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Kinetics of Heterogeneous Photocatalytic Decomposition of Phenol over Anatase TiO_2 Powder

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The photocatalytic decomposition of phenol over anatase TiO_2 powder followed the first-order kinetics, upto high conversions, of which the apparent rate constant k_{ap} depended on initial concentration of phenol $[\text{phenol}]_0$, $[TiO_2]$, O_2 pressure p_{O_2}, and incident light intensity I. The dependence of the initial reaction rate Ω_0 on $[\text{phenol}]_0$ showed characteristic curvature convex to the concentration axis. The p_{O_2} dependence of both Ω_0 and k_{ap} was very similar each other and showed characteristic curvature to the p_{O_2} axis. The dependence of both Ω_0 and k_{ap} on $[\text{phenol}]_0$ was affected by the $[TiO_2]$ and I. Both Ω_0 and k_{ap} were proportional to I below *ca.* 1×10^{-5} mol m^{-2} s^{-1} and to $I^{1/2}$ above 2×10^{-5} mol m^{-2} s^{-1}. The activation energy was 10 kJ/mol. The results were satisfactorily explained by the equation;

$$\Omega=\phi_{\cdot\mathrm{OH}}I_a{}^n\frac{K_{O_2}p_{O_2}}{1+K_{O_2}p_{O_2}}\cdot\frac{[\text{phenol}]}{[\text{phenol}]_0+\beta},$$

where Ω is the reaction rate; $\phi_{\cdot\mathrm{OH}}I_a{}^n$, a parameter related to the formation rate of ·OH radicals or real reactive species; K_{O_2}, the equilibrium constant of Langmuir adsorption of O_2; β, the ratio of the combined first-order rate constant of the reaction of ·OH with species other than organic compounds to the second-order rate constant of the reaction of ·OH with phenol.

In the previous paper,[1] we have reported on the reaction pathway of the photocatalytic decomposition of phenol in oxygenated aqueous suspensions of anatase TiO_2 as follows. Hydroxyl radicals are real reactive species responsible for the reaction. They are formed not only by the reaction of holes with adsorbed H_2O or OH^{-1}, but also *via* H_2O_2 from $O_2^{\dot{-}}$ formed by electron trapping of adsorbed O_2. Phenol are decomposed *via* its hydroxylated compounds into the final products of CO_2 and H_2O. It is interesting from the viewpoint of wastewater treatment that phenol is completely mineralized to CO_2 in the presence of TiO_2 powder under solar irradiation without both aeration and mixing of the solution.

In the present paper, effects of initial concentration of phenol, TiO_2 loading, partial pressure of O_2 in a gas bubbled, incident light intensity, and temperature on the reaction rate were investigated at the optimum pH 3.5. A kinetic equation was proposed to explain the experimental results satisfactorily.

Experimental

Lightly-reduced anatase TiO_2 prepared previously[1] was used as a photocatalyst. The experimental procedure was the same as mentioned in the previous paper,[1] except where noted.

The photocatalytic reaction was carried out in two types of photoreactors at pH 3.5. One (named reactor I) was the same as used previously.[1] The other (named reactor II) was a 200 cm^3 beaker with both four pieces of baffles and a water jacket. A quantity of TiO_2 was suspended in 100 cm^3 of a phenol solution by stirring magnetically. Air was bubbled through the suspension at the rate of 50 cm^3 min^{-1}. The suspension was irradiated from the upside of the beaker by a parallel UV-light, which was obtained by passing the light from a 500 W high-pressure mercury lamp (Ushio Electric Co., USH-500D) through both a $CuSO_4$ solution (0.24 M (1 M=1 mol dm^{-3}), 10 cm) and a band-pass filter (Toshiba Co., UVD-25 or UVDIC) and was substantially composed of 366, 334, and 313 nm light. The irradiated area was 27 cm^2 and the depth of the suspensions was 3.5 cm. The light intensity was adjusted by using wire meshes and/or Pyrex glass plates as neutral filters. The suspension was kept at a constant temperature (usually 25 °C) by circulating thermostated water through the jacket.

The average diameter of TiO_2 powder in the suspensions was measured by means of a highly-directional photoprobe.[2]

Results

Effects of Both Initial Concentration of Phenol and Partial Pressure of O_2. The photocatalytic decomposition of phenol followed the first-order reaction kinetics (Eq. 1) upto high conversions.[1]

$$-\ln\left(\frac{[\text{phenol}]}{[\text{phenol}]_0}\right)=k_{ap}t \tag{1}$$

where $[\text{phenol}]_0$ is initial concentration of phenol; k_{ap}, the apparent first-order rate constant; t, the reaction time. The dependence of initial reaction rate Ω_0 and k_{ap} on $[\text{phenol}]_0$ is shown in Figs. 1 and 2, respectively. The k_{ap} depended on $[\text{phenol}]_0$, indicating that the reaction was not a simple first-

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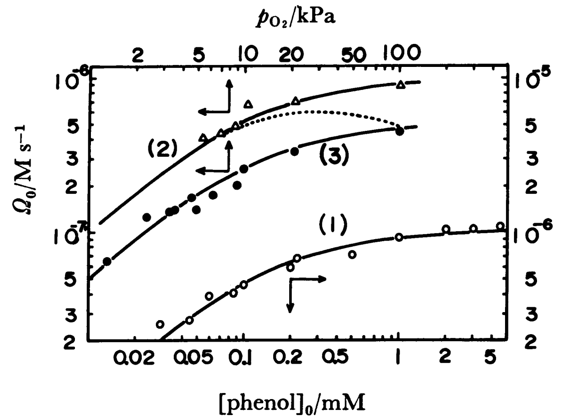

Fig. 1. Dependence of Ω_0 on both [phenol]$_0$ and p_{O_2}. Reactor I and [TiO$_2$] = 6.3 mg cm^{-3}. (1) p_{O_2} = 101 kPa; (2) [phenol]$_0$ = 1 mM; (3) [phenol]$_0$ = 0.1 mM. The solid lines were calculated from Eq. 10 with $\phi_{\cdot OH}I_a^n$ = 1.12 μM s^{-1}, β = 0.12 mM, and K_{O_2} = 0.11 kPa^{-1}.
The dotted line was calculated from Eqs. 10 and 17 with $\phi_{\cdot OH}I_a^n$ = 1.12 μM s^{-1}, K_{O_2} = 0.11 kPa^{-1}, and $k_d/(k_{ph}K_{ph})$ = 10 μM.

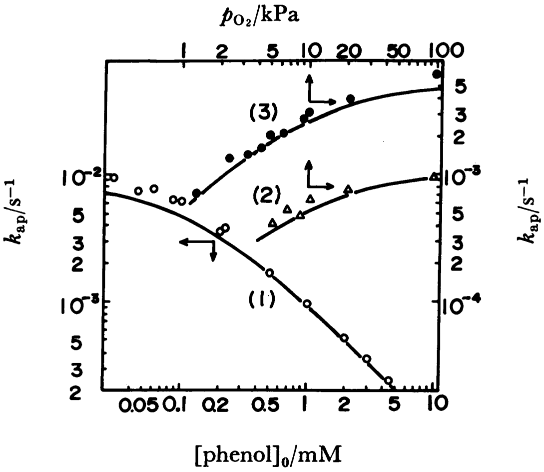

Fig. 2. Dependence of k_{ap} on both [phenol]$_0$ and p_{O_2}. The experiments were the same as in Fig. 1. The solid lines were calculated from Eq. 21 with the same values of the parameters as used in Fig. 1.

order one. Figures 1 and 2 also show the dependence of Ω_0 and k_{ap} on the partial pressure of O$_2$, p_{O_2}, in a bubbled gas, respectively. As has been reported previously,[1] the dependence of Ω_0 on p_{O_2} was represented by Eq. 2.

$$\Omega_0 \propto \frac{K_{O_2}p_{O_2}}{1+K_{O_2}p_{O_2}} \tag{2}$$

where K_{O_2} is the equilibrium constant of Langmuir adsorption of O$_2$. It is noted that the dependence of k_{ap} on p_{O_2} was almost the same as that of Ω_0.

As shown in Figs. 3 and 4, the dependence of both

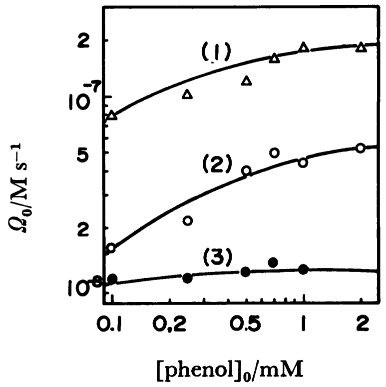

Fig. 3. Dependence of Ω_0 on [phenol]$_0$. Reactor II and p_{O_2} = 21 kPa. (1) I = 3.5 × 10^{-4} mol m^{-2}s^{-1} and [TiO$_2$] = 1.2 mg cm^{-3}; (2) I = 3.5 × 10^{-4} mol m^{-2}s^{-1} and [TiO$_2$] = 0.15 mg cm^{-3}; (3) I = 4.1 × 10^{-6} mol m^{-2}s^{-1} and [TiO$_2$] = 1.2 mg cm^{-3}. The solid lines were calculated from Eq. 10 with the corresponding set of the parameter values listed in Table 2.

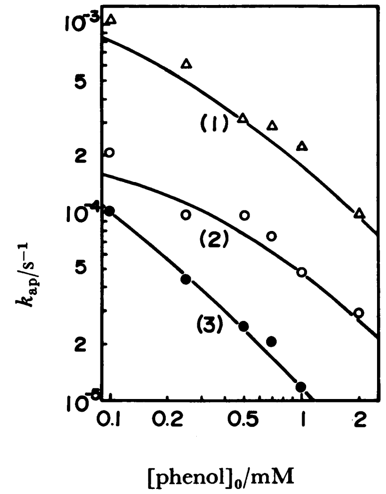

Fig. 4. Dependence of k_{ap} on [phenol]$_0$. The experiments were the same as in Fig. 3. The solid lines were calculated from Eq. 21 with the same values of the parameters as used in Fig. 3.

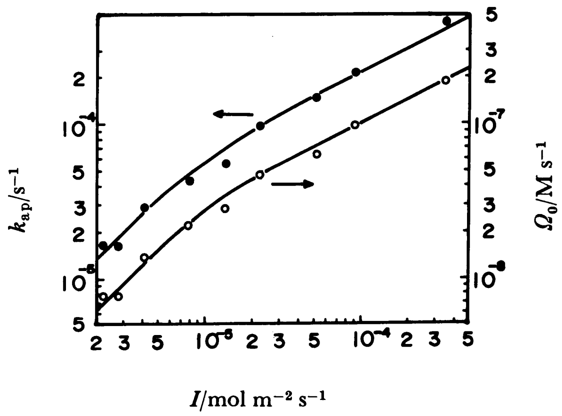

Fig. 5. Light-intensity dependence of both Ω_0 and k_{ap}. Reactor II, p_{O_2} = 21 kPa, [phenol]$_0$ = 0.5 mM, and [TiO$_2$] = 2.0 mg cm^{-3}.

Ω_0 and k_{ap} on [phenol]$_0$ depended on light intensity I and [TiO_2].

Effect of Light Intensity. Figure 5 shows light-intensity dependence of both Ω_0 and k_{ap}. Both Ω_0 and k_{ap} were proportional to I below *ca.* 10 μmol m^{-2} s^{-1} and to $I^{1/2}$ *ca.* above 20 μmol m^{-2} s^{-1}. The square-root dependence of Ω_0 in I indicates that the reaction was limited by the recombination of photogenerated hole-electron pairs. The experiments carried out both in the reactor I and without dense neutral filters in the reactor II were in the region of this dependence.

The effective intensity of sunlight was evaluated to be *ca.* 4 μmol m^{-2} s^{-1} from both the Ω_0 value of 1.9×10^{-8} M s^{-1} for [phenol]$_0$=1 mM and the quantum yield of 10% for 366 nm.[1] This is in the region of linear dependence of Ω_0 on I.

Effect of [TiO_2]. Figure 6 shows variation of [phenol] with reaction time for the suspensions with different concentrations of TiO_2. When the suspensions were stirred for only 15 min in the dark prior to the reaction, the patterns of the reaction curves observed for the dilute suspensions were quite different from that expected from Eq. 1, as shown by the solid line (3) as an example. On the other hand, when they were stirred for more than 60 min prior to the reaction, such a deviation from Eq. 1 was not observed even for the dilute suspensions, as shown by the solid line (2) as an example. This was related to a change of dispersion state of TiO_2 powder. Table 1 shows the variation of average diameter $\bar{d}_p$ of TiO_2 powder in a suspension during a run. When the suspensions were not stirred sufficiently prior to the reaction, the dispersion state of the powder was much improved by UV-irradiation, probably because of accumulation of surface charge,[3] resulting in gradual increases of the light-absorption rate and consequently of the reaction rate for the dilute suspensions. For the suspensions stirred sufficiently prior to the reaction, a decrease of $\bar{d}_p$ caused by UV-irradiation was not large and was furthermore attained in only several min after light on. Therefore, in this case it hardly affects the reaction curves. The results concerning both Ω_0 and k_{ap} mentioned here were obtained for the suspensions stirred for more than 60 min prior to the reaction.

TABLE 1. VARIATION OF $\bar{d}_p$ OF TiO_2 POWDER IN A SUSPENSION DURING A RUN[a)]

$\bar{d}_p/\mu m$	Stirring conditions
1.88	15 min in the dark
0.98	60 min in the dark
0.76	7 min under UV-irradiation[b)]
0.78	20 min under UV-irradiation[b)]

a) Reactor II, [TiO_2]=0.20 mg cm^{-3} and pH 3.5. The $\bar{d}_p$ was 0.17 μm for the suspension where TiO_2 powder was completely dispersed by use of sodium hexametaphosphate. b) The suspension was stirred for 60 min in the dark prior to UV-irradiation.

As shown in Fig. 7, the [TiO_2] dependence of both Ω_0 and k_{ap} was very similar each other. In the high concentration region above 5 mg/cm^3, both Ω_0 and k_{ap} were independent of [TiO_2] at a low light intensity, while they still increased with an increase of [TiO_2] at a high light intensity.

Effect of Temperature. Figure 8 shows the temperature dependence of both Ω_0 and k_{ap}. The activation energy of both Ω_0 and k_{ap} was about

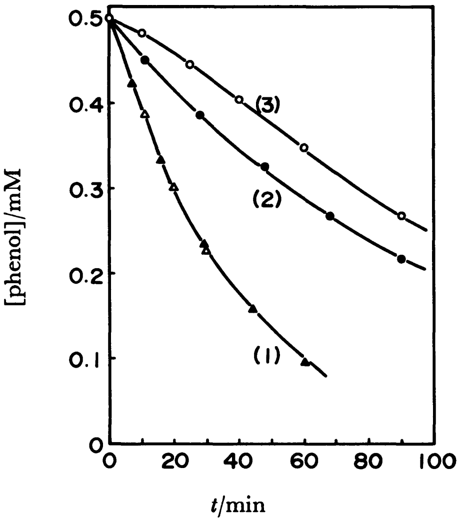

Fig. 6. Effect of stirring time prior to the reaction on the reaction curves.
Reactor II and p_{O_2}=21 kPa. The suspensions were stirred for either 15 min (○ and △) or 60 min (● and ▲) in the dark prior to the reaction.
○ and ●: [TiO_2]=0.3 mg cm^{-3}; △ and ▲: [TiO_2]=2.0 mg/cm^3. The solid lines (1) and (2) were calculated from Eq. 1. The solid line (3) was drawn by eyes.

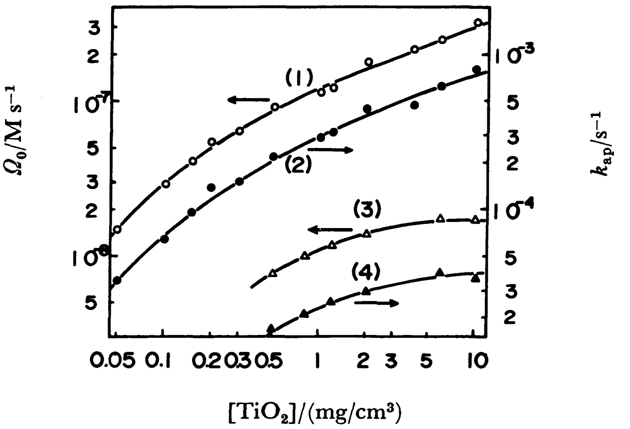

Fig. 7. Dependence of both Ω_0 and k_{ap} on [TiO_2].
Reactor II, [phenol]$_0$=0.5 mM, and p_{O_2}=21 kPa.
(1) and (2): $I=3.5\times10^{-4}$ mol m^{-2}s^{-1}; (3) and (4): $I=4.1\times10^{-6}$ mol m^{-2}s^{-1}.

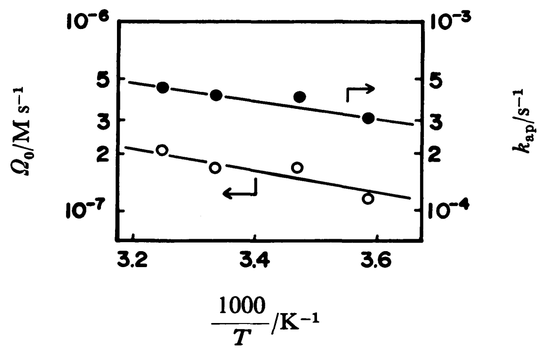

Fig. 8. Temperature dependence of both Ω_0 and k_{ap}. [phenol]$_0$=0.5 mM, p_{O_2}=21 kPa, [TiO$_2$]=1.2 mg/cm^3, and I=3.5×10^{-4} mol m^{-2}s^{-1}.

10 kJ/mol. This value was in the same range as those obtained for oxalic acid (13 kJ/mol)[4] and for formic acid (11 and 17 kJ/mol)[5,6], although being smaller than that obtained for 2-propanol (31 kJ/mol).[7] It was much smaller than that (48 kJ/mol) obtained for oxidation of phenol by means of Fentons' reagent.[8]

Discussion

Influence of Mass Transfer Rate on the Reaction Rate. It is clear from no influence of gas-bubbling rate on both Ω_0 and k_{ap} that mass transfer rate at gas-liquid interface did not affect the reaction rate. On the other hand, there remains the possibility that mass transfer rate at liquid-solid interface might affect the reaction rate, because both Ω_0 and k_{ap} increased with an increase of [TiO$_2$] upto the highest concentration investigated here at a high light intensity, as shown in Fig. 7. The following consideration, however, objects this possibility.

The reaction rate Ω is expressed by Eq. 3 in terms of volumetric mass transfer coefficient $k_s a$.

$$\Omega = (k_s a)_A (c_{A,l} - c_{A,s}), \qquad (3)$$

where $c_{A,l}$ and $c_{A,s}$ are the concentrations of species A in the bulk liquid and at the external surface of the particles, respectively. For very fine spherical particles $k_s a$ is given by Eq. 4.[9]

$$k_s a = \frac{12\, D\, m_p}{\bar{d}_p^{\,2} \rho_p}, \qquad (4)$$

where D is diffusion coefficient; m_p, mass of the particles per unit volume of a suspension; ρ_p, density of the particles. If we consider mass transfer of phenol in a dilute suspension with [TiO$_2$]=0.12 mg cm^{-3}, the value of $(k_s a)_{\text{phenol}}$ is evaluated to be 0.55 s^{-1}, using D=8.9×10^{-6} cm^2 s^{-1},[10] $\bar{d}_p$=0.77 μm, and ρ_p=3.90 g/cm^3. In the case of an experimental result of Ω_0=4×10^{-8} M s^{-1} with [phenol]$_0$=0.5 mM, I=3.5×10^{-4} mol m^{-2} s^{-1}, and [TiO$_2$]=0.12 mg/cm^3, the ratio of [phenol]$_s$/[phenol]$_l$ is evaluated to be 0.9998. The similar values of the ratio of $c_{A,s}/c_{A,l}$ are evaluated for other species such as O$_2$, ·OH, and the intermediate products. This fact indicates that the results mentioned above were not affected by mass transfer rate at liquid-solid interface at all.

Chemical Kinetics. Simple Langmuir-Hinshelwood kinetics have been applied to the photocatalytic reaction of trichloroethylene,[11] chloromethanes[12], halide ions,[13] and aliphatic carboxylic acids.[4,6] In these reports, only the dependence of Ω_0 on initial concentration of the substrates has, however, been investigated. As mentioned above, the photocatalytic decomposition process of phenol had the following important characteristics. (1) Upto the high conversions, the reaction apparently proceeded according to the first-order kinetics with k_{ap} depending on [phenol]$_0$ p_{O_2}, [TiO$_2$], and I. (2) The dependence of Ω_0 on [phenol]$_0$ showed characteristic curvature convex to the concentration axis. (3) The p_{O_2} dependence of both Ω_0 and k_{ap} was very similar each other and showed characteristic curvature convex to the p_{O_2} axis. (4) The dependence of both Ω_0 and k_{ap} on [phenol]$_0$ was affected by [TiO$_2$] and I. A chemical kinetic model is proposed as follows, in order to explain these characteristics.

The rate determining step of the reaction is reasonably considered to be the formation of ·OH radicals or real reactive species, because they react very rapidly with phenols; for example, k=1.4×10^{10} M^{-1} s^{-1} for phenol.[14] The reaction rate is, therefore, given by the product of formation rate of ·OH, $\Omega_{\cdot\text{OH}}$, and the probability of the reaction of ·OH with phenol, P_{ph}.

$$\Omega = \frac{-\text{d[phenol]}}{\text{d}t} = \Omega_{\cdot\text{OH}}\, P_{\text{ph}} \qquad (5)$$

Judging from the initial steps of the photocatalysis mentioned in the previous paper,[1] $\Omega_{\cdot\text{OH}}$ is proportional to the number of hole-electron pairs escaped from the recombination. O$_2$ adsorbed on TiO$_2$ surface prevents the recombination by trapping an electron. Therefore, $\Omega_{\cdot\text{OH}}$ is reasonably considered to be expressed by Eq. 6.

$$\Omega_{\cdot\text{OH}} = \frac{\phi_{\cdot\text{OH}} I_a^{\,n} K_{O_2} p_{O_2}}{1 + K_{O_2} p_{O_2}}, \qquad (6)$$

where $\phi_{\cdot\text{OH}}$ is a constant related to the yield of formation of ·OH; I_a, rate of light absorption; n, a constant representing the dependence of $\Omega_{\cdot\text{OH}}$ on I.

Hydroxyl radicals react with phenol and its intermediates with second-order rate constants of k_{ph} and k_I (k_{I_i} for an intermediate I$_i$), respectively. They also react with the other species such as electrons and

$O_2^{\dot{-}}$ ions[15] with a combined first-order rate constant of k_d.

$$\left.\begin{array}{l} \cdot OH + e \longrightarrow OH^- \\ \cdot OH + O_2^{\dot{-}} \longrightarrow O_2 + OH^- \end{array}\right\} \tag{7}$$

The following three cases are assumed concerning the reaction of ·OH with phenol and its intermediates.

Case I. We assume that ·OH radicals react with the species being either in bulk liquid phase or at the interface. Then, P_{ph} is given by Eq. 8.

$$P_{ph} = \frac{k_{ph}[\text{phenol}]}{k_{ph}[\text{phenol}] + \sum_i k_{I_i}[I_i] + k_d}, \tag{8}$$

where the summation of the second term of the denominator is taken over every intermediate. Moreover, we assume that Eq. 9 holds to a fairly good approximation over a long period of reaction time.

$$k_{ph}[\text{phenol}] + \sum_i k_{I_i}[I_i] = k_{ph}[\text{phenol}]_0 \tag{9}$$

Then, Ω is expressed by Eq. 10.

$$\Omega = \phi_{\cdot OH} I_a^n \frac{K_{O_2} p_{O_2}}{1 + K_{O_2} p_{O_2}} \cdot \frac{[\text{phenol}]}{[\text{phenol}]_0 + \beta}, \tag{10}$$

$$\beta = k_d / k_{ph}. \tag{11}$$

Case II. We assume that ·OH radicals react with the species adsorbed on TiO_2 surface in competition with O_2. Then, P_{ph} is given by Eq. 12.

$$P_{ph} = \frac{k_{ph}\theta_{ph}}{k_{ph}\theta_{ph} + \sum_i k_{I_i}\theta_{I_i} + k_d}, \tag{12}$$

where θ_{ph} and θ_{I_i} are the surface coverages of phenol and an intermediate I_i, respectively. Both phenol and its primary intermediates were hardly adsorbed on TiO_2 surface.[1] Moreover, the p_{O_2} dependence of both Ω_0 and k_{ap} was not affected by $[\text{phenol}]_0$. Judging from these facts, Eq. 13 holds.

$$1 + K_{O_2} p_{O_2} \gg K_{ph}[\text{phenol}] + \sum_i K_{I_i}[I_i], \tag{13}$$

where K_{ph} and K_{I_i} are the equilibrium constants of phenol and an intermediate I_i, respectively. Therefore, θ_{ph} and θ_{I_i} is given by Eqs. 14 and 15, respectively.

$$\theta_{ph} = \frac{K_{ph}[\text{phenol}]}{1 + K_{O_2} p_{O_2}} \tag{14}$$

$$\theta_{I_i} = \frac{K_{I_i}[I_i]}{1 + K_{O_2} p_{O_2}} \tag{15}$$

Moreover, we assume that Eq. 16 holds to a fairly good approximation over a long period of reaction time.

$$k_{ph}K_{ph}[\text{phenol}] + \sum_i k_{I_i}K_{I_i}[I_i] = k_{ph}K_{ph}[\text{phenol}]_0 \tag{16}$$

Then, we obtain the same equation as Eq. 10, although in this case β is expressed by Eq. 17 instead of Eq. 11.

$$\beta = \frac{k_d(1 + K_{O_2} p_{O_2})}{k_{ph}K_{ph}} \tag{17}$$

Case III. We assume that ·OH radicals react with the species adsorbed at the sites different from the adsorption sites of O_2. Then, P_{ph} is given by Eq. 12, where θ_{ph} and θ_{I_i} are expressed by Eqs. 18 and 19 instead of Eqs. 14 and 15, respectively.

$$\theta_{ph} = K_{ph}[\text{phenol}] \tag{18}$$

$$\theta_{I_i} = K_{I_i}[I_i] \tag{19}$$

Moreover, we assume Eq. 16 as in Case II. Then, we obtain the same equation as Eq. 10, although in this case β is expressed by Eq. 20.

$$\beta = \frac{k_d}{k_{ph}K_{ph}} \tag{20}$$

Concerning [phenol], Eq. 10 is a first-order kinetic equation with the rate constant k_{ap} expressed by Eq. 21.

$$k_{ap} = \frac{\phi_{\cdot OH} I_a^n K_{O_2} p_{O_2}}{(1 + K_{O_2} p_{O_2})([\text{phenol}]_0 + \beta)} \tag{21}$$

Both Eqs. 10 and 21 have three adjustable parameters of $\phi_{\cdot OH} I_a^n$, K_{O_2}, and β. The solid lines in Fig. 1 were calculated from Eq. 10 with $\phi_{\cdot OH} I_a^n = 1.12\,\mu M\,s^{-1}$, $K_{O_2} = 0.11\,kPa^{-1}$, and $\beta = 0.12\,mM$. These values were determined to give best fit of the calculated lines with the experimental results. The solid lines in Fig. 2

TABLE 2. KINETIC PARAMETERS OBTAINED FOR VARIOUS EXPERIMENTAL CONDITIONS[a)]

	Experimental conditions		Kinetic parameters		
	I / mol m^{-2} s^{-1}	[TiO_2] / mg cm^{-3}	$\phi_{\cdot OH} I_a^n$ / M s^{-1}	β / mM	K_{O_2} / kPa^{-1}
(1)	≈ 10^{-3}	6.3	1.12×10^{-6}	0.12	0.11
(2)	3.5×10^{-4}	1.2	2.2×10^{-7}	0.15	0.11
(3)	3.5×10^{-4}	0.15	6.8×10^{-8}	0.30	0.11
(4)	4.1×10^{-6}	1.2	1.2×10^{-8}	0.02	0.11

a) (1): Reactor I and $p_{O_2} = 101$ kPa; (2)—(4): Reactor II and $p_{O_2} = 21$ kPa.

were calculated from Eq. 21 with the same values of the parameters. They were in good agreement with the experimental results.

The solid lines in Figs. 3 and 4 were calculated from Eqs. 10 and 21, respectively, with the values of the parameters listed in Table 2. They were also in good agreement with the experimental results obtained for different conditions of I and [TiO$_2$]. As can be seen from Table 2, there is a tendency that the β value is small for the case with both a high value of [TiO$_2$] and a low value of I. This is due to the dependence of k_d on both [TiO$_2$] and I; judging from Eq. 7, k_d is reasonably considered to be reduced with an increase of [TiO$_2$] and with a decrease of I. Thus, Eq. 10 satisfactorily explains the experimental results.

In Case II, β should depend on p_{O_2}, as expressed by Eq. 17. For the experiments shown in Fig. 2, the value of $k_d/(k_{ph}K_{ph})$ in Eq. 17 was evaluated to be 10 μM using the β and K_{O_2} values (0.12 mM and 0.11 kPa^{-1}, respectively) obtained with p_{O_2}=101 kPa. The relation of Ω_0 *vs.* p_{O_2} for [phenol]=0.1 mM was calculated from Eqs. 10 and 17 with $\phi_{\cdot OH}I_a{}^n$= 1.12 μM s^{-1}, K_{O_2}=0.11 kPa^{-1} and $k_d/(k_{ph}K_{ph})$=10 μM. As shown by the dotted line in Fig. 1, the calculated relation of Ω_0 *vs.* p_{O_2} is quite different from the experimental one, indicating that Case II is ruled out for the present reaction.

At the present, we have no idea concerning which one between Cases I and III is more appropriate for the present reaction. The Ω_0 values of hydroquinone and pyrocatechol were 70 and 65% of that of phenol observed under the same conditions, respectively, while the reaction of ·OH with phenols has been reported to be diffusion-controlled.[14] Appreciable amounts of undetected compounds having very short retention times in liquid chromatograms were produced at the initial stage of the reaction of hydroquinone and pyrocatechol.[1] Phenol, hydroquinone, and pyrocatechol were hardly adsorbed on TiO$_2$ powder.[1] Judging from these facts, both Eqs. 9 and 16 appear to be the resonable assumptions.

In order to discuss the dependence of both Ω_0 and k_{ap} on [TiO$_2$], it is necessary to know the local rate of light absorption of TiO$_2$ powder in the reactor. At the present, we have no information about it. The experiments are in progress.

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References

1) K. Okamoto, Y. Yamamoto, H. Tanaka, M. Tanaka, and A. Itaya, *Bull. Chem. Soc. Jpn.*, **58**, 2015 (1985).

2) M. Tanaka, A. Itaya, and K. Okamoto, *Kagaku Kogaku Ronbunshu*, **10**, 551 (1984); P. H. Calderbank, *Trans. Instn. Engrs.*, **36**, 443 (1958).

3) W. W. Dunn, Y. Aikawa, and A. J. Bird, *J. Am. Chem. Soc.*, **103**, 3456 (1981).

4) J. M. Herrmann, M. N. Mozzanega, and P. Pichat, *J. Photochem.*, **22**, 333 (1983).

5) H. Yoneyama, N. Matsumoto, T. Furusawa, and H. Tamura, *Nippon Kagaku Kaishi*, **1984**, 253.

6) M. Bideau, B. Claudel, and M. Otterbein, *J. Photochem.*, **14**, 291 (1980).

7) P. R. Harvey, R. Rudham, and S. Ward, *J. Chem. Soc., Faraday Trans. 1*, **79**, 1381 (1983).

8) M. Sudo, T. Yonebayashi, and K. Koide, 18th Autumn Meeting of The Society of Chemical Engineers of Japan, Fukuoka, October 1984, Abstr. No.SD210.

9) R. V. Chaudhari and P. A. Ramachandran, *AIChEJ*, **26**, 177 (1980).

10) "Kagaku Kogaku Binran," ed by Inst. Chem. Eng. Jpn., Maruzene (1978), P. 68.

11) A. I. Pruden and D. F. Ollis, *J. Catalysis*, **82**, 404 (1983).

12) C.-Y. Hsiao, C.-L. Lee, and D. F. Ollis, *J. Catalysis*, **82**, 418 (1983).

13) J.-M. Herrmann and P. Pichat, *J. Chem. Soc., Faraday Trans. 1*, **76**, 1138 (1980).

14) G. E. Adams and B. D. Michael, *Trans. Faraday Soc.*, **63**, 1171 (1967); E. J. Land and M. Ebert, *ibid.*, **63**, 1181 (1967).

15) G. Munuera, V. Rives-Arnau, and A. Saucedo, *J. Chem. Soc., Faraday Trans. 1*, **75**, 736 (1979); D. T. Sawyer and M. J. Gibian, *Tetrahedron*, **35**, 1471 (1979).