

Destruction of 2-Chlorophenol from Wastewater and Investigation of By-products by Ozonation

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This study investigates the ozonation kinetics of 2-chlorophenol in wastewater under acidic condition. Intermediates and by-products generated during the process were rigorously identified and quantified. The major by-products are four carboxylic acids: tartaric acid, oxalic acid, maleic acid, and hydroxymalonic acid. The generation of these organic acids is in agreement with theoretical predictions. But hydroxylated compounds are more favorable to produce than their corresponding non-hydroxylated ones. Based on the information concerning the generation of organic acids and other aromatic intermediates, the complete reaction pathways toward mineralization can be proposed and mathematically modeled. The fitted second-order rate constants are in the same order of magnitude with the results from other studies. Using these oxidation pathways and the corresponding kinetic model, by-products generated in ozonation process can be predicted. This can help in optimizing the design and operation of any subsequent treatment processes.

Keywords : 2-Chlorophenol, Ozonation, Intermediates, Kinetic model, Mechanism.

Introduction

The contamination of chlorophenols in many lakes and rivers has resulted in serious environmental problems for decades.^{1,2} These compounds are highly toxic and human carcinogenic even at low concentrations. Most of these compounds are biologically recalcitrant. Therefore, when a fast and effective removal method is considered, the advanced oxidation process (AOP) has the highest potential. Among various AOP processes, the ozonation is one of the most economical one since the operation is easy and no other chemical except ozone is needed. Ozone gas can be readily generated through an ozone generator by passing an electrical charge to oxygen or air. Ozone has a standard reduction potential under an acidic condition of about 2.1 volts, and has a great water solubility; therefore, it can react extremely fast with soluble organics and oxidize them to smaller or less toxic molecules. Recent researches have shown that the ozonation process is effective in removing a wide variety of organic contaminants.^{3,4}

In the past, researchers focused only on measuring the disappearance of the parent compound during ozonation.^{5,6} More recently, they have focused on understanding the intermediates and by-products generated in the process.^{7,8} This information is crucial since sometimes by-products could be more toxic than the parent compounds.⁹ Therefore, it is important to understand the oxidation mechanisms and pathways so that the ozonation process can be better controlled to generate favorable and less toxic by-products. In addition, any subsequent treatment processes can be greatly improved with this information. Although oxidation products and pathways of chlorophenols in ozonation have been speculated,

little attempt has been made to confirm the products and model the pathways. In this study, all the possible by-products during the course of ozonation were rigorously identified using chemical derivatization method. In addition, the concentration distributions of those compounds identified were monitored as a function of time. A possible oxidation pathway was proposed based on this information. Finally, a mathematical model consisting of various consecutive and parallel reactions was developed and fitted to the experimental results.

Experimental Section

Figure 1 shows the experimental set-up. The ozone generator is from Welsbach Co. (Philadelphia, PA). A pressurized air tank from Keen Co. (Wilmington, DE) was connected to

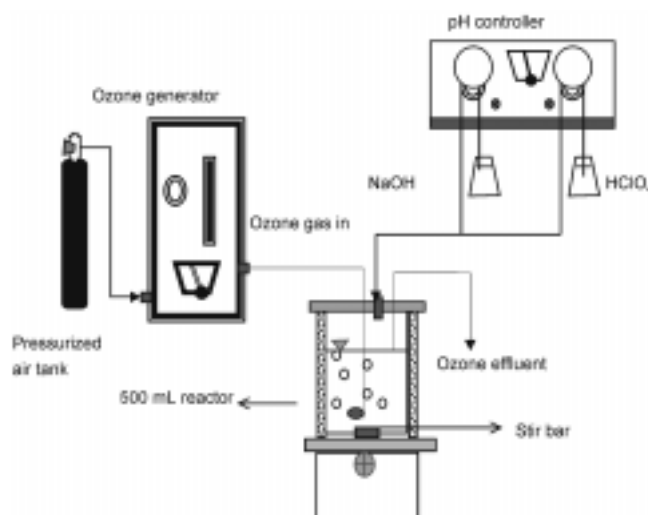


Figure 1. Experimental set-up of the aqueous ozonation system.

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the inlet of the generator to provide oxygen. The generator was run for at least 60 min until ozone concentration reached its steady-state level before experiment. The 2-chlorophenol (2-CP) solution in the experiment had a concentration of 100 mg/L with a pH of 3. The total volume of 2-CP solution used in each experiment is 500 mL. Ozone gas concentrations in and out of the column were monitored by the iodometric method with potassium iodide as absorbing solution. Immediately after ozone absorption, the KI solution was acidified to liberate iodine before titration with sodium thiosulfate. Each experiment was performed at a semi-batch condition mixing with a magnetic stirring bar. The ozone gas applied had a concentration of 6.3 mg- O_3/L_g and a flow rate of 100 mL/min throughout the experiment.

In qualitative experiment to confirm identity of oxidation by-products, each sample with a volume of 100 mL was taken at 30, 60, and 90 minutes, respectively. These samples were concentrated 50 times using a rotary evaporator (Brinkmann Co., Westbury, NY) to ensure a high response in chemical identification. And then, the concentrated samples were derivatized using the silylation method. Each sample was first evaporated to dryness in a vial under a gentle stream of nitrogen at a temperature of 40 °C. This was done on the Reacti-VapTM system (Pierce Co., Rockford, IL). After all the moisture was removed, 100 μ L of silylation reagent (BSTFA + 1% TMCS, Pierce Co.) plus 2 mL of pyridine was added for derivatization reaction under 70 °C for 60 minutes. After reaction, the sample was cooled down to room temperature and then analyzed with GC/MS.

The intermediates generated during the ozonation were analyzed by gas chromatography-mass spectrometric system equipped with a HP5971 mass selective detector and DB-5 capillary column (30 m \times 0.25 mm i.d. \times 0.33 μ m, film thickness). Prior to injection, the sample was derivatized using silylation method. In silylation, the sample (5 mL) was first evaporated to dryness, and then 100 μ L silylation reagent (BSTFA + 1% TMCA) and 1 mL pyridine were added for reaction. The reaction was carried out at 65 °C for 60 min. The injection temperature was 250 °C and the column temperature, initially 70 °C was held constant for 3 min., and then increased to 280 °C at temperature rate of 10 °C/min over 24 min run time. The GC/MS interface line was maintained at 300 °C. The mass selective detector was scanned at rate of 1.2 seconds per decade from mass 50 to 550. The mass spectra were produced using the standard electron ionization (70 eV) in electron impact (EI) mode.

In another series of quantitative experiment, to quantify the concentration of oxidation by-products, samples of 10 mL were withdrawn at pre-determined reaction times and immediately mixed with 0.5 mL of 10^{-2} M $Na_2S_2O_3$ to quench any reactions with residual ozone in the sample. A HPLC system (Hewlett-Packard, series 1100) with a reversed phase C-18 VydacTM column (50 mm \times 0.5 mm; Vydac Co., Hesperia, CA) was used to analyze 2-CP and other aromatic intermediates. The same system with a SupelcogelTM ion-exclusion chromatographic column (C-610H, 30 cm \times 7.8 mm; Supelco Co., Bellefonte, PA) was used to analyze car-

boxylic acids. The eluent to separate 2-CP and other aromatic intermediates was a mixture of acetonitrile and buffer solution (H_3PO_4/NaH_2PO_4 ; pH = 3.00), and to separate carboxylic acids was 0.1% H_3PO_4 . To determine the chloride ion concentration in each sample, a DionexTM ion chromatographic system with a conductivity detector was used. The eluent was a mixture of 80% H_2O , 10% acetonitrile, and 10% of 191 mM NaOH: the flow rate was 1 mL/min and the injection loop was 50 μ L in volume. Chloride ion concentration was also monitored in situ by an Orion (Model 96-17B) specific combination electrode.

Results and Discussion

The silylation technique for GC/MS analysis have been successful in identifying the reaction products of 2-CP by hydroxyl radicals generated with ozonation. The reaction products generated from the oxidation of 2-CP by ozonation was analyzed by GC/MS with or without silylation. Without silylation, only parent compound peak, 2-CP, and no intermediate peaks were observed. However, with silylation intermediate peaks were observed. Figure 2 shows the typical ion chromatogram of derivatized oxidation products of 2-CP after 60 minutes of ozonation. Eight peaks are observed, and the mass spectra of four main peaks 2, 6, 7, 8 are given, representatively in Figure 3. The first two peaks, 1 and 2, with retention times at 11.8 and 12.3 minutes are the under-

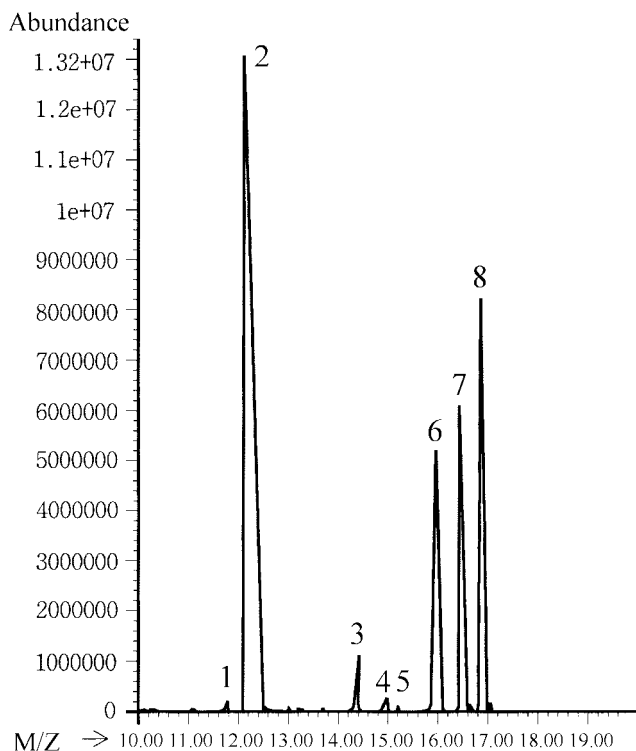


Figure 2. Total ion chromatogram by the electron impact GC/MS analysis of the oxidation products of 2-chlorophenol with silylation. Experimental condition: $[O_3] = 6.3$ mg/Lg; flow rate 100 mL/min, $[2\text{-chlorophenol}] = 10^{-3}$ M, $I = 1.3 \times 10^{-2}$ M $NaNO_3$, pH = 3.0.

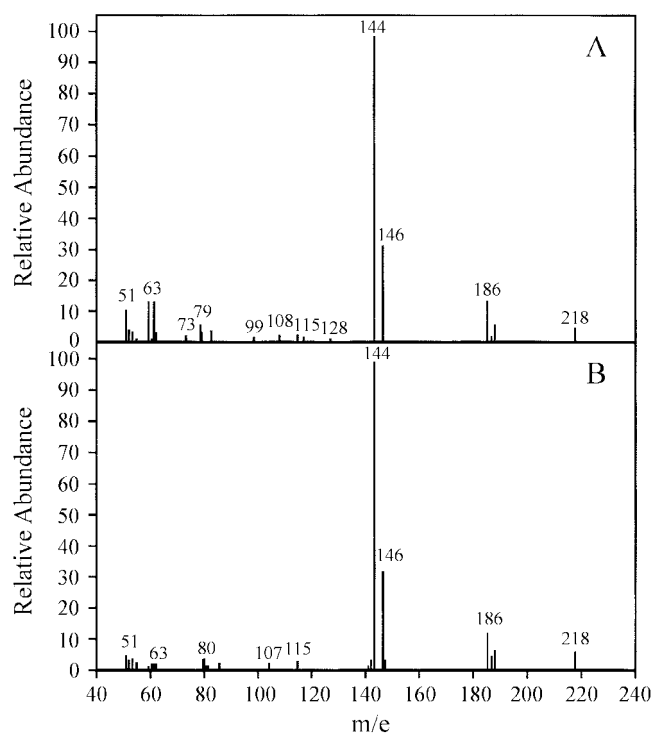


Figure 3. Mass spectra of intermediate A (3-chlorocatechol) and B (chlorohydroquinone) ozonation of 2-chlorophenol.

ivatized and derivatized parent compounds, 2-chlorophenol, respectively. The next group of peaks, 3, 4, and 5 with retention times 14.3, 14.9, and 15.6 minutes, corresponds to the incompletely derivatized chlorodihydroxybenzene products, which shows that only one of two hydroxyl groups of chlorohydroxybenzenes has been converted to the silyl group by the derivatized silylation reagent.

The major product peak, 6, 7, and 8, with retention times, 16.0, 16.5, and 16.9 minutes, are the completely derivatized chlorodihydroxybenzene products, whose mass spectra show the same molecular ion peak, M^+ , at m/e 218 and the same base peak, $M-[Si-(CH_3)_3]^+$ at m/e 144 as the derivatized chlorodihydroxybenzene standard. The difference in m/e values between the M^+ and $M-[Si-(CH_3)_3]^+$ peaks is due to the loss of silyl radicals, which implies the presence of OH radicals. The mass spectra of these two peaks of derivatized intermediates A and B with retention time 14.9(16.5) and 15.6(16.9) min. show a near 3 : 1 ratio of isotope ion peaks at m/e 144 and 146, indicating the presence of a chlorine atom, which also shows isotope ion peaks at m/e 35 and 37. A slight difference in other fragment ion peaks is observed between peak A and B, which implies that these two intermediates have similar chemical structures. Chlorodihydroxybenzenes are suggested as the peaks A and B, which also have two hydroxyl ions and one chlorine atom. Essentially, these three isomeric products show mass spectra similar to each other, except for slight differences in the fragment ion peaks such as m/e 51, 63, 79, 108, 115, 186, and 218. For example, the relative abundances of peaks 6 and 7 at m/e 51 and 79 are larger than peak 8 and the relative abundance of peak 7 at m/e 108 is larger than peaks 6 and 8. With a

Table 1. GC/MS analysis of qualitative experiment result

Q ^a	Authentic chemical formula ^b
90%	HOCH ₂ COOH (Glycolic acid)
64%	(COOH) ₂ (Oxalic acid)
95%	HOCH ₂ COCH ₂ OH (N/A)
91%	HOCH ₂ CH(OH)CH ₂ OH (Glycerol)
83%	COOHCOCH(CH ₃) ₂ (3-Methyl-2-oxobutyric acid)
95%	HOOC(CH ₂) ₂ COOH (Succinic acid)
91%	HOOCCH=CHCOOH (Maleic acid)
56%	HOOCCH(CH ₃)COOH (Methylmalonic acid)
91%	HOOCCHOHCOOH (Hydroxymalonic acid)
72%	HOOC(CHOH) ₂ COOH (Tartaric acid)
91%	HOOCCH ₂ CHOHCOOH (Malic acid)

^aQ is the match quality when compared with the spectrum in the NIST database; ^bThe authentic structure is obtained by substituting TMS group (*i.e.*, Si(CH₃)₃) with hydrogen atom from the silylated compounds identified by GC/MS.

comparison of both retention times and mass spectra of these three peaks 6, 7, and 8 are identified as the derivatized 3-chlorocatechol, 4-chlororesorcinol and chlorohydroquinone, at m/e 144, respectively.

Table 1 shows the results of qualitative experiment by the GC/MS. Comparing the mass spectra of the silylated compounds and the spectra in the database (NIST Mass Spectral Library, 1998), one can confirm their identities. It is seen from Table 1 that most identified compounds have a high match quality. Since the silylation reaction replaces the hydrogen on the carboxylic group with a trimethyl silyl (TMS) group, the TMS must be substituted with hydrogen atom to become the compound prior to silylation (*i.e.*, the authentic carboxylic acid). Therefore, the authentic organic acids produced in ozonation process can be reduced (see Table 1). These organic acids have two to four carbons. Most of these acids are common. However, a few of them are very specific and sometimes not commercially available. The standard solutions of these identified organic acids were prepared and analyzed using HPLC. Therefore, the relation between retention time and identity of these acids in HPLC system can be established.

Figure 4 shows the chromatograms of samples analyzed prior to ozonation (Figure 4(a)) and after 90 minutes of ozonation (Figure 4(b)). It is evident that several high peaks which are not seen prior to ozonation appeared in Figure 4(b). These peaks were identified by comparing the retention time with those of standards established previously. The identities of these acids are listed in the figure.

Figure 5 shows the results of carboxylic acid concentrations as a function of ozonation time. The results indicate that the identified organic acids with unsaturated carbon-carbon bonds (*i.e.*, muconic acid and maleic acid) have very low concentrations compared to the compounds with saturated carbon-carbon bonds (*i.e.*, tartaric acid, oxalic acid, glycolic acid). This is mainly due to high reactivity of those unsaturated carbons, which normally have much larger rate constants.⁵ It is evident from Figure 5 that the chloride ion concentration increases almost proportionally to 2-CP de-

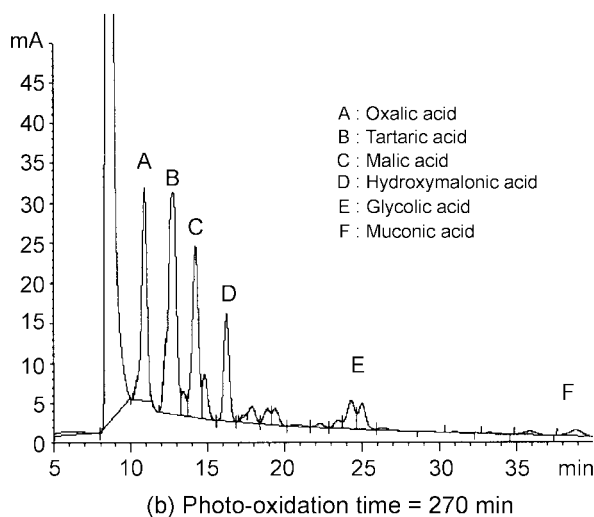
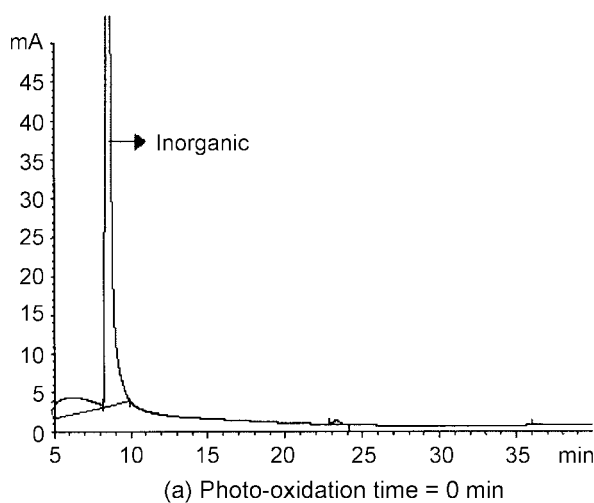


Figure 4. HPLC chromatogram of carboxylic acid analysis using the ion-exclusion column. (a) Initial sample before ozonation starts (ozonation time = 0 minute). The only peak is the inorganics which cannot be retained in the acid column. (b) Sample taken after 90 minutes of ozonation. The identity of each peak is listed.

gradation. In addition, low concentrations of both 3-chlorocatechol (3-CCA) and chlorocatechol (CCA) were detected. From the results, it is possible that the dechlorination occurs either as a first step immediately after 2-CP removal or as a second step after 3-chlorocatechol and chlorocatechol removal. This also implies that chloride does not exist in the compounds after the aromatic ring cleavages. Therefore, the formation of hydroxylated hydroquinone (HHQ) probably proceeds before ring cleavage.

Four reaction products, catechol, 3-chlorocatechol, 4-chlororesorcinol, and chlorohydroquinone are observed from the oxidation of 2-CP by ozonation. A reaction scheme used to describe the formation of reaction products is given in Scheme 1.

The first product is due to the attack of hydroxyl radical at the position of chlorine located the ortho position.¹⁰ The other three compounds are products generated from the hydroxylation of 2-CP at the position of hydrogen located at ortho, meta, and para sites, respectively. With a 84.7%

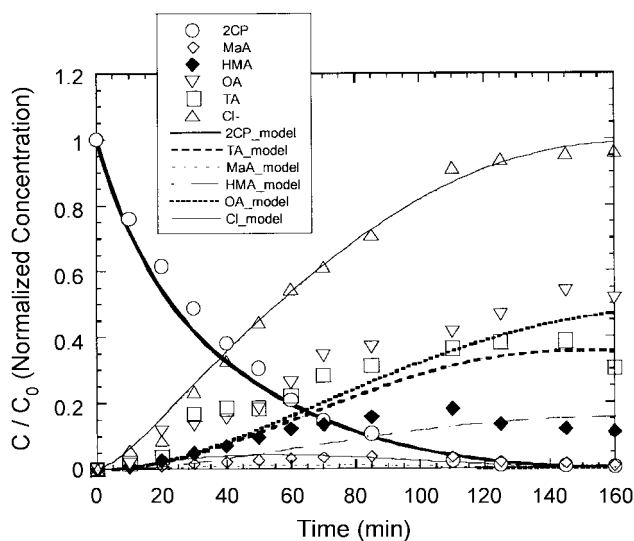
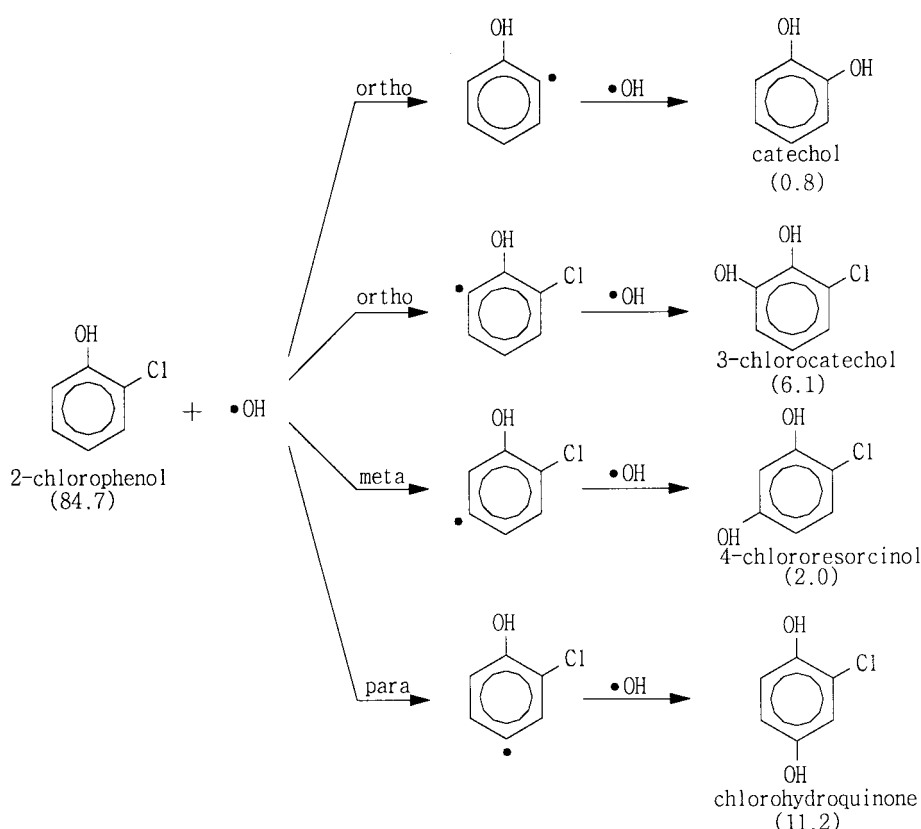


Figure 5. Results of quantification of various oxidation by-products in ozonation of 2-chlorophenol. Marked symbols are experimental results, and lines are results from the kinetic modeling. 2CP = 2-Chlorophenol; MaA = Maleic Acid; HMA = Hydroxymalonic acid; OA = Oxalic Acid; TA = Tartaric Acid; Cl⁻ = Chloride.

conversion of 2-CP, the % product yield of catechol is 0.8, the % yield of 3-chlorocatechol is 6.1, the % yield of 4-chlororesorcinol is 2.0, and the product yield of chlorohydroquinone is 11.2%. Apparently, the ortho and para hydroxylated products (3-chlororesorcinol and chlorohydroquinone) are the main reaction product, whereas the meta hydroxylated product (3-chlororesorcinol) and dechlorinated product (catechol) are less important products (Figure 6).

That the dechlorination pathway is less important can be explained by the electron-withdrawing properties of chlorine group. The formation of a lesser amount of 4-chlororesorcinol can be explained by the electron donating properties of the hydroxyl group located on the ring of monochlorophenols. The hydroxyl groups are stronger ortho and para directing groups,¹¹ which are able to stabilize the intermediate radicals at the ortho and para position rather than the meta position. As a result, the generation of ortho and para products will be higher than that of the meta product.

Further oxidation of hydroxylated hydroquinone leads to muconic acid (MuA), which has been identified as a precursor of various short-chain carboxylic acids.^{12,13} Four major short-chain carboxylic acids found are tartaric acid (TA), oxalic acid (OA), maleic acid (MaA) and glycolic acid (GA). Tartaric acid along with other two acids, malic acid and succinic acid (see Table 1), are possibly formed from either oxidation of muconic acid or maleic acid. Since maleic and succinic acid concentrations are insignificant compared to tartaric acid, it can be concluded that the by-products with more hydroxylated groups are more preferable during oxidation. The majority of oxalic acid can generate at the same time as muconic and maleic acids are oxidized to tartaric acid. Some oxalic acid can be generated from the oxidation of tartaric as well; however, this is probably not an important



Scheme 1. The initial reaction products observed from 2-chlorophenol.

one since tartaric acid has a much smaller second-order rate constant with respect to ozone compared to muconic and maleic acids. The pathway for the generation of glycolic acid is similar to that of acetic acid from muconic acid.¹⁴ According to this pathway, muconic acid is first oxidized to malonic acid, and then to acetic acid. It is seen from Table 1 that hydroxymalonic acid (*HMA*) appears instead of malonic acid, and the product is glycolic acid instead of acetic acid. These observations further enforce the conclusion that hydroxylated products are more preferable. All those carboxylic acids with saturated carbon-carbon bonds (*i.e.*, tartaric, oxalic, and hydroxymalonic acids) are stable compounds and remain as major ozonation by-products.

The above oxidation pathways can be described in Figure 6. To kinetic model this system, several assumptions were made. First, oxidation reactions between ozone and any organic intermediates or by-products were assumed to be second-order with respect to ozone and the organic, respectively.⁵ Second, the two-film theory² was employed in describing the gas-liquid mass transfer process. Since there are multiple consecutive and parallel reactions involved in this pathway, a system of kinetic equations can be derived:

$$\frac{d[2CP]}{dt} = -(k_1 + k_2)[2CP][O_3] \quad (1)$$

$$\frac{d[3CCA]}{dt} = k_1[2CP][O_3] - k_3[3CCA][O_3] \quad (2)$$

$$\frac{d[CHQ]}{dt} = k_2[2CP][O_3] - k_4[CHQ][O_3] \quad (3)$$

$$\frac{d[HHQ]}{dt} = k_3[3CCA][O_3] - k_4[CHQ][O_3] - k_5[HHQ][O_3] \quad (4)$$

$$\frac{d[MuA]}{dt} = k_5[HHQ][O_3] - (k_6 + k_7 + k_8 + k_9)[MuA][O_3] \quad (5)$$

$$\frac{d[TA]}{dt} = k_6[MuA][O_3] - k_{10}[TA][O_3] + k_{13}[MaA][O_3] \quad (6)$$

$$\frac{d[MaA]}{dt} = k_8[MuA][O_3] - k_{11}[MaA][O_3] - k_{13}[MaA][O_3] \quad (7)$$

$$\frac{d[HMA]}{dt} = k_9[MuA][O_3] - k_{12}[HMA][O_3] \quad (8)$$

$$\frac{d[OA]}{dt} = k_7[MuA][O_3] + k_{10}[TA][O_3] + k_{11}[MaA][O_3] - k_{15}[OA][O_3] \quad (9)$$

$$\frac{d[GA]}{dt} = k_{12}[HMA][O_3] - k_{14}[GA][O_3] \quad (10)$$

$$\frac{d[CO_2]}{dt} = k_{15}[OA][O_3] + k_{14}[GA][O_3] \quad (11)$$

$$\frac{d[Cl^-]}{dt} = k_3[3CCA][O_3] + k_4[CHQ][O_3] \quad (12)$$

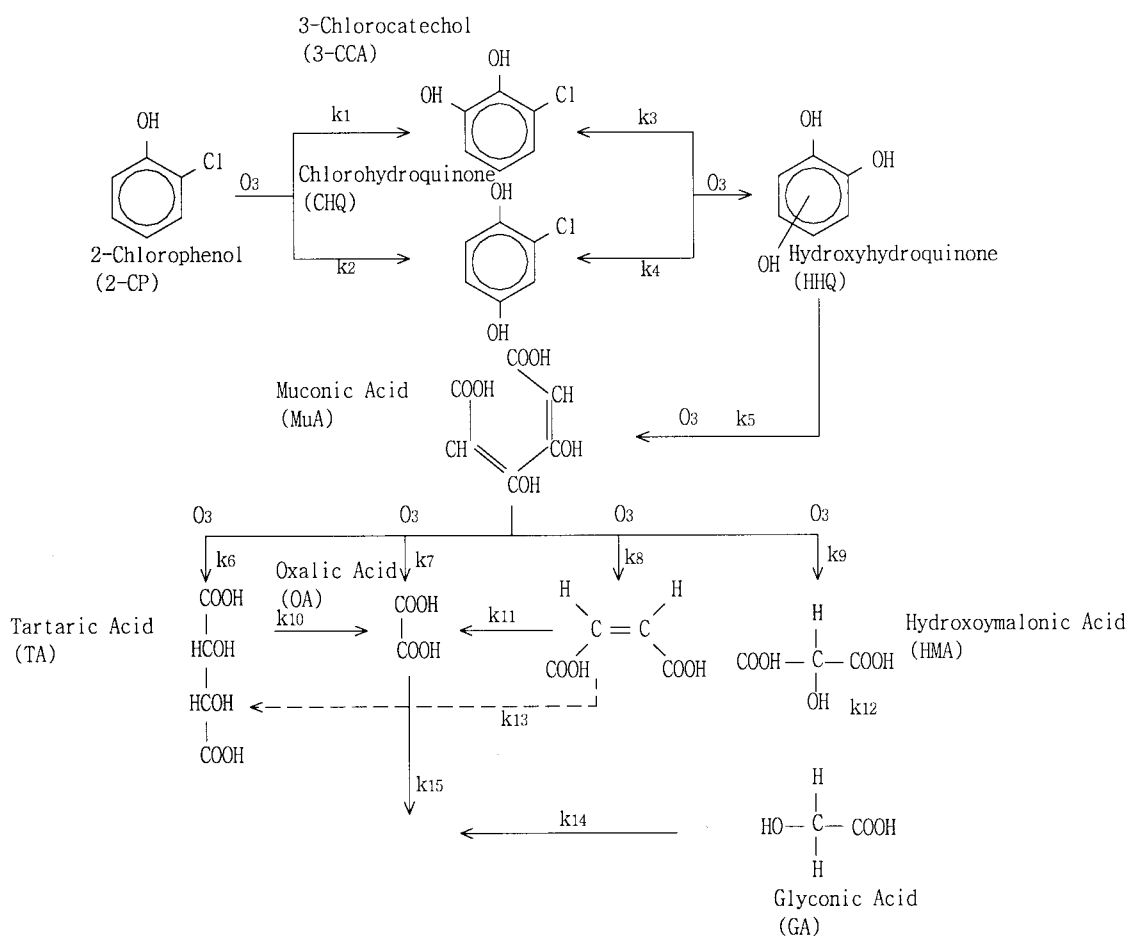


Figure 6. Proposed reaction pathways of ozonation of 2-chlorophenol under acidic condition.

$$\begin{aligned} \frac{d[O_3]}{dt} = & K_{La}(O_3^* - O_3) - (k_1 + k_2)[2CP][O_3] \\ & - k_3[3CCA][O_3] - k_4[CHQ][O_3] \\ & - k_5[HHQ][O_3] - (k_6 + k_7 + k_8 + k_9)[MuA][O_3] \\ & - k_{10}[TA][O_3] - k_{11}[MaA][O_3] - k_{12}[HMA][O_3] \\ & - k_{13}[GA][O_3] - k_{14}[OA][O_3] - k_{15}[GA][O_3] \end{aligned} \quad (13)$$

where k_i is the second-order reaction rate constant ($M^{-1}sec^{-1}$) between ozone and each organic compound in Figure 6, K_{La} is the volumetric mass transfer coefficient (sec^{-1}), O_3^* is the saturated ozone concentration at the gas-liquid interface, and the abbreviation for each reactants can be seen from Figure 6. This system of ordinary differential equations has an initial constant 2-CP (i.e., $t = 0$, $[2CP] = 5.45 \times 10^{-4} M$) and initial zero concentrations for all other species. The K_{La} value used is $0.01 sec^{-1}$, which is around the average of various aerated reactors.¹⁵ These equations were solved numerically by fourth-order Runge-Kutta method, and MATLABTM was the programming language employed. The second-order rate constants obtained from fitting the model are listed in Table 2 and the fitted results are shown as lines in Figure 5. These fitted rate constants have the same order of magnitude with other independent studies.⁵ Therefore, this reaction pathways

Table 2. Fitted results from kinetic modeling

Compound	$z_i k_i^a$ ($M^{-1}sec^{-1}$)
2-Chlorophenol (2CP)	1500
3-Chlorocatechol (3CCA)	3600
Chlorohydroquinone (CHQ)	3600
Hydroxyhydroquinone (HHQ)	9000
Muconic Acid (MuA)	6000
Tartaric Acid (TA)	100
Maleic Acid (MaA)	6000
Hydroxymalonic Acid (HMA)	10
Oxalic Acid (OA)	0.01
Glycolic Acid (GA)	0.01

^a z_i is the stoichiometric coefficient between ozone and each compound, and k_i is the second order rate constant.

and kinetic modeling can properly describe the concentration change during the course of ozonation.

Conclusions

The ozonation by-products generated under an acidic condition are mainly organic carboxylic acids. From this study, an easy and accurate analytical method was established to monitor the organic acid as a By-products generated by

ozonation. This procedure can also be applicable for future analysis of ozonation on various organic contaminants. Final stable compounds found in this study have relatively low reaction rate constants (see Table 2) compared to the parent compound (2-CP); therefore, it is no longer economical to degrade these organic acids by ozonation when the parent compound is entirely removed. Since these short-chain organic acids are favorable for biological degradation, a biological treatment unit following the ozonation process should be considered. The kinetic mathematical model can describe the concentration change of the parent compound, chloride ion, and several other organic acids well with reasonable rate constants.

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