

The Oxidative Coupling Reaction of 2,6-Dimethylphenol with Heterogeneous Basic Copper(II) Catalysts

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The oxidation of 2,6-dimethylphenol by heterogeneous basic copper(II) catalyst (CuCl_2 -KOH system) without amine such as pyridine under an oxygen atmosphere resulted in the formation of the corresponding coupling products, polyphenylene oxide (C-O coupling product) and diphenoquinone (C-C coupling product). The KOH/ CuCl_2 ratio was found to be the main factor which controls the coupling manner, namely, the increase of this ratio was favorable for C-O coupling, whereas C-C coupling product was liable to be preferentially obtained under a low KOH/ CuCl_2 ratio. The effect of the variation in base and copper(II) salt on the product yield and/or the reaction rate were discussed in terms of the catalytic activity of the basic copper(II) system formed. In contrast to hitherto reported homogeneous copper complex catalysts, it was found that the heterogeneous basic copper(II) system in the absence of oxygen could not catalyze the oxidative coupling reaction of 2,6-dimethylphenol. The role of oxygen was discussed on the basis of esr spectra of the mixed system consisting of the catalyst and 2,6-dimethylphenol. From the esr measurement of the mixed system under an oxygen atmosphere, the corresponding polymer radical was observed.

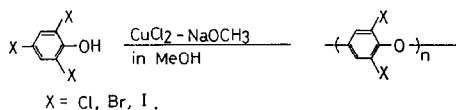
INTRODUCTION

The oxidative coupling reaction of 2,6-dimethylphenol to its corresponding C-O coupling (polyphenylene oxide) and/or C-C coupling (diphenoquinone) products has been carried out with various homogeneous and heterogeneous catalysts. The copper-amine system, which is an excellent catalytic oxidant, was developed by Hay (1). Heterogeneous oxidants such as silver oxide (2), activated manganese dioxide (3), lead dioxide (3) and sodium bismuthate (4) have been reported to be one-electron phenolic oxidants.

Hay's typical homogeneous system consists of a copper complex prepared by autoxidation of cuprous chloride in pyridine. Replacement of cuprous chloride by cupric chloride as a catalyst in pyridine causes inactivity for the oxidative coupling reaction of 2,6-dimethylphenol. On the other hand, homogeneous basic copper(II)-pyridine complex (cupric chloride-pyridine system in which a base such as KOH was added) has been found to produce an active catalyst (5).

In a preliminary communication (6), it was reported that 2,4,6-trihalophenols

reacted under relatively mild conditions with a heterogeneous copper(II) chloride–sodium methoxide system without amine as a ligand to give the corresponding poly-(dihalophenylene oxide). This finding, that the heterogeneous basic copper(II) system without amine forms active species for the oxidative displacement reaction of halophenols, has stimulated renewed interest in investigation of the application of heterogeneous basic copper(II) system to the oxidative coupling reaction of 2,6-dimethylphenol. With this background, it was anticipated that the heterogeneous basic copper(II) system (containing copper(II) salt and base such as KOH) would form active species for the oxidative coupling reaction of 2,6-dimethylphenol.



In the present paper, we report the oxidative coupling reaction of 2,6-dimethylphenol with the heterogeneous basic copper(II) system under a variety of reaction conditions. The selectivity of reaction products, C–O coupling and/or C–C coupling, was found to vary with the ratio of copper(II) salt to KOH. This basic copper(II) system with KOH as base, differs from the previously reported homogeneous basic copper(II) system (5), in that it was found not to catalyze the oxidative coupling reaction of 2,6-dimethylphenol in the absence of oxygen. The properties of the heterogeneous basic copper(II) system were studied by esr measurement and discussed in connection with its catalytic function and the role of oxygen.

EXPERIMENTAL METHODS

The ir spectra were obtained on a Hitachi 215 type spectrophotometer. The nmr spectra were recorded on a JEOL-3H-60 spectrometer in CDCl_3 , TMS being chosen as the internal standard. The esr

spectra were taken by using a JEOL-2BSX type spectrometer with a 100 kHz modulation unit. The magnetic field was calibrated with Mn(II) ion and potassium peroxyamine disulfonate. The microanalyses were performed at the elemental analysis center of Kyoto University.

Materials

2,6-Dimethylphenol was purified by recrystallization from *n*-hexane. Copper(II) chloride was prepared by heating the dihydrate of copper(II) chloride at 110–120°C for 3 hr under vacuum. The other copper(II) salts were used without further purification. The methanol used was refluxed with magnesium powder and distilled twice.

Oxidative Coupling Reaction of 2,6-Dimethylphenol

All the reactions were conducted at $30 \pm 0.2^\circ\text{C}$. The requisite amount of both methanol solutions of copper(II) chloride and of potassium hydroxide were taken in a round-bottomed reaction vessel fitted with mechanical stirrer, gas-inlet tube and condenser. A known quantity of a methanol solution of 2,6-dimethylphenol was added. Then vigorous stirring was continued for the prescribed time under an oxygen atmosphere. The products were worked up as follows: Where only polymer was obtained, the reaction mixture was poured into 200 ml of methanol containing a little concentrated hydrochloric acid stirred magnetically. The precipitate was filtered off and washed with methanol containing HCl. Where only diphenoquinone was obtained, the reaction mixture was decomposed with aqueous HCl solution, the diphenoquinone was filtered off and dried. Where both polymer and diphenoquinone were produced, the mixed product was filtered after decomposition of the catalyst and separated using a Soxhlet extractor and hot methanol. In all the cases described above, the filtrate

was colorimetrically analyzed to determine the amount of diphenoquinone dissolved ($\lambda_{\max} = 415$ nm). It was ascertained that the other products were not present in the filtrate by thin layer chromatography (tlc) in benzene on silica gel. The reactions with the other copper(II) salts and/or bases were carried out by a procedure analogous to that described above. Infrared spectra of polymer and diphenoquinone were, respectively, identical with those of poly(2,6-dimethyl-1,4-phenylene oxide) and 3,3',-5,5'-tetramethyl-4,4'-diphenoquinone obtained with a homogeneous cuprous chloride-pyridine catalyst. The nmr spectrum of the polymer in CDCl_3 showed absorptions at $\tau 3.54$ and $\tau 7.91$ with the area ratio of 1:3. The former signal was assigned as the phenylene ring protons and the latter as the methyl protons. The elemental analysis of the polymer was as follows: Anal.: calcd for $\text{C}_8\text{H}_8\text{O}$: C, 79.97; H, 6.71; found: C, 79.69; H, 6.97. Intrinsic viscosities of some of the polymers were measured with a Ubelhode type viscometer at 25°C in chloroform. The nmr signals of diphenoquinone at $\tau 7.90$ and $\tau 2.38$ are due to the methyl protons and ring protons, respectively (the area ratio, 3:1). The elemental analysis of the product diphenoquinone was as follows: Anal.: calcd for $\text{C}_8\text{H}_8\text{O}$: C, 79.97; H, 6.71; found: C, 79.95; H, 6.91.

In the case of the reaction under a nitrogen atmosphere, the methanolic solutions of the catalytic system and 2,6-dimethylphenol were outgassed with nitrogen by bubbling nitrogen through them for 5 hr before mixing. Then the reaction was conducted over a period of 5 hr under nitrogen after which, neither polymer or diphenoquinone was found. Thin-layer chromatography of the reaction solution showed no spots other than that of the starting material.

The amount of oxygen absorption was measured by a usual pressure-constant type gas absorption equipment.

Isolation of Basic Copper(II) Complex

The basic copper(II) complex was prepared by mixing both methanolic solutions of copper(II) chloride and KOH (KOH/ CuCl_2 mole ratio, 1.14) and collecting by filtration. The ir spectrum of the basic copper(II) complex isolated showed a strong and broad peak near 3400 cm^{-1} .

Oxidative Coupling Reaction of 2,6-Dimethylphenol with Basic Copper(II) Complex

A 0.5 g sample of basic copper(II) complex isolated by the procedure described above was added to 50 ml of methanolic solution in which was dissolved 1.0 g (0.0082 mole) of 2,6-dimethylphenol. After stirring the reaction mixture under oxygen at 30°C for 5 hr, only diphenoquinone was produced in the yield of 8%, and no polymer was obtained.

Oxidative Coupling Reaction of 2,6-Dimethylphenol in Filtrate Resulting from Isolation of Basic Copper(II) Complex

A 1.22 g sample (0.01 mole) of 2,6-dimethylphenol was dissolved in 50 ml of the filtrate resulting from isolation of basic copper(II) complex mentioned above. The homogeneous reaction mixture was allowed to react at 30°C under an oxygen atmosphere for 3 hr. But no reaction products were obtained, and starting phenol was recovered quantitatively.

Oxidative Coupling Reaction of 2,6-Dimethylphenol with a System Formed of Both the Basic Copper(II) Complex Isolated and Methanolic Solution Containing KOH

A 0.7 g sample of basic copper(II) complex isolated from the method noted above was added to 25 ml of methanol. Into the heterogeneous solution, 25 ml of methanolic solution containing 1.12 g (0.01 mole) of 2,6-dimethylphenol and 0.64 g (0.01 mole) of KOH was poured. The resulting heterogeneous mixture was re-

acted for 3 hr under an oxygen atmosphere. Only the polymer was formed in 39% yield.

Electron Spin Resonance Spectra of the System Consisted of 2,6-Dimethylphenol and Basic Copper(II) Complex

The methanolic solution containing the prescribed amount of basic copper(II) catalyst and 2,6-dimethylphenol was reacted under oxygen for 5 min at ca. -40°C . After this treatment, oxygen supply was replaced with nitrogen, and the reaction mixture was allowed to stand for 20 min. Under a nitrogen atmosphere, the resulting precipitate was collected by filtration and transferred to an esr sample tube. The esr spectrum of the precipitate isolated at ca. -20°C was also measured. In the case of measurement of the reaction system out-gassed under vacuum, the esr sample tube consisted of a main sample tube with a side tube. The methanolic solutions of basic copper(II) catalyst and 2,6-dimethylphenol were placed in the main sample tube and the side tube, respectively. After degassing under vacuum, the esr sample tube was sealed off. After mixing the two methanolic solutions in a sample tube and removal of methanol from the main sample tube to the side tube by vacuum distillation, the solid sample was measured with esr equipment at room temperature.

RESULTS AND DISCUSSION

The Oxidative Coupling Reaction of 2,6-Dimethylphenol with Heterogeneous Basic Copper(II) Catalyst

The result of reaction of 2,6-dimethylphenol with basic copper(II) catalyst is presented in Table 1. No other products except polymer (C-O coupling product) and diphenoquinone (C-C coupling product) were obtained in the reaction conditions. As seen in Table 1, the copper(II) chloride by itself in methanol has no catalytic activity and neither does methanolic solution containing only KOH. Thus

TABLE 1
Oxidative Coupling Reaction of 2,6-Dimethylphenol with Basic Copper(II) Catalyst^a

CuCl ₂ (mole/ liter)	KOH (mole/ liter)	KOH/ CuCl ₂	Yield (%) ^b	
			Polymer	Dipheno- quinone
0.00	0.20	—	0	0
0.01	0.20	20	3	0
0.02	0.20	10	25 ^c	0
0.025	0.20	8	38	0
0.050	0.20	4	40	0
0.150	0.20	1.33	69 ^d	Tr
0.175	0.20	1.14	79 ^e	Tr
0.20	0.00	0	0	0
0.20	0.05	0.25	0	28
0.20	0.10	0.5	0	36
0.20	0.15	0.75	31	12
0.20	0.20	1	47 ^f	22
0.20	0.30	1.5	56	8
0.20	0.40	2	38	0
0.20	0.50	2.5	4	0
0.20	0.80	4	2	0
0.20	1.00	5	Tr	0
0.40	0.20	0.5	0	26
0.60	0.20	0.33	0	33

^a 2,6-Dimethylphenol: 0.2 mole/liter; solvent: 50 ml of methanol; temp: 30°C ; time: 5 hr; O₂ atmosphere.

^b Based on 2,6-dimethylphenol.

^c Intrinsic viscosity at 25°C in chloroform: 0.30 dl/g.

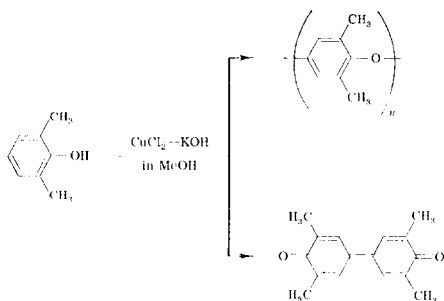
^d Intrinsic viscosity at 25°C in chloroform: 0.24 dl/g.

^e Intrinsic viscosity at 25°C in chloroform: 0.20 dl/g.

^f Intrinsic viscosity at 25°C in chloroform: 0.30 dl/g.

basic copper(II) complex consisting of copper(II) chloride and potassium hydroxide catalyzes the oxidative coupling reaction of 2,6-dimethylphenol. It was observed that both total yield and selectivity vary with KOH/CuCl₂ ratio. At constant CuCl₂ or KOH concentration, the general trend was found that a ratio more than 1 favors the C-O coupling, on the other hand C-C coupling product is preferentially obtained when the ratio is less than 1 although no products were yielded when the ratio was

very high or low. It appears that one of the major factors which controls the coupling manner is the ratio of KOH to copper(II) chloride.



In order to obtain more direct information concerning the function of KOH, isolation of the copper(II) complex was attempted. Although the definite structure and/or composition of the basic copper(II) complex could not be determined, it is reasonable to consider that in the isolated basic copper(II) complex, hydroxyl groups are included because of its infrared spectrum, elemental analysis (for KOH/CuCl₂ = 1.14; C, 0.00; H, 1.72) and the reaction condition for preparation. Also because of

its insolubility in common solvents, the basic copper(II) complex seems to be a polynuclear chain structure, supported by esr spectrum of the isolated basic copper(II) complex (see below).

Reaction of 2,6-dimethylphenol with the isolated basic copper(II) complex (KOH/CuCl₂ = 1.14) in methanol solvent yielded only the diphenylquinone. On the other hand, only the polymer was produced where 2,6-dimethylphenol in methanol with an equivalent of KOH was reacted with the isolated basic copper(II) complex (KOH/CuCl₂ = 1.14). These results are of interest in connection with the function of KOH for the present reaction. The result of Table 1 that the increase of KOH favors C-O coupling is compatible with the result with the isolated catalyst. It may be concluded from these results that OH⁻ ion which is soluble in methanol rather than basic copper(II) complex itself controls the coupling manner to give either C-O or C-C coupling product. The fact that ir and esr spectra of isolated basic copper(II) complexes were only slightly different despite the variation of the ratio of copper(II) chloride to KOH upon the preparation seems to show the basic copper(II) complex isolated has only one kind of active species, not depending on the condition of preparation. In the case of large KOH/CuCl₂ ratio, free OH⁻ ion in methanol will increase the concentration of corresponding phenolate anion. The increase of phenolate anion may favor C-O coupling rather than C-C coupling. Although there is no clear answer concerning the reason why the increase of phenolate anion favors C-O coupling it is concluded that the amount of KOH in methanol has an important role for the selectivity of coupling manner.

It has been well known (1) that the role of oxygen in the oxidative coupling reaction of 2,6-dimethylphenol with copper(I)-pyridine system is to keep copper(I) ion in divalent state. Thus 2,6-dimethylphenol can be reacted in the absence of oxygen

TABLE 2

Effect of CuCl₂/2,6-Dimethylphenol on the Oxidative Coupling Reaction under an Oxygen or a Nitrogen Atmosphere^a

CuCl ₂ (mole/ liter)	CuCl ₂ / 2,6-Di- methyl- phenol (mole ratio)	KOH/ CuCl ₂ (mole ratio)	Reac- tion time (hr)	Yield ^b (%)	
				Poly- mer	Di- phen- oqui- none
0.2 ^c	1	1	3	47	38
0.02 ^c	0.1	1	6	68	16
0.2 ^c	1	2	3	0	38
0.02 ^c	0.1	2	14	1	26
0.27 ^d	1.33	1.33	5	0	0
0.1 ^d	0.5	1	5	0	0

^a 2,6-Dimethylphenol: 0.2 mole/liter; solvent: 50 ml of MeOH; temp: 30°C.

^b Based on 2,6-dimethylphenol.

^c Under an oxygen atmosphere.

^d Under a nitrogen atmosphere.

providing more than an equivalent of copper(II) ion is present. Table 2 shows the effect of the ratio of $\text{CuCl}_2/2,6$ -dimethylphenol under oxygen or nitrogen. Even at copper(II) chloride concentration less than equivalent based on 2,6-dimethylphenol, the reaction products were obtained in moderately good yields although the reaction rate tends to become slower. This result shows that also in the present copper(II) system, redox process of copper ion by oxygen occurred. However, surprisingly, no products could be obtained with present catalytic system under a nitrogen atmosphere as shown in Table 2. Though explanation of the result is difficult, the oxygen seems to have another role in addition to keeping copper ion in the divalent state. The role of oxygen in this catalytic system is discussed below in connection with esr spectra of the basic copper(II) complexes and the reaction systems prepared under an oxygen and/or a nitrogen atmosphere.

As shown in Table 3, some copper(II) halides other than copper(II) chloride were found to catalyze the present oxidation, but $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ did not act as a catalyst under identical reaction conditions. Thus, halogen atom appears to be necessary as a ligand. Figure 1 shows that the oxygen absorption rate with copper(II) chloride is faster than with copper(II) bromide. It is obvious from Fig. 1 that copper(II) halide as a catalyst influences the reaction rate. It has been reported (1) that in the oxidative coupling reaction of 2,6-dimethylphenol with copper(II) halide modified suitably in amine, the active catalyst is a basic salt as follows:

$\text{X}-\text{Cu}-\text{OH}$ (X = halogen atom). The first step in the reaction appears to be:

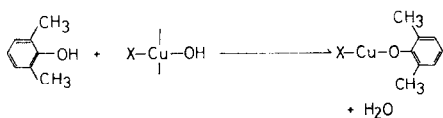


TABLE 3
Effect of Copper(II) Salt on Oxidative Coupling Reaction^a

Copper(II) salt	Yield (%) ^b	
	Polymer	Diphenoquinone
CuCl_2	47	22
CuBr_2	53	12
$\text{CuF}_2 \cdot 2\text{H}_2\text{O}$	27	0
$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	0	0
$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	0	0

^a 2,6-Dimethylphenol: 0.2 mole/liter; time: 3 hr; copper(II) salt: 0.2 mole/liter; KOH: 0.2 mole/liter; temp: 30°C; O_2 atmosphere; solvent: 50 ml of MeOH.

^b Based on 2,6-dimethylphenol.

Although the composition of present basic copper(II) complex is ambiguous, it seems reasonable to assume the basic copper(II) complex includes halogen and hydroxyl group. Our present concern is to consider the difference of the reaction rates with the difference of the reaction rates with ligand substitution scheme given above. Arakawa and Miyamoto (7) discussed the initial rate of the oxidative coupling reaction of 2,6-dimethylphenol with copper-amine complex in terms of substitution

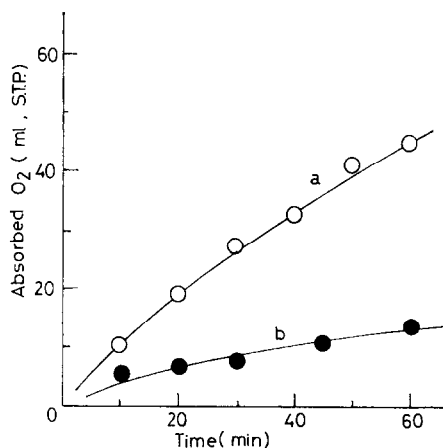


FIG. 1. Absorbed O_2 vs reaction time. 2,6-Dimethylphenol: 0.1 mole/liter; Cu(II) salt: 0.1 mole/liter; KOH: 0.1 mole/liter; temp: 30°C; solvent: 50 ml of methanol. (a) CuCl_2 -KOH; (b) CuBr_2 -KOH.

TABLE 4
Effect of Base on Oxidative Coupling Reaction^a

Base	Yield (%) ^b	
	Polymer	Dipheno-quinone
CH ₃ ON _a ^c	73	3
<i>n</i> -C ₂ H ₅ ON _a ^d	58	3
tert-C ₄ H ₉ ON _a	6	0

^a 2,6-Dimethylphenol: 0.2 mole/liter; time: 3 hr; temp: 30°C; copper(II) chloride: 0.2 mole/liter.

^b Based on 2,6-dimethylphenol.

effect of ligand. It is reasonable to postulate in the present system that the substitution by phenolate anion takes place on OH⁻ rather than on X⁻, as has been reported previously (8). Because Cl⁻ ion has more strong electron-accepting power than Br⁻ ion based on the electronegativity, the

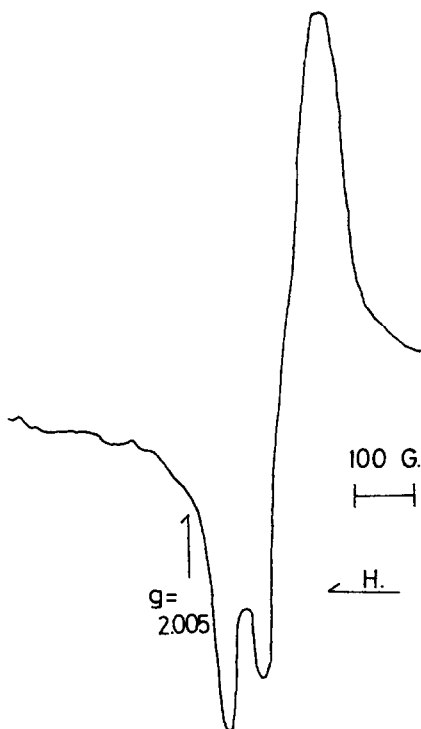


Fig. 2. Electron spin resonance spectrum of heterogeneous basic copper(II) complex (KOH/CuCl₂ = 1.14).

cationic charge on copper atom of copper(II) chloride will be larger in comparison with copper(II) bromide system. Due to the difference of cationic charge on copper ion the copper(II)-phenolate complex considered as an intermediate may be formed more easily with copper(II) chloride rather than with copper(II) bromide. Also the steric factor may play an important part. Thus phenolate anion in copper(II) bromide system may be more difficult to approach on copper ion since Br⁻ ion is larger in size than Cl⁻ ion. As discussed above, charge on copper ion and steric factor around copper(II) ion must influence the reaction rate on the basis of the assumption that the corresponding phenoxo-copper(II) complex is formed in the process of the initial stage of oxidation as has been considered in the homogeneous system.

It is of interest to investigate the effect of base on coupling yield. The result in which some bases other than KOH were utilized is presented in Table 4. The coupling product was afforded in a poor yield when treated with sodium tert-butoxide. This result may be once again attributed to the sterically hindered tert-butoxide group considered as a ligand coordinated to the copper(II) ion.

Electron Spin Resonance Measurement of Basic Copper(II) System and Reaction Intermediate

We have used esr spectroscopy to study the structure and nature of the basic copper(II) system and the intermediate of the oxidation of 2,6-dimethylphenol with basic copper(II) system. Figure 2 shows the esr spectrum of basic copper(II) complex (KOH/CuCl₂ = 1.14, mole ratio) prepared under an oxygen atmosphere. This spectrum is a typical one of amorphous copper(II) complex which has three components of *g*-tensor. In order to investigate the intermediate state of the present oxidation reaction, the mixed system of the basic copper(II) complex and 2,6-

dimethylphenol was followed by esr measurement. At first, the degassed mixed system was measured as shown in Fig. 3. Evidently in the absence of oxygen, the esr spectrum consists of one broad peak and its signal/noise ratio is small. In the case of the presence of oxygen, 2,6-dimethylphenol and basic copper(II) complex were mixed in methanol under a low temperature (see Experimental section), and Fig. 3b and c show the esr spectra of the mixed system prepared at -40 and -20°C , respectively. In contrast to the esr spectrum in the absence of oxygen, one sharp peak is observed near $g = 2.00$ in addition to the absorption peak based on copper(II) ion. This newly generated

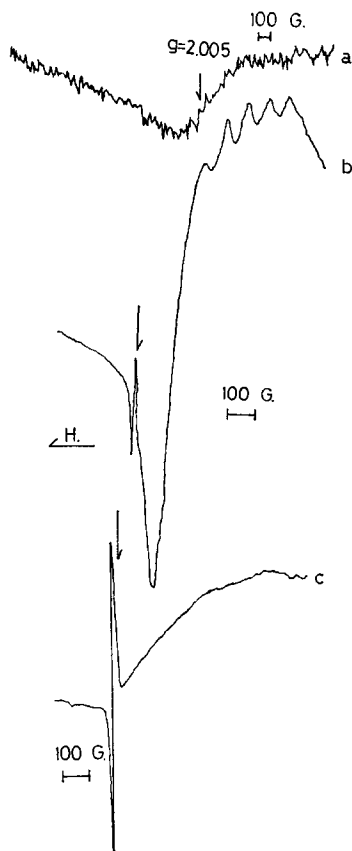


FIG. 3. Electron spin resonance spectra of mixed reaction system. (a) Under vacuum; (b) at -40°C under an oxygen atmosphere; (c) at -20°C under an oxygen atmosphere.

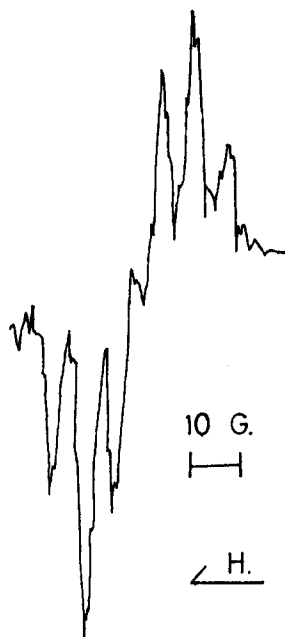


FIG. 4. Electron spin resonance spectrum near $g = 2.00$ in Fig. 3c under magnification.

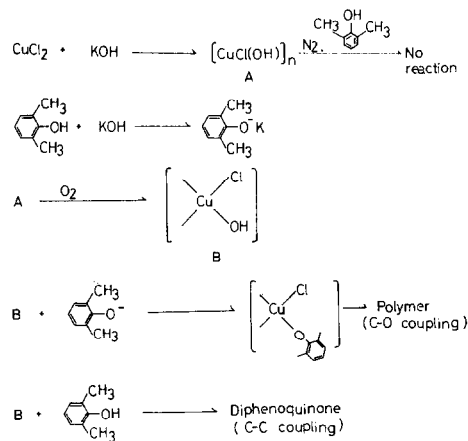
peak is considered the organic radical derived from 2,6-dimethylphenol. Furthermore, the absorption peak based on copper(II) ion in Fig. 3b is fairly different from that in the spectrum under a nitrogen atmosphere. The esr spectrum on the basis of the copper(II) ion in Fig. 3b has four peaks at g_{11} and large one peak at g_{\perp} , and is considered as a typical anisotropic spectrum in which the interaction between copper(II) ions is weak or not present. The esr spectrum in Fig. 3c is explained as a later stage in the reaction than that in Fig. 3b, judging from the preparation conditions of the two samples. The sharp peak near $g = 2.00$ in Fig. 3c is larger than in Fig. 3b. The absorption peak based on the organic radical is revealed under magnification in Fig. 4. In Fig. 4, a basic pattern of seven lines (coupling constant, ca. 6 G) can be seen, though no subsplittings were observed because of low S/N ratio and resolving power. This spectrum seems to be a polymer radical (ρ). In contrast to the one in Fig. 3b, the esr peak based on

copper(II) ion in Fig. 3c became a broad one in which the anisotropy of g -value was not at all clear. To discuss the differences of esr spectra between the mixed systems under oxygen and in the absence of oxygen is of interest from the point of view, not only of the structure of catalyst but also of the role of oxygen. In the amorphous nondiluted paramagnetic species, the strong interaction between spin-spin dipole is anticipated as one cause of broadening of the esr absorption line (10). According to this interpretation, the mixed system in the absence of oxygen may have the stronger interaction between copper(II) ions, based on its broad esr line. Thus it may be considered that the polynuclear array of copper(II) ions in the absence of oxygen through the bridged ligands such as OH^- and/or Cl^- is anticipated to be more rigid. On the contrary, the polynuclear chain of copper(II) ion under an oxygen atmosphere may more easily dissociate into mononuclear-like planar copper(II) complex in which the interaction between copper(II) ions is weak, as evidenced in Fig. 3b. It is reasonable to consider that this assumed mononuclear-like copper(II) system under an oxygen atmosphere is more easy to replace ligand than rigidly bounded polynuclear system. Thus the role of oxygen may be thought to dissociate and/or weaken the bonds of the polynuclear copper(II) system and facilitate the replacement of hydroxy anion by phenolate anion, in addition to the role of reoxidation of copper ion. Due to the information obtained from the esr data, the cause of the inactivity of the basic copper(II) system under a nitrogen atmosphere may be attributed to the difficulty of formation of copper(II)-phenoxo complex, which is considered as an intermediate. In the homogeneous basic copper(II) complex with anime such as pyridine, the effect noted above may be ignored since the bond between copper(II) ion and ligand in the homogeneous system are much weaker than

that of heterogeneous polynuclear copper(II) system.

Since the first order phenoxy radical of 2,6-dimethylphenol could not be observed with heterogeneous basic copper(II) system under the present measurement condition, we attempted to use 2,6-di-*tert*-butyl-4-methylphenol as a phenol derivative. It was found that the corresponding phenoxy radical was generated with the present catalytic system, which result shows that the heterogeneous basic copper(II) system acts as a one-electron transfer reagent, as well as the homogeneous basic copper(II) system (5-b).

The proposed reaction pathways to coupling products are shown in Scheme I.



SCHEME I

Complex A is a polynuclear basic copper(II) complex. This complex has no catalytic activity in the absence of oxygen. Complex B may have mononuclear-like structure or nonbridged OH group. A possible mechanism leading to C-O coupling involves a phenolate anion, which can be formed with OH^- ion. This clearly explains the necessity of an excess OH^- ion for C-O reaction. On the other hand, C-C coupling product may be obtained by direct oxidation of 2,6-dimethylphenol with complex B.

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