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Density Functional Theory Based Model Calculations for Accurate Bond Dissociation Enthalpies. 3. A Single Approach for X−H, X−X, and X−Y (X, Y = C, N, O, S, Halogen) Bonds

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Molecule and radical enthalpies were computed using five model chemistries, which are differentiated by the method used for calculating geometries and scaled frequencies. For all the models, electronic energies were calculated using density functional theory (DFT) at the B3P86/6-311G(2d,2p) level of theory, which was selected following tests involving six hybrid functionals and three basis sets. The models were assessed for their ability to accurately predict the bond dissociation enthalpies (BDEs) of 34 X−H bonds and 28 X−X and X−Y bonds, where X, Y = C, N, O, S, and halogen. The mean absolute error (MAE) of the BDEs relative to experiment predicted using each of the five models is: AM1 = 2.1, PM3 = 1.7, HF/3-21G(d) = 1.6, B3P86/3-21G(d) = 1.4, and B3P86/6-31G(d) = 1.5 kcal/mol. The B3P86/6-311G(2d,2p)//B3P86/3-21G(d) and B3P86/6-311G(2d,2p)//B3P86/6-31G(d) models perform as well as G3(MP2) (MAE = 1.5) for the bonds in the test set and with a substantially lower computational cost. The models also perform well for Si−H bonds and for Si−X (X = C, N, O) bonds in radicals but not for Si−X bonds in closed-shell molecules. Comparisons are also made to a reparametrized version of B3LYP, which is also shown to perform well for most bonds in the test set. The models are shown to be applicable to the study of olefin line growth on silicon surfaces, an area of research in which we are currently involved. The basis set dependence of the X−H BDEs is examined. The shortcomings of the present models are discussed, with particular emphasis on the failure of various DFT methods to adequately describe molecules with extensive delocalization.

1. Introduction

Bond dissociation enthalpies (BDEs) are important thermodynamic quantities that contribute to the understanding of a diversity of processes ranging from enzyme mechanisms to surface chemistry. BDEs have been well studied both experimentally and theoretically and there continues to be a steady stream of work in the field from practitioners in both areas.[3] The substantial theoretical work can likely be attributed to the increasing ability of computational techniques to predict BDEs in reasonable agreement with experimental values at a fraction of the cost in manpower resources. In general, however, experimental BDE data have large uncertainties (2−3 kcal/mol and more in some cases), making the development and comparisons of new computational techniques challenging. For example, in a 1998 review of bond dissociation enthalpies of silicon-containing compounds, Becerra and Walsh[4] upwardly revise Si−H BDEs in methylsilanes alone by ca. 3−4.5 kcal/mol compared to their review from 10 years earlier. This illustrates the importance of continued efforts in this area of research.

We have been involved in the development of density functional theory based model chemistries for BDE calculations. Our principal goal in developing models for calculating BDEs is to formulate approaches that are reasonably reliable and can yield quick results even when applied to large molecular systems. We have particular interest in antioxidant[5] and silicon surface (organosilane) chemistry,[6] where the molecular systems of interest can contain several hundred atoms.

Our early efforts showed that BDEs and proton affinities (PAs) for X−H molecules and electron affinities (EAs) for $X^\bullet$ radicals are accurately predicted using models based on electronic energies calculated at the (RO)B3LYP/6-311+G(2d,2p) level.[7] The use of lower level methods such as the semiempirical AM1[8] and B3LYP[9,10]/6-31G(d) to energy minimize molecule and radical structures and to calculate (scaled) vibration frequencies yielded results in excellent agreement with the full (RO)B3LYP/6-311+G(2d,2p) treatment and experiment, while substantially reducing the computational cost of the calculations. These B3LYP based model chemistries also require that the exact enthalpy for the hydrogen atom be used to obtain BDEs in good agreement with experiment, despite the fact that the error in the enthalpy at that level of theory is ca. 1.35 kcal/mol. Thus, the use of the exact hydrogen atom enthalpy amounts to an empirical correction. One of the serious drawbacks of the B3LYP based models is their inability to accurately calculate the BDEs for X−X and X−Y (X,Y ≠ H) bonds. For example, the BDEs for the central bonds in H_2O_2 and C_2H_6 are underestimated by 3.1 and 3.9 kcal/mol, respectively.

In follow-up work,[11] we explored alternative models that better describe X−X and X−Y BDEs. Our studies, which were largely guided by the extensive DFT benchmarking performed by Curtiss et al.[12] showed that BDEs for bonds of these types were well predicted using (RO)B3P86[9,13]/6-311G(d,p) based models. As in our earlier work,[7] the use of lower level methods for geometry and frequency calculations was shown to reduce computational cost with little or no loss in accuracy except in a few, well-understood cases. However, (RO)B3P86/6-311G(d,p)

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based models consistently produced X−H BDEs that were overestimated for small test cases by 4−15 kcal/mol depending on how the energy of the hydrogen atom was calculated.

We continue to be motivated to find a (hybrid) DFT based model approach that allows us to compute accurate BDEs at a minimum of computational cost because the molecular systems in which we are interested are becoming ever larger. Thus, to be able to engage in "high-throughput" studies (of, for example, molecules that display appropriate line-growth properties on silicon surfaces), the ideal DFT based model should be applicable to X−H, X−X, and X−Y bonds, use a computationally inexpensive method for the intensive geometry optimization and vibration frequency calculations, and employ the smallest possible basis set for the energy calculations.

The continual development of new functionals gives us the opportunity to assess new models for BDE calculations. We surveyed the ability of six functionals (B3LYP, B3P86, B3PW91,[9,14] BHandHLYP,[15] PBE1PBE,[17] and mPW1PW91[18]) each using three basis sets (6-31G(d), 6-311G(d,p), and 6-311G-(2d,2p)) for their ability to accurately predict 10 representative X−H, X−X, and X−Y bonds (these data are collected in Table S1 in the Supporting Information). Our preliminary efforts once again led us to the B3P86 functional as the best choice for use in our model.

In this work, we report on the ability of the B3P86 functional to predict accurate BDEs and explore B3P86 based model chemistries for calculations on X−H, X−X and X−Y (X, Y = X, Y = C, N, O, Si, S, halogen) bonds. In particular, we show that a marginal increase in the basis set size over our previous work[11] results in a substantial improvement in X−H BDEs and a slight improvement in BDEs involving heavy atoms and thus provides a single approach for calculating accurate X−H, X−X, and X−Y BDEs. The use of lower level methods for geometry and frequency calculations, which greatly improves the speed of the calculations and extends their range of applicability, is studied in detail. The basis set dependencies of C−H BDEs are discussed along with application of the developed models to organosilane chemistry. Comparisons to a reparametrized version of the B3LYP approach are made and shortcomings of the present models are discussed, including difficulties associated with treating delocalized systems.

2. Methods of Calculation

The X−H BDEs for 34 molecules and the X−X or X−Y BDEs for 28 molecules were tested. The molecules were chosen on the basis of the availability of reasonably reliable experimental BDE data and are representative of molecules that are involved in biochemical, atmospheric, and surface processes. Generally speaking, the experimental BDE data we use have uncertainties of ca. 2 kcal/mol. There are questions as to how to compare calculated results to experimental data of varying degrees of uncertainty. For the sake of simplicity, however, the experimental data are treated as though they all have the same uncertainty. Another important consideration is how to go about selecting a single experimental value from among a large number of different values covering a large (e.g., 5 kcal/mol) range. In this study, we have attempted to select BDE data from reviewed sources and/or more recent experimental sources.

The calculation of a BDE can be separated into two parts. The first part of the problem (part A) involves finding the optimum structures of the molecule and the radicals. At the same level of treatment, zero-point energies and the vibrational contributions to the enthalpy must be evaluated by performing frequency calculations on the optimized molecule and radical structures. In the second part of the problem (part B), the electronic energy for each of the components in the dissociation reaction are calculated at their respective minimima, as determined in part A. At any given level of theory, the geometry optimization and frequency calculations of part A are far more computationally costly that the single-point energy calculations of part B. Therefore, efficient (i.e., fast) model chemistries can be designed for the calculation of BDEs by using lower level and hopefully reliable methods for A and higher level methods with large basis sets for B. If one is only interested in computing BDEs,[19] then the accuracy of the approach used for A is, in principle, unimportant. In our experience,[5,7,11] we find that even very low levels of theory can be used for A and that errors arising in part B due to inaccuracies in predicted molecular (radical) geometry cancel and yield quite satisfactory BDE results. We explore in this work the applicability of lower level methods for the geometry and frequency calculation phase of BDE calculations.

All calculations were performed with the Gaussian-98 package of programs.[16] The models tested in this work are differentiated by the computational method used for geometry optimization and frequency calculations. The geometries of the molecules and radicals were optimized using the AM1,[8] PM3,[20] HF/3-21G(d), B3P86/3-21G(d), or B3P86/6-31G(d) levels of theory. Our previous work has shown that performing geometry optimizations using basis sets larger than 6-31G(d) results in very little change in BDE. Frequency calculations were performed following the geometry calculations to obtain the zero-point vibrational energy (E_{ZP}) and vibrational enthalpy ($H_{T,\mathrm{vib}}$) corrections for the bond dissociation process and to verify that the optimized structures are true minima. For the semiempirical frequencies, the scale factor of 0.973 was that used in ref 7 for AM1 frequencies. The HF/3-21G(d) scale factor (0.89) was adapted from the work of Scott and Radom.[21] A scale factor of 0.986 was used for both the B3P86/3-21G(d) and B3P86/6-31G(d) based models and was taken from ref 21. It is worth noting that the vibrational contribution to the BDE is on the order of 8.8 kcal/mol for a 130 kcal/mol X−H bond at 298.15 K. Consequently, a reduction in scale factor from 1.00 to 0.95 results in a 0.4 kcal/mol change in the BDE. The use of scale factors for vibrational corrections becomes less important for smaller BDEs. Following the frequency step, the electronic energy, E_{el}, is computed at the B3P86/6-311G(2d,2p) level. The molecule/radical enthalpy is obtained by

$$H_T^\circ = E_{\mathrm{el}} + E_{\mathrm{ZP}} + H_{T,\mathrm{vib}} + 4RT \qquad (1)$$

where the quantity $4RT$ accounts for the enthalpic contributions due to translation and rotation in a nonlinear molecule and includes a PV term.[22] For atoms, this term becomes $(5/2)RT$. For the system X−Y, the BDE at 298.15 K is then computed as

$$\mathrm{BDE(X{-}Y)} = H_{298}^\circ(\mathrm{X}^\bullet) + H_{298}^\circ(\mathrm{Y}^\bullet) - H_{298}^\circ(\mathrm{XY}) \qquad (2)$$

We note that the hydrogen atom electronic energy is taken to be the value computed at the B3P86/6-311G(2d,2p) level despite the fact that it is lower than the exact value by 11.6 kcal/mol. This differs from our previous approach[7] where the electronic energy of the hydrogen atom was set to −0.5 hartree. We note, again, that the use of this exact value in our previous work amounts to nothing more than an empirical correction, used to improve agreement between theory and experiment. Such a correction is unnecessary in the present work.

Where possible, the data are compared to BDEs calculated using the G3(MP2) model,[23] which has been shown to predict enthalpies of formation with an average absolute deviation of 1.30 kcal/mol relative to experiment. Therefore, this work also serves to validate the use of G3(MP2) for BDE calculations.

3. Results and Discussion

The model chemistries studied in this work are based on computing E_{el} at the B3P86/6-311G(2d,2p) level, which was selected from our preliminary survey of six functionals (data given in Table S1, Supporting Information). We performed additional basis set tests on the BDEs of 21 compounds that confirm that 6-311G(2d,2p) provides the best balance between calculation time and accuracy, as measured by the mean absolute error (MAE) of these BDEs from experiment. The data from these tests are provided in Table S2 of the Supporting Information section.

The computed BDEs for 34 X−H bonds are collected in Table 1a and the BDEs for 28 X−X and X−Y bonds are listed in Table 1b. For convenience, the models will be identified by the method by which geometry optimizations were performed and the G3(MP2) model will be referred to by name. Where necessary, calculated geometries will be compared to those obtained using the B3P86/6-31G(d) method. The data are organized in order of increasing computational effort of the method used for the geometry optimization and frequency calculation parts of the model. Based on the total time required for the frequency calculations for 91 compounds, the relative times for the B3P86/6-311G(2d,2p)//method models are 1:1:18:85:229 for the AM1, PM3, HF/3-21G(d), B3P86/3-21G(d), and B3P86/6-31G(d) methods, respectively. For comparative purposes, the calculation time by G3(MP2) for the benzene molecule was 3.7 times that using B3P86/6-311G(2d,2p)//B3P86/6-31G(d).

Statistical analyses of the data by bond type are provided at the end of each subsection. These analyses include mean absolute error (MAE), root-mean-square error (RMSE), and maximum error (MaxE), which are computed relative to experimental values and have units of kcal/mol. Because the E_{el} term in eq 1 is evaluated at the same level of theory in all the B3P86 based models, the comparisons of the BDEs predicted with each of these models provide an indication of how well the geometry optimization methods perform.[24]

3.1. X−H BDEs. The C−H BDEs reported in Table 1a represent the largest subset of bonds in our test group. The BDEs using all the models are in very good agreement with the available experimental values, with MAEs ranging from 1.9 kcal/mol for the AM1 model to 1.3 kcal/mol for the B3LYP/6-31G(d) model. G3(MP2) performs marginally better for the C−H set, giving a MAE of 1.2 kcal/mol. The RMSE values for all the models and G3(MP2) are also quite low, ranging from 2.4 to 1.5 kcal/mol. The MaxE values for all models are due to apparent underestimations in the C−H BDE of 1,4-pentadiene. The AM1 based model has the largest MaxE, at 5.1 kcal/mol, a value that is improved to ca. 3.3 kcal/mol upon use of either of the B3P86 models. This error may be due to difficulties that DFT methods have with delocalized systems (see section 3.5.2). G3(MP2) predicts the C−H BDE for 1,4-pentadiene to within 0.1 kcal/mol of the experimental value and has a MaxE of 2.7 kcal/mol for the C−H BDE in cyclopropane.

Four N−H bonds are listed in Table 1a. All models predict BDEs that are in excellent agreement with experiment, with the notable exception of the AM1 derived N−H BDEs for hydrazine. The semiempirical AM1 method incorrectly predicts a N_2H_4 structure in which the dihedral angle between nitrogen lone pairs is 180° and the N−N bond length is 0.04 Å too short. These inaccuracies result in a higher E_{el} for the parent structure and a lower BDE. This effect was noted in our previous work.[7] PM3 also predicts a similar structure for hydrazine but an N−N bond that is too long by 0.02 Å provides a slightly lower E_{el} for the molecule, relative to the AM1 model, and thus a BDE in better agreement with experiment.

For the five O−H bonds in the table, all the models perform well except for the treatment of HOO−H. In this case, the excellent agreement between the AM1 derived BDE and experiment is fortuitous. The structure of the parent molecule is incorrectly predicted to be planar (with the dihedral angle being 180°) and the O−O bond length is too long by about 0.1 Å whereas the peroxyl radical has an equally long O−O bond so errors in E_{el} tend to cancel. The structure for hydrogen peroxide is also predicted to be planar using HF and B3P86 when 3-21G(d) basis sets are used.[25] However, the predicted bond lengths are reasonable and so little error is found in the BDEs determined with these models.

Si−H bonds have been included in Table 1a despite the fact that Si is not one of the title atoms listed (for reasons that will be clear in section 3.5.1). The BDEs for this subgroup are well predicted with all of the models, with the exception of the AM1 based model, which severely overestimates the Si−H BDE in trimethylsilane. This error results from Si−C bond lengths in the trimethylsilyl radical that are too short by ca. 0.1 Å by the AM1 method. For the other models, the trihalosilanes are generally the largest contributors to the BDE errors where the models tend predict BDEs that are too low by 3.5−4.0 kcal/mol. The G3(MP2) BDEs for these silanes are also too low (by 3.4 and 2.6 kcal/mol for F_3SiH and Cl_3SiH, respectively.).

Only two S−H BDEs are included in this study. The HS−H BDE is overestimated and the PhS−H is underestimated by all of the models but not by G3(MP2).

To summarize, the statistical information for all the X−H BDEs is provided at the bottom of Table 1a and absolute values of the differences of the calculated BDEs from the experimental values are summarized in histograms in Figure 1. Overall, the X−H BDEs are predicted with MAEs of less than 2 kcal/mol using all of the models. The B3P86 based models perform better than the semiempirical and HF based models over the broad range of BDE values (ca. 40 kcal/mol) for molecules containing a diversity of substituents. The histograms clearly show that the AM1 model has the poorest performance with three BDEs in error by 5−7 kcal/mol and the PM3 results are clustered closer to zero with fewer outliers. This is significant because our previous "low-level" models were based exclusively on the AM1 geometry and frequency calculations.[26] As the geometry optimization method improves, the errors in BDE tend to be more clustered around 0 kcal/mol and there are fewer BDEs with large errors. The HF/3-21G(d) model tends to perform slightly better than the semiempirical models. For both of the B3P86 models the errors are nearly identical, indicating that the smaller basis set can be used for geometry optimizations and frequency calculations with little or no loss in the quality of predicted BDEs but with a significant savings in computational effort for larger molecules. A comparison of the B3P86 models with G3(MP2) shows that these different methods predict essentially identical results.

3.2. X−X and X−Y BDEs. The C−C BDEs results listed in Table 1b show reasonable agreement with experiment. The values for H_3C-CF_3, H_3C-CH_3, and $H_3C-C_2H_5$ calculated with all of the models are within ca. 2 kcal/mol of experiment. For $PhCH_2-CH_3$, the semiempirical and HF/3-21G(d) models

TABLE 1: Calculated BDEs Using Various B3P86/6-311G(2d,2p) Based Models[a]

bond	AM1	PM3	HF/3-21G(d)	B3P86/3-21G(d)	B3P86/6-31G(d)	G3(MP2)	exptl
(a) X−H BDEs							
C−H							
Ph−H	113.6	114.0	112.9	113.2	113.3	115.8	113.3^b
H_2CCH−H	114.3	113.4	111.6	111.1	111.2	110.6	110.6^b
F_3C−H	105.2	107.3	106.0	106.4	106.0	106.6	106.3^b
c-C_3H_6	110.1	110.1	109.5	108.6	108.7	109.0	106.3^c
H_3C−H	106.4	106.2	106.6	106.2	106.5	104.1	104.8^b
H_3CCH_2−H	102.1	102.3	102.1	101.5	101.7	101.1	100.5^b
$H_3CCH_2CH_2$−H	102.1	102.4	102.4	101.7	101.9	101.4	101.0^b
$HOCH_2$−H	95.7	96.6	96.5	95.7	96.0	97.7	98.1^b
Cl_3C−H	95.6	96.9	93.9	93.4	93.6	93.6	95.8^b
$HCOCH_2$−H	94.3	95.4	98.2	95.5	95.3	95.5	94.3^d
$NCCH_2$−H	95.3	95.9	95.2	95.6	95.7	96.2	94.8^d
OCH−H	93.4	92.0	89.0	88.7	88.7	88.1	90.2^b
$PhCH_2$−H	89.1	89.5	89.1	89.7	90.0	91.9	89.7^b
$C_4H_5CH_2$−H	80.0	80.4	80.2	81.1	81.2	82.5	83.0^c
$(H_3C_2)_2CH$−H	70.9	71.8	71.8	72.6	72.8	76.1	76.0^c
MAE	**1.9**	**1.8**	**1.8**	**1.3**	**1.3**	**1.2**	
RMSE	**2.4**	**2.1**	**2.1**	**1.6**	**1.6**	**1.5**	
MaxE	**5.1**	**4.2**	**4.2**	**3.4**	**3.2**	**2.7**	
N−H							
H_2N−H	108.8	109.9	106.9	106.9	107.7	106.6	108.6^b
H_3CNH−H	100.8	101.7	99.9	99.4	99.1	99.5	100.0^c
PhNH−H	92.1	92.2	90.4	90.7	91.8	93.2	89.7^e
H_2NNH−H	77.1	79.5	81.9	82.2	81.3	82.3	82.2^d
MAE	**2.1**	**2.1**	**0.7**	**0.8**	**1.2**	**1.5**	
RMSE	**2.8**	**2.1**	**0.9**	**1.0**	**1.3**	**2.0**	
MaxE	**5.1**	**2.7**	**1.7**	**1.7**	**2.1**	**3.5**	
O−H							
HO−H	119.3	119.1	118.6	118.3	118.4	117.8	118.8^f
CH_3CH_2O−H	103.9	104.0	105.7	104.8	104.2	105.8	104.6^d
$(C_4N_2H_3)O$−H^g	89.9	90.2	92.0	90.2	89.8	92.1	91.1^h
PhO−H	87.5	87.2	88.8	88.2	87.8	89.6	87.4^i
HOO−H	89.6	84.6	88.7	85.6	84.6	86.6	87.8^j
MAE	**0.9**	**1.0**	**0.9**	**0.9**	**1.1**	**1.3**	
RMSE	**1.0**	**1.6**	**1.0**	**1.2**	**1.6**	**1.5**	
MaxE	**1.8**	**3.2**	**1.4**	**2.2**	**3.2**	**2.2**	
Si−H							
F_3Si−H	99.7	99.8	99.9	99.6	99.9	99.8	103.3^k
$(CH_3)_3Si$−H	100.9	97.7	93.7	93.4	93.4	93.8	94.9^k
Cl_3Si−H	94.9	92.5	90.9	90.5	90.6	91.8	94.4^k
$(CH_3)_2SiH$−H	96.6	95.7	93.0	92.7	92.7	92.9	93.5^k
CH_3SiH_2−H	93.8	93.5	92.3	91.9	91.9	91.9	92.7^k
SiH_3−H	91.9	92.1	91.6	91.4	91.3	90.9	91.7^k
$PhSiH_2$−H	92.4	92.0	89.0	89.1	89.2	92.2	91.3^k
SiH_3SiH_2−H	89.3	89.3	88.8	88.5	88.5	88.3	88.9^k
MAE	**2.0**	**1.6**	**1.4**	**1.7**	**1.7**	**1.4**	
RMSE	**2.8**	**1.9**	**2.0**	**2.2**	**2.1**	**1.7**	
MaxE	**6.0**	**3.5**	**3.5**	**3.9**	**3.8**	**3.5**	
S−H							
HS−H	92.3	93.1	92.7	92.6	92.7	90.6	90.1^b
PhS−H	79.9	80.4	78.2	79.7	79.8	82.7	83.5^l
Total (for 34 Bonds)							
MAE	**1.8**	**1.7**	**1.6**	**1.4**	**1.5**	**1.2**	
RMSE	**2.5**	**2.1**	**2.1**	**1.8**	**1.8**	**1.6**	
(b) X−X and X−Y BDEs (X,Y ≠ H)							
C−C							
H_3C−CN	125.6	126.4	125.5	126.1	126.3	122.7	121.8^b
H_3C−CF_3	99.0	99.4	100.0	100.5	100.3	102.5	101.4^b
H_3C−CH_3	89.0	89.9	89.4	89.4	89.9	88.5	89.7^b
H_3C−C_2H_5	86.7	87.4	86.7	86.4	86.9	88.1	88.2^b
$PhCH_2$−CH_3	73.2	72.2	73.3	74.3	74.7	79.3	77.6^m
MAE	**2.6**	**2.6**	**2.2**	**2.1**	**2.0**	**1.0**	
RMSE	**2.9**	**3.3**	**2.7**	**2.6**	**2.5**	**1.1**	
MaxE	**4.4**	**5.4**	**4.3**	**4.3**	**4.5**	**1.7**	
C−N							
H_3C−NH_2	84.7	87.3	83.2	83.6	84.1	85.6	84.9^c
H_3C−$NHCH_3$	80.5	81.9	79.4	79.4	79.2	80.4	82.2^c
$PhCH_2$−NH_2	70.9	73.6	69.2	70.6	71.2	74.2	74.0^b
PhNH−CH_3	70.3	69.1	69.4	70.2	70.9	73.8	71.4^c
H_3C−NO_2	59.7^n	57.8^n	58.1	59	59.1	59.5	62.0^b
MAE	**1.7**	**1.9**	**3.0**	**2.3**	**2.0**	**1.5**	
RMSE	**2.0**	**2.4**	**3.3**	**2.5**	**2.3**	**1.8**	
MaxE	**3.1**	**4.2**	**4.8**	**3.4**	**3.0**	**2.5**	

TABLE 1: (Continued)

bond	AM1	PM3	HF/3-21G(d)	B3P86/3-21G(d)	B3P86/6-31G(d)	G3(MP2)	exptl
(b) X−X and X−Y BDEs (X,Y ≠ H) (Continued)							
C−N							
H_3C-NH_2	84.7	87.3	83.2	83.6	84.1	85.6	84.9[c]
$H_3C-NHCH_3$	80.5	81.9	79.4	79.4	79.2	80.4	82.2[c]
$PhCH_2-NH_2$	70.9	73.6	69.2	70.6	71.2	74.2	74.0[b]
$PhNH-CH_3$	70.3	69.1	69.4	70.2	70.9	73.8	71.4[c]
H_3C-NO_2	59.7[n]	57.8[n]	58.1	59	59.1	59.5	62.0[b]
MAE	**1.7**	**1.9**	**3.0**	**2.3**	**2.0**	**1.5**	
RMSE	**2.0**	**2.4**	**3.3**	**2.5**	**2.3**	**1.8**	
MaxE	**3.1**	**4.2**	**4.8**	**3.4**	**3.0**	**2.5**	
C−O							
H_3C-OH	91.8	93.4	91.6	91.7	92.2	90.2	92.0[o]
$H_3C-OC_2H_5$	80.2	81.8	82.1	81.9	81.8	84.1	82.5[b]
$PhCH_2-OH$	79.1	79.5	78.2	79.3	79.8	82.1	81.0[o]
$PhO-CH_3$	61.5	62.7	62.9	63	62.9	66.7	63.5[p]
MAE	**1.6**	**1.1**	**1.1**	**0.8**	**0.7**	**1.9**	
RMSE	**1.8**	**1.2**	**1.5**	**0.9**	**0.8**	**2.1**	
MaxE	**2.3**	**1.5**	**2.8**	**1.7**	**1.2**	**3.2**	
C−S							
H_3C-SH	71.2	74.4	73.9	73.9	74.1	73.1	73.6[b]
$H_3C-SC_2H_5$	70.2	71.0	70.6	70.4	70.8	72.0	72.7[b]
C−Halide							
C_2F_5-F	123.4	125.2	124.8	124.6	124.9	125.9	126.8[c]
H_3C-F	110.5	111.2	110.5	110.4	111.1	109.5	109.8[b]
$PhCH_2-F$	98.3	98.8	97.9	98.6	99.5	101.4	98.7[b]
H_3C-Cl	84.6	85.0	84.6	84.7	84.9	82.8	83.8[b]
C_2F_5-Cl	81.0	82.6	82.2	82.5	82.4	86.2	82.7[c]
$PhCH_2-Cl$	69.9	70.3	69.9	71	71.0	74.5	72.2[c]
H_3C-Br	73.5	73.4	73.2	73.2	73.1	p	72.1[m]
C_2F_5-Br	65.7	66.1	68.6	68.8	69.0	p	68.7[c]
$PhCH_2-Br$	59.0	57.9	58.4	59.2	59.5	p	57.6[c]
MAE	**1.7**	**1.2**	**1.0**	**0.9**	**1.1**	**1.8**	
RMSE	**1.9**	**1.4**	**1.2**	**1.1**	**1.2**	**2.1**	
MaxE	**3.4**	**2.6**	**2.3**	**2.2**	**1.9**	**3.5**	
Homonuclear							
$HO-OH$	44.0	52.6	51.6	50.8	53.1	47.5	50.4[o]
$HS-SH$	56.8	63.6	63.2	63.4	63.4	62.2	66.0[r]
H_2N-NH_2	62.1	67.8	65.5	65.9	66.4	63.7	68.2[b]
MAE	**7.2**	**1.7**	**2.2**	**1.8**	**2.4**	**3.7**	
RMSE	**7.4**	**1.9**	**2.4**	**2.0**	**2.4**	**3.8**	
MaxE	**9.2**	**2.4**	**2.8**	**2.6**	**2.7**	**4.5**	
Total (for 28 Bonds)							
MAE	**2.5**	**1.6**	**1.7**	**1.5**	**1.5**	**1.7**	
RMSE	**3.2**	**2.1**	**2.2**	**1.9**	**1.8**	**2.1**	

[a] The theoretical method used for the geometry optimization and frequency calculation stage of the model calculations is given across the top. The G3(MP2) and experimental BDEs are also shown. All values are in kcal/mol. [b] Using heats of formation obtained from the NIST database.[28] [c] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493−532. [d] Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744−2765. [e] MacFaul, P. A.; Wayner, D. D. M.; Ingold, K. U. *J. Org. Chem.* **1997**, *62*, 3413−3414. [f] Ruscic, B.; Wagner, A. F.; Harding, L. B.; Asher, R. L.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Song, Y.; Qian, A.; Ng, C.-Y.; Liu, J.; Chen, W.; Schwenke, D. W. *J. Phys. Chem. A* **2002**, *106*, 2727−2747. [g] 5-Pyrimidinol [h] Reference 5b. [i] Wayner, D. D. M.; Lusztyk, E.; Page, D.; Ingold, K. U.; Mulder, P.; Laarhoven, L. J. J.; Aldrich, H. S. *J. Am. Chem. Soc.* **1995**, *117*, 8737−8744. [j] Ramond, T. M.; Blanksby, S. J.; Kato, S.; Bierbaum, V. M.; Davico, G. E.; Schwartz, R. L.; Lineberger, W. C.; Ellison, G. B. *J. Phys. Chem. A.* **2002**, *106*, 9641−9647. [k] Reference 4. [l] Borges dos Santos, R. M.; Muralha, V. S. F.; Correia, C. F.; Guedes, R. C.; Costa Cabral, B. J.; Martinho Simoes, J. A. *J. Phys. Chem. A* **2002**, *106*, 9883−9889. [m] Reference 3a. [n] Frequencies determined numerically. [o] Using heats of formation from reference b and the $^{\bullet}OH$ heat of formation from footnote e. [p] Suryan, M. M.; Kafafi, S. A.; Stein, S. E. *J. Am. Chem. Soc.* **1989**, *111*, 1423−1429. [q] Bromine cannot be treated with G3(MP2). [r] Reference 31.

predict BDEs that are slightly lower than the B3P86 based models, which underestimate the experimental BDE by ca. 2.9 kcal/mol. For this bond, G3(MP2) overestimates the value by 1.7 kcal/mol. The BDEs of H_3C-CN predicted using all of the models differ from experiment by 4−5 kcal/mol. The calculated G3(MP2) BDE for the H_3C-CN bond is predicted to be within 1 kcal/mol of the experimental value of 121.9 kcal/mol. However, a G2 treatment[27] gives the BDE as 124.3 kcal/mol, which is closer to the values of 125.5−126.4 kcal/mol predicted by the models.

The C−N and C−O BDEs are all predicted to be within ca. 3 kcal/mol of experiment. For the latter group, the G3(MP2) results indicate that method to be in worse agreement with experiment than all of the models. It is interesting to note that G2 predicts the $H_3C-OC_2H_5$ BDE to be 86.8 kcal/mol,[27] 3.6 kcal/mol higher than experiment and 2.7 kcal/mol higher than the G3(MP2) value. For comparison, the BDE for H_3C-OCH_3 is 85.9 kcal/mol by G2[27] (*lower* than the calculated value for $H_3C-OC_2H_5$) and 82.9 kcal/mol from experiment.[28,29]

We have only included two molecules containing C−S bonds in our study.[30] For H_3C-SH, all models predict BDEs to within 1 kcal/mol of experiment, with the exception of the AM1 based model, which gives a BDE too low by 2.4 kcal/mol. This poor result is due to the AM1 method predicting the C−S bond length to be too short by ca. 0.1 Å. All of the models predict BDEs that are too low by ca. 2 kcal/mol for $H_3C-SC_2H_5$.

A larger number of carbon−halogen BDEs are included in Table 1b. In general, all of the models perform better than G3-

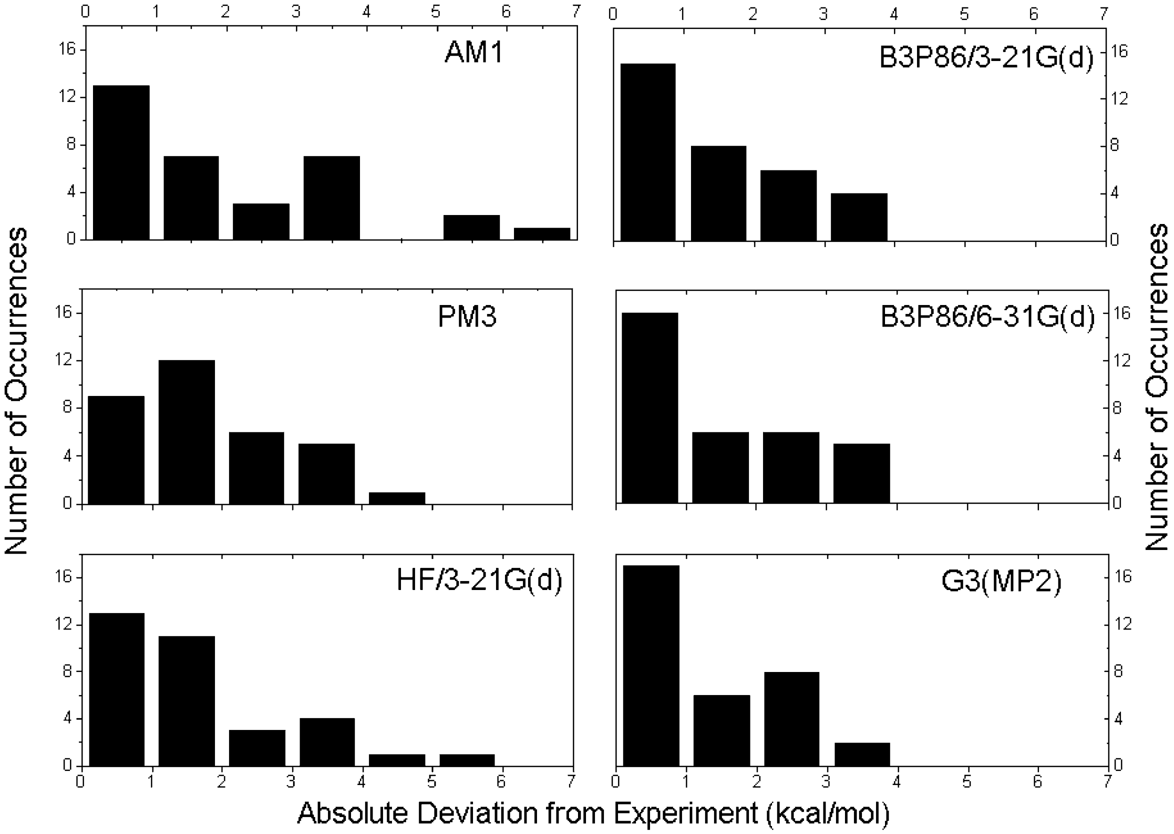

Figure 1. Histograms of the absolute errors in computed X−H BDEs, in kcal/mol, using the various models relative to experiment.

(MP2) for these bonds. G3(MP2) cannot yet be used for molecules containing bromine. However the G2 method gives a H_3C-Br BDE of 73.6 kcal/mol,[11] in good agreement with the values of 73.1−73.5 kcal/mol predicted by the models.

The final entries in Table 1b are the central bonds in hydrogen peroxide, hydrogen sulfide and hydrazine. As noted previously,[7,11] AM1 geometries for these molecules are generally in large disagreement with experiment, presumably because of poorly described lone pair−lone pair interactions. This results in errors of ca. 6−10 kcal/mol for the AM1 based BDEs for these compounds. Although the PM3 method also predicts geometries for these compounds that are substantially different from the B3P86/6-31G(d) ones (for example, planar vs nonplanar structure for H_2O_2), bond lengths predicted using the two methods are in reasonable agreement and so the PM3 based model BDEs have errors of less than 3 kcal/mol relative to experiment. BDEs using the other models agree quite well with experiment. It is interesting to note that G3(MP2) predicts all of the BDEs for this group to be too low. In particular, the G3(MP2) H_2N-NH_2 BDE is too low by 4.5 kcal/mol. G2 BDEs[32] for HO−OH and H_2N-NH_2 are in much better agreement with the results from our models and with experiment. However, the HS−SH G2 BDE is lower than the tabulated experimental value by 3.2 kcal/mol.[33]

The performance of the models is summarized at the bottom of Table 1b, where the statistical information for all the X−X and X−Y BDEs is given, and in Figure 2, which shows the absolute values of the errors of the calculated BDEs from the experimental values. The MAE of the X−X and X−Y BDEs using the AM1 model is somewhat higher than the corresponding value for the X−H BDEs (2.5 vs 1.8 kcal/mol). The other models, including the PM3 based one, have MAEs and RMSEs for the heavy bonds that are within 0.2 kcal/mol of those computed for the X−H bonds. For "heavy−heavy" bonds, the PM3 based model turns in a performance superior to the AM1 based model. The histograms in Figure 2 reflect these findings, with the AM1 BDE error data being equally distributed between 0 and 4 kcal/mol with additional outliers from 4 to 10 kcal/mol. Again, this is significant because our previous "low-level" models for X−X and X−Y BDEs were based exclusively on the AM1 geometry and frequency calculations. For the other models, the errors in BDEs tend to cluster closer to zero with improved performance with the increasing level of geometry optimization. The B3P86 based models perform slightly better than G3(MP2) for the X−X and X−Y BDEs.

Ultimately, all of the models presented in this work, with the exception of the AM1 based model, are capable of providing a balanced and accurate treatment of X−H, X−X, and X−Y bonds involving C, N, O, S, and halogen atoms. Additional data show that Si−H BDEs are also accurately computed (as are Si−X bonds in doublet radicals but Si−X bonds in closed-shell systems are not, vide infra). The present models are an improvement over the models we have proposed previously[7,11] in that better agreement with experimental BDEs is achieved. The models require less computational effort than the previously proposed models because the E_{el} calculations are performed within the unrestricted, open-shell formalism[7,11] and the basis sets used contain no diffuse functions.[7] In addition, the present models do not require the use of empirical corrections to the energies of reactants and products.

3.3. Basis Set Independence of C−H BDEs. In the preliminary studies for this work, we found that C−H BDEs display little dependence on basis set size. For the 15 C−H BDEs we studied, the BDEs determined using B3P86/6-31G(d)//B3P86/6-31G(d) have a MAE of only 0.8 kcal/mol relative to the B3P86/6-311G(2d,2p)//B3P86/6-31G(d) model. Similar

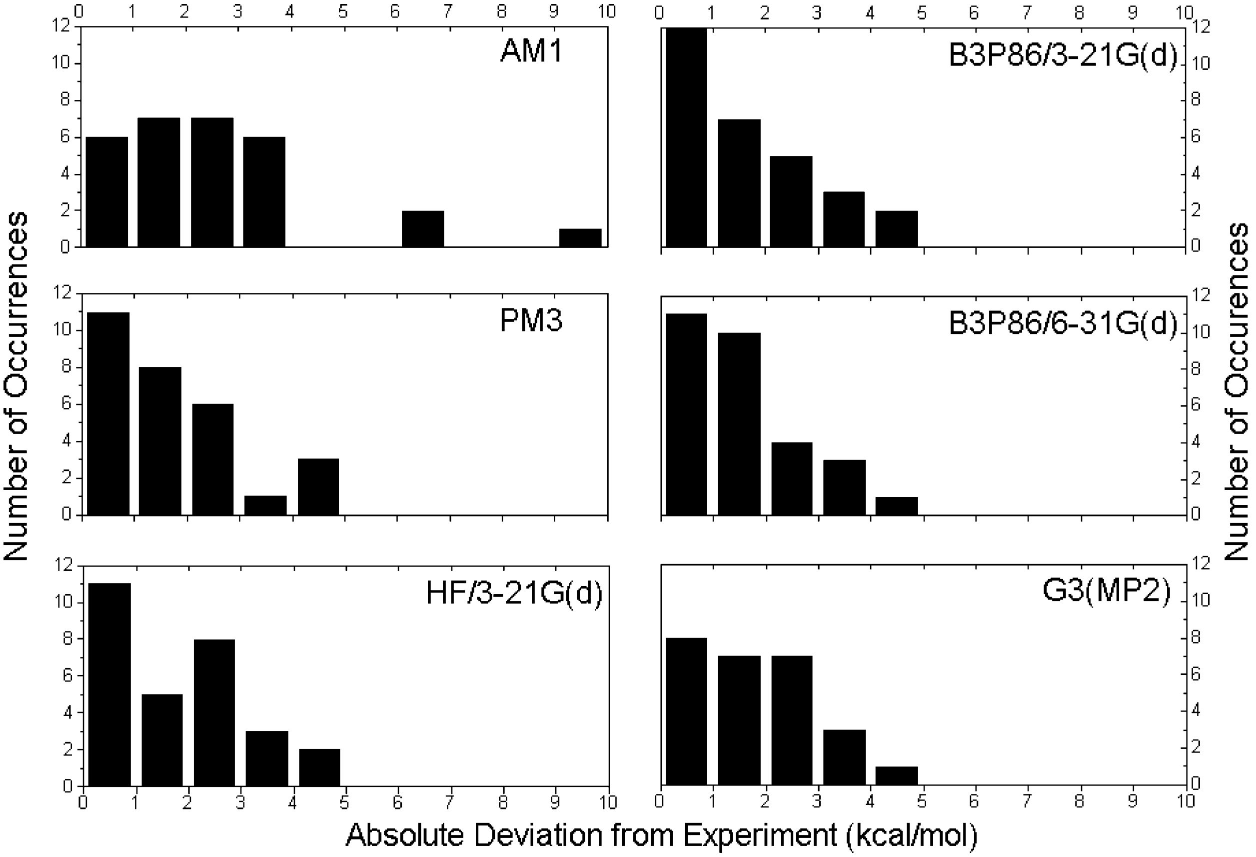

Figure 2. Histograms of the absolute errors in computed X−X and X−Y BDEs, in kcal/mol, using the various models relative to experiment. Note that the G3(MP2) data set has three fewer entries than the other data sets (see Table 1).

results were found using HF/3-21G(d) geometries and frequencies (MAE = 0.6 kcal/mol relative to HF/3-21G(d) model BDEs). These data are summarized in the Table S3 in the Supporting Information. This lack of basis set dependence on C−H BDEs is fully consistent with the findings of Korth and Sicking[34] who saw quite good agreement between theory and experiment for a series of substituted methanes using B3LYP/6-31G(d,p) and (PU)MP2/6-31G(d,p). Chandra and Uchimaru[35] made similar observations for C−H BDEs in halogen-substituted methanes but found, as did we,[7] that the water O−H BDE was strongly basis set dependent.

In general, the basis set dependence of the electronic energy for atoms increases across a row of the periodic table, as does their correlation energy. (This is illustrated in Figure S1, in the Supporting Information, which shows that the B3P86 E_{el} for boron and fluorine decreases by ca. 4.5 and 26.8 kcal/mol, respectively, in going from 6-31G(d) to 6-311+G(3df) basis sets.) Hydrides of the first row atoms follow a similar trend, but the molecular energies have a larger basis set dependence than do the atoms and this dependence increases for XH_n with increasing hydrogenation (increasing n). This is due to the polarizing influence of the attached hydrogen atoms and the need for more flexible basis sets to describe the polarized electron density. Thus, the basis set dependence of the BDEs of these systems reflects the differential of the basis set dependence in XH_n and XH_{n-1}. Table 2 shows the basis set dependence of the molecules (XH_n) and radicals (XH_{n-1}) of the hydrides of the first row. Over the range of closed-shell hydrides, BH_3 to HF (of which all but BH_3 are isoelectronic), the maximum values of B3P86 basis set dependence increase from 5.8 to 39.1 kcal/mol. For the open-shell radicals ($BH_2^{\bullet}$ to $F^{\bullet}$, of which all but $BH_2^{\bullet}$ are isoelectronic), the basis set dependence of the electronic energy is lower than that for the molecules, with the maximum values spanning the range 5.9−26.8 kcal/mol. Hence, BDEs for this series of hydrides display increasing basis set dependencies over the range 0.6 (H_2B-H) to −13.4 (H−F) kcal/mol. Si−H BDEs show even less basis set dependence than C−H BDEs (data not shown).

3.4. Comparisons to Modified B3LYP. Recently, Kang and Musgrave introduced a reparametrization of Becke's three-parameter hybrid functional[9] designed to predict accurate BDEs and barrier heights.[36] This modified B3LYP (mB3LYP) energy, used previously with 6-311+G(3df,2p) basis sets, incorporates empirical corrections for the difference between the number of α and β electrons and for the number of lone pairs and/or π-bonds. Given the excellent performance demonstrated by mB3LYP in the prediction of hydrocarbon BDEs[36a] and the apparent absence of studies in the literature of the application of mB3LYP to other bond types, a comparison with the present models is in order.

Using B3P86/6-31G(d) geometries and frequency information, BDEs were calculated with E_{el} computed using mB3LYP/6-311+G(3df,2p) for a subset of 15 bonds[37] listed in Table 1. The data are collected in Table S4 (Supporting Information) along with the corresponding G3(MP2) results and B3P86/6-31G(d) based model results from Table 1. The present model gives MAE, RMSE, and MaxE values of 1.2, 1.5, and 3.3 kcal/mol for this subset of bonds compared to 2.0, 2.9, and 8.1 kcal/mol for mB3LYP. The large deviation in the mB3LYP BDEs is due to the underestimation of the O−O bond strength in hydrogen peroxide and overestimations in the C−halide BDEs. The present model is also faster than mB3LYP due to the use of smaller basis sets for the calculation of E_{el}. However,

TABLE 2: Basis Set Dependence of the B3P86 Energies of Hydrides of the p-Block, First Row Elements and of Their BDEs[a]

basis set	6-31G(d)	6-31+G(d)	6-311G(d,p)	6-311G(2d,2p)	6-311+G(2d,2p)
E_{el}(H)	1.1	1.1	0.0	0.0	0.0
E_{el}(BH_3)	5.8	5.0	1.5	0.5	0.5
E_{el}(BH_2)	5.9	4.4	1.3	0.5	0.4
BDE(BH_2−H)	1.2	0.4	−0.2	0.0	−0.1
E_{el}(CH_4)	10.8	9.9	2.0	0.4	0.3
E_{el}(CH_3)	11.4	9.4	2.5	1.2	0.5
BDE(CH_3−H)	1.7	0.5	0.5	0.7	0.1
E_{el}(NH_3)	23.3	18.8	6.4	4.0	0.8
E_{el}(NH_2)	19.3	16.2	5.5	3.3	0.8
BDE(NH_2−H)	−3.0	−1.5	−0.8	−0.6	0.0
E_{el}(H_2O)	32.9	25.9	9.5	6.6	1.6
E_{el}(OH)	25.2	20.2	6.3	4.9	1.2
BDE(OH−H)	−6.6	−4.6	−3.1	−1.7	−0.3
E_{el}(HF)	39.1	26.9	9.3	7.0	1.4
E_{el}(F)	26.8	19.2	4.0	3.9	0.6
BDE(F−H)	−11.2	−6.7	−5.3	−3.1	−0.8

[a] The E_{el} data shown are relative to the B3P86/6-311+G(3df,3pd) values. All values are in kcal/mol.

TABLE 3: BDEs for Si−X (X = C, N, O, Si) Bonds Using Four of the Five Models of This Work and G3(MP2)[a]

bond	AM1	PM3	HF/3-21G(d)	B3P86/6-31G(d)	mB3LYP//B3P86/6-31G(d)	G3(MP2)	exptl
(a) Closed-Shell Molecules							
H_3Si-CH_3	84.8	85.2	85.5	85.5	88.0	86.8	89.6
$CH_3SiH_2-CH_3$	87.1	87	86.4	86.4	89.4	88.6	91.1
$(CH_3)_2SiH-CH_3$	92.3	89.4	87.4	87.4	90.7	90.3	92.5
$(CH_3)_3Si-CH_3$	93.5	91.4	88.2	88.1	91.8	91.8	94.2
$(CH_3)_3Si-OH$	125.8	130.8	126.5	127.1	129.9	130.2	132.6
$(CH_3)_3Si-OCH_2CH_3$	108.6	112.8	111.3	111.1	117.3	120.2	122.4
$(CH_3)_3Si-NHCH_3$	100.6	98.8	95.2	94.5	100.8	102.2	100.1
$(CH_3)_3Si-N(CH_3)_2$	92	90.4	87.5	86.3	93.6	96.9	97.5
$H_3Si-SiH_3$	73.5	72.8	73.0	72.8	75.2	74.1	76.7
$(CH_3)_3Si-Si(CH_3)_3$	81.3	76.5	71.9	71.5	76.1	79.5	79.3
MAE	**4.2**	**4.1**	**6.3**	**6.5**	**2.5**	**2.0**	
RMSE	**5.7**	**4.7**	**6.7**	**7.0**	**2.8**	**2.2**	
(b) Open-Shell Molecules							
$H_3Si-CH_2CHCH_3$	19.1	20.1	21.6	21.6	20.2	19.5	
$H_3Si-OC(CH_3)_2$	18.3	21.8	24.0	25.9	27.8	27.6	
$H_3Si-NC_5H_5$	22.1	21.5	24.1	23.7	25.7	25.5	
$H_3Si-CH_2CHC_6H_5$	29.4	29.7	31.9	30.4	29.7	27.2	
$H_3Si-OCH_2C_6H_5$	33.8	36.0	37.4	37.6	40.5	36.9	
$(CH_3)_3Si-CH_2CH_2$	28.3	27.1	25.1	24.8	24.8	25.4	
$(CH_3)_3Si-OCH_2$	40.6	43.3	40.3	41.3	45.1	43.3	
MAE[b]	**3.4**	**2.2**	**2.2**	**1.7**	**1.4**		
RMSE[b]	**4.3**	**2.9**	**2.7**	**1.9**	**1.8**		

[a] The mB3LYP/6-311G(2d,2p)//B3P86/6-31G(d) BDEs are presented in lieu of the B3P86/3-21G(d) model results, which are within 0.5 kcal/mol of the B3P86/6-31G(d) model BDEs. The experimental values are taken from footnote k of Table 1. All values are in kcal/mol. [b] Calculated relative to the G3(MP2) data.

mB3LYP does perform better for X−X and X−Y bonds involving silicon, as discussed in the next section.

3.5. Shortcomings of the Present Models. *3.5.1. Bonds Involving Silicon.* As shown in section 3.1, the present models are adequate for the calculation of Si−H bonds. However, we have left silicon out of the title of this work because the BDEs of X−X and X−Y bonds involving silicon are predicted, using the present models, to be in very poor agreement with both experimental and G3(MP2) values for closed-shell molecules. This is illustrated by the data in Table 3 for a number of Si−X bonds. Because the two B3P86 based models tend to perform equally well, we replaced the B3P86/3-21G(d) model with mB3LYP.

The data in Table 3a clearly show that the present models perform very poorly for the calculations of Si−X bonds. The models predict Si−C BDEs that are lower than experiment by more than 4 kcal/mol for methylsilane with the errors increasing with increasing methyl substitution on the silicon. The AM1 based model tends to be in better agreement with experiment, largely due to the accumulation of error in E_{el} because of poorly predicted silyl radical geometries. For example, the Si−C bond length by AM1 tends to be underestimated by ca. 0.06 Å in the silanes and underestimated by ca. 0.09 Å in the silyl radicals. Consequently, the silane BDEs, which start out too low in methylsilane, “catch up” to the experimental value for the Si−C BDE in tetramethylsilane because the differential in the error in the Si−C bond lengths between molecule and radical increases the BDE.

The situation is worse for Si−O and Si−N bonds. For trimethylhydroxysilane and trimethyl-*N*-methylaminosilane, the B3P86/6-31G(d) based model underestimates the Si−O and Si−N BDEs by ca. 5.5 kcal/mol. These errors increase to ca. 11 kcal/mol underestimations in $(CH_3)_3Si-OC_2H_5$ and $(CH_3)_3Si-N(CH_3)_2$. The AM1 based model and, to a lesser extent, the PM3 based model BDEs for these systems show significant deviations from the B3P86/6-31G(d) results. Errors in BDEs on the order of 4 kcal/mol in disilane and ca. 8 kcal/mol for hexamethyldisilane are obtained with the higher level models.

The errors in these various Si−X BDEs using mB3LYP are much lower (MAE = 2.5 kcal/mol compared to 6.5 kcal/mol

TABLE 4: C−C BDEs for Some Delocalized Molecules, Expressed Relative to the Ethane C−C BDE, As Determined by Each Method[a]

bond	$H_2CCHCH_2{-}CHCH_2$	$PhCH_2{-}CH_3$	$H_2CCHCH_2{-}CH_3$	$PhCH_2{-}CH_2Ph$	$H_2CCHCH_2{-}CH_2CHCH_2$
exptl	−2.4	−12.1	−13.2	−24.5	−27.0
G3(MP2)	−2.8	−9.2	−14.2	−17.5	−28.2
MB3LYP	−6.3	−14.3	−17.2	−28.3	−34.4
MPW1K	−6.6	−14.6	−17.3	−29.1	−34.7
BH&HLYP	−6.7	−14.0	−17.1	−27.9	−34.3
B3P86	−8.0	−15.1	−17.9	−30.0	−35.8
B3LYP	−8.4	−15.7	−18.1	−31.1	−36.4
BLYP	−10.2	−17.1	−19.1	−34.1	−38.3

[a] Experimental values are shown for comparison. The BDEs for all of the methods, except G3(MP2), used the B3P86/6-31G(d) geometries and scaled frequencies. The experimental values are taken from footnote m of Table 1. All values are in kcal/mol. The absolute values for the C−C BDEs in ethane are 89.7 (experimental, see Table 1), 88.5, 91.5, 87.0, 83.4, 89.9, 86.0, 85.1 kcal/mol from top to bottom in order of the entries in the first column in the table.

for the B3P86/6-31G(d) based model) indicating that mB3LYP might make a good choice for applications involving these bond types. However, care should also be taken when this functional is applied (cf. BDE($(CH_3)_3Si{-}OC_2H_5$) too low by 5.1, BDE(HO−OH) too low by 8.1 kcal/mol, and weak C−C bonds, see below). Difficulties may also be encountered when dealing with bond dissociations where the reactants and products are open-shell species. For example, mB3LYP underestimates the enthalpy for the process $H_3COO^\bullet \rightarrow H_3C^\bullet + {}^3\Sigma_g^-\ O_2$ by ca. 6 kcal/mol relative to G3(MP2), whereas the present models perform well for this type of bond.[38]

We are not certain as to the origin of the poor behavior of the models for Si−X bonds, especially in light of their excellent performance for the many bond types in Table 1. However, additional calculations on N−O BDEs in nitroxides reveal errors of similar magnitudes when compared to G3(MP2) results, indicating that the problem is not specific to Si−X bonds. The BDE errors in the Si−X bonds can be reduced by up to 3 kcal/mol, depending on the molecule, if a 6-311+G(3df) locally dense basis set[39] is applied to the silicon atom. However, this correction is not large enough to compensate for the errors in a number of the BDEs listed in Table 3a. Additional calculations with hybrid DFT methods that use an even mix of Hartree−Fock and Slater exchange (like mB3LYP) tend to give better results than present models (see additional discussion in section 3.5.2). We therefore recommend that the present models not be applied to Si−X BDEs of the types listed in Table 3a and instead suggest the use of mB3LYP/6-311G(2d,2p)//B3P86/6-31G(d). Alternatively, HF/3-21G(d) and B3P86/3-21G(d) geometries and frequencies can be used.

The poor treatment of Si−X bonds in closed-shell molecules is even more surprising in light of the excellent agreement between BDEs predicted using the present models and G3(MP2) for similar bonds in open-shell molecules (see Table 3b). This is quite fortuitous because we have a particular interest in these types of BDEs because they are representative of the reaction enthalpies associated with the key addition reaction that occurs in the line-growth of olefins on silicon surfaces.[6,40] (The AM1 and PM3 based models do underestimate the Si−O bond length, which leads to an underestimation of the Si−O BDEs.) To explore the sources of error in the Si−O BDE in $(H_3C)_3Si{-}OCH_2CH_3$ and the absence of appreciable error in the Si−O BDE in $(H_3C)_3Si{-}OCHCH_3$, we calculated the C−H BDE of the central methyl group of the ethoxyl radical using the B3P86/6-31G(d) based model and found it to be in poor agreement with the G3(MP2) value (19.8 vs 14.7 kcal/mol, respectively). This makes it difficult for us to assign the sources of error for Si−X BDEs.

3.5.2. C−C Bonds in Delocalized Molecules. In a recent study of cumulenes and poly-ynes, Woodcock et al. concluded that gradient corrected functionals, like those used in this work, overstabilize highly delocalized systems.[41] Similar findings were noted by Pratt et al. who recently examined C−H BDEs in delocalized systems.[42] Using our present B3P86/6-31G(d) based model, G3(MP2), and a number of other methods (including mB3LYP), we calculated the C−C BDEs for a number of molecules where electronic delocalization is present to varying degrees. In all cases, except for G3(MP2), we used the B3P86/6-31G(d) geometries and frequency data and the 6-311G(2d,2p) basis set for single-point energies so that the methods can be compared solely on the basis of their calculation of E_{el}. These data are presented in Table 4, relative to the C−C BDE in ethane.

The data in Table 4 indicate that G3(MP2) predicts the relative C−C BDEs in fairly good agreement with experiment, but with a large deviation of 7.0 kcal/mol for dibenzyl. The density functional methods tend to have errors that increase with decreasing C−C BDE. For example, the errors in ΔBDE predicted by mB3LYP/6-311G(2d,2p) ranges from 2.2 to 7.4 kcal/mol (note that errors are reduced to a range of 1.9−7.0 kcal/mol when 6-311+G(3df,2p) basis sets are used with mB3LYP). The BHandHLYP and MPW1K[43] data are in excellent agreement with the mB3LYP results, indicating that the errors tend to decrease when a higher ratio of Hartree−Fock (HF) exchange is included in the functional and that the results are not affected by the correlation functional. Woodcock et al. noted a reduction in errors associated with cumulene and poly-yne heats of formation when an even mix of HF and Slater exchange was employed in the functional they used. The errors tend to be higher with the other DFT methods, including the errors in the ΔBDEs predicted with the present B3P86/6-31G(d) based model (cf. a range of 3.0−8.8 kcal/mol). Errors in the ΔBDEs predicted by hybrid functionals are highest using B3LYP and are even worse for BLYP. This is consistent with recent comments by Perdew et al. which point out that functionals incorporating generalized gradient approximations tend to fail for simple metals.[17] The mB3LYP errors could also be reduced if a “half π-bond” correction (analogous to the π bond correction already employed with mB3LYP), which amounts to ca. 3.9 kcal/mol, is used. However, the use of these types of corrections can be problematic and is not recommended.[38]

4. Summary

We have characterized model chemistries that utilize the AM1, PM3, HF/3-21G(d), B3P86/3-21G(d), and B3P86/6-31G(d) methods for geometry optimization and (scaled) frequency calculations, combined with electronic energies calculated with B3P86/6-311G(2d,2p), for their ability to calculate accurate BDEs for X−H, X−X, and X−Y (X,Y = C, N, O, S, halogen) bonds. This level of theory was chosen on the basis of a survey of six commonly available functionals. The survey shows that, contrary to a recent study,[44] the B3P86 functional predicts BDEs in better agreement with experiment than other functionals. Overall, the models perform uniformly well for the indicated bond types with the MAE relative to experiment for the entire test set being 2.1 kcal/mol or less.

In our previous work, we based our lowest level (i.e., fastest) model on AM1 geometry optimizations and frequency calculations. However, we have found in this work that the PM3 model performs generally better than the AM1 model for all the bonds, viz., MAEs of 1.7 vs 1.8 kcal/mol (for X−H bonds) and 1.6 vs 2.5 kcal/mol (X−X and X−Y bonds) for PM3 vs AM1, respectively. Therefore, the PM3 based model is recommended to users interested in applying a very fast model to obtain BDEs to within ca. 3 kcal/mol of experiment for most bonds.

We have shown that semiempirical methods can fail to produce accurate geometries for molecules with O−O, N−N, and S−S moieties. In these or other cases of unusual (but well-recognized) failures in semiempirical methods, an economical alternative for BDE calculations is required. The HF/3-21G(d) model performs better than the PM3 model for X−H bonds (MAE = 1.6 kcal/mol) but slightly worse for X−X, X−Y bonds (MAE = 1.7 kcal/mol) and represents a suitable alternative to the PM3 based model.

In some cases spin contamination in the HF wave function can lead to results that are not reliable. Density functional methods tend not to suffer from spin contamination problems. The B3P86/3-21G(d) model, a "low cost" alternative to the HF/3-21G(d) model, was shown to perform very well for all bond types (MAEs of 1.4 (X−H) and 1.5 (X−X, X−Y) kcal/mol). There is effectively no difference between this model and our highest level model by MAE, RMSE, and MaxE measures.

Our highest level model, which is based on B3P86/6-31G(d) geometries and (scaled) frequencies, displays performance similar to the B3P86/3-21G(d) based model (MAEs of 1.5 (X−H) and 1.5 (X−X, X−Y) kcal/mol). These results are on par with those obtained using G3(MP2), but the model is considerably less computationally intensive than G3(MP2). We therefore recommend the use of the B3P86/6-31G(d) model to calculate the BDEs for bonds involving C, N, O, S, halogen atoms and for Si−H bonds.

We have shown that the basis set dependence of X−H BDEs in the simple, first row hydrides increases across the periodic table and is due to a differential in the basis set dependence of electronic energy with the degree of hydrogenation. For B−H and C−H BDEs, very little basis set dependence in BDE is found and so a small basis set can be used to obtain accurate BDEs for these types of bonds. Increasingly larger basis sets are required for N−H, O−H, and F−H BDEs.

The present models fail to predict accurate BDEs for Si−X bonds in closed-shell silanes. For example, in the case of $(CH_3)_3Si-OC_2H_5$, the BDE calculated using the present B3P86/6-31G(d) model is too low by 11.3 kcal/mol relative to experiment and 9.1 kcal/mol lower than the G3(MP2) value. Functionals that use a more even mixture of Hartree−Fock and Slater exchange tend to perform better for these types of bonds. The Si−X BDEs in open-shell molecules are predicted by the present models to be in excellent agreement with G3(MP2) data, indicating that these models can be used to study (radical) addition reactions involving silicon surfaces.[6,40]

In agreement with recent work by Woodcock et al.,[41] we have found that DFT methods tend to produce results in poor agreement with experiment when applied to delocalized systems. We showed that various DFT functionals predict relative BDEs for weak C−C bonds in delocalized molecules that are too low compared to experiment. Some of the error is mitigated with those methods that include a nearly even mixture of Hartree−Fock and Slater exchange.

Supporting Information Available: Tables S1−S4 and Figure S1 as described in the text. BDE results for a number of antioxidant model molecules. Components of the molecule and radical enthalpies as determined using the five models, G3(MP2) enthalpies and B3P86/6-31G(d) optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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