TABLE II (*Concluded*)

	Formula	Subs., g.	Vol. of N in cc.	Nitrogen, % Calcd.	Nitrogen, % Found
3	$C_{14}H_{19}ON_3Cl_2$	0.1728	22 (31°, 743.3 mm.)	13.29	13.35
4	$C_{17}H_{25}ON_3$	.1396	19.1 (32°, 749.8 mm.)	14.63	14.39
5	$C_{17}H_{25}O_3N_3$	.1737	21.6 (33.5°, 749.5 mm.)	13.16	12.95
6	$C_{17}H_{25}ON_3$	.1535	20.5 (30°, 750.1 mm.)	14.63	14.22
7	$C_{21}H_{31}ON_3$	.1785	21.1 (32.5°, 745.6 mm.)	12.31	12.32
8	$C_{21}H_{29}ON_3$	.1504	18.1 (36°, 748 mm.)	12.39	12.31
9	$C_{24}H_{25}ON_3$	.2103	21.9 (31°, 747.1 mm.)	11.32	10.98
10	$C_{19}H_{23}ON_3$	.1643	21.4 (31°, 746 mm.)	13.59	13.71
11	$C_{25}H_{27}O_2N_3$	.1915	19.0 (34°, 747.3 mm.)	10.47	10.27

Summary

1. Di-*p*-cymylurea is obtained in small amount by the action of urea upon aminocymene hydrochloride in aqueous solution. The best method is to heat aminocymene and urea together at 150–170°.

2. *p*-Cymylurea is best prepared by the action of potassium cyanate upon aminocymene in glacial acetic acid solution.

3. 2-*p*-Cymyl-4-semicarbazide is best made by the action of hydrazine hydrate on *p*-cymylurea.

4. *p*-Cymylsemicarbazide yields semicarbazones with the following ketones: acetone, methyl ethyl ketone, α,γ-dichloro-acetone, mesityl oxide, acetoacetic ester, cyclohexanone, camphor, carvone, benzophenone, acetophenone and benzoin. The products are very stable. The reactions are immediate except those with camphor, carvone and the purely aromatic ketones. These require some acetic acid and a period of heating.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

THE INDUCED CHLORINATION OF ETHYLENE DICHLORIDE. THE EFFECT OF OXYGEN UPON THE REACTION BETWEEN ETHYLENE AND CHLORINE

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Gaseous chlorine and gaseous ethylene react to form ethylene dichloride. The reaction takes place upon the surface of the containing vessel.[1,2]

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2 \qquad (1)$$

The reaction rate may be expressed by the equation

$$-\frac{d(C_2H_4)}{dt} = K_a'' (C_2H_4)(Cl_2)$$

in which the bracketed formulas represent partial pressures of the respective gases. The specific reaction rate varies with the nature of the

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[1] Stewart and Fowler, THIS JOURNAL, **45**, 1014 (1923).

[2] Norrish, *J. Chem. Soc.*, **123**, 3006 (1923).

catalytic surface,[3] but under given conditions is constant over wide variations in the pressures of the reactants. The experiments upon which these conclusions are based were carried out in the presence of air and in glass vessels whose surfaces were only superficially dried. Water is known to be a catalyst for the addition reaction.[2,4]

Stewart and Fowler[1] made their experiments at such concentrations that ethylene dichloride did not separate as a liquid. Norrish[2] worked at higher pressures, but states that the specific reaction rate, under the conditions mentioned above, was unaltered by the separation of the liquid. In the total absence of water or other catalyst the reaction does not take place,[3,4] and there is some evidence[1] that the reaction is autocatalytic.

The present paper concerns experiments carried out with thoroughly pure dry reactants and in glass vessels which were evacuated at a pressure of 1×10^{-6} mm. of mercury and at a temperature of 500° to remove all traces of water and oxygen from the walls.

Under these conditions there is an inhibition period and the reaction, when once started, is autocatalytic, with a marked increase in reaction rate accompanying the deposition of liquid. Besides the addition reaction, substitution occurs, and the facts suggest that the latter reaction is induced by the former. The effect of oxygen is to decrease the induced reaction, presumably by dissipating the energy of the exothermic addition reaction.

Experimental Method

Description of Apparatus and Preparation of Materials.—Figure 1 shows diagrammatically the reaction system. The apparatus was constructed of pyrex glass. The reaction vessel A was of three hundred cubic centimeters' capacity. All the connecting lines were of 2 mm. inside diameter except that leading from Stopcock 4 into A, which was 1 mm. inside diameter.

A and E and the attached capillaries (to within a few centimeters of the stopcocks) could be baked out at any temperature up to 550° by means of an electric oven. While baking was in progress, the stopcocks were kept cool by a blast of air. After the baking was completed the oven was replaced by an oil thermostat. This was controlled by hand to one tenth of a degree, the oil being pumped around the bulb at a constant rate.

The ethylene was made by dropping ethylene dibromide on zinc. It was washed with 95% alcohol, then passed over calcium chloride and phosphorus pentoxide and liquefied in a liquid air trap. A middle fraction of the liquid ethylene was distilled slowly at low pressure into the ethylene supply system, which was composed of several small traps containing small amounts of phosphorus pentoxide so that the ethylene was continually in contact with the drying agent. Between experiments the ethylene was kept frozen in one of the traps by means of a liquid-air bath. Before each experiment the ethylene system was evacuated for half an hour to an hour to the vapor pressure of solid ethylene.

The chlorine used was taken from a tank of liquid chlorine, passed over calcium chloride and liquefied in a trap with liquid air. The first fourth of the chlorine was

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[3] Norrish and Jones, *J. Chem. Soc.*, **126,** 55 (1926).

[4] Brooks and Humphrey, *J. Ind. Eng. Chem.*, **9,** 750 (1917).

distilled away; the next half of the original was distilled slowly into the supply system at low pressure and sealed off for use in the experiments; it was then handled in a manner similar to that described for the ethylene. Analysis showed that the chlorine contained one and eight-tenths mole per cent. of hydrogen chloride as an impurity. As it subsequently appeared that hydrogen chloride had no important effect on the reactions studied, it was not thought worth while to attempt the removal of the hydrogen chloride.

Other substances were introduced to the reaction bulb through Stopcocks 9, 8 and 5. In the case of vapors they were first liquefied in G and subjected to high vacuum before introduction to A. The course of the reaction was followed at constant volume by means of a double manometer system. One leg of a constant level mercury manometer was connected by a 2-mm. capillary tube to the reaction bulb through Stopcocks 1 and 4. During a reaction the two sides of the mercury column of this manometer were maintained at constant level by adjusting the pressure on a second mercury manometer. The probable error in readings in the rapid reactions was not greater than 1 mm., and the readings for the slow reactions were accurate to 0.5 mm. The ratio of volumes of reaction flask and manometer system was approximately 100:3.

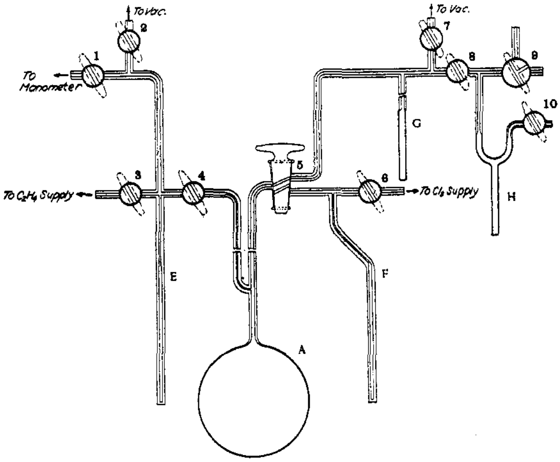

Fig. 1.

Experimental Procedure.—After baking at high temperature under vacuum for several hours, the furnace was removed and replaced by the oil-bath. All light was excluded from A and connections by black coverings. The substance (oxygen, ethylene dichloride, etc.), whose effect was being studied was then introduced through Stopcocks 9, 8 and 5; 5 was then closed and 1 and 4 were opened to determine the pressure of the substance in A. Stopcock 4 was then closed and the manometer system swept out with ethylene, through 3 and 1. Ethylene pressure in E was next built up greater than the pressure in A and 4 opened, the pressure being then increased until the total pressure in the system was equal to the pressure of the substance in A plus the desired pressure of ethylene in A; 4 was then closed and the pressure in the manometer system built up further with ethylene to a few centimeters greater than the expected initial total pressure in A after the introduction of chlorine; 3 was then closed. The desired amount of chlorine from the supply system was liquefied in F at approximately −30°. All lights in the room were turned out except the small ruby bulbs on the manometers; 5 was turned to connect F and A and a water-bath placed on F. As soon as the chlorine was evaporated into A, 5 was closed and 4 opened, and the initial total pressure in A noted. Less than a minute elapsed from the time of starting to admit chlorine to A to the time of making the first reading. In general an accurate determination of the total initial pressure was obtained; in those cases where the initial reaction rate was rapid, a satisfactory extrapolation to zero time could be made. At the start of the reaction the partial pressure of each substance in the reaction bulb was accurately known. The manometer system contained pure ethylene equal to the total pressure in A and as the reaction progressed some of this expanded into A in amount proportional to the pressure drop. Since the relative volumes of the manometer system and A were known, a correction could be applied for this effect in making rate calculations. Moreover, since this expansion was from the manometer system into the reaction bulb, it served to prevent any substance from leaving the reaction vessel.

The Determination of End-Products.—At the end of the reaction the condensable gases and vapors were frozen out in G or H with liquid air. Any non-condensable gases present were removed through 10. When the pressure in A dropped to zero, 5 was closed and the vapor evacuated through 8 and 9 and through a bubbler containing water. In those experiments where there was an excess of chlorine, potassium iodide was included in the bubbler contents. The iodine was titrated with 0.1 *N* sodium thiosulfate solution and any hydrogen chloride present was determined by titrating with standard sodium hydroxide solution. Ethylene dichloride did not hydrolyze in the time allowed and the amount of hydrogen chloride present did not interfere with the thiosulfate titration. The amounts of the residual gases were expressed in terms of their respective partial pressures.

In most cases there was excess of ethylene at the end of the reaction. The amount of hydrogen chloride formed was a measure of the amount of substitution reaction and, since the initial chlorine was accurately known, it was possible to calculate the amount of addition reaction and hence the amount of ethylene used up. Knowing the amounts of addition product (ethylene dichloride) and substitution product (trichloro-ethane), the volume of the reaction vessel, and assuming Raoult's Law, it was possible to calculate the vapor pressure of the liquid.

The sum of the final hydrogen chloride pressure, the final vapor pressure and the final ethylene or chlorine must be equal to the final pressure observed for the experiment. This was found to be true within a millimeter of mercury pressure in every case.

Experimental Results

When ethylene and chlorine were allowed to react in a darkened glass flask from whose surface all volatile substances had been removed by means of prolonged evacuation at 500°, the following observations were made. There was a short inhibition period, followed by an autocatalytic reaction. The reaction rate became relatively high as soon as the reaction products separated as liquids upon the walls. A high proportion of the reacting chlorine was used up to produce hydrogen chloride, according to the reactions

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2 \qquad (I)$$

$$C_2H_4Cl_2 + Cl_2 \longrightarrow C_2H_3Cl_3 + HCl \qquad (II)$$

Reaction II was not independent of Reaction I. Oxygen gas decreased the total reaction rate and tended to eliminate Reaction II.

The Inhibition Period.—In Fig. 2 the pressure of the reacting system is plotted against the time for several typical experiments carried out in the same vessel. Experiment 4–1 was performed before the reaction flask was evacuated at high temperatures and therefore the form of the plot corresponds closely to those of similar plots previously reported.[1] Succeeding experiments gave erratic results, but in each of them there was marked autocatalysis and indication of a true inhibition period. About twenty experiments were carried out before it was felt that the surface conditions were reproducible, the chief difficulty being complete evacuation of the walls.[5]

In no case, in the absence of oxygen, could the reaction be inhibited for more than a few minutes. The plot of Expt. 5-8 (Fig. 2) shows the effect of 3.1 cm. of mercury pressure of oxygen, in which an inhibition period of fifty-five minutes was observed. It is believed that this inability to prolong the inhibition period indefinitely was due to the autocatalytic feature of the reaction. It started in some unbaked portion of the capillary connections and gradually extended to the reaction flask.[6]

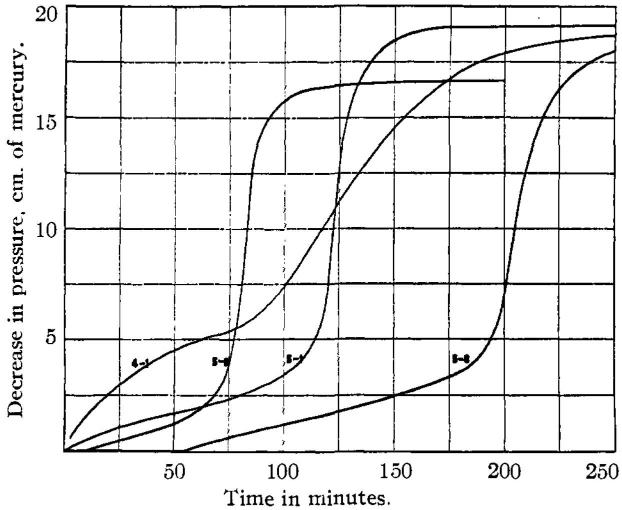

Fig. 2.—The effect of surface evacuation and of oxygen upon the catalysis of the reaction between ethylene and chlorine gases. Conditions: Curve 4-1, evacuated at room temperature; Curves 5-1, 5-9, prolonged evacuation at 500°; Curve 5-8, dry oxygen gas introduced after evacuation.

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[5] After each experiment the system was evacuated at 100° for an hour; then the temperature was raised to 500° and dry oxygen admitted to burn off any film of carbonaceous matter. The evacuation was then carried to 1×10^{-6} mm. of mercury pressure for several hours before the succeeding experiment. In the earlier experiments there was evidence of incomplete evacuation, since in spite of a very good vacuum before admitting the reactants, some gas which was non-condensable in liquid air appeared after the reaction was over. Eventually this no longer happened.

[6] Nitrogen gas as well as oxygen served to prolong the inhibition period by slowing diffusion in the capillaries. Faulty manipulation of the manometer, causing convection currents in the capillaries, hastened the apparent start of the reaction.

It is important to note that the evacuated surface was not a catalyst for the reaction.

The Substitution Reaction.—As the evacuation of the walls progressed an increasing amount of hydrogen chloride appeared among the reaction products. Under given initial concentrations of reactants, however, this appeared to reach a maximum when about thirty-five to forty mole per cent. of the initial chlorine was used up in the substitution reaction. An attempt was made to increase this amount in two ways, first by introducing ethylene dichloride vapor or liquid as an initial constituent, second, by using a large excess of chlorine over ethylene. The results are presented in Table I, in which the experiment number gives the order in which the experiments were performed although, for the sake of clarity, they are grouped in a different order. The influences of some other factors are also indicated.

TABLE I

THE EFFECT OF CERTAIN VARIABLES UPON THE CHLORINATION OF ETHYLENE DICHLORIDE DURING ITS FORMATION FROM ETHYLENE AND CHLORINE

Temperature: Expt. 4-1, 26.5°; Expts. 5-1 to 5-9, 18.5°; Expts. 5-10 to 6-11, 20.0°. Initial HCl content, 1.8 mole per cent. of the chlorine

Expt. no.	Initial pressures (cm. of mercury) C_2H_4	Cl_2	Other substances	Molal ratio HCl formed to Cl_2 used up
4-1	17.7	14.7	None (?)	0.08
5-1	16.2	15.1	None (?)	.20
5-3	16.5	15.1	None (?)	.08
5-6	15.8	16.4	None (?)	.19
5-7	16.3	16.4	None	.32
5-9	16.2	16.1	None	.38
6-4	15.9	30.5	$C_2H_4Cl_2$, 3.7	.47
6-5	16.8	7.85	$C_2H_4Cl_2$, 5.4	.47
6-6	16.3	3.0	$C_2H_4Cl_2$, 6.1	.34
6-7	15.9	3.0	$C_2H_3Cl_3$, 1.4	.19
6-10	14.8	5.2	$C_2H_3Cl_3$, 1.6	.26
6-11	5.4	15.0	$C_2H_3Cl_3$, 1.6	.38
6-8	16.3	2.63	$C_2H_4Cl_2 + C_2H_3Cl_3$, 3.8	.33
6-9	5.0	15.1	$C_2H_4Cl_2 + C_2H_4Cl_3$, 3.7	.496
5-4	15.9	15.6	O_2, 0.1	.17
5-5	15.8	16.3	O_2, 0.2	.24
5-8	15.3	15.5	O_2, 3.1	.10
6-1	16.6	17.5	O_2, 35.1	.105
6-2	16.8	17.1	O_2, 3.1, $C_2H_3Cl_3$, 1.6	.18
6-3	16.2	17.5	H_2O, 0.1	.31
5-10	16.2	17.1	N_2, 3.0	.39
5-11	16.1	17.2	N_2, 4.7; $C_2H_4Cl_2$, 1.8	.46
5-12	16.5	16.9	N_2, 7.9; $C_2H_4Cl_2$, 6.1	.48
5-2	8.4	7.85	None (?)	.02

A maximum of one-half the reacting chlorine was used in Reaction II, even when excess chlorine remained in contact with the reaction products for a period several times as long as the half period of the reaction itself. This maximum was approached closely only when the vapor phase was initially nearly saturated with ethylene dichloride (6.1 cm. of mercury pressure). Hence in the absence of such vapor, that is, in the initial stages of an experiment such as Expt. 5–7, the reaction was probably largely addition. On the other hand, some substitution took place before the actual separation of liquid. This was shown by a comparison of such plots as appear in Fig. 2, with respect to the magnitude of the observed pressure change at which the reaction became very rapid. When the hydrogen chloride content was high (Expts. 5–7, 5–9) this point corresponded to about three centimeters of mercury, but when it was low (Expts. 4–1, 5–3, 6–1) the pressure change was about five centimeters before the rapid reaction set in. Since the vapor pressures of the ethylene dichloride and trichloro-ethane are, respectively, 6.1 cm. and 1.6 cm. at 20.0°, and since the appearance of a rapid reaction corresponds in time with the separation of liquid, then the compound of low vapor pressure started to form before the gas phase became saturated with ethylene dichloride.

Similarly, Expts. 6–6 and 6–8 suggest that the mere presence of the liquid phase does not ensure the maximum substitution reaction if the ethylene concentration is high and the chlorine concentration low. Experiment 5–2 indicates that if both are low in concentration the substitution reaction is inhibited. However, Expt. 6–4, toward its end, duplicated the concentration condition of Expt. 5–2, but with liquid present, and yielded nearly the maximum substitution. There is no doubt that liquid ethylene chloride facilitates the substitution (Reactions I and II), and that low concentrations of reactants favor addition only.

The presence of trichloro-ethane apparently decreased the chance of the substitution reaction (Expts. 6–11 and 6–9).

Oxygen gas definitely tends to decrease the amount of Reaction II but does not entirely eliminate it on an evacuated surface. It also causes Reaction I to go more slowly, although this effect will be made the subject of a separate paper. A small amount of oxygen is almost as effective as a large amount. Attempts were made to reproduce the original glass surface by exposing it to moist air at 100° for several hours, cooling the system and then evacuating at room temperature. In every instance the freshly adsorbed gas was quickly removed, giving rise to the characteristic substitution reaction. On the other hand, the original surface was difficult to evacuate.

Nitrogen gas and water vapor had no apparent effect upon the induced substitution reaction.

Other investigators[4] report the formation of trichloro-ethane as a side reaction during the addition of ethylene to chlorine. That it was the sole product of substitution in this case is made probable by the facts mentioned above. Further, the total reaction products from several experiments were collected in Bulb G (Fig. 1) by condensation in liquid air and then allowed to evaporate. After the ethylene and hydrogen chloride had volatilized, the remaining liquid was condensed in E (Fig. 1) and its vapor pressure measured at 20.0°. The liquid was then allowed to distil slowly into A and the vapor pressure of the residue measured from time to time. The vapor pressure slowly dropped from 5.8 cm. of mercury to 1.5 cm., at which point about 7% of the original liquid remained, and finally to 1.2 cm. when 2% of the liquid remained. Since the higher chlorinated ethanes have still lower vapor pressures, it is apparent that they were not present in appreciable quantities.[7]

The Catalyst.—The existence of an inhibition period in the presence of an evacuated surface, with or without oxygen gas, and in the presence of hydrogen chloride, indicated that none of these or any combination of them was a catalyst. Experiments were therefore made with the other products of the reaction, ethylene dichloride and trichloro-ethane, present at the start of the reaction. The results are presented graphically in Fig. 3. In Expts. 6–4, 6–5 and 6–6 ethylene dichloride vapor was used as a possible catalyst (see Table I). In Expts. 6–7, 6–10 and 6–11 pure trichloroethane vapor was present at the beginning of the reaction; in Expts. 6–8 and 6–9 the mixed liquids were present.

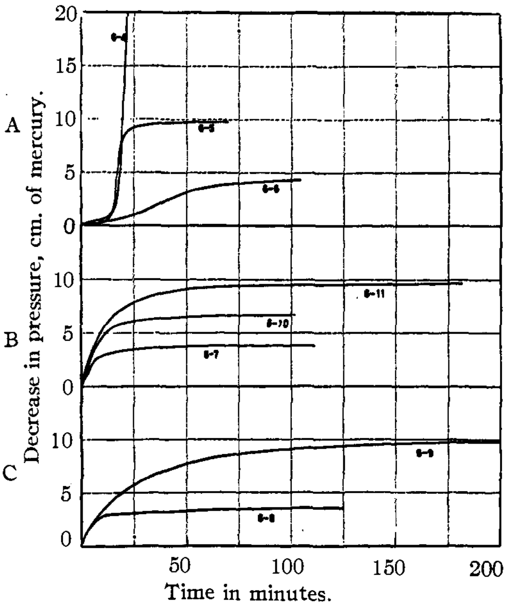

Fig. 3.—Catalysis of the reaction between ethylene and chlorine gases by (A) ethylene dichloride vapor, (B) trichloro-ethane vapor, (C) the mixed liquids.

In each case using the ethylene dichloride vapor, the initial reaction

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[7] It was found impossible to separate fully the liquid reaction products by such distillations because of the small amount available. The above measurements indicated the futility of an analysis of the mixture. The total liquid formed and collected could be measured in volume from the known dimensions of the bomb G. It always corresponded within experimental error (5%) to the volume of liquid to be expected from the reactants and hence the carbonaceous film left upon the glass constituted but a minute fraction of the total products.

rate was very low, suggesting in fact a short inhibition period.[8] The autocatalytic part of these reactions could be due either to an approach to saturation of the vapor, with eventual separation of liquid, or to the production of trichloro-ethane, or both. The absence of any suggestion of an inhibition period in those experiments in which trichloro-ethane vapor was initially present indicates definitely that this compound was a catalyst. The above-mentioned curves represent the experimental observations and take no account of the larger pressure changes to be expected, for a given amount of ethylene reacted, after the saturation of the gas phase with vapor. In every case liquid started to separate some time before the maximum reaction rate was reached. This showed that a relatively large amount of liquid was necessary to produce the optimum catalytic conditions, perhaps because it first separated in droplets rather than as a coherent surface film.

In the absence of oxygen, either liquid, or a mixture of them, is a powerful catalyst, but in the presence of oxygen, or upon an unbaked surface, the separation of liquid is not accompanied by a large increase in specific reaction rate (Expts. 4–1 and 5–8, Fig. 2 and Ref. 2).

It may be concluded that upon an evacuated surface the trichloroethane vapor is a more powerful catalyst than is the ethylene dichloride vapor; that upon an evacuated surface in the presence of oxygen the addition reaction is catalyzed by the vapors, but less effectively than in its absence; and that upon an unevacuated surface neither vapor is an effective catalyst. The liquids are each effective catalysts but apparently less effective in the presence of oxygen. The order of their catalytic activity in the absence of oxygen is undetermined, but in the presence of oxygen ethylene dichloride is somewhat the better catalyst.[9]

Discussion of Results

The Induced Substitution Reaction.—Since ethylene dichloride is not ordinarily chlorinated under the conditions of time and temperature of the experiments described above, the formation of the trichloro-ethane is brought about as a result of the addition reaction. The course of the reaction and the role of the oxygen may be represented as follows. The starred formulas represent either molecules of sufficiently high energy content to react, as compared to the unstarred molecules of average energy content, or complex compounds with the catalyst. The equilibria indicated by the arrows are arbitrary assumptions.

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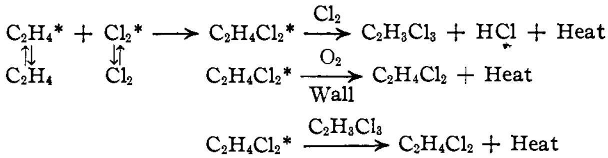
[8] The initial abnormal pressure drop in Expts. 6–6 and 6–7 was possibly due to experimental difficulty. It occurred also in Expt. 5–1 (Fig. 2). If it be significant, it would suggest a rapid reaction involving a small amount of adsorbed ethylene.

[9] The experimental data upon which this conclusion is based are not included in this paper; the difference in the catalytic activity is small (40%), hence it may be presumed that any mixture of the two liquids insures constant catalytic activity.



$$\begin{tikzcd}[column sep=small]
C_2H_4^* \arrow[d, shift left] & + & Cl_2^* \arrow[d, shift left] \arrow[r] & C_2H_4Cl_2^* \arrow[r, "Cl_2"] & C_2H_3Cl_3 + HCl + \text{Heat} \\
C_2H_4 \arrow[u, shift left] & & Cl_2 \arrow[u, shift left] & C_2H_4Cl_2^* \arrow[r, "O_2", "\text{Wall}"'] & C_2H_4Cl_2 + \text{Heat} \\
 & & & C_2H_4Cl_2^* \arrow[r, "C_2H_3Cl_3"] & C_2H_4Cl_2 + \text{Heat}
\end{tikzcd}$$

In the absence of the addition reaction ethylene dichloride molecules do not become activated sufficiently for chlorination.[10]

The fact that the presence of liquid ethylene dichloride, at least in the form of a film, increases the chance of the substitution, suggests the transfer of the activation energy to other molecules of the same kind. In effect the liquid dilutes the various deactivators and prolongs the life of the activated form, but this view requires the assumption of relatively slow dissipation of the activation energy among ethylene dichloride molecules as compared to a thermal equilibrium rapidly established in the presence of oxygen or of trichloro-ethane.[11,12]

In view of the facts regarding the catalysis of the reaction it appears likely that the molecular species represented by the symbols $C_2H_4^*$ and Cl_2^* are in reality complex aggregates of ethylene and chlorine with ethylene dichloride or trichloro-ethane. These aggregates may be within the liquid film or adsorbed upon the glass surface. That the latter concept is important is suggested by the fact that a trace of adsorbed gas within the walls during the early experiments reduced the amount of the substitution reaction, and was itself displaced and appeared in the gas phase at the conclusion of the reaction. These effects could have occurred only if the reaction involved the glass surface. On the other hand, if this were the only reaction area, the separation of liquid should introduce a diffusion factor and decrease the rate of the reaction. Since the presence of a liquid film increased the reaction rate it must be assumed either that there is a rapid homogeneous reaction within the film, or that the liquid surface is a better catalyst or that some other influence increases the reaction rate. These factors will be considered in detail in a separate communication. It is sufficient to note now that when the glass surface with adsorbed water is itself a catalyst (Expt. 4–1, Fig. 2) not only is the amount of substitution reaction diminished but also the catalytic effect of the condensing vapor is lessened. When the surface is not a catalyst, due to evacuation of water from it, oxygen gas reduces both the amount of substitution and the reaction rate, even in the presence of

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[10] The chlorine used in the substitution may or not require independent activation. Another alternative assumption would utilize the energy of reaction to activate the chlorine to a degree sufficient for the substitution of an unactivated ethylene dichloride molecule.

[11] Christiansen and Kramers, *Z. physik. Chem.*, **104**, 451 (1923).

[12] N. A. Milas, *Proc. Nat. Acad. Sci.*, **14**, 844 (1928), presents a case of induced polymerization of styrene and refers to other results of a similar character.

the liquid. It seems probable (1) that the glass surface functions as an adsorbing medium for any catalyst; (2) that the reaction is normally initiated on this surface; (3) that the energy liberated by the reaction may be transmitted to a liquid film if the glass is slow to adsorb it; (4) that this energy may induce the substitution reaction; (5) that in the absence of light and water[13] the normal liquid phase reaction is very slow; (6) that in the absence of deactivators a liquid-phase addition reaction may be induced by the glass surface reaction; (7) that oxygen is neither a catalyst nor an inhibitor for the addition reaction, but serves very effectively in maintaining equilibrium in the thermal distribution among the molecules, thus preventing induced or chain reactions.[14]

The Specific Reaction Rate.—By assuming that after the separation of the reaction products as liquids the catalytic conditions were constant, the rates of the reaction under different conditions may be compared. The law governing the rate may be expressed

$$-\frac{\mathrm{d}(\mathrm{C_2H_4})}{\mathrm{d}t} = \mathrm{K}'' \, (\mathrm{C_2H_4})(\mathrm{Cl_2}) \qquad (1)$$

In order to evaluate the concentrations of the reactants at any instant from their initial concentrations and from the measured change in pressure, the amount of the substitution reaction taking place and the vapor pressure of the deposited liquid must be known.

Consider first the case that the reaction is simple addition. If a and b are the initial pressures of ethylene and chlorine, respectively, and x the amount, expressed in pressure, of ethylene that has reacted, then

$$\frac{\mathrm{d}x}{\mathrm{d}t} = K_a'' \, (a - x)(b - x) \qquad (2)$$

Since the rate-determining step of the substitution reaction is this same reaction, but for each ethylene molecule reacting two chlorine molecules are used up, then for a reaction in which the maximum of substitution occurs the expression becomes

$$\frac{\mathrm{d}x}{\mathrm{d}t} = K_s'' \, (a - x)(b - 2x) \qquad (3)$$

The numerical values of K_a'' and K_s'' should be identical under given catalytic conditions. In this paper it is intended to establish only that the above expressions are true within certain limits, namely, in the presence of oxygen to insure Reaction I (addition) as the main reaction and in the presence of excess chlorine (but no oxygen) to insure the maximum of substitution (Reactions I and II). Under these conditions the specific

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[13] H. S. Davis, This Journal, 50, 2769 (1928).

[14] The fact that the reaction takes place only upon the surface (or liquid film) would minimize the importance of radiation as a means of transfer of energy from one molecule to another. Moreover, the reaction as studied in this paper was very susceptible to light from electric globes, which brought about a gas-phase reaction. This effect is under investigation.

reaction rates are the lowest obtained for an evacuated surface. Under other conditions the reaction was faster and the specific reaction rates were not constant during the period of constant catalytic conditions.[15]

Tables II and III present the data as calculated from the experimental observations (see section on Experimental Procedure). In Expt. 6–1 (Table II) the values of K_a'' are not calculated from the beginning because of the separation of liquid during the reaction, with attendant change in the catalytic surface. Also it was impossible to interpret the observed change in pressure in the presence of partial substitution; hence it was assumed that all of this substitution occurred in the early stages of the reaction while the chlorine concentration was high. Similarly in Expt. 6–9 (Table III) the small amount of simple addition was presumed to occur after the chlorine concentration became low.

The agreement of the two specific reaction rates with each other is very good in consideration of the assumption regarding equal catalytic activity

TABLE II

EXPERIMENT 6–1

The specific rate of formation of ethylene dichloride from gaseous ethylene and chlorine, in the presence of 35.1 cm. of oxygen gas and with the liquid reaction products condensed on an evacuated glass surface. Chlorine was used up in substitution (10.5% of initial chlorine) during the first part of the reaction only. Pressures are in centimeters of mercury and time is in minutes.

$$K_a'' = \frac{2.3}{(a-b)t} \log \frac{b(a-x)}{a(b-x)}$$

Time, min.	Vapor pressure, cm.	C_2H_4 pressure, a, cm.	Cl_2 pressure, b, cm.	$K_a'' \times 10^3$
0	0.00	16.6	17.40	...
460	4.60	8.66	7.16	...
470	4.85	7.28	5.73	3.2
480	5.00	6.23	4.63	3.6
490	5.08	5.51	3.86	3.6
500	5.15	5.01	3.31	3.4
510	5.18	4.62	2.87	3.5
520	5.20	4.32	2.54	3.1
530	5.21	4.08	2.28	2.9
540	5.22	3.90	2.08	2.6
550	5.23	3.77	1.94	2.0
575	5.25	3.48	1.65	1.8
600	5.27	3.25	1.41	1.9
625	5.28	3.06	1.21	2.0
650	5.29	2.89	1.03	2.3
703	5.30	2.62	0.75	2.3
792	5.30	2.40	.52	1.7
852	5.30	2.25	.37	2.5
912	5.30	2.14	.25	3.1
1000	5.30	1.90	.00	Av. 2.6

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[15] The reason for this is suggested in Factor 6 in the preceding section. It will be discussed in detail in a later paper.

TABLE III

EXPERIMENT 6–9

The specific rate of formation of 1,2,2-trichloro-ethane from gaseous ethylene and chlorine in the presence of a mixture of ethylene dichloride and trichloro-ethane condensed on an evacuated glass surface. Chlorine was used in simple addition (0.4%) at the end of the reaction only. Pressures are in centimeters of mercury and time is in minutes.

$$K_s'' = \frac{2.3}{2(a - b/2)t} \log \frac{b/2(a - x)}{a(b/2 - x)}$$

Time, min.	Vapor pressure, cm.	C_2H_4 pressure, a, cm.	Cl_2 pressure, b, cm.	$K_s'' \times 10^3$
0	3.7	5.00	15.10	...
5	3.55	4.07	13.15	2.7
10	3.45	3.43	11.80	2.5
15	3.40	2.92	10.75	2.7
20	3.35	2.57	10.00	2.2
25	3.34	2.29	9.40	2.2
30	3.33	2.05	8.90	2.3
35	3.32	1.83	8.45	2.5
40	3.31	1.64	8.05	2.6
45	3.30	1.48	7.70	2.4
50	3.30	1.31	7.35	3.2
55	3.30	1.20	7.10	2.2
60	3.30	1.10	6.90	2.4
65	3.30	1.01	6.70	2.4
70	3.30	0.93	6.55	2.6
75	3.30	.87	6.40	1.8
80	3.30	.82	6.30	1.9
85	3.30	.77	6.22	2.2
90	3.30	.73	6.10	1.5
95	3.30	.705	6.03	1.0
100	3.30	.68	5.98	1.2
00	3.30	.25	4.90	Av. 2.2

in the two cases. The trend of the constants is quite characteristic. In experiments made under other conditions the trend involved from five to ten times this minimum rate, but in such cases the specific reaction rate constant decreased toward the end of the reaction and approached the same value.

Attempts were made to show that the reaction rate was independent of the concentration of the one or other reactant, but without success.

Diffusion in either the gas phase or liquid film is not an important factor in determining the rate; calculations show that for the fastest reactions about 10^5 molecules strike the surface for each one that reacts.

Summary

Under certain circumstances gaseous ethylene and gaseous chlorine react quantitatively to form ethylene dichloride. Under other circumstances they form only 1,2,2-trichloro-ethane and hydrogen chloride. The specific reaction rates for the two reactions are the same. The

substitution reaction is induced by the addition reaction, the heat of formation of ethylene dichloride being utilized to promote the formation of trichloro-ethane.

In the absence of water and light the reactions are autocatalytic.

Oxygen inhibits the utilization of the reaction energy to promote substitution. Nitrogen and water have little effect in this respect. Oxygen and excess chlorine reduce the specific reaction rate to the same minimum value. It is suggested that besides the induced substitution reaction there is also an induced addition reaction.

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THE FRACTIONAL PRECIPITATION OF CELLULOSE ACETATE AND SOME PROPERTIES OF THE FRACTIONS

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Introduction

It is well known that cellulose acetates may be prepared that have widely different physical properties but identical chemical compositions. These differences are commonly ascribed to some difference in state of aggregation or molecular weight of the cellulosic micelles. Several synthetic organophilic colloids—polyvinyl acetate,[1] polyindene,[2] polycinnamalfluorene[3] and polystyrene[2]—have been shown to be mixtures of polymers representing a rather wide range of polymerization of the monomer; it also has been shown that the physical properties of these colloids are intimately connected with the range of sizes of the molecular aggregates present.

The easiest method yet found for fractionating such mixtures is a precipitation process which makes use of the fact that the more highly polymerized components are the first to precipitate from a solution when a precipitating liquid is added. It has been found possible to adapt this method to the case of cellulose acetate and show that a representative material is a mixture of acetates having widely different characteristics.

Materials.—All the experiments reported here were made on a single sample of cellulose acetate prepared by subjecting a dope acetylated triacetate to acid hydrolysis until the product was soluble in acetone. The acetyl number determined by the Eberstadt[4] method was 44.50.

Methods of Fractionation.—Two procedures were used to separate

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[1] G. S. Whitby, J. G. McNally and W. Gallay, *Trans. Roy. Soc. Canada*, **22**, 27 (1928).

[2] H. Staudinger, *Ber.*, **59**, 3019 (1926).

[3] G. S. Whitby and J. R. Katz, THIS JOURNAL, **50**, 1160 (1928).

[4] Eberstadt, "Dissertation," University of Heidelberg, **1911**; Knoevenagel, *Z. angew. Chem.*, **27**, 507 (1914).