296 *J. Org. Chem.* 1988, *53*, 296-300

Direct Conversion of Benzene to Hydroquinone. Cooperative Action of Cu(I) Ion and Dioxygen

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Received September 4, 1987

Hydroquinone (or benzoquinone) and phenol are obtained from the aqueous-phase reaction of benzene with hydroxyl radical generated in the combined system of Cu(I) ion and dioxygen. The relative yield of hydroquinone to phenol (n = HQ/PhOH) varies substantially with the change in the solution pH ($n = 0.4$ at pH 1.3 and $n = 6$ at pH 3.5). Factors affecting the n value have been studied extensively by comparing reactivites of OH radical generated in several different means such as γ-ray radiolysis or Fenton's reaction. Extraneously high n values were only obtained when both oxygen and Cu(I) ion were present simultaneously in the reaction media. All of the experimental findings are consistent with the mechanism that involves several successive intermediates, hydroxycyclohexadienyl radical, its oxygen adduct (peroxy radical), and the reducton product of the peroxy radical (hydroperoxide). Oxygen is necessary to produce peroxy radical and Cu(I) ion to produce hydroperoxide. A somewhat complex behavior of pH effect has also been discussed.

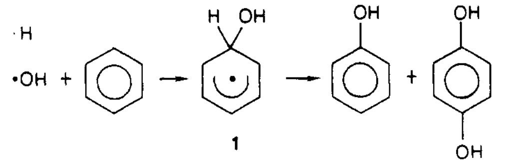
I. Introduction

In a series of papers,[1-6] we have shown that benzene is readily oxidized by dioxygen to form phenolic compounds in sulfuric acid solutions containing Cu^+ ion. Mechanistic studies[5,6] indicated that the active species responsible for the phenolic products is hydroxyl radical produced by the reactions in eq 1 and 2. Hydroxyl radicals thus produced

$$2Cu^+ + O_2 + 2H^+ = 2Cu^{2+} + H_2O_2 \qquad (1)$$

$$Cu^+ + H_2O_2 + H^+ = Cu^+ + OH + H_2O \qquad (2)$$

can react with benzene to form hydroxycyclohexadienyl radicals, radical 1, which lead to the formation of phenolic products (eq 3). The processes composing the whole sequence of reaction 3 are believed to be more or less the same as those proposed for the reaction of Fenton's reagent.[7-9] It is somewhat surprising that the combination of Cu^+ ion and dioxygen as the OH radical source has never been studied at any systematic level.



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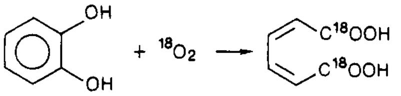
The use of Cu^+ ion in place of Fe^{2+} of the Fenton's reagent has several advantages; i.e., (1) external supply of H_2O_2 is unnecessary, (2) continuous operation of reaction 3 is readily accomplished by utilizing electrolytic regeneration of Cu^+ ion,[2,3] and (3) selectivity of the phenolic products is remarkably high.[5,6] Besides these, it must be a noticeable character of the present reaction system that an appreciable amount of hydroquinone is produced without any complicated treatment.[5,6] Although the Fenton reaction of benzene has been studied extensively,[7-9] the formation of hydroquinone has never been reported before our finding. Very recently, the formation of hydroquinone in the oxidation with the Cu^+/O_2 system has been confirmed by Wismeijer et al.,[10,11] who were stimulated by our previous papers.[1-4]

In a previous study using ^{18}O tracer,[5] we demonstrated that two oxygen atoms in the hydroquinone molecule are incorporated in two separate steps, not in one step from a single oxygen molecule. This finding seems to be inconsistent with the mechanisms of the biological dioxygenation reactions, since dioxygenases (EC. 1.13.) are believed to catalyze reactions in which both atoms of a single oxygen molecule are incorporated into the substrate.[12,13] Furthermore, the enzymatic dioxygenations of aromatic compounds usually introduce two oxygen atoms into ortho positions, not in para positions as was found in the Cu^+/O_2 system. For instance, pyrocatechase (EC.1.13.11.1) catalyzes oxidative cleavage of catechol to *cis,cis*-muconic acid (eq 4). It seems very important to make clear the difference, if it exists, in the mechanism of dioxygenation reactions occurring in the enzymatic and Cu^+/O_2 systems. Undoubtedly, enzymatic reactions take place at near neutral conditions. On the other hand, the oxidation with the Cu^+/O_2 system has been carried out in 0.05 M H_2SO_4 and accordingly the reaction mechanism proposed was for the reaction in acidic conditions.[5,6] There is no proof that the same mechanism can be applied to the reactions occurring in neutral pHs. In addition, even though the skeleton of the oxidation pathway for the Cu^+/O_2 system has been proposed, there remain many uncertainties about the facters affecting reaction branching



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[1] Sasaki, K.; Ito, S.; Saheki, Y.; Kinoshita, T.; Yamasaki, T.; Harada, J. *Chem. Lett.* **1983**, 37.

[2] Sasaki, K.; Ito, S.; Kinoshita, T.; Harada, J. *Chem. Lett.* **1983**, 445.

[3] Kinoshita, T.; Harada, J.; Ito, S.; Sasaki, K. *Angew. Chem. Suppl.* **1983**, 599.

[4] Ito, S.; Sasaki, K. *Yuki Gosei Kagaku Kyoukaishi* **1983**, *41*, 839.

[5] Kunai, A.; Hata, S.; Ito, S.; Sasaki, K. *J. Org. Chem.* **1986**, *51*, 3471.

[6] Ito, S.; Yamasaki, T.; Okada, H.; Okino, S.; Sasaki, K. *J. Chem. Soc., Perkin Trans. 2*, in press.

[7] Walling, C.; Johnson, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 363.

[8] Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125.

[9] Kunai, A.; Hata, S.; Ito, S.; Sasaki, K. *J. Am. Chem. Soc.* **1986**, *108*, 6012.

[10] van Gent, J.; Wismeijer, A. A.; Peter Rit, A. W. P. G.; van Bekkum, H. *Tetrahedron Lett.* **1986**, *27*, 1059.

[11] Wismeijer, A. A. Thesis, Delft University of Technology, 1987; p 39.

[12] Sheldon, R. A.; Kochi, J. K. *Metal-catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; p 232.

[13] Nomenclature Committee of the International Union of Biochemistry, *Enzyme Nomenclature*; Academic Press: New York, 1979; p 108.

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Table I. Oxidation of Benzene with Hydroxyl Radical from Various Sources at 25 °C

			products (μmol)				HQ + BQ
OH source	pH	atm	PhOH	HQ	BQ	CA	PhOH
CuCl/O_2[a]	1.3	air	78	28	trace	1.5	0.36
	1.3	O_2	58	18	3.5	trace	0.37
	3.5	air	35	68	18	trace	2.5
	3.5	O_2	19	40	73	trace	6.0
CuCl/H_2O_2[a]	1.3[b]	N_2	24	1.2	trace	trace	0.050
	1.3[c]	N_2	153	8.3	trace	3.0	0.054
	3.5[c]	N_2	170	14	trace	2.2	0.082
irradiated water[d]	1.3	air	3.0	0.13	trace	0.22	0.043
	1.3	O_2	5.0	0.10	trace	0.14	0.020
	3.5	air	2.8	0.16	trace	trace	0.057
	3.5	O_2	4.3	0.23	trace	trace	0.053
Fenton's reagent[e]	1.3	O_2	30	1.9	trace	trace	0.063
	3.5	O_2	30	6.8	trace	1.5	0.23

[a] CuCl = 1 mmol. [b] H_2O_2 = 0.125 mmol. [c] H_2O_2 = 0.5 mmol. [d] 1.08 kGy in 30 min. [e] $FeSO_4$ = 0.5 mmol, H_2O_2 = 0.25 mmol.

which appear repeatedly in the whole reaction sequence. Unless the detailed mechanism at each branching step is clear, the mechanism cannot be said to be elucidated. This is particularly important when one considers the practical application of this oxidation. In this paper, we examine the detailed mechanism for the dioxygenation of benzene with the Cu^+/O_2 and other hydroxylation systems such as Fenton's reagent and γ-irradiated water at higher pHs. An important role of the Cu(I) ion in the process of decomposing a dioxygen adduct of hydroxycyclohexadienyl radical has been pointed out.

II. Experimental Section

Analysis. All of the phenolic products were determined with reversed-phase high-performance liquid chromatography as described elsewhere.[5,6] Normally, excess benzene remaining in the reactant solution was removed by streaming nitrogen before HPLC analysis. When, however, *p*-benzoquinone was in the products, it was extracted from the aqueous solution with fresh benzene and both the aqueous and benzene layers were analyzed separately.

Oxidation of Benzene with Cu(I)/O_2. The standard procedure employed is as follows. To a 100-mL Erlenmeyer flask with a ground glass stopper, 25 mL of a base solution containing 0.75 mL (8.4 mmol) of benzene was placed. The base solution used was either 0.1 M acetate buffer (pH 2.9–5.5) or 0.05 M H_2SO_4 (pH 1.3). The oxidation was initiated by adding 99 mg (1 mmol) of copper(I) chloride. The reaction was continued at 25 °C under in an atmosphere of N_2–O_2 mixture at the desired ratio for 2 h during which the flask was shaken vigorously with a mechanical shaker. Both aqueous and benzene layers were then subjected to the HPLC analysis.

Oxidation of Benzene with Cu(I)/H_2O_2. Both benzene (0.75 mL) and CuCl (99 mg, 1 mmol) were initially taken in 25 mL of a deoxygenized base solution under vigorous agitation. The reaction was started by adding 0.5 mmol of H_2O_2 dropwise and continued over a period of 1 h.

γ-Ray Radiolysis. In a test-tube of 12 mm of diameter, 2 mL of a base solution containing 0.1 mM EDTA was placed and was saturated with either air or pure O_2. After adding 70 μL of benzene to the buffer solution and shaking for 15 min, the solution was irradiated with γ-rays (^{60}Co, 10 kCi) for 30 min. The dose measured by a Fricke dosimeter was 1.08 kGy. The irradiated solution was analyzed after removing the excess benzene by a stream of N_2 gas.

Fenton's Oxidation of Benzene. Base solution (25 mL) of various pHs containing 20 mM (0.5 mmol) of $FeSO_4$ and 0.75 mL of benzene was taken in a 100-mL Erlenmeyer flask with a rubber stopper. The whole solution was first thermostated at 25 °C and deoxygenated with streaming nitrogen. The reaction was started by adding 2.5 mL of 100 mM H_2O_2 slowly through a capillary tube and was continued for 1 h under a nitrogen atmosphere.

Oxidation of Phenol with Cu(I)/O_2. To 25 mL of a base solution containing 3 mM of phenol was added 99 mg (1 mmol) of copper(I) chloride. The solution was shaken for 1 h at 25 °C under aerial atmosphere.

III. Results and Discussion

1. Requirements for the Formation of Hydroquinone. The active species generated from Cu^+/O_2 in acidic solutions has been established to be a hydroxyl radical.[6] The detection of hydroquinone in the oxidation of benzene with the Cu^+/O_2 system,[1-6] therefore, prompted us to reexamine the yields of hydroquinone in the oxidation of benzene with other hydroxylating reagents, which are believed to involve the hydroxyl radical. Three hydroxylating reagents other than the Cu^+/O_2 system were chosen, i.e., copper(I) chloride plus hydrogen peroxide under N_2 atmosphere (with Cu^+ but without O_2), γ-irradiated water under O_2 atmosphere (without Cu^+ but with O_2), and the Fenton's reagent under O_2 atmosphere (with Fe^{2+} and O_2). Results of the hydroxylations at pH 1.3 and 3.5 are summarized in Table I. It is clearly indicated that under the anerobic conditions (column 2), the relative yield of HQ/PhOH is very low (less than 0.1). A striking feature appears in the result of radiolysis (column 3), where only a trace amount of hydroquinone was detected although a plenty of oxygen was in the reaction system. Similarly, the molar ratio HQ/PhOH is unexpectedly low in the oxygenated Fenton system, although the value at pH 3.5 is higher than that at pH 1.3.

From these seemingly contradicting results, however, one can draw a definite conclusion. That is, for a preferential formation of hydroquinone, the presence of oxygen is the least requirement but not the sufficient condition, and, in order to be sufficient, the presence of a stronger reducing agent, copper(I) ion, is necessary. Ferrous ions in the Fenton system are thought to be insufficient in their reducing ability.

The results with the Cu^+/O_2 system in Table I also show that the relative yield of hydroquinone (plus benzoquinone) to phenol depends on the pH, while the effect of the concentration of O_2 is not straightforward. The effects of these reaction conditions on the product distribution, therefore, are investigated systematically in the following section.

2. Factors Affecting the Product Distribution. The effect of pH on the product distribution is summarized in Figure 1, which shows clearly that the sum of hydroquinone (HQ) and *p*-benzoquinone (BQ) increases steadily with increasing pH up to pH 4.6 and, at the same time, the yield of phenol decreases by keeping the total yield unchanged. At a more basic pH range, the yield of each product decreases rapidly due to perhaps, some secondary reasons such as reduced solubility of Cu(I) ion and/or the enhancement of further oxidaton of phenolic products. The reason why the product distribution has such a strong dependence on the solution pH cannot be answered at this

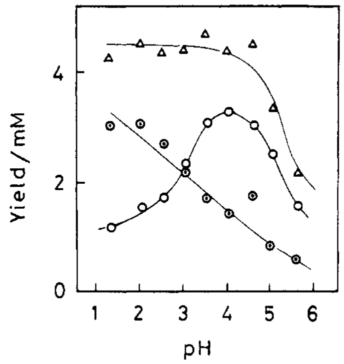


Figure 1. Effect of pH on the product distribution: (○) hydroquinone plus *p*-benzoquinone, (◎) phenol, (△) total yield (40 mM CuCl, benzene saturated, aerial atmosphere, 25 °C).

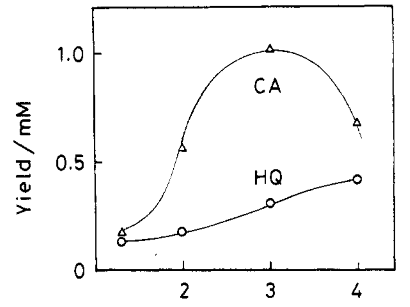


Figure 2. Aerial oxidation of phenol (40 mM CuCl, 3 mM phenol, 25 °C).

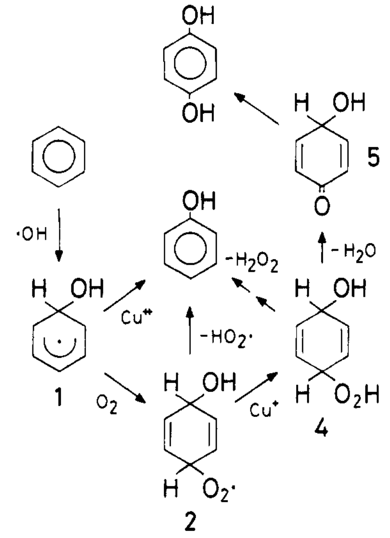
stage and will be discussed later together with the effect of other factors.

p-Benzoquinone is not appreciably formed at pH 1.3. Above pH 2.9, the formation of *p*-benzoquinone becomes noticeable and at pH 4.6 the molar ratio of benzoquinone to hydroquinone goes up as high as 8. The increasing yield of benzoquinone at higher pHs should be attributed to the enhanced rate of the oxidation of hydroquinone with O_2 and/or copper(II) ion.

In contrast to hydroquinone, the yield of catechol (CA) is almost unaffected by the change of pH and is less than one-tenth that of hydroquinone in the pH range 1.3–5.6. If the yield of catechol at various pHs is plotted (Figure 1), the data fall on the ordinate axis and thus are omitted. In other word, the paraselectivity found in the Cu^+/O_2 system is independent of the pH of the reaction media. Accordingly, one can conclude that the mechanism of dioxygenation in the Cu^+/O_2 is quite different from that of the biological system.

From the curve behavior of Figure 1, one might consider hydroquinone to be the secondary product derived from phenol which is readily oxidized at higher pHs. The possibility of this mechanism seems, however, to be deniable from three lines of evidence. First, during the progress of the reaction at pH 1.3, the molar ratio of hydroquinone to phenol, HQ/PhOH, is almost constant (ca. 0.3) over the whole reaction time.[6] If the primary product, phenol, is further oxidized to hydroquinone with OH radical, the accumulation curve to phenol must have a maximum or it must reach a saturation value when the starting material is in large excess and the molar ratio HQ/PhOH should vary as a function of time. Secondly, when phenol is oxidized as the starting material in place of benzene, the yield of catechol always exceeds hydroquinone over the pH range of 1.3–3.5, as shown in Figure 2. Finally, as demonstrated in Table I, the product distribution in the reaction of benzene with OH radical generated from different sources differs case by case (see Table I). The preferential formation of hydroquinone is observed only when both copper(I) ion and dioxygen are present in solutions of higher pH value. This fact can only be explained by considering the branched path mechanism, which is outlined in Scheme I. Accordingly, we may safely conclude that most of the hydroquinone is produced without passing through phenol as the intermediate. Probably, a minor yield of catechol may provide a measure of the consecutive process which passes through phenol.

Scheme I



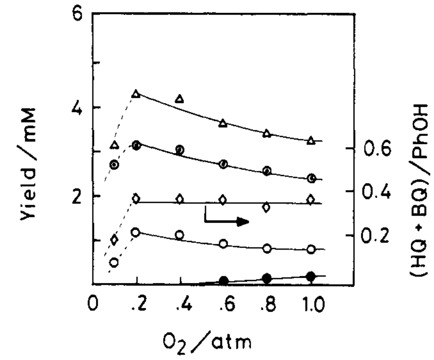


Figure 3. Effect of O_2 pressure on the yield of phenols at pH 1.3: (○) hydroquinone, (●) *p*-benzoquinone, (◎) phenol, (△) total yield, (◇) (hydroquinone + *p*-benzoquinone)/phenol (40 mM CuCl, benzene saturated, 25 °C).

Although the oxidation of benzene with Fenton's reagent has been studied extensively,[7,8] most of the past experiments have been carried out under anaerobic conditions and no systematic information for the effect of oxygen is available. As a reflection of this, nobody has paid attention to the production of hydroquinone or benzoquinone in the Fenton system. We have already shown that, even in the Fenton system, an appreciable amount of *p*-benzoquinone is formed.[9] This suggests that dioxygen plays an essential role for producing quinones.

Figures 3 and 4 indicate the effect of oxygen partial pressure on the relative yield of the sum of hydroquinone and benzoquinone compared with phenol, Q/PhOH, studied at two different pHs. It is clearly indicated that the effect of oxygen partial pressure appears differently at the two pH values concerned. The effect is not so much pronounced at pH 1.3, though the total yield decreases slightly with increasing $P(O_2)$ except the region of very low $P(O_2)$ (<0.2).[6] On the other hand, at pH 3.5, the total yield is unchanged but the yield of *p*-benzoquinone increases

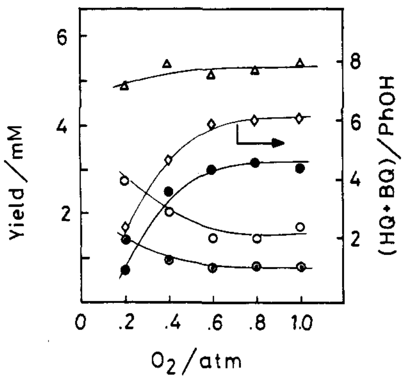
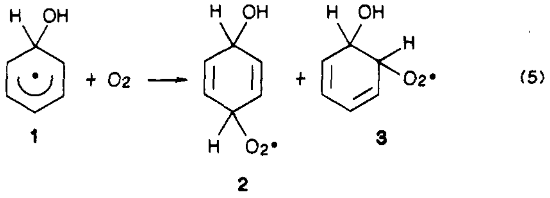


Figure 4. Effect of O_2 pressure on the yield of phenols at pH 3.5 (40 mM CuCl, benzene saturated, 25 °C). The symbols are the same as in Figure 3.

markedly and those of phenol and hydroquinone decrease with increasing oxygen pressure up to $P(O_2) = 0.6$.

The most striking change between Figures 3 and 4 is the product ratio Q/PhOH, which is constant at pH 1.3 but varies at pH 3.5 as a function of the oxygen partial pressure. Undoubtedly, at pH 3.5, at least two reactions leading to phenol and hydroquinone, respectively, are competing with each other at the region of $P(O_2) < 0.6$. The difference in Figures 3 and 4 can be simply explained as follows. It is well established that in the oxidation of benzene either with the Fenton's reagent or with the irradiated water, radical **1** is oxidized either with O_2[14,15] to give peroxy radicals **2** and **3** (eq 5) or with copper(II) ion[7,8] to give phenol (eq 6). The formation of peroxy radicals **2** and **3** has been detected spectroscopically by Dorfman et al.[14] and was confirmed separately by a tracer experiment.[9]



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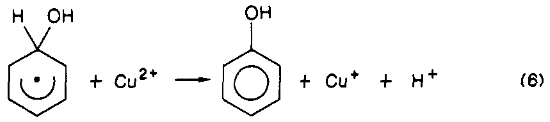

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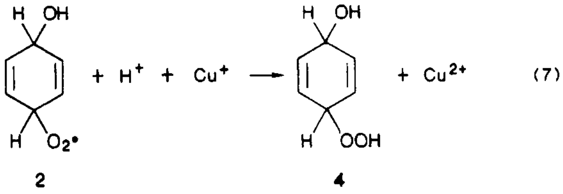
The competing reactions which bring about the difference in Figures 3 and 4 should thus be reactions 5 and 6. In a reaction occurring at low pH, the contribution of reaction 6 seems to negligible and branching at the stage of radical **1** becomes also negligible at least when $P(O_2)$ exceeds 0.2 (Figure 3). As a result, the main route goes through radical **2**. The contribution of reaction 6 seems, however, to become more and more important with increasing pH so that an appreciable effect of $P(O_2)$ appears in Figure 4. Even at pH 3.5, as long as the oxygen partial pressure is high enough ($P(O_2) > 0.6$, see Figure 4), the contribution of reaction 6 becomes again negligible. The reason why the direct path (reaction 6) is useless at lower pH but becomes useful at higher pHs can be ascribed to the pH dependence of redox potential of the (redical **1**)/PhOH couple which should decrease by an amount of 60 mV/pH. In any case, when plenty of O_2 is present in the system, the main reaction is the formation of peroxy radicals **2** (and **3**) and the branching competition shifts to somewhere after the stage of radical **2**, where the effect of pH and Cu(I) ion clearly appears.

3. Reaction Mechanism. Now it is clear that the role of Cu(I) ion is not restricted only for generating OH radical (eq 1 and 2) but has some additional function during the processes of degradating peroxy radical **2**. Although unequivocal specification of the reaction route is difficult, we tentatively assume the following sequence for this. The key role of Cu(I) ion is considered to be the reduction of radical **2** to hydroperoxide **4** (eq 7).



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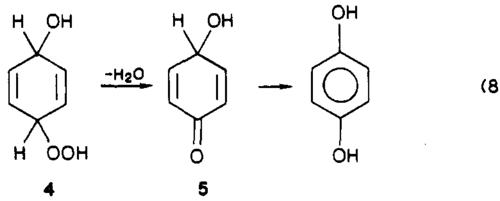
Hydroperoxide **4** will then dehydrate to give quinol **5**, which readily tautomerizes to hydroquinone (eq 8). The



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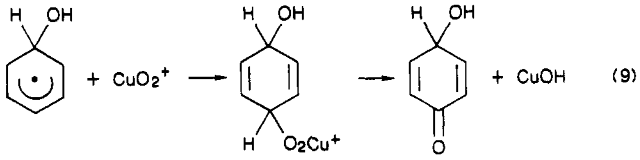
dehydration reaction of **4** to **5** is analogous to a base-catalyzed decomposition of hydroperoxide to give a carbonyl compound originally noticed by Kornblum.[16]

The selective formation of para-dioxygenated product in the present system seems to be peculiar, since the biological dioxygenations catalyzed by dioxygenases usually give ortho-dioxygenated products.[12,13] The reason why only a trace amount of catechol is produced in the Cu^+/O_2 system is not clear at the present stage of our knowledge. It is at least unlike that molecular oxygen attacks selectively 4-position of radical **1**, since more catechol than hydroquinone was observed in the radiolysis system (Table I). It may be a reasonable explanation that the ortho-addition intermediate **3** undergoes preferential detachment of HO_2 radical to yield phenol. In regard to this problem, kinetic studies on the oxidation of Cu(I) complexes with O_2 hitherto reported[17-19] may provide an alternative explanation. All of them concluded the existence of Cu(I)–O_2 complex during the oxidation of certain coordinated compounds of Cu(I) with O_2. The existence of such a complex cannot be ruled out in our reaction system. If the attacking species onto radical **1** is a bulky Cu(I)–O_2 complex and not a simple dioxygen molecule, the steric hindrance at the ortho position might result in a selective formation of para adduct (radical **2**), and reactions 5, 7, and 8 should be replaced by reaction 9. In any case, the two characteristics



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[14] Dorfman, L. M.; Taub, I. A.; Bühler, R. E. *J. Chem. Phys.* **1962**, *36*, 3051.

[15] Barakrishnan, I.; Reddy, M. P. *J. Phys. Chem.* **1970**, *74*, 850.

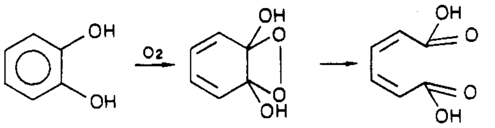
[16] Kornblum, N.; De La Mare, H. E. *J. Am. Chem. Soc.* **1951**, *73*, 880.

[17] Pecht, I.; Anbar, M. *J. Chem. Soc. A* **1968**, 1902.

[18] Zuberbühler, A.; Kaden, T. *Chimia* **1969**, *23*, 416.

[19] Buxton, G. V.; Green, J. C.; Sellers, R. M. *J. Chem. Soc., Dalton Trans.* **1976**, 2160.

in the enzymatic oxygenations, i.e., (1) two oxygen atoms of a single oxygen molecule are incorporated and (2) into ortho positions of aromatic compounds, should be closely related to each other. The formation of a cyclic peroxide as an intermediate can explain the differences from the Cu^+/O_2 system (eq 10).



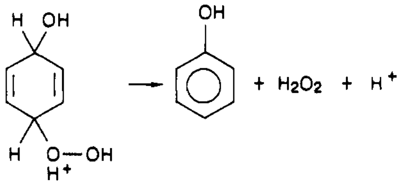
(10)

Reilly also found that *p*-benzoquinone was produced selectively (80%) from the aerial oxidation of phenol in acetonitrile which contained CuCl.[20] Catechol was not a primary product.

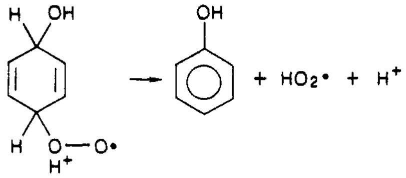
By a ^{18}O tracer experiment, we have demonstrated that two oxygen atoms in the hydroquinone molecule are incorporated in two separate steps.[5,9] One of those is incorporated at the stage of forming radical 1, and the other at the stage of forming peroxy radical 2. The present results are quite consistent with this. A minimal reaction scheme for producing phenol and hydroquinone is shown in Scheme I, where several less important steps such as the deactivation of radical 1 via cation radical,[7,8] the dimerization of radical 1 to yield biphenyl,[7,8] consecutive oxidation of phenol to hydroquinone and catechol, and the anaerobic oxidation of hydroquinone to *p*-benzoquinone are omitted for simplicity. The outside routes in Scheme I are the consecutive reactions to lead to hydroquinone. In the whole sequence, there are at least three branching points connected to phenol. First, radical 1 has to choose either the shortest way to phenol or to go through peroxy radical 2 depending upon the solution pH, relative concentration of Cu(II) ion and oxygen partial dressure (Figure 3 and 4). When the reaction proceeds under anaerobic conditions, all of the phenol is produced exclusively by the former route. On the contrary, in aerated acid solutions of pH <2, the formation of radical 2 becomes predominant and the direct conversion of radical 1 to phenol becomes unimportant. This fact has already been pointed out in our previous paper which dealt with oxygen effect on Fenton's reaction.[9] When, however, the acidity of solution is weakened, a larger supply of oxygen is demanded in order to sustain the predominant formation of radical 2. As a consequence, at pH 3.5, a higher oxygen partial pressure ($P(O_2) > 0.6$) is required (Figure 4).

Radical 2, at the second branching point, has to again choose either the elimination of HO_2 to give phenol (Dorfman path)[14] or the reduction of Cu(I) to give hydroperoxide 4. The reaction occurring under aerobic conditions but in the absence of any reducing agent, such as the reactions in columns 3 and 4 in Table I, are thought to pass through the Dorfman's route. The route connecting radical 2 to hydroperoxide 4 is the reduction reaction and necessitates the presence of Cu(I) ion. Although Fe^{2+} ion in the Fenton system seems to be useful, its reducing ability is limited. This is the reason for the poor yield of hydroquinone and benzoquinone as observed in Table I.

Among the factors affecting the relative yield of hydroquinone, the effect of pH was found of primary importance at least apparently. Although the essential part of the reaction sequence leading to hydroquinone has now been established as expressed in Scheme I, there still remains a question about the stage where the pH effect appears primarily. The effect appearing in the branching reactions of radical 1 has already been discussed in the foregoing section. In order to lead the reaction toward hydroquinone, it is a prerequisite to convert radicals 1 to 2 efficiently. Accordingly, the pH effect on the hydroquinone/phenol ratio should be explained by the pH dependence of the decomposition rates of radicals 2 and/or the hydroperoxide 4. The detachment of H_2O_2 from hydroperoxides is known to be accelerated by acid[21] (eq 11). Similarly, elimination of the peroxy group from radical 2 may be promoted by the presence of H^+ (eq 12).



(11)



(12)

If the decomposition of hydroperoxide 4 and/or radical 2 according to reactions 11 and/or 12 slows down at higher pHs, or alternatively, the dehydration of hydroperoxide 4 to quinol 5 according to reaction 9 is promoted at higher pHs,[16] the yield of hydroquinone should increase as observed. The pH effect cannot be attributed to changes in the reduction rate of radical 2 with Cu(I) ion to give hydroperoxide 4, since the pH dependence of the redox potential of the (radical 2)/(hydroperoxide 4) couple predicts that lower pH favors the formation of 4.

Continuous production of hydroquinone can be realized if we employ the electrolytic regeneration of Cu^+ species. Work along this line is now in progress.

Acknowledgment. We thank Professor Takahisa Ichikawa and Dr. Nobuaki Ohta for the use of the ^{60}Co 10-kCi irradiator of Hiroshima University. A part of this study was supported by Grants-in-Aid for Scientic Research from the Ministry of Education, Science and Culture (Nos. 61470081 and 62607001).

Registry No. PhH, 71-43-2; Cu(I), 17493-86-6; O_2, 7782-44-7; H_2O_2, 7722-84-1; PhOH, 108-95-2; $^{\cdot}OH$, 3352-57-6; *p*-HOC_6H_4OH, 123-31-9; benzoquinone, 106-51-4; Fentons' reagent, 36047-38-8.

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[20] Reilly, E. L. Br. Pat. 1 511 813, 1978, to Du Pont.

[21] Plesničar, B. *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; p 555.