# ATOMIC CHLORINATION OF SIMPLE HYDROCARBON DERIVATIVES IN THE GAS PHASE

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## I. INTRODUCTION

After the classical studies in the thirties (162, 171) an intensive study of photochlorination reactions was started about ten years ago.

Several systems have been studied in detail, others more as a general survey. The primary object of this work has been to compute rate constants of elementary reactions, bond dissociation energies, energies of activation, entropies of free radicals and transition states, and to understand these results in the light of theories of rate processes. Rate constants of about 100 elementary reactions are known (63, 71) and the present possibilities and limitations of explaining these rate constants by means of the activated complex theory have been discussed (118, 124, 154, 187).

Direct observations of single elementary reactions have been made only in some work on atom and free radical recombinations. It is hoped that techniques like flash photolysis and shock waves together with analytical tools like mass spectrometry and electron spin resonance will give more information about such reactions. Up to the present time the main results have been obtained from a kinetic analysis based on a reasonable reaction scheme and the use of some special kinetic techniques. Among these the techniques of intermittent light and competing reactions are most useful.

When one measures over-all rates of complex reactions such as atomic chlorinations, involving two or more chain carriers, special care must be taken in determining reaction orders to interpret the experimental data.

In some reactions, the reaction order with respect to one reactant is a simple multiple of $^1/_2$ and remains constant throughout the reaction. The measurement of the rate at any instant is then equivalent to the measurement of the initial rate and an integration method can be used to calculate the over-all rate constant.

Usually the reaction rate is not a simple function of

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the reactant concentrations and the order varies during the course of the reaction. This difficulty can sometimes be avoided and the interpretation can be simplified by an adequate choice of experimental conditions. Some reactions however present a great intrinsic complexity which has been shown to be due to consecutive reactions and require a detailed analysis.

In this way the comprehensive study of photochlorinations has led to important improvements in the techniques of kinetic analysis. Many problems such as variable reaction orders, true induction periods, and induction periods due to the Draper effect (24a,b,c, 82) are now more clearly understood. The study of competitive reactions has not only permitted the measurement of a number of elementary rate constants (83, 124, 158), but has also thrown new light on the mechanism of inhibition (63, 139). At present the photochlorination of methane, ethane, and ethylene and all their chlorinated derivatives are well understood and good values for all relevant elementary constants are available (63). Such questions as the point of attack of a chlorine atom on an asymmetric chlorinated ethylene, the difference in reactivities of isomeric chlorinated ethanes (62, 88a), the *cis–trans* isomerization of 1–2 dichloroethylene (11), and the kinetic isotope effect are being clarified (44).

These improvements and the knowledge of numerous elementary constants permit one to arrive at a better understanding of the pyrolysis of chlorinated hydrocarbons (88), as well as of the mode of action of halogenating reagents like haloimides (3) for which new reactions have been predicted (137).

Within the scope of these studies, a very satisfactory general picture is obtained. There are, of course, several questions which remain unsettled and which shall be discussed in this review. One of these is the possibility of observing an unstable intermediate addition product between an olefin and a chlorine atom (10, 11, 13, 54); another is the occurrence of chlorine-chlorine atom recombinations and the possibility of observing them (12, 43).

From a discussion of the thermodynamic properties of free radicals involved in these reactions it appears that the data on the strengths of certain bonds are not quite satisfactory (88). An effort to obtain better data by a study of photobromination reactions ought to be worthwhile.[3]

In this paper the progress that has been made in the methods of analysis of complex reactions shall be described. Next the results shall be presented and a few questions, that are still unsettled, shall be mentioned. Finally the significance of the results shall be discussed in terms of activated complex theory.

## II. KINETIC ANALYSIS

### A. CHOICE OF MECHANISM

Already in the thirties it was clearly understood (28, 57, 162, 171) that light absorbed by chlorine molecules leads to photodissociation to atoms and that the subsequent reactions, recognized as chain reactions, proceed by these atoms. Bodenstein and his group assumed that a chlorine atom abstracts a hydrogen atom from a saturated hydrocarbon or adds to a double bond forming in both cases a hydrocarbon or chlorinated hydrocarbon radical. In the phosgene synthesis the corresponding radical is COCl. The reaction chain should proceed alternately by a chlorine atom and a free radical.

Rollefson, on the other hand, showed that the observed kinetic properties could equally well be explained by a chain mechanism in which the chain carriers are Cl and $Cl_3$ (77, 162, 163).

The lack of logic with which the choice between Bodenstein and Rollefson's mechanism has been treated by different authors is striking (23). To our knowledge only Noyes and Leighton (148) have established a clear and valid criterion for this choice. This criterion, however, has not been used prior to the work of Chiltz, Mahieu, and Martens (45). Another method of distinguishing between these two mechanisms has been proposed and used more recently (38), but it is open to criticism.

Using either the Bodenstein or the Rollefson mechanism, similar reaction steps have been proposed for different substances but in none of these earlier studies (162, 171) was an attempt made to put forward a general reaction scheme. Such a general scheme (96) may be written for addition reactions as

$$\begin{array}{rll}
Cl_2 \rightarrow 2Cl & (I_a) & \\
A + Cl \rightarrow ACl & k_2 & \\
ACl + Cl_2 \rightarrow ACl_2 + Cl & k_3 & \\
ACl \rightarrow A + Cl & k_4 & \\
ACl_2 + Cl \rightarrow ACl + Cl_2 & k_5 & (1) \\
Cl + Cl + M \rightarrow Cl_2 + M & k_6 & \\
ACl + Cl \rightarrow ACl_2 \text{ (or Cl or H abstraction)} & k_7 & \\
ACl + ACl \rightarrow \text{dimerization or disproportionation} & k_8 &
\end{array}$$

and for substitution reactions

$$\begin{array}{rll}
Cl_2 \rightarrow 2Cl & (I_a) & \\
RH + Cl \rightarrow R + HCl & k_2' & \\
R + Cl_2 \rightarrow RCl + Cl & k_3 & \\
R + HCl \rightarrow RH + Cl & k_4' & \\
RCl + Cl \rightarrow R + Cl_2 & k_5 & (2) \\
Cl + Cl + M \rightarrow Cl_2 + M & k_6 & \\
Cl + R \rightarrow RCl \text{ (or Cl or H abstraction)} & k_7 & \\
R + R \rightarrow \text{dimerization or disproportionation} & k_8 &
\end{array}$$

Whatever ethylenic hydrocarbon A or saturated hydro-

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(3) Such studies have been started now in this Laboratory.

carbon RH reacts with a mixture of chlorine atoms and chlorine molecules, this scheme is supposed to be valid.

The advantage of choosing a mechanism, even arbitrarily, lies in the fact that this gives the possibility of devising a limited number of tests in order to check it. In some cases A and RH may be chosen so that the free radicals ACl and R become identical: some rate constants measured in the system A + Cl or RH + Cl then have identical values. This method has been used extensively for tetrachloroethylene and pentachloroethane (1, 61, 83) and for trichloroethylene and the two tetrachloroethanes (59, 62).

This scheme is also assumed to be valid in mixtures. In such cases all reactions of A, RH, and all intermediates with stable products and free radicals must be considered. This approach has proved most fruitful in the study of competitive systems (83, 115) and where reaction products can react further (63).

In order to show that a Bodenstein type generalized mechanism and not a Rollefson type mechanism must be used, the criterion proposed by Noyes and Leighton (148) has been developed as follows (45, 80). For an addition reaction both mechanisms can be written in the general form

$$\begin{array}{rll} \mathrm{Cl_2 \rightarrow 2Cl} & (I_a) & \\ \mathrm{X + Cl \rightleftarrows R} & k_2,\ k_4 & \\ \mathrm{R + Y \rightleftarrows ACl_2 + Cl} & k_3,\ k_5 & \\ \mathrm{Cl + Cl + M \rightarrow Cl_2 + M} & k_6 & (3) \\ \mathrm{Cl + R \rightarrow chain\ breaking} & k_7 & \\ \mathrm{R + R \rightarrow chain\ breaking} & k_8 & \end{array}$$

In a Bodenstein type mechanism $X = A$, $Y = Cl_2$, and $R = ACl$; in a Rollefson type mechanism $X = Cl_2$, $Y = A$, and $R = Cl_3$.

This general scheme yields the following rate equation

$$v = I_a^{1/2}k_3(\mathrm{Y})[k_6\mathrm{M}\alpha^2 + k_7\alpha + k_8]^{-1/2} \tag{4}$$

where $\alpha = (\mathrm{Cl})/(\mathrm{R})$.

In this rate equation a term occurs which depends only on $(Cl_2)$; for the Bodenstein mechanism the constant $k = k_3/k_8^{1/2}$ while for the Rollefson mechanism $k = k_2/(k_6\mathrm{M})^{1/2}$. In the latter case the chain terminating step would be the recombination of chlorine atoms and $k$ would depend on the total pressure; this has never been observed. Furthermore $k$ would not depend on the nature of the reactants and would have the same value for all atomic chlorinations. Accurate measurements have shown that these constants have identical values for $C_2Cl_4$ and $C_2Cl_5H$ where the intermediate free radical is the same, *i.e.*, $C_2Cl_5$, but different values for say $CHCl_3$, $C_2HCl_3$, and $C_2HCl_5$. This can be explained only by the Bodenstein mechanism.

### B. OVER-ALL REACTION ORDER

#### 1. *Simple Reaction Orders and their Identification*

For a given initiation step (87, 131) the order of the reaction depends on the type of chain terminating step. A simple order is expected if there is only one type of chain breaking.

It is well known that over-all reaction orders can be determined either by differential (*e.g.*, van't Hoff's) or integration methods. The latter should be avoided for determining unknown reaction orders; it has been shown (80) in the case of the photochlorination of trichloroethylene that the integration method hardly permits one to distinguish between $n = 1$, $^3/_2$, or 2.

#### 2. *Complex Reaction Orders*

Usually the reaction rate is not a simple function of the reactant concentrations. Two cases are to be distinguished. In the first (photochlorination of $C_2Cl_4$, $C_2Cl_5H$, (61, 83), $CCl_3H$ (45) for instance) the rate depends not only on the concentrations of the reactants but also on the ratio of their concentrations because of competition between two chain-breaking steps. The rate is given by

$$v = I_a^{1/2}k_3(\mathrm{Cl_2})/[k_3k_7(\mathrm{Cl_2})/k_2'(\mathrm{CHCl_3}) + k_8]^{1/2} \tag{5}$$

If van't Hoff's method is used, one has to distinguish, as did Letort (133), between $n$, the "order in the course of the reaction," and $n_0$, the "order in the initial conditions."

In the eq. $\log v = \log k + n \log (\mathrm{Cl_2})/(\mathrm{Cl_2})_0$, $n$ is constant during the course of the reaction only if $(\mathrm{Cl_2})/(\mathrm{CHCl_3}) = 1$. Increasing or decreasing values of $n$ are found during the course of the reaction if this ratio is higher or lower (45, 80, 81, 139). On the other hand for each value of this ratio $n_0 = {}^3/_2$ but for different ratios, different parallel straight lines are found for $\log v_0$ *vs.* $\log (\mathrm{Cl_2})_0$ as is essentially seen from equation 5. Integration methods have frequently led (173, 174, 185, 200) to erroneous conclusions. Equations of the type of equation 5 are best analyzed by plots of inverse squares $(\mathrm{Cl_2})^2I_a/v_0^2$ as a function of concentrations, inverse concentrations, or concentration ratios as for example equation 33 (43, 44).

In the second case (the photochlorination of methane for instance) consecutive reactions occur. From the rate equation identical with that for the chlorination of chloroform $(CHCl_3)$ is simply replaced by $(CH_4)$, a reaction order $n = {}^3/_2$ is expected. Actually the experimental order is very high, up to seven (63), and a strong autoinhibition occurs which cannot be explained by the back reactions (2.4′) and (2.5′) (50). A similar situation occurs in the photochlorination of methyl chloride. In such cases great care must be taken in extrapolating to the initial rates. Methods equivalent to integration of the reaction rate, as used by some authors (201, 202), obviously have no significance when the variation of the rate during the course of the reaction is not known.

The situation is different again in competitive systems like $C_2Cl_4 + CH_4 + Cl_2$, because of mutual inhibition of the reactions. Here too only van't Hoff's plot is useful for determining initial rates and verifying how the reaction rate varies with the concentration (63, 83).

### 3. *Perturbations*

Initial rate determinations by van't Hoff's method or by direct measurement can be perturbed by different phenomena that occur at the start of the reaction; such as a true induction period resulting from the slow building up of the steady state concentrations of intermediates or an induction period due to the Draper effect.

An instance of the former has been observed in the dehydrochlorination of pentachloroethane for which the rate is given by (83)

$$v = \mathrm{d}p/\mathrm{d}t = \frac{I_a^{1/2}\{k_4 - k_2(C_2Cl_4)[k_4 + k_3(Cl_2)]/[k_2(C_2Cl_4) + k_2'(C_2Cl_5H)]\}}{\{k_8 + k_7[k_4 + k_3(Cl_2)]/[k_2(C_2Cl_4) + k_2'(C_2Cl_5H)]\}^{1/2}} \quad (6)$$

A simplified form of this equation

$$v = I_a^{1/2}(k_2'k_4/k_7)^{1/2}(C_2Cl_5H)^{1/2} \quad (7)$$

assuming $k_2(C_2Cl_4) \ll k_2'\,(C_2Cl_5H)$, $k_3(Cl_2) \ll k_4$, and $k_8 \ll k_7k_4/k_2'(C_2Cl_5H)$ yields a reaction order $^1/_2$ with respect to $(C_2Cl_5H)$ (4). Only the latter two assumptions, however, are justified and then only at high temperature (60, 83). In fact $k_2(C_2Cl_4)/k_2'(C_2Cl_5H)$ is not negligible as soon as small quantities of $C_2Cl_4$ appear and a complicated form of the order plot is obtained (83). This is explained as follows. The duration (2, 24a,b) of the induction period (see section C) $t_i \approx 4\tau_s$, where the steady state life-time of the chains

$$\tau_s = 1/2I_a^{1/2}k_t^{1/2} = [k_2'(C_2Cl_5H)/2^2\,I_ak_7k_4]^{1/2} \approx 0.2 \text{ sec.} \quad (8)$$

This means that the rate is undistinguishable from the steady state rate only after $t_i$. This corresponds to the initial increase in rate. Before the steady state initial rate corresponding to $C_2Cl_4 \approx 0$ is reached, however, such a quantity of $C_2Cl_4$ has been formed that equation 7 must be corrected by a factor $f = \{1 - 1/[1 + k_2(C_2Cl_4)/k_2'(C_2HCl_5)]\}^{1/2}$.[4] From known values of the constants in $f$ a satisfactory $n = {}^1/_2$ plot of equation 6 is obtained (83).

The importance of temperature gradients in gas phase chlorinations has been demonstrated recently (24c, 82). Disregarding their effect would not only introduce errors in rate constants and activation energies but even errors concerning the mechanism.

From the preceding discussion it appears that there are great risks in drawing the initial rate as the slope of the straight line through a few initial experimental points. This is only justified for more or less constant and low values of the reaction order $n$. Even in such cases the fraction of substance which has reacted being $\alpha$, an error of approximately $n\alpha$ is made in the initial rate; this means that only low values of $\alpha$ can be accepted and therefore the analytical systems must be of very high sensitivity and accuracy. Even though van't Hoff's method for determining reaction orders and initial rates is a tedious procedure, it seems by far the safest method. In addition, following the reactions up to a considerable degree of conversion often yields further valuable information (115).

Another source of perturbations appears when a new reaction cell is used. Reaction orders are erratic and irreproducible and values of initial rates fluctuate widely. Only after a certain number of runs do the results become reproducible. Similar effects have often been mentioned in the literature (15, 40), the "preliminary runs" being considered necessary for "conditioning the wall." This phenomenon seems to consist in the replacement of adsorbed layers by hydrocarbon derivatives. These layers have vapor pressures less than $10^{-5}$ mm. as measured with a Penning gage and seem to consist of polymeric chlorinated derivatives. The effect of conditioning can be explained either by an inhibition of the chain breaking at the wall or by an increased chain initiation on the layers (40). The first explanation is in agreement with the very low recombination coefficient mentioned below; while the absence of dark reactions at low temperature seems to rule out the second explanation.

## C. LIFE-TIME OF CHAINS WITH SEVERAL CHAIN CARRIERS

Measurements in intermittent light of the rate of nonbranching chain reactions with one chain carrier are equivalent to measurements of the life-time of the chain if this rate depends on a power $n \neq 1$ of the absorbed light intensity (36, 56). Applied to the simple scheme

$$\begin{array}{rl} A + h\nu \rightarrow 2R & \text{initiation} \\ R + A \rightarrow C + R & \text{propagation} \\ 2R \rightarrow R_2 & \text{chain breaking} \end{array}$$

the stationary state life-time $\tau_s$ of the chain is given by

$$\tau_s = (R_s)/2k_i(A) = 1/2[k_i(A)k_t]^{1/2} \quad (9)$$

where $(R_s)$ is the steady state concentration of the radical R. $\tau_s$ is obtained from measurements of rates in intermittent light $v_i$ and steady light $v_s$, from the duration of the light flash $t$ and the ratio $r$ of dark to light period

$$y = v_i/v_s = (\bar{R})_i/(R)_s = \{1 + (1/m)\ln[1 + rm/(1 + (R)_s/(R)_1)]\}/(r + 1) \quad (10)$$

where $m = t/\tau_s$ and $(\bar{R})_i$ and $(R)_1$ are, respectively, the mean concentrations of R and its concentration

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[4] The formula in ref. 83 gives $f^2$ and not $f$.

TABLE I

PARAMETERS OF EQUATION 12

| $r$ | 1 | 2 | 3 | 5 |
|---|---|---|---|---|
| $a$ | 0.172 | 0.265 | 0.331 | 0.388 |
| $b$ | 1.005 | .971 | .944 | .889 |
| $y$ min.[a] | 0.835 | .76 | .70 | .62 |
| $y$ max.[a] | .94 | .92 | .90 | .89 |
| $\frac{\Delta m/m}{\Delta v/v_s}$[b] | 22 | 17 | 15 | 15 |

[a] Limiting values between which equation 12 yields log $m$ values within 1% of the theoretical. [b] Factor by which the error in rate measurements is multiplied when $m$ is calculated.

at the end of a light period in intermittent light. $(\mathrm{R})_1$ is obtained from

$$(\mathrm{R})_s/(\mathrm{R})_1 = \{-rm + [r^2m^2 + 4rm(e^{2m} + 1) \times (e^{2m} - 1) + 4]^{1/2}\}/2 \tag{11}$$

Usually equations 10 and 11 are solved numerically (tables are given (36) and experimental results are compared to a plot of $y$ or $y(r + 1)^n$ *vs.* log $m$); from the value $m$ thus obtained and the measured $t$, the value of $\tau_s$ is calculated.

It is easy to see from a plot of equation 11 that only for values of $m$ about 1.5 to 10 does $y$ vary considerably, and therefore only in that region can valid measurements of $m$ be performed. These can however be simplified (2) because there log $m$ is, within about 1%, a linear function of $y$, *viz.*

$$y = (v_i/v_s)(r + 1)^{1/2} = -a \log m + b \tag{12}$$

written here for the case of a $^1/_2$ power light intensity dependence. The parameters of this equation are given in Table I. The advantage of this equation is threefold. First it permits one to calculate immediately the incidence of experimental error, which becomes

$$\Delta m/m = (2.3/a)\Delta y \tag{13}$$

or assuming $\Delta v_i = \Delta v_s = \Delta v$

$$\Delta m/m = (2.3/a)(1 + r + y^2)^{1/2}\ \Delta v/v_s \tag{14}$$

As seen in Table I the relative error in $m$, which is practically the error in $\tau_s$ is about 15 times the relative error $\Delta v/v_s$ on rate measurements. The consequences of this, when small variations of $\tau_s$ with temperature or with reactant concentrations are studied, are easily estimated. Next the use of equation 12 permits one to choose experimental conditions so as to minimize $\Delta m/m$. Finally it permits one to calculate $\tau_s$ from each experiment, which is particularly useful in complex reactions, where $\tau_s$ is a function of concentrations.

Correction factors for equations 10 and 11 have been calculated for such things as penumbra effects (37), dark reactions (140), non-uniform absorption (37), and monomolecular chain breaking (159, 166). In some cases these corrections are of a certain importance, in many cases their significance may be questioned in view of the enormous amplification of experimental error (equation 16 and Table I).

This result has been extended (2) to chains with two or more chain carriers; for a photochlorination, the over-all rate, calculated from scheme (1), is given by

$$v = k_3(\mathrm{Cl}_2)(\mathrm{R}) \tag{15}$$ [5]

(R) can be calculated by the steady state approximation. $(\mathrm{R})_s = I_a^{1/2}/k_t^{1/2}$ and $v_s = k_3(\mathrm{Cl}_2)(I_a/k_t)^{1/2}$ where $v_s$ is the stationary rate. Two conditions are necessary for integrating the rate equation. The real rate must be indistinguishable from $v_s$, *i.e.*

$$k_3/k_t < 2\epsilon/0.893(\mathrm{Cl}_2)_0 \tag{15a}$$

where $\epsilon/(\mathrm{Cl}_2)_0$ is the relative accuracy of measuring concentrations. This means that the time required for a measurable amount of reaction (46) must be large compared to the life-time of the chain $\tau_s$. Further the ratio of the concentrations of two chain carriers must be practically equal to the steady state ratio, *i.e.*, the concentration ratio (Cl)/(R) must have reached its "stationary value" before the concentrations themselves reach their "stationary values." This condition is met for long chains where $\tau_{\mathrm{Cl}}$ and $\tau_{\mathrm{R}}$ are small compared to the time between two measurements $t_1$.

Table II shows that this condition is always met in photochlorinations.

Therefore for such complex mechanisms as those considered here, the life-time of the chains can be written

$$\tau_s = (1 + \alpha)/2I_a^{1/2}k_t^{1/2} \tag{16}$$

where $\alpha = (\mathrm{Cl})/(\mathrm{R}) = [k_3(\mathrm{Cl}_2) + k_4]/[k_2(\mathrm{A}) + k_2'(\mathrm{RH})]$ and $k_t = k_8 + \alpha k_7 + \alpha^2 k_6\mathrm{M}$. Even if $k_6$ is neglected, this yields such complicated equations as

$$\tau_s = \frac{1 + [k_4 + k_3(\mathrm{Cl}_2)]/[k_2(\mathrm{A}) + k_2'(\mathrm{RH})]}{2I_a^{1/2}\{k_8 + k_7[k_4 + k_3(\mathrm{Cl}_2)]/[k_2(\mathrm{A}) + k_2'(\mathrm{RH})]\}^{1/2}} \tag{17}$$

It is obviously difficult to analyze such a complex function experimentally due to limited accuracy with which the life-time is measured. It is more useful to introduce (9, 38, 61, 167) a reduced time parameter

$$t' = 2t\, I_a(\mathrm{Cl}_2)/v_s \tag{18}$$

It then follows

$$t'/m = 1/k_3 + [k_4 + k_3(\mathrm{Cl}_2)]/[k_2(\mathrm{A}) + k_2'(\mathrm{RH})]k_3 \tag{19}$$

This permits one (38, 53, 61) to measure the rate constant of chain propagation ($k_3$) and the ratio (Cl)/(R), which is obtained from the second term of equation 19.

### D. THE LIFE-TIME OF THE ACTIVATED ACl* RADICALS FORMED IN REACTION (1.2)

In the association reaction (1.2) 17 to 23 kcal. per mole are liberated. The possibility of observing the

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(5) The reaction step $k_5$ in the scheme equations 1 and 2 has always been neglected on energetic grounds; see also Table III.

Table II

Stationary Conditions

Life-time: $\tau_s = (1 + \alpha)/2I_a^{1/2}k_t^{1/2}$; $\tau_{\mathrm{Cl}} = 1/k_2(\mathrm{A})$; $\tau_{\mathrm{R}} = 1/[k_3(\mathrm{Cl_2}) + k_4]$

| Reaction | Equation 15a | Temperature interval, °K. | $\tau_s$ | $\tau_a$ | $\tau_R$ | log Φ | Ref. |
|---|---|---|---|---|---|---|---|
| Addition (low temp.) | $k_3(\mathrm{Cl_2})/k_8$ | | | | | | |
| $\mathrm{Cl_2 + C_2Cl_4 = C_2Cl_6}$ | $10^{-6}$ | 360–450 | $3 \times 10^{-1}$ | $2 \times 10^{-7}$ | $2 \times 10^{-3}$ | 2.5 | (61) |
| $\mathrm{Cl_2 + C_2HCl_3 = C_2HCl_5}$ | $4 \times 10^{-6}$ | 350–410 | $10^{-1}$ | $10^{-8}$ | $10^{-4}$ | 3.3 | (53) |
| Addition (high temp.) | $k_3(\mathrm{Cl_2})/[k_7k_4/k_2(\mathrm{A})]$ | | | | | | |
| $\mathrm{Cl_2 + C_2Cl_4 = C_2Cl_6}$ | $10^{-7}$ | 520–560 | $4 \times 10^{-2}$ | $2 \times 10^{-7}$ | $1.5 \times 10^{-6}$ | 2.2 | (61) |
| $\mathrm{Cl_2 + CO = COCl_2}$ | $10^{-6}$ | 300–350 | $3 \times 10^{-2}$ | $6 \times 10^{-9}$ | $4 \times 10^{-9}$ | 3.6 | (38) |
| Dehydrochlorination | $k_2(\mathrm{A})/k_7$ | | | | | | |
| $\mathrm{C_2Cl_5H = C_2Cl_4 + HCl}$ | $1.6 \times 10^{-3}$ | 400–470 | $2 \times 10^{-1}$ | $3.5 \times 10^{-6}$ | $4 \times 10^{-5}$ | 3.8 | (61) |

Legend: (A) $\approx 2 \times 10^{-3}$ in ref. 61; (A) $\approx 10^{-2}$ in ref. 38 and 53; $I_a = 10^{-8}$ einstein l.$^{-1}$ sec.$^{-1}$ except for the dehydrochlorination where $I_a = 1.4 \times 10^{-10}$. $\tau$: order of magnitude of the life-times in the middle of the temperature interval; Φ: chain length, molecules formed per quantum absorbed: $\{k_3(\mathrm{Cl_2})/[k_3(\mathrm{Cl_2}) + k_4]\}\ (2\tau_s/\tau_{\mathrm{R}})$; $\alpha = [k_3(\mathrm{Cl_2}) + k_4]/k_2(\mathrm{A}) = \tau_{\mathrm{Cl}}/\tau_{\mathrm{R}}$.

excited ACl* radical which is primarily formed and probably in a vibrationally excited state has been discussed (10, 11, 12, 13, 51, 54). A reaction scheme is proposed in which steps (1.2) and (1.4) are replaced by

$$\left.\begin{array}{rl} \mathrm{A + Cl \rightarrow ACl^*} & (k_2) \\ \mathrm{ACl^* \rightarrow A + Cl} & (k_\alpha) \\ \mathrm{ACl^* + Cl_2 \rightarrow A + Cl_3} & (k_\beta) \\ \mathrm{ACl^* + Cl_2 \rightarrow ACl + Cl_2} & (k_\gamma) \end{array}\right\} \quad (20)$$

A further activation step, the reverse of $k_\gamma$, must also be added

$$\mathrm{ACl + Cl_2 \rightarrow ACl^* + Cl_2} \quad (k_{-\gamma})$$

The general form of rate equation 4 is still valid and one finds

$$\alpha = (\mathrm{Cl})/(\mathrm{R}) = [k_4 + k_3(\mathrm{Cl_2})]/k_2(\mathrm{A}) \quad (21)$$

The significance of $k_4$, however, is now

$$k_4 = [k_\alpha + k_\beta\,(\mathrm{Cl_2})](k_3 + k_{-\gamma})/k_\gamma \quad (22)$$

If many degrees of freedom contribute to the activation process (20.$-\gamma$), $k_{-\gamma} \gg k_3$, and if simultaneously $k_\beta\,(\mathrm{Cl_2}) \ll k_\alpha$ the decomposition of ACl is a first-order monomolecular reaction as observed for $\mathrm{C_2Cl_5}$ and $\mathrm{C_2HCl_4}$ at temperatures above 400°K. (83, 115). On the other hand it has been assumed in the case of the chlorinated ethyl radicals containing less than 3 Cl atoms that $k_3 \gg k_{-\gamma}$ and $k_\alpha \approx k_\beta\,(\mathrm{Cl_2})$; this assumption is used to explain the *cis–trans* isomerization of $\mathrm{C_2H_2Cl_2}$ (11, 12), the photochlorination of vinyl chloride and ethylene (54, 170), and competitive chlorinations of ethylenes (13). A severe test (equation 27) of this assumption is obtained in the competitive chlorination of $\mathrm{C_2H_6}$—$\mathrm{C_2H_4}$; no indication of the sequence (20) could be observed and at this limit of the series it appears certain that $k_{-\gamma} \gg k_3$ (84).

It should be noted here that the occurrence of vibrationally excited HCl molecules in the $\mathrm{H + Cl_2 \rightarrow HCl + Cl}$ reaction has been proved by infrared chemiluminescence (38a, 40a, 155a). The possibility of further reaction of the excited HCl has been discussed recently (176a).

### E. COMPETITIVE SYSTEMS

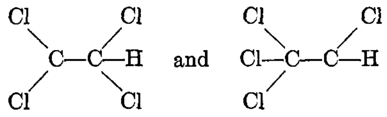
The usual steady state treatment applied to the photochlorination of simple hydrocarbons like $\mathrm{C_2Cl_5H}$ yields (61) the rate equation

$$-\mathrm{d(Cl_2)}/\mathrm{d}t = I_a^{1/2}k_3(\mathrm{Cl_2})\{k_8 + k_7[k_4 + k_3(\mathrm{Cl_2})]/ [k_2(\mathrm{C_2Cl_4}) + k_2'(\mathrm{C_2Cl_5H})]\}^{-1/2} \quad (23)$$

Equation 6 leads to a pressure maximum corresponding to the competition dehydrochlorination–addition for

$$k_2k_3/k_2'k_4 = (\mathrm{C_2Cl_5H})/(\mathrm{Cl_2})(\mathrm{C_2Cl_4}) \quad (24)$$

This has been observed and used for the measurement of the complex rate constant $k_2k_3/k_2'k_4$ (60, 83). A similar method permits one (59, 62) to distinguish between isomeric radicals such as



(25)

A competition addition–dehydrochlorination is also observed when one follows the photochlorination of trichloroethylene to a large extent of reaction (41, 85, 115).

Addition–substitution, substitution–substitution, and addition–addition competitions have been extensively studied to determine elementary rate constants.

A study of the chlorination of mixtures of $\mathrm{H_2}$ and NO (8) has allowed measurements of the elementary rate constant of the reaction $\mathrm{H_2 + Cl \rightarrow H + HCl}$. This value has been used (157, 158, 187) to obtain the elementary rate constants of hydrogen abstraction from $\mathrm{CH_4}$, $\mathrm{CH_3Cl}$, $\mathrm{C_2H_6}$, $\mathrm{C_2H_5Cl}$, $\mathrm{C_3H_8}$ by competitive experiments using gas chromatographic analysis. Several cross-checks have been performed (122, 124, 125), and the hydrogen abstraction from $\mathrm{CH_2Cl_2}$, $\mathrm{CHCl_3}$ has been studied.

Measurements of the ratio of addition to substitution rates have been made (45, 60, 83) to determine the rates of addition of a chlorine atom to the $C_2Cl_4$ double bond. This has also furnished checks for the parameters measured previously (122, 124, 125); the values are in fair agreement. In simple cases of substitution–substitution competition, the ratio of rates is given by

$$v_{RH}/v_{R'H} = k_2(RH)/k_2'(R'H) \qquad (26)$$

which can be immediately integrated (44, 125). A somewhat more complicated situation occurs in addition–substitution and addition–addition competitions. One finds

$$v_s/v_a = [k_2'(RH)/k_2(A)][1 + k_4/k_3(Cl_2)] \qquad (27)$$

and

$$v_a/v_a' = [k_2(A)/k_2'(A')][1 + k_4'/k_3'(Cl_2)]/[1 + k_4/k_3(Cl_2)] \qquad (28)$$

These equations can, of course, not be integrated and it is necessary to extrapolate to initial rates, *i.e.*, to conditions in which well defined concentrations of RH, A, A′, and $Cl_2$ exist. These extrapolations are not easy due to complex and usually high reaction orders as discussed in section F (equation 29).

Even more complex situations arise when substitution and dehydrochlorination compete; very generally then, addition must be considered also and equations as complex as 23 and 6 are obtained somewhat different according to whether the radicals R and ACl are identical or not. These equations have been used to study the hydrogen abstraction from $C_2HCl_5$ (83) and the two $C_2H_2Cl_4$ (59).

Equations 27 and 28 have been used to obtain values of $k_4$ and $k_4'$ and can thus be interpreted as a measure of the relative importance of activation, reaction, or deactivation (equations $20.-\gamma$; 1.3; $20.\gamma$) of the ACl radical (11, 12, 13, 54, 84).

A competition technique had already been used (143) to study the photochlorination of mixtures of $CHCl_3$ and $CDCl_3$; this problem has been reinvestigated using careful kinetic analysis (44).

Competition techniques can also be used when chlorine does not attack two reactants, but two or more sites in one reactant (40, 88a, 122); the rate of hydrogen abstraction from *n*-butane, isobutane (7), and *n*-butylhalides (74) and 2 halobutanes (75) has been studied; the order of reactivity for the hydrogen atoms is as follows

tertiary > secondary > primary

A similar problem is the competition addition–α-substitution in compounds such as propylene (123, 189) or the reactivity in the liquid phase (3, 137, 193, 194) of chlorinating agents such as *n*-chloroimides or alkyl hypochlorites.

### F. SINGULARITIES IN OVER-ALL RATES

Several chlorination reactions show complex orders. Some of these can be reduced to simple orders by the choice of adequate experimental conditions, in other cases though, the behavior of the reaction is more peculiar and needs a careful kinetic analysis to be understood; this is true for the over-all rate of single reactions in mixtures or when the reaction products can in turn act as reactants.

#### 1. *Over-all Rates of Single Reactions in Mixtures*

In a mixture where addition and substitution take place simultaneously the total rate of chlorine disappearance is given by

$$v^* = v + v' = \{k_2(A)/[1 + k_4/k_3(Cl_2)] + k_2'(R'H)\}I_a^{1/2}/(k_t/\alpha^2 + k_t^m/\alpha\beta + k_t'/\beta^2)^{1/2} \qquad (29)$$

where

$$\alpha = (Cl)/(ACl) = [k_3(Cl_2) + k_4]/k_2(A)$$
$$\beta = (Cl)/(R) = k_3'(Cl_2)/k_2'(R'H)$$

$k_t^m$ refers to a new mixed chain-breaking step between two different radicals.

Three distinct situations are to be expected according to whether the principal chain-breaking step is the same as in pure addition, as in pure substitution, or whether mixed chain breaking predominates.

In the first case $k_t/\alpha^2 \gg k_t'/\beta^2 + k_t^m/\alpha\beta$. The addition rate remains unchanged, but the substitution is inhibited and the over-all rate constant of the addition is numerically equal for the mixture and for "pure" addition. This occurs when one measures the rate of chlorine addition to tetrachloroethylene in mixtures with methane, methyl chloride, and methylene chloride (63); the addition order with respect to chlorine is $n = {}^3/_2$. The rate of substitution in the mixture is given by

$$v' = I_a^{1/2}[k_2'(R'H)/k_2(A)][k_3(Cl_2) + k_4]/k_t^{1/2} \qquad (30)$$

and shows "an order in the initial condition" $n_0 = {}^3/_2$. The substitution order varies during the course of the reaction with the ratio (R′H)/(A). If that ratio increases the order decreases and inversely.

When the chain breaking is the same as in pure substitution, *i.e.*, $k_t'/\beta^2 \gg k_t/\alpha^2 + k_t^m/\alpha\beta$, the substitution is not inhibited while the addition reaction is.

Finally, when $k_t^m/\alpha\beta \gg k_t/\alpha^2 + k_t'/\beta^2$, both reactions are inhibited. This was shown to occur in mixtures of tetrachloroethylene and chloroform (45). Here the main chain breaking is

$$CCl_3 + C_2Cl_5 \rightarrow \text{inactive products} \quad (k_9)$$

and the usual steady state treatment leads to the rate equation

$$(vv')^{1/2} = I_a^{1/2}(k_3k_3'/k_9)^{1/2}(Cl_2) \qquad (31)$$

TABLE III

| Reactions | $CH_4$ $E_A$ | $CH_4$ log $A$ | $CH_3Cl$ $E_A$ | $CH_3Cl$ log $A$ | $CH_2Cl_2$ $E_A$ | $CH_2Cl_2$ log $A$ | $CHCl_3$ $E_A$ | $CHCl_3$ log $A$ |
|---|---|---|---|---|---|---|---|---|
| $Cl + R'H \rightarrow R' + HCl$ | 3.9 | 10.7 | 3.1 | 10.5 | 3.1 | 10.4 | 3.3 | 10.2 |
| $R' + Cl_2 \rightarrow R'Cl + Cl$ | 2.3 | 9.9 | 3.0 | 9.6 | 4.0 | 9.0 | 6.0 | 8.7 |
| $R' + HCl \rightarrow R'H + Cl$ | 5.0 | 9.0 | 8.2 | 9.1 | 11.2 | 9.0 | 13.4 | 8.8 |
| $R'Cl + Cl \rightarrow R' Cl + Cl_2$ | 25.0 | 11.0 | 21.4 | 11.0 | 21.0 | 11.0 | 18.9 | 11.3 |
| $R' + Cl \rightarrow R'Cl$ | 0 | 11.6 | 0 | 11.4 | 0 | 11.4 | 0 | 11.4 |
| $R' + R' \rightarrow$ ..... | 0 | 10.5 | 0 | 9.6 | 0 | 9.4 | 0 | 8.8 |

| Reactions | $C_2H_4$ $E_A$ | $C_2H_4$ log $A$ | $C_2H_3Cl$ $E_A$ | $C_2H_3Cl$ log $A$ | $C_2H_2Cl_2$ $E_A$ | $C_2H_2Cl_2$ log $A$ | $C_2HCl_3$ $E_A$ | $C_2HCl_3$ log $A$ | $C_2Cl_4$ $E_A$ | $C_2Cl_4$ log $A$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $Cl + R \rightarrow RCl\ (R')$ | 0 | 10.2 | 0 | 10.2 | 0 | 10.0 | 0 | 9.8 | 0 | 9.4 |
| $R' + Cl_2 \rightarrow RCl_2 + Cl$ | 1.0 | 9.4 | 1.0 | 8.8 | 2.5 | 8.7 | 5.2 | 8.8 | 5.4 | 8.3 |
| $R' \rightarrow R + Cl$ | 23.6 | 13.9 | 23.8 | 13.8 | 20.3 | 13.7 | 20.4 | 13.7 | 16.8 | 12.8 |
| $RCl_2 + Cl \rightarrow R' + Cl_2$ | 21.3 | 11.3 | 20.6 | 11.3 | 20.4 | 11.3 | 18.3 | 11.3 | 19.5 | 11.4 |
| $R' + Cl \rightarrow RCl_2$ | 0 | 11.3 | 0 | 11.3 | 0 | 11.3 | 0 | 11.5 | 0 | 11.0 |
| $R' + R' \rightarrow$ ..... | 0 | 10.1 | 0 | 9.8 | 0 | 9.5 | 0 | 9.3 | 0 | 8.7 |

| Reactions | $C_2H_6$ $E_A$ | $C_2H_6$ log $A$ | $C_2H_5Cl$ $E_A$ | $C_2H_5Cl$ log $A$ | $C_2H_4Cl_2$ $E_A$ | $C_2H_4Cl_2$ log $A$ | $C_2H_3Cl_3$ $E_A$ | $C_2H_3Cl_3$ log $A$ | $C_2H_2Cl_4$ $E_A$ | $C_2H_2Cl_4$ log $A$ | $C_2HCl_5$ $E_A$ | $C_2HCl_5$ log $A$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Cl + R'H \rightarrow R' + HCl$ | 1.0 | 11.0 | 1.5 | 10.5 | 3.0 | 10.4 | 3.5 | 10.5 | 3.3 | 10.8 | 3.3 | 9.8 |
| $R' + Cl_2 \rightarrow R'Cl + Cl$ | 1.0 | 10.1 | 1.0 | 2.0 | 1.0 | 8.8 | 2.5 | 8.7 | 5.2 | 8.8 | 5.4 | 8.3 |
| $R' + HCl \rightarrow R'H + Cl$ | 8.1 | 9.3 | 9.1 | 9.0 | 10.2 | 8.9 | 11.2 | 8.5 | 10 | 8.5 | 10.8 | 7.8 |
| $R'Cl + Cl \rightarrow R' + Cl_2$ | 21.5 | 11.3 | 21.3 | 11.3 | 20.6 | 11.3 | 20.4 | 11.3 | 18.3 | 11.3 | 19.5 | 11.4 |
| $R' + Cl \rightarrow R'Cl$ | 0 | 11.3 | 0 | 11.3 | 0 | 11.3 | 0 | 11.3 | 0 | 10.9 | 0 | 11.0 |
| $R' + R' \rightarrow$ ... | 0 | 10.5 | 0 | 10.1 | 0 | 9.8 | 0 | 9.5 | 0 | 9.3 | 0 | 8.7 |

which permits one to measure the over-all rate constant $(k_3k_3'/k_9)^{1/2}$.

The competitive chlorination of $C_2Cl_4$ and $C_2Cl_5H$ is a special case of this type of reaction where the two reactants yield the same free radical.

### 2. *Consecutive Reactions*

The chlorinations of methane, methyl chloride, and methylene chloride are equivalent to chlorinations of mixtures since the reaction products can also be chlorinated.

For two competing reactants one can write the total rate of chlorine disappearance in the form

$$-d(Cl_2)/dt = v_A^* + v_B^* = I_a^{1/2} k_3(Cl_2)(1 + \Phi) \times [k_t + k_t'(\alpha/\beta)^2 + k_t(\alpha/\beta)]^{-1/2} \quad (32)$$

where $v_A^*$ and $v_B^*$ are the rates of disappearance of reactants A and B in the mixture and $\Phi$ is the relative yield of each type of radical.

Equation 32 can be generalized for three or more competitive reactions.

The good agreement between experimental points and the theoretical prediction from equation 32 has been shown (63).

It is astonishing that in previous studies on photochemical (201, 202) or thermal (153) chlorination of methane the inhibition by reaction products has never been stated; neglecting the inhibition leads to misinterpretation of the experimental results.

Purely formal treatments (116a, 174a) of such complex reactions as the chlorination of methane and its chlorinated derivatives, disregarding the mechanism, do not seem useful and may be misleading for technological applications for which they are intended.

## III. RESULTS AND DISCUSSION

### VALUES OF RATE CONSTANTS, FREQUENCY FACTORS, ACTIVATION ENERGIES

Table III summarizes all available data on rate constants of the six elementary steps of schemes 1 and 2 which determine the rate of photochlorination of methane, ethane, ethylene, and all their chlorinated derivatives; no distinction is made, however, between isomeric compounds since available data would be insufficient for that purpose. Most data were obtained by the kinetic analysis of photochlorination reactions in steady or in intermittent light, or by competition techniques. Results on the recombination of methyl and ethyl radicals obtained by the intermittent light technique in different systems (89, 116, 121, 167) or by mass spectrometric studies (135) have been used. The few available data on the chlorine atom recombination will also be considered (35, 43, 47, 48, 106a, 149, 150).

The discussion is subdivided into four groups of compounds: 1. "Chlorination of $CHCl_3$, $C_2Cl_4$, $C_2HCl_5$, and CO," 2. "Chlorination of $CH_4$ and its Derivatives," 3. "Chlorination of Other Derivatives of $C_2H_4$ and $C_2H_6$," 4. "Chlorination of Higher Hydrocarbons."

This subdivision will appear reasonable because in these different groups the course of the reaction differs in a typical manner and the quality of some results is also typically different.

For similar reasons the "Pyrolysis of Chlorinated Compounds" will be discussed in a separate section (5), even though the results have been used in Table III. Finally a brief survey of "Other Halogenating Agents" will be given in section 6.

### 1. *Chlorination of $CHCl_3$, $C_2Cl_4$, $C_2HCl_5$, and CO*

In one respect these reactions are the simplest because the products cannot be further chlorinated. The over-all rate is given by equations of the form of 4 or 5. The first term is predominant for trichloroethylene up to 410°K. (53, 115) and for tetrachloroethylene up to 370°K. (61), and thus $k_3/k_8^{1/2}$ in steady light and $k_3$ as well as $k_8$ in intermittent light have been measured.

At higher temperatures the second term becomes more important and in $C_2Cl_4$ predominates above 470°K. In the intermediate region it is useful (45, 61) to make plots of the function

$$Y = I_a(Cl_2)/v_0^2 = k_8/k_3^2 + k_7[k_4 + k_3(Cl_2)]/k_2k_3^2(C_2Cl_4) \quad (33)$$

*vs.* $(Cl_2)/(C_2Cl_4)$ or $1/(C_2Cl_4)$. This allows one to extend the temperature range of measured $k_3/k_8^{1/2}$ values in steady light, of $k_3$ in intermittent light, and to measure the complex constant $k_7k_4/k_2$ (61). $k_3/k_8^{1/2}$ and $k_3$ have also been measured for the reaction of $C_2HCl_5$ (61) and $k_3/k_8^{1/2}$ and $(k_2k_3/k_7)^{1/2}$ for $CHCl_3$ (45, 63). Using further competition experiments in systems containing $CH_4$, $CH_3Cl$, $CH_2Cl_2$, $CHCl_3$, $C_2Cl_4$, $C_2HCl_5$ all relevant $k_2$ values were obtained (83). In the competition $C_2HCl_5$–$C_2Cl_4$ equations 25 and 27 yield further combinations of constants and finally the equilibrium constants obtained from thermodynamic data yield $k_5$ and $k_4'$ (88).

Actually in the system $C_2Cl_4$–$C_2HCl_5$ a number of parameters exceeding the number of rate determining constants has been measured; the system is thus highly overdetermined (61, 83).

The reaction of $C_2HCl_3$ above 410°K. gives rise to a complex stoichiometry

$$C_2HCl_3 + Cl_2 \rightarrow C_2HCl_5$$
$$C_2HCl_5 \rightarrow C_2Cl_4 + HCl$$
$$C_2Cl_4 + Cl_2 \rightarrow C_2Cl_6$$

This has been analyzed (115) by means of a new mass spectrometric technique (85) and has given the values of $k_2$, $k_4$, and $k_7$; $k_5$ has been obtained from the equilibrium constant.

For $CHCl_3$ no sector experiments have been made. If $k_7 = 10^{11.4}$ is estimated on the basis of measurements on $CH_4$ (see below), $C_2Cl_4$, and $C_2HCl_3$, values of $A_3$ and $A_8$ are obtained which are very nicely in line with others in Table III. The accuracy in the $C_2HCl_3$, $C_2Cl_4$, $C_2HCl_5$ systems as well as for most of the $k_2'$ values is about ±0.5 kcal. for $E$ and ±0.2 for log $A$; in a few instances such as for $CHCl_3$ higher error limits are possible as discussed below.

For the phosgene synthesis in steady light from 280 to 328°K. the rate equation

$$v = I_a^{1/2}k_3(Cl_2)[k_2(CO)/k_7k_4]^{1/2} \quad (34)$$

has been found (29, 30, 38) and rate constants have been given. Investigations by the sector technique (38) should yield the ratio $\alpha = Cl/COCl$ with the help of an equation equivalent to equation 19. A mechanism with three chain carriers Cl, $Cl_3$, COCl has also been considered.

The life-time of the chains is then given by

$$\tau_s = (1 + \alpha + \beta)/2I_a^{1/2}k_t^{1/2} \quad (35)$$

where $\beta = Cl_3/COCl$ is proportional to $(Cl_2)$. Since $\tau_s$ was actually found to be independent of the chlorine pressure (except for the $I_a$ dependence) (38), it may be concluded that $\beta \ll 1 + \alpha$. This does not permit one to discard the Rollefson mechanism. It could in fact be possible that $\beta$ is negligible, within the *experimental error limits* which are not small (see Table I), and that chains are nevertheless propagated by $Cl_3$. In fact in the reactions reviewed here there is no doubt that Cl atoms *do* propagate chains even though $\alpha$ is not measurable (Table II) except in the case of the phosgene synthesis.

Interesting conclusions can be drawn from existing data on the phosgene synthesis. Equation 34 implies that in the general equation $k_7\alpha \gg k_6M\alpha^2$ or $k_8$. From the rate constants given in (38) (see Table III) and the maximum and minimum CO pressure used one obtains $k_8 < 10^{11}$ l. mole$^{-1}$ sec.$^{-1}$ and $k_6 \leq 10^{11.4}$ l.$^2$ mole$^{-2}$ sec.$^{-1}$ at room temperature.

The rate of recombination of Cl atoms at room temperature, with $Cl_2$ as a third body, would therefore be slightly lower than that of Br with $Br_2$ (33, 34, 78) and about ten times lower than that of I with $I_2$ (156).

The thermal chlorination of CO proceeds, according to (31) by

$$v = (k_1/k_6)^{1/2}\, k_3(Cl_2)^{3/2}\, k_2(CO)/k_4 \quad (36)$$

If the equilibrium $k_1/k_6$ here is established homogeneously, $k_6M\alpha \gg k_7$ and $k_6 \simeq 10^{12}$; if a wall reaction contributes to the recombination, as suggested by these authors, a smaller $k_6$ results. From (31, 38) it can be estimated that, between 500 and 600°K., reactions 6 and 7 are about equally important. If $k_7$ is known, this provides a ready measure of $k_6$ if $M = Cl_2$. Recent experiments (43) have shown that log $k_6 = 9.9 \pm 0.5$ at 502.4°K., $9.85 \pm 0.5$ at 552.3°K., and $9.70 \pm 0.5$ at 598.9°K. In fact the large error limits are only due to the discrepancy between the values given for $k_4/k_2$ (29, 30, 38). Measurements are presently performed to improve the knowledge of this ratio. The values of $k_6$ can be compared with a room temperature value (149, 150) and diverging results obtained in shock tube experiments either by direct measurements (35) or from the reverse reaction (106a). It should be pointed out that high temperature measurements are subject to experimental difficulties due to the occurrence of the radiative recombination of chlorine atoms (153a, 177b, 187a). A thorough discussion of the temperature dependence is premature; nevertheless, we believe it may be definitely stated that any value of log $k_6 > 11.5$ (107, 132) at about 300°K. is in contradiction with experimental results.

On the other hand, the rate of diffusion of chlorine atoms to the wall and the resulting heterogeneous chain breaking have been discussed (145, 156). A similar discussion can be applied for the reactions studied here: A considerable fraction of the chains would be terminated on the wall if the recombination coefficient at the wall is of the order of unity. An accurate value of $^1/_2$ for the reaction order with respect to the absorbed light intensity was always observed in Pyrex vessels (53, 83, 115) in cases in which the Draper effect can be neglected or if adequate corrections (82) are applied. The same has been observed in smaller quartz reaction vessels for the synthesis of $COCl_2$ (38) and the photochlorination of $C_2HCl_3$ (53). Further, in experimental conditions differing considerably, a perfect agreement of the rate constants for the latter reaction has been obtained at Leeds and at Brussels (42, 53). These facts permit us to conclude that heterogeneous reaction must represent less than 2%. This leads to a recombination coefficient at the walls less than $10^{-5}$.

It is of interest to restate this perfect agreement of rate constants of trichloroethylene measured using either $\lambda = 3660$ Å. or $\lambda = 4358$ Å. The increase of the energy of the light quanta by about 14 kcal. mole$^{-1}$ thus has no influence on the rate. This shows that there is no variation of the primary photochemical yield of chlorine dissociation and confirms the general opinion that this yield is 1.

### 2. *Chlorination of $CH_4$ and its Derivatives*

The reaction of $CH_4$, $CH_3Cl$, and $CH_2Cl_2$ is complicated by the fact that, as soon as quite small amounts of products are formed, these react in turn and interfere with the course of the over-all reaction. High reaction orders are found (63) for extrapolating to initial rates. This difficulty is further increased by the fact that these initial rates have to be fitted to a two-parameter equation, *e.g.*, equation 5. It would therefore be possible to determine rate constants with an accuracy comparable to that quoted in the preceding section (III1) only if the analytical methods permitted one to measure amounts of products of less than 1% with a precision of better than 1%.

A few facts nevertheless facilitate the solution of these difficulties. All values of $k_2'$ have been measured (124, 125, 139) by a competition technique on which numerous cross-checks have been performed. $k_8$ for methane, *i.e.*, the rate of recombination of $CH_3$ radicals has been measured in the acetone photolysis (89, 121) and by a mass spectrometric technique (135). Thus a plot of the inverse square of equation 5 as for equation 33 yields $k_3$, $k_8k_2'/k_3k_7$, and $k_7$. Finally, a tedious procedure of fitting the data for $CHCl_3$ to equation 32 for $CH_2Cl_2$, these data to the same equation for $CH_3Cl$ and ultimately for $CH_4$, and repeating this entire procedure until the best fit for the whole series is obtained, has led to the figures given in Table III (63). The product $k_4'k_5$ is obtained from thermodynamic data, $E_4'$ and $E_5$ from bond dissociation energies; the values of $k_4'$ obtained in this way are in excellent agreement with direct measurements (50). A constant value log $A_5 = 10^{11}$ is assumed in rough agreement with the values resulting from actual measurements in the systems $CHCl_3$, $C_2Cl_4$, $C_2HCl_3$.

It is remarkable that the log $A_2'$, log $A_3$, and $E_3$ values and hence also the log $A_4'$, log $A_5$, and $E_5$ values agree extremely well with activated complex calculations (118). The disagreement concerning $E_2'$ values will be discussed in section IVB.

### 3. *Chlorination of Other Derivatives of $C_2H_4$ and $C_2H_6$*

The chlorinations of 1,1,2,2- and 1,1,1,2-tetrachloroethane have been studied extensively. All the elementary rate constants have been determined (59); it has also been shown that in the photochlorination of trichloroethylene, the attack of a chlorine atom in the double bond yields principally the 1,1,2,2-tetrachloroethyl radical. The elementary rate constants of $C_2HCl_3$ and $C_2H_2Cl_4$ given in Table III, are calculated from (59, 115).

The addition of chlorine to the lower chlorinated ethylenes has also been studied (107, 169). The elementary rate constants of addition reactions have been given previously (10, 63). The value of log $k_2$ for $C_2H_4$ has been checked experimentally (84) and is in perfect agreement with the earlier estimated value (63). The values of log $k_2$ from $C_2H_3Cl$ to $C_2HCl_3$ are in good agreement with recent results (10, 12, 13, 54, 115) if zero activation energy is assumed. The resulting dissociation energies of chlorinated free radicals $D$(C–Cl) are in good agreement with data obtained from pyrolysis reactions (16, 18, 19, 21, 22, 111, 113) and refer to nonactivated species. The over-all activation energies and quantum yields of these reactions have been reviewed (107); combined with more recent data on the over-all reaction rates in steady and intermittent light (12, 13, 54), these permit one to calculate $k_3$, $k_8$. The latter constant has been measured by a direct method for $C_2H_5$ radicals (116). A constant value log $k_7 = 11.3 \pm 0.3$ was assumed in each case in agreement with theoretical provisions. It should be noted that the recombination of 2 monochloroethyl radicals goes principally by dimerization and not disproportionation (197). Recent results have been obtained on the recombination of trichloromethyl and monochloroethyl radicals (163a). Similar experiments are being performed for the higher chlorinated ethyl radicals.

The product $k_4k_5$ is calculated from the thermodynamic equilibrium constant; where $A_2$, $A_3$, $A_4$ are known, this leads to $\log A_5 = 11.3$. Assuming this frequency factor to be constant throughout the series yields either $A_2$ or $A_3$ values well in line with the measured ones.

For the substitution reactions, most of the rate constants are the same as for the corresponding ethylene ($k_3$, $k_5$, $k_7$, $k_8$). The over-all rate constants for $C_2H_6$ have been measured recently (114), using the known values of $k_8$ (116) and $k_2'$ (71, 125, 158); this yielded $k_3$ and $k_7$. The rate of hydrogen abstraction $k_2'$ was also measured for ethyl chloride (158), both tetrachloroethanes (59), and pentachloroethane (83); the values for the di- and trichloroethanes have been measured recently (88a) as well as the point of attack on the asymmetrically substituted derivatives. The values given in Table III refer to the symmetric compounds. The equilibrium constants yield $k_4'k_5$ and thus $k_4'$ since $k_5$ is known from the corresponding addition reaction. For the tetrachloroethanes, the standard entropy is not known (see Table IV); $\log A_4' = 8.5$ has been interpolated for both $C_2H_3Cl_3$ and $C_2H_2Cl_4$.

Experiments have also been performed on the photochemical addition of chlorine to tetrafluoroethylene and trifluoromonochloroethylene (39). The narrow range of the experimental conditions however makes the results doubtful.

### 4. *Chlorination of Higher Hydrocarbons*

Numerous studies have been made to determine the relative reactivities of C–H bonds toward a chlorine atom in higher paraffins or their substituted derivatives, among these were propane (102), *n*-butane (7, 102) and isobutane (7), *n*-butylhalides (74), 2-halobutanes (73, 75), *n*-pentane (102), and *n*-hexane (40). Similar experiments were performed with bicyclane (129). As a rule the reactivities of C–H bonds increase from primary to tertiary. This was also observed in competitive experiments (122, 125) yielding not only the relative reactivities but also the values of the elementary rate constants of hydrogen abstraction. These experiments were performed with propane, *n*- and isobutane, neopentane, cyclopropane, and cyclobutane.

A similar technique was used to measure the rate of addition of a chlorine atom to the ethylene, propylene, and isobutene double bonds (98). These systems are complicated by the occurrence of rapid heterogeneous dark reactions even at room temperature. Such effects were observed in the chlorination of propane (204, 205), but no kinetic treatment was given in these earlier studies.

The influence of the molecular structure of paraffins on their over-all chlorination rates was also investigated for *n*-pentane, *n*-hexane, *n*-heptane, 2,3-dimethylbutane, and 2,2,4-trimethylpentane (40). It was found that the rate of monochlorination increases with increasing chain length and decreases with chain branching.

The point of attack of a chlorine atom on monosubstituted benzene in the gas phase has also been extensively studied (64, 65, 66). These reactions were recognized as proceeding by a free radical scheme similar to that of the paraffins, the peculiarity being the unexpected reactivity of the *meta* position.

Little, however, is known about the mechanism and the over-all rates of these reactions. The photochlorination of toluene vapor has been studied (161), but the results are very doubtful due to the integration method used in the interpretation.

### 5. *Pyrolysis of Chlorinated Compounds*

The gas phase pyrolysis of chloroalkanes has been studied extensively. These reactions proceed either by a molecular mechanism or by a chain mechanism (15, 113). Chain mechanisms were found in the pyrolysis of dichloromethane (108, 188), chloroform (176), 1,2-dichloroethane (18, 111),[6] trichloroethane (22), 1,1,2,2-tetrachloroethane (20), pentachloroethane (110), hexachloroethane (52), and oxalylchloride (184) while the pyrolysis of ethyl chloride (19, 26a), 1,1-dichloroethane (19, 100), 1-chloropropane (17), 2-chloropropane (16), 1,2-dichloropropane (16), 1-chlorobutane (17, 101), 2-chlorobutane (136), and *t*-butyl chloride (21) occur by a molecular process. Arguments have also been advanced that methyl chloride (108a, 177a) and chloroform (177) pyrolyze by a nonchain mechanism.

A general scheme has been proposed for the free radical mechanism (112) comprising the following steps

$$
\begin{aligned}
\mathrm{AHCl} &\rightarrow \mathrm{AH} + \mathrm{Cl} && k_1 \\
\mathrm{Cl} + \mathrm{AHCl} &\rightarrow \alpha(\beta\mathrm{ACl} + \mathrm{HCl}) && \\
&\rightarrow (1 - \alpha)(\mu\mathrm{ACl} + \mathrm{HCl}) && k_2 \\
\mu\mathrm{ACl} &\rightarrow \mathrm{A} + \mathrm{Cl} && k_4 \\
\mathrm{Cl} + \mathrm{AH} &\rightarrow \mathrm{AHCl} && k_7
\end{aligned}
$$

For completeness the following steps ought to be added

$$
\begin{aligned}
\mathrm{AH} &\rightarrow \mathrm{A'H} + \mathrm{Cl} && k_4'\text{[7]} \\
\mathrm{Cl} + \beta\mathrm{ACl} &\rightarrow \mathrm{ACl_2} && k_7' \\
\mathrm{Cl} + \mu\mathrm{ACl} &\rightarrow \mathrm{ACl_2} && k_7''
\end{aligned}
$$

This scheme makes it possible to predict whether a given pyrolysis is molecular or proceeds by free radicals. If $\alpha = 1$, the hydrogen abstraction reaction ($k_2$) gives

---

(6) The photolysis of this compound proceeds by the same mechanism (203).

(7) Except for $C_2H_5Cl$, 1,1-$C_2H_4Cl_2$, 1,1,1-$C_2H_3Cl_3$.

TABLE IV

RATE CONSTANTS FOR PYROLYSIS OF CHLORINATED ETHANES

| Reaction | Calculated values | Experimental | Temperature interval, °K. | Limiting values Calcd. | Limiting values Exptl. | Ref. |
|---|---|---|---|---|---|---|
| $1,2\text{-}C_2Cl_2H_4 \rightarrow C_2ClH_3 + HCl$ | $-52.500/4.57T + 12.8$ | $-47.000/4.57T + 10.8$[a] | 635–758 | −5.3 to −2.4 | −5.4 to −2.7 | (112) |
| $1,1,1\text{-}C_2Cl_3H_3 \rightarrow C_2Cl_2H_2 + HCl$ | $-49.600/4.57T + 12.6$ | $-47.900/4.57T + 12.53$ | 661–697 | −3.8 to −3.0 | −3.4 to −2.5 | (112) |
| $1,1,2,2\text{-}C_2Cl_4H_2 \rightarrow C_2Cl_3H + HCl$ | $-48.300/4.57T + 12.6$ | $-36.500/4.57T + 9.6$ | 536–635 | −6.8 to −3.3 | −5.3 to −2.6 | (112) |
| $C_2Cl_5H \rightarrow C_2Cl_4 + HCl$ | $-45.100/4.57T + 12.5$ | $-48.000/4.57T + 13.0$ | 680–711 | −2.0 to −1.4 | −2.4 to −1.8 | (110) |

[a] NOTE ADDED IN PROOF.—Recent experiments (55a) yield $-53.100/4.57T + 13.35$ between 637 and 754°K.

only a $\mu$ radical (87), *i.e.*, one which can yield the unsaturate A by a C–Cl dissociation, the radical chain is most important. The kinetic analysis leads then to the following rate expressions

$$v_1 = (k_1k_2k_4/k_7'')^{1/2}(\mathrm{AHCl}) \tag{37a}$$

or

$$v_2 = (k_1k_2k_4/k_7)^{1/2}(\mathrm{AHCl}) \tag{37b}$$

depending on whether the AH radical dissociates faster than it combines with a chlorine atom or the reverse. If $\alpha \neq 0$, the right hand side of equations 37a and 37b should be multiplied by $(1 - \alpha)^{1/2}$ for small values of $\alpha$, whereas for large values the rate equations become

$$v_3 = k_1 \frac{1-\alpha}{\alpha} \cdot (\mathrm{AHCl}) \tag{37c}$$

or

$$v_4 = (k_1k_7'/k_7) \cdot \frac{1-\alpha}{\alpha} \cdot (\mathrm{AHCl}) \tag{37d}$$

The transition from equations 37a to 37c or 37b to 37d is obtained by setting $v_1 = v_3$ or $v_2 = v_4$; using reasonable values (55a) for the rate constants one finds that this should occur at about $\alpha \approx 10^{-6}$ to $10^{-8}$.[8] The over-all rate constants of equations 37c and 37d have activation energies of approximately 75 kcal./mole instead of 50 kcal./mole in equations 37a and 37b. Measured values of $\alpha$ actually lie around 0.6 to 0.8, and thus the "chain length" drops below unity and the molecular process predominates in these cases.

An effort is currently being made (55a) to relate the mechanism of pyrolysis of other asymmetric ethanes to the reactivity of the different C–H bonds toward chlorine atoms.

Table IV shows a comparison of the experimental values of over-all rate constants of pyrolysis and the values calculated from chlorination studies. For di-, tri-, and pentachloroethane the agreement is quite good, especially when one takes into account the difficulties caused by the Draper effect, induction periods, and subsequent reactions of pyrolysis products in the measurement of pyrolysis rate constants. Furthermore, in spite of the special care with which the experiments were done, the small temperature intervals in which measurements could be made reduce the accuracy of the activation energies. For tetrachloroethane the agreement is less good; it should be pointed out though that the small activation energy found here (112) does not fit in with the heat of addition of two chlorine atoms to the double bond of dichloroethylene (94.6 kcal. mole$^{-1}$).

The pyrolysis of the chloroalkenes has also been studied. The reactions for allyl chloride (90), trichloroethylene (91), and both 1,2-dichloroethylenes (92, 93) are very complicated due to the simultaneous occurrence of molecular, chain, and heterogeneous processes. The molecular contribution to the reaction was either true mono- or bimolecular and was interpreted in terms of Slater's theory (179).

The reactions of chloroalkenes are much slower than those of chloroalkanes and therefore must not be taken into account in the mechanism of the latter.

### 6. *Other Halogenating Agents*

The phosgene photolysis has been used as a source of chlorine atoms in the gas phase (197, 197a) permitting to work in the absence of molecular chlorine.

Reactions of other halogenating agents have usually been studied in solution. Even though it is not intended here to review reactions in solution it seems interesting to discuss here a few cases. The particular interest of these reagents lies in their specificity; several substances have been used such as hypochlorites (193, 194), sulfuryl chloride (25), or haloimides (58). The latter have been intensively studied because of their interest in organic synthesis (103, 168).

It is generally accepted (192) that haloimides and particularly N-chloro- and N-bromosuccinimides react with hydrocarbons by a chain mechanism involving radicals or atoms. The nature of the chain carriers is still uncertain. The succinimidyl radical (27) or the chlorine atom (3, 5), respectively, yield the following schemes

I

$$\mathrm{SNX} \rightarrow \mathrm{SN} + \mathrm{X} \tag{1}$$

$$\mathrm{SN} + \mathrm{RH} \rightarrow \mathrm{R} + \mathrm{SNH} \tag{2}$$

$$\mathrm{R} + \mathrm{SNX} \rightarrow \mathrm{RX} + \mathrm{SN} \tag{3}$$

---

(8) NOTE ADDED IN PROOF.—This means that the addition of $10^{-6}$ to $10^{-8}$ ethyl chloride would inhibit the pyrolysis of 1,2-dichloroethane by about a factor of two. In fact, recent measurements (55a) have shown that such an inhibition occurs only when about $10^{-3}$ ethyl chloride is added. This discrepancy has been attributed to the occurrence of the chain transfer step

$$1,1\text{-}C_2H_4Cl + 1,2\text{-}C_2H_4Cl_2 \rightarrow C_2H_3Cl_2 + C_2H_5Cl \qquad (k_{tr})$$

This is checked now by a careful kinetic analysis.

II

$$\begin{aligned} SNX &\rightarrow SN + X && (1)\\ X + RH &\rightarrow R + HX && (2)\\ HX + SNX &\rightarrow SNH + X_2 && (2')\\ R + X_2 &\rightarrow RX + X && (3) \end{aligned}$$

In a recent review (192), scheme II has been discarded. The arguments though are not convincing; in fact most experimental features favor scheme II. The special reactivity of N-halosuccinimides toward H atoms in the "$\alpha$" position to a double bond cannot be explained by scheme I nor can the addition reaction (55). It should be noted that no careful kinetic study has been performed that yielded evidence for scheme I. An attempt to prove the validity of scheme I on the basis of rate measurements (128) gave results favorable to scheme II (178). This study was based on measurements of the rate of bromination of toluene by N-bromosuccinimide. If this reaction proceeds by the succinimidyl radical, the rate constants of hydrogen abstraction should be different from the one obtained for bromination by bromine; actually the same was found as would be expected if the reaction proceeds by halogen atoms (178). The electron acceptor properties of the intermediate cannot be used to distinguish between these mechanisms (55, 128) since the succinimidyl radical and the halogen have similar properties. The influence of light, chain initiators, and inhibitors has been studied (55); unfortunately yields rather than reaction rates were measured. Peroxides were shown to increase the reaction rate considerably. Light is also an accelerator, this is quite interesting since N-bromosuccinimide does not absorb at the wave length used (151, 172), but the halogen molecules involved in scheme II do.

On the basis of scheme II (3, 5), the relative rates of substitution and addition should be given by

$$v_s/v_a = (k_{2s}'/k_{2a})[1 + K/(Cl_2)]$$

Experimental confirmation of this equation has been given recently (137).

Measurements have also been made on the hydrogen deuterium isotope effect in the hydrogen abstraction from toluene (196). If scheme II is valid, the isotope effect should be the same for SNCl and $Cl_2$ and for SNBr and $Br_2$ but should be different for SNCl and SNBr while reverse conclusions should be drawn if scheme I is valid. Experimental results are given here.

| | SNBr | SNCl | $Cl_2$ | $SO_2Cl_2$ |
|---|---|---|---|---|
| $k_H/k_D$ | 3.59 ± 0.05 | 1.59 ± 0.05 | 1.47 ± 0.02 | 1.73 ± 0.05 |

From these it is apparent that the reactions do not involve an N-succinimidyl radical; $SO_2Cl_2$ seems to react not only by Cl atoms but, to a small extent at least, by another species.

The *cis–trans* transposition in cyclohexene induced by haloimides has also been interpreted in terms of scheme II (137).

## IV. THEORETICAL RELATIONS

### A. THERMODYNAMIC DATA

Many elementary rate constants of atomic chlorinations have been determined by direct measurements; some have been calculated from the thermodynamic equilibrium constant (88). These rate constants in turn permit one to calculate dissociation energies of stable compounds and heats of formation, entropies, and dissociation energies of free radicals or activated states involved in these reactions.

Thermodynamic data used for the calculation of Table III[9] have been given earlier (88) and were taken principally from ref. 142 and 180. They are reliable to within ±1 kcal. mole$^{-1}$ for the heats of formation and to ±1 e.u. for the entropies.[10]

Only in the cases of $C_2Cl_5H$ (88, 139, 144) and $C_2Cl_6$ (88, 139, 181) is there still an uncertainty of 4 e.u. The values given in (139) have been calculated using additivity rules (109) which have been checked for known compounds. It is believed that such methods can lead to errors amounting to 1–3 e.u. On the other hand, experimental results on the photochlorination of $C_2Cl_4$ and $C_2Cl_5H$ (83) give good support for the higher values given in (88, 191). This is based, on the one hand, on the frequency factors $A_4'$ and $A_5$ and, on the other hand, on the calculated entropy of $C_2Cl_5$ and a reasonable estimate relating values as $S(C_2Cl_5H)$ and $S(C_2Cl_5)$ (186). However, there is no good reason to discard the lower values $S(C_2Cl_5H) = 91.0$ e.u. (144) and $S(C_2Cl_6) = 90.4$ e.u. (181). These would yield $\log A_5 = 10.8$ for $C_2HCl_3$; $\log A_5 = 12.6$ and $\log A_4' = 7.7$ for $C_2HCl_5$ in Table III. In that table, the frequency factors were calculated using the intermediate values for $S(C_2Cl_5H)$ and $S(C_2Cl_6)$.

### *Dissociation Energies*

For the chlorinated methanes a monotonous decrease of the dissociation energies $D$(C–Cl) from $CH_3Cl$ to $CCl_4$ has been assumed (88, 139) as for $D$(C–Br) from $CH_3Br$ to $CBr_4$ and from $CH_3Br$ to $CCl_3Br$ (175).

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(9) We wish to thank Dr. D. R. Stull (The Dow Chemical Co., Midland, Mich.) who has drawn our attention to numerous papers (76, 94, 97, 105, 106, 134, 138, 141).

(10) Heats of formation of gaseous 1,1-$C_2H_2Cl_2$, *cis*-1,2-$C_2H_2Cl_2$, *trans*-1,2 $C_2H_2Cl_2$, and $C_2Cl_4$ given in ref. 126 and 127 should be discarded. The following heats of formation should be used instead; 1,1-$C_2H_4Cl_2$: −30.4 kcal. mole$^{-1}$; 1,2-$C_2H_4Cl_2$: −31.4 (119, 142, 180, 182); 1,1,2-$C_2H_3Cl_3$: −35.9 (119); $C_2H_3Cl$: +8.0 (32, 130, 142); 1,1-$C_2H_2Cl_2$: +0.3 (182); *cis*-1,2-$C_2H_2Cl_2$: −0.4 (119, 147, 180); *trans*-1,2-$C_2H_2Cl_2$: −0.8 (119, 147); and $C_2HCl_3$: −1.8 (119, 180). Entropies calculated from ref. 126 must also be considered suspect and are not taken into account. $S°_{298}$ 1,1,1-$C_2H_3Cl_3$: 76.4 e.u. can be calculated from the value for the standard liquid state (142) and an interpolated value of 22 ± 1 e.u. for the entropy of vaporization; for $S°_{298}$ $C_2H_3Cl$: 63.1 e.u. (160); *trans*-1,2-$C_2H_2Cl_2$: 70.2 e.u. (126, 155); $C_2HCl_3$: 77.6 e.u. (6); 1,1,2-$C_2H_3Cl_3$: 78.8 e.u. (99) should be used.

This assumption leads to the following values for the dissociation energies of $CH_2Cl$–H and $CHCl_2$–H:

| | $D$(R–H) | $D$(R–Cl) | $E_1'$ |
|---|---|---|---|
| $CH_4$ | 102(49, 120) | 80.6 | 3.9 |
| $CH_3Cl$ | 98 | 76 | 3.1 |
| $CH_2Cl_2$ | 95 | 75 | 3.1 |
| $CHCl_3$ | 93(176, 183) | 71.4 | 3.3 |

The activation energy of hydrogen abstraction presents a minimum for $CH_3Cl$ and $CH_2Cl_2$; if the above assumption is correct, the Polanyi–Evans relation (67) $E \sim \alpha D$ as used (190) is not valid in this series (see next section). Even though the values of $D$(R–H) for methane (72) and chloroform (68) could be somewhat different, this would not significantly change the trend in the series (139).

On the other hand, the existing values for $D(C_2H_5–H)$ and $D(C_2H_4Cl–H)$ (49) and the activation energies given in Table III permit one to calculate a constant value of 96 ± 1 kcal. mole$^{-1}$ for $D$(C–H) in the whole series of chlorinated ethanes.

Since the addition of the chlorine atom to a double bond occurs with nearly zero activation energy, the dissociation energy $D$(C–Cl) in the intermediate free radicals is equal to $E_4$ (88). The values are in good agreement with those obtained from the over-all rate constants of pyrolysis reactions (16, 18, 19, 21, 55a, 111, 113).

### B. TRANSITION STATE THEORY

In the evaluation of rate constants by transition state theories, reactions with activation energy and reactions with zero activation energy are treated separately.

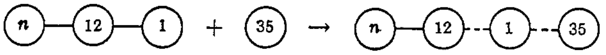
#### 1. *Reactions with Activation Energy*

Activated complex theory has been applied to hydrogen abstraction by halogen atoms in a rather primitive manner either by assuming an angular complex (86) or by neglecting vibrational entropy changes (187); the agreement between calculation and experiment was very poor. It has been pointed out (154) that the latter simplification can cause considerable error; in fact, a complete calculation of the classical partition functions for a linear complex yielded good results for the chlorination of methane. Calculations have also been made on the assumption that the complexes are linear with bonds 0.18 Å. longer than normal single bonds and that the vibrational modes of C–H–X bonds in the complex have the same force constants as those in the H–H–Cl complex (69, 70, 71). Although this is an evident over-simplification, the results were fairly satisfactory. The application of this method to the chlorinated methanes has been discussed at length (124).

Frequency factors for a number of hydrogen abstraction reactions have been calculated (198) in excellent agreement with experimental data. Reasonable empirical rules for bond distances (152), force constants (14), and Wilson's F–G matrix method (199) were used to obtain the structure and mechanical properties of the activated complex. The "input data" required are essentially the following: (i) equilibrium internuclear distances, (ii) force constants for vibrations (104), (iii) dissociation energies of the bond involved in the reaction.

In a similar way the reaction occurring in the photochlorination of chlorinated hydrocarbons was treated (118). In the London, Polanyi, Eyring, Sato model (79, 164, 165), the potential energy of activation $V_a$ is a complex function of $Q$, $\alpha$, and $\Delta$. The coulombic and exchange integrals $Q$ and $\alpha$ are evaluated from the Morse function considering $\Delta$ as a parameter which is adjusted empirically (195). In the bond energy bond order (117) model, the dissociation energy $D$ of a bond of order $n$ is assumed to be related to the dissociation energy of a single bond $D_s$ by the expression $D = D_s n^p$ where the bond order in the complex is determined from the saddlepoint condition $\delta V_a/\delta n = 0$. The index $p$ (or Sato's $\Delta$) is chosen in such a manner that the calculated and experimental energies are approximately equal. Because the potential energy of activation includes the zero point energies of complex and reactants, this is done by successive approximations; evidently no better agreement need be sought than is warranted by existing data. Pre-exponential factors, activation energies, and kinetic isotope effects for an entire series of reactions can then be found by fitting a single arbitrary parameter ($p$ or $\Delta$) to the kinetic data of a single reaction in the series.

Calculations were made (118) for two series of reactions: (i) hydrogen abstraction by chlorine atoms, (ii) chlorine atom transfer. For the former a linear complex



was assumed where reduced emphasis is given to the atoms not taking a direct part in the reaction. The resulting expression for the rate constant in cm.$^3$ mole$^{-1}$ sec.$^{-1}$ is

$$k = B_e B_\sigma\, 4.62 \times 10^{11} \left(\frac{F_1}{F_1^{\neq}}\right)^{1/2} \left(\frac{F_{\phi 1}}{F_{\phi}^{\neq}{}_1}\right) \left(\frac{R_1}{R_1^{\neq}}\right)^2 \times \frac{\left(\frac{T}{1000}\right)^{3/2} \left(\frac{\omega^*}{1000W}\right)}{(F_2^{\neq})^{1/2} F_\phi} R_2^2 \frac{\Gamma^* \Pi\Gamma^{\neq}}{\Pi\Gamma} \exp(-V_a/RT)$$

where

$B_e$ = product of electronic partition functions
$B_\sigma$ = product of rotational symmetry numbers
$F_i$ = force constants of normal modes (the superscript $\neq$ denotes the complex)
$R_i$ = bond lengths
$\omega^*$ = imaginary frequency along the reaction coördinate
$W$ = function of force constants of activated complex
$\Pi\Gamma$ = product of partition functions
$\Gamma^*$ = correction for tunneling through potential energy barrier
$V_a$ = potential energy of activation related to experimental activation energy by $V_a = E_a - \theta RT$ where $\theta$ is a term allowing for zero point energy and thermal enthalpy of the reactants and the complex.

TABLE V

COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED RATE CONSTANTS

| Cl + ... | $CH_4$ | $CH_3Cl$ | $CH_2Cl_2$ | $CHCl_3$ |
|---|---|---|---|---|
| $E$ calcd. | 3.6 | 1.6 | 0.9 | 0.8 |
| $E$ obsd. | 3.9 | 3.1 | 3.1 | 3.3 |
| log $A$ calcd.$^a$ | 13.5 | 13.4 | 13.1 | 12.8 |
| log $A$ obsd. | 13.7 | 13.5 | 13.4 | 13.2 |
| $Cl_2$ + ... | $CH_3$ | $CH_2Cl$ | $CHCl_2$ | $CCl_3$ |
| $E$ calcd. | 4.1 | 4.5 | 4.6 | 5.1 |
| $E$ obsd. | 2.3 | 3.0 | 4.0 | 6.0 |
| log $A$ calcd. | 13.0 | 12.6 | 12.4 | 12.1 |
| log $A$ obsd. | 12.9 | 12.6 | 12.0 | 11.7 |

$^a$ Cc. mole$^{-1}$ sec.$^{-1}$.

For chlorine atom transfer, linear reactants and complex were assumed

giving a rate constant of the form

$$k = B_e B_\sigma \, 3.20 \times 10^9 \left(\frac{F_1}{F_1^{\neq}}\right)^{1/2} \left(\frac{R_1^{\neq}}{R_1}\right)^2 \times \frac{\left(\frac{T}{1000}\right)^{5/2} \left(\frac{\omega^*}{1000W}\right)}{(F_2^{\neq})^{1/2} F_{\phi 1} F_{\phi 2}} R_2^2 \, \frac{\Gamma^* \Pi \Gamma^{\neq}}{\Pi \Gamma} \exp(-V_a/RT)$$

The agreement between calculated pre-exponential factors and activation energies and the experimental values was very satisfactory for both hydrogen abstraction from saturated hydrocarbons and chlorine atom transfer reactions. Arrhenius $A$ factors for hydrogen abstraction from chlorinated methanes and ethanes were also predicted with reasonable success. The experimental activation energies for these reactions, however, are considerably higher than those calculated (see Table V). Since the theory has dealt successfully with many similar reactions the disagreement was thought due to an extraneous effect. An explanation has been suggested by the authors in terms of nonbonding interactions with the approaching Cl atom which causes the formation of an H–R–Cl–Cl complex. Only those atoms which have sufficient energy to overcome the Cl–Cl dispersion forces would go on to form the Cl–R–H–Cl hydrogen transfer complex. A test of this hypothesis ought to be provided by the H/D kinetic isotope effect where this extraneous effect is canceled out and which should therefore be correctly predicted by the theory. With this aim, the kinetic isotope effect in the photochlorination of $CH_4$–$CD_4$, $CHCl_3$–$CDCl_3$, and $C_2H_6$–$C_2D_6$ has recently been investigated (44). The results are in good agreement with the calculated effect. Similar results were found in a recent study on the kinetic isotope effect in the chlorination of dideuteriomethane (141a). Experiments were also performed (44) on $H_2$–$D_2$ + Cl and were in good agreement with previous results and calculations (26).

### *2. Reactions with Zero Activation Energy*

These were treated (118) using Gorin's model (95), which assumes a central attractive potential and unchanging internal structure. The theory, which does not involve any adjustable parameters, calculates the rate at which complexes cross over into the spherical shell of diameter $R_c$ inside which the attractive forces exceed centrifugal forces and a close encounter is possible. Calculations were made for some 20 reactions involving radical recombination, disproportionation, and addition of a chlorine atom to a double bond. The rate constants were correctly predicted for the class of reactions as a whole but several large scale trends were not foreseen. More detailed analysis shows that for a large fraction of the possible rotational states of the complex, the assumption of central attractive forces breaks down. For them, the outer nonbonding atoms are within each other's van der Waals radius before the radicals come within the critical distance $R_c$. This is true of the $CH_3$ radical recombination, whose rate is correctly predicted, as well as of $CCl_3$ where theory and experiment differ by two powers of 10. The observed decrease in rate of recombination of radical with increasing chlorination is only qualitatively explained in terms of noncentral Cl–Cl forces.

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