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Liquid-phase Oxidation Catalyzed by Cu(II)–Cl. II. Chloride Ion Transfer during the Oxidation of Cyclohexene

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Cyclohexene was oxidized in glacial acetic acid with a Cu(II)-Cl catalyst. In addition to the main oxidation products, 3-cyclohexenyl chloride, 3-cyclohexenyl acetate, 2-chlorocyclohexanol-(1), cyclohexene oxide, and hydrogen chloride were produced. The mechanism of the formation of these compounds was investigated in detail: the deactivation of the catalyst was explained by chloride ion transfer.

Previously it has been reported that, in the liquid-phase oxidation of cyclohexene in glacial acetic acid, the catalytic activity of cupric chloride was greatly increased by the addition of various alkali chlorides which formed complexes with copper.[1] As the reaction proceeded, however, the catalyst was deactivated owing to the consumption of chloride ion, but the mechanism of this deactivation could not be elucidated fully.

In this work, we have attempted to analyze the reaction products in detail in order to explain the consumption of chloride ion during the reaction.

Experimental

3-Cyclohexenyl acetate was obtained from cyclohexenol and acetyl chloride.[2] 2-Chlorocyclohexanol-(1) was prepared by the reaction of cyclohexene with hypochloric acid[3] and trans-dichlorocyclohexane by the reaction of cyclohexene with molecular chlorine.[4] Anhydrous cupric acetate was obtained by dehydration of cupric acetate monohydrate. G. R. grade commercial *t*-butyl hydroperoxide (*t*-butyl HPO) and cyclohexene oxide were used without further purification. Other reagents were obtained and purified as described previously.[1]

The oxidation apparatus used was the same as in the previous work.[1] It was confirmed that the reactions were not controlled by the diffusion of oxygen into the liquid phase. *t*-Butyl HPO was decomposed under a nitrogen atmosphere.

The reaction products were analyzed with a Hitachi 063 Gas Chromatograph equipped with a flame ionization detector, a Hitachi 215 Infrared Spectrophotometer, and a Hitachi RMU-6L Mass Spectrometer. The conditions for the operation of the gas chromatograph were as follows: (1) Column packing—Ethylhexyl sebacate/Chromosorb 101 (5 : 1); Carrier gas-N_2 (30 ml/min); Column temperature—80∼100 °C, and (2) Column packing—Ethylhexyl sebacate (2 m); Carrier gas-N_2 (30 ml/min); Column temperature—115 °C.

Results and Discussion

Accumulation of By-products during the Oxidation of Cyclohexene. The main products were cyclohexenyl hydroperoxide (cyclohexenyl HPO), cyclohexenol, and cyclohexenone, which were analyzed as described previously.[1] In addition, 3-cyclohexenyl chloride, 3-cyclohexenyl acetate, 2-chlorocyclohexanol-(1), cyclohexene oxide, and a trace amount of trans-dichlorocyclohexane were detected in this work. However, cyclohexene oxide was detected only in the later stages of the oxidation. Fig. 1 shows the amounts of 2-chlorocyclohexanol-(1), 3-cyclohexenyl acetate, and 3-cyclohexenyl chloride formed together with the amount of oxygen absorbed. These curves all show a maximum when the rate of oxidation begins to decrease.[5] The amounts of main products formed after twenty minutes were 0.037 mol/l of cyclohexenyl HPO, 0.071 mol/l of cyclohexenone, and 0.015 mol/l of cyclohexenol. Table 1 shows the yield of 3-cyclohexenyl chloride plus 2-chlorocyclohexanol-(1) after various reaction times. From the table it may be seen that almost all the chloride ion added was transferred to organic chlorine compounds after forty to sixty minutes. Chloride ion forms complexes with cupric acetate in glacial acetic acid and increases its

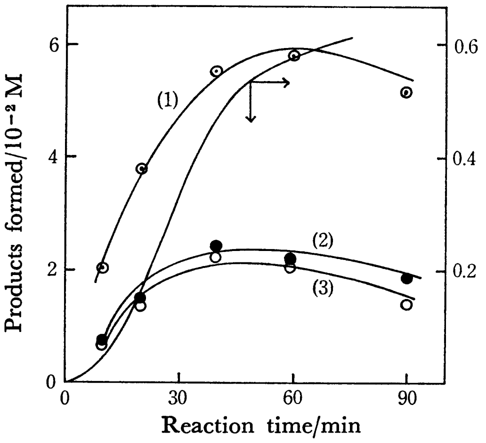

Fig. 1. Production of by-products in the oxidation of cyclohexene in glacial acetic acid at 60 °C.
$[Cu(OAc)_2]=8.1\times10^{-3}$ M; $[LiCl]=8.0\times10^{-2}$ M; [Cyclohexene] = 4.94 M
(1) 2-Chlorocyclohexanol-(1)
(2) 3-Cyclohexenyl acetate
(3) 3-Cyclohexenyl chloride

Table 1. Yield of chlorinated products in the oxidation of cyclohexene at 60 °C

Reaction time/min	[3-Cyclohexenyl chloride + 2-chlorocyclohexanol-(1)]/%[a]
10	32.8
20	63.8
40	97.6
60	98.3
90	80.0

$[Cu(OAc)_2]=8.1\times10^{-3}$ M, $[LiCl]=8.0\times10^{-2}$ M, [Cyclohexene] = 4.94 M, Solvent: AcOH, a) Based on LiCl.

TABLE 2. REACTION OF THE OXIDATION PRODUCTS WITH Cu(II)-Cl-*t*-butyl HPO IN GLACIAL ACETIC ACID AT 60 °C

Reactant (0.1 M)	[Cu(II)-Cl]/10^{-3} M[a]	*t*-Butyl HPO/M	H_2O/M	2-Chlorocyclo-hexanol-(1) /%
Cyclohexenol	8.0	0.10	0	0
Cyclohexenone	8.0	0.10	0	0
Cyclohexenyl HPO	8.0	0	0	trace
3-Cyclohexenyl chloride	8.0	0.10	0	0
3-Cyclohexenyl chloride	8.0	0.10	2.5	0
Cyclohexene	8.0	0.10	2.5	trace
trans-Dichlorocyclohexane	8.0	0.10	2.5	0

a) $Cl^-/Cu=10$

activity in the oxidation of hydrocarbons.[1,6)]

$$Cu(OAc)_2 \xrightarrow{Cl^-} Cu(OAc)Cl \xrightarrow{Cl^-} CuCl_2 \xrightarrow{Cl^-} \cdots\cdots$$

From this and the results shown in Fig. 1 and Table 1, we concluded that chloride ion transfer occurred to form these organic chlorine compounds and an inactive cupric acetate. This is the reverse of the reaction shown above. In the following sections we discuss the mechanisms of the formation of these by-products.

Formation of 3-Cyclohexenyl Acetate 3-Cyclohexenyl acetate may be formed in one of the following three possible ways. The first is an esterification of cyclohexenol, one of the oxidation products, with acetic acid.

$$ROH + AcOH \rightarrow ROAc \qquad (1)$$

R: cyclohexenyl-

The second is a chloride ion transfer oxidation of cyclohexenyl radical, an intermediate radical in the oxidation of cyclohexene, by the catalyst. This is followed by acetolysis of the resulting 3-cyclohexenyl cyloride. The chloride ion transfer to cyclohexenyl radical would occur and compete with attack by oxygen, the rate constant of which is close to the diffusion controlled limit.[7)]

$$R\cdot + Cu(II)Cl_x(OAc)_y \rightarrow RCl + Cu(I)_{x-1}(OAc)_y \qquad (2)$$

$$RCl + AcOH \rightarrow ROAc \qquad (3)$$

The third is a direct acetate ion transfer oxidation of cyclohexenyl radical.

$$R\cdot + Cu(II)Cl_x(OAc)_y \rightarrow ROAc + Cu(I)_x(OAc)_{y-1} \qquad (4)$$

To investigate the possibility of the first two mechanisms, cyclohexenol and 3-cyclohexenyl chloride were refluxed in glacial acetic acid at 60 °C. For cyclohexenol (initial concentration of 0.29 mol/l), only about 2% of 3-cyclohexenyl acetate was produced after sixty minutes. The yield of cyclohexenol in the oxidation after a reaction time of twenty minutes was about 0.014 mol/l, therefore the quantity of 3-cyclohexenyl acetate formed by esterification of cyclohexenol would be calculated to be less than $0.014\times0.02=0.00028$ mol/l. Actually the yield of 3-cyclohexenyl acetate was 0.015 mol/l after twenty minutes (see Fig. 1), so the esterification of 3-cyclohexenol can be excluded. The result for 3-cyclohexenyl chloride is shown in Fig. 2. This figure shows that the yield of 3-cyclohexenyl acetate reaches about 20% after sixty minutes. However, as shown in Fig. 1, 3-cyclohexenyl acetate accumulated from the beginning of the reaction and in almost the same amount as 3-cyclohexenyl chloride. From the results shown in Figs. 1 and 2, it seems that the formation of 3-cyclohexenyl acetate by the acetolysis of 3-cyclohexenyl chloride, although it does occur, is not the main but

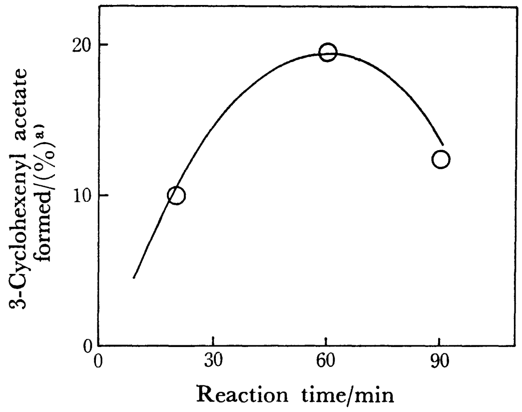

Fig. 2. Formation of 3-cyclohexenyl acetate from 3-cyclohexenyl chloride in glacial acetic acid at 60 °C. [3-Cyclohexenyl chloride] = 0.40 M
a) Based on 3-cyclohexenyl chloride

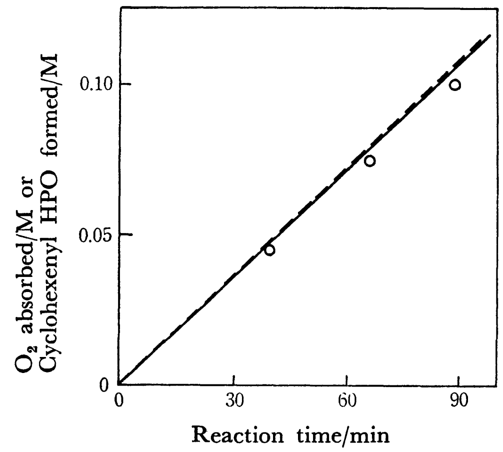

Fig. 3. Oxidation of cyclohexene initiated by azobisisobutyronitrile in glacial acetic acid at 60 °C.
---- In the absence of cupric acetate
—— In the presence of cupric acetate
○ Cyclohexenyl HPO formed
$[Cu(OAc)_2]=8.0\times10^{-3}$ M; [Azobisisobutyronitrile] = 6.0×10^{-2} M; [Cyclohexene] = 4.94 M

the side route.

Next the effect of cupric acetate on the cyclohexenyl radical in the oxidation of cyclohexene was investigated. As cupric acetate in the absence of lithium chloride was inactive in initiating the oxidation, azobisisobutyronitrile was added. Figure 3 shows that the shapes of the two oxidation curves which correspond to the reaction with and without cupric acetate are almost the same. Moreover, in the presence of cupric acetate, more than 95% of cyclohexenyl HPO was obtained, showing an inactivity of cupric acetate in decomposing the HPO. Though a trace amount of 3-cyclohexenyl acetate (less than 1.4% based on oxygen absorbed) was produced after a reaction time of ninety minutes, the yield was too low compared with that obtained in the oxidation. From these results, it appears that cupric acetate itself is inactive and does not interact with cyclohexenyl radical. However, it does not mean that the active cupric acetate-chloride ion complex, $Cu(II)Cl_x(OAc)_y$, does not transfer acetate ion. As stated earlier, because 3-cyclohexenyl acetate and 3-cyclohexenyl chloride seem to be formed in a competitive process, it is preferable to assume that 3-cyclohexenyl acetate is formed by the acetate ion transfer oxidation of cyclohexenyl radical by the active catalyst system (Eq. (4)). However, this cannot be proved using the present experimental technique.

Formation of 2-Chlorocyclohexanol-(1). We assumed that 2-cyclohexanol-(1) was formed by the chlorination of the olefinic bond of cyclohexenol or cyclohexenone with Cu(II)–Cl–HPO.[8] So these compounds were treated with cupric acetate-lithium chloride-*t*-butyl HPO and the results are shown in Table 2. Other oxidation products, together with cyclohexene, were also treated in a similar manner. As water was assumed to be produced in the oxidation, the effect of addition of it was also discussed. From the table it may be seen that chlorination of cyclohexenol or cyclohexenone did not occur. It is also seen that other compounds are not intermediates for 2-chlorocyclohexanol-(1).

Next we investigated the reaction of cyclohexene oxide, which was formed in a later stage of the oxidation, with the catalyst. From Fig. 4, we can see that cyclohexene oxide reacted rapidly with the catalyst to produce 2-chlorocyclohexanol-(1) almost quantitatively (based on lithium chloride added) after twenty minutes. This indicates that chloride ion transfer from the catalyst to cyclohexene oxide is the main route leading to 2-chlorocyclohexanol-(1). As the chlorination shown above proceeded rapidly, cyclohexene oxide could not be detected in the early stages of the oxidation when the catalyst still had active chloride ion.

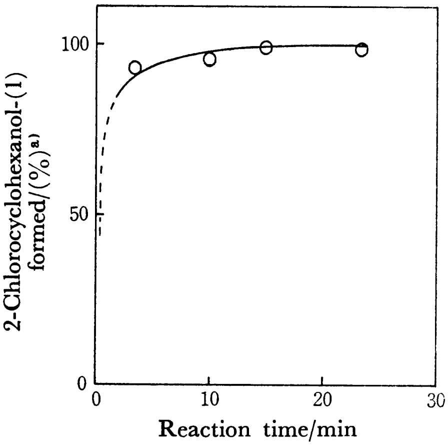

Fig. 4. Reaction of cyclohexene oxide with Cu(II)–Cl in glacial acetic acid at 60 °C.
$[Cu(OAc)_2]=8.6\times10^{-3}$ M; $[LiCl]=8.2\times10^{-2}$ M; [Cyclohexene oxide]=0.11 M
a) Based on LiCl

Formation of Hydrogen Chloride. As shown in Fig. 1 and Table 1, the total quantity of chloride ion in the chlorinated products had a maximum value during the reaction, that is, in the later stages of the reaction it became less than that added initially as lithium chloride. As no other chlorinated products were detected, it was assumed that chloride ion was transferred to hydrogen chloride. Therefore cyclohexene was oxidized by Cu(II)–Cl (Cu : Cl=1 : 50) and the gaseous products were analyzed. As was expected, a considerable amount of hydrogen chloride, which was not measured, was detected by the gas chromatograph in the later stages of the oxidation.[9]

Mechanism of Chloride Ion Transfer. From the results obtained so far, the mechanism of the chloride ion transfer from the catalyst can be summarized as follows.

$$Cu(OAc)_2 + Cl^- \rightarrow CuCl_x(OAc)_y \tag{5}$$

$$RH \rightarrow R\cdot \xrightarrow{O_2} ROO\cdot \tag{6}$$

$$ROO\cdot + RH \rightarrow ROOH + R\cdot \tag{7}$$

$$ROOH + CuCl_x(OAc)_y \rightarrow \text{radicals} \tag{8}$$

$$ROO\cdot + RH \rightarrow \text{Cyclohexene oxide} + RO\cdot \tag{9}$$

$$\text{Cyclohexene oxide} + CuCl_x(OAc)_y \xrightarrow{H^+} \text{2-Chlorocyclohexanol-(1)} + CuCl_{x-1}(OAc)_y \tag{10}$$

$$R\cdot + CuCl_x(OAc)_y \rightarrow RCl + CuCl_{x-1}(OAc)_y \tag{2}$$

$$RCl + AcOH \rightarrow ROAc + HCl \tag{3}$$

$$R\cdot + CuCl_x(OAc)_y \rightarrow ROAc + CuCl_x(OAc)_{y-1} \tag{4}$$

In the first step cupric acetate forms complexes with chloride ion. (Eq. (5)) Equations (6) and (7) are the propagation steps. In Eq. (8) cyclohexenyl HPO is decomposed by the catalyst and the active radicals are formed. Cyclohexene oxide would be produced by the reaction of cyclohexenylperoxy radical with cyclohexene (Eq. (9)),followed by chloride ion transfer to give 2-chlorocyclohexanol-(1). (Eq. (10)) In Eq. (2) the ligand transfer oxidation of cyclohexenyl radical occurs and 3-cyclohexenyl chloride is formed. A part of the 3-cyclohexenyl chloride formed suffers an acetolysis by acetic acid to give 3-cyclohexenyl acetate. (Eq. (3)) Hydrogen chloride produced in this process partly diffuses into the gas phase and partly remains in the liquid phase to form complexes with copper again. The acetate ion transfer oxidation of cyclohexenyl radical (Eq. (4)) should occur as the main route for the formation of 3-cyclohexenyl acetate, although this could not be confirmed in this work.

The deactivation of the catalyst occurs by the chloride ion transfer as shown by Eqs. (2) and (10) to form inactive cupric acetate. The direct chlorination of the olefinic bonds of cyclohexene or its oxidation products[8] does not proceed owing to the presence of cyclohexene oxide or cyclohexenyl radical which reacts with the catalyst more rapidly than those compounds.

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References

1) S. I. Imamura, T. Banba, and Y. Takegami, This Bulletin, **46**, 856 (1973)

2) K. Richter, *J. Prakt. Chem.*, **111**, 385 (1925).

3) H. Gilman, "Organic Syntheses", Coll. Vol. I, p. 158 (1956).

4) B. Carroll, D. G. Kubler, H. W. Davis and A. M. Whaley, *J. Amer. Chem. Soc.*, **73**, 5382 (1951).

5) It was found that 3-cyclohexenyl acetate was unstable toward Cu(II)–Cl–HPO and decomposed to some unknown compounds with lower boiling points. This seems to lower its yield in the later stages of the reaction.

6) S. I. Imamura, T. Sumi, M. Teramoto, and Y. Takegami, Proceedings of the sixth Symposium on Oxidation, Tokyo, p. 54 (1972).

7) C. L. Jenkins and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 856 (1972).

8) Chlorination of olefins by Cu(II)–Cl was found to be markedly accelerated in the presence of HPO. For example, cyclohexene was chlorinated almost quantitatively to produce trans-dichlorocyclohexane by Cu(II)–Cl–*t*-butyl HPO under a nitrogen atmosphere at 30 °C. A detailed investigation of this phenomenon is under way.

9) A Hitachi 063 Gas Chromatograph equipped with a thermal conductivity detector was used.