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Liquid Phase Chlorination of Olefins with Cupric Chloride. III. Effect of Additives and Kinetics

Takashi KOYANO and Osamu WATANABE
Central Research Laboratory, Toa Nenryo Kogyo Co., Oi-machi, Iruma-gun, Saitama

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Chlorination of 1-octene with cupric chloride has been investigated in methanol at 110—130°C. The yield of 1,2-dichlorooctane (I) increased by addition of lithium chloride in the reaction mixture, while that of 1-chloro-2-methoxyoctane (II) decreased. Addition of water and cuprous chloride markedly retarded the reaction. The initial rates of formation of I and II could be expressed as $v=k[\text{octene}]_0\ [\text{CuCl}_2]_0^{1.6}$ and $v=k[\text{octene}]_0\ [\text{CuCl}_2]_0$, respectively. These results can be explained as an initial formation of a complex between olefin and cupric chloride molecule, followed by competitive attack on the complex by chloride ion and methanol. In the less polar reaction media containing more octene, the ratio of I/II increased. This may be ascribed to the steric effect of cupric chloride in the intermediate.

In our previous investigations on the mechanism of chlorination of olefins with cupric chloride in liquid phase, the initial formation of an open-type cationic intermediate by electrophilic addition of cupric chloride to the olefin and the succeeding competitive attacks on the intermediate by the second chlorinating species and the solvent have been suggested.[1,2] However, the nature of this second chlorinating agent has not been clarified and we have continued the study in order to understand the reaction thoroughly. This paper reports the effect of additives on product composition and the kinetic results for the reaction of octene in methanol.

Results

All reactions were carried out by a sealed tube technique. Octene was selected as the olefin because of its relatively low vapor pressure at the reaction condition and convenience in analysis of the products by gas chromatography. The products consised of 1,2-dichlorooctane (I) and 1-chloro-2-methoxyoctane (II). Effects of reaction medium and added lithium chloride on the product composition are shown in Table 1.

The product composition is subject to the influence of cupric chloride concentration and the products ratio I/II decreases as the reaction progresses.[1] This can be predicted from the different rate orders in cupric chloride for the formations of I and II. Therefore, the data should be compared at the same conversion of cupric chloride, when the effects of environment on the products ratio are discussed. The rate of methanolysis of I or II is sufficiently small even in the presence of cupric chloride under the reaction conditions and can be ignored.

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[1] T. Koyano, This Bulletin, **43**, 1439 (1970).
[2] T. Koyano, *ibid.*, **43**, 3501 (1970).

TABLE 1. EFFECT OF ADDITIVES

MeOH (vol%)	Octene (vol%)	Solvent (vol%)	LiCl (mol/*l*)	Time (hr)	Conversion ($CuCl_2$ %)	Products ratio I/II
90	10			1	8.4	1.29
				1.5	11.4	1.16
				2	13.6	1.07
				2.5	15.6	0.96
				3	17.3	0.86
98	2			3	8.9	1.11
95	5			3	13.3	0.99
85	15			1.5	13.3	1.17
80	20			1	11.1	1.36
75	25			1	13.6	1.40
90	5	H_2O 5		3	12.4	1.25
90	5	*n*-C_7H_{16} 5		3	11.5	1.16
90	10		0.1	3	32.8	2.95
			0.2	3	43.4	10.63
			0.4	3	54.7	34.71
			0.6	3	59.5	61.50
0	10	EtOH 90		3	17.1	1.32[a]

$CuCl_2$ 0.20 mol/*l*, 125°C

a) ratio of dichloride/ethoxychloride

Increase of octene content in the reaction solution increased the portion of I in the products. However, the conversion was not increased linearly in proportion to the octene content, probably due to marked retardation effect of cuprous chloride formed as well as to instability of the intermediate cationic complex in less polar media. Partial replacement of octene by heptane reduces the rate but the ratio I/II is the same as that in the case of octene without heptane. Thus, the effect of octene except for the action as a reactant resembles that of heptane, which means that it seems to be related to polarity of the solution.

Addition of water retarded the reaction. In discussing the product composition of this case, a possibility of nucleophilic attack of water may also have to be taken into account, although no apparent peaks of hydroxylic compounds were observed in the gas chromatogram and no hydroxylic products have been reported in the reactions with styrene in the presence of hydrated or added water.[3-5]

A comparatively large I/II ratio in ethanol solvent reaction can be attributed to its low polarity, although steric disadvantage of ethanol as an attacking agent at the reaction center should also be duly considered. It should be noted that steric inhibition is not important in the chlorination of ethylene.[6]

When lithium chloride was added in the reaction system, both the conversion of cupric chloride and the ratio I/II increased considerably with the amount of the salt. It is noteworthy that, in contrast to the striking increase in yield of I, that of II decreased; *i.e.*, on additions of lithium chloride in 0, 0.1, 0.2, 0.4, and 0.6 mol/*l*, the yields of II were 9.3, 8.3, 3.7, 1.5, and 1.0% on the basis of cupric chloride.

The reaction was followed by titrating cuprous chloride formed. Since the reaction was inhibited significantly by the presence of cuprous chloride, the rates were expressed by initial rates in order to avoid complication as made by Walling[7] and Uemura *et al.*[5] The results are given in Table 2.

TABLE 2. RATE OF REACTION

Temp. (°C)	Octene (mol/*l*)	$CuCl_2$ (mol/*l*)	Additive (mol/*l*)	$v_1 \times 10^6$	$v_2 \times 10^6$
110	0.200	0.305		0.44	0.23
		0.500		0.92	0.36
		0.692		1.54	0.53
120	0.191	0.085		0.09	0.13
		0.100		0.13	0.16
		0.202		0.44	0.34
		0.497		1.79	0.80
		0.619		2.78	1.11
	0.212	0.195	*n*-C_8H_{18} 0.394	0.40	0.28
	0.401	0.195	*n*-C_8H_{18} 0.200	0.68	0.51
	0.600	0.195		1.02	0.77
	0.597	0.256		1.36	0.80
		0.325	CuCl 0.063	0.28	0.84
		0.325	CuCl 0.063 LiCl 0.061	0.82	0.94
		0.323		1.78	0.98
125	0.204	0.119		0.35	0.41
		0.201		0.80	0.71
		0.484		3.28	1.58
130	0.204	0.110		0.61	0.74
		0.208		1.81	1.27
		0.480		6.17	2.48
		0.658		9.72	3.58

v_1: initial rate of formation of I (mol/*l* sec)

v_2: initial rate of formation of II (mol/*l* sec)

In changing octene concentration, a suitable amount of *n*-octane was added to compensate the change of solvent polarity. The rate of formation of I was approximately 0.9 th order and that of II was 1st order in octene. Hence the initial rates may be expressed by the following equations, where v_1 and v_2 are the initial rates for I and II, respectively, and k_1 and k_2 are the corresponding rate constants.

$$v_1 = k_1[\text{octene}]_0[\text{CuCl}_2]_0{}^m \qquad (1)$$

$$v_2 = k_2[\text{octene}]_0[\text{CuCl}_2]_0{}^n \qquad (2)$$

Terms concerned with cuprous chloride, water and other additives can be excluded from these equations when these materials are not present in the initial step of reaction. Plots of log v_1 and log v_2 *vs.* log $[\text{CuCl}_2]_0$ show straight lines at each temperature. From the slopes of the lines m and n were calculated and the results are summarized in Table 3 together with the corresponding k_1, k_2, and entropies of activation. Energies of activation were calculated to be 29.9 kcal/mol for I and 29.0 kcal/mol for II.

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[3] K. Ichikawa, S. Uemura, T. Hiramoto, and Y. Takagaki, *Kogyo Kagaku Zasshi*, **71**, 1657 (1968).

[4] S. Uemura, T. Hiramoto, Y. Takagaki, and K. Ichikawa, *ibid.*, **72**, 2390 (1969).

[5] S. Uemura, Y. Takagaki, and K. Ichikawa, *ibid.*, **72**, 2577 (1969).

[6] T. Koyano, K. Kaneko, and O. Watanabe, *ibid.*, **74**, 211 (1971).

[7] A. Lorenzini and C. Walling, *J. Org. Chem.*, **32**, 4008 (1967).

TABLE 3. KINETIC RESULTS

Temp. (°C)	m	n	$k_1\times10^5$ (l^m/mol^m ·sec)	$k_2\times10^5$ (l/mol ·sec)	$\varDelta S_1$ (e.u.)	$\varDelta S_2$ (e.u.)
110	1.6	1.0	1.32	0.38	−3.3	−8.2
120	1.7	1.1	3.23	0.98	−3.6	−8.2
125	1.6	1.0	5.04	1.55	−3.7	−8.3
130	1.6	0.9	9.29	2.56	−3.4	−8.2

$\varDelta S_1$: entropy of activation for formation of I
$\varDelta S_2$: entropy of activation for formation of II

Discussion

The decrease in absolute yield of II which took place when lithium chloride was added strongly suggests that the amount of certain active species responsible for formation of II decreased in the reaction mixture. Since the concentration of methanol did not change practically in these instances, another factor, *viz.*, the concentration of cupric chloride molecule integrated over the reaction time, must have decreased. Nevertheless, the yield of I increased. Thus, it should be assumed that the second chlorinating species for I differs from cupric chloride molecule and increases on addition of lithium chloride. Chloride ion might be such a reactive species. If this is true, the reactions are represented by the following rate equations.

$$v_1 = k_1[\text{octene}][\text{CuCl}_2][\text{Cl}^-] \qquad (3)$$

$$v_2 = k_2[\text{octene}][\text{CuCl}_2][\text{MeOH}] \qquad (4)$$

Cupric chloride molecule exists probably as a distorted octahedral complex in methanol solution, and replacement of the coordinating methanol with the olefin is indispensable for initiation of the reaction. However, addition of water decreases the concentration of cupric chloride molecule by substituting chlorine in the complex as a result of its high coordinating power.[8] Water can also substitute the coordinating methanol. Since water is not so readily replaced by an olefin, a much weaker ligand, initial formation of the reaction intermediate complex should be seriously hindered.

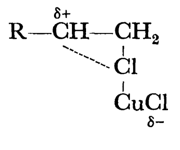
$$\text{CuCl}_2(\text{MeOH})_4 \xrightleftharpoons{\text{olefin}} [\text{CuCl}_2\cdot\text{olefin}](\text{MeOH})_3 \longrightarrow \text{reaction}$$

$$\uparrow\downarrow \text{H}_2\text{O}$$

$$[\text{CuCl}(\text{H}_2\text{O})(\text{MeOH})_4]^+\text{Cl}^- \text{ (inactive)}$$

$$\text{CuCl}_2(\text{H}_2\text{O})(\text{MeOH})_3 \text{ (less active)}$$

When the solution becomes less polar by increasing addition of octene, dissociation of cupric chloride should become less favorable and the concentration of chloride ion smaller. However, experimental results were contrary to those predicted from the chloride ion concentration. Therefore, in these cases, the ratio of k_1 to k_2 must have changed and overshadowed the change of chloride ion concentration.[11] A possible interpretation is that the charge separation between Cl–CuCl is disadvantageous in less polar solvents and Cl–CuCl bond becomes tighter, that is, more bulky around the cationic center in the intermediate complex.



This assumption is in line with the explanation for stereochemical behavior in the chlorination of inner olefins by cupric chloride.[2] Then, the attack of methanol is more restricted than that of chloride ion. The smaller entropy of activation, although the difference was not remarkable, favors the view that the activation complex for the formation of II is more crowded than the one for the formation of I and the attack of methanol is more sensitive to steric factors.

The formation of I was 1.6th order in cupric chloride added while that of II followed 1st order kinetics. The lower rate order for II indicates that major part of II was not formed by methanolysis of I, but directly through a different route. This kinetic observation is another evidence for the competitive reactions.

It is interesting that Uemura *et al.* reported the rate order in chlorination of styrene was 1.8th order in cupric chloride in 1-propanol solution.[5] If the chlorination takes place by the action of one mole of cupric chloride molecule and one mole of chloride ion, the reaction order must be much smaller than 2 in cupric chloride added, $[\text{CuCl}_2]_0$. On the other hand, the rate would be approximately proportional to $[\text{CuCl}_2]_0^2$, if two moles of cupric chloride molecules participate in the reaction. This may be evident when the concentrations of cupric chloride molecule and chloride ion are expressed in terms of $[\text{CuCl}_2]_0$, and Eqs. (3) and (5), are rewritten:[12]

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[8] According to the spectrochemical series,[9] ligand field splitting increases in the following order. In fact, the order of ligand
$\text{Cl}^- < \text{ROH} < \text{H}_2\text{O}$
field strength toward Cu^{2+} has been shown to be EtOH $<$ H_2O[10]

[9] L. E. Orgel, "An Introduction to Transition Metal Chemistry (Ligand Field Theory)," Methuen Co., London (1960), p. 96.

[10] N. J. Friedman and R. A. Plane, *Inorg. Chem.*, **2**, 11 (1963).

[11] If the formation of I is explained by the attack of 2 moles of cupric chloride molecules, the tendency can be understood by considering the change in concentration of cupric chloride molecule. However, this possibility can be denied for several reasons given in this paper.

[12] For the sake of simplification, assume that the dissociation of CuCl_2 in methanol is only of the type

$$\text{CuCl}_2 \rightleftharpoons \text{CuCl}^+ + \text{Cl}^-$$

$$K = \frac{[\text{CuCl}_2]}{[\text{CuCl}^+][\text{Cl}^-]}$$

Concentrations of $[\text{Cl}^-]$ and $[\text{CuCl}_2]$ are calculated to be

$$[\text{Cl}^-] = \frac{1}{2K}(\sqrt{4KC_0+1}-1)$$

$$[\text{CuCl}_2] = \frac{1}{4K}(\sqrt{4KC_0+1}-1)^2$$

where C_0 is the formal concentration of CuCl_2.
Then,

$$v_1' = k'[\text{CuCl}_2][\text{Cl}^-] = \frac{k'}{8K^2}(\sqrt{4KC_0+1}-1)^3$$

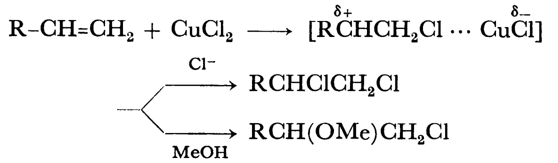
$$v_1'' = k''[\text{CuCl}_2]^2 = \frac{k''}{16K^2}(\sqrt{4KC_0+1}-1)^4$$

From the fact that the formation of II is 1st order in $[\text{CuCl}_2]_0$, $(\sqrt{4KC_0+1}-1)$ could be simplified as $\sqrt{4KC_0}$. Then, we have as first approximation

$$v_1' \propto C_0^{3/2}, \qquad v_1'' \propto C_0^2$$

$$v_1 = k_1'[\text{octene}][\text{CuCl}_2]^2 \qquad (5)$$

Our results seem to fit the former case. Thus, we presume that the chlorination occurs mostly by attack of chloride ion[13] on the intermediate complex formed between cupric chloride molecule and olefin. Possibility of participation of other anionic species such as CuCl_3^- and CuCl_4^{2-} can not strictly be ruled out. However, such species are supposed to be less nucleophilic because of their anionic charge dispersion over large molecules and also sterically less advantageous as compared to chloride ion. Then, the overall reaction sequence is represented by the following scheme, the second steps being rate-determining.



$$\text{R-CH=CH}_2 + \text{CuCl}_2 \longrightarrow [\overset{\delta+}{\text{R}}\text{CHCH}_2\text{Cl}\cdots\overset{\delta-}{\text{Cu}}\text{Cl}] \begin{cases} \xrightarrow{\text{Cl}^-} \text{RCHClCH}_2\text{Cl} \\ \xrightarrow[\text{MeOH}]{} \text{RCH(OMe)CH}_2\text{Cl} \end{cases}$$

Addition of cuprous chloride suppressed the reactions significantly. If all the added cuprous chloride form one to one complexes with cupric chloride[14] and the complexes are inert or at least far less reactive than cupric chloride itself,[7] active cupric chloride concentration would be 0.262 mol/*l* in our experiment. Therefore, v_1 should be larger than that in the case of cupric chloride concentration at 0.256 mol/*l*. However, v_1 was five times smaller while v_2 was slightly larger than those expected. These results indicate that the main reason for the decrease of v_1 is other than the decrease of cupric chloride molecule. A plausible explanation is that chloride ion plays an important role in the formation of I and the concentration of chloride ion decreased by complex formation with cuprous chloride. Although the complex Cu_2Cl_3 may actually exist in the reaction solution, the predominant cuprous chloride complexes would still be CuCl_2^- and CuCl_3^{2-}.[14]

The fact that existence of oxygen is disadvantageous for the formation of dichloride has been interpreted by the same sort of consideration, *i.e.*, the decrease of chloride ion.[6]

Addition of lithium chloride together with cuprous chloride did not compensate the retardation completely. A fairly large portion of lithium chloride seems to exist undissociated in the reaction solution.

Experimental

Materials. 1-Octene (Schuchardt, München) was dried over Na_2SO_4 and distilled under N_2 before use, which was gas-chromatographically pure. Methanol (GR, Koso Chemical Co.) was distilled from Mg(OMe)_2 under N_2. Anhydrous cupric chloride and lithium chloride were of GR grade (Koso). Cuprous chloride was prepared by the reduction of cupric chloride with sodium sulfite under N_2[15]. 1,2-Dichlorooctane was prepared by the chlorination of 1-octene with sulfuryl chloride in the presence of benzoyl peroxide[16] (bp 67—68°C/4 mmHg). 1-Chloro-2-methoxyoctane was synthesized by the action of *t*-butyl hypochlorite on 1-octene in methanol.[17]

Analytical Methods. Cupric chloride was determined by iodometry.[1] Cuprous chloride was titrated with 0.1 N ceric ammonium sulfate solution using ferroin as an indicator.[18,19] The reaction products were analyzed by gas chromatography. Conditions (apparatus, column, temperature and carrier gas): (A). Shimadzu GC-4APT, Apiezon L on Chromosorb W, 150°, He; (B). Shimadzu GC-5F, Silicone DC-200 on Diasolid L, 160°, N_2.

Procedure. In each 15 m*l* sealed tube was placed 10 m*l* of the prescribed reaction mixture under N_2. After an appropriate period of heating in a constant temperature bath (±0.05°C) the sealed tube was taken out and cooled in ice-water. The reaction solution was subjected to gas chromatography. All the solution was then poured into 10 m*l* of 0.1 M ferric ammonium sulfate solution (in 3 M H_2SO_4) and the cuprous ion was titrated with a standard ceric solution. Since the products practically consisted of only I and II, the amount of consumed cupric chloride was divided between I and II in the proportion of the analytical result by gas chromatography, and the amounts of formation were calculated.[20] The rate of reaction was very sensitive to retardation caused by the products. Therefore, the initial rate of formation was conveniently calculated by reading the reaction time at 2% conversion from the time-conversion plot.

Methanolysis of I. A 10 m*l* solution of I (0.114 mol/*l*) with CuCl_2 (1.0 mol/*l*) in MeOH was heated at 120°C in a 15 m*l* glass sealed tube. After 13 hr a trace of II was detected in the solution, and after 19.5 hr 1.6% of I was converted to II.

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[13] or a loosely connected ion pair, *e.g.*, a solvent separated ion pair.

[14] H. McConnell and N. Davidson, *J. Amer. Chem. Soc.*, **72**, 3168 (1950).

[15] R. N. Keller and H. D. Wycoff, "Inorganic Syntheses," Vol. II, ed. by W. C. Fernelius, McGraw-Hill Book Co., New York (1946), p. 1.

[16] M. S. Kharasch and A. F. Zavist, *J. Amer. Chem. Soc.*, **73**, 964 (1951).

[17] C. F. Irwin and G. F. Hennion, *ibid.*, **63**, 858 (1941).

[18] I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience, New York (1957), p. 121.

[19] L. F. Hatch and R. R. Estes, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 136 (1946).

[20] One mole of either product is assumed to be formed by the consumption of two moles of cupric chloride.