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Liquid-phase Oxidation Catalyzed by Cu(II)-Cl. III. Oxidation of 1,2,3,4-Tetrahydronaphthalene

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1,2,3,4-Tetrahydronaphthalene was oxidized in the presence of copper(II) acetate in glacial acetic acid. An addition of lithium chloride which formed complexes with copper(II) ion highly accelerated the reaction, and the initiating process was found to be the decomposition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide by the copper(II)-chloride ion complexes. However, only about 8% of the decomposition contributed the initiation, and it was suggested that the larger part of the decomposition proceeded through a non-ionic mechanism. Spectrophotometric and ESR experiments suggested that one of the accelerating effects of the chloride ion was due to its action to decompose the inactive copper(II) acetate dimer and form active copper(II)-chloride ion complexes and that the order of the activity of the complexes was $CuCl^+ < CuCl_2 < CuCl_3^-$, $CuCl_4^{2-}$.

Copper(II) salts are well-known to form complexes with alkali chloride in glacial acetic acid, in aqueous solutions, or in acetonitrile, and extensive data on these complexes are available.[1-6)]

Previously we carried out the oxidation of cyclohexene catalyzed by copper(II) salts in glacial acetic acid and found that the reaction was highly accelerated by an addition of various alkali chlorides.[7)] During the reaction, however, the chloride ion was consumed by a chlorination of cyclohexene or of the oxidation products and a rapid deactivation of the catalyst occurred.[8)] However, the mechanism of the oxidation has not been discussed in detail.

This paper deals with the oxidation of 1,2,3,4-tetrahydronaphthalene and the decomposition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide by copper(II) acetate–lithium chloride for the investigation of the catalytic action and of the effect of the chloride ion.

Experimental

Commercial 1,2,3,4-tetrahydronaphthalene (tetralin) was washed with 5% aqueous sodium hydroxide and concentrated sulfuric acid, and distilled twice under a reduced pressure. 1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide (THP) was obtained by an autoxidation of tetralin and purified twice by recrystallization from petroleum ether.[9)] Glacial acetic acid and acetonitrile were purified by the usual methods, and anhydrous copper(II) acetate was obtained by a dehydration of copper(II) acetate dihydrate. 1,2,3,4-Tetrahydro-1-naphthol (α-tetralol) was prepared by the reduction of 1,2,3,4-tetrahydro-1-naphthalenone (α-tetralone) followed by a fractional distillation.[10)] Commercial α-tetralone and other G. R. grade reagents were used without further purification.

The apparatus used in the oxidation and the procedures were the same as described in the previous paper.[7)] The rate of the oxidation was confirmed not to be controlled by the diffusion of oxygen into the liquid phase.

The decomposition of THP was carried out under a nitrogen atmosphere. In a 100 ml reaction vessel immersed in a constant temperature water bath, acetic acid and a known amount of THP were stirred until a desired temperature (usually 37 °C) was reached. Then a known amount of the catalyst solution was added and the reaction started. The reaction was followed by an iodometry of the remaining THP.

The analysis of the products was carried out using a Hitachi 063 gas chromatograph. The conditions were as follows: (1) Column packing-PEG 6000 (1 m); Carrier gas-N_2 (30 ml/min); Column temperature-150 °C, 180 °C, and (2) Column packing-Chromosorb 101 (1 m); Carrier gas-He (30 ml/min); Column temperature-150 °C.

The ESR and electronic spectra of the catalyst were observed at room temperature by the use of a JES-PE spectrometer and a Hitachi 125 spectrophotometer, respectively.

Results and Discussion

Visible Spectra of Copper(II) Acetate-Lithium Chloride in Glacial Acetic Acid. Visible spectra of the copper(II) acetate–lithium chloride were observed in glacial acetic acid varying the concentration of lithium chloride and the result is shown in Table 1. As the concentration of lithium chloride is increased, the absorption maximum shifts from 680 nm to the higher wavelength region, and the color of the solution gradually changes from blue to green and finally to yellow. The result suggests that the acetate anion of copper(II) acetate is replaced by the chloride ion and complexes which posess copper–chloride ion bondings are formed.[1)] In the subsequent sections, we

$$Cu^{2+} \underset{K_1}{\overset{Cl^-}{\rightleftharpoons}} CuCl^+ \underset{K_2}{\overset{Cl^-}{\rightleftharpoons}} CuCl_2 \underset{K_3}{\overset{Cl^-}{\rightleftharpoons}} CuCl_3^- \underset{K_4}{\overset{Cl^-}{\rightleftharpoons}} CuCl_4^{2-} \qquad (1)$$

call these complexes Cu(II)–Cl.

TABLE 1. ABSORPTION SPECTRA OF Cu(II)–Cl IN AcOH

$LiCl/Cu(OAc)_2$[a)]	λ_{max}/nm
1	680
2	690
3	700
4	710
5	750
6	>800
10	>800

$[Cu(OAc)_2] = 2.0 \times 10^{-3}$ M.
a) Molar ratio.

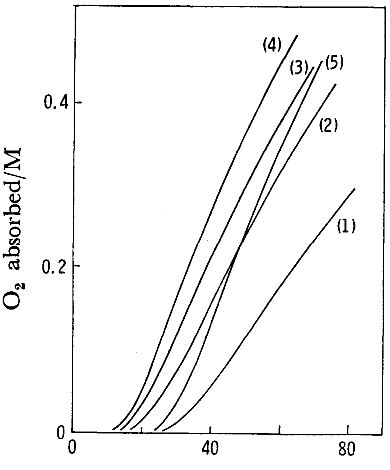

Fig. 1. Oxidation of tetralin catalyzed by Cu(II)-Cl in AcOH at 80 °C.
$[Cu(OAc)_2]=2.0\times10^{-3}$ M, [Tetralin]$=1.25$ M.
$[LiCl]/(M\times10^{-3})$: (1) 2.0, (2) 6.0, (3) 8.0, (4) 10.0, and (5) 20.0.

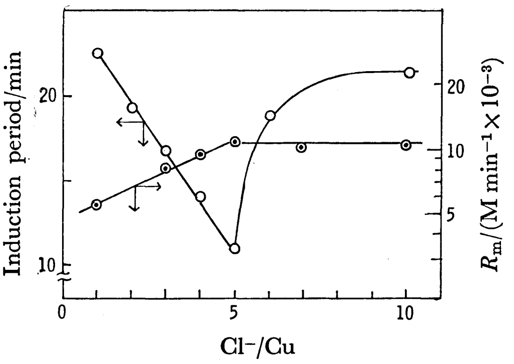

Fig. 2. Effect of LiCl in the oxidation of tetralin in AcOH at 80 °C.
$[Cu(OAc)_2]=2.0\times10^{-3}$ M, [Tetralin]$=1.25$ M.

Oxidation of Tetralin Catalyzed by Cu(II)-Cl at 80 °C. Tetralin was oxidized at 80 °C in the presence of Cu(II)-Cl. Figure 1 shows that the chloride ion has an accelerating effect on the reaction, while copper(II) acetate itself was inactive in the absence of lithium chloride. In Fig. 2 the maximum rate of oxidation (R_m) and the induction period are plotted against the molar ratio of chloride ion to copper(II) ion at the constant concentration of copper(II) ion. It is shown that, with the increase in the concentration of chloride ion, R_m increases and reaches a maximum at the molar ratio near five and, then, remains constant. The induction period also takes a minimum at the molar ratio of five and is rather prolonged in the higher concentration region of chloride ion.

In Fig. 3 the accumulation of the oxidation products is shown. The yield of α-tetralone is much higher than that of α-tetralol. The yield of THP is considerably low and there is no steady state concentration of THP. The low yield of THP suggests the high activity of Cu(II)-Cl to decompose THP.

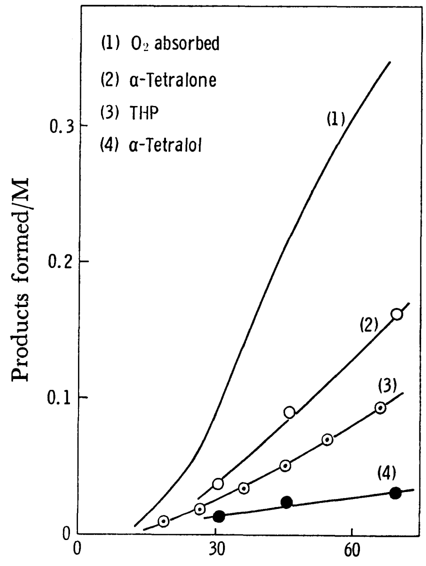

Fig. 3. Product distribution in the oxidation of tetralin catalyzed by Cu(II)-Cl in AcOH at 80 °C.
$[Cu(OAc)_2]=2.0\times10^{-3}$ M, [Tetralin]$=1.25$ M, [LiCl]$=1.0\times10^{-2}$ M.

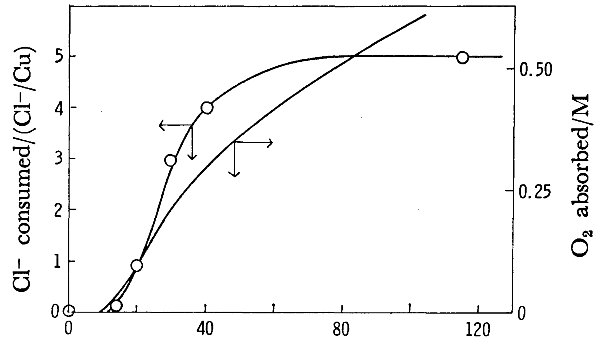

Fig. 4. Consumption of Cl⁻ during the reaction at 80 °C.
$[Cu(OAc)_2]=2.0\times10^{-3}$ M, [LiCl]$=1.0\times10^{-2}$ M, [Tetralin]$=1.25$ M.

Table 2. Time dependence of absorption spectrum in the oxidation of tetralin in AcOH at 80 °C

Reaction time/min	λ_{max}/nm
0	750
15	740
20	710
30	690
40	680
55	680
115	680
180	680

$[Cu(OAc)_2]=2.0\times10^{-3}$ M; [LiCl]$=1.0\times10^{-2}$ M.

The color of the solution changed in the course of the reaction from yellow to green and finally to blue, which suggested that the state of the catalyst gradually changed. The visible spectra of the reaction mixture were observed during the reaction and the result is given in Table 2. We see that the absorption maximum of the catalyst shifts to the shorter

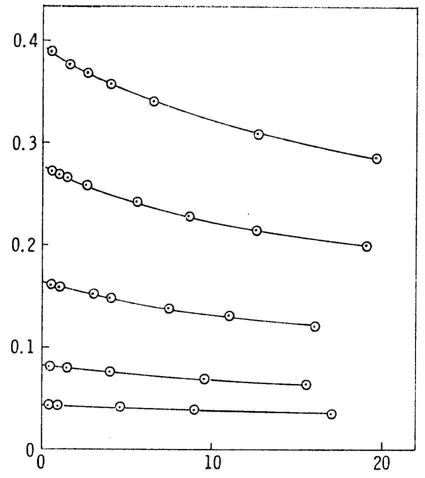

Fig. 5. Decomposition of THP catalyzed by Cu(II)-Cl in AcOH at 37 °C.
$[Cu(OAc)_2]=2.0\times10^{-3}$ M, $[LiCl]=2.0\times10^{-2}$ M.

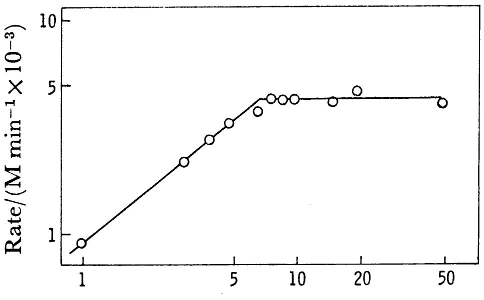

Fig. 6. Effect of LiCl in the decomposition of THP catalyzed by Cu(II)-Cl in AcOH at 37 °C.
$[Cu(OAc)_2]=8.0\times10^{-3}$ M, $[THP]=0.10$ M.

wavelength region as the reaction proceeds, and after 40 min the absorption at 680 nm begins to appear. The chloride ion seems to be consumed during the reaction and change to inactive organic chlorine compounds.[7,8,11] The quantity of the chloride ion consumed during the reaction was roughly estimated from Table 2 by the use of the chloride ion to copper(II) ion molar ratio *vs.* absorption maxima data listed in Table 1, and the result is shown in Fig. 4. It may be seen that the consumption of chloride ion occurs as soon as the induction period is over. The state of the catalyst changes in this manner during the reaction, so, it is impossible to carry out a kinetic discussion from the measurement of R_m's.

Decomposition of THP Catalyzed by Cu(II)-Cl. THP was decomposed by Cu(II)-Cl in glacial acetic acid at 37 °C and the result is shown in Fig. 5.[12] Copper(II) acetate without lithium chloride was found to be inactive as in the oxidation of tetralin. Kochi reported that copper(II) salts do not decompose hydroperoxides directly and that an induction period exists at the initial stage of the reaction.[13] In the present result, however, no induction period exists, indicating that Cu(II)-Cl decomposes THP directly.

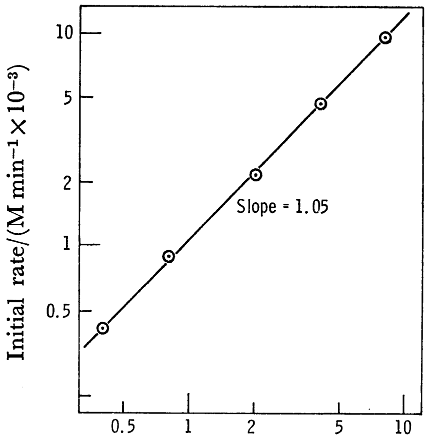

Fig. 7. Decomposition of THP catalyzed by Cu(II)-Cl in AcOH at 37 °C.
$[THP]=0.17$ M, $Cl^-/Cu=10$.

Table 3. PRODUCT DISTRIBUTION IN THE DECOMPOSITION OF THP CATALYZED BY Cu(II)-Cl[a)]

Solvent	Temp. /°C	ϕ_3CH	α-Tetralone /%[b)]	α-Tetralol /%[b)]	H_2O /%[b)]
AcOH	50	0	79.6	7.2	93.4
AcOH	50	0.34	71.0	5.0	
AcOH	70	0	66.8	7.5	
CH_3CN	37	0	79.5	12.6	

$[THP]=0.17$ M; $[Cu(OAc)_2]=8.0\times10^{-3}$ M; $[LiCl]=8.0\times10^{-2}$ M.
a) The Products were analyzed after the decomposition was completed. b) Based on the initial concentration of THP.

Figure 6 shows the rate dependence on the concentration of chloride ion at the constant concentration of copper(II) ion. The rate increases with the increase of chloride ion up to the molar ratio of chloride ion to copper(II) ion of eight, after which it remains almost constant. It was found that Cu(II)-Cl gradually changed to inactive copper(II) acetate during the reaction, and the amount of THP decomposed before the catalyst was deactivated increased with the increase of the concentration of chloride ion. The accelerating effect of chloride ion shown in Fig. 6 resembles to that in the oxidation of tetralin (Fig. 2), which indicates that the catalytic action of Cu(II)-Cl in the decomposition of THP is correlated to that in the oxidation of tetralin.

Figure 7 shows the rate dependence on the concentration of Cu(II)-Cl ($Cl^-/Cu=10$). From this and the result shown in Fig. 5, the initial rate of the decomposition of THP by Cu(II)-Cl ($Cl^-/Cu=10$) is expressed as

$$-d[THP]/dt=k[Cu(II)\text{-}Cl]^{1.05}[THP]^{1.28} \qquad (2)$$

The products in the decomposition of THP were α-tetralol, α-tetralone, α-tetralyl acetate, water, and a high-boiling unknown product. In Table 3 the yields of α-tetralone and α-tetralol after the reaction was completed are shown. The yield of α-tetralone is much higher than that of α-tetralol, and water is producuced almost quantitatively. Triphenylmethane,

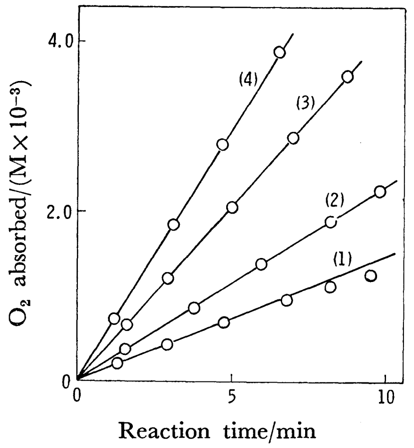

Fig. 8. Oxidation of tetralin catalyzed by Cu(II)–Cl–THP in AcOH at 37 °C.
[Tetralin] = 1.26 M, [THP] = 0.1 M, $Cl^-/Cu = 10$, $[Cu(OAc)_2]/(M\times10^{-3})$: (1) 0.5, (2) 1.0, (3) 3.0, and (4) 6.0.

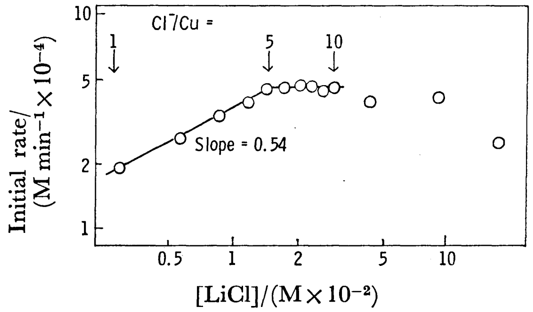

Fig. 9. Effect of LiCl in the oxidation of tetralin catalyzed by Cu(II)–Cl–THP in AcOH at 37 °C. $[Cu(OAc)_2] = 3.0\times10^{-3}$ M, [THP] = 0.1 M, [Tetralin] = 1.26 M.

which is a good hydrogen donor in radical reactions, does not increase the yield of α-tetralol, suggesting that the reaction proceeds mainly by an ionic or a molecular mechanism. In the case of acetonitrile solvent, chloride ion also accelerated the decomposition of THP catalyzed by copper(II) acetate and the product distribution was similar to that in glacial acetic acid. (see Table 3). Although the unknown product was not analyzed and the amount of α-tetralyl acetate was not determined, the disagreement in the material balance shown in Table 3 is considered to be due to the formation of these by-products.[7,8]

Oxidation of Tetralin Initiated by Cu(II)–Cl–THP at 37 °C. As shown in the previous sections, the catalytic activity of Cu(II)–Cl in the oxidation of tetralin was correlated to that of the decomposition of THP; the decomposition of THP by Cu(II)–Cl is suggested to be effective in initiating the oxidation. Therefore, a series of experiments was carried out as described below, assuming that the intiation step is the decomposition of THP by Cu(II)–Cl. A known amount of THP was added at the beginning of the oxidation and the rate dependences on the concentrations of THP, tetralin, copper(II) acetate, and chloride ion were observed. Figure 8 shows an example of the oxidation catalyzed by Cu(II)–Cl–THP at 37 °C. The reaction proceeds without any induction period and at a constant rate, which enables us to carry out the kinetic investigation from the measurement of the initial rates. The change of the catalyst state due to the consumption of chloride ion will be neglected in the initial stage of the reaction.

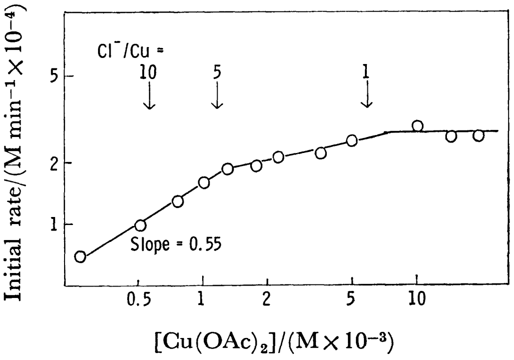

Fig. 10. Effect of $Cu(OAc)_2$ in the oxidation of tetralin catalyzed by Cu(II)–Cl–THP in AcOH at 37 °C. $[LiCl] = 6.0\times10^{-3}$ M, [THP] = 0.1 M, [Tetralin] = 1.26 M.

The effect of chloride ion was investigated again and the results are shown in Figs. 9 and 10. Figure 9 shows the rate dependence on the chloride ion concentration at a constant concentration of copper(II) ion. The rate is proportional to $[Cl^-]^{0.54}$ up to the chloride ion to copper(II) ion molar ratio of five, then remains constant, and is rather decreased by an addition of excess chloride ion. As Fig. 10 shows, at the constant concentration of chloride ion, the rate is proportional to $[Cu(II)]^{0.55}$ unless the molar ratio becomes less than five. In the molar ratio range below five, the rate does not increase so much with the increase in the copper(II) ion concentration. When the concentration of copper(II) ion exceeds that of chloride ion, the rate becomes independent of the copper(II) ion concentration; that is, an excess copper(II) ion over chloride ion does not take part in the oxidation. The effect of chloride ion shown above is the same as that in the decomposition of THP except that an excess chloride ion (more than ten molar ratio) retards the oxidation. These observations indicate clearly that the presence of copper–chloride ion bonds is inevitable for the catalyst to be active and that the most active catalyst is formed in the chloride ion to copper(II) ion molar ratio range from five to ten.

The rate dependences on the concentrations of tetralin, Cu(II)–Cl ($Cl^-/Cu = 10$), and THP are shown by dotted lines in Figs. 11—13. From these results, the apparent rate equation for the oxidation of tetralin is obtained as shown below.

$$-dO_2/dt = k_1[RH]^{1.05}[Cu(II)\text{-}Cl]^{0.53}[THP]^{0.68} \qquad (3)$$

RH : Tetralin

Oxidation Mechanism. On the basis of the results obtained in the preceding sections, it is suggested that Cu(II)–Cl produces active radicals by an interaction with THP in the initiation step. Therefore, the mechanism of the oxidation of tetralin is

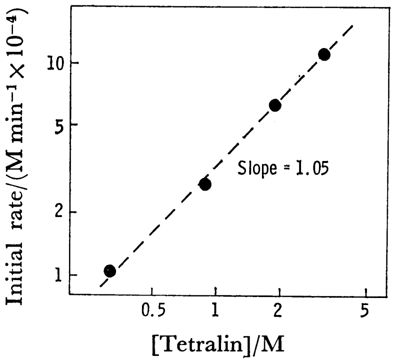

Fig. 11. Oxidation of tetralin catalyzed by Cu(II)-Cl-THP in AcOH at 37 °C. Rate dependence on [Tetralin].
$[Cu(OAc)_2]=3.0\times10^{-3}$ M, $[LiCl]=3.0\times10^{-2}$ M, [THP]=0.1 M.

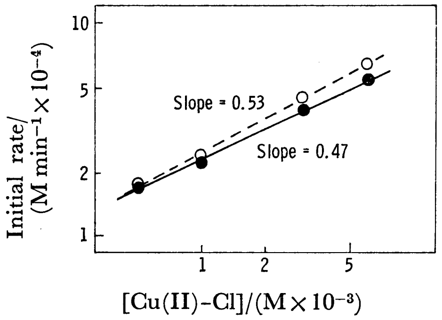

Fig. 12. Oxidation of tetralin catalyzed by Cu(II)-Cl-THP in AcOH at 37 °C. Rate dependence on [Cu(II)-Cl]. [THP]=0.09 M, [Tetralin]=1.26 M, $Cl^-/Cu=10$.

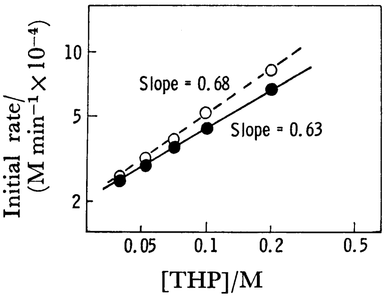

Fig. 13. Oxidation of tetralin catalyzed by Cu(II)-Cl-THP in AcOH at 37 °C . Rate dependence on [THP].
$[Cu(OAc)_2]=3.0\times10^{-3}$ M, $[LiCl]=3.0\times10^{-2}$ M, [Tetralin]=1.26 M.

represented as follows.

$$\text{THP} + \text{Cu(II)-Cl} \xrightarrow{\text{RH}} \text{R}\cdot \qquad (4) \quad R_i$$

$$\text{R}\cdot + O_2 \longrightarrow \text{ROO}\cdot \qquad (5)$$

$$\text{ROO}\cdot + \text{RH} \longrightarrow \text{THP} + \text{R}\cdot \qquad (6) \quad k_p$$

$$2\text{ROO}\cdot \longrightarrow \text{Inactive products} + O_2 \qquad (7) \quad 2k_t$$

When the kinetic chain length is short, the amount of oxygen evolved in step (7) cannot be neglected. Taking this into consideration and by the use of a steady state approximation, the rate of the oxygen absorption is expressed as

Table 4. Dependence of R_i on THP concentration[a)]

[THP]/M	R_i/M min⁻¹
0.050	3.78×10^{-5}
0.068	5.31×10^{-5}
0.090	8.07×10^{-5}
0.130	1.30×10^{-4}
0.260	2.88×10^{-4}

a) Reaction condition is the same as described in Fig. 13.

Table 5. Dependence of R_i on catalyst concentration[a)]

[Cu(II)-Cl]/M	R_i/M min⁻¹
5.0×10^{-4}	1.75×10^{-5}
1.0×10^{-3}	3.45×10^{-5}
3.0×10^{-3}	8.07×10^{-5}
6.0×10^{-3}	1.78×10^{-4}

a) Reaction condition is the same as described in Fig. 12.

$$-dO_2/dt = k_p/\sqrt{2k_t}[\text{RH}]\sqrt{R_i} + R_i/2 \qquad (8)$$

From this rate expression, the dependences of R_i on the concentrations of Cu(II)-Cl and THP were investigated as follows. The value of $k_p/\sqrt{2k_t}$ was obtained as $4.0\times10^{-3}l^{1/2}\,s^{-1/2}$ in the oxidation of tetralin initiated by AIBN at 37 °C.[14)] This value was substituted into Eq. 8, and the values of R_i are calculated at each concentration of the reactants from the data shown in Figs. 12 and 13. The results are listed in Tables 4 and 5, and afford R_i expressed as

$$R_i = k_2[\text{Cu(II)-Cl}]^{0.98}[\text{THP}]^{1.25} \qquad (9)$$

We see that the rate dependences on the concentrations of Cu(II)-Cl and THP are similar to those in the decomposition of THP by Cu(II)-Cl. (Eq. 2)

As mentioned before, when the kinetic chain length is short, the contribution of $R_i/2$ cannot be neglected in Eq. 8. Therefore, the values of $R_i/2$ are calculated from Tables 4 and 5, and substracted from the overall rates of the oxidation shown by dotted lines in Figs. 12 and 13. The solid lines thus obtained afford the following rate expression in which the contribution of $R_i/2$ is excluded.

$$-dO_2/dt = k_3[\text{RH}]^{1.05}[\text{Cu(II)-Cl}]^{0.47}[\text{THP}]^{0.63} \qquad (10)$$

This is in good agreement with rate relation (11) which is obtained by substituting Eq. 9 into the first term of the right of Eq. 8.

$$-dO_2/dt \propto k_p/\sqrt{2k_t}[\text{RH}]^{1.0}[\text{Cu(II)-Cl}]^{0.49}[\text{THP}]^{0.63} \qquad (11)$$

From the discussion shown above, it can be concluded that the formation of active radicals by the interaction of Cu(II)-Cl with THP is the main initiating step in the oxidation of tetralin.

Efficiency of the Initiation by Cu(II)-Cl-THP. In order to investigate the nature of the decomposition of THP by Cu(II)-Cl, the efficiency of the initiation by Cu(II)-Cl-THP was investigated. As described in the previous sections, the rate of the initiation (R_i) was expressed by Eq. 9. Under the same condition, the rate of the decomposition of THP (R) was observed.

Table 6. Efficiency of radical production in the decomposition of THP catalyzed by Cu(II)-Cl in AcOH at 37 °C

Cu(II)-Cl/M	R/M s^{-1}	R_i/M s^{-1}	Efficiency/%[a]
5.0×10^{-4}	2.25×10^{-4}	1.75×10^{-5}	7.8
8.0×10^{-4}	3.70×10^{-4}	2.80×10^{-5}	7.6
1.0×10^{-3}	4.70×10^{-4}	3.45×10^{-5}	7.3
			a. v. 7.6

a) Efficiency$=R_i/R\times100$

In Table 6 the values of R_i and R are listed. The fourth column in the table shows the values of $R_i/R\times100$ which indicate the efficiency of the production of active radicals in the reaction of Cu(II)-Cl with THP shown by Eq. 4. We see that only 7—8% of the decomposition contributes to the initiation. From this and the effect of triphenyl methane upon the product distribution shown in Table 3, it is suggested that the larger part of the decomposition proceeds through an ionic or a molecular mechanism such as a dehydration of THP to produce ketone and water as the product distribution shows.

$$\mathrm{THP}\xrightarrow{\mathrm{Cu(II)\text{-}Cl}}\begin{cases}\text{Non-radical mechanism} & \\ \quad\vee & (\mathrm{H_2O+R{=}O}) \quad (12)\\ \text{Radical mechanism} & \quad (13)\end{cases}$$

ESR and Electronic Spectra of Cu(II)-Cl in Glacial Acetic Acid. Copper(II) ion forms various chloro complexes in glacial acetic acid as shown by Eq. 1. To clarify the active species both in the oxidation of tetralin and in the decomposition of THP, and also to investigate the effect of chloride ion, ESR and electronic spectra of Cu(II)-Cl were observed

As copper(II) ion has an unpaired electron in its 3d-orbitals, its ESR signal must be observed. However, as shown in Fig. 14, copper(II) acetate in glacial acetic acid has no signal. This phenomenon can be explained by the following fact. That is, copper(II) acetate has a dimer structure as indicated by Fig. 15 and the distance between each copper atom is only 2.64 Å, indicating an extensive quenching of the spin moments of the copper(II) ions.[17] When lithium chloride is added, an asymmetric signal with two small peaks near the center appears, which suggests that the copper(II) acetate dimer is decomposed and monomer species are formed. By means of spectrophotometry and magnetic susceptibility measurement, Sawada *et al.*, also reported that copper(II) acetate is dimerized in glacial acetic acid and that an addition of chloride ion affords monomer species which have copper–chloride ion bonds.[18] In Fig. 16 the intensity of the signal relative to that of the Mn^{2+} external standard is plotted against the molar ratio of chloride ion to copper(II) acetate. The intensity increases with the increase of the concentration of chloride ion

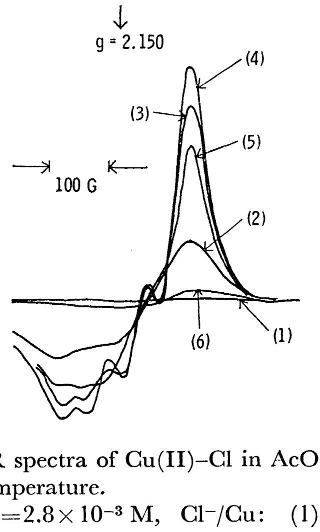

Fig. 14. ESR spectra of Cu(II)-Cl in AcOH measured at room temperature.
$[\mathrm{Cu(OAc)_2}]=2.8\times10^{-3}$ M, Cl$^-$/Cu: (1) 0, (2) 1, (3) 3, (4) 5, (5) 10, and (6) 200.

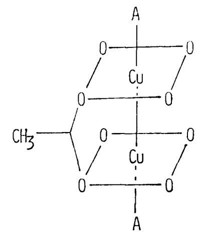

Fig. 15. Structure of Cu(OAc)$_2$. Only one bridging group is shown.[17]

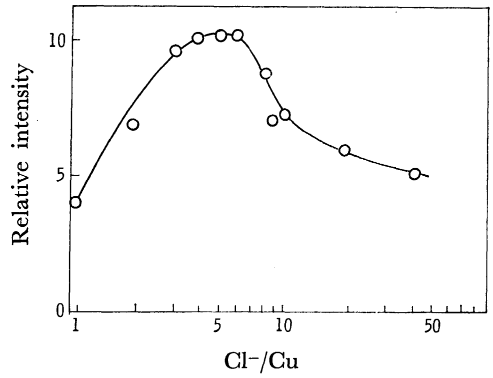

Fig. 16. Relative intensity of the ESR spectrum of Cu(II)-Cl in AcOH measured at room temperature. $[\mathrm{Cu(OAc)_2}]=2.8\times10^{-3}$ M.

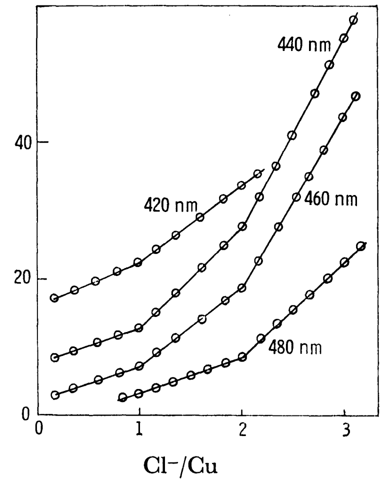

Fig. 17. Molar ratio plot for Cu(II)-Cl in AcOH measured at room temperature.

and reaches a maximum at the molar ratio from four to eight. In the oxidation of tetralin, the active catalyst was formed in the molar ratio range from five to ten, and, in the decomposition of THP, the maximum rate is attained at the molar ratio of eight and, then, remains constant. Although a slight discrepancy in the effect of chloride ion exists between these two cases, it is clear that one of the accelerating effects of the chloride ion is to decompose the dimer structure of copper(II) acetate (inactive) and to form monomer species (active) by coordinating to the copper(II) ion.

The formation of Cu(II)–Cl was investigated spectrophotometrically on the basis of the molar ratio method. Figure 17 shows the plots of ε, the absorption coefficient of Cu(II)–Cl, at 420, 440, 460, and 480 nm against the chloride ion to copper(II) acetate molar ratio. At the molar ratios of one and two, the slopes of the ε-molar ratio lines change. This indicates that the equilibrium constants, K_1 and K_2, are large enough to afford mono- and dichloro complexes almost quantitatively at the corresponding molar ratios. However, the catalytic activity of Cu(II)–Cl continues to increase up to the molar ratio of five or above both in the oxidation of tetralin and in the decomposition of THP. This indicates clearly that the order of the activity of Cu(II)–Cl is $CuCl^+ < CuCl_2 < CuCl_3^-$, $CuCl_4^{2-}$.

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