REACTIONS BETWEEN ETHYLENE CHLORIDE AND CHLORINE.

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The fact that, when ethylene and chlorine are mixed, a mixture of various chlorinated products in various proportions is formed, has been reported by several investigators.(1) Albert Maier(1) observed that when chlorine and ethylene are mixed in proportion of 2:1 at a temperature between 20° and 30°, the products are found to be 70% 1,1,2-trichlorethane, 15% ethylene chloride, 5% 1,1,2,2-tetrachlorethane, and 10% higher chlorinated products. The difficulties arising from the complex nature of the reaction implicate to the study not only theoretical but also practical importance. Mitsukuri and Kinumaki(2) found that only ethylene chloride is formed when the experiment is carried out at low temperature. Besides, Taylor and Hildebrand(3) published a paper on the solubility of chlorine in ethylene bromide, a compound similar to ethylene chloride, and it was conventionally considered that there was no reaction between chlorine and ethylene chloride; but the evidences so far obtained by the present author definitely show that there are reactions between chlorine and ethylene chloride.

In view of these facts, the study of the reactions of chlorine with ethylene chloride would be very much interesting for clarifying the nature of chlorination of hydrocarbons. Although the work is not yet completed, the purpose of this paper is to point out some of important facts so far found along with some suggestions for the future work.

Materials. Ethylene chloride, from Takeda (b.p. 83.0°), after treated with phosphorus pentoxide and calcium chloride, was subjected to fractional distillation several times, and only the middle portions were used (refractive index 1.44240(4) for H_α-line at 25°).

Chlorine, vaporized from ordinary commercial liquid chlorine in cylinder, was passed through water, concentrated sulphuric acid, and a phosphorus pentoxide tube, condensed by cooling with liquid air or liquid nitrogen, and

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(1) A. Maier, German Patent, 522959, Aug. 26, 1926; Stewart and Smith, *J. Am. Chem. Soc.*, **51** (1929), 3091; P. Askenasy and A. Hieler, German Patent, 549341, May 13, 1930.

(2) Mitsukuri and Kinumaki, *J. Chem. Soc. Japan*, **53** (1932), 398.

(3) Taylor and Hildebrand, *J. Am. Chem. Soc.*, **45** (1923), 682.

(4) S. Hamai, This Bulletin, **8** (1933), 297.

vaporized again. This process was repeated three times, the initial and the last portions being rejected each time.

Reaction of Chlorine and Liquid Ethylene Chloride. Chlorine was passed into ethylene chloride in the reaction chamber as shown in Fig. 1. The three ends of the inlet tube A are covered with platinum foils, each with a fine hole, so as to form very minute bubbles of chlorine in ethylene chloride. Chlorine was passed for various lengths of time, from 2 to 5 hours, at 50°. The whole reaction vessel was kept in a thermostat, rapeseed oil being used as the thermostat liquid. The rate of flow of chlorine was adjusted to 125–250 c.c. per minute. After a certain time the solution was taken out, washed with sodium hydroxide, dried with calcium chloride, and subjected to fractional distillation. No trace of expected substitution products was obtained. Similar experiments were carried out at 25° and 30°, and chlorine was passed for 2–5 hours with and without radiation by a mercury lamp at both temperatures.

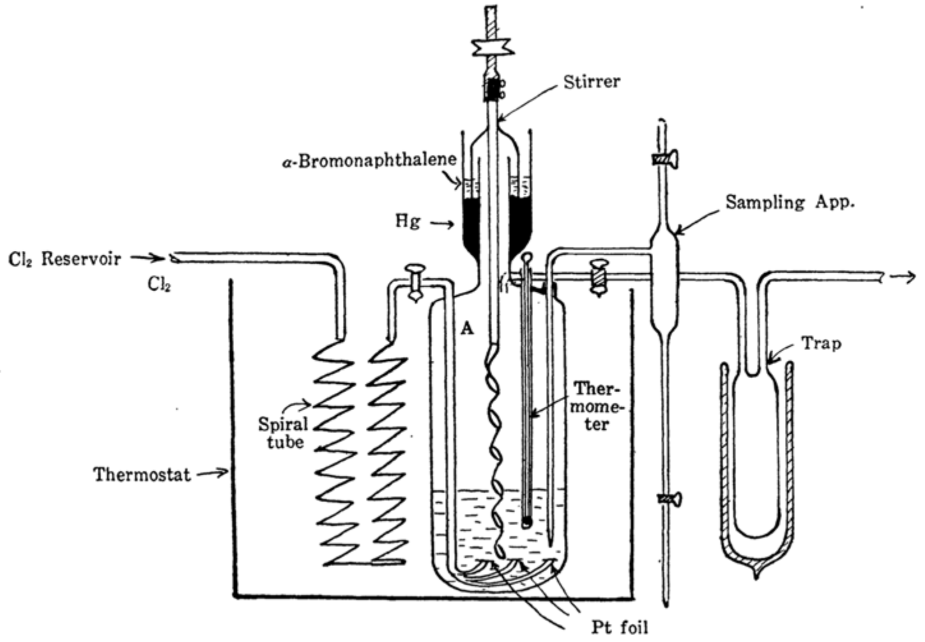

Fig. 1.

In no case, on treating the mixture as mentioned above, any compound of higher boiling point than ethylene chloride was found; however at the outside of the chamber, in the tube where possibly ethylene chloride vapour diffused when chlorine was led into the liquid by opening the stopcock, and in one of the traps attached directly to the reaction chamber, the formation of a white crystalline substance was observed after a long while. It was found to be hexachlorethane by its odour somewhat like camphor and m.p. 185°.

In another experiment ethylene chloride was mixed with about one fourth its volume of carbon tetrachloride, and the reaction was carried out under radiation by a mercury lamp.(5) On the following day a crystalline substance was noticed on the wall of the chamber after the solution was taken out, and also the crystals were found, as in the previous case, in the chlorine trap which is attached to the spiral tube of the inlet just outside the thermostat (not shown in the figure).

Correlating with other evidences from previous experiments, this fact possibly means that higher chlorinated derivatives may be formed only where the concentration of chlorine is high and the partial vapour pressure of ethylene chloride is relatively low. This is also concordant with the facts which will be discussed later. Formation of hydrogen chloride is also noticed; this is just as much concordant with the fact that platinum foils used at the ends of the inlet tube was found corroded, for chlorine alone can not possibly corrode platinum, but can with hydrogen chloride. Therefore, the fact that it was unable to find any trace of substituted compounds when the substitution of chlorine for hydrogen in ethylene chloride was tried is probably due to the reasons: (1) the substitution is so slow that on passing chlorine the reaction is not very appreciable, and (2) the substituted amount is too small to be detected by fractional distillation.

In order to see the effect of hydrogen chloride on the reaction, chlorine alone was passed into pure ethylene chloride in one vessel, and in the other, chlorine was passed into ethylene chloride mixed with hydrogen chloride gas, and both were allowed to stand for several hours. Ethylene chloride containing hydrogen chloride decolorized chlorine much faster than that without hydrogen chloride gas. This apparently shows that hydrogen chloride acts as a catalyst in chlorination of ethylene chloride. On fractional distillation, it was found that 1,1,2-trichlorethane was formed (b.p. 113.5°, the refractive index 1.47345(6) for H_α-line at 25°). In the previously mentioned experiments (flow method), no substituted compound was found except C_2Cl_6 formed in the vapour phase. However, definite evidences of substitution were obtained when the static method was employed. Ethylene

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(5) Effect of mercury lamp radiation may not be found so much noticeable unless more precise measurement is carried out.

(6) Unpublished data.

chloride was put in the vessel as shown in Fig. 2, the system was evacuated, and chlorine was passed in by opening the stopcock A, which was then closed. The temperature measured outside the vessel rose in one case from 16° to 21°, and in other cases, from 16.75° to 22.75° and from 17° to 47°.

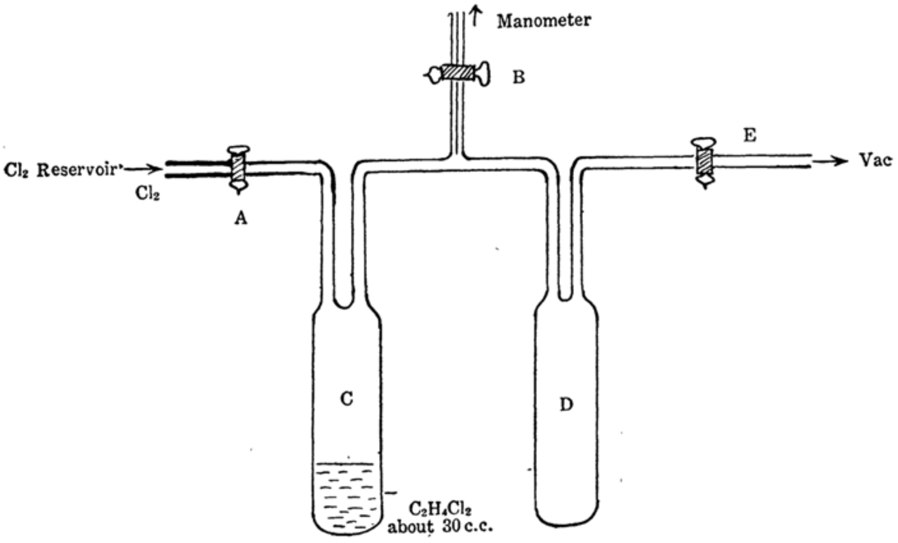

Fig. 2.

Moreover, the mercury-α-bromonaphthalene manometer indicated the rise of pressure from 14.35 cm. to 189.0 cm. at 17°, and from 76.0 cm. to 126.0 cm. at 18°.

At first the reaction is very slow, but after a certain time it becomes appreciable and gradually faster, showing a possible existence of an induction period. More experiments have been carried out and although they are not strictly quantitative, all of them have shown that chlorine, though slowly, reacts with ethylene chloride with the rise of temperature and increase of pressure. The increase of pressure is possibly due to the difference in solubilities of chlorine and hydrogen chloride in ethylene chloride. (Absorption of hydrogen chloride by ethylene chloride is now under investigation. The solubility of hydrogen chloride is much smaller than that of chlorine. The details will be published soon.) Hexachlorethane was noticed on the walls particularly at part D in Fig. 2 agreeing to the evidences found in the previous cases, and from the liquid part merely trichlorethane was obtained by fractional distillation. The formation of trichlorethane on mixing chlorine with ethylene chloride was demonstrated again in the attempt(7) of measuring the solubility of chlorine in ethylene chloride; in this attempt no concordant results for the solubility were observed owing to the reaction between them.

Stewart and Smith(8) in the experiment of the reaction between ethylene and chlorine observed that, as soon as liquid ethylene chloride was formed on the wall of the reaction vessel, the rate of reaction became faster corresponding to the so-called induced substitution as caused by energy given out by excited ethylene chloride molecules, and they found trichlorethane and hydrogen chloride but no other higher chlorinated compounds. But the fact that ethylene chloride reacts with chlorine shows that trichlorethane formation is not necessarily be induced by addition reaction as suggested by Stewart and Smith. It can be independent, and furthermore, energy necessary for substitution can be supplied from other sources such as collision or possible excitation of chlorine to higher quantum states (Energy of excited chlorine as found from the spectral data is 0.233 volt(9) (heat of dissociation)).

Reaction Between Ethylene Chloride Vapour and Chlorine. In order to study the nature of the gaseous reaction between ethylene chloride and chlorine the following scheme has been carried out.

The reaction chamber was connected to the ethylene chloride reservoir and after allowing its vapour into the chamber, the stopcock was closed, the pressure of ethylene chloride vapour being maintained slightly lower than the saturated vapour pressure. The vapour was mixed with chlorine by opening the stopcock and after closing it the mixture was left for various lengths of time at various temperatures, the whole vessel being immersed in the thermostat. The experiments were carried out with mixtures in various proportions (Table 1).

Table 1.

Tem. (°C.)	$\frac{P_{Cl_2}}{P_{C_2H_4Cl_2}}$	Time (hrs.)
35	4.5	3
35	3	1/2
35	4	3
25	2.3	4
25	5	$2\frac{1}{3}$
25	2.3	3

The gaseous mixture was then condensed by cooling with liquid air or liquid nitrogen. It was found, however, that the reaction is extremely slow, and

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(7) Discordant results have been found in several experiments of measuring the solubility of chlorine in ethylene chloride by a procedure somewhat similar to Taylor and Hildebrand's for measuring the solubility of chlorine in ethylene bromide, *J. Am. Chem. Soc.*, **45** (1923), 682.

(8) Stewart and Smith, *J. Am. Chem. Soc.*, **52** (1930), 2869; **51** (1929), 3091.

(9) International Critical Table, Vol. 5.

where chlorine is largely in excess hexachlorethane formation predominates in the gaseous phase and no other reaction is appreciable, while in the reaction between liquid ethylene chloride and chlorine there occurs trichlorethane formation especially on the surface (liquid-vapour interface) as semiquantitatively observed by the rise of temperature along the liquid-gas interface. This fact is concordant with the theoretical consideration that on the interface the concentration of chlorine is much higher than inside the body of ethylene chloride into which chlorine has been dissolved, favouring naturally the substitution reaction by chlorine.

Thus some important facts about the reactions between chlorine and ethylene chloride both in liquid and vapour phases have been pointed out, although they are not based strictly on quantitative data because of the complex nature of the reactions as well as lack of a suitable method of measurement. It is hoped that a more detailed study will be reported some time.

Some Suggestions for the Future Work. There are several investigators(10) who have studied infra-red absorption bands which are attributed to the carbon-hydrogen linkage in carbon hydrogen compounds as well as in their chlorine derivatives; furthermore Smith and Board(11) observed that substitution of chlorine for hydrogen in tetrachlorethane causes a remarkable decrease in the intensity of absorption in each of the characteristic absorption bands without any evident shift of its position, and a similar phenomenon takes place in the transformation from dichlorethylene to trichlorethylene. Such compounds as carbon disulphide and carbon tetrachloride have no such bands. Smith and Board(11) also state that the intensity is approximately a direct function of the number of hydrogen-carbon linkages. Later Spence and Easley(12) studied more carefully infra-red absorption bands of halogen derivatives of ethane, some fourteen compounds including the series of $C_2H_4Cl_2$, $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2HCl_5 and C_2Cl_6, and found that, as concluded by several previous investigators already, the mentioned absorption bands are due to carbon-hydrogen linkages, the intensity of absorption is a function of the number of C-H-linkages, and the bands completely vanish in hexachlorethane as in the case of carbon tetrachloride.

Looking over these papers, it is rather interesting to notice that the intensity of absorption decreases with chlorine substitution without shift of

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(10) Ellis, *Phys. Rev.*, (2), **23** (1924), 48; *J. Opt. Soc. Am.* **8** (1924), 1; Coblentz, *Bur. Stand. Sci. Paper*, No. 148 (1921).

(11) Smith and Board, *J. Am. Chem. Soc.*, **48** (1926), 1512.

(12) B. J. Spence and M. A. Easley, *Phy. Rev.*, **34** (1929), 730.

the positions of bands, and that might be an available method for the study of chemical reactions in which chlorine substitution occurs and for which the ordinary conventional method of attack is not suitable, when the reaction is rather slow. Making use of the infra-red absorption phenomena we might be able to investigate chemical reactions which otherwise could not be easily studied. Whether it is practically useful or not must be decided by actual experiments.

Summary.

(1) In the reaction between chlorine and ethylene chloride in the liquid phase 1,1,2,-trichlorethane is the principal product and in the gaseous phase the formation of hexachlorethane predominates.

(2) The reaction between gaseous chlorine and liquid ethylene chloride seems to occur mainly on the liquid gas interface.

(3) Hydrogen chloride gas dissolved in the mixture catalytically accelerates the reaction.

(4) There seems to exist an induction period in the reaction between ethylene chloride and chlorine possibly owing to catalytic acceleration by either hydrogen chloride or substituted product or both in later stage.

(5) In the gaseous reaction between chlorine and ethylene chloride the formation of hexachlorethane predominates especially when chlorine exists largely in excess to ethylene chloride vapour.

(6) A suggestion is made as to the method of study on chemical reactions, especially on chlorination reaction (substitution).

In conclusion, the author wishes to express his hearty thanks to Prof. S. Mitsukuri for his interests and kind advices, and is also very grateful that a part of the expenses of this experiment were covered by the research funds granted to Prof. S. Mitsukuri by the Imperial Academy and the Saito Gratitude Foundation.

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