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Comment

Comment on “The enthalpy of the O–H homolytic dissociation: Basis-set extrapolated density functional theory and coupled cluster calculations” by B.J. Costa Cabral and S. Canuto [Chem. Phys. Lett. 406 (2005) 300–305]

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Abstract

Costa Cabral and Canuto [B.J. Costa Cabral, S. Canuto, Chem. Phys. Lett. 406 (2005) 300] have studied the O–H bond dissociation enthalpy in water, hydrogen peroxide, methanol, phenol and catechol using a number of theoretical methods. Their choice of experimental O–H bond dissociation enthalpies for phenol and catechol are not the best available values and led them to several erroneous conclusions about the performance of methodologies they tested. In this work, we present more rigorous experimental O–H bond dissociation enthalpies for phenol and catechol and discuss the implications these data have on the conclusions presented by Costa Cabral and Canuto. We also demonstrate the importance of the inclusion of higher-order excitations in the coupled-cluster treatment of bond dissociation enthalpy of the O–H bond in H₂O₂ and HOO•.

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Costa Cabral and Canuto [1] have tested four density functional theory (DFT) methods and couple-cluster with single and double excitations (CCSD), with basis set extrapolation, for their ability to predict O–H bond dissociation enthalpies (BDEs) in five compounds. We address in this communication several short-comings of that report.

The successful evaluation of theoretical methods, as is presented in [1], critically depends on the choice of the experimental data to which the computed results are compared. The reference data for the O–H BDEs in H₂O, H₂O₂, and CH₃OH used in [1] appear to be well chosen. However, the reference values they used for the O–H BDE in phenol are 88.7, 90.1 ± 3, and 85.8 ± 2 kcal/mol, implying that the O–H BDE in phenol is somewhere between 84 and 93 kcal/mol. We have recently presented a critical reevaluation of a number of gas- and liquid-phase

studies dealing with the O–H BDE in phenol. This led us to recommend an O–H BDE for phenol of 86.7 ± 0.7 kcal/mol [2]. This value is at the thermodynamic standard state of 1 atmosphere, which is also the standard state for computational studies. Table 1 summarizes the phenol BDE data.

For catechol, Costa Cabral and Canuto used an O–H BDE of 82.5 ± 1.2 kcal/mol as their reference experimental value. Two separate gas-phase studies on the rate of thermolysis of the O–C bond in 2-OHC₆H₄O–CH₃, using the very low pressure pyrolysis method, have been reported [3,4]. It was found that the O–C BDE in 2-OHC₆H₄OCH₃ is 7.2 kcal/mol lower than that in C₆H₅O–CH₃. This substantial decrease in the O–C BDE is the result of two effects. Firstly, the strong electron donating ortho OH group ($\sigma_p^+ = 0.78$ [5], $\sigma_o^+ = 0.66 \times \sigma_p^+$ [6]) acts to lower the BDE by destabilizing the parent 2-OHC₆H₄OCH₃ molecule and stabilize the 2-OHC₆H₄O• relative to a hydrogen atom substituent [7]. Secondly, the lowest energy

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Table 1

Summary of the bond dissociation enthalpies (BDE) of the O–H bond in phenol (kcal/mol) discussed in [1,2]

Reaction	BDE	Comment
$\text{C}_6\text{H}_5\text{O}-\text{H} \rightarrow \text{C}_6\text{H}_5\text{O}^\bullet + \text{H}^\bullet$	$85.8 \pm 1.9^{\text{a}}$	Negative ion cycle
	88.7^{b}	Recommend value ^b
	$90.1 \pm 3.1^{\text{c}}$	Negative ion cycle
	$86.7 \pm 0.7^{\text{d}}$	Re-evaluated value ^d

^a L.A. Angel, K.M. Ervin, J. Phys. Chem. A 108 (2004) 8346.

^b R.M. Borges dos Santos, J.A. Martinho Simões, J. Phys. Chem. Ref. Data 27 (1998) 707.

^c V.F. DeTuri, K.M. Ervin, Int. J. Mass Spectrom. 175 (1998) 123.

^d Ref. [2].

conformations of 2-OHC₆H₄OCH₃ and 2-OHC₆H₄O[•] have intramolecular hydrogen bonds between the hydrogen of the hydroxyl group and the oxygen of the methoxyl group and the oxygen-centered radical, respectively. The strength of the intramolecular hydrogen bond in the radical is higher than that in 2-OHC₆H₄OCH₃ [6,8] because O[•] is electron enriched due to its strong electron withdrawing ability [7]. Because the substituent effects on O–C BDEs and O–H BDEs are quite similar [4], and hydrogen bonding enthalpies in 2-OHC₆H₄OCH₃ and in 2-OHC₆H₄OH are almost identical [6], the O–H BDE in 2-OHC₆H₄O–H (catechol) can be taken to be 7.2 kcal/mol lower than the O–H BDE in phenol.

In addition, Zhang [9] recently compiled the rate constants, *k*, for hydrogen abstraction by peroxy radicals from various substituted phenols, including catechol. These were plotted against measured O–H BDEs (excluding catechol) to yield an Evans–Polanyi type plot between log(*k*) and the O–H BDE. From the linear plot it can be determined that the O–H BDE in catechol is 6.9 kcal/mol lower than that in phenol. The Zhang study ignored the effects of hydrogen bonding which will influence the kinetic and the thermodynamic data.

Further corroborating the above are the results of the time-resolved photoacoustic calorimetric (PAC) liquid phase study by Correia et al. [10] on the O–H BDEs for phenol and catechol. It is critical that solvent effects be taken into consideration before a BDE obtained by the PAC method can be presented as a gas phase value. The solvent effect involves the formation of an intermolecular hydrogen bond between the solute (phenol or the phenoxyl radical) and the solvent. The difference in the hydrogen bond enthalpies between the parent phenol and the phenoxyl radicals convolutes the experimentally determined heat of reaction. Accepting that the intermolecular hydrogen bonding enthalpies for phenol and catechol are identical within the accuracy of the experiment, the O–H BDE in catechol is found to be 6.8 kcal/mol lower than that in phenol. It should be noted that the accuracy of the relative BDEs in a PAC study on a family of related compounds (i.e. substituted phenols) is much higher than the absolute values. For example, Correia et al. report the gas phase O–H BDE for phenol as 89.5 kcal/mol (at 1 atm) which is 2.8 kcal/mol

Table 2

Summary of the relative bond dissociation enthalpies (ΔBDE) of the O–H bond in catechol (kcal/mol), referenced to phenol, obtained from literature sources

Reaction	ΔBDE
$2\text{-OHC}_6\text{H}_4\text{O}-\text{H} \rightarrow 2\text{-OHC}_6\text{H}_4\text{O}^\bullet + \text{H}^\bullet$	7.2^{a}
	7.2^{b}
	6.9^{c}
	6.8^{d}

^a Ref. [3].

^b Ref. [4].

^c Ref. [9].

^d Ref. [10].

too high and may be associated with an improper accounting of the solvent interactions.

These four independent studies, the results of which are summarized in Table 2, demonstrate that the O–H BDE in catechol is 7.0 ± 0.2 kcal/mol lower than that in phenol. With the recommended O–H BDE for phenol of 86.7 kcal/mol, it follows that the O–H BDE for catechol is 79.7 ± 0.9 kcal/mol.

In light of the discussion presented above, the conclusions arrived at by Costa Cabral and Canuto that basis set extrapolated CCSD provides BDEs for the five compounds with near chemical accuracy (± 1 kcal/mol) is a slight exaggeration. Differences between the highest-level CCSD results reported in [1] and the best available experimental BDEs range from 1.5 to 2.4 kcal. Furthermore, the authors of [1] argue about the importance of extrapolation to the basis set limit but do not include the effects of higher-order (i.e. triples and higher) substitutions in their coupled-cluster calculations (mainly due to the computational costs associated with those calculations). However, it is well known [11] that a complete wavefunction solution is arrived at through the use of both complete, one-particle basis set and N-particle bases expansions. Therefore, the predicted BDEs in [1] are expected to be in disagreement with results obtained from a more complete wavefunction treatment. In our recent work [2], we showed that the O–H BDE in phenol calculated by using the Thruhlar [12] extrapolation scheme with the CCSD(T)/aug-cc-pV(D-T)Z energies to be 91.2 kcal/mol and is in poor agreement with almost all of the available experimental data. Therefore, the conclusion that the extrapolated CCSD BDEs for the five compounds are nearly within chemical accuracy of the experimental BDEs selected by Costa Cabral and Canuto is coincidental.

To demonstrate the effects of higher-levels of treatment, we calculated (using the GAUSSIAN-03 package [13]) the O–H BDE in H₂O₂ using a number of approaches. We began by verifying that the B3LYP/cc-pVTZ geometries used in [1] for H₂O₂ and HOO[•] are essentially identical to the structures obtained using CCSD/cc-pVTZ. The vibration frequencies obtained at the CCSD/cc-pVTZ level lead to a BDE that is 0.1 kcal/mol less than that obtained by using B3LYP/cc-pVTZ frequencies, as in [1]. We then evaluated

Table 3

Bond dissociation enthalpies (BDE) for the O–H bond in H₂O₂ obtained at different levels of theory^{a,b,c}

Method/Basis//CCSD/cc-pVTZ			Δ BDE
Basis	CCSD(T)	CCSD	
cc-pVDZ	78.54	78.26	0.28
cc-pVTZ	84.98	84.20	0.78
cc-pVQZ	86.43	85.55	0.88
cc-pV5Z	86.89	85.98	0.91
cc-pV6Z	87.00	86.08	0.91

All values are in kcal/mol.

^a The BDEs obtained using the Martin 2–3 (cc-pV(DZ-TZ)) extrapolation scheme [15] are: 87.24 kcal/mol by CCSD(T) and 86.29 kcal/mol by CCSD, giving a Δ BDE of 0.96 kcal/mol.

^b Extrapolated (cc-pVDZ-cc-pVTZ, [15]) BDEs using the QCI method: 87.21 kcal/mol by QCISD(TQ) and 86.95 by QCISD(T), giving a Δ BDE of 0.26 kcal/mol.

^c The experimental BDE is 87.8 ± 0.5 kcal/mol [14].

the effects of the non-iterative inclusion of triple excitations on the molecule and radical energies by performing CCSD(T)/cc-pVXZ//CCSD/cc-pVTZ calculations. These results are collected in Table 3. With the cc-pVDZ basis set, the differences in the CCSD(T) and CCSD BDEs is only 0.28 kcal/mol. However, BDEs obtained at the CCSD(T) level using bases ranging in size from cc-pVTZ to cc-pV6Z are 0.78–0.91 kcal/mol higher than those obtained using CCSD. As the basis set size is increased, the calculated BDEs approach the experimental BDE from below. At the CCSD(T)/cc-pV6Z//CCSD/cc-pVTZ level, the O–H BDE in H₂O₂ is predicted to be 87.0 kcal/mol, in reasonable agreement with the experimental value of 87.8 ± 0.5 kcal/mol [14]. Additionally, we found that core–valence correlation effects (CCSD(T)/cc-pCVTZ vs. CCSD(T)/cc-pVTZ) were small, increasing the BDE by 0.06 kcal/mol. We also calculated the effect of the inclusion of quadruples non-iteratively by computing the differences in BDEs at the QCISD(TQ)/cc-pVXZ//CCSD/cc-pVTZ and QCISD(T)/cc-pVXZ//CCSD/cc-pVTZ levels with X = D,T. The extrapolated results (using the method in [15]) give a QCISD(TQ)–QCISD(T) Δ BDE of 0.26 kcal/mol. Finally, scalar relativistic effects on the BDE were determined (using the MOLPRO package [16]) with the Douglas–Kroll approximation [17] and with CCSD(T)/cc-pVTZ to be -0.10 kcal/mol. Summing the core–valence correlation and quadruples correction into the CCSD(T)/cc-pV6Z//CCSD/cc-pVTZ BDE gives a calculated BDE of 87.2 kcal/mol which is nearly within the error bars of the experimental value.

Similar calculations were performed for the O–H BDE in HOO• and the results are shown in Table 4. High-level calculations on HOO• were recently reported in the literature [18]. In this case, the non-iterative inclusion of triple excitations reduces the calculated BDE by amounts ranging from 0.61 kcal/mol (cc-pVDZ) to 0.23 kcal/mol (cc-pV6Z). Incorporating the effects (as described above) of core–valence correlation (-0.12 kcal/mol), non-iterative quadruples (-0.26 kcal/mol), and scalar relativistic effects

Table 4

Bond dissociation enthalpies (BDE) for the O–H bond in HOO obtained at different levels of theory^{a,b,c}

Method/Basis//CCSD/cc-pVTZ			Δ BDE
Basis	CCSD(T)	CCSD	
cc-pVDZ	40.69	41.29	-0.61
cc-pVTZ	47.16	47.53	-0.37
cc-pVQZ	48.51	48.78	-0.27
cc-pV5Z	49.02	49.26	-0.23
cc-pV6Z	49.11	49.34	-0.23

All values are in kcal/mol.

^a The BDEs obtained using the Martin 2–3 (cc-pV(DZ-TZ)) extrapolation scheme [15] are: 49.44 kcal/mol by CCSD(T) and 49.73 kcal/mol by CCSD, giving a Δ BDE of -0.23 kcal/mol.

^b Extrapolated (cc-pV(DZ-TZ), [15]) BDEs using the QCI method: 49.36 kcal/mol by QCISD(TQ) and 49.62 by QCISD(T), giving a Δ BDE of -0.26 kcal/mol.

^c The experimental BDE, obtained from heats of formation [14], is 48.9 ± 0.5 kcal/mol.

(-0.09 kcal/mol) into the CCSD(T)/cc-pV6Z value (49.11 kcal/mol) yields a final O–H BDE in HOO• of 48.6 kcal/mol, in excellent agreement with the experiment. We note that the BDE obtained from the (DZ-TZ) extrapolated CCSD(T) energies (see footnote a of Table 4) overestimates the BDE by more than 0.5 kcal/mol.

The conclusion made in [1] that the CBS-QMPW1 O–H BDEs for phenol and catechol (given in Table 3, footnote e of that work) are in poor agreement with the experiment is not correct in light of the available experimental O–H BDEs for the two compounds (86.7 ± 0.7 and 79.7 kcal/mol for phenol and catechol, respectively). We also reported that CBS-QB3 performed well for phenol and related compounds [2].

Finally, the finding that B3P86 predicts BDEs in reasonable agreement with the experiment for the five compounds is not new. We showed sometime ago that B3P86/6-311G(2d,2p) can be used to calculate BDEs for a wide variety of bonds in good agreement with the experiment [19]. The basis sets used in our model was chosen to give the balance between speed and accuracy. Nevertheless, we showed that our selected bases produced results in good agreement with the large (valence) basis set limit for a number of test compounds. (See the Supporting Information Section of [19].)

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