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Liquid Phase Chlorination of Olefins with Cupric Chloride

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Reactions of olefins with cupric chloride were studied in methanol at 100—140°C. The reactivity of olefins was in the order, ethylene>propylene>1-butene>2-butenes. A considerable amount of 1-chloro-2-methoxy compounds were found in the reaction products of 1-olefins. Competitive formation of dichloride and methoxychloride was suggested. Chlorination of 2-butenes leads to *meso*- and *dl*-2,3-dichlorobutanes, their ratio being invariable regardless of the starting material *cis*- or *trans*-2-butene. The mechanism is discussed in terms of ionic intermediates.

Although there are a number of investigations on the chlorination of unsaturated organic compounds by cupric chloride, the mechanism of the reaction is somewhat ambiguous. For the liquid phase chlorination of aromatic compounds a polar mechanism[1] or a mechanism involving homolytic decomposition of the π-complex between cupric chloride and the aromatic compound[2] has been proposed. Chlorination of alkenes in the vapor phase has been accepted to proceed through chloronium ion intermediates.[3] However, participation of both radical and ionic mechanisms has recently been demonstrated.[4]

Only a few reports have appeared on the chlorination of simple olefins in liquid phase. Although the photo-induced chlorination of olefinic compounds was noted earlier,[5] the thermal chlorination in aqueous phase was not reported until 1967.[6] Recently, the reaction in alcoholic media has been described in some detail.[7] However, efforts have been concentrated mostly on reaction with styrene and interpretation for the reaction with alkene is not conclusive.

We found that a considerable amount of methoxychloride is formed in addition to the anticipated dichlorides in the chlorination of alkenes in methanol. The object of this paper is to elucidate the mechanism of this type of reaction. A detailed description from the synthetic point of view will be presented later.

Results and Discussion

Several simple olefins were allowed to react with cupric chloride in methanol at 120°C (Table 1). The reactivity based on the conversion of cupric chloride was in the order, ethylene>propylene>

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[1] J. C. Ware and E. E. Borchert, *J. Org. Chem.*, **26**, 2263, 2267 (1961).

[2] D. C. Nonhebel, *J. Chem. Soc.*, **1963**, 1216.

[3] R. P. Arganbright and W. F. Yates, *J. Org. Chem.*, **27**, 1205 (1962)

[4] P. P. Nicholas and R. T. Carroll, *ibid.*, **33**, 2345 (1968).

[5] J. K. Kochi, *J. Amer. Chem. Soc.*, **84**, 2121 (1962).

[6] M. L. Spector, H. Heinemann and K. D. Miller, *Ind. Eng. Chem., Process Des. Develop.*, **6**, 327 (1967).

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

TABLE 1. REACTION OF OLEFINS

Olefin	(mol)	$CuCl_2$ (mol)	Conversion ($CuCl_2$ %)	Product(mmol) A	B	C
C_2H_4	0.90	0.10	84.7	8.8	30.3	1.3
	1.47	0.20	98.5	33.6	57.3	1.6
	0.86	0.30	93.7	55.2	72.8	2.8
C_3H_6	0.92	0.20	90.0	31.8	34.9	trace
1-C_4H_8	0.65	0.20	72.1	27.6	19.5	trace
cis-2-C_4H_8	0.55	0.20	64.9	34.5*	0.9	0
trans-2-C_4H_8	0.67	0.20	57.0	42.6**	1.7	0

Ta autoclave reaction, MeOH 120 m*l*, 120°C, 3 hr
Product (RCHXCHYR′)
A: X=Cl, Y=Cl; B: X=Cl, Y=OMe;
C: X=OMe, Y=OMe
* *meso* 63.4%, *dl* 36.6%
** *meso* 65.5%, *dl* 34.5%

1-butene>2-butenes. This is in line with the facility of complex formation of the olefins with silver ion.[8] This suggests initial formation of olefin-copper complex such as acetylene-copper(II) complex speculated by Castro,[9] rather than olefin-chlorine complex deduced by Arganbright in the vapor phase reaction.[3]

Considerable amounts of methoxy compounds were found in the products. In the reaction of ethylene the ratio of 1,2-dichloroethane (I) to 2-chloroethyl methyl ether (II) increases with increase in the amount of cupric chloride present. This may be interpreted by assuming competitive reactions of the intermediate with chloride ion[10] and with methanol, in sharp contrast to the styrene chlorination reported by Ichikawa[7] where a consecutive reaction has been claimed. Although methanolysis of I is accelerated by the presence of cupric chloride (Table 2), the rate is too small to explain the present data. Since the rate of methanolysis of I is not greater than that of II (Table 3), a simple calculation for the consecutive first order reactions clearly shows that the formation of II by methanolysis should be much less than that actually obtained.[11] In accordance with this, a fairly large quantity of II was produced in the reaction at 100°C, whereas no 1,2-dimethoxyethane (III), which is presumed to be produced exclusively by methanolysis, was detected in the products (Table 4). This means that the methanolysis of I is negligible at this temperature and II is formed through a different route. As is expected, addition of chloride ion favors the formation of I significantly.

A tendency for the ratio of I/II to be larger in the lower temperature reaction may be ascribed to the lower conversion of cupric chloride, *viz.*, the products consist of only those formed at the higher cupric chloride concentration. The fact

TABLE 2. EFFECT OF $CuCl_2$ ON METHANOLYSIS OF I

$CuCl_2$ (mmol)	CuCl (mmol)	Yield (%) I	II	III
25	0	88.6	3.0	0
12	12	94.2	1.7	0
4	20	90.9	1.1	0
0	25	89.6	0.7	0

Test tube reaction, I 12 mmol, MeOH 10 m*l*, 140°C, 3 hr

TABLE 3. METHANOLYSIS OF I AND II

Reactant	Additive (mmol)	Yield (%) I	II	III
I	none	67.5	19.3	5.9
	ZnO 60	41.6	22.3	27.9
II	none	—	61.0	32.1
	ZnO 30	—	34.2	59.4

Sealed tube Reaction, I or II 50 mmol, MeOH 25 m*l*, 180°C, 6 hr

TABLE 4. REACTION OF ETHYLENE

Temp. (°C)	Additive	Conversion ($CuCl_2$ %)	Product (mmol) I	II	III
100		25.1	2.19	1.22	0
120		66.2	4.46	3.91	0.07
140		92.3	5.82	5.85	0.17
	Air*	72.7***	6.04	6.15	0.29
	LiCl**	84.4	7.29	3.17	0.09
160		98.0	5.45	5.21	0.65
180		100.0	4.18	3.54	1.45

Test tube reaction, C_2H_4 50 kg/cm^2, MeOH 10 m*l*, $CuCl_2$ 25 mmol, 3 hr
* 25 kg/cm^2
** 20 mmol
*** Assuming that one mole of the product is formed by use of two moles of $CuCl_2$, the total selectivity of products based on $CuCl_2$ is 140%.

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[8] M. A. Bennet, *Chem. Rev.*, **62**, 612 (1962).

[9] C. E. Castro, E. J. Gaughan and D. C. Owsley, *J. Org. Chem.*, **30**, 587 (1965).

[10] Although the real attacking species on the intermediate to form I is not fully clear at this stage, its concentration should be higher with the higher cupric chloride concentration due to equilibria in the system.

$$Cu^{++} + Cl^- \rightleftharpoons CuCl^+$$
$$CuCl^+ + Cl^- \rightleftharpoons CuCl_2$$
$$CuCl_2 + Cl^- \rightleftharpoons CuCl_3^-$$

[11] In the consecutive first order reactions,

$$A \xrightarrow{k_1} B \xrightarrow{k_1'} C$$

the equation $\ln([A]_0/[A])=[B]/[A]$ can be derived when $k_1=k_1'$. However, 0.37 $[A]_0$ is the largest possible solution of [B] for this equation, and [C] should be 0.27 $[A]_0$ in this case. When $k_1<k_1'$, $[B]=0.5\ [A]_0$ can not satisfy the equations given in literature.[12]

[12] W. J. Moore, "Physical Chemistry," 3rd Ed., Prentice-Hall Inc., Englewood Cliffs, N. J. (1962), p. 266

Table 5. Effect of reaction time on products ratio

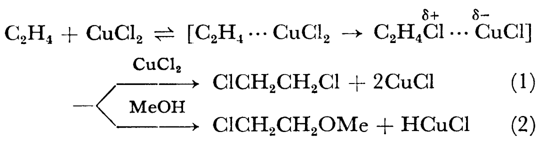
Time (hr)	Conversion ($CuCl_2$%)	Yield(mmol) I	Yield(mmol) II	Net Yield* (mmol) I	Net Yield* (mmol) II	II/I
0.5	24.8	12.1	12.2	12.1	12.2	1.01
1.0	40.5	18.3	21.3	6.2	9.1	1.47

Ta autoclave reaction, C_2H_4 0.55 mol (charged at the reaction temperature), MeOH 120 m*l*, $CuCl_2$ 0.20 mol, 100°C

* Yield of products during the initial and the following 30 min.

that the ratio is larger in the earlier stage of reaction at a temperature is also attributable to the same reason (Table 5).

These observations can be rationalized by the following mechanism.



$$C_2H_4 + CuCl_2 \rightleftharpoons [C_2H_4\cdots CuCl_2 \rightarrow \overset{\delta+}{C_2H_4Cl}\cdots\overset{\delta-}{CuCl}]$$

$$\xrightarrow{CuCl_2} ClCH_2CH_2Cl + 2CuCl \qquad (1)$$

$$\xrightarrow{MeOH} ClCH_2CH_2OMe + HCuCl \qquad (2)$$

$$HCuCl + CuCl_2 \rightarrow 2CuCl + HCl \qquad (3)$$

The olefin-copper complex initially formed is transformed into a cationic chlorine complex[13] which is the common intermediate for the formations of dichloride[14] and methoxychloride. Evidence for an ionic intermediate comes from the fact that the products from 1-butene consist of only both 1,2-dichlorobutane and 1-chloro-2-methoxybutane. No other compounds were detected. When methanol attacks the intermediate complex, the resulting HCuCl[15] is rapidly oxidized by another mole of cupric chloride to yield two moles of cuprous chloride and one mole of hydrogen chloride. Cupric chloride undergoes disproportionation only at high temperatures.[9,16] None of the present data suggests the participation of chlorine molecule.[17]

It should be noted that the presence of air reduces the apparent conversion of cupric chloride, regenerated from cuprous chloride and hydrogen chloride (produced according to equation (3)) by oxidation, to increase the total yield of products based on consumed cupric chloride as high as 140% (Table 4).

$$CuCl + HCl + \tfrac{1}{4}O_2 \rightarrow CuCl_2 + \tfrac{1}{2}H_2O \qquad (4)$$

This furnishes a hint for a possible catalytic reaction analgous to usual oxychlorination.

Table 6. Reaction of 2-butenes

Reactant (%) *trans*	Reactant (%) *cis*	Recovered Gas (%) *trans*	Recovered Gas (%) *cis*	Product (mmol) A	Product (mmol) B
100.0	0	93.4	6.6	23.0*	1.1
4.5	95.5	6.8	93.2	12.9**	0.8***

Glasslined autoclave reaction, 2-C_4H_8 0.25 mol, MeOH 150 m*l*, $CuCl_2$ 0.10 mol, 140°C, 3 hr

A: 2,3-dichlorobutane

B: *erythro*-2-chloro-3-methoxybutane

* *meso* 62.5%, *dl* 37.5%

** *meso* 59.0%, *dl* 41.0%

*** A small amount of *threo* compound was also detected.

When *cis*- and *trans*-2-butenes were subjected to reaction, isomeric dichlorides were formed. However, the ratio of *meso*- to *dl*-dichlorides is almost independent of the starting material 2-butene (Tables 1 and 6). Although interconversion of 2-butenes has occurred slightly, the extent is by no means sufficient to account for the result. The stability of the dichlorides was examined to show that both the isomerization and the methanolysis do not take place significantly under the reaction condition. Therefore, the invariable *meso*/*dl* ratio must be determined during the course of reaction. A mechanism which accounts for the results is that the intermediate complex has considerable open-chain character[18] and is in equilibrium between two isomeric forms[20] by rotation around the central C–C bond faster than the attack of nucleophiles. Since the intermediate originally from *trans*-2-butene is less crowded than the one from the *cis* isomer by separating two methyl groups apart, it must be more stable. Thus, by

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[13] The structure of this complex is under investigation and will be discussed in succeeding papers.

[14] Equation (1) does not necessarily mean that the attacking species is cupric chloride but it simply shows the stoichiometry on the dichloride side.

[15] Existence of the cation CuH^+ and its reaction with cupric ion yielding cuprous ion have been demonstrated; J. Halpern, E. R. Mcgregor and E. Peters, *J. Phys. Chem.*, **60**, 1455 (1956).

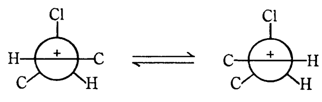
[16] M. C. Ball and R. F. M. Coultard, *J. Chem. Soc.*, *A*, **1968**, 1417.

[17] a) When methanol solution (10 m*l*) of cupric chloride (25 mmol) was heated at 140°C for 3 hr in a test tube, more than 90% of $CuCl_2$ was recovered unchanged. b) No substituted products were detected, *e.g.*, by gas chromatography (Condition *VI*). The products from 1-butene exhibited only two peaks (methoxychloride 9.0 min and dichloride 9.5 min) during 46 min running.

[18] In this respect the intermediate is dissimilar to the strongly bridged chloronium ion intermediates in the chlorination of 2-butenes by chlorine molecule.[19]

[19] R. C. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, **87**, 5172 (1965).

[20] Scheme of equilibrium:



succesive *trans* addition of chloride ion, *meso*-dichloride predominates over *dl*-isomer. A σ-bonded complex, $Cl(CH_3)CHCH(CH_3)CuCl$, is unlikely to exist under the reaction conditions, although it can not be strictly ruled out.

Experimental

Materials. Olefins were commercially available. Ethylene, 99% pure grade (Nihon Sekiyu Kagaku Co.); propylene, pure grade (Takachiho Chemical Industrial Co.); 1-butene, 99.7% pure grade (Matheson Co.); *cis*- and *trans*-2-butenes, pure grade (Takachiho). Cupric chloride was anhydrous GR grade (Koso Chemical Co.). Methanol was GR grade (Koso), refluxed and distilled from magnesium methoxide[21] under N_2. 1,2-Dichloroethane, GR grade (Koso), and 2-chloroethyl methyl ether, chemical grade (Koso), were distilled after drying over $CaCl_2$. Other materials were the purest reagents commercially available.

Analytical Methods. *a*) Unchanged Cu(II) was determined by iodometry.[22] *b*) Reaction products were analyzed by gas chromatography. The conditions (apparatus, column, temperature, carrier gas) were as follows: *I*. Shimadzu GC-2C, dioctyl sebacate (plus sebacic acid) on Chromosorb W (DOS column), 100°C or 120°C, He; *II*. Shimadzu GC-2C, Triton X-305 on Diasolid L, 80°C, He; *III*. Shimadzu GC-1C, DOS column, 120°C; He; *IV*. Shimadzu GC-1C, Triton X-305 on Diasold L, 130°C, He; *V*. Shimadzu GC-1C, propylene carbonate plus glutaronitrile on Chromosorb W, room temp., He; *VI*. Shimadzu GC-4APT, DOS column, 100°C (program 4°C/min) max. 140°C, He; *VII*. Perkin-Elmer 226 (H_2 flame detector), Silicone DC-550 (300 ft capillary), 30°C (12 min, program 10°C/min) max. 120°C, N_2. *c*) IR spectra were measured by JASCO IR-G spectrophotometer. d) NMR spectra were measured by JEOL JNM-C-60H spectrometer.

Autoclave Reaction. Into a N_2 purged 300 m*l* Ta lined autoclave (with an agitator and a thermo-well made of Ta metal) were placed $CuCl_2$ and methanol, and the measured amount of olefin was added from a pressure bottle. The autoclave was heated with an electric oven with stirring. The reaction time was shown as the heating time after the autoclave reached the prescribed temperature (±1.0°C). After the reaction, the autoclave was immediately cooled with water to room temperature. Cuprous chloride was filtered off from the reaction solution, followed by extraction with methanol. The combined methanol solution was subjected to titration and gas chromatographic analysis (Conditions *I* and *II*, with toluene as the internal standard). The results are summarized in Table 1.

Test Tube Reaction. Since cupric chloride is very corrosive to steel, the methanol solution (10 m*l*)[23] was taken in a 45 m*l* glass test tube and placed in a 100 m*l* stainless steel autoclave. In the autoclave was placed 30 m*l* methanol in order to adjust partial pressure and minimize vaporization of the reactant methanol. After being flushed with N_2, ethylene was introduced, and the autoclave was heated (±1.0°C) for 3 hr with an oven without stirring. The reaction solution and the outside solution were taken out and analyzed separately. The combined results are shown in Table 4.

The same procedure was applied to methanolysis of I, in which N_2 (50 kg/cm^2) was used in place of ethylene (Table 2).

Methanolysis of I and II. The reaction was carried out in a 50 m*l* glass sealed tube, which was heated (±1.0°C) in a 500 m*l* autoclave with shaking (75/min). The products were analyzed by gas chromatography (Condition *I*). The results are listed in Table 3.

Reaction of 1-Butene. In a 500 m*l* glass lined autoclave (with a stirrer made of Ta metal) was placed cupric chloride (0.10 mol) in 150 m*l* of anhydrous methanol, followed by addition of 13.8 g (0.25 mol) of 1-butene. The autoclave was heated at 140°C in an oil bath for 3 hr with stirring. After cooling, the reaction solution was analyzed by gas chromatography (Condition *I*, 120°C). The products were 1,2-dimethoxybutane (trace, retention time 10.5 min), methoxychlorobutane (IV) (1.94 g (14.8 mmol), 13.5 min), and 1,2-dichlorobutane (1.42 g (11.2 mmol), 15.2 min), which were identified by comparing their retention times with those of the synthesized samples. No higher boiling products were detected by programmed gas chromatography.[17b] When the reaction mixture was heated with KOH in a sealed tube at 150°C for 1 hr, the peak at 10.5 min increased while the other two peaks disappeared. This shows that the peak at 10.5 min corresponds to 1,2-dimethoxybutane.

Product IV showed a single peak also in a capillary column gas chrotmaography (Condition *VII*), showing it consisted of a single product. The NMR and IR spectra of IV, which was separated by fractionation and preparative gas chromatography (Condition *III*), were identical with those of synthesized 1-chloro-2-methoxybutane. (NMR (CCl_4 solution): τ 9.05 (triplet, 3H), τ 8.37 (multiplet, 2H), τ 6.54 (singlet, 3H, τ 6.4—6.9 (multiplet, 3H)).

Synthesis of 1,2-Dichlorobutane. Chlorine gas was introduced slowly into 1-butene (10 m*l*) at −20°C with stirring. About 2 m*l* of pure (>99%) 1,2-dichlorobutane (confirmed by NMR and IR) was isolated from the higher substituted substances by fractionation using a spinning band column.

Synthesis of 1-Chloro-2-methoxybutane. This was carried out by modification of olefin chlorination with *t*-butyl hypochlorite[24] and the product was purified by preparative gas chromatography (Condition *III*).

Reaction of 2-Butenes. A methanol solution of cupric chloride was charged in a 500 m*l* glass lined autoclave, and 2-butene was then pressured in from a pressure bottle. The autoclave was heated at 140°C (±1.0°C) in an oil bath with stirring for 3 hr. After cooling to room temperature, gas chromatographic analysis was conducted on both gaseous (Condition *V*) and liquid (Condition *I*) products. The results are presented in

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21) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C Heath Co., Boston (1955), p. 289.

22) W. T. Elwell and D. Price, "Comprehensive Analytical Chemistry," Vol. Ic, ed. by C. L. Wilson and D. W. Wilson, Elsevier Publishing Co., Amsterdam (1962), p. 371.

23) If the volume exceeds 10 m*l*, the $CuCl_2$ solution might splash out into the autoclave on purging and on heating.

24) C. F. Irwin and G. F. Hennion, *J, Amer. Chem Soc.*, **63**, 858 (1941).

Table 6.

Synthesis of 2,3-Dichlorobutane.[25] 2-Butene was allowed to react with chlorine gas under a dry ice condenser. The products were purified by preparative gas chromatography (Condition *IV*). (NMR(CCl_4 solutions): *meso* (from *trans*), τ 8.39 (doublet, 3H), τ 6.01 (multiplet, 1H); *dl* (from *cis*), τ 8.45 (doublet, 3H), τ 5.82 (multiplet, 1H)). IR spectrum of *dl*-dichloride agreed with the standard chart (Sadtler No. 12165).

A mixture of 0.5 g (4 mmol) of *meso*- and *dl*-2,3-dichlorobutanes, 0.22 g (1.7 mmol) of $CuCl_2$, and 0.17 g (1.7 mmol) of CuCl in 5 m*l* of MeOH was heated in a 10 m*l* sealed glass tube at 140°C for 3.3 hr. Gas chromatographic analysis (Condition *I*) revealed that no isomerization and no detectable extent of methanolysis occurred under the reaction condition: a feed composed of *meso* 99.8% and *dl* 0.2% yielded a mixture of *meso* 99.7% and *dl* 0 3%, while a feed of *meso* 1.7% and *dl* 98.3% gave a mixture of *meso* 1.6% and *dl* 98.4%.

Synthesis of 2-Chloro-3-methoxybutane. The method of olefin chlorination with *t*-butyl hypochlorite[24] was applied to the synthesis. From *trans*-2-butene, the main product (assigned to *erythro*-2-chloro-3-methoxybutane) appeared at 16.3 min in the gas chromatogram (Condition *I*, 100°C) with a small amount of *meso*-dichloride at 18.2 min. On the other hand, *threo*-compound from *cis*-2-butene showed a peak at 17.3 min with *dl*-dichloride at 20.5 min.

The author is indebted to Professor Naoki Inamoto for valuable discussions. He also wishes to thank Mr. Katsumi Kaneko for his assistance in part of this work.

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[25] H. J. Lucas and C. W. Gould, Jr., *J. Amer. Chem. Soc.*, **63**, 2541 (1941).