Density Functional Theory Based Model Calculations for Accurate Bond Dissociation Enthalpies. 2. Studies of X−X and X−Y (X, Y = C, N, O, S, Halogen) Bonds[†]

G. A. DiLabio*

Department of Chemistry, Carleton University and Ottawa-Carleton Chemistry Institute,
1125 Colonel By Drive, Ottawa, ON Canada K1S 5B6

D. A. Pratt[‡]

Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive,
Ottawa, ON Canada K1A 0R6

Received: October 31, 1999; In Final Form: December 16, 1999

The bond dissociation enthalpies for a set of 30 compounds containing X−Y (X, Y = C, N, O, S, halogen) bonds are computed using density functional theory based model approaches with the B3P86 functional. These types of bonds were chosen because of their particular importance in free radical organic and bioorganic chemistry, specifically redox chemistry and atom transfer reactions. A series of test calculations on hydrogen peroxide, propane, and methyl chloride led to the choice of the 6-311G(d,p) basis set for optimum performance in terms of speed and accuracy. Three models are defined and tested. The lowest level model, which is capable of treating systems containing more than 30 non-hydrogen atoms, predicts bond dissociation enthalpies with a mean absolute deviation of 2.38 kcal/mol relative to experiment. For a subset of 21 molecules, the two higher-level models predict results with mean absolute deviations of 1.88 and 2.19 kcal/mol relative to experiment. Test calculations on X−H bond energetics indicate that two separate approaches are required for the accurate treatment of both X−Y and X−H bonds.

1. Introduction

The accurate calculation of bond dissociation enthalpies (BDE's) has long been an important application of quantum mechanical techniques. For some time, it has been recognized that in order to obtain BDE's to within 1−2 kcal/mol of experimental values, extensive correlation treatments and large basis sets are necessary. Such approaches are applied in model calculations such as G2, where several ab initio methods, including the QCISD(T)/6-311G(d,p) approach, are used to obtain molecular enthalpies.[1] The primary shortcoming of the G2 approach is the high-order dependence of the computational effort on the number of electrons in (and hence the size of) the chemical system. Consequently, the G2 model is limited to small molecules.

Density functional theory (DFT) techniques, such as the B3LYP approach,[2,3] have recently experienced a surge in popularity, arguably due to much more favorable scaling than ab initio methods. As a result of this lower-order scaling, DFT approaches are often the only alternative for treating larger molecular systems. However, the results from calculations using these techniques typically do not yield the desired “chemical” accuracy, i.e., 1−2 kcal/mol, one can obtain from higher-level ab initio treatments.

We have addressed some of these concerns (in part 1 of this study) by formulating a series of B3LYP-based model approaches which are capable of predicting accurate X−H (X = C, N, O, S) bond dissociation enthalpies (BDE's), electron affinities (EA's), and proton affinities (PA's) for a variety of molecules.[4] The model that is most applicable to larger systems utilizes the semiempirical AM1[5] approach for geometry and frequency determination. The electronic energy component of the enthalpy is computed at the AM1 minimum using the restricted open-shell (RO)B3LYP method with 6-311+G(2d,2p) basis sets. This model predicts BDE's, EA's, and PA's to within about 2 kcal/mol of experimental values and is capable of easily treating molecules with up to 15 non-hydrogen centers. The primary drawback of this model is the inability of the B3LYP functional to predict accurate BDE's for heavy (X−X, X−Y) bonds, which are typically underestimated by 3−6 kcal/mol. For example, the bond dissociation enthalpies for hydrogen peroxide (O−O), anisole (O−CH_3), and benzyl bromide (C−Br) are predicted to be lower than their corresponding experimental values by 3.1, 4.2, and 5.2 kcal/mol, respectively.[6] Other approaches, such as the IMOMO-G2(MS) method developed by Froese, et al.,[7] combine density functional theory and ab initio techniques to determine bond dissociation enthalpies. These authors have had some success with the approach, showing that it is capable of predicting the BDE's of substituted benzene systems to within a few kcal/mol of the experimental value, depending on the level and the complexity of the treatment.[8]

Homolytic bond dissociation enthalpies (BDE's) have long been considered an important thermodynamic quantity. Most recently, interest in BDE's has come from the free radical community, where they are important in governing the exothermicity and indirectly, the rate, of a given radical forming reaction (e.g., the decomposition of a peroxide) or radical transformation (e.g., an atom transfer reaction). Both of these reaction types are relevant in biological chemistry, where C−H,

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* Corresponding author. E-mail: gdilabio@carl.ccs.carleton.ca.

[†] Part 1 is as follows: Theoretical Study of X-H Bond Energetics (X = C, N, O, S): Application to Substituent Effects, Gas-Phase Acidities, and Redox Potentials. *J. Phys. Chem. A* **1999**, *103*, 1653-1661.

[‡] Present address: Department of Chemistry, Vanderbilt University, Box 1822, Station B, Nashville, TN, 37235.

10.1021/jp9938617 CCC: $19.00

O−H, S−H, O−O, and S−S BDE's contribute to an overall understanding of cellular redox processes and the reactivity of antioxidants.[9] Furthermore, X−H and C−Y BDE's are important in understanding many free radical transformations important in organic synthesis.[10] Since the majority of radical forming reactions occur via cleavage of X−X bonds (most often O−O) and any atom transfer involves cleavage of X−H and X−Y bonds (most often X−H and C-halogen), it is useful to have a method or model capable of predicting accurate X−H, X−Y, and X−X BDE's.

In addition to providing information that is critical to elucidate many of the mechanisms which govern free radical processes in chemistry and biology, accurate X−Y bond dissociation enthalpies can also be used to derive the heats of formation for large molecules. By determining accurate BDE's associated with fragmenting a large molecule into smaller segments and combining these values with the accurately known experimental (or computational) heats of formation for the segments, the heats of formation for large molecules can be determined.

In a recent study, Curtiss et al. examined the G2 method and seven DFT procedures for their ability to compute accurate heats of formation ($\Delta_f H°_{298}$) for a set of 148 molecules.[11] They concluded that, of the DFT approaches, the B3LYP/6-311+G-(3df,2p) model calculations predicted $\Delta_f H°_{298}$ values with the smallest average absolute deviation (3.11 kcal/mol). However, a detailed examination of the data in ref 11 reveals that X−X and X−Y (X, Y = C, N, O) BDE's for 19 compounds predicted using the B3LYP model have a large average error of −5.8 kcal/mol. The DFT method that produces among the worst heats of formation, with an average absolute deviation of about 18 kcal/mol, is B3P86.[2,12] Nevertheless, the B3P86 bond dissociation enthalpies predicted for the same 19 compounds show an average deviation from experiment of only −0.5 kcal/mol. This indicates that the B3P86 approach shows potential for providing accurate X−X and X−Y bond energetics.

In this paper, we extend our work on the development of DFT-based model calculations for calculating X−H bond energetics[4] by examining the applicability of the B3P86 approach to the determination of accurate X−X and X−Y (where X, Y = C, N, O, S, halogen) bond dissociation enthalpies. We begin by assessing a variety of balanced basis sets by computing the O−O BDE in hydrogen peroxide, the C−C BDE in propane, and the C−Cl BDE in methyl chloride with the (RO)B3P86 functional. The optimum basis set is then used within a series of model approaches to determine the bond dissociation enthalpies for 30 representative molecules. The general applicability of the computational models is then discussed.

2. Test Calculations on Hydrogen Peroxide, Propane, and Methyl Chloride

To determine the optimal basis set with which to proceed, the restricted open-shell (RO) B3P86 method is applied, with a series of balanced basis sets, to determine the terms that contribute to the molecular enthalpies using the Gaussian-94 package of programs.[13] More details are provided in the next section. The accuracy of the computed bond dissociation enthalpies and the basis set size serve as our selection criteria. Enthalpies are determined by computing the electronic energies and correcting for zero-point energies and vibrational, rotational, and translational enthalpies as given by standard formulas.[14]

The calculated bond dissociation enthalpies, at $T = 298$ K, for hydrogen peroxide, propane, and methyl chloride are presented in Table 1. Balanced basis sets are varied from double-ζ + polarization (DZ+P) quality (6-31G(d,p)) to the largest available split-valence basis set (6-311++G(3df,3pd)) available in the Gaussian-94 database.

TABLE 1: Computed Bond Dissociation Enthalpies for Hydrogen Peroxide, Propane, and Methyl Chloride in kcal/mol

basis set	BDE (HO−OH)	BDE ($H_3C-C_2H_5$)	BDE (H_3C-Cl)
6-31G(d,p)	55.4	91.4	86.4
6-311G(d,p)	53.2	88.2	85.2
6-311G(2d,2p)	55.2	89.2	87.0
6-311++G(2d,2p)	52.7	88.1	86.3
6-311++G(3df,3pd)	53.5	88.4	87.7
experiment[a]	51	88.9	83.1

[a] References for experimental data given in Table 2.

The largest errors in BDE are observed with the 6-31G(d,p) basis set where BDE's are overestimated by 2.5−4.4 kcal/mol. Extending the basis set from double- to triple-ζ in the valence space significantly improves results, with values bracketing the experimental BDE's by −0.7 to +2.2 kcal/mol. The use of double polarization functions increases the BDE for hydrogen peroxide and methyl chloride by about 2 kcal/mol relative to the 6-311G(d,p) value and by 1 kcal/mol for propane. Further increases in the basis set size substantially increase computational times without significantly improving BDE's, illustrating the diminishing returns associated with the use of very large basis sets. Given the results listed in Table 1, the optimum balance between speed (smallest basis set) and accuracy (BDE) is obtained with the 6-311G(d,p) basis.

3. Methods of Calculation

A series of 30 molecules involving C−Y (Y = C, N, O, S, F, Cl, Br), O−O, S−S, and N−N bonds was tested. The Gaussian-94 package of programs was used for all the calculations.[13] First, optimized geometries and scaled vibration frequencies, for zero-point energies (ZPE) and vibrational enthalpy corrections (H_{vib}), were obtained using one of three low-, medium-, and high-level procedures (denoted LLM, MLM, and HLM). These were followed by single-point DFT calculations using the (RO)B3P86[2,12] functional with 6-311G(d,p) basis sets, as per the results of section 2, to obtain the electronic energies (E_e) of the systems. These values were summed, along with enthalpic corrections for translation ($^3/_2RT$) and rotation ($^3/_2RT$) plus an additional RT term, to obtain the enthalpy at $T = 298$ K, given by $H°_{298} = E_e + \text{ZPE} + H_{vib} + 4RT$. In the case of atoms, the enthalpic corrections total $^5/_2RT$.[14] Bond dissociation enthalpies (BDE's), for example in the reaction $R-X \rightarrow R^\bullet + X^\bullet$, are then determined by: $\text{BDE} = (H°_{298}(R^\bullet) + H°_{298}(X^\bullet)) - H°_{298}(RX)$.

The low-level model (LLM) for computing enthalpies makes use of the semiempirical AM1[5] procedure for calculating minimum energy geometries and frequencies. Following our previous work[4] and that of Scott and Radom,[16] vibrations are scaled by a factor of 0.973 to obtain zero-point energies (ZPE) and vibrational enthalpy corrections (H_{vib}) at $T = 298$ K. The single-point energy//geometry/frequency calculations involved in this low-level model are denoted (RO)B3P86/6-311G(d,p)//AM1/AM1, where it is understood that open-shell systems are treated with (RO)B3P86. This model is appropriate for systems containing up to 30 heavy (i.e., non-hydrogen) atoms on a low-end workstation since the geometry and frequency determinations are rapid using AM1.

The medium-level model (MLM) uses (U)MP2(Full)/6-31G-(d) for geometry optimizations and (U)HF/6-31G(d) for the determination of vibrational frequencies, where open-shell systems are treated in an unrestricted formalism. Frequencies are scaled by a factor of 0.9135.[4,16] Geometry optimizations and frequency calculations are much more time-consuming than using LLM but are generally more reliable, in particular for systems involving O−O or S−S bonds. The MLM approach is denoted (RO)B3P86/6-311G(d,p)//(U)MP2(Full)/6-31G(d)/(U)-HF/6-31G(d). Note that the methods for determining geometries and frequencies correspond to those used in the G2 approach of Curtiss, et al.[1] This model, like the low-level model, mixes unrestricted and restricted, open-shell formalisms. However, it is important to note that geometries and frequencies determined using unrestricted, open-shell treatments are known to reproduce the restricted, open-shell results.[17] Molecular enthalpies are determined (in all the models presented here) using a restricted, open-shell treatment which effects the energies of the radicals. As we have shown previously for X−H BDE's,[4] and will show below for X−Y systems, this teatment of radicals results in superior X−Y bond dissociation enthalpies. This medium-level model is applicable to systems containing up to ca.20 heavy atoms on a high-end workstation.

Finally, we define a high-level model (HLM) to which the performance of the LLM and MLM approaches can be compared. The HLM is simply the application of (RO)B3P86/6-311G(d,p) for the determination of geometries, frequencies, and molecular energies and is denoted (RO)B3P86/6-311G(d,p)//(RO)B3P86/6-311G(d,p)/(RO)B3P86/6-311G(d,p). Frequencies determined using this model were scaled by a factor of 0.9806.[4,16] HLM is applicable to molecular systems containing up to 10 heavy atoms.

It should be noted that the procedures and models outlined above are similar in spirit to those developed in our work on X−H bond energetics but they differ in a number of ways. In our previous work, single-point energies were determined using (RO)B3LYP/6-311+G(2d,2p), an approach which underestimates X−X and X−Y BDE's. In addition, our previous models required extensive visualizations in order to identify and correct for vibrations that correspond to rotations. We have since found that, in most cases, bond dissociation enthalpies are relatively insensitive to such corrections and have omitted them in the models presented in this work.

4. Results and Discussion

The bond dissociation enthalpies of 30 representative compounds determined using the LLM, MLM, and HLM models are listed in Table 2 with available experimental data. In the case of substituted benzenes, only the LLM approach was used for BDE evaluations due to resource limitations. For comparison, G2 values from ref 11 are also included in the table. In a few cases, G2 calculations (outlined in ref 1) were performed to obtain BDE's with which the results from the model calculations could be compared. As pointed out in the recent work by Froese and Morokuma,[8] accurate experimental data with which to compare are scarce. For several of the molecules studied in this work, the experimental BDE's were evaluated from experimental heats of formation. However, the experimental BDE's listed in Table 2 are believed to be reasonable, with uncertainties estimated to be in the range of 1−3 kcal/mol.

4.1. H_3C-Y Bond Dissociation Enthalpies. In general, all H_3C-Y systems presented in Table 2 have computed bond dissociation enthalpies that are higher than the corresponding experimental values. The high-level model BDE's show the least agreement with experiment, with a mean absolute deviation (MAD) of 2.56 kcal/mol. These results are in line with the findings for the HO−OH, $H_3C-C_2H_5$, and H_3C-Cl BDE's (see section 2), where the results indicated overestimated BDE values. The medium-level model calculations are in much better agreement with experiment, displaying a lower deviation of 1.95 kcal/mol. Differences between the MLM and HLM bond dissociation enthalpies can be traced to minor disagreements in the electronic energy (E_e) component of the enthalpies for the parent molecules. As expected, HLM predicts E_e values that are slightly lower than those determined using MLM (recall that MLM uses MP2=Full/6-31G(d) to obtain geometries while HLM uses (RO)B3P86/6-311G(d,p)). For the radical species, however, there is better agreement between HLM and MLM

TABLE 2: Bond Dissociation Enthalpies for 30 Representative Compounds Using Three Model Approaches Along with Available Experimental and G2 Data and Mean Absolute Deviations (MAD) (All Values in kcal/mol)

compound	LLM	MLM	HLM	G2[a]	exptl
H_3C-Y Bond Dissociation Enthalpies					
H_3C-NO_2	61.1	60.8	61.2	62.8	60.8[b]
H_3C-Br	74.9	75.7	76.4	73.6*	70.0[c]
H_3C-SH	72.8	74.7	75.2	74.9	74.7[d]
H_3C-Cl	84.8	85.1	85.2	84.6*	83.1[e]
H_3C-NH_2	87.4	86.4	86.7	85.6	85.6[d]
H_3C-CH_3	91.2	91.6	92.1	90.8	90.1[d]
H_3C-OH	93.0	92.9	93.5	93.6	92.4[d]
H_3C-CF_3	101.5	102.2	102.5		101.4[e]
H_3C-F	110.4	111.7	112.1	112.4*	109.8[e]
H_3C-CN	128.4	128.2	130.5	124.3	121.9[d]
MAD	1.95	1.95	2.56	1.58	
$X-X$ and $X-Y$ Bond Dissociation Enthalpies					
$(CH_3)_3CO-OC(CH_3)_3$	26.9	36.3	35.9		38.0[b]
HO−OH	45.1	52.4	53.2	50.5	51[b]
HS−SH	52.6	59.7	60.0		66.0[b]
H_2N-NH_2	65.5	69.2	69.4	66.4	67.4[d]
C_2F_5-Br	67.1	69.5	69.4		68.5[c]
$H_3C-SC_2H_5$	70.3	71.3	71.6		73.7[f]
C_2F_5-Cl	80.2	82.0	82.0		82.9[c]
$H_3C-OC_2H_5$	80.5	80.5	80.3	86.8	83.0[d]
$H_3C-NHCH_3$	83.4	81.9	82.2		82.2[b]
$H_3C-C_2H_5$	88.6	87.9	88.2	90.4	88.9[d]
C_2F_5-F	123.9	125.2	125.1		126.9[c]
MAD	4.06	1.82	1.85	1.95	
ArX-Y Bond Dissociation Enthalpies					
$ArS-CH_3$	62.1				59.9[g]
$ArCH_2-Br$	61.6				60.8[h]
$ArO-CH_3$	64.5				63.4[i]
$ArCH_2-Cl$	70.8				70.4[j]
$ArNH-CH_3$	71.8				71.4[c]
$ArCH_2-NH_2$	74.5				74.0[e]
$ArCH_2-CH_3$	76.6				77.2[e]
$ArCH_2-OH$	81.7				81.4[e]
$ArCH_2-F$	99.7				98.6[k]
MAD	0.82				
total MAD	2.38	1.88	2.19		

[a] Computed from the G2 heats of formation from ref 11. Values marked with asterisks were computed in this work. [b] Reference 15. [c] *CRC Handbook of Chemistry and Physics*, 76th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1995. [d] Computed from experimental heats of formation tabulated in ref 11. [e] Computed from heats of formation as listed in the National Institute of Standards and Technology on-line database. Standard Reference Data Program 69, November 1998 Release. http://webbook.nist.gov. [f] Value for H_3C-SCH_3 derived from experimental heats of formation tabulated in ref 11. [g] See text for details. [h] Laarhoven, L. J. J.; Born, J. G. P.; Arends, I. W. C. E.; Mulder, P. *J. Chem. Soc. Perkin Trans. 2* **1997**, 2307. [i] Suryan, M. M.; Kafafi, S. A.; Stein, S. E. *J. Am. Chem. Soc.* **1989**, *111*, 1423. [j] Averaged from the range of results provided in: Andreiux, C. P.; Le Gorande, A.; Saveant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 6892. [k] Zavitsas, A. A. *J. Phys. Chem.* **1987**, *91*, 5573.

E_e terms. Consequently, bond dissociation enthalpies are somewhat higher using HLM compared to MLM.

The low-level model, in which geometries and frequencies are determined using the AM1 method, predicts H_3C-Y bond dissociation enthalpies in good agreement with MLM values. The LLM mean absolute deviation in BDE is 1.95 kcal/mol. In all cases, the electronic energy component of the LLM enthalpies is higher than the corresponding MLM and HLM values. The good agreement between LLM and MLM or HLM BDE's can therefore be attributed to significant error cancellation. For LLM, the higher BDE's (relative to MLM) are the result of radical zero-point energies and vibrational enthalpies that are higher than those predicted using the MLM model.

The disagreement between calculated and experimental BDE's of methyl bromide and methyl nitrile contribute significantly to the MAD values for all three models as well as the G2 model. Results for other carbon−bromine species presented in Table 2 show excellent agreement with experiment, suggesting that the accepted H_3C-Br value of 70 kcal/mol may be in error. The G2 BDE for methyl bromide of 73.6 kcal/mol (computed presently) seems to support this conclusion. The results for methyl nitrile are also in reasonable agreement with the G2 result,[11] which is higher than the experimental value by 2.4 kcal/mol. Re-evaluating the MAD's, omitting the methyl bromide and methyl nitrile BDE's, yields 1.01, 0.94, and 1.33 kcal/mol for LLM, MLM, and HLM, respectively. A similar evaluation using the G2 BDE's gives an MAD of 1.19 kcal/mol.

4.2. X−X and X−Y Bond Dissociation Enthalpies. In general, the HLM procedure performs well for this group and compares well with the available G2 BDE's. The overall MAD for this set of BDE's is 1.85 kcal/mol, lower than that determined for the H_3C-Y bonds. The sulfide bond in H_2S_2 is treated very poorly, with a BDE predicted to be too low by 6.0 kcal/mol. Test calculations indicate that increasing the basis set size to 6-311+G(2d,2p) brings the BDE into exact agreement with experiment. Evaluations of the bond dissociation enthalpy of other sulfur−heteroatom and sulfur−carbon species, however, show no significant ($<$0.2 kcal/mol) change in BDE's with the larger basis, indicating that the original 6-311G(d) basis set for sulfur may only be inadequate for disulfide linkages. Further test calculations in which a locally dense 6-311+G(2d) basis set[18] is placed on the sulfur atom yields a HS−SH BDE (65.3 kcal/mol) that agrees with experiment while maintaining the good agreement observed for compounds in which an S−Y bond is broken. Consequently, a locally dense basis set approach is recommended for the treatment of disulfide bonds. The poor H_2S_2 BDE contributes about 30% to the MAD for this set of compounds.

The MLM bond dissociation enthalpies, as for the methyl C−Y bonds, are slightly lower than the HLM values for reasons outlined in section 4.1. As in the HLM treatment of H_2S_2, MLM underestimates the BDE by 6.3 kcal/mol due to basis set effects. Overall, MLM results are in better agreement with HLM BDE's for this set of molecules, with the MAD for the procedure/molecular subset being 1.82 kcal/mol. Removal of the poor H_2S_2 value reduces the MAD to 1.37 kcal/mol. Using a locally dense 6-311+G(2d) basis on the sulfur atoms in H_2S_2 improves the BDE to 65.0 kcal/mol.

The low-level model performs quite poorly for several members in this set. Specifically, BDE's for $(CH_3)_3CO-OC(CH_3)_3$, H_2O_2, and H_2S_2 are underestimated by 11.1, 5.9, and 13.4 kcal/mol, respectively. In the case of H_2S_2, a locally dense sulfur basis set improves the BDE to 58.3 kcal/mol. However, for all three compounds, the majority of the error can be traced to poor AM1 bond lengths in those being broken. As noted in our previous work,[4] AM1 predicts the O−O separation in hydrogen peroxide to be 1.30 Å compared to an experimental value of 1.46 Å. Consequently, the parent H_2O_2 is destabilized relative to the dissociation fragments, lowering the BDE by 6.2 kcal/mol. Similar effects are observed in di-*tert*-butyl peroxide and hydrogen persulfide. To some extent, the poorly predicted (AM1) dihedral angle in hydrazine contributes to the underestimated LLM bond dissociation enthalpy but the net error is much smaller in this case since the MLM and HLM overestimate this BDE. One possibility for bypassing the difficulties associated with these systems, while still maintaining the computational advantages of the LLM, is to perform a two level ONIOM-type (MP2 = high, AM1 = low)[19] optimization on the O−O or S−S fragment followed by the single-point B3P86 procedure described here.

Despite the difficulties noted above, the low-level model performs reasonably well. The MAD for this set of molecules is 4.06 kcal/mol, a value which is reduced to 1.78 kcal/mol upon removal of peroxide and persulfide species. The accurate determination of C_2F_5-X (X = F, Cl, Br) BDE's indicates that molecules containing multiple heavy centers can be accurately treated using the these models.

4.3. Aromatic X−Y (ArX−Y) Bond Dissociation Enthalpies. Because of the computationally intensive geometry/frequency determinations inherent in the MLM and HLM approaches, the bond dissociation enthalpies for aromatic systems were determined using only the low-level model. However, we may conclude from the results presented in sections 4.1 and 4.2 that LLM bond dissociation enthalpies, with a few well understood exceptions, agree well with those determined using the higher-level treatments.

In general, aromatic X−Y bond dissociation enthalpies are very accurately predicted using LLM. The MAD for this set of molecules is only 0.82 kcal/mol. The largest deviation is observed for the (methylthiol)−benzene compound, whose BDE is predicted to be 2.2 kcal/mol higher than experiment. However, the experimental value for this species was estimated from the isodesmic reaction, $ArS-CH_3 + H-CH_3 \rightarrow ArS-H + H_3C-CH_3$. The enthalpy of reaction was determined using the enthalpies of formation[20] for the reaction participants then experimental BDE's for $H-CH_3$, $ArS-H$, and H_3C-CH_3 were used with the enthalpy of reaction to estimate the value of 59.9 ± 3.0 kcal/mol for the S−C bond in $ArS-CH_3$. This BDE is almost 10 kcal/mol lower than the 69.4 kcal/mol value reported by McMillen and Golden.[15]

4.4. X−H Bond Dissociation Enthalpies. In previous work, we developed a series of model approaches that were shown to accurately reproduce experimental X−H BDE's.[4] These models are similar to those developed in this work but, as pointed out earlier, differ in that single-point electronic energies are determined using the (RO)B3LYP/6-311+G(2d,2p) approach, while the models described here use (RO)B3P86/6-311G(d,p) for X−Y BDE's. In addition, the X−H models compensated for overestimated B3LYP hydrogen atom energy by setting the value to −0.500 au.

Clearly, it is desirable to have one model that can be applied to both X−H and X−Y thermochemistry so that chemically and biologically relevant mechanisms (such as those mentioned in the Introduction) can be treated in a balanced way. Since the X−H DFT-based models tend to predict X−Y BDE's that are too low, it is worthwhile to test the current models to examine their applicability to the determination of accurate X−H bond

TABLE 3: Bond Dissociation Enthalpies for Representative X−H Species (Values in kcal/mol)

bond	HLM (ref 4)[a]	HLM (this work)[b] (E_e(H) = −0.5 au)	HLM (this work)[c]	exptl
HO−H	118.3	129.6	119.3	119.3 ± 0.05
H_2N−H	107.6	120.3	110.0	108.2 ± 0.3
H_3C−H	105.8	119.0	108.7	104.9 ± 0.1

[a] Using the high-level model of ref 4 for the determination of X−H BDE's, where enthalpies are evaluated using (RO)B3LYP/6-311+G(2d,2p). [b] Using the high-level model presented in this work with the hydrogen atom energy taken as −0.500 00 au. [c] Using the high-level model presented in this work taking the hydrogen atom energy, −0.518 52 au, as predicted by B3P86/6-311G(d,p).

energetics. Values for X−H BDE's were computed for H_2O, NH_3, and CH_4 using three procedures and are compared to the experimental values listed in ref 4.

The X−H bond dissociation enthalpies in the second column of Table 3 are those determined using the (RO)B3LYP/6-311+G(2d,2p) model of ref 4. As previously noted, the models in ref 4 compensated for the hydrogen atom energy that is too low by setting the value to −0.500 au. This correction amounts to 1.5 kcal/mol, which is enough to raise the predicted BDE's to within 1 kcal/mol of the accepted values. Next are the BDE's determined using the high-level model outlined in the this work; that is, the electronic energy evaluations are performed using (RO)B3P86/6-311G(d,p) with hydrogen atom energies taken as −0.500 au. These values overestimate the experimental values by 10−15 kcal/mol for the three species. Finally, BDE's are reported using the high-level model of this work but using the B3P86/6-311G(d,p) energy for the hydrogen atom, a value that is too low by 10.3 kcal/mol. The BDE's in this case are in much better agreement with the experimental values but are up to 4 kcal/mol too high. In the case of the B3LYP-based models,[4] radical enthalpies are predicted to be too low relative to the parent molecules resulting in X−X and X−Y BDE's that are underestimated. For X−H bonds, the dissociation fragments include the energy-corrected hydrogen atom and only one overly stable radical and, therefore, X−H BDE's are predicted with that model to be only 1−2 kcal/mol too low. However, the data in Table 2 suggest that radical enthalpies determined using B3P86 tend to be slightly high while the results listed in Table 3 indicate that the hydrogen atom enthalpy is too high. This suggests that X−H BDE results may improve upon the introduction of energy-lowering corrections for the hydrogen atom but this would require extensive testing. We are currently experimenting with models involving open-shell corrections of the type used in the G2 approach[1] with limited success.

This analysis indicates that neither the DFT-based model approach presented in this work nor that of ref 4 is capable of accurately determining bond dissociation enthalpies for both X−H and X−Y systems. Nevertheless, the X−H models of ref 4 and the heavy atom models of this study can be used in conjunction with each other to determine the *thermodynamics* of systems involving cleavage of both types of bonds.

5. Conclusions

We have demonstrated for 30 representative molecules that accurate X−Y bond dissociation enthalpies can be determined using one of three DFT-based model approaches. The low-level model ((RO)B3P86/6-311G(d,p)//AM1/AM1) is capable of treating molecules of containing about 30 heavy (non-hydrogen atoms) on a low-end workstation. The LLM predicts BDE's for the test compounds with a mean absolute deviation from experiment of 2.38 kcal/mol. For processes involving the cleavage of an O−O or S−S bond, LLM greatly underestimates BDE's due to poorly predicted AM1 bond lengths. An evaluation of the MAD without these compounds yields a value of 1.60 kcal/mol. A future study is being considered in which the LLM will be applied to the determination the heats of formation of large molecules.

The speed and accuracy of the LLM approach presented here is illustrated by a comparison to a recent IMOMO study by Vreven and Morokuma.[21] In that work, the authors calculate the C−C BDE's for a series of hydrocarbons. They find that their best-performing method (G2MSr/ROMP2) predicts BDE's for 18 compounds with a root mean sqaure error of 2.4 kcal/mol relative to experiment. For the largest compound in that study, H_3C−CMePh_2, the authors report a BDE of 72.9 kcal/mol compared to the experimental value of 69 ± 2 kcal/mol.[15] The LLM approach outlined in this work predicts a value of 65.9 kcal/mol, in better agreement with the experimental quantity by 0.8 kcal/mol. However, the IMOMO value required over 2 days of computer time on their resources while the LLM result was obtained in 6.5 h on a Pentium III 450 MHz personal computer.

The medium-level model ((RO)B3P86/6-311G(d,p)//(U)MP2-(Full)/6-31G(d)/(U)HF/6-31G(d)) was applied to a 21 molecule subset of the test species. This procedure is capable of treating up to 20 heavy atoms and predicts bond dissociation enthalpies with an MAD of 1.88 kcal/mol.

The high-level model, which is simply the straightforward application of (RO)B3P86/6-311G(d,p), was also applied to a 21 molecule subset of the test species. Bond dissociation enthalpies had a mean absolute deviation from experiment of 2.19 kcal/mol.

Test calculations were also performed to determine the X−H BDE's of H_2O, NH_3, and CH_4. The results indicated that, while our previous models accurately reproduced these bond dissociation enthalpies, the models presented in this work overestimate them by up to 4 kcal/mol. As a result, for the accurate determination of X−Y and X−H BDE's, two different types of model calculations must be used. Nonetheless, important insights into biologically and chemically relevant processes can be obtained from the application of both the X−H[4] and X−Y DFT-based models.

Acknowledgment. We thank J. S. Wright for helpful comments made during the preparation of the manuscript and for support for G.A.D. through NSERC Canada. D.A.P. thanks NRC Canada and NSERC Canada for their support.

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