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Invited review

Bond dissociation enthalpies in benzene derivatives and effect of substituents: an overview of density functional theory (B3LYP) based computational approach

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Abstract

In this review, we have mainly focused on the recent computational studies on the bond dissociation enthalpies (BDE) of the X–H bonds of the *para* and *meta* substituted benzene derivatives ($3Y\text{-}C_6H_4X\text{–}H$ and $4Y\text{-}C_6H_4X\text{–}H$ with X = O, S, Se, NH, PH, CH_2, SiH_2 and Y = H, F, Cl, CH_3, OCH_3, NH_2, CF_3, CN, NO_2). In addition, the remote substituent effects on the BDE(X–H), the radical stability and parent one have also been discussed in terms of the calculated ground state effect, radical effect and total effect. Model chemistry of ROB3LYP/6-311++G(d,p)//B3LYP/6-311G(d,p) can reproduce the BDE values with the accuracy of 1.0–2.0 kcal/mol. The good linear correlations between Hammett constants and BDE values were discovered for both *para* and *meta* substitutions in phenols, thiophenols, benzeneselenols, anilines and phenylposphines with the R-squared lager than 0.94. In contrast, it does not occur in case of toluenes and phenylsilanes.

Keywords. Benzene derivatives, density functional theory, bond dissociation enthalpies, substituent effects, radical effect, ground state effect, total effect, Hammett constants.

1. INTRODUCTION

The chemistry of benzene derivatives, especially in phenol, thiophenol, benzeneselenol, aniline, phenylphosphine, toluene, phenylsilane and their derivatives continues to attract considerable interest [1-3]. Compounds bearing these structures ranging from synthetic compounds to the natural extracts from leaves, trees and roots have several indispensable applications in our daily life [4-6]. Among the most fundamental aspect in chemical and biochemical studies, the molecular structures, energetics, reactivity and their interrelationships are of crucial importance. For example, in a chemical reaction there are disruption and formation of chemical bonds. The making and breaking of bonds is the basis of all chemical transformation. A sound knowledge of the energies required to break bonds and the energies released upon their formation is fundamental to understanding chemical processes. The energy required to homolytic bond cleavage at 298 K and 1 atm corresponds to the enthalpy of reaction: $A\text{–}B \rightarrow A^{\bullet} + B^{\bullet}$, which is defined as the bond dissociation enthalpy of the A–B bond and symbolized by BDE(A–B) [7]. It should be noted that by definition of IUPAC, the bond dissociation energy is sometimes called the bond dissociation enthalpy (or bond enthalpy), but these terms may not be strictly equivalent [8]. Conversely, if the radicals A and B recombine to form the molecule AB, then thermal energy equivalent to the bond dissociation enthalpy is released, according to the first law of thermodynamics [9].

Hence it is essential to establish reliable data of bond dissociation enthalpies (BDEs) as direct information about the strength of the relevant chemical bond in order to understand the inherent reaction mechanism. Therefore, the BDEs already provide valuable criteria for the analysis and selection of antioxidants derived from the natural compounds extracted from plants.

The bond strength of a given bond can be experimentally measured or computationally calculated. It exists many experiments that allow measuring the bond dissociation enthalpy [10]. Despite compilations of experimental thermochemical data for many molecules, there are numerous species for which there are no available. In addition, the data in the compilations are sometimes incorrect [11].

Experimental measurements of thermochemical processes are often expensive, difficult and need a careful manipulation, so it is highly desirable to have computational methods that can make reliable predictions and inexpensive [9]. With the recent advances in computation methods and computer capacity, this becomes more and more reality.

To the best of our knowledge, there has been no recent review on the B3LYP method for predicting the accurate BDEs in benzene derivatives and their analogues as well as the effect of substituents at the *para* and *meta* positions of the benzene ring, a short review on these topics is urgent and necessary. For the results, this review includes several sections organized in three parts. In the first part, the model chemistry of ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) was analyzed and evaluated by comparing the calculated results with the available experimental values as well as by benchmarking against the other computational methods. Conventionally, the model to the right of the double slash *i.e.* B3LYP/6-311G(d,p) is the one at which the molecular geometry was optimized and the model to the left of the double slash *i.e.* ROB3LYP/6-311++G(2df,2p) is the one at which the energy is computed. In case of radical species, specification of a restricted open shell wave function for the Becke3LYP hybrid functional requires the ROB3LYP keyword, while the unrestricted version denoted as UB3LYP is applied for geometrical optimization of the radicals. The second one, the homolytic bond dissociation enthalpies of the X−H bonds (X = O, S, Se, NH, PH, CH_2 and SiH_2) of the related benzene derivatives have been reviewed and evaluated by using ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p). In addition, the updated BDEs for a series of aniline derivatives and phenylsilane analogues were also calculated using the same procedure of computational method. The third part of this review, the effect of *para* and *meta* substituents on the BDE(X−H) have been critically analyzed considering the nature of substituent and the substituted position. The idea of a quantitative description of the substituent effect on rates and equilibria of chemical reaction (log(k) or log(K), respectively) by use of a linear regression in which the nature of the substituent (X) is described numerically by a substituent constant was ingenious and opened a great field for further investigations [12]. Therefore in this review the correlations of Hammett's substituent constants with the BDE(X−H) values have also been explored.

2. METHODOLOGY FOR PREDICTING BDE(X−H)s

Because of the important of bond dissociation enthalpy in many reactions, the accurate determination of BDE is an urgent task for both experimental and computational researchers and this continues to be a steady stream of work in the field from practitioners in both areas [13].

2.1. Experimental methods

Experimental determinations of BDE are still limited to simple or small molecules and are insufficient in many practical cases, in which large and complex systems have frequently to be treated [14]. In addition, experimental BDE data have large uncertainties (2.0-3.0 kcal/mol and more in some cases), making the development and comparisons of new computational technique challenges. A very concise of description of experimental methods can be found in details from Ref. [15] and references therein. For a given X−H bond in polyatomic molecules, three applicable techniques are usually proposed: *i*) The study of radical kinetics; *ii*) Photoionization mass spectrometry (PIMS) and *iii*) the acidity/electron affinity cycle. The abstraction of a hydrogen atom and creation of radical is considered in the study of radical kinetics. In this method, the concentration of atoms, free radicals, and molecules at one or several temperatures using various detecting methods [16].

Spectrometry method is used to predict the BDEs of the bond of diatomic molecules in gas phase. Mass spectrometry is a powerful tool for the study of molecular thermochemistry. There are several mass spectrometry methods used to investigate in molecular thermochemistry such as electron impact, guided ion beam, high pressure, photoionization mass spectrometry and so on [9, 15, 17]. Photoionization mass spectrometry uses a tunable light source to dissociatively ionize a target species and measures ion intensities versus photon energy and this method is widely used for the X−H bond [9].

2.2. Computational methods

In computational approach, the homolytic X−H bond dissociation enthalpies at 298.15 K and 1 atm for the

AXH molecule can be estimated from the expression.

$$\mathrm{BDE(X{-}H)} = H_f(\mathrm{AX}^\bullet) + H_f(\mathrm{H}^\bullet) - H_f(\mathrm{AXH}) \quad (1)$$

Where H_f's are the enthalpies of the different species at 298.15 K and 1 atm. The enthalpy of each species was calculated from the following equation:

$$H_f = E_0 + \mathrm{ZPE} + H_{trans} + H_{vib} + H_{rot} + \mathrm{RT} \quad (2)$$

Where ZPE is zero point energy, H_{trans}, H_{vib}, H_{rot} are the standard temperature correction term calculated with the equilibrium statistical mechanics with harmonic oscillator and rigid rotor approximation.

In this review, the computational calculations for thiophenols, phenylphosphines, toluenes were performed using the Gaussian 03 software and the computational calculations for phenols, benzeneselenols and phenylsilanes were newly carried out using Gaussian 09 software [18].

2.3. Benchmark the computational methods for determining BDE

Based on the equations (1) and (2), a larger number of theoretical studies have been carried out over the last decade to assess the accuracy of the computational procedures for predicting the BDE [13, 14, 19-42]. Radom and coworkers [28, 43] investigated the performance of a variety of theoretical methods for the calculation of radical stabilization energies of six substituted methyl and vinyl radicals. The conclusion confirmed that UHF (unrestricted Hatree Fock) and PMP (Projected Møller-Plesset) performed poorly for radicals with significant spin contamination in the wave function. On the other hand, the calculation using RMP2/6-311+G(2df,p) single point energies were computationally inexpensive. The results for BDE using several composite methods like CBSRAD, G3(MP2)-RAD and the high level G2 [44], CBS-4 [44], W_1' showed the reasonable agreement with the experimental values. Guo and coworkers applied ONIOM-G3B3 method to predict the bond dissociation enthalpies (BDEs) of coenzyme Q, flavonoids, olives, curcumins, indolinonic hydroxylamines, phenothiazines, edaravones and antioxidants used as food additives as well as the C–H and N–H BDEs of ribonucleosides and deoxyribonucleosides [31, 34]. Especially, the DFT are now capable of providing excellent agreement with benchmark binding energies of a variety of dimers systems [45]. It also appears obligatory to use the DFT methods which can dramatically decrease the CPU time *vs.* ab initio methods of similar accuracy [42]. In 1999, Dilabio and Pratt tested three DFT based procedures to evaluate the BDE(1)for a variety of molecules containing C–H, O–H, N–H and S–H. The results showed that ROB3LYP/6-311++G(2d,2p)/AM1; ROB3LYP/6-311++G(2d,2p)//(U)MP2(fu)/6-31G(d)/HF/6-31G(d) and ROB3LYP/6-311++G(2d,2p)//(U)B3LYP/6-31G(d)/B3LYP/6-31G(d) can generate the BDEs of these bonds with the accuracy of 1.0 to 2.0 kcal/mol [46].

The recent studied on phenol [47], thiophenol, [29] benzeneselenol [48], phenylphosphine [49] and toluene [50] and have showed that calculations with ROB3LYP/6-311++G(2df,2p)/B3LYP/6-311G(d,p) procedure using Gaussian suit of program can predict the BDEs of O–H, S–H, Se–H, P–H and C–H with the accuracy within 1–2 kcal/mol. To validate this procedure, a number of small compounds have been calculated and benchmarked. In case of S–H bond, the BDE(S–H) of two model systems namely H_2S and CH_3SH for which exact experimental results are known were calculated and compared. The calculated BDE(S–H) values for H_2S and CH_3SH are 91.5 and 86.8 kcal/mol [29], respectively, which are very close to the experimental values of 91.2±0.7 kcal/mol for the former and 87.4±0.5 kcal/mol for the latter molecule [15]. A set of small compounds in which the central atoms belong to the group VA including PH_3, NH_3, and AsH_3 were calculated using different DFT methods with a variety of basis set then being compared with the results at CCSD(T) and MP2 with a larger basis set such as aug-cc-pvTZ. The sequential results for BDE(P–H), BDE(N–H) and BDE(As–H) based on ROB3LYP/6-311++G(2df,2p) are 81.3, 107.4 and 76.1 kcal/mol, being very agreement with the experimental data of 83.9±0.5; 108.0±0.3 and 76.3±0.2 kcal/mol [15], respectively. Moreover, the calculated results for BDEs using several density functionals like B3P86, B3PW91 and O3LYP at the same basis set of 6-311++G(2df,2p) based on the optimized structures and frequency calculations at B3LYP/6-311G(d,p) have been evaluated for a variety of compounds having P–H, N–H, As–H, C–H bonds. In fact, the ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) procedure could be used as an accurate model for determining the bond strength of various types of bonds in organic molecules [48-52].

3. THE ROB3LYP/6-311G(2DF,2P)/B3LYP/6-311G(D,P) CALCULATED FOR X−H BOND IN BENZENE DERIVATIVES

3.1. The homolytic X−H bond dissociation enthalpies of C_6H_5X−H (X = O, S, Se, NH, PH, CH_2, SiH_2)

Very recently, BDEs were computed for a variety of bonds in aromatic compounds such as C_6H_5X−H where X = O, S, Se, NH, PH, CH_2 and SiH_2. In terms of predicting the reliable values of BDEs, the computational procedure of B3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) could be used as an accurate model. First, in this section, once again we reviewed the validation of this computational procedure for calculating the BDE(X−H) of phenol, thiophenol, benzeneselenol, aniline, benzenephenylphosphine, toluene and phenylsilane. The calculated BDE(X−H) values (X = O, S, Se, NH_2, PH_2, CH_3, SiH_3) are given in Table 1 along with the available experimental values. It should be noted that there are a number of experimental values for the studied aromatic compounds and these estimated values vary in a wide range. Therefore, the analysis as well as the comparison with the available experimental values are necessary for reconfirming the efficacy of ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) procedure. First, the calculated BDE(O−H) for phenol using ROB3LYP/6-311++G(2df,2p) based on the optimized structure at B3LYP/6-311G(d,p) is 87.5 kcal/mol, being very close to the experimental value of 87.3±1.5 kcal/mol measured using photoacoustic calorimetry (TR-PAC) [53]. Although there are several experimental values of the O−H BDE, varying within a wide range from 84.4 kcal/mol to 91.0 kcal/mol, [15, 21, 53-64] but the recommended data for BDE(O−H) of phenol is 88.0 ± 1.5 kcal/mol [15] which is larger than that in this study about 1.5 kcal/mol. It should be indicated that the ROB3LYP usually raises the BDE to be close the accurate values than the UB3LYP. The predicted value of BDE(O−H) for phenol using UB3LYP/6-311++G(2d,2p)/B3LYP/6-311G(d,p) was 82.2 kcal/mol [65] which is underestimated the experimental value. In case of thiophenol, the experimental BDE(S-H) values also vary within in a wide range of 79.4 to 83.5 kcal/mol [66-70]. The most recent value (83.4 kcal/mol) was determined from the time resolved photoacoustic calorimetry (TR-PAC) experiment by dos Santos *et al.* [71]. It should be noted here the margin of error is very large up to 4 kcal/mol in this measurement. The calculated BDE(S−H) in this review is very close to that estimated by Venimadhavan *et al.* (79.4 kcal/mol) [68]. Especially for BDE(Se−H) of benzeneselenol, there is a larger deviation between the calculated value using ROB3LYP/6-311++G(2df,2p) given in Table with the experimental values. This can be explained on the basis of the existence of two lower lying electronic states of C_6H_5S radical, namely $^2A'$ and $^2A''$ and the calculated BDE(Se−H) in table 1 is predicted for the latter one.

Table 1: The calculated BDE(X−H) of C_6H_5XH (X = O, S, Se, NH, PH, CH_2, SiH_2) using ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p)

X	Calculated values (in kcal/mol)	Experimental values [a] (in kcal/mol)
O	87.5	89.5±1.0; 88.3±1.5; 88.0±1.5; 87.3±1.5 [10, 53]
S	79.5	83.3±2; 79.4 [68]; 80.0; 80.8; 83.5±1.1
Se	73.5	67.0; 78.0±4.0
N	92.4[b]	88.0±2.0; 92.3; 89.1; 89.7
P	76.3	N/A
C	89.4	87.9±1.5; 88.1±2.2; 88.6; 88.5±1.5; 89.6±1.0
Si	89.6[b]	88.2 [17]

[a] All experimental values can be found in Ref. [15] and references therein. For specific values, references are given right behind. [b] in this work.

For aniline, our calculated BDE(N−H) is 92.4 kcal/mol, larger than those experimental values of 89.1 and 89.7 kcal/mol using pulse radiolysis and photoacoustic calorimetry, respectively [15, 72, 73]. However our predicted value is close to value of 92.3 kcal/mol determined by Bordwell *et al* using the measured pK_a of aniline ($C_6H_5NH_2$) in DMSO and oxidation potential (E_{ox}) of aniline anion (C_6H_5NH) [72, 74]. Our estimated value is 1.0 kcal/mol slightly larger than that reported by Guo and coworker using G3 method [31] and Gomes *et al* using B3LYP methods [75]. For phenylphosphine, although no experimental value for BDE(P−H) is available, using the same procedure for calculation, the value should be 76.3 kcal/mol.

The ROB3LYP calculated BDE(C−H) in CH_3 group of toluene is reported to be 89.4 kcal/mol, which is very close to the recent experimental value of 88.5±1.5 kcal/mol [15]. The Si−H BDE of phenylsilane was calculated using ROB3LYP/6-311++G(2df,2p) method to be 89.6 kcal/mol. This value is of 1.4 kcal/mol higher than the experimental value 88.2 kcal/mol at 298.15 K [17]. However, the predicted values using unrestricted B3LYP with small basis set of 6-311G(d,p) and restricted MP2 at the 6-311++G(d,2p) are underestimated the experimental values.

Similar underestimation of BDEs was also found in number of former study not only for silane centered radicals but also for oxygen-, sulfur-, carbon-, and phosphine centered radicals. This leads to a critical conclusion that ROB3LYP appears to be the best choice for estimating the BDE of compounds containing X−H bonds.

3.2. The homolytic BDE(X−H) of a series of *para* and *meta* substituted Y-C_6H_5X−H (X = O, S, Se, NH, PH, CH_2, SiH_2 and Y = H, F, Cl, CH_3, OCH_3, NH_2, CF_3, CN and NO_2)

In fact, this procedure has been further developed and applied on various types of bonds. We subsequently presented the calculated results based on this model for a series of benzene derivatives described in figure 1.

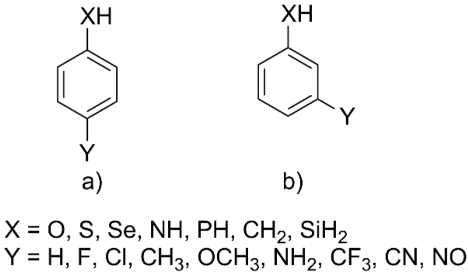


Figure 1: Benzene derivatives and their related substituents

The calculated BDE(X−H) of 4Y-C_6H_4X−H and 3Y-C_6H_4X−H (X = O, S, Se, NH, PH, CH_2, SiH_2) are also given in tables 2 and 3, respectively. It is also interesting to observe how the BDE(X−H) value changes with the change of substituent at the *para* and *meta* position of the benzene ring.

Table 2: The ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) calculated BDE(X−H) of 4Y-C_6H_4X−H

Substituent Y	BDE(X−H) (kcal/mol)						
	O−H	S−H	Se−H	N−H	P−H	C−H	Si−H
H	87.5	79.5	73.5	92.4	76.3	89.8	89.6
F	85.4	77.8	73	91.0	76.3	89.8	89.7
Cl	86.1	78	73.3	91.9	76.2	89.6	89.6
CH_3	85.1	77.5	72.7	90.8	76	89.4	89.5
OCH_3	81.3	75.9	71.4	88.3	75.7	88.9	89.5
NH_2	77.9	74.1	70	85.9	75	88.1	89.2
CF_3	90.4	81.3	75.4	95	76.7	90.1	89.6
CN	89.4	81.4	75.3	95	76.5	89.4	89.4
NO_2	91.7	82.5	76.4	96.5	76.9	89.3	89.3

Table 3: The ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) calculated BDE(X−H) of 3Y-C_6H_4X−H

Substituent Y	BDE(X−H) (kcal/mol)						
	O−H	S−H	Se−H	N−H	P−H	C−H	Si−H
H	87.5	79.5	73.5	92.4	76.3	89.8	89.6
F	88.4	80.3	74.5	93.5	76.5	90.1	89.7
Cl	88.4	80.3	74.4	93.6	76.5	90.1	89.7
CH_3	86.9	79.3	73.5	92.0	76.2	89.7	89.0
OCH_3	86.1	79.0	74.2	93.2	76.5	90.2	89.7
NH_2	86.9	79.3	73.5	92.1	76.3	89.9	89.6
CF_3	89.5	80.6	74.9	94.7	76.7	90.3	89.7
CN	90.3	81.1	74.7	94.9	76.9	90.6	89.8
NO_2	90.7	81.4	75.2	95.2	77.1	90.6	89.8

3.2.1. X belongs to class O category

From the columns containing data for BDE of O–H, S–H, Se–H, N–H and P–H bond of Table 4, it can be observed that the effect of electron donating group (EDG) and electron withdrawing group (EWG) is opposite. Strong electronic donating substituents like OCH_3 and NH_2 at the *para* position result in sharp decrease for the BDE(X–H), except for X = P. For EWG, there is also an increase of the X–H BDE in which a larger enhancement is found for *p*-NO_2. The change of the BDEs also depends on the nature of X atom and can be placed in the order O > N > S > Se > P.A similar change of BDE values in Table 5 is also found when a substituent is at the *meta* position. A dramatically BDE(X–H) decrease with the presence of electron donating group (EDG) was found when X is N. In case of O, S and Se the difference between the parents and the corresponding *meta* substituted derivatives is within 0.0-1.5 kcal/mol. For EDG, the change is more pronounce with the increase of BDE about 1.1–4.1 kcal/mol. However, when X is P, the substituent effect is not meaningful with the change is less than 1 kcal/mol for both EDG and EWG.

3.2.2. X belongs to class S category

The change of X–H BDE of two series of aromatic compounds, Y-C_6H_4X–H with X is C or Si with that of the parent one C_6H_5X–H is presented in the two last columns of tables 4 and 5. It is clear from the BDE values in table 4 that the effect of *para* substituents on the BDE(C–H) value of toluene and BDE(Si–H) of phenylsilane are not very significant, except for the strong EDGs, like NH_2. For *meta* substitution, the effect of substituents on X–H BDE is almost trivial (yable 5). It is apparent that the *para* substituents on toluenes and phenylsilanes have different effects than that observed for phenols and anilines. However, the *meta* substituent effect on the BDE(C–H) or BDE(Si–H) follows the same pattern as that is observed for phenols and anilines.

Table 4: The change of BDE(X–H) of 4Y-C_6H_4X–H upon *para* substitution (in kcal/mol)

Y	*para* substituents: 4Y-C_6H_4X–H						
	O–H^a	S--H^b	Se–H^c	N–H^d	P–H^e	C–H^f	Si–H^d
H	0.0	0.0	0	0	0.0	0.0	0.0
F	-2.1	-1.7	-0.5	-1.4	0.0	0.0	0.1
Cl	-1.4	-1.5	-0.3	-0.5	-0.1	-0.2	0.0
CH_3	-2.4	-2.0	-0.8	-1.6	-0.3	-0.4	-0.1
OCH_3	-6.2	-3.6	-2.1	-4.1	-0.6	-0.9	-0.1
NH_2	-9.6	-5.4	-3.5	-6.5	-1.3	-1.7	-0.4
CF_3	2.9	1.8	1.9	2.6	0.4	0.3	0.0
CN	1.9	1.9	1.8	2.6	0.2	-0.4	-0.2
NO_2	4.2	3.0	2.8	4.1	0.6	-0.5	-0.3

^{a,b,c,e,f} Data taken from Refs. [47], [29], [48], [49], [50], respectively; ^{d} In this work

The change of $\Delta BDE_{\mathbf{4Y}}$ = BDE(X–H) of 4Y-C_6H_4XH - BDE(X–H) of C_6H_5XH.

Table 5: The change of BDE(X–H) of 3Y-C_6H_4X–H upon *meta* substitution (in kcal/mol)

Y	*meta* substituents: 3Y-C_6H_4X–H						
	O–H^a	S–H^b	Se–H^c	N–H^d	P–H^e	C–H^f	Si–H^d
H	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F	0.9	0.8	1.0	-1.2	0.2	0.3	0.1
Cl	0.9	0.8	0.9	-0.5	0.2	0.3	0.1
CH_3	-0.6	-0.2	0.0	-0.5	-0.1	-0.1	-0.6
OCH_3	-1.4	-0.5	0.7	-3.9	0.2	0.4	0.1
NH_2	-0.6	-0.2	0.0	-6.0	0.0	0.1	0.0
CF_3	2.0	1.1	1.4	1.7	0.4	0.5	0.1
CN	2.8	1.6	1.2	2.4	0.6	0.8	0.2
NO_2	3.2	1.9	1.7	4.1	0.8	0.8	0.2

^{a,b,c,e,f} Data taken from Refs. [47], [29], [48], [49], [50], respectively; ^{d} In this work

The change of $\Delta BDE_{\mathbf{3Y}}$ = BDE(X–H) of 3Y-C_6H_4XH - BDE(X–H) of C_6H_5X.

4. SUBSTITUENT EFFECTS AND HAMMETT EQUATION

Substituent effects are among the most important structural effects influencing the chemical, physical and biological properties of a chemical species. The substituent is a small part of molecule which can be introduced by a simple chemical operation, particularly when it replaces a hydrogen atom. The substituent modified the properties of the molecule but does not alter its general character. The substituent effects are always an attractive subject for chemists [5, 12, 47].

The Hammett equation and its extended forms have been one of the most widely used means for the study and interpretation of organic reactions and their mechanisms [78, 79]. Almost every kind of organic reaction has been treated *via* Hammett equation or its modified forms, Hammett proposed that there is a relationship between the rate of a reaction and the equilibrium constant. As a result, the correlation of Hammett's substituent constant with bond dissociation enthalpies has also been found [12, 76, 78, 80].

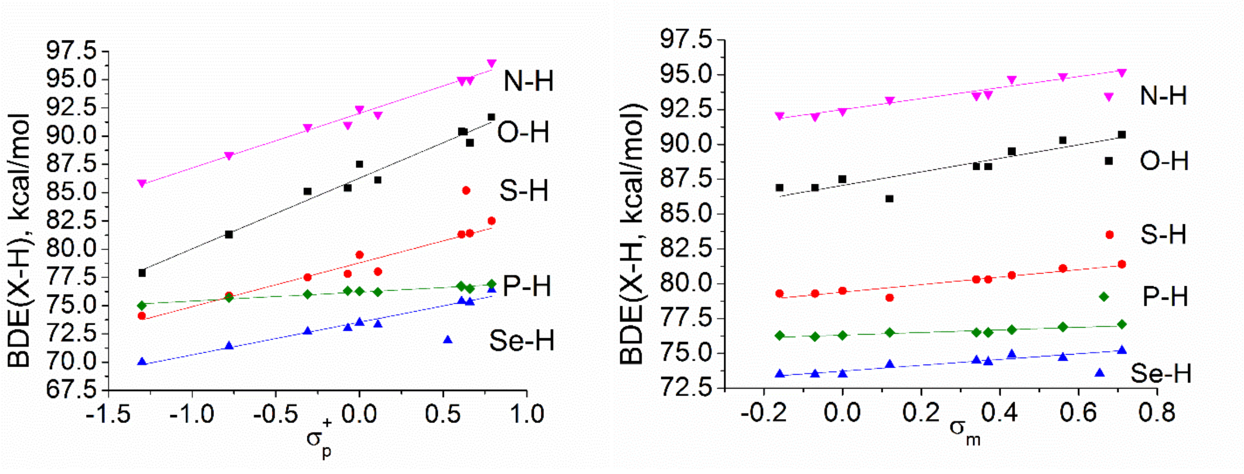
Under this regard, the substituent constant σ at the reaction site of *para* and *meta* is usually discussed in terms of the stability of the radical which is generated from the parent molecule.

Figure 2 shows that the BDE(X−H) when substituent is placed at the *para* position of the aromatic ring depends strongly on the nature of substituent and the effect is much less in the case of *meta* site. Indeed, the correlation of original Hammett (σ) becomes poorer when the substituents were conjugated with the reaction center. This problem was resolved by defining a new constant. Actually, depending on the hetero atom *e.g.* O, S, Se, N, P, C, Si, a suitable modified Hammett parameter has been chosen for such correlation [4, 6]. For example, in case of phenols and anilines, when a lone pair of electrons on the O and N atom could be delocalized on the substituents like *p*-CN and *p*-NO_2 a modified Hammett $\sigma^-$is proposed. On the other hand, a modified Hammett σ^+ proposed by Brown and his colleagues is used when substituents conjugated with a reaction center which could effectively delocalized and since it accounts for through conjugation effects, which will be important for electron-donor groups at the *para* position. In the case of *meta* substituents, the σ_m^+ and σ_m values are found to be virtually the same [47].

4.1. Correlation between Hammett constants and BDE(X−H), in which X belongs to class O category

Figure 2 shows a Hammett's plot for the BDE(X−H) values of *para* 4Y-C_6H_4X-H (X = O, S, Se, N, P) and σ_p^+. The σ_p^+ values were taken from the compilations of Hammett parameters by Hansch, Leo and Taft [78].

The obtained equations from such correlations between the modified Hammett constants (σ^+_p and σ_m) and the BDE(X−H) at the *para* and *meta* of Y-C_6H_4X−H (X = O, S, Se, NH, PH) can be express as follow:



(a) (b)

Figure 2: Plot of BDE(X−H) of the 4Y-C_6H_4X−H and 3Y-C_6H_4X−H (X = O, S, Se, NH and PH) with the Hammett constant σ_p^+ and σ_m, respectively

For 4Y-C_6H_4X−H:

Phenol: $\text{BDE(O−H)} = 6.2559\sigma_p^+ + 86.290 \quad R^2 = 0.9714$ (3)

Thiophenol: BDE(S–H) $= 3.8817\sigma_p^+ + 78.792$ $R^2 = 0.9492$ (4)
Benzeneselenol BDE(Se–H) $= 2.8876\sigma_p^+ + 73.540$ $R^2 = 0.9740$ (5)
Aniline BDE(N–H) $= 4.8444\sigma_p^+ + 92.023$ $R^2 = 0.9823$ (6)
Phenylphosphine BDE(P–H) $= 0.7976\sigma_p^+ + 76.203$ $R^2 = 0.9449$ (7)
For 3Y-C_6H_4X–H:
Phenols: BDE(O–H) $= 4.8707\sigma_m + 87.055$ $R^2 = 0.8194$ (8)
Thiophenols: BDE(S–H) $= 2.6924\sigma_m + 79.401$ $R^2 = 0.8797$ (9)
Benzeneselenols: BDE(Se–H) $= 2.0705\sigma_m + 73.738$ $R^2 = 0.9252$ (10)
Anilines; BDE(N–H) $= 3.9474\sigma_m + 95.502$ $R^2 = 0.9398$ (11)
Phenylphosphines: BDE(P–H) $= 0.9284\sigma_m + 76.318$ $R^2 = 0.8742$ (12)

The R-squared is a statistical measure of how close the data are to the fitted regression line. The higher the R-squared, the better the model fits the data. Based on the equations (3) to (12), an impressive linear correlation ($R^2 > 0.97$) is observed between the BDE(X–H) and σ_p^+ for benzeneselenols ($R^2 = 0.9735$), phenols ($R^2 = 0.9714$) and thiophenols ($R^2 = 0.95$). The BDE(X–H) values of this group increase with the increasing electron withdrawing ability of the substituent (*i.e.* higher value for σ_p^+ especially with X has a lone pair of electron like O, S and Se. For example, when X = O, S and Se, the BDE(X–H)s increase with the amount of 4.20, 3.01 and 2.84 kcal/mol, respectively. The existence of an electron lone pair at the spin centered atom make the radical stabilized by EWG but destabilized by EDG [47, 77, 78]. For instance, the EDGs like CH_3, OCH_3, NH_2 reduce the BDE(O–H)s with the amount of 2.40, 6.20 and 9.60 kcal/mol, respectively due to the destabilization of the radicals generated from the parent aromatic derivatives. In the meantime, the substituents also affect in the stability the ground state. To further understand the effect of a substituent on the strength of the X–H bond, the ground state effect (GE) and radical effect (RE) can be calculated from the exchange reactions between benzeneselenols and related species in figure 3 [48].

Figure 4 illustrates the change of BDE values based on the calculated GE and RE for Y-C_6H_4SeH. In both radicals and parents, the effect of F and Cl is insignificant and the total effect (TE = RE-GE) is very small. EWGs at *para* position tend to stabilize the parents but not the radicals. However, the latter parameter is larger thus leading to the negative TE value. For EDGs, an opposite trend is observed for the radical stability and the parent one. The RE values are found to be larger than the GE counterpart. Therefore the TE values remain considerably positive [48].

4.2. Correlation between Hammett constants and BDE(X–H), in which X belongs to class S category

Toluene and phenylsilane are the aromatic compounds with methyl (–CH_3) and silyl (–SiH_3) groups replacing one hydrogen in benzene ring which are classified as the class S category. This is due to methyl and silyl groups without any lone pair and all electrons are used in single bonds with three hydrogens and one carbon of benzene ring. Because

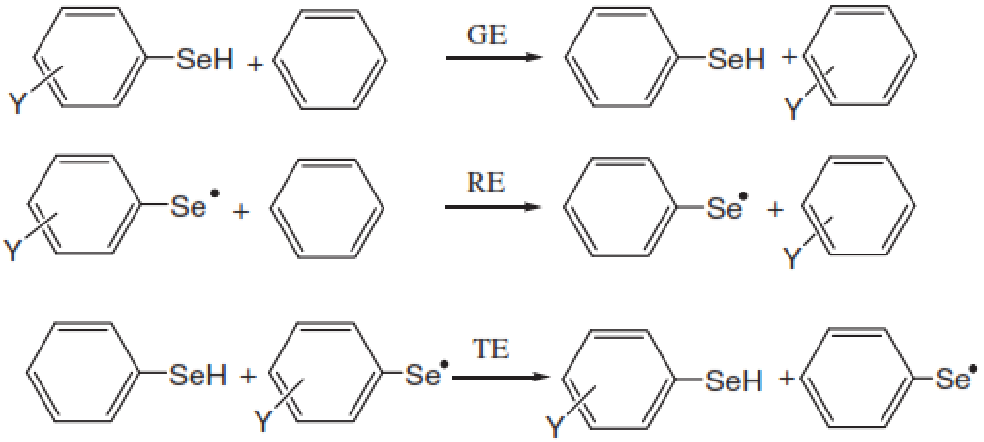


Figure 3: The exchange reactions for calculating GE and RE
(Reprinted from Ref. [48])

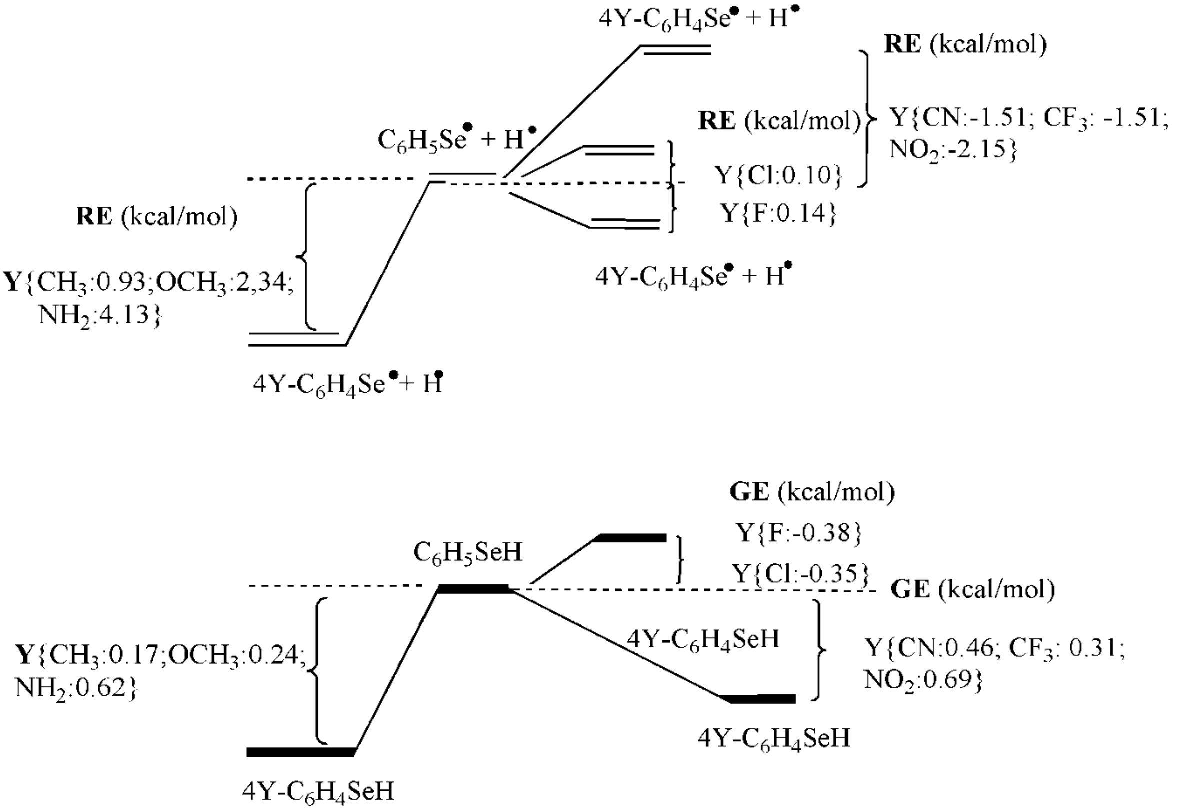


Figure 4: Calculated GE and RE for 4Y-C_6H_4Se-H with Y = H, F, Cl, CH_3, OCH_3, NH_2, CF_3, CN, NO_2. (Reprinted from Ref. [48])

of the S pattern, both toluenes and phenylsilanes do not inhibit of the good correlation between BDE(C–H) or BDE(Si–H) with the Hammett constants. The correlations between the Hammett σ_p^+ and σ_m constants and BDE(C–H)s and BDE(Si–H)s in substituted toluenes and phenylsilanes were displayed in figure 5.

For *para* substitution, in case of toluene and phenylsilane, the linear regressions between BDE(X–H)s (X = CH_2 and SiH_2) with σ_p^+ shown in figure 5 are very poor. However, for *meta* substitution, the correlation is slightly better for C–H bond but still very poor for Si–H bond. The Hammett regression result for the BDE(C–H) changes *verus* σ_m constant is expressed in equation (13).

$$\text{BDE(C–H)} = 0.9699x + 89.897 \quad R^2 = 0.8184 \quad (13)$$

This leads to a conclusion that the direction and magnitude of the effect of Y- substituents on the X–H bonds in 4Y- and 3Y-C_6H_4XH compounds have some dependence on the polarity of the X–H bond undergoing homolytic dissociation [81].

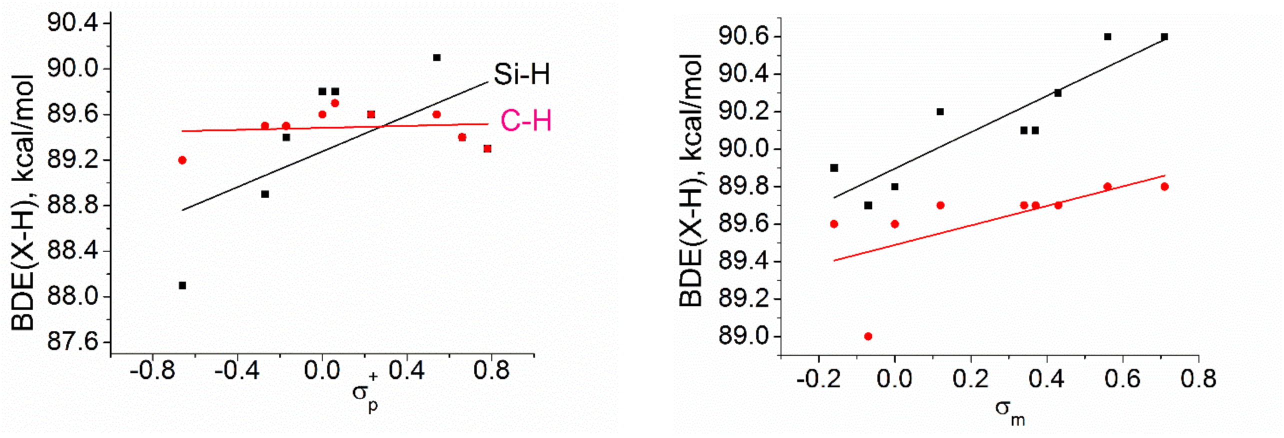


Figure 5: Plot of BDE(X–H) of the 4Y-C_6H_4X-H and 3Y-C_6H_4X-H (X = CH_2, SiH_2) with the Hammett constant σ_p^+ and σ_m, respectively

5. CONCLUSION AND OUTLOOK

Up today, computational chemistry has evolved into a powerful tool to be used to study in many areas. In this review, the computational quantum chemical methods based on B3LYP functional have been applied to determine the bond dissociation enthalpies of a variety of substituted benzenes derivatives. In searching for suitable methods to be used in the evaluation of BDEs, the good performance of the density functional theory using restricted open-shell formalism ROB3LYP at the basis set of 6-311++G(2df,2p) in conjunction with geometries optimized at the B3LYP/6-311G(d,p) level has been demonstrated by its capacity to reproduce the BDEs of a series of X−H bond types in a range of substituted aromatic compounds YC_6H_4XH (X= O, S, Se, NH, PH, CH_2 and SiH_2; Y = H, F, Cl, CH_3, OCH_3, NH_2, CF_3, CN and NO_2). The calculated BDEs of the studied benzene derivatives have been reviewed and hence the model chemistry of ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) is defined as a convenient and economic manner, but with reliable results as compared to available experimental values with the accuracy of 1.0-2.0 kcal/mol.

Depending on the nature of centered atom X, which is polar or non-polar, the behavior of substituents at the *para* and *meta* position is quite different. The success of correlation between Hammett constants was found for substituted benzene derivatives with hetero atom X belongs to class “O” category including phenols, thiophenols, benzeneselenols, anilines and phenylphosphines. In contrast, the poor correlations are seen between BDE values of the C−H and Si−H bonds in toluenes and phenylsilanes, respectively with the Hammett substituent constants at the *para* and *meta* position of aromatic ring. Small effects of the Y-substituents have similarly observed for both C−H and Si−H bonds in substituted toluenes and phenylsilanes.

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