The Chlorination of Ethylene in Alcohol

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It is well known that the chlorination of ethylene in aqueous solution yields ethylene chlorohydrine and dichloride. About the reactions, there are number of investigations, especially about the factor which is likely to determine the ratio of two additions, between ethylene and hypochlorous acid on the one hand, and between ethylene and chlorine on the other.(1)(2)(3)

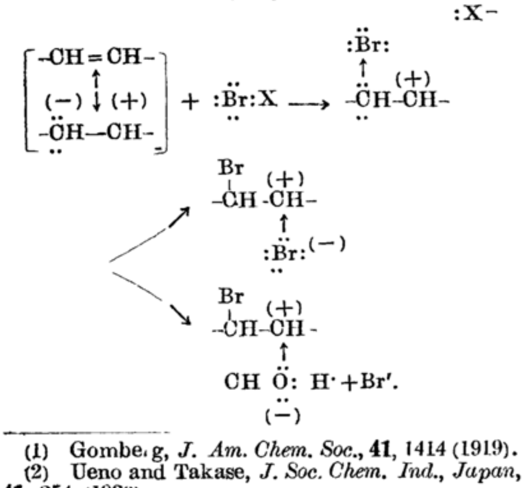
$$\begin{array}{ccc} H_2O+Cl_2 & \rightleftarrows & HOCl+H^{\cdot}+Cl' \\ & \downarrow CH_2=CH_2 \downarrow & \\ ClCH_2CH_2Cl & & ClCH_2CH_2OH \end{array}$$

Lately it was found that in other solvents as alcohol,(4)(5)(6)(7) phenol(8) or organic acid,(9) the chlorination proceeded in a quite similar way and gave the substance which would be obtained by the addition of the alkyl, aryl or acyl hypochlorite corresponding to the reactive solvent, together with dichloride,

$$-CH=CH-+Cl_2 \xrightarrow{ROH} -CH(OR)CHCl- + -CHClCHCl-$$

$$\xrightarrow{RCOOH} -CH(OCOR)CHCl- + -CHClCHCl-,$$

and it was also found that the chlorine atom added to ethylenic linkage might be obtained from a compound in which chlorine atom was linked to oxygen,(4)(5) nitrogen,(8) or a very negative organic radical as chloronitroform $ClC(NO_2)_3$,(10) instead of molecular chlorine. Recently Bartlett and Tarbell(7) stated that the reaction of this type might proceed as follows: one unsaturated carbon atom of the olefine donated a pair of electrons to bind the electrophylic halogen atom of the halogenating agent, while the nucleophillic addendum, either an anion or a negative fragment taken from a neutral solvent molecule, supplied a pair of electrons to form a linkage with other unsaturated carbon atom, *e g.*,



So the reaction might be trimolecular, instead of dimolecular between olefine and hypochlorous acid or its derivatives. But the ratio of two products, chlorohydrine or its derivative and dichloride, seems to vary according to the kinds of the reactive solvent,(5)(8)(9) ethylenic linkage,(6) or chlorinating agent.(5) And the reaction condition itself, which was likely to influence the ratio of two products, has been less investigated, so the more detailed study of the chlorination of ethylene in alcohol is intended by the present authors to make clear the mechanism on the one hand, and to use the reaction for the preparation of chlorohydrine ether on the other. As the chlorinating agent, molecular chlorine was used.

From −40° to 10° the chlorination of ethylene proceeded rapidly and gave ethylene chlorohydrine ethyl ether and ethylene dichloride almost quantitatively. In this range of temperature, the higher the temperature, the greater the velocity was, but the ratio of both products scarcely changed, indicating that the temperature affected both additions in the same degree. Above 10°, acetaldehyde was produced as the result of the oxidation of alcohol by chlorine and the higher the temperature, the more the amount and the less the ratio of the ether in the reaction products was. When methyl alcohol was used as solvent, no oxidation was observed even at 20°. (Table 1) However, the fractional distillation of the reaction products was more defficult than the case of ethyl alcohol, owing to the little difference of their boiling points (Dichloride 84°, chlorohydrine methyl ether 92°)

Table 1
The Effect of Temperature

Temp., °C.	Yield of dichloride, %	Yield of chloroether, %	Acetaldehyde
−40	33	54	none
−10	34	56	〃
− 5	30	53	〃
0	33	51	〃
5	31	54	〃
10	32	50	trace
20	32	45	some
30	36	26	much

Ethyl alcohol 4.0 mol, chlorine 1.0 mol, ethylene 2.0 mol.

Many catalysts of halogen-addition or -substitution (nucleophilic), as chloride of Hg, Al or Fe, were found to accelerate the both in the same degree, unless these substances did not markedly change the concentration of chloride ion in the reaction mixture. Active carbon, which adsorbed ethylene and chlorine on the porous surface, accelerated both additions, too. Such catalyst could not be found as to accelerate selectively only one of both additions, except urea, in the presence of which the ratio of the chloroether-formation seemed to increase somewhat.

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(1) Gomberg, *J. Am. Chem. Soc.*, **41**, 1414 (1919).

(2) Ueno and Takase, *J. Soc. Chem. Ind., Japan*, **41**, 254 (1938).

(3) Hiratsuka, *J. Chem. Soc. Japan*, **58**, 1177 1937).

(4) Conat and Jackson, *J. Am. Chem. Soc.*, **46**, 1727 (1924); **48**, 2166 (1926).

(5) Likosherstov and Petrov, *J. Gen. Chem., U. S. S. R.*, **5**, 1348 (1935); *C. A.*, **30**, 2174 (1936).

(6) Meinell, *Ann.*, **510**, 129 (1934); **516**, 273 (1936).

(7) Bartlett and Tarbell, *J. Am. Chem. Soc.*, **58**, 466 (1936).

(8) Likosherstov and Arkhangel'skaya, *J. Gen. Chem., U.S.S.R.*, **7**, 1914 (1937); *C. A.*, **32**, 519 (1938).

(9) Weber, Hennion and Vogt, *J. Am. Chem. Soc.*, **61**, 457 (1939).

(10) Schmidt; Ascherl and Kuilling, *Ber.*, **57**, 1876 (1926).

On the other hand, hydrogen chloride produced during the ethoxy-and chlorine-addition, inhibited this addition selectively and the more the reaction proceded, the greater the ratio of the dichloride-formation became. When the concentration of chloride ion in the solution reached to 1/2 *N*, the formation of chloroether decreased remarkably and scarcely stopped till it became 2 *N*. The ether was obtained as main product only in the case of large excess of alcohol. (See Table 2.)

Table 2

The Effect of the Ratio of Reactants

Ethanol, mol	Chlorine, mol	Chlorine, ml./min.	Ethylene, mol	Ethylene, ml./min.	Yield of dichloride, %	Yield of chloroether, %	Final concn. of Cl
3.0	2.5	85	5.5	185	58	28	2.3
4.0	2.0	90	4.0	180	44	40	1.8
5.0	1.8	95	3.8	200	37	46	1.6
7.5	2.5	95	5.0	150	34	49	1.4
4.0	1.2	85	2.2	155	35	50	1.3
4.0	1.0	—	1.7	—	29	53	1.2
8.0	1.0	—	2.1	—	25	59	1.0
2.0	2.0	80	—	—	73	12	2.5
10.0	0.5	—	1.0	170	8	76	0.8

At 10°, yields were based upon the amount of chlorine introduced.

When the sufficient amounts of hydrogen or ammonium chloride were added to the solution at the beginning of the chlorination, no chlorohydrine ether was formed, though chlorine and ethylene reacted rapidly, giving ethylene dichloride as the sole product. While the presence of a considerable amount of sulfuric acid showed no effect to the ratio of both additions, though some polymerisation of ethylene occured by the acid. Acetic acid was the same, except that some other products (probably ethylene chlorohydrine acetate) were formed. So this apparent inhibition of ethoxy- and chlorine-addition was mainly due to chloride ion in the solution, and the effect of hydrogen ion was not so great.

In the presence of suitable chloride ion-combining substances such as Ag^+ or Pb^{++}, the ratio of chlorohydrine ether in the reaction mixtures increased greatly. Alkaline, which neutralized the hodrogen ion produced during the reaction, did not increase the chlorohydrine ether formation, but inhibited both additions at various degrees, as long as the concentration of chloride ion did not change by the effect of the cation. In these cases, the accumulation of insoluble chloride or the presence of insoluble neutralizating agent as ferric hydroxide seemed to affect adversely for the dissolving of the reacting gases into the solution. The adversed effects followed in the order : $Fe(OH)_3 \gg KCl$, $NaCl > NH_4Cl$, $Ca(OH)_2$.

Table 3

The Effect of Many Substances

Addition of		Yield of dichloride, %	Yield of chloroether, %	Remarks
2*N*-HCl		96	0	Addition-velocity increased.
N/2-HCl		88	6	〃
N/2-NH_4Cl		78	11	
Ammonia*	(a)	0	48	
〃	(b)	14	40	
〃	(c)	30	54	
NaOH(equiv. to Cl)		2	25	Large amount of acetaldehyde was formed.
$Ca(OH)_2$(〃)		26	45	
$Fe(OH)_3$(〃)		0	18	Ethylene was scarcely adsorbed.
ZnO (〃)		25	59	$ZnCl_2$ produced, catalyzed.
MgO (〃)		27	53	
PbO (〃)		10	68	
		8	74	
$AgNO_3$ (〃)		0	50	A nitro-ester was formed?
$Pb(NO_3)_2$(〃)		6	62	
$Pb(CH_3COO)_2$(〃)		17	56	An acetate was formed.
30% Water		31	25	Large amount of ethylene chlorohydrine and ββ'-dichloroethyl ether were produced.
Active carbon	1 g.	41	57	Adsorption of ethylene was very rapid.
$HgCl_2$	1 g.	39	54	The velocity of additions increased.
$AlCl_3$	1 g.	38	53	〃
$FeCl_3$	1 g.	40	52	〃
Urea	1 g.	30	57	〃
	5 g.	31	65	〃
	10 g.	27	68	〃
	30 g.	18	69	〃
N-Acetic acid		35	50	Other chloro-compounds were formed.
N-Sulfuric acid		33	43	Some coloration occurred, with polymerisation of ethylene.

At 10°, ethyl alcohol 4.0 moles, chlorine 1.0 mole, ethylene 1.5 to 2.0 moles. The yield was based on the amount of chlorine introduced. * Ammonia was continuously introduced as gas; (a) large excess, (b) to maintain neutral, (c) slight acidic. The others were added at the beginning of the reaction.

$\gg$ PbO, $AgNO_3$, $PbCl_2$, $AgCl$. Those of the last four were very weak, so in the presence of oxide, nitrate, or acetate of Ag or Pb, ethylene chlorohydrine ether could be obtained in excellent yield.

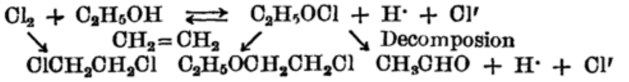
In addition, the formation of small amounts of $\beta\beta'$-dichloro-diethylether was found, which increased with increment of water contents in the ethanol solution and of the reaction time. So it seemed to be produced according to the following reactions These results were summarized in Table 3.

$$CH_2 = CH_2 + H_2O + Cl_2 \longrightarrow ClCH_2CH_2OH$$

$$CH_2=CH_2+ClCH_2CH_2OH+Cl_2 \longrightarrow ClCH_2CH_2OCH_2CH_2Cl$$

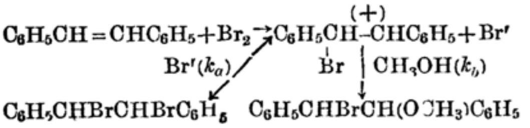
Disscussion

It was supposed that ethyl hypochlorite was the intermediate of chloroether and the reaction proceeded as follows(5).



$$\begin{array}{l} Cl_2 + C_2H_5OH \rightleftarrows C_2H_5OCl + H^{\cdot} + Cl' \\ \searrow \quad CH_2=CH_2 \swarrow \qquad \searrow \text{Decomposion} \\ ClCH_2CH_2Cl \quad C_2H_5OCH_2CH_2Cl \quad CH_3CHO + H^{\cdot} + Cl' \end{array}$$

The facts that the greater acetaldehyde forms, the less chlorohydrine ether, but the amount of dichloride produced, remains constant, might support this assumption. Recently, similar addition of bromine to stilbene in methanol was examined by Bartlett and Tarbell.(7) According to them, the relative amounts of the dibromide and methoxy bromide in the reaction products varied with varing concentration of bromide ion in a way that it was consistent with the assumption that the positively charged intermediate might react in the following two ways.



$$\begin{array}{l} C_6H_5CH=CHC_6H_5+Br_2 \rightleftarrows C_6H_5\overset{(+)}{CH}-CHC_6H_5 + Br' \\ \qquad\qquad Br'(k_a) \swarrow \qquad\quad \underset{Br}{|} \quad \downarrow CH_3OH(k_b) \\ C_6H_5CHBrCHBrC_6H_5 \quad C_6H_5CHBrCH(OCH_3)C_6H_5 \end{array}$$

So the relative amount of methoxybromide was equal to $k_b/[k_b+k_a(Br')]$, where (Br') represented the concentration of bromide ion and k the reaction constant of the above reaction. And the possibility that the bromohydrine ether might result from the direct additon of methyl hypobromite seemed to be disposed of kinetics, the rate being first order in stilbene and indepenedent of the acidity of the solution.

Our results that halide type catalysts accelerate both additions,(11) and that chloride ion inhibits the chloroether-formation selectively, and that the effect of hydrogen ion to the ratio of both reaction products is not so great, seem not only to be inconsistent with their assumption, but also even to verify it. But their equation does not agree with our results. It might be partially due to the other factor such as solubility- or activity-change of ethylene in the salt solution(3) or the difference of the dissociation coefficient of various chlorides (NH_4Cl, $NaCl$ or HCl in alcohol). But the fact that the effect of chloride ion concentration to the chloroether-formation showed no simple relation as the bromination of stilben, might indicate that the solvolytic reaction proceeded by the more complex passes.

Urea seems to affect the reaction as halogenating catalyst(12) in the one hand, and as chloride ion-combining substance in the other.

Experimental Part

Ethylene.—The unsaturated hydrocarbon was prepared from ethyl alcohol by the use of acid clay (Takeda Pure Chemicals, Ltd.) as catalyst in quartz tube at 450° to 500°.(13) The issuing gases were passed through a water-cooling condenser, receiver of the condensate, two washing bottles containing water and then one containing concentrated sulfuric acid. Its purity was more than 98 per cent, freed from higher olefines.

Chlorine was produced from concentrated hydrochloric acid and potassium bichromate and washed with water in ordinary way. Its purity was more than 99 per cent.

Procedure.—200 to 1000 ml. of ethyl alcohol (96 per cent) was placed in a cylindrical bottle (diameter, 7.5 cm.), which was provided with 2 gas inlet tubes at the bottom and a tightly fitting stopper having 3 holes. The one was for an efficient sealed stirrer, the second carried a tube for connection with a trap cooled below −10°, and the third carried a thermometer. Ethylene and chlorine were introduced into alcohol through a flowmeter from the two gas inlet tubes at the bottom of the vessel, and the former was kept enough in excess over the latter to keep the reaction solution colorless, while the temperature of the solution controlled in the range of ± 3° by the suitable cooling and efficient stirring. Chlorine was adsorbed very rapidly and the issuing gas from the trap contained only ethylene in this condition.

After the definite amounts of chlorine was introduced, the mixture was added with the three times of water and the separated lower oil layer was washed with concentrated calcium chloride, sodium carbonate solution and water respectively and then dried with calcium chloride overnight. The upper aqueous layer was distilled and the fraction below 75° was added with the three times of water. Small amount of the separated oil was treated same as the oily layer above described. Then combined dried oil was distilled by fractionating column.

Ethylene dichloride...... b. p. 84°–85°, d (15°) 1.261. Cl % found: 68.21, 69.07. Calculated: 70.70.

Ethylen chlorohydrine ethylether .. .b. p. 105°–107.5°, d (15°) 1.040, n (D, 20°) 1.418. Cl % found:

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(11) It is posturated that the catalyst of this type accelerates the formation of the positively charged intermediate.

(12) Li, *J. Am. Chem. Soc.*, **69**, 1065 (1945).

(13) Katsuno, *J. Soc. Chem. Ind., Japan*, **42**, 908 (1939).

34.02, 33.84. Calculated: 32.65.

The distillation residue was dissolved in ether, and the ether solution was washed with solution of sodium carbonate and water, then dried with calcium chloride. After the removal of the solvent by distillation on a water-bath, the remaining oil was redistilled.

ββ'-Dichloro-diethylether ...... b. p. 170°–173° (uncorr.) d (15°) 1.228, n (D, 20°) 1.457. Cl % found: 46.52, 47.36. Calculated: 48.86.

The approximate estimation of the ratio of dichloride and chloroether in the reaction mixtures could be done by the difference of the specific gravities between the two, if the amount of dichloroether was less than few per cent.

When the chlorination was done above 10°, some amounts of acetaldehyde was detected in the trap and the fore-run fraction (below 40°) of the upper aqueous layer. It was identified as p-nitro-phenylhydrazone (m. p. 128°), dimedone derivative (m. p. 139°–140°) and semicarbazone (m. p. 163°).

A number of substance shown in Table 3, except ammonia, were divided into very fine powder and added to alcohol in some portion during the introduction of gases. Ammonia was added through a flowmeter from the gas inlet tube with ethylene.

Properties of chlorohydrine ether as synthetic material or solvent are now on study.

In conclusion, the authors wish to express their thanks to Prof. Shiro Akabori, who gave many valuable advices and encouragements.

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