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# Oxidation of 2,4-Di-*t*-butylphenol with Hydrogen Peroxide Catalyzed by Bis(ethylenediamine)copper(II) Complexes

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2,4-Di-*t*-butylphenol (**1**) was efficiently oxidized with $H_2O_2$ in methanol in the presence of bis(ethylenediamine)copper(II) (Cu(II)(en)$_2$) complexes. Activity of the Cu(II) complexes was strongly dependent on the structure of the en ligands, as in the cases of the $O_2$ oxidation of phenol **1**.[1)] In the $H_2O_2$ oxidation of **1**, ens having none of *N*-alkyl substituent were of the most efficient. By addition of $H_2O_2$, stable Cu(II)(en)$_2$ complexes exhibited a new absorption at 340 nm, which was assigned to Cu(II)-en-$H_2O_2$ (1 : 2 : 1) complexes. Furthermore, the rapid-scanning spectrophotometry proved that quadruple Cu(II)-en-phenol **1**-$H_2O_2$ (1 : 1 : 1 : 1) complexes were the key intermediate for the oxidation of **1**. The initial velocity can be summarized in the equation $v=k[H_2O_2]^1[\text{phenol } \mathbf{1}]^1[\text{Cu(II)(en)}_2]^1$. The oxidation mechanism of phenol **1** with $H_2O_2$ is proposed.

In the previous papers[1,2)] reported on the autoxidation of phenols with molecular oxygen catalyzed by bis(*N*-alkylethylenediamine)copper(II) (abbreviated as Cu(II)(*N*-Ren)$_2$ (R=alkyl group) hereafter; the related complexes are also shown by the same type of abbreviation) complexes, we showed that the most active complexes were those derived from sterically overcrowded ens around the nitrogen atoms. This paper deals with the oxidation of 2,4-di-*t*-butylphenol (**1**) by hydrogen peroxide. Oxidation of phenols with hydrogen peroxide in the presence of Cu(II)-amine complexes has been scantly reported with exception of the hydroxylation of phenols.[3)] Compared with molecular oxygen, hydrogen peroxide is a stronger oxidant and has a higher coordinating ability to copper(II). We have investigated Cu(II) complexes of a series of ens bearing *N*-alkyl or *C*-alkyl substituents to determine how the structure of en ligands affects the oxidation of phenol **1**. Only en and *C*-alkyl ens having none of *N*-alkyl substituent formed active Cu(II) complexes in this oxidation. Using such complexes, the initial stage of the oxidation was kinetically examined.

## Results and Discussion

Phenol **1** was oxidized in methanol with hydrogen peroxide under a set of standard conditions (see Experimental section) except for minor deviations specified, if any. The oxidation of phenol **1** with hydrogen peroxide, as well as that with molecular oxygen,[1,2)] afforded only 3,3′,5,5′-tetra-*t*-butyl-2,2′-dihydroxybiphenyl (**2**) and its oxidation product, i.e., 2,4,7,9-tetra-*t*-butyloxepino[2,3-*b*]benzofuran (**3**).

**[I] Phenol Oxidation with Hydrogen Peroxide Catalyzed by Cu(II)(en)$_2$ Complexes.** The results of the oxidation of phenol **1** with hydrogen peroxide in the presence of **stable** Cu(II)(en)$_2$ complexes are shown in Table 1, together with their stability constants.[4)] In Tables 1 and 2, the relative oxidation activities of Cu(II)(en)$_2$ complexes are expressed as the percent yields of biphenol **2** for the first 10 min of oxidation, because the amount of benzofuran **3** produced during this period was negligible.

In the presence of the stable complexes, yields of biphenol **2** exceeded over 20% without exception, proving that hydrogen peroxide acted as a two-electron oxidant. Since oxidation was carried out under the conditions at hydrogen peroxide/phenol **1** (molar ratio) of 0.19, yields of **2** could not exceed over 19% if we would assume that one molecule of hydrogen peroxide oxidized only one molecule of phenol **1**. In

Table 1. Oxidation of Phenol **1** with Hydrogen Peroxide in the Presence of Cu(II)(en)$_2$ Complexes

| Diamine R : $CH_3$ | Product[a,b)] **2**/% | Stability const. $\log K_T$[4)] |
|---|---|---|
| *dl*-$H_2N$-CHR-CHR-$NH_2$ | 22.5 | 21.21 |
| $H_2N$-$CH_2$-$CH_2$-$NH_2$ | 21.1 | 20.13 |
| *meso*-$H_2N$-CHR-CHR-$NH_2$ | 21.1 | 20.06 |
| $H_2N$-CHR-$CH_2$-$NH_2$ | 21.8 | 20.06 |
| $H_2N$-$CR_2$-$CH_2$-$NH_2$ | 20.5 | 19.58 |

a) Standard conditions. b) Benzofuran **3**: trace.

Table 2. Oxidation of Phenol **1** with Hydrogen Peroxide in the Presence of Cu(II)(*N*,*N*′-$R_2$en)$_2$ Complexes

| (RNH-$CH_2$)$_2$ R | $CH_3OH$ Product[a-c)] **2**/% | $CH_3OH$-$H_2O$ (9 : 1) Product[b,d)] **2**/% |
|---|---|---|
| $CH_3$ | 2.9 | 9.5 |
| $C_2H_5$ | 2.4 | 7.7 |
| *n*-$C_3H_7$ | 1.9 | 8.0 |
| *i*-$C_3H_7$ | 1.8 | 8.5 |
| *n*-$C_4H_9$ | 2.4 | 10.0 |
| *i*-$C_4H_9$ | 3.6 | 11.9 |
| *s*-$C_4H_9$ | 3.9 | 13.8 |
| *t*-$C_4H_9$ | 2.6 | 2.9[e)] |

a) Standard conditions. b) Benzofuran **3**: trace. c) The yields of biphenol **2** increased little after the first 1 min of the oxidation. d) Standard conditions except for solvent. e) Absorption spectra showed the decomposition of the Cu(II)-complex by $H_2O$.

the absence of either copper(II) or en, phenol **1** was hardly oxidized to biphenol **2** under the same conditions (0.5—2.2%).

The copper(II) complexes of a series of *N,N′*-$R_2$ens were examined similarly (Table 2). All of the complexes were less active in the oxidation reactions. In the oxidation with molecular oxygen,[1] the less stable and tetrahedral copper(II) complexes which had alkyl branching on the carbon attached to nitrogen were the most active. The Cu(II) complexes could undergo facile coordination of phenolate anion and facile electron transfer from phenolate anion to Cu(II). Hydrogen peroxide of the high coordinating ability to Cu(II) complexes would expel diamine ligands or/and phenolate anion coordinated to Cu(II). Actually, addition of hydrogen peroxide to the concentrated methanolic solution of unstable Cu(II)(*N,N′*-(*t*-butyl)$_2$en)$_2$ complex resulted in the formation of a dark brown precipitate. The precipitate was proved to be peroxo-copper complexes with the luminol test (see Experimental section).

Too quick and exclusive replacement of diamine ligands or/and phenolate anion by hydrogen peroxide molecules in the less stable diamine complexes would block the oxidation of phenol **1**. This was confirmed by the reactions using 1 : 9 mixture of water and methanol as a solvent (Table 2), where yields of biphenol **2** increased by a factor of 3 to 5.[5] In the mixture, the hydrogen bond[6] between water and hydrogen peroxide would reduce concentration of hydrogen peroxide which is able to coordinate to copper complexes. Consequently, the succesive coordination of hydrogen peroxide to copper complexes would be retarded and the oxidation of phenol **1** would be facilitated. Furthermore, increase of concentration of phenol **1** in solution heightened yields of biphenol **2**, owing to impediment to the succesive coordination of hydrogen peroxide (Fig. 1). Those results indicate that the diamine complexes of copper(II) bearing both hydrogen peroxide and phenol **1** are indispensable for the oxidation of **1**.

**[II] The Mechanism of Oxidation of Phenol 1.** **(1) Effect of en/Cu(II) Ratio.** In methanolic solutions of copper(II) and ens, only 1 : 1 and 1 : 2 complexes were detected spectrophotometrically.[1] In the presence of copper(II) chloride and en, yields of biphenol **2** were affected by ratios of en to Cu(II) (Fig. 2). The maximum yield of biphenol **2** was achieved at en/Cu(II) ratio of 2/1. In the reaction at the higher ratio than 2/1, decrease of yields of **2** as well as appearance of an induction period was observed. On the other hand, in the mixtures of *N,N′*-$R_2$ens and Cu(II) which formed the less stable complexes, the maximum yield of **2** was achieved at the higher ratio than 2/1, but with no induction period. These observations suggest that Cu(II)(en)$_2$ complexes are the active catalysts. Excess en molecules surrounding the stable Cu(II)(en)$_2$ complex could impede the ligand exchange by hydrogen peroxide and/or phenol **1**, while, in the cases of the less stable complexes, presence of excess diamines surrounding Cu(II) may be advantageous for reproducing the active catalytic species.

**(2) Spectral Studies.** By addition of phenol **1**, a solution of less stable Cu(II)(*N,N′*-$R_2$en)$_2$ complexes exhibited a broad absorption at the region of 350—600 nm, whereas the spectrum of the stable Cu(II)(en)$_2$ complex was slightly changed by addition of **1** at 370—440 nm. Since in the latter case the absorbance at 410 nm increased with time, gradual coordination of phenol **1** to the stable Cu(II)(en)$_2$ complexes was substantiated. On the other hand, addition of hydrogen peroxide to a solution of the stable Cu(II)(en)$_2$ complexes exhibited absorption maximum at either 340 or

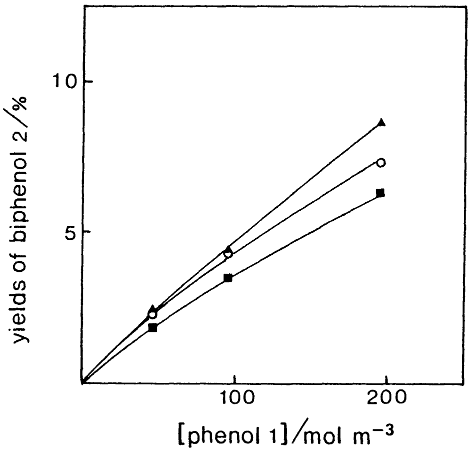


Fig. 1. Effect of phenol **1** concentration in oxidation of **1** in the presence of Cu(II)(*N,N′*-$R_2$en)$_2$ complexes. R: $C_2H_5$ ▲; *n*-$C_3H_7$ ■; *n*-$C_4H_9$ ○.

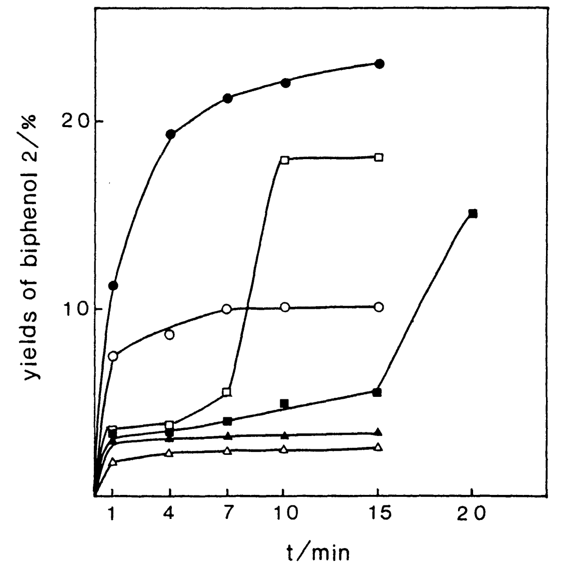


Fig. 2. Effect of en/Cu(II) ratio in oxidation of phenol **1**. en/Cu(II): 0.5 △; 1 ▲; 1.5 ○; 2 ●; 3 □; 4 ■; $2.43\times10^{-3}$ mol of phenol **1**, $6.06\times10^{-6}$ mol of $CuCl_2$ and $4.56\times10^{-4}$ mol of $H_2O_2$ in 50 mL of methanol.

360—400 nm, which was depending on added amount of hydrogen peroxide. The absorption at 340 nm appeared at the relatively lower molar ratio of hydrogen peroxide in solution. However, examination by rapid-scanning spectrophotometry even at the higher molar ratio of hydrogen peroxide showed absorption ($\lambda_{max}$ 340 nm) at the initial stage after mixing Cu(II)(en)$_2$ complex with hydrogen peroxide. Keeping the concentration of Cu(II)(en)$_2$ complex in solution at a constant, we added different amount of hydrogen peroxide and followed change of the absorbance at 340 nm by a stopped flow method. Initial increasing rate of the absorption at 340 nm was the first order with respect to initial concentrations of hydrogen peroxide (Fig. 3). Therefore, under our conditions the absorption at 340 nm was attributed to ternary Cu(II)-en-$H_2O_2$ (1 : 2 : 1) complexes, but not to hydroxo- or alkoxo-bridged copper(II) binuclear complexes which showed the characteristic absorption at 350—400 nm.[7] While, the absorption at 360—400 nm observed in the presence of the higher molar ratio of hydrogen peroxide would be formed via a complex showing the absorption at 340 nm. The similar broad absorption at around 360—400 nm was exhibited by addition of hydrogen peroxide to a solution of less stable Cu(II)-(*N*,*N*′-R$_2$en)$_2$ complexes. The absorption probably arise from Cu(II)-ens-$H_2O_2$ (1 : 1 : 2) complexes.

Then, applying rapid-scanning spectrophotometry, we examined appearence of an intermediate after mixing Cu(II)(en)$_2$ complex, phenol **1**, and hydrogen peroxide. By the addition of hydrogen peroxide, a solution of Cu(II)(en)$_2$-phenol **1** exhibited an absorption spectrum having maximum at 370 nm. The same spectrum appeared as well when a mixture of $H_2O_2$-phenol **1** was added to a solution of Cu(II)(en)$_2$ complex.[8] Thus, the absorption maximum at 370 nm could be attributed to a quadruple Cu(II)-en-$H_2O_2$-phenol **1** (1 : 1 : 1 : 1) complex. In order to examine the formation and decay processes of the quadruple complex, the absorbance at 370 nm was traced (Fig. 4 ). As shown in Fig. 4, absorbance at 370 nm reached rapidly at a maximum, but falled then, and began to rise again gradually. This phenomenon indicates that besides of the quadruple Cu(II)-en-$H_2O_2$-phenol **1** complex the other species which has absorption at around 370 nm was accumulating in the solution with time. Actually, Cu(II)-en-biphenol **2** (reaction product)-$H_2O_2$ complex had absorption at around 370 nm. Thus, although exact trace of the quadruple Cu(II)-en-$H_2O_2$-phenol **1** complex was not carried out, it might be concluded that the quadruple complex was formed and reasonably stable.

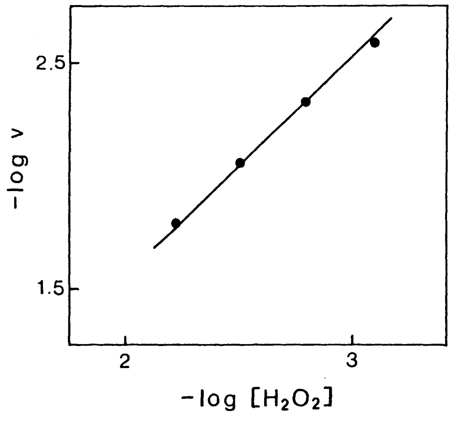


Fig. 3. Dependence of initial rate of the formation of the absorption at 340 nm on hydrogen peroxide concentration. [$CuCl_2$]=0.97 mol m$^{-3}$, [en]=1.94 mol m$^{-3}$, [$H_2O_2$]=0.76—6.06 mol m$^{-3}$ in methanol, at 25 °C.

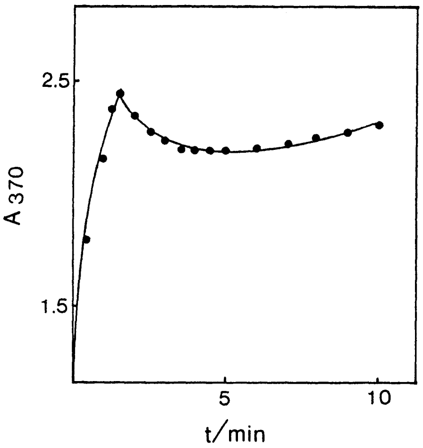


Fig. 4. Absorbance behavior at 370 nm indicating the formation of quadruple complex. 4.85×10$^{-5}$ mol of $CuCl_2$, 9.7×10$^{-5}$ mol of en, 2.43×10$^{-3}$ mol of phenol **1** and 1.21×10$^{-3}$ mol of $H_2O_2$ in 50 mL of methanol.

Table 3. Oxidation of Phenol **1** with Hydrogen Peroxide

| [$H_2O_2$]$_{initial}$/mol m$^{-3}$ | Biphenol **2**/%$^{a,b)}$ |
|---|---|
| 0.76 | 93 |
| 1.52 | 89 |
| 3.03 | 83 |
| 6.06 | 78 |

a) [$CuCl_2$]=0.121 mol m$^{-3}$, [en]=0.242 mol m$^{-3}$ and [phenol **1**]=48.5 mol m$^{-3}$. The oxidation was carried out in methanol at 25 °C for 7 min. b) Yields of biphenol **2** were estimated on the basis of hydrogen peroxide added, taking account of the experimental results that hydrogen peroxide acted as a two-electron oxidant (see Text).

On the other hand, addition of hydrogen peroxide to a solution containing unstable Cu(II)(*N*,*N*′-R$_2$en)$_2$ complexes and phenol **1** exhibited similarly the absorption at about 370 nm, but it disappeared within about 0.1 s. The instability of Cu(II)-*N*,*N*′-R$_2$en-$H_2O_2$-phenol **1** complexes might be responsible for less activity in the oxidation of **1**.

**(3) Kinetic Studies.** The kinetics were studied in the presence of the stable Cu(II)(en)$_2$ complex. The initial rate ($v$) of the reaction ([biphenol **2**]$_{initial}$/min$^{-1}$)

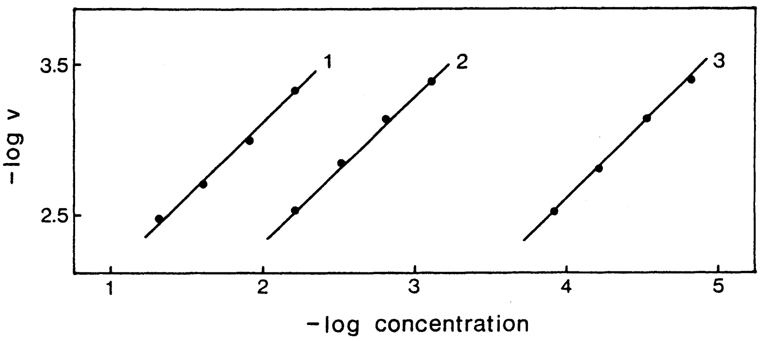


Fig. 5. Kinetic plots.
1: [phenol **1**]=6.06—48.5 mol m$^{-3}$, 2: [$\mathrm{H_2O_2}$]=0.76—6.06 mol m$^{-3}$, 3: [Cu(II)-en]=$1.52\times10^{-2}$—$1.21\times10^{-1}$ mol m$^{-3}$. Other conditions were as follows: [phenol **1**]=48.5 mol m$^{-3}$, [$\mathrm{H_2O_2}$]=6.06 mol m$^{-3}$ and [Cu(II)-en]=0.121 mol m$^{-3}$ in methanol at 25 °C.

was determined. The initial rate increased linearly with concentration of hydrogen peroxide. From plots of log $v$ against log [$\mathrm{H_2O_2}$], the dependence on [$\mathrm{H_2O_2}$] is of the first order. The dependence on [phenol **1**] and [$\mathrm{Cu(II)(en)_2}$ complex] are also of the first order, respectively (Fig. 5). From those results, the following empirical rate expression was deduced.

$$v = k[\mathrm{H_2O_2}]^1[\text{phenol }\mathbf{1}]^1[\mathrm{Cu(II)(en)_2}\text{ complex}]^1$$

Consequently, the kinetic results as well as spectral data indicate that under our conditions the oxidation of phenol **1** was not catalyzed by copper(II)-binuclear complexes.

The Cu(II)-en complex catalyzes decomposition of hydrogen peroxide.[9] Therefore, in the kinetic studies of the oxidation, we controlled conditions so that the oxidation of **1** can exclusively proceed (see Experimental section).

**(4) Control Experiments.** To determine whether free hydroxyl or hydroperoxyl radical which might be generated in our reactions could oxidize phenol **1** to biphenol **2**, first we attempted oxidation of **1** with free hydroxyl radical produced by photodecomposition of hydrogen peroxide.[10] After irradiation of the methanolic solution containing hydrogen peroxide and phenol **1** for 2 h, about 50% of hydrogen peroxide was decomposed. However, phenol **1** was wholly recovered and no oxidation product was detected by high performance liquid chromatography and by thin layer chromatography. Prior to the oxidation of **1**, hydroxyl radical would be quenched by methanol.[11]

Table 4. Decomposition of Hydrogen Peroxide Catalyzed by $\mathrm{Cu(II)(en)_2}$ Complexes. Control Experiments

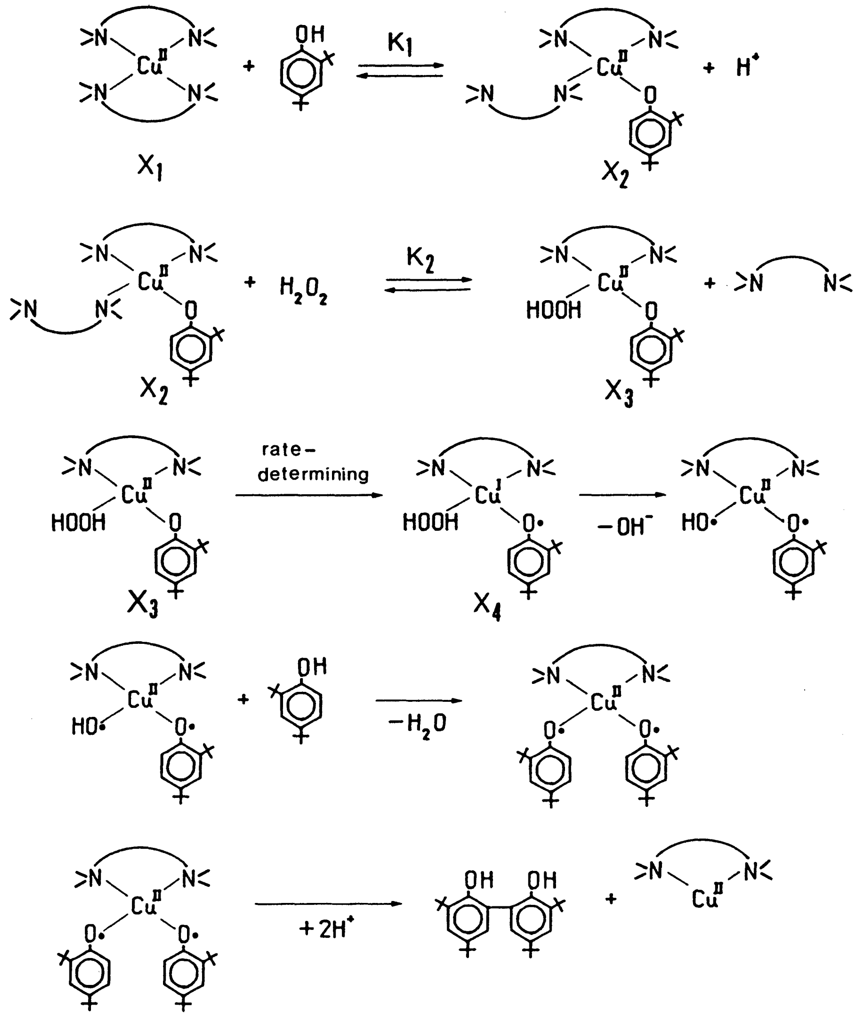
| Diamine | Decomposition[a)] $\mathrm{H_2O_2}$/% | |
|---|---|---|
| less stable Cu(II)-complex | | |
| $(\mathrm{CH_3NH\text{-}CH_2})_2$ | 84 | [7.7][b)] |
| $(n\text{-}\mathrm{C_3H_7NH\text{-}CH_2})_2$ | 80 | [5.0] |
| $(n\text{-}\mathrm{C_4H_9NH\text{-}CH_2})_2$ | 75 | [6.4] |
| stable Cu(II)-complex | | |
| $(dl\text{-}\mathrm{H_2N\text{-}CHCH_3})_2$ | 33 | [60] |
| $(\mathrm{H_2N\text{-}CH_2})_2$ | 44 | [56] |
| $(meso\text{-}\mathrm{H_2N\text{-}CHCH_3})_2$ | 38 | [56] |

a) The decomposition of hydrogen peroxide was examined in the absence of **1**. The conditions were the same as those used in b), except for **1**. b) The yields of biphenol **2** in the oxidation of **1** under standard conditions.

Secondly, the decomposition of hydrogen peroxide catalyzed by $\mathrm{Cu(II)(en)_2}$ complexes was studied in the absence of phenol **1**. The results are shown in Table 4, together with yields of biphenol **2** obtained in the studies of the oxidation of **1**. The less stable Cu(II)-($N,N'$-$\mathrm{R_2}$en)$_2$ complexes decomposed hydrogen peroxide efficiently, but were less active in the oxidation of **1**. In the stable $\mathrm{Cu(II)(en)_2}$ complexes, yields of **2** exceeded considerably those expected to be produced by the decomposition products of hydrogen peroxide. While hydrogen peroxide in the presence of various metal ions (including copper(II)) or their complexes has been reported to oxidize 4-substituted phenols to hydroperoxidation products at the 4-position,[12] none of hydroperoxidation products was detected in the present studies.

In conclusion, under our conditions, phenol **1** was not oxidized with decomposition products of hydrogen peroxide, e.g., free hydroxyl or hydroperoxyl radical. Oxidation of **1** was achieved within the coordination sphere of the quadruple Cu(II)-en-$\mathrm{H_2O_2}$-phenol **1** complex.

**(5) The Mechanism of Oxidation of Phenol 1.** The oxidation of phenol **1** was carried out within the coordination sphere of mononuclear Cu(II)-en-$\mathrm{H_2O_2}$-phenol **1** complex and two molecules of **1** for each molecule of hydrogen peroxide was oxidized to biphenol **2**. The reaction sequence consisting with these results and kinetics as well as the spectral data is given in Scheme 1. Spectroscopic studies demonstrated similarly that under our conditions the quad-



Scheme 1.

ruple complex $\mathbf{X_3}$ was produced via the coordination of **1** to Cu(II)-diamine complex $\mathbf{X_1}$. The formation of the quadruple complex $\mathbf{X_3}$ depended on the molar ratio of hydrogen peroxide to phenol **1**. A large excess of **1** would hinder coordination of hydrogen peroxide to Cu(II)-diamine-phenol **1** complex $\mathbf{X_2}$ and bring about an induction period into the whole sequence of reactions. On the contrary, for excess of hydrogen peroxide, yields of biphenol **2** were lowered with increasing concentration of hydrogen peroxide. Cu(II)-en-$H_2O_2$ (1 : 1 : 2) complex[9c] which is responsible for the decomposition of hydrogen peroxide would be formed in competition with the quadruple complex $\mathbf{X_3}$.

After forming the quadruple complex $\mathbf{X_3}$, phenolate anion would transfer an electron to hydrogen peroxide through copper.[13] The redox potential of Cu(II) complexes having two nitrogen donors is optimum for reduction of Cu(II).[9c] While, hydrogen peroxide is reduced with the generation of hydroxyl radical. The radical was not quenched by methanol because of the coordination with Cu(II) complex and oxidized another molecule of **1** by the participation of copper(II). The whole process in which one molecule of hydrogen peroxide oxidized two molecules of **1** is consistent with the experimental results.

In the reaction, the reduction process of hydrogen peroxide of complex $\mathbf{X_4}$ might be rate-determining step, but this could be unlikely judging from redox potentials of both copper(II) complexes[14] and hydrogen peroxide. Then we assumed that complexes $\mathbf{X_1}$, $\mathbf{X_2}$, and $\mathbf{X_3}$ were in fast equilibrium and the process in which phenolate anion of the quadruple complex $\mathbf{X_3}$ transferred an electron to Cu(II) was the rate-determining step. By the assumptions a rate expression is deduced as follows,

$$v = k'[\text{complex } \mathbf{X_3}] \tag{1}$$

$$\begin{aligned} K_1 &= [\text{complex } \mathbf{X_2}][\text{H}^+]/[\text{complex } \mathbf{X_1}][\text{phenol } \mathbf{1}] \\ K_2 &= [\text{complex } \mathbf{X_3}][\text{en}]/[\text{complex } \mathbf{X_2}][\text{H}_2\text{O}_2] \\ K_1K_2 &= [\text{complex } \mathbf{X_3}][\text{H}^+][\text{en}]/ \\ &\quad [\text{complex } \mathbf{X_1}][\text{phenol } \mathbf{1}][\text{H}_2\text{O}_2] \end{aligned} \tag{2}$$

from Eqs. 1 and 2

$$v = k'K_1K_2[\text{H}_2\text{O}_2][\text{phenol } \mathbf{1}][\text{complex } \mathbf{X_1}]/[\text{H}^+][\text{en}] \tag{3}$$

Since all complexes in Scheme 1 were catalytic species, they would be in low concentrations and in steady state. Then, [$H^+$] and [en] which were mainly subjected to the respective concentrations of complexes $\mathbf{X}_1$ and $\mathbf{X}_2$ would be constant.

$$v = k''[H_2O_2][\text{phenol } \mathbf{1}][\text{complex } \mathbf{X}_1] \qquad (4)$$

The rate expression (Eq. 4) consists with the foregoing empirical rate expression.

## Experimental

GLC analyses were carried out on a JEOL Model JGC-20K equipped with 3% Apiezone L grease on Celite 545 NAW column. HPLC analyses were performed using methanol as a eluent on a Shimadzu Model LC-3A liquid chromatograph with Zorbax ODS column. Ultraviolet and visible spectra were taken using a Shimadzu UV-300 spectrophotometer. Stopped flow method and rapid scan technique were performed on an Otuka Denshi RA-401 stopped flow system equipped with RA-415 rapid scan system, gas driving device and RA-451 data processor. Temperature of a thermostat used in the kinetic measurement was controlled (±0.15 °C) by using a Komatsu-Yamato Coolnics CTR-220. Spectrophotometric determination of hydrogen peroxide was performed on a Shimadzu Model Double-Beam Spectrophotometer UV-140-02. The photoreactions were carried out on a Eichosha PIL-120, a low-pressure mercury lamp with quartz housing: $\Phi = 7.74\times10^{-5}$ (using a potassium tris(oxalato)ferrate(III) actinometer) in the decomposition reaction of hydrogen peroxide under the conditions used.

**Materials.** Anhydrous copper(II) chloride was prepared by heating the dihydrate in an oven at 100 °C for 20 h. Hydrogen peroxide (30%) was obtained from Santoku Kagaku Kogyo Co. and concentration was determined by iodometry before use. *dl*- And *meso*-2,3-butanediamine,[15] *N,N'*-dipropyl- and *N,N'*-dibutylethylenediamines (*N,N'*-(propyl)$_2$en and *N,N'*-(butyl)$_2$en)[16] and 3,3',5,5'-tetra-*t*-butyl-2,2'-dihydroxybiphenyl (**2**)[17] were prepared by procedures given in literatures.

**Standard Conditions. Oxidation of 2,4-Di-*t*-butylphenol (1).** Phenol **1** ($2.43\times10^{-3}$ mol) and the en ($1.21\times10^{-5}$ mol) were dissolved in methanol, and the volume was made up to 50 mL by adding methanol. Under a nitrogen atmosphere, anhydrous copper(II) chloride ($6.06\times10^{-6}$ mol) and hydrogen peroxide ($4.56\times10^{-4}$ mol) were added successively to the mixture and the oxidation was conducted at 25 °C for 10 min. The products were only biphenol **2** and its oxidation product, 2,4,7,9-tetra-*t*-butyloxepino[2,3-*b*]benzofuran (**3**).[1] The yields of product **2** were determined by GLC.

**The Luminol Test.** Addition of hydrogen peroxide ($4.85\times10^{-3}$ mol) to the methanolic solution (100 mL) containing anhydrous copper(II) chloride ($9.7\times10^{-5}$ mol) and *N,N'*-(*t*-butyl)$_2$en ($1.94\times10^{-4}$ mol) resulted in a precipitate, which was separated by centrifugation. The precipitate was thoroughly washed with methanol to remove free hydrogen peroxide and suspended in methanol. The suspension of the precipitate produced luminescence by addition of the luminol reagent.[18]

**Effect of en/Cu(II) Ratio.** In the presence of Cu(II)-en mixtures of various ratios, phenol **1** was oxidized under standard conditions.

**Spectral Studies. Ultraviolet and Visible Absorption Spectra:** In various combinations of phenol **1** ($4.85\times10^{-4}$ mol), biphenol **2** ($2.43\times10^{-4}$ mol), anhydrous copper(II) chloride ($9.7\times10^{-6}$ mol), the en ($1.94\times10^{-5}$ mol), and hydrogen peroxide ($4.85\times10^{-4}$—$7.6\times10^{-6}$ mol), the absorption spectra of a methanolic solution (10 mL) of the mixture were taken using a spectrophotometer.

**Rapid Scanning Spectra:** Conditions were the same as those used in ultraviolet and visible absorption spectra, and the absorption spectra at 295—485 nm were obtained using a stopped flow system at 25 °C.

**Formation Kinetics of the Absorption at 340 nm by Stopped-Flow Method:** Concentrations of anhydrous copper(II) chloride (0.97 mol m$^{-3}$) and en (1.94 mol m$^{-3}$) were kept constant and concentration of hydrogen peroxide was varied from 0.76 mol m$^{-3}$ to 6.06 mol m$^{-3}$. The change of the absorbance at 340 nm was followed by a stopped flow system at 25 °C. In every case, the result was accumulated about 10 times.

**Absorbance Behavior at 370 nm:** Phenol **1** ($2.43\times10^{-3}$ mol) and en ($9.7\times10^{-5}$ mol) were dissolved in 50 mL of methanol. Under a nitrogen atmosphere, anhydrous copper(II) chloride ($4.85\times10^{-5}$ mol) and hydrogen peroxide ($1.21\times10^{-3}$ mol) were added successively to the mixture at 25 °C. The sample was taken out of the reaction solution and the absorbance at 370 nm was measured on a spectrophotometer.

**Kinetic Measurements.** Bis(ethylenediamine)copper(II) complexes catalyzed both the oxidation of phenol **1** with hydrogen peroxide and the decomposition of hydrogen peroxide. For the purpose of carrying out the oxidation of **1** exclusively (Table 3), concentration of hydrogen peroxide was lowered from that under standard conditions by a factor of 2/3. Other conditions were the same as standard. The initial rate of the reaction ([product **2**]$_{\text{initial}}$/min$^{-1}$) was determined by GLC.

**Control Experiments. Photoreaction:** Phenol **1** ($1.21\times10^{-2}$ mol) was dissolved in methanol, and the volume was made up to 250 mL by adding methanol. The solution was then placed in an inside-irradiation-type reaction flask equipped with a low-pressure mercury lamp. Under a nitrogen atmosphere, hydrogen peroxide ($2.28\times10^{-3}$ mol) was added to the solution and the irradiation was conducted at 30 °C for 2 h. The reaction mixture was analyzed by TLC (HPTLC-Fertigplatten Kieselgel 60 $F_{254}$ Merck/benzene). Phenol **1** and biphenol **2** were determined by HPLC. The rate of decomposition of hydrogen peroxide was determined by iodometry.

**Decomposition of Hydrogen Peroxide in the Absence of Phenol 1:** Conditions were the same as those used in the oxidation, except for absence of **1**. The samples were taken out of the reaction solution and mixed with titanium(IV) chloride in 6 mol dm$^{-3}$ HCl. The absorbance of titanium-$H_2O_2$ complex was measured at 450 nm on a spectrophotometer.[19]

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