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A Kinetic Study of a Homogeneous, Unimolecular Gaseous Decomposition Reaction.

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A KINETIC STUDY OF A HOMOGENEOUS, UNIMOLECULAR
GASEOUS DECOMPOSITION REACTION

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN
LOUISIANA STATE UNIVERSITY

BY

HAROLD ARTHUR FREDIANI

MAY, 1937
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ABSTRACT

The present investigation is a study of the decomposition characteristics of several organic and inorganic compounds.

Suitable equipment for high temperature gaseous kinetic studies, comprised of a photoelectrically operated high temperature bath, an automatically operated pressure regulator containing a glass diaphragm has been developed.

Iodine trichloride, dimethyl and diethyl carbonates were found to be unsuitable for such a study because the former was difficult to prepare in a state of known purity while the latter decomposed heterogeneously.

The reaction rates for the dimethyl and diethyl carbonates decomposition were determined under varying surface conditions and definitely shown to be heterogeneous.

Ethyl chlorocarbonate decomposes homogeneously in the gas phase between 150 and 195°C. and from 20 to 700 mm. of mercury pressure. The rate constant over this range of temperatures has been found to be given by the equation:

\[ k = 5.5 \times 10^{10} \times C^{\frac{x}{RT}} \]
It has been noted that the rate constant decreases with a decrease in initial pressure in accordance with the modified collision hypothesis. In comparing the adequacy of the various equations and theories tending to explain homogeneous unimolecular gas reactions it has been calculated that the degrees of freedom required for the molecule studied are nine according to the simpler of these theories (that of Hinshelwood, known as Theory I), and fourteen in the Rice and Ramsperger and Kasel theories (Theories II and III).

In general, Theories II and III are shown to fit the experimental facts most adequately, the numerical calculations being in favor of Theory III.

The effect of $N_2$ and $CO_2$ on the reaction rate has been determined.

Further investigations are under way at present with the aim of studying the effect of other gases and low pressures upon the reaction. A monochromator is also in the process of construction for the photochemical study of this reaction in the gas, liquid and solution phases. It is hoped that when these further studies are complete interesting information correlating reaction rates in various states may be obtained.
INTRODUCTION

"The entire field of physical chemistry might perhaps be divided into Thermodynamics, which is essentially legislative in character, and Kinetics, which is essentially executive. The former subject stipulates changes which are permitted and describes conditions from which no change is allowed; it is left to the latter to say what will actually occur.---

"It is, then, of the greatest practical and theoretical importance to understand the principles which govern the rates of chemical reaction.---

"Physics has always been relatively helpless in treating liquids, which have neither the simple structure of a crystal nor the convenient dilution of a gas. It seems desirable on that account that any attempt to discover the fundamental principles in the field of reaction rates should not begin with the baffling complexities of liquid reactions. The reactions of solids are rather rare, and almost never homogeneous, so that the gaseous state is clearly indicated as the most suitable for such an attempt."
"It is true that there is only a limited amount of experimental material dealing with the rates of gas reactions."

This statement of Kassel (1), if it is a representative expression of the facts of the field of kinetics, will, in itself, be sufficient for the undertaking of any original research in kinetics—particularly the discovery and study of a homogeneous, unimolecular gas reaction. Perhaps the explanation of the last statement in the quotation from Kassel lies in the fact that the field is comparatively new and that the chemist of past generations was primarily interested in production and "cost factors" rather than in the purely theoretical concepts of chemical changes.

Kinetics is still sadly lacking in well-tested, proven hypotheses that are applicable to all cases. In order to postulate kinetic theories that will hold over a range of reactions, it is necessary to base them upon kinetic studies which are simple and free from complications. It would not only be difficult but it would be inadvisable to attempt to obtain fundamental kinetic relationships by
studying reactions which are exceedingly complex in mechanism.

The simplest reaction suitable for kinetic study is the homogeneous, unimolecular gas reaction, in which both reactant and products are gaseous in character and are not affected by the surface of the enclosing wall. A unimolecular gas reaction sensitive to wall effects is still of little value from a theoretical standpoint due to our lack of knowledge of catalytic processes. We should, therefore, attempt to develop an unfailing mechanism for the explanation of homogeneous, unimolecular reactions. This may then be used to advantage in the study of catalysis, solvent effect and other environmental influences.

Hinshelwood (2) states that, at present, a very considerable number of gaseous unimolecular reactions are known. A surprisingly small number of these are homogeneous and of simple nature.

Three outstanding theories seem at present applicable to unimolecular gas reactions. The data available is meager and evenly divided. It does not permit us to choose one of
these and say that it is the true theory with which to explain all reactions on a kinetic basis.

This study was started with the aim of discovering an unstudied, homogeneous unimolecular gas reaction, compiling data and utilizing the data obtained to test the three theories in vogue at present and so determine which of these is closest to the ultimate truth. While the study is still far from being complete it is our belief that enough has been done to add appreciably to our fund of knowledge in the field of kinetics.
REVIEW OF THE LITERATURE

It is generally accepted that only activated molecules undergo reaction. This fact was first noted by Arrhenius (3) when he observed that the empirical constant $E$ in the equation

$$\frac{d \ln k}{dT} = \frac{E}{RT}$$

which he proposed as giving the quantitative relationship between the change in rate of a reaction with temperature has the dimensions of energy. This fact was deduced from a study of van't Hoff's equilibrium equation. Tolman (4) has more recently shown, as a result of the application of statistical mechanics, that the equation is essentially correct. It is generally agreed that activated molecules are those having an energy content greater than the average. This excess energy is not in the form of displaced electrons but is rather increased vibrational energy. Fundamentally this is all that we may say with certainty. The mechanism by which molecules become activated was in doubt until quite recently. One of the earlier theories advanced to explain activation was the Radiation Hypothesis of
Chemical Reaction promoted jointly by W. C. M. Lewis (5), Trautz (6) and Perrin (7). According to their reasoning the most important means by which molecules became activated was by their reaction with quanta of light in the infra red region of the spectrum. This theory was especially designed to account for the activation of molecules in unimolecular reactions as it was argued then that these reactions could not depend upon collision for activation. However, Langmuir (8) showed as early as 1920 that the observed reaction rates could not be accounted for by this hypothesis. Further arguments against the theory were put forth (9), the strongest being that increase in the intensity of light of the calculated wave length for a given reaction did not increase the reaction rate. Though this hypothesis failed in its original purpose, it served to stimulate the interest in kinetic research to such an extent that it may be said to mark the beginning of modern kinetics.

With the failure of the radiation hypothesis it became necessary to develop more completely the alternate, or collision, theory.
This concept, activation by collision, is not so difficult to realize as might appear at first glance. If one considers, then, that through collision a molecule takes on enough energy to become activated one might readily conceive that, although the molecule possesses enough, or even more than enough, energy to decompose, it might take some small interval of time for this energy to localize itself in the proper position within the molecule for it to decompose. Then, if the number of molecules confined in a definite space were large and the collision frequency correspondingly great, the rate of reaction would necessarily be governed by the rate of localization within the molecule. This was the basis of Lindemann's (10) argument. Another mechanism by which activation could be produced by collision is that proposed by Christiansen and Kramers (11). According to their reasoning an activated molecule may break up to form its reaction products. The resulting products, due to the activation energy previously present in the reactant molecule and any added energy due to the heat of reaction, may be considered as
being in highly excited states. By collision they may transfer this energy to another reactant molecule and cause its activation. Thus collisions would tend to propagate the reaction essentially by means of energy chains.

According to both of these mechanisms, if the original concentration of reactant molecules is made small, and collision frequency becomes correspondingly small, the frequency of collision will then become the rate determining factor. This predicts that, at low pressures, the specific reaction rate should fall off appreciably. This is in direct contradiction to Perrin's (12) assumption that unimolecular reactions should be totally independent of the initial concentration, or pressure, and that if one were to expand a gas, theoretically to zero pressure, the rate would remain constant. If Perrin's assumption proved to be correct it could be argued that the mechanism of unimolecular reactions could not be explained on a collision basis.

Until 1925 the decomposition of nitrogen pentoxide was the only known gaseous unimolecular reaction. It had been studied at length
by Daniels and Johnston (13) and others down to low pressures. Its velocity constant did not seem to fall off. This was contrary to the collision theory. Moreover, when irradiated strongly with wave lengths of light that should theoretically have accelerated the reaction (14), no effect was noticed. Thus the one reaction tended to throw out both kinetic theories prevalent at that time. However, after 1926 other unimolecular gas reactions were discovered, all of which showed a definite decrease in specific reaction rate at lower pressures. Other studies were then made with nitrogen pentoxide (15, 16, 17) and it was found that a definite decrease in rate occurred at pressures below 0.06 mm. This, of course, substantiated the collision theory and nullified Perrin's arguments.

And so it has become evident that activation, even in the case of unimolecular reactions, must be explained on a basis of molecular collisions. It is here that difficulties arise. Having granted that activation occurs through collision of molecules, one must necessarily designate the exact implication of
activation. The general concession is that when a molecule contains a definite amount of energy equal to or greater than a given energy $E_o$ (which is necessarily greater than the average energy content of the molecules) that molecule may be considered as being in an activated condition. Under any given conditions the number of molecules in this activated state may be roughly calculated from Boltzman's equation:

$$\frac{n'}{n} = e^{-\frac{E_o}{RT}} \quad (2)$$

where $n'$ = the number of activated molecules;

$n$ = the total number of molecules.

Here the term $e^{-\frac{E_o}{RT}}$ represents the fraction of molecules having an energy content equal to or greater than $E_o$. It can readily be shown from this equation and from the simple gas laws, for a specific case considering $E_o$ as being 25,000 cals., that an increase in temperature of only 10° C., while increasing the total kinetic energy of a mol of gas by only about 32%, practically triples the number of molecules having the energy content of 25,000 cals. This is in accord with the large
temperature coefficients of most reactions.

Now, although activated molecules are necessary for a reaction to occur, it is not necessarily true that all activated molecules undergo reaction. Let us suppose that a molecule, through collision with another, obtains enough energy to become activated. In the next instant of time any one of a number of things may occur:

(a) The molecule may react—

(in our special case we are considering merely the breakdown of a single molecule into two or more simpler ones).

(b) It may collide with a wall, lose energy and become deactivated.

(c) It may collide with an unactivated molecule and lose sufficient energy to become deactivated.

(d) It may collide with another activated molecule in which case one will become deactivated. Considering the relatively small number of activated molecules present at one time, however, this last effect is negligible. If one assumes that at every collision a statistical redistribution of energy occurs, then it can be shown that prac-
tically every collision involving an activated molecule results in deactivation. This has been substantiated by the calculations of Lindemann (10), Rodebush (18), Christiansen (19), Hinshelwood (20), Fowler and Rideal (21), Rice and Ramsperger (22), Rice (23) and Kassel (24).

Using these facts three slightly different, though related, theories have been reached. The chief differences in these theories are due to the following trends of thought. In what is generally known as Theory I, proposed by Hinshelwood (25), the fact is recognised that the energy in an activated molecule must be localized at a definite point within the molecule before reaction can occur. This important contribution was first made by Christiansen (26) who showed that the degrees of freedom within molecules must be taken into consideration. Hinshelwood, however, in this theory holds that the excess energy above the minimum ($E_0$) required for activation has no effect on the specific rate. In Theory II, proposed by Rice and Ramsperger (22), the excess energy above $E_0$ is taken into considera-
tation. However, they assume that the energy must be localized in one square term. Theory III, proposed by Kassel (24) shortly after the theory of Rice and Ramsperger is essentially the same as II except that in his derivation Kassel considers that the energy must be centered in a single degree of freedom which necessarily involves two square terms.

All three of these theories are merely attempts to account for two things:

1. If one assumes that the energy of activation is derived from the kinetic energy of impact between two molecules (which holds for bimolecular reactions) it is found experimentally that most unimolecular reactions are much faster than the rate calculated from the simple Arrhenius equation. In fact, in the gaseous decomposition of acetone (27) at 300° absolute, 10^5 times as many molecules react in unit time as are theoretically calculated.

2. The decrease in the specific reaction rate with increasing dilution (i.e., the low pressure effect).

The development of Theory I may be summarized as follows (28):
All of the internal degrees of freedom of the molecule are taken into consideration and the assumption is made that all the kinds of energy in a large number of these degrees of freedom may combine, or add to the impact energy transfer, to constitute the energy of activation. G. N. Lewis and D. F. Smith (29), Hinshelwood (25), and Fowler and Rideal (21) have shown mathematically that in considering a molecule of "n" square terms, the factor \( \mathbb{E}^{\frac{E}{RT}} \left( \frac{E}{RT} \right)^{k_n} \) rather than the Boltzmann factor \( \mathbb{E}^{-\frac{E}{RT}} \) determines more accurately the probability of that molecule having an internal energy equal to or greater than \( E_0 \). With this important substitution it is found that for the proper value of "n" this factor leads to much larger results than the simpler Boltzmann term. Temperature has relatively the same effect on this factor as on the older form. If we now consider a gas in statistical equilibrium the following may be stated:

If \( N \) is the total number of molecules present, \( N_i \) the number in an activated state then:
Due to activation and deactivation by collision we may consider $Z_1$ as the number of molecules entering the activated state in unit time and $Z_2$ the number leaving. As we are considering a state of equilibrium the following must be true: $Z_1 = Z_2$. Since it is accepted that every collision of an activated molecule leads to its deactivation we may then consider $Z_2$ as being equal to the number of collisions entered into by activated molecules in unit time. Since $Z_2$ is equivalent to the total number of collisions occurring in unit time multiplied by the ratio of the number of activated molecules to the total number of molecules present, substituting the appropriate values from equation (3) we get:

$$Z_2 = \frac{Z}{N} N \frac{e^{-\frac{E}{RT}}}{\left(\frac{E}{RT}\right)^{\frac{1}{2}} n^{-1}} \left(\frac{1}{2} n^{-1}\right)!$$

This expression neglects the extremely small number of collisions between two activated molecules.

If the equilibrium originally postulated is considered as being disrupted by the removal...
al -- through reaction -- of some of the molecules entering the activated state then \( z_1 \) may be considered as being the maximum rate for their reformation. Lindemann says that at the higher pressures where \( k \) is unaffected by slight changes in initial pressure \( z_1 \) must be greater than the observed rate of reaction since it is not a determining factor in actually measuring \( k \). Then, if this be true, it is reasonable to assume that just at the pressure where the constant begins to fall off, the rate of reaction is just sufficient to keep up the reaction rate. By determining, then, the pressure at which the rate just starts to fall and equating the expression for the rate of activation and the actual number of molecules reacting one may determine the numerical value of \( n \). The method usually used in determining the limiting pressure to use is to plot \( 1/k \) against \( 1/p \) and draw the best curve to fit the experimental points. According to Hinshelwood's theory this should be a straight line. Theories II and III predict this plot to be a curve concave to the \( 1/p \) axis. The value of the intercept which the curve crosses
on the 1/k axis is then taken as the limiting value for p, i.e. the lowest pressure before which k starts to fall off.

Since a new factor has been used for the Boltzmann term the energy of activation is no longer equal to E, as in the Arrhenius equation, but to $E + (\frac{2}{3}n-1)RT$. This may be arrived at by substituting in the Arrhenius equation the proper factor:

$$k = S \frac{E}{RT} \left( \frac{E}{RT} \right)^{\frac{1}{2}n-1} \left( \frac{1}{2}n-1 \right)!$$

by taking logarithms and differentiating:

$$\frac{d \ln k}{d T} = \frac{E - \left( \frac{1}{2}n-1 \right)RT}{RT^2}$$

The final form being:

$$\left[ \frac{-E}{RT} \left( \frac{E}{RT} \right)^{\frac{1}{2}n-1} \right] \left( \frac{1}{2}n-1 \right)! = \frac{k_{obv}}{\text{Total no. molecules present/cc.}} \times \frac{\text{Total no. collisions/cc./sec.}}{\text{Total no. collisions/cc./sec.}}$$

The total number of collisions is arrived at from:

$$Z = 3.9 \sigma^2 n^2 \sqrt{\frac{RT}{M}}$$

where:

$Z =$ number of collisions/cc./second

$\sigma =$ molecular diameter

$n =$ number of molecules/cc.

$R = 8.315 \times 10^7$

The number of molecules per cc. is obtained from
the simple gas equation:

\[ N = \frac{PV}{RT} \times 6.02 \times 10^{23} \]  

(9)

Hinshelwood states that there is no apparent relationship between the number of square terms calculated (n) and molecular structure.

It may be noted that in his derivation Hinshelwood considers that activated molecules having an excess of energy above \( E_0 \) react at the same rate as molecules having the minimum energy required for activation.

Theories II and III have both been arrived at in similar fashion through quantum mechanics, where the various quantum states possible of the molecules are considered. Individual reaction rates (relatively) are arrived at for molecules in different quantum states and the observed rate calculated by summing over all the quantum states possible.

It is assumed that \( k_j \) is the specific reaction rate for molecules in the j quantum state. Furthermore, for a molecule to react at all, at least m quanta of energy must be localized in one or more particular degrees of freedom. Then it may be stated that for values of j that are less than m, \( k_j = 0 \); for values of j equal to or great-
er than \( m \), \( k_j = \lambda \). The energy necessary to break the bond involved in the reaction is \( \hbar \gamma \).

With these assumptions the reaction rate at high pressures is reached as being:

\[
K_\infty = \lambda \left( 1 - e^{-\frac{\hbar \gamma}{RT}} \right) \sum_{j=m}^{\infty} \binom{j+s-1}{s-1} e^{-\frac{j\hbar \gamma}{RT}}
\]  

(10)

The number of molecules having \( j \) quanta are:

\[
N_j = N \binom{j+s-1}{s-1} \left( 1 - e^{-\frac{\hbar \gamma}{RT}} \right) e^{-\frac{j\hbar \gamma}{RT}}
\]  

(11)

The final term being essentially the binomial expansion:

\[
\sum_{j=m}^{\infty} \binom{j+s-1}{s-1} e^{-\frac{j\hbar \gamma}{RT}} = 1 + s e^{-\frac{\hbar \gamma}{RT}} + \frac{s(s+1)}{2!} e^{-\frac{2\hbar \gamma}{RT}} + \ldots
\]  

(12)

By further assumptions and simplifications Rice and Homan (22) show that equation (8) may be reduced to the simple Arrhenius form. For the specific rate at any pressure they derive:

\[
K = \frac{1}{N} \sum_{j=m}^{\infty} k_j Z_j
\]  

(13)

where \( Z_j \) is the actual number of molecules per ml containing \( j \) quanta. Since \( k_j \) is zero when \( j \) is less than \( m \) and a constant \( \lambda \) when \( j \) is equal to or greater than \( m \), substituting in (13) and comparing with (10) and (11) they arrive at the conclusion that:

\[
K = \frac{\lambda}{1 + \frac{\lambda}{aN}} \sum_{j=m}^{\infty} \frac{N_j}{N} = \frac{K_\infty}{1 + \frac{\lambda}{aN}}
\]  

(14)
\[
\frac{K_\infty}{K} = 1 + \frac{\lambda}{aN} = 1 + \frac{\lambda \frac{kT}{aP}}{
\]

Thus far the theory is exactly the same as Theory I although arrived at in a more rigorous manner by quantum mechanics. This theory predicts that a plot of \(1/k\) against \(1/p\) (or \(1/\beta\)) should result in a straight line having a slope of \(1/\sqrt{T}\). This prediction is not borne out by experimental values.

Thus the important innovation is introduced that activated molecules containing an excess of energy above \(E_0\) will tend to decompose relatively faster than those molecules having the minimum energy required for activation.

Then, considering a molecule with \(S\) degrees of freedom, \(j\) quanta of energy, and assuming that at least \(m\) quanta must be located in one degree of freedom for reaction to occur, the probability that under these conditions at least \(m\) quanta will be localized in the one given degree of freedom is:

\[
\frac{j! (j-m+s-i)!}{(j-m)! (j+s-i)!} \quad \text{(Ref. 20)}
\]

From this Kassel then assumes:

\[
K_j = A \frac{j! (j-m+s-i)!}{(j-m)! (j+s-i)!}
\]

(16)
where \( \mathcal{A} \) is merely a proportionality factor.

From equation (15) Rice, Ramsperger and Kassel arrive at the following, in place of equation (15):

\[
\frac{K}{K_\infty} = \left( 1 - e^{-\frac{A\mathcal{L}}{RT}} \right)^S \sum_{p=0}^\infty \frac{\left( \frac{p + S - 1}{p} \right)}{e^{\frac{\mathcal{A}}{R(T)}}} \frac{p!}{(p+m)!(p+s-1)!} \frac{m!}{p!(p+m+s-1)!}
\]

Equation (17) then predicts that as \( P \) increases the numerator decreases (due to the exponent of \( E \)) and that the ratio \( K/K_\infty \) decreases with an increase in temperature. Using quantum formulas throughout, Kassel (24) gives as the final form, in place of the Arrhenius equation:

\[
K_\infty = \lambda e^{-\frac{E_\infty}{RT}} \left[ \frac{1}{(s-1)!} \left( \frac{E}{RT} \right)^{s-1} + \frac{1}{(s-2)!} \left( \frac{E}{RT} \right)^{s-2} + \cdots + 1 \right]
\]

In arriving at this equation, Kassel states that precise assumptions had to be made as to the oscillator frequencies. In order to obviate these assumptions Rice (31) used a statistical method of treatment and obtained for his final form:

\[
K_\varepsilon = K_\infty c \frac{e^{\frac{E_\varepsilon}{RT}}}{\sqrt{K_\tau T}} \frac{(E - E_0)^{S-\frac{1}{2}}}{E^{S-1}}
\]

\( (19) \)
wherein $S$ is the actual number of degrees of freedom within the molecule under consideration. It is numerically equal to:

$$S = 3(n-1)$$

(20)

where $n$ is the actual number of atoms in the molecule (32). In considering these degrees of freedom translational and rotational energy are neglected as the former is not within the molecule itself and the latter is negligible in comparison to the vibrational. Not all of the theoretically calculated degrees of freedom for a specific molecule need necessarily be taken into consideration (33, 34).

The foregoing is essentially a brief resume of both Theories II and III. Mention may be made of the fact that in their derivations Kassel's differs from that of Rice and Ransperger in the consideration of the oscillators in the molecule. Kassel assumes that the energy for the breakdown must be localized in a single degree of freedom, involving $2(n)$ square terms, while Rice and Ransperger assume the energy to localize in but a single square term.

A brief survey of the known unimolecular, homogeneous gas reactions may now be in order.
The classical study, of course, is that of Daniels and Johnston (13) on the gaseous decomposition of nitrogen pentoxide. Although a great deal of the theory of kinetics is based on the experimental data of this reaction it is generally recognized that it is not as simple as might be desired since the mechanism has been suggested to be:

(a) \( \text{N}_2\text{O}_5 = \text{N}_2\text{O}_3 + \text{O}_2 \)

(b) \( \text{N}_2\text{O}_3 = \text{NO} + \text{NO}_2 \) (Ref. 35)

(c) \( \text{NO} + \text{N}_2\text{O}_5 = 2\text{NO}_2 \)

Further complications lie, of course, in the equilibrium maintained between the di- and the tetroxide:

\[ 2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4 \]

The reaction stands alone inasmuch as no fall off in the reaction rate is observed until one reaches an extremely low pressure. It undoubtedly is the most accurately studied. A large number of well known kineticians have investigated this reaction over all possible pressure ranges, as well as in the presence of nitrogen dioxide (36, 37, 39), oxygen (37), nitrogen (39), phosphorous pentoxide and specially prepared forms of nitrogen pentoxide (40). It has also been studied in solution (41, 35).
by Kyring and Daniels (42).

Although the decomposition of gaseous acetone has been shown to be homogeneous and unimolecular by Hinshelwood and Hutchison (43) the products are not simple as it decomposes at 500 °C into carbon monoxide and two methyl groups which then combine to form various hydrocarbons. Its mechanism has been postulated by Rice and Vollrath (44):

\[
\begin{align*}
(a) & \quad CH_3COCH_3 = CH_4 + CH_2=CO \\
(b) & \quad 2CH_2=CO = C_2H_4 + 2CO
\end{align*}
\]

Reaction (b) is considered as being slow and the results obtained are generally considered as too unreliable for use in determining the value of present theories.

The temperature of the decomposition is so high as to make it difficult to study in solution and determine the relationship between its decomposition rates under varying conditions.

The gaseous decomposition of propionic aldehyde is also unimolecular and homogeneous, although it, too, decomposes at a high temperature, yields a variety of hydrocarbons and acts abnormally at pressures below eighty mm (45).

The diethyl ether decomposition is homo-
gaseous down to a pressure of 150 mm. although the reaction occurring can only be explained as being approximately:

\[(a) \quad C_2H_5OC_2H_5 = CO + 2CH_4 + 2CO_2H_4\]

An appreciable amount of ethane, though neglected in the stoichiometric equation, is found to be present in the reaction chamber and the final pressure is, at most, found to be only 100% greater than the initial (46), showing that it is far from being a simple reaction.

Dimethyl ether likewise, (47) acts abnormally even at relatively high pressures. Furthermore, since the reaction is considered as being:

\[(a) \quad CH_3OCH_3 = CH_4 + HCHO\]
\[(b) \quad HCHO = CO + H_2\]

the intermediate formation of formaldehyde is an undesirable complication.

The isomerism of pinene in the gaseous state (48) is one of the few ideal gas reactions for our purpose. Its reaction velocity has been found to be the same in the gaseous state, in pure liquid and in solution in various solvents. Unfortunately, it has not been studied at low pressures.
Although Ramsperger (49) found that the decomposition of asomethane is unimolecular and homogeneous, the reaction products are by no means simple, although the principle reaction is:

(a) $\text{CH}_3\text{N} : \text{NCH}_3 = N_2 + \text{C}_2\text{H}_6$

Possible side reactions postulated are:

(b) $\text{CH}_3\text{N}_2\text{CH}_3 = \text{C}_2\text{H}_4 + \text{H}_2 + N_2$

(c) $2\text{CH}_3\text{N}_2\text{CH}_3 = \text{C}_2\text{H}_4 + 2\text{CH}_4 + 2N_2$

The specific rate does not drop as the reaction proceeds, as one would expect it to, because of the reduced partial pressure of the reactant, showing that the reaction products probably affect the reaction in some manner.

Aisisopropane (50), although it decomposes unimolecularly and homogeneously between 250 and 490° C. from 46 to 25 mm. pressure, follows two distinct paths:

(a) $\text{C}_7\text{H}_7\text{N} : \text{NCO}_2\text{H} = N_2 + \text{C}_2\text{H}_6$ (about 85%)

(b) $\text{C}_7\text{H}_7\text{N} : \text{NCO}_2\text{H} = N_2 + \text{C}_2\text{H}_6 + \text{C}_2\text{H}_6$ (about 15%)

The conversion of dimethyl maleate into dimethyl fumarate (51, 52) appears to be homogeneous and unimolecular although the product formed gradually undergoes decomposition itself.

The conversion of maleic acid into fumeric
in the liquid state (53) has also been studied by Höjendohle although it generally is believed that this reaction was due to ion catalysis because of its low energy of activation.

The decomposition of ethylene oxide is also said to be homogeneous (54). However, it has been claimed that inert gases cause the specific rate to decrease. This is in direct contradiction to all our present theories and the work done on this compound has not been sufficient to warrant our stressing its importance too greatly.

The decomposition of sulphuryl chloride was at first reported as a homogeneous reaction although later studies (56, 56, 57) showed it to be heterogeneous. The original work (by Smith) was done with the commercial product, which, it is believed, contained enough camphor to apparently appreciably affect the reaction rate.

The decomposition of ethyl bromide, studied by Vernon and Daniels (58), has been found to be homogeneous and unimolecular, although the reaction is complicated by the reverse reaction occurring. Four methods may be used to calculate the specific rate, two of these giving
concordant results. It clearly shows itself to be unimolecular at the early stages at low pressures. However, its stoichiometric relationships do not leave much choice with respect to the application of Theories II or III in determining the rate constant at low pressures.

It is evident from the above that kineticians are still in need of simpler, unimolecular, homogeneous reactions for further study.
The bath employed was a five gallon stone jar placed in a galvanized iron pull and lagg ed with two inches of filtercell. Hydrogenated cottonseed oil was used in the bath. A turbine stirrer, using an induction motor for power, was used to keep the oil circulating rapidly.

Although reference has been made to the use of vaseline and lubricating oil baths it was found that no mineral oil or vaseline could be obtained which did not smoke and decompose above 200°C. Metal baths were possible but their comparatively high cost made the oil more desirable. The cottonseed oil used smoked at temperatures above 175°C but after a relatively short period of use blackening of the oil occurred, the smoking became less noticeable and, with good ventilation in the room, the bath could be used satisfactorily up to 150°C.

Three specially wound resistance coils, each capable of dissipating 400 watts, which could be turned on by appropriate switches either in series or in parallel to give an input up to 1200 watts.
constituted the permanent heater. These coils were mounted on a one-half inch transite board placed in the bottom of the jar. Besides this heating unit, two 150 watt hairpin type heaters were connected to the line through a 460 ohm rheostat, used as a potentiometer, to give a partial regulation of the heat input. These two sets of heaters were adjusted so as to maintain the bath to within one degree of the desired temperature. The exact temperature regulation was obtained by means of a 200 watt light bulb with an all-weather socket operated by the thermoregulator. The bath itself was mounted on a hydraulic jack which permitted the bath to be rapidly raised or lowered. The reaction vessel could be connected, evacuated and sealed off and then the bath, already at the temperature desired, raised to completely surround it in a minimum of time with much greater safety to the operator and the glass system.

Thermoregulator

The thermoregulator consisted of a Leeds and Northrup platinum resistance thermometer, immersed in the bath close to the reaction
vessel. Before use the thermometer was calibrated (Fig. 1). It was then connected to a type F leads and Northrup reflecting galvanometer through a Wheatstone bridge with compensating leads. A galvanometer light, modified to use a 60 C.P. 6 volt automobile headlight bulb, operated at twelve volts, was set (Fig. 3) one meter from the galvanometer with an appropriate lens system to concentrate as much light as possible on the galvanometer mirror. The lamp was air-cooled to prevent overheating. A Weston photoelectric cell was then placed four meters from the galvanometer. At zero scale reading the light fell directly upon the most active part of the cell. The cell was connected through a miniature relay-power relay system to the regulated 200 watt bulb heater. The system was so arranged that the galvanometer light falling directly upon the cell turned the auxiliary heater on. As the bath heated the Wheatstone bridge became unbalanced, the light swung off the cell and the heater turned off. When the bath cooled, the light swung slowly back to the cell. As soon as enough light was striking the cell to actuate the miniature relay, the heater turned on. While
in operation the light was found to fluctuate from the cell to a position approximately ten centimeters distant from the edge of the cell. Addition of 0.1 Ω resistance to the thermometer side of the bridge (equivalent to 5.05°C) caused the galvanometer light to move a distance of eight meters along a line passing through the photronic cell and perpendicular to the galvanometer mirror. Thus, theoretically, the system was sensitive to 0.003°C. Actually at 200°C, the bath remained constant to ± 0.01°C.

This is a much simpler arrangement than that of Daniels and Vernon (58) and, because of the great distance between the galvanometer mirror and photronic cell, more sensitive. Förster and Gruner (59) describe a high temperature thermostat but base their regulator on a small bath kept at a much lower temperature. This method did not seem to be sufficiently accurate for our study. Other high temperature thermoregulators, primarily based on the photoelectric cell principle, are those of Walsh and Milas (60), Vedder and Evans (61), Barnes and Antasi (62), L. B. Smith (63), Southard and Andrews (64), Borkun (65), Label and Hancock
Lange and Voos (69) also describe a photo-electric thermostatic control, and, although usable up to 1000 °C, it appears less sensitive than the set-up described.

Reaction Vessel.

Because of the greater simplicity and accuracy the static rather than the dynamic method was decided upon for this study. After numerous attempts to obtain data by means of the simpler Minshewood apparatus proved it to be inaccurate and unsatisfactory, recourse was had to a modified form of Daniels' (73) method. This consists in studying the reaction at constant volume and measuring the rate of reaction by the increase in pressure occurring. The pressure at any time within the reaction vessel is determined by dynamic balancing against the pressure in an outside system, which is, in turn, measured by means of a capillary mercury manometer. The construction of the reaction vessel is shown in Fig. 2a, while the system
as a whole is pictured in Fig. 2. In Fig. 2a "M" is a 25 x 150 mm. pyrex testtube that has sealed into it a glass diaphragm, "E", connecting to the outside balancing system, and two side arms "H" and "L". The glass diaphragm consists of a thin walled bulb, flattened on the bottom "G". One end of a small diameter pyrex tube "F" is sealed to the flattened portion of the bulb and a No. 20 platinum wire sealed to the other. A second piece of the No. 20 platinum wire "B" with a ball end is sealed through the side of the body of the tube so that its end is close to the platinum wire "D". This wire "D" is in turn connected by 50 mm. of No. 44 platinum wire to a third piece of No. 20 wire "A". The side arm "L" is of 4 mm. pyrex glass and is connected by pressure tubing to the vacuum pump. The side arm "H" is essentially a "Y" tube. In "Y" is placed a glass enclosed hammer "J" and around it is wound a wire coil constituting an electromagnet. The reactant material is introduced into "H" within a small, sealed thin-walled bulb "K". The reaction vessel and outside system are evacuated. In actual practice, in order to exclude any traces of oxygen, the whole system was evac-
A. Volume Flask
b. Vacuum Pump
c. Reaction Flask
d. Rubber Connection
e. Reaction Bulb
f. Mercury Well
g. Inlet Valve
h. Pressure Equalizer
i. 110 Volt Relay
j. Mercury Relay
k. Power Transformer
l. Hg. Manometer

Fig. 2.
ated with a gas collecting Gecco pump for half an hour. One atmosphere of nitrogen was then bled in and the system re-evacuated. This was repeated two or three times and finally, when a pressure of approximately 0.006 mm, was obtained, the side arm L was sealed off with a hand torch. The hammer J was lifted by the electromagnet and H tapped gently until the bulb K fell into the depression E. The bulb was then broken by the fall of the hammer, letting the reactant material diffuse throughout the vessel. The constant temperature bath was raised rapidly until the entire reaction vessel was submerged. As decomposition occurred the pressure inside the vessel became momentarily greater than the pressure in the outside system. This caused the thin glass diaphragm to move inward, swinging arm D until D made contact with B. A mercury relay J in Fig. 2 was connected through B and A (Fig. 2A). When contact was made the mercury relay actuated the power relay I (Fig. 2). The long arm h on this relay then gently tapped the protruding tip of the automobile valve g and permitted air from the atmosphere to leak into the hal-
ancing outside system ("a" in Fig. 2). As soon as the pressure in this outside system became equal to that within the reaction vessel, the glass diaphragm straightened, breaking contact between "B" and "D" (Fig. 2A), stopping the outside leak. The pressure in the outer system was then read off the mercury manometer "1" (Fig. 2). The glass diaphragm was very sensitive, making and breaking contact during the course of a run as fast as two or three times per second. The mercury column in the manometer fell quite smoothly, following the course of the reaction closely. The improvements of this apparatus over that of Daniels are:

1. A glass enclosed hammer to break a bulb containing the reactant after the vessel had been completely sealed off.

2. An automatically operated pressure regulator. This eliminated the personal element in adjusting the balancing pressure.

In the original apparatus the side arm "L" (Fig. 2A) consisted of a "U" tube with rubber connections so arranged that the flask could be evacuated with the capillary tip of the bulb extending well into the side arm of the flask.
After the flask had been evacuated the tip of the capillary was broken, the liquid vaporized into the flask and the side arm sealed off. Thus during the process of sealing some of the vapors were in contact with the hot glass. Furthermore, the diaphragm leads were connected to a galvanometer through a battery. When the pressure increased sufficiently to cause contact, the galvanometer needle deflected and the operator adjusted the pressure in the outside system by manipulating a stopcock. The balancing system used in this work consisted essentially of a three liter round bottom flask ("a" in Fig. 2) which had a large enough volume so that an appreciable leak was needed to effect a small pressure change but permitted no appreciable lag.

Before being used on a run, newly blown glass diaphragms were broken in by repeated flexing. This was done by partially evacuating the reaction flask and then permitting the vacuum pump to keep on working on the outside system only. At first, contact was not made and broken at exactly the same pressure but after being in operation for approximately half an hour it was found that the zero point of the diaphragm became
constant. This zero point had to be determined for each diaphragm constructed. It was found that after being used four or five times in the neighborhood of 200°C, the diaphragm no longer gave concordant results and was discarded. This was probably due to crystallization and loss of pliability of the thin glass.

The flask and tubes were thoroughly cleaned before using. They were boiled in cleaning solution, then in concentrated nitric acid to remove any carbon that might be present and finally rinsed thoroughly with distilled water.

In this type of apparatus all of the reactant material is maintained at the desired temperature and there is no opportunity for contact with mercury, stopcock grease, rubber tubing or any other foreign material that might possibly act as a catalyst. Moreover, there is no need for a "correction factor" to take care of the gases in the dead space level, outside the bath, as in most apparatus described in the literature.

To test the homogeneity of a reaction duplicate runs were made at the same temperature and approximately identical initial pressures, once with an empty vessel and once with a vessel having an increased surface. The increase in surface was obtained by partially filling the
vessel with ground glass or glass wool. The ground glass was of pyrex ground to 100 mesh and the glass wool of soda lime glass. Both of the packing materials were boiled in concentrated nitric acid and rinsed with distilled water before use. A reaction is considered to be homogeneous if identical reaction rates are obtained.
MATERIALS INVESTIGATED

Methyl formate was the first compound studied. A search of the literature indicated that Bairstow and Minchelwood (74) had found this compound to undergo heterogeneous decomposition. These two workers further claimed that the reaction could be catalyzed by iodine to present an apparently homogeneous decomposition but was probably complicated by a secondary reaction, i.e.:

(a) \( \text{CH}_3\text{CHOH} = \text{H}_2\text{O} + \text{CO} \)

(b) \( 2\text{CH}_3\text{OH} = 2\text{CH}_4 + 2\text{H}_2\text{O} + \text{CO} \)

Reaction (b) probably occurring in various steps. Since the presence of iodine was required to make the reaction appear homogeneous the compound was discarded.

It was next decided that the decomposition of iodine trichloride might be suitable for study. It is known fact (75) that when liquid chlorine is passed over solid iodine two chlorides form, depending on the amount of chlorine used. The trichloride is a solid, melting at 53° C., that slowly undergoes decomposition, even in the solid state, to form \( \text{Cl}_2 \) gas and iodine monochloride. The decomposition of the trichloride is complete at 67° C. Since its decomposition products are a
gas (Cl₂) and a solid (ICl) which exists in two forms, i.e., an unstable form melting at 14 °C. which gradually changes to a stable form melting at 27.2 °C., it appeared that this would be a good compound to study. At that stage of the work we were still attempting to use the Hinshelwood type of apparatus for preliminary investigations and no concordant results could be obtained because of the violent action of the liberated chlorine gas on the mercury in the manometer. The trichloride was prepared by a modified form of the method used by Cornog and Harges (76) in the preparation of the monochloride for their studies. This method proved to be much simpler and yielded a product as good as the more complicated method suggested by Truesdail and Beyer (77). The work was discontinued on this compound since it was extremely difficult to determine whether the substance obtained was pure trichloride or a mixture of the tri- and mono-forms.

Trimethyl ammonium bromide was another of the compounds considered. It was prepared by passing CH₃Br (formed by dropping HBr into hot CH₃OH) through a solution of trimethyl amine in
absolute ether at -5°C. The impure product, obtained by evaporating off the ether, was purified (according to the suggestion of Dr. J. L. E. Erickson) by recrystallizing three times from a hot 10% ethyl alcohol solution, washing with absolute alcohol and drying at 60°C. The final product obtained was pure white, had no odor of trimethyl amine and analyzed 58.37% Br (theoretical = 58.39%). Although it is known that this compound decomposes to form trimethyl amine and methyl bromide when heated to 150°C., the decomposition of the pure substance appeared to be so slow as to be unsuitable for kinetic study.

Due to the similarity in structure of methyl formate, the methyl and ethyl carbonates and chlorocarbonates, it was decided to investigate this group of compounds. Preliminary investigation showed that diethyl carbonate decomposes (above its boiling point - 112°C.) yielding diethyl ether and carbon dioxide. This is in accord with the literature (78). Dimethyl carbonate, diethyl carbonate, ethyl chlorocarbonate and methyl chlorocarbonate were obtained from the Eastman Kodak Co. and the study reported in this paper started. The dimethyl and diethyl carbonates were used as obtained and although decomposition
was found to occur in the region of 250 °C. It was learned that both reactions were heterogeneous, being appreciably catalyzed by addition of either glass wool or ground glass to the reaction vessel.

**TABLE I**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Initial Pressure</th>
<th>$K$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl carbonate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>103 mm Hg</td>
<td>$4.30 \times 10^{-3}$</td>
<td>unpacked</td>
</tr>
<tr>
<td>13</td>
<td>143 mm Hg</td>
<td>$3.20 \times 10^{-2}$</td>
<td>packed</td>
</tr>
<tr>
<td>21</td>
<td>141 mm Hg</td>
<td>$4.18 \times 10^{-3}$</td>
<td>unpacked</td>
</tr>
<tr>
<td>Diethyl carbonate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>59 mm Hg</td>
<td>$1.64 \times 10^{-2}$</td>
<td>unpacked</td>
</tr>
<tr>
<td>14</td>
<td>102 mm Hg</td>
<td>$1.48 \times 10^{-2}$</td>
<td>&quot;</td>
</tr>
<tr>
<td>17</td>
<td>117 mm Hg</td>
<td>$9.51 \times 10^{-2}$</td>
<td>packed</td>
</tr>
</tbody>
</table>

Ethyl chloroformate was then investigated and results obtained with the commercial product which led us to believe that homogenous, unimolecular decomposition to ethyl chloride and carbon dioxide occurred between 150 °C. and 200 °C. The commercial product (b.p. 92-94 °C.) was purified as follows: 250 ml of the substance were placed in a round bottom flask connected to a three foot fractionating column and distilled. The first
and last 100 ml. were discarded, the intermediate 50 ml. being retained. This intermediate portion was refractionated, using a Beckman thermometer to determine the boiling point range. The first 20 ml. were discarded again and the intermediate 10 ml. having a boiling range of 0.02°C. retained for study. The portion finally retained was placed in a ground glass stoppered bottle and kept in a desiccator until used. Eighty small Victor Joyer bulbs were prepared and filled, the contents varying from 12.8 to 13.3 mgs. of chloroethyl carbonate.

When these bulbs had been all used a fresh batch was prepared using another refractionated portion of the carbonate. Some 250 bulbs were prepared.
The volume of the reaction vessel was obtained with distilled water. A bulb, containing the material to be studied, was then chosen with a weight of material calculated to give approximately the desired initial pressure. The bath was brought to the proper temperature and the vessel evacuated, rinsed and sealed as previously described. Pressure equal to approximately one half the initial pressure to be obtained was then bled into the outside balancing system and the bulb broken. It was found that if the pressure difference between the reaction vessel and the balancing system were permitted to become too great the glass diaphragm between the two ruptured. After breaking the reaction bulb by means of the electromagnetically operated hammer the bath was quickly raised so as to completely surround the reaction vessel and the time noted.

The pressure, indicating the rate of decomposition, was then read off the mercury manometer at definite time intervals. The pressure gradually increased until decomposition was complete and then remained constant. The exact initial pressure was taken to be one half the final constant pressure eventually reached.
hen the reaction vessel was sealed off at side tube "J" (Fig. 2A) care was taken to leave a small tip on the end of this tube. After a reaction had gone to completion, the bath was lowered by means of the hydraulic jack, leaving the reaction vessel exposed. A piece of pressure tubing was connected to the vacuum pump and slipped over the sealed tip of tube "J". The pressure in the tubing was lowered so as to be approximately the same as that within the reaction vessel and the tip broken off. This prevented a rapid rush of air from suddenly entering the glass diaphragm and permitted collecting gas samples for analysis.

The final products obtained were analysed for \( \text{CO}_2 \) and \( \text{C}_2\text{H}_6\text{Cl} \) content by means of an Ostert apparatus. In order to obtain sufficient material for an accurate analysis a special type of vessel was used. It consisted of the bulb from a 250 ml. distilling flask with two pieces of glass tubing sealed on, one being of 8 mm. diameter glass, the second of 2 mm. One end of the 2 mm tubing was sealed off, a sealed tube containing approximately 0.5 g. of ethyl chloroacetate introduced through the large tube, the whole system evacuated, rinsed with nitrogen through a three way stopcock,
re-evacuated and sealed off. The small bulb was then broken by shaking the vessel and the whole submerged in the constant temperature bath before a regular run was to be made. At the end of the run the auxiliary vessel was taken from the bath and cooled. The lower end of the small tubing was submerged in an ice-salt mixture at about -10°C. The ethyl chloride present liquified and collected in the tip of this small tube. This tip was then drawn off, leaving the CO₂ gas in the larger bulb and the ethyl chloride sealed in a smaller bulb. The CO₂ was then transferred to the burette by connecting the larger arm, by pressure tubing, to the inlet stopcock and breaking the tip of the smaller tube under a slightly acidic water solution. By lowering the leveling bulb of the burette the dilute acid was drawn into the reaction bulb and the CO₂ in turn drawn into the burette. The volume of CO₂ obtained was then measured, checked by absorption in 40% KOH solution, corrected to standard pressure and temperature.

The ethyl chloric acid was broken, by means of a glass rod, below the surface of a cold solution of AgNO₃. The precipitated AgCl was filtered off, washed with dilute HNO₃, dissolved with an
Excess of ammonia water to separate it from glass fragments, reprecipitated, dried and weighed. A typical analysis is as follows:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>175 °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulb No.</td>
<td>11</td>
</tr>
<tr>
<td>Tare</td>
<td>0.4963 g.</td>
</tr>
<tr>
<td>Sample</td>
<td>0.8098 g.</td>
</tr>
<tr>
<td>Weight $\text{AgCl} \cdot \text{CO}_2$</td>
<td>0.3125 g.</td>
</tr>
<tr>
<td>Volume $\text{CO}_2$ obtained</td>
<td>68.21 ml. (at 21 °C. and 764 mm.)</td>
</tr>
<tr>
<td>Volume $\text{CO}_2$ after absorption</td>
<td>68.00 ml.</td>
</tr>
<tr>
<td>Corrected volume $\text{CO}_2$</td>
<td>62.95 ml. (at S.T. and P.)</td>
</tr>
<tr>
<td>Theoretical volume $\text{CO}_2$</td>
<td>64.30 ml.</td>
</tr>
<tr>
<td>Deviation from theoretical $\text{CO}_2$</td>
<td>2.4%</td>
</tr>
</tbody>
</table>

Cl content

<table>
<thead>
<tr>
<th>Weight of crucible</th>
<th>19.2184 g.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{AgCl}$</td>
<td>19.6185 g.</td>
</tr>
<tr>
<td>Weight of $\text{AgCl}$</td>
<td>0.4031 g.</td>
</tr>
<tr>
<td>Theoretical weight</td>
<td>0.4111 g.</td>
</tr>
<tr>
<td>Deviation from theoretical</td>
<td>0.27%</td>
</tr>
</tbody>
</table>


**EXPERIMENTAL RESULTS**

The experimental data obtained are shown in Table II and graphically in Figures 4-14.

**TABLE II**

150 °C.

<table>
<thead>
<tr>
<th>Time in min.</th>
<th>Bulb A-58</th>
<th></th>
<th>Bulb A-15</th>
<th></th>
<th>Bulb B-1</th>
<th></th>
</tr>
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<tbody>
<tr>
<td></td>
<td>( P_t )</td>
<td>Log C</td>
<td>( P_t )</td>
<td>Log C</td>
<td>( P_t )</td>
<td>Log C</td>
</tr>
<tr>
<td>1</td>
<td>116</td>
<td>2.058</td>
<td>74</td>
<td>1.644</td>
<td>175</td>
<td>2.244</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>2.017</td>
<td>76.3</td>
<td>1.597</td>
<td>175</td>
<td>2.228</td>
</tr>
<tr>
<td>4</td>
<td>131</td>
<td>1.992</td>
<td>79</td>
<td>1.556</td>
<td>175</td>
<td>2.244</td>
</tr>
<tr>
<td>6</td>
<td>134</td>
<td>1.978</td>
<td>80.5</td>
<td>1.539</td>
<td>175</td>
<td>2.228</td>
</tr>
<tr>
<td>8</td>
<td>137</td>
<td>1.959</td>
<td>81.5</td>
<td>1.521</td>
<td>130</td>
<td>2.228</td>
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<tr>
<td>10</td>
<td>139.5</td>
<td>1.946</td>
<td>83.1</td>
<td>1.501</td>
<td>186</td>
<td>2.228</td>
</tr>
<tr>
<td>15</td>
<td>141.0</td>
<td>1.900</td>
<td>85.6</td>
<td>1.483</td>
<td>194</td>
<td>2.228</td>
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<tr>
<td>20</td>
<td>156</td>
<td>1.896</td>
<td>87.1</td>
<td>1.464</td>
<td>191</td>
<td>2.228</td>
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<tr>
<td>25</td>
<td>167.5</td>
<td>1.865</td>
<td>89</td>
<td>1.445</td>
<td>109</td>
<td>2.196</td>
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<tr>
<td>30</td>
<td>161</td>
<td>1.849</td>
<td>90.5</td>
<td>1.425</td>
<td>215</td>
<td>2.196</td>
</tr>
<tr>
<td>35</td>
<td>165.5</td>
<td>1.820</td>
<td>92.4</td>
<td>1.407</td>
<td>123</td>
<td>2.196</td>
</tr>
<tr>
<td>40</td>
<td>169</td>
<td>1.814</td>
<td>93.3</td>
<td>1.389</td>
<td>22.9</td>
<td>2.196</td>
</tr>
<tr>
<td>45</td>
<td>172</td>
<td>1.795</td>
<td>95</td>
<td>1.363</td>
<td>238</td>
<td>2.196</td>
</tr>
<tr>
<td>50</td>
<td>177</td>
<td>1.778</td>
<td>96</td>
<td>1.350</td>
<td>244</td>
<td>2.196</td>
</tr>
<tr>
<td>60</td>
<td>181.5</td>
<td>1.741</td>
<td>98</td>
<td>1.312</td>
<td>208</td>
<td>2.022</td>
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150°C.

FIG 4

PRESSURE MM HG

TIME IN MIN

A15

B6

A30

A39

B1
FIG. 7

195°C

Pressure (mm Hg)

Time in min.

- A-13
- C-6
- C-8

25 mm. CO₂
50 mm. N₂
195°C

- B-15
- 88
- A-3
- C-5

Pressure (mm Hg)

Time in min.

FIG 8

50 MM N₂
HIGH PRESSURE CURVES

PRESSURE (mm Hg)

TIME IN MIN

Fig. 9
Since the only products of the reaction are carbon dioxide and ethyl chloride the equation for the reaction is:

\[ C_2H_5OCOCl = C_2H_5Cl + CO_2 \]

Employing the following symbols:

- \( P_1 \) = initial pressure of ethyl chlorocarbonate.
- \( P_L = P_{CO_2} \) = partial pressure of carbon dioxide.
- \( P_2 = P_{C_2H_5Cl} \) = partial pressure of ethyl chloride.
- \( P = P_{C_2H_5OCOCl} \) = partial pressure of ethyl chlorocarbonate undecomposed.

Since for every mol of reactant one mol of \( CO_2 \) and one mol of \( C_2H_5Cl \) (or two mols of products) are formed, then:

1. \( P_f = \text{final pressure} = P_L + P_3 \)
2. and: \( P_L = P_3 \)
3. also: \( P_2 = \frac{1}{2} P_1 \)

Then at any time \( t \) during the reaction the pressure at that time is:

4. \( P_t = P + P_L + P_3 \)
5. But \( P_L = P_3 = (P_1 - P) \)
6. Therefore: \( P_t = \frac{3}{2}(P_1 - P) + P \)
7. \( P = 2P_1 - P_t \)
8. Then: \( P = 2P_1 - P_t \)
Thus the concentration of undecomposed ethyl chloro-carbonate (proportional to its partial pressure) is given by equation (8).

The curves obtained by plotting pressure against time are typical log curves (Figs. 4, 5, 6, 7, 8, 9). These curves were originally plotted on large size graph paper. The rate of the reaction may be considered as being a function of these curves. Figure 9 shows well the relative rate of reaction at different temperatures. It is understood, of course, that all of the runs made could not be plotted and inserted in this paper as many of the curves would have come too close together. However, the curves included are representative.

The specific reaction rate was obtained from the slope of the lines in Figures 10-14. The elementary equation for unimolecular reactions is mathematically expressed as:

$$\frac{-dc}{dt} = kc$$

Only a single substance reacts and its rate of decomposition \((79)\) is directly proportional to its concentration. This is, of course, but one expression of the law of exponential growth in which \(c\) is the concentration of material and \(\frac{-dc}{dt}\) is the rate at which the concentration de-
Integrating we get:
\[ \int \frac{dc}{c} = \int k dt \]
\[ \ln c = kt + \text{constant of integration} \]

(or) \[ \log c = \frac{k}{2.303} t + \text{constant of integration} \]

Thus, a plot of \( \log c \) against time should give a straight line. The negative of the slope of this line multiplied by 2.303 gives the value of \( k \) (velocity constant). As can be seen from figures 10-14, in our case plotting the log of \((E_1 - E_t)\) (directly proportional to the concentration) against time yielded straight lines. The slope of these lines was obtained by using the numerical values of the points obtained in each run and calculating by the method of least squares. The fact can be shown mathematically (30) that the slope of the straight line best fitting a large number of points may be calculated from the equation:

\[
(9) \quad m = \frac{(x_1 y_1 + x_2 y_2 + \cdots + x_n y_n) - (x_1 + x_2 + \cdots + x_n)(y_1 + y_2 + \cdots + y_n)}{(x_1^2 + x_2^2 + \cdots + x_n^2) - (x_1 + x_2 + \cdots + x_n)^2} \]

Each value of \( k \) reported in Table III was calculated by multiplying the negative of the slope obtained from this equation by 2.303. \( K_{\infty} \) in this
table was taken as the average of the specific velocity values for the high pressure runs. Figure 14 shows well the effect of temperature on the rate of reaction by means of the different slopes obtained at different temperatures.

**Table III**

Temperature = 160 °C.

\[ k_\infty = 0.00760 \]

<table>
<thead>
<tr>
<th>( P_1 ) (mm.)</th>
<th>( k/\text{min.} )</th>
<th>( k/k_\infty )</th>
<th>( \log P_1 )</th>
<th>( \log (k/k_\infty \times 10) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>0.00769</td>
<td>0.936</td>
<td>2.012</td>
<td>0.994</td>
</tr>
<tr>
<td>177*</td>
<td>0.00787</td>
<td>1.009</td>
<td>2.048</td>
<td>1.002</td>
</tr>
<tr>
<td>126</td>
<td>0.00481</td>
<td>0.617</td>
<td>2.097</td>
<td>0.790</td>
</tr>
<tr>
<td>116</td>
<td>0.00749</td>
<td>0.980</td>
<td>2.062</td>
<td>0.992</td>
</tr>
<tr>
<td>106</td>
<td>0.00472</td>
<td>0.605</td>
<td>2.022</td>
<td>0.782</td>
</tr>
</tbody>
</table>

*vessel packed*

Temperature = 176 °C.

\[ k_\infty = 0.04515 \]

<table>
<thead>
<tr>
<th>( P_1 ) (mm.)</th>
<th>( k/\text{min.} )</th>
<th>( k/k_\infty )</th>
<th>( \log P_1 )</th>
<th>( \log (k/k_\infty \times 10) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>146*</td>
<td>0.0449</td>
<td>0.995</td>
<td>2.031</td>
<td>0.993</td>
</tr>
<tr>
<td>112</td>
<td>0.0446</td>
<td>0.988</td>
<td>2.016</td>
<td>0.995</td>
</tr>
<tr>
<td>177</td>
<td>0.0459</td>
<td>1.0171</td>
<td>2.146</td>
<td>1.007</td>
</tr>
<tr>
<td>176*</td>
<td>0.0406</td>
<td>0.8996</td>
<td>2.246</td>
<td>0.964</td>
</tr>
<tr>
<td>152*</td>
<td>0.0348</td>
<td>0.771</td>
<td>2.182</td>
<td>0.887</td>
</tr>
<tr>
<td>131</td>
<td>0.0365</td>
<td>0.911</td>
<td>2.110</td>
<td>0.910</td>
</tr>
<tr>
<td>1.6*</td>
<td>0.0328</td>
<td>0.749</td>
<td>2.100</td>
<td>0.875</td>
</tr>
<tr>
<td>85</td>
<td>0.0276</td>
<td>0.612</td>
<td>1.930</td>
<td>0.706</td>
</tr>
<tr>
<td>45</td>
<td>0.0163</td>
<td>0.688</td>
<td>1.654</td>
<td>0.768</td>
</tr>
</tbody>
</table>

*vessel packed*
Table III, contd.

Temperature = 195 °C.

\( k_\infty = 0.1015 \)

<table>
<thead>
<tr>
<th>( P_1 ) (mm)</th>
<th>( k )/min</th>
<th>( k/k_\infty )</th>
<th>( \log P_1 )</th>
<th>( \log (k/k_\infty \times 10) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>179</td>
<td>0.183</td>
<td>1.0083</td>
<td>2.258</td>
<td>1.003</td>
</tr>
<tr>
<td>176</td>
<td>0.180</td>
<td>0.9917</td>
<td>2.214</td>
<td>0.997</td>
</tr>
<tr>
<td>151</td>
<td>0.128</td>
<td>0.7603</td>
<td>2.179</td>
<td>0.882</td>
</tr>
<tr>
<td>85</td>
<td>0.114</td>
<td>0.5381</td>
<td>1.930</td>
<td>0.798</td>
</tr>
<tr>
<td>20</td>
<td>0.102</td>
<td>0.3820</td>
<td>1.510</td>
<td>0.750</td>
</tr>
</tbody>
</table>

The influence of temperature in the normal high pressure decomposition rate is shown in Figure 15.

The energy of activation calculated from the simple Arrhenius equation and from the slope of this straight line, calculated by the method of least squares, is 29,410 cal. per mole. From this value are calculated the values of \( \theta \), in the equation:

\[ k = \varepsilon e^{-E/RT} \]

as seen in Table IV.
FIG. 15

Log $K_{eq} \times 10^3$

$1/T \times 10^3$
Thus, the rate of this reaction may be obtained from the equation:

\[ k = 5.5 \times 10^{10} \times e^{-\frac{29410}{RT}} \]

or

\[ \ln k = 24.736 - \frac{29410}{RT} \]

The magnitude of \( s \), while slightly smaller than similar values obtained in most unimolecular reactions (81), fits in with the understanding of this factor as put forth by Rice and Gershinowitz (82). The order of magnitude of the energy of activation is approximately the same as that of ethyldene diacetate and its homologues studied by Coffin (83, 84).
The Arrhenius Equation

In practice, it is conventional to indicate the rate of a reaction by the equation suggested by Arrhenius in 1889 (3). It is at present understood that the simple equation is strictly applicable for the calculation of the steady state values only. It is evident from Table III that the initial pressure of ethyl chlorocarbonate has an appreciable effect on its rate of decomposition. The simple equation, then, although suitable for use when the initial pressure is relatively high, does not hold over the entire range of the reaction. This is probably due to the fact that although activated molecules were postulated by Arrhenius he did not take into consideration the localization of energy within the molecule or the probability that molecules having a large excess of energy, above $E_0$, react faster.

Theory I

Hinshelwood first proposed a theory which attempted to account for the decrease in the specific reaction velocity constant in the low pressure region. The principle concept of this theory is that it postulates a time lag between activation and subsequent decomposition. Mathematically
this is expressed as:

\[
\frac{\text{No. molecules reacting/cc./sec.}}{\text{Total No. collisions/cc./sec.}} = \frac{e^{-\left(\frac{E + (3n-1)RT}{RT}\right)}\left[\frac{E + (3n-1)RT}{RT}\right]^{\frac{3n-1}{2}}}{(3n-1)!}
\]

The basis of this postulate was that the localization of energy within particular vibrational bonds of the molecule was a time consuming operation.

**Theories II and III**

In deriving the equations for a more general form of the modified collision hypothesis Rice and Ramsperger and Kassel do not only make allowance for the localization of energy within particular vibrational bonds of the molecule, which accounts for the time lag, but also take into consideration that molecules in a higher quantum state, that is, molecules having energy greater than the minimum activation energy, will, as a result of this excess energy, react faster. According to these theories all molecules having an internal energy greater than \(E_0\), irrespective of the distribution of this energy among the internal degrees of freedom, are considered as being in the activated state. During the interval between collisions, this energy is undergoing a continual redistribution process within the molecule. When sufficient energy is
localized in a single vibrational bond, the molecule decomposes.

It has been shown by Kassel (24) that the Hinshelwood equation may be considered as being a special, simpler form of Rice and Hamperger's (22) more general theory. In order to obviate unnecessary complications we base the following calculations for all of the theories upon the symbols proposed by Rice and Hamperger. If we assume that \( N \) is the total number of molecules per unit volume and \( \pi \) the fraction of molecules in the activated state as calculated from Boltzman's distribution law then \( NW \) is the actual number of activated molecules per unit volume at relatively high pressures. If we then let \( aNW \) represent the number of collisions of activated molecules per cc. per second at high pressures, this will also represent the rate of deactivation at high pressures since every collision of an activated molecule leads to its deactivation. The rate of deactivation at lower pressures then becomes equal to \( a2Z \) (where \( Z \) is the actual number of activated molecules per unit volume). The number of molecules decomposing per unit volume is \( bZ \) (where \( b \) is a constant). At high pressures the
rate of activation (by collision) is greater than the sum of the rates of reaction and deactivation (since the measured reaction rate remains constant) and at very low pressures it is less, so we may consider some limiting pressure as being a steady state at which the rate of activation = rate of reaction + rate of deactivation, whence:

\[ \text{rate of activation} = \text{rate of reaction} + \text{rate of deactivation} \]

from which:

\[ a = \frac{\text{rate of activation}}{\text{rate of reaction} + \text{rate of deactivation}} \]

Setting

\[ K = \text{fraction of molecules decomposing per unit time} \]

then \( K = \text{fraction of molecules decomposing per unit time at higher pressures where the reaction rate is constant over a range of initial pressures.} \)

Therefore:

\[ K = \frac{bW}{m} \]

and

\[ k = \frac{aW}{m + \frac{p}{m} + kT \frac{kT}{m}} \]

where \( p = \text{initial pressure} \)

\( k = \text{gas constant/molecule}. \)

The term \( a^2 \) is the kinetic theory collision factor and has been shown by Jeans (35) to be calculated from:

\[ a = 4\sigma^2 \sqrt{\frac{\pi kT}{m}} \]
where \( \sigma \) = molecular diameter

\( m = \text{molecular weight of the gas} \).

Then considering the molecule to consist of harmonic oscillators, from classical statistical mechanics,

\[
W = \int_{\mathcal{E}_0}^{\infty} \mathcal{E} \, d\mathcal{E} = \int_{\mathcal{E}_0}^{\infty} \left( \frac{\mathcal{E}}{kT} \right)^{\frac{n-2}{2}} e^{-\frac{\mathcal{E}}{kT}} \frac{d\mathcal{E}}{kT} = \frac{1}{(\frac{n}{2})!} \left( \frac{\mathcal{E}_0}{kT} \right)^{\frac{n-2}{2}} e^{-\frac{\mathcal{E}_0}{kT}} \left( 1 + \frac{n-2}{2} \frac{kT}{\mathcal{E}_0} + \cdots \right)
\]

If the second and all higher terms may be neglected this reduces to

\[
W = \frac{1}{(\frac{n}{2})!} \left( \frac{\mathcal{E}_0}{kT} \right)^{\frac{n-2}{2}} e^{-\frac{\mathcal{E}_0}{kT}}
\]

(7)

and

\[
\bar{\kappa} = \frac{k\infty}{1 + \theta/p}
\]

(8)

Equation (8) may also be written in the form:

\[
\frac{1}{\bar{\kappa}} = \frac{1}{k\infty} + \frac{\bar{\kappa}}{k\infty} \cdot \frac{1}{p}
\]

(9)

This is fundamentally the equation of Hinshelwood and theory b. From it a plot of \( 1/\bar{\kappa} \) against \( 1/p \) should result in a straight line with a slope of \( \theta/k\infty \) and an intercept of \( 1/k\infty \). The test for this equation is shown in Figure 16. This plot shows the limiting pressure value (the pressure at which one should theoretically expect a de-
THEORETICAL LINE CALG. FROM: $K = \frac{K_{\infty}}{1 + \frac{\theta}{\theta^*}}$

○ EXPERIMENTAL POINTS

FIG. 16

$\frac{1}{K} \times 10^{-3}$

$\frac{1}{P} \times 10^2$
crease in the rate constant) to be 40 mm. The discrepancy between the actually obtained points and the theoretically obtained straight line (from eqn. 9) leads one to believe that this theory does not fit the facts very well. The value of "n" in equation (1) has been calculated as follows:

\[
\frac{C \cdot \left( \frac{E+(\frac{1}{2}n-1)R \cdot T}{RT} \right)^n}{(\frac{1}{2}n)!} = \frac{\text{No. molecules reacting/ } \text{sec.}}{\text{Total No. collisions/ } \text{sec.}}
\]

The total number of molecules is obtained from the simple gas equation:

\[
N = \frac{PV \times 6.06 \times 10^{23}}{RT} = 40 \times 6.06 \times 10^{23} \times \frac{108.5}{760 \times 82.06 \times 448} = 8.69 \times 10^{17} \text{ molecules per cm.}
\]

The number of molecules reacting is then obtained from the observed high pressure rate constant:

\[
K = 7.5 \times 10^{-4} / \text{sec.}
\]

\[
\text{No. molecules reacting/ } \text{cm. } \text{sec.} = \Delta N = 7.5 \times 10^{-4} \times 8.69 \times 10^{17} = 6.52 \times 10^{14}
\]

The molecular diameter of ethyl chlorocarbonate is:

density = 1.138 g./cm. in liquid state

Therefore: molecular volume = \[
\frac{108.5}{1.138 \times 6.06 \times 10^{23}} = 1.08 \times 10^{-22} \text{ cm.}^3/\text{molecule.}
\]

The volume of a sphere is \[
\frac{4\pi r^3}{3}
\]
where \( \sigma \) = diameter of the sphere.

Then:

\[
\frac{\pi \sigma^3}{6} = 1.58 \times 10^{-22}
\]

\[
\sigma^3 = \frac{1.58 \times 10^{-22}}{\pi} 
\]

\[
\sigma = \sqrt[3]{\frac{1.58 \times 10^{-22}}{\pi}} = 6.7 \times 10^{-8} \text{ cm.}
\]

The number of collisions/cc/sec is then obtained from the following equation:

\[
Z = \frac{3.9 \sigma^2 N^2}{kT} \text{ where } k = 8.315 \times 10^7 \text{ mole./kcal.}
\]

\[
= 3.9 \times \frac{3.7^2}{10^{-16}} \times 3.65^2 \times 10^{12} \times \frac{8.315 \times 10^7 \times 448}{108.5}
\]

\[
= 2.44 \times 10^{26} \text{ collisions/cc/sec at } 175^\circ C.
\]

Then the right hand term in the equation reduces to:

\[
\text{No. molecules reacting/cc/sec} = 6.67 \times 10^{-12}
\]

\[
\text{Total no. collision科尔/cc/sec.} = 2.44 \times 10^{26} \times 6.67 \times 10^{-12}
\]

The left hand term may be simplified as follows:

\[
e^{\left(\frac{E + (\frac{1}{2}n-1)R^2}{RT}\right)} \times \frac{E + (\frac{1}{2}n-1)R^2}{RT}^{\frac{1}{2}n-1}
\]

\[
(\frac{1}{2}n-1)!
\]

\[
e^{\frac{-E}{RT}} \times e^{-(\frac{1}{2}n-1)} \times \left[\left(\frac{E}{RT}\right)^{\frac{1}{2}n-1}\right]^{\frac{1}{2}n-1}
\]

\[
(\frac{1}{2}n-1)!
\]

Taking logarithms:

\[
(\frac{1}{2}n-1)\log\left[\frac{E}{RT} + (\frac{1}{2}n-1)\right] = \frac{4.43 \times E}{RT} - (\frac{1}{2}n-1) \times 4.43 - \log \left(\frac{1}{2}n-1\right)
\]

\[
= \log \left(2.67 \times 10^{-12}\right) = -11.5731
\]
Various values of \( n \) were then substituted in this equation to determine which would fit the closest. The value of \( n \) found to give the best results by this method was 9.

Theories II and III.

Rice and Kamsperger (Theory II) consider that as soon as the energy is localized in one squared term the molecule becomes reactive while Kassel (Theory III) assumes that the energy must be localized in two squared terms. It might be pertinent here to elucidate on the significance and meaning of "squared terms" designated in the mathematical expressions by the symbol "n". In this paper "n" represents the total number of quadratic terms by means of which the energy of activation is defined. This idea was put forth concurrently and independently by Hinshelwood (30) and Fowler and Rideal (11). Although three squared terms are required to define the total kinetic energy of a molecule (36) only the resultant component along the line of centers (in a single direction) need be considered for collisional purposes. For the collision of two molecules two terms are required to define the kinetic energy, each defining the translational energy of one molecule. Certain
of the internal vibrational bonds of each molecule also contribute to activation energy. Considering all of the internal degrees of freedom involved and assuming that the vibrations are simple each contributes two additional squared terms; one for the kinetic and one for the potential vibrational energy.

The equations given under Theory I are essentially those of Rice and Ramsperger and merely need clarification as to the terms used. In equation (9) the constant \( C_1 \) has the following value:

\[
C_1 = \frac{K_{0}^{\frac{1}{2}} \left( kT \right)}{4 \sqrt{\pi \sigma^2}} \cdot \frac{\beta^2}{4m \pi} \cdot \frac{C_{0}^{\frac{1}{2}}}{C_{0}^{\frac{1}{2}}}
\]

The term \( K_0 \) used in equations (7) and (10) is not the simple energy of activation as determined by the Arrhenius equation. As used by Hinshelwood \( E_0 \) actually has the value \( E + (\frac{n-1}{2})RT \) where \( E \) is the Arrhenius value. From previous calculations the value of \( n \) required for the Hinshelwood equation has been shown to be 9. This gives for the value of the energy of activation according to Theory I

\[
29,410 + 3,140 = 32,550 \text{ calories.}
\]

The value of \( E_0 \) as well as the value of \( n^* \) in terms of Theory II and III may easily be calculated from equation (7) in the following manner.
knowing the Arrhenius value of $E$ the fraction of molecules in the activated state ($W$) was determined at three different temperatures.

(a) At $160^\circ C$. 
\[ W = \frac{e^{-E/RT}}{n!} \]
\[ \log W = - \frac{E \times 4.343}{RT} = \frac{29.410 \times 4.343}{1.9865 \times 4.8} = -15.059 \]

(b) At $175^\circ C$. 
\[ \log W = - \frac{29.410 \times 4.343}{1.9865 \times 4.8} = -14.181 \]

(c) At $195^\circ C$. 
\[ \log W = - \frac{29.410 \times 4.343}{1.9865 \times 4.8} = -12.645 \]

Taking logs from equation (7) we have:

\[ \log W = - \log \left( \frac{n}{2} \right) + \left( \frac{n-1}{2} \right) \log \frac{E_0}{RT} - \frac{4.343 \times E_0}{RT} \]

Then for the three temperatures taken:

(d) $\log W_{160^\circ C} = - \log \left( \frac{n}{2} \right) + \left( \frac{n-1}{2} \right) \log \frac{E_0}{1.9865 \times 4.8} - \frac{4.343 \times E_0}{1.9865 \times 4.8}$

(e) $\log W_{175^\circ C} = - \log \left( \frac{n}{2} \right) + \left( \frac{n-2}{2} \right) \log \frac{E_0}{1.9865 \times 4.8} - \frac{4.343 \times E_0}{1.9865 \times 4.45}$

(f) $\log W_{195^\circ C} = - \log \left( \frac{n}{2} \right) + \left( \frac{n-3}{2} \right) \log \frac{E_0}{1.9865 \times 4.8} - \frac{4.343 \times E_0}{1.9865 \times 4.25}$

Substituting the calculated numerical values for $\log W$ and subtracting equation (e) from (d) and (f) from (e), we have:
(d) - (e)

\[ g - 15.039 + 14.251 = \log \left( \frac{n}{2} \right) - \log \left( \frac{n-2}{2} \right) \times \]

\[
\log \left[ \frac{E}{1.9385 \times 428} \right] - \log \left[ 1.9385 \times 448 \right] \\
+ - 4.843 E \left[ \frac{1}{1.9385 \times 428} - \frac{1}{1.9385 \times 448} \right] \\
\]

(h) \[ = .808 = \left( \frac{n-2}{2} \right) \log \left[ \frac{E \times 1.9385 \times 448}{E_0 \times 1.9385 \times 428} \right] - 2.8 \times 10^{-5} E_0 \\
= \left( \frac{n-2}{2} \right) (.026) - 2.8 \times 10^{-5} E_0 \\
\]

\[ E_0 = \frac{.808 \times 10^{-5}}{2.8 \times 10^{-5}} \]

(i) (e) - (f)

\[ E_0 = \left( .606 \right) \left( \frac{n-2}{2} \right) \left( .019 \right) \]

\[ = 2.1 \times 10^{-5} \]

Equating the right hand portions of (h) and (i)

\[ \frac{(.808)(n-2)(.026)}{2.8 \times 10^{-5}} = \left( .606 \right) \left( \frac{n-2}{2} \right) \left( .019 \right) \]

\[ = 2.1 \times 10^{-5} \]

\[ 2.1 (.808 .012n -.026) = 2.8 (.606 .0095n -.019) \]

\[ n = 14 \]

Substituting back in (h) for the numerical value of \( E_0 \)

we find

\[ E_0 = \frac{.808 \times 10^{-5}}{2.8 \times 10^{-5}} = \frac{.606 \times 10^{-5}}{2.1 \times 10^{-5}} \]

\[ = \frac{.804 \times 10^{-5}}{2.8} = 34.430 \text{ calories.} \]
A test for Theories II and III may be obtained by plotting \( \log \frac{k}{k_\infty} \) against \( \log p_1 \). Because of the dependence of \( k \) upon \( \Theta \), in the equation given by Vernon and Daniels, i.e.

\[
(11) \quad \log \frac{k}{k_\infty} = \log p_1 - \log (p_1 - \Theta),
\]

this plot should result in a curved line concave to the \( \log p_1 \) axis. This has been done in Figure 17 using the previously calculated values for \( \Theta \) and molecular diameter. The data seems to fit the theoretical curve quite well.

It has often been suggested that in attempting to fit theoretical curves to experimental data one may assume that the molecular diameter of a compound may be considered to be effectively much greater for activating and deactivating collisions than that calculated in the ordinary way from kinetic theory. This was suggested by Fowler and Rideal on the basis that all of the energy of two molecules colliding may flow into one molecule. However, Mitchellwood (87) points out, "The difficulty about this suggestion is that the calculation of bimolecular reaction rates can be carried out with the ordinary diameter; it is therefore rather an ad hoc procedure to alter them to explain one or two unimolecular reactions."

A method of determining the applicability of Theories II and III to the experimental values is
Fig. 17

THEORETICAL CURVE FROM EQUATION II

O ACTUAL DATA

Log. $K/K_\infty$

Log. $P_i$

-1.0

-0.75

-0.50

-0.25

0
obtained by comparing the actual value of $E_o$ calculated from the equation of both theories and noting its relationship to the Arrhenius value. According to Theory II the Arrhenius value for $E$ should be less than the critical energy by $\frac{1}{2}kT$. According to Theory III the difference between the two energy values should be $\left(\frac{n-2}{2}\right)kT$ (22).

The value previously calculated for $E_o$ has been found to be 34,430 calories/mol. while the Arrhenius value obtained from Figure 15 is 29,410 cals. The difference between the two is about 5,000 cals. At 175°C the value of $\frac{1}{2}kT$ is merely 450 cals. while the value for $\left(\frac{n-2}{2}\right)kT$ is (taking $n$ as 14) 5.5kT having a numerical value of 4,900 cals. This last value agrees well with the theoretically calculated value and leads us to believe that Theory III fits our data better.

Some of the fundamental concepts of these modified theories may be briefly reviewed here. At higher pressures where the measured rate is directly dependent upon the breakdown of the molecule itself, the collision frequency is great enough to keep a sufficient supply of activated molecules present, and a first order rate for the reaction should be expected. At low pressures
where the primary factor governing the rate of the reaction is collision frequency (a bimolecular mechanism) with the subsequent production of activated molecules one would expect the reaction to become a second order one. At intermediate pressures, then, one would expect a continuously changing order, being essentially a transition from the first to second order. At extremely high pressures the collision frequency may become so great as to give a sufficiently rapid deactivation process through collision, that enough molecules in the activated state are not present at any given time to keep up the first order reaction rate. Then at very high pressures the reaction should again tend to become of second order. Due to a lack of the proper equipment it was impossible to study this reaction at the extreme pressure limits. The range covered, from the data obtained, appears to be from the lower transition point (from first to second order) into the truly first order region.

In plotting the log C against time curves it can be seen that the initial values, during the first few minutes, do not fall exactly upon the straight line obtained over the major portion of the reaction. This can be seen in Figures 10 and 11.
When the values of the concentration and time for this period were plotted according to bimolecular theory, it was found that this part of the reaction corresponded to a second order rate. A plot of the reciprocal of the concentration against time, for second order reactions, should result in a straight line. This is exemplified in Figure 18 where these values are plotted for typical results of the studies made. From this figure it can readily be seen that during the very early stages the reaction is definitely of second order. Although a McLeod gauge and a mercury vapor pump were built with the intentions of following our reaction down into the very low pressure region and determining exactly the pressure at which the entire reaction remains in the second order state, it was decided that it would be better for the present to make a thorough examination in the transition and relatively higher pressure region and leave the very low and very high pressure regions to be studied in the near future. The region studied is generally considered as the best for determining the values of Theories I, II and III. An exhaustive study into the very low pressure region will give, however, very
conclusive proof as to whether Theory II or III is to be preferred.
EFFECT OF FOREIGN MATERIALS

The presence of inert gases in the reaction vessel during the course of a reaction is a further important factor in the study of unimolecular gaseous reactions. It is generally believed that inert gases help to maintain the Maxwell-Boltzmann quota of activated molecules. Thus, if to a low concentration of reactant is added sufficient inert gas to give an appreciable total pressure it might be expected that the rate of the reaction would be raised from the theoretical low pressure rate to a higher value. This is, of course, due to the fact that a collision between a reactant molecule and an inert gas molecule may lead to activation just as well as collisions between two reactant molecules. In fact it has actually been found in certain cases (32, 69, 89), most notably hydrogen, that there is more possibility in producing an activated molecule by collision of a reactant molecule with a hydrogen molecule than by a collision of two reactant molecules.

Since nitrogen had been used to flush out the reaction vessel before use and since carbon dioxide was one of the reaction products runs were made with N₂ or CO₂ present. The data for these are
tabulated in Table II and are graphically shown in Fig. 13. It can be seen from these curves that, although the initial pressure of ethyl chlorocarbonate itself was relatively low the reaction rate approximated the high pressure rate, indicating that the Maxwell-Boltzmann factor was maintained. This was common to both nitrogen and carbon dioxide. The fact that a relatively high concentration of carbon dioxide caused an increase, rather than a decrease, in the specific rate is substantial indication that no reverse reaction occurred. Moreover, inasmuch as the introduction of CO₂ does not increase the reaction rate over that of the steady state (Kₐ) is also evidence that this product of the reaction is in no way serving to catalyze its decomposition.

Further investigation is under way at present to determine more rigidly, as well as quantitatively, the effects of these and other gases. It is our purpose, also, to investigate the reaction both in the liquid phase and in solution. Photochemical as well as thermal activation will be employed for studying the reaction. Such work should afford a closer articulation and better correlation of gas and solution kinetics.
SUMMARY

1. It has been found that iodine trichloride, though decomposing at low temperatures, is not suited for kinetic study because of the difficulty of preparing it in a pure state free from the monomer form and further because it yields heterogeneous products over the thermal decomposition range.

2. Dimethyl and diethyl carbonates have been found to decompose, in the region of 200 °C., unimolecularly in the gaseous state; this decomposition being a heterogeneous reaction catalyzed by the surface of the enclosing vessel.

3. Ethyl chlorocarbonate has been found to decompose homogeneously and by a unimolecular mechanism between 150 and 195 °C. and over pressure ranges from 20 to 700 mm. of mercury. It is, therefore, a reaction quite suitable for kinetic study. The study of this reaction was made in an all-glass system completely immersed in an oil thermostat, photoelectrically controlled. The reaction was followed by noting the increase in pressure occurring as recorded by a glass barostat.

4. The specific rate of the reaction in the high pressure region is given by the equation:
5. It has been found that at low pressures, the rate constant falls appreciably, substantiating the modified collision hypothesis for molecular activation.

6. The hypothesis suggested by Kassel and familiarly known as Theory III has been found to best interpret the experimental data over the pressure ranges investigated.

7. No appreciable reverse reaction occurs.

8. CO₂ and N₂ are without effect upon the reaction except insofar as they serve to increase the rate of activation by maintaining the Maxwell-Boltzmann energy distribution.
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BIOGRAPHY

Harold Arthur Frediani was born in New York City on December 23, 1911. His primary education was obtained in the public schools of the City of New York.

After being graduated from New Utrecht High School he attended New York University for two years. At the end of this time he accepted an industrial position which he retained until the summer of 1933.

Voluntarily resigning his position he continued his higher education at the State University of Iowa. He was graduated from this institution with the B. A. degree in 1934.

He remained at Iowa on a research appointment from June 1934 until July 1936 at which time he received the M. S. degree in Chemistry.

In 1935 he was appointed a teaching fellow at Louisiana State University and began work upon this investigation which has continued until the present time.
EXAMINATION AND THESIS REPORT

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Title of Thesis: A Kinetic Study Of A Homogeneous, Unimolecular Gaseous Decomposition Reaction

Approved:

Date:

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