

Kinetics of the degradation of 2-chlorophenol by ozonation at pH 3

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Abstract

Prediction of byproduct distribution during ozonation is of importance to the design of treatment process. In this study, degradation products in direct ozonation of 2-chlorophenol in aqueous solution were identified by employing the chemical derivatization technique, specifically, silylation. Transient distribution of degradation products, in a semi-batch reactor under three ozone dosages were identified and determined by HPLC analysis. An empirical degradation pathway was proposed to describe the ozonation reaction. A mathematical protocol consisting of 11 equations and 12 rate constants was developed to solve and optimize the kinetic parameters. Modeling results revealed that the empirical pathway was capable of predicting the ozonation reaction at the beginning phase under a higher ozone dosage (e.g., greater than 6 mg/L_g). The degree of agreement between predicted and experimental data decreased as the ozone dosage decreased to 1.2 mg/L_g. Results suggested that there was a dosage-dependent pathway in the direct ozonation of 2-chlorophenol.

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1. Introduction

Ozonation treatment, both in indirect and direct reaction modes, has been proved to be effective in degrading recalcitrant organic contaminants. Indirect ozonation alone or in combination with H₂O₂/UV has been applied in abating various organic contaminants [1–3]. Direct ozonation has the advantage of high selectivity, which warrants its specific application in killing microorganisms, oxidizing minerals as well as organic contaminants that have reactive functional groups in water treatment. It is this selectivity that a low ozone dosage is usually sufficient to achieve hygienic, organoleptic, and chemical goals of water purification [4].

Because the nature of degradation byproducts was of great interest to environmental health, new drinking water regulations have now established maximum concentration levels (MCLs) not only for parent compounds per se but also for their degradation byproducts in various stages and forms of water treatment [5]. In addition, the integrated process of utilizing ozonation as

pretreatment and biodegradation as a follow-up treatment has become a promising cost-effective option in water purification [6–8]. Consequently, insight into the distribution of degradation byproducts in ozonation will help optimize the subsequent biological unit via providing information on the composition of feed constituents. On the whole, there is an urgent need to understand how degradation byproducts distribute, what kinetic model can describe their distribution, and what affects their distribution during ozonation treatment.

Degradation byproducts of aromatic compounds were determined using chemical derivatization methods in a few studies [9,10]. These products consist of short-chain compounds such as alcohols, aldehydes, acid anhydrides, and carboxylic acids with carbon numbers ranging from 2 to 6. In addition to the ring-cleavage mechanism, other reaction mechanisms such as anomalous ozonolysis and oxidative coupling may play important roles in these reactions [11]. For example, anomalous reactions could participate in the direct ring-cleavage mechanism and lead to the formation of maleic, tartaric, and dihydroxymaleic acids. Also, it was reported that polymeric compounds were detected during oxidative coupling of chlorophenols [12–14]. Such polymerization is taking place by initial formation of transition-state peroxide and subsequent rearrangement of aromatic radicals [15].

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With respect to ozonation of 2-chlorophenol in aqueous solution, early studies mainly focused on the degradation rate of 2-chlorophenol itself [16,17] and its stoichiometric relationships with ozone [18]. Later, aromatic intermediate products such as *o*-dihydroxybenzene [19] and aromatic quinone [2,20], and carboxylic acids such as oxalic and glyoxylic acids were found [21]. The degradation pathway was suggested to be complex and the secondary reactions were believed to be important [19]. An attempt was made to model the formation of aromatic quinone in acidic condition, and it was found that effects of stoichiometrics were sophisticated and further detailed experimental data were needed [2].

The goal of this study was to establish a model to predict transient distributions of intermediates and byproducts pertinent to direct ozonation process, exemplified by 2-chlorophenol, under various ozone dosages. Due to the complexity of the oxidation pathway and potential unknown reactions involved, the pathway was developed empirically according to byproduct information obtained from experiments. Theoretical reaction kinetics to the production of a few byproducts was simplified in order to fulfill the proposed pathway. Based on this empirical model, kinetic rate constants were then globally optimized using experimental data. Although the approach adopted in this study was empirical, it provides a practical tool to predict transient distribution of byproducts during direct ozonation. Specific objectives of this study were: (1) to identify and quantify degradation products so as to elucidate the degradation pathway, (2) to optimize rate constants in the empirical model, and (3) to investigate ozone dosage effects on product distribution dynamics.

2. Materials and methods

Ozonation experiments were conducted in a semi-batch stirred reactor, where ozone gas (100 mL_g/min) was continuously purged through a fine-bubble glass diffuser into a glass cylinder (500 mL) that was completely mixed with a magnetic stirring bar. Three ozone gas concentrations, e.g., 1.2, 6.3, and 12.5 mg/L_g, were applied. The ozone generator was manufactured by the Welsbach Company (Philadelphia, PA, USA). The solution of 2-chlorophenol (2CP) with a concentration of 100 mg/L was prepared with deionized distilled water from its pure liquid. To study the direct oxidation reaction, the solution pH was adjusted to 3 using a strong acid (1 M HClO₄).

Ozone gas concentrations in and out of the reactor were monitored by the iodometric method, and dissolved ozone concentrations were determined by the indigo method [22]. Prior to ozonation of 2-chlorophenol, the physical mass transfer coefficient of this specific system was determined by passing the ozone gas into deionized distilled water (pH 3) in the absence of any organic compounds. Dissolved ozone was measured as a function of time. The physical absorption model was subsequently fitted to the transient data to determine the overall mass transfer coefficient (k_{La}).

During the ozonation of 2CP, separate identification and quantification experiments were carried out. In the identification step, samples of 10 mL were withdrawn using a syringe from the sampling port at selected times. Immediately after collection

the samples were mixed with 0.1 mL of 0.1 M Na₂S₂O₃ as to quench further oxidation reactions. The samples were then acidified with 0.1 mL of 1 M HClO₄, and then extracted with 1 mL dichloromethane for 48 h. After extraction, the samples in the dichloromethane layer were analyzed using GC/MS (HP Models 5890 and 5971). As to the aqueous phase sample after extraction, a volume of 6 mL was transferred to the Reacti-VialTM vial (Pierce Chemical Co., Rockford, IL, USA), and 0.1 mL of 1 M NaOH was added to the sample. This sample was then evaporated to dryness under a gentle stream of nitrogen with a Reacti-VapTM evaporator. The last traces of moisture were removed by adding 0.1–0.5 mL of methylene chloride, which forms azeotrope. The solvent was removed under the same condition as the evaporation operation. In each completely dry sample, 75 μL of BSTFA (*N,O*-bis(trimethylsilyl)trifluoroacetamide) with 10% of TMCS (trimethylchlorosilane) was added, capped, and mixed at a temperature of 40 °C for 15 min to complete the silylation reaction. The silylated samples were then analyzed by GC/MS. In the quantification step, identical experiments as in the identification were conducted except only a sample volume of 2 mL was taken at selected times. These samples were quenched with Na₂S₂O₃ and alkalized (with 1 M NaOH) to prevent any vaporization and then was stored under refrigeration in glass vials for subsequent total organic carbon and HPLC analyses.

An HPLC system (Hewlett-Packard, series 1100) with a reversed phase C-18 VydacTM column (Vydac Co., Hesperia, CA, USA) was used to quantify 2CP and other aromatic intermediates. The same system with a SupelcogelTM ion-exclusion chromatographic column C-610H (Supelco Co., Bellefonte, PA, USA) was used to analyze carboxylic acids. To determine the chloride ion concentration in each sample, a DionexTM ion chromatographic system with a conductivity detector was used. The TOC analyzer Dohrmann DC-190 (Rosemount Analytical Inc., Orrville, OH, USA) was used for organic carbon analysis.

3. Mathematical modeling

In a reaction-controlled regime, the rates of change in the concentration of reactant (P_i), dissolved ozone (O_{3L}), and gaseous ozone (O_{3g}) can be expressed as the following equations [2]:

$$\frac{d[P_i]}{dt} = \sum_i \pm k_i [P_i][O_{3L}] \quad (1)$$

$$\frac{d[O_{3L}]}{dt} = k_{La} \left(\frac{[O_{3g}]}{H} - [O_{3L}] \right) - \sum_i k_i [P_i][O_{3L}] \quad (2)$$

$$V_g \frac{d[O_{3g}]}{dt} = Q_g ([O_{3g(in)}] - [O_{3g}]) - k_{La} \left(\frac{[O_{3g}]}{H} - [O_{3L}] \right) V_L \quad (3)$$

where k_i is the rate constant between dissolved ozone (O_{3L}) and the reactant (P_i), k_{La} the overall mass transfer coefficient, H the Henry's constant of ozone, V_g the gas content in the reactor, V_L the liquid volume in the reactor, and Q_g is the ozone gas flow rate. For this specific system, the dimensionless Henry's constant

used was 3.354 [23], the Q_g was 100 mL_g/min, the gas holdup in the reactor was determined to be around 10%, and the k_{La} value was measured in a separate experiment. This leaves a series of k_i 's as only unknowns in the governing equations. Depending upon the number of reactants present in a system, Eqs. (1) and (2) are subject to expand to include all available reactants and to consider all potential reactions taking place simultaneously. The Runge–Kutta method was employed to solve the above coupled ordinary differential equations using program codes written in MATLABTM (The MathWorks, Inc., Natick, MA, USA). To globally optimize rate constants in the model system, the random walk method utilizing the golden section technique for step size computation was applied [24]. The objective function (f) used in the optimization was set to be:

$$f = \sum_i \sum_j [C_i(t_j) - C_i^*(t_j)]^2 \quad (4)$$

where $C_i(t_j)$ and $C_i^*(t_j)$ represent the experimental and fitted concentrations of a specific product i at a specific time of t_j , respectively.

4. Results and discussion

4.1. Kinetic modeling of degradation byproducts

Traces of 2-chlorophenol, 3-chlorocatechol (3CICA), chlorohydroquinone (CIHQ), and phthalic acid were detected in GC/MS analysis of the dichloromethane phase. Organic acids identified by silylation include acetic, valeric, 2-propenoic, maleic, succinic, propionic, dihydroxymaleic, malonic, hydroxymalonic, muconic, oxalic, tartaric, and phthalic acids. Although more than 10 products were identified from GC/MS analysis, only muconic (MUCA), tartaric (TART), dihydroxymaleic (DHMA), maleic (MALA), and oxalic acids (OA) were quantified, while others were too dilute to be quantified.

Based upon the product information obtained, reaction pathways under direct ozone reactions can be hypothesized as presented in Fig. 1(a), where major products are produced via aromatic ring cleavage. Compounds in the parentheses are those being positively identified in this study. Other organic acids identified but not shown in the figure are produced via the unknown reactions, which refer to any other reaction routes besides the ring-cleavage route illustrated in Fig. 1(a). Table 1 summarizes dimensionless peak concentrations of each product under three different ozone concentrations. When the gaseous ozone equals 6.3 and 12.3 mg/L_g, the total mass of each of all C6 (six carbons) compounds is less than 6% of the initial mass of 2-chlorophenol, whereas tartaric acid is more than 54%. This implies that the above ring-cleavage pathway in Fig. 1(a) alone cannot produce the entire mass of tartaric acid under higher ozone dosages (e.g., >6 mg/L_g). Accordingly, there must be unknown reactions that can yield the substantial mass of tartaric acid observed. In light of the above observation, analogous assumption on the other two C4 products (i.e., maleic and dihydroxymaleic acids) can be made, that is, parts of their mass are resulted from unknown reactions as well.

Table 1

Maximum normalized concentrations of various products under three different ozone concentrations within specific experimental reaction times^{a,b}

| Compound name | 1.2 mg/L | 6.3 mg/L | 12.3 mg/L |
|----------------------|----------|----------|-----------|
| Chlorohydroquinone | 0.035 | 0.025 | 0.025 |
| 3-Chlorocatechol | 0.012 | 0.01 | 0.012 |
| Muconic acid | 0.03 | 0.018 | 0.022 |
| Maleic acid | 0.003 | 0.025 | 0.023 |
| Tartaric acid | 0.08 | 0.54 | 0.54 |
| Dihydroxymaleic acid | 0 | 0.13 | 0.15 |
| Oxalic acid | 0 | 0.25 | 0.1 |

^a Reaction times for O₃ of 1.2, 6.3, and 12.3 mg/L are 60, 120, and 300 min, respectively.

^b Concentrations are normalized to the initial 2-chlorophenol concentration.

In order to facilitate the modeling effort, the reaction pathway is simplified as illustrated in Fig. 1(b). Some products such as C3 compounds that were not quantified by HPLC are not included. This empirical pathway is used to simulate the experimental data. The unknown reaction pathway is assumed to take place via an intermediate compound, E₁, which leads to the production of maleic, tartaric and, and dihydroxymaleic acids. Consequently, the following mass balance equation for the E₁ compound can be written:

$$\frac{d[E_1]}{dt} = k_E[2CP][O_{3L}] - (k_{E4} + k_{E5} + k_{E6})[E_1][O_{3L}] \quad (5)$$

where k_E is the second-order rate constant for the reaction between ozone and 2-chlorophenol with the production of E₁, k_{E4} , k_{E5} , and k_{E6} are the second-order rate constants for the reactions between ozone and E₁ with the production of maleic, tartaric and dihydroxymaleic acids, respectively. Since no detectable unknown peaks representing E₁ was observed in the chromatograms, it is thus assumed that the concentration of E₁ is close to zero. Therefore, one can further assume that its transient distribution is at steady state, and the following equation representing E₁ can be obtained:

$$[E_1] = \frac{k_E[2CP][O_{3L}]}{(k_{E4} + k_{E5} + k_{E6})[O_{3L}]} \quad (6)$$

Furthermore, according to the empirical pathway in Fig. 1(b) one can write the mass balance equation for tartaric acid (TART) as:

$$\begin{aligned} \frac{d[TART]}{dt} &= k_{E4}[E_1][O_{3L}] + k_9[MALA][O_{3L}] \\ &\quad - k_{10}[TART][O_{3L}] \end{aligned} \quad (7)$$

By substituting [E₁] in Eq. (6) into Eq. (7), one has the following rate expression:

$$\begin{aligned} \frac{d[TART]}{dt} &= k_4[2CP][O_{3L}] + k_9[MALA][O_{3L}] \\ &\quad - k_{10}[TART][O_{3L}] \end{aligned} \quad (8)$$

where k_4 equals $(k_{E4}k_E)/(k_{E4} + k_{E5} + k_{E6})$, which represents the apparent second-order rate constant for the reaction between ozone and 2-chlorophenol with the production of tartaric acid.

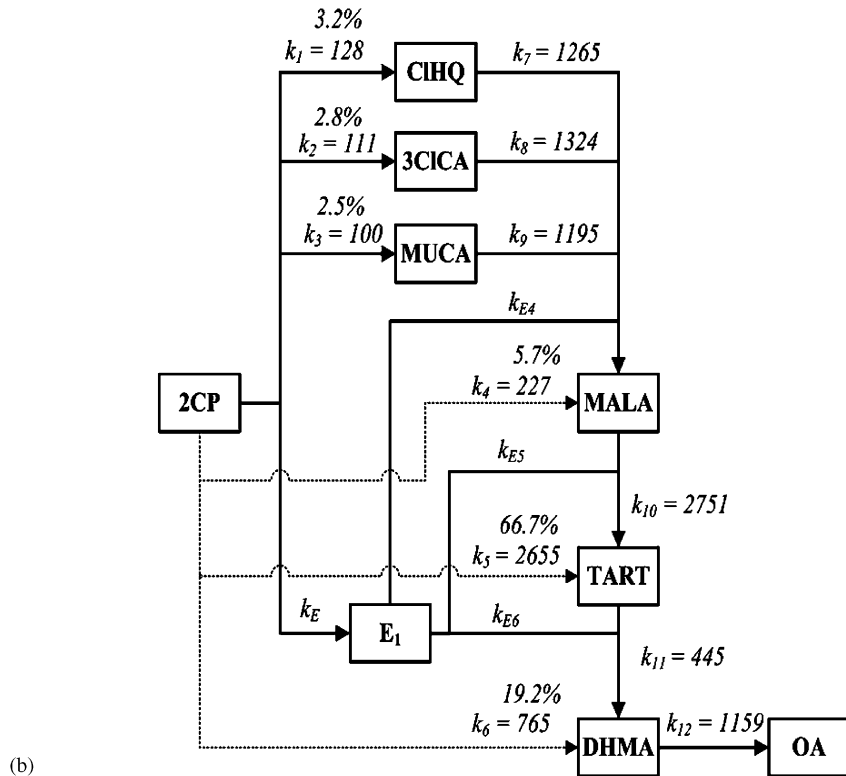
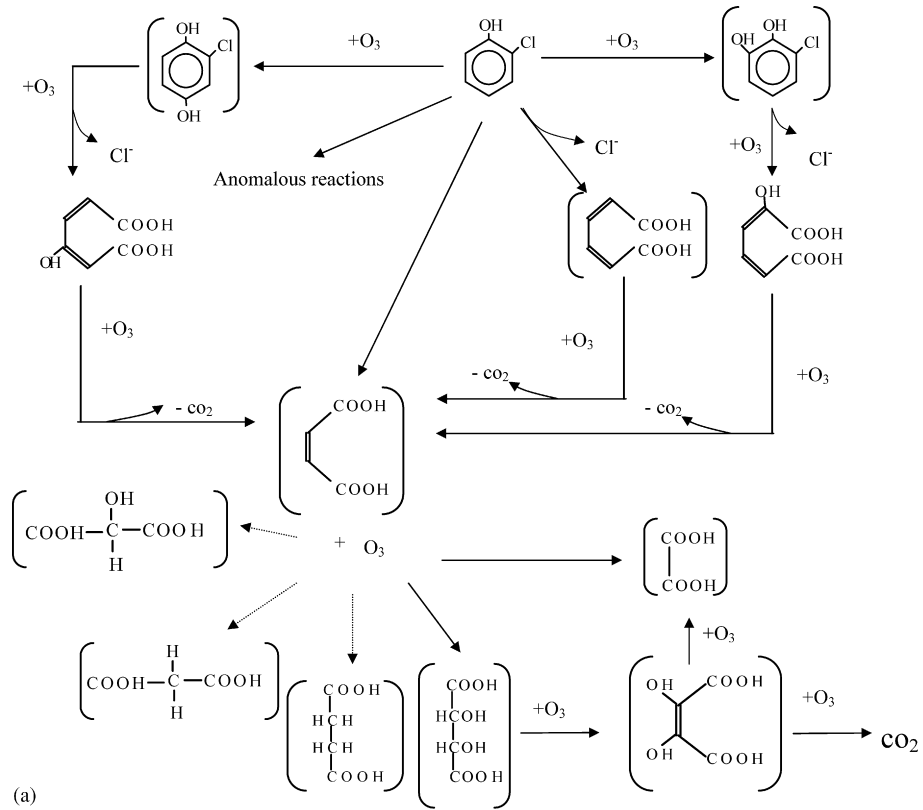


Fig. 1. (a) Proposed degradation pathways of 2CP oxidation. Compounds in the parentheses are the ones that have been positively identified using GC/MS analysis. Others are hypothetical intermediate compounds. (b) Simplified 2-chlorophenol (2CP) oxidation pathway in direct ozone reactions. Byproduct compounds include chlorhydroquinone (ClHQ), 3-chlorocatechol (3CICA), muconic acid (MUCA), maleic acid (MALA), tartaric acid (TART), dihydroxymaleic acid (DHMA), and oxalic acid (OA). Unknown reactions were assumed to take place via the E₁ compound. Dashed lines represent direct production from 2CP to various products.

Table 2
Kinetic equations describing degradation pathways presented in Fig. 1(b)

$$\begin{aligned} \frac{d[2CP]}{dt} &= -(k_1 + k_2 + k_3 + k_4 + k_5 + k_6)[2CP][O_{3L}] \\ \frac{d[CIHQ]}{dt} &= k_1[2CP][O_{3L}] - k_7[CIHQ][O_{3L}] \\ \frac{d[3CICA]}{dt} &= k_2[2CP][O_{3L}] - k_8[3CICA][O_{3L}] \\ \frac{d[MUCA]}{dt} &= k_3[2CP][O_{3L}] - k_9[MUCA][O_{3L}] \\ \frac{d[MALA]}{dt} &= k_7[CIHQ][O_{3L}] + k_8[3CICA][O_{3L}] + k_9[MUCA][O_{3L}] \\ &\quad + k_4[2CP][O_{3L}] - k_{10}[MALA][O_{3L}] \\ \frac{d[TART]}{dt} &= k_5[2CP][O_{3L}] + k_{10}[MALA][O_{3L}] - k_{11}[TART][O_{3L}] \\ \frac{d[DHMA]}{dt} &= k_6[2CP][O_{3L}] + k_{11}[TART][O_{3L}] - k_{12}[DHMA][O_{3L}] \\ \frac{d[OA]}{dt} &= k_{12}[DHMA][O_{3L}] \\ \frac{d[Cl]}{dt} &= (k_3 + k_4 + k_5 + k_6)[2CP][O_{3L}] \\ \frac{d[O_{3L}]}{dt} &= k_{La} \left(\frac{[O_{3g}]}{H} - [O_{3L}] \right) - (k_1 + k_2 + k_3 + k_4 + k_5 + k_6)[2CP][O_{3L}] \\ &\quad - k_7[CIHQ][O_{3L}] - k_8[3CICA][O_{3L}] - k_9[MUCA][O_{3L}] \\ &\quad - k_{10}[MALA][O_{3L}] - k_{11}[TART][O_{3L}] - k_{12}[DHMA][O_{3L}] \\ V_g \frac{d[O_{3g}]}{dt} &= Q_g([O_{3g(in)}] - [O_{3g}]) - k_{La} \left(\frac{[O_{3g}]}{H} - [O_{3L}] \right) V_L \end{aligned}$$

By the same approach, the equation describing the production of dihydroxymaleic acid and maleic acid can also be developed. Furthermore, it was assumed that the chloride ion was freed immediately upon 2-chlorophenol degradation except when intermediates, chlorohydroquinone and chlorocatechol were formed. As to the production of CO₂, theoretically, CO₂ could be produced from all C4 compounds and unknown reactions as well. If one wishes to consider all possible conditions, extra five rate constants have to be included. For the sake of simplicity, its production is not included in the simplified model.

Comprehensively, a total of 11 ordinary differential equations as shown in Table 2 were established to mathematically describe the simplified pathway in Fig. 1(b). By conducting the gas absorption experiment in pure water at pH 3, the k_{La} value for the semi-batch reactor was found to be 0.015 s⁻¹ and was incorporated into the modeling. Data collected under ozone concentrations of 6.3 and 12.3 mg/L_g were applied to optimize the 12 rate constants. Optimized values of rate constants are shown in Fig. 1(b).

For dissociating compounds, their second-order rate constants (k_{O_3}) can be expressed by the general equation: $k_{O_3} = ak_{B-} + (1 - \alpha)k_{HB}$, where α is the degree of deprotonation (or dissociation) and is expressed by $\alpha = 1/(10^{pK_a - pH} + 1)$ with pK_a being the acidity (or dissociation) constant, k_{HB} and k_{B-} being rate constants with respect to the non-dissociated (or protonated) and the dissociated (or deprotonated) forms of the organic acid, respectively. Given $pK_a = 8.3$, $k_{HB} = 600 \text{ M}^{-1} \text{ s}^{-1}$, and $k_{B-} = 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for 2-chlorophenol [16], the computed k_{O_3} at pH 3 is $3607 \text{ M}^{-1} \text{ s}^{-1}$. In fact, the summation of k_1 – k_6 (i.e., $3986 \text{ M}^{-1} \text{ s}^{-1}$) actually represents the apparent rate constant of reaction of dissolved ozone with 2-chlorophenol, and is very close to the value independently obtained from the general equation (i.e., $k_{O_3} = \alpha k_{B-} + (1 - \alpha)k_{HB}$). The mass transfer coefficient (k_L) of ozone in bub-

ble columns from two other independent studies were found to be 1.7×10^{-4} [25] and 2×10^{-4} m/s [26]. With the diffusion coefficient D_{O_3} of 2×10^{-9} m²/s for dissolved ozone [27] and other parameters estimated above, the Hatta number, $\gamma = \sqrt{D_{O_3} k_{O_3} [2CP]} / k_L$, is found to be less than one (e.g., $\gamma = \sqrt{(2 \times 10^{-9})(3986)(7.8 \times 10^{-4})} / (2 \times 10^{-4}) = 0.39$), implying a slow reaction regime. The system is not completely reaction-controlled ($\gamma < 0.3$) and, thus the enhancement factor has to be considered to account for reactions in the film. However, the enhancement factor calculated is nearly unity, suggesting that the physical absorption condition can still be applied. It should be noted that as reaction proceeds, the 2-chlorophenol concentration decreases. Also, concentrations of degradation products are low and their rate constants with ozone are not as high as 2-chlorophenol. This means that the Hatta number estimated above would be the maximum value in the system. Therefore, the Hatta number of the system should become smaller as reaction proceeds. This justifies the validity of the governing equations in the system.

The mass percentage of 2-chlorophenol converted via a specific route, η_i , can be calculated by the equation, $\eta_i = k_i / \sum_{i=1}^6 k_i$. Thus, the percentages via the k_1 – k_6 routes were computed and their values are listed in Fig. 1(b). It is seen that the routes leading to the formation of C6 compounds account for only about 8.5% of the total 2-chlorophenol reacted. The rest products are predominantly converted via the k_4 – k_6 routes. As can be seen later, modeling results indicate that ozone concentration affects only the emerging time of the peak concentration of a specific compound, not the value of the peak concentration. In other words, according to the model no matter what ozone concentration is applied, the peak concentration observed during a run will always be the same under a fixed initial 2-chlorophenol concentration. The reason for this is because the mass balance requirements must be satisfied in the modeling.

4.2. Dynamic distribution of 2-chlorophenol and its degradation products

Experimental data of 2-chlorophenol degradation are shown in Fig. 2 together with modeling results obtained from the scheme presented in Fig. 1(b). It is evident that there are good agreements between experimental and modeled results during the early reaction phase (e.g., 20, 30, and 100 min for ozone concentration of 1.2, 6.3, and 12.3 mg/L_g, respectively). Fig. 3 illustrates the experimental and modeled results of C6 compounds. In general, modeling results of both chlorohydroquinone and 3-chlorocatechol are closer to experimental data at ozone concentrations of 6.3 and 12.3 than at 1.2 mg/L_g. This implies that the proposed simplified pathway can better reflect reactions taking place at higher ozone concentrations. Fig. 4 compares experimental data and modeled results of C4 products. For all three compounds, there are excellent agreements under higher ozone concentrations, while significant gaps exist at the lowest ozone concentration of 1.2 mg/L_g. These phenomena observed so far suggest that ozone concentration itself can probably affect the reaction pathway. When the ozone concentration is above

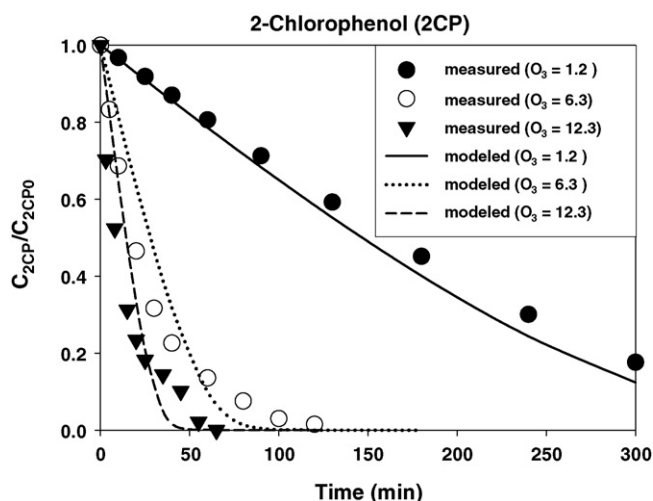
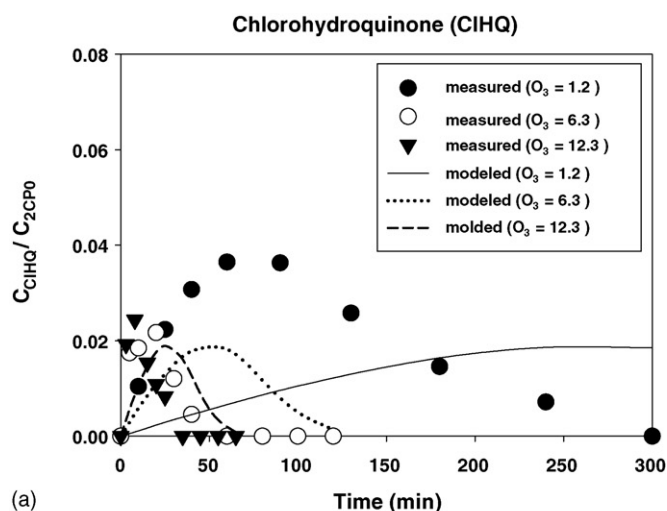


Fig. 2. Residual concentrations of measured and modeled 2-chlorophenol, C_{2CP} , as a function of time during ozonation treatment under various gaseous ozone concentrations of 1.2, 6.3, and 12.3 mg/L_g. Data are normalized to the initial 2-chlorophenol concentration (C_{2CP0}) of 7.8×10^{-4} M.

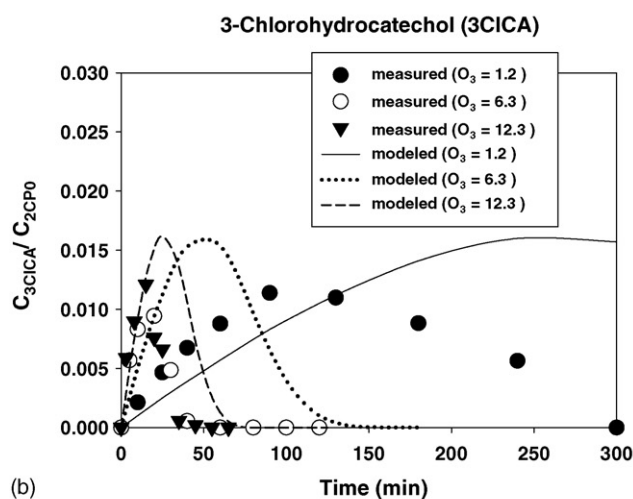
a particular value, the empirical pathway applies. Otherwise, different pathways are needed to explain product distributions. Based on results of this study, it appears that this critical value was between 1.2 and 6.3 mg/L_g.

Oxalic acid was the major end products quantified and its distribution is shown in Fig. 5(a). Unlike C4 compounds, during the first 60 min of the reaction experimental data appear to be independent of ozone dosage at concentrations greater than 6 mg/L_g, whereas modeling results show significant dosage-dependent trends. The oxalic acid concentration at 12.3 mg/L_g of ozone is likely to be higher than 6.3 mg/L_g if measurements are made till 120 min. Compared to other products, oxalic acid has the largest deviation at higher ozone concentrations, which is probably because dihydroxymaleic acid is degraded to products besides oxalic acid when the ozone concentration is 12.3 mg/L_g. At ozone concentration of 1.2 mg/L_g, no significant oxalic acid is detected during the entire course of reaction, but the model predicts a mass of 3% within 300 min. Additionally, Fig. 5(b) shows results of the other end product, CO₂, which is obtained from TOC analysis. From the CO₂ data, it is estimated that ozonation mineralized more than 30 and 10% of 2-chlorophenol at ozone concentrations of 6.3 and 1.2 mg/L_g, respectively.

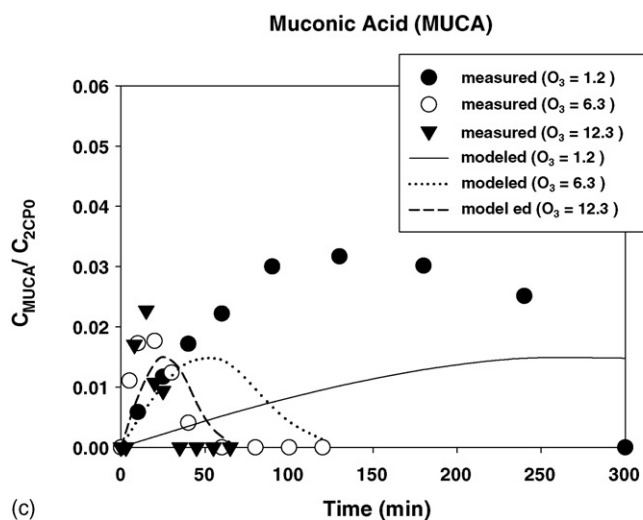
Furthermore, there is an excellent agreement between modeling results and experimental data of chloride ion except for the lowest ozone concentration as illustrated in Fig. 5(c). This verifies that chloride ion is freed immediately upon reaction between ozone and 2-chlorophenol at ozone concentrations greater than 6 mg/L_g. Finally, Fig. 6 shows the mass balance relationship of 2-chlorophenol and all products as a function of time in terms of carbon. These results were obtained by adding the mass of all compounds generated at each specific ozone dosage in Figs. 2–5. Generally, experimental data can account for over 80% of carbon mass at the initial reaction period (ca. 50 min), but fail to further reckon the carbon mass as the reaction time is prolonged. This



(a)



(b)



(c)

Fig. 3. Residual concentrations of measured and modeled six-carbon products as a function of time during ozonation treatment under various gaseous ozone concentrations of 1.2, 6.3, and 12.3 mg/L_g. Data are normalized to the initial 2-chlorophenol concentration (C_{2CP0}) of 7.8×10^{-4} M: (a) chlorohydroquinone (C_{ClHQ}), (b) 3-chlorocatechol (C_{3CICA}), and (c) muconic acid (C_{MUCA}).

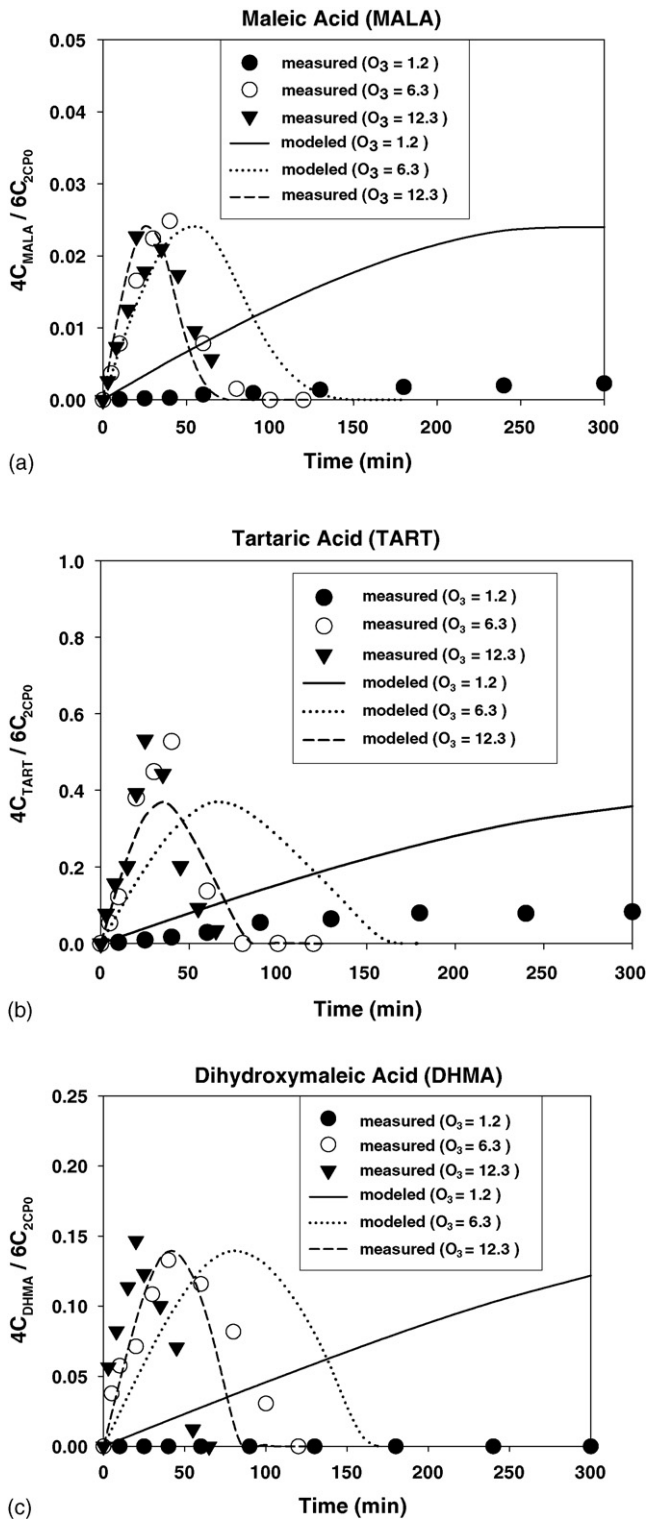


Fig. 4. Residual carbon concentrations of measured and modeled four-carbon products as a function of time during ozonation treatment under various gaseous ozone concentrations of 1.2, 6.3, and 12.3 mg/L_g. The initial 2-chlorophenol concentration (C_{2CP0}) is 7.8×10^{-4} M. The data are normalized to the initial total carbon number of $6C_{2CP0}$: (a) maleic acid (C_{MALA}), (b) tartaric acid (C_{TART}), and (c) dihydroxymaleic acid (C_{DHMA}).

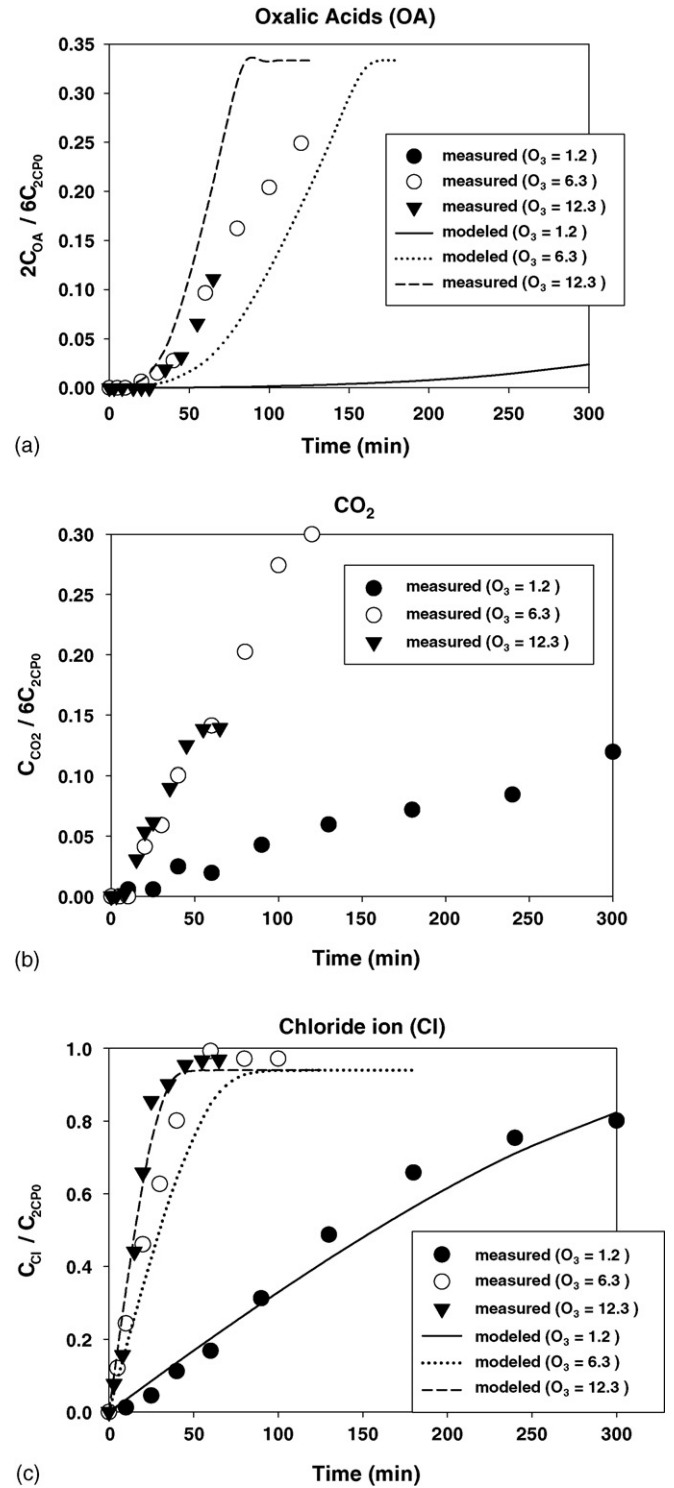


Fig. 5. Residual carbon and chloride concentrations for: (a) oxalic acid (C_{OA}), (b) CO_2 (C_{CO_2}), and (c) chloride ion (C_{Cl}).

suggests that other non-quantifiable products play an important role in determining the mass balance, and that these products become more important as reactions proceed. From information obtained in the identification experiment, these non-quantifiable products mainly consist of many short-chain carboxylic acids with micro-concentration in each.

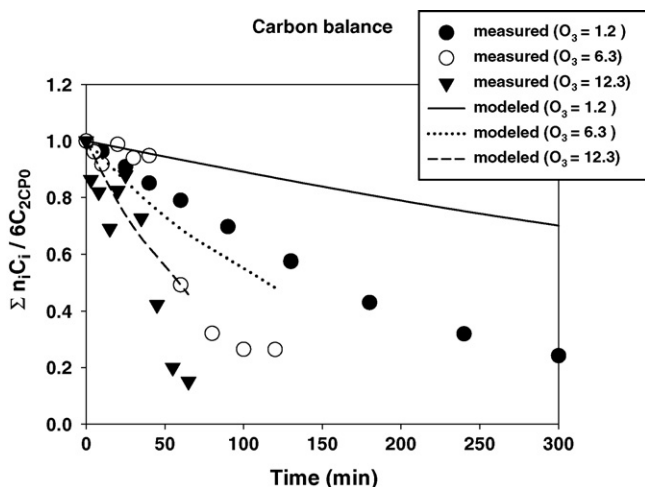


Fig. 6. Total mass of carbon atoms from measured and modeled results normalized to the initial total carbon numbers of $6C_{2CP0}$. The n_i value in the y-axis represents the number of carbons in the product i .

5. Conclusions

Based on the empirical kinetics with 12 optimized rate constants, it is possible to account for more than 90% of byproduct mass via the pathway of unknown intermediates. Transient distribution of products during the degradation of 2-chlorophenol by ozonation can be predicted to a limited degree using the empirical kinetics. If the ozone gas concentration is greater than 1.2 mg/L_g, the model prediction of most products agrees well with experimental data except for oxalic acid. Predominantly, good fits between experimental and modeled results are obtained at the early phase (e.g., within ca. 50 min). Final mass balance implies that short-chain carboxylic acids with micro-concentration would be important if the ozonation time prolongs. Ultimately, if ozonation is applied for a limited time, the empirical pathway together with the corresponding mathematical modeling provides a tool that can predict the degradation rates of not only the parent compound, but also various byproducts during ozonation.

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