A Kinetic Study of Ozone-Phenol Reaction in Aqueous Solutions

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The present research concerns mechanism and rate of reaction between dissolved ozone and phenol in homogeneous solutions. The stopped-flow technique was employed to obtain absorbances during reactions; the kinetic experiments were conducted at temperatures varying from 5° to 35°C in aqueous solutions with *p*H values ranging from 1.5 to 5.2.

The kinetic data indicated that the absorbance of a mixed solution increased rapidly in the very early portion of the reaction and then declined slowly in the remaining period. The rate of reaction in the early period was first order with respect to both phenol and ozone concentrations. The rate constant increased with *p*H value and temperature, and an activation energy of 5.74 K cal/mole was obtained. Further tests showed that the dissolved ozone was consumed completely in the first period and that in the second period the intermediate products were decomposed without depletion of ozone. Catechol, *o*-quinone, hydroquinone, oxalic acid, humic acid, and a dimer were identified from mass spectra as products of the ozonization reaction.

A free radical mechanism, with initiation of an electrophilic reaction for the formation of catechyl radical, has been proposed to explain the experimental data for phenol-ozone reaction in aqueous solutions. According to the proposed mechanism, the reaction path through the attachment to ortho position is much more favorable compared with that through the paraposition because of geometric advantage, though quinones and hydroxyphenol can be formed through parallel paths. The products of reaction detected in this research, therefore, are accountable by this mechanism. A rate equation derived on the basis of this mechanism also agrees well with that observed from the kinetic experiments.

SCOPE

Ozonization has been considered as a promising method for tertiary treatment of liquid industrial wastes. Although ozone injection technique has been applied in several industrial plants for treatment of phenolic waste, scientific information concerning the process is inadequate. In the past studies, experiments were conducted using gas-liquid contacting reactors, and the kinetic data were obscured by influences of mass transfer on rate measurements. Therefore, the stopped-flow technique was applied in this research to study kinetics of ozonization of phenol in homogeneous solutions. Influences of *p*H value and temperature on the reaction rate also were investigated. Products of the reaction were identified utilizing the technique of gas chromatography and mass spectrometry. On the basis of the experimental results, a mechanism of the reaction between phenol and dissolved ozone in aqueous solutions has been suggested.

CONCLUSIONS AND SIGNIFICANCE

Rapid reaction between dissolved ozone and phenol in aqueous solutions was studied successfully utilizing the stopped-flow technique. Absorbances measured during the early life of the reaction (as short as a few milliseconds) were important in determining the rate of consumption of ozone. The reaction was second order (first order with respect to both phenol and ozone concentrations) in the early period to form intermediates, and decomposition of the intermediates followed in the latter period of the reaction. For the experiments carried out at temperatures ranging from 5° to 35°C in the aqueous solutions with *p*H values varying from 1.5 to 5.2, the reaction rate constant increased with *p*H value and temperature. The Arrhenius equation was applied to correlate the effect of temperature on the reaction yielding a constant activation energy of 5.74 K cal/mole. This result suggests that the overall kinetics was controlled by a single-step reaction, though the mechanisms of reaction were very complex. By employing the method of gas chromatography and mass spectrometry, catechol, *o*-quinone, hydroquinone, oxalic acid, humic acid, and a dimer were identified as products of the ozonization reaction.

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A free radical mechanism, with initiation of an electrophilic reaction for the formation of catechyl radical, has been proposed to explain the experimental data for phenol-ozone reaction in the aqeous solutions. According to the proposed mechanism, the reaction path through the attachment to orthoposition is much more favorable compared with that through the paraposition because of geometric advantage. Nevertheless, both quinones and hydroxyphenol may be formed through the parallel paths. The rate equation derived on the basis of this mechanism agrees well with that observed from the kinetic experiments.

In the ozone treatment of wastewater containing phenol, it may be desirable to operate the process in neutral or acidic solution to achieve a fast rate of depletion of phenol and slow rate of decomposition of ozone. Because of formation of the intermediate products, complete oxidation of phenol to carbon dioxide may not be attainable in the ozone injection process.

Phenol is a common constituent of wastewater from many industrial processes including dye, gas, coke, and synthetic-resin manufacturers, petroleum refineries, tar distilleries, plastic, steel, and textile industries. Conventional treatment of phenolic wastewater by chlorination often results in accentuation of disagreeable taste in the effluent. Furthermore, chlorination of industrial wastewater may cause serious problems (Labine, 1959; Sliter, 1974; ES&T, 1976) because of formation of toxic residues. Therefore, many states have adopted stringent regulations concerning content of phenol allowable in effluents discharged from various industrial facilities.

Biological or activated sludge treatment have the advantages of low initial and operation costs to degrade phenol in wastewater, but the concentration of phenol can hardly be reduced to a level permissible for discharge under a reasonable retention time. Thus, it has been a common practice to utilize chemical oxidations for secondary or tertiary treatment of the wastes following biological treatments (Labine, 1959). Ozonization is a promising method in tertiary treatment (McCarthy and Smith, 1974; Sliter, 1974) of drinking and wastewaters because of high oxidizing potential of ozone. Therefore, the present work was undertaken to study kinetics of reactions between ozone and phenol in aqueous solutions.

Studies of ozonization of phenol in aqueous solutions have been reported by several investigators using gas-liquid contacting systems. Eisenhauer (1968) detected catechol and *o*-quinone in reaction solutions and suggested that phenol was consecutively oxidized down further to muconic acid, maleic acid, oxalic acid, and carbon dioxide. Bauch et al. (1970) reported that the mole ratio of ozone consumed to phenol was the predominant factor in determining the final products. At the mole ratio of 7, glycol acid, maleic acid, oxalic acid, and carbon dioxide were formed through formation of ozonide. On the other hand, Razumovskii et al. (1972) proposed a mechanism of ozone-phenol reaction through formation of free radicals. Gould and Weber (1976) found presence of catechol, hydroquinone, glyoxyl, glyoxlic acid, and oxalic acid in the reaction solutions. Anderson (1977) reported that the reaction rate between ozone and phenolate ion was at least twenty-seven times faster than the rate between ozone and molecules of phenol.

The above investigators all reported that the reaction between ozone and phenol was first order with respect to phenol. Since the reaction rates were measured in gas-liquid systems, the reaction rate constants were found to change with hydrodynamic conditions.

Reaction between ozone and phenol in a homogeneous liquid phase has never been reported by any previous investigator. In this research, the kinetics of ozone-phenol reaction in homogeneous aqueous solutions was investigated using a stopped-flow method. Such a study is advantageous in eliminating the interference of mass transfer on measurements of reaction rates. Products of the reaction were identified by the technique of gas chromatography and mass spectrometry. On the basis of the experimental results, a mechanism of the reaction between ozone and phenol has been suggested. Effects of *p*H value and temperature on the rate of reaction also were determined.

EXPERIMENTAL PROCEDURES

A Durrum-Gibson Model D-110 stopped-flow spectrophotometer was used for the kinetic study. The flow diagram and function of the stopped-flow spectrophotometer has been described in our earlier report (Kuo et al., 1977). Before kinetic measurements, the mechanical shock and Schlierin effects were tested and found insignificant in affecting the kinetic data.

The stock solution of phenol (0.536M) was prepared in a volumetric flask which was wrapped with aluminum foil and stored in a cool dark place to avoid possible degradation. This freshly prepared stock solution was used within 1 wk. Aqueous solutions of phenol were obtained by dilution of the stock solution in buffer solutions controlled by phosphates and acids to maintain desirable *p*H values. The ionic strength of the solution was kept at 0.45 by adding appropriate amount of sodium sulfate. All chemicals used were ACS grade reagents from Fisher Company.

Ozone gas was produced from a Welsbach Model T-408 ozonator using extra dry, pure oxygen. The ozone solution was obtained by bubbling ozone gas into a buffer solution which was contained in a gas washing bottle. The gas washing bottle was immersed in an isothermal bath to maintain a temperature identical to that of circulating water in the stopped-flow spectrophotometer system.

Before each experiment, solutions of ozone and phenol were stored in two separate drive syringes in the stopped-flow spectrophotometer system. By actuating the flow actuator, the two solutions were mixed rapidly in a mixing jet and allowed to flow through an observation cuvette where the mixed solution was stopped abruptly. The reaction was followed by continuous measurements of the absorbance of the mixed solution (Li, 1977).

EXPERIMENTAL RESULTS

Nature of Reactions

The kinetic data indicated that the absorbance of the mixed solution increased very rapidly in the very early life of a reaction and then declined slowly in the remaining life. The first and second periods of the reaction curve are illustrated in Figure 1 using different time scales. The rate of the first reaction was found to depend upon initial concentrations of both ozone and phenol. In the second portion, however, the rate of reaction was influenced only by the initial concentration of ozone. This indicated that in the first period of the reaction, intermediates were formed from the reaction of ozone and phenol and that in the second period decomposition and/or ozonization of the intermediates were involved.

A test was carried out to determine the nature of the reactions in the second portion. Two equal volumes (10 ml) of aqueous solutions of phenol and ozone were mixed. Immediately after mixing, nitrogen gas was introduced into the solution to bubble for 12 s, and then absorbance of the solution was measured as function of time. The experiment was repeated following the same procedure but with a longer period of bubbling (3 min). The experimental data indicated that there was no difference in the absorbance curves for both cases. Blank tests also were made by bubbling nitrogen gas in saturated solution of ozone. In a solution of 20 ml, the dissolved ozone was swept out of the solution and removed completely in 10 s. These results imply that the dissolved ozone was not involved in the second period of the ozone-phenol reactions. Thus, it may be concluded that in the second step the intermediates were decomposed without consumption of ozone. Therefore, it was only necessary to utilize the early period of the experimental data to study the rate of depletion of ozone.

Rate of Ozone Consumption

In spite of the complex nature of the mechanism of the reactions between ozone and phenol, the overall reaction can be expressed as

$$C_6H_5OH + rO_3 \rightarrow \text{products} \tag{1}$$

and the rates of depletion of ozone and phenol can be written as

$$-\frac{1}{r}\frac{d[O_3]}{dt} = -\frac{d[C_6H_5OH]}{dt} = k[C_6H_5OH]^m\,[O_3]^n \tag{2}$$

Values for r, m, and n can only be determined from experimental results.

If phenol is in large excess in a solution, then, $k[C_6H_5OH]^m$ can be regarded as a constant during the course of the reaction. Thus, Equation (2) can be rewritten as

$$\frac{d[O_3]}{dt} = -r\,k'[O_3]^n \tag{3}$$

where

$$k' = k[C_6H_5OH]_0{}^m \tag{4}$$

Equation (3) can be integrated to yield

$$\frac{[O_3]}{[O_3]_0} = e^{-rk't} \quad \text{for} \quad n = 1 \tag{5}$$

and

$$\left\{\frac{[O_3]}{[O_3]_0}\right\}^{1-n} - 1 = \frac{(n-1)}{[O_3]_0{}^{1-n}}\,rk't \quad \text{for} \quad n \neq 1 \tag{6}$$

Since absorbances were measured, the experimental data were correlated from the following relationship between ozone concentrations and absorbances:

$$\frac{[O_3]}{[O_3]_0} = \frac{D(t) - D_1}{D(0) - D_1} \tag{7}$$

D_1 is the asymptotic value of the absorbance measured in the first periods of reaction as shown in Figure 1. Derivations of Equation (7) were given by Li (1977). By substituting Equation (7) into Equations (5) and (6), the rate equations can be transformed to

$$rk't = -\ln\frac{D(t) - D_1}{D(0) - D_1} \quad \text{for} \quad n = 1 \tag{8}$$

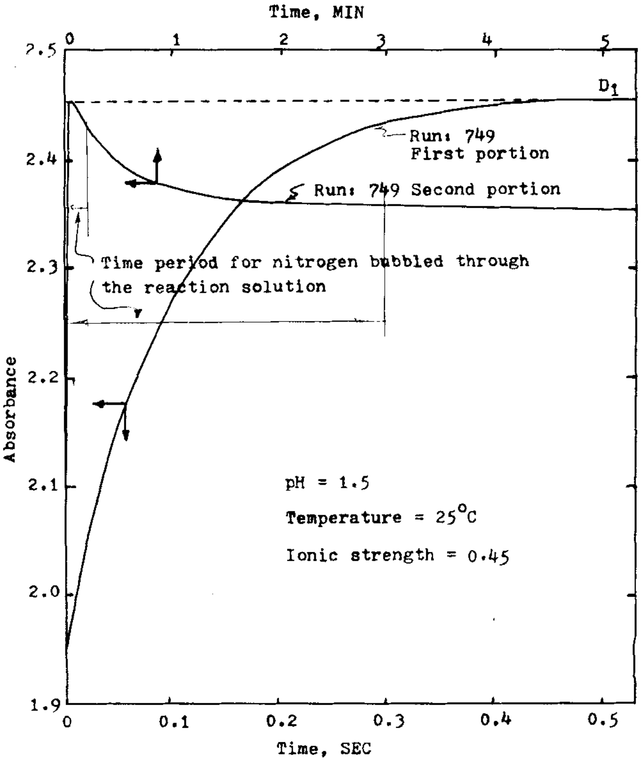


Fig. 1. Reaction curve of ozonization of phenol.

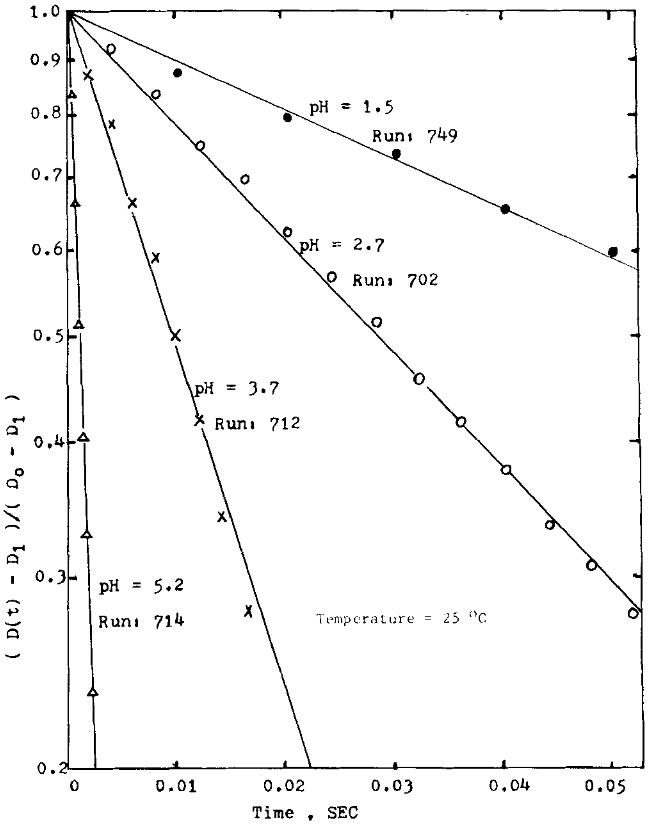


Fig. 2. Phenol-ozone reaction curves in semilogarithmic plot.

TABLE 1. REACTION RATE CONSTANT OF PHENOL-OZONE REACTION AT 25°C

pH	Run No.	$[PhOH]_0 \times 10^2$ M	k', s^{-1}	k, $M^{-1} s^{-1}$
1.5	752	0.700	6.75	964.3
1.5	749	0.583	5.33	914.2
1.5	750	0.583	4.92	843.9
1.5	753	0.350	2.91	831.4
1.5	754	0.350	2.90	828.6
1.5	755	0.292	2.89	989.7
				avg. $k = 895.4$
2.7	710	0.700	12.73	1 819
2.7	702	0.583	10.63	1 823
2.7	709	0.467	10.24	2 193
2.7	708	0.350	7.67	2 191
2.7	707	0.292	7.18	2 459
				avg. $k = 2\,097$
3.7	729	0.700	22.25	3 179
3.7	730	0.700	28.70	4 100
3.7	712	0.583	20.64	3 540
3.7	728	0.350	17.29	4 940
3.7	727	0.350	19.60	5 600
3.7	726	0.292	14.15	4 846
3.7	725	0.292	13.28	4 548
				avg. $k = 4\,393$
5.2	735	0.700	158.4	22 630
5.2	736	0.700	189.4	27 060
5.2	713	0.583	106.6	18 280
5.2	714	0.583	191.5	32 850
5.2	734	0.350	66.2	18 910
5.2	733	0.350	160.3	45 800
5.2	732	0.292	134.8	46 160
5.2	731	0.292	73.5	25 170
				avg. $k = 29\,520$

$$rk't = \frac{[O_3]_0^{1-n}}{n-1}\left[\left(\frac{D(t)-D_1}{D(0)-D_1}\right)^{1-n} - 1\right] \quad \text{for } n \neq 1 \quad (9)$$

The kinetic data from the first period of the reaction were correlated by Equations (8) and (9) using assumed values of n. The experimental data were best fitted for $n = 1$, implying that the reaction was first order with respect to ozone concentration. These correlations are demonstrated in Figure 2 by plotting $[(D(t) - D_1)/(D(0) - D_1)]$ vs. the reaction time in a semilogarithmic scale to yield straight lines. The values of rk' then can be obtained from the slopes of the straight lines (Li, 1977).

The stoichiometric ratio r has been shown to vary from 1 to 5 by several previous investigators (Bauch, 1970; Eisenhauer, 1968; Razumovskii et al., 1972). In this research, the value of r was found to be 2 by using the aminoantipyrine method to determine the phenol concentrations (Emerson, 1943; Martin, 1949) before and after reaction with a known amount of ozone. If we use the r value of 2, the pseudo first-order reaction rate constant k' can be calculated, and the values at 25°C are shown in Table 1 and Figure 3. Results obtained for other temperatures are given elsewhere (Li, 1977).

The order with respect to phenol concentration m can be determined by plotting k' vs. the initial concentration of phenol in a logarithmic scale. A straight line can be obtained in such a plot as indicated by Equation (10):

$$\log k' = \log k + m \log [C_6H_5OH]_0 \quad (10)$$

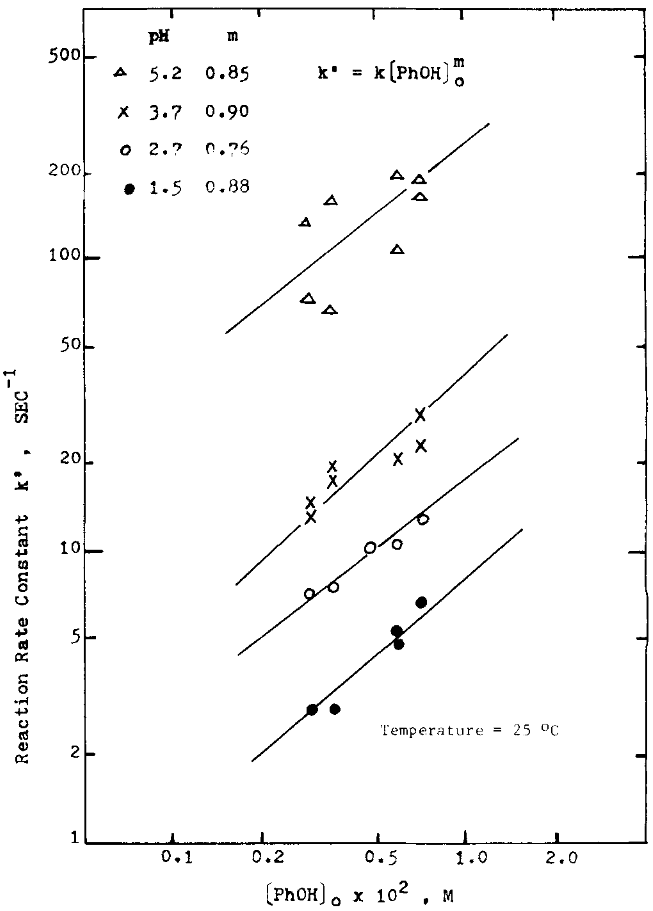


Fig. 3. Determination of reaction order with respect to phenol.

The slopes of these straight lines are equal to m for the experimental runs. Using the method of least squares, the average value of m was obtained to be 0.85 as shown in Figure 3. This result seems to suggest that the reaction was first order with respect to phenol concentration. The second-order reaction rate constant k then can be calculated from the Equation (4) and is included in Table 1.

From the above analysis, the rate equation for ozone-phenol reaction in aqueous solution is determined as

$$-\frac{1}{2}\frac{d[O_3]}{dt} = -\frac{d[C_6H_5OH]}{dt} = k\,[C_6H_5OH]\,[O_3] \quad (11)$$

At a constant temperature, the rate constant k varied only with pH of the aqueous solution. The average values of k for pH of 1.5, 2.7, 3.7, and 5.2 are given in Table 1 for experiments conducted at 25°C. The results in the table indicate that k increases with pH value of the reaction solution, and the rate of increases is faster in the range of higher pH values. This seems to indicate that ozone molecules react with both phenol molecules and phenolate ions. As reported by Anderson (1977), the rate of ozone-phenolate reaction was faster than that of ozone-phenol reaction. At a higher pH value, more phenolate ions are dissociated from phenol molecules, and, therefore, a higher reaction rate constant is obtained. Because of the limitation of stopped-flow spectrophotometer, rate constants for solutions with pH value higher than 5.2 have not been obtained.

For solutions of the same pH value, the temperature dependence of k may be correlated by the Arrhenius equation as shown in Figure 4. The activation energy obtained from slopes of the straight lines is 5.74 Kcal/mole at pH

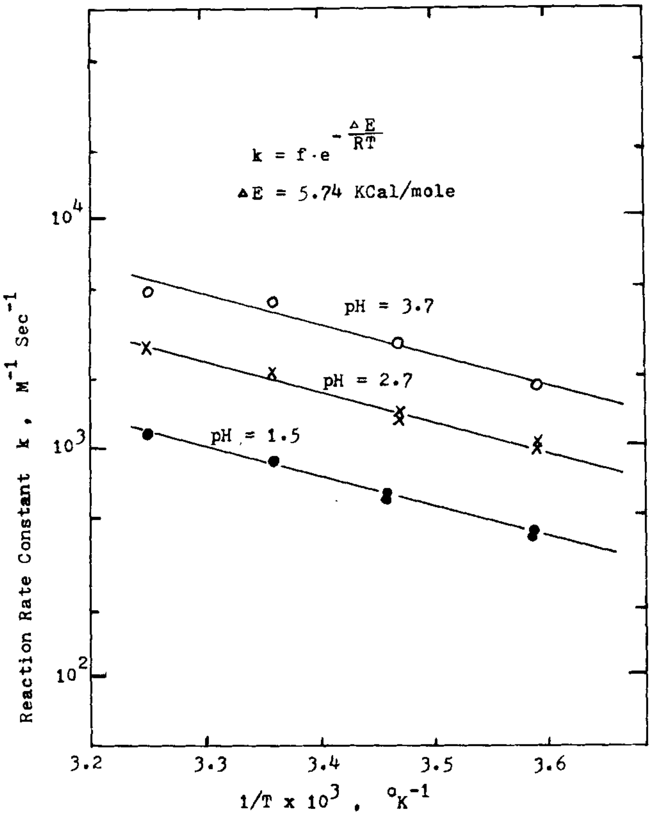


Fig. 4. Effect of temperature on rate constant.

values of 1.5, 2.7, and 3.7. This result tends to suggest that the kinetics of ozone-phenol reaction is controlled by a single step reaction, though the actual mechanism of reaction may be quite complex.

Reaction Products

Although the rate equation has been formulated and rate constants calculated from the experimental data, kinetic data usually are insufficient to derive a complete and unique reaction mechanism because of ambiguity in mechanistic interpretation of the rate law (Haim, 1966). Such ambiguity may be circumvented by using other information including results of identification of final products and explanation of formation of intermediates.

For identification of the final products, a saturated ozone solution of 200 ml was mixed with 3.7 ml of phenol solution at a concentration of 0.01 M. About 100 ml of the mixed solution was then extracted by ether four times, using 25 ml in each extraction. The extracted solutions were combined and evaporated at room temperature to 0.5 ml. Samples of the concentrated ether solution were injected into a Hewlett Packard Model 700 gas chromatograph using OV-17 (6 ft × ⅛ in.) as the separation column. Results of the chromatogram are shown in Figure 5.

Standard solutions were prepared by dissolving pure reagents of phenol, catechol, hydroquinone, *p*-benzoquinone, and oxalic acid in ether. Using the same separation column, chromatograms of these standard solutions were obtained as shown in Figure 6. By comparing retention times of the peaks in Figures 5 and 6, oxalic acid (peak number 1), catechol (peak number 4), and hydroquinone (peak number 5) can be verified.

Identification of the two unknown peaks (numbers 3 and 6) from the chromatograms was not possible by comparing the retention times with those of standard reagents including *p*-benzoquinone, trans-trans muconic acid, fumaric acid, tataric acid, and resocinol. In order to identify these two unknown products, a GC-Mass Spectrometer (Perkin-Elmer Model 270) was used. The mass spectra of peaks number 3 and 6 are shown in Figure 7 and 8, respectively. From Figure 7, the peak number 3 can be verified to be the chromatogram of *o*-quinone with a very small amount of humic acid.

The mass spectrum shown in Figure 8 gives a parent peak at the mass number of 220. This molecular weight

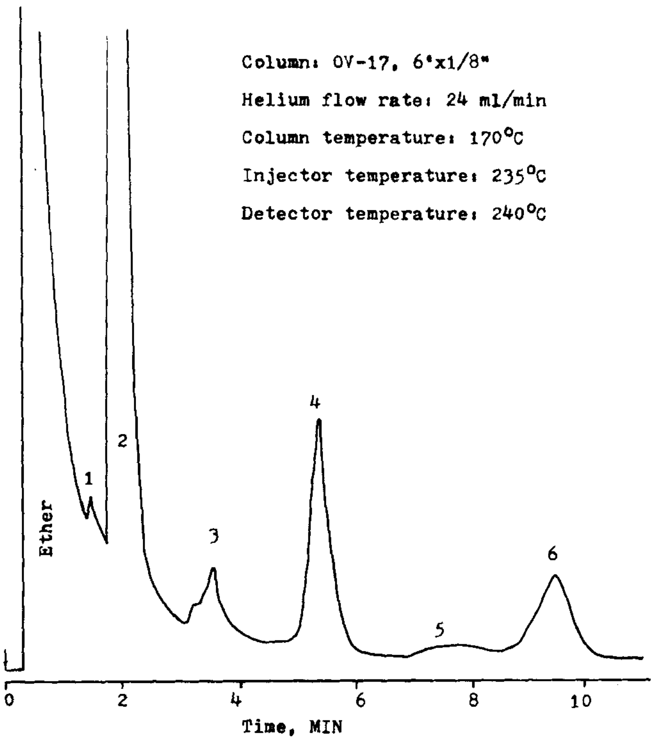


Fig. 5. Gas chromatogram of phenol—ozone reaction products in aqueous solution.

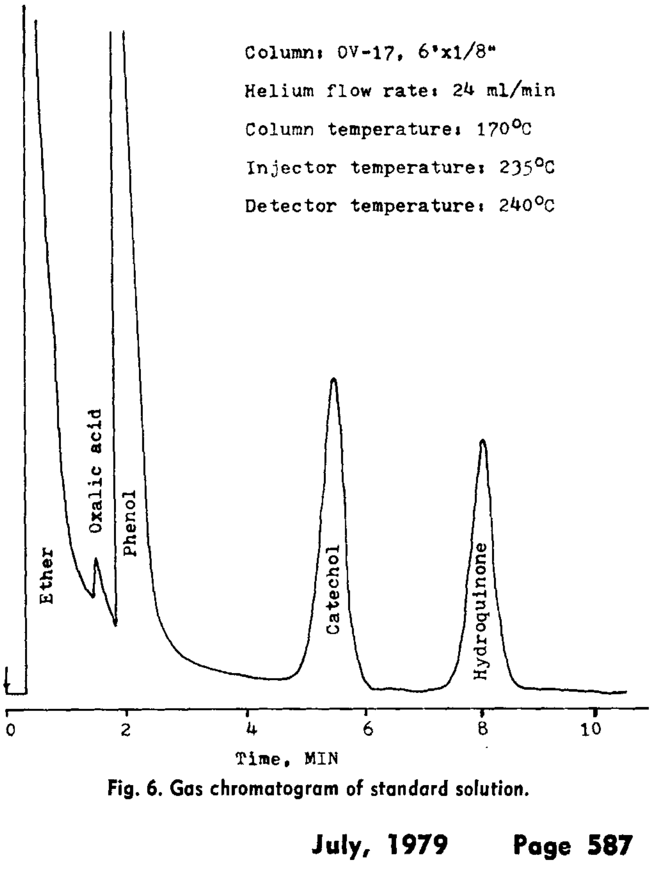


Fig. 6. Gas chromatogram of standard solution.

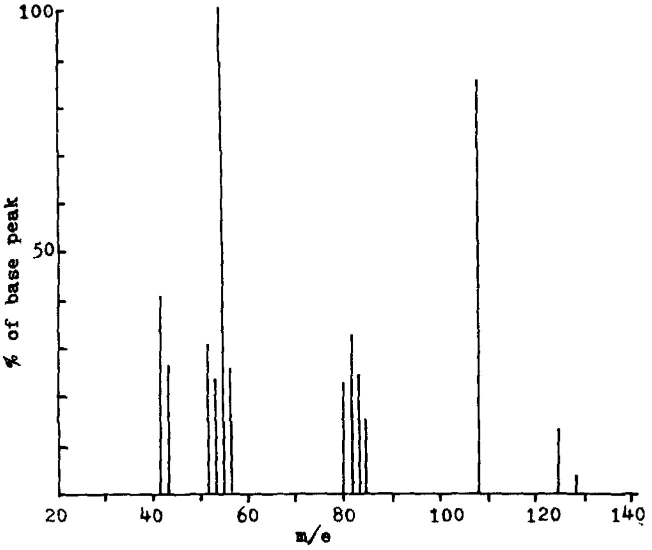


Fig. 7. Mass spectrum of No. 3 peak.

of 220 is larger than that of muconic acid (molecular weight = 142), the largest molecule expected in the reaction solution. This suggests that a dimer might have been formed during the reactions.

MECHANISM OF THE REACTION

Experimental Evidences

Eisenhauer (1968) proposed a mechanism of consecutive reaction between phenol and ozone in aqueous solution. He postulated that phenol can be oxidized consecutively to catechol, *o*-quinone, muconic acid, fumaric acid, oxalic acid, and carbon dioxide. According to the mechanism, the reaction in the first step is first order with respect to both phenol and ozone concentrations, and only a small amount of quinones and acids can be produced. In the present research, however, significant quantities of *o*-quinone, oxalic acid, and a dimer were observed, and the absorbance of the solution during the course of reaction could not be accounted for from the molar absorptivities of phenol ($\epsilon_{245} = 300$) and/or hydroquinone ($\epsilon_{245} = 850$). Therefore, the mechanism proposed by Eisenhauer can not be applied to explain the experimental results obtained in this research.

Another parallel-consecutive reaction mechanism was proposed by Baily (1972). According to his proposition, phenol may be oxidized to form catechol and muconic acid, and further ozonization of catechol may result in production of muconic acid through *o*-quinone as an intermediate. Under this condition, the reaction is first order with respect to ozone but is not first order with respect to phenol unless the second and third steps proposed by Baily (1972) are negligible. Also, appreciable quantities of catechol and muconic acid should be produced as final products. Again, this mechanism can not be applied to explain significant quantities of *o*-quinone, oxalic acid, and a dimer formed in the experiments carried out in the present research.

Formation of Free Radicals

In order to obtain additional information, the molar absorptivity of the intermediate was calculated. In a liquid phase, the absorbance may be calculated from the Beer law. Therefore, under the assumption of additive property of the absorbance, the following equations can be formulated:

TABLE 2. MOLAR ABSORPTIVITY, CHROMOPHORE AREA AND EQUIVALENT DIAMETER OF THE INTERMEDIATE

pH	Average $\epsilon_{\text{intermediate}}$	Effective chromophore area $\times 10^{16}$ cm^2	Equivalent diameter $\times 10^8$ cm
1.5	7 589	0.87	1.05
2.7	7 026	0.81	1.02
3.7	5 707	0.66	0.92
5.2	4 668	0.54	0.83

$$D_0 = b \cdot [\epsilon C_6H_5OH \cdot (C_6H_5OH)_0 + \epsilon_{O_3} \cdot (O_3)_0] \tag{12}$$

$$D_1 = b \cdot [\epsilon C_6H_5OH \cdot (C_6H_5OH)_1 + \epsilon_{\text{intermediate}} \, (\text{intermediate})] \tag{13}$$

Since the concentration of phenol was in large excess in the reaction solution and ozone was completely consumed, we have

$$[C_6H_5OH]_0 = [C_6H_5OH]_1 \tag{14}$$

$$[\text{Intermediate}]_1 = \tfrac{1}{2}[O_3]_0 \tag{15}$$

From Equations (12) through (15), inclusive, the molar absorptivity of the intermediate can be derived:

$$\epsilon_{\text{intermediate}} = 2\left[\frac{D_1 - D_0}{b \cdot [O_3]_0} + \epsilon_{O_3}\right] \tag{16}$$

The average values of $\epsilon_{\text{intermediate}}$ at pH values of 1.5, 2.7, 3.7, and 5.2 are given in Table 2.

A semiempirical equation has been suggested by Braude (Jaffe and Orchin, 1965) to correlate the maximum molar absorptivity and effective chromophore area:

$$\epsilon = 0.87 \times 10^{20} \, a \tag{17}$$

The effective chromophore area is defined as the area where falling light is completely absorbed. This absorbed light energy causes a transition of electrons from ground state to excited state and results in a high absorbance.

From Equation (17), the effective chromophore area of the intermediate can be estimated, and the results are included in Table 2. These values are smaller than the chromophore area of π-bond which usually has the value of about 2×10^{-16} cm^2.

By considering the chromophore area of a sphere, an equivalent diameter may be obtained from

$$d = (4\,a/\pi)^{1/2} \tag{18}$$

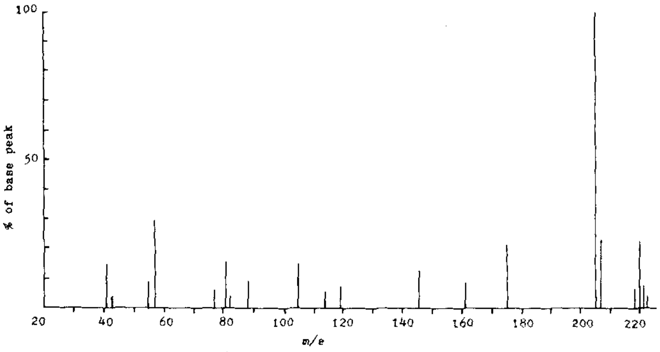
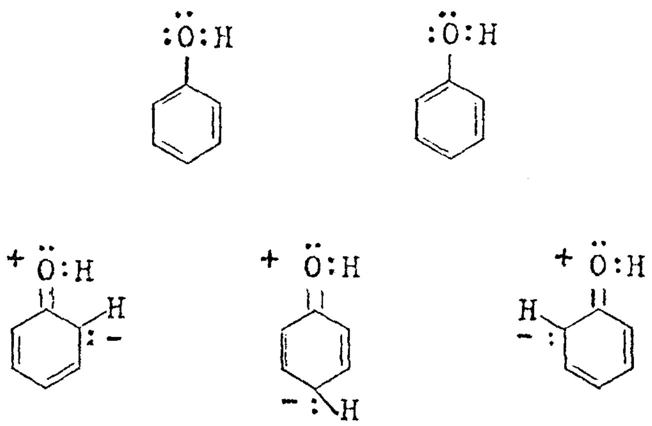


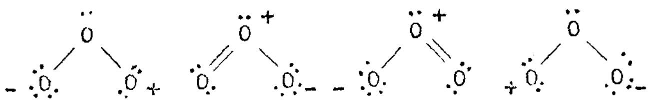
Fig. 8. Mass spectrum of No. 6 peak.

As can be seen from Table 2, the calculated results show that the equivalent diameter has the same dimension as that of an atom, 10^{-8} cm. This implies that the electron, which absorbed light and yielded high absorbance in the first portion of the reaction, might be an unpaired electron of a free radical.

From the view point of resonance, the molecules of phenol may be presented in the aqueous solution with the following configurations:

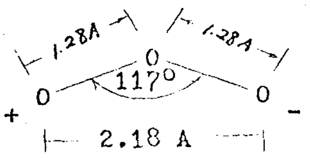


Because of resonance, the electron density at ortho or para position of the ring is higher than that at meta position; the positions with high electron density are more active compared with other positions in inducing electrophilic addition. The resonance of ozone molecules may be expressed as

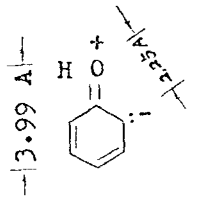


The first step in the ozonization of phenol is known to be an electrophilic addition (Bailey, 1958). Thus, the positive charged side of the ozone molecules would tend to attack the positions of high electron density in the phenol molecules. This could result in production of catechol twice as much as that of hydroquinone. However, the amount of catechol was much more than twice of hydroquinone in the experiments conducted in this research. This might be attributed to the effect of geometric factor as discussed below.

The geometric dimensions of ozone and phenol can be found from many textbooks (Cotton, 1967; Morrison, 1966):

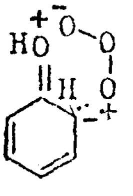


Ozone

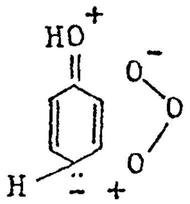


Phenol

The distance between the positive and negative charged sides of the ozone molecule is about 2.18 A. This value is very close to the distance from the negative charged ortho position to the positive charged oxygen of the phenol molecule. When the positive charged oxygen of the ozone is attached to the ortho position, the negative charged side becomes close to the positive charged oxygen of the phenol molecule. This results in neutralization of electric charge and reduction of potential energy of the transition state (Morrison, 1966). Consequently, the reaction of ozone with phenol at the ortho position becomes favorable. On the other hand, a favorable geometric factor does not exist in the attachment of ozone at the para position of phenol molecule. Therefore, the electrophilic addition at the para position is not as easy as that at the ortho position. This might explain the reason of production of catechol at a quantity more than twice of hydroquinone in the ozone-phenol reaction products. This geometric consideration can be visualized in the following picture:

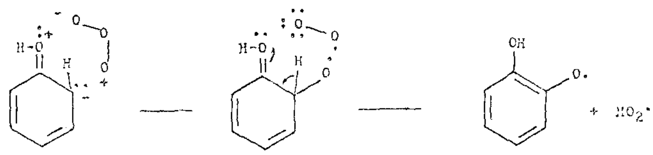


Ortho position
attachment



Para position
attachment

During the transition state in the electrophilic addition at the ortho position, the compound also may undergo an electron rearrangement forming a free radical of catechol and a radical HO_2. The initial steps for formation of the free radicals are



Phenol and ozone — Transition state — Free radicals

Mechanism Proposed

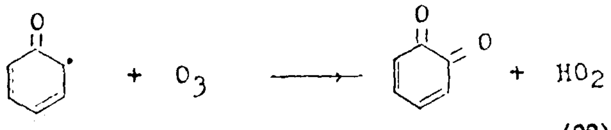
The reaction between phenol and ozone is initiated mainly by an electrophilic attachment to form a catechyl free radical as discussed above:

(19)

Following the initial step for formation of the free radicals, a series of chain reactions may take place as follows:

(20)

(21)



(22)

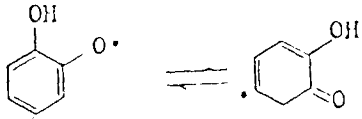
From the above chain reactions, catechol and *o*-quinone may be formed by parallel steps. The chain reaction may be terminated by the following steps:

$$HO\cdot + HO\cdot \rightarrow H_2O_2 \qquad (23)$$

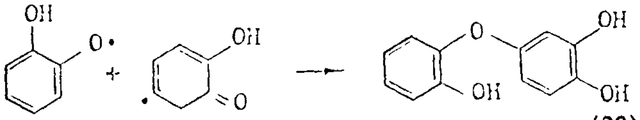
$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2 \qquad (24)$$

According to the above mechanism of free radical reaction, hydrogen peroxide may be formed during the reaction as indicated by Equations (21), (23), and (24). Hydrogen peroxide and *o*-quinone were detected by Iscaas (1922) and Stein and Weiss (1951).

According to the mechanism proposed, a stable dimer could be formed through the isomerization of the catechyl free radical (Thompson, 1964):



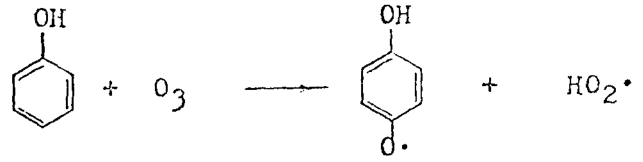
(25)



(26)

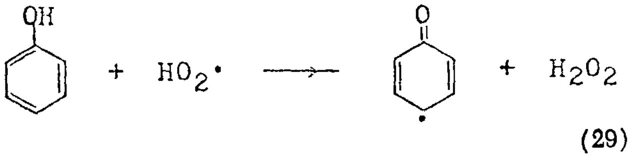
The compound indicated by the peak number 6 in gas chromatogram was quite stable and is suspected to be the dimer produced through the reaction step (26).

In addition to the major reaction steps discussed above, some minor reactions also could occur. These include attachment of ozone to the para position of the ring to undergo the following reactions:



(27)

(28)

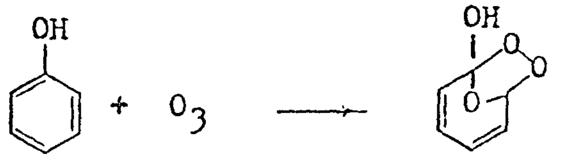


(29)

(30)

Since the minor reactions through the above steps are insignificant, the amount of quinhydrone formed by combination of hydroquinone and *p*-benzoquinone may be neglegible.

In the solution, an ozonide could be formed by an attachment of the ozone molecule to the π bond of the ring (Bailey, 1958):

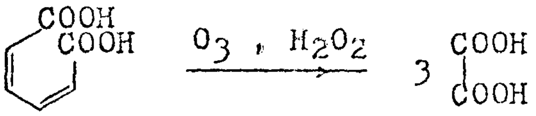


(31)

Although the structure is not well understood, the ozonide is known to be unstable and can be easily decomposed through opening of the ring to form muconic acid:

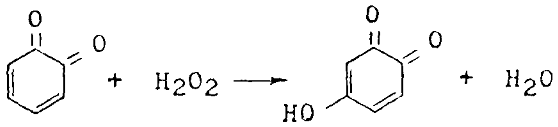
(32)

Since muconic acid has not been detected in the present work, it is likely that the unsaturated hydrocarbon was oxidized further to oxalic acid:

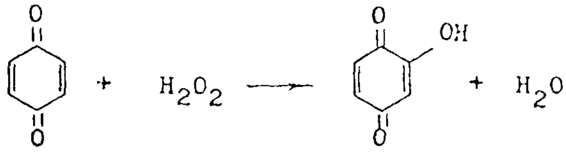


(33)

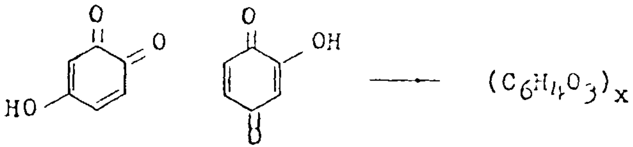
A small quantity of humic acid found in the final products was probably formed through the following reaction steps:



(34)

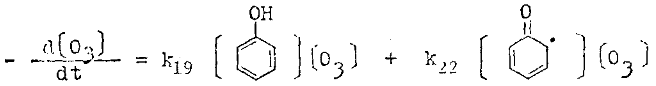


(35)



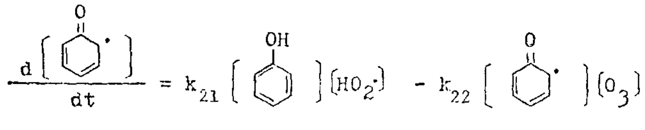
(36)

Derivation of a rate equation taking into account all above-mentioned reactions is difficult. Nevertheless, the following equation can be derived to account for ozone consumed in the major reaction steps from (19) to (26), inclusive:

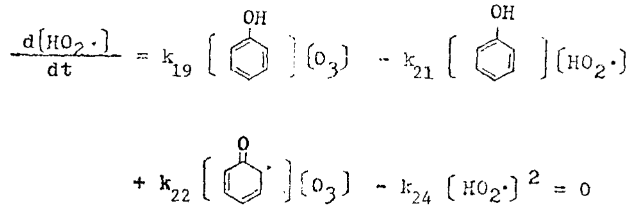


(37)

Under the assumption of steady state (identical rates of formation and disappearance of an intermediate), we have

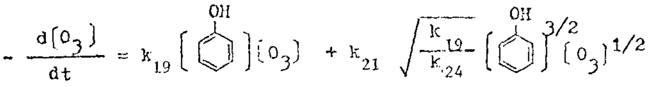


$$\frac{d[C_6H_5O\cdot]}{dt} = k_{21}[C_6H_5OH][HO_2\cdot] - k_{22}[C_6H_5O\cdot][O_3] = 0 \qquad (38)$$



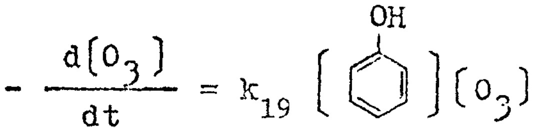
$$\frac{d[HO_2\cdot]}{dt} = k_{19}[C_6H_5OH][O_3] - k_{21}[C_6H_5OH][HO_2\cdot] + k_{22}[C_6H_5O\cdot][O_3] - k_{24}[HO_2\cdot]^2 = 0 \qquad (39)$$

By combining Equations (37), (38), and (39), the following rate equation can be derived:



$$-\frac{d[O_3]}{dt} = k_{19}[C_6H_5OH][O_3] + k_{21}\sqrt{\frac{k_{19}}{k_{24}}}[C_6H_5OH]^{3/2}[O_3]^{1/2} \qquad (40)$$

Since the reaction for termination of the radical $HO_2\cdot$ is usually much faster than that for initiation of the radical, it may be reasonable to assume that k_{24} is much larger than k_{19}. Under this condition, the second term on the right-hand side of Equation (40) may be neglected, and the rate equation can be simplified to



$$-\frac{d[O_3]}{dt} = k_{19}[C_6H_5OH][O_3] \qquad (41)$$

The above equation implies that the reaction is first order with respect to both phenol and ozone concentrations. This is in agreement with the results obtained from the present experiments. A slight deviation from the first order to phenol concentration might be attributed to the fact that a small fraction of phenol was consumed in the minor reactions. Equation (41) also shows that the reaction is controlled by a single step reaction. This is confirmed by analyses of the experimental data to yield a constant activation energy at various pH values of the aqueous solutions as discussed in an earlier section. Consequently, the mechanism proposed in this research can be employed to explain both the kinetic data and the formations of the final products identified in this research.

It should be mentioned that under the conditions of experiments, the rate of decomposition of ozone was slow compared with that of ozonization of phenol (Kuo et al., 1977; Li, 1977). Therefore, the decomposition was insignificant in influencing the rate of ozone consumption in the ozonization reactions.

NOTATION

a = effective chromophore area, cm^2
b = length of the optical path, cm
d = equivalent diameter, cm
D = absorbance at time t
D_0 = initial absorbance
D_1 = asymptotic absorbance measured in first period of reaction
ΔE = activation energy, K cal $mole^{-1}$
f = frequency factor, l $mole^{-1}$ s^{-1}
k = second-order reaction rate constant, l $mole^{-1}$ s^{-1}
k_i = reaction rate constant for the reaction given in Equation (i)
k' = pseudo first-order reaction rate constant, s^{-1}
m = reaction order with respect to phenol
n = reaction order with respect to ozone
r = stoichiometric ratio
R = gas constant, cal $°K^{-1}$ $mole^{-1}$
T = absolute temperature, °K
t = reaction time, s
ϵ = molar absorptivity, l $mole^{-1}$ cm^{-1}

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