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Liquid-phase Oxidation Catalyzed by Cu(II)-Cl System. I. Oxidation of Cyclohexene

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Oxidation of cyclohexene catalyzed by Cu(II)–Cl systems was carried out in glacial acetic acid. The oxidation of cyclohexene with cupric chloride was highly accelerated by addition of various alkali chlorides. The decomposition of cyclohexenyl hydroperoxide, an intermediate product of the oxidation, was also accelerated by this catalyst system. Salts other than alkali chlorides had little effect. It was concluded that the activation of copper catalyst was due to the chloride ions which form a complex with copper. In the course of the reaction the catalyst loses its activity through ligand exchange with solvent molecule, acetic acid.

It is well known that the solubility of cupric salt is increased by the formation of complexes with alkali chlorides in acetic acid or acetonitrile. These catalyst systems are often used in the chlorination of olefines.[1] Tamura used these systems in the synthetic reaction of vinyl acetate and discussed the form of the catalyst and its behaviour.[2]

We have studied the oxidation of cyclohexene in detail to clarify the effect of various alkali chlorides on the catalytic activity of cupric chloride.

Experimental

Cyclohexene was synthesized by the dehydration of cyclohexanol.[3] The crude cyclohexene was washed with 5% aqueous sodium hydroxide, distilled twice and stored under nitrogen. Cyclohexenyl hydroperoxide was obtained by the autooxidation of cyclohexene. Cyclohexenol was obtained by the reduction of cyclohexenyl hydroperoxide with triphenylphosphine and cyclohexenone by the decomposition of cyclohexenyl hydroperoxide with cupric chloride–pyridine system.[4] Acetic acid was purified by the standard method. Cupric chloride and other reagents (anhydrous, GR grade) were used without further purification.

Oxidation was carried out using a reactor equipped with an atmospheric pressure gas burette. Fifteen ml of the mixture of cyclohexene and acetic acid containing a catalyst was warmed to the desired temperature (60°C) in a nitrogen atmosphere. Nitrogen was then replaced with oxygen and the reaction started. The decomposition of cyclohexenyl hydroperoxide was carried out in a nitrogen atmosphere and the rate of reaction was followed by iodometric titration of the remaining hydroperoxide.

Analysis of oxidation products was carried out using a Hitachi gas chromatograph 063 equipped with a frame-ionization detector. The column packing was *n*-decyl phthalate (1 m length) and the column temperature was 70—120°C (5°C/min). Visible spectra were measured by means of a Toshiba-Beckman UV spectrophotometer DBG.

Results and Discussion

Catalytic Activity of Cu(II)-Cl System. The effect of lithium chloride on the catalytic activity of cupric chloride was investigated and the results are shown in Fig. 1 and Table 1. In all cases, retardation of the reaction occurs after some uptake of oxygen. During the constant uptake of oxygen the reacting system is yellowish green or green but a deep blue colour appears

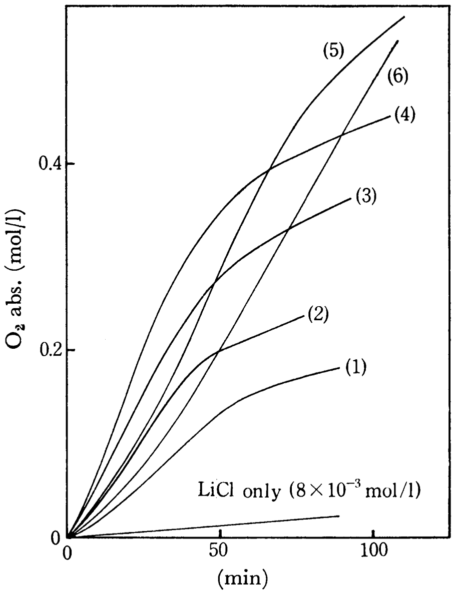

Fig. 1. Effect of LiCl on the oxidation catalyzed by $CuCl_2$. AcOH: 10 ml. Cyclohexene: 5 ml. $CuCl_2$: 8×10^{-3}mol/l. 60°C. LiCl ($\times10^3$mol/l) (1) 0, (2) 8, (3) 24, (4) 48, (5) 80, (6) 200.

TABLE 1. R_m AND MAXIMA OF ABSORBED O_2

LiCl ($\times10^3$M)	R_m ($\times10^3$M/min)	Max. O_2absd(M)
0	3.82	0.136
8	6.82	0.164
24	8.45	0.237
48	10.90	0.306
80	9.13	0.461
200	6.90	0.821

AcOH: 10 ml.
Cyclohexene: 5 ml.
$CuCl_2$: 8×10^{-3}mol/l. 60°C.

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[1] K. Ichikawa, S. Uemura, Y. Takagaki, and T. Hiramoto, *Bull. Jap. Petrol. Inst.*, **12**, 77 (1970).

[2] M. Tamura and A. Yasui, *Kogyo Kagaku Zasshi*, **72**, 558 (1969).

[3] H. Gilman, "Organic Synthesis," Coll. Vol. I, p. 183, (1956).

[4] Cyclohexenone is obtained exclusively in the decomposition of cyclohexenyl hydroperoxide by cupric chloride in pyridine solution. This was reported by T. Banba, S. I. Imamura, and Y. Takegami at the 5th Oxidation Symposium in Osaka. (December 3, 1971).

after the retardation of oxygen uptake. Though the maximum rate of oxygen absorption (R_m) increases with an increase in the amount of lithium chloride added, a large excess (more than seven parts to one part of copper) results in a decrease in the rate. On the other hand, the maximum quantity of absorbed oxygen defined as the quantity of oxygen absorbed before the retardation occurs, increases linearly with the increase in the concentration of lithium chloride added. It is clear that lithium chloride increases and maintains the activity of the catalyst. As shown in Fig. 1 lithium chloride without copper salt has little activity.

Table 2. R_m and maxima of absorbed O_2

Additive ($\times 10^3$M)		R_m($\times 10^3$ M/min)	Max. O_2absd(M)
LiCl	8	6.32	0.161
	24	8.45	0.238
	48	10.90	0.306
$MgCl_2$	8	5.13	0.185
	24	7.68	0.202
	48	8.28	0.328
NaCl	8	6.72	0.196
	24	10.17	0.311
	48	11.37	0.518
KCl	8	9.73	0.184
	24	13.25	0.390
	48	14.00	0.546
LiBr	8	6.22	0.112
	24	6.32	0.131
	48	4.12	0.136
LiF	8	4.82	0.161
	24	5.60	0.109
	48	5.78	0.098
Li_2CO_3	8	6.22	0.136
	24	6.45	0.169
	48	6.03	0.174
$LiNO_3$	8	6.22	0.145
	24	7.98	0.145
	48	8.98	0.147

AcOH: 10 ml. Cyclohexene: 5 ml.
$CuCl_2$: 8×10^{-3} mol/l. 60°C.

Table 3. Oxidation activity and λ_{max} of copper salt-LiCl system

Catalyst	Activity	λ_{max}(mμ)
$CuCl_2$	○	—
+LiCl	○	760
Cu(acac)$_2$	×	673
+LiCl	○	710
CuF_2	×	672
+LiCl	○	674
$Cu_3(PO_4)_2 3H_2O$	×	—
+LiCl	○	780
$CuCO_3$	×	—
+LiCl	○	—
Cu-st*	×	675
+LiCl	○	770

* st: stearate

The effects of various alkali metal chlorides and lithium salts on the catalytic activity of the cupric chloride were investigated and the results are shown in Table 2. We see that the addition of magnesium chloride, sodium chloride, or potassium chloride increases the maximum quantity of absorbed oxygen and the maximum rate of oxygen absorption (R_m) as in the case of lithium chloride, but the addition of lithium fluoride, lithium bromide, lithium carbonate, and lithium nitrate has little effect. It has been reported that lithium salts, which have a considerable covalent character, have a catalytic activity for oxidation through the activation of a molecular oxygen[5] or through the homolysis of a peroxide.[6] However, in our experiments no such general effect could be seen with lithium salts except for lithium chloride as mentioned above. The order of the effect is found to be $KCl > NaCl > LiCl \fallingdotseq MgCl_2$. The greater the ionic character of the added chloride, the more effective for the oxidation. It can be said that the effect of the additives on the catalytic activity of copper salt is due to the anionic part, namely chloride ion, the activity of copper salt increasing through complex formation with chloride ions. In Table 3 the activity of various copper compounds–lithium chloride systems is shown together with the visible spectra. All copper salts tested are inactive with the exception of cupric chloride. However, oxidation takes place on addition of lithium chloride to these salts. The visible spectra of the inactive copper salts show an absorption at about 670 mμ, while the active catalyst systems containing lithium chloride have absorption in a wavelength region greater than 710 mμ The absorption seems to indicate the formation of various types of complexes. The effect of chloride ion on the catalytic activity of transition metals other than copper was also studied. In Table 4 the effect of lithium chloride on the catalytic activity of cobalt, nickel, and manganese chlorides is given. Hardly any or no effect can be seen for chlorides of other transition metals.

The accumulation of cyclohexenyl hydroperoxide in the reaction system was measured at oxygen uptake

Table 4. Oxidation of cyclohexene with MCl_2–LiCl system

Catalyst	LiCl ($\times 10^2$mol/l)	R_m ($\times 10^3$mol/l·min)
$CuCl_2$	0	2.61
	2.4	8.45
$CoCl_2$	0	12.91
	2.4	14.41
$NiCl_2$	0	1.26
	2.4	1.24
$CrCl_2$	0	1.49
	2.4	1.51
$MnCl_2$	0	3.16
	2.4	3.55

AcOH: 10 ml. Cyclohexene: 5 ml, 60°C.
[Catalyst]: 8×10^{-3}mol/l.

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5) K. Ohkubo and T. Yamabe, *Bull. Jap. Petrol. Inst.*, **12**, 123 (1970).

6) J. K. Kochi, B. M. Graybill, and M. Kurz, *J. Amer. Chem. Soc.*, **86**, 5257 (1964).

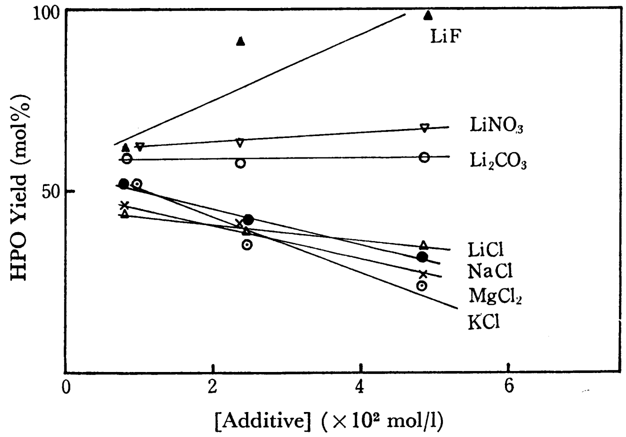

Fig. 2. Effect of additives on hydroperoxide (HPO) yield.
AcOH: 10 ml. Cyclohexene: 5 ml. $CuCl_2$: 8×10^{-3}mol/l. 60°C O_2absd: 0.136 mol/l.

of 0.136 mol/l. The results are given in Fig. 2. The addition of lithium carbonate or lithium nitrate has no effect upon the hydroperoxide yield, but in the case of various chlorides, the higher the concentration of the chloride, the lower the yield.

Product Distribution. The product distribution of the cyclohexene oxidation catalyzed by cupric chloride-lithium chloride system was investigated. Main products were cyclohexenyl hydroperoxide, cyclohexenol, and cyclohexenone. Two unknown high boiling products, I and II, were detected. Product I showed an infrared absorption at 1730 cm^{-1} due to carbonyl group and the product II at 3450 cm^{-1} due to hydroxyl group.[7] It was found that the product II contained chlorine. The relation between the product distribution at the point where the oxygen uptake amounted to 0.136 mol/l and the quantity of lithium chloride added is shown in Fig. 3. We see that as the concentration of lithium chloride increases, the yield of the hydroperoxide decreases and that of cyclohexenone increases. The higher the concentration of lithium chloride, the lower the total yield of these products and on the contrary, the higher the total yield of the unknown products; which is not shown in the figure. Thus it seems that the chloride ion is consumed by the chlorination of the reaction product.[8]

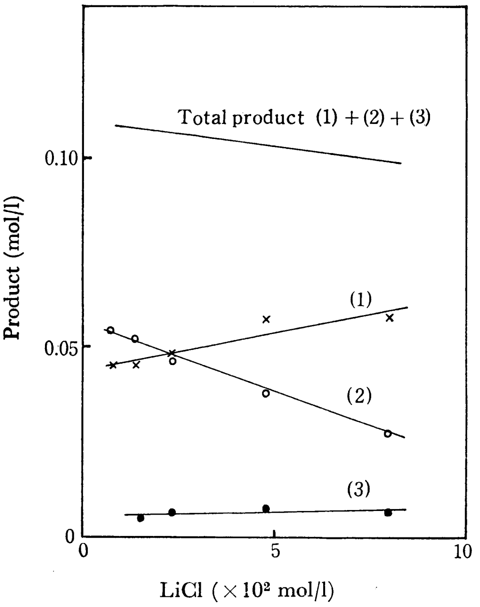

Fig. 3. Effect of LiCl on the product distribution.
AcOH: 10 ml. Cyclohexene: 5 ml. $CuCl_2$: 8×10^{-3}mol/l. 60°C O_2absd.: 0.136 mol/l. (1) Cyclohexenone, (2) Cyclohexenyl hydroperoxide, (3) Cyclohexenol.

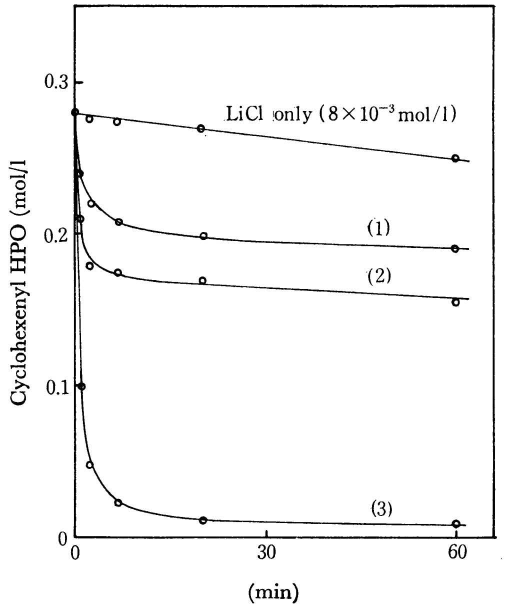

Fig. 4. Decomposition of cyclohexenyl HPO catalyzed by $CuCl_2$–LiCl.
AcOH: 10 ml. Cyclohexane: 10 ml. $CuCl_2$: 8×10^{-3}mol/l. 60°C LiCl (mol/l) (1) 0, (2) 8×10^{-3}, (3) 8×10^{-2}.

Decomposition of Cyclohexenyl Hydroperoxide Catalyzed by Cu(II)-Cl System. It was found that the addition of alkali chlorides decreased the yield of hydroperoxide, and thus the effect of lithium chloride on the decomposition of hydroperoxide catalyzed by copper salt was investigated. The result is given in Fig. 4. In this case also, lithium chloride increases the catalytic activity of the cupric chloride remarkably. Decomposition of hydroperoxide in the presence of lithium chloride alone does not proceed so much. The promotion of the catalytic activity by lithium chloride seems to be caused by the complex formation with copper. The decomposition curves resemble that of the oxidation of cyclohexene, *viz.*, retardation occurs after the decomposition of a certain amount of hydroperoxide, the colour of the solution turning from yellowish green to deep blue. The quantity of the hydroperoxide decomposed by the time retardation occurs is proportional to the concentration of lithium chloride added. It seems that lithium chloride increases the rate of decomposition of hydroperoxide and consequently increases that of oxidation.

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[7] By comparison with standard sample, substances I and II proved not to be 3-chlorocyclohexanone or 3-chlorocyclohexanol formed by the chlorination of the conjugated cyclohexenone which is one of the oxidation products. Moreover, they both did not correspond to 2-chlorocyclohexanone or cyclohexyl acetate.

[8] After the retardation occurred, chloride ion was scarcely detected in the solution with silver nitrate.

Change of the Dissolved State of the Catalyst System. In the oxidation of cyclohexene, the colour of the solution changes from yellowish green to green and finally to deep blue in the course of the reaction. Thus the visible spectra of the reaction system were observed and the effect of lithium chloride upon the change of the state of the catalyst was discussed. At the beginning of the reaction a feeble absorption is observed at 760 mμ which seems to be due to the Cu(II)–Cl complex.2) Soon after oxidation takes place, the absorption disappears and a new absorption appears at 680 mμ. From a comparison with the standard reagent, the absorption proved to be due to the cupric acetate which seemed to be formed through the ligand exchange of the catalyst with the solvent molecule, acetic acid. The time dependence of absorption is given in Fig. 5.

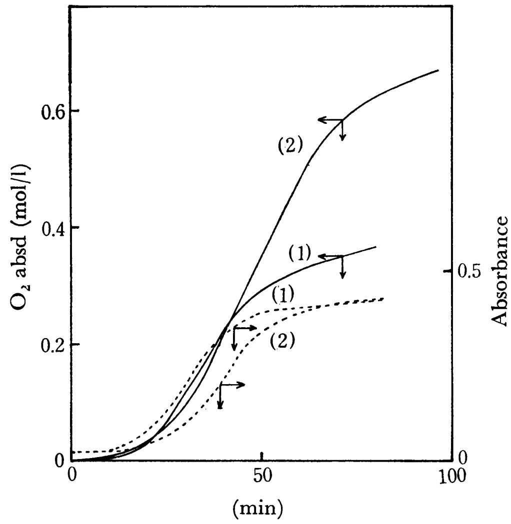

Fig. 5. Time dependence of the visible spectrum (λ_{max}=680mμ)
AcOH: 10 ml. Cyclohexene: 5 ml. $CuCl_2$: 8×10^{-3}mol/l.
60°C LiCl (mol/l) (1) 8×10^{-3}, (2) 4.8×10^{-2}.

We see that the absorbance increases during the reaction until the point where the rate of the oxidation begins to decrease and then remains constant. It seems that all the copper turns to cupric acetate at the end of the reaction. When the quantity of the lithium chloride increases, the time is lengthened at which the absorbance becomes constant [Curve (2), Fig. 5]. At the point where the catalyst became deactivated, addition of more lithium chloride recovered the activity of the system. This shows that the inactive cupric acetate is partly changed to the active Cu(II)–Cl complex. It can thus be concluded that lithium chloride contributes to maintain the activity of the catalyst and deactivation is caused by the consumption of chloride ions and the solvent molecules enter into the ligand site of the copper forming inactive cupric acetate.

Effect of the Catalyst Concentration. Dependence of the oxidation rate on the catalyst concentration was investigated. When the concentration of the copper catalyst is increased at a constant concentration of lithium chloride, R_m increases but reaches its maximum value at the concentration of copper about 2.4×10^{-2} mol/l, then remains constant [Curve (1), Fig. 6]. When the concentration of lithium chloride was made to vary at a constant concentration of copper [Curve (2)], R_m reaches the maximum value for a mole ratio of lithium to copper, *ca.* 7: 1, then begins to decrease. The concentration of the Cu(II)–Cl was made to vary at constant lithium to copper concentration of unity. It is shown that R_m also reaches the maximum value at the complex concentration of about 2.0×10^{-2} mol/l and then decreases [Curve (3)]. In all cases the maximum value of R_m is about 1.0×10^{-2} mol/l·min. From curves (2) and (3), it seemes that excess lithium chloride retards the reaction. An explanation for the phenomenon may be that excess lithium chloride blocks the active sites of the copper catalyst and prevents hydroperoxide molecules from approaching them. Another explanation may be that while the active species is $CuCl_3^-$, excess lithium chloride forms a complex of the type $CuCl_4^{2-}$9) which retards the reaction.

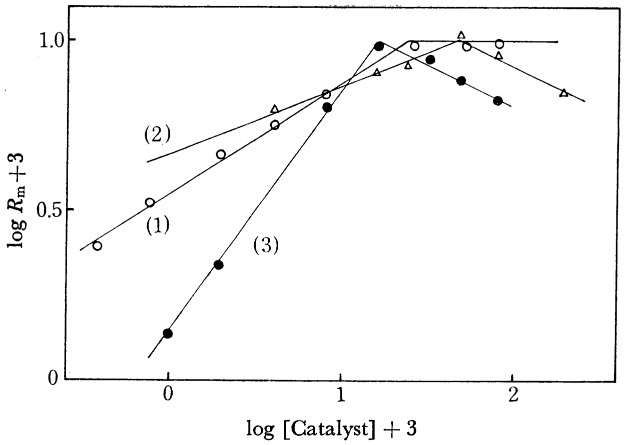

Fig. 6. R_m *vs.* catalyst concentration.
AcOH: 10 ml. Cyclohexene: 5 ml. 60°C.
(1) [$CuCl_2$] Dependence, [LiCl] 8×10^{-3}mol/l.
(2) [LiCl] Dependence, [$CuCl_2$] 8×10^{-3}mol/l.
(3) $\begin{bmatrix} CuCl_2\text{–}LiCl \\ 1 : 1 \end{bmatrix}$ Dependence

Oxidation Scheme. From the results so far obtained, the oxidation mechanism is schematically drawn as follows.

$$CuCl_2 + Cl^- \rightleftarrows CuCl_3^-\ (CuCl_4^{2-}) \qquad (1)$$

$$RH \longrightarrow R\cdot \qquad (2)$$

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (3)$$

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot \qquad (4)$$

$$ROOH + CuCl_3^-\ (CuCl_4^{2-}) \longrightarrow ROO\cdot \text{ or } RO\cdot \qquad (5)$$

$$CuCl_3^-\ (CuCl_4^{2-}) \xrightarrow[O_2,\ S]{AcOH} Cu(OAc)_2 + \text{Chlorination product} \qquad (6)$$

$$\big\downarrow Cl^-$$

$$Cu(Cl)(OAc),\ CuCl_2,\ CuCl_3^-,\ CuCl_4^{2-} \qquad (7)$$

In reaction (1) the copper salt forms a complex with chloride ions. It seems that the complex is not of a single form but a mixture of various forms. In reactions (2)—(4) cyclohexenyl hydroperoxide is formed.

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9) C. L. Jenkins and J. K. Kochi, *J. Org. Chem.*, **36**, 3103 (1971).

In reaction (5) the hydroperoxide is decomposed by the Cu(II)–Cl complex. The increase in the rate of oxidation seems to be due to the high activity of the complex to promote the step. As shown in reaction (6), during oxidation, presumably in the decomposition of hydroperoxide, some ligand exchange occurs through the chlorination of a third body (cyclohexene or its oxidation product), represented by S in reaction (6), and cupric acetate is formed causing deactivation of the catalyst system. In reaction (7) addition of alkali metal chlorides to the deactivated system restores the activity of the system.

In conclusion, it can be said that in acetic acid solvent, chloride ion increases and maintains the catalytic activity of the copper salt as its ligand.

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