

Trends in R–X Bond Dissociation Energies (R• = Me, Et, *i*-Pr, *t*-Bu, X• = H, Me, Cl, OH)

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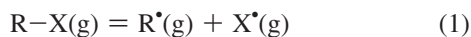
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Abstract: Trends for R–X bond dissociation energies have been examined with density functional methods of B3LYP, BMK, M06-2X, MC3MPW, B2PLYP, MCG3-MPW, and XYG3, as well as G3, MCG3/3, G3X, and G4 theories as functions of alkylation (i.e., R• = Me, Et, *i*-Pr, *t*-Bu) and X• substitution (i.e., X• = H, Me, Cl, OH). The results highlight the physical origin of success or failure of each method and demonstrate the good agreement with experimental results for G4, MCG3-MPW, and XYG3. The last holds great promise as a reliable method that is applicable to larger systems.

1. Introduction

Chemistry is fundamentally about making and breaking bonds. For a basic understanding of a chemical process, one has to account for how much energy is required for the cleavage of the old bonds in the reactants and how much energy will be released to form new bonds in the products. Accurate bond dissociation energies (BDEs) are mandatory, as the equilibrium constant K_{eq} is very sensitive to any error in the BDEs. An error of 1, 2, or 3 kcal/mol can lead to an error of a factor of 5, 29, or 158, respectively, in the equilibrium constant K_{eq} at 298 K.¹ Finding trends of relative BDEs can be even more important both practically and fundamentally. Such trends may highlight the active sites most accessible to a reagent,² and the knowledge of substitution effects on relative BDEs can be very helpful for the rational synthesis of a target structure.³

The homolytic BDE of R–X is defined as the enthalpy change of the dissociation reaction in the gas phase at 298 K and 1 atm:¹



where the indicated bond is broken and the products are radicals (•). BDE may be obtained by supplying the

experimental or calculated heat of formation (HOF, $\Delta_f H^\circ$) for each species as in eq 2.

$$BDE(R-X) = \Delta_f H^\circ(\text{eq 1}) = \Delta_f H^\circ(R^{\bullet}) + \Delta_f H^\circ(X^{\bullet}) - \Delta_f H^\circ(RX) \quad (2)$$

People have varied X• in accordance with their electronegativities (e.g., H, CH₃, Cl, OH) and R• in accordance with their degree of alkylation (i.e., R• = (CH₃)_nCH_{3-n} where $n = 0, 1, 2$, and 3 for Me = CH₃, Et = CH₃CH₂, *i*-Pr = (CH₃)₂CH, and *t*-Bu = (CH₃)₃C, respectively.^{4–6} Relative BDEs to the CH₃–X bond are effectively the enthalpy changes for the X-transfer reaction between CH₃ and R• = (CH₃)_nCH_{3-n}:



$$\Delta BDE = \Delta_f H^\circ(\text{eq 3}) = BDE(CH_3-X) - BDE(R-X) \quad (4)$$

In particular, when X• = H, the enthalpy change for eq 3 is usually defined as the radical stabilization energy (RSE) for the radical R•.^{7,8} Such a concept of the ordering of alkyl radical stabilities has proven to be extremely useful in explaining the kinetics and thermodynamics of many chemical reactions.

The majority of experimental BDE data suffer from an uncertainty of 1 to 2 kcal/mol,¹ and this is a continuing source

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of debate and controversy. The high-level theoretical calculations, on the other hand, should produce reasonable absolute BDEs, but more significantly, they should produce even more accurate trends based on the assumption that the uniform treatment of a series of BDEs to calculate Δ BDEs should enhance the prospect of a cancellation of errors.^{5–7} In this work, we show that this is not always true with Δ BDE trend calculations for the widely used composite method such as the G3 method⁹ and some popular density functional theory (DFT) methods such as B3LYP^{10–13} and BMK.¹⁴ We demonstrate that the recently introduced G4,¹⁵ although at higher expense, is a significant improvement over G3, while the multicoefficient extrapolated density functional theory, MCG3-MPW,¹⁶ shows very good agreement with the experiment at a comparable cost of G3. The newly developed fifth-rung¹⁷ XYG3 functional¹⁸ offers particular promise as a reliable method that is applicable to larger systems than do G4 and MCG3-MPW.

It is challenging to calculate accurate BDE via eq 2 for many theoretical methods. As the unpaired electron does not have a partner electron sharing the same space, the open-shell radicals are inherently different from their closed-shell parent molecule.¹⁷ Accurate BDE calculations demand treatment of the open-shell and closed-shell species on an equivalent footing. The widely used B3LYP fails badly in this context, whose BDE errors accumulate as the molecules become large along with alkylation.^{5–7,20–23} The situation is likely to be improved in calculating Δ BDE, as eq 3 is isodesmic,^{24,25} holding radicals, C–X bonds, and other bond types in both sides. However, Coote and co-workers⁶ showed that many popular density functional methods (BLYP,^{11,12} PBE,²⁶ B3LYP,^{10–13} B3P86,^{12,27} BB1K,²⁸ MPW1K,²⁹ KMLYP,³⁰ BMK,¹⁴ etc.) overestimate the stabilizing effect on BDEs in going from $R^\bullet = \text{Me}$ to $R^\bullet = t\text{-Bu}$, leading in some cases to incorrect qualitative behavior. Among the DFT methods they examined, they claimed that BMK showed the smallest systematic errors in Δ BDE and provided very reasonable predictions of BDE.⁶ The present work confirms the poor behavior of B3LYP but reveals some inherent weaknesses of BMK by doing energy decomposition analysis of the contributions to Δ BDEs from the exchange and correlation functionals.

A recent important development in DFT is the M06 family of functionals,³¹ which currently provides the highest accuracy with a broad applicability for chemistry. Similar to that for its predecessor M05,³² the development of these functionals involved using four alkyl bond dissociation energies (i.e., the ABDE4 set including R–CH₃ and R–OCH₃ with R = Me and *i*-Pr) as the training set. We test M06-2X here for its applicability to the R–X bond series as functions of alkylation (i.e., $R^\bullet = \text{Me}$, Et, *i*-Pr, *t*-Bu) and X[•] substitution (i.e., X[•] = H, Me, Cl, OH).

2. Computational Details

Unless otherwise stated or defined by the method per se, the equilibrium geometry of each molecule or radical was optimized at the level of B3LYP/6-311+G(d,p).^{10–13,33,34} Analytical harmonic frequency was calculated at the same level to give zero-point energy (ZPE, with scaling factor

0.9877¹⁸) and thermo-corrections and to ensure that each geometry corresponded to a true local minimum. The final electronic energy was obtained by single point calculation at the level of 6-311+G(3df,2p)^{33,34} for all DFTs other than MC3MPW³⁵ and MCG3-MPW.¹⁶

B3LYP^{10–13} is currently the most popular DFT method. It is one of the first hybrid functionals that replaces some portion of the local exchange energy with the exact exchange energy E_x^{exact} .

$$E_{\text{xc}}^{\text{B3LYP}}[\rho] = E_{\text{xc}}^{\text{SVWN}} + c_1(E_x^{\text{exact}} - E_x^{\text{S}}) + c_2\Delta E_x^{\text{B}} + c_3\Delta E_c^{\text{LYP}} \quad (5)$$

Here, ΔE_x^{B} ¹¹ and ΔE_c^{LYP} ¹² are the generalized gradient approximation (GGA) correction terms to the local density approximation (LDA) exchange-correlation SVWN.^{36,37} The three mixing parameters are $\{c_1, c_2, c_3\} = \{0.20, 0.72, 0.81\}$. BMK¹⁴ and M06-2X³¹ improve B3LYP by also including the ingredient of kinetic energy density (i.e., hybrid meta-GGAs), whose functional forms can be found in the original papers.^{14,31}

The MC3MPW method is one of the first doubly hybrid DFTs,³⁵ whose total energy was defined as

$$E_{\text{tot}}^{\text{MC3MPW}} = d_2 E_{\text{tot}}(\text{SAC/DIDZ}) + (1 - d_2) E_{\text{tot}}(\text{MPWX/MG3S}) \quad (6)$$

Here, MPWX is a one-mixing-parameter hybrid DFT²⁹ using mPW exchange³⁸ and PW91 correlation³⁹ functionals, and MG3S is a 6-311+G(3d2f,2df,2p) basis set,^{34,35,40} which uses 3d2f polarization on the second-row, 2df polarization on the first row, and 2p on hydrogen. SAC/DIDZ can be expressed as

$$E(\text{SAC/DIDZ}) = E(\text{HF/DIDZ}) + d_1 \Delta E(\text{MP2/DIDZ}) \quad (7)$$

where DIDZ stands for the 6-31+G(d,p) basis set.^{34,41} The name MC3 suggests that this is a multicoefficient method that contains three parameters.³⁵ The mixing parameters are $d_1 = 1.339$ and $d_2 = 0.266$. The percentage of the exact exchange in MPWX is 38%. MC3MPW scales formally as N^5 where N is the number of atoms. Since the scaling-all-correlation (SAC) method^{42,43} was employed to extrapolate MP2/DIDZ calculations to the limit of full dynamic correlation of the valence electrons and a complete one-electron basis set for the valence electrons, MC3MPW was found to be more accurate than the conventional hybrid method without an appreciable increase of computational cost.³⁵

The MCG3-MPW method is also a doubly hybrid DFT.¹⁶ It combines the G3-like component calculations such as HF/6-31G(d), MP2/MG3S, MP4SDQ/6-31G(2df,p), QCISD/6-31G(d), etc. with hybrid DFT of MPWX/MG3S using eight mixing parameters. MCG3-MPW scales formally as N^7 . Its cost is smaller than that of the G3 theory, as full MP4 is replaced with MP4SDQ.

B2PLYP is a widely recognized doubly hybrid functional.^{44,45} It employs a hybrid GGA functional defined in eq 8, which may be called B2LYP,⁴⁶ as it contains two mixing parameters (i.e., $\{a_x, a_c\} = \{0.53, 0.73\}$).

$$E_{xc}^{B2LYP} = a_x E_x^{exact} + (1 - a_x) E_x^B + a_c E_c^{LYP} \quad (8)$$

This B2LYP functional cannot be used alone, whose mere purpose is to generate the Kohn–Sham (KS) orbitals and orbital eigenvalues for the MP2-like perturbative correlation energy evaluation. The final form of B2PLYP is completed as

$$E_{xc}^{B2PLYP}[\rho] = E_{xc}^{B2LYP} + (1 - a_c) E_c^{MP2} \quad (9)$$

Unlike that in MC3MPW,³⁵ where Hartree–Fock orbitals are used for a conventional MP2 calculation, the reference wave function in B2PLYP does not satisfy the Brillouin theorem. Nevertheless, single contributions are neglected in B2PLYP.^{44,45} There are several new functionals (i.e., B2T-PLYP,⁴⁷ B2K-PLYP,⁴⁷ B2GP-PLYP,⁴⁸ B2 π -PLYP,⁴⁶ ROB2-PLYP,⁴⁹ UB2-PLYP⁴⁹), which are constructed in the same way as B2PLYP but use different $\{a_x, a_c\}$ parameters.

XYG3¹⁸ is a new version of doubly hybrid functional. It has the form as

$$E_{xc}^{XYG3}[\rho] = E_{xc}^{SVWN} + e_1(E_x^{exact} - E_x^S) + e_2\Delta E_x^B + e_3(E_c^{MP2} - E_c^{LYP}) + \Delta E_c^{LYP} \quad (10)$$

It was developed on the basis the adiabatic connection formalism^{50–55} using initio slope of the exchange–correlation potential energy defined rigorously as the second-order correlation energy in the Görling–Levy theory (GL2)⁵⁶ of coupling-constant perturbation expansion, which demands^{56,57}

$$E_c^{GL2} = E_c[\rho_{1/\lambda}]|_{\lambda=0} \quad (11)$$

The validity of eq 11 is critically dependent on the quality of density and orbitals generated by the corresponding exchange–correlation functional, such that eq 11 was suggested to be used as a check for the accuracy of an approximate correlation functional.⁵⁶ YXG3 omits the single contribution as B2PLYP does to approximate E_c^{GL2} as E_c^{MP2} , while it differs from B2PLYP by using B3LYP to generate the density used to calculate the DFT energy and orbitals from which the PT2 term is computed. We assume, on the basis of the generally good performance of B3LYP, that the B3LYP orbitals are a reasonably good approximation to the real (unknown) KS orbitals to better fulfill the requirement of the Görling–Levy theory than do the B2LYP orbitals used in B2PLYP.

G3 is a widely used composite method.⁹ It uses MP2(full)/6-31G(d) geometries for energy evaluations and scaled HF/6-31G(d) frequencies for ZPE and H_{0-298} . The G3 energy is effectively at the QCISD(T, Full)/G3Large level through a series of calculations at lower levels. The G3Large basis set is similar to 6-311+G(3d2f,2df,2p). G3X is a modification of G3 theory.⁵⁸ The new features include (1) B3LYP/6-31G(2df,p) geometry, (2) B3LYP/6-31G(2df,p) ZPE (scaling factor 0.9854), (3) addition of a g polarization function to the G3Large basis set for second-row atoms at the Hartree–Fock level, and (4) revised empirical higher-level correction (HLC). G4 is the latest successor to G3,¹⁵ which modifies G3 in five ways: (1) B3LYP geometry and ZPE as those in G3X, (2) G3LargeXP (with XP standing for extra polariza-

Table 1. Mean Absolute Deviations (MADs, kcal/mol) for Heats of Formation ($\Delta_f H^\circ$) of R $^\bullet$ Radicals and RX Compounds, As Well As for Bond Dissociation Energies (BDEs) of R–X Bonds^{a,b}

no.	methods	$\Delta_f H^\circ(R^\bullet)$	$\Delta_f H^\circ(RX)$	BDE(R–X) ^c
1	B3LYP	1.91 (2.57)	4.25 (11.52)	5.98 (11.91)
2	BMK	0.73 (1.39)	1.37 (3.97)	1.44 (3.93)
3	M06-2X	0.95 (1.25)	1.50 (3.33)	1.21 (2.51)
4	MC3MPW	2.13 (3.70)	1.04 (2.75)	1.47 (2.90)
5	B2PLYP	3.81 (7.50)	7.04 (11.69)	2.93 (6.11)
5*	B2PLYP*d	1.07 (2.80)	3.47 (7.98)	3.05 (5.94)
6	XYG3	0.72 (1.05)	0.84 (2.12)	1.00 (2.01)
7	MCG3-MPW	0.84 (1.15)	1.33 (2.42)	0.61 (1.69)
8	G3	0.51 (1.07)	0.38 (1.23)	0.83 (1.95)
9	MCG3/3	0.29 (0.49)	1.84 (3.59)	1.33 (3.49)
10	G3X	0.42 (0.86)	0.23 (0.71)	0.64 (1.50)
11	G4	0.43 (0.59)	0.17 (0.50)	0.76 (1.33)

^a For a given entry, the maximum absolute error is given in parentheses. The best two values based on the smallest MADs are in boldface, which are resulted from the methods with (nos. 1–7) or without (nos. 8–11) using DFT components. ^b See Tables S1–S3 for details, Supporting Information. ^c BDE(R–X) = $\Delta_f H^\circ(R^\bullet) + \Delta_f H^\circ(X^\bullet) - \Delta_f H^\circ(RX)$. ^d B2PLYP* results are taken from ref 45, using a very large CQZV3P basis set including core-polarization functions as originally recommended by Grimme.

tion functions) as the replacement of G3Large basis set, (3) extrapolated HF limit energies, (4) CCSD(T), in substitution for QCISD(T), and (5) revised HLC.

Besides the Gn series developed by Curtiss and co-workers,^{9,15,40,58} Truhlar's group developed a series of multicoefficient correlation methods (MCCMs⁵⁹). Here, we examine the MCG3/3 method, the best performer of this family, being a G3 analogy of MCCM-version 3. As the full MP4 energy component in G3 is removed, MCG3/3 is faster than G3. The HLC scheme is not adopted in MCG3/3. Instead, six parameters are used to linearly mix the energy components from wave function theory (WFT) methods of different levels and basis sets. The salient difference between MCG3/3,⁵⁹ MC3MPW,³⁵ and MCG3-MPW¹⁶ is that there is no DFT component in the first method.

After being armed with total electronic energy, we calculate the standard HOF in the same manner as Curtiss et al.^{9,15,40,58} by first subtracting the calculated atomization enthalpies, using a scaled ZPE for the molecule, from the known experimental HOFs of the isolated atoms at 0 K and then adding the calculated thermo-corrections (H_{0-298} K) for the molecule, as well as H_{0-298} K for elements in their standard states from experiments. Spin–orbit (SO) corrections are also included in the present work.⁹ Having HOFs on hand, we calculate BDEs and Δ BDEs as enthalpy changes, as defined in eqs 2 and 4.

Calculations were performed by using the Gaussian 03 suite of programs.³⁴ For Truhlar's M06 suite of functionals,³¹ calculations were carried out by using Jaguar.⁶⁰

3. Results and Discussion

Table 1 summarizes the mean absolute deviations (MADs) and maximum absolute deviations (MAXs) for HOFs^{61–63} of radicals (R $^\bullet$ = Me, Et, *i*-Pr, and *t*-Bu) and RX compounds with X $^\bullet$ = H, Me, Cl, and OH. MADs and MAXs for R–X BDEs are also presented in Table 1 (the detailed results can

be found in Tables S1–S3, Supporting Information). The experimental uncertainties cited in the present work for HOFs are all below 0.5 kcal/mol.^{61–63} These are good representative systems, showing how alkylation and X[•] substitution will affect the R–X bond strengths.^{5–7,20–23} In addition to B3LYP and BMK, we focus on some “new generation” functionals M06-2X,³¹ MC3MPW,³⁵ B2PLYP,^{44,45} XYG3,¹⁸ and MCG3-MPW¹⁶ in the present work. Results from G3,⁹ G3X,⁵⁸ and G4,¹⁵ as well as those from MCG3/3,⁵⁹ are also included in Table 1 for comparison.

B3LYP leads to MADs of 1.91 and 4.25 kcal/mol for HOFs of R[•] radicals and RX compounds, respectively. These errors unfortunately accumulate,^{20–23} increasing MAD to 5.98 kcal/mol for BDE prediction. On the other hand, B2PLYP leads to 3.81 and 7.04 kcal/mol for HOFs of radicals R[•] and RX compounds, respectively. MAD is decreased, due to error cancellation, to 2.93 kcal/mol for BDE calculations. It is noteworthy that the present B2PLYP results are obtained at the 6-311+G(3df,2p) level. Using a very large CQZV3P basis set including core-polarization functions as originally recommended by Grimme^{44,45} will reduce MADs of HOFs to 1.07 for R[•] and 3.47 for RX. Nevertheless, we find that the quadruple- ζ -quality basis sets slightly degrade the R–X BDE calculations (MAD = 3.05 kcal/mol, see Tables S1–S3 for details). BMK, M06-2X, MC3MPW, XYG3, and MCG3-MPW present the best DFT methods currently available for HOFs and BDEs calculations (c.f. Table 1 and Tables S1–S3). Their MADs for BDE predictions are all below 1.50 kcal/mol, approaching “chemical accuracy”. G3, G3X, and G4 all display MADs below 0.51 kcal/mol for HOFs and below 0.83 kcal/mol for BDEs, being most satisfactory. Notably, MCG3-MPW displays the lowest MAD (0.61 kcal/mol) for BDEs, even surpassing that of the G4 method.

Δ BDEs defined in eqs 3 and 4 examine how alkylation by successive replacement of H in CH₃X with methyl group affects the C–X bond. In terms of HOFs, Δ BDE may also be written as

$$\Delta\text{BDE} = \Delta\Delta_f H^\circ(\text{R}^\bullet) - \Delta\Delta_f H^\circ(\text{RX}) \quad (12)$$

where $\Delta\Delta_f H^\circ(\text{R}^\bullet) = [\Delta_f H^\circ(\text{CH}_3) - \Delta_f H^\circ(\text{R}^\bullet)]$ and $\Delta\Delta_f H^\circ(\text{RX}) = [\Delta_f H^\circ(\text{CH}_3\text{X}) - \Delta_f H^\circ(\text{RX})]$. Equation 12 clearly demonstrates that the Δ BDE trend is a composite effect of the stability change of R[•] and that of RX along with alkylation, while the latter depends on the electronic nature of X[•] ligands.^{4–8} If $\Delta\Delta_f H^\circ(\text{R}^\bullet) > \Delta\Delta_f H^\circ(\text{RX})$ and $\Delta\text{BDE} > 0$, Δ BDE goes up with increasing alkylation. On the other hand, if $\Delta\Delta_f H^\circ(\text{R}^\bullet) < \Delta\Delta_f H^\circ(\text{RX})$ and $\Delta\text{BDE} < 0$, Δ BDE goes down with increasing alkylation. Experimentally,^{61–63} it was found that, when X[•] = H and Me, one has $\Delta\Delta_f H^\circ(\text{R}^\bullet) > \Delta\Delta_f H^\circ(\text{RX})$. This has been attributed mainly to the increasingly stronger hyperconjugation⁶⁴ in radicals than in RX from R[•] = Me to R[•] = *t*-Bu. Thus, we see that Δ BDE goes up with increasing alkylation, as shown in Figure 1. When X[•] = Cl and OH, one has $\Delta\Delta_f H^\circ(\text{R}^\bullet) < \Delta\Delta_f H^\circ(\text{RX})$. This effect of X[•] has been attributed to the increasing contribution of the ionic R⁺X[−] configuration for electronegative X[•] substituents.^{4–8} Such stabilization of R–X increases with increasing alkylation and leads to an increase

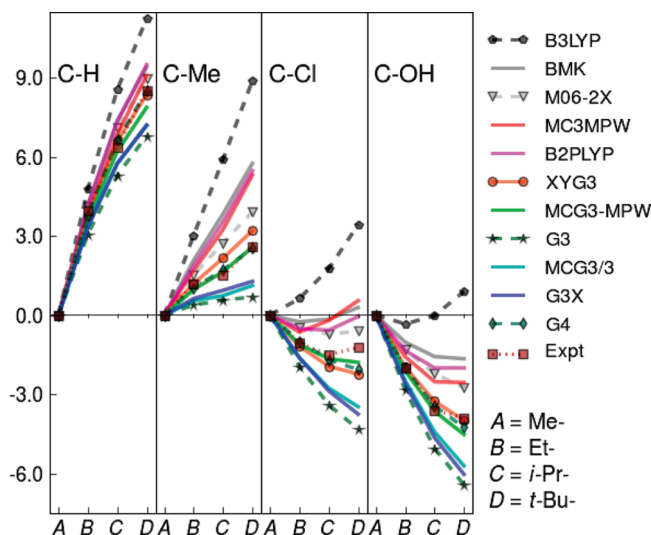


Figure 1. Trends of Δ BDE (kcal/mol) for R–X (R[•] = Me, Et, *i*-Pr, and *t*-Bu; X[•] = H, Me, Cl, and OH).

in the R–X BDEs, despite the accompanying increase of R[•] stability.^{4–8} Hence, in these cases, we see that Δ BDE goes down with increasing alkylation (Figure 1). B3LYP results clearly violate such trends qualitatively for X[•] = Cl or OH. Instead of going down from R[•] = Me to R[•] = *t*-Bu, it erroneously goes up. It was claimed that the incorrect qualitative behavior of B3LYP Δ BDE for electronegative X[•] substituents is a result from overestimation of the stabilizing effect on BDEs, giving $\Delta\Delta_f H^\circ(\text{R}^\bullet)$ too large in going from R[•] = Me to R[•] = *t*-Bu.^{4–8} Instead, we find that B3LYP actually underestimates the increasing rates with alkylation for $\Delta\Delta_f H^\circ(\text{R}^\bullet)$. The experiments give $\Delta\Delta_f H^\circ(\text{R}^\bullet) = 22.76$ kcal/mol from R[•] = Me to R[•] = *t*-Bu (See Table S4, Supporting Information). The corresponding B3LYP values are 18.02, being too low by 4.74 kcal/mol. On the other hand, B3LYP also underestimates the increasing rates with alkylation for $\Delta\Delta_f H^\circ(\text{RX})$. The experimental value for $\Delta\Delta_f H^\circ(\text{ROH})$ from R[•] = Me to R[•] = *t*-Bu is 26.65 kcal/mol (See Table S4), while the corresponding B3LYP value is only 17.13, falling short by 9.52 kcal/mol. Thus, we conclude that the erroneous Δ BDE trend is in fact due to a more severe underestimation tendency for $\Delta\Delta_f H^\circ(\text{RX})$ than for $\Delta\Delta_f H^\circ(\text{R}^\bullet)$.

Most surprisingly, Figure 1 uncovers the quantitative failure of the G3 method for predicting the Δ BDE trend, despite its good performance for BDE prediction (see Table 1). It is indisputable that the G3 Δ BDE slopes are too gentle when X[•] = H and Me, whereas Δ BDEs decrease too fast when X[•] = Cl and OH. Table 2 shows that G3 has an error as high as 1.24 kcal/mol for $\Delta\Delta_f H^\circ(\text{R}^\bullet)$, and the error in $\Delta\Delta_f H^\circ(\text{RX})$ adds up, leading to MAD = 1.50 and MAX = 3.10 kcal/mol for Δ BDE! Figure 1 illustrates that G3X and MCG3/3 only marginally improve over G3, whereas G4, MCG3-MPW, and XYG3 are very satisfactory in predicting the Δ BDE trend. Table 2 shows that MADs for Δ BDE associated with G4, MCG3-MPW, and XYG3 are 0.21, 0.26, and 0.32 kcal/mol, respectively (See Tables S4–S6 for more details, Supporting Information). We recall that, as eq 3 is isodesmic, holding radicals, C–X bonds, and other bond types in both sides, errors for Δ BDE should be even smaller

Table 2. Mean Absolute Deviations (MADs, kcal/mol) for Relative Heats of Formation ($\Delta\Delta_f H^\circ$) and Relative Bond Dissociation Energies (ΔBDEs)^{a,b}

no.	methods	$\Delta\Delta_f H^\circ(\text{R}^\bullet)^\circ$	$\Delta\Delta_f H^\circ(\text{RX})^\circ$	$\Delta\text{BDE}(\text{R}-\text{X})^d$
1	B3LYP	2.33 (4.74)	5.48 (11.02)	3.16 (6.28)
2	BMK	1.16 (1.67)	0.59 (2.25)	1.45 (3.14)
3	M06-2X	0.31 (0.62)	0.56 (1.43)	0.79 (1.38)
4	MC3MPW	2.77 (3.65)	1.75 (3.08)	1.04 (2.70)
5	B2PLYP	4.10 (6.76)	5.30 (9.62)	1.21 (2.86)
5*	B2PLYP* ^e	1.86 (3.56)	3.54 (6.98)	1.68 (3.42)
6	XYG3	0.23 (0.33)	0.30 (0.92)	0.32 (1.01)
7	MCG3-MPW	0.14 (0.41)	0.37 (0.64)	0.26 (0.65)
8	G3	1.24 (1.80)	0.31 (1.30)	1.50 (3.10)
9	MCG3/3	0.27 (0.39)	0.78 (1.86)	1.05 (2.25)
10	G3X	1.00 (1.55)	0.30 (0.97)	1.10 (2.53)
11	G4	0.19 (0.27)	0.21 (0.57)	0.21 (0.84)

^a For a given entry, the maximum absolute error is given in parentheses. The best two values based on the smallest MADs are in boldface, which are resulted from the methods with (nos. 1–7) or without (nos. 8–11) using DFT components. ^b See Tables S4–S6 for details. ^c $\Delta\Delta_f H^\circ(\text{R}^\bullet) = \Delta_f H^\circ(\text{CH}_3) - \Delta_f H^\circ(\text{R}^\bullet)$ and $\Delta\Delta_f H^\circ(\text{RX}) = \Delta_f H^\circ(\text{CH}_3\text{X}) - \Delta_f H^\circ(\text{RX})$. ^d $\Delta\text{BDE} = \text{BD}^\circ(\text{CH}_3\text{X}) - \text{BDE}(\text{R}-\text{X}) = \Delta\Delta_f H^\circ(\text{R}^\bullet) - \Delta\Delta_f H^\circ(\text{RX})$. ^e B2PLYP* results are taken from ref 45, using a very large CQZVP basis set including core-polarization functions as originally recommended by Grimme.

Table 3. Mean Absolute Deviations (MADs, kcal/mol) for Hartree–Fock and Correlation Contributions to the Relative Bond Dissociation Energies ΔBDEs , Using the Corresponding G4 Values As References^{a,b,c}

no.	methods	$\Delta\text{BDE}(\text{HF})$	$\Delta\text{BDE}(\text{corr.})$	$\Delta\text{BDE}(\text{ZPE}+)$
1	B3LYP	2.23	1.17	0.05
2	BMK	0.87	2.10	0.05
3	M06-2X	2.01	1.17	0.05
4	MC3MPW	1.12	0.66	0.00
5	B2PLYP	1.21	0.40	0.05
6	XYG3	0.49	0.52	0.05
7	MCG3-MPW	0.36	0.50	0.00
8	G3	0.12	0.93	0.41
9	MCG3/3	0.16	0.98	0.00
10	G3X	0.17	0.85	0.00
11	G4	0.00	0.00	0.00

^a ΔBDEs are decomposed in terms of Hartree–Fock (HF) contributions, correlation contributions (corr.), and zero-point-energy plus thermo-contributions (ZPE+). ^b See Tables S7–S9 for details. ^c The best two values based on the smallest MADs are in boldface, which are resulted from the methods with (nos. 1–7) or without (nos. 8–11) using DFT components.

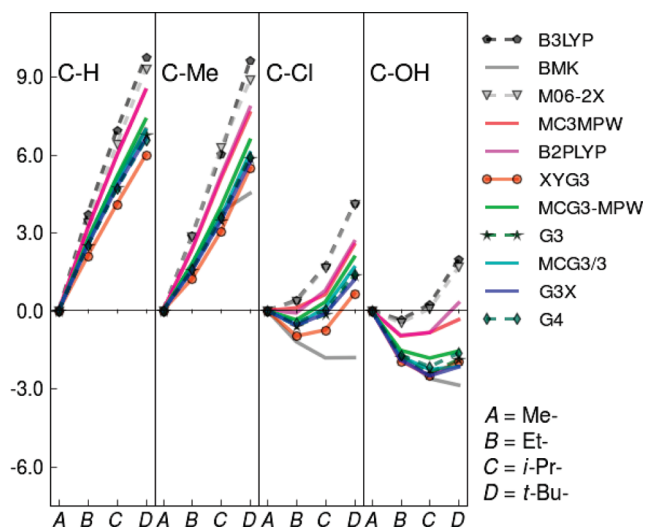
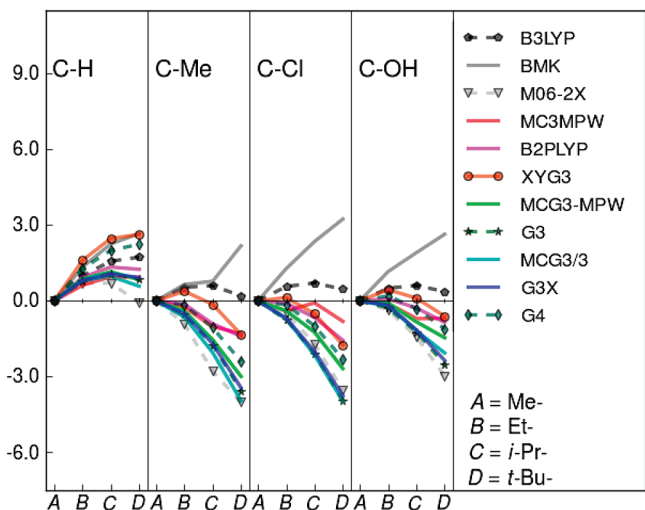
than that of BDE for a theoretical method to be satisfactory. Indeed, MADs decrease from BDE to ΔBDE for all methods other than BMK, G3, and G3X.

In order to better understand the physical origin of success or failure of each method, we use G4 energies as references and decompose ΔBDE in terms of Hartree–Fock (HF) contributions, correlation contributions (corr.), and zero-point-energy plus thermo-contributions (ZPE+).

$$\Delta\text{BDE} = \Delta\text{BDE}(\text{HF}) + \Delta\text{BDE}(\text{corr.}) + \Delta\text{BDE}(\text{ZPE}+) \quad (13)$$

The data are summarized in Table 3 with details in Tables S7–S9 (Supporting Information), which are depicted in Figures 2 and 3.

Let us first address $\Delta\text{BDE}(\text{ZPE}+)$. G4, G3X, and Truhlar's MC methods all use B3LYP/6-31G(2df,p) geometries and the corresponding scaled ZPE.¹⁵ All other DFT calculations

**Figure 2.** Hartree–Fock contribution to ΔBDE trends of $\text{R}-\text{X}$ (kcal/mol).**Figure 3.** Correlation contribution to ΔBDE trends of $\text{R}-\text{X}$ (kcal/mol).

employ B3LYP/6-311+G(d,p) geometries and the corresponding scaled ZPE,¹⁸ which lead, on average, to $\Delta\text{BDE}(\text{ZPE}+)$ divergence from the G4 results by only 0.05 kcal/mol. G3, on the other hand, uses MP2(full)/6-31G(d) geometries and scaled HF/6-31G(d) ZPE,⁹ giving a higher MAD (0.41 kcal/mol) in this quantity. Figure 2 demonstrates that the G3 HF contribution, obtained with HF/G3Large, is quite close to G4 HF results extrapolated to the basis set limit. G3 MAD for $\Delta\text{BDE}(\text{HF})$ with respect to the G4 data is only 0.12 kcal/mol. Figure 3 and Table 3 clearly disclose that it is the deficiency in G3 correlation contribution, i.e., $\Delta\text{BDE}(\text{corr.})$, that results in the unsatisfactory performance in quantitatively predicting ΔBDE trends. This holds true for G3X and MCG3/3 methods.

It would be interesting to compare DFT results with those of G4 in terms of $\Delta\text{BDE}(\text{HF})$ and $\Delta\text{BDE}(\text{corr.})$. Although it should be kept in mind that the distinction between exchange and correlation is different in DFT and WFT methods, and $\Delta\text{BDE}(\text{HF})$ in fact contains more information than just that of exchange, we do believe that the trends should be in parallel. Figure 2 demonstrates that B3LYP and

M06-2X display very similar behavior for $\Delta\text{BDE}(\text{HF})$. They diverge from the G4 values most significantly with MADs = 2.23 and 2.01 kcal/mol, respectively, but they both have a similar trend to that of G4. BMK, on average, seems to be in reasonable agreement with G4 $\Delta\text{BDE}(\text{HF})$ with MAD = 0.87 kcal/mol. Figure 2, on the other hand, reveals that BMK may have a problem with its exchange functional. For $\text{X}^* = \text{H}$, there is a strong increase of $\Delta\text{BDE}(\text{HF})$ with increasing alkylation, and BMK faithfully reproduces this trend. When $\text{X}^* = \text{Me}$, BMK shows a reduced rate of increase for $\Delta\text{BDE}(\text{HF})$ from *i*-Pr to *t*-Bu, which is not shown in the G4 data. For $\text{X}^* = \text{Cl}$, the BMK trend for $\Delta\text{BDE}(\text{HF})$ is in sharp contrast to the G4 trend. BMK suggests that it is all the way downward from Me to *i*-Pr with a plateau from *i*-Pr to *t*-Bu, whereas G4 shows an initial decrease from Me to Et, followed by a steady increase from Et to *t*-Bu. Even though BMK's trend for $\text{X}^* = \text{OH}$ is good from Me to *i*-Pr, it differs from G4 $\Delta\text{BDE}(\text{HF})$ by 1.22 kcal/mol from *i*-Pr to *t*-Bu. We notice that MC3MPW and B2PLYP give a qualitatively good $\Delta\text{BDE}(\text{HF})$ trend, although its MAD (1.12 and 1.21 kcal/mol, respectively) is less satisfactory from a quantitative point of view. We suggest that updating $E(\text{HF}/\text{DIDZ})$ in eq 7 to $E(\text{HF}/\text{MG3S})$ would improve MC3MPW prediction of the $\Delta\text{BDE}(\text{HF})$ trend.

Figure 3 displays the correlation contribution to the ΔBDE trend. As compared to Figures 1 and 2, it is immediately clear that the ΔBDE trend is generally HF-dominant. Interestingly, while $\Delta\text{BDE}(\text{HF})$ leads to similar uprising trends for both $\text{X}^* = \text{H}$ and Me, it is $\Delta\text{BDE}(\text{corr.})$ that distinguishes them, leading to an attenuated trend for $\text{X}^* = \text{Me}$. Indeed, as X^* becomes more electronegative and R^* becomes more alkylated, the correlation effect eventually turns ΔBDE curve downward.

Figure 3 shows that the BMK results are anomalous when G4 $\Delta\text{BDE}(\text{corr.})$ data are taken as references. This functional clearly displays an opposite trend for electronegative substituents X^* . Figure 3 also shows that the B3LYP $\Delta\text{BDE}(\text{corr.})$ is too mild, being unable to pull the overall ΔBDE trend downward for electronegative X^* along with alkylation. On the other hand, even though M06-2X correlation makes little contribution to ΔBDE for $\text{X}^* = \text{H}$, it starts to overshoot the G4 correlation, resulting in a deep decrease of $\Delta\text{BDE}(\text{corr.})$ with increasing alkylation (Figure 3). Such a correlation contribution is compensated by the sharp increase of $\Delta\text{BDE}(\text{HF})$ in the opposite direction (Figure 2), giving a net reasonable performance for BDE and ΔBDE (MAD = 1.21 for BDE and 0.79 kcal/mol for ΔBDE). Interestingly, $\Delta\text{BDE}(\text{corr.})$ from all doubly hybrid functionals (nos. 4–7, see Table 3) are in good agreement with that of G4, suggesting the importance of its second-order perturbation term. Even though B2PLYP $\Delta\text{BDE}(\text{corr.})$ is most satisfactory, it cannot be balanced with the B2PLYP $\Delta\text{BDE}(\text{HF})$, making its overall performance (i.e., MAD = 2.93 for BDE and 1.21 kcal/mol for ΔBDE) less satisfactory. Figures 2 and 3 demonstrate that MCG3-MPW's $\Delta\text{BDE}(\text{HF})$ and $\Delta\text{BDE}(\text{corr.})$ are both in close parallel with the G4 counterparts, with MADs of 0.36 and 0.50 kcal/mol, respectively (see Table 3). G4 is the most accurate and most expensive Gaussian-n type method with explicit extrapolation of

Hartree–Fock energy and using correlation methods up to CCSD(T), while the less expensive MCG3-MPW by taking linear combinations of DFT method with WFT single-level methods to inexplicitly extrapolate toward complete configuration interaction has achieved similar (if not better) accuracy. Most significantly, Figures 2 and 3 demonstrate that XYG3's $\Delta\text{BDE}(\text{HF})$ and $\Delta\text{BDE}(\text{corr.})$ are also in good parallel with the G4 counterparts, with MADs of 0.49 and 0.52 kcal/mol, respectively. The comprehensively good performance for BDE and ΔBDE trends suggests that XYG3 gets the right answer for the right reason with a correct description of the fundamental physics. As XYG3 formally scales as N^5 , it offers a valuable alternative to the N^7 methods, especially when the latter become prohibitively expensive.

4. Conclusion

Recently, we proposed a doubly hybrid functional, XYG3,¹⁸ which shows very good performance for the calculations of the standard heats of formation, reaction barrier heights, as well as nonbonded interaction. In the present work, we examined the XYG3 performance to calculate bond dissociation energies using R–X ($\text{R}^* = \text{Me}, \text{Et}, i\text{-Pr}, t\text{-Bu}$; $\text{X}^* = \text{H}, \text{Me}, \text{Cl}, \text{OH}$) as a representative system. We compared the XYG3 results with those of other state-of-art DFT methods such as doubly hybrid functionals MC3MPW, B2PLYP, MCG3-MPW, and hybrid meta-GGAs (M06-2X and BMK), and the most widely used hybrid GGAs (B3LYP), as well as those from WFT-based composite methods of G3, G3X, MCG3/3, and G4. We conclude the following:

(1) BDEs can be calculated as the energy difference of HOFs (atomization energies), and ΔBDEs are defined here as BDE trends as functions of alkylation and X^* substitution. Our calculations show that errors can accumulate or cancel out in calculating energy differences, such that BDE and ΔBDE carry additional information as compared to the widely used HOF that is important for the judgment of functional performance for “real” chemistry.

(2) Jointly with others,^{5–7,20–23} the present work confirms B3LYP's poor performance for BDE calculations, leading to a MAD of 5.98 kcal/mol. B2PLYP yields a MAD of around 3 kcal/mol regardless of the standard 6-311+G(3df,2p) basis set or the very large CQZV3P basis set including core-polarization. MADs for BDE predictions are 1.47 (MC3MPW), 1.44 (BMK), 1.21 (M06-2X), and 1.00 kcal/mol (XYG3), approaching the G3 and G4 results (MAD = 0.8 kcal/mol). MCG3-MPW leads to the smallest MAD (0.61) for this set of BDEs.

(3) B3LYP fails in qualitative prediction of ΔBDE trends for electronegative substituents $\text{X}^* = \text{Cl}$ or OH, leading to MAD = 3.16 with MAX = 6.28 kcal/mol. Our calculations show that even G3 falls short quantitatively in these cases, giving MAD = 1.50 with MAX = 3.10 kcal/mol. XYG3, MCG3-MPW, and G4 are all satisfactory with MADs = 0.32, 0.26, and 0.21 and MAXs = 1.01, 0.65, and 0.84 kcal/mol, respectively.

(4) Using G4 energy terms as references, our calculations display the anomalous behaviors of BMK in $\Delta\text{BDE}(\text{HF})$ and

Δ BDE(corr.), downplaying its role as a reliable tool for Δ BDE trend calculations. Δ BDE(HF) and Δ BDE(corr.) from XYG3 and MCG3-MPW are all in close parallel with the G4 counterparts, suggesting that these methods have captured the physical essence of the R–X bond as functions of alkylation and X^{*} substitution, and demonstrating the power of combining DFT and WFT methods as an efficient way of doing accurate electronic structure calculations.

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Supporting Information Available: Experimental and calculated heats of formation; experimental and calculated bond dissociation energies; Hartree–Fock and correlation contributions to the relative bond dissociation energies; optimized geometries at the levels of B3LYP/6-311+G(d,p), B3LYP/6-31G(2df,p), UMP2/6-31G(d), and UHF/6-31G(d). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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