

## The Oxidative Coupling of 2,6-Dimethylphenol Catalyzed by Basic Copper(II) Complexes

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The oxidative coupling reaction of 2,6-dimethylphenol has been studied using basic copper(II) catalytic systems, the heterogeneous complexes derived from copper(II) chloride, and potassium hydroxide, sodium hydroxide, and sodium methoxide in a methanol solution. With these basic copper(II) catalysts, the oxidation products were poly(2,6-dimethyl-1,4-phenylene oxide) (C-O coupling) and 3,3',5,5'-tetramethyldiphenquinone (C-C coupling). The reaction time, the inorganic base added, and the mole ratio of base to copper(II) chloride were found to affect the course of oxidation and/or the selectivity of products. The KOH/CuCl<sub>2</sub> mole ratio was particularly sensitive to the oxidation activity and the coupling manner of 2,6-dimethylphenol. The kinetic data obtained from the oxygen absorption rate showed that the rate was first-order in the 2,6-dimethylphenol concentration and oxygen partial pressure, respectively. On the other hand, the rate was found to be independent of the concentration of the basic copper(II) catalyst for the higher concentrations, and ca. one-half-order for the lower concentrations of the basic copper(II) catalyst. On the basis of the kinetic result, a reaction scheme is proposed in which the phenol-O<sub>2</sub> species interacts with the heterogeneous basic copper(II) complex to form a phenol-O<sub>2</sub>-Cu(II) intermediate. This reaction is the rate-controlling step. It was suggested that the basic copper(II) complex might be termed as a "heterogenized homogeneous catalyst."

### INTRODUCTION

Copper ions have been shown to act as catalysts in the oxidation of organic substrates by molecular oxygen (1). It is well known that the complexation of Cu(II) ions by certain ligands modifies its catalytic activity. Since the discovery by Hay and his group on 2,6-dimethylphenol polymerization by oxidative coupling catalyzed with homogeneous copper(I) chloride-pyridine-O<sub>2</sub> system (2), the development of the oxidative coupling polymerization of 2,6-disubstituted phenol with a variety of catalytic systems has been described by many workers (2, 3). The copper(I) chloride-pyridine-O<sub>2</sub> catalytic system is a novel example of a transition metal coordination catalysis in a homogeneous solution. The study of phenol oxidation with a catalytic system involving a copper-nitrogen coordinate linkage might clarify the mechanism of

certain important enzymes of an oxidase type and shed light on the subject.

A heterogeneous catalytic system such as transition metal ions attached to an insoluble support has been well known to have several practical advantages. Thus, the reaction products are easily separated from the catalyst and the latter is available to use again. The halogen displacement polymerization of 2,4,6-trihalogenophenol with a heterogeneous basic copper(II) catalytic system without an amine under relatively mild reaction conditions has been reported to give the corresponding poly(dihalo-phenylene oxide) (4). Also, it has been reported that the heterogeneous basic copper(II) system (containing copper(II) salt and inorganic base such as KOH) could form an active species for the oxidative coupling reaction of 2,6-dimethylphenol (5). In the study, the KOH/CuCl<sub>2</sub> mole ratio was found to be the main factor which controls

the coupling manner; namely, increasing this ratio was favorable for C–O coupling whereas the C–C coupling was preferentially obtained under a low KOH/CuCl<sub>2</sub> mole ratio. Furthermore, the properties of the heterogeneous basic copper(II) systems were studied by ESR measurements (5). Very little is known of the primary mechanistic process which generates the phenoxy radicals by the heterogeneous basic copper(II) catalyst. In seeking to extend this work, we present in this paper the kinetic data on the oxidative coupling of 2,6-dimethylphenol under various reaction conditions. We also wish to report the effects of the catalytic composition, reaction time, and concentration of copper(II) chloride on the reactivity and/or the coupling manner.

#### EXPERIMENTAL

The infrared spectra were obtained with a Hitachi recording spectrophotometer, Model EPIG 2. Visible ray spectra were measured by a Nippon Bunkko spectrophotometer, Model UVIDEC-420. All spectra were obtained in 1-cm quartz cells at room temperature. Microanalyses were performed by the Microanalysis Center, Kyoto University.

*Materials.* 2,6-Dimethylphenol was purified by recrystallization from n-hexane. Reagent grade anhydride copper(II) chloride was used after drying at 110°C under vacuum for 2 hr. Reagent grade KOH, NaOH, and NaOCH<sub>3</sub> were used without further purification. Methanol was refluxed with magnesium metal and distilled.

*Oxidative coupling reaction of 2,6-dimethylphenol with heterogeneous basic copper(II) complex.* The oxidation reactions were run in a 50-ml round-bottom flask, which was connected with a mechanical stirrer, a cooler, a gas inlet tube, a dropping funnel, and maintained in a thermostated water bath. The desired copper(II) chloride was dissolved in methanol, and a methanolic solution of sodium methoxide was added to the resultant clear-green homogeneous copper(II) solution. A meth-

anolic solution of 2,6-dimethylphenol in a dropping funnel was added to the catalytic system. The reaction mixture was stirred vigorously for the prescribed time under an oxygen atmosphere. In the case of the reaction under a nitrogen atmosphere, nitrogen gas was introduced to both the methanolic solutions of catalyst and 2,6-dimethylphenol for 30 min and then the reaction was started by the method previously described. Details of the identification of the oxidation products were presented in a previous paper (5). The products obtained were identified as poly(2,6-dimethyl-1,4-phenylene oxide) and/or 3,3',5,5'-tetramethyl-4,4'-diphenoquinone by their ir spectra and elementary analyses.

*Isolation of basic copper(II) catalyst.* In a methanolic solution of CuCl<sub>2</sub>, a methanolic solution of KOH was added dropwise under a magnetic stirring. The resultant precipitate was filtered out and dried under vacuum.

*Oxygen absorption measurement.* Oxygen absorption measurements during the oxidative coupling reaction of 2,6-dimethylphenol were carried out in a constant pressure gas absorption apparatus consisting of a reaction vessel with a magnetic stirrer connected to a gas buret and a U-tube manometer. The reaction vessel, which was thermostated at 30°C, was attached to a pressure-equalized dropping funnel to which a methanolic solution of 2,6-dimethylphenol was added. The whole reaction system was saturated with oxygen for 40 to 60 min under vigorous stirring. When equilibrium was obtained, the 2,6-dimethylphenol solution was added to the catalytic solution in the reaction vessel. The oxygen consumptions at constant pressure were measured at regular time intervals.

#### RESULTS

*Oxidative coupling reaction of 2,6-dimethylphenol with basic copper(II) catalytic system.* The heterogeneous basic copper(II) catalytic systems used here were CuCl<sub>2</sub>–KOH, CuCl<sub>2</sub>–NaOH, and CuCl<sub>2</sub>–

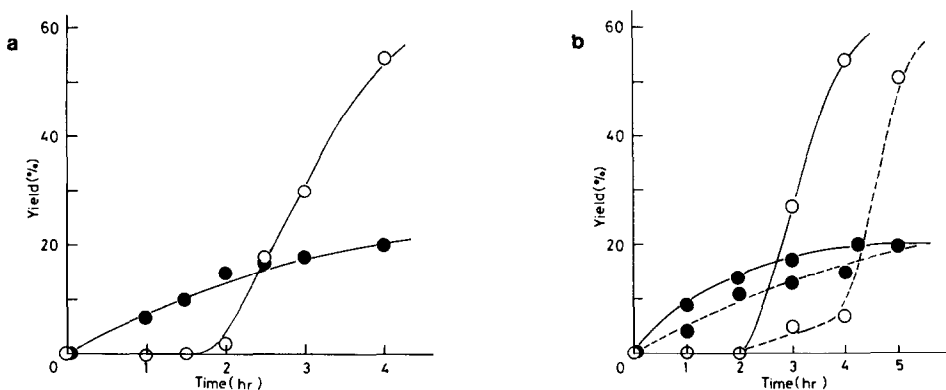


FIG. 1. Dependence of the oxidative coupling products on reaction time. 2,6-Dimethylphenol, 0.2 mole/liter; reaction temp, 30°C; O<sub>2</sub> atmosphere, 1 atm; solvent, 50 ml of MeOH; ○, polyphenylene oxide (C–O coupling); ●, diphenoquinone (C–C coupling); (a) CuCl<sub>2</sub>–KOH system; (b) —, CuCl<sub>2</sub>–NaOH system; ---, CuCl<sub>2</sub>–NaOCH<sub>3</sub> system.

NaOCH<sub>3</sub> systems. The oxidation products were poly(2,6-dimethylphenylene oxide) (C–O coupling product) and/or 3,3',5,5'-tetramethyl-4,4'-diphenoquinone (C–C coupling product) irrespective of the catalytic system studied. Figure 1 indicates the dependence of the yield of the oxidative coupling products on reaction time. Diphenoquinone increased with the reaction time immediately after the reaction starts. On the other hand, the behavior of the polymer yield is notable as shown in Fig. 1: the long induction period and the rapid acceleration after the onset of the reaction. It should be pointed out that the behaviors of the yield of the oxidation products vs reaction time with these three catalytic systems (Figs. 1a, b) were similar, irrespective of the heterogeneous basic copper(II) catalytic system.

Figure 2 shows the effect of the concentration of CuCl<sub>2</sub> (KOH/CuCl<sub>2</sub> mole ratio = 1) on the yields of the oxidative coupling products. It is evident that the increase of the CuCl<sub>2</sub> concentration resulted in an increase of both the C–O and C–C coupling product yields at the initial stage, but further increase of the concentration of CuCl<sub>2</sub> leveled off the yields. Particularly, the yield of the C–O coupling product (polymer) tended to decrease with the increase of the

CuCl<sub>2</sub> concentration at more than 0.012 mole/liter. A similar behavior of the catalyst concentration on the yield of the C–C coupling product (diphenoquinone) has already been reported for the selective C–C coupling reaction of 2,6-dimethylphenol catalyzed by the copper(II) nitrate–acetonitrile complex (6).

It has been suggested that the main factor which controls the coupling manner (C–O and/or C–C coupling) was the KOH/CuCl<sub>2</sub> mole ratio (5). Thus, it was reported that an increase of this ratio was favorable for the C–O coupling, whereas the C–C coupling

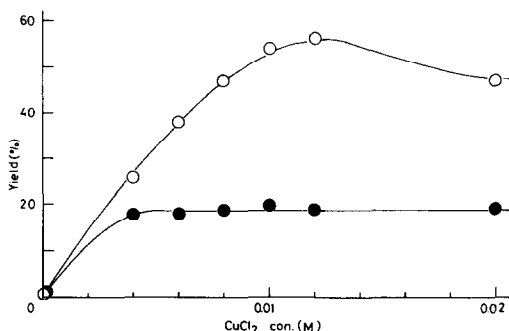


FIG. 2. Dependence of the yield of the oxidative coupling products on the concentration of CuCl<sub>2</sub>. 2,6-Dimethylphenol, 0.2 mole/liter; KOH/CuCl<sub>2</sub> (mole ratio = 1); reaction temp, 30°C; O<sub>2</sub> atmosphere, 1 atm; reaction time, 4 hr; solvent, 50 ml of MeOH; ○, polyphenylene oxide; ●, diphenoquinone.

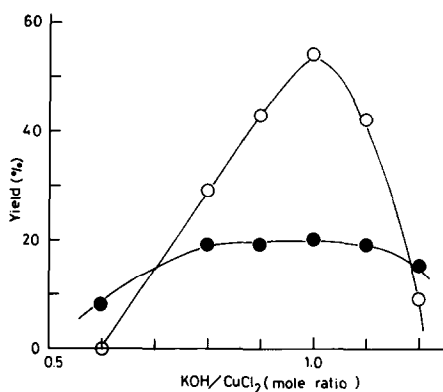


FIG. 3. Dependence of the yield of the oxidative coupling products on the KOH/CuCl<sub>2</sub> mole ratio. 2,6-Dimethylphenol, 0.2 mole/liter; CuCl<sub>2</sub>, 0.01 mole/liter; reaction temp, 30°C; O<sub>2</sub> atmosphere, 1 atm; solvent, 50 ml of MeOH; reaction time, 4 hr; ○, polyphenylene oxide; ●, diphenoquinone.

product was preferentially obtained under low KOH/CuCl<sub>2</sub> ratios. To see the effect of the KOH/CuCl<sub>2</sub> mole ratio on both the oxidation activity and the coupling mode systematically, 2,6-dimethylphenol was reacted with various mole ratios of KOH/CuCl<sub>2</sub>. Figure 3 indicated the relationship between the yield of the oxidative coupling product vs the KOH/CuCl<sub>2</sub> mole ratio under a constant concentration of CuCl<sub>2</sub>. As has been reported previously (5), the C-C coupling product was formed almost selectively at low KOH/CuCl<sub>2</sub> mole ratios, though the yields of diphenoquinone were low. Also, it is evident that the yield of the C-O coupling product increased with the increase of the KOH/CuCl<sub>2</sub> mole ratio in the range of the mole ratios of less than 1. However, it must be noted that at a mole ratio of more than 1, the yields of the C-O and C-C coupling products decreased inversely. Particularly, the activity for the C-O coupling mode decreases markedly with the increase of the ratio at the KOH/CuCl<sub>2</sub> mole ratios of more than 1. Thus, the selectivity for the C-O coupling product has been shown to have a maximum value at a KOH/CuCl<sub>2</sub> mole ratio of approximately 1. Table 1 indicates the effect of the base/CuCl<sub>2</sub> mole ratio on the oxidation activity

and the oxidative coupling manner. Only copper(II) chloride itself, without a base such as KOH, had no activity for the oxidative coupling reaction of 2,6-dimethylphenol. Instead of using a CuCl<sub>2</sub>-KOH system as a catalyst, Cu(OH)<sub>2</sub> was independently sampled as a catalyst for this reaction; however, it had no catalytic activity. The use of CH<sub>3</sub>ONa as a base tended to have a similar effect as KOH for both the oxidation activity and the oxidative coupling manner, though the sensitivity of the CH<sub>3</sub>ONa/CuCl<sub>2</sub> mole ratio on the oxidative coupling mode seemed to be higher than the corresponding sensitivity for the KOH/CuCl<sub>2</sub> mole ratio.

The oxidative coupling reaction of 2,6-dimethylphenol, catalyzed with a CuCl<sub>2</sub>-KOH system, was evaluated under a nitrogen, instead of an oxygen atmosphere, to test the role of oxygen. No oxidative coupling product was obtained, however, under a nitrogen atmosphere, even when 1:1 molar of the CuCl<sub>2</sub>-KOH catalyst (KOH/CuCl<sub>2</sub> mole ratio = 1) was treated with 2,6-dimethylphenol.

Figure 4 indicates the oxygen amount consumed vs reaction time for the oxidative coupling of 2,6-dimethylphenol with CuCl<sub>2</sub>-KOH, -NaOH, and -NaOCH<sub>3</sub> catalytic systems. The rates of the oxygen ab-

TABLE I  
Oxidative Coupling Reaction of 2,6-Dimethylphenol  
Catalyzed by Basic Copper(II) Complexes<sup>a</sup>

Cu(II) salt	Base	Base/CuCl <sub>2</sub> (mole ratio)	Reaction time (hr)	Product yield (%)	
				C-O	C-C
CuCl <sub>2</sub>	—	0	4	0	0
Cu(OH) <sub>2</sub>	—	0	4	0	0
CuCl <sub>2</sub>	KOH	0.5	10	0	11
		1.0	4	54	20
		1.5	6.5	0	11
		20	4	17	0
		NaOCH <sub>3</sub>	0.5	5.5	0
1.0	5.5		51	20	
1.2	5.5		0	11	
1.5	5.5		0	Trace	

<sup>a</sup> 2,6-Dimethylphenol, 0.2 mole/liter; Cu(II) salt, 0.01 mole/liter; O<sub>2</sub> atmosphere, 1 atm; solvent, 50 ml of MeOH.

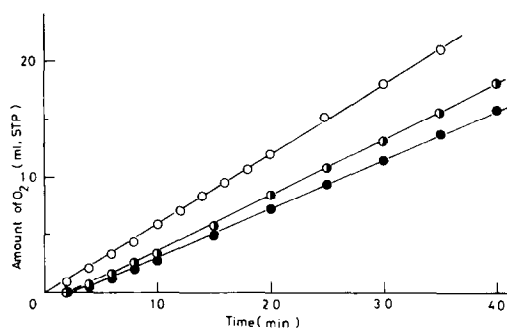


FIG. 4. Dependence of the amount of oxygen absorbed on the reaction time. 2,6-Dimethylphenol, 0.2 mole/liter;  $\text{CuCl}_2$ , 0.01 mole/liter; Base/ $\text{CuCl}_2$  (mole ratio), 1; reaction temp,  $30^\circ\text{C}$ ;  $\text{O}_2$  atmosphere, 1 atm; solvent, 50 ml of MeOH;  $\circ$ ,  $\text{CuCl}_2$ -KOH system;  $\odot$ ,  $\text{CuCl}_2$ -NaOH system;  $\bullet$ ,  $\text{CuCl}_2$ - $\text{NaOCH}_3$  system.

sorption obtained from the three slopes are shown in Table 2. Changing the base did not result in a striking difference in the oxidative activity, though the order of the activity was  $\text{KOH} > \text{NaOH} > \text{NaOCH}_3$ .

The basic copper(II) complex, isolated by a filtration of the heterogeneous methanolic solution of  $\text{CuCl}_2$  and KOH (KOH/ $\text{CuCl}_2$  mole ratio = 1, 0.1 g), was used as a catalyst for the oxidative coupling reaction of 2,6-dimethylphenol (Table 3). In a methanol solvent, the isolated basic copper(II) system was found to have an activity for 2,6-dimethylphenol oxidation comparable with that of the nonisolated catalytic system. This result indicates that the heterogeneous parts of the basic copper(II) complex are active species for 2,6-dimethylphenol

oxidation; however, a benzene solvent made the isolated catalytic system nonactive for the oxidative coupling of 2,6-dimethylphenol. It is interesting to note that by using the corresponding phenoxide anion dissolved from the methanolic solution of KOH, instead of an original 2,6-dimethylphenol as a reactant, only the C-O coupling product was obtained with the isolated catalytic system, though the oxidation activity became rather low.

*Kinetics of 2,6-dimethylphenol oxidation catalyzed with basic copper(II) system.* In order to check the significance of gas-liquid mass transfer, the effect of stirrer speed on the initial oxygen absorption rate was studied at  $30^\circ\text{C}$  with the heterogeneous basic copper(II) catalyst (KOH/ $\text{CuCl}_2$  mole ratio = 1). The rates were found to be independent of the speed of agitation at more than 1400 rpm which suggests that gas-to-liquid mass transfer resistance is negligible under this reaction condition (Fig. 5).

The rate of oxygen absorption ( $r$ ) dependence on 2,6-dimethylphenol concentration was indicated in Fig. 6a as a log-log plot. Figure 6b illustrates the relationship between the rate and the partial pressure of oxygen. As evidenced from Figs. 6a,b, both graphs are straight lines with slopes of 1. This result indicates that the rate is first-order in the concentration of 2,6-dimethylphenol and the partial pressure of oxygen, respectively. On the other hand, the log-

Catalyst system	Oxygen absorption rate ( $r$ ) (mole/s)
$\text{CuCl}_2$ -KOH	$4.0 \times 10^{-7}$
-NaOH	$3.6 \times 10^{-7}$
- $\text{NaOCH}_3$	$3.2 \times 10^{-7}$

<sup>a</sup> 2,6-Dimethylphenol, 0.2 mole/liter;  $\text{CuCl}_2$ , 0.01 mole/liter; Base, 0.01 mole/liter;  $\text{O}_2$  atmosphere, 1 atm; solvent, 50 ml of MeOH; reaction temp;  $30^\circ\text{C}$ .

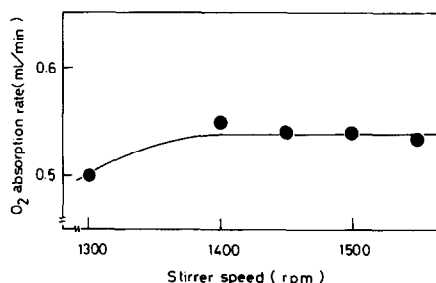


FIG. 5. Effects of stirrer speed on the rate of the oxygen absorption. 2,6-Dimethylphenol, 0.2 mole/liter;  $\text{CuCl}_2$ , 0.01 mole/liter; KOH/ $\text{CuCl}_2$  (mole ratio), 1; reaction temp,  $30^\circ\text{C}$ ;  $\text{O}_2$  atmosphere, 1 atm; solvent, 50 ml of MeOH.

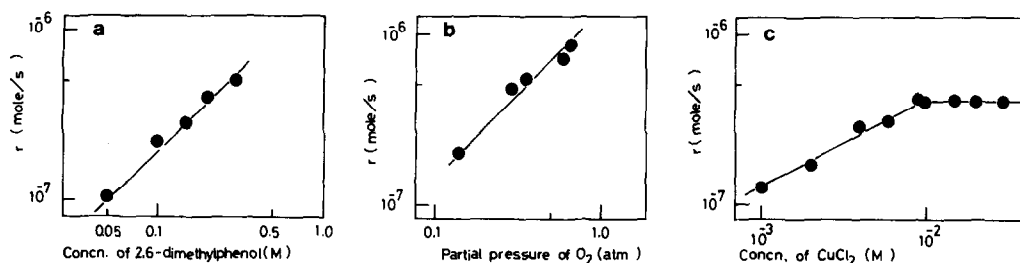


FIG. 6. Log-log plots of oxygen absorption rates versus the concentration of 2,6-dimethylphenol, the partial pressure of oxygen, and the concentration of  $CuCl_2$ . (a)  $CuCl_2$ , 0.01 mole/liter; KOH, 0.01 mole/liter; reaction temp,  $30^\circ C$ ;  $O_2$  atmosphere, 1 atm; solvent, 50 ml of MeOH; (b) 2,6-dimethylphenol, 0.2 mole/liter;  $CuCl_2$ , 0.01 mole/liter; KOH, 0.01 mole/liter; reaction temp,  $30^\circ C$ ; solvent, 50 ml of MeOH; (c) 2,6-dimethylphenol, 0.2 mole/liter; reaction temp,  $30^\circ C$ ;  $O_2$  atmosphere, 1 atm; solvent, 50 ml of MeOH.

log plot between the rate and the concentration of  $CuCl_2$  is shown in Fig. 6c. The plot shows a folded straight line, in which, at low-level copper(II) chloride concentrations, the slope of this straight line is ca. 0.5, and at high levels of the copper(II) chloride, the rate is independent of the copper(II) concentration. Thus, the slope is zero. From the results obtained above, the rate equation may be represented as

$$r = \frac{k \cdot (2,6\text{-Dimethylphenol}) \cdot (O_2) \cdot (Cu(II))^{1/2}}{1 + k' \cdot (Cu(II))^{1/2}} \quad (1)$$

*Reuse of basic copper(II) catalyst.* Efforts were made to reuse the basic copper (II) catalyst (KOH/ $CuCl_2$  mole ratio = 1) in the oxidation of 2,6-dimethylphenol. At first, the amount of oxygen absorbed during the reaction was measured with the reaction time. After the amount of oxygen absorbed nearly leveled off, the same amount of 2,6-dimethylphenol as the first run was added in the reaction mixture and again, the amount of oxygen absorption was followed with the reaction time. This result is illustrated in Fig. 7 where the initial concentration of 2,6-dimethylphenol was  $3.2 \times 10^{-2}$  mole/liter. The slopes of the oxygen absorption amount vs reaction time for the initial and the second runs were almost similar to each other, as evidenced from Fig. 7. Thus, this result seems to indicate that the present basic copper(II) catalyst is reusable

without an appreciable loss in the oxidation activity.

#### DISCUSSION

Only copper(II) chloride and only KOH had no activity for the 2,6-dimethylphenol oxidation. Also, although copper(II) hydroxide ( $Cu(OH)_2$ ) was used as a catalyst for the oxidative coupling of 2,6-dimethylphenol, it was found that no oxidation product was obtained and the starting phenol was recovered quantitatively. On the other hand, from the study on the effect of KOH/ $CuCl_2$  mole ratio on the oxidative coupling, the catalyst with the composition of KOH/ $CuCl_2$  = 1 was found to have a maximum

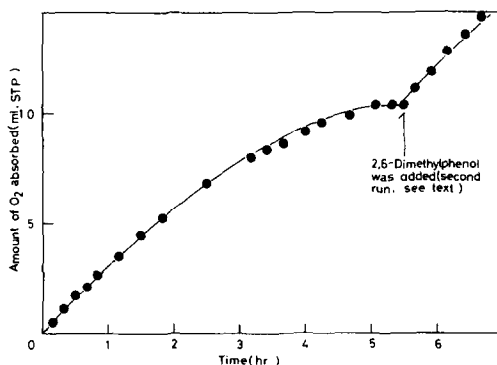


FIG. 7. The amount of oxygen absorbed versus reaction time. 2,6-Dimethylphenol, 0.032 mole/liter;  $CuCl_2$ , 0.015 mole/liter; KOH, 0.015 mole/liter; reaction temp,  $30^\circ C$ ;  $O_2$  atmosphere, 1 atm; solvent, 50 ml of MeOH.

activity for the present oxidation reaction. Judged from the series of experimental results, the active catalytic series for the oxidative coupling reaction of 2,6-dimethylphenol seem to be polymeric or oligomeric species which had a composition of  $\text{Cu Cl}(\text{OH})$  and were bridged by  $\text{OH}^-$  and  $\text{Cl}^-$  ligands. This consideration may be supported furthermore by the fact that the isolated heterogeneous part of the basic copper(II) system had a catalytic activity for the 2,6-dimethylphenol oxidative coupling reaction.

It must be noted that the heterogeneous part of the basic copper(II) catalytic system had a catalytic activity for the phenol oxidative coupling. We carefully observed the state of the heterogeneous basic copper(II) catalyst at the initial stage of the oxidative coupling reaction. After ca. 5 min, the heterogeneous part of the basic copper(II) catalytic system dissolved in the methanol solvent to result in seemingly the homogeneous-like catalytic system. The separation of the heterogeneous part of the basic copper(II) catalyst from the methanolic reaction solution by filtration was tried ca. 5 min after the oxidative coupling reaction of 2,6-dimethylphenol. No precipitate, except a small amount of red crystal of diphenquinone, was obtained by the filtration. It may be of interest to consider the behavior of the heterogeneous basic copper(II) catalyst at the initial stage of the oxidation in connection with the result obtained previously (5) by ESR measurement of the basic copper(II) catalyst. Thus, an ESR spectrum, assigned to a monomer-like planar copper(II) complex, was observed at the atmosphere of the oxidation reaction of 2,6-dimethylphenol. This was observed in place of a broad ESR peak which was observed under vacuum and may be caused by a strong interaction between a spin-spin dipole observed in a polynuclear array of copper(II) ions (5). From these experimental observations, it may be reasonable to suppose that under an oxygen atmosphere and in the presence of 2,6-dimethylphenol,

TABLE 3

Oxidative Coupling of 2,6-Dimethylphenol Catalyzed by Isolated Basic Copper(II) Complexes<sup>a</sup>

Catalyst ( $\text{CuCl}_2/\text{KOH}$ mole ratio = 1)	Solvent	Product yield (%)		Initial $\text{O}_2$ absorption rate (mole/s)
		C-O	C-C	
Isolated system <sup>b</sup>	MeOH	57	19	$3.0 \times 10^{-7}$
	MeOH <sup>c</sup>	20	0	$1.6 \times 10^{-7}$
	Benzene	0	0	—
Nonisolated system <sup>d</sup>	MeOH	55	20	$4.0 \times 10^{-7}$

<sup>a</sup> 2,6-Dimethylphenol, 0.2 mole/liter; reaction temp, 30°C;  $\text{O}_2$  atmosphere, 1 atm; reaction time, 4 hr; solvent, 50 ml.

<sup>b</sup> Isolated catalyst, 1 g.

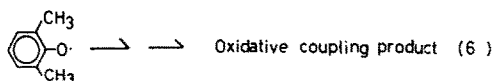
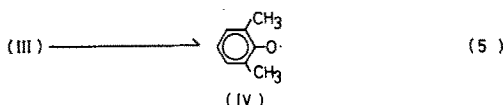
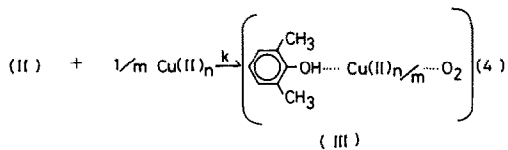
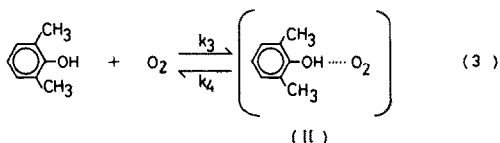
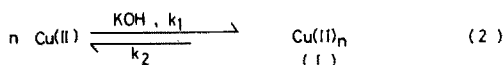
<sup>c</sup> KOH (0.2 mole/liter) was taken in the dropping funnel, in which the methanolic solution of 2,6-dimethylphenol (0.2 mole/liter) has been already introduced.

<sup>d</sup> 2,6-Dimethylphenol, 0.2 mole/liter; reaction time, 4 hr; reaction temp, 30°C;  $\text{O}_2$  atmosphere, 1 atm;  $\text{CuCl}_2$ , 0.01 mole/liter; KOH, 0.01 mole/liter.

the basic copper(II) catalyst shows the catalytic activity in the homogeneous state that has a mononuclear copper(II) complex structure rather than a polynuclear copper(II) complex structure. In other words, the present basic copper(II) catalytic system may be termed as a "heterogenized, homogeneous catalyst." As has been suggested previously (5), the role of oxygen may be thought to dissolve or weaken the bonds of the polynuclear copper(II) system to form a homogeneous system from a heterogeneous system and facilitate the replacement of a hydroxy anion by a phenolate anion in addition to the role of the reoxidation of copper ions. In fact, in a benzene solvent, the isolated heterogeneous basic copper(II) catalyst remained in a heterogeneous state during the oxidation reaction of 2,6-dimethylphenol, and no product of the oxidative coupling reaction was obtained as shown in Table 3.

It has been found that the basic copper(II) system acts as a one-electron transfer reagent by the ESR measurement of 2,6-*tert*-butyl-4-methylphenol with the basic copper(II) catalyst (5), as well as the homogeneous basic copper(II) system (7, 8). Thus, a one-electron transfer from 2,6-dimethylphenol moiety to the basic copper

(II) species in a phenoxo-copper(II) intermediate complex results in the corresponding phenoxy radical, which, in turn, couples to give the corresponding oxidative coupling product. Although we have no direct information on the reaction intermediate at the present stage, the reaction scheme for the oxidative coupling of 2,6-dimethylphenol catalyzed by the heterogeneous basic copper(II) complex



Reaction scheme

may be considered as a plausible reaction on the basis of the kinetic data and the properties of the observed catalytic system. At first, copper(II) chloride can react with KOH to form the corresponding polymeric (or oligomeric) basic copper(II) species  $\text{Cu(II)}_n$ , Eq. (2). 2,6-Dimethylphenol and oxygen molecules weakly interact with each other to form species (II). It is suggested that species (II) reacts with the polymeric basic copper(II) species to form a copper(II)-phenoxo moiety complex (III) in the rate-determining step. Species (III) can yield the corresponding phenoxy radical in a fast electron transfer process (Eq. (5)) that will yield an oxidative coupling prod-

uct via some coupling processes (Eq. (6)). If, as suggested, the rate-determining step is Eq. (4), the rate of this reaction will be expressed by

$$r = k \cdot \text{(II)} \cdot \{\text{Cu(II)}_n\}^{1/m} \quad (7)$$

By applying the steady state approximation (Bodenstein approximation) to species (II), we can obtain

$$\text{(II)} = \frac{k_3 \cdot \left( \text{2,6-dimethylphenol} \right) \cdot (\text{O}_2)}{k_4 + k \cdot \{\text{Cu(II)}_n\}^{1/m}} \quad (8)$$

Also, it can be expressed that if  $K_1 = k_1/k_2$ ,

$$\{\text{Cu(II)}_n\} = K_1 \cdot \{\text{Cu(II)}\}^n \quad (9)$$

Then, the reaction rate ( $r$ ) can be expressed in the form of Eq. (10) by replacement of Eq. (8) to Eq. (7)

$$r = \frac{k \cdot k_3 \cdot K_1^{1/m} \cdot (\text{O}_2) \cdot \{\text{Cu(II)}\}^{n/m} \cdot \left( \text{2,6-dimethylphenol} \right)}{k_4 + k \cdot K_1^{1/m} \cdot \{\text{Cu(II)}\}^{n/m}} \quad (10)$$

Equation (10) may be expressed in the form

$$r = k \cdot k_3 \cdot K_1^{1/m} \cdot k_4^{-1} \cdot (\text{O}_2) \cdot \{\text{Cu(II)}\}^{n/m} \cdot \left( \text{2,6-dimethylphenol} \right) \quad (11)$$

on the assumption that  $k_4 \gg k \cdot K_1^{1/m} (\text{Cu(II)})^{n/m}$ . On the other hand, if  $k_4 \ll k \cdot K_1^{1/m} (\text{Cu(II)})^{n/m}$ , Eq. (10) may be expressed in the form

$$r = k_3 \cdot (\text{O}_2) \cdot \left( \text{2,6-dimethylphenol} \right) \quad (12)$$

Equations (10), (11), and (12) are consistent with the observed kinetic behavior of the basic copper(II) complex which catalyzes the oxidative coupling of 2,6-dimethylphenol, though we have no information on the structures of the intermediate species (II) and (III) at this stage.

Finally, some comments may be given on the factor which governs the oxidative coupling manner in the basic copper(II) cata-



lytic system. In the oxidative coupling reaction of 2,6-dimethylphenol, catalyzed with the isolated basic copper(II) complex, the introduction of an equivalent amount of KOH, as 2,6-dimethylphenol formed the C–O coupling product selectively, is shown in Table 3. In contrast, an appreciable amount of C–C coupling product was produced under the same reaction condition as stated before, except for the absence of the excess KOH. From the results, the presence of the corresponding phenolate anion, liberated by the interaction of 2,6-dimethylphenol with the added KOH under the former reaction condition, may be responsible for a selective C–O coupling production in the oxidative coupling of 2,6-dimethylphenol. In comparison with free 2,6-dimethylphenol, which forms the intermediate phenol–Cu(II) complex (such as species (III)) with the basic copper(II) complex through hydrogen bonding, the corresponding phenolate anion may be able to more strongly interact with Cu(II) ions in the basic copper(II) complex. The difference of the interaction of the phenol moiety with the basic copper(II) complex may be suggested as one of the factors that govern the oxidative coupling manner in the oxidative coupling of 2,6-dimethylphenol catalyzed by the basic copper(II) complex.

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#### REFERENCES

1. Pecht, I., Levitzki, A., and Anbar, M., *J. Amer. Chem. Soc.* **89**, 1587 (1967); Hewitt, D. G., *J. Chem. Soc. C* 2967 (1971); Ogata, Y., Sawaki, Y., Mibae, J., and Morimoto, T., *J. Amer. Chem. Soc.* **86**, 3854 (1964); Ogata, Y., and Morimoto, T., *J. Org. Chem.* **30**, 597 (1965); Jackson, E. L., *J. Amer. Chem. Soc.* **68**, 1438 (1946); Takahashi, H., Kajimoto, T., and Tsuji, T., *Synth. Commun.* **2**, 181 (1972); Tsuji, J., and Takayanagi, H., *J. Amer. Chem. Soc.* **96**, 7349 (1974); Kinoshita, K., *Bull. Chem. Soc. Jpn.* **32**, 777, 780 (1959); Terentev, A. P., and Mogilyanskii, Y. D., *Dokl. Akad. Nauk SSSR* **103**, 91 (1955); *Chem. Abstr.* **50**, 4807e (1956); Tsuji, J., Takahashi, H., and Kajimoto, T., *Tetrahedron Lett.* 4573 (1973); Bullock, F. J., and Tweedie, J. F., *J. Med. Chem.* **13**, 261 (1970); Van Rheenen, V., *Tetrahedron Lett.* 985 (1969); Van Rheenen, V., *J. Chem. Soc. D* 314 (1969); Malhotra, S. K., Hostynek, J. H., and Lundin, A. F., *J. Amer. Chem. Soc.* **90**, 6565 (1968).
2. Hay, A. S., Blanchard, H. S., Endres, G. F., and Eustance, J. W., *J. Amer. Chem. Soc.* **81**, 6335 (1959); Endres, G. F., Hay, A. S., and Eustance, J. W., *J. Org. Chem.* **28**, 1300 (1963); Hay, A. S., *J. Polym. Sci.* **58**, 581 (1962); Finkbeiner, H., Hay, A. S., Blanchard, H. S., and Endres, G. F., *J. Org. Chem.* **31**, 549 (1966); Hay, A. S., *Adv. Polym. Sci.* **4**, 496 (1967); Hay, A. S., *Polym. Eng. Sci.* **16**, 1 (1976); and references cited therein.
3. Taylor, W. I., and Battersby, A. R., "Oxidative Coupling of Phenols." Dekker, New York, 1968; Staffin, G. D., and Price, C. C., *J. Amer. Chem. Soc.* **82**, 3632 (1960); Lindgren, B. O., *Acta Chem. Scand.* **14**, 1203 (1960); McNelis, E., *J. Org. Chem.* **31**, 1255 (1966); Carrick, W. L., Karapinka, G. L., and Kwiatkowski, G. T., *J. Org. Chem.* **34**, 2388 (1969); Kon, E., and McNelis, E., *J. Org. Chem.* **40**, 1515 (1975); White, D. M., and Klopfer, H. J., *J. Polym. Sci. Part A-1* **8**, 1427 (1970); Hall, J. R., *Polym. Lett.* **4**, 463 (1966); Bruce, J. M., and Pauley, S. E., *Polymer* **10**, 701 (1969); Hay, A. S., Shenian, P., Gowan, A. C., Erhardt, P. E., Haaf, W. R., and Theberge, J. E., "Encyclopedia of Polymer Science and Technology," Vol. 10, p. 92. Wiley, New York, 1969; Kresta, J., Tkac, A., Prikrýl, R., and Malik, L., *Makromol. Chem.* **176**, 157 (1975); Schouten, A. J., Wiedijk, D., Borkent, J., and Challa, G., *Makromol. Chem.* **178**, 1341 (1977); Hudec, P., *J. Catal.* **53**, 228 (1978); Schouten, A. J., Prak, N., and Challa, G., *Makromol. Chem.* **178**, 401 (1977); Schouten, A. J., Challa, G., and Reedijk, J., *J. Mol. Catal.* **9**, 41 (1980); Meinders, H. C., and Challa, G., *J. Mol. Catal.* **7**, 321 (1980); Meinders, H. C., Van Bolhuis, F., and Challa, G., *J. Mol. Catal.* **5**, 225 (1979); Schouten, A. J., Noordeggraaf, D., Jekel, A. P., and Challa, G., *J. Mol. Catal.* **5**, 331 (1979).
4. Tsuruya, S., Kawamura, T., and Yonezawa, T., *J. Polym. Sci. Part B* **7**, 709 (1969); Tsuruya, S., Okumoto, K., and Yoshimatsu, T., *J. Polym. Sci., Polym. Chem. Ed.* **16**, 379 (1978); Tsuruya, S., and Yoshimatsu, T., *J. Catal.* **58**, 444 (1979).
5. Tsuruya, S., Nakamae, K., and Yonezawa, T., *J. Catal.* **44**, 40 (1976).
6. Tsuruya, S., Kishikawa, Y., Tanaka, R., and Kuse, T., *J. Catal.* **49**, 254 (1977).
7. Tsuruya, S., Shirai, T., Kawamura, T., and Yonezawa, T., *Makromol. Chem.* **132**, 57 (1970).
8. Tsuruya, S., Kinumi, K., Hagi, K., and Masai, M., *J. Mol. Catal.* **22**, 47 (1983).