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Aqueous phase ozonation of chlorophenols

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Abstract

This research investigates the kinetics and mechanisms of the reactions between dissolved ozone and mono-chlorophenols in distilled water. The stoichiometric determination indicates that three moles of ozone are required for complete conversion of each mole of chlorophenol. A stopped-flow spectrophotometer system was applied to obtain the kinetic data. *p*-Chlorophenol is the most reactive of the three isomers with ozone yielding second order rate constants of 10 800–56 000 $1/M$ s as the temperature increases from 10 to 35 °C. The ozonation reaction is first order in ozone, and independent of the concentration of *o*- or *m*-chlorophenol. The kinetic results suggest that the reactions of the three isomers are governed by different pathways though all of the ozonation reactions might be initiated by electrophilic addition.

1. Introduction

Like many phenolic compounds, chlorophenols are highly toxic and used widely in the manufacture of pesticides, insecticides, herbicides, fungicides, intermediates of dyes, and other industrial chemicals. Chlorination of phenols during the disinfection of waste water also produces chlorophenols. These result in contamination of many lakes and water streams by chlorophenols [1–3]. Although they can be degraded by bacteria and by plants in some instances [4], environmental conditions are often unfavorable for the biological degradation processes to occur. Thus, the removal or destruction of these compounds by other chemical or physical means is often required. One of these methods, chemical oxidation by ozone, is considered in this work.

Reactions of chlorophenols with ozone in aqueous media have been investigated by several researchers. Shuval and Peleg [5] and Gilbert [6, 7] observed the rate of formation of chloride ion during ozonation of *o*- and *p*-chlorophenol. Complete removal of chlorophenols, rupture of aromatic ring and formation of intermediates by the reactions between chlorophenols and ozone were reported by Dore and

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co-workers [8,9]. Prengle [3] found the enhancement of the ozonation rate of chlorinated compounds by ultraviolet light irradiation to produce carbon dioxide. The chlorophenols also can be oxidized by hydrogen peroxide/iron system, as indicated by Keating et al. [1]. Although some pathways of the ozonation have been discussed by the above investigators, information on kinetics of the ozonation reactions is scarce.

In the present research, the stoichiometry of the ozonation reactions was determined. By utilizing a stopped-flow reactor, kinetic data for the rapid reactions were obtained and analyzed to obtain the reaction orders and rate constants for the ozonation of mono-chlorophenols. Possible mechanisms of the ozonation reactions also were suggested.

2. Experimental details

A Welsbach Model T-408 ozonator was employed to produce ozone gas using extra dry, pure oxygen. An aqueous solution of dissolved ozone was prepared by bubbling the ozone gas in distilled water for 10–30 min. By dissolving appropriate amounts of a chlorophenol isomer (ACS reagent, 99.9%, purchased from Aldrich Chemical Company) in distilled water, an aqueous solution of the isomer was prepared. Prior to the preparation, however, the distilled water was treated with ozone for destruction of any contaminants. The pH value of a solution was measured before and after an experiment by using a Beckman Model H2 glass electrode pH meter. No control of the pH value of a reaction mixture was attempted in the kinetic experiments because of reactive nature of chlorophenols with buffer reagents [2], as confirmed by preliminary tests.

A stopped-flow spectrophotometer (Hi-Tech Model SF-51) system equipped with a data acquisition subsystem was employed to conduct the kinetic experiments. The system is designed for studying rapid reactions between two liquid reactants under isothermal condition by water circulation. Changes in the optical absorbance of a reacting solution following mixing of the reactants (within one millisecond) can be measured as a function of the reaction time at a fixed wavelength within 200–800 nm.

Preliminary tests indicated that strong absorbances were exerted by chlorophenols in water at the wavelength of about 220 nm. The absorbances decreased to minimum values in the range 250–260 nm. In the kinetic experiments, ozone was chosen as the limiting reactant because of its lower solubility in water than that of chlorophenols. Therefore, the wavelength was set at 260 nm to allow maximum contribution of the limiting reactant to the total absorbance of a solution [10], and minimize errors in analysis of the absorbance data.

3. Analysis of kinetic data

The mechanism of the reaction between dissolved ozone and a chlorophenol isomer in the aqueous medium is quite complex, as suggested by the earlier investigators

[5–9, 11]. Nonetheless, the depletion rate of ozone is likely controlled by simultaneous reactions involving the self-decomposition of dissolved ozone and the reaction between ozone and the chlorophenol. These overall reactions can be expressed in the following forms:

$$A(O_3) \rightarrow 3/2O_2 \cdot \tag{1}$$

$$aA + bB\ (C_6H_5ClO) \rightarrow Ps \tag{2}$$

The reaction rate of the limiting reactant A (ozone) in the above parallel reactions can be written as:

$$-dC_A/dt = k_1 C_A^l + k_2 a C_A^m C_B^n . \tag{3}$$

In the above equation, C_A and C_B are the concentrations of ozone and chlorophenol, respectively. The order of the self-decomposition of ozone is l, and the orders of the ozonation reaction with respect to the concentrations of ozone and chlorophenol, respectively, are m and n.

The decomposition rate of ozone is substantially slower than the ozonation rate under the experimental conditions [10], as confirmed by the preliminary tests. Thus, the first term on the right-hand side of Eq. (3) can be ignored. With the chlorophenols (B) in large excess in the experiments, Eq. (3) can be simplified to:

$$-dC_A/dt = k' C_A^m , \tag{4}$$

where the apparent rate constant is

$$k' = k_2 a C_B(0)^n . \tag{5}$$

Integration of Eq. (4) yields

$$C_A(t)/C_A(0) = \exp[-k't] \quad \text{for } m = 1 \tag{6}$$

and

$$[C_A(t)/C_A(0)]^{1-m} = 1 + (m-1)C_A(0)^{m-1} k't \quad \text{for } m \neq 1 . \tag{7}$$

The absorbance of a dilute mixture can be taken as the sum of the absorbances of individual components, as dictated by Beer's law and confirmed by the preliminary tests. The following equation, therefore, can be derived to relate the ozone concentrations with absorbances measured in an experiment [12]:

$$[S(t) - S(\infty)]/[S(0) - S(\infty)] = C_A(t)/C_A(0) , \tag{8}$$

where $S(t)$ is the absorbance of the reacting mixture measured at time, t, and $S(\infty)$ is the asymptotic absorbance of the solution at the end of a reaction period. By utilizing the relationships given in Eqs. (4)–(8), inclusive, the absorbance data can be analyzed to obtain the orders and rate constants of the reaction.

4. Stoichiometry of the ozonation

Experiments were conducted to determine the quantity of ozone required for complete destruction of a chlorophenol. In each experiment, a solution containing excessive amount of dissolved ozone was mixed with a solution containing known quantity of chlorophenol at room temperatures (20–25 °C). The residual amount of ozone was determined by the iodimetric titration at 90 s after mixing of the two reactants to allow complete depletion of the chlorophenol. Three initial concentrations of each chlorophenol isomer (0.125×10^{-4}–0.5×10^{-4} M) were used, and the experiments were repeated several times at each concentration. As shown in Fig. 1, the fraction of ozone consumed in the reaction is plotted against the initial ratio of moles of ozone to chlorophenol. The figure indicates that the dissolved ozone was consumed completely for cases of three moles of ozone per mole of chlorophenol or less initially. On the other hand, if the ratio was higher than three, then a residual amount of ozone was detected after the reaction. Therefore, the results of the experiments show that three moles of ozone are required for complete destruction of each mole of a chlorophenol isomer. This finding ($a = 3, b = 1$) can be applied in Eq. (5) to calculate the rate constants of the ozonation reactions from the kinetic data, as discussed in the next section. It should be noted that the residual ozone fractions varied widely in Fig. 1. The scatter in the data seems to suggest that following the initial conversion of the

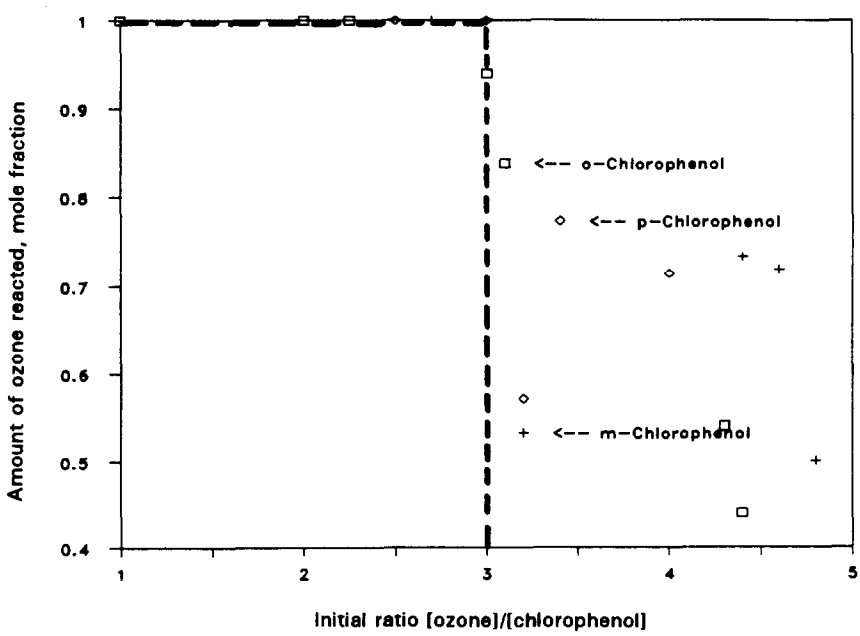

Fig. 1. Stoichiometric ratio.

parent chlorophenols, further oxidation reactions proceeded to form carbon dioxide and other end-products.

The stoichiometry of the ozonation of chlorophenol has been estimated to vary from 3 to 5 mol of ozone per mole of chlorophenol [6–9]. The requirement of 3 mol of ozone per mole of chlorophenol obtained in this work tends to agree with the postulation of the hexagon formula of Kekule, as discussed by Haijman and Wibaut [13]. They suggested that the benzene ring of an aromatic species behaves as a compound with three double bonds and that the six carbon–carbon bonds in the benzene nucleus are equivalent. Accordingly, three moles of ozone per mole of chlorophenol are required to rupture the aromatic ring in the initial stages of the reaction. With continued ozonation and complete oxidation to carbon dioxide, more than three moles are required, as reported by the earlier investigators [6–9].

5. Kinetics of the oxidation

The stopped-flow equipment was applied to study the ozonation rates of the three chlorophenols in distilled water containing excessive amounts of chlorophenols. The initial concentrations of chlorophenols varied from 0.0005 to 0.002 M, and those of ozone ranged from 0.5×10^{-4} to 2.5×10^{-4} M. The absorbance data measured during the reactions are tabulated elsewhere [8].

Typical absorbance behaviors during the ozonation of the three chlorophenols are illustrated in Fig. 2. For a reaction mixture, the absorbance decreased very rapidly following complete mixing of the two reactants (within 0.001 s), as indicated in the figure. The rapid decline of the absorbances during the initial period suggested fast reactions between the chlorophenols and dissolved ozone. Following the initial change, the absorbances continued to drop gradually approaching minimum values in no more than 0.3 s. The absorbances might increase slightly in a latter period possibly due to high absorbances exhibited by some reaction products.

The asymptotic absorbance at the completion of an ozonation reaction in the first period can be estimated, and the kinetic data analyzed utilizing Eqs. (5)–(8), inclusive. The regression analysis of the absorbance data indicates that the oxidation of a chlorophenol is first order ($m = 1$) with respect to the concentration of ozone. This result is illustrated in Fig. 3 by plotting the absorbance data (given in Fig. 2) according to the semi-logarithmic scale yielding straight lines, as dictated by Eq. (6). The apparent rate constants, k', can be calculated from the slopes of the linear plots or from results of the regression work.

The regression analysis gives the first order kinetics as the best result with the correlation coefficient of greater than 0.96. In general, the first order kinetics implies that the straight line goes through the origin in the semi-logarithmic plot. For several runs (for example line C in Fig. 3), however, the first few data points fluctuated widely, and were discarded for the purpose of obtaining the best slope, and in turn, the rate constant. At a given initial and operating conditions, at least three experimental runs were carried out to insure that the kinetic data are reproducible. Details of the

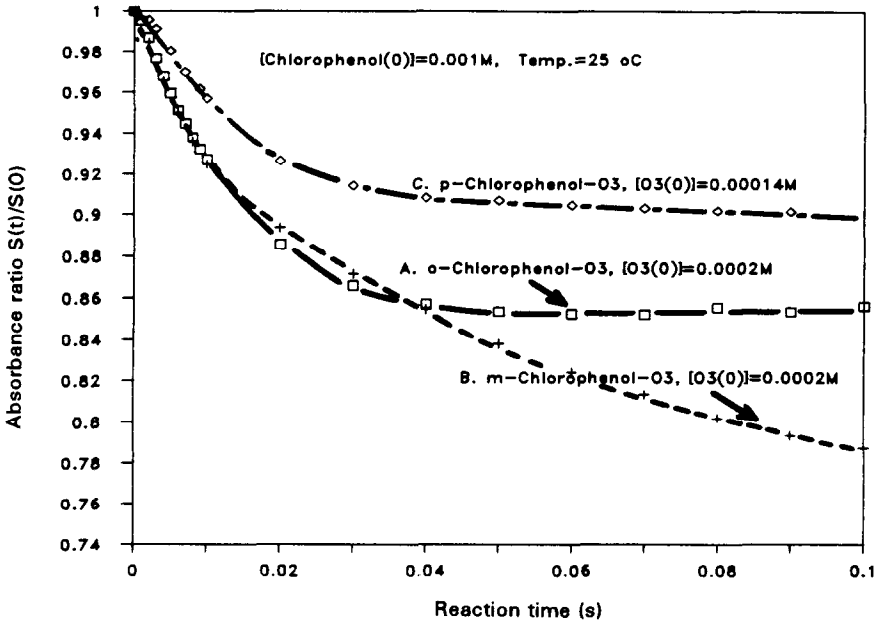

Fig. 2. Absorbance during reaction.

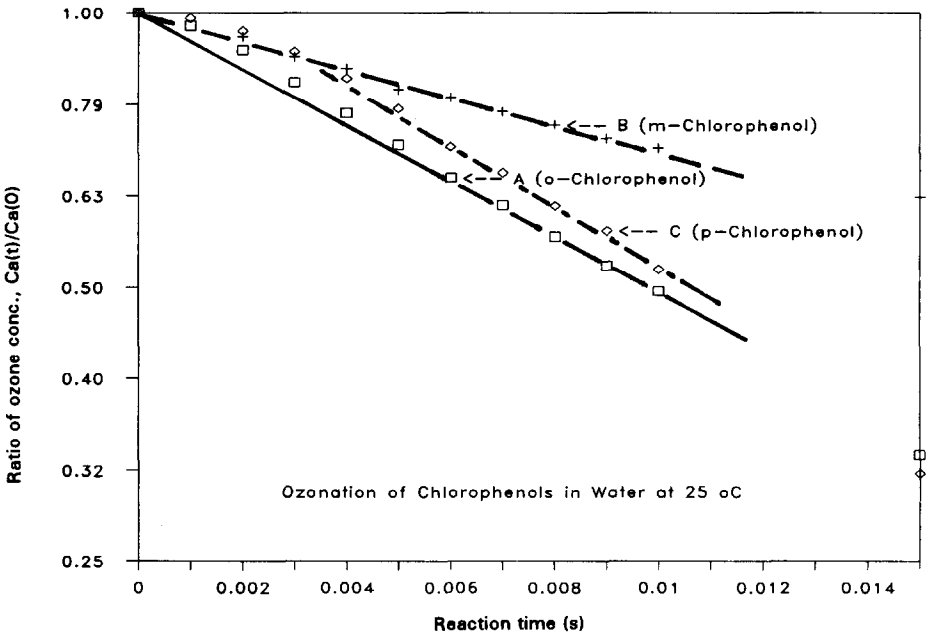

Fig. 3. Correlation of kinetic data.

experimental data and regression analyses are given in the thesis [14]. For the average rate constants calculated and presented in this work, the maximum deviation is 7.8% from the individual results.

The calculated results indicate that the apparent rate constant is sensitive to the initial concentration of *p*-chlorophenol, but is nearly independent of the concentration of *o*- or *m*-chlorophenol. As the temperature increases from 10 °C to 40 °C, the apparent rate constant, k', varies in the ranges of 31–120 and 10–33 1/s for the ozonation reactions of *o*- and *m*-chlorophenol, respectively. For the ozonation of *p*-chlorophenol at 25 °C, the apparent rate constant increases in the range of 36–134 1/s as the initial concentration increases from 0.0005 to 0.002 *M*.

The apparent rate constants obtained at 25 °C are plotted against the initial concentrations of the chlorophenol isomers on logarithmic scale in Fig. 4. The order with respect to the concentration of a chlorophenol isomer, n, at the fixed temperature then can be estimated from the slope of such a plot, as dictated by Eq. (5). Fig. 4 demonstrates that the ozonation reaction is independent of the concentrations of *o*- and *m*-chlorophenol ($n = 0$), and that the reaction rate is proportional to the concentration of *p*-chlorophenol ($n = 1$). Thus, the kinetics of the ozonation reaction is first order overall for the ozonation of *o*-chlorophenol and *m*-chlorophenol. For the reaction between *p*-chlorophenol and ozone, the reaction is first order in each reactant yielding a second order kinetics for the overall reaction.

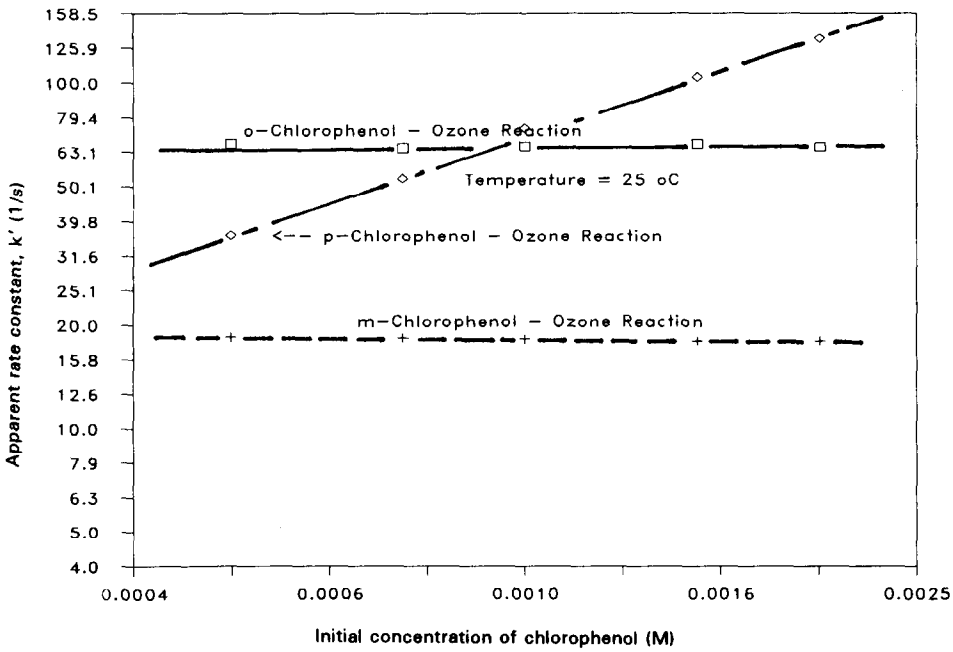

Fig. 4. Apparent rate constant.

The overall rate constants, k_2, can be computed from Eq. (5) on the basis of the stoichiometric requirement of three moles of ozone for complete conversion of each mole of chlorophenol ($a = 3, b = 1$) obtained in this work. In the temperature range of 10–40 °C, the average rate constant increases from 10.2 to 39.8 1/s for the ozonation of *o*-chlorophenol, and 3.3–10.9 1/s for the oxidation of *m*-chlorophenol. For the reaction between *p*-chlorophenol and dissolved ozone, the overall rate constant varies from 10 800 to 56 000 $1/M$ s as the temperature increases from 10 °C to 35 °C. Because of limitation of the stopped-flow reactor, reliable results were not obtainable for the extremely rapid oxidation of *p*-chlorophenol at temperatures above 35 °C.

6. Discussion of the kinetic results

The results of the kinetic experiments indicate that the chlorophenol isomers are reactive with ozone in aqueous media. The rapid depletion of ozone results in the absorbance decline of a reaction mixture to approach an asymptotic value in a short period (less than 0.3 s). The reaction rates are comparable with that of the phenol–ozone reaction investigated earlier by Li et al. [12]. For instance, the overall rate constants are 21.9 1/s, 6.1 1/s and 23 600 $1/M$ s, respectively, for the ozonation reactions of *o*-, *m*- and *p*-chlorophenol in distilled water at 25 °C. At the same experimental condition, the rate constant for the ozonation of phenol is 29 500 $1/M$ s [12]. Among the three isomers, *p*-chlorophenol is the most reactive, and *m*-chlorophenol is the least reactive species in the temperature range investigated.

The temperature dependence of the rate constant is shown in Fig. 5. As suggested by the Arrhenius equation, a linear relationship exists in the semi-logarithmic plot of the rate constant versus the reciprocal of the absolute temperature. The activation energies are estimated to be 7.9, 7.5 and 11.3 k cal/mol for the ozonation of *o*-, *m*- and *p*-chlorophenol, respectively. It should be noted that electronic components of the analytical instruments are estimated to yield possible error of about 10% in the measurements. Therefore, the difference in the activation energies for the oxidation of *o*- and *m*-chlorophenol is considered statistically insignificant. The reaction rate is enhanced by the temperature for all three chlorophenols. As the temperature increases from 10 °C to 40 °C, the rate constant increases by a factor of about 3.9 and 3.3 times, respectively, for the ozonation of *o*- and *m*-chlorophenol. The rate of increase is faster for the *p*-chlorophenol–ozone system (5.2 times in the temperature range 10–35 °C).

No kinetic data are reported here for the ozonation reactions in buffer solutions, as indicated earlier. In the preliminary experiments, different reagents were used to prepare acidic buffer solutions. For example, two solutions of the same pH value of 2 were made separately using sodium phosphate and phosphoric acid in one, and hydrochloric acid and potassium chloride in another. Following the mixing of the dissolved ozone and chlorophenol contained in the buffer solutions with sodium phosphate and phosphoric acid, the absorbance increased gradually during the entire reaction life. In the mixture using hydrochloric acid and potassium chloride as the reagents, on the other hand, the absorbance declined and then increased after about 0.1 s. The opposite trends in the absorbance behaviors tend to confirm the literature

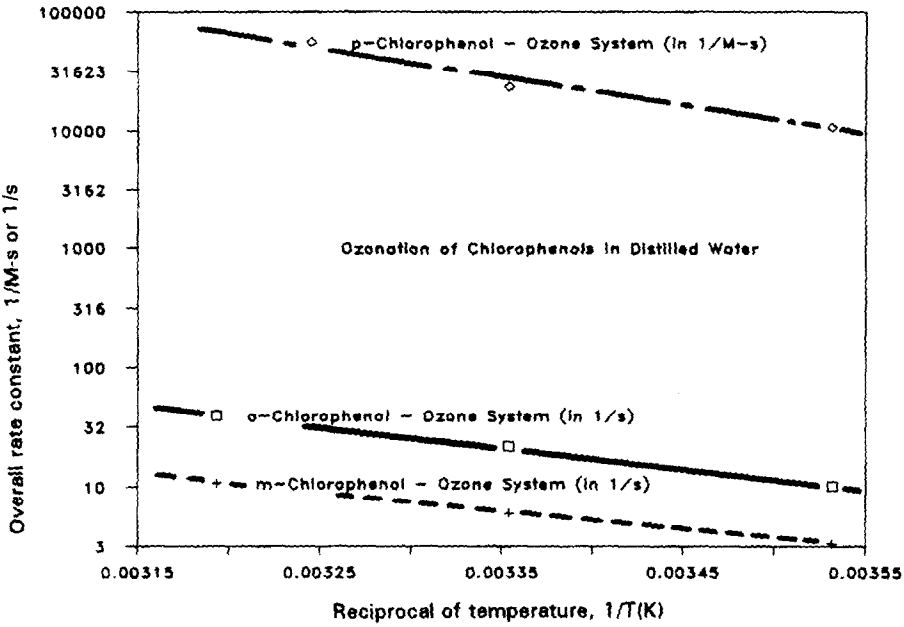

Fig. 5. Overall reaction rate constant.

report [2] that the reagents are reactive with chlorophenols to form sodium or potassium salts. The absorbances of the solutions observed in these preliminary experiments could not be those exhibited by the reaction mixtures of ozone and chlorophenols. Therefore, it is not feasible to investigate the kinetics of the ozonation reactions of chlorophenols in buffer solutions.

Contrary to the ozonation reactions of many organic compounds, the ozonation of *o*- or *m*-chlorophenol is not second order overall, as suggested in the literature [15]. At room temperature, Hoigne and Bader [15] reported that for the ozonation of *o*-chlorophenol in the pH range of 1.8–4.0, the second order, rate constant is about 1100 $1/M$ s for the molecular reaction and that the rate constant for the overall reaction including the molecular and hydroxyl radical reactions is 66 000 000 $1/M$ s at the pH value of 8. For the reaction of *p*-chlorophenol in the pH range 1.5–6.0, they gave the rate constant of 500–700 $1/M$ s for the molecular reaction. At the pH value of 8, the molecular and hydroxyl radical reactions yielded the overall rate constant of 34 000 000 $1/M$ s [15]. The results of this work show the overall rate constants of 21.9 1/s for the ozonation of *o*-chlorophenol and 23 600 $1/M$ s for the reaction of *p*-chlorophenol in distilled water (with the pH value of about 5.1) at 25 °C. Although an exact comparison is not possible, the rate constants obtained in this work are much larger than those reported by Hoigne and Bader [15] for the molecular reaction of ozone with the chlorophenols. Since the buffer reagents are reactive with chlorophenols to form salts, as discussed earlier, the rate constants reported by these authors could be those for the reactions between the salts and ozone instead of the molecules

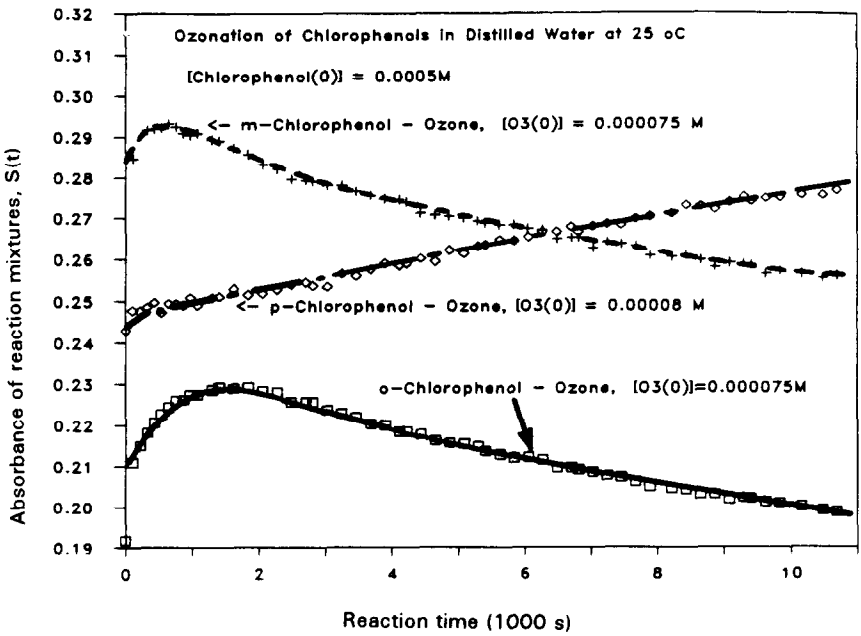

Fig. 6. Long term absorbance behavior.

of chlorophenols. The predominant role of the hydroxyl radicals, suggested by Hoigne and Bader [15], could not be confirmed because of the difficulty in studying the reaction kinetics in alkaline buffer solutions.

The long term absorbance behaviors of the reaction mixtures of chlorophenols and ozone also were investigated, as illustrated in Fig. 6. This figure reveals that the reacting solutions of *o*- and *m*-chlorophenol exhibit different absorbance behaviors from that of *p*-chlorophenol during the entire reaction life. For the ozonation of *o*- and *m*-chlorophenol, the absorbance increased rapidly to a maximum, and then declined gradually during the remaining life. Perhaps, this is indicative of formation of intermediates (ozonides) of high absorbances following the initial attack of ozone molecules. Further reaction or decomposition of the ozonides without ozone might be responsible for the gradual decline in the absorbance in the second period. The continued increase in the absorbance during the ozonation of *p*-chlorophenol for the entire reaction life might be attributable to high absorbances exhibited by the intermediate and final products of the reaction.

7. Mechanisms of the reactions

As discussed above, the overall kinetics and the absorbance behaviors all tend to suggest different mechanisms of reactions with ozone for the three isomers. The ozonation of *p*-chlorophenol seems to follow a different pathway from that of the

ozonation of *o*- and *m*-chlorophenol. Since ozone was the limiting reactant in the kinetic experiments, the dissolved ozone was depleted completely in the initial attack to form the ozonides. In the second period, the reactions or decomposition of the ozonides proceeded without ozone. As confirmed by the stoichiometric determination, three moles of ozone per mole of chlorophenol are required for the complete conversion to rupture the aromatic ring.

As discussed by the earlier investigators, chlorophenols are expected to undergo the ozonation reactions by mechanisms similar to those of phenol since they are phenolic derivatives. The mechanism for the initial reaction of ozone with the phenolic compounds is known to be an electrophilic addition [11]. Thus, the first step in the attack of ozone tends to occur at the ortho and para positions. These are positions of high electron density, and are more active compared with other positions in deducing electrophilic addition because of the resonance donated effect. Also, the ortho and para positions are more stable than the meta position because of resonance donation of the oxygen electrons. Consequently, the reaction of ozone attack at these positions becomes more favorable [11].

In the electrophilic attachment, the positively charged side of the ozone molecules would tend to attack the aromatic ring at both the ortho other than chlorine site and para position of the molecules of the chlorophenols. According to this mechanism, the ozonation of *o*- or *m*-chlorophenol would tend to form chlorinated aliphatic intermediates initially, as suggested by Shuval and Peleg [5]. In the ozonation of *o*-chlorophenol, Shuval and Peleg [5] reported that covalent C–Cl bonds on the aromatic ring were broken with ozone and that the active oxidation species attacked the aromatic ring at a site or sites other than the chlorine position. These resulted in production of the chlorinated aliphatic compounds as intermediates. This possible path of reaction is illustrated in Fig. 7 for the ozonation of *o*-chlorophenol. Similar reaction path is probably followed in the oxidation of *m*-chlorophenol, as suggested by the results of the kinetic experiments.

The intermediates would tend to decompose upon continued ozonation. The subsequent decomposition could result in the release of chlorine ion from the chlorinated aliphatic compounds, as reported by Gilbert [6, 7], and production of oxalic acid as a final product. The observation of Shuval and Peleg [5] was confirmed by Gilbert [6, 7]; he also found that chloride ion was first detected only after 40% of the *o*-chlorophenol was degraded. The rupture of the aromatic ring by ozonation also was reported by Dore et al. [9].

The ozonation of *p*-chlorophenol also is expected to initiate by electrophilic addition; the positively charged side of the ozone molecules would tend to attack at the ortho and para positions. In this case, however, chlorine ions might be released from the aromatic ring in the beginning of the reaction to form catechol because of the effect of electron-donating resonance. This result is consistent with the finding of Gilbert [6, 7]. Unlike the oxidation of *o*-chlorophenol, Gilbert [6, 7] reported the production of chloride ion in the beginning of the ozonation of *p*-chlorophenol. Further oxidation would tend to rupture the aromatic ring, and continued ozonation might result in formation of oxalic acid. The reaction path for the mechanism of oxidation of *p*-chlorophenol is illustrated in Fig. 8. Although oxalic acid could be

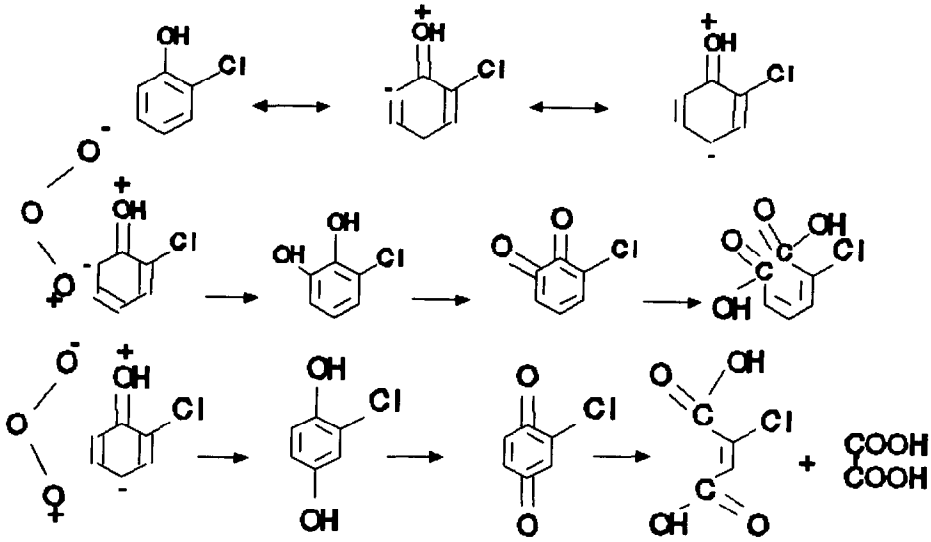

Fig. 7. Mechanism of ozonation of *o*-chlorophenol.

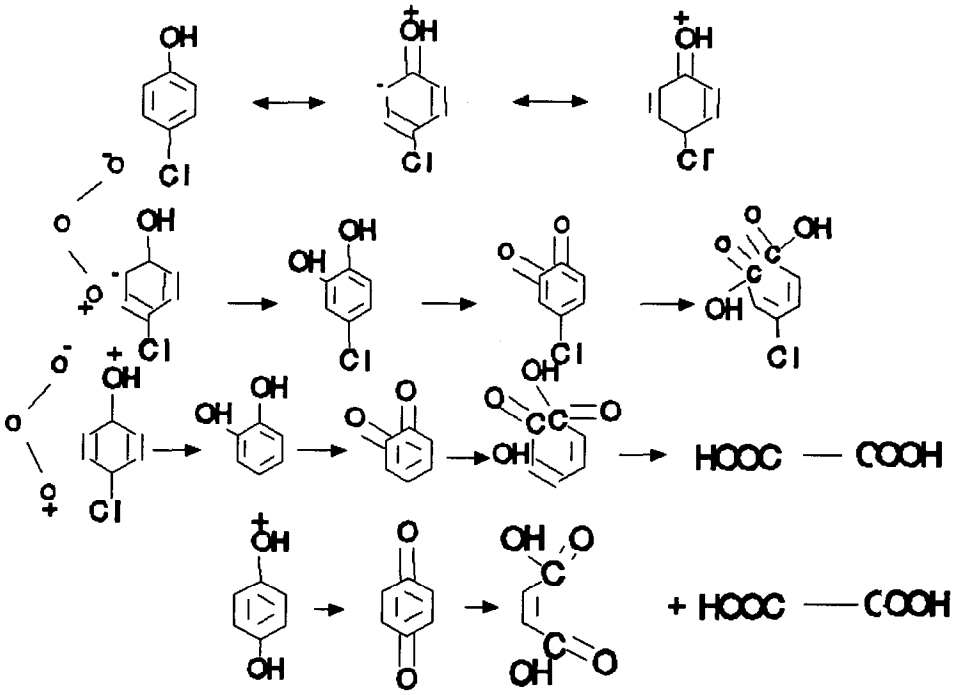

Fig. 8. Mechanism of ozonation of *p*-chlorophenol.

formed as a final product in the ozonation reactions of all three isomers, the oxidation might proceed by different paths of reactions.

As discussed above, the suggested mechanisms of the reactions seem to agree with the results reported in the literature [6, 7, 3] for the ozonation of *o*- and *p*-chlorophenol. Decoret et al. [8] indicated that complete removal of chlorophenols in pure water at low acidic pH of 4.5–6.0 was possible. As suggested by Dore et al. [9], the ozonation reaction of substituted phenols may result in formation of *o*- and *p*-benzoquinone, and the nature and position of the substituent seem to be a determinant factor in the orientation of the reaction. It should be mentioned, however, that the final products of the ozonation of mono chlorophenols have never been reported by the earlier researchers though some products of dichlorophenol–ozone reaction were identified [5–7]. Because of the different reaction paths, the absorbances and overall kinetics exhibited by the reaction mixtures could be different for the reactions of the three isomers. Therefore, the reaction mechanisms suggested above are consistent with the literature information as well as the results of the kinetic investigation conducted in this work. It should be mentioned that no steric effect has been observed by any previous investigators. In the present work, the kinetic experiments were carried out in dilute solutions, and the steric factors are unlikely to affect the measurements and calculated results.

It is well known that the aqueous phase decomposition of ozone may produce hydroxyl radical. Subsequent free radical reactions between the hydroxyl radical and chlorophenols could be significant if the hydroxyl radical is present at a sufficient concentration level; the second order rate constant for the rapid hydroxyl radical reactions is of the order of 1×10^8–1×10^{12} $1/M$ s [15]. The decomposition rate of ozone is accelerated rapidly in alkaline solutions, the first order decomposition constant increases from about 0.005 1/s in the neutral solution to about 20 1/s in the alkaline solution of the pH value of 11 at 25 °C [10]. Therefore, the hydroxyl radical reactions may play the major role in controlling the reaction pathways in the alkaline solutions. In the distilled water (the pH value of about 5.1) at 25 °C, however, the dissolved ozone decomposes slowly yielding the average first order rate constant of about 0.0002 1/s, as indicated by the preliminary tests. With the slow rate of decomposition of ozone, and in turn, the formation of hydroxyl radical at insignificant concentration level, the ozonation reaction is predominant by the direct oxidation between the chlorophenols and ozone molecules. This conclusion is similar to that observed in the earlier studies of the ozonation of several phenolic compounds [11, 14, 12].

8. Conclusions

The following conclusions can be drawn from this research:

(1) The stoichiometric determination yields the requirement of three moles of ozone for complete conversion of one mole of a chlorophenol. The result tends to

support the postulation of hexagon formula of Kekule indicating equivalent conformation of a benzene ring.

(2) The overall kinetics of the ozonation of *o*- or *m*-chlorophenol is first order with respect to the concentration of ozone and independent of the concentrations of the chlorophenols. For the ozonation of *o*-chlorophenol, the rate constant increases from 10.2 to 39.8 1/s, and for the ozonation of *m*-chlorophenol the rate constant changes from 3.3 to 10.9 1/s, as the temperature ranges from 10 °C to 40 °C. The activation energies are 7.9 and 7.5 k cal/mol, respectively for the ozonation of *o*- and *m*-chlorophenol.

(3) The overall kinetics of the ozonation of *p*-chlorophenol is second order with first order each in the concentrations of ozone and *p*-chlorophenol. The reaction rate constant varies from 10 800 to 56 000 $1/M$ s as the temperature increases from 10 °C to 35 °C in distilled water. *p*-Chlorophenol is the most reactive species of the three isomers with ozone yielding an activation energy of 11.3 k cal/mol.

(4) The ozonation of all chlorophenols is likely initiated by electrophilic addition of ozone molecules, but different pathways might be followed depending upon the position of chlorine atom. The reaction mechanisms suggested in this work seem consistent with the kinetic results and absorbance behaviors obtained in this research, and the analytical results reported in the literature.

9. Nomenclature

a	stoichiometric ratio for the limiting reactant, A
b	stoichiometric ratio for the excessive reactant, B
C_A	concentration of the limiting reactant, A (ozone)
C_B	concentration of the excessive reactant, B (chlorophenol)
k_1	rate constant for self-decomposition reaction of ozone
k_2	overall rate constant for the ozonation reaction
k'	apparent rate constant
l	order of self-decomposition reaction of ozone
m	order with respect to ozone in the ozonation reaction
n	order with respect to chlorophenol in the ozonation reaction
Ps	products of ozonation reactions
S	absorbance of the reaction mixture or solution
t	reaction time

Acknowledgements

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