Oxidation of 2,4-Di-t-butylphenol with t-Butyl Hydroperoxide Catalysed by Copper(II)–Ethylenediamine Complexes

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In the oxidation of 2,4-di-t-butylphenol (**1**) with $\mathrm{Bu^tO_2H}$ in alcohols in the presence of $\mathrm{Cu^{II}}$–ethylenediamine (including *N,N'*-dialkylethylenediamines) (abbreviated to EDA) (1:2) complexes, the solvents are partly oxidized to the corresponding aldehydes or ketones in a competitive manner with phenol (**1**), while $\mathrm{Bu^tO_2H}$ is quantitatively reduced to $\mathrm{Bu^tOH}$. Suitable solvents, *e.g.*, chlorobenzene, used in the oxidation of (**1**) are found to be inert. Activity of the copper(II) complexes in the oxidation of phenol (**1**) is strongly dependent on the structure of the EDA ligands, as in the case of the oxidation of the phenol (**1**) by O_2 or H_2O_2. In the $\mathrm{Bu^tO_2H}$ oxidation of (**1**), the greatest degree of efficiency is brought about by the combination of copper(II) and *N,N'*-di-t-butyl-EDA. The initial stage of the oxidation of the phenol (**1**) has been kinetically investigated. The reaction velocity can be summarized by the equation:

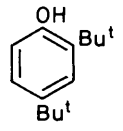
$$v = k[\mathrm{Bu^tO_2H}][\text{phenol } (\mathbf{1})][\mathrm{Cu^{II}}\text{–EDA}]$$

Taking into account the results of the product analyses and kinetics, a mechanism for the oxidation of the phenol (**1**) with $\mathrm{Bu^tO_2H}$ catalysed by $\mathrm{Cu^{II}}$–EDA complexes is proposed.

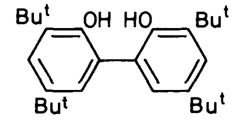
In the previous papers,[1–3] it was shown that in the oxidation of phenols by molecular oxygen or hydrogen peroxide in the presence of $\mathrm{Cu^{II}}$–ethylenediamine (including *N,N'*-dialkylethylenediamines) complexes, the efficiency is controlled by the stability of $\mathrm{Cu^{II}}$–EDA complexes, and by the co-ordinating ability and the oxidizing power of oxidants. This indicates that the oxidation is achieved within the co-ordination sphere of copper(II) complexes. This paper deals with the oxidation of 2,4-di-t-butylphenol (**1**) by t-butyl hydroperoxide for the series of $\mathrm{Cu^{II}}$–EDA-catalysed oxidations. Oxidation by molecular oxygen or hydrogen peroxide, differs from this in that it uses t-butyl hydroperoxide-oxidized alcohols as solvents rather than the unoxidised alcohols of the corresponding aldehydes or ketones. We have investigated a series of copper(II) complexes ligated with EDA to determine how the structure of EDA ligands affects the oxidation of phenol (**1**). The most active complex was formed between copper(II) and *N,N'*-di-t-butyl-EDA. The initial stage of the oxidation of (**1**) in a suitable solvent was kinetically examined in the presence of the most active copper(II) complexes.

Results and Discussion

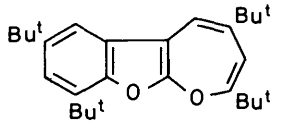
Phenol (**1**) was oxidized with t-butyl hydroperoxide under a set of standard conditions (see the Experimental section) except for minor specific modifications. The oxidation of phenol (**1**) with t-butyl hydroperoxide afforded only 3,3',5,5'-tetra-t-butyl-2,2'-dihydroxybiphenyl (**2**) and its oxidation product, *i.e.*, 2,4,7,9-tetra-t-butyloxepino[2,3-*b*]benzofuran (**3**). These products are the same as those formed in the oxidation by molecular oxygen or hydrogen peroxide.[1,3] The amount of benzofuran (**3**) formed was negligible under the present oxidations.



(**1**)



(**2**)



(**3**)

Phenol Oxidation with t-Butyl Hydroperoxide Catalysed by $\mathrm{Cu^{II}}$–N,N'-*Di-t-butyl*-EDA (1:2) *Complex.*—(*a*) *In alcohols.* In the presence of $CuCl_2$ and/or *N,N'*-di-t-butyl-EDA, the phenol (**1**) was oxidized in methanol with t-butyl hydroperoxide to give the biphenyldiol (**2**) (Table 1). The present work considers whether copper(II) chloride itself with methanol as the solvent catalyses oxidations of the phenol (**1**). Methanol was oxidized to formaldehyde, but not to formic acid.† The yields obtained for (**2**) were much less than those for formaldehyde (runs 3 and 4).

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† After the addition of small amounts of formaldehyde in a reacting solution, phenol (**1**) in the presence of *N,N'*-di-t-butyl-EDA–$\mathrm{Cu^{II}}$ complex was oxidized by t-butyl hydroperoxide in 2-methylpropan-2-ol to give (**2**), but formic acid was not produced. However, the yield of (**2**) and the amount of consumed t-butyl hydroperoxide decreased with increasing amount of formaldehyde added. Presumably, formaldehyde destroys the $\mathrm{Cu^{II}}$–diamine complexes. This is supported by the fact that the addition of formaldehyde to a solution of *N,N'*-di-t-butyl-EDA–$\mathrm{Cu^{II}}$ complex resulted in the formation of a pale-blue precipitate.

Table 1. Oxidation of phenol (**1**) with t-butyl hydroperoxide in methanol.[a]

Run	Catalyst[b]	Bu^tO_2H consumed/ 10^{-3} mol	Oxidation products/10^{-3} mol	
			(**2**)[c]	HCHO[d]
1	—	0	0.005	0
2	Diamine	0.01	0.005	0
3	$CuCl_2$	0.21	0.044	0.17
4	$CuCl_2$ + Diamine	1.17	0.22	0.93

[a] The phenol (**1**) (2.43×10^{-3} mol) in 50 cm^3 of solution was oxidized with Bu^tO_2H (1.22×10^{-3} mol) for 20 min at 25 °C. [b] $CuCl_2$ (2.43×10^{-5} mol) and/or diamine (4.85×10^{-5} mol). Diamine: *N,N′*-di-t-butyl-EDA. [c] Benzofuran, trace. [d] Formic acid was not formed.

Table 2. Oxidation of phenol (**1**) with t-butyl hydroperoxide in the presence of Cu^{II}-*N,N′*-di-t-butyl-EDA complex.[a]

Solvent Alcohol	Bu^tO_2H consumed/ 10^{-3} mol	Bu^tOH/ 10^{-3} mol	Oxidation Products/ 10^{-3} mol		
			(**2**)[b]	Aldehyde	Ketone
MeOH	1.17	1.20	0.22	0.93	—
EtOH	1.17	1.15	0.16	0.93	—
PrOH	1.19	1.16	0.17	0.91	—
Pr^iOH	1.19	1.13	0.14	—	0.86
BuOH	1.19	1.08	0.17	0.86	—
Bu^tOH	1.18	—	0.61	—	—
Pe^tOH[c]	1.11	1.11	0.40	—	—

[a] The conditions were the same as those indicated in Table 1, except for solvents. [b] Benzofuran, trace. [c] $Pe^t = C_2H_5C(CH_3)_2$.

Table 3. Oxidation of the phenol (**1**) with t-butyl hydroperoxide in the presence of Cu^{II}–*N,N′*-di-t-butyl-EDA complex in aprotic solvents.

Solvent	Oxidation[a] (%)		Decomposition[b] (%)
	Bu^tO_2H (consumed)	(**2**)	Bu^tO_2H
o-$C_6H_4Cl_2$	89.0	78.4	11.8
C_6H_5Cl	89.4	74.4	8.9
C_6H_6	87.6	73.6	7.4
$CHCl_3$	59.0	50.6	0
C_5H_5N	11.3	12.0	5.4
Me_3CN	7.0	7.2	1.0

[a] The phenol (**1**) (2.43×10^{-3} mol) and *N,N′*-di-t-butyl-EDA (6.06×10^{-6} mol) in 50 cm^3 of solution. $CuCl_2$ (3.03×10^{-6} mol) and Bu^tO_2H (6.06×10^{-4} mol) were added to the solution and the oxidation was carried out at 25 °C for 4 min. Yields of (**2**) were estimated on the basis of Bu^tO_2H added, taking account of the experimental results that Bu^tO_2H is a two-electron oxidant. [b] Decomposition of Bu^tO_2H was performed in the absence of (**1**), under the same conditions.

Table 4. Oxidation of phenol (**1**) with t-butyl hydroperoxide in the presence of Cu^{II}–EDA complexes in benzene.[a]

$RNH-[CH_2]_2-NHR$ R	(**2**)[b] (%)
H	0.6
Me	0.8
Et	3.7
Pr	4.2
Pr^i	29.0
Bu	3.6
Bu^i	5.2
Bu^s	28.7
Bu^t	42.0

[a] Standard conditions. [b] Benzofuran, trace.

To examine the effect of alcohols on the oxidation of phenol (**1**), methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, 2-methylpropan-2-ol, and 2-methylbutan-2-ol were studied (Table 2). Primary and secondary alcohols were oxidized effectively under the present conditions to the corresponding aldehydes or ketones, but tertiary alcohols resisted oxidation. As the results show, yields of (**2**) after oxidation in primary or secondary alcohols were reduced in comparison with those obtained in tertiary alcohols by a factor of 0.5–0.2. The amounts (mol) of consumed t-butyl hydroperoxide together with the amount of 2-methylpropan-2-ol produced agreed with the sum of the yields (mol) of oxidation products of phenol (**1**) and alcohols. This implies that t-butyl hydroperoxide acted as a two-electron oxidant, to give a quantitative amount of 2-methylpropan-2-ol.

(*b*) *In aprotic solvents.* Oxidation of the phenol (**1**) was carried out under similar conditions in aprotic solvents which are resistant to oxidation by t-butyl hydroperoxide, (*i.e.*, *o*-dichlorobenzene, chlorobenzene, benzene, chloroform, pyridine, and acetonitrile). The yields of (**2**) and the amount of t-butyl hydroperoxide consumed are shown in Table 3. In Table 3, the percentage yields of (**2**) were estimated on the basis of the amount of t-butyl hydroperoxide added. The yields of (**2**) were in excess of 100% based on the assumption that one molecule of the hydroperoxide oxidized only one molecule of phenol (**1**). The results proved that t-butyl hydroperoxide and H_2O_2 both acted as two-electron oxidants.[3] In these solvents, the yields of (**2**) corresponded approximately to the amounts of consumed t-butyl hydroperoxide, and oxidation products of solvents were not observed. A series of aromatic solvents which do not have co-ordinating ability to copper(II) were more effective, while pyridine and acetonitrile were less effective, because of their strong ligation to copper(II).

The copper(II) salts themselves were used to catalyse the decomposition of t-butyl hydroperoxide,[4] and a fairly large number of oxidations of phenols with t-butyl hydroperoxide in the presence of metal salts [including copper(II) salts] have been reported.[4d,4f,5] The oxidizing species were ascribable to free t-butylperoxyl and/or t-butoxyl radicals which are generated in the reaction of metal ions with the hydroperoxide. However, under our conditions, including Cu^{II}–EDA complexes, decomposition of t-butyl hydroperoxide in the absence of (**1**) took place to a very small extent in these solvents (Table 3), and in the presence of Cu^{II}–EDA complexes oxidation of (**1**) in toluene or cumene, both quite strong hydrogen-atom donors, still gave high yields of (**2**) (75 %) and the oxidation products of toluene or cumene were not obtained. In conclusion, phenol (**1**), and the alcohols were not oxidized by free t-butoxyl or t-butylperoxyl radical under our conditions. This implies that the oxidations are achieved within the co-ordination sphere of copper(II).

Phenol Oxidation by t-Butyl Hydroperoxide Catalysed by a Series of EDA–Cu^{II} *Complexes.*—In aprotic solvents, the phenol (**1**) was oxidized in the presence of a series of EDA–Cu^{II} complexes. The relative activities of the EDA–Cu^{II} complexes on the oxidation were affected to a small extent by the solvents examined with the exception of pyridine, but the absolute values of the reactivity varied considerably from one complex to another (see Table 4 for a typical example).

On the whole, the relative activities of the Cu^{II}–EDA complexes were similar to those which were observed in the oxidation of the phenol (**1**) by molecular oxygen.[1] The most

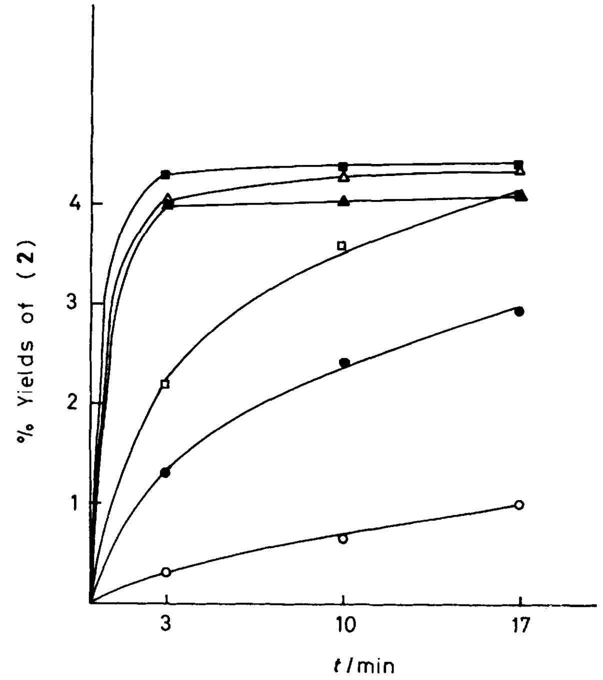

Figure 1. Effect of diamine:copper(II) ratio on the oxidation of phenol (**1**). Diamine/copper(II): ○, 0:1; ●, 0.5:1; □, 1:1; ■, 2:1; △, 4:1; ▲, 6:1. The phenol (**1**) (2.43×10^{-3} mol), $CuCl_2$ (3.03×10^{-6} mol) and $\mathrm{Bu^tO_2H}$ (6.06×10^{-4} mol) in benzene (50 cm^3).

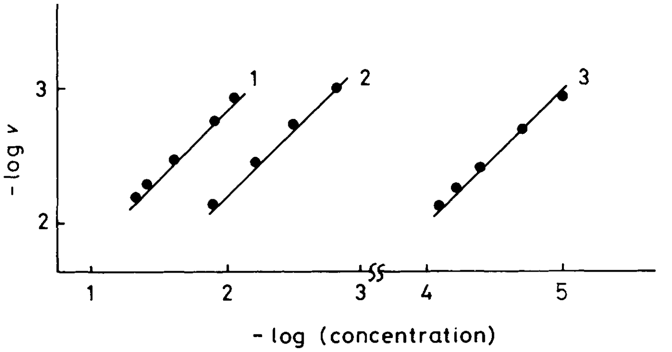

Figure 2. Kinetic plots: 1, [(**1**)] = 9.09–48.5 mol m^{-3}; 2; [$\mathrm{Bu^tO_2H}$] = 1.53–12.2 mol m^{-3}, 3; [$\mathrm{Cu^{II}}$–EDA] = 0.76×10^{-2}–6.06×10^{-2} mol m^{-3}. Other conditions were as follows: [(**1**)] = 48.5 mol m^{-3}, [$\mathrm{Bu^tO_2H}$] = 12.2 mol m^{-3} and [$\mathrm{Cu^{II}}$–EDA] = 6.06×10^{-2} mol m^{-3} in benzene at 25 °C.

active copper(II) complexes were those derived from *N,N′*-di-t-butyl-, *N,N′*-di-s-butyl- and *N,N′*-di-isopropyl-EDA, in which steric crowding around the nitrogen atom was very large.* Comparing with hydrogen peroxide, t-butyl hydroperoxide would have weak co-ordinating ability towards $\mathrm{Cu^{II}}$–EDA complexes, owing to the bulky t-butyl group. Thus, the apparent co-ordinating ability towards $\mathrm{Cu^{II}}$–EDA complexes could be similar to molecular oxygen. In pyridine, however, the activities of all $\mathrm{Cu^{II}}$–EDA complexes examined were similar but the yields of (**2**) were quite low (6.0 %). In these cases, the $\mathrm{Cu^{II}}$–pyridine complex could be the catalyst, because EDA molecules ligated to copper(II) ions could be exchanged with pyridine.

The Mechanism of Oxidation of Phenol (**1**).—(*a*) *Effects of the diamine: copper*(II) *ratio.* In the presence of copper(II) chloride and *N,N′*-di-t-butyl-EDA, the yields of the biphenyldiol (**2**) in benzene were affected by the ratios of diamine to copper(II). The results are shown in Figure 1. The maximum yield of (**2**) was achieved at a diamine:copper(II) ratio of 2:1, implying that the 2:1 complex is the most active catalyst. At a ratio higher than 2:1, the yields of (**2**) decreased slightly. However, even under the conditions in which 1:1 complexes could be preferentially formed, the yield of biphenyl (**2**) was still rather high. The 1:1 complexes would also be active. This is quite different from the oxidation by molecular oxygen or hydrogen peroxide.[1,3] The 1:1 and 2:1 mixtures of a series of EDA and $CuCl_2$ in benzene showed visible absorption maxima at 700–835 and 570–825 nm, respectively. Since the mixture of 3:1 or of higher ratio showed the same absorption maxima at 570–825 nm, formation of the 2:1 complexes could be inferred.

(*b*) *Kinetic studies.* The kinetics of the oxidations were studied in the presence of the active $\mathrm{Cu^{II}}$–*N,N′*-di-t-butyl-EDA (1:2) complex. The initial rate of the reaction $\{[(\mathbf{2})]_{\text{initial}}\ \mathrm{min^{-1}}\}$ was determined. The initial rate (v) and the yields of (**2**) decreased in the presence of a large excess of either phenol (**1**) or t-butyl hydroperoxide. Thus for the oxidation, there is an optimum ratio of combination for phenol (**1**), copper(II), EDA, and t-butyl hydroperoxide molecules. This suggests that the oxidation proceeds *via* an intermediate consisting of the quadruple $\mathrm{Cu^{II}}$–EDA–(**1**)–$\mathrm{Bu^tO_2H}$. Within the limiting concentration ranges of each of the species given below, the kinetics were shown to follow closely the simple product of the three components. The initial rate increased linearly with concentration of t-butyl hydroperoxide, where the initial concentration of the hydroperoxide was varied from 1.53–12.2 mol m^{-3}. From plots of log v *vs.* log [$\mathrm{Bu^tO_2H}$], the dependence on [$\mathrm{Bu^tO_2H}$] is found to be first order. The dependence on [(**1**)] and [$\mathrm{Cu^{II}}$–EDA] is also first order; concentrations of (**1**) and the $\mathrm{Cu^{II}}$–EDA complex were varied from 9.09–48.5 mol m^{-3} and from 7.60×10^{-3}–6.06×10^{-2} mol m^{-3}, respectively (Figure 2). From these results, the following empirical rate expression (1) was deduced.

$$v = k[\mathrm{Bu^tO_2H}][\text{phenol }(\mathbf{1})][\mathrm{Cu^{II}}\text{–EDA complex}] \quad (1)$$

(*c*) *The mechanism of oxidation.* In the present oxidations, one molecule of $\mathrm{Bu^tO_2H}$ oxidizes two molecules of phenol (**1**) to (**2**), while $\mathrm{Bu^tO_2H}$ was reduced to $\mathrm{Bu^tOH}$. The reaction sequence consistent with these results is given in the Scheme.

Co-ordination of (**1**) to the $\mathrm{Cu^{II}}$–EDA complex (**X1**) was ascertained spectroscopically.[3] Since decomposition of $\mathrm{Bu^tO_2H}$ took place in the absence of (**1**), it was obvious that $\mathrm{Bu^tO_2H}$ co-ordinated to the complex (**X1**). Complex (**X3**) would be formed *via* co-ordination of both (**1**) and $\mathrm{Bu^tO_2H}$ to complex (**X1**). The solvents which strongly co-ordinate to copper(II), *e.g.*, pyridine and acetonitrile, would inhibit the formation of complexes (**X2**) and (**X3**). In particular, pyridine may destroy complex (**X1**) and form a $\mathrm{Cu^{II}}$–pyridine complex. Formation of complex (**X3**) would be dependent on the stability of complex (**X1**).

In stark contrast with the oxidation of (**1**) by molecular oxygen, copper(II) chloride in the absence of EDA catalyses the oxidation of (**1**) to give a reasonable yield of (**2**). The results suggest that phenolate anion can transfer an electron to $\mathrm{Bu^tO_2H}$ through copper(II) in the quadruple complex (**X3**). The configuration of complex (**X3**) would affect the rate of electron transfer. After having received an electron $\mathrm{Bu^tO_2H}$ generates $\mathrm{Bu^tO^{\bullet}}$. Since, in our oxidation, quenching of $\mathrm{Bu^tO^{\bullet}}$ by H-donation by toluene or cumene was not observed, the $\mathrm{Bu^tO^{\bullet}}$ must be in the sphere of the copper(II) complex in order to oxidize a further molecule of (**1**).

Alternatively, the reduction process involving $\mathrm{Bu^tO_2H}$ in

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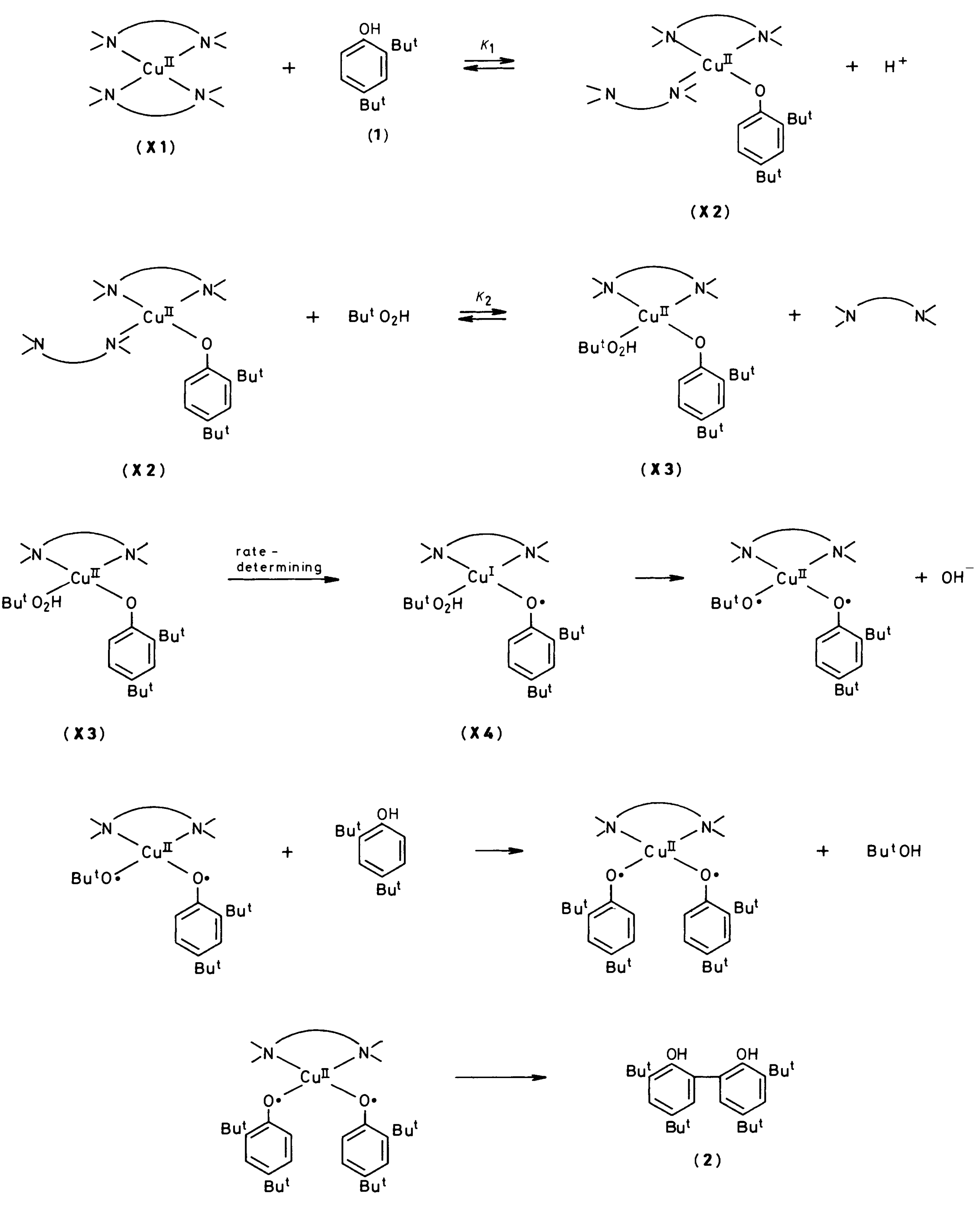
* The copper(II) complexes ligated with highly alkylated EDA are less stable and forced to have a tetrahedral configuration. In general, copper(II) complexes of tetrahedral configuration are expected to undergo facile electron acceptance.[1,6]



Scheme.

complex (**X4**) might be the rate-determining step, but this is unlikely considering the redox potentials of both copper(II) complexes[7] and Bu^{t}O$_2$H. Since the complexes (**X1**), (**X2**), and (**X3**) could be in rapid equilibrium, a one-electron transfer process from phenolate anion to copper(II) within complex (**X3**) would be the rate-determining step, therefore. By assuming the processes given above, the rate expression is derived as follows, from (2) and (3).

Table 5. Oxidation of phenol (**1**) with molecular oxygen, hydrogen peroxide, or t-butyl hydroperoxide in the presence of Cu^{II}–EDA complexes in methanol.[a]

RNH–[CH$_2$]$_2$–NHR			Oxidation Products/10^{-3} mol		
R	Oxidant	Oxidant consumed/ 10^{-3} mol	(**2**)	(**3**)	HCHO[b]
Bu^t	O_2	—	0.30	0.51	0
	H_2O_2	0.68	0.06	tr.	0
	Bu^{t}O$_2$H	1.17	0.22	tr.	0.93
H	O_2	—	0.005	tr.	0
	H_2O_2	1.12	0.51	tr.	0
	Bu^{t}O$_2$H	0	0.007	tr.	0

[a] The conditions were the same as those indicated in Table 1. Bu^{t}O$_2$H was replaced with H_2O_2 (1.22 × 10^{-3} mol) or O_2 was bubbled through the mixture at atmospheric pressure. [b] Formic acid was not formed.

Table 6. Oxidation of methanol with t-butyl hydroperoxide in the presence or absence of (**1**).[a]

	Bu^{t}O$_2$H consumed/10^3 mol	Oxidation Products/ 10^3 mol	
		(**2**)[b]	HCHO[c]
CuCl$_2$ + diamine[d]	0.17	—	0.12
CuCl$_2$ + diamine[d] + phenol (**1**)	1.17	0.22	0.93
CuCl$_2$	0.003	—	tr.
CuCl$_2$ + phenol (**1**)	0.21	0.044	0.17

[a] The conditions were the same as those indicated in Table 1. [b] Benzofuran, trace. [c] Formic acid was not formed. [d] Diamine: *N,N'*-di-t-butyl-EDA.

$$v = k'[(\mathbf{X3})] \qquad (2)$$

$$\begin{aligned} K_1 &= [(\mathbf{X2})]/[(\mathbf{X1})][\text{2,4-di-t-butylphenol}] \\ K_2 &= [(\mathbf{X3})]/[(\mathbf{X2})][\mathrm{Bu^tO_2H}] \\ K_1K_2 &= [(\mathbf{X3})]/[(\mathbf{X1})][\mathrm{Bu^tO_2H}][\text{2,4-di-t-butylphenol}] \qquad (3) \end{aligned}$$

$$v = k'K_1K_2[\mathrm{Bu^tO_2H}][\text{2,4-di-t-butylphenol}][(\mathbf{X1})] \qquad (4)$$

The rate expression [equation (4)] is consistent with the foregoing empirical rate expression.

Oxidation of Methanol.—In Table 5, oxidations of (**1**) in methanol by molecular oxygen, hydrogen peroxide, and t-butyl hydroperoxide are compared. In the oxidation with these oxidants, Cu^{II}-unsubstituted EDA complex cannot catalyse the oxidation of methanol. The Cu^{II}–unsubstituted EDA complex was active in the oxidation of (**1**) with hydrogen peroxide, although the same copper(II) complex was inactive in the oxidation of (**1**) with molecular oxygen or t-butyl hydroperoxide. However, in the presence of *N,N'*-di-t-butyl-EDA–Cu^{II} complex, only t-butyl hydroperoxide was active in the oxidation of methanol to formaldehyde. The oxidation by molecular oxygen or t-butyl hydroperoxide in the presence of *N,N'*-di-t-butyl-EDA–Cu^{II} complex afforded a large quantity of (**2**) or (**3**), but molecular oxygen was too weakly oxidising to oxidize methanol. In the oxidation with the hydrogen peroxide–*N,N'*-di-t-butyl-EDA–Cu^{II} system, decomposition of hydrogen peroxide proceeded predominantly. It is highly probable that hydrogen peroxide co-ordinates strongly to copper(II) and quick electron transfer to copper(II) initiates the decomposition, Cu^{II}-complex was destroyed and dark-brown precipitates formed. Unlike hydrogen peroxide, the rather weak reducing power of t-butyl hydroperoxide makes the decomposition difficult and the weak co-ordinating ability of t-butyl hydroperoxide might not compete with co-ordination of (**1**) and methanol. Thus, the formation of the quadruple complex consisting of *N,N'*-di-t-butyl-EDA–Cu^{II}–t-butyl hydroperoxide–methanol is a prerequisite for the oxidation of methanol.

We investigated further whether methanol is oxidized by t-butyl hydroperoxide in the absence of (**1**). The results are shown in Table 6, together with those for the oxidation of (**1**) in methanol. In the oxidation of (**1**) catalysed by Cu^{II}–*N,N'*-di-t-butyl-EDA complex, a great deal of formaldehyde was formed in contrast with the oxidation of (**2**). As mentioned above, both (**1**) and methanol were oxidized within the co-ordination sphere of copper(II). Taking account of redox potentials of both phenol (**1**) and methanol, the electron transfer to copper(II) is found to be favourable for (**1**). t-Butyl hydroperoxide which receives an electron from phenolate anion through copper would be reduced to t-butoxyl radical. The radical co-ordinated to copper(II) would not directly oxidize methanol. The high yield of formaldehyde suggests that phenoxyl radical within the co-ordination sphere of copper(II) complex participates in the oxidation of methanol. In the absence of (**1**), the decomposition product of t-butyl hydroperoxide, *i.e.*, t-butylperoxyl radical, would oxidize methanol. Under our conditions, the radical must also co-ordinate to copper(II), since molecular oxygen which is formed from two free t-butylperoxyl radicals was not detected. Copper(II) chloride itself could not oxidize methanol in the absence of EDA and (**1**).

Experimental

G.c. analyses were carried out on a JEOL Model JGC-20K and JEOL Model JGC-1100. The g.c. columns used were as follows: (*i*) Porapak T for formaldehyde, formic acid, acetaldehyde, acetone, and 2-methylpropan-2-ol, (*ii*) Dinonyl phthalate 20% on Celite 545 for propionaldehyde, butyraldehyde, and 2-methylpropan-2-ol. H.p.l.c. analyses were performed using methanol as an eluant on a Shimadzu Model LC-3A liquid chromatograph with Zorbax ODS column. U.v.–vis. spectra were taken using a Shimadzu UV300 spectrophotometer. Temperature used in the kinetic measurement was controlled (±0.15 °C) by using a Komatsu-Yamato Coolnics CTR-220 thermostat. Detection of molecular oxygen was performed on a Hempel apparatus.

Materials.—Anhydrous copper(II) chloride was prepared by heating the dihydrate in an oven at 100 °C for 20 h. t-Butyl hydroperoxide (70%) was obtained from Sigma and concentration was determined by iodometry before use.[8] *N,N'*-Dipropyl- and *N,N'*-dibutyl-EDA[9] and 3,3',5,5'-tetra-t-butyl-2,2'-dihydroxybiphenyl (**2**)[10] and 2,4,7,9-tetra-t-butyloxepino[2,3-*b*]benzofuran (**3**)[10] were prepared by procedures given in the literature.

Standard Conditions.—Oxidation of 2,4-*di-t-butylphenol* (**1**). The phenol (**1**) (2.43×10^{-3} mol) and the EDA (6.06×10^{-6} mol) were dissolved in benzene, and the volume was made up to 50 cm^3 by the addition of benzene. Under a nitrogen atmosphere, a methanolic solution (0.5 cm^3) containing anhydrous copper(II) chloride (3.03×10^{-6} mol) and t-butyl hydroperoxide (6.06×10^{-4} mol) were added successively to the mixture and the oxidation was conducted at 25 °C for 10 min. The products were (**2**) and its oxidation product, benzofuran (**3**).[1] The yields of product (**2**) were determined by h.p.l.c.

Oxidation of Phenol (**1**) *in Alcohols.*—Phenol (**1**) (2.43×10^{-3} mol) and *N,N′*-di-t-butyl-EDA (4.85×10^{-5} mol) were dissolved in an alcohol, and the volume was made up to 50 cm^3 by the addition of an alcohol. Under a nitrogen atmosphere, anhydrous copper(II) chloride (2.43×10^{-5} mol) and t-butyl hydroperoxide (1.22×10^{-3} mol) were added successively to the mixture and the oxidation was conducted at 25 °C for 20 min. The yields of the biphenyldiol (**2**), aldehydes, ketones, formic acid, and 2-methyl propan-2-ol were determined by h.p.l.c. or g.c. t-Butyl hydroperoxide was determined by iodometry.[8]

Decomposition of t-Butyl Hydroperoxide in the Absence of (**1**).—Conditions were the same as the standard, except for the absence of (**1**). The samples were removed from the reaction solution and the amounts of t-butyl hydroperoxide consumed for the first 4 min of the reaction were determined by iodometry.[8]

Spectroscopic Studies.—Ultraviolet and visible absorption spectra. In various combinations of anhydrous copper(II) chloride (9.7×10^{-6} mol) and EDA (4.85×10^{-6}–3.88×10^{-5} mol), the absorption spectra of a benzene solution (10 cm^3) of the mixture were taken using a spectrophotometer.

Effects of the Diamine: *Copper*(II) *Ratio.*—In the presence of the Cu^{II}–diamine mixture of various ratios, phenol (**1**) was oxidized under standard conditions.

Kinetic Measurements.—Phenol (**1**) was oxidized under standard conditions for 10 min. The initial rate of the reaction $\{[(\mathbf{2})]_{\text{initial}}\ \text{min}^{-1}\}$ was determined by h.p.l.c.

Oxidation of Phenol (**1**) *with Molecular Oxygen or Hydrogen Peroxide in Methanol.*—Conditions were the same as those in the oxidation of (**1**) with t-butyl hydroperoxide in alcohols, except for the oxidant. In place of t-butyl hydroperoxide, hydrogen peroxide (1.22×10^{-3} mol) was added to the mixture or molecular oxygen was bubbled through the mixture at atmospheric pressure. The yields of the biphenyldiol (**2**), benzofuran (**3**), and formaldehyde were determined by h.p.l.c. or g.c. Hydrogen peroxide was determined by iodometry.

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