J. Phys. Chem. A **2003,** *107,* 9991−9996

Accurate Calculations of Bond Dissociation Enthalpies with Density Functional Methods

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Received: July 19, 2003; In Final Form: September 25, 2003

The homolytic dissociation enthalpies of various bonds (C−H, N−H, O−H, S−H, X−H, C−C, C−N, C−O, C−S, and C−halogen) have been computed by using five density functional methods (B3LYP, MPW1PW91, B3PW91, B3P86, and MPW1P86). The quality of these methods is comprehensively evaluated on the basis of the available experimental bond dissociation enthalpies, and it is found that the MPW1P86 has the best agreement, while B3LYP performs the largest deviations. Large deviations also are found at the sophisticated CCSD(T) level of theory. The restricted open-shell method underestimates the radical stability.

Introduction

Bond dissociation enthalpies (BDE) are one of the important properties of molecules for considering their decomposition reactivities.[1−4] Experimental determinations of BDE are still limited to simple or small molecules and are insufficient in many practical cases, in which large and complex systems have frequently to be treated. Recent development of first-principle-based computational chemistry approaches has provided an alternative way to obtain accurate BDE ideally for any molecule of interest.[5] However, these approaches have to be carefully selected in order to calculate accurate BDE with reasonable computational costs. Of the available computational chemistry methods, ab initio methods have been proven to be accurate only at highly correlated post Hartree−Fock levels of theory. For example, the G2 and CCSD(T) methods were proven to be accurate but practicable only for small molecules.[6−10] The IMOMO method, which combines several methods at different levels of theory, expanded the capability to larger systems than those of the CCSD(T) limit,[11−14] but this kind of method is still very limited for many practical applications.

Computational methods from density functional theory (DFT) are good alternatives in predicting properties of large molecules because of their favorable scaling and therefore low computational costs.[15,16] Among several approaches (B3LYP, B3PW91, MPW1PW91, and B3P86)[3] which underestimate the C−C BDE systematically, the B3P86 values show the best agreement with the available experimental data. DiLabio has reported a similar effect.[4] This indicates that the available DFT methods have not reached the limit of the Kohn−Sham scheme of quantum mechanics. This can be considered as functional deficiencies in currently available methods, appealing for a continuous improvement of the existing functionals and their combinations.[5,15,17−20] The latest development in this direction has been discussed in the recent seminar of density functional theory.[21]

As we are focusing on the accurate estimation of BDE, we should keep in mind that the available DFT methods have not fully reached the thermochemistry consistency. For example, B3P86 can reproduce the BDE satisfactorily, but the heats of formation are far from acceptable,[22] indicating that the thermochemistry procedures using DFT methods need to be reexamined. Nevertheless, for the calculations of BDE, we believe that a solid reference system can be satisfied in the available theoretical tools for bond energies, providing an opportunity for us to discuss the theoretical implications from the comparison of theoretical BDE with the experimental ones, expecting that both theoretical and experimental chemists could get benefits from these comparisons. In this work, we expanded the combinations of the exchange-correlation functional (MPW1P86) to test the DFT limit in calculations of BDE for several sets of molecules containing different chemical bonds.

Computational Methods

All calculations were carried out using the Gaussian 98 program.[23] Geometries of molecules and related radical species were optimized at the (U)B3LYP/6-31G(d) level. The B3LYP/6-31G(d) method has been used for structure optimizations in many works, showing that this choice is feasible in terms of high accuracy requirements and practical, acceptable computational cost.[3,4,24] Subsequent frequency calculations at the same level verify the optimized structures to be ground states without imaginary frequencies (NImag = 0) and provide thermal data (E_{th}, 298 K). Single point energies for the optimized structures of the molecules and radicals concerned were computed with different DFT methods and the more flexible 6-311+G(d,p) basis set. All energetic calculations are on the basis of the ground-state structures, for either the neutral or radical fragments. The BDE at 298 K were calculated by using the thermochemical scheme supplied by Gaussian[25] as in the following equation: $\mathrm{BDE}_{298}(\mathrm{R}_1{-}\mathrm{R}_2) = [\Delta_f H_{298}(\mathrm{R}_1) + \Delta_f H_{298}(\mathrm{R}_2)] - \Delta_f H_{298}(\mathrm{R}_1{-}\mathrm{R}_2)$, in which $\mathrm{R}_1{-}\mathrm{R}_2$ is the neutral molecule, and R_1 and R_2 are the corresponding radicals.

Apart from the methods used in our previous studies,[3] we propose a new combination of MPW1[17] for the exchange functional and the P86 nonlocal correlation functional provided by Perdew 86[20] (MPW1P86[26]). These treatments are applied for a systematic improvement in BDE calculations to the DFT limit for understanding both exchange and correlation effects.

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10.1021/jp0361125 CCC: $25.00

TABLE 1: Computed BDE (kcal/mol, 298 K, with the 6-311+G(d,p) Basis Set), Compared with the Available Experimental Data

bond	B3LYP	B3PW91	MPW1PW91	B3P86	MPW1P86	(RO)B3P86	CCSD(T)	exp	exp[h]	exp[i]
					C−H					
CH_3−H	102.8	101.8	100.9	105.5	105.2	106.4	100.4	104.9 ± 0.1[a]	104.9 ± 0.1	104.9 ± 0.1
C_2H_5−H	98.3	97.3	96.5	100.8	100.7	101.9	96.6	101.1 ± 0.4[b]	101.1 ± 0.4	101.1 ± 0.4
$(CH_3)_2CH$−H	94.6	93.7	93.1	97.2	97.2	98.3		95.1 ± 1[c]	97.8 ± 0.5	98.6 ± 0.4
$(CH_3)_3C$−H	92.1	90.9	90.4	94.6	94.7	95.6		93.2 ± 2[c]	96.7 ± 0.3	96.5 ± 0.4
Ph−H	110.4	109.1	108.5	112.8	112.8	113.7		110.9 ± 2[d]	113.2 ± 0.7	112.9 ± 0.6
$PhCH_2$−H	87.1	86.8	86.2	90.1	90.1	92.1		88.5 ± 1.5[b]	89.8 ± 0.4	89.7 ± 0.6
$Ph(CH_3)CH$−H	83.7	83.1	82.6	86.3	86.4	88.2		85.4 ± 1.5[e]	85.4 ± 1.5	
$(Ph)_2CH$−H	78.7	78.5	78.3	81.6	81.9	83.4		84 ± 2[e]	81.4	
$(Ph)_2CH_3C$−H	78.7	78.0	77.7	81.0	81.3	82.7		81 ± 2[e]	81.1 ± 1.9	
					O−H, S−H, N−H					
HO−H	114.8	114.5	113.1	118.7	117.9	119.6	112.5	119.3 ± 0.05[b]	119.1 ± 0.96	118.8 ± 0.1
PhO−H	82.9	83.4	83.1	87.0	87.3	89.4		87.3 ± 1.0[a]	86.6 ± 1.9	90 ± 3
HS−H	88.0	88.0	87.2	91.4	91.2	92.2	86.0	91.2 ± 0.7[d]	91.2 ± 0.7	
PhS−H	75.5	75.8	75.3	79.0	79.0	80.1		79.1 ± 2.0[f]	83.3 ± 2.0	
NH_2−H	104.6	104.2	103.2	108.1	107.7	109.1	101.7	108.2 ± 0.3[g]	108.2 ± 0.3	107.6 ± 0.1
CH_3NH−H	96.0	95.7	94.9	99.4	99.3	100.5		100.0 ± 2.5[d]	100.0 ± 2.5	
PhNH−H	88.1	88.5	88.0	92.0	92.1	94.4		92.3 ± 2.0[g]	92.3 ± 2.0	
					X−H					
F−H	132.9	132.2	130.2	136.7	135.4	137.6	129.0	135.9 ± 0.3[d]	136.3	136.25 ± 0.01
Cl−H	100.1	100.7	99.7	104.2	103.9	105.0		103.2 ± 0.1[d]	103.2	103.15 ± 0.03
Br−H	88.3	88.5	87.6	92.0	91.7	92.6		87.4 ± 0.5[d]	87.6	87.54 ± 0.05

[a] Reference 28. [b] Reference 29. [c] Reference 30. [d] Reference 31. [e] Reference 13. [f] Reference 32. [g] Reference 4. [h] Reference 33. [i] Reference 2.

In addition, we also used the restricted open-shell method to test the energy accuracy of these radicals.

Results and Discussion

B3LYP and B3P86 were used in the previous studies of DiLabio[4] for X−H and X−Y calculations of BDE (X, Y = C, N, O, S, halogen). It was concluded that two different models are needed for determining X−H and X−Y BDE (B3LYP for X−H bonds and B3P86 for X−Y bonds). Chandra[27] calculated the C−H BDE of haloalkanes by the B3LYP method and got reasonable results. Previous studies for calculating R−H BDE, although extensive, have not conducted a systematic investigation on the performances of available DFT methods. The computed data are compared to the available experimental values[2,4,13,28−33] in Table 1, and the results are discussed separately.

C−H Bonds. The C−H bonds of nine hydrocarbon molecules were calculated with five DFT methods. As given in Table 1, both B3P86 and MPW1P86 have nearly the same results, and they are very close to the experimental data. Since both methods have the same correlation functional, one might conclude that B3 and MPW1 exchange functionals have nearly the same effects on the calculations of BDE. Combining both B3 and MPW1 exchange functionals with the PW91 correlation functional results in the largest deviation (up to 5.5 kcal/mol). This indicates that the PW91 correlation functional is insufficient. As expected from our pervious study for C−C bonds,[3] B3LYP gives less satisfactory results and the related deviation is ∼4 kcal/mol. In addition to these DFT results, we have performed two sophisticated CCSD(T) calculations on CH_4 and C_2H_6, and the C−H BDE are underestimated by 5 kcal/mol systematically. The relative trend of these methods for C−H BDE is MPW1P86 ≈ B3P86 > B3LYP > B3PW91 ≈ MPW1PW91 ≈ CCSD(T).

O−H, S−H, N−H, and X−H Bonds. In addition to the C−H bonds, we calculated some simple hydrogen to heteroatom bonds to investigate the functional dependence. As given in Table 1, both B3P86 and MPW1P86 have nearly the same results, in very good agreement with the available experimental data. Large deviations are found for B3LYP, B3PW91, and MPW1PW91, as for the C−H bonds. It is also worthy of note that the highly correlated CCSD(T) underestimates BDE once again by 5−6 kcal/mol. It is therefore obvious to conclude that MPW1P86 and B3P86 perform the best for determining X−H bond energies.

For the hydrogen halide bonds, very good agreement between theory and experiment in BDE is found for F−H and Cl−H at MPW1P86 and B3P86. In contrast, B3LYP, MPW1PW91, and B3PW91 underestimate these BDE by 3−5 kcal/mol. The largest underestimation for the F−H bond is at CCSD(T) by 7 kcal/mol. This raises a question on the sufficiency of this sophisticated correlation method. On the other hand, both B3P86 and MPW1P86 calculated BDE for Br−H are larger than the experimental value by 4 kcal/mol, and those at B3LYP, B3PW91, and MPW1PW91 are close to the experimental value.

C−C Bonds. The performance of C−C BDE calculations using four functionals has been addressed in our previous study.[3] Although B3P86 gives the best agreement, we have to note that all these four methods underestimate the C−C BDE in general, instead of presenting well-balanced statistics with both positive and negative deviations. On the basis of the pronounced performance of MPW1P86 on X−H bonds, we have redone our calculations on 16 molecules having available experimental data.[1,2,30,33−36] These results are compared with the other DFT methods used in our previous work in Table 2.

As shown in Table 2, MPW1P86 improves the quality of the calculated BDE of C−C bonds by an average magnitude of 1.4 kcal/mol in comparison with the B3P86 results, and the largest difference of 3.1 kcal/mol is found for $(Ph)_2CH$−$CH(Ph)_2$. It is interesting to note that the difference between MPW1P86 and B3P86 depends on the size of molecules studied; that is, the larger the molecules, the bigger the difference. The average absolute deviation of MPW1P86 for 14 molecules is only 1.2 kcal/mol, as compared with those of 1.9 kcal/mol of B3P86, 3.5 kcal/mol of MPW1PW91, 4.6 kcal/mol of B3P86, and 6.7 kcal/mol of B3LYP, respectively. Detailed analysis shows that MPW1P86 has both negative and positive deviations, while the other functionals have only underestimated BDE. The systematic trend implies that the current theoretical functionals should be

TABLE 2: Computed BDE (kcal/mol, 298 K, with the 6-311+G(d,p) Basis Set), Compared with the Available Experimental Data

bond	B3LYP	B3PW91	MPW1PW91	B3P86	MPW1P86	(RO)B3P86	exp	exp[f]	exp[g]
CH_3-CH_3	84.3	85.9	86.4	88.6	89.1	90.5	90.4 ± 0.3[a]	89.9 ± 0.5	90.1 ± 0.1
$C_2H_5-CH_3$	81.4	83.0	83.8	85.7	86.6	87.7	85.8 ± 1[a]		89.0 ± 0.4
$Ph-CH_3$	96.4	97.9	98.8	100.8	101.9	102.7	101.8 ± 2[a]		103.5 ± 0.6
$(CH_3)_2CH-CH_3$	78.7	80.3	81.3	83.2	84.4	85. 2	85.7 ± 1[a]		88.6 ± 0.4
$(CH_3)_3C-CH_3$	76.0	77.6	78.8	80.7	82.2	82.7	84.1 ± 1[a]		87.5 ± 0.4
$PhCH(CH_3)-CH_3$	66.4	68.5	69.7	71.2	72.6	74.0	74.6 ± 1.5[a]		
$PhCH_2-C_2H_5$	66.3	68.6	69.8	71.2	72.6	74.2	71.8 ± 1[a]	70.3 ± 1	76.7 ± 0.7
$PhCH_2-CH_2CH_2CH_3$	66.9	69.2	70.5	71.9	73.3	74.9	72.1 ± 1[a]	70.0 ± 1	
$PhCH_2-CH_3$	69.1	71.4	72.3	73.9	75.0	76.9	75.8 ± 1[a]	79.4 ± 1	77.6 ± 0.6
$Ph-Ph$	108.0	109.5	110.8	112.9	114.5	114.7	113.7[b]		118 ± 0.1
$PhCH_2-Ph$	79.6	82.0	83.4	84.8	86.5	87.7	89.6[b]		97 ± 1
$(Ph)_2CH-CH_3$	60.2	62.9	64.3	65.4	67.1	68.2	67.6[b,c]	72.0 ± 2	
$PhCH_2-CH_2Ph$	54.1	57.1	58.5	59.5	61.1	63.5	61.4[b,d]		65.2 ± 0.9
$PhCH_2CH_2-CH_2Ph$	66.8	69.0	70.3	71.6	73.0	74.6	73.9[b]		
average deviation	6.7	4.6	3.5	1.9	1.2	1.3			
$(Ph)_2CH-CH_2Ph$	43.4	46.7	48.8	49.3	51.6	53.2	57.8[b,e]		
$(Ph)_2CH-CH(Ph)_2$	32.7	36.9	39.7	39.8	42.9	43.4	47.5[b,e]		

[a] Reference 30. [b] Reference 1. [c] Reference 34. [d] Reference 35. [e] Reference 36. [f] Reference 33. [g] Reference 2.

reexamined, especially when molecular size is extended to the range that has not been considered during the development of the functionals.

For B3P86, the computed data for $PhCH_2-Ph$, $(Ph)_2CH-CH(Ph)_2$, and $(Ph)_2CH-CH_2Ph$ are lower than the experimental values by 4.8, 7.7, and 8.5 kcal/mol, respectively. Here MPW1P86 gives smaller deviations (3.1, 4.6, and 6.2 kcal/mol), but these differences are still too large. Thus, we appeal to a refinement in experimental work for the BDE of these large molecules, for which thermochemistry data are difficult to measure.

On the basis of the better performance of MPW1P86 in energy, one might ask if it can also perform better in geometry. Thus, test calculations were carried out for a set of molecules. Taking phenylethane as an example, the MPW1P86/6-311+G-(d,p) C−C BDE with the B3LYP/6-31G(d) geometry (75.0 kcal/mol) is larger than that with the MPW1P86/6-31G(d) geometry (73.2 kcal/mol), and the former is closer to the experimental value (75.8 kcal/mol). As for diphenylethane, the value of the C−C BDE with different geometries has the same trend, and the results of MPW1P86/6-311+G(d,p) BDE with the B3LYP geometry (61.1 kcal/mol) are higher than those with the MPW1P86 geometry (59.1 kcal/mol). These indicate that the relative energies with the B3LYP structures are more reasonable than those with the MPW1P86 geometries by around 2 kcal/mol.

C−N, C−O, C−S, and C−Halogen Bonds. The BDE of these bonds have been investigated computationally by several authors.[37] They found that MP2, CCDS(T), and G2[6−14] methods with large basis sets and proper corrections could provide reliable BDE values, while the tested B3LYP approach failed in most cases. In a more systematic way, DiLabio et al.[4] have investigated DFT approaches in calculating BDE, and found that B3P86 with proper basis sets produced good BDE. B3P86 has been taken as a basis of more sophisticated combined models for BDE calculations.

To examine the DFT performances, we extend our calculations to the X−Y BDE (X, Y = C, N, O, S, halogen) with the best-performed MPW1P86. The high level CCSD(T) method is applied to affordable molecules (small enough) for further comparisons. The calculated BDE values were listed in Table 3 with available experimental values from different sources.[2,4,30,31,33,38,39] It is worthy of note that the experimental BDE from different sources also bring about uncertainties due mainly to the experimental limitations, as we are reminded by many authors.[1,2,30,40,41]

C−N Bonds. We calculated seven C−N bonds with reliable experimental BDE values (values of different sources are very close, Table 3). It can be found that B3P86 and MPW1P86 have almost the same performance with average deviations of less than 1.5 kcal/mol. The other DFT methods bring typically deviations of more than 2.5 kcal/mol, of which B3LYP has the largest average absolute error, 5.6 kcal/mol. The CCSD(T) approach brings about a 5 kcal/mol error for H_3C-NH_2. In general, a quality trend observed in C−C BDE is again recovered: MPW1P86 ≈ B3P86 > MPW1PW91 ≈ B3MPW91 > B3LYP for all DFT methods used.

C−O and C−S Bonds. In six C−O bonds, one C−O bond in $PhOCH_3$ has a large deviation between the experimental values from different sources. Nevertheless, the MPW1P86 and B3P86 BDE values are within the range of experimental BDE. For $PhCH_2O-CH_3$, large negative deviations are found between the experimental and calculated values, while for CH_3-OCH_3 large positive deviations (3−4 kcal/mol) are found, although both of them work better than CCSD(T). In regard to these irregularities, we should be aware that experimental values need to be strictly verified, and the theoretical deficiencies implied should be considered in further studies.

The C−S BDE is produced with the highest error, about 5−6 kcal/mol, for the set of compounds used. The large deviations in S−C calculations indicate that all DFT methods and CCDS-(T) fail to fit the available experimental data. The fundamental reasons come again from experimental inconsistency and theoretical deficiencies for practically existing nonlocal effects. However, in general, the quality trend observed for C−C and C−N bond calculations has been maintained.

C−Halogen Bonds. For the C−halogen bonds calculated in this work, experimental data are quite reliable because of acceptable fluctuations between the BDE values from different sources. It is interesting that calculated values with our best method, MPW1P86, are very close to the experimental ones and B3P86 behaves equally well, with typical errors around 1 kcal/mol. Again the quality trend as in C−C bonds is repeated, indicating that the MPW1P86 combination can be extended to C−halogen BDE.

One reviewer[42] has suggested the use of a restricted open-shell method for all the radicals in BDE calculations to check our results, preventing the possible spin contamination, which

TABLE 3: Computed BDE (kcal/mol, 298 K, with the 6-311+G(d,p) Basis Set), Compared with the Available Experimental Data

bond	B3LYP	B3PW91	MPW1PW91	B3P86	MPW1P86	(RO)B3P86	CCSD(T)	exp^a	exp^b	exp	exp^f	exp^g
C−N												
CH_3-NH_2	79.1	80.9	81.2	83.9	84.3	85.9	79.8		84.9 ± 1.1			85.2 ± 0.3
$C_2H_5-NH_2$	78.2	80.0	80.5	83.0	83.7	85.0		84	81.6 ± 2			84.8 ± 0.4
$Ph-NH_2$	98.3	100.4	100.9	103.6	104.4	105.5		104	102 ± 2			104.2 ± 0.6
$PhCH_2-NH_2$	65.7	68.2	68.9	71.1	72.0	74.1		71.9 ± 1		74.0^c	71.1 ± 1.	71.7 ± 0.7
$PhNH-CH_3$	64. 8	67.5	68.4	70.3	71.5	73.7		67.7	71.4 ± 2		71.4 ± 1.9	
$PhCH_2-NHCH_3$	60.2	62.8	63.9	65.7	67.2	68.8		68.7 ± 1	68.7 ± 2		68.7 ± 1.9	
$PhCH_2-N(CH_3)_2$	55.0	57.6	59.3	61.0	62.8	64.1		60.9 ± 1	62.1 ± 2		62.1 ± 1.9	
C−O												
CH_3O-CH_3	74.6	75.8	76.2	79.0	79.7	84.8	78.7		83.3 ± 1			83.2 ± 0.9
$C_2H_5-OCH_3$	75.1	76.3	76.9	79.6	80.5	85.4			81.8 ± 1	83.0^c		85.0 ± 1.1
$PhCH_2O-CH_3$	73.0	74.2	74.9	77.4	78.4	79.5		67.0			67.0	
$PhO-C_2H_5$	56.6	58.6	59.9	61.7	63.2	65.1		64.0	63.0 ± 1.5		63.1 ± 1.5	
$Ph-OCH_3$	91.2	92.9	93.6	96.4	97.5	102.1		98				101.0 ± 1.0
$PhO-CH_3$	56.1	58.2	59.3	61.2	62.6	64.6		57 ± 2	63.8 ± 1	63.4^{c,d}	56.9 ± 1.9	
C−S												
CH_3S-CH_3	65.7	68.2	68.8	70.6	71.4	72.4	69.2		77.2 ± 2		73.6 ± 0.8	
$PhS-CH_3$	56.2	59.0	59.8	61.2	62.2	63.4		67.5 ± 2	69.4 ± 2	59.9^c	69.4 ± 1.9	
$PhCH_2-SCH_3$	50.3	53.4	54.4	55.6	56.8	58.5		59.4 ± 2	61.4 ± 2		61.4 ± 1.9	
C−X												
$Ph-F$	121.6	122.1	121.4	125.7	125.3	127.5		125	125.2			127.2 ± 0.7
$Ph-Cl$	89.5	92.3	92.8	95.0	95.7	96.7		95	95.7 ± 2			97.1 ± 0.6
$Ph-Br$	77.6	80.1	80.6	82.7	83. 4	84.2		80	80.2		80.5 ± 1.9	84.0 ± 1.0
$PhCH_2-F$	93.7	94.5	93.9	97.8	97.5	100.7				98.6^e		98.7 ± 0.7
$PhCH_2-Cl$	64.3	67.3	67.7	69.6	70.2	72.4		69	72.2 ± 1.5	70.4^c		74.0 ± 1.0
$PhCH_2-Br$	54.3	57.0	57.5	59.2	59.8	61.8		55	57.6 ± 1.5	60.8^c		63.0 ± 1.0

[a] Reference 31 [b] Reference 30. [c] Reference 4. [d] Reference 38. [e] Reference 39. [f] Reference 33. [g] Reference 2.

TABLE 4: Computed BDE (kcal/mol, 298 K, with the 6-311+G(d,p) Basis Set), Compared with the Available Experimental Data

bond	B3LYP	B3PW91	MPW1PW91	B3P86	MPW1P86	(RO)B3P86	G2^a	G2MP2^a	exp^a
CCl_3-Cl	58.7	61.5	62.0	64.2	65.0	65.8	71.8	72.8	69.9 ± 2.1
C_2Cl_5-Cl	57.6	61.2	62.2	64.2	65.4	65.9	74.5	75.5	71.5 ± 2.8
CCl_3-CCl_3	53.9	56.7	58.6	60.5	62.9	62.1	77.6	77.7	70.1 ± 3.5

[a] Reference 40.

may cause the unsatisfactory radical energies. For simplicity, we used the (RO)B3P86 functional, and the computed data are listed in Tables1-4 for comparison. In general, results at (RO)-B3P86 are higher than those at (U)B3P86. For X−H bonds, most of the (RO)B3P86 results are higher than the experimental data, and they appear to be not as accurate as those at B3P86 and MPW1P86. For X−Y bonds (Table 1), results at (RO)-B3P86 are larger than those at (U)B3P86, and the former also are larger than the available experimental values. Thus, one might consider that the restricted open-shell method underestimates the radical energies, in contrast to the unrestricted open-shell method. The same trend is found for C−C bonds (Table 2) and C−N, C−O, and C−S as well as C−halogen bonds (Table 3). On the basis of these changes, it is to be expected that all other functionals within the restricted open-shell wave function should have larger BDE than those with unrestricted open-shell wave functionals. Indeed, this is found for phenylethane as an example; the restricted open-shell results (kcal/mol) with different functionals show the same order as that of unrestricted results, but the former results, (RO)B3P86 [76.9] > (RO)MPW1PW91 [76.0] > (RO)B3MPW91 [74.5] > (RO)-B3LYP [71.9], are larger than the later results, B3P86 [73.9] > MPW1PW91 [72.3] > B3MPW91 [71.4] > B3LYP [69.1]. On the other hand, it is necessary to point out that both (RO)-B3P86 and B3P86 perform better than (RO)B3LYP and B3LYP by around 5 kcal/mol. On this basis, (RO)MPW1P86 should also give larger BDE values than MPW1P86, and the consequence will be that the (RO)MPW1P86 overestimates BDE values as compared with the experimental values.

Further Remarks

The BDE calculations with B3LYP, B3PW91, MPW1PW91, B3P86, and MPW1P86 have shown that proper combinations of exchange and correlation functionals can systematically improve the quality of calculated BDE to the limit of the Kohn−Sham scheme of quantum mechanics; namely, the magnitudes of systematic underestimation of BDE by well established methods can be eliminated or reduced. This observed trend, when other factors (basis set) are kept unchanged, can be a starting point to discuss the performances and problems implied in the currently available functionals, although we have to be aware that one could not predict the errors of these DFT methods only from an intimate knowledge of their functional features. The benchmark results from this work may serve as a kind of probe for the systematic improvement of DFT methods.

The functionals used in this work and available from the published domain have not been fully evaluated in a comprehensive way. MPW1P86 differs from MPW1PW91 in correlation functional, and shows remarkably improved behavior. To fully understand the quality sequences of theses DFT methods for different bond dissociations is a very complicated matter. Nevertheless, the trend in C−C BDE calculations is systematically sufficient for a comprehensive comparison and, in turn, provides an opportunity to verify the related functionals.

A systematic comparison has been shown in Figure 1, in which the deviations for the C−C bonds tested are displayed. Of 16 C−C bonds in different molecules (Table 2), the 2 experimental BDE values (nos. 15 and 16) with the greatest

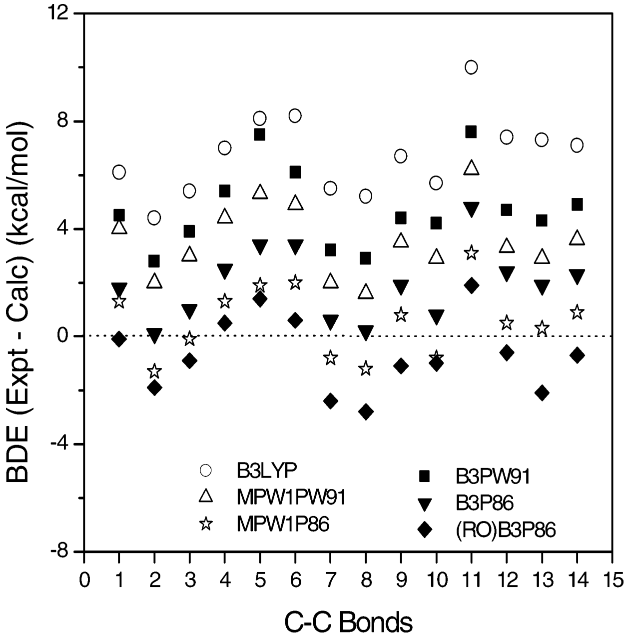

Figure 1. Deviation of calculated C−C BDE.

uncertainties are not included; this is because MPW1P86 does not show any reasonable deviations such as those for the other C−C bonds (no. 1−14). For these 14 C−C bonds, MPW1P86 brings the calculated BDE values to the accuracy level of experimental BDE with both positive and negative deviations, while the other four methods have only positive deviations from experimental BDE. We may consider that this essential difference between MPW1P86 and the other four methods may come from a significant deficiency existing in the four combinations. Comparing the results in Figure 1, similar variation trends are found for other bonds (Tables 1 and 3).

Corresponding to the phenomena observed in our BDE calculations, several theoretical studies[17−20] have continuously dealt with the improvement of existing functionals by using more rigorous theoretical assumptions or constraints. These works partially reflected the theoretical genesis of the deficiencies of existing DFT methods. For the correlation part in popular DFT methods available, Becke[15] has found that the LYP correlation does not meet two of the four “minimal” theoretical requirements, which are attainment of a uniform electron gas limit and distinct treatment of opposite-spin and parallel-spin relations, and the P86 and PW91 correlation formulas do not meet the requirement of perfect self-interaction (exactly zero interaction energy in one electron system).

For the exchange part, Adamo and Barone[18] pointed out that the B functional, despite yielding very useful computational models, does not obey some of the most important physical conditions that must be satisfied by an exact exchange functional, and they therefore developed a new version of the exchange functional denoted as MPW1 with improved long-range behavior and adiabatic connection relations on the basis of Perdew and Wang’s work (PW91).

Among all the DFT methods tested in this work, the theoretical consequences are that the MPW1P86 combination may benefit largely from a better exchange functional with improved long-range (low density gradient region) capability as well as a well-established correlation functional and, therefore, gain the highest accuracy in our BDE calculations. This is true especially in C−C bond calculations for large and complex molecules, in which many factors may constitute the significance of the long-range contribution to the molecular-fragment energies, and in addition, the quality of effectively counting local effects has not been attenuated. However, it should be mentioned that it is by no means perfect to have only MPW1P86 functionals because our knowledge has not been sufficient to fully understand all theoretical aspects implied in real molecular systems.

Apart from the generality that should be seriously concerned in theoretical exploration, the above discussion appeals to us to consider in a more practical way in chemistry the complexity of the systems that we are interested in. What we are not satisfied with is that all these tested methods have large deviations for almost all C−S bonds and failed to predict correct C−Cl BDE in CCl_4 and C_2Cl_6 and C−C BDE in C_2Cl_6, as listed in Table 4.[40] This improvement from (U)B3P86 to (RO)B3P86 is still too small for the C−Cl bonds. This appeals for a further investigation of the existing DFT methods, and new and general functional approaches are expected to meet all these needs.

Conclusions

In our previous work, we have shown the ability of B3LYP, B3PW91, MPW1PW91, and B3P86 to reproduce the C−C bond dissociation enthalpies and found that all BDE were underestimated, despite the best performance of B3P86. It has been shown in this work that such systematic underestimation can be eliminated or reduced with the combination of the MPW1 exchange functional and the P86 correlation functional. This trend is not only found for C−C and C−H bonds but also found for the C−N, C−S, C−O, and C−halogen bonds. This work not only is a benchmark for further improvement and development of both exchange and correlation functionals, but also provides a reliable method for the study of the bond dissociation reactions associated with radical species, as found in gas phase chemistry and biological processes. It is found that the restricted open-shell method underestimates the stability of the related radical in a systematic way and gives larger BDE values as compared with those of the unrestricted method.

Acknowledgment. This work was supported by the Chinese Academy of Sciences (No. [2002] 437) and the Committee of Science and Technology of China (project 863, No. 2001AA523010).

Supporting Information Available: Tables of total electronic energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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