ARTICLE

Theoretical Study of the C−Cl Bond Dissociation Enthalpy and Electronic Structure of Substituted Chlorobenzene Compounds

Rui-zhou Zhang[a], Xiao-hong Li[a,b∗], Xian-zhou Zhang[c]

a. *College of Science, Henan University of Science and Technology, Luoyang 471003, China*
b. *Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China*
c. *College of Physics & Information Engineering, Henan Normal University, Xinxiang 453007, China*

Quantum chemical calculations were used to estimate the bond dissociation energies (BDEs) for 13 substituted chlorobenzene compounds. These compounds were studied by the hybrid density functional theory (B3LYP, B3PW91, B3P86) methods together with 6-31G∗∗ and 6-311G∗∗ basis sets. The results show that B3P86/6-311G∗∗ method is the best method to compute the reliable BDEs for substituted chlorobenzene compounds which contain the C−Cl bond. It is found that the C−Cl BDE depends strongly on the computational method and the basis sets used. Substituent effect on the C−Cl BDE of substituted chlorobenzene compounds is further discussed. It is noted that the effects of substitution on the C−Cl BDE of substituted chlorobenzene compounds are very insignificant. The energy gaps between the HOMO and LUMO of studied compounds are also investigated and from this data we estimate the relative thermal stability ordering of substituted chlorobenzene compounds.

Key words: Density functional theory, Bond dissociation enthalpy, Substituent effect, Substituted chlorobenzene compound

I. INTRODUCTION

The cleavage of the C−Cl bond in homogeneous media and with electrochemical devices has attracted a great deal of attention recently [1-3]. The carbon radicals formed are intermediates in the photodecomposition and oxidation reactions of halogenated hydrocarbons which represent an important source of halogen atoms in the atmosphere [4,5]. Electron transfer on a neutral molecule RX that undergoes bond breaking can proceed by means of a concerted process or in successive steps through the RX⁻· radical. Kopinke *et al.* investigated three infinitely water-soluble reductant [6], and carried out mechanism and kinetics studies of the chemical reactions concerned. Benassi *et al.* investigated the reductive electron transfer on the benzyl chloride and benzotrichloride with MO *ab initio* methods [7]. However, much work only focused upon the rearrangement and fragmentation reactions. Accurate theoretical study on the bond length characteristics of chlorobenzene and its derivatives, which is of fundamental importance for the radical chemistry and the organic materials and can be obtained by calculating the bond dissociation energy (BDE), is still unavailable.

A sound knowledge of BDE is fundamental to a bet-

ter understanding of diverse chemical processes ranging from combustion reactions to enzyme catalysis. For many organic reactions, the substituted chlorobenzene compounds are often used as radical sources. For most small and medium size chlorinated organic compounds here, experimental BDEs are not always determined directly. They can be derived from the heat of formation $\Delta H_f^{\ominus}$ as explained in Ref.[8], which shows that most of the experimental measurements have the high precision required to calculate standard enthalpies of formation to within 1 kJ/mol accuracy. But for large molecules, especially unstable molecules, it is very difficult to experimentally determine the radical stability of these molecules. Therefore, it is very important to find reliable theoretical calculations and predictions of BDE for chlorinated organic compounds.

Different calculational methods are generally applied to compute the BDE for various kinds of molecular systems. For example, the B3LYP method considered by Jursic can produce satisfactory N−H BDE for the chemical system [9]. Li *et al.* used B3PW91 method to predict the accurate BDEs of the S−NO bond for S-nitrosothiols [10]. For the C−Cl bond in substituted chlorobenzene compounds, there are very few reports on the BDEs. Whether the computational methods listed above are suitable to produce the reliable results for substituted chlorobenzene compounds is still not known. If we can discover an accurate calculation method to compute BDEs of the C−Cl bond, it would be possible to use this method to predict those

───────
∗Author to whom correspondence should be addressed. E-mail: lorna639@163.com

molecules whose experimental BDEs are not available. These predictions will also be helpful to understand electron transfer, mechanism and kinetics of chlorinated organic compounds.

The composite *ab initio* methods such as CBS-Q are definitely reliable for the BDE calculations. Recently, Fu *et al.* using over 200 experimental BDE data, demonstrated that the CBS-Q method could predict diverse BDE values within 8 kJ/mol of the experimental values [11]. Density functional theory (DFT) method, which is cheaper than the composite *ab initio* methods, does not suffer much from the spin contamination problem and therefore, is also an attractive computational option for BDE.

In this work, a systematic comparison of the BDEs for the C−Cl bond dissociation of 13 substituted chlorobenzene compounds was performed. All the BDEs are calculated by employing the hybrid density functional theory (B3LYP, B3PW91, B3P86) methods with 6-311G** and 6-31G** basis sets. By comparing the calculated results with the available experimental values, the suitability of the hybrid DFT methods for computing reliable bond dissociation energies of the C−Cl bond in substituted chlorobenzene compounds is discussed. Substituent effect on the C−Cl BDE of chlorinated organic compounds is further discussed. In addition, the energy gaps between the HOMO and LUMO of substituted chlorobenzene compounds are also investigated.

II. METHODS AND COMPUTATIONAL DETAILS

All calculations were performed with the Gaussian 03 computational package [12]. Geometry optimizations and subsequent normal mode analyses at the corresponding equilibrium structures were performed for the products of the different bond scission reactions in which a single Cl group was removed from the parent structure. The equilibrium geometries and bond dissociation energies were obtained using the Becke-style three-parameter DFT [13] with the Lee-Yang-Parr correlation function (LYP) [14,15], the Perdew-Wang 91 expression (PW91) [16], and Perdew's 86 (P86) [17]. All calculations were performed with 6-311G** and 6-31G** basis sets. The normal mode analysis for each structure resulted in no imaginary frequencies for the remaining $3N-6$ vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to a local minimum on the potential energy surface.

The C−Cl bond strength is obtained by calculating the homolytic bond dissociation energy, which is defined here as the enthalpy change of the dissociation reaction:

$$R - X \rightarrow R \cdot + X \cdot \qquad (1)$$
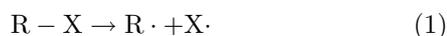
The bond dissociation energy of the R−X bond is computed from the heats of formation at 298.15 K of the

species involved in the dissociation, *i.e.*:

$$E_{\mathrm{BDE}} = \Delta_f H_{\mathrm{R}}^\ominus + \Delta_f H_{\mathrm{X}}^\ominus - \Delta_f H_{\mathrm{RX}}^\ominus \qquad (2)$$

For the substituted chlorobenzene compounds studied here, the BDE is defined as the difference between the zero-point-corrected energy of the parent molecule and that of the products of the unimolecular dissociation in which a Cl group is removed. For example, for 2-Cl-C$_6$H$_4$Cl, the BDE is

$$\mathrm{BDE} = E(C_6H_4Cl) + E(Cl) - E(2\text{-}Cl\text{-}C_6H_4Cl) \qquad (3)$$

The average errors of the BDEs for the B3LYP, B3PW91, and B3P86 methods are determined by calculating the average absolute error ($\varepsilon_{\mathrm{aae}}$), defined as:

$$\varepsilon_{\mathrm{aae}} = \frac{1}{N} \sum_{i=1}^{N} |x_i - c_i| \qquad (4)$$

where x_i represents the experimental data, c_i denotes the calculated values, and N is the number of experimental or calculated data.

III. RESULTS AND DISCUSSION

A. The C−Cl BDE of the substituted chlorobenzene compounds calculated by employing various methods

Tables I and II summarize the C−Cl BDE values of the substituted chlorobenzene compounds calculated by various quantum chemistry methods. From Tables I and II, it is noted that the BDE calculated by B3LYP functional is the smallest and the biggest BDE is calculated by the B3P86 functional. The BDEs increase on average 9.03 kJ/mol from the B3LYP functional to the B3PW91 functional. The same trend is also found, and even stronger, from the B3PW91 functional to the B3P86 functional. In addition, it is noted that all values in Tables I and II follow the same trend, the larger the basis set used, the smaller the BDE value. In the case of B3LYP method, the BDE of 4-CH$_3$CO-C$_6$H$_4$Cl is 377.58 kJ/mol when the 6-31G** basis set is used, but it changes to 371.23 kJ/mol when the 6-311G** basis set is used.

B. Agreement between theoretical and experimental C−Cl BDE

The calculated and experimental C−Cl BDE of the substituted chlorobenzene compounds are listed in Tables I and II. The experimental data are obtained from Ref.[18]. It is noted that the BDE calculated by B3LYP method for most studied molecules are very poor. For B3LYP/6-31G** and B3LYP/6-311G** methods, the average absolute differences are 14.51 and 21.37 kJ/mol, respectively, which is outside our desired target accuracy for chemical predictions. In Tables I and II, the largest deviations are found for 2-4-5-Cl-C$_6$H$_2$Cl (−26.25 and −32.69 kJ/mol, respectively), and we can

TABLE I Computed C−Cl BDE at 298 K for removal of a Cl group in studied molecules by using various DFT methods with 6-31G** basis set[a].

	BDE/(kJ/mol)			BDE$_{exp}$/(kJ/mol) [18]
	B3LYP/6-31G**	B3PW91/6-31G**	B3P86/6-31G**	
C_6H_5Cl	377.37 (−21.82)	386.27 (−12.92)	397.60 (−1.59)	399.19
2-CF_3-4-Cl-C_6H_3Cl	366.08 (−11.37)	374.40 (−3.05)	386.78 (9.33)	377.45
2-CF_3-C_6H_4Cl	365.42 (−23.32)[b]	373.61 (−15.13)	386.02 (−2.72)	388.74
2-CH_3-C_6H_4Cl	376.83 (−14.84)	385.98 (−5.68)	398.19 (6.52)	391.67
2-Cl-C_6H_4Cl	369.60 (−15.80)	379.29 (−6.10)	391.37 (5.98)	385.40
3-CH_3CO-C_6H_4Cl	374.99 (−10.41)	384.10 (−1.30)	395.43 (10.03)	385.40
3-Cl-5-Cl-C_6H_3Cl	370.72 (−24.29)	379.75 (−15.26)	391.16 (−3.85)	395.01
3-Cl-C_6H_4Cl	373.90 (−1.46)	382.89 (7.52)	394.26 (18.89)	375.36
3-F-4-Cl-C_6H_3Cl	375.16 (−7.73)	384.14 (1.25)	395.51 (12.62)	382.89
4-CF_3-C_6H_4Cl	376.37 (−12.37)	385.44 (−3.30)	396.77 (8.03)	388.74
4-CH_3CO-C_6H_4Cl	377.58 (−4.47)	386.57 (4.51)	397.98 (15.93)	382.05
4-Cl-C_6H_4Cl	377.20 (−14.46)	386.23 (−5.43)	397.60 (5.94)	391.67
2-4-5-Cl-C_6H_2Cl	368.34 (−26.25)	378.16 (−16.43)	390.20 (−4.39)	394.59
Mean absolute deviation	14.51	7.53	8.14	

[a] Zero-point energies are taken into account.
[b] The value in the parenthesis is the deviation from computed BDE for experimental one.

TABLE II Computed BDE at 298 K for removal of a Cl group in studied molecules by using various DFT methods with 6-311G** basis set[a].

	BDE/(kJ/mol)			BDE$_{exp}$/(kJ/mol) [18]
	B3LYP/6-311G**	B3PW91/6-311G**	B3P86/6-311G**	
C_6H_5Cl	370.68 (−28.51)	381.97 (−17.22)	393.46 (−5.73)	399.19
2-CF_3-4-Cl-C_6H_3Cl	357.47 (−19.98)[b]	368.68 (−8.78)	381.26 (3.80)	377.45
2-CF_3-C_6H_4Cl	356.76 (−31.98)	367.84 (−20.9)	380.42 (−8.32)	388.74
2-CH_3-C_6H_4Cl	369.60 (−22.07)	381.34 (−10.32)	393.76 (2.09)	391.67
2-Cl-C_6H_4Cl	362.87 (−22.53)	375.20 (−10.20)	387.53 (2.13)	385.40
3-CH_3CO-C_6H_4Cl	368.47 (−16.93)	379.92 (−5.48)	391.42 (6.02)	385.40
3-Cl-5-Cl-C_6H_3Cl	364.54 (−30.47)	376.03 (−18.98)	387.57 (−7.44)	395.01
3-Cl-C_6H_4Cl	367.46 (−7.90)	378.88 (3.51)	390.37 (15.01)	375.36
3-F-4-Cl-C_6H_3Cl	368.84 (−14.04)	380.25 (−2.63)	391.75 (8.86)	382.89
4-CF_3-C_6H_4Cl	369.89 (−18.85)	381.30 (−7.44)	392.84 (4.10)	388.74
4-CH_3CO-C_6H_4Cl	371.23 (−10.83)	382.64 (0.59)	394.17 (12.12)	382.05
4-Cl-C_6H_4Cl	370.68 (−20.98)	382.05 (−9.61)	393.59 (1.92)	391.67
2-4-5-Cl-C_6H_2Cl	361.90 (−32.69)	374.32 (−20.27)	386.65 (−7.94)	394.59
Mean absolute deviation	21.37	10.46	6.58	

[a] Zero-point energies are taken into account.
[b] The value in the parenthesis is the deviation from computed BDE for experimental one.

see that all of the B3LYP calculated results underestimate the BDE for the compounds studied here. Although the hybrid B3LYP method is a popular computational tool which can produce an extraordinary agreement between the computed and experimental energies for some small polar molecules [19-21], it is clear that this method is not suitable to predict highly accurate bond dissociation energies for the chlorinated organic compounds containing the C−Cl bond.

It is also noted that the mean absolute deviation between the B3PW91/6-311G** results and experiments is about 10.46 kJ/mol, which is somewhat smaller than those found by B3LYP method. The mean absolute deviation, however, between B3PW91/6-31G** results and experiments is 7.53 kJ/mol, which is in good agreement with the experimental value. It is noted from Table I that there are four compounds for which the deviations from experimental values for B3PW91/6-31G**

method are larger than 12.50 kJ/mol, and the maximum deviation is found for 2-4-5-Cl-C_6H_2Cl (16.43 kJ/mol).

In Tables I and II, we can see that the mean absolute deviation between the B3P86/6-31G** results and experiments is about 8.14 kJ/mol, which is somewhat smaller than those found by B3LYP method, but larger than those found by B3PW91/6-31G** method, while the mean absolute deviation between B3P86/6-311G** results and experiments is only 6.58 kJ/mol, which is in extraordinarily good agreement with the experimental value. In the case of 4-Cl-C_6H_4Cl, the B3P86 method in the 6-311G** basis set yields the most accurate C−Cl bond dissociation energy of 393.59 kJ/mol, only a 1.92 kJ/mol deviation from the experimental value. It is noted from Table II that there is one compound for which the deviation from experimental values for B3P86/6-311G** method is larger than 12.50 kJ/mol and the maximum deviation for B3P86/6-311G** method is found for 3-Cl-C_6H_4Cl (15.01 kJ/mol). Because of the smaller mean absolute deviation and the smaller number of the compounds with the deviation from experimental value bigger than 12.50 kJ/mol, the B3P86 method with 6-311G** basis set is the best method to compute dissociation energies for chlorinated organic compound studied.

From Tables I and II, we can see that the BDEs of the C−Cl bond depend strongly on the calculation method. The mean absolute deviation decreases from 14.51 kJ/mol to 7.53 kJ/mol when B3LYP/6-31G** method is replaced by B3PW91/6-31G** method; while it reduces from 21.37 kJ/mol to 6.58 kJ/mol when B3LYP method with 6-311G** basis set is replaced by B3P86/6-311G** method. In addition, it is also noted that the BDEs of the C−Cl bond depend strongly on the basis set. The mean absolute deviation increases from 7.53 kJ/mol (Table I) to 10.46 kJ/mol (Table II) when the 6-31G** basis set in the B3PW91 model is replaced by the 6-311G** basis set, while it decreases from 8.14 kJ/mol to 6.58 kJ/mol when the 6-31G** basis set in the B3P86 model is replaced by the 6-311G** basis set, which implies that B3P86 DFT method is sensitive to the basis sets.

In addition, it is also noted that the BDE computed by B3P86/6-311G** method for 4-CH_3CO-C_6H_4Cl is the biggest, while the BDE of other compounds are all smaller than that of 4-CH_3CO-C_6H_4Cl, especially the BDE of 2-CF_3-C_6H_4Cl is the smallest, which means that 2-CF_3-C_6H_4Cl has the highest chemical activity while 4-CH_3CO-C_6H_4Cl has the lowest chemical activity. In addition, it is noted that the position of the substituent group has great effect on the BDEs of the compounds selected. For example, the BDEs of 2-Cl-C_6H_4Cl, 3-Cl-C_6H_4Cl and 4-Cl-C_6H_4Cl are 387.53, 390.37, and 393.59 kJ/mol, respectively. For 4-Cl-C_6H_4Cl, it is also found that the BDE decreases when an H atom is substituted by other substituent group such as F or CF_3 group.

C. The substituent effects on the C−Cl BDE

The substituent effects on BDE can be reflected by comparing the BDE of a substituted molecule with that of the parent molecule, *i.e.* substituent effect ΔBDE=BDE(X-C_6H_4Cl)−BDE(C_6H_5Cl). If the substituent effect is positive, the corresponding substituent increases the BDE, otherwise, the substituent lowers the BDE. Using DFT method, we studied a series of substituted X-chlorobenzene, where X includes both electron donating and electron withdrawing groups such as X=CF_3, CH_3, Cl, and CH_3CO. The results in Table III show that the effects of substitution on the BDE of substituted chlorobenzene are very insignificant. For example, substitutent groups p-CF_3, p-CH_3CO, and p-Cl have hardly any effect on the BDEs of the parent X-C_6H_4Cl. The same conclusion can be obtained for single substituent groups such as m-Cl, m-CH_3, o-CH_3CO, o-Cl and for two or three substituent groups 2-CF_3-4-Cl, 3-Cl-5-Cl, 3-F-4-Cl, and 2-4-5-Cl.

It is also noted that the groups in meta position exert stronger influence upon the BDE of the C−Cl bond than the groups in para position. For example, m-Cl and m-CF_3 groups have greater effect on the BDE than p-Cl and p-CF_3 groups. The largest decrease in BDE amounts to about −14.13 kJ/mol for B3PW91/6-311G** method for the substituent group m-CF_3. Compared to chlorobenzene, it is noted from Table III that the electron-withdrawing groups decrease the C−Cl BDE, while the electron-donating substituent groups increase the BDE. For example, m-Cl, m-CF_3, and p-CF_3 groups decrease the BDE of chlorobenzene and the substituent effects for B3LYP/6-311G** method are −3.22, −13.92, and −0.79 kJ/mol, respectively. While p-Cl group has little effect on the BDE of chlorobenzene and the substituent effect is zero. In addition, it is noted

TABLE III ΔBDE values of substituted chlorobenzene compounds calculated with 6-311G** basis set.

Substituent	ΔBDE/(kJ/mol)		
	B3LYP	B3PW91	B3P86
H	0	0	0
2-CF_3-4-Cl	−13.21	−13.29	−12.2
3-Cl-5-Cl	−6.14	−5.94	−5.89
3-F-4-Cl	−1.84	−1.72	−1.71
2-4-5-Cl	−8.78	−7.65	−6.81
o-CH_3CO	−1.07	−0.21	−0.29
o-Cl	−7.81	−6.77	−5.93
m-Cl	−3.22	−3.09	−3.09
m-CF_3	−13.92	−14.13	−13.04
m-CH_3	−1.08	−0.63	0.29
p-CF_3	−0.79	−0.67	−0.62
p-CH_3CO	0.55	0.67	0.71
p-Cl	0	0.08	0.13

TABLE IV The calculated energy gaps ΔE between the HOMO and LUMO of the substituted chlorobenzene compounds (energy in 10^{-3} a.u.).

Compounds	ΔE (B3LYP)		ΔE (B3PW91)		ΔE (B3P86)	
	6-31G**	6-311G**	6-31G**	6-311G**	6-31G**	6-311G**
2-CF$_3$-4-Cl-C$_6$H$_3$Cl	209.29	206.26	209.56	206.65	209.69	206.72
2-CF$_3$-C$_6$H$_4$Cl	222.25	219.52	223.03	220.47	223.25	220.64
2-CH$_3$-C$_6$H$_4$Cl	231.67	229.05	232.27	229.88	232.51	230.01
2-Cl-C$_6$H$_4$Cl	226.95	223.94	227.29	224.48	227.47	224.57
3-CH$_3$CO-C$_6$H$_4$Cl	191.10	191.19	190.22	190.34	190.72	190.77
3-Cl-5-Cl-C$_6$H$_3$Cl	227.42	224.77	227.86	225.49	228.10	225.61
3-Cl-C$_6$H$_4$Cl	227.32	224.27	227.82	225.00	227.98	225.04
3-F-4-Cl-C$_6$H$_3$Cl	216.66	214.15	216.72	214.43	216.90	214.48
4-CF$_3$-C$_6$H$_4$Cl	224.78	22.24	225.42	223.24	225.64	223.40
4-CH$_3$CO-C$_6$H$_4$Cl	190.78	191.14	189.82	190.14	190.36	190.62
4-Cl-C$_6$H$_4$Cl	220.00	216.57	220.24	216.99	220.29	216.94
2-4-5-Cl-C$_6$H$_2$Cl	210.25	206.96	210.08	206.98	210.14	206.93

that different calculation methods do not affect ΔBDE values significantly. For these reasons, density functional method can be regarded as a suitable tool for the C−Cl ΔBDE calculations of the substituent chlorinated organic compounds.

D. The energy gaps between the HOMO and LUMO of substituted chlorobenzene compounds

The energy gaps between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are important properties in several chemical processes. The energy of the HOMO (E_{HOMO}) measures the electron donating character of a compound and the energy of the LUMO (E_{LUMO}) measures its electron accepting character [22-27]. The HOMO-LUMO gap, *i.e.* the difference in energy between the E_{HOMO} and E_{LUMO}, is an important stability index [28]. In reactions of a nucleophile with an electrophile, the interaction between the HOMO of the nucleophile with the LUMO of the electrophile contributes to the attraction between the two reactants. Studying HOMO and LUMO is expected to show whether or not the reaction is feasible and the relatively thermal stability of an individual molecule in the gas phase. A large HOMO-LUMO gap implies high stability for the molecule in the sense of its lower reactivity in chemical reactions [29]. Also, it is of great interest to discuss the compound's thermal stability at an electron level. The calculated energy gaps between the HOMO and LUMO ($\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$) of substituted chlorobenzene compounds at various levels are displayed in Table IV.

From Table IV, it is noted that the ΔE values from three DFT methods are similar to each other. The compound which has the biggest value of the energy gap between the HOMO and LUMO at B3LYP/6-31G** is 2-CH$_3$-C$_6$H$_4$Cl and the energy gap value is 0.23167 a.u.,

which shows that 2-CH$_3$-C$_6$H$_4$Cl is the most stable compound among the substituted chlorobenzene compounds. The compounds which have the smallest value of the energy gap between the HOMO and LUMO at B3LYP/6-31G** are 4-CH$_3$CO-C$_6$H$_4$Cl and 3-CH$_3$CO-C$_6$H$_4$Cl and the energy gap values are all about 0.19 a.u., which shows that 4-CH$_3$CO-C$_6$H$_4$Cl and 3-CH$_3$CO-C$_6$H$_4$Cl are the least stable compounds among the studied compounds. The values of the energy gaps between the HOMO and LUMO of 2-CF$_3$-C$_6$H$_4$Cl, 2-Cl-C$_6$H$_4$Cl, 3-Cl-5-Cl-C$_6$H$_3$Cl, 3-Cl-C$_6$H$_4$Cl, 4-CF$_3$-C$_6$H$_4$Cl, and 4-Cl-C$_6$H$_4$Cl are about 0.22 a.u., which shows that these compounds have similar stability and are less stable than 2-CH$_3$-C$_6$H$_4$Cl. The values of the energy gaps between the HOMO and LUMO of 2-4-5-Cl-C$_6$H$_2$Cl, 2-CF$_3$-4-Cl-C$_6$H$_3$Cl, and 3-F-4-Cl-C$_6$H$_3$Cl are about 0.21 a.u.

Because a large HOMO-LUMO gap implies high stability for the molecule in the sense of its lower reactivity in chemical reactions, 2-CH$_3$-C$_6$H$_4$Cl has the highest stability and lowest reactivity among the compounds selected, when it is attacked by free group, while 4-CH$_3$CO-C$_6$H$_4$Cl and 3-CH$_3$CO-C$_6$H$_4$Cl have lower stability and higher reactivity.

IV. CONCLUSION

In this work, the bond dissociation energies of the C−Cl bond for 13 substituted chlorobenzene compounds were calculated by hybrid DFT B3P86, B3LYP, and B3PW91 methods. By comparing all the computed results with the experimental ones, it is noted that B3P86/6-311G** method can yield the most accurate BDE of the C−Cl bond, which has an average absolute deviation of 6.58 kJ/mol. Substituent effect on the C−Cl BDE of substituted chlorobenzene compounds is further discussed. It is noted that the effects of substi-

tution on the C−Cl BDE of substituted chlorobenzene compounds are very insignificant, so DFT can be regarded as a suitable tool for the C−Cl ΔBDE calculations of the substituted chlorobenzene compounds. In addition, we also investigated the energy gaps between the HOMO and LUMO of studied compounds and estimated the relative thermal stability ordering. It is found that 2-CH_3-C_6H_4Cl is the most stable compound among the substituted chlorobenzene compounds, while 4-CH_3CO-C_6H_4Cl and 3-CH_3CO-C_6H_4Cl are the least stable compounds.

V. ACKNOWLEDGMENT

[1] (a) A. J. Fry, *Synthetic Organic Electrochemistry*, 2nd Edn., New York: Wiley, (1989).
(b) D. Peters, *in Organic Electrochemistry*, 3rd Edn., H. Lund, and M. M. Baizer, Ed., New York: Marcel Dekker, 361 (1991).

[2] J. M. Saveant, Adv. Phys. Org. Chem. **26**, 1 (1990).

[3] L. Eberson, *Electron Transfer Reactions in Organic Chemistry*, Berlin: Springer Verlag, 159 (1987).

[4] B. J. Finlayson-Pitts and J. N. Pitts, *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*, New York: Academic Press, 241 (1999).

[5] J. S. Francisco and M. M. Maricq, Adv. Photochem. **20**, 79 (1995).

[6] F. D. Kopinke, K. Machenzie, R. Koehler, and A. Georgi, Appl. Catal. A General. **271**, 119 (2004).

[7] R. Benassi, C. Bertarini, and F. Taddei, J. Chem. Soc. Perkin Trans. **2**, 2263 (1997).

[8] A. A. Boyd, B. Noziere, and R. Lesclaux, J. Phys. Chem. **99**, 10815 (1995).

[9] B. S Jursic, J. Mol. Struct.: THEOCHEM **366**, 103 (1996).

[10] X. H. Li, R. Z. Zhang, and X. D. Yang, J. Mol. Struct.: THEOCHEM **817**, 43 (2007).

[11] Y. Fu, X. Y. Dong, Y. M. Wang, L. Liu, and Q. X. Guo, Chin. J. Chem. **23**, 474 (2005).

[12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, Ö. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian* 03 (*Revision B*.01), Pittsburgh, PA: Gaussian, Inc., (2003).

[13] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[14] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[15] B. Miehlich, A. Savin, H. Stoll, and H. Preuss, Chem. Phys. Lett. **157**, 200 (1989).

[16] J. P. Perdew and Y. Wang, Phys. Rew. B **45**, 13244 (1992).

[17] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).

[18] Y. R. Luo, *Handbook of Bond Dissociation Energies in Organic Compounds*, Beijing: Science Press, 137 (2004).

[19] B. S. Jursic, J. Mol. Struct.: THEOCHEM **366**, 103 (1996).

[20] B. S. Jursic, J. Mol. Struct.: THEOCHEM **422**, 253 (1998).

[21] B. S. Jursic, Int. J. Quantum. Chem. **62**, 291 (1997).

[22] A. Korolkovas, *Fundamentos da Farmacologia Molecular*, Guanabara: Rio de Janeiro, 139 (1982).

[23] B. Clare, Theor. Chim. Acta **87**, 415 (1994).

[24] A. B. F. Da Silva and M. Sc. Thesis, Universidade de Säo Paulo, Brazil, (1985).

[25] E. J. Ariens, *Drug Design*, New York: Academic Press, 469 (1971).

[26] L. B. Kier, *Molecular Orbital Studies in Chemical Pharmacology*, Berlin: Springer, 105 (1970).

[27] A. Burger, *Medicinal Chemistry*, New York: Wiley-Interscience, 118 (1970).

[28] D. F. V. Lewis, C. Ioannides, and D. V. Parke, Xenobiotica **24**, 401 (1994).

[29] Z. Zhou and R. G. Parr, J. Am. Chem. Soc. **112**, 5720 (1990).