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Bond Dissociation Energies and Radical Stabilization Energies: An Assessment of Contemporary Theoretical Procedures

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Various contemporary theoretical procedures have been tested for their accuracy in predicting the bond dissociation energies (BDEs) and the radical stabilization energies (RSEs) for a test set of 22 monosubstituted methyl radicals. The procedures considered include the high-level W1, W1′, CBS-QB3, ROCBS-QB3, G3-(MP2)-RAD, and G3X(MP2)-RAD methods, unrestricted and restricted versions of the double-hybrid density functional theory (DFT) procedures B2-PLYP and MPW2-PLYP, and unrestricted and restricted versions of the hybrid DFT procedures BMK and MPWB1K, as well as the unrestricted DFT procedures UM05 and UM05-2X. The high-level composite procedures show very good agreement with experiment and are used to evaluate the performance of the comparatively less expensive DFT procedures. RMPWB1K and both RBMK and UBMK give very promising results for absolute BDEs, while additionally restricted and unrestricted X2-PLYP methods and UM05-2X give excellent RSE values. UM05, UB2-PLYP, UMPW2-PLYP, UM05-2X, and UMPWB1K are among the less well performing methods for BDEs, while UMPWB1K and UM05 perform less well for RSEs. The high-level theoretical results are used to recommend alternative experimental BDEs for propyne, acetaldehyde, and acetic acid.

1. Introduction

The effect of substituents on the thermodynamic stability of radicals is of widespread chemical interest. There have been numerous experimental[1,2] and theoretical[3] studies carried out to quantify such effects, and the topic has recently been reviewed.[4] The homolytic bond dissociation energy (BDE) is recognized as an important thermodynamic quantity that can provide a measure of radical stability. For CH_3X molecules, the C−H BDE is defined as the enthalpy change for the reaction

$$CH_3X \rightarrow \bullet CH_2X + \bullet H \qquad (1)$$

A related convenient measure of the effect of a substituent on the stability of a radical, relative to its effect in the parent closed-shell molecule, is the radical stabilization energy (RSE). For monosubstituted methyl radicals, viz, $\bullet CH_2X$, the RSE is commonly defined as the energy change in the isodesmic reaction:

$$\bullet CH_2X + CH_4 \rightarrow CH_3X + \bullet CH_3 \qquad (2)$$

Equivalently, the radical stabilization energy is equal to the difference between the bond dissociation energy (BDE) of the reference species (in this case, methane) and the bond dissociation energy of the substituted species:

$$\mathrm{RSE}(\bullet CH_2X) = \mathrm{BDE}(CH_4) - \mathrm{BDE}(CH_3X) \qquad (3)$$

Defined in this way, a positive value for the RSE implies a net stabilization of the substituted radical with respect to the reference radical relative to the same effect in the parent closed-shell species, while a negative value implies a net destabilization. Because the errors for any particular theoretical method in the calculation of absolute BDEs are generally systematic, cancellation of errors in eq 3 might be expected to lead to improved results for RSEs.

In previous work,[5] we investigated the performance of a variety of theoretical methods for the calculation of radical stabilization energies of six substituted methyl and vinyl radicals. We found that the commonly used UMP procedure, and to a lesser extent UHF and PMP, performed poorly for radicals with significant spin contamination in the wave function. On the other hand, the RSEs calculated with RMP2/6-311+G(2df,p) single-point energies on RMP2/6-31G(d) or UB3-LYP/6-31G(d) optimized geometries were computationally inexpensive and generally good.

More recently, we studied the BDEs and RSEs associated with a series of 22 monosubstituted methyl radicals at the CBS-RAD, G3(MP2)-RAD, RMP2, UB3-LYP, and RB3-LYP levels of theory.[3] The high-level W1′ method was also used for a subset of the smaller species in the set. Most of the substituents (except those with an electronegative inductive effect) were found to stabilize the radical center, either by permitting delocalization of the unpaired electron into an adjacent π system, through hyperconjugative interaction, or by having a three-electron bonding interaction between the unpaired electron at the radical center and a nonbonding pair of electrons on the heteroatom. In a manner similar to that of a previous study,[6] CBS-RAD was found to give results close to those of W1′, proving to be a reliable and efficient procedure for calculating free radical thermochemistry. G3(MP2)-RAD also showed reasonable agreement with W1′ and CBS-RAD. Single-point calculations with the less expensive RB3-LYP/6-311+G(3df,2p)//RB3-LYP/6-31G(d), RMP2/6-311+G(3df,2p)//RMP2/6-31G(d), and RMP2/6-311+G(3df,2p)//UB3-LYP/6-31G(d) methods gave satisfactory performance, while RSEs calculated by UB3-LYP/6-311+G(3df,2p)//UB3-LYP/6-31G(d) showed somewhat larger deviations.

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There have been a number of subsequent theoretical studies of bond dissociation energies.[7−12] The most extensive study among these was that of Guo et al.,[7] who tested the reliability of experimental values for the BDEs of 200 molecules against high-level CBS-Q and G3 results. They also tested the reliability of several DFT methods. They reported that although DFT methods are popular as inexpensive alternatives of sophisticated ab initio methods for the calculation of BDEs, the underestimation of BDEs is always a disadvantage for most DFT methods and the magnitude of the underestimation varies from system to system. This matches the observation of many previous and later studies.[3,12−14] Nevertheless, the hybrid functional B3-P86, in combination with Pople basis sets like 6-311+G(d,p) or 6-311G(2d,2p) on UB3-LYP/6-31G(d) or B3-P86/6-31G(d) geometries, has been recommended[10−12,15] on the basis of its modest underestimation of BDEs. Yao et al.[11] and Fu et al.[12] found that the restricted DFT methods that they examined predicted larger BDE values than their unrestricted counterparts.

In this paper, we extend our previous study[3] of the assessment of theoretical procedures in calculating the effect of substituents on radical stabilization energies in two ways. First, access to improved computational resources has allowed the extension of W1 (or W1′) calculations[16] to most of the larger species in the test set. Second, more recently introduced procedures including the restricted-open-shell variant of CBS-QB3,[17] namely ROCBS-QB3,[18] a modified G3X(MP2) procedure,[19] namely G3X(MP2)-RAD,[20] and the double-hybrid density functional procedures UB2-PLYP,[21] RB2-PLYP, UMPW2-PLYP,[22] and RMPW2-PLYP, as well as several hybrid density functionals, viz, UBMK, RBMK,[23] UMPWB1K, RMPWB1K,[24] UM05,[25] and UM05-2X,[25,26] have been tested for their performance with regard to radical thermochemistry. W2 calculations[16a] have also been performed for a small set of radicals for which our other theoretical results showed large deviations from currently recommended experimental BDEs. We use the same set of carbon-centered radicals as in ref 3 to enable a consistent comparison of results.

2. Theoretical Procedures

Standard ab initio molecular orbital theory[27] and density functional theory (DFT)[28] calculations were carried out with the Gaussian 03,[29] Molpro 2002.6,[30] Aces II,[31] and NWCHEM 5[32] computer programs. Bond dissociation energies and associated radical stabilization energies at 0 K were calculated with a number of theoretical procedures for the set of 22 reactions from ref 3 that lead to carbon-centered radicals. It has previously been found that the geometries optimized at the UB3-LYP/6-31G(d) and RB3-LYP/6-31G(d) levels are generally very similar for the radicals under examination. Unless otherwise noted, RB3-LYP/6-31G(d) geometries[3] were used throughout this study to enable consistent comparisons. Harmonic vibrational frequencies were computed at the RB3-LYP/6-31G(d) level and used (after appropriate scaling)[33] to provide zero-point vibrational energies (ZPVEs).[3] For the W1, W1′, CBS-QB3, and ROCBS-QB3 methods, we used the prescribed geometries and ZPVEs, specifically, UB3-LYP/cc-pVTZ (for W1), UB3-LYP/cc-pVTZ+1 (for W1′, where +1 indicates additional d-type inner polarization function for second- and third-row atoms), and UB3-LYP/6-311G(2d,d,p) (for CBS-QB3 and ROCBS-QB3). To facilitate comparisons with W1, W2 calculations were also carried out using UB3-LYP/cc-pVTZ geometries. Calculations on radicals that were performed with a restricted-open-shell reference wave function are designated with an “R” prefix, while calculations using an unrestricted wave function are designated with a “U” prefix.

We have chosen W1 as the benchmark theoretical method, as it has been shown to give good agreement with reliable experimental thermochemistry.[16a] For systems containing second-row and third-row elements, the W1′ procedure,[16b] in which the basis set sequence for extrapolations, AVDZ+2d, AVTZ+2d, and AVQZ+2d1f, replaces the W1 sequence, AVDZ+2d, AVTZ+2d1f, and AVQZ+2d1f, for second- and third-row elements, has been used.[34] W1 and W1′ results for a subset of the radicals surveyed in this study have been previously published[3] but with the use of Martin’s original three-point extrapolation procedure. In the present study, later recommendations[35] to use a two-point extrapolation and to exclude from the correlation space the very deep-lying (1s) orbitals on second-row elements in core-correlation calculations have been followed. We loosely refer to these procedures (W1 and W1′) collectively as W1 within the text.

For three radicals, $\bullet CH_2COOH$, $\bullet CH_2CHO$, and $\bullet CH_2C{\equiv}CH$, for which the BDE and RSE values predicted by the W1 method show large differences from currently recommended experimental values,[2] we also used the higher-level W2[16a] procedure to try to resolve the apparent discrepancy between theory and experiment. In these calculations, the W2 method was employed in conjunction with the use of UB3-LYP/cc-pVTZ geometries and the two-point extrapolation procedure,[35] as well as the more rigorous Douglas−Kroll method at the CCSD(T)/MTsmall level[36] for obtaining the scalar relativistic correction.

Additional high-level composite procedures, G3(MP2)-RAD,[20] G3X(MP2)-RAD,[20] CBS-QB3,[17] and its recently formulated restricted-open-shell variant, ROCBS-QB3,[18] were also used to determine BDEs and RSEs. It is of interest to see how the performance of G3X(MP2)-RAD compares with that of G3-(MP2)-RAD, how CBS-QB3 compares with ROCBS-QB3, and how they all compare with W1.

Finally, single-point calculations were carried out on the RB3-LYP/6-31G(d) optimized geometries using a variety of standard DFT methods in combination with the 6-311+G(3df,2p) basis set. The restricted and unrestricted versions of the double-hybrid methods, B2-PLYP[21] and MPW2-PLYP,[22] and the hybrid meta GGAs, BMK,[23] and MPWB1K,[24] as well as the unrestricted versions of the M05[25] and M05-2X[25,26] functionals, were tested for their performance in calculating absolute and relative bond dissociation energies. BMK and MPWB1K are generally regarded as cost-effective DFT methods for calculating thermochemistry.[8h] UM05 and UM05-2X[25,26] are hybrid meta exchange-correlation functionals designed for thermochemistry, thermochemical kinetics, and noncovalent interactions, with UM05-2X specially recommended for calculating bond dissociation energies for systems that do not include metal atoms. B2-PLYP[21] and MPW2-PLYP[22] are double-hybrid density functionals related to B-LYP and MPW-LYP. Besides including a proportion of exact HF exchange, they also include a perturbative second-order correlation contribution. These functionals have been very recently introduced by Grimme[21,22] and have been found to show promising performance in calculating thermochemical properties.

3. Results and Discussion

3.1. Bond Dissociation Energies. Bond dissociation energies for the monosubstituted methanes calculated at various levels of theory are compared with experiment in Table 1. The mean deviations (MDs), mean absolute deviations (MADs), and largest deviations (LDs), both from experimental values and from the W1 results, are also listed.

3.1.1. Experimental Data. A comprehensive and critical compilation of experimental BDE data has been published by

TABLE 1. Comparison of Calculated Bond Dissociation Energies for $CH_3X \rightarrow \bullet CH_2X + \bullet H$ with Experimental Values (0 K, kJ mol^{-1})

radical ($\bullet CH_2X$)	UBMK	RBMK	UMPWB1K	RMPWB1K	UMO5	UMO5-2X	UB2-PLYP	RB2-PLYP	UMPW2-PLYP	RMPW2-PLYP	G3(MP2)-RAD	G3X(MP2)-RAD	CBS-QB3	ROCBS-QB3	W1^a	expt^b
$\bullet CH_3$	428.6	432.7	430.4	434.4	423.5	426.7	421.9	425.7	422.7	426.7	428.4	429.1	434.2	433.4	432.3	432.4 ± 0.4
$\bullet CH_2NH_2$	376.5	380.4	375.8	380.1	373.9	376.2	371.6	375.2	372.6	376.5	384.1	383.9	384.6	383.9	383.0	386.8 ± 8.4
$\bullet CH_2OH$	391.5	395.3	391.1	395.2	388.8	392.4	386.7	390.2	387.6	391.5	396.8	396.6	399.1	398.5	397.0	395.8 ± 0.63
$\bullet CH_2OCH_3$	391.3	394.9	393.0	395.5	388.8	392.9	386.4	389.8	387.5	391.3	397.3	397.1	399.4	398.9	397.1	395.7^c
$\bullet CH_2F$	414.3	417.9	412.8	416.6	410.6	414.2	407.7	411.3	408.6	412.4	415.9	416.0	419.6	419.0	417.5	417.4 ± 4.2
$\bullet CH_2CH_3$	413.1	417.6	411.3	415.5	402.9	410.3	405.9	409.9	406.6	410.7	414.2	414.5	418.0	417.3	416.5	413.0 ± 1.3
$\bullet CH_2CH_2CH_3$	416.2	420.5	415.3	419.1	406.4	413.6	409.1	412.9	409.8	413.9	415.9	417.8	420.9	420.1	419.6	414.8 ± 2.1
$\bullet CH_2CF_3$	436.5	440.8	435.8	438.7	425.8	433.4	427.4	431.2	428.4	432.4	436.1	434.8	440.8	440.0	438.4	439.3 ± 4.5
$\bullet CH_2CF_2CF_3$	433.0	437.3	433.1	435.5	422.8	430.5	424.5	428.3	425.5	429.5	433.3	433.2	437.3			
$\bullet CH_2PH_2$	399.7	404.5	399.5	404.7	391.7	399.6	394.6	399.0	395.3	400.1	405.1	405.2	405.8	405.9	405.4^a	
$\bullet CH_2SH$	392.7	397.4	387.0	392.1	381.6	387.3	382.5	386.5	383.5	388.0	392.2	391.8	392.8	392.5	390.9^a	386.3 ± 8.4
$\bullet CH_2Cl$	409.9	414.5	404.0	408.7	398.4	404.8	400.1	404.2	400.9	405.4	407.2	406.7	410.5	410.1	409.3^a	411.9 ± 2.3
$\bullet CH_2Br$	412.8	417.5	409.8	414.6	402.7	414.1	406.3	410.3	407.1	411.4			424.1			410.3 ± 2.4
$\bullet CH_2BH_2$	382.8	385.9	386.0	388.6	381.8	385.0	380.5	383.2	381.1	383.9	388.3	388.2	391.5	391.8	391.4	
$\bullet CH_2CH{=}CH_2$	356.0	368.2	353.2	367.0	340.3	351.3	351.5	356.6	351.5	358.7	357.7	358.0	359.4	359.0	362.0	363.5 ± 3
$\bullet CH_2C{\equiv}CH$	371.4	381.7	368.5	380.0	357.7	368.8	367.4	370.6	367.9	372.8	375.7	376.2	376.1	377.3	378.7	377.7 ± 4.2^d
$\bullet CH_2C_6H_5$	368.4	377.9	366.8	377.4	353.4	365.7	368.8	368.8	368.7	370.7	369.5	369.8	374.3	370.2	373.2	370.7 ± 5.0
$\bullet CH_2CHO$	390.0	398.9	387.4	397.5	382.4	385.9	386.5	389.0	386.6	390.6	393.4	393.1	393.3	394.9	395.8	392.6^{c,e}
$\bullet CH_2COOH$	405.3	410.7	403.7	409.0	395.4	401.4	398.0	401.4	398.7	402.7	407.2	406.9	409.1	409.4	408.6	407.7 ± 3.3^f
$\bullet CH_2COOCH_3$	405.0	410.3	403.5	408.4	394.6	401.3	397.5	400.9	398.3	402.2	406.8	406.3	408.8	409.0	409.0	401.1 ± 10.5^g
$\bullet CH_2OCOCH_3$	406.1	409.8	405.8	409.4	399.6	407.5	401.1	404.6	402.1	405.9	410.3	408.9	412.3	411.4	414.8	398.4^c
$\bullet CH_2CN$	394.0	403.4	390.1	401.1	381.6	391.9	388.9	391.0	389.3	393.0	396.4	397.6	396.4	398.0	399.2	399.5 ± 4.2
$\bullet CH_2NO_2$	412.5	417.7	413.2	418.7	404.3	412 .6	407.9	411.3	408.9	412.8	416.8	417.7	417.7	417.8	418.8	409.7^c
MD(W1)^h	−4.6	1.1	−5.9	0.0	−13.1	−6. 5	−10.3	−6.9	−9.6	−5.5	−2.1	−2.0	0.3	0.0		
MAD(W1)^h	4.8	2.9	5.9	1.8	13.1	6.5	10.3	6.9	9.6	5.5	2.3	2.2	1.7	1.3		
LD(W1)^h	−8.8	6.5	−10.1	−5.4	−21.7	−10 .7	−11.5	−10.3	−12.7	−8.9	−4.5	−5.9	−2.8	−3.5		
MD(expt)^{c,g,h}	−2.7	3.3	−4.8	1.5	−12.3	−5. 0	−8.9	−5.4	−8.2	−4.0	−1.3	−1.2	2.4	0.8	0.7	
MAD(expt)^{c,g,h}	4.0	4.2	4.9	3.1	12.3	5.6	8.9	5.5	8.2	4.4	2.8	2.8	4.0	2.5	2.1	
LD(expt)^{c,g,h}	−10.2	11.1	−15.1	−11.6	−12.7	−10 .3	−10.1	−7.4	−23.2	−12.2	5.9	±5.5	13.8	6.2	4.8	

[a] W1′ calculations for systems containing second- and third-row elements. [b] Bond dissociation energies at 0 K calculated using experimental BDEs at 298 K from ref 2, unless otherwise noted, with the thermal corrections to 0 K obtained at the RB3-LYP/6-31G(d) level. [c] Species without experimental error bars are not included in the statistics. [d] Calculated using the experimental BDE for propyne reported by Tsang.[37] [e] Calculated using the experimental BDE for acetaldehyde reported by Cummings and Kebarle.[38] [f] Calculated using the experimental BDE for acetic acid reported by Lagoa et al.[39] [g] Species with experimental uncertainties greater than ±10 kJ mol^{-1} are not included in the statistics. [h] MD, MAD, and LD are mean deviation, mean absolute deviation, and largest deviation, respectively, from W1 and experimental values.

Luo.[1] The uncertainties for most of the experimental data listed in Table 1 lie in the 4−8 kJ mol^{-1} range. For most molecules, we have compared our theoretical data with the BDEs recommended by Luo, as summarized in the CRC Handbook of Chemistry and Physics.[2] However, for a small number of molecules (see below), where the recommended values showed large deviations from the results obtained with the benchmark W1 and other high-level theoretical methods, W2 calculations were employed to further assess the accuracy of the theoretical predictions. For these cases, we end up recommending alternative experimental values,[37−39] with uncertainties equal to or even smaller than those for the previously recommended values.

3.1.2. W1 and W2. Examination of Table 1 shows that there is generally close agreement between the W1 BDEs and experimental values. The overall mean absolute deviation of W1 results from experiment is 2.1 kJ mol^{-1}.[40] This close agreement of W1 results with experiment, coupled with the established good performance of W1 with larger test sets of thermochemical data,[35] gives us reasonable confidence in accepting W1 as a benchmark.

The large variation among the experimental BDEs reported in the literature demands caution in selecting appropriate experimental data against which the theoretical results can be compared. Among molecules for which there are significant discrepancies between the latest recommended experimental BDEs[2] and our best calculated values are propyne, acetaldehyde, and acetic acid. For example, when compared with those experimental values (365.6 ± 4.2, 389.2 ± 9.2, and 393.4 ± 12.1 kJ mol^{-1}, respectively), the W1 BDEs for propyne, acetaldehyde, and acetic acid show deviations of +13.1, +6.6, and +15.2 kJ mol^{-1}, respectively. The other high-level methods included in this study also give comparable deviations.

The higher level W2 method was employed to further probe the accuracy of the theoretical results in these cases. W2 predicts bond dissociation energies of 378.8 kJ mol^{-1} for propyne, 395.7 kJ mol^{-1} for acetaldehyde, and 409.2 kJ mol^{-1} for acetic acid, results that are all within 1 kJ mol^{-1} of the corresponding W1 BDEs. Examination of the Luo compendium[1] shows that alternative experimental BDE estimates of Tsang,[37] Cummings and Kebarle,[38] and Lagoa et al.[39] for propyne, acetaldehyde, and acetic acid, respectively, are in much closer agreement with the theoretically predicted BDEs. Our theoretical results therefore suggest that the currently recommended experimental BDEs for propyne, acetaldehyde, and acetic acid should be replaced by the alternative experimental values[37−39] of 377.7 ± 4.2, 392.6, and 407.7 ± 3.3 kJ mol^{-1}, respectively.

The experimental BDEs for nitromethane and methyl acetate (in its dissociation to methyl acetyloxy radical) are reported without experimental error bars and also show large deviations of +9.1 and +16.5 kJ mol^{-1}, respectively, from W1. New experimental data would be of great interest for these species.

3.1.3. Other High-Level Composite Methods. Among the other composite methods tested, ROCBS-QB3 shows the best agreement with W1 for the evaluation of BDEs, with a mean absolute deviation of 1.3 kJ mol^{-1}. The largest deviation of −3.5 kJ mol^{-1} from W1 occurs for propene. The mean absolute deviation of ROCBS-QB3 from experiment (2.5 kJ mol^{-1}) is almost the same as the MAD of W1 from experiment (2.1 kJ mol^{-1}).

Standard CBS-QB3 performs almost as well, with an MAD(W1) of 1.7 kJ mol^{-1}. CBS-QB3 overestimates the BDEs of propane and of two species containing second-row or third-row elements, methanethiol and bromomethane, by 6.1, 6.5, and 13.8 kJ mol^{-1}, respectively, in comparison with experimental values. However, these deviations are not significantly different from the W1 results for the first two species. In general, both ROCBS-QB3 and CBS-QB3 give reliable bond dissociation energies.

G3X(MP2)-RAD also performs reasonably well, showing an MAD of 2.2 kJ mol^{-1} from W1, a slightly larger deviation than that found for the CBS techniques. G3X(MP2)-RAD predicts BDE values very similar to those of G3(MP2)-RAD,[3,41] the latter showing a mean absolute deviation of 2.3 kJ mol^{-1} from W1.

Interestingly, in comparison with experiment, both G3X-(MP2)-RAD and G3(MP2)RAD show an MAD of 2.8 kJ mol^{-1} and show LDs of ±5.5 and ±5.9 kJ mol^{-1}, respectively, which are all smaller than the corresponding deviations shown by CBS-QB3.

3.1.4. DFT Methods. Of the various DFT procedures, RMPWB1K performs the best for BDEs, with an MAD of 1.8 kJ mol^{-1} from W1 and an MAD of 3.1 kJ mol^{-1} from experiment. RBMK also performs well, with an MAD of 2.9 kJ mol^{-1} from W1. Considering the modest cost of these methods, these results are encouraging and are consistent with results of another recent study.[8g] The unrestricted variants UMPWB1K and UBMK do not perform as well and tend to systematically underestimate the BDEs, with MDs consistently being negative. Nevertheless, the mean absolute deviation of UBMK from experiment is still just 4.0 kJ mol^{-1}.

UM05 shows the poorest agreement with W1, with an MAD of 13.1 kJ mol^{-1}. However, there is a significant improvement in going from UM05 to UM05-2X (MAD(W1) = 6.5 kJ mol^{-1}).

Among the double-hybrid X2-PLYP functionals tested in this study, the restricted versions, RMPW2-PLYP (MAD(W1) = 5.5 kJ mol^{-1}) and RB2-PLYP (MAD(W1) = 6.9 kJ mol^{-1}) give better BDE values than their unrestricted counterparts. However, both the restricted and unrestricted X2-PLYP methods consistently underestimate the bond dissociation energies.

It is worth noting that the MD(expt) values of the unrestricted DFT methods tested in this study show that the UDFT methods tend to underestimate the experimental bond dissociation energies. This trend has previously been reported for several DFT methods,[3,7−15] including the popular B3-LYP functional.[11,14,15] With the exception of RBMK and RMPWB1K, the restricted DFTs in the present study also underestimate BDEs but the extent of underestimation is smaller than with the unrestricted methods, which arises because the restricted DFTs tend to predict higher (less negative) total energies than their unrestricted counterparts for open-shell species. A more comprehensive comparison of restricted versus unrestricted DFTs will be discussed elsewhere.[42]

3.2. Radical Stabilization Energies. The isodesmic reaction that defines the radical stabilization energies (eq 2) offers a good prospect for significant cancellation of errors. As a consequence, the methods that perform less well in predicting BDEs may still produce acceptable radical stabilization energies. Table 2 presents a comparison of calculated and experimental RSEs.

3.2.1. W1 and Other Composite Methods. As noted earlier, W1 gives accurate BDEs, and this is carried over to the RSEs calculated at this level. W1 shows a mean absolute deviation of 2.1 kJ mol^{-1} from experiment for the RSEs.

Consistent with the BDE results, ROCBS-QB3 gives slightly better RSE values (MAD(W1) = 1.4 kJ mol^{-1}) than CBS-QB3 (MAD(W1) = 1.7 kJ mol^{-1}). However, with the exception of cyanomethyl, carboxymethyl, and benzyl radicals, the CBS-QB3 and ROCBS-QB3 results are remarkably similar and differ from one another by less than 1 kJ mol^{-1}. As a whole, the performances of both the CBS methods are commendable as far as accuracy and computational costs are concerned. This

TABLE 2. Comparison of Calculated Radical Stabilization Energies with Experimental Values (0 K, kJ mol^{-1})

radical (•CH_2X)	UBMK	RBMK	UMPWB1K	RMPWB1K	UMO5	UMO5-2X	UB2-PLYP	RB2-PLYP	UMPW2-PLYP	RMPW2-PLYP	G3(MP2)-RAD	G3X(MP2)-RAD	CBS-QB3	ROCBS-QB3	W1[a]	expt[b]
•CH_2NH_2	52.0	52.3	54.6	54.3	49.6	50.5	50.3	50.5	50.1	50.2	44.2	45.2	49.5	49.5	49.3	45.6 ± 8.4
•CH_2OH	37.0	37.4	39.3	39.1	34.6	34.3	35.3	35.5	35.1	35.2	31.6	32.5	35.1	34.9	35.3	36.5 ± 0.63
•CH_2OCH_3	37.3	37.7	37.4	38.9	34.6	33.8	35.6	35.9	35.2	35.4	31.0	32.0	34.7	34.5	35.2	36.6[c]
•CH_2F	14.3	14.8	17.6	17.8	12.9	12.5	14.2	14.4	14.1	14.3	12.4	14.5	14.6	14.5	14.8	15.0 ± 4.2
•CH_2CH_3	15.4	15.1	19.1	18.9	20.6	16.4	16.0	15.9	16.2	16.0	14.1	14.5	16.2	16.2	15.8	19.3 ± 1.3
•$CH_2CH_2CH_3$	12.4	12.1	15.1	15.2	17.1	13.1	12.9	12.8	12.9	12.8	12.5	13.3	13.3	13.3	12.7	17.6 ± 2.1
•CH_2CF_3	−8.0	−8.1	−5.4	−4.4	−2.3	−6.7	−5.5	−5.5	−5.6	−5.7	−7.7	−5.7	−6.6	−6.6	−6.1	−6.9 ± 4.5
•$CH_2CF_2CF_3$	−4.5	−4.7	−2.7	−1.1	0.7	−3.8	−2.6	−2.5	−2.7	−2.8	−4.9		−3.1			
•CH_2PH_2	28.9	28.2	30.9	29.7	31.7	27.1	27.4	26.8	27.4	26.6	23.3	23.9	28.4	27.5	27.0	
•CH_2SH	35.9	35.3	43.4	42.2	41.9	39.4	39.5	39.2	39.3	38.7	36.1	37.3	41.4	40.9	41.4	46.1 ± 8.4
•CH_2Cl	18.7	18.1	26.4	25.6	25.1	21.9	21.9	21.6	21.8	21.3	21.1	22.4	23.7	23.3	23.0	20.5 ± 2.3
•CH_2Br	15.7	15.2	20.6	19.7	20.7	12.6	15.6	15.5	15.6	15.3			10.1			22.1 ± 2.4
•CH_2BH_2	45.8	46.7	44.4	45.8	41.7	41.7	41.4	42.5	41.7	42.8	40.1	40.9	42.7	41.6	40.9	
•$CH_2CH{=}CH_2$	72.5	64.5	77.2	67.4	83.2	75.4	70.5	69.2	71.2	68.0	70.7	71.1	74.8	74.4	70.3	68.9 ± 3
•$CH_2C{\equiv}CH$	57.1	51.0	61.9	54.4	65.8	57.9	54.5	55.1	54.9	53.9	52.6	52.9	58.1	56.1	53.6	54.7 ± 4.2[d]
•$CH_2C_6H_5$	60.2	54.8	63.6	57.0	70.1	61.0	53.1	57.0	54.0	56.0	58.9	59.2	59.9	63.2	59.1	61.6 ± 5.0
•CH_2CHO	38.6	33.8	43.0	36.9	41.0	40.8	35.4	36.8	36.1	36.1	34.9	36.0	40.9	38.5	36.6	39.8[c,e]
•CH_2COOH	23.3	21.9	26.7	25.4	28.1	25.3	23.9	24.3	24.0	24.0	21.2	22.1	25.1	24.0	23.7	24.7 ± 3.3[f]
•CH_2COOCH_3	23.6	22.4	26.9	25.9	28.8	25.4	24.4	24.8	24.5	24.5	21.5	22.8	25.4	24.4	23.3	31.3 ± 10.5[g]
•CH_2OCOCH_3	22.5	22.8	24.6	24.9	23.8	19.2	20.9	21.2	20.6	20.8	18.0	20.2	21.9	22.0	17.5	34.0[c]
•CH_2CN	34.6	29.3	40.3	33.3	41.9	34.8	33.1	34.7	33.5	33.7	31.9	31.5	37.8	35.4	33.1	32.8 ± 4.2
•CH_2NO_2	16.1	15.0	17.2	15.6	19.1	14.1	14.0	14.4	13.9	13.9	11.6	11.4	16.5	15.6	13.5	22.7[c]
MD(W1)[h]	0.9	−0.6	4.1	2.3	4.5	0.7	0.0	0.4	0.1	0.0	−2.0	−1.1	1.6	1.1		
MAD(W1)[h]	2.3	2.9	4.1	2.8	4.8	1.6	1.0	1.2	1.0	1.1	2.1	1.6	1.7	1.4		
LD(W1)[h]	−5.5	−6.1	8.2	7.5	12.9	5.1	−6.0	3.7	−5.1	3.3	−5.3	−4.1	4.7	4.6		
MD(expt)[c,g,h]	−1.2	−3.2	3.0	0.5	3.6	−0.7	−1.7	−1.3	−1.5	−1.8	−2.8	−1.9	−0.4	0.2	−0.8	
MAD(expt)[c,g,h]	3.3	4.3	4.0	2.7	5.1	3.4	3.0	2.7	3.0	2.8	3.2	2.8	3.6	2.6	2.1	
LD(expt)[c,g,h]	−10.2	−10.8	9.0	8.7	14.3	−9.5	−8.5	−6.9	−7.6	−7.4	−9.9	−8.8	−12.0	5.5	−4.9	

[a] W1′ calculations for systems containing second- and third-row elements. [b] Bond dissociation energies at 0 K calculated using experimental BDEs at 298 K from ref 2, unless otherwise noted, with the thermal corrections to 0 K obtained at the RB3-LYP/6-31G(d) level. [c] Species without experimental error bars are not included in the statistics. [d] Calculated using the experimental BDE for propyne reported by Tsang.[37] [e] Calculated using the experimental BDE for acetaldehyde reported by Cummings and Kebarle.[38] [f] Calculated using the experimental BDE for acetic acid reported by Lagoa et al.[39] [g] For all species with experimental uncertainties less than ±10 kJ mol^{-1}. [h] MD, MAD,and LD are mean deviation, mean absolute deviation,and largest deviation, respectively, from W1 and experimental values.

result is complementary to an earlier assessment study[5] that finds reasonable error cancellation and good RSE values for CBS methods. G3X(MP2)-RAD performs comparably well to the CBS methods in the calculation of RSEs, with an MAD of 1.6 kJ mol^{-1} from W1. Unlike the case for BDEs, the RSEs predicted by G3(MP2)-RAD show slightly larger deviations than those shown by G3X(MP2)-RAD, with MADs of 2.1 kJ mol^{-1} from W1 and 3.2 kJ mol^{-1} from experiment.

As found for the BDEs, the calculated RSEs for three radicals, viz, $\bullet CH_2C\equiv CH$, $\bullet CH_2COOH$, and $\bullet CH_2OCOCH_3$, show improved agreement with experiment if our newly recommended experimental BDEs[37−39] are used. W2 results for propargyl radical (53.6 kJ mol^{-1}), formylmethyl radical (36.7 kJ mol^{-1}), and carboxymethyl radical (23.2 kJ mol^{-1}) lie within 0.1 kJ mol^{-1} of the W1 RSE values, in further support of these experimental results. Additionally, our results suggest a reexamination of experimental thermochemical data for $\bullet CH_2OCOCH_3$ and $\bullet CH_2NO_2$.

3.2.2. DFT Methods. DFT methods show improved accuracy in predicting RSEs compared with BDEs. Specifically, all the tested DFT methods in this study give quite reasonable mean absolute deviations from experiment, in the range 3−5 kJ mol^{-1}.

The restricted and unrestricted X2-PLYP functionals give the best RSE values, showing mean absolute deviations of around 1 kJ mol^{-1} with respect to W1. However, the LDs from W1 suggest that the RB2-PLYP and RMPW2-PLYP give more reliable RSE values than their unrestricted variants.

UM05-2X gives good RSEs, with an MAD of 1.6 kJ mol^{-1} compared with W1 and 3.4 kJ mol^{-1} compared with experiment. UBMK also gives reasonable RSEs, with an MAD of 2.3 kJ mol^{-1} from W1. Both RMPWB1K and RBMK perform slightly less well and show larger deviations from experiment (MAD values of 2.7 and 4.3 kJ mol^{-1}), yet they are in reasonable agreement with W1 (MAD of 3.0 kJ mol^{-1}). The performance of UMPWB1K and UM05 is less good, as both these methods systematically overestimate RSEs by approximately 4.4 kJ mol^{-1} compared with W1.

We note that the superior performance of the X2-PLYP and UM05-2X methods for calculating RSEs contrasts with their performance for the previously discussed BDEs. The UBMK and RBMK functionals perform well for the estimation of both BDEs and RSEs. While the restricted form of the BMK functional performs better than the unrestricted form for the calculation of BDEs, for RSEs the converse is true. The UM05 functional performs less well for RSEs and, particularly, for BDEs.

4. Conclusions

Systematic assessment of the accuracy of quantum chemistry methods is an essential prerequisite for their routine use for predicting radical thermochemistry. In this study, the performance of a variety of contemporary theoretical procedures in calculating the BDEs and RSEs of monosubstituted methyl radicals is assessed. In the light of experimental uncertainties, the standard W1 method is used as the benchmark. Taken together with the results of our previous work,[3] we have reached the following conclusions:

(1) We find that the restricted-open-shell variant in the CBS family of methods, ROCBS-QB3, gives the best agreement with W1 for BDEs, with an MAD(W1) of just 1.3 kJ mol^{-1}. CBS-RAD comes in next with an MAD from W1 of 1.6 kJ mol^{-1}, while CBS-QB3 shows an MAD(W1) of 1.7 kJ mol^{-1}. The various CBS methods show very similar performance in predicting RSEs. In short, ROCBS-QB3, CBS-RAD, and CBS-QB3 represent reliable and efficient procedures for calculating the thermochemistry of carbon-centered radicals.

(2) G3X(MP2)-RAD performs slightly less well than the CBS methods in the calculation of BDEs. However, the RSEs predicted by G3X(MP2)-RAD compare well in accuracy with those predicted by the CBS methods. G3(MP2)-RAD performs comparably to G3X(MP2)-RAD for the test set under study.

(3) Very good BDE values, comparable to those obtained by the high-level composite methods, are produced by the RMPWB1K and RBMK methods, with MAD values from W1 of 1.8 and 2.9 kJ mol^{-1}, respectively. RMPWB1K provides the best agreement with experimental BDEs, showing a mean absolute deviation of 3.1 kJ mol^{-1}. UBMK, UMPWB1K, and UM05-2X perform less well and systematically underestimate the BDE values by 4.8, 5.9, and 6.5 kJ mol^{-1} (from W1), respectively. Still larger deviations are shown by the UM05 and UB2-PLYP methods, yet they give better results than UB3-LYP (MAD(W1) = 13.8 kJ mol^{-1}) and RMP2 (MAD(W1) = 16.7 kJ mol^{-1}).

(4) In a manner similar to that of many other DFT functionals, all the unrestricted DFT methods tested in this study tend to underestimate the bond dissociation energies. The extent of underestimation is relatively smaller for BDEs predicted by restricted DFTs.

(5) Most of the DFT methods that show poor performance in predicting absolute BDEs perform significantly better in calculating RSEs, which points to a systematic cancellation of errors in the latter through the use of an isodesmic reaction. Among the DFT methods examined in this study, the restricted and unrestricted double-hybrid X2-PLYP procedures yield the best RSE values (MAD(W1) = 1.0−1.2 kJ mol^{-1}), in contrast to their poorer prediction of BDEs. UM05-2X (MAD(W1) = 1.6 kJ mol^{-1}) and UBMK (MAD(W1) = 2.3 kJ mol^{-1}) give comparably good RSE values, while the UM05 and UMPWB1K functionals perform less well for RSEs.

(6) For three radicals, $\bullet CH_2C\equiv CH$, $\bullet CH_2COOH$, and $\bullet CH_2CHO$, W2 and W1, as well as other theoretical procedures employed in this study and in our previous study,[3] all give energies that lead to large deviations from previously recommended experimental BDEs.[1,2] We therefore recommend alternative experimental BDEs[37−39] for the production of these radicals from propyne, acetic acid, and acetaldehyde, respectively. We also recommend that the BDEs associated with $\bullet CH_2OCOCH_3$ and $\bullet CH_2NO_2$ be reexamined.

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Supporting Information Available: Table S1, containing the total energies that led to the BDEs and RSEs of Tables 1 and 2, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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