Bull. Chem. Soc. Jpn., 55, 666—671 (1982) [Vol. 55, No. 3

Heterogeneous Photocatalytic Reactions on Semiconductor Materials. III. Effect of pH and Cu^{2+} Ions on the Photo-Fenton Type Reaction

Masamichi Fujihira,* Yoshiharu Satoh, and Tetsuo Osa
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980

(Received June 29, 1981)

The effect of pH and Cu^{2+} ions on the heterogeneous photocatalytic oxidation of toluenes by H_2O_2 formed from dissolved O_2 in the presence of illuminated TiO_2 powders, *i.e.* "the photo-Fenton type reaction," was investigated. At low and high pH, a total amount of products increased drastically compared with that of the additive free system (pH 7). In the acidic region (aqueous H_2SO_4), side-chain oxidation prevailed over cresol formation and benzaldehyde was formed quite selectively at pH 1. Oxidation of the side chain in preference to hydroxylation of aromatic ring was also observed in the alkaline region (aqueous NaOH). By adding Cu^{2+} ion to the aqueous H_2SO_4 (pH 1 and 2), the yield of benzaldehyde increased further and cresols, benzyl alcohol, and bibenzyl were formed newly in high yields. At high Cu^{2+} concentrations (pH 2), the cresol formation in preference to the side-chain oxidation was attained. The observation was in good agreement with the Fenton reaction reported in which Cu^{2+} and Fe^{3+} ions are added as oxidants for the intermediate products, such as hydroxycyclohexadienyl and benzyl radicals, formed by HO· attack to toluene. Cu^{2+} ion was more preferable to Fe^{3+} ion as the oxidant, since "short circuiting" by Cu^{2+} due to the reversible redox reaction at semiconductor particles was much lower than that by Fe^{3+}. By adding a large amount of Cl^- ions to the Cu^{2+}–H_2SO_4 aqueous system, no oxidation of toluene resulted.

Previously we described the heterogeneous photocatalytic oxidation of aromatic compounds by the illuminated semiconductor powders under the air atmosphere.[1–3] By this new synthetic method, all the products expected from the Fenton reaction[4] were obtained when the reactions were carried out in the aqueous solutions.[1,2] For example, phenol and biphenyl from benzene and benzaldehyde, cresols, and bibenzyl from toluene were obtained. From the distribution of these products[1] and from the effect of the semiconductor materials on the reaction,[2] it was concluded that the reaction proceeded *via* the same mechanism as the Fenton reaction and consequently the reaction was named "the photo-Fenton type reaction."[1,2] The real oxidant in the aqueous TiO_2 systems was considered to be the hydroxyl radical, HO·, which is formed either from the cathodic reaction product, H_2O_2, (Eqs. 1—3 and 5—7) as in

$$h\nu \longrightarrow e^- + h^+ \tag{1}$$

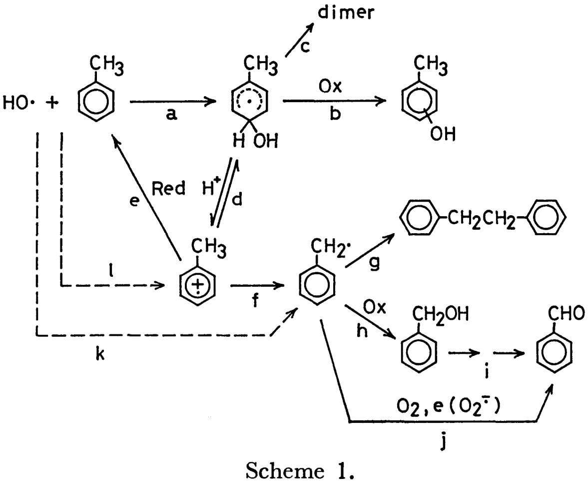
$$2h^+ + H_2O \longrightarrow 1/2O_2 + 2H^+ \tag{2}$$

$$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2 \tag{3}$$

Fenton's reagent[5] or from the anodic oxidation of OH^- or H_2O (Eqs. 8 and 22).[6–11] The role of hydroxyl radicals was also suggested in the photodecomposition of hydrocarbons in oxygen-containing aqueous solutions at platinized TiO_2.[12]

On the other hand, the reaction proceeded differently, when TiO_2 powders suspended in the aromatic hydrocarbon themselves were irradiated. For example, irradiation of toluene gave benzaldehyde under the air, and gave bibenzyl under nitrogen very selectively.[3] The observation under the air atmosphere corresponded well to the reported results for vapor-phase oxidation of alkyltoluenes by oxygen in contact with UV irradiated TiO_2 in which alkylbenzaldehydes were yielded selectively.[13] The difference in the distribution of the products caused by the absence of water was interpreted by proposing the other mechanism.[3] In this mechanism, oxidation was initiated by the anodic oxidation of toluene by a photogenerated hole to form a toluene cation radical[14] and inexistence of the reactive oxidant, HO· was assumed. The mechanism explained well not only the absence of the hydroxylated products, but also the reason for failure in oxidation of benzene in the absence of water.[3]

If we compare the results observed in the presence and absence of water, we will readily come to the conclusion that a distinctive feature of "the photo-Fenton type reaction" in the presence of water is its ability to hydroxylation of aromatic rings. Consequently in the present work, we investigated the effect of the solution conditions such as pH and Cu^{2+} ions on "the photo-Fenton type reaction," because these solution conditions are well known in the usual Fenton reaction[4] to affect the distribution of the products, especially the ratio of the yield of hydroxylated product to that of side-chain oxidation product (Scheme 1). We will also describe the effect of these factors on the total yield of product.



Scheme 1.

Experimental

As a photocatalyst, 99.99% anatase from Rare Metallic Co. was used as received. Each photocatalyst (1 g), in a mixture of aqueous solution of various pH's (100 cm^3) and toluene (5 cm^3), was irradiated for 2 h by a 500 W high pressure mercury arc lamp in a 100 cm^3 Pyrex glass round bottomed flask with a condenser cooled with running water. The solutions were prepared using doubly distilled water and reagent grade chemicals without further purification. To keep the solution saturated with oxygen in the air and to maintain homogeneous mixing of the suspension, the solution was stirred by a magnetic stirrer. After photolysis, the solution was made acidic by HCl addition, then extracted with ether, and finally concentrated under a reduced pressure. A Shimadzu GC-4CM gas chromatograph was used for the analysis of the products. The injection temperature was 250 °C and the column temperature was programmed from 140 °C to 180 °C at the raising rate of 1 °C min^{-1}. Nitrogen was used as the carrier gas at the flow rate of 30 $cm^3\,min^{-1}$. The column used was 2 m × 3ϕ SUS packed with 10% Lanoline on Chromosorb W. Identification of products was based on comparison of the retention times of samples and standards. Acetophenone was used as the internal standard material for quantitative analysis. The amount of a gaseous product, CO_2, was determined by the method in the literature.[12] Total amount of products and the quantum yield were calculated on the basis of the amount of the starting material transformed. Therefore 1 mol of cresols, benzaldehyde, or benzyl alcohol counted as 1 mol of products while 1 mol of bibenzyl counted as 2 mol of product. The number of incident photons (s^{-1}) was estimated by the use of a calibrated Hamamatsu silicon photocell model S 1337-1010 BQ on the assumption that irradiated light through a Toshiba UV filter UV-D35 mainly consisted of photons of 365 nm.

Results and Discussion

Effect of pH. The effect of pH on the distribution of the products and on the total yield of product is shown in Table 1. In these experiments, pH was controlled by adding H_2SO_4 or NaOH and the solutions were irradiated without UV filter except for run Nos. 2 and 3. On calculation of quantum yields, effective light intensity without UV filter was assumed to be about 1.9 times stronger than that with the filter on the basis of the previous results for neutral systems (pH 7).[2] It seems quite reasonable because the quantum yields calculated on the assumption for the experiments at pH 1 with and without the filter are in good agreement with each other (Nos. 1 and 2). By merely adding H_2SO_4, the total amount of products increased with increase in H_2SO_4 concentrations and at pH 1 it becomes about 5 times more than that of additive free system. Although the amount of CO_2 evolved was not determined for every run of the experiment, about 100 µmol of CO_2 was evolved at pH 7 while only a trace amount of CO_2 was detected at pH 1. The suppression of CO_2 formation may explain partly the high yield at low pH.[15] There has been also prediction that the Haber-Weiss reaction can be a potential HO· radical source in the absence of metal impurities at high and low pH.[16] It is also clear from the data in the acidic region (Nos. 1—4) that the yield of side-chain oxidation products prevailed over the yield of cresols and at pH 1 benzaldehyde was formed quite selectively. The total yields increased also with increase in pH in the alkaline region and preferential oxidation of the side chain becomes clearer with increase in pH. But as the side-chain oxidation products, not only benzaldehyde but also bibenzyl was formed and the latter yield is rather higher than the former yield (Nos. 9 and 10) in contrast with the results at pH 1.

The pH dependence of the heterogeneous photocatalytic oxidation of toluene in the acidic region can be interpreted reasonably with reference to the mechanism of the Fenton reaction as previously.[1,2] In the Fenton reaction, H_2O_2 decomposes into hydroxy radical and hydroxide anion by the reductive cleavage with ferrous ion as follows:[4]

$$H_2O_2 + Fe^{2+} \longrightarrow HO^- + HO\cdot + Fe^{3+} \qquad (4)$$

In the present system, where the metal ion catalyst for HO· formation such as Fe^{2+} was not added, we considered the following four reactions are responsible for HO· formation as probable paths.[1,2] HO· formed is very reactive and takes part in the hydroxyla-

TABLE 1. EFFECT OF pH ON YIELDS FOR PHOTO-FENTON TYPE REACTION OF TOLUENE

Run No.	pH	Product (µmol)[c]								Total[d]	Quantum[d] yield/%
		BzOH	PhCHO	*o*-Cr	*m*-Cr	*p*-Cr	BiBz	Dimer	CO_2	µmol	
1	1	3.8	418.2	—	—	—	18.7	—		459.4	1.14
2	1[a]	trace	234.3	—	—	—	—	—	trace	234.3	1.08
3	2[a]	trace	133.7	8.9	3.8	2.7	—	—		149.1	0.69
4	3	trace	84.2	7.5	3.7	1.7	4.7	1.4		106.5	0.26
5	4	—	27.0	31.3	20.2	10.3	11.0	5.4		110.8	0.28
6	7[b]	—	27.3	30.5	19.2	11.2	—	5.0	81.2	88.2	0.22
7	11	—	11.0	19.9	23.8	9.1	18.5	8.0		100.8	0.25
8	12	—	25.1	41.0	39.5	17.5	2.3	trace		127.7	0.32
9	13	trace	46.6	19.9	19.4	6.7	63.8	9.7		220.2	0.55
10	14	trace	58.5	1.5	0.6	0.3	106.0	0.5		272.9	0.68

a) With UV filter. b) Without H_2SO_4 and NaOH. c) BzOH = benzyl alcohol, PhCHO = benzaldehyde, Cr = cresol, BiBz = bibenzyl. d) Calculated by excluding dimer.

$$H_2O_2 + O_2^{\cdot -} \longrightarrow HO\cdot + OH^- + O_2 \quad (5)$$

$$H_2O_2 + h\nu \longrightarrow 2HO\cdot \quad (6)$$

$$H_2O_2 + e^-(TiO_2) \longrightarrow HO\cdot + OH^- \quad (7)$$

$$H_2O(ads) + h^+ \longrightarrow HO\cdot + H^+ \quad (8)$$

tion of aromatic ring and the side-chain oxidation of alkylbenzenes *via* the mechanism as shown in Scheme 1.[17–19] Steps for which there is substantial evidence[18] are indicated by solid arrows, others which are also discussed by dashed arrows. It indicates that most hydroxyl radical attack on aromatics occurs *via* addition, a, to yield hydroxycyclohexadienyl radicals. This is in agreement with conclusions by previous researchers[17–19] and the frequent detection of the hydroxycyclohexadienyl radical by spectroscopic means[20,21] and is strongly supported by the present result described later that phenolic products can be detected in every system in the presence of adequate oxidant, particularly Cu^{2+}, and can be made the major products. This shows that direct side-chain attack, k, cannot be more than a minor reaction path.[22] The rates of hydroxyl radical reactions with aromatics are much faster than would be anticipated for side-chain hydrogen abstraction.[18] In order to account for an apparent high reactivity of aromatic alcohols compared with benzene, Hamilton has proposed either path, l (perhaps concerted with f) or initial formation of a π complex.[23] It is, however, suggested from a correlation of the rate constants with Hammett substituent constant σ[24,25] that sulfate radical anions, $SO_4^{\cdot -}$, form the cation radicals by an electron transfer from the ring to $SO_4^{\cdot -}$ while hydroxyl radicals add to the aromatic ring to form hydroxycyclohexadienyl radicals.

If pH of the solution becomes low, the hydroxycyclohexadienyl radical, will be changed promptly to a radical cation (route d in Scheme 1).[21] The formed cation radical has been known to lose a proton irreversibly to give a benzyl radical (route f) which undergoes dimerization to bibenzyl in the absence of oxidant (route g) or side-chain oxidation to benzyl alcohol (route h) or benzaldehyde (route h and i or route j) in the presence of oxidant. In the systems described above, there is no oxidant added such as Cu^{2+} and Fe^{3+} ions, and therefore only dissolved oxygen acts as the oxidant. Since the yield of benzyl alcohol is much less than that of benzaldehyde (Nos. 1 and 2), benzaldehyde may be formed directly *via* a route j in the presence of dissolved oxygen as in the oxidation in aromatic hydrocarbons.[3] The selective formation of benzaldehyde agrees well with the reaction with Fenton's reagent generated electrochemically in the presence of oxygen.[26] With increase in pH, cresols formation by oxidation of hydroxycyclohexadienyl radical with dissolved oxygen (route b) seems to prevail over the side-chain oxidation described above due to slow down in the water elimination reaction to cation radicals (route d). Above pH 3, another product which may be attributable to a dimer as biphenyl was also detected (route c).

In the alkaline region especially at extremely high pH where only a small amount of cresols was obtained (No. 10), it seems difficult to explain the reaction only by the above described mechanism for the Fenton reaction. For example in such a high pH region, the concentrations of H_2O_2 and $HO\cdot$ are lowered by deprotonation as follows:

$$H_2O_2 \longrightarrow HO_2^- + H^+ \quad (pK_a = 11.62)^{27)} \quad (9)$$

$$HO\cdot \longrightarrow O^- + H^+ \quad (pK_a = 11.9^{28,29)} \text{ and } 11.8^{30)}) \quad (10)$$

Consequently, it is preferable to propose the additional mechanism for the reaction in this pH region. Fortunately, it has been already demonstrated[22,31–34] by pulse radiolysis studies that benzyl radicals can be produced in irradiated aqueous solution by the reaction of O^- with toluene at high pH. Although $HO\cdot$ radicals add to the aromatic ring much more rapidly than they abstract hydrogen from an aliphatic side chain, the situation is reversed when $HO\cdot$ is converted into O^-. At $pH > 13$, the main reaction in irradiated solutions of toluene involves abstraction of H from the methyl group to produce the corresponding benzyl radicals. Consequently, the preferential oxidation of side-chain at high pH ($pH > 13$) in Table 1 can be interpreted by the further reactions of the benzyl radicals formed by this hydrogen abstraction by O^-. In the presence of oxygen, O^- reacts with O_2 very rapidly to form the ozonide ion with the rate constant of $2.6 \times 10^9\ M^{-1}\,s^{-1}$.[35] However, from careful pulse radiolysis studies, Gall and

$$O^- + O_2 \longrightarrow O_3^- \quad (11)$$

Dorfman[36] concluded that O^- species through thermal dissociation reaction is again the true reactive species in the presence of O_3^-.

$$O_3^- \longrightarrow O_2 + O^- \quad (12)$$

Although the explanation given above is most probable, the alternative mechanism described below was considered at first as a probable mechanism which is similar to the mechanism for the reaction in the absence of water described previously.[3]

$$h\nu \longrightarrow e^- + h^+ \quad (13)$$

$$C_6H_5CH_3 + h^+ \longrightarrow C_6H_5CH_3^{+}\cdot \quad (14)$$

$$C_6H_5CH_3^{+}\cdot \longrightarrow C_6H_5CH_2\cdot + H^+ \quad (15)$$

$$C_6H_5CH_2\cdot \longrightarrow 1/2(C_6H_5CH_2)_2 \quad (16)$$

$$C_6H_5CH_2\cdot + O_2 \longrightarrow C_6H_5CH_2O_2\cdot \quad (17)$$

$$C_6H_5CH_2O_2\cdot + e^- \longrightarrow C_6H_5CHO + OH^- \quad (18)$$

Instead of Eqs. 17 and 18, the alternatives are possible as follows:

$$O_2 + e^- \longrightarrow O_2^{\cdot -} \quad (19)$$

$$C_6H_5CH_2O_2\cdot + O_2^{\cdot -} \longrightarrow C_6H_5CHO + OH^- + O_2 \quad (20)$$

$$C_6H_5CH_2\cdot + O_2^{\cdot -} \longrightarrow C_6H_5CHO + OH^- \quad (21)$$

This seems to be rationalized by the consideration of pH dependent change in energy levels of the band edges of TiO_2[37,38] and the redox potentials of species in solution as shown in Fig. 1. For lack of data, the redox potential of toluene/toluene cation radical measured in acetonitrile[39] is adopted in place of that

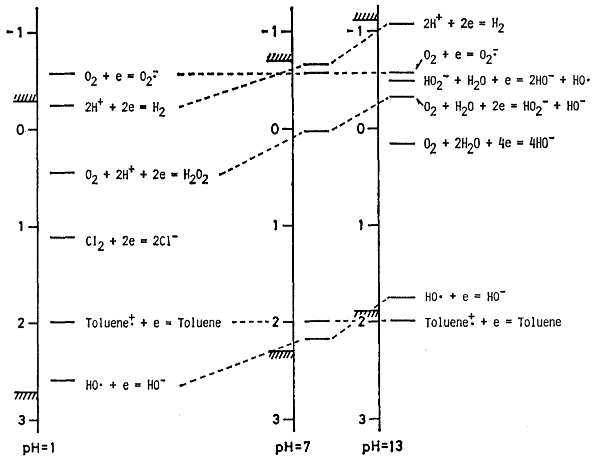


Fig. 1. Changes in position of conduction-band and valence-band edges of TiO_2[37,38] and redox potentials of solution species[39,42,46] in V *vs.* SCE by pH of the aqueous solution.

in water. The potential should be more cathodic than the value shown in Fig. 1 due to the higher solvation energy of cation radical in water than in acetonitrile.[40] Taking this into account, it can be reasonably proposed that toluene is oxidized directly into cation radical even at high pH (Eq. 14) as well as HO^- by positive holes created in the valence band.

$$HO^- + h^+ \longrightarrow HO\cdot \qquad (22)$$

Previously the reaction under the air in the absence of water only gave benzaldehyde,[3] but bibenzyl was also formed in the aqueous alkaline solution. The difference may be partly due to the lower solubility of oxygen in water than that in toluene[41] and partly due to the shorter life time of superoxide ion in water[42] than that in hydrocarbon. Furthermore the direct formation of cation radical by positive holes can be considered reasonably as a parallel initiation reaction as well as the reaction initiated *via* addition by $HO\cdot$ at $pH<12$, since the cation radical formed by $SO_4^{\cdot-}$ gave the similar isomer distributions to those obtained by $HO\cdot$,[43] but in a strongly alkaline solution, applicability of this parallel mechanism cannot be ascertained since conversion of $SO_4^{\cdot-}$ to $HO\cdot$ should compete with attack on toluene[44] and the $HO\cdot$–O^- equilibrium becomes significant as described above. If it prevailed, reversible hydration by water to hydroxycyclohexadienyl radicals from the cation radical (route d)[21] would give more phenolic compounds even at high pH. Anyhow, the very low yield of cresols at pH 14 indicates that contribution of the Fenton type reaction by $HO\cdot$ radical is very low, but it is not negligible in contrast with the previous results in the absence of water[3] due to the equilibrium of reaction of Eq. 10.

In addition to the above described pH dependence of CO_2 formation[15] and the yield of Haber-Weiss reaction,[16] the following will partly account for the present observation as to the effect of pH on the total yield of products. In neutral solution, the equilibrium of reaction route d lies to so far to the hydroxycyclohexadienyl radical side and furthermore the rate of reaction route b is limited by the oxidation with dissolved oxygen in the absence of additional oxidants. Consequently if there is another path through which hydroxycyclohexadienyl radicals decay, this accounts for the minimum in the total yield of product in the neutral region. The Hückel theory predicts that the hydrogenated aromatic radical, $ArH\cdot$, derived from alternant hydrocarbons should have the same half-wave potentials, about -1.1 V *vs.* SCE, since the highest occupied orbital into which a further electron is uptaken is the non-bonding molecular orbital. This fact was ascertained experimentally by Dietz and Peover.[45] Due to its higher electronegativity of HO than H, the reduction potential of hydroxycyclohexadienyl radical can be considered reasonably to be more positive than that of cyclohexadienyl radical of -1.1 V *vs.* SCE. Consequently there is a possibility for hydroxycyclohexadienyl redical to be reduced to yield toluene and HO^- by either electron from conduction band of TiO_2 or superoxide ion. In the alkaline region, the direct formation of benzyl radical by O^- as described above may account for the increase in total yield.

Effect of Cu^{2+} Ions. The effect of Cu^{2+} ion concentrations at pH 1 and pH 2 on "the photo-Fenton type reaction" is summarized in Table 2. On run Nos. 2, 3, and 11—17, pH of the solution was adjusted by adding H_2SO_4, while in run Nos. 18 and 19, HCl was used as acids and in the latter case NaCl was also added. As is evident from the mechanism shown in Scheme 1, the total yield of product will be expected to increase if oxidants are added in the acidic region where the Fenton type reaction mechanism was found to be applicable. This is because the reactions of routes b and h will be accelerated and the backward reaction (route e) will be retarded by the addition of oxidants. As one would expect, the side-chain oxidation products increased by addition of 10 mM Cu^{2+} ions at pH 1 (No. 11). Absence of cresols seems to be reasonable since the reaction between hydroxycyclohexadienyl and cation radicals (route d) lies to the cation radical side at such a very low pH.[4] It is also worthy of note that bibenzyl and benzyl alcohol were formed in additon to benzaldehyde. Cresols formation by further increase in Cu^{2+} ion concentrations (Nos. 12—14) seems to be due to the acceleration of route b which is so high as to be able to compete with the reaction to cation radical (route d). Among the side-chain oxidation products, bibenzyl decreased dramatically with increase in Cu^{2+} ion concentration according to our expectation from Scheme 1. Sudden increase in benzyl alcohol yield by addition of Cu^{2+} ions supports the above interpretation that benzaldehyde was formed directly *via* route j in the presence of only oxygen. The further increase in the formation of benzaldehyde and almost the constant yield of benzyl alcohol with increase in Cu^{2+} ion concentration up to 50 mM indicate that a part of benzaldehyde was formed *via* the intermediate benzyl alcohol in the presence of Cu^{2+} ions (routes h and i). In the presence of high concentration of Cu^{2+} ions (Nos. 13 and 14), cresols formation increased, but the total yield decreased with

TABLE 2. EFFECT OF Cu^{2+} CONCENTRATION ON YIELD FOR PHOTO-FENTON TYPE REACTION OF TOLUENE[a)]

Run No.	pH	$[Cu^{2+}]$ mM	Product (μmol) BzOH	PhCHO	*o*-Cr	*m*-Cr	*p*-Cr	BiBz	Total μmol	Quantum yield/%
2	1	0	trace	234.3	—	—	—	—	234.3	1.08
11	1	10	182.4	315.3	trace	—	—	201.5	901.1	4.17
12	1	50	188.1	646.4	80.7	7.6		70.8	1064.4	4.93
13	1	200	186.8	540.4	130.8	54.7		19.0	950.3	4.40
14	1	500	141.9	206.8	133.0	73.7		8.8	573.0	2.65
3	2	0	trace	133.7	8.9	3.8	2.7	—	149.1	0.69
15	2	50	—	123.9	101.9	44.5	21.1	7.9	307.3	1.42
16	2	200	trace	111.3	208.2	89.7	67.5	—	476.7	2.21
17	2	500	—	24.5	120.9	57.1	50.2	—	252.7	1.17
18	2[b)]	200	—	60.5	165.9	90.0	65.4	—	381.8	1.77
19	2[c)]	200	—	—	—	—	—	—	0	0

a) All experiments were done with UV filter and pH of solutions were controlled by adding H_2SO_4 unless otherwise noted. 1 M = 1 mol dm^{-3}. b) 10 mM HCl aqueous solution. c) 3.4 M NaCl in 10 mM HCl aqueous solutinn.

increase in Cu^{2+} concentration. This tendency was also observed in the experiments carried out at pH 2 (Nos. 3, 15—17). At this pH, by adding Cu^{2+} oxidation occurred on the ring in preference to the side chain and furthermore the yield of the side-chain oxidation products rather decreased compared with the result in the absence of Cu^{2+}. In spite of addition of Cu^{2+}, benzaldehyde may be formed mainly *via* route j at this pH as only little benzyl alcohol and bibenzyl are formed. At present the reason for this is not clear. Among the experiments done in H_2SO_4 aqueous solutions, 500 mM of Cu^{2+} ions at pH 2 gave the highest ratio of the yield of hydroxylated products to that of side-chain oxidation products.

In addition to acceleration of routes b and h and retardation of route e, it may be possible that addition of Cu^{2+} ions also increases the total yield by the action of Cu^+ ions, formed by the oxidation reactions in route b and h, as a catalyst for the Fenton type reaction as follows:

$$H_2O_2 + Cu^+ \longrightarrow HO\cdot + OH^- + Cu^{2+} \tag{23}$$

Here Cu^+ ion is unstable thermodynamically[46)] because Cu^+ ion easily disproportionates to Cu^{2+} and Cu metal in H_2SO_4. The decrease in the total yield observed in the high Cu^{2+} concentration, which is not so obvious as in Fe^{2+} addition described previously[1,2)] can be attributed to the "short circuiting" reactions as follows:

$$Cu^{2+} + 2e^- \longrightarrow Cu \tag{24}$$

$$Cu + 2h^+ \longrightarrow Cu^{2+} \tag{25}$$

Sluggishness of Reaction 25, may be the main reason for inefficiency of the "short circuiting" reaction of Cu^{2+} ions.[47)]

If chloride ion is added, cuprous ion will be stable thermodynamically by complex formation[46)] as shown in Eqs. 26—28. The redox couple would also expected to be active as a catalyst for HO· formation.[48)] The result at pH 2 by adding HCl is shown in run No. 18. Almost comparable result to that observed with H_2SO_4 solution was obtained in the aqueous HCl solution, but no product was formed when 3.4 M NaCl was added further (No. 19). The latter result may be explained by the "short circuiting" reaction of the following reversible redox reactions:

$$Cu^{2+} + Cl^- + e^- \longrightarrow CuCl \tag{26}$$

$$CuCl + h^+ \longrightarrow Cu^{2+} + Cl^- \tag{27}$$

where, in high Cl^- concentration, cuprous chloride is in equilibrium with its complexes with chloride anion as follows:[49)]

$$n\mathrm{CuCl} + m\mathrm{Cl}^- \rightleftharpoons \mathrm{Cu}_n\mathrm{Cl}_{m+n}{}^{m-} \tag{28}$$

The preferential hole quenching by the undesirable anodic reaction of chloride anions:[50)]

$$2Cl^- + 2h^+ \longrightarrow Cl_2 \tag{29}$$

also seems to be responsible for no oxidation of toluene.

In conclusion, lowering pH and adding Cu^{2+} ions increased the quantum yield of the heterogeneous photocatalytic oxidation of toluene up to 5% as to total products, which is about 20 times more efficient than that observed in the additive free system. The effect of these solution conditions on the distribution of products was very similar to those observed in the usual Fenton reactions in the acidic media containing H_2O_2, Fe^{2+}, and Cu^{2+}. In the alkaline media, O^-, deprotonated form of HO·, abstracts H from side-chain of toluene rather than adds to the aromatic ring and consequently the side-chain oxidation products were formed in preference to the phenolic compounds. In other words, the selective formation of benzaldehyde, bibenzyl, or cresols was possible by controlling pH and/or adding Cu^{2+} ions. By these observations we could confirm further the previous conclusion that the real oxidant in the aqueous TiO_2 system is the hydroxyl radical as in Fenton's reagent. Cu^{2+} ion was not so serious as Fe^{2+} for decreasing the yield due to the "short circuiting" by its redox reaction occurring at the same semiconductor particle, unless the solution contained a large amount of Cl^- ions.

References

1) M. Fujihira, Y. Satoh, and T. Osa, *Nature*, **293**, 206

(1981).

2) M. Fujihira, Y. Satoh, and T. Osa, *Chem. Lett.*, **1981**, 1053.

3) M. Fujihira, Y. Satoh, and T. Osa, *J. Electroanal. Chem.*, **126**, 277 (1981).

4) C. Walling, *Acc. Chem. Res.*, **8**, 125 (1975).

5) H. J. H. Fenton, *J. Chem. Soc.*, **65**, 899 (1894).

6) M. D. Archer, *J. Appl. Electrochem.*, **5**, 17 (1975).

7) G. A. Korsunovskii, *Russ. J. Phys. Chem. (Engl. Transl.)*, **52**, 1314 (1978).

8) M. V. Rao, K. Rajeshwar, V. R. P. Verneker, and J. DuBow, *J. Phys. Chem.*, **84**, 1987 (1980).

9) J. M. Kowalski, K. H. Johnson, and H. L. Tuller, *J. Electrochem. Soc.*, **127**, 1969 (1980).

10) S. Sato and J. M. White, *J. Phys. Chem.*, **85**, 336 (1981).

11) C. D. Jaeger and A. J. Bard, *J. Phys. Chem.*, **83**, 3146 (1979).

12) I. Izumi, W. W. Dunn, K. O. Wilbourn, F. F. Fan, and A. J. Bard, *J. Phys. Chem.*, **84**, 3207 (1980); I. Izumi, F. F. Fan, and A. J. Bard, *ibid.*, **85**, 218 (1981).

13) M. N. Mozzanega, J. M. Herrman, and P. Pichat, *Tetrahedron Lett.*, **1977**, 2965.

14) T. Kanno, T. Oguchi, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, **21**, 467 (1980).

15) B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, **100**, 5985 (1978).

16) J. Weinstein and B. H. J. Bielski, *J. Am. Chem. Soc.*, **101**, 58 (1979).

17) C. R. E. Jefcoate, J. R. L. Smith, and R. O. C. Norman, *J. Chem. Soc., B*, **1969**, 1013.

18) C. Walling and R. A. Johnson, *J. Am. Chem. Soc.*, **97**, 363, (1975).

19) M. K. Eberhardt and M. I. Martinez, *J. Phys. Chem.*, **79**, 1917 (1975).

20) L. M. Dorfman, I. A. Taub, and R. E. Bühler, *J. Chem. Phys.*, **36**, 3051 (1962).

21) K. Sehested, J. Holcman, and E. J. Hart, *J. Phys. Chem.*, **81**, 1363 (1977).

22) K. Sehested, H. Corfitzen, H. C. Christensen, and E. J. Hart, *J. Phys. Chem.*, **79**, 310 (1975).

23) M. E. Snook and G. A. Hamilton, *J. Am. Chem. Soc.*, **96**, 860 (1974).

24) P. Neta, V. Madhaven, H. Zemel, and R. W. Fessenden, *J. Am. Chem. Soc.*, **99**, 163 (1977).

25) P. Neta and L. M. Dorfman, *Adv. Chem. Ser.*, **81**, 222 (1968).

26) T. Matsue, M. Fujihira, and T. Osa, *J. Electrochem. Soc.*, **128**, 2565 (1981).

27) "Handbook of Chemistry and Physics," 54th ed, CRC Press, Cleveland (1973), p. D-130.

28) J. Rabani and M. S. Matheson, *J. Am. Chem. Soc.*, **86**, 3175 (1964).

29) J. Rabani and M. S. Matheson, *J. Phys. Chem.*, **70**, 761 (1966).

30) J. L. Weeks and J. Rabani, *J. Phys. Chem.*, **70**, 2100 (1966).

31) P. Neta, M. Z. Hoffman, and M. Simic, *J. Phys. Chem.*, **76**, 847 (1972).

32) P. Neta and R. H. Schuler, *J. Phys. Chem.*, **77**, 1368 (1973).

33) H. C. Christensen, K. Sehested, and E. J. Hart, *J. Phys. Chem.*, **77**, 983 (1973).

34) M. K. Eberhardt and M. Yoshida, *J. Phys. Chem.*, **77**, 589 (1973).

35) G. E. Adams, J. W. Boag, and B. D. Michael, *Nature*, **205**, 898 (1965).

36) B. L. Gall and L. M. Dorfman, *J. Am. Chem. Soc.*, **91**, 2199 (1969).

37) J. M. Bolts and M. S. Wrighton, *J. Phys. Chem.*, **80**, 2641 (1976).

38) E. C. Dutoit, F. Cardon, and W. P. Gomes, *Ber. Bunsenges. Phys. Chem.*, **80**, 475 (1976).

39) E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963).

40) S. Hayano and M. Fujihira, *Bull. Chem. Soc. Jpn.*, **44**, 2051 (1971).

41) R. Battino and H. L. Clever, *Chem. Rev.*, **66**, 395 (1966).

42) D. T. Sawyer and M. J. Gibian, *Tetrahedron*, **35**, 1471 (1979).

43) C. Walling, D. M. Camaioni, and S. S. Kim, *J. Am. Chem. Soc.*, **100**, 4814 (1978).

44) E. Hayon, A. Treinin, and J. Wilf, *J. Am. Chem. Soc.*, **94**, 47 (1972).

45) R. Dietz and M. E. Peover, *Trans. Faraday Soc.*, **62**, 3536 (1966).

46) D. Dobos, "Electrochemical Data," Elsevier, Amsterdam (1975).

47) H. Reiche, W. W. Dunn, and A. J. Bard, *J. Phys. Chem.*, **83**, 2248 (1979).

48) J. F. Skinner, A. Glasel, L. Hsu, and B. L. Funt, *J. Electrochem. Soc.*, **127**, 315 (1980).

49) J. J. Fritz, *J. Phys. Chem.*, **84**, 2241 (1980); **85**, 890 (1981).

50) T. Kobayashi, H. Yoneyama, and H. Tamura, *Chem. Lett.*, **1979**, 457; *J. Electroanal. Chem.*, **122**, 133 (1981).