

Prediction of Hydroxyl Substitution Site(s) of Phenol, Monochlorophenols and 4-Chloronitrobenzene by Atomic Charge Distribution Calculations

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The predictions of the radical reaction sites for phenol, 2-, 3- and 4-chlorophenols (CPs) and 4-chloronitrobenzene (CNB) were studied by atomic charge distribution calculations. The atomic charge distributions on each atom of these molecules were obtained using the CHelpG and MK (Merz-Kollman/Singh) methods with the optimized structural parameters determined by DFT calculation at the level of BLYP/6-311++G(d,p). By comparing the experimentally obtained hydroxyl addition site(s) and the calculated atomic charges on carbon atoms of phenol and CPs, we found that hydroxyl substitution by oxidation reaction mainly occurred to the carbon(s) with high atomic charges. With these results, we were easily able to predict the position(s) of the ·OH reaction site(s) of phenol, CPs and CNB through atomic charge distribution calculations.

Key Words: Atomic charge distribution, CHelpG, MK, Hydroxyl radical reaction

Introduction

Chlorophenols (CPs) have widely been used as pesticides, germicides, and wood preservatives and have largely been used in the manufacturing processes of products using leather, fiber, and pulp paper.¹ CPs contain toxic elements and there have recently been reported several cases of CP contaminating soil and underground water.² Thus, a variety of treatment methods, such as reductive dechlorination,³ ultraviolet (UV) irradiation,^{4,5} ozone oxidation,⁶ and Fenton oxidation,⁷ have been studied in order to dispose of CPs contamination.

The research that has been most actively carried out is the reductive dechlorination of CPs³ using anaerobic microorganism. However, this method takes a long time for the CPs to decompose, and is not applicable in case of high concentration contamination. On the other hand, the UV treatment^{4,5} refers to a method that dechlorinates CPs with a UV light and has the ability to dispose of high concentrated CPs at a comparatively low price, compared to other treatments. However, this method has limitations. When it is used in real circumstances where suspended solids are present in the water, the UV light irradiates poorly and the treatment efficiency is drastically decreased. In the meantime, there have been several studies being performed on the oxidation process using catalysts produced by ozone oxidation⁶ and Fenton oxidation.⁷ These methods pose as an effective treatment technology to complement the weaknesses of the UV method. This treatment removes chlorines by reacting CPs with ·OHs generated by ozone or Fenton reaction. These ozone and Fenton oxidation methods have the merits of short processing time and the possibility of application even in a turbid target solution.

Thus, to remove the harmful chlorinated organic compounds efficiently, including CPs which are the by-products of industrial processes, a variety of experimental^{3,7} and theoretical^{8,16} studies are being carried out. To evaluate the photo degradation characteristics of chlorinated organic compounds, several

studies using the density functional theory (DFT) method have been reported.⁸⁻¹¹ However, studies that analyze the radical reaction of chlorinated organic compounds including phenol by using the DFT method have not been reported yet. Until recently, there have merely been studies predicting the reaction of formaldehyde with alkaline phenol among phenol compounds based on the calculation of the atomic charges.¹²⁻¹⁴ Thus, to understand the ·OH substitution reaction of phenols, CPs and CNB at the molecular level, it is important to predict what products are made in radical reaction by Fenton or ozone. A deep comprehension of the ·OH reaction mechanism of these harmful chlorinated organic compounds is also important. In addition, establishing such an accurate and easy technique to predict the products generated after the radical reaction helps a highly reliable prediction of the decomposition possibility by the radical reaction. Also, the reacting site(s) and products made during the decomposition of many kinds of chlorinated organic compounds are also easily and rapidly predicted. The method mentioned above is expected to make a great contribution to induce reliable optimal factors in the design of means for decomposing and disposing pollutants such as radicals. Therefore, we investigated the position(s) of the radical reaction site(s) on phenol, CPs and CNB using atomic charge distribution calculations.

Calculation

In this study, to predict the decomposition products of phenol, CPs and CNB using ·OH radical, the plane figures of all the molecules in this study were drawn using the ChemDraw program.¹⁷ In addition, the three-dimensional features of these figures were confirmed with the Chem3D program using the CS Chem3D program package.¹⁷ With the Chem3D program, the Gaussian input files were created to run the Gaussian-98 program.¹⁸

We also carried out density functional theory calculations

with Becke's exchange functional (BLYP)^{19,20} to obtain the optimized geometrical parameters of the molecules at the level of BLYP/6-311++G(d,p). The ·OH attacks the atom on benzene ring of each molecule which has strongly electrophile. Therefore, the atomic charge distributions were calculated for the carbon of the benzene ring using the CHelpG²¹ and MK (Merz-Kollman/ Singh)^{22,23} methods with these optimized molecular structures.

Results and Discussion

Hydroxyl group substitution by oxidation. Under the ozone oxidation reaction,²⁴ the ·OH is generated by the underwater ozone decomposition. However, in an oxidation reaction with the presence of a catalyst such as the Fenton reaction,²⁵ the radical is produced from hydrogen peroxide (H₂O₂) in the coexistence of a catalyst (Fe²⁺ and etc.). The ·OH generated in this way attacks the carbon with a benzene ring, creating a reactive product in the form of a hydroxyl compound or making a product with a benzene ring open. These reactive products are attacked again by ·OH or other kinds of radicals and create the final products that have been further oxidated.²⁶⁻²⁸

Literary research on radical decomposition. Table 1 shows the physical and chemical characteristics of phenol, CPs, and CNB, which are target substances in this study. As seen in Table 1, all the target substances show high relative boiling points, so it seems that the volatilization possibility of these target substances in the ozone and Fenton oxidation test under the open system, which has been reported in the literature,^{6-7,15-16,26-28} is low. In addition, as the octanol/water partition coefficients of CPs and CNB reach high peaks, they have been the focus of important research subjects because

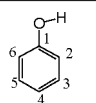
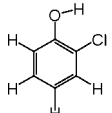
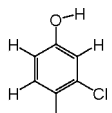
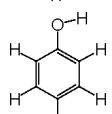
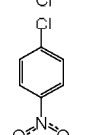
those substances may end up highly concentrated in the biological organisms through the food chain.

Table 2 shows the oxidation products reported in the experiments using target substances. As shown in Table 2, all the oxidation products reported in the literature^{26-28,31-32} indicate the compound structure in which a hydroxyl group (-OH) has been substituted from the original target substance.

Atomic charge calculation. Due to the electron deficiency of a benzene ring, the decomposition of phenol, CPs, and CNB using OH radical oxidation begins with the strong electrophilic ·OH's attack on the carbon(s) of benzene ring. Thus, it is best to review the electron density of the carbon found in a benzene ring in analyzing the oxidation reaction. In other words, the higher the value of negative charge of the carbon forming the benzene rings of phenol, CPs, and CNB reach high points, the easier the attack by the electrophilic ·OH is made. Accordingly, in this study, concerning the molecular structure obtained from the BLYP/6-311++G(d,p) optimization, the atomic charge distribution of each carbon atom using CHelpG and MK charges method was calculated and the results are shown in Table 3.

Looking at the values of CHelpG and MK charge in the Table 3, we found that carbon 6 has the highest negative electric charge of -0.272 and -0.345, respectively, followed by carbon 2 with -0.200 and -0.261 and carbon 4 with -0.157 and -0.179. In the experimental results, the catechol (CT) also generated after the -OH group was substituted in carbon 6 or carbon 2 and the hydroquinone (HQ) generated after the -OH group was substituted in the catechol (CT) and carbon 4 are considered as products.³³⁻³⁶ In most cases,³⁴⁻³⁶ the produced quantity of CT was higher than that of HQ. This shows the identical tendency that the negative charges of carbon 6 and

Table 1. Chemical properties of considered CPs.^{29,30,a}

Structure	Name	w _m	b.p./°C	LogK _{ow}
	phenol	94.11	182	1.46
	2-chlorophenol	128.55	176	2.15
	3-chlorophenol	128.55	214	2.52
	4-chlorophenol	128.55	220	2.39
	4-chloronitrobenzene	157.55	242	2.39

^aAbbreviations used: w_m, molecular weight; b.p., boiling point; K_{ow}, octanol-water partition coefficient.

Table 2. Literature summary of ozone and Fenton oxidation of CPs.

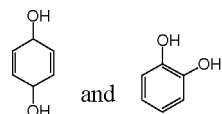
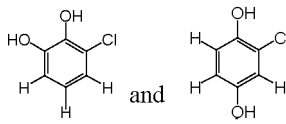
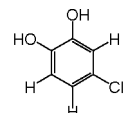
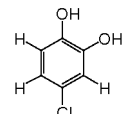
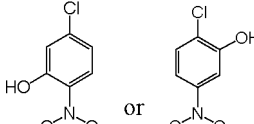
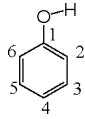
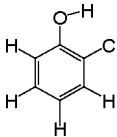
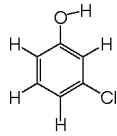
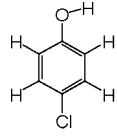
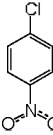
Target	Oxidation products	Reference
phenol		33-35
2-chlorophenol		26, 37, 38
3-chlorophenol		40
4-chlorophenol		28, 39
4-chloronitrobenzene		32

Table 3. Comparison of atomic charges of radical reaction products of phenol, monochlorophenols and 4-chloronitrobenzene.

Target Substance	Position	Charges	
		MK	CHelpG
	1	0.472	0.407
	2	-0.261	-0.200
	3	-0.083	-0.049
	4	-0.179	-0.157
	5	-0.049	-0.016
	6	-0.345	-0.272
	1	0.500	0.425
	2	-0.158	-0.079
	3	-0.022	-0.040
	4	-0.222	-0.166
	5	-0.057	-0.026
	6	-0.321	-0.261
	1	0.440	0.411
	2	-0.295	-0.294
	3	0.042	0.161
	4	-0.101	-0.134
	5	-0.157	-0.091
	6	-0.282	-0.205
	1	0.480	0.417
	2	-0.416	-0.323
	3	0.028	0.018
	4	-0.023	0.025
	5	-0.030	-0.039
	6	-0.304	-0.225
	1	-0.034	0.065
	2	0.038	-0.021
	3	-0.273	-0.130
	4	0.206	0.067
	5	-0.273	-0.130
	6	0.038	-0.021

carbon 2 reach higher values than those of carbon 4 as a result of calculating charges.

As a result of the calculation of CHelpG and MK, the atomic charge of 2-chlorophenol which chlorine was substituted in the *ortho* position of phenol, reached highest values with -0.261 and -0.321, respectively, at the carbon 6 and followed by -0.166 and -0.222 at the carbon 4. These results of CHelpG and MK accurately correspond with those of products generated by the substitution of OH group in carbon 6 and carbon 4 in the previous studies.^{37,38}

The CHelpG and MK charges of 4-chlorophenol generated by the substitution of chlorine in the *para* position of phenol, the carbon 2 reached very high negative values with -0.323 and -0.416, respectively, and with -0.225 and -0.304, respectively, at the carbon 6. Meanwhile, carbon 3 has positive charges with 0.018 and 0.028 and carbon 5 has very small negative charges with -0.039 and -0.030. As a result, based on the position of OH of phenol, it seems that carbons 2 and 6 located in the *ortho* positions are easily attacked by ·OH, whereas carbons 3 and 5 in the *meta* positions rarely caused

·OH to be substituted due to a positive charge or a small negative one. These results showed the correspondence with those of the previous experimental report³⁹ that only 4-chlorocatechol created by the substitution of OH is generated at the *ortho* position and 4-chloro-1,3-dihydroxybenzene is not produced.

The charge of 3-chlorophenol (3-CP) generated by the substitution of chlorine at the *meta* position reached very high values at the carbon 2 with -0.294 and -0.295, respectively, and at the carbon 6 with -0.205 and -0.282, respectively, in CHelpG and MK. The carbon 4 reached the second highest negative value with -0.134 in CHelpG but it showed a value of -0.101, which was lower than -0.157 of the carbon 5 in MK. In the experimental report,⁴⁰ the initial product percentage of 3-chlorocatechol generated by the substitution of OH at the carbon 2 position reached 8%. 4-chlorocatechol generated in the same way at the carbon 6 position reached 15%, and that at the carbon 4 reached 3%. Looking at these results, we found that the CHelpG charge is more appropriate than the MK charge in predicting the OH substitution by radical oxidation reaction on 3-CP.

In case of the CNB, the values of CHelpG and MK charges at the carbons 3 and 5 which are symmetrically located, indicated as -0.130 and -0.273, respectively. Meanwhile, the carbons found in other positions indicated positive charges or negative charges of very small value. In the literature,³² it was reported that 5-chloro-2-nitrophenol (5-Cl-2-NP) and 2-chloro-5-nitrophenol (2-Cl-5-NP) are all generated. However, considering the results of charge calculation obtained in this study, it was predicted that the products generated by hydroxyl substitution reaction using ·OH reaction will be 5-Cl-2-NP and the amount of produced 2-Cl-5-NP will be small or almost none.

Conclusions

The following results were obtained by comparing the atomic charge values calculated by using the CHelpG and MK methods with optimized structure of BLYP/6-311++G(d,p) with the oxidation products of phenol, three kinds of CPs, and CNB reported in the literatures.

1. Based on the comparison of the experimental results, it has been identified that the OH group originating from ·OH was substituted at the position of the carbon whose negative charge distribution among the benzene ring of the target compound was highly dense.
2. In the case of 3-CP, the CHelpG charge value was more efficiently used than MK charge value in predicting radical oxidation products.
3. In the case of CNB, judging from the charge calculation, it is expected that 5-Cl-2-NP is more advantageous than 2-Cl-5-NP as OH substitute product by ·OH reaction.

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