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Heterogeneous Photocatalytic Decomposition of Phenol over TiO_2 Powder

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The photocatalytic decomposition of phenol in oxygenated aqueous suspensions of lightly-reduced anatase TiO_2, being the most satisfactory among the semiconductors investigated from the standpoint of the photocatalytic activity and stability, has been investigated at the optimum pH 3.5. The products at the initial stage of the reaction were hydroquinone, pyrocatechol, 1,2,4-benzenetriol, pyrogallol, and 2-hydroxy-1,4-benzoquinone. These intermediates underwent further photocatalytic oxidation *via* acids and/or aldehydes finally into CO_2 and H_2O. A reaction scheme involving hydroxyl radicals as real reactive species has been proposed. Although H_2O_2 was formed *via* O_2^{-} produced by electron trapping of adsorbed oxygen, its concentration remained constant at a low value during the reaction. About 0.7 mole of O_2 was consumed for the consumption of one mole of phenol at the initial stage of the reaction. These results indicated that hydroxyl radicals were formed not only *via* holes but also *via* H_2O_2 from O_2^{-}. It was interesting from the viewpoint of wastewater treatment that phenol was completely mineralized to CO_2 in the presence of TiO_2 powder under solar irradiation without both aeration and mixing of the solution.

Photocatalytic effects of semiconductors have been of much interest from the view point of solar energy utilization. They have been applied not only to produce useful chemicals,[1] but also to convert pollutants in waste streams to innocuous or less harmful form.[2–8] For example, by heterogeneous photocatalysis of some *n*-type semiconductors such as TiO_2 and ZnO, CN^-, and $Cr_2O_7^-$ in aqueous solutions are converted to CNO^- and Cr^{3+}, respectively.[2,3,5,6] In dilute aqueous solutions, chlorinated hydrocarbons such as $CHCl_3$ and trichloroethylene are completely mineralized to HCl and CO_2.[8] Chlorinated aromatics such as polychlorinated biphenyls also undergo photocatalytic dechlorination to give less harmful products.[2] These facts indicate some potential for phtocatalytic treatment of wastewater utilizing sunlight.

Phenol is a refractory and common compound in industrial wastes, and there is interest in developing a new type of chemical treatment of phenol. Kawaguchi and Uejima have studied on phtocatalytic decomposition of phenol in aqueous suspensions of ZnO.[7] They observed that the decomposition process apparently obeyed the first-order reaction kinetics, and detected hydroquinone and pyrocatechol as the main products. The photocatalytic decomposition process of phenol has not, however, been clarified in detail yet.

In the present paper, the photocatalytic decomposition of phenol was studied at several semiconductor powders. For aqueous suspensions of lightly-reduced anatase, the most satisfactory photocatalyst, the dependence of the reaction rate on pH, partial pressure of O_2 and $[Cu^{2+}]$, the consumption rate of O_2, and variation of $[H_2O_2]$ during the reaction were investigated to clarify the initial steps of the photocatalysis. The intermediate products were investigated to clarify the reaction pathway. The photocatalytic decomposition under solar irradiation was also investigated. The reaction kinetics of the process will be reported elsewhere.[9]

Experimental

Materials. As photocatalysts, TiO_2 (anatase and rutile), ZnO, α-Fe_2O_3, and CdS were used as received from Wako Pure Chemical Co., except for anatase. Anatase powder was reduced in a stream of hydrogen at 520 °C for 6 h. The lightly-reduced anatase had a specific area of $38\ m^2\ g^{-1}$, as determined by BET nitrogen adsorption, and was used in this paper except where noted. Cu-deposited anatase powder was prepared by UV-irradiating a deaerated suspension of lightly-reduced anatase in the presence of $CuSO_4$ (0.1 mM ($1\ M=1\ mol\ dm^{-3}$)).[10]

All chemicals were of reagent grade (Wako Pure Chemical Co.). Solutions were prepared with distilled deionized water.

Photocatalytic Experiments. The majority of the reaction was carried out in a photochemical reactor which was fitted with a 100 W high-pressure mercury lamp (Ushio Electric Co., UM-102) surrounded by a Pyrex glass thimble. A 0.23 M solution of $CuSO_4\cdot 5H_2O$ was circulated through the thimble to cool the reaction solution and to help filter out short-wavelength light. The $500\ cm^3$ reaction vessel formed a gas-tight seal around the lamp and had four ports for gas inlet and outlet, sampling, and pH measurement.

In typical experiments, 2.5 g of catalyst powder was suspended in $400\ cm^3$ of 1 mM phenol solution by stirring magnetically. A gas was bubbled through this solution at the rate of $220\ cm^3\ min^{-1}$. In the experiments using anatase, pH of the solution was adjusted by adding an appropriate amount of a H_2SO_4 or KOH solution to the suspension. In the other experiments, it was not adjusted. During a run, the reaction solution was maintained at

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25 °C, and *ca.* 3 cm^3 samples were taken at given time intervals. After being sampled, the suspensions were centrifuged and the centrifugates were subjected to the analyses.

To measure quantum yield of phenol decomposition, the reaction was also carried out in a rectangular cell at 25 °C. With bubbling oxygen gas slowly and stirring magnetically, 15 cm^3 of a 1 mM phenol solution suspended with 95 mg anatase was irradiated through a front side of the cell by a monochromatized and parallel light from a 500 W xenon lamp. The incident light intensity was measured by means of a potassium ferrioxalate actinometer.[11)]

Analyses. Phenol and the reaction products were analyzed by means of a high-performance liquid chromatography (Hitachi, 635-A) with a column packed with ODS gel (Toyosoda Co., ODS-120A). An aqueous solution of 50% methanol or 0.2% acetic acid[12)] was used as an eluting solvent. Products were identified by comparing both the retention times and the ratios of absorbance monitored at two different wavelengths between samples and standards. Total organic carbon (TOC) content was measured using a TOC analyzer (Shimazu, TOC-10A). COD was measured by the acidic method using a COD analyzer (Bionic Instrument Co., COD-510E). The amount of CO_2 produced was determined either from a reduction in TOC of the reaction solution or as $BaCO_3$ precipitated by passing the effluent gas into a $Ba(OH)_2$ solution. The amount of carbonyl groups produced was measured by treating the reaction solution with a 1 M aqueous HCl solution of 2,4-dinitrophenylhydrazine and following the consumption of hydrazine spectrometrically. H_2O_2 was analyzed spectrometrically using $TiOSO_4$ as the reagent.[13)] Zn^{2+} and Ti^{4+} were analyzed spectrometrically using Xylenol Orange and 8-quinolinol, respectively, as the reagents.[14)] The partial pressure of O_2 of a bubbled gas was measured using a gaschromatography (Shimazu, TC-4A) with a column packed with silica gel.

Adsorption. 20 cm^3 of a 0.5 mM phenol solution and a certain quantity (0.1—3 g) of reduced anatase powder were added to 50 cm^3 flask with a tight stopper. After the suspension was magnetically stirred for 10 h at 25 °C, the TiO_2 powder was removed by centrifugation and the absorbance of the solution was measured against a blank solution.

Solar Experiments. In the experiments using sunlight, 10 g of reduced anatase and 1.2 dm^3 of 1 mM phenol solution were placed in a rectangular cell with a Pyrex glass cover. As the solution was not stirred during a run, the anatase powder covered the bottom of the cell. The deposited layer of anatase (510 cm^2 in the surface area) was illuminated with sunlight through the solution layer (2.3 cm in depth). Cu-deposited anatase was also used. The pH of the solution was initially set at 3.5, but it was not controlled during a run. The experiments were carried out in August in Ube located in lattitude 34° north. The temperature of the reaction solution was in the range of 30 to 55 °C. The weather was clear to partly cloudy.

Results and Discussion

Photocatalytic Activity and Stability of Semiconductors. Figure 1 shows reduction of phenol concentration with reaction time t for oxygenated aqueous suspensions of several semiconductors. As shown in Fig. 1, the reaction followed the first-order reaction kinetics (Eq. 1) concerning to [phenol].

$$\ln([\text{phenol}]/[\text{phenol}]_0) = -k_{\text{ap}}\, t \qquad (1)$$

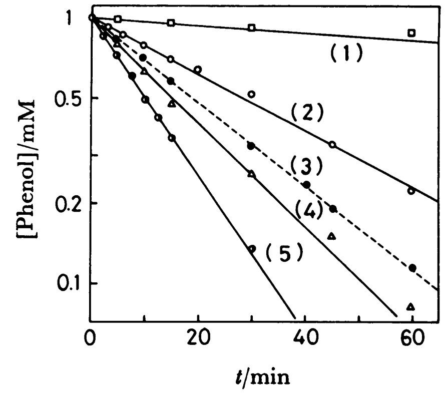


Fig. 1. Reduction of [phenol] with reaction time for the oxygenated aqueous suspensions of semiconductor powders. The ordinate is taken on a log scale. (1) CdS, (2) anatase at pH 6.5, (3) anatase at pH 3.5, (4) ZnO, and (5) reduced anatase at pH 3.5.

Table 1. Comparison between the photocatalytic activities of semiconductors

Semiconductor	pH	k_{ap}[a)]/$10^{-4}\ \text{s}^{-1}$
None	6.5	0
Rutile TiO_2	6.5	0
Anatase TiO_2	6.5	4.0
Anatase TiO_2	3.5	6.1
Reduced anatase	3.5	10.5—9.2[b)]
CdS	—	0.7
α-Fe_2O_3	—	0
ZnO	7	≈7.5

a) $[\text{phenol}]_0 = 1.0$ mM. b) The k_{ap} values were scattered in this range between different lots of anatase samples.

The photocatalytic activity of semiconductors was, therefore, compared by use of the values of the apparent rate constant, k_{ap}, shown in Table 1. It was in the order of reduced anatase>ZnO>anatase-(untreated)≫CdS. Rutile used in the present paper did not have the activity at all.

The photochemical stability of anatase and ZnO was checked by measuring the concentration of Ti^{4+} and Zn^{2+} ions dissolved out during the reaction. No trace of Ti^{4+} ions dissolved out was detected for the anatase suspensions, even after the reaction was continued till phenol disappeared completely, indicating that TiO_2 is very stable photochemically in aqueous solutions.[3)] On the other hand, a significant quantity of Zn^{2+} was detected for ZnO suspensions; for example $[Zn^{2+}]$=0.93 mM, after the reaction was performed for 1 h. This quantity of Zn^{2+} corresponded to about 1% of ZnO loaded and was roughly equal to the quantity of consumed phenol. It is known that a ZnO electrode undergoes anodic photocorrosion according to Eq. 2.

$$ZnO + 2h^+ \longrightarrow Zn^{2+} + O^* \quad (2)$$

This reaction occurs in an aqueous solution of formic acid or alchohols as well as in an inert electrolyte solution.[15] ZnO powder is, therefore, not suitable to a photocatalyst for wastewater treatment.

Among the semiconductors investigated here, lightly-reduced anatase was the most satisfactory from the standpoint of the photocatalytic activity and stability. The experiments mentioned below were, therefore, carried out using lightly-reduced anatase.

Effects of pH, Partial Pressure of O_2 and Addition of Cu^{2+}. Figure 2 shows the effect of pH on both the initial reaction rate Ω_0 and k_{ap}. It is noted that pH 3.5 is the optimum for the photocatalytic decomposition of phenol.

As shown in Fig. 3, Ω_0 depended on the partial pressure of O_2 in the bubbled gas, p_{O_2}. Under a N_2 gas bubbled, the reaction hardly occurred. The pattern of Fig. 3 suggests that the reaction rate is controlled by the quantity of O_2 adsorbed on TiO_2 surface in the Langmuir mode;

$$\Omega_0 \propto K_{O_2}p_{O_2}/(1+K_{O_2}p_{O_2}), \quad (3)$$

where K_{O_2} is the equilibrium constant of adsorption of O_2. The solid lines in Fig. 3, which were calculated from Eq. 3 with the K_{O_2} value of 0.11 kPa^{-1}, were in good agreement with the experimental results.

Figure 4 shows variation of the concentration of O_2 dissolved, $[O_2]$, with reaction time. When an anatase suspension without phenol was irradiated with UV-light, a small quantity of O_2 was consumed in the first run. After aeration, the suspension was reirradiated. O_2 was hardly consumed in the second run. After the second run, an appropriate amount of a concentrated phenol solution was added to the suspension to prepare a 1 mM phenol solution. As shown by the line (3) in Fig. 4, O_2 disappeared rapidly in this phenol solution under the UV-irradiation. In the experiments without the preirradiation in the absence of phenol, O_2 disappeared in the similar manner. About 0.7 mole of O_2 was consumed for the consumption of 1 mole of phenol at the initial stage of the reaction, as shown by the dotted lines in Fig. 4.

Table 2 shows the values of quantum yield, ϕ, of the reaction. These values were obtained in the range of the low light intensity where Ω_0 was proportional to it. The reaction proceeded only by light of wavelength shorter than 400 nm, because anatase has a band gap of 3.23 eV (corresponding to 388 nm).[16] The ϕ was almost constant for wavelength shorter than 370 nm, being in agreement with the action spectrum observed for water reduction over platinized

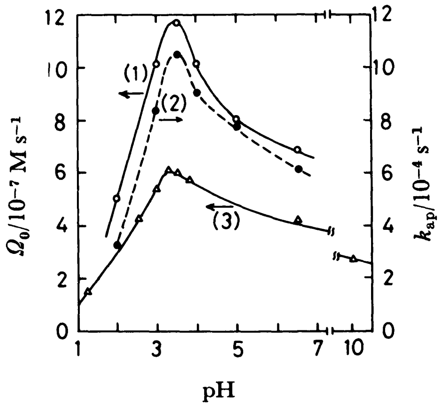


Fig. 2. Effect of pH on both Ω_0 and k_{ap}.
$[\text{phenol}]_0 = 1.0$ mM and $p_{O_2} = 101$ kPa.
Anatase: (1) and (2) reduced, (3) untreated.

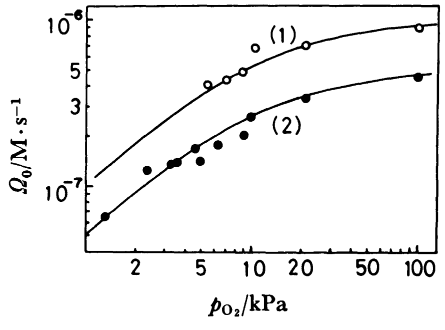


Fig. 3. Effect of p_{O_2} on Ω_0 at pH 3.5.
$[\text{phenol}]_0$: (1) 1.0 mM and (2) 0.1 mM.
The solid lines were calculated from Eq. 3 with $K_{O_2} =$ 0.11 kPa^{-1}.

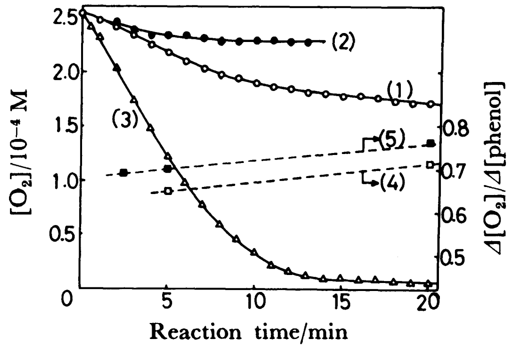


Fig. 4. Variations of $[O_2]$ with reaction time and the consumed mole ratio of O_2 to phenol, $\Delta[O_2]/\Delta[\text{phenol}]$, at pH 3.5.
$[\text{phenol}]_0 = 1.0$ mM for (3)—(5).
(1) First run in the absence of phenol; (2) second run: after the first run, the suspension was aerated for 5 min prior to the irradiation; (3) third run: after the second run, an appropriate amount of phenol was added to the suspension and it was aerated for 5 min prior to the irradiation; (4) $\Delta[O_2]/\Delta[\text{phenol}]$ for the third run; (5) $\Delta[O_2]/\Delta[\text{phenol}]$ for experiments without the pre-irradiation in the absence of phenol.

Table 2. Quantum yield of the reaction at pH 3.5[a)]

Wavelength/nm	ϕ/%
430	0
400	1.0
370	10.6
340	11.8

a) For reduced anatase, [phenol] = 1.0 mM, at 25 °C, and in the range of low light-intensity.

anatase.[17)]

For oxygenated aqueous suspensions of anatase, hydroxyl radicals have been considered to be reactive species responsible for the photocatalytic reactions of benzene,[18)] toluene,[19)] benzoic acid,[20)] and so on.[21)] They also seem reactive species responsible for the present reaction, because the photocatalytic decomposition of phenol proceeded *via* its hydroxylated compounds such as hydroquinone and pyrocatechol as will be mentioned in the following section. The initial steps of the photocatalysis are considered as follows.

Judging from the fact that Ω_0 was proportional to the square root of the incident light intensity, as will be reported elsewhere,[9)] the reaction rate was limited by the recombination of photogenerated hole-electron pairs, under the present experimental conditions. The dependence of Ω_0 on p_{O_2} expressed by Eq. 3, therefore, indicates that oxygen adsorbed on anatase surface prevents the recombination of hole-electron pairs by trapping electrons. Superoxide ions are thus formed.[18—23)]

$$O_2(a) + e^- \longrightarrow O_2^{\cdot -} \qquad (4)$$

It is likely that H_2O_2 is formed from $O_2^{\cdot -}$ according to the following reactions.[20—22,24)]

$$O_2^{\cdot -} + H^+ \longrightarrow HO_2\cdot \qquad pK_a = 4.88 \qquad (5)$$

$$HO_2\cdot + HO_2\cdot \longrightarrow H_2O_2 + O_2 \qquad k = 7.6\times10^5\ M^{-1}\,s^{-1} \qquad (6)$$

$$O_2^{\cdot -} + HO_2\cdot \longrightarrow O_2 + HO_2^- \qquad k = 8.5\times10^7\ M^{-1}\,s^{-1} \qquad (7)$$

$$HO_2^- + H^+ \longrightarrow H_2O_2 \qquad pK_a = 1.5\times10^{-12} \qquad (8)$$

The values of pK_a and k were cited from Ref. 25. It has been suggested that ·OH radicals are formed from H_2O_2 by anyone of the following reactions.[19,22)]

$$H_2O_2 \xrightarrow{h\nu} 2\cdot OH \qquad (9)$$

$$H_2O_2 + O_2^{\cdot -} \longrightarrow \cdot OH + OH^- + O_2 \qquad (10)$$

$$H_2O_2 + e^- \longrightarrow \cdot OH + OH^- \qquad (11)$$

On the other hand, holes react with either H_2O or OH^- adsorbed on anatase surface to give ·OH radicals.[16,18—22)]

$$H_2O(a) + h^+ \longrightarrow \cdot OH + H^+ \qquad (12)$$

$$OH^-(a) + h^+ \longrightarrow \cdot OH + OH^- \qquad (13)$$

It is ambiguous to what extent the routes of formation of ·OH *via* H_2O_2 are important as compared with ones *via* holes. Mattews has reported that the former routes are negligible as compared with the latter ones.[21)] In order to clarify this point, $[H_2O_2]$ in the reaction solutions was measured under the typical experimental conditions. It increased over first *ca.* 10 min and subsequently remained almost constant at 15 μM. The low value of $[H_2O_2]$ in the steady state suggests that formation of H_2O_2 according to Eqs. 4—8 was in a balance with its decomposition according to Eqs. 9—11. The fact that 0.7 mol of O_2 was consumed for the consumption of 1 mol of phenol is an additional support for the importance of formation of ·OH radicals *via* H_2O_2, as will be mentioned in the following section.

Figure 5 shows the effect of $[Cu^{2+}]$ on both Ω_0 and k_{ap}. A small quantity of Cu^{2+} less than 0.1 mM increased both Ω_0 and k_{ap} by a factor of *ca.* 2, suggesting that the effect is catalytic. On the other hand, a large quantity of Cu^{2+} rather reduced them. It has been observed that Cu^{2+} ions reduce the extent of hole-electron recombination by trapping photogenerated electrons;[10)]

$$Cu^{2+} + e^- \longrightarrow Cu^+ \xrightarrow{e^-} Cu \qquad (14)$$

The reduced forms, in turn, prevents the recombination by trapping holes;

$$Cu + h^+ \longrightarrow Cu^+ \xrightarrow{h^+} Cu^{2+} \qquad (15)$$

If a small quantity of Cu^{2+} effectively prevents hole-electron recombination even in the oxygenated suspensions, either holes or electrons escaped from the recombination produce ·OH radicals *via* the corresponding routes, resulting in the promotion of the reaction. Because a couple of Eqs. 14 and 15 is the short-circuiting reaction of Cu^{2+},[10,19)] a large quantity

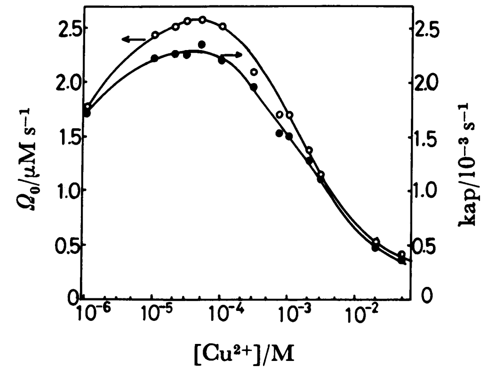


Fig. 5. Effect of $[Cu^{2+}]$ on both Ω_0 and k_{ap} at pH 3.5. $[\text{phenol}]_0 = 1.0$ mM and $p_{O_2} = 101$ kPa. With $[Cu^{2+}]=0$, $\Omega_0 = 0.96$ μM/s and $k_{ap} = 0.92\times10^{-3}\,s^{-1}$.

of Cu^{2+} rather retards the reaction. This is the most probable explanation for the result shown in Fig. 5. An alternative explanation is based on the effect of Cu^{2+} as a catalyst for the Fenton reaction.[26]

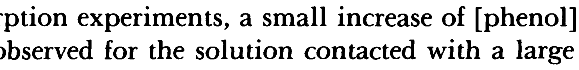
$$Cu^+ + H_2O_2 \longrightarrow \cdot OH + OH^- + Cu^{2+}, \qquad (16)$$

$$\cdot RHOH + Cu^{2+} \longrightarrow ROH + H^+ + Cu^+, \qquad (17)$$

where $\cdot$RHOH is a hydroxy adduct of a reactant RH. This effect, however, is unlikely to be significantly responsible for the promotion of the reaction, because the formation of $\cdot$OH radicals *via* H_2O_2 seems to occur sufficiently fast even in the absence of Cu^{2+} ions as mentioned above.

In the oxygenated suspensions, oxygen acts as both a trap for a photogenerated electron and an oxidant for a hydroxy adduct of the reactant (see Eqs. 19—23). In the deaerated suspensions, Cu^{2+} ions probably act in these two modes in place of O_2 according to Eqs. 14 and 17, although formation of $\cdot$OH by the routes *via* H_2O_2 does not occur. The values of Ω_0 were 0.20 and 0.28 $\mu M\, s^{-1}$ for the deaerated suspensions containg 50 μM and 1 mM of Cu^{2+}, respectively, while the reaction does not occur in the absence of Cu^{2+}. These values of Ω_0 corresponded to *ca.* 20 and 30% of the value for the oxygenated suspensions without Cu^{2+}. This fact also suggests the importance of the routes of formation of $\cdot$OH *via* H_2O_2.

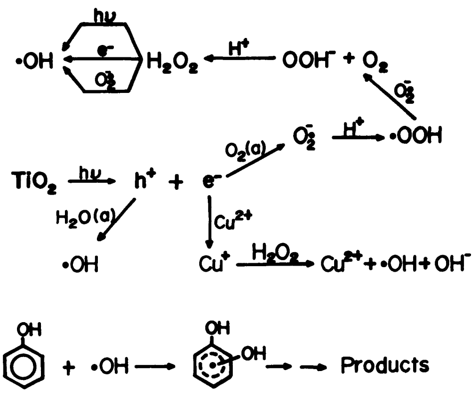
There remains the possibility that photogenerated holes react with phenol adsorbed on anatase to give dihydroxycyclohexadienyl radicals *via* phenol radical cations, as has been recently proposed for the photocatalytic oxidation of benzene by Hashimoto *et al.*[27]



(18)

The energy of holes in the valence band of TiO_2 is about -7.5 eV and is high enough for holes to react easily with H_2O and organic compounds.[28] Therefore, the probability of the reaction of holes with phenol is considered to be roughly proportional to the surface coverage of adsorbed phenol. In the adsorption experiments, a small increase of [phenol] was observed for the solution contacted with a large amount of TiO_2 powder; for example, Δ[phenol]= 0.11 mM for $[TiO_2]$=50 mg cm^{-3}. This indicates that phenol was hardly adsorbed on TiO_2 powder, as compared with water. Therefore, the path expressed by Eq. 18 is not considered to be significantly responsible for the case of phenol at least.

On the bases of the above-mentioned results and discussion, a mechanism shown in Scheme 1 is proposed for the initial steps of the photocatalysis.



Scheme 1.

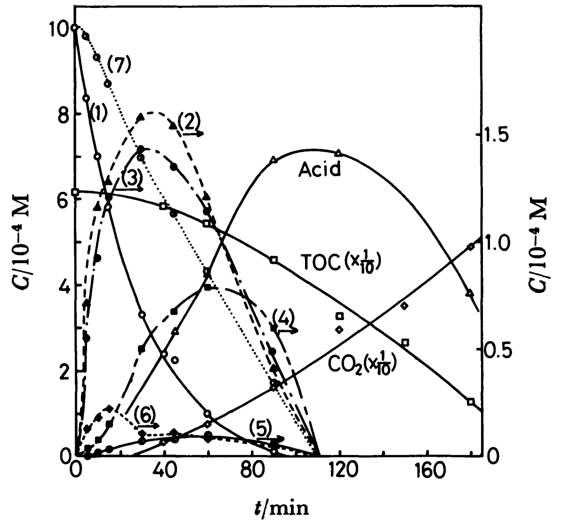


Fig. 6. Variation of concentration of the reaction products and TOC with reaction time at pH 3.5 and p_{O_2} = 101 kPa.

(1) phenol, (2) CC, (3) HQ, (4) HHQ, (5) PG, (6) HBQ and (7) total concentration of the detected aromatic compounds.

Intermediate Products and Reaction Pathway. The reaction products identified from liquid chromatograms were hydroquinone (abbreviated as HQ), pyrocatechol (CC), 1,2,4-benzenetriol (HHQ), pyrogallol (PG), 2-hydroxy-1,4-benzoquinone (HBQ), and 1,4-benzoquinone (BQ). Many peaks having very short retention times were enhanced with increasing reaction time. These peaks seemed to be attributed to very polar products like aldehydes and carboxylic acids, but were not analyzed in detail.

Figure 6 shows variation of the concentration of the products and TOC with reaction time. The concentration of acids was obtained from an amount of a KOH solution added to the reaction solution in order to maintain its pH at 3.5. BQ was detected by an amount less than 1 μM till phenol disappeared. At the degrees of conversion of 16, 42, and 80%, the combined amounts of HQ, CC, HHQ, PG, and HBQ corresponded to 90, 68, and 48% of consumed phenol, respectively. With a decrease of the mole ratio of the detected aromatic compounds to consumed phenol, [acids] increased rapidly. These results indicate that

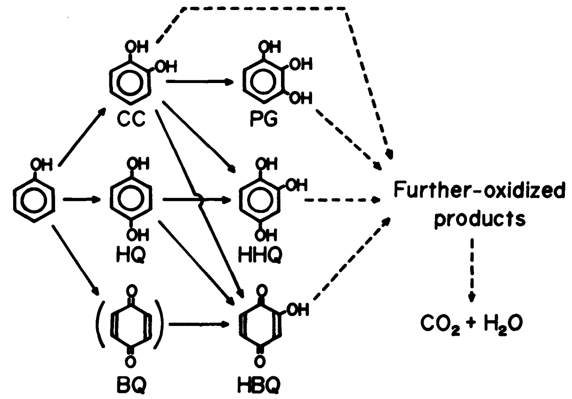
HQ, CC, HHQ, PG, and HBQ are the products at the initial stage of the reaction and undergo further photocatalytic oxidation to yield the very polar intermediate products like carboxylic acids and aldehydes. These aromatic intermediates disappeared in about ten min after disappearence of phenol. After reaching a maximum at that time, [acids] decreased with increasing reaction time. CO_2 began to be detected at the conversion of about 75%. By the reaction for 3 h, about 80% of the carbon quantity of loaded phenol was mineralized to CO_2.

Table 3 shows the distribution of the products for the photocatalytic reaction of HQ, CC, and HHQ. In spite of low conversions, about 50% of consumed pyrocatechol became undetected products having one or two carbonyl groups, suggesting that the attack of ·OH on CC brings about cleavage of benzene ring with a probability of about 50% to yield aldehydes and/or carboxylic acids. Judging from Fig. 6 and Table 3, the reaction pathway shown in Scheme 2 is the most likely. HQ and CC are the major primary products. HHQ is formed as the major secondary product *via* either HQ or CC. PG is formed *via* CC as the minor secondary one. Thus, the photocatalytic decomposition of phenol mainly proceeds *via* its hydroxylated compounds. This is very similar to the case of radiolysis of phenol in aerated aqueous solutions.[29] On the other hand, it is noted that HBQ is formed not only as the minor primary product but also as the minor secondary one *via* either HQ or CC. A possible explanation for these facts is as follows. Hydroxyl radicals react easily with phenol to yield dihydroxycyclohexadienyl radicals.[30] Most of the radicals react with O_2 according to Eqs. 19 and 20. Some of the radicals undergo the unimolecular elimination of water to yield phenoxyl radicals,[30] which react with O_2 to yield HBQ *via* BQ according to Eq. 21.

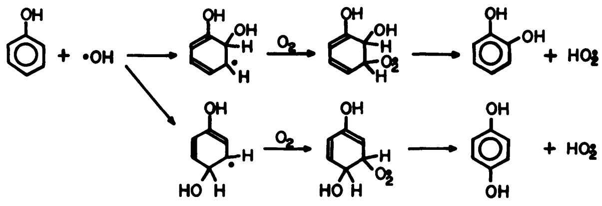
Table 3. Distribution of the products at the initial stage of the reaction[a)]

Reactant	Conversion %	Yield/% HQ	CC	HHQ	PG	HBQ	Undetected
Phenol	16.0	33.3	43.6	2.1	0.3	7.9	12.8[b)]
HQ	10.7	—	0	64.8	0	11.1	24.1[b)]
HQ	19.0	—	0	63.3	0	7.5	29.1[b)]
CC	9.8	0	—	33.7	11.8	5.8	48.7[b)]
CC	16.5	0	—	34.0	12.5	4.4	49.1[b,c)]
HHQ	6.2	0	0	—	0	0	100

a) $[\text{reactant}]_0 = 1$ mM, $[TiO_2] = 3.0$ mg cm^{-3}, and at pH 3.5. b) In liquid chromatograms, large peaks with retention times of 5.5 and 3.3 min were observed for the reaction solutions of HQ and CC, respectively. c) The reaction solution contained 0.11 mM of carbonyl groups, which corresponded to 1.3 mole per one mole of CC changed to undetected products.



Scheme 2.



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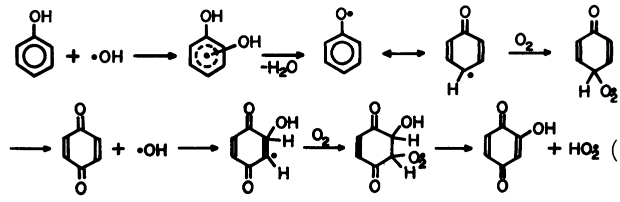
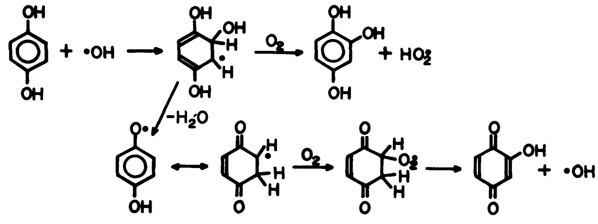


(21)

Similar reactions occur for HQ and CC. For example;



(22)

(23)

HO_2· radicals produced by Eqs. 19—21 can regenerate ·OH radicals *via* Eqs. 5—11. If the formation of ·OH *via* H_2O_2 according to Eqs. 4—11 is fully operative, 0.67 and 1.05 mole of O_2 will be necessary to consumption of one mole of phenol according to Eqs. 19 and 20 and Eq. 21, respectively. Taking the product distribution shown in Table 3 into account, it is estimated that 0.70 mol of O_2 is consumed for consumption of one mole of phenol. This estimation is in agreement with the experimental result shown in Fig. 4, indicating that the importance of formation of ·OH radicals *via* H_2O_2.

It has been reported that H_2 was not formed for photocatalytic reaction of some organic compounds

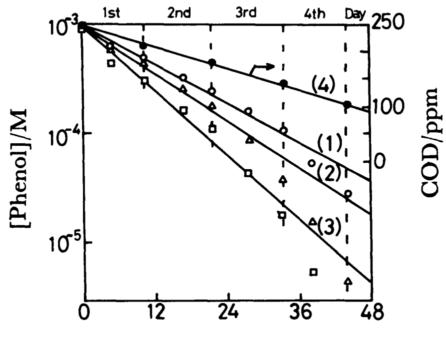


Fig. 7. Reduction of [phenol] and COD with reaction time under solar irradiation.
(1) and (4) anatase; (2) anatase in the presence of Fe^{3+} (50 μM); (3) Cu-deposited anatase.
The experimental conditions are given in the text.

in oxygenated solutions.[8,32] Therefore, the complete decomposition of phenol seems to be expressed by Eq. 24.

$$C_6H_5OH + 7\,O_2 \longrightarrow 6\,CO_2 + 3\,H_2O \qquad (24)$$

Photocatalytic Decomposition under Solar Irradiation. Figure 7 shows reduction of [phenol] and COD under solar irradiation. Control experiments with irradiated solutions with or without Cu^{2+} (50 μM) in the abscence of anatase showed very little decomposition of phenol occurred under these conditions. In the presence of anatase covering the bottom, phenol disappeared according to Eq. 1, without the serious influence of changes in both weather and height of the sun. Phenol was decomposed by the average rate of 8.6 mmol m^{-2} d^{-1} over first two days. By using Cu-deposited anatase powder, the reduction rate was increased appreciably. This catalyst, however, was not useful for wastewater treatment, because Cu deposited were dissolved into the reaction solution according to Eq. 15.

COD was reduced linearly with irradiation time. Since the photocatalytic decomposition proceeded by hydroxylation of phenol and its intermediate products according to Scheme 2, it is reasonable that a reduction in COD is proportional to an amount of ·OH radicals produced and therefore to an irradiation time. It is interesting from the viewpoint of wastewater treatment that phenol is completely mineralized to CO_2 and H_2O in the presence of anatase powder under solar irradiation without both aeration and mixing of the solution.

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