# Prediction of Accurate Thermochemistry of Medium and Large Sized Radicals Using Connectivity-Based Hierarchy (CBH)

Arkajyoti Sengupta and Krishnan Raghavachari*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405, United States

ⓢ Supporting Information

ABSTRACT: Accurate modeling of the chemical reactions in many diverse areas such as combustion, photochemistry, or atmospheric chemistry strongly depends on the availability of thermochemical information of the radicals involved. However, accurate thermochemical investigations of radical systems using state of the art composite methods have mostly been restricted to the study of hydrocarbon radicals of modest size. In an alternative approach, systematic error-canceling thermochemical hierarchy of reaction schemes can be applied to yield accurate results for such systems. In this work, we have extended our connectivity-based hierarchy (CBH) method to the investigation of radical systems. We have calibrated our method using a test set of 30 medium sized radicals to evaluate their heats of formation. The CBH-rad30 test set contains radicals containing diverse functional groups as well as cyclic systems. We demonstrate that the sophisticated error-canceling isoatomic scheme (CBH-2) with modest levels of theory is adequate to provide heats of formation accurate to ~1.5 kcal/mol. Finally, we predict heats of formation of 19 other large and medium sized radicals for which the accuracy of available heats of formation are less well-known.
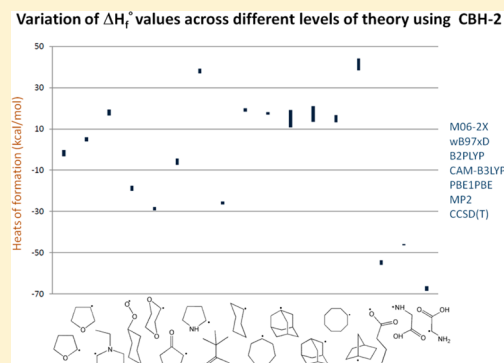
Radicals play an important role in many diverse areas such as combustion, photochemistry, atmospheric chemistry, and polymer chemistry. Understanding the kinetics and thermodynamics of chemical reactions in these fields requires a knowledge of the accurate thermochemistry of many important radicals.[1,2] With scientific interest turning toward environmental conservation through search for alternate energy fuels and protection of the ozone layer, an increased importance is given to understanding the mechanistic features of the underlying chemical reactions.[3−6] While the experimental isolation and investigation of these unstable species has its own problems, the complications from spin contamination and the frequent choice of inadequate basis sets for study have hindered accurate computational studies of these radicals.[7−9] Even popular databases such as NIST,[10] Active Thermochemical Tables (ATcT),[11] and others[12−14] fail to report the thermochemical parameters of some radicals that are of high interest in the aforementioned fields. A key challenge for modern thermochemistry lies in overcoming these limitations of the paucity of available data.

The present state-of-the-art ab-inito tool box includes composite methods[15−26] that offer highly accurate atomization energies and heats of formation. Derivatives of these methods have also been developed for application to open shell systems.[21,27−29] However, they frequently involve expensive and lengthy computations that restrict them to small molecules. To circumvent the multiple rigorous calculations, Goldsmith et al. have performed RQCISD(T)/cc-PV∞QZ//B3LYP/6-311++G(d,p) calculations for 219 small molecules including many radicals.[30] However, even these calculations are computation-

ally expensive and are not feasible for molecules containing more than eight heavy (non-hydrogen) atoms.

Resorting to chemical reactions that can offer systematic error cancellation to evaluate accurate thermochemical properties with the use of modest levels of theory for large molecules has had a long history,[31] starting from Pople's isodesmic scheme.[32−34] Numerous schemes such as homodesmotic scheme,[35] hyperhomodesmotic,[36] isogeitonic,[37] and n-homodesmotic[38] have been developed for evaluation of accurate thermochemical properties. However, some of these schemes suffer from definition-based inconsistencies, while others involve arduous requirements of bond and hybridization matching.

To overcome the above set of problems, connectivity-based hierarchy (CBH) was developed in our group. It is a systematic and automated protocol of an error cancellation-based thermochemical hierarchy applicable to all closed shell organic molecules.[39] Accurate heats of formation were obtained with both density functional methods[39] as well as wave function-based methods using modest basis sets.[40] Recently, we employed CBH for the prediction of heats of formation of two sulfur containing amino acids: cysteine and methionine.[41] Superior error cancellation through the isoatomic scheme (CBH-2) offered results in agreement with the available G3MP2 and W2−F12 calculations.[42,43] These results demonstrated the success of the method with the modest levels of
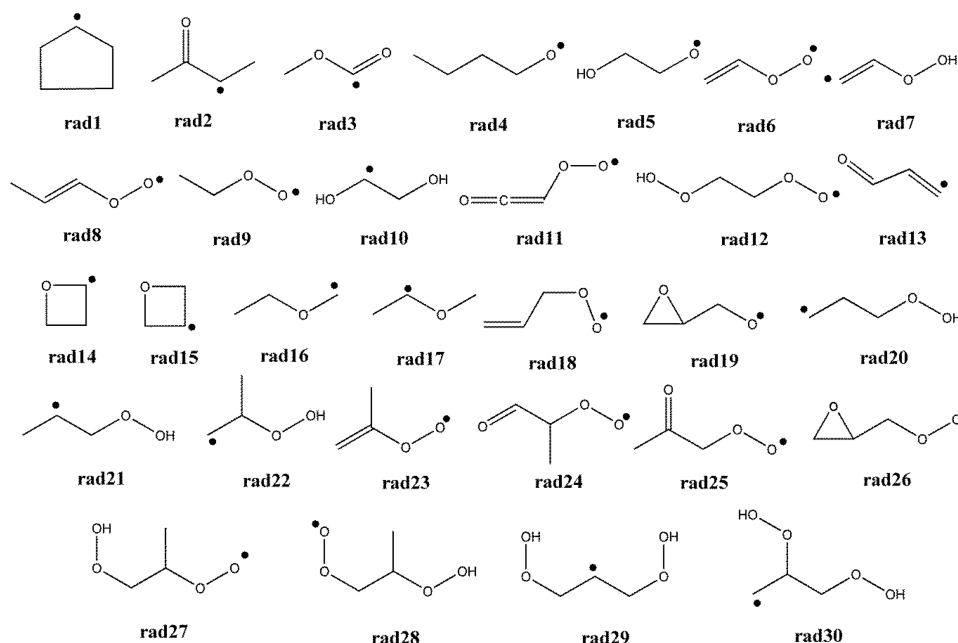
Figure 1. CBH-rad30 test set of 30 doublet radicals.

theory for a range of organic molecules containing multiple functional groups.

For ease of comprehension, a succinct account of CBH is provided herein. More details are provided in our previous studies.[39−41] CBH has several rungs, called CBH-0, CBH-1, CBH-2, CBH-3, etc. At CBH-0, all the heavy atoms are extracted by simple hydrogen termination (C as CH$_4$, N as NH$_3$, etc.). CBH-1 is formally the same as the isodesmic bond separation scheme. At the isoatomic CBH-2 rung, the immediate chemical environments of all the heavy atoms are preserved. At CBH-3, the immediate chemical environments of all the heavy atom bonds are preserved. Similarly, additional higher rungs can also be defined easily. However, for reasons mentioned in the above paragraphs, we restrict the discussions to the CBH-1 and CBH-2 rungs, with a specific emphasis on the CBH-2 (isoatomic) rung. Using these reaction energies and based on Hess's law, accurate enthalpies of formation are then computed.

In this study, we extend our application of CBH to open shell systems to compute heats of formation of medium and large sized radicals. The purpose of this study is 2-fold. First, we demonstrate that the atom-centric rung CBH-2[44] is sufficient for evaluation of accurate thermochemical properties for medium-sized radicals even with modest levels of theory. Similar to our previous studies, we found that a greater conservation of bond connectivities allows CBH-2 to yield heats of formation within the experimental errors with significantly less demanding calculations. Second, we predict heats of formation of 19 medium and large sized radicals. The recent study of Wheeler and co-workers of their "generalized bond separation reactions" (GBSRs)[45] on 27 radicals involved computation of CCSD(T)/cc-pVTZ energies for evaluation of the heats of formation of the fragments involved in the homodesmotic, and hyperhomodesmotic reactions (CBH-3). While higher CBH rungs can offer great error cancellation, the unavailability of heats of formation of the CBH fragments restricts their use. We demonstrate herein that the CBH-2 scheme is efficient and yields heats of formation of such radicals

within 1−2 kcal/mol even with modest levels of theory using above-mentioned databases.[10−14,30]

■ COMPUTATIONAL DETAILS

All the calculations have been performed using the Gaussian 09[46] suite of programs. Geometry optimizations of all species were carried out at B3LYP/6-311+G(d,p) level or MP2/6-311+G(d,p) levels of theory. The associated harmonic frequencies were scaled by a factor of 0.9854 in the case of the B3LYP optimizations and 0.9445 in the case of the MP2 optimizations. The optimized geometries were all characterized as minima without any imaginary frequencies. Geometry optimizations were followed by single-point calculations with 12 different density functional methods having different exchange and correlation functionals. The error cancellation at the CBH rungs were tested with Handy's long-range corrected CAM-B3LYP,[47] Minnesota functionals M05-2X[48] and M06-2X,[49] the pure GGA PBE,[50] the long-range corrected pure GGA LC-ωPBE,[51] hybrid functionals B3LYP[52,53] and PBE1PBE,[54] Grimme's dispersion-corrected GGA B97-D[55,56] and ωB97xD by Head-Gordon and co-workers,[57] Boese and Martin's BMK,[58] and double hybrid functional B2PLYP.[59] Along with the aforementioned density functionals, error cancellation schemes were also evaluated for wave function-based methods such as HF, MP2, and CCSD(T).

The single point energies obtained using these different methods were added to the thermal corrections to the enthalpies at 298.15 K to determine the heats of formation. Three modest-sized basis sets including Pople-style 6-31+G-(d,p) and 6-311++G(3df,2p) and Dunning-style aug-cc-pVDZ have been used in single point calculations to study the effect of the basis sets. We use these practical and modest basis sets to evaluate their significant error cancellations using CBH. Consistent with our idea of balancing the computational cost of CBH with the desired levels of accuracy, computationally expensive CCSD(T)/6-311++G(3df,2p) calculations were avoided. Instead, we used an additivity-based approach to get the CCSD(T)/6-311++G(3df,2p) energies, that is,

$$E(CCSD(T)/6\text{-}311\text{++}G(3df,2p))$$

$$= E(CCSD(T)/6\text{-}31\text{+}G(d,p))$$

$$+ E(MP2/6\text{-}311\text{++}G(3df,2p))$$

$$- E(MP2/6\text{-}31\text{+}G(d,p))$$

■ CBH-RAD30 TEST SET

The test set for the evaluation of the systematic error cancellation at CBH-2 for open shell systems consists of 30 radicals, shown in Figure 1. These 30 radicals all have doublet ground states and contain diverse functional groups (carboxyl, alkoxy, peroxy, alkylperoxide, etc.) and different hybridizations. In addition, the test set contains five cyclic systems, through which the effect of ring strain is illustrated. Our results using CBH are compared to the available experimental heats of formation or RQCISD(T)/cc-pV∞QZ//B3LYP/6-311++G-(d,p) calculations by Goldsmith et al.[30] B3LYP and MP2 optimized geometries were used for the single point calculations with various density functional and wave function-based theoretical methods. While our results with both B3LYP and MP2 optimized geometries are in very good agreement with the reference values, for the sake of brevity herein, we only provide results (reaction energies and heats of formation) with B3LYP optimized geometries.[60] The $\langle S^2 \rangle$ values of the radicals are provided in the Supporting Information.

The reactions corresponding to CBH-1 and CBH-2 schemes are provided in Tables S3 and S4, respectively, in the Supporting Information. Reaction energies for the radicals with different density functionals and wave function-based methods at CBH-1 and CBH-2 are compared in Figure 2.
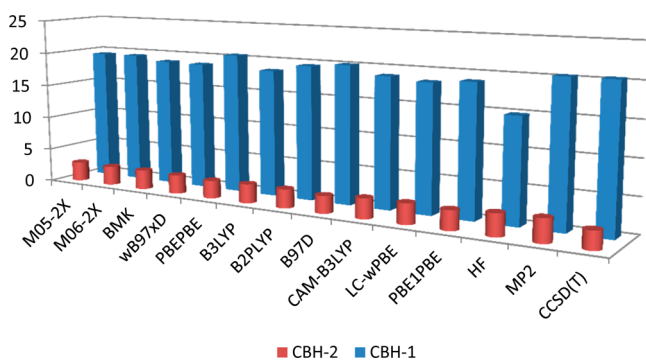
Figure 2. Mean absolute reaction energies (kcal/mol) of 25 acyclic radicals calculated with various levels of theory for their CBH-1 and CBH-2 reaction schemes.

These energy trends for the acyclic systems are similar to our findings from previous studies: the reaction energies for the different levels of theory are in the range 17−20 kcal/mol and 2−4 kcal/mol at CBH-1 and CBH-2, respectively. Thus, the sharp decrease in the magnitude of the reaction energies on going from CBH-1 to CBH-2, reflective of the increased matching of the bond types and hybridizations, is very similar to our previous observations for closed shell systems.[39,41]

Next, we calculated heats of formation of the 30 radicals in the CBH-rad30 test set at room temperature (298.15 K) using the heats of formation of the components involved.[61] The sophisticated error cancellation at CBH-2 over CBH-1 (Figure 2) results in lower mean absolute deviations (MAD) of the

heats of formation of the radicals (given in Table 1) for the former. Since our goal is to furnish accurate thermochemistry

Table 1. Mean Absolute Deviations (kcal/mol) of Calculated Heats of Formation of 30 Radicals Using 6-311++G(3df,2p) Basis Set at Various Levels of Theory Using CBH[a]

method	cyclic molecules (5)		acyclic molecules (25)	
	CBH-1	CBH-2	CBH-1	CBH-2
M05-2X	2.20	2.08	1.16	1.20
M06-2X	1.52	1.62	1.24	1.24
BMK	2.04	1.18	1.76	1.21
ωB97xD	1.54	0.78	1.67	1.14
PBEPBE	1.54	2.40	2.10	1.52
B3LYP	1.34	1.90	2.23	1.28
B2PLYP	0.68	1.04	1.28	1.20
B97-D	2.04	3.00	1.78	1.51
CAM-B3LYP	2.18	0.74	1.58	1.10
LC-ωPBE	1.16	1.60	1.87	1.08
PBE1PBE	1.48	0.98	2.08	1.21
HF	4.20	0.76	5.10	1.26
MP2	2.12	0.88	1.69	1.29
CCSD(T)	1.00	0.58	1.28	1.34

[a]The geometries were obtained at the B3LYP/6-311+G(d,p) levels of theory. The 6-311++G(3df,2p) basis set was used throughout for single point calculations. CCSD(T)/6-311++G(3df,2p) energies obtained by extrapolation. The number of cyclic and acyclic molecules in the test set is written in parentheses.

with modest levels of theory, we focused on the heats of formation obtained at the CBH-2 rung. It is important to note that we avoided going beyond the CBH-2 rung, as the experimental heats of formation of many of the individual components involved in the higher rungs are not known. However, we do note that an accurate method, such as CCSD(T) that recovers a large fraction of the correlation energy for molecules,[62−64] can yield accurate results at both CBH-1 and CBH-2 levels. In addition, the fragments involved at CBH-1 are smaller and their heats of formation are frequently available with greater precision, resulting in heats of formation that are in good agreement with the known reference values of the radicals. If necessary, CCSD(T) calculations at CBH-1 can be used to evaluate unavailable heats of formation of fragments involved at higher CBH rungs. This strategy is used later for the evaluation of the heats of formation of some larger radical systems (vide infra).

Table 1 provides the MAD of heats of formation at CBH-1 and CBH-2 calculated with different levels of theory. Table 2 lists the heats of formation for the individual molecules in the test set with the best performing density functional and wave function-based methods. The complete data for all the methods is listed in the Supporting Information (Tables S11 and S12). The most striking observation from Table 1 is that, for the acyclic systems, the MAD of the heats of formation of the 30 radicals at CBH-2 (Table 1, column 5) *falls within a narrow range (1.1−1.5 kcal/mol) for all the methods*. Even with HF, the MAD of the heats of formation decreases from a value of 5.1 kcal/mol at CBH-1 to 1.3 kcal/mol at CBH-2. The double hybrid B2PLYP performs much better than the popular B3LYP functional, particularly at CBH-1. The dispersion-corrected functionals B97-D and ωB97xD, as well as the long-range corrected functionals LC-ωPBE and CAM-B3LYP, perform much better at CBH-2 than at CBH-1. Similar observations

Table 2. Calculated Heats of Formation (kcal/mol) of the 30 Radicals in CBH-rad30 Test Set at CBH-2 with the Best Set of DFTs and Wavefunction-Based Methods[a]

species	literature	M06-2X	ωB97xD	B2PLYP	CAM-B3LYP	PBE1PBE	MP2	CCSD(T)
rad1	25.3[b]	28.6	27.8	26.6	27.1	26.5	27.0	27.4
rad2	−16.8[b]	−17.0	−16.8	−16.9	−16.9	−17.0	−17.4	−16.7
rad3	−37.6[c]	−37.4	−37.3	−37.6	−37.5	−37.4	−37.5	−37.4
rad4	−15.0[d]	−12.5	−12.5	−12.4	−12.3	−12.3	−12.7	−12.8
rad5	−39.3[c]	−37.5	−37.5	−37.3	−37.3	−37.3	−37.3	−37.5
rad6	27.5[c]	25.3	25.5	25.1	25.3	25.1	27.0	24.7
rad7	53.5[c]	53.8	53.6	53.7	53.7	53.7	54.6	53.3
rad8	19.2[c]	18.0	18.0	17.6	18.0	17.8	19.9	17.3
rad9	−5.0[c]	−5.3	−5.4	−5.4	−5.3	−5.3	−5.4	−5.3
rad10	−50.0[c]	−46.5	−46.4	−46.3	−46.3	−46.3	−46.2	−46.5
rad11	19.2[c]	19.4	19.0	18.4	19.0	18.8	21.2	17.9
rad12	−21.5[c]	−22.0	−22.1	−21.8	−21.5	−21.9	−22.2	−22.3
rad13	44.4[c]	43.2	43.2	42.8	43.3	43.0	49.1	43.5
rad14	24.4[c]	26.8	24.6	24.5	25.5	24.3	25.3	24.8
rad15	30.6[c]	32.6	30.6	30.3	31.2	30.2	31.2	30.8
rad16	−7.3[c]	−7.1	−7.2	−7.2	−7.1	−7.1	−7.3	−7.3
rad17	−8.6[c]	−8.1	−8.2	−8.2	−8.1	−8.1	−8.4	−8.4
rad18	21.2[c]	22.3	22.0	21.8	22.2	22.2	21.9	21.7
rad19	−2.7[c]	−2.9	−3.3	−4.5	−2.8	−4.3	−3.3	−2.8
rad20	6.8[c]	5.2	5.3	5.4	5.5	5.4	5.0	5.0
rad21	4.6[c]	4.1	4.4	3.9	4.5	4.5	3.9	3.6
rad22	4.1[c]	2.7	2.8	2.7	3.0	3.1	2.3	2.3
rad23	16.0[c]	13.4	13.7	13.4	13.9	13.3	15.9	13.0
rad24	−28.7[c]	−29.6	−29.4	−29.6	−29.3	−29.3	−29.7	−29.9
rad25	−32.0[c]	−32.0	−32.1	−32.0	−31.8	−32.0	−32.0	−32.4
rad26	−3.8[c]	−4.0	−4.4	−5.5	−3.7	−5.4	−4.4	−3.9
rad27	−31.2[c]	−34.3	−33.5	−33.0	−32.7	−33.2	−33.9	−34.2
rad28	−31.1[c]	−34.0	−33.1	−32.4	−32.1	−32.5	−33.4	−33.9
rad29	−15.6[c]	−13.6	−13.1	−13.2	−12.3	−12.5	−13.7	−14.1
rad30	−15.8[c]	−15.8	−15.4	−15.0	−14.9	−14.9	−15.9	−16.2

[a]Basis set 6-311++G(3df,2p) was used to obtain all the energies. CCSD(T)/6-311++G(3df,2p) energies obtained by extrapolation. Geometries were optimized at B3LYP/6-311+G(d,p). [b]Ref 76. [c]Ref 30. [d]Ref 77.

with B97-D and LC-ωPBE were reported by Wheeler and co-workers, where the performance of these functionals improved at higher reaction classes.[45] This is partly due to the smaller molecular size of fragments involved in CBH-1 that do not fully benefit from the improved long-range description relative to the larger reference molecules used in CBH-2. Among the different density functionals, CAM-B3LYP, ωB97xD, and LC-ωPBE resulted in minimum MADs.

Among wave function-based methods, the MADs of heats of formation were similar for MP2 and CCSD(T) at CBH-2. However, for some of the radicals namely, **rad6, rad8, rad11, rad13,** and **rad23** the heats of formation evaluated by MP2 and CCSD(T) (Table S10 in Supporting Information) varied by more than 2 kcal/mol. On further examination, we observed that most of these radicals suffer from significant spin contamination ($\langle S^2 \rangle$ values at the HF level greater than 0.8). It is well-known for the MP2 calculations that the spin contamination can slightly raise the total energies due to presence of a high energy spin state. This suggests that accurate error cancelation through our CBH schemes may not be observed in such cases. However, the CBH schemes for these radicals (Table S4 in Supporting Information) are such that the one of the fragments also has a similar spin contamination, the MP2 results are thus off by only 2 kcal/mol against the CCSD(T) results for most of the radicals. For CCSD(T), spin contamination tends to have less effect on the results, and thus,

for the above-mentioned radicals, the CCSD(T) results are in excellent agreement with the reference values. To verify that our extrapolated CCSD(T) results (that use the MP2 energies from larger basis sets) did not suffer from any artifacts, we performed direct CCSD(T)/6-311++G(3df,2p) calculations (without any extrapolation) on the three systems with the largest spin contamination. We observe that the reaction energies and hence the heats of formation calculated by extrapolated and nonextrapolated CCSD(T)/6-311++G-(3df,2p) are in excellent agreement (Table S21 in Supporting Information) for **rad2, rad7,** and **rad13** having $\langle S^2 \rangle$ values 0.886, 0.955, and 1.109 respectively. Hence, we prescribe our extrapolated CCSD(T)/6-311++G(3df,2p) calculations to provide accurate heats of formation for radicals having significant spin contamination.

The situation for the cyclic molecules is somewhat different, though it should be noted that the number of examples is small. As noted previously,[40] the strain energy in such molecules may not be canceled as well in the CBH reaction schemes. This leads to larger reaction energies for strained molecules (than for the unstrained acyclic systems), even at CBH-2. However, the calculated heats of formation are still very accurate with good levels of theory. In particular, it is observed that the MP2 and CCSD(T) yield heats of formation within 1 kcal/mol. In the case of the density functionals, the MADs of heats of formation for cyclic systems occur over the broader range 0.7−3.0 kcal/

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mol, even at CBH-2. This appears to be due to the fact that among the five cyclic systems, two derivatives each of oxirane and oxetane involve high strain energies that are not uniformly described with the different functionals, leading to a larger spread of reaction energies (Table S10 in Supporting Information) resulting in larger calculated deviations. Cyclopentanyl radical (**rad1**) suffers less ring strain, and hence, the CBH-2 reaction energies are small, akin to acyclic systems. Overall, despite the high reaction energies for the ring strained radicals, the calculated heats of formation at CBH-2 are in good agreement with the available literature values. However, B97-D and PBEPBE performed comparatively poorly for the cyclic systems. Overestimation of reaction energies by B97-D was also reported by Wheeler and co-workers leading to disagreement with the CCSD(T)/CBS reference values at lower reaction classes.[45] CAM-B3LYP, ωB97xD, and PBE1PBE outperformed the other density functionals at CBH-2.

Among the Minnesota functionals, M06-2X performed better than M05-2X at CBH-2 for all the ring strained cyclic systems. The performance of long-range corrected functional CAM-B3LYP improves dramatically from CBH-1 to CBH-2 for the cyclic systems as seen from Table 1. The hybrid form of PBE functional, PBE1PBE (commonly known as PBE0) that uses 25% exact exchange, performed much better than the pure PBE functional for cyclic as well as acyclic systems. Finally, additional calculations with the smaller Pople's 6-31+G(d,p), and Dunning's aug-cc-pVDZ basis sets performed with the B2PLYP functional showed that the trend in our results are consistent across different basis sets at both CBH-1 and CBH-2 (Table 3).

Table 3. Mean Absolute Deviations (kcal/mol) of Calculated Heats of Formation with Different Basis Sets Using B2PLYP Functional

	cyclic		acyclic	
basis set	CBH-1	CBH-2	CBH-1	CBH-2
6-311++G(3df,2p)	0.68	1.04	1.28	1.20
6-31+G(d,p)	1.10	1.25	0.76	1.17
aug-cc-pVDZ	1.96	1.27	0.88	1.20

■ PREDICTION OF HEATS OF FORMATION OF 19 RADICALS

In this section, we predict heats of formation of 19 medium and large sized radicals at CBH-2.[65] Heats of formation of some of these radicals are experimentally reported with large or missing uncertainty or there are a few cases where different computational studies are in disagreement. We perform our calculations with the best density functionals and wave function-based methods (MP2 and CCSD(T)) to evaluate accurate heats of formation of these radicals. Figure 3 represents the structures of the 19 radicals consisting of bicyclic systems as well as radicals containing O and N heteroatoms.

In order to derive accurate heats of formation in good agreement with experiments, it may be important to take into account other low lying conformations in addition to the lowest energy conformer.[41,66,67] Thus, we performed conformational search for each of these radicals and included the conformers having a population of greater than 5%, as they contribute significantly to the overall heat of formation. We first calculated the individual enthalpies of formations for each conformation

(ΔH_i) and then obtain the weighted enthalpy of formation (ΔH) as

$$\Delta H = \sum_{i=1}^{n} X_i \Delta H_i$$

where n is the number of conformations considered.[68] X_i refers to the weight of the ith conformer and is obtained by Boltzmann-weighting the relative free energies (referenced to the lowest energy conformer) as

$$X_i = \left\{ \frac{e^{-\Delta G_i / RT}}{\sum_{i=1}^{n} e^{-\Delta G_i / RT}} \right\}$$

The first three radicals considered (**1−3**) have low experimental uncertainties. The two conformers of THF-2-yl (**1**) were found to have C1 point group symmetry. The calculated heat of formation of **1** after taking account of both conformers is −1.5 kcal/mol with CCSD(T), within 1 kcal/mol of the experimental value. The different DFT methods have a range of over 3 kcal/mol, with the largest deviation for PBE1PBE and the lowest deviation for M06-2X (Table 4). Similarly, two different conformers of THF-3-yl (**2**) also have C1 symmetry. The calculated heats of formation of **2** at various levels of theory are in good agreement with the previous results and with experiment.[69] Two low energy conformers were considered for **3**, which resulted in values that are in agreement with the experimental results at both MP2 and CCSD(T) levels. However, an important factor must be noted. The CBH-2 scheme for the radical **3** involved certain fragments whose heats of formation were unknown. In such cases, we have applied CCSD(T) calculations at CBH-1 (Table S18 in Supporting Information) to derive the heats of formation for those fragments. This is a useful strategy that can extend the range of applicability of our CBH approach to more important systems.

The calculated heat of formation of species **4** differs from the available experimental value by over 12 kcal/mol. The calculated results are internally consistent between the different density functionals as well as wave function-based methods. The calculated spin contamination in the starting UHF wave function is also small for both conformers, and should not lead to any significant deficiency. Thus, the heat of formation obtained by CCSD(T) calculations at CBH-2 should be more reliable than the experiments. The calculated heats of formation of radicals 1,4-dioxan-2-yl (**5**) and cyclopentanon-2-yl (**6**) differ by a smaller amount from the experimental reports. However, the experimental results report larger uncertainities in these values. The calculated values for **5** are within these uncertainties while a residual deviation is noted for **6** at the CCSD(T) level. We recommend the use of our CCSD(T) calculated heats of formation in such instances.

Four other monocyclic systems, namely pyrrolidin-2-yl (**7**), cyclohexyl (**9**), cycloheptyl (**10**), and cyclooctanyl (**13**) were also tested. The calculated heats of formation were mostly in agreement with experimental results (Table 4) except for cycloheptyl (**10**). Our calculations for cycloheptyl resulted in values that differ by 5 kcal/mol from experiment, and hence, we recommend use of our calculated values. Many of the density functionals also show similar performance for the simpler cyclic hydrocarbon systems.

Next, we performed calculations for some bicyclic systems like adamantan-1-yl (**11**), adamantan-2-yl (**12**), norborn-1-yl
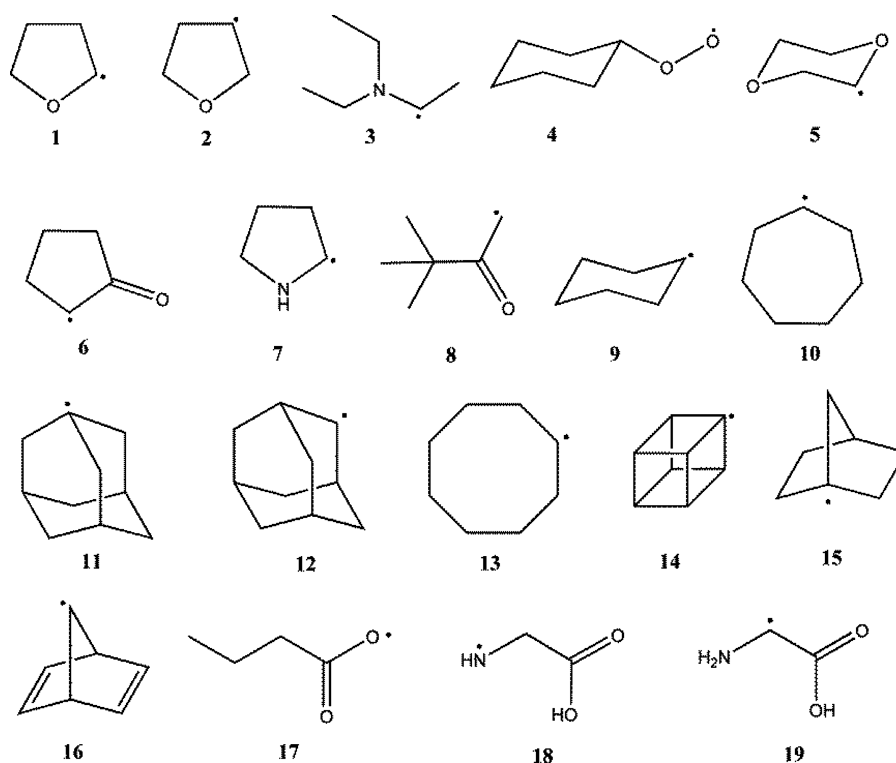
Figure 3. Structures of 19 radicals whose heats of formation are predicted using CBH-2 at various levels of theory.

Table 4. Enthalpies of Formation (kcal/mol) of Radicals 1−19 Taking into Account Multiple Conformations at the CBH-2 Rung[a]
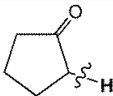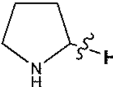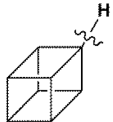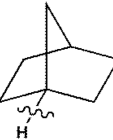
species	literature	M06-2X	ωB97xD	B2PLYP	CAM-B3LYP	PBE1PBE	MP2	CCSD(T)
1	−0.5 ± 1.0[b]	−0.3	−2.4	−2.5	−2.2	−3.3	−1.6	−1.5
2	3.6 ± 1.0[b]	5.8	5.5	4.4	5.3	4.5	4.0	4.0
3	16.4 ± 0.5[c]	17.8	17.3	18.5	19.2	18.9	16.8	16.6
4	−6.0 ± 2.5[c]	−17.6	−18.3	−19.1	−18.1	−18.6	−19.9	−19.4
5	−31.5 ± 3.0[c]	−28.0	−28.7	−28.8	−28.1	−29.0	−29.0	−29.5
6	−10.0 ± 3.0[c]	−4.5	−5.7	−6.8	−6.4	−7.3	−6.7	−5.3
7	34.1 ± 3.0[c]	39.1	38.1	37.2	37.7	37.0	37.4	37.5
8	−27.6 ± 3.0[c]	−26.3	−25.9	−25.7	−25.2	−25.4	−26.6	−26.4
9	18.0 ± 1.5[c]	20.0	19.6	18.8	19.4	19.0	18.4	18.7
10	12.1 ± 1.0[c]	17.9	17.1	17.3	18.1	17.8	16.6	16.7
11	12.3[c]	19.1	17.4	13.8	16.9	15.0	10.9	12.7
12	14.8[c]	21.0	18.7	15.4	17.8	16.1	13.5	15.1
13	14.2[c]	14.6	13.9	15.2	16.5	16.0	13.3	13.5
14	198.6 ± 4.0[c]	199.3	191.3	186.4	188.6	184.1	197.2	194.5
15	32.6 ± 2.5[c]	44.0	43.3	40.3	42.6	40.8	38.5	39.7
16	122.3 ± 1.9[c]	115.8	114.5	110.4	114.1	111.4	106.6	109.5
17	−59.6[d]	−55.6	−55.5	−53.7	−55.3	−55.3	−55.8	−55.9
18	−43.2[e]	−46.3	−46.1	−45.9	−46.0	−46.3	−46.0	−46.0
19	−66.7[e]	−68. 0	−67.8	−67.6	−68.0	−68.1	−68.3	−66.4

[a]The geometries were obtained at the B3LYP/6-311+G(d,p) level of theory. 6-311++G(3df,2p) basis set was used to obtain all the energies. CCSD(T)/6-311++G(3df,2p) energies obtained by extrapolation. The individual weights and heats of formation for the different conformers are provided in the Supporting Information. [b]Ref 69. [c]Ref 76. [d]Ref 77. [e]Ref 73.

(**15**), and norborna-2,5-dien-7-yl (**16**). To the best of our knowledge, we are the first to calculate heats of formation of such radicals. In addition, an increased interest in bridgehead C−H bond dissociation enthalpies in recent papers[70,71] has encouraged us to use our CBH-2 scheme to predict accurate thermochemistry for such important systems. The heats of formation of **11** and **12** obtained by CCSD(T) calculations led to values that differ from experimental results by 0.4 and 0.3

kcal/mol, respectively. The uncertainty of the experimental results was not listed and so our CCSD(T) calculations suggest that 12.7 and 15.1 kcal/mol are accurate heats of formation of **11** and **12**. The density functionals show a relatively broad range of 7 kcal/mol. The tricyclic cubyl (**14**) radical was also studied. Despite the ring strain and the corresponding high reaction energies, our results are within the larger uncertainty of the experiment results (Table 4). The density functionals had

Table 5. Bond Dissociation Energies (BDE) of Radicals Taking into Account Multiple Conformations at the CBH-2 Rung in kcal/mol

The broken bonds (**boldface** = dissociated atom)	Literature	Present work[a]
	94.8[b]	94.0
	90.1 ± 2.4[c]	90.4
	102 ± 4,[d] 106.9[e]	102.4
	96.7 ± 2.5,[b] 105.7 ± 2.0,[f] 107.3[g]	104.9

[a]BDEs were calculated using heats of formation obtained by our CCSD(T) calculations. [b]Ref 78. [c]Ref 79. [d]Ref 80. [e]Ref 81. [f]Ref 70. [g]Ref 71.

substantial deviations for this system, except M06-2X. Hence, for highly strained systems, it may be useful to explore the performance of higher CBH rungs to see if the performance is more uniform across different methods.

Next, for norborn-1-yl (**15**) and norborna-2,5-dien-7-yl (**16**) radicals, the calculated and experimental heats of formation are in disagreement, as seen in Table 4. The calculated heats of formation using CCSD(T) are 39.7 and 109.5 kcal/mol against the experimental value of 32.6 ± 2.5 and 122.3 ± 1.9 kcal/mol respectively for **15** and **16**. The spin contaminations for radicals **15** and **16** are also very small, suggesting that they do not play a role in this discrepancy. Previous ab initio calculations along with bond and group equivalent schemes on radical **15** by Allinger et al. resulted in a value of 38.0 kcal/mol,[72] in concordance with our result. We thus recommend the calculated values of 39.7 and 109.5 kcal/mol for the radicals **15** and **16** and suggest further analysis of the experiments. The results using different density functional methods, while they show some variations, are closer to the CCSD(T) values. For radical **17** three different conformers were considered for the determination of its heat of formation. The heats of formation of **17** were found to be −55.9 and −55.3 kcal/mol with CCSD(T) and PBE1PBE calculations, respectively, which are in agreement with the available experiments. The results obtained with other density functionals are in close agreement with the ones obtained with CCSD(T).

Two different glycine derived radicals **18** and **19** were also studied. G2(MP2) calculations on these radicals were performed by Yu et al. in 1995.[73] However, despite all the advances since then, no other studies have reported heats of formation of such amino acid derived radicals. We applied our CBH-2 on these glycine derived radicals to obtain their accurate heats of formation. Two low energy lying conformers for radical **19** were taken into account for the evaluation of its heat of formation. The calculated $\langle S^2 \rangle$ suggests little spin contamination, and thus, the present scheme can be used for the evaluation of their heats of formation. The CCSD(T) heat of formation of nitrogen-centered radical **18** was found to be

−46.0 kcal/mol, which differs by 3 kcal/mol from the previous G2(MP2) calculations using an isodesmic reaction scheme. A detailed examination suggests that part of this discrepancy is partly due to the fact that Yu et al. used a value 43.5 kcal/mol for ΔH_f° for $CH_3NH^\bullet$, while we used an improved value of 42.3 kcal/mol.[14] It should be noted that the success of any such hierarchy depends on the accuracy of the available heats of formation. However, for the carbon-centered radical **19**, the heat of formation was calculated to be −66.4 kcal/mol with CCSD(T), which is in good agreement with the G2(MP2) calculations. Overall, with modest levels of theory at CBH-2, we can derive accurate heats of formation of amino-acid derived radicals.

While most of the radicals studied here yield results in excellent agreement with previous experimental results, some of them differ by more than the experimental uncertainty. For a few select cases where the deviations are large (**6**, **7**, **14**, and **15**), we obtained bond dissociation energies (BDE) of the corresponding closed shell analogues to assess the accuracy of our calculated thermochemistry of radicals (Table 5). The C−H BDEs were obtained using our CCSD(T) calculated heats of formations of the radicals[74] and heats of formation of the corresponding closed shell systems.[75] Table 5 compares our calculated BDEs with previous experimental or theoretical results. For radicals **6** and **7**, where the calculated ΔH_f° values differ significantly from the experimental results, we observe that our BDEs are in good agreement with the previous experimental results. Thus, the BDEs can be better reproduced with our calculated ΔH_f° values of the radicals than with the corresponding experimental values. The inconsistencies of the experimental ΔH_f° values with the BDEs leads us to recommend the CCSD(T) calculated ΔH_f° values for radicals **6** and **7** over the experimental values. Similarly, for cubane with C−H bond cleavage resulting in radical **14**, the calculated BDE is well within the experimental errors. For radical **15**, a set of rigorous CBS-Q calculations were recently performed that resulted in a value of 107.3 kcal/mol for the C−H BDE.[71] We find that using our calculated ΔH_f° value of **15**, the resulting

C−H BDE (104.9 kcal/mol) is closer to the reported value 107.3 kcal/mol than when the experimental ΔH_f° value is used (97.8 kcal/mol). Thus, we recommend CCSD(T) calculated ΔH_f° values for these radicals having significant deviations from the experimental ΔH_f° values.

CONCLUSIONS AND SCOPE

In this work, we have applied our connectivity-based hierarchy (CBH)[39] to evaluate accurate thermochemical parameters of 30 organic radicals containing various functional groups. We find that similar to our previous findings for closed shell molecules,[39−41] the CBH-2 scheme is sufficient for obtaining accurate thermochemistry for open shell systems having low spin contamination. Both cyclic and acyclic systems were tested with density functionals and wave function-based methods. The results obtained by long-range density functionals and dispersion corrected functionals are in good agreement with the expensive CCSD(T) calculations. Among the DFT methods, CAM-B3LYP, PBE1PBE, and ωB97xD gave the best results for both cyclic and acyclic systems with the CBH-2 schemes. Additionally, the heats of formation of 19 large and medium sized radicals have been calculated at CBH-2 with DFTs and wave function-based methods that performed best for our test set. For most of these 19 radicals, the calculated heats of formation are within the reported experimental uncertainties. For a chosen set of such radicals, we observed a good agreement of the concerned C−H bond dissociation energies (BDE) with available experimental or computed BDEs. Hence, we propose that calculations at CBH-2 with the chosen DFTs and wave function-based methods can be used for prediction of heats of formation of organic radicals. CBH-2 can further be applied for evaluation of accurate bond dissociation energies (BDE), ring strain energies, and reaction energies corresponding to radical addition and polymerization. Interesting applications with complex systems such as radical cations and radical anions are under progress.

ASSOCIATED CONTENT

Ⓢ Supporting Information

CBH-1 and CBH-2 reaction schemes for all the 30 radicals in CBH-rad30 test set, CBH-2 reaction schemes for radicals **1−19**, and the corresponding electronic energies at various levels of theory, structures of the optimized geometries of all the conformers used, and Cartesian coordinates of all the 49 radicals are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*Email: kraghava@indiana.edu.

Notes
The authors declare no competing financial interest.

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(60) Table S13 and Table S14 in the Supporting Information contain the calculated reaction energies and heats of formation of the 30 radicals of CBH-rad30 test set at CBH-1 and CBH-2 using MP2 optimized geometries.

(61) Table S20 in Supporting Information contains a complete list of heats of formation of CBH fragments and their references.

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(65) Refer Table S15 in Supporting Information for CBH-2 schemes for radicals **1−19**.

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