PHOTO-OXIDATION OF PHENOLS WITH OZONE

TSUTAO OTAKE, SETSUJI TONE, KOJI KONO
AND KATSUMI NAKAO

*Department of Chemical Engineering,
Osaka University, Toyonaka 560*

The aqueous-phase photo-ozonization of phenols in concentrations ranging from 800 ppm to 1500 ppm was carried out by employing two kinds of reactors, one being a bubble column and the other a stirred cell having a gas-liquid free interface. The oxidation of phenols with ozone alone was also performed for comparison.

The kinetic data from the stirred cell revealed that both photo-ozonization and ozonization fell into the fast pseudo-first order regime for simultaneous mass transfer and reaction. The intrinsic reaction rate constants for the degradation of various phenolic compounds were determined, based on the chemical absorption theory, from the data of the ozonizations in the bubble column over a wide range of variables.

Product distributions were elucidated for removal of phenol and of its primary and secondary oxidation products. The overall reaction pathway was regarded as being comprised of the two successive oxidation series, each of which produced the same smaller molecules. The pH value as well as ultraviolet light intensity exerted negligible influence on the overall reaction pathway, but they enhanced the rate of each oxidation step.

Ultraviolet radiation promoted remarkably the efficiency of ozone absorption in the later stage of ozonization rather than the application of higher pH.

Introduction

Much attention has been given to advanced wastewater treatment processes not only for environmental protection but also for water reuse. Particularly, ozonization^{7,9,10,13} and photo-ozonization^{14,16} are potentially effective in removing refractory compounds and toxic impurities.

There have been a few studies^{5,6,16} on the rate and efficiency of ozonization. Unfortunately, there are apparent inconsistencies in the literature. This is considered due to the different reactivity of ozone in water^{2,3,8}, and to the difficulty in separating the effects of chemical kinetic process and ozone mass transfer between the gas and liquid phases⁷.

The purpose of this paper is to study the reaction of ozone with dilute solutions of phenolic compounds, a common aromatic component in industrial wastes. Ozonization as well as photo-ozonization were carried out by using both bubble column and stirred cell with gas-liquid free interface to evaluate effects of important variables such as concentrations of ozone and phenolic compound, pH of the reaction mixture, substituent group of phenol, temperature and ultraviolet radiation intensity. The study was limited to the determination of (a) kinetic regime for mass transfer and reaction, (b) the rate at which a phenolic compound was

destroyed by ozone, (c) its ozonization products and their behavior under continued application of ozone and (d) the efficiency of ozone consumption.

1. Experimental

Figure 1 is a schematic drawing of the apparatus. The Pyrex glass bubble column (volume: 2000 ml) was run batchwise with respect to the liquid phase, and a sintered glass plate as gas distributor was placed at the center of the bottom. A cylindrical low-pressure mercury lamp (40 watts) was positioned at the axis of the column.

To evaluate the kinetic regime for chemical absorption, a stirred cell with gas-liquid free interface (volume: 500 ml, gas-liquid interfacial area: 53.2

Fig. 1 Schematic diagram of experimental apparatus

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(a) Ozonization

(b) Photo-ozonization

Fig. 2 $2(\sqrt{[A]_0} - \sqrt{[A]})$ vs. reaction time

Fig. 3 $\log k_1$ vs. $\log [O_3]_i$ for phenol degradation

cm²) was employed, being equipped with two stirrers to homogenize the respective phases. Kinetic data were obtained under the condition that the rate of ozonization was virtually unaffected by stirring speed.

The reactor was charged with feedwater containing the desired amount of a phenolic compound. When the solution temperature reached the desired level, the reaction was started by introducing ozone and air mixture of desired concentration. Gas flow rate was such that superficial gas velocity u_g exerted negligible influence on the rate of ozonization. Liquid samples were withdrawn periodically and analyzed for concentrations of the reactant and its oxidation products with a high-performance liquid chromatograph. Dur-

ing the reaction, pH of the reaction mixture and the ozone concentration of the exit gas stream were measured by a pH meter and the standard iodometric procedure, respectively. The scope of the experiment and the analytical procedures used are listed in Table 1.

2. Results and Discussion

2.1 Kinetic regime for mass transfer and reaction

The rates of chemical absorption of ozone per unit interfacial area, N_{O_3} , were obtained by using the stirred cell. These data proved that the following condition was satisfied:

$$3 < \beta \equiv N_{O_3}/k_L[O_3]_i \ll q \equiv D_A[A]/D_{O_3}[O_3]_i$$

Here the values of k_L were estimated from the results of Teramoto *et al.*¹⁵⁾ and Yano *et al.*¹⁸⁾, since the order of magnitude of k_L sufficed for the determination of kinetic regime. The values of D_{O_3} were estimated by the method of Wilke *et al.*¹⁷⁾. The values of D_A ¹¹⁾ and $[O_3]_i$ ¹²⁾ were available in the literature.

Both ozonization and photo-ozonization are, therefore, regarded as the fast pseudo-first order regime for chemical absorption. In other words, the degradation rate of a phenolic compound is controlled by the diffusion rate of ozone in the liquid film.

2.2 Effect of ozone and phenolic compound concentrations

For the fast pseudo-first order regime with the assumed second order reaction between dissolved ozone and phenolic compound A, the apparent rate of disappearance of A, taking account of mass transfer, is given by

$$-d[A]/dt = k[A]^{1/2}[O_3]_i \quad (1)$$

$$k = a\sqrt{k_0 D_{O_3}} \quad (2)$$

where k is apparent reaction rate constant and a gas-liquid interfacial area per unit volume of the liquid phase.

With a constant concentration of the dissolved ozone the integrated form of Eq. (1) is

$$2(\sqrt{[A]_0} - \sqrt{[A]}) = k_1 t \quad (3)$$

$$k_1 = k[O_3]_i \quad (4)$$

Figures 2 (a) and (b) show a plot of $2(\sqrt{[A]_0} - \sqrt{[A]})$ versus t for the ozonization and photo-ozonization of various phenolic compounds, respectively. All the data in Fig. 2 were obtained in the bubble column during the earlier stage of oxidation so that the amount of ozone consumed by the consecutive oxidation might be negligible. As shown in the figure, the result for each ozonization gives a straight line through the origin. Thus the overall reaction was found to be a half-order with respect to phenolic compound. Figure 3 is a logarithmic plot of k_1 , the slope of straight line of Fig. 2, versus $[O_3]_i$. The value of $[O_3]_i$ was approximated

Table 1 Experimental conditions and analytical procedures

Raw materials	Phenol, <i>p</i> -Nitrophenol, <i>p</i> -Aminophenol, <i>m</i> -Aminophenol, Hydroquinone, Resorcinol, <i>p</i> -Benzoquinone
Initial concentration of raw materials	800–1500 mg/l
Ozone concentration	800–1800 ppm
Superficial gas velocity	1.0–3.5 cm/sec
pH	2–11
Reaction time	60–180 min
Reaction temperature	5–25°C
Light source	Low-pressure mercury lamp (40W)
Measurement of pH	pH meter
Measurement of ozone concentration	Iodometry
Analysis of raw materials and products	High-performance liquid chromatograph (Shimadzu-Du Pont Model LC-830) Detector: UV spectrophotometer Column: Zorbax SIL, Zipax SAX (Shimadzu-Du Pont)

by the liquid-phase concentration in equilibrium with the logarithmic mean value of ozone partial pressures at the inlet and outlet of the reactor. The ozone partial pressure at the outlet was obtained by averaging the instantaneous value over the reaction time. This figure shows that the degradation rate is first-order with respect to ozone.

Recently, Wako¹⁶⁾ reported that for photo-ozonization using a high-pressure mercury lamp the phenol removal rate was a half- and first-order with respect to phenol and ozone, respectively. The result is considered to correspond to the above reaction rate expression, i. e., Eqs. (1) and (2) for the fast pseudo-first order regime of simultaneous mass transfer and reaction.

2.3 Effect of reaction conditions on k_0

For the ozonization carried out in the bubble column, superficial gas velocity u_G greater than 2.5 cm/sec exerted practically no influence on the removal rate of phenolic compound. This may be because the interfacial area does not increase at gas velocities above 2.5 cm/sec under the present experimental conditions.

The constant interfacial area a of the bubble column can be evaluated based on Eq. (1) by knowing the values of the overall rate $-d[A]/dt$, the diffusivity of ozone D_{O_3} and the intrinsic rate constant k_0 . The last is determined from the kinetic data of ozonization in the stirred cell with a known interfacial area. When the value of a is known, the intrinsic rate constant k_0 can be calculated by using Eq. (2) from the data of ozonization in the bubble column over wide ranges of variables such as ozone and phenolic compound concentrations, pH, substituent group, temperature and ultraviolet light intensity.

Under the present experimental conditions, the values of a were found to be 5 to 8 cm²/cm³. Based on

Fig. 4 Relationship between k_0 and pH

the present value of k_L ¹⁾, the values of k_0 determined in the above work were shown to satisfy the condition that $\beta = \gamma = (3 \text{ to } 10) \ll q = (500 \text{ to } 700)$. That is, the fast pseudo-first order regime was well established in the bubble column considering that the estimated values of a and k_L would be somewhat larger than the actual ones, which might be nearly equal to the values for the foam bed.

1) **Effect of pH** Figure 4 represents the result of the effect of pH on k_0 for phenolic compounds. The value of k_0 is found to increase remarkably with pH. This is probably because the higher value of pH is advantageous for an increase in concentration of phenolate ion, which would promote electrophilic addition of ozone to phenolic compound according to the Bailey mechanism⁴⁾.

The rate constant for ozonization with ultraviolet radiation is seen to be greater than that for ozonization alone. A fractional increase in rate constant due to ultraviolet radiation is also found to remain almost constant regardless of pH.

2) **Effect of substituent group** Figure 5 presents a Hammett's plot of the reaction rate constants for various phenolic compounds. In both ozonization and photo-ozonization the reaction constant ρ , that is, slope of a straight line is found to be clearly negative. This supports the supposition that electrophilic reaction of ozone would proceed. The difference between the values of ρ for *m*- and *p*-substituted phenols suggests that electrophilic attack of ozone on the aromatic ring may take place at *o*- and *p*-positions.

3) **Effect of temperature** The activation energy of the rate of *p*-nitrophenol removal by ozone was found to be 16.2 kcal/mol from the Arrhenius' plot of the intrinsic rate constant, k_0 . According to Wako¹⁶⁾,

Fig. 5 Hammett's plot of reaction rate constant

Fig. 6 Effect of ultraviolet light intensity on rate constant for phenol degradation

the apparent activation energy for phenol photo-ozonization is 6.3 kcal/mol. These results agree satisfactorily, since Eq. (2) shows that the apparent activation energy corresponds to nearly half the intrinsic one.

4) Effect of ultraviolet light intensity The radiation intensity was varied by using aqueous potassium nitrate filter solution of different concentrations. The filter solution was passed through a coolant annulus surrounding a cylindrical lamp. The radiation through the reaction mixture was regarded as being nearly monochromatic light of wave length 253.7 nm, since its other major fraction of wave length 184.9 nm was readily absorbed in water.

If the intrinsic rate constant for photo-ozonization, $k_{0,i}$, is assumed to be the sum of the rate constant for ozonization k_0 and the contribution due to ultraviolet light intensity, $k_{0,i}$ is represented as follows:

$$k_{0,i} = k_0 + \alpha(I/I_0)^n \quad (5)$$

where I/I_0 is relative intensity of ultraviolet light, that is, the ratio of the incident light intensity after transmission by the filter solution to that without the solution, and both α and n are empirical constants. The values of $k_{0,i}$ are for an average ultraviolet light intensity in the reactor which is proportional to I . Hence the value of α is dependent on reactor geometry.

(a) Ozonization

(b) Photo-ozonization

Fig. 7 Variation of intermediate concentration with time for phenol degradation

Figure 6 shows the plot of $(k_{0,i} - k_0)$ against I/I_0 according to Eq. (5). This figure shows that $n=1.0$ and $\alpha=1.75 \times 10^3$.

The effect of ozone decomposition on its reaction with phenolic compounds in water was considered to be negligible since the rate of phenol disappearance was several thousand to ten times as large as that of ozone decomposition depending on the pH value from 6 to 10.

2.4 Behavior of major intermediates and reaction scheme

Figures 7 (a) and (b) illustrate the variation of product concentration with time during a typical run for phenol degradation by ozonization and photo-ozonization, respectively. The presence of hydroquinone, catechol, *p*-benzoquinone, *cis-cis*-muconic acid and maleic acid in the reaction mixture was established by high-performance liquid chromatography. Oxalic acid and carbon dioxide were also detected. The product distribution is seen to be similar in each case. This suggests that the phenol oxidation mechanism of ozonization is identical to that of photo-ozonization, although the rates are different. In the same way, comparison of the product distribution obtained for different values of pH suggested that the reaction mechanism was not changed by pH value.

When the reaction between phenol and ozone was

Table 2 Summary of reaction condition and product distribution in research on oxidation of phenol by ozone

Researcher	Ozone feed rate $\times 10^3$ [mol/min]	Initial conc. of phenol $\times 10^3$ [mol/l]	Ozone dose rate [mol O_3 /mol phenol/min]	Initial pH	Temp. [$^{\circ}C$]	Reactor type and volume	Ozone flow rate [l/min]	Type of oxidation	Products identified
Eisenhauer ⁵⁾	0.1–0.4	0.5–3	0.06–0.6	3–9	20–50	Cylindrical vessel with sintered glass dispersion tube; 1000 ml	0.1–0.5	Thermal oxidation	Catechol, (Hydroquinone), <i>o</i> -Benzoquinone, (<i>p</i> -Benzoquinone) <i>cis-cis</i> -Muconic acid, (Maleic, Fumaric and Oxalic acids), Carbon dioxide
Gould and Weber ⁶⁾	0.4–1.8	0.1–1	0.8–28	2–11	23 ± 2	Cylindrical vessel with glass plate diffuser; 500 ml	0.5–1.3	Thermal oxidation	Catechol, Hydroquinone, Glyoxal, Glyoxylic acid, Oxalic acid
Wako ¹⁶⁾	0.6–1	10–200	0.1–0.16	2–10	13–43	Flask with gas feed pipe; 300 ml	2	Photo-oxidation with high pressure mercury lamp	Hydroquinone, <i>p</i> -Benzoquinone, <i>cis-cis</i> -Muconic acid, Glyoxylic acid, Maleic acid
Otake <i>et al.</i>	0.1–1.3	8–15	0.02–0.1	2–11	5–25	Cylindrical vessel with sintered glass plate diffuser; 2000 ml	3–12	Photo-oxidation with low pressure mercury lamp	Hydroquinone, Catechol, <i>p</i> -Benzoquinone, <i>cis-cis</i> -Muconic acid, Maleic acid, Oxalic acid, Carbon dioxide

conducted in unbuffered solution, the pH of the system decreased rapidly to a nearly constant value between 2 and 3. The final pH value was found to be reached roughly at the maxima of the concentrations of the aromatic intermediates and to be almost equal to the pH of the lower fatty acid such as maleic acid.

To elucidate the phenol oxidation mechanism, the product distribution was determined for the degradation of hydroquinone and *p*-benzoquinone, which are assumed to be the primary and secondary degradation products of phenol, respectively. From comparison of these data, we propose a reaction pathway as shown in Fig. 8. The reason why the concentrations of intermediates such as quinone, muconic acid and maleic acid have their maximum values in the earlier stage of the reaction may be the fact that the reaction is confined within the liquid film.

Until the maxima of the aromatic intermediate concentrations were reached, the amount of phenol reacted, i. e., the difference between the initial concentration of phenol and the concentration at any time, agreed satisfactorily with that calculated from the product distributions by assuming that one mole of ozone reacts with one mole of reactant in each oxidation step shown in Fig. 8. After the concentration maxima, the difference between them increased progressively with time. This is partly because such lower carbon fragments as oxalic acid and carbon dioxide, etc., which may be produced predominantly in the later stage of the oxidation, were not determined in the present work.

For phenol removal a reaction scheme similar to that in the present work was suggested by Eisenhauer⁵⁾ for ozonization and by Wako¹⁶⁾ for photo-ozonization,

Fig. 8 Reaction pathway for phenol degradation with ozone

based on qualitative evidence rather than on such quantitative data as product distributions. On the other hand, according to Gould and Weber⁶⁾, in the earlier stages of ozonization the concentration of glyoxal and glyoxylic acid is sufficiently higher than that of the hydroxylated species, that is, hydroquinone and catechol, and during the later stages the concentration of oxalic acid rises very slowly.

The inconsistency among the reported product distributions of phenol removal by ozone is considered due to the difference in reaction conditions such as ozone and phenol concentrations, pH and gas-liquid flow pattern. **Table 2** shows the range of variables covered by various investigators and the reported products of the ozonolysis of phenol. The table suggests that the ozone dose rate⁵⁾, defined as moles of ozone fed per minute per mole of phenol initially present, may exclusively control the product distribution.

2.5 Ozone consumption

The ozone consumption can be calculated from the difference between the amount of ozone supplied and that leaving the reactor. The latter is obtained from the ozone concentration of the exit gas and its flow

Table 3 Characteristics of oxidation of phenol by ozone

Characteristics	The earlier stage of reaction		The later stage of reaction	
	Ozonization	Photo-ozonization	Ozonization	Photo-ozonization
Efficiency of ozone absorption η^*	0.96	1.00	0.68	0.80
Number of C=C double bonds	Nearly constant	Nearly constant	Decreased linearly with ozone supplied	Decreased in the same way more rapidly
Dependency of η on pH	η increased from 0.85 to 1.0 with pH (pH=3 to 11)	Nearly the same as for ozonization	η had almost constant value of 0.68 (pH=3 to 9)	η had almost constant value of 0.80 (pH=3 to 9)
Compounds present predominantly	Aromatic compounds such as phenol, hydroquinone and catechol		Aliphatic compounds such as maleic and oxalic acids	
Plausible reaction mechanism	Ionic reaction of aromatic compounds with ozone		Free radical reaction of aliphatic compounds with ozone	

* The reaction condition is the same as that for Fig. 7.

Fig. 9 Relationship between ozone consumption and phenol removal

rate. **Figure 9** represents the interrelationship among the ozone supplied to the reaction mixture per unit amount of phenol present initially μ , fractional degradation of phenol f , efficiency of ozone absorption η and the ratio of ozone consumed to degrade phenol itself to ozone absorbed ξ . μ corresponds to reaction time. The amount of ozone consumed to remove phenol was calculated from decrease in phenol concentration during the reaction, taking into account the fact that one mole of phenol reacts with one mole of ozone⁵⁾.

In **Fig. 9**, the efficiency of ozone absorption for each ozonization is found to be near 100% before all the phenol present initially has disappeared. It is obvious that the fractional degradation of phenol for photo-ozonization is greater than that for ozonization at the same value of μ . In the latter case, after consumption of about four molecules of ozone per molecule of phenol, namely $\mu=4$, practically all the phenol present originally has been destroyed. This result is in close agreement with that of Eisenhauer⁵⁾ and Gould and Weber⁶⁾. Further, the higher ξ of photo-ozonization implies that ultraviolet radiation is ef-

fective and specific to the oxidation of phenol toward the first degradation products of ozonization. In the present work, the specificity of ultraviolet light was most remarkable for *p*-benzoquinone removal. Therefore, if the earlier stage of oxidation of a phenolic compound is sufficient to satisfy pollution prevention requirements, it is seen that photo-ozonization can remove substantially all the phenolic compound at a smaller consumption of ozone compared to ozonization.

2.6 Critical ozone dosage

A plot of the amount of ozone absorbed versus that of ozone supplied made a sharp transition from one linear relationship to another (the figure is omitted). The breakpoint, that is, the transition point, occurred approximately at the maximal aromatic intermediate concentrations for both ozonization and photo-ozonization. The critical ozone dosage was defined as the amount of ozone supplied corresponding to the breakpoint.

The same feature was observed for a plot of the number of carbon-carbon double bonds versus the amount of ozone supplied. For convenience, the earlier and later stages of the reaction were defined as the periods before and after the critical ozone dosage, respectively. **Table 3** represents the distinction between the two stages. It clarifies that an increase in pH has no advantage for increasing the efficiency of ozone absorption in the later stage and that the ultraviolet radiation is more advantageous for higher efficiency in that stage. This is probably due to the difference in reaction mechanism between the two stages as shown in **Table 3**.

In brief, the critical ozone dosage may be used as a valuable indicator for the rational design of any ozonization process.

Conclusions

An ozone ultraviolet radiation process, that is, photo-ozonization, was investigated to obtain basic information for improving the rate and efficiency of

waste ozonization. The results obtained are summarized as follows.

1) Both ozonization and photo-ozonization of various phenolic compounds were found to fall into the fast pseudo-first order regime for simultaneous mass transfer and reaction. Overall reaction rate expression as well as intrinsic reaction rate constants were determined based on the chemical absorption theory.

2) Product distributions were elucidated for removal of phenol and of its primary and secondary oxidation products. The overall reaction pathway of phenol removal was shown to comprise successive oxidation series, each of which produced smaller molecules. Both ozonization and photo-ozonization were found to follow the same reaction scheme.

3) The pH value and the ultraviolet light intensity were found to exert negligible influence on the overall reaction pathway, but did enhance the rate of each oxidation step.

4) As an indicator for rational design of ozonization process, the critical ozone dosage was introduced. In the later stage of ozonization, corresponding to ozone dosage greater than the critical one, the ultraviolet radiation was proved to be more advantageous for improving the efficiency of ozone absorption, whereas the application of the higher pH showed no advantage.

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Nomenclature

$[A]$	= concentration of phenolic compound	[mol/l]
a	= gas-liquid interfacial area per unit liquid volume	[cm ² /cm ³]
D_A	= diffusivity of phenolic compound in liquid phase	[cm ² /sec]
D_{O_3}	= diffusivity of ozone in liquid phase	[cm ² /sec]
f	= fractional conversion of phenolic compound	[—]
I/I_0	= relative intensity of ultraviolet light	[—]
k	= apparent rate constant	[l ^{1/2} /mol ^{1/2} ·sec]
k_0	= intrinsic rate constant of second-order reaction	[l/mol·sec]
$k_{0,i}$	= k_0 for ultraviolet irradiation	[l/mol·sec]
$k_{0,s}$	= k_0 for substituted phenol	[l/mol·sec]
k_L	= liquid-phase mass transfer coefficient	[cm/sec]
N_{O_3}	= rate of chemical absorption of ozone	

	per unit interfacial area	[mol/cm ² ·sec]
n	= order with respect to ultraviolet light intensity	[—]
$[O_3]$	= concentration of ozone in liquid phase	[mol/l]
q	= $D_A[A]/D_{O_3}[O_3]_i$	[—]
t	= time	[sec]
u_G	= superficial gas velocity	[cm/sec]
α	= constant in Eq. (5)	[l/mol·sec]
β	= reaction factor (Hatta number)	[—]
γ	= $\sqrt{k_0[A]D_{O_3}/k_L}$	[—]
η	= efficiency of ozone absorption	[—]
μ	= ratio of ozone supplied to phenolic compound present initially	[—]
ξ	= ratio of ozone consumed to remove phenolic compound alone compared to ozone absorbed	[—]
ρ	= reaction constant	[—]
σ	= substituent constant	[—]
<Subscripts>		
0	= initial value	
i	= gas-liquid interface	

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