THE REACTION BETWEEN ETHYLENE DERIVATIVES AND THE HALOGENS

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Received March 30, 1943

CONTENTS

I. Introduction 27
II. Reactions between olefins and fluorine 28
III. Reactions between olefins and chlorine 28
  A. Photochemical reactions 28
  B. Thermal reactions 31
IV. Reactions between olefins and bromine 32
  A. Photochemical reactions 32
  B. Thermal reactions 34
  C. Mechanism of the olefin-bromine reaction 36
  D. Influence of substituents 43
V. Reactions between olefins and iodine 46
VI. The general mechanism of the olefin-halogen reaction 49

I. INTRODUCTION

Considerable work on the addition reactions of olefins and the halogens has been published since the first preparation of ethylene dichloride by a group of Dutch workers (25), but a systematic investigation of the problem is comparatively recent history. The considerable industrial use of olefins and of their halogenated products in recent times has not been without its repercussions on the purely scientific side, and it is useful and necessary to consider the development of the subject and to survey the present position.

The greater part of the early work has been essentially of a qualitative nature, with no serious attempt to study the mechanism of the reaction. Also, an analysis of published work reveals that surprisingly few compounds have been the subject of study. The most important early work was on the reactions in the gaseous phase, between ethylene and chlorine and between ethylene and iodine, studied by Michael Faraday (29). In a remarkable communication to the Royal Society, Faraday observed that with equal proportions the addition reaction is complete, with excess olefin reaction stops after the addition, and with excess halogen substitution follows the addition reaction,—all the reactions being carried out in bright sunlight. Faraday observed that these reactions can also take place in the dark, though much more slowly. In the reaction between

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ethylene and iodine, however, the photochemical reaction appears to have stopped with the formation of addition compound, no hydrogen iodide being evolved.

Subsequent work in the nineteenth century does not indicate the same thoroughness of investigation. Generally carbon disulfide has been the solvent (30, 55, 56, 57, 59, 119, 120, 121, 122) in which the reactions were carried out. Carbon tetrachloride and chloroform have been used in some cases (13, 57, 66, 67). In the case of gaseous olefins, reactions in the gas phase were studied first. In all cases the addition compounds were obtained, and in some cases substitution products were found in connection with chlorine and bromine additions (7, 53, 84, 92). For convenience of treatment, the problem may be considered under various headings.

II. REACTIONS BETWEEN OLEFINS AND FLUORINE

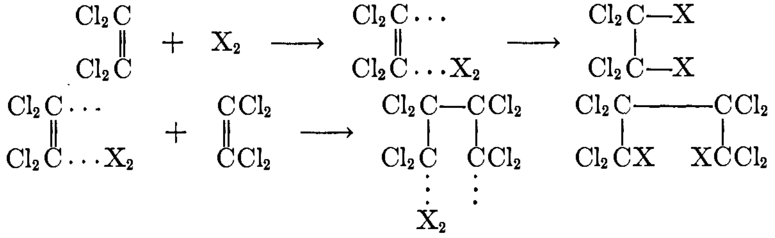
The considerable reactivity of fluorine has been a serious impediment in the study of the olefin–fluorine reaction. As may be expected, any fruitful results are possible only with comparatively inert olefins. Humiston and coworkers (45) observed that tetrachloroethylene reacts readily with fluorine, the products isolated being hexachloroethane, carbon tetrafluoride, and carbon. They suggested that the reaction probably proceeds as follows:—

$$C_2Cl_4 + 2F_2 \rightarrow 2Cl_2 + C_2F_4$$

$$C_2F_4 \rightarrow CF_4 + C$$

$$C_2Cl_4 + Cl_2 \rightarrow C_2Cl_6$$

The later investigations of Bockemüller (20) led to a somewhat different result. By the action of fluorine on a solution of tetrachloroethylene in dichlorodifluoromethane at −80°C. the addition compound, tetrachlorodifluoroethane, was formed, and also a by-product containing double the number of carbon atoms. To explain this behavior, following Meisenheimer (61) and taking into account the work of Hunter and Yohe (46) that provides some evidence for an activated olefin molecule with a free electron pair, the mechanism of the reaction was represented as follows:



$$\begin{array}{c}\mathrm{Cl_2C}\\ \| \\ \mathrm{Cl_2C}\end{array} + \mathrm{X_2} \longrightarrow \begin{array}{l}\mathrm{Cl_2C}\cdots\\ \|\\ \mathrm{Cl_2C}\cdots\mathrm{X_2}\end{array} \longrightarrow \begin{array}{l}\mathrm{Cl_2C{-}X}\\ |\\ \mathrm{Cl_2C{-}X}\end{array}$$

$$\begin{array}{l}\mathrm{Cl_2C}\cdots\\ \|\\ \mathrm{Cl_2C}\cdots\mathrm{X_2}\end{array} + \begin{array}{c}\mathrm{CCl_2}\\ \|\\ \mathrm{CCl_2}\end{array} \longrightarrow \begin{array}{cc}\mathrm{Cl_2C}{-} & \mathrm{CCl_2}\\ | & |\\ \mathrm{Cl_2C} & \mathrm{CCl_2}\\ \vdots & \vdots\\ \multicolumn{2}{c}{\mathrm{X_2}}\end{array} \quad \begin{array}{ccc}\mathrm{Cl_2C} & \text{———} & \mathrm{CCl_2}\\ | & & |\\ \mathrm{Cl_2CX} & & \mathrm{XCCl_2}\end{array}$$

III. REACTIONS BETWEEN OLEFINS AND CHLORINE

A. Photochemical reactions

Michael (63, 64, 65), Massot (49), and Kirchhoff (52) found addition reactions with very little side reactions occurring between the olefins studied by them and chlorine, in the presence of sunlight. In solution in carbon disulfide or carbon tetrachloride, Liebermann (57) found that the cinnamic acid–chlorine reaction gave a mixture of optical isomerides. Later Nasarow (73) observed that the reaction between cinnamic acid and chlorine in carbon tetrachloride takes place fairly rapidly even in the dark and showed that, for any temperature, the dark reaction must be separated from the total reaction. Taking this into account, he obtained for the photochemical reaction a temperature coefficient of 1.402. A more complete investigation was carried out by Berthoud and Porret (17). They found that the photochemical addition of chlorine is approximately independent of acid concentration, is proportional to the concentration of chlorine, and is a function of the light intensity. The results obtained by these workers differed from those of Basu (9), who suggested an atom-chain mechanism, in which the length of the chain is proportional to the energy of the monochloro compound formed in the first stage of the reaction. The later workers obtained a value of the quantum yield as variable, about 2.4, and a thermal temperature coefficient of 1.5. Following the work on bromine addition, these workers suggested the following chain mechanism to explain their results:

$$Cl_2 + h\nu \rightarrow Cl + Cl$$

$$A + Cl \rightarrow ACl$$

$$ACl + Cl_2 \rightarrow ACl_2 + Cl$$

$$2ACl \rightarrow X$$

In consideration of the complex nature of the substituents in cinnamic acid, it may be expected that olefin hydrocarbons and halogenated olefins may give better information on the mechanistic side. With the exception of ethylene and tetrachloroethylene, work in this direction has been practically nil.

Stewart and Weidenbaum (108a), working with methylethylethylene, found that the photochemical reaction involves both substitution and addition. They made the rather surprising observation that substitution is favored by increased olefin concentration, while an increased chlorine concentration favors addition. Stewart and coworkers (103, 106, 107, 108, 108a) have made a thorough study of this reaction, an investigation ranging over several years. In an early work (106) the observation was made that both addition and substitution reactions take place, the addition reaction inducing the substitution. In the absence of moisture and light the reaction is found to be autocatalytic, oxygen functioning as an inhibitor. A chain mechanism involving activated molecules is also suggested for the thermal reaction. The later photochemical investigations showed that the reaction is proportional to the concentration of chlorine at constant intensity of light and independent of the concentration of ethylene. There is the significant observation that in a mixture of hydrogen, chlorine, and ethylene, while no hydrogen reacted, the ethylene–chlorine reaction went to completion both in the dark and in light. The addition compound functioning as a solvent enhanced the reaction rate, reducing the extent of substitution. There is in pentane solution a high degree of substitution, the extent depending on the ethylene–chlorine ratio. Two alternative mechanisms leading to the same kinetic equation

$$-\frac{d(Cl_2)}{dt} = kI_{abs.} = kI_0(Cl_2)$$

have been suggested.

$$Cl_2 + h\nu \rightarrow 2Cl$$

$Cl + Cl_2 \rightarrow Cl_3$	$Cl + C_2H_4 \rightarrow C_2H_4Cl$
$Cl_3 + C_2H_4 \rightarrow C_2H_4Cl_3$	$Cl_2 + C_2H_4Cl \rightarrow C_2H_4Cl_3$
$C_2H_4Cl_3 \rightarrow C_2H_4Cl_2 + Cl$	$C_2H_4Cl_3 \rightarrow C_2H_4Cl_2 + Cl$
$C_2H_4Cl_3 + \text{wall} \rightarrow C_2H_4Cl_2 + \frac{1}{2}Cl_2$	$C_2H_4Cl_3 + \text{wall} \rightarrow C_2H_4Cl_2 + \frac{1}{2}Cl_2$

While one has to admit that an atom-chain mechanism is most likely in the photochemical reaction, it is rather difficult to explain how there is no reaction with hydrogen, when it is used as a diluent. Presumably the lower energy of activation of 3 kilocalories for the over-all reaction arrived at by Sherman, Quimby, and Sutherland (101) provides one reason for the addition reaction taking precedence.

The photochlorination of the *cis*- and *trans*-dichloroethylenes has been thoroughly investigated by Müller and Schumacher (70, 71), using light of 4360 Å. between 80° and 95°C., the reactant concentration being maintained below a pressure of 100 mm. With an absorption rate of 10 to 15 quanta per minute, the quantum yield is given as 7×10^3 molecules. These authors observe that the reactions of both the *cis* and the *trans* forms are similar, with the same absolute velocity. At low pressures, below 20 mm., the reaction seems to be influenced by olefin concentration, but at higher pressures the velocity equation is given as

$$+\frac{d(C_2H_2Cl_4)}{dt} = kI_{abs.}^{1/2}(Cl_2)$$

Oxygen is observed to have a marked retarding influence and in the chain mechanism suggested by the authors it is presumed to react with ACl radicals. These authors observed a similar effect in the photochlorination of trichloroethylene. While with our present knowledge it is not possible to arrive quantitatively at the extent of mutual group interactions in influencing the additive reactivity of the double bond, it seems rather strange that with two olefins of widely different dipole moments, no difference in reactivity should be observed. The authors have been able to confirm in a later paper (71) the observation on the influence of oxygen by the isolation of oxygenated compounds. With a low temperature coefficient and a quantum yield of 40, a chain mechanism is suggested involving the formation of a peroxide. The interpretation, however, is complicated by the formation of carbon dioxide, phosgene etc.

Dickinson and coworkers (26, 27, 28) have studied the photochlorination of ethylene both in the gaseous phase and in solution. In both cases, in the absence of oxygen, the quantum yields were of the order of several hundred, and the best interpretation is possibly by a mechanism identical with that of Berthoud and Béraneck (15, 16).

$$
\begin{array}{lll}
(1) & Cl_2 + h\nu \rightarrow 2Cl & \phi I_a \\
(2) & C_2Cl_4 + Cl \rightarrow C_2Cl_5 & k_2 \\
(4) & C_2Cl_5 + Cl_2 \rightarrow C_2Cl_6 + Cl & k_4 \\
(6) & Cl + Cl \rightarrow Cl_2 & k_6 \\
(7) & Cl + C_2Cl_5 \rightarrow C_2Cl_6 & k_7 \\
(8) & 2C_2Cl_5 \rightarrow C_2Cl_4 + C_2Cl_6 & k_8 \\
 & \text{or} & \\
 & 2C_2Cl_4 + Cl_2 &
\end{array}
$$

The non-appearance of the olefin concentration in the reaction-rate equation indicates that every chlorine atom reacts according to equation 2. The observation by Müller and Schumacher (70, 71) of a pressure limit when the olefin concentration affects the reaction, evidently represents the lower limit of concentration at which all chlorine atoms may be expected to react by reaction 2. The inhibitory effect of oxygen and the detection of carbonyl chloride bring this in line with other observations on like reactions. In the presence of oxygen, even at 40°C., there is no perceptible reaction, while in the absence of it there is slight thermal reaction. These authors suggest an alternative method of formulating the mechanism, though Berthoud's mechanism may account for the observations equally well.

B. Thermal reactions

While the photochemical reactions appear to have been well investigated, the studies of the thermal reactions are very few and comparatively recent. Norrish and Jones (75) observed the remarkable effect of the nature of the reaction surface on the gas reaction; they found that the reaction proceeds only in the presence of a polar surface and that the thermal reaction is essentially heterogeneous with apparently no homogeneous reaction.

In dissociating solvents like acetic acid and nitrobenzene (97), the addition of chlorine to *cis*- and *trans*-cinnamic acids gives bimolecular constants, the *cis* acid adding nearly four times faster than the *trans* acid. While dilution appears to have no effect on the value of k_2 in both solvents, the constants tend to diminish with increased dilution in the case of the *trans* acid. The bearing of this and of the values of the Arrhenius parameters on the mechanism is discussed in greater detail in a later section.

Mention should also be made of Tishchenko's work (113) on tetrasubstituted ethylenes. The results indicate that the polarization of the double bond at the quaternary atom leads to anomalous reaction with chlorine. With increasing number of chlorine atoms in the alkyls attached to the quaternary carbon atom, addition increases, while substitution diminishes.

A comparison of the thermal and photochemical reactions with the meager data available indicates an apparently clear-cut demarcation between the two types. The photochemical change appears essentially to depend on the dissociation of the chlorine molecules into atoms with chains involving atomic chlorine, while the thermal reaction probably proceeds by a mechanism involving molecular chlorine.

IV. REACTIONS BETWEEN OLEFINS AND BROMINE

A. Photochemical reactions

While the olefin–chlorine reaction has been studied in the presence of light to a considerable extent, controlled photochemical reactions between olefins and bromine have been studied in comparatively few cases. The work done, however, is sufficient to indicate that the photochemical reactions involving the halogens are essentially similar, though the exact mechanisms may differ.

The preliminary observations of Sudborough and Thomas (109, 110, 111) indicate the enormous influence exerted by light on this reaction. The results of Hofmann and Kirmreuther (43), though comparable amongst themselves, can at best be taken only as qualitative, since the photochemical reactions have not been studied under sufficiently rigidly controlled conditions. The work of Plotnikow (81, 82, 83) on the reactions between bromine and compounds of the structure $R_1R_2C{=}CR_3R_4$ led to the following conclusions: the reaction appears to be in equilibrium which depends upon temperature, the temperature coefficient being of the order of 1.4; the concentration of the reactants, the solvent, the intensity of light (the reaction rate varying as the square of the intensity of light), and the nature of the substituents (R_1, R_2, R_3, and R_4) affect the reaction rate. Plotnikow considers that in the photochemical reaction bromine atoms are definitely involved.

The most thoroughly investigated reactions have been with cinnamic acid, stilbene, and tetrachloroethylene. In a thorough and comprehensive study, Berthoud and coworkers (15, 16) found that, for strong absorption of light, the reaction rate was found to accord with the equation

$$-\frac{d(Br_2)}{dt} = k'I_0^{1/2}(Br_2)$$

and for weak absorption it is

$$k''I_0^{1/2}(Br_2)^{3/2}$$

wherein I_0 stands for the intensity of the incident light. The experimental data indicate clearly a chain mechanism and these authors suggest the following scheme:

$$\begin{array}{lll}
(1) & Br_2 + h\nu \rightarrow 2Br & I_{abs.} \\
(2) & A + Br \rightarrow ABr & k_2 \\
(4) & ABr + Br_2 \rightarrow ABr_2 + Br & k_4 \\
(6) & Br + Br \rightarrow Br_2 & k_6 \\
(7) & ABr + Br \rightarrow ABr_2 & k_7 \\
(8) & ABr + ABr \rightarrow ABr_2 + A & k_8 \\
 & \qquad\qquad \text{or} & \\
 & \qquad\qquad 2A + Br_2 &
\end{array}$$

It is clear that the primary process involves the dissociation of the bromine molecule into atoms, while the proportionality of the rate constant with bromine concentration indicates that the rate-determining step involves bromine molecules. These authors consider that the velocity constant is independent of the olefin concentration, but an examination of the values shows a progressive fall with decreasing concentration of olefin. Reactions 2 and 4 constitute the chain, while reactions 6, 7, and 8 serve as chain-terminating steps. Since the reaction appears to depend essentially on the halogen concentration, reaction 4 is probably the rate-determining step, while reaction 2 is relatively fast. Also, if reaction 2 is sufficiently fast, the chain-breaking mechanisms 6 and 7 may be neglected compared with reaction 8. The non-appearance of the olefin concentration in the experimental equation of these authors indicates that this is largely true. Hence the reaction-velocity equation may be written as

$$-\frac{\mathrm{d}(\mathrm{Br_2})}{\mathrm{d}t} = I_a + k_4(\mathrm{ABr})(\mathrm{Br_2})$$

For the stationary state,

$$(\mathrm{ABr}) = \frac{\phi^{1/2} I_a^{1/2}}{k_4^{1/2}}$$

and hence

$$-\frac{\mathrm{d}(\mathrm{Br_2})}{\mathrm{d}t} = I_a + \frac{k_4 \phi^{1/2}}{k_4^{1/2}} I_a^{1/2}(\mathrm{Br_2})$$

This equation will agree with the experimental rate equation for long chains, i.e., where the chain-breaking mechanism (reaction 8) is negligible when compared with reaction 4. It is interesting to note that *trans*-cinnamic acid, apparently the compound used by these authors, reacts approximately at the same rate as stilbene. These authors' figures for the velocity constant led to a value of the energy of activation for the reaction of 11,500 calories for cinnamic acid in carbon tetrachloride.

Bauer and Daniels (12) have examined the photobromination of cinnamic acid from 0° to 30°C. and over a concentration range of 2×10^{-3} to 8×10^{-3} moles per liter. Their results clearly indicate again a chain mechanism with varying quantum efficiency from 1 to 15, dependent on bromine concentration as well as temperature. The primary photochemical process involves the activation of a bromine molecule, and this is followed by a photoexcited thermal reaction. This thermal reaction, measured by $\phi - 1 = \theta$, is suppressed either by dilution of bromine or by low temperature. A linear relationship between log θ and the reciprocal of the absolute temperature is considered to support the energy chain mechanism.

$$\mathrm{Br_2} + h\nu = \mathrm{Br_2^*}$$

$$\mathrm{Br_2^*} + \mathrm{A} = \mathrm{ABr_2'}$$

$$\mathrm{ABr_2'} + \mathrm{Br_2} = \mathrm{Br_2''} + \mathrm{ABr_2}$$

$$\mathrm{Br_2''} + \mathrm{A} = \mathrm{ABr_2''}$$

$$\mathrm{ABr_2''} + \mathrm{Br_2} = \mathrm{Br_2'''} + \mathrm{ABr_2}$$

Later work by Willard and Daniels (23) with tetrachloroethylene, together with their own work on cinnamic acid (12), appears to indicate the pronounced inhibitory effect of oxygen on the course of the reaction; in fact, in the absence of oxygen the thermal bromination of cinnamic acid is too fast to measure. This mechanism, together with those of Ghosh and Purkayastha (37), are dealt with in detail in a later section. The work of Purkayastha (89) is, however, of doubtful value in understanding the course of the reaction. One finds a rather surprising statement that "this period of gradually increasing velocity is called the period of induction," and the calculations indicated in the paper, neglecting the induction period in the accepted sense of the term, obviously cannot lead to a correct conclusion.

B. Thermal reactions

The first important observation is that of Plotnikow (80), who studied the bromination of ethylene in the dark in petroleum ether at −78° to −100°C. and obtained the results shown in tables 1 and 2. The reaction was followed by observing the change in volume of the reactants. When only one reactant was in excess, a unimolecular constant was obtained, while with both in comparable proportions, bimolecular constants were obtained. This author, however, reports a reaction giving rising constants, but does not investigate the question of catalysis. In the light of later observations (1, 3, 4, 115), these results may be interpreted as arising from the presence, in all but one case, of adequate amounts of the catalyst, hydrogen bromide, to eliminate both induction period and autocatalysis. There is also this further complication that in the non-polar solvent (petroleum ether) used, there is a possibility of a heterogeneous reaction.

TABLE 1

Bromination of ethylene

ETHYLENE	BROMINE	VELOCITY CONSTANT k_1
a = constant	b = 0.024 moles/liter	0.19
a = constant	b = 0.0201 moles/liter	0.17
a = constant	b = 0.0143 moles/liter	0.24
a = 0.0327 moles/liter	b = constant	0.35

The observations of Stewart (104) of the same reaction in the gas phase in the presence of oxygen indicate an essentially heterogeneous reaction with practically no evidence for the homogeneous part. With a constant surface, the reaction rate was found to be proportional to the concentration of reactants, there being no deviation from a bimolecular reaction. Water vapor was found to catalyze the reaction and the initial rate appeared to be greater than the later course of the reaction, an abnormality which the author attributed to wall catalysis. The heterogeneous nature of the gaseous reaction has been confirmed by Norrish (74), who has clearly established the close correlation between the reaction rate and the polar nature of the surface. In a later paper, Stewart (105) observed autocatalysis in the same reaction and also obtained a negative temperature coefficient. This is indicative of a trimolecular mechanism for the heterogeneous reaction.

A more complete investigation by G. Williams (117) of the surface reaction at room temperature in glass vessels indicated a simple addition reaction, followed by supplementary reactions when the bromine is in excess, a behavior recalling the observations of Faraday (29). The kinetics of the reaction was found to be complex, with a negative temperature coefficient and an order of reaction varying with the surface. This author has provided clear evidence that the reaction involves more than one stage. For a given surface, reduction of temperature or increase of pressure of the reactants appears to lower the order of the reaction, while for a given surface and reaction order, the rate constant appears to depend only on the bromine concentration. The catalytic effect of water was pronounced, and it was found that the transition from the second- to the first-order kinetics is favored by a wet surface and a high bromine–ethylene ratio. The product of the reaction is also reported to increase the rate, besides inducing a homogeneous reaction.

TABLE 2

Bromination of ethylene

ETHYLENE	BROMINE	VELOCITY CONSTANT k_2
moles per liter	*moles per liter*	
0.0451	0.0362	6.6
0.0126	0.0126	6.8
0.01885	0.01885	6.4

The work on chloroethylenes (42) is not sufficiently accurate to warrant conclusions as to the nature of the addition reaction. The results of Herz and Rathmann indicated an induction period of about 800 min. with tetrachloroethylene, but the results on di- and tri-chloroethylenes were different, the difference being obviously due to uncontrolled catalytic conditions. The recent investigations of G. Williams (118) on vinyl bromide constitute an important advance in our knowledge of the reaction in the gas phase. The exact mechanism is discussed in relation to the reaction in solution later, but it may be stated here that the study has shown that the reaction is a trimolecular one, is heterogeneous, and involves molecular and not atomic bromine.

In an earlier communication Williams and James (116), from a study of the addition of bromine to a number of unsaturated acids like cinnamylideneacetic, crotonic, and cinnamic acids and their derivatives in chloroform and carbon tetrachloride, divided the reactions into three groups: (*1*) rapid addition followed by substitution accounting for the production of hydrogen bromide with falling k_2 values, e.g., in the case of cinnamylideneacetic acid; (*2*) a slow but measurable addition with an induction period, e.g., in the cases of crotonic and cinnamic acids; (*3*) no measurable addition under the conditions investigated.

These authors found that hydrogen bromide was an effective catalyst, and considered that the mechanism of the dark reaction is different from that of the photochemical one. While the results reported appear to indicate that the reaction in both solvents is homogeneous, the experiments in carbon tetrachloride may not be expected to be so. In a subsequent communication (50) James has shown that the three isomorphic forms of *cis*-cinnamic acid react at the same rate, contrary to the observations of Meyer and Pukall (62).

The first observation leading to doubt as to the correctness of all the earlier work was that of D. M. Williams (115), who clearly demonstrated that with ethylene in carbon tetrachloride the addition reaction shows a clear induction period of many minutes depending on the concentration of bromine (11 min. in one case), and the curve drawn from his data shows all the characteristics of a chain reaction (reference 4, page 293). This observation has been confirmed by Anantakrishnan and Ingold (1). Using acetic acid as solvent, Williams obtained apparently bimolecular constants, the deviation from this being more marked with rise of temperature. In interpreting his results, Williams stated that "the addition of the acetoxy group instead of the second bromine does not take place to a detectable extent." This is to be expected, in view of the observations of Hennion, Vogt, and Weber (39), if the solution had initially contained any hydrogen bromide. We find qualitative evidence in the case of bromine additions, confirming the observations of Hennion and coworkers, to the effect that Williams' statement that the intermediate production of hydrogen bromide is not sufficient to account for the fact that there is no inhibition period when the addition occurs in acetic acid requires revision (3, 4, 95). It is our experience that unless rigid care is exercised to exclude moisture and hydrogen bromide from the reactants the inhibition period fails to be noticed.

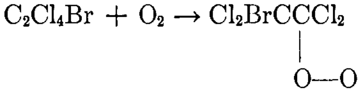
It is necessary to mention here that the choice of solvent is extremely important in following the reactions in solution. Alcohols and esters which are definitely known to react with bromine are unsuitable for any mechanistic studies or interpretation of group influences, while non-polar solvents like carbon tetrachloride and carbon disulfide, which might approximate to the conditions in the gas phase, suffer from the handicap of a possible non-homogeneity in the reactions in solution. Under controlled conditions at ordinary temperatures, the best solvents appear to be methylene chloride, chloroform, and acetic acid.

C. Mechanism of the olefin–bromine reaction

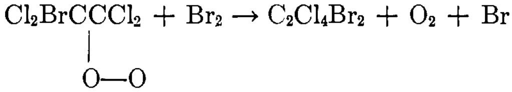
Though in the case of a decomposition like that of nitrogen pentoxide the reaction in the gas phase and in solution, as well as thermal and photochemical reactions, follows more or less the same mechanism, in the case of reactions like the present some difference may be expected. The work of Francis and of Terry and Eichelberger (33, 112) has clearly demonstrated that in halogen additions in solution, it is only molecular bromine that takes part in the reaction. Also the conditions of the dark reaction could reasonably be expected to involve the activated bromine molecule rather than atomic bromine, though addition may take place in stages.

For the photochemical reaction, three main mechanisms have been suggested,—the mechanisms of Berthoud and Béraneck (*loc. cit.*), of Ghosh and coworkers, and of Daniels and coworkers. The mechanism suggested by Daniels and Bauer has already been given; the modified mechanism suggested by Daniels and Willard in their later communication, and the mechanism of Ghosh and coworkers are given below.

	Mechanism of Ghosh and coworkers (36)	*Mechanism of Willard and Daniels (23)*
(1)	$Br_2 + h\nu \rightarrow 2Br$	$Br_2 + h\nu \rightarrow Br + Br$
(2)	$Br + Br \rightarrow Br_2$	$C_2Cl_4 + Br \rightleftharpoons C_2Cl_4Br$
(3, 4)	$Br + Br_2 \rightleftharpoons Br_3$	$C_2Cl_4Br + Br_2 \rightleftharpoons C_2Cl_4Br_2 + Br$
(5)	$Br_3 + A \rightarrow ABr_2 + Br$	$Br + Br \rightarrow Br_2$



$$C_2Cl_4Br + O_2 \rightarrow \underset{O—O}{Cl_2BrCCCl_2}$$



$$\underset{O—O}{Cl_2BrCCCl_2} + Br_2 \rightarrow C_2Cl_4Br_2 + O_2 + Br$$

The mechanism of Berthoud suffers frôm the disability that it involves small temperature coefficients. Daniels has shown that Ghosh's mechanism is difficult to maintain, as the energy of addition of Br_3 to the double bond will be greater than that of Br_2 by about 10,000 calories. Further, the mechanism suggested leads to a rate law of the form

$$-\frac{d(Br_2)}{dt} = k_3\left[\frac{I_{abs.}}{k_2}\right]^{1/2}(Br_2)\,\frac{k_5(A)}{k_5(A) + k_4}$$

The last factor on the right-hand side could be tested only by a sufficient variation of experimental conditions, and in the absence of such evidence it is possible to fit in their results with other mechanisms as well. The formation of Br_3 molecules involves an energy of activation of 10,000 calories, which is approximately the difference between the $^2P_{3/2}$ and $^2P_{1/2}$ states of the bromine atom, but this observation of Ghosh is not of much significance, since we do not have any experimental evidence to lead us to the conclusion that the $^2P_{1/2}$ bromine is more reactive than $^2P_{3/2}$.

In order to account for the course of the addition reaction, together with the inhibitory effect of oxygen on the photochemical reaction, Daniels and Willard (23) have suggested a mechanism taking into account the fact that the product of the reaction has an inhibitory effect as well. With tetrachloroethylene as the olefin, the concentration of the unsaturated compound does not appear to be involved in the rate, and the photochemical reaction appears to have a very small temperature coefficient. The mechanism involves a free radical containing a bromo compound, and this intermediate is considered to explain also the reversibility of the reaction at higher temperatures. While small amounts of oxygen accelerate the photobromination, large amounts have the reverse effect, presumably owing to photosensitized oxidation.

From his study of the heterogeneous gas reaction in the dark, Norrish (74) was led to conclude that the reaction consists in the polarizing of the reactant molecules by *association with a polar catalyst* either in gaseous, surface, or liquid phase. The kinetic studies of G. Williams (117) again indicate a chain mechanism, and in order to account for the apparent effect of water, he suggested a bromine–water complex, adsorbed on the glass surface, which reacts with ethylene. While Daniels found for the photochemical reaction that the products had an inhibitory effect, Williams noted that the products increased the rate of reaction. But Kinumaki *et al.* (51) appear to have found that, even in the dark reaction, the results are the same as those of Daniels. The only other study in the gaseous phase with a view to elucidation of the mechanism is that of G. Williams (118), who investigated the reaction between vinyl bromide and bromine. He found for the rate expression the equation,

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = (\text{olefin})(\text{Br}_2)^2 k_3$$

the heterogeneous reaction having a negative temperature coefficient. With the olefin in excess, an apparent bimolecular constant is obtained, while in other cases an initial rapid reaction of the third order, followed by a reduced reaction of the third order, appears to result. Inert surfaces, however, require a different rate expression,

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = k_2(\text{olefin})(\text{Br}_2)$$

while the introduction of water vapor restores third-order kinetics. The following mechanism has been suggested to account for the observations:

$$\text{Olefin} + \text{Br}_2 \rightarrow \text{Intermediate complex}$$

$$\text{Intermediate complex} \rightarrow \text{Dibromo compound}$$

While this mechanism probably explains the gas reaction, which is essentially heterogeneous, the homogeneous reaction in solution in polar solvents may not conform to it.

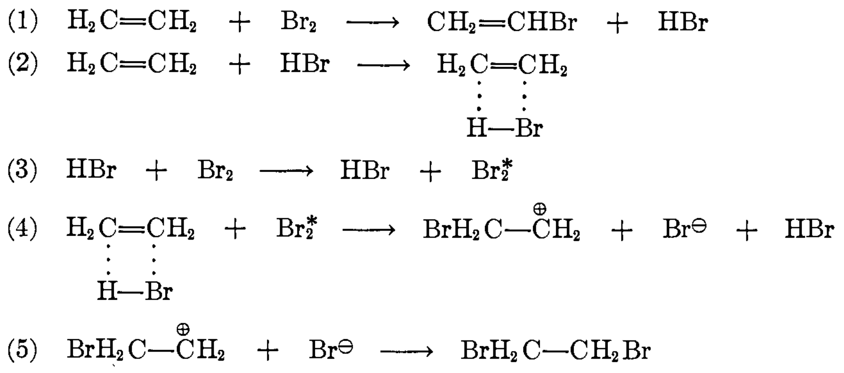
With the available evidence it is very difficult to decide whether the dark reactions in non-polar solvents like carbon tetrachloride and carbon disulfide are to be considered homogeneous or heterogeneous. The observations of D. M. Williams, which show all the characteristics of a chain reaction, can, however, be considered so far as the positive catalytic effect of hydrogen bromide is concerned. With polar solvents the reaction appears to be clearly homogeneous, and these reactions therefore lend themselves to clearer mechanistic studies. The alternative mechanisms that have been proposed are essentially those of Robertson and coworkers, and those of the authors of this review.

It is relevant to mention here that the reactions studied for elucidating the mechanism have all been with α,β-unsaturated acids. It has been observed (60, 98) that the reaction is not influenced by oxygen or peroxides, so that any mechanism suggested may ignore for the present the peroxide effect, observed with simple olefins in gaseous photochemical reactions.

All earlier work on the olefin–bromine reaction gave bimolecular constants and pseudo-monomolecular constants with one of the reactants in excess. That this is no true representation of the actual reaction is seen when one examines the observations of Plotnikow, who obtained rising constants, and the vagarious constants obtained by Herz and Mylius (40, 41), Hofmann and Kirmreuther (43), and Sudborough and Thomas (109, 110, 111). Even in the case of the gas reactions, whether thermal or photochemical, work during the last decade has reduced the number of apparently simple bimolecular reactions to two. It is not, therefore, unlikely that in solutions also one has to expect a similar state of affairs. Systematic work on many reactions in solutions involving organic compounds has shown that these earlier notions, which ascribed simple mechanisms to them, must give place to chain mechanisms involving atoms, free radicals, and activated complexes (98).

Robertson *et al.* consider that the reactions between halogens and olefins involve a trimolecular mechanism and suggest that it is probably similar to that of G. Williams. Taking the reaction between bromine and *cis*- and *trans*-cinnamic acids, in both acetic acid and carbon tetrachloride, it is suggested that in the polar solvent the velocity depends on (*1*) the rate of conversion of the *trans* to the *cis* form, (*2*) the rate of addition to the *trans* form, and (*3*) the rate of addition to the *cis* form. The function of hydrogen bromide is considered to be to accelerate the isomeric change. The experiments in carbon tetrachloride indicate a heterogeneous reaction below 50°C. and a homogeneous trimolecular reaction above that. These authors remark that hydrogen bromide is not a catalyst in the addition of bromine to *cis*-cinnamic acid. The case of acrylic acid, however, seems to provide the difficulty. So far as aliphatic unsaturated compounds are concerned we are unable to get trimolecular constants, the catalyzed reactions invariably giving good bimolecular constants. The difference might be attributed partly to the purity of bromine employed. The elimination of hydrogen bromide is a difficult process, and in most cases the experimental details do not indicate that this catalyst had been eliminated from the bromine used. In all cases that we have examined, a very clear, strictly reproducible, and well-defined period of induction is observed, and this varies with the nature of the groups attached to the olefinic linkage. Activating groups in general diminish the induction period, while deactivating groups have the opposite effect.

A trimolecular reaction does not necessarily preclude binary intermediate compounds. The problem can logically be simplified by considering that a binary collision may involve a certain duration whether an association compound is formed or not, this duration being a function of the structure of the molecules and of intermolecular forces. This complex formed may then be involved in a collision with a further molecule in the process. Considered in this form the trimolecular mechanism of Robertson reduces to the following mechanism proposed by us (3):



$$\text{(1)}\quad H_2C{=}CH_2 + Br_2 \longrightarrow CH_2{=}CHBr + HBr$$

$$\text{(2)}\quad H_2C{=}CH_2 + HBr \longrightarrow \underset{H{-}Br}{\underset{\vdots\quad\vdots}{H_2C{=}CH_2}}$$

$$\text{(3)}\quad HBr + Br_2 \longrightarrow HBr + Br_2^*$$

$$\text{(4)}\quad \underset{H{-}Br}{\underset{\vdots\quad\vdots}{H_2C{=}CH_2}} + Br_2^* \longrightarrow BrH_2C{-}\overset{\oplus}{C}H_2 + Br^{\ominus} + HBr$$

$$\text{(5)}\quad BrH_2C{-}\overset{\oplus}{C}H_2 + Br^{\ominus} \longrightarrow BrH_2C{-}CH_2Br$$

This takes into account the definite and pronounced influence of hydrogen bromide on the reaction, at any rate in polar solvents. In the association complex that is formed, the place of hydrogen bromide may be taken by any other catalyst, like iodine chloride or quinoline. As we have pointed out (3, 4, 5, 114), the catalytic influence of any of these reagents is not the same for all compounds. The presence of sufficient activating groups attached to the olefin residue may reduce the need for external activation and the reaction may appear to obey second-order kinetics without the catalyst (see table 3). At lower temperatures none of the three acids gave any constants (Anantakrishnan and Venkataraman), though the induction periods clearly indicated the influence of activating groups. Table 3 demonstrates that the part of the catalyst can be eliminated if adequate structural and thermal activations are present. It may be logical to expect that similar apparent bimolecular reactions may become possible even at low temperatures with suitable substituents. Under such conditions it may become difficult to distinguish between this chain mechanism and the one suggested by G. Williams.

While considering the problem of mechanism it is necessary to see whether the initiation of addition is by positive halogen or by negative. As indicated earlier, the work of Francis (33) and of Terry and Eichelberger (112) suggests the positive halogen as the initiator. From *a priori* considerations and from the experimental evidence in which activating groups are systematically introduced, Ingold and coworkers have shown that the existing observations are best reconciled by adopting the same view. Ogg (76), however, questions the validity of the above mechanism of Ingold (47) and the slightly modified mechanism of Carothers (22), on the ground that it leads one to expect identical products—a mixture of meso and *dl* halides from *cis–trans* isomers, contrary to experimental evidence. Also he has suggested the following mechanism in which addition is initiated by negative bromine:

$$CHR{=}CHR + Br^{\ominus} \rightarrow CHRBr{-}\overset{\ominus}{C}HR$$

$$RHBrC{-}\overset{\ominus}{C}HR + Br{-}Br \rightarrow RCHBr{-}HCRBr + Br^{\ominus}$$

This mechanism requires catalysis by bromide ions, which is apparently supported by earlier work. Ogg considers that his mechanism explains the stability of the intermediate compound, the formation of stereoisomeric addition products from *cis–trans* isomers, and the generally observed *trans* addition of halogens. His contentions, however, are difficult to maintain. The observed influence of substituents on additive reactivity is not compatible with initiation of attack by negative halogen except where an "electron sink" is attached to the olefin residue. Also in the case of non-aqueous solvents, where ionization of hydrogen bromide may not be expected, the catalytic influence cannot be as simple as the one postulated by Ogg.

Further, Roberts and Kimball (93), in attempting to explain the results of Bartlett and Tarbell (8), postulated for the intermediate compound a structure of the ethylene oxide type as an improvement over the ones suggested by Robinson (97a) and by Ingold (47). These authors consider "that free rotation about the C—C bond is not to be expected. If this structure is assumed one of the orbitals of C^+ must be completely empty. The X atom, on the other hand, has three orbitals occupied by pairs of electrons. The arrangement is such that a co-ordinate link will almost be certainly formed by sharing of one of the pairs of electrons of the halogen with the unoccupied orbital of the carbon. Another possible structure of the ion is one in which the positive charge is on the halogen. The X^+, being isoelectronic with a member of the oxygen family, should show a valence of two, i.e., it should form a structure of the ethylene oxide type

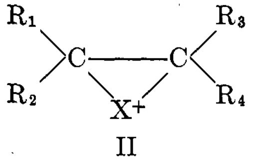
TABLE 3

The reaction between bromine and three α,β-unsaturated acids in acetic acid at 50°C.

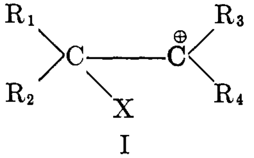
ACID	CONCENTRATION OF REACTANTS	CATALYST CONCENTRATION*	VALUES OF $100k_2$ FOR PER CENT REACTION					VALUES† OF k_3 FOR PER CENT REACTION				
			10%	15%	20%	30%	40%	10%	15%	20%	30%	40%
Crotonic....	$M/30$	Nil	2.45	2.69	2.88	3.37	3.88	3.11	3.51	3.89	4.91	6.22
Crotonic....	$M/30$	11.01	9.06	8.62	8.52	8.67	8.85	11.5	11.3	11.5	12.6	14.2
Tiglic.......	$M/30$	Nil	12.2	13.2	14.0	15.8		15.4	17.2	18.9	23.0	
Tiglic.......	$M/30$	11.01	30.3	31.2	31.5	31.4	30.3	38.4	40.7	42.5	45.7	48.5
β,β-Dimethylacrylic....	$M/30$	Nil	78.6	79.0	77.8	76.2	73.0	132	133	140	151	166
β,β-Dimethylacrylic....	$M/60$	Nil	45.0	47.1	47.8	49.8	50.6	114	123	129	145	162

* Molar percentage of catalyst per mole of each reactant.

† Concentrations are expressed in gram-moles per liter; unit of time, minute; values of k_3 are calculated using Robertson's equation (95).



II



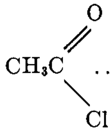
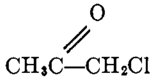
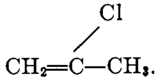
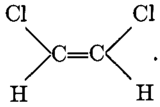
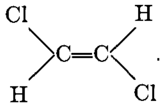
I

From the electronic point of view structures I and II are identical. The difference between the ionization potential of carbon (11.22 volts) and that of a halogen (e.g., 11.8 volts for bromine) is so small that the actual structure of the ion is undoubtedly between I and II. Since the two carbons in either structure are joined by a single bond and by a halogen bridge, a free rotation is not to be expected."

If, however, R_1 and R_3 or R_2 and R_4 are similarly charged groups (e.g., $COO^{\ominus}$), there may be sufficient repulsion between them to overcome the restraining force of the double linkage and rotation to the opposite configuration may take place before the second step of the reaction occurs. The ionization potentials of chlorine and of iodine are also not far removed from that of carbon, and a similar mechanism involving resonance between the two structures is possible for these halogens. The case of fluorine is different. The general *trans* addition is also explained by assuming the addition of X or some other atom or molecule to approach one of the carbon atoms from the side opposite to the X atom already present, thus being similar to the three-atom reaction type proposed by London

TABLE 4

Efficiencies of reaction of halides with sodium

COMPOUND	NUMBER OF COLLISIONS FOR ONE SUCCESSFUL TRANSFORMATION	COMPOUND	NUMBER OF COLLISIONS FOR ONE SUCCESSFUL TRANSFORMATION
CH_3I	1		100
CH_3Br	50		10
CH_3Cl	10,000	$CH_2{=}CHCl$	11,000
CH_3F	10,000,000		5,500
CH_3CH_2Cl	7,000		1,800
$(CH_3)_2CHCl$	3,300		2,600
$CH_3CH_2CH_2CH_2Cl$	3,300		
$(CH_3)_3CCl$	1,500		

(58) and developed by Polanyi (86, 87) and Olson (78, 79). This similarity probably accounts for the group influences on atomic reactions observed by Polanyi (85) which are analogous to their influence on olefin–halogen reactivity (see table 4).

It may not be out of place to mention here that the abnormally rapid addition of bromine to crotonaldehyde has been explained by Ingold and Anantakrishnan (2) as due to the initiation of attack by negative bromine, consequent on the development of a positive charge on the α-carbon atom due to the powerful electron-attracting carbonyl link. Compounds of this type may conform to Ogg's mechanism but it will be interesting to note if there are other such instances. Some work is in progress in these laboratories to test this aspect of the problem.

D. *Influence of substituents*

Before the advent of the electronic theory of organic reactions, very little quantitative work had been done on the influence of substituents on the rate of addition of halogens to ethylenic derivatives. Any little work done merely classified groups into two types, activating and deactivating. The degree of accuracy and the inadequate control of catalysis precluded any definite classification.

TABLE 5

Rate constants for the bromination of olefins

OLEFIN	RATE CONSTANT
Ethylene	0.006
Propylene	0.200
Isobutene (butene-2)	60
Trimethylethylene	250
Diisobutylene	20

Bauer and Moser (10, 11), from their studies on the addition of bromine to stilbene, methylstilbene, α-phenylcinnamonitrile, cinnamic acid, and bromocinnamic acid, found that C_6H_5, Br, COOH, and CN deactivate, while CH_3 probably activates. Sudborough and Thomas' experiments (109, 110, 111) on the rate of addition of bromine to a series of unsaturated acids, under uncontrolled catalytic conditions, indicated that the introduction of the methyl group facilitates addition, and that conjugated systems containing the carboxyl group and the α,β-ethylenic linkage react more readily than the simple ethylenic conjugated system. In addition, reference may be made to the several dynamical investigations on bromine addition by Herz and Mylius (40, 41), Brüner and Fischler (21), Hofmann and Kirmreuther (43), and Reich, Van Wijck, and Waelle (91). Davis was the first to give a quantitative idea of the effect of substituents. From his experiments on the olefin–bromine reaction he gave the data in table 5 for the comparative reactivity of methyl-substituted ethylenes.

Also, indications of a competitive method are found in Davis' procedure for studying the relative velocity of bromination.

The first important work on a quantitative study of the influence of substituents on the reactivity of ethylenic compounds is that of Ingold and coworkers (1, 2, 48). A competitive method was developed for the comparison of the reactivity, and it was found that the few necessary prerequisites for such comparisons are satisfied under the experimental conditions used (4). The relative rates of addition of bromine to ethylene and its simple derivatives were found to be consistent with theory and the possibility of an inverted mutual action, with several substituents, has also been demonstrated in one case (48).

From *a priori* considerations, taking into account related work on aromatic substitution and on tautomerism, Ingold and Ingold (48) classified substituent groups as shown in table 6. The work of Anantakrishnan and Ingold (*loc. cit.*) suggests that one may predict the comparative rate of addition of bromine to an ethenoid compound, if the effect exerted by each substituent is known quantitatively, in compounds with closely related structures.

TABLE 6

Classification of substituent groups

(1) $+I$ $:C \leftarrow CH_3$	(4) $-I + T$ $:C \rightarrow \overset{\curvearrowleft}{Br}$
(2) $-I$ $:C \rightarrow \overset{\oplus}{N}(CH_3)_3$	(5) $+I +T$ $:C \leftarrow O^{\ominus}$
(3) $-I -T$ $:\overset{\curvearrowright}{C \rightarrow} COOH$	(6) $+I -T$ $:C \leftarrow COO^{\ominus}$
(7) $\pm T$ $:\underset{\curvearrowleft}{\overset{\curvearrowright}{C \leftarrow C_6H_5}}$	

In comparing the influence of substituents on additive reactivity, it is essential to bear in mind the rôle of solvent, catalyst, and temperature. In the same solvent, temperature may not exert any great influence on the reduced velocity (i.e., the ratio of the rate of reaction with a given substance relative to the rate with ethylene), if other conditions are the same (see table 7). A change of solvent, however, affects the values considerably. While the introduction of a methyl group at the same carbon atom in the case of propylene increases the velocity constant about threefold in methylene chloride solution, in the case of crotonic acid addition of a methyl group in a similar position increases the velocity constant twentyfold at 35.5°C. in acetic acid solution and about thirteenfold at 50°C. (i.e., for crotonic acid and dimethylacrylic acid). Though quantitative comparisons are not possible in the present stage of investigations, the difference is noteworthy. No doubt, a strict comparison of the two instances raises the question of mutual group interaction, arising from the complication of a carboxyl group, but solvent effect cannot be a negligible factor. The known formation of a complex with acetic acid by iodine suggests that some association of the bromine molecule with acetic acid may not be unlikely and this association necessarily implies influence on the course of reactions in this solvent. Until we have adequate evidence to prove the absence of heterogeneity, comparisons of reactions in carbon tetrachloride cannot have much value.

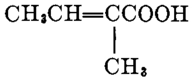
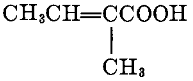
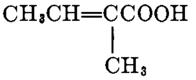
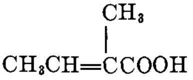
TABLE 7

Effect of temperature on reduced velocity

COMPOUND	REDUCED VELOCITY AT −35°C. (48)	REDUCED VELOCITY AT −78°C. (2)
$H_2C{=}CH_2$	1	1
$C_6H_5CH{=}CH_2$	3.24	3.35
$CH_3CH{=}CH_2$		2.03
$C(CH_3)_2{=}CH_2$	5.5	5.53
$C(CH_3)_2{=}CHCH_3$		10.4
$C(CH_3)_2{=}C(CH_3)_2$	13.6, 14.0	14.0
$CH_2{=}CHCOOH$	0.03	Small
$CH_2{=}CHBr$	0.03	Small
$CH_2{=}CHCHO$		1.5
$CH_3CH{=}CHCHO$		3.0
$CH_3CH{=}CHCOOH$		0.26

TABLE 8

Relative rates of addition of bromine by olefinic compounds

SOLVENT	X	Y	$\frac{k_X}{k_Y}$
Methylene chloride at −78°C. (references 1, 2)	$CH_3CH{=}CH_2$	$CH_2{=}CH_2$	2
	$(CH_3)_2C{=}CH_2$	$CH_3CH{=}CH_2$	2.8
	$(CH_3)_2C{=}CHCH_3$	$(CH_3)_2C{=}CH_2$	1.9
	$(CH_3)_2C{=}C(CH_3)_2$	$(CH_3)_2C{=}CHCH_3$	1.4
	$CH_3CH{=}CHCHO$	$CH_2{=}CHCHO$	2
Acetic acid at 35°C.	 $CH_3CH{=}\underset{\substack{\mid\\ CH_3}}{C}COOH$	$CH_3CH{=}CHCOOH$	5.2
Acetic acid at 35°C. (references 3, 4, 5)	$(CH_3)_2C{=}CHCOOH$	 $CH_3CH{=}\underset{\substack{\mid\\ CH_3}}{C}COOH$	3.9
Acetic acid at 50°C.	 $CH_3CH{=}\underset{\substack{\mid\\ CH_3}}{C}COOH$	$CH_3CH{=}CHCOOH$	3.7
Acetic acid at 50°C.	$(CH_3)_2C{=}CHCOOH$	 $CH_3CH{=}\overset{\substack{CH_3\\ \mid}}{C}COOH$	3.5

The rôle of catalysts is more difficult to interpret. Investigations have shown that a variety of catalysts (1, 3, 21, 40, 41, 114, 116, 118) is available, and in all cases they are polar compounds that can associate with an olefin or form loose complexes with bromine. The influence of oxygen on these reactions has also to be more fully investigated, though in the case of α,β-unsaturated acids this has been shown to be absent (60, 98).

With these limitations it is possible to draw certain tentative conclusions as to the influence of structure on additive reactivity. For this purpose consider the data presented in table 8.

It is clearly seen that the introduction of an alkyl group has a pronounced activating effect which is cumulative. Other things remaining constant, the symmetry or asymmetry of groups introduced exerts considerable influence. The tables also clearly indicate that before a generalized quantitative interpretation is attempted, we have to know more about the liquid state and about the mutual interaction of groups.

V. REACTIONS BETWEEN OLEFINS AND IODINE

Comparatively little work has been done in this field. Almost the only exhaustive study has been with ethylene and iodine, but even here the photochemical addition reaction does not seem to have been studied in the gaseous state.

Mooney and Ludlam (68) have studied the equilibrium "ethylene + iodine $\rightleftharpoons$ ethylene iodide" in the gaseous state between 10° and 65°C., while Arnold and Kistiakowsky (6) have studied the thermal decomposition of ethylene iodide between 200° and 250°C. The former authors find that the kinetics of the reaction can be expressed by the rate equation

$$\frac{\mathrm{d}P}{\mathrm{d}t} = k'P_{\mathrm{EI}_2} - kP_{\mathrm{E}} \cdot P_{\mathrm{I}_2}$$

the intergrated form of which gives

$$k = \frac{1}{t}\,\frac{2.303}{P_{\mathrm{I}_2}}\log_{10}\left[\frac{P - P_0}{P - \underline{P}}\right]$$

where P is the equilibrium pressure, P_0 the initial pressure, and $\underline{P}$ the pressure at the time of measurement. Increasing values of k from 1.2×10^{-3} to 4×10^{-3} are obtained and the authors have also evaluated the value of k'. The pressure–time curve clearly indicates an autocatalytic reaction, though dealing with an equilibrium; calculation shows that the curve is not of the $e^{-\phi t}$ type. The authors have also made the interesting observation that the heat of decomposition obtained from the log $K - 1/T$ curve gives a value of 22 kilocalories at 50°C. and 13 kilocalories at 30°C.

The work of Arnold and Kistiakowsky (6) leads to a slightly different reaction-rate equation:

$$\frac{\mathrm{d}[\mathrm{EI}_2]}{\mathrm{d}t} = k[\mathrm{EI}_2] + k'[\mathrm{EI}_2]\,[\mathrm{I}_2]^{1/2}$$

Though it has been suggested that the gaseous decomposition is homogeneous, it is difficult to reconcile this with the observation of these authors that alteration in the surface volume ratio leads to a variation in the velocity constant for decomposition. Considering the reactions with other halogens it is more likely that this is also an essentially heterogeneous reaction in the gas phase. Though experiments on the gas reaction are not many, the reactions in solution, especially in carbon tetrachloride, have been the subject of a fairly complete investigation.

The work of Iredale and Martin (49) indicates a definite period of induction, an initial zero-order reaction followed by a monomolecular reaction and finally by an uncatalyzed bimolecular reaction. Increase of surface or cleaning the reaction vessel with hydrogen fluoride accelerates the reaction, which, however, continues on the same course. It is found that mercury vapor has to be removed if the gas reaction is to be complete. Taking into account all these observations, the following mechanism has been suggested:

(1) $I\text{ (glass)} + C_2H_4I_2 = I{-}I\text{ (glass)} + C_2H_4I$

(2) $C_2H_4I + C_2H_4I_2 = C_2H_4 + I_2 + C_2H_4I$

(3) $C_2H_4I = C_2H_4 + I$

(4) $C_2H_4I_2 + I = C_2H_4I + I_2$

(5) $C_2H_4 + I = C_2H_4I$

(6) $I\text{ (glass)} + C_2H_4I = C_2H_4I_2$

(7) $I\text{ (glass)} + I = I{-}I\text{ (glass)}$

(8) $I + I_2 = I_3$

The evidence for the full scheme is, however, inadequate and a further reason for doubt is provided by the author's statement that the results are not reproducible. From a consideration of available experimental evidence Ogg (77) has shown that the reaction is best represented by a chain mechanism rather than the single stage visualized by Arnold and Kistiakowsky (6). Since generally reactions in solution in non-polar solvents like carbon tetrachloride have been found to correspond largely to gas-phase reactions, these results may also be taken to indicate the probable course of gas reaction.

Schumacher and coworkers have shown (100) that the decomposition is sensitized by the photochemical or thermal dissociation of iodine, leading to an experimental rate equation:

$$-\frac{d(C_2H_4I_2)}{dt} = kI^{1/2}_{\text{abs.}}(C_2H_4I_2) \qquad \text{(I)}$$

Varying quantum yields indicate a chain mechanism for the reaction, the primary process being dissociation of iodine molecules into atoms, combined with a secondary process, common to the thermal mechanism:

(1) $I_2 + h\nu \rightarrow 2I$

(2,3) $C_2H_4 + I \rightleftharpoons C_2H_4I$

(4,5) $C_2H_4I + I_2 \rightleftharpoons C_2H_4I_2 + I$

(6) $I + I\ (+M) \rightarrow I_2(+M)$

Assuming a constant third body recombination of iodine atoms and a stationary concentration of the free radical C_2H_4I, this chain mechanism leads to a rate equation:

$$-\frac{d(C_2H_4I_2)}{dt} = \frac{k_5 \frac{\phi^{1/2}}{k_6^{1/2}} I_{abs.}^{1/2}(C_2H_4I_2)}{1+\frac{k_4(I_2)}{k_3}} - \frac{k_2 \frac{\phi^{1/2}}{k_6^{1/2}} I_{abs.}^{1/2}(C_2H_4)}{1+\frac{k_3}{k_4(I_2)}}$$

If the ethylene concentration is small, as in the initial stage of photolysis, the second term of the equation cancels out, while if the denominator of the first term becomes small, it reduces to equation I. The inaccuracy of these simplifying assumptions in the later stages of the reaction and the limitations in the range of stationary concentration in an element of volume lead to the observed deviation of the experimental results from the simplified rate equation.

Mooney and Reid (69) were the first to observe the autocatalytic nature of the reaction in solution and the catalytic influence of free iodine. Their observation that the initial slopes of the curves are proportional to the square root of the iodine concentration is a precursor of the chain mechanism involving iodine atoms. Polissar's (88) work has shown that at temperatures at which the reaction rate is conveniently measurable, the reverse reaction is also facilitated. Having thermal dissociation of iodine as the initial step, Schumacher (99) derived a mechanism analogous to that of Berthoud and Béraneck (*loc. cit.*) for bromine addition, with necessary alterations, taking into account the reversibility of the reaction. Using this mechanism and assuming stationary concentration of C_2H_4I and I

(1,6) $I_2 \rightleftharpoons 2I$

(2,3) $C_2H_4 + I \rightleftharpoons C_2H_4I$

(4,5) $C_2H_4I + I_2 \rightleftharpoons C_2H_4I_2 + I$

he obtained the reaction-velocity equation

$$+\frac{d[C_2H_4I_2]}{dt} = \frac{k_2 K_{I_2}^{1/2}[C_2H_4][I_2]^{1/2}}{1+\frac{k_3}{k_4[I_2]}} - \frac{k_5 K_{I_2}^{1/2}[C_2H_4I_2][I_2]^{1/2}}{1+\frac{k_4[I_2]}{k_3}}$$

which, if the term $\frac{k_4}{k_3}(I_2)$ is small or $\frac{k_3}{k_4(I_2)}$ large, simplifies to

$$+\frac{d[C_2H_4I_2]}{dt} = \frac{k_2 k_4 K_{I_2}^{1/2}}{k_3}[C_2H_4][I_2]^{3/2} - k_5 K_{I_2}^{1/2}[C_2H_4I_2][I_2]^{1/2}$$

the actual experimental rate equation obtained by Polissar. Ogg has shown that Kistiakowsky's work in the gas phase also leads to the same result and that Polissar failed to notice the uncatalyzed unimolecular decomposition observed by Arnold and Kistiakowsky (6), presumably owing to its being suppressed at the lower temperatures at which he worked.

Mention may be made also of the careful studies of Forbes and Nelson (31, 32) on the photoiodination of the simpler olefins in chloroform solution at −55°C. The reaction has been found to depend on light intensity and on concentration of the reactants, and the varying quantum yields lead as before to a chain mechanism. They make the significant observation that oxygen is without effect on the quantum yield, and the thermal iodination of the butenes in liquid Freon (CCl_2F_2) was complete within a few minutes even at −150°C.

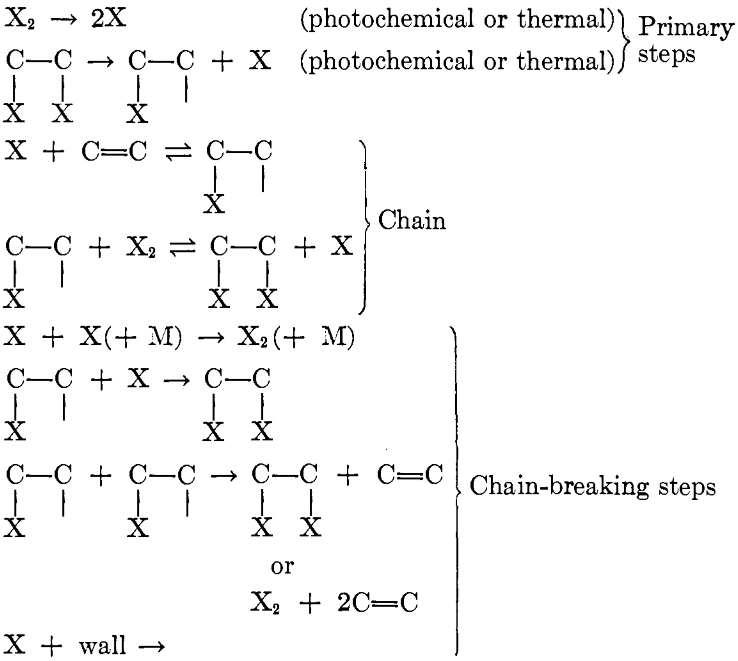
Robertson (94) and Bythell have studied the addition of iodine to a number of allyl derivatives in nitrobenzene, acetic acid, hexane, and carbon tetrachloride. In the last two solvents, the reaction is found to be heterogeneous, the course of the reaction being generally analogous to the bromine addition.

More recently Ghosh and coworkers (18, 19, 34, 35) have studied the addition of iodine to β-amylene and to α-pinene in a number of solvents. In the chain mechanism suggested by these authors for the thermal reaction they postulate the I_6 molecule as taking part in the reaction in preference to smaller polymers. Apart from the work of Groh (38), all studies lead to the existence of only I_2 and I_4 molecules in solution, and the recent magnetic susceptibility studies of Rao and Govindarajan (90) point more to a possible ionization than to the existence of higher polymers of iodine in solution. Further, it is very difficult to accept the view that iodine should behave so differently from the other halogens. The volatility of carbon disulfide and the temperatures used for the experiment, under the conditions stated, preclude any accurate results. The choice of α-pinene is also rather unfortunate, because of a possible Wagner–Meerwein change in the course of the reaction. Doubt is thrown on the results of the photochemical reaction also, when variations in the velocity coefficient of as much as 12 per cent with concentration are found to be neglected.

As yet the olefin–iodine reaction has not received adequate attention in the shape of a systematic study either in polar solvents or for variations in reactivity with systematic structural changes on lines similar to those with bromine.

VI. THE GENERAL MECHANISM OF THE OLEFIN–HALOGEN REACTION

The trend of observations of photochemical and thermal reactions between the different halogens and the carbon–carbon double bond indicates clearly that two different but general mechanisms should explain the course, one for the thermal and the other for the photochemical change. In the case of photochemical reactions, while the essential chain mechanism involves absorption of light quanta by halogens, photoactivation of the olefin cannot be excluded, judging from the photodissociation of olefins. The best general mechanism suggested appears to be that of Leighton (54).



(1a), (1b) $X_2 \rightarrow 2X$ (photochemical or thermal)

(1c) $\underset{X}{C}-\underset{X}{C} \rightarrow \underset{X}{C}-C + X$ (photochemical or thermal)

Primary steps

(2), (3) $X + C{=}C \rightleftharpoons \underset{X}{C}-C$

(4), (5) $\underset{X}{C}-C + X_2 \rightleftharpoons \underset{X}{C}-\underset{X}{C} + X$

Chain

(6) $X + X(+ M) \rightarrow X_2(+ M)$

(7) $\underset{X}{C}-C + X \rightarrow \underset{X}{C}-\underset{X}{C}$

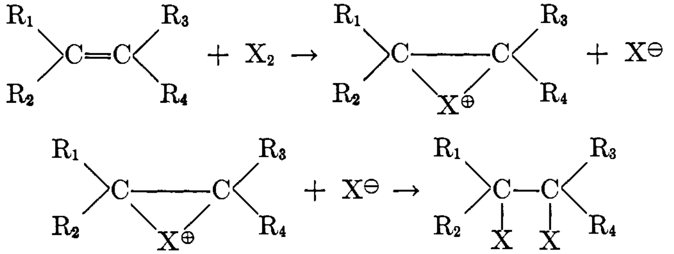
(8) $\underset{X}{C}-C + \underset{X}{C}-C \rightarrow \underset{X}{C}-\underset{X}{C} + C{=}C$ or $X_2 + 2C{=}C$

(9) $X + \text{wall} \rightarrow$

Chain-breaking steps

From considerations of the $\frac{k_4}{k_3}$ (X_2) ratio and its variation with temperature, Leighton concludes that there is adequate evidence for the free radical cum atom chain mechanism, the life of the free radical practically determining the rate. The objection has been raised that the formation of a free radical as an intermediary step necessarily implies that *cis–trans* isomers should lead to the same products, *dl* and meso forms. In actual practice, however, these stereoisomers generally give different products in which one or the other predominates.[3] Also we have to infer from the work of Meisenheimer (61) and of Berthoud (14) that the addition of halogens takes place in *trans* positions, and oriented addition is incompatible with a free-radical mechanism unless some other factor that implies restricted rotation, even with a system containing a sextet, is taken into account. The interconversion of fumaric and maleic acids during halogenation, however, is a difficulty for this alternative scheme.

A better explanation of experimental observations is provided by the work of Roberts and Kimball (93), who suggest for the two steps



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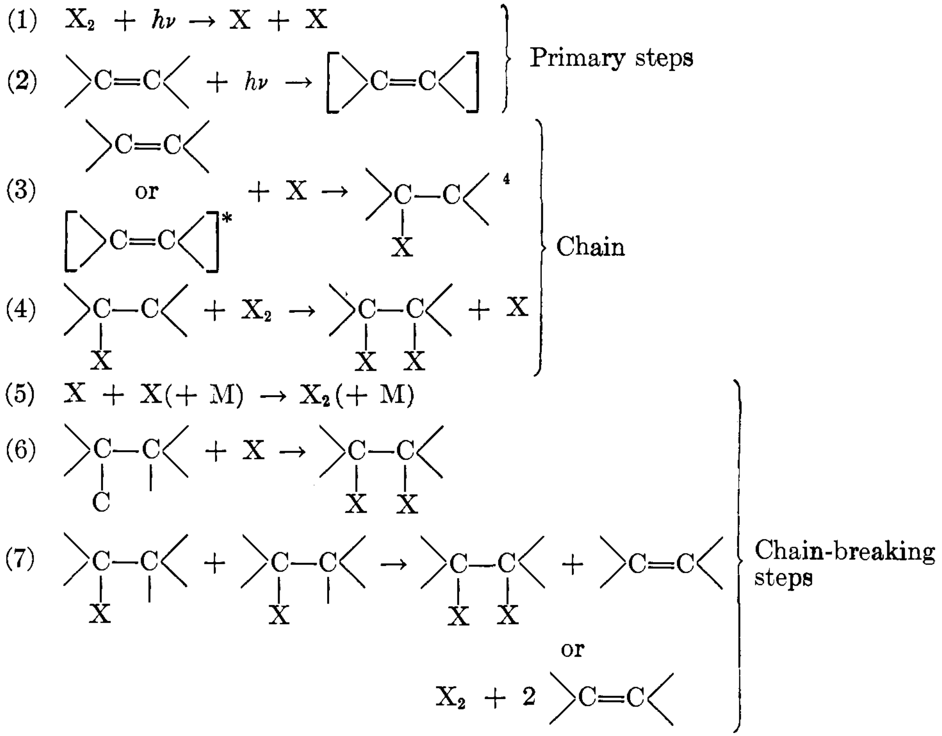
[3] See Freudenberg: *Stereochemie*, p. 520. Verlag Franz Deuticke, Vienna (1933).

Ogg has objected to an initiation of attack by positive halogen on the ground that a carbon atom with a sextet is unstable. A resonance hybrid of the type suggested, however, gets over this difficulty and is not impossible, since the ionization energies of the halogens other than fluorine is not far different from that of carbon.

Neither the mechanism of Leighton nor that of Roberts and Kimball explains the rôle of catalysts in this reaction. A polar surface has been generally found essential in the gas reaction, while compounds like hydrogen bromide, iodine monochloride, etc., exert at least in solutions a pronounced effect in bromine addition. The authors have taken this into account in the tentative scheme suggested (3). Possibly the true mechanism is some kind of a combination of this scheme with that of Roberts and Kimball. The reaction may be visualized as involving the following steps:

- (*i*) Activation of halogen—thermal, photochemical, or catalytic.
- (*ii*) Activation of the double bond by
  - (*a*) external factors, (*b*) internal factors.
- (*iii*) Reaction between the two activated molecules in two steps, the first one being the rate-determining step.

Photochemical



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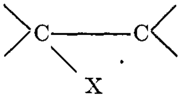
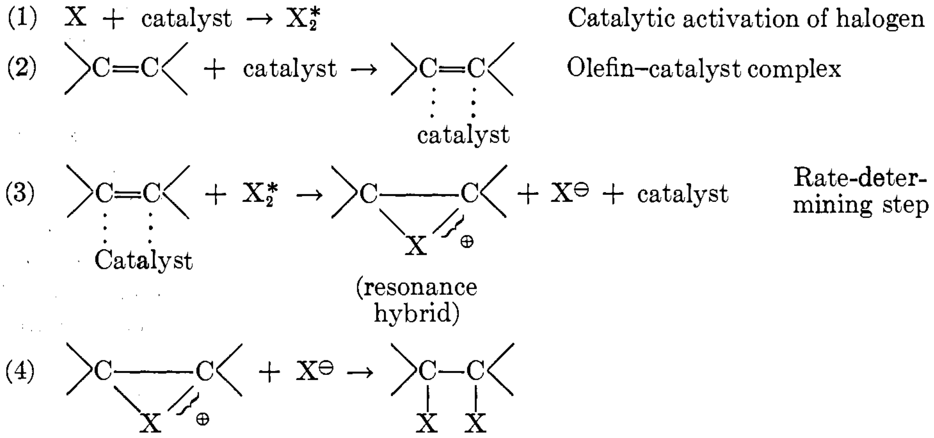
[4] Instead of assuming a free radical, this step may be represented as involving a singlet link



which might account for the predominance of one of the products.

Thermal



Catalytic activation of halogen

Olefin–catalyst complex

Rate-determining step

The extent to which a catalyst influences the reaction will depend on the degree of activation of the double bond, either thermally or by the presence of activating groups or both. The more the activation by internal factors, i.e., structural influences, the less the influence of external catalytic agents and *vice versa.* The revised scheme suggested can also explain the interconversion of geometrical isomers which depends on whether the reverse reaction, i.e., the rate-determining step in the thermal reaction, or further addition takes place. The formation of a complex with the catalyst accounts also for the varying *PZ* values with systematic changes in structure that indicate the importance of the phase of collision prior to combination. Whether a reaction gives an apparent trimolecular or bimolecular or at times even pseudo-monomolecular constant depends on which of the several steps determines the rate and this is turn depends on the experimental conditions.

The general trend, however, is to indicate that no great difference may be expected among the halogens in this kind of reaction, the behavior of the first member being exceptional on account of its extreme reactivity. Possibly the stability of fluorine as a positive halogen is so small and the ionization energy so different from that of carbon, that the postulated intermediate steps are ruled out, with only a rupture of the olefin leading to a variety of fluorinated products. The others conform to the gradation one might expect from their behavior in other reactions.

It should also be stated that the addition of halogens to olefins is of such a general nature that, irrespective of the substituent groups, the general mechanism should be unaltered, since the reactivity is essentially a function of the polarizability of the double bond. This expectation is confirmed by the observations of Kharasch and Roth on hydrogenation of olefins (reference 44, page 94).

Before concluding, it is interesting to note the variation in the parameters of the Arrhenius reaction-velocity equation with the halogen on the one hand and the structure of the olefin on the other. The energy of activation decreases from chlorine to iodine (101) though, as has been found experimentally, the values of *E* can be considerably reduced by the presence of activating groups or by catalysts or both. But the significant result is that the probability factor in all the cases turns out to be several powers of ten smaller than the value one might expect theoretically. This brings out clearly that in the formation of a transition state the relative orientation of the reacting olefin and halogen is as important as the frequency of collision on account of the number of degrees of freedom involved, and any adequate interpretation can be possible only after more systematic investigations.

The reactions under discussion present further examples of the apparently simple bimolecular type becoming a complex chain type of reactions.

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