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Gas-Phase Thermodynamic Properties of Dichlorophenols Determined from Density Functional Theory Calculations

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Density functional theory has been used to investigate gas-phase thermodynamic properties of phenol and dichlorophenols. Molecular geometries, energies, and vibrational frequencies were computed at the B3LYP and BP86 levels of theory. At $T = 298.15$ K, calculated standard enthalpies of formation are in excellent agreement with experimental data. The average deviation between calculated and experimental values is of about 2.3 kJ/mol, and in some cases, theoretical values fall within experimental uncertainty. Other properties for which only a few experimental results were available in the literature were also calculated, namely, O−H homolytic bond dissociation energies, gas-phase acidities, ionization energies, and proton and electron affinities.

Introduction

The thermodynamic properties of chlorinated phenols are of major relevance due to their impact on stratospheric ozone depletion and to their role as precursors of air pollutants.[1−4] The emission of these substances to the atmosphere is associated with practical combustions such as incineration of waste materials. The combustion method is being or intended to be intensively implemented in the European Union (EU). In some countries, this passes by modification of cement plant facilities. The main reason presented for application of the combustion approach by EU governments is that this is one of the cleanest methods for waste disposal. However, some voices have been raised against co-incineration of hazardous materials and populations in the vicinity of cement plants are becoming increasingly alarmed. The argument against co-incineration relies on the fact that some chemicals, when burned under those conditions observed in cement furnaces, produce extremely toxic substances such as dioxins. Among these chemicals, chlorinated phenols, commonly used as pesticide components, insecticides, and antimicrobial agents, are known precursors of chlorinated dioxins.[2] Phenol itself is very important to the chemistry of living organisms, and in some cases chlorophenols are produced as metabolites in certain species of flora and fauna. However, these natural sources of chlorophenols are thought to represent a negligible contribution to overall chlorinated dioxin environmental levels.

Incineration is the recommended method for the disposal of large amounts of chlorinated phenols, but necessary precautions include the security of complete combustion. Further understanding of such systems is needed in order to perform a controlled incineration. Nevertheless, thermochemical data are still scarce for the majority of halogenated phenols, which is even more dramatic for gas-phase reactions involving these compounds. It is noteworthy that phenols are highly reactive molecules due to formation of phenoxy radicals, these being important intermediates in many biological and industrial processes due to their role in antioxidant activity.[3,4] The energetics of the O−H bond in phenol and substituted phenols was recently reviewed by Santos et al.[5] Thermodynamic data reported in this review paper for dichlorophenols concern the homolytic O−H bond dissociation enthalpy, BDE, for 3,5-dichlorophenol, being of 14 ± 4 kJ/mol higher to the same value for phenol. This value is based on the experimental BDEs reported by Bordwell, Arnett and co-workers.[6,7] Also, for the 3,5-isomer, the experimental gas-phase acidity is 1399 ± 8.8 kJ/mol.[8] The experimental gas-phase standard enthalpies of formation $\Delta_f H_m°(g)$ of the disubstituted chlorophenol series were reported by Ribeiro da Silva et al.[9] These authors derived the gas-phase values from condensed-phase standard molar enthalpies of formation and enthalpies of sublimation, obtained by rotating-bomb calorimetry and Calvet microcalorimetry, respectively. The ionization energy IE of the 2,6-dichlorophenol isomer can also be found in the literature as 834.6 ± 1.9 kJ/mol.[10] From a theoretical point of view and as far as we are aware, only a few studies devoted to the thermodynamics of monosubstituted chlorophenols have been reported. Suryan et al. used the semiempirical AM1 method to calculate gas-phase BDEs.[11] Other authors employed more sophisticated methods based in the density functional theory, DFT, to obtain accurate energies by consideration of correlation effects. Different computational schemes were engaged to optimize molecular geometries and to introduce thermal corrections. The local density, LD, and the generalized gradient-corrected, GG, approximations have been used by Wu and Lai[12] to optimize the molecular geometry of *p*-chlorophenol and also to obtain the corresponding BDE. More recently, the hybrid B3LYP method was used to calculate the BDEs of both *m*-chlorophenol and *p*-chlorophenol.[13,14] Miranda[15] used a combination of Hartree−Fock, HF, second-order Moller−Plesset, MP2, and DFT methods to obtain BDEs, $\Delta_f H_m°(g)$, and gas-phase acidities of the three chlorophenol isomers. The HF/3-21G* computational scheme was used to correct the energy calculated at the MP2/6-31G* or B3LYP/6-31G* levels of theory on the HF/6-31G* optimized geometry. The B3LYP computed values for the $\Delta_f H_m°(g)$ were −129.3 kJ/mol (*o*-chlorophenol), −126.5 kJ/mol (*m*-chlorophenol), and −124.4 kJ/mol (*p*-chlorophenol), while the BDE and gas-phase acidity satisfactorily agree with published experimental val-

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ues.[5,16] However, the agreement of the computed BDE values at the B3LYP/6-31G*//HF/6-31G* level (ref 15) and experimental BDE data is considerably worse than those at B3LYP/6-31G** level (ref 13). This was expected due to the complete absence of correlation energy in the HF theory.

The work herein presented is devoted to the determination of several gas-phase thermodynamic properties for the six dichlorophenol isomers. First, this work is intended to fill the lack of thermochemical information on dichlorophenols and also to use theoretical calculations in the interpretation of isomeric effects and in the prediction of new values. Second, we aim to compare calculated parameters with available experimental data, to clarify some existing discrepancies arisen by application of different experimental techniques. This is especially evident for the case of the experimental O−H bond dissociation energy in phenol, in which a wide range of values has been proposed, see ref 5 and references therein. Finally, this work will provide a ground test for the applicability of these theoretical methods for prediction of structural, vibrational and thermochemical parameters, still unavailable for a wide variety of aromatic compounds.

Theoretical Calculations

Density functional calculations within the Kohn−Sham formalism were carried out for geometry optimization of phenol and of the six dichlorophenol isomers, and their corresponding phenoxyls and phenoxydes as well. Two different approaches were considered, namely the B3LYP three-parameter hybrid method proposed by Becke[17] and the BP86 exchange−correlation functional. These calculations were performed by means of the GAMESS−UK suite of programs.[18,19] The former functional comprises an exchange-correlation functional that mixes the nonlocal Fock exchange with the gradient-corrected form of Becke[20] and adds the correlation functional proposed by Lee et al.[21] while the BP86 method is based on the Becke's 1988 exchange and on the Perdew's 86 correlation functionals.[20,22] In the present work, the atomic electron density was described by the standard polarized double-ζ split valence basis set DZVP.[23]

The association of the B3LYP method with a relatively large basis set was proven to be an excellent computational choice.[13,26] This approach was found to provide very good molecular geometries comparable to those obtained using more accurate and much more computer resources demanding CCSD(T) or QCISD methods together with a medium sized basis set.[25,26] Therefore, use of an extended basis set is needed but, unfortunately, this unables application of these accurate methods to the majority of chemical compounds in which the chemists are interested, i.e., big size molecules and compounds containing heavy atoms. The excellency of the hybrid approach is also confirmed by the good agreement observed for phenoxyl radical's vibrational frequencies and spin densities computed at DFT/6-31G(d) level of theory and those calculated using the CASSCF/6-311G(2d,p) approach.[27]

In this work, vibrational frequencies have also been calculated at the same levels of theory used in the optimization procedure. This is used to correct the computed electronic energy values for zero-point energies, ZPE, as well as translational, rotational, and vibrational contributions to the enthalpy at $T = 298.15$ K. Usually, the determination of spin contamination is based in the $\langle S^2 \rangle$ value. However, in DFT methods the computation of $\langle S^2 \rangle$ is not trivial since construction of the Slater determinant is based on the Kohn−Sham orbitals. Therefore, direct calculation of $\langle S^2 \rangle$ is not possible and is approximated by considering a system of noninteracting electrons with the same ground-state density. Wang et al.[28] have shown that this approach provides reasonable estimates of spin contamination. In the present work, for the open-shell radical species, the values of $\langle S^2 \rangle$ were carefully checked. The s-square values were found to be of about 0.75, an indication of pure doublets states with no spin contamination.

Results and Discussion

Computed geometrical parameters of phenol and of the six dichlorophenol isomers, obtained by full optimization at the B3LYP/DZVP and BP86/DZVP levels of theory are in excellent agreement with experimental data. Geometric and energetic data are given as Supporting Information. In fact, the average deviation between B3LYP/DZVP geometry of phenol and that from microwave experiments[29] is 0.006 Å for bond lengths and 0.2° for bond angles. Further, the maximum deviation observed is 0.014 Å for the O−H bond length and 0.6° for the $H_2-C_2-C_3$ angle. Bond lengths computed at BP86/DZVP level of theory are generally longer than those computed at the B3LYP/DZVP level and consequently are farther from experimental numbers. The substitution of hydrogen by chlorine atoms does not considerably affect phenol geometry. It should be pointed here that the hydroxyl hydrogen atom points toward the chlorine atom at the closest position, i.e., toward the chlorine in *ortho* position in 2,3-, 2,4-, 2,5-, and 2,6-dichlorophenols and toward the chlorine in *meta* position in 3,4- or 3,5-isomers. For example, when replacing a hydrogen atom in the *ortho* position, there are maximum changes, in the O−H bond distance of 0.003 Å and in the $O-C_1-C_2$ or C_1-C_2-Cl bond angles of 2.2°. The presence of the one chlorine atom neighboring the hydroxyl group shortens the C_1-O bond length by 0.019 Å. Other differences between bond lengths in *ortho*-substituted dichlorophenols and in phenol are negligible. Consequently, these effects are even more imperceptible for the 3,4- and 3,5-dichlorophenols.

The B3LYP and BP86 energies at $T = 0$ K were corrected for $T = 298.15$ K by introducing the thermal corrections calculated at the same level of theory. This is simply accomplished by performing a vibrational frequencies calculation at the optimized geometry for each molecule. These corrected energies show that 2,5-dichlorophenol is the most stable species, whereas the 3,4-isomer is the most unstable one. As it happens with the *ortho*-chlorophenol species, the most stable dichlorophenols are those in which the chlorine and the hydroxyl hydrogen atoms are close to each other. The distance between the hydrogen atom of the OH group and the chlorine atom in the *ortho* position is 2.402 Å, at the B3LYP/DZVP level. Therefore, it could be argued that the B3LYP energy difference, of about 12 kJ/mol, between the two possible conformations in the 2,3-isomer reflects some kind of hydrogen bonding stabilization. However, this effect is due to high steric hindrance if the oxygen lone pairs, which occupy more space than the hydrogen atom, point toward the chlorine atom. Interestingly, it is possible to believe that chlorine atoms placed in adjacent position do not interact with each other since the energetic difference between the two conformations of 2-chlorophenol is 13 kJ/mol, almost the same difference referred above for the two possible conformations of 2,3-dichlorophenol. A contrasting result was obtained for the 2,3 and 2,4-dichlorophenols and for the 3,4- and 3,5-isomers in which the B3LYP/DZVP energetic difference is noticeable, of about 8 and 11 kJ/mol, respectively. Corrected total energies were used to calculate the absolute homolytic O−H BDEs, at $T = 298.15$ K, of phenol and of the

TABLE 1: Absolute and Relative Bond Dissociation Energies for Phenol and the Six Dichlorophenols at $T = 298.15$ K[a]

	O−H BDE (kJ/mol)							
	UB3LYP/DZVP		ROB3LYP/DZVP		ROB3LYP/6-311++G(2df,2p)		exptl	
compound		Δ		Δ		Δ		Δ
phenol	336.9		346.6		366.8		371.3 ± 2.3[b]	
2,3-dichlorophenol	347.0	(+10.1)	356.2	(+9.6)	375.5	(+8.7)		
2,4-dichlorophenol	340.2	(+3.3)	348.1	(+1.5)	366.6	(−0.2)		
2,5-dichlorophenol	347.5	(+10.6)	356.3	(+9.7)	375.4	(+8.6)		
2,6-dichlorophenol	339.5	(+2.6)	347.4	(+0.8)	366.4	(−0.4)		(−1)[c]
3,4-dichlorophenol	337.4	(+0.5)	346.3	(−0.3)	364.8	(−2.0)		
3,5-dichlorophenol	345.9	(+9.0)	356.5	(+9.9)	375.1	(+8.3)		(17.1)[d] (11.2)[e]

[a] Three different theoretical approaches were used; see text for further details. ΔBDEs, given in parentheses, were obtained as BDE($C_6H_3Cl_2OH$) − BDE(C_6H_5OH). [b] Absolute BDE recommended in ref 5, selected from a list of experimental BDEs falling in the range ∼365−375 kJ/mol. [c] Relative BDE calculated from selected values for 2,4,6-trichlorophenol and 4-chlorophenol in ref 5. [d] Relative BDE following the combination of oxidation potential measurements and pK_{HA}, ref 6. [e] Relative BDE obtained from titration calorimetry and second-harmonic ac voltammetry experiments, ref 7.

six dichlorophenols which are listed in Table 1. The values herein reported provide information about the effect on homolytic O−H BDE caused by the position of chlorine atoms in the aromatic ring. The BDE was calculated by considering the following equation:

$$\mathrm{BDE} = H[C_6H_3X_2O^\bullet] + H[H^\bullet] - H[C_6H_3X_2OH] \quad (1)$$

where H[Y] refer to the enthalpies at $T = 298.15$ K of each species involved in the homolytic O−H dissociation. The enthalpy of the hydrogen atom at 298.15 K, was calculated from the exact energy, −0.50000 au, which becomes after thermal corrections −0.49764 au. This is due to the self-energy problem in DFT methods.

For the set of compounds investigated in this work and as far as we know, only the experimental homolytic O−H BDE of phenol can be found in the literature. For this compound, direct comparison of calculated (U)B3LYP/DZVP and experimental BDE values for phenol results in a significant difference, cf. left column in Table 1. The calculated value is 34 kJ/mol lower than the recommended number by Santos et al.[5] In fact, the generality of the computational methodologies fails in the determination of BDE in phenol. In a previous work, both ab initio and DFT methods combined with large basis sets have been used by Brinck et al. to calculate the absolute homolytic BDE for phenol.[13] The computed BDEs are also consistently lower than the experimental data with a single exception for the MP4/6-31G* energy calculation based on an optimized geometry at the MP2/6-31G* level of theory, which is only 6 kJ/mol higher than the recommended experimental value. Also, the supposedly more sophisticated CCSD(T)/6-31G*//MP2/6-31G* approach gives a value far below the experimental one. A nice agreement between CCSD(T) and experimental BDE of phenol is found if the CCSD(T) energies are corrected for limited basis set effects. This is done by adding the energetic difference between the MP2/6-311G(2d,p) and MP2/6-31G* approaches. Similarly, if basis set corrections are included in the MP4 approach, the small difference found between the MP4/6-31G* and experimental values increases drastically. The basis set effect is not important for the B3LYP hybrid method. On going from the B3LYP/6-31G**//B3LYP/6-31G** to the B3LYP/6-311G(2d,p)//B3LYP/6-31G** approach, the correction in the BDE of phenol is of only 0.8 kJ/mol. Despite the consistent failure of computational chemistry in the determination of accurate homolytic O−H BDE, Brinck et al.[13] report, for a series of monosubstituted phenols, that the B3LYP method yields very good relative BDEs. Further, theoretical and experimental ΔBDEs, calculated as BDE(C_6H_4XOH) − BDE(C_6H_5OH), seldom differ by more than ∼5 kJ/mol, falling within the experimental uncertainty. In fact, for the series of isomers of dichlorophenol, available experimental relative BDEs are in good agreement with the B3LYP/DZVP values, cf. Table 1. Thus, absolute BDEs reported in Table 1 for dichlorophenols may be considered erroneous, but ΔBDEs may be interpreted as reliable data. Very recently, it was reported for a series of substituted phenols that it was possible to compute BDE values in good agreement with experiment.[14,30] This was achieved by employing on the DFT calculations, the energies of the open-shell radicals, a restricted-open (RO) procedure similar to the ROHF formalism. These ROB3LYP energies were computed at the B3LYP/DZVP geometries by means of the Gaussian 98[31] suite of programs since open-shell formalism is not available in GAMESS−UK package. First, we have simply calculated the energy of the radicals using the same DZVP basis set. The new set of results is also compiled in Table 1, but, from direct comparison of the computed and experimental BDE for phenol, this approach yields a value which still far from the experimental one. However, ΔBDEs agree perfectly with available experimental values. In a previous work, Chandra and Uchimaru[14] tested the BDE variation with basis set size and conclude that the computed and experimental values converge if the size of the basis set is increased. Thus, using the B3LYP/DZVP geometries, a new set of calculations was performed by using a significantly larger basis, namely, the 6-311++G(2df,2p).[32,33] A nice improvement is found for the O−H BDE of phenol, as the computed value, 366.8 kJ/mol, falls into the range of experimental derived absolute BDEs, 365−375 kJ/mol. Relative BDEs are close to the values computed at UB3LYP/DZVP and ROB3LYP/DZVP levels of theory. This finding gives further support to the conclusion that relative BDEs are good even if a low level of theory is used. Therefore, new BDEs may be derived by adding the experimental BDE for phenol and calculated ΔBDEs. Given that one cannot find significantly different O−H bond lengths between the various dichlorophenols, different ΔBDEs seem to be a consequence of the position of the chlorine atoms in the aromatic ring. The positive ΔBDE values reflect bond destabilization considering as reference the O−H bond in phenol. From the compilation of BDEs in ref 5 it can be observed that *ortho* substitution always destabilizes the O−H bond. This is due to repulsive steric interaction that is relieved upon O−H bond cleavage. Thus, analyzing data in Table 1 for the 2,n-dichlorophenols, it is concluded that when the second chlorine atom enters positions 4 or 6, ΔBDEs become smaller than when the second chlorine

TABLE 2: Computed and Experimental Standard Enthalpies of Formation at $T = 298.15$ K: Differences Δ of Computed Values to the Corresponding Experimental Numbers in Parentheses

	$\Delta_f H_m°(g)$ (kJ·mol^{-1})						
	BP86/DZVP		B3LYP/DZVP		B3LYP/6-311++G(2df,2p)[a]		exptl
compound		Δ		Δ		Δ	
phenol	−97.09	(−0.73)	−92.10	(+4.26)	−92.97	(+3.39)	−96.36 ± 0.59[b]
2,3-dichlorophenol	−149.6	(+2.0)	−148.2	(+3.4)	−149.7	(+1.9)	−151.6 ± 2.5[c]
2,4-dichlorophenol	−152.1	(+4.2)	−151.1	(+5.2)	−152.1	(+4.2)	−156.3 ± 1.9[c]
2,5-dichlorophenol	−157.7	(+0.7)	−156.7	(+1.7)	−157.9	(+0.5)	−158.4 ± 2.4[c]
2,6-dichlorophenol	−145.9	(+0.4)	−144.2	(+2.1)	−145.8	(+0.5)	−146.3 ± 1.5[c]
3,4-dichlorophenol	−143.3	(+7.0)	−143.5	(+6.8)	−143.3	(+7.0)	−150.3 ± 2.5[c]
3,5-dichlorophenol	−149.6	(−1.4)	−149.7	(−1.5)	−149.6	(−1.4)	−148.2 ± 1.5[c]

[a] B3LYP/6-311++G(2df,2p) energies computed at the optimized B3LYP/DZVP geometry. [b] Experimental values were taken from ref 35. [c] Experimental values were taken from ref 9.

TABLE 3: B3LYP Absolute Acidities $\Delta_{Acid}G°$ for Phenol and for the Several Dichlorophenol Isomers, Calculated from the Enthalpy $\Delta_{Acid}H°$ Associated with the Reaction $C_6H_3X_2OH \rightarrow C_6H_3X_2O^- + H^+$ and Ionization Energies IE Associated with the Reaction $C_6H_3X_2OH \rightarrow C_6H_3X_2OH^+ + e^-$

	$\Delta_{Acid}H°$ (kJ·mol^{-1})		$\Delta_{Acid}G°$ (kJ·mol^{-1})		IE (kJ·mol^{-1})	
	calcd	exptl	calcd	exptl	calcd	exptl
phenol	1455.1	1466.1 ± 2.5[a] 1460.9 ± 8.4[c]	1423.8	1432 ± 8.4[b]	799.3	820.9 ± 0.1[c]
2,3-dichlorophenol	1409.7		1377.1		825.1	
2,4-dichlorophenol	1408.3		1375.6		807.0	
2,5-dichlorophenol	1402.1		1369.6		821.3	
2,6-dichlorophenol	1401.2		1368.7		822.3	834.6 ± 1.9[d]
3,4-dichlorophenol	1402.6		1369.4		804.8	
3,5-dichlorophenol	1392.6	1399 ± 8.8[b]	1360.7	1370 ± 8.4[b]	838.7	

[a] Ultraviolet photoelectron spectroscopy experiments, ref 36. [b] Pulsed ion cyclotron resonance studies, ref 8. [c] From results compiled by Lias et al., refs 37 and 38. [d] Molecular photoelectron spectroscopy data, ref 10.

atom goes into positions 3 or 5. This is due to the fact that substituents at *para* and *ortho* positions can engage in resonance effects that are significantly diminished if the substituent goes to the *meta* position. In the other two isomers of dichlorophenol, the difference between ΔBDEs calculated for 3,4- and 3,5-dichlorophenols, ∼9−10 kJ/mol, gives a measure of the resonance effects which take place when chlorine is at the *para* position.

The gas-phase enthalpy of the six dichlorophenols, at $T = 298.15$ K, was calculated considering the computed enthalpies of the species in the following isodesmic reaction:

$$C_6H_3Cl_2OH + C_6H_6 \rightarrow C_6H_5OH + C_6H_4Cl_2 \qquad (2)$$

and the standard enthalpies of formation of benzene, phenol, and dichlorobenzene. This reaction was preferred since individual enthalpies of formation of the considered molecules are experimentally well established. Dichlorobenzene isomers instead of chlorobenzene were included in order to eliminate errors that might arise from neglecting Cl−Cl interaction effects. Then, using the $\Delta_f H_m°(g)$ of benzene, phenol, and of the appropriate dichlorobenze isomer, the $\Delta_f H_m°(g)$ of each of the six dichlorophenols was estimated. The estimated $\Delta_f H_m°(g)$ are listed in Table 2 and compared with the experimental data of Ribeiro da Silva and collaborators.[9] Average deviation between calculated and experimental values is in the 2.3−3.6 kJ/mol interval, being the lower value found for BP86/DZVP. Some of theoretical values fall within experimental uncertainty. It is worth to notice that the BP86/DZVP approach together with isodesmic reaction 1, yields a $\Delta_f H_m°(g)$ of phenol which differs by only 0.7 kJ/mol from the experimental value, an excellent result if it is compared with the value computed by using the B3LYP energies, either with the DZVP or 6-311++G(2df,2p) basis sets. Also, $\Delta_f H_m°(g)$ of phenol reported in Table 2 is also much closer to experiment when compared with the number given in the Gaussian-3 paper, $\Delta = 6.7$ kJ/mol.[34] In that work, the authors have applied the B3LYP hybrid method but a different reaction was used. In reaction 2, the lack of a term accounting for proximity effects between the OH group and the chlorine atom in *ortho*-substituted phenols does not seem to produce any significant error in the calculated values. This can be easily checked from the deviation between experimental and estimated $\Delta_f H_m°(g)$ for 2,3- and 3,4-dichlorophenols or between 2,5- and 3,5-dichlorophenols. This confirms that the energetic difference between the two 2,3-dichlorophenol conformers is not due to the possible formation of a hydrogen bond.

Absolute acidities and ionization energies were also calculated for the seven molecules considered in the present work, and the corresponding B3LYP values are listed in Table 3. Numbers from calculations with the DZVP basis set are not given since they are too low when compared with available experimental data. BP86 yield absolute acidities ∼10−15 kJ/mol consistently smaller than B3LYP/DZVP values and the latter are also lower than results computed with the largest basis set by ∼10 kJ/mol. This means that the good agreement between the BP86 and the experimental results found for $\Delta_f H_m°(g)$ of the dichlorophenols is not achieved in the case of acidities and ionization energies. The $\Delta_{acid}G°$ and $\Delta_{acid}H°$ values from B3LYP/6-311++G(2df,2p)//B3LYP/DZVP reported in Table 3 are in rather good agreement with available experimental data: the results for phenol and 3,5-dichlorophenol fall within experimental uncertainty. Considering the ionization energies of dichlorophenols, as far as we are concerned, only a single experimental value is available in the literature, namely that for the 2,6-isomer. The IE computed value is ∼10 kJ/mol below the experimental number and a similar behavior is found for phenol but, in this case, the difference is larger. This means

TABLE 4: Proton and Electron Affinities for Phenoxy and the Six Different Isomers of Dichlorophenoxy: The Auxiliary Experimental Data Taken from Reference 5

	PA ($kJ\cdot mol^{-1}$)			*EA* ($kJ\cdot mol^{-1}$)		
	estimated[a]	BP86[b]	B3LYP[b]	estimated[c]	BP86[d]	B3LYP[d]
phenoxy	862 (860.2 ± 1.3)[e]	858	850	218 (217.4 ± 0.6)[f]	212	198
2,3-dichlorophenxy	847	838	835	272	271	261
2,4-dichlorophenxy	856	851	846	265	263	255
2,5-dichlorophenxy	851	846	839	280	278	269
2,6-dichlorophenxy	841	833	830	272	270	262
3,4-dichlorophenxy	856	851	845	269	267	258
3,5-dichlorophenxy	833	830	824	289	288	277

[a] Estimated employing eq 3. [b] Calculated as $H[C_6H_3X_2O^\bullet] - H[C_6H_3X_2OH^+] + (5RT)/2$, eq 5. [c] Estimated emplying eq 4. [d] Calculated as $H[C_6H_3X_2O^\bullet] - H[C_6H_3X_2OH^-]$, eq 6. [e] Experimental values taken from ref 39. [f] Experimental values taken from ref 36.

that none of the DFT approaches used in the present work yields reliable IE values.

The quantities reported in Table 3, combined with estimated BDEs were used to calculate proton, PA, and electron affinities, EA, for the highly reactive radicals, using the following approximate equations:

$$\mathrm{BDE}[C_6H_3X_2OH] = \mathrm{PA}[C_6H_3X_2O^\bullet] + \mathrm{IE}[C_6H_3X_2OH] - \mathrm{IE}[H] \quad (3)$$

$$\mathrm{BDE}[C_6H_3X_2OH] = \mathrm{EA}[C_6H_3X_2O^\bullet] + \Delta_{\mathrm{acid}}H°[C_6H_3X_2OH] - \mathrm{IE}[H] \quad (4)$$

The estimated BDEs are obtained by addition of Δ*B*DEs calculated at the B3LYP/6-311+G(2df,2p)//B3LYP/DZVP level of theory (Table 1) to the experimental BDE of phenol. A consistent deviation in computed IEs led to the inclusion of a +20 kJ/mol correction prior to calculation of PAs. Also, in a similar way, the absolute acidities were corrected by +10kJ/mol before calculation of EAs following eq 4. Final PAs and EAs for $C_6H_3X_2O^\bullet$ radicals, calculated using auxiliary experimental data from ref 5, are listed in Table 4. In this table are compiled also the same quantities but calculated by direct application of equations:

$$\mathrm{PA}[C_6H_3X_2O^\bullet] = H[C_6H_3X_2O^\bullet] - H[C_6H_3X_2OH^+] + (5RT)/2 \quad (5)$$

$$\mathrm{EA}[C_6H_3X_2O^\bullet] = H[C_6H_3X_2O^\bullet] - H[C_6H_3X_2OH^-] \quad (6)$$

In eq 5, the term 5*RT*/2 stands for the enthalpy of H^+ species. The values herewith reported show a small difference between the proton affinities calculated for phenoxy and dichlorophenoxys. However, the same is not verified for electron affinities where larger differences are found. Concerning proton affinities, the application of eq 3 yields a set of results in which the PA for phenoxy radical is in good agreement with experiment. Thus, it should be expected that the correction introduced in the IE of phenol behave well in the case of the dichlorophenols. Further, PAs estimated with eq 3 may be used as a reference to test the performance of DFT approaches used in the present work. Using eq 5, if the BP86 and B3LYP results are compared, it is shown that the BP86 exchange-correlation functional yields results which are closer to the kinetic experimental value of Hoke et al.[39] in the case of phenoxy radical and also to the results estimated by employing eq 3. Turning our discussion to the calculated EAs, the 10 kJ/mol correction used seems adequate since the estimation by use of eq 4 yields an *EA* for phenol in close agreement with experiment. Again, comparison of the DFT methods with these results show that the BP86 results are closer to the experimental values. In fact, the BP86 calculated *EA* for phenol is 212 kJ/mol, which is only 5 kJ/mol lower than the experimental value, 217.4±0.6 kJ/mol, whereas the B3LYP/DZVP result is 198 kJ/mol, ∼20 kJ/mol lower than the experimental value.

Conclusions

The present computational study allowed the obtention of new and important thermodynamic parameters that characterize the gas-phase chemistry of dichlorophenols. Whenever possible, the computed values for standard enthalpies of formation, homolytic bond dissociation energies, acidities, ionization energies and proton and electron affinities were compared with experimental data. Globally, agreement between theory and experiment is quite good. However, care must be taken since it is shown that this agreement depends on the approach used. All approaches used seem to adequately yield good values of $\Delta_f H_m°(g)$ for phenol and for the six isomers of dichlorophenol. Differences are small but not negligible, i.e., the BP86/DZVP model is comparable to the B3LYP/6-311++G(2df,2p)//B3LYP/DZVP approach but both are better than B3LYP/DZVP. Interesting enough, close inspection of computed standard enthalpies of formation show a larger deviation for the 3,4-dichlorophenol isomer, which can suggest the re-determination of the experimental value. The computation of O−H bond dissociation energy shows that even with a restricted-open model, if a large basis set is not used, the absolute BDEs are not comparable with experimental values. However, despite the approach used, unrestricted or restricted-open formalism to compute energies of the radicals, small or large basis set, the relative BDEs are always comparable and may be compared with experimental results. The computation of absolute acidities show again that a large basis set is needed, being the results computed at the B3LYP level together with the larger basis set comparable with experimental numbers. However, we suggest a correction of 10 kJ/mol to the computed values. The three approaches considered in the present work fail also in the determination of ionization energies. A correction of 20 kJ/mol is suggested to the B3LYP/DZVP results. These two correction values are supported by the excellent agreement found for *PA*s and *EA*s of phenoxy and dichlorophenoxy radicals estimated by use of eqs 3 and 4. Finally, it is shown that the BP86/DZVP approach yields excellent PAs and EAs in good agreement with available experimental data and that the B3LYP/DZVP method consistently underestimates these quantities by ∼10−15 kJ/mol.

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Supporting Information Available: Table S1, geometric parameters for phenol and dichlorophenols. Tables S2–S13: total energies and thermal corrections to the energy for the neutral, radicals, cations, and anions of phenol and dichlorophenols. This material is available free of charge via the Internet at http://pubs.acs.org.

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