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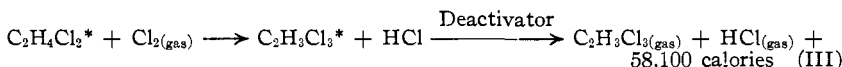
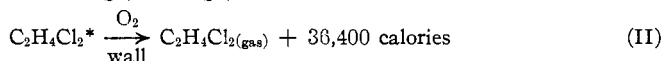
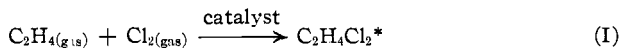
THE INDUCED ADDITION OF ETHYLENE AND CHLORINE

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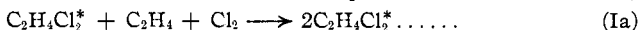
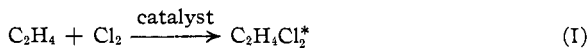
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In a previous paper¹ it was shown that when chlorine gas and ethylene gas react at the surface of the containing vessel, there is formed momentarily a product which is not ordinary ethylene dichloride. This intermediate product may either react rapidly with chlorine to yield 1,1,2-trichloro-ethane and hydrogen chloride or it may be converted into stable ethylene dichloride. This latter step is promoted by oxygen. These changes are expressed in the following equations, the reactants being considered as gases although the reaction takes place upon the wall.



The starred formula represents the intermediate compound of high energy content, which appears only at the surface and may involve the catalyst in its composition or be adsorbed upon the glass surface. Evidence that it is an activated form of ethylene dichloride is presented later.

We now propose to examine the mechanism by which the reaction energy is used to induce the first reaction (Equation I). This reaction is the rate determining step of the total reaction and its specific reaction rate is assumed to have two components. First there is the thermal component, or specific thermal reaction rate, with which the reaction energy is not concerned. This rate is determined by the catalytic conditions and the temperature. The reaction is autocatalytic under the conditions used and the catalyst is the reaction product, ethylene dichloride or trichloro-ethane, which, if present as a liquid film upon the surface, is considered to be of constant activity. The second component is the induced reaction rate, whose magnitude depends upon that of the thermal rate, and upon the length of the reaction chains²



and by Equation III



¹ Stewart and Smith, THIS JOURNAL, 51, 3082 (1929).

² The efficiency of propagation of the chains is very low, otherwise the reaction rate would approach that of an explosion. Occasional explosions in highly condensed systems support this mechanism.

If we assume that for the reaction product to act as a catalyst it must be activated, then for the thermal rate the activated catalyst is in thermal equilibrium with the main mass of the catalyst, whereas the induced component of the reaction is caused by the production during the reaction of activated catalyst in excess of thermal equilibrium.³ The sum of these two components is the quantity experimentally determined and is termed the enhanced specific reaction rate.

The method of experimentation has already been described.

The Specific Thermal Reaction Rate

Subsequent to the series of experiments described in the previous paper, the addition reaction⁴ was studied in the presence of oxygen to insure the minimum of any induced reactions. In this way the purely catalytic influence of trichloro-ethane and of ethylene dichloride could be compared.

Table I gives a summary of the results. In the last column the second order reaction rate constants are given as an arithmetical average of the various values calculated by intervals, together with the mean deviation

TABLE I

THE RELATIVE CATALYTIC EFFECTS OF LIQUID FILMS OF ETHYLENE DICHLORIDE, TRICHLORO-ETHANE AND OF A MIXTURE OF THE TWO, DEPOSITED UPON AN EVACUATED GLASS SURFACE, UPON THE RATE OF ADDITION OF ETHYLENE AND CHLORINE GASES

Pressures are in centimeters of mercury. $dx/dt = K''_a(a-x)(b-x)$. Pressure of oxygen, 35.0 cm.

Part A. Temperature, 20.0°						
Expt.	Catalyst	Vapor pressure		Initial concentrations		$K''_a \times 10^3$ (average)
		Initial	Final	Chlorine (a)	Ethylene (b)	
7-2	C ₂ H ₄ Cl ₂	6.1	6.0	5.7	16.10	1.8±0.10
7-3	C ₂ H ₃ Cl ₃	1.8	2.5	5.09	14.89	1.3±0.15
7-4	Mixture	3.6	3.9	4.28	15.59	1.5±0.26
7-5	Mixture	3.6	3.8	14.52	4.26	1.3±0.10
7-6	Mixture	3.6	4.5	13.51	13.43	3.1±0.35
Part B. Temperature, 10.3°						
7-7	Mixture	2.5	2.9	4.78	14.41	3.7±0.15

³ Direct activation of ethylene and chlorine through collision, sufficient to bring about reaction, seems unlikely since alone they do not react at all upon dry glass surfaces. For the thermal reaction at least, the catalyst must be adsorbed upon the surface. The fact that the thermal reaction rate has a negative temperature coefficient indicates the reversible formation of a compound or "complex" between the catalysts and reactants.

⁴ In this paper the term "addition reaction" refers to that series of steps as outlined above which results only in ethylene dichloride (I and II). The term "substitution reaction" correspondingly denotes trichloro-ethane as the sole (organic) product (I and III). The term "induced addition reaction" involves only the rate-determining step (Equation I, Ia or Ib) of these two reactions and indicates an enhanced rate of either addition or substitution, depending upon the nature of the following reaction. "Induced substitution" refers only to Equation III.

from the average. There was no pronounced trend in the constants for any one experiment.

The variation of the specific reaction rate with variation in the composition of the liquid phase is small, in the presence of a large amount of oxygen. The numerical magnitude of the constants reported in the previous paper are in good agreement when all the factors governing the reaction rate are considered. It would appear that ethylene dichloride is a better catalyst than is trichloro-ethane, but this conclusion is inconsistent with the data presented in the previous paper. It is believed that the trichloro-ethane is the better catalyst (when adsorbed) and is also a more efficient deactivator, so that the difference in reaction rates in Expts. 7-2 and 7-3 is simply an indication that the chain or induced part of the reaction is more inhibited by trichloro-ethane than by ethylene dichloride. As will appear later, chlorine is a powerful deactivator, so that its inability to reduce the constant in Expt. 7-5 to a lower value than 1.3×10^{-3} may be taken as an indication that this value, with the mixed liquids as catalyst, represents the true thermal specific reaction rate. It is important to note that large variations in the composition of the liquid film produce small changes (40%) in this specific reaction rate, as compared to the effect (1000%) of oxygen (see next section). In Table I we have the first indication of the effect upon the specific reaction rate of the *relative proportion* of the reactants. When either one is in excess, the reaction is slower, excess chlorine being more effective than excess ethylene in lowering the specific reaction rate. This fact alone indicates the existence of an induced addition reaction even in the presence of thirty-five centimeters' pressure of oxygen and with the mixed liquids as a film upon the surface. Excess of ethylene almost eliminates the chain reaction, and excess of chlorine reduces the reaction rate to the thermal value. Finally it must be presumed either that the catalytic activity of ethylene dichloride and of trichloro-ethane are nearly equal, or that only one (trichloro-ethane) is the effective catalyst, regardless of its relative amount. The latter view is supported by the existence of an inhibition period when saturated ethylene dichloride *vapor* is initially present but not in the presence of trichloro-ethane vapor. The catalyst is active only when adsorbed upon the wall, which accounts for the effectiveness of small amounts as compared to large amounts. On this view, liquid ethylene dichloride is not a strong catalyst, but as a liquid supports the induced part of the enhanced reaction rate.

The deactivating conditions described above seem adequate largely to eliminate the induced substitution (Equation III). For this purpose oxygen appears almost specific. Water vapor had little effect upon the substitution.

The Enhanced Reaction Rate

In the absence of oxygen the specific rate of the reaction is much greater

than in its presence. Table II presents the results of some typical experiments.⁵

TABLE II

THE ENHANCED SPECIFIC REACTION RATE BETWEEN ETHYLENE AND CHLORINE IN THE ABSENCE OF OXYGEN, WATER OR LIGHT

Catalyst, liquid reaction products; temperature, 20.0°; pressures in cm. of mercury; time in minutes. A is the pressure of ethylene, B that of chlorine and x that of the ethylene used up, then, (1) $\frac{dx}{dt} = K_a''(A - x)(B - x)$ (2) $\frac{dx}{dt} = K_s''(A - x)(B - 2x)$. The constant is calculated by intervals, and the pressures correspond to the times of the first and last constant calculated.

	Expt. 5-9		Expt. 6-4		Expt. 6-5		Expt. 7-1	
	Partial pressures Initial	Final	Partial pressures Initial	Final	Partial pressures Initial	Final	Partial pressures Initial	Final
C ₂ H ₄	11.72	7.15	14.25	0.64	15.93	13.02	15.30	13.01
Cl ₂	7.35	0.35	27.5	1.25	6.02	0.10	5.2	0.22
Vapor	1.85	2.60	3.4	2.6	4.90	3.80	6.1	5.3
	Time	$K_s'' \times 10^3$	Time	$K_s'' \times 10^3$	Time	$K_s'' \times 10^3$	Time	$K_s'' \times 10^3$
	80	..	16	..	14	..	0	..
	81	8.7	17	11.5	15	11.1	1	10.6
	82	10.4	18	16.7	16	14.8	2	14.8
	83	13.7	19	18.2	17	15.5	3	28.1
	84	16.6	20	22.0	18	16.0	4	21.4
	85	$K_a'' \times 10^3$	21	34.6	19	14.7	5	13.8
	86	17.4	22	32.7	20	15.3	6	9.5
	87	17.9	23	32.7	21	11.9	7	7.1
	88	16.0	24	31.3	22	$K_a'' \times 10^3$	8	5.5
	89	16.0	25	31.3	25	10.8	9	6.5
	90	14.3	27	20.2	32	8.0		
	91	13.1	29	19.7				
	93	13.0	31	21.0				
	95	10.9	33	$K_a'' \times 10^3$				
	97	10.0	44	..				
	99	9.4	49	21.5				
	101	9.5	54	27.0				
	105	10.2	59	23.0				

The law for the reaction rate which is here used would not seem to be satisfactory, since a marked trend in the constants usually is found. Other laws, such as those involving other powers of the pressures than unity, were less satisfactory. Moreover, under deactivating conditions this law is very satisfactory and the increase in the magnitude of the constants over the values given in Table I, together with the trends, finds a reasonable explanation on the basis of the factors developed in the succeeding section.

The enhanced specific reaction rate is seen to be from five to twenty times that of the thermal rate. Accordingly, upon the assumption that the

⁵ If the reaction were mostly substitution, but partly addition, the addition reaction was presumed to occur exclusively at the end of the reaction when the chlorine concentration was low. There would be a short period in which the two reactions would be concurrent, *i. e.*, Equation I being succeeded in part by Equation II and in part by Equation III, but finally the latter would disappear.

thermal reaction initiates the induced chains, these chains are seen to involve on the average from five to twenty links. The product formed by the induced reaction is then over 80% of the total, and the enhanced rate is largely dependent upon factors affecting the induced reaction.

Discussion of Results

Variables Affecting the Enhanced Specific Reaction Rate.—These may be listed as follows: (1) catalyst for the thermal reaction, (2) the extent of the liquid film, (3) ratio of the pressures of the reactants, (4) actual pressures of the reactants, (5) deactivators other than the reactants and products, (6) temperature.

The first variable has already been considered. The other variables are used in tentative explanation of the apparent autocatalysis after separation of the liquid film, and the decrease in the constant toward the conclusion of the reaction (Table II).⁶ Since the specific thermal reaction rate is constant in the presence of the liquid film and affected only slightly by small variations in its composition, this autocatalysis is to be ascribed to an effect upon the induced reaction of a changing condition within the film itself. The continued formation of the reaction products as liquids, with drainage to the bottom of the vessel, leads to a steady state condition of maximum opportunity for the induced reaction. The reaction within the liquid film (or accompanying its presence) is not thermally initiated, but is induced within the liquid phase by the thermal reaction occurring at the glass-liquid or glass-vapor interface. This statement is proved by the facts that separation of liquid in the presence of oxygen does not cause such a large increase in reaction rate, and that upon ordinary glassware the reaction is not autocatalytic. Hence the increasing reaction rate is connected with the setting up of a steady condition of the liquid film, modified by any changes in composition of the film during the reaction. A higher vapor pressure indicates a higher percentage of ethylene dichloride. This in turn permits an increased chance of induced addition reaction (greater specific enhanced reaction rate) and also an increased chance of the induced substitution reaction (Equation III). Thus in Expt. 7-1, in the presence of liquid ethylene dichloride and excess ethylene, the reaction is very rapid, somewhat autocatalytic (no inhibition period), and *completely substitution*.

The third and fourth variables account for the falling off in the specific reaction rate of the enhanced reaction. This phase of the work is still under investigation, since the evidence concerning them is confused with changing composition and character of the liquid film. Table I presents

⁶ At zero time there was no vapor present in Expt. 5-9 so that considerable time elapsed before the separation of liquid and any reasonable approach to constant catalytic conditions. In Expts. 6-4 and 6-5 there were 3.7 and 5.4 cm. pressure of ethylene dichloride present at zero time, respectively, and in Expt. 7-1 liquid ethylene dichloride was present at zero time.

the best evidence that the chance of an induced addition reaction is increased when the reactants are in equal concentrations. There is reason to believe the maximum chance should occur at this point under otherwise given conditions. Table III presents what other evidence there is that excess of either reactant in the absence of oxygen reduces the specific reaction rate.

TABLE III

THE EFFECT OF THE RELATIVE PROPORTIONS OF THE REACTANTS UPON THE SPECIFIC ENHANCED REACTION RATE UNDER FAIRLY CONSTANT CATALYTIC CONDITIONS AND UNIFORMITY OF LIQUID FILM

Temperature, 20.0°. All pressures are in cm. of mercury. No oxygen or water present.

Expt.	Vapor pressure	Pressure of reactants		$K_a'' \times 10^3$	$K_s'' \times 10^3$
		Chlorine	Ethylene		
6-4	2.6	5.0	3.8	..	31
6-9	3.3	6.0	0.7		1.5
6-4	2.6	1.5	2.0	22	
5-9	2.1	1.5	8.5	16	
6-5	3.9	1.5	13.8		16
6-8	3.7	1.5	15.7	8	
7-1	5.8	1.5	13.6		25
6-4	2.6	7.5	5.0	32	
6-9	3.7	15.1	5.0		2.7
6-4	2.6	0.9	1.5	22	
6-9	3.3	7.7	1.5		2.5

Excess of chlorine is very effective in eliminating the chain reactions, excess of ethylene less so. The results of Expt. 7-1 again indicate that the composition of the liquid film is very important in determining the extent of the induced reaction, or the length of the reaction chains.

The chance that the reaction energy is used to induce further reaction is greatest when there is equal chance of collision of the reactants with the activating center. If there is a greater chance of chlorine molecules striking this center than of ethylene, the reaction energy will be dissipated among the chlorine molecules, and *vice versa*.⁷ Thus a decrease in the specific rate constant is to be expected if one constituent is used up at a different

⁷ The inefficiency of propagation of the chains infers a high sensitivity to deactivators, which is inconsistent with the fact that the total quenching of the induced part of the reaction has been difficult to achieve. The answer to this anomaly may lie in part in the heterogeneous character of the reacting system; on the other hand, since both chlorine and ethylene may act as deactivators as well as reactants, the length of the chain may depend in part upon the ratio of their concentrations, and within limits be largely independent of their actual concentrations. This factor must be studied further, but it suggests that increase in reactant concentration automatically increases the deactivation capacity and, conversely, if one is depending upon excess of one reactant, as in the present instance, to help eliminate the chains, a very large excess may be required. Adsorbed oxygen, trichloro-ethane and chlorine appear to be the best deactivators, but none is effective in traces only.

rate than the other, leaving one in increasing excess as the reaction proceeds, and even at equal concentrations the specific reaction rate may decrease with decreasing concentration of the reactants. This was observable in Expt. 7-6 (Table I) in which, after the pressures of ethylene and chlorine fell to 2 cm. of mercury, the constant for the reaction dropped to the value 2.3×10^{-3} . A further explanation of this decrease in rate could be found in the idea that the uniformity of the film of liquid influenced the induced reaction. As the reaction slows, the rate of deposition of liquid lessens and the character of the film may change. The heterogeneous character of the reaction suggests other factors such as adsorption and diffusion which may play a smaller part in this effect.

The fifth and sixth variables require no further comment. Three experiments (not included above) made at 10.0° in the absence of oxygen indicate a negative temperature coefficient for the enhanced reaction rate, with some indication that at lower temperatures a positive coefficient might be found, *i. e.*, the induced reaction may disappear faster with lowering temperature than is compensated for by the negative temperature coefficient of the thermal reaction.

The Reaction Mechanism and the Nature of the Intermediate Product.—The equations presented above represent the proposed mechanism of the reaction. Only one mole of hydrogen chloride is formed for each mole of ethylene that reacts, even in the presence of liquid ethylene dichloride and excess of chlorine. It seems evident that the energy of addition is available to induce the exothermic substitution, and the substitution may induce the addition, but the total energy of the two reactions is not utilized to induce further chlorination. There are three possible reasons for this. First, the trichloro-ethane may rapidly distribute the excess energy to the walls, or other inert substances, before the collisions occur which are necessary to promote further substitution. Second, the energy may not be transferable from the trichloro-ethane to ethylene dichloride and chlorine in such a way as to induce substitution, even though collisions could take place during the life time of the energy laden trichloro-ethane. The total energy might be transferred to another molecule of the same kind, but not to one of a different kind. Third, the evolution of hydrogen chloride may be a factor in the rapid distribution of the reaction energy.

Whenever trichloro-ethane is formed, the chain reaction leading to *chlorination* is broken, and the question arises as to whether the reaction energy is ever actually transferred to a second molecule in such a way as to activate that molecule for a specific reaction. The induced substitution reaction (Equation III) need not presume such a transfer, since the molecule chlorinated may be the precise molecule formed in the addition reaction (Equation I). However, it was shown in the previous article that the presence of ethylene dichloride enhanced the chance of the substitution

reaction, and that the presence of other substances, notably oxygen, decreased that chance.

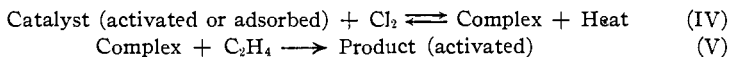
This effect of the ethylene dichloride could be explained as follows. (1) Of all the deactivators present, ethylene dichloride is the only one which could receive the reaction energy and utilize it to promote a substitution. This presumes a transference of energy of high intensity from one molecule to another. The chance of an ethylene dichloride molecule possessing the energy would depend in part upon the relative concentrations of the various substances present and hence the chance of substitution would increase in the presence of ethylene dichloride. (2) Normal ethylene dichloride might prolong the life of an activated ethylene dichloride through association, or, in the liquid film, by offering mechanical protection or a medium of existence apart from the wall where it was formed. (3) Chlorine is a deactivator and, having received the energy of reaction, its chance of taking part in a substitution reaction would be enhanced by the presence of ethylene dichloride. However, the fact that when chlorine does act as a deactivator the amount of substitution does not exceed the maximum represented by the above equations, would appear to eliminate this view from serious consideration.

There is, then, good reason to believe that a normal ethylene dichloride molecule may receive the reaction energy, being itself activated sufficiently to react with chlorine; but the source of the energy is a "nascent" ethylene dichloride, termed above an "intermediate product," and except for their energy content the two molecules are identical. Equation II then becomes reversible under these specific conditions, *i. e.*, the source of the activation energy is an ethylene dichloride molecule of high energy content.

It should also be noted that although the reactions represented by Equations I and II may be reversible, the intermediate addition product is usually not in equilibrium with either the reactants or the final product during the reaction. Its formation is the slow step in the total reaction, and its rate of formation depends upon other processes, such as activations or complex formation, involving the reactants and catalysts. These in turn are in true equilibria, except as noted hereafter.

The thermal reaction requires a catalyst, which in the case of an evacuated glass surface is either ethylene dichloride or trichloro-ethane, or both, which are adsorbed.³ The negative temperature coefficient of the rate of the reaction indicates an equilibrium involved in the rate determining step, of the type

³ If water is present it is preferentially adsorbed and the reaction is not autocatalytic. Upon a paraffin surface there is no adsorption and no reaction. It is probable that if the dry liquid reaction products were used as a solvent, in the dark, there would be little or no homogeneous reaction.



The equilibrium represented by Equation IV involves not the catalyst as a whole, but only that portion capable of entering into complex formation, such as some activated form. The reason that the surface-adsorbed catalyst is more effective than the liquid may be that adsorption stabilizes the complex formation or lowers the activation energy. To the extent that the catalyst may become activated in the liquid phase, a liquid phase reaction will take place.

It is then apparent that the intermediate reaction product (Equation I) is a potential catalyst itself, and represents an amount of activated catalyst in excess of that in true thermal equilibrium. By Equation IV this means a higher concentration of the complex chlorine addition product and hence a faster or enhanced specific reaction rate.

According to this picture of the mechanism, there is no essential difference between the thermal and the induced reactions. Photons, or any other source of activation within the liquid phase, might induce the reaction, and there is evidence⁹ that light induces a gas phase reaction under the conditions of the present experiments. Of particular importance is the idea that by this mechanism the reaction energy *need* not be transferred at all from one molecule to another to induce the rate-determining step of the reaction. The presence of the liquid film brings about a faster reaction either by permitting the surface-formed intermediate to escape from the surface with its energy, thereby initiating a reaction chain within the liquid, or receives this energy by transfer with the same result.

Summary

The addition of ethylene and chlorine is probably a chain reaction, being self-induced. The role of the catalyst for the thermal reaction and the mechanism of the induced reaction are discussed.

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⁹ To be presented in a separate communication.