Experimentally Unavailable Product Branching Ratios for Biofuel Combustion: The Role of Anharmonicity in the Reaction of Isobutanol with OH. *J. Am. Chem. Soc.* **2014**, *136*, 5150–5160.
- (17) Porterfield, J. P.; Bross, D. H.; Ruscic, B.; Thorpe, J. H.; Nguyen, T. L.; Baraban, J. H.; Stanton, J. F.; Daily, J. W.; Ellison, G. B. Thermal Decomposition of Potential Ester Biofuels. Part I: Methyl Acetate and Methyl Butanoate. *J. Phys. Chem. A* **2017**, *121*, 4658–4677.
- (18) Oyeyemi, V. B.; Dieterich, J. M.; Krisiloff, D. B.; Tan, T.; Carter, E. A. Bond Dissociation Energies of C10 and C18 Methyl Esters from Local Multireference Averaged-Coupled Pair Functional Theory. *J. Phys. Chem. A* **2015**, *119*, 3429–3439.

- (19) Li, X.; Xu, X.; You, X.; Truhlar, D. G. Benchmark Calculations for Bond Dissociation Enthalpies of Unsaturated Methyl Esters and the Bond Dissociation Enthalpies of Methyl Linolenate. *J. Phys. Chem. A* **2016**, *120*, 4025–4036.
- (20) Zhang, L.; Zhang, P. Towards High-Level Theoretical Studies Of Large Biodiesel Molecules: An ONIOM [QCISD(T)/CBS:DFT] Study of Hydrogen Abstraction Reactions of $C_nH_{2n+1}COOC_mH_{2m+1}$ + H. *Phys. Chem. Chem. Phys.* **2015**, *17*, 200–208.
- (21) Wang, Q.-D. Theoretical studies on the hydrogen abstraction reactions of methyl esters with HO_2 radical and the following β -scission reactions. *J. Phys. Org. Chem.* **2017**, *30*, No. e3668.
- (22) Blanksby, S. J.; Ellison, G. B. Bond Dissociation Energies of Organic Molecules. *Acc. Chem. Res.* **2003**, *36*, 255–263.
- (23) O'Reilly, R. J.; Karton, A.; Radom, L. Effect of Substituents on the Strength of N–X (X = H, F, and Cl) Bond Dissociation Energies: A High-Level Quantum Chemical Study. *J. Phys. Chem. A* **2011**, *115*, 5496–5504.
- (24) Pedley, J. B. *Thermochemical Data and Structure of Organic Compounds*; Thermodynamics Research Center: Texas A & M University: College Station, TX, 1994.
- (25) Chen, E. C. M.; Albyn, K.; Dussack, L.; Wentworth, W. E. Determination of Bond Dissociation Energies from Dissociative Thermal Electron Attachment. *J. Phys. Chem.* **1989**, *93*, 6827–6832.
- (26) Akbar Ali, M.; Violi, A. Reaction Pathways for the Thermal Decomposition of Methyl Butanoate. *J. Org. Chem.* **2013**, *78*, 5898–5908.
- (27) Giri, B. R.; AlAbbad, M.; Farooq, A. High-Temperature Unimolecular Decomposition of Ethyl Propionate. *Chem. Phys. Lett.* **2016**, *664*, 184–190.
- (28) El-Nahas, A. M.; Navarro, M. V.; Simmie, J. M.; Bozzelli, J. W.; Curran, H. J.; Dooley, S.; Metcalfe, W. Enthalpies of Formation, Bond Dissociation Energies and Reaction. Paths for the Decomposition of Model Biofuels: Ethyl Propanoate and Methyl Butanoate. *J. Phys. Chem. A* **2007**, *111*, 3727–3739.
- (29) *Theory and Applications of Computational Chemistry The First Forty Years*; Dykstra, C., Frenking, G., Kim, K., Scuseria, G., Eds; Elsevier: Amsterdam, The Netherlands, 2005; pp 1–7.
- (30) Pelucchi, M.; Cavallotti, C.; Ranzi, E.; Frassoldati, A.; Faravelli, T. Relative Reactivity of Oxygenated Fuels: Alcohols, Aldehydes, Ketones, and Methyl Esters. *Energy Fuels* **2016**, *30*, 8665–8679.
- (31) Somers, K. P.; Simmie, J. M. Benchmarking Compound Methods (CBS-QB3, CBS-APNO, G3, G4, W1BD) against the Active Thermochemical Tables: Formation Enthalpies of Radicals. *J. Phys. Chem. A* **2015**, *119*, 8922–8933.
- (32) Metcalfe, W. K.; Dooley, S.; Curran, H. J.; Simmie, J. M.; El-Nahas, A. M.; Navarro, M. V. Experimental and Modeling Study of $C_5H_{10}O_2$ Ethyl and Methyl Esters. *J. Phys. Chem. A* **2007**, *111*, 4001–4014.
- (33) Yang, B.; Westbrook, C. K.; Cool, T. A.; Hansen, N.; Kohse-Höinghaus, K. Fuel-specific Influences on the Composition of Reaction Intermediates in Premixed Flames of three $C_5H_{10}O_2$ Ester Isomers. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6901–6913.
- (34) Gdanitz, R. J.; Ahlrichs, R. The Averaged Coupled-Pair Functional (ACPF): A Size-Extensive Modification of MR CI(SD). *Chem. Phys. Lett.* **1988**, *143*, 413–420.
- (35) Gdanitz, R. J. A New Version of the Multireference Averaged Coupled-Pair Functional (MR-ACPF-2). *Int. J. Quantum Chem.* **2001**, *85*, 281–300.
- (36) Oyeyemi, V. B.; Keith, J. A.; Carter, E. A. Accurate Bond Energies of Biodiesel Methyl Esters from Multireference Averaged Coupled-Pair Functional Calculations. *J. Phys. Chem. A* **2014**, *118*, 7392–403.
- (37) Oyeyemi, V. B.; Krisiloff, D. B.; Keith, J. A.; Libisch, F.; Pavone, M.; Carter, E. A. Size-Extensivity-Corrected Multireference Configuration Interaction Schemes to Accurately Predict Bond Dissociation Energies of Oxygenated Hydrocarbons. *J. Chem. Phys.* **2014**, *140*, No. 044317.
- (38) Krisiloff, D. B.; Carter, E. A. Approximately Size Extensive Local Multireference Singles and Doubles Configuration Interaction. *Phys. Chem. Chem. Phys.* **2012**, *14*, 7710–7717.
- (39) Dieterich, J. M.; Carter, E. A. Assessment of a Semi Integral-Direct Local Multi-reference Configuration Interaction Implementation Employing Shared-Memory Parallelization. *Comput. Theor. Chem.* **2015**, *1051*, 47–56.
- (40) Radom, L.; Lathan, W. A.; Hehre, W. J.; Pople, J. A. Molecular orbital theory of the electronic structure of organic compounds. VIII. Geometries, energies, and polarities of C_3 hydrocarbons. *J. Am. Chem. Soc.* **1971**, *93*, 5339–5342.
- (41) Wheeler, S. E.; Houk, K. N.; Schleyer, P. V. R.; Allen, W. D. A Hierarchy of Homodesmotic Reactions for Thermochemistry. *J. Am. Chem. Soc.* **2009**, *131*, 2547–2560.
- (42) Ramabhadran, R. O.; Raghavachari, K. Theoretical Thermochemistry for Organic Molecules: Development of the Generalized Connectivity-Based Hierarchy. *J. Chem. Theory Comput.* **2011**, *7*, 2094–2103.
- (43) Ramabhadran, R. O.; Sengupta, A.; Raghavachari, K. Application of the Generalized Connectivity-Based Hierarchy to Biomonomers: Enthalpies of Formation of Cysteine and Methionine. *J. Phys. Chem. A* **2013**, *117*, 4973–4980.
- (44) Sengupta, A.; Ramabhadran, R. O.; Raghavachari, K. Accurate and Computationally Efficient Prediction of Thermochemical Properties of Biomolecules Using the Generalized Connectivity-Based Hierarchy. *J. Phys. Chem. B* **2014**, *118*, 9631–9643.
- (45) Sengupta, A.; Raghavachari, K. Prediction of Accurate Thermochemistry of Medium and Large Sized Radicals Using Connectivity-Based Hierarchy (CBH). *J. Chem. Theory Comput.* **2014**, *10*, 4342–4350.
- (46) Ramabhadran, R. O.; Raghavachari, K. Extrapolation to the Gold-Standard in Quantum Chemistry: Computationally Efficient and Accurate CCSD(T) Energies for Large Molecules Using an Automated Thermochemical Hierarchy. *J. Chem. Theory Comput.* **2013**, *9*, 3986–3994.
- (47) Sengupta, A.; Ramabhadran, R. O.; Raghavachari, K. Breaking a Bottleneck: Accurate Extrapolation to “Gold Standard” CCSD(T) Energies for Large Open Shell Organic Radicals at Reduced Computational Cost. *J. Comput. Chem.* **2016**, *37*, 286–295.
- (48) Sengupta, A.; Raghavachari, K. Solving the Density Functional Conundrum: Elimination of Systematic Errors To Derive Accurate Reaction Enthalpies of Complex Organic Reactions. *Org. Lett.* **2017**, *19*, 2576–2579.
- (49) Kromann, J. C.; Welford, A.; Christensen, A. S.; Jensen, J. H. Random versus Systematic Errors in Reaction Enthalpies Computed Using Semiempirical and Minimal Basis Set Methods. *ACS Omega* **2018**, *3*, 4372–4377.
- (50) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; et al. *Gaussian16, Revision A.03*, (2016); Gaussian Inc. Wallingford CT.
- (51) Mardirossian, N.; Head-Gordon, M. Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals. *Mol. Phys.* **2017**, *115*, 2315–2372.
- (52) Hait, D.; Head-Gordon, M. Delocalization Errors in Density Functional Theory Are Essentially Quadratic in Fractional Occupation Number. *J. Phys. Chem. Lett.* **2018**, *9*, 6280–6288.
- (53) Oyeyemi, V. B.; Keith, J. A.; Pavone, M.; Carter, E. A. Insufficient Hartree–Fock Exchange in Hybrid DFT Functionals Produces Bent Alkynyl Radical Structures. *J. Phys. Chem. Lett.* **2012**, *3*, 289–293.