The Kinetics of the Decomposition of Ethyl-Chlorocarbonate.

George Francis Kirby

Louisiana State University and Agricultural & Mechanical College

Follow this and additional works at: https://repository.lsu.edu/gradschool_disstheses

Part of the Chemistry Commons

Recommended Citation
https://repository.lsu.edu/gradschool_disstheses/7814

This Dissertation is brought to you for free and open access by the Graduate School at LSU Scholarly Repository. It has been accepted for inclusion in LSU Historical Dissertations and Theses by an authorized administrator of LSU Scholarly Repository. For more information, please contact gradetd@lsu.edu.
MANUSCRIPT THESES

Unpublished theses submitted for the master's and doctor's degrees and deposited in the Louisiana State University Library are available for inspection. Use of any thesis is limited by the rights of the author. Bibliographical references may be noted, but passages may not be copied unless the author has given permission. Credit must be given in subsequent written or published work.

A library which borrows this thesis for use by its clientele is expected to make sure that the borrower is aware of the above restrictions.

LOUISIANA STATE UNIVERSITY LIBRARY
THE KINETICS OF THE DECOMPOSITION OF
ETHYL CHLOROCARBONATE

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

By

George Francis Kirby, Jr.
B. A., Louisiana College, 1936
M. S., Louisiana State University, 1938
1940
ACKNOWLEDGMENT

The author wishes to express his sincere appreciation for the advice and assistance of Dr. A. R. Choppin, who directed this work.
TABLE OF CONTENTS

I. Introduction ............................................. 1
II. Review of the Literature ................................. 4
III. The Static Method ....................................... 15
   1. Experimental ........................................... 15
   2. Results .................................................. 17
   3. Discussion of Results (I) ............................. 35
IV. The Dynamic Method ..................................... 39
   1. Experimental ........................................... 39
   2. Results .................................................. 49
   3. Discussion of Results (II) ............................. 54
V. Analytical Procedures ................................... 56
VI. The Semi-Empirical Calculation of
    Activation Energy ....................................... 58
VII. Conclusion ............................................ 63
VIII. Summary ............................................ 65
IX. Bibliography ........................................... 69
X. Vita ..................................................... 78
TABLE OF ILLUSTRATIONS

1. Pressure - Time Curves in the Presence of Foreign Gases ... 22
2. First Order Rate Curves ............................................. 23
3. Rate Curves, Chlorine and Hydrogen as Foreign Gases .......... 24
4. The Effect of Water Vapor ........................................... 25
5. Pressure - Time Curves, Nitric Oxide as Foreign Gas .......... 26
6. First Order Rate Influence of Nitric Oxide ....................... 27
7. Induction Time - Partial Pressure of Nitric Oxide ............ 28
8. Low Pressure Approach to Second Order Rate .................... 33
9. Pressure - Rate Constant at 175° ................................ 34
10. Diagram of Dynamic Apparatus ....................................... 46
11. Calibration of Flowmeter ............................................ 47
12. Vapor Pressure ...................................................... 48
ABSTRACT

The investigation reported here deals with the kinetics of the gas phase decomposition of ethyl chlorocarbonate. The reaction has previously been studied in this laboratory and found to be homogeneous and unimolecular. Several lines of approach are described in the present report in an attempt to more comprehensively develop the kinetic treatment of the reaction.

The low pressure region has been investigated, and the specific rate constant has been found to decrease below 175 mm., approaching a second order rate quite closely as the pressure reaches the order of 10 mm. This is in agreement with the collision theory for complex molecules.

The effects of foreign gases have been extensively studied. Carbon dioxide, nitrogen and oxygen are normal in their effect, acting to maintain the high pressure rate effectively. Carbon tetrachloride, benzene and nitrous oxide cause slight depressions, and hexane a slight increase. These substances may be considered as comparatively inert relative to the reaction, and their effect points toward a mechanism with few complicating factors.

Water vapor reacts with ethyl chlorocarbonate in the gas phase and the products slightly catalyze the decomposition of any chlorocarbonate in excess. Chlorine catalyzes the decomposition. This catalysis may involve
the walls, since its extent does not depend on the partial pressure chlorine.

Nitric oxide at low partial pressures has very little effect, but as the partial pressures are increased an induction period appears, followed by reaction at rates slightly above normal. This effect is anomalous, and eludes explanation on the basis of the present work. Its description is apparently reduced to chemical interaction or to a specialized wall effect. Nitric oxide is normally used to detect chains propagated by the aliphatic free radicals, indicating their presence by a total inhibition of the chain carried reaction. In this capacity it is effective at very low partial pressures. Obviously some other effect is present in the case of ethyl chlorocarbonate.

The dynamic method was used to investigate the initial minutes of the reaction. Here the gas was allowed to flow through a thermostated reaction tube and the products were chemically analyzed. This method showed the rate to be higher at the beginning of the reaction. This is in accord with the idea that the walls might have some effect on the reaction, becoming deactivated after a few minutes of contact with the reactant and products.

Analytical work, both chemical and spectrographic, indicates that the overwhelming portion of the reaction is simple in nature, supporting the kinetic data which indicates that the reaction can be adequately described by some simple mechanism.
On the basis of the experimental work, this mechanism is most logically taken as an internal rearrangement of the ethyl chlorocarbonate molecule with the formation of ethyl chloride and the elimination of carbon dioxide.

The calculation of the activation energy of such a reaction has been initiated, using the semi-empirical method of treatment. This calculation demonstrates the existence of a well defined energy barrier whose value is in fair agreement with the experimentally determined energy of activation. A further refinement of the calculations should lead to even more satisfactory results.
INTRODUCTION

The recent theories of chemical kinetics and their supporting experimental data have provided very clear pictures of the fundamental processes of activation and reaction. Many of the details of speed and mechanism, however, remain uncertain. The field remains open for pioneer work, and there will long be a place for precise application of experiment to theory.

In chemical kinetics the simplest method of approach is through the study of reactions in the gaseous state. Here the complicating and obscure effects of solvent action are avoided. In addition the kinetic theory of gases, as developed by mathematical physics, affords a considerable amount of detailed information about the internal state of gases.

The most important factor in the theory of kinetics is the activation of molecules. Reactions have been activated by molecular collisions, light quanta and electrons. Photochemical work is capable of precision and conciseness to a greater extent than electronic. More common and of enormous importance is the study of reactions which proceed through molecular collisions, with their great thermal effects.

To such reactions the theoretical kineticians have devoted concerted attention in recent years. They have been provided with many reactions whose characteristics are quite favorable, and with a few which approach ideal behavior.
The literature abounds with articles dealing with reaction velocity. But many of these are invalidated by an inadequate consideration of the topics of study or by a failure to eliminate errors of experiment. So insidious are these sources of error that they were long ignored. Among them may be found the effects of lubricants and other foreign materials, inadequate treatment of dead spaces, temperature distribution etc. While experimental workers have been slow in refining their techniques, theoretical work has in many cases forged steadily ahead. However, the great complexity of many reactions limits the field to the treatment of a few fundamental cases.

Experimental studies (22) of decomposition reactions have been about equally distributed between the static and the dynamic methods of analysis. In the one method the volume of the reactant is held constant and the reaction is followed by a change in pressure or by intermittent sampling. In the other the reaction space remains constant and the volume of the gas is allowed to change. A sensibly constant pressure gradient is maintained by a flow gradient throughout the reaction space. The merits of these methods have been sources of disagreement; but it seems evident that each will maintain a sphere of usefulness in which it excels. Certainly their interrelation in the determination of questionable points for a single reaction will continue to be of value.

Such a check has been found desirable in the study of
ethyl chlorocarbonate. The dynamic method has been used to secure additional valuable information regarding wall effects, low pressure reaction rates and the mechanism of the initial stages of the reaction.

This investigation has attempted to employ all available techniques in the establishment of the reaction involved as an adequate kinetic study. Particular attention has been given to the probable mechanism and to its general adaptability to the modern theories of kinetics.
A few gas phase reactions involving decomposition have been studied quantitatively from the kinetic standpoint. A small number of these are simple organic reactions similar to ethyl chlorocarbonate. Some of these, as listed by Daniels (12), have become quite generally accepted as legitimate first order reactions. But the progress in the field has not been so imposing as the later references might indicate. The cautious and discordant note struck by Pease (43) during a recent symposium on the subject is sharply reminiscent of the earlier uncertainty which pervaded the field.

The last quarter century has been the proposal of the radiation hypothesis of Lewis (36) and Perrin, and its subsequent discard as a result of the work of Langmuir (32) and other investigators. During the earlier years of this period the theory of Lindemann (37) suggested a very real insight into the rate problem. The contributions of Christiansen (5), Rice (50), Hinshelwood (26) and Kassel (30) were refinements of value.

These developments of theory have been sufficiently well supported by experiment, and by 1935 the opinion prevailed that the existing theories of unimolecular reactions were essentially correct and that they should require only minor improvements in the near future.

The succeeding years of experimentation have largely borne out this idea. Further illuminating treatments of
the activated state and of the frequency factor in the Arrhenius equation have made little change in the older theories.

A general summary of the unimolecular decomposition of complex molecules is as follows. Molecules become activated by collision and then react or become deactivated by collision. The rate of activation depends on the frequency of collision and there is a time lag for localization of energy in some effective bond of the molecule. At normal pressures the number of activated molecules decomposing is very small compared to the total number becoming deactivated. A comprehensive discussion of this elaborated collision theory, and much of the mathematical treatment has been given by Frediani (23). This expanded theory has been successful in explaining most of the anomalies of the simple collision hypothesis, viz., the absolute value of the activation energy of unimolecular reactions and the fact that the rates of unimolecular reactions are independent of collision frequency.

Competing with this hypothesis and increasing in favor at the present time is the hypothesis of chain reactions. Such a reaction is most simply defined as one in which the products successively react with the initial material in a series of cycles. This sort of mechanism can be used to show the attainment of a steady state in which the concentration of material for the rate determining step is proportional to the concentration of the initial material.

Such chains are predominantly thought to be
stoichiometrical in nature; that is, they are thought to proceed through successive chemical steps. Formerly many chain reactions were explained on the basis of "energy chains". In this type of reaction the products were supposed to transmit their excess thermal energy to reactant molecules with this process leading to further reaction. However, at present the majority opinion favors the stoichiometrical chain. The phenomenon of negative catalysis can be satisfactorily explained only by a stoichiometrical chain mechanism. The process also furnishes an ideal explanation of explosive reactions.

Bound inevitably to the chain reaction mechanism is the use of free radicals in chain construction. The importance and application of free radical chains to chemical kinetics may be credited chiefly to F. O. Rice (51). His methods of analysis coupled with spectroscopy have contributed greatly to our knowledge of these fleeting molecular fragments.

The elaborated collision hypothesis is not to be considered as opposing the chain theory. Both are undoubtedly needed in the expanding scheme of kinetics, and there will be an increasing number of reactions explained by each. Indeed, there seem to be certain reactions which need both hypotheses for a complete explanation. Hinshelwood has postulated two competing mechanisms in the decomposition of several organic compounds. This discrimination has been made possible by the development of a method for detecting the presence of chains initiated by the aliphatic free
The method depends on the fact that nitric oxide combines with the molecular fragments and thus acts as a chain breaker. A chain reaction occurring at pressures lower than an atmosphere is almost completely inhibited by the addition of quantities of nitric oxide of the order of 1 mm. This inhibition has been summarized in an article by Hinshelwood and Staveley (57). Later investigations (15, 52) by others have shown its effectiveness for such chains as are carried by aliphatic free radicals.

By comparing the rates of reactions inhibited in this manner with the uninhibited rates some reactions have been found to proceed partly through short chains and partly by a mechanism of internal rearrangement. The radical propagated chains become predominant at high temperatures and pressures in the absence of wall effects. This method has also served as an auxiliary indication of chain length.

Still a further point to be considered in discussing these hypotheses is the more tangible one of practicability. While the collision theory is very efficient in describing simple reactions, the mathematical treatment of its more refined phases often becomes quite involved. The theory might work reasonable well for, let us say, the initial scission of a molecule in the radical producing step. But such a step often makes up a very minor part of a complex chain reaction. These succeeding steps would multiply the difficulties of application many times, so that any advantage of preciseness would be lost to the elaborated
collision method in a maze of uncertain calculations. Here the chain mechanism is at its best. Recognizing the uncertainties involved it describes the situation by a series of logical steps, chosen for their utility and so arranged that their summation gives a fair picture of the overall process. The accuracy of the estimation of the rates of these individual steps, and their energies of activation are often not highly accurate. For this reason, and because it would be difficult to define precisely the outcome of several competing mechanisms it seems that predictions of rate and products must remain definitely limited in accuracy. The chain hypothesis finds this no disadvantage, but is content with a highly probable description which fits the experimental facts.

In view of the developments outlined above the investigation of any reaction in regard to mechanism must take these two methods of approach into account. Most reactions can be made to conform satisfactorily with one of the hypotheses. With these theoretical descriptions as a foundation the experimentalist has now to further test their utility, and furnish other material for their possible perfection.

The Arrhenius equation is still of great importance to the kineticist. With amazing accuracy it relates reaction velocity and temperature over wide ranges. Let us examine it qualitatively for a moment:

\[ k = se^{-E/RT} \]
The term $s$ is temperature variable, but compared to the exponential variation of $E$, it may usually be considered constant. Obviously then a fair estimation of $E$ would enable quite accurate predictions of the specific rate constant $k$. It is to this end that much theoretical work has been directed during the past decade. Chemical reactions take place when existing bonds break and new ones are formed. Ordinarily these two processes are simultaneous, though they can take place through complete separation and subsequent combination. For such a rearrangement to take place the system must increase in energy. This energy will vary with the manner of decomposition. If the new bond is formed along such a path that the old bond is gradually supplanted the active centers will reach a point in time when the two bonds are of approximately the same length, following which the new bond will become stabilized and the old completely disrupted. This path required the minimum energy for reaction. The maximum energy is required for complete dissociation and combination from points of zero potential. Calculations may then be made on the basis of interatomic distances. Complete considerations must include all possible atomic interactions, a stupendous task. But certain valid assumptions greatly simplify this treatment. One of these is to consider the nuclear energy constant and work only with the electronic. However, the solutions of the Schrödinger wave equation for even such a simplified case would be very difficult. The approximation
of London (38) has been used by Eyring (18, 19) to circumvent this difficulty. While not physically rigorous the method has been successful in predicting activation energies in agreement with those determined by experiment.

The empirical equation of Morse:

\[ E = D(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}) \]

is employed to describe the energy of the system in terms of the interatomic distances. Here \( E \) is the energy, \( D \) the heat of dissociation plus zero point energy, \( r_0 \) the normal interatomic distance, \( r \) the actual distance and \( a \) is constant. The values of \( D \) are derived from spectroscopic data, and \( r_0 \) from a number of physical methods.

If a three dimensional contour map is made, plotting as coordinates the two interatomic distances concerned and the energy of the system the reaction may be traced over its minimum energy path. Such a path, usually symmetrical, will be found over the energy surface. Only the binding electrons are considered, and the atoms are assumed to be held together by fixed proportions of coulombic and interchange binding energy. Eyring (19) has had success in setting these values at 14% and 86% respectively, though actually rather wide variations have been noted. The total energy equations for systems of three to nine electrons have been evaluated and placed in convenient form. These equations are functions of each important interatomic distance, taking the percentage of coulombic and interchange energy as constant. The part of the total energy contained in each single bond is
evaluated by means of the Morse equation mentioned above. By summation the total energy of the system is obtained. These calculations may often be reduced in number if made in the neighborhood of the correct distances. Contour lines connecting will form a contour map of the various energy paths of the reaction, showing one path whose energy of activation is a minimum.

This method has been used with success in a number of chemical reactions, though the results are often in error by as much as 3 kilocalories. It is especially useful in the treatment of relative rates, where errors common to all calculations are not significant. A very good example of the chemical application of the method is the treatment of all the possible reactions between ethylene and the halogens as carried out by Sherman and Sun (55). Other applications are fairly numerous. This so-called "semi-empirical" method is now quite familiar to chemists. While it may be reemphasized that the treatment is not rigorous (11), it is justified by the success of its predictions.

Related qualitatively to the above system, but much more satisfactorily developed, is the "transition state" (20) method, largely the work of Eyring (21), Pelzer and Wigner (44), and qualitatively suggested by Rodebush (53) and Lakéé (31). This method is purely statistical in treatment. The transition state, or activated complex, is considered to be an abnormal intermediate which decomposes
to give the products of the reaction. One immediately sees the similarity to the solution theory of Bronsted.

If the activated complex be a real state, then it is possible to write the equilibrium constant between the reactants and complex, and to set up a general equation for the velocity:

\[ k = pKv = p \frac{f^* k'T}{f} \frac{e^{-E/RT}}{h} \]

where \( K \) is the equilibrium constant mentioned above, \( v \) the average rate at which the molecules of the activated complex attain the energy of activation, \( p \) the probability that the activated complex will decompose to give the products and \( k' \) the Boltzmann constant; \( f^* \) and \( f \) are the partition functions for the activated complex and the normal molecules respectively.

Since thermodynamically

\[ K = e^{S/R} e^{-H/RT} \]

the above equation may be written

\[ k = p \frac{k'T}{h} e^{S/R - H/RT} \]

The term \( \frac{k'T}{h} \) has been identified with the parameter \( s \) in the Arrhenius equation and has been suggested as being related to the entropy concept. This is at slight variance with Hinshelwood who prefers to separate the quantity into two others, one related to the collision number, the other acting as a probability factor involving all other variables. It is of interest here to mention the suggestion that \( E_\text{r} \)
activation energy, is probably temperature variable, and that an entropy of activation must exist if this is true. Present experimental methods are not sufficiently accurate to amplify this point further.

At first sight it may appear that there is a great deal of divergence in the theoretical methods of approach. Actually this is not the case. Hinshelwood (27) points the virtual equivalence of the collision theory and the transition state method, and is corroborated by Polanyi (45).

Returning for a while to the experimental side, there is no indication of gas phase reaction velocity measurements having been made previously on the alkyl chlorocarbonates aside from the study of isobutyl chlorocarbonate; this decomposition, studied by Lessig (35) was found to be quite complex at the temperatures involved.

It might be of interest to indicate the possible modes of thermal decomposition of the chlorocarbonates as a whole, since they are exemplified by fairly simple reactions and follow the obvious paths. Phenyl chloroformate (3) decomposes according to the reaction:

$$2C_6H_5-O-COCl \rightarrow C_6H_5-O-C^0 -O-C_6H_5 + COCl_2$$

Trichloromethyl chloroformate follows either of two mechanisms:

$$\text{Cl}_3\text{C} - \text{COCl} \xrightarrow{\text{heat}} 2\text{COCl}_2$$

$$\text{Cl}_3\text{C} - \text{COCl} \xrightarrow{\text{AlCl}_3} \text{CCl}_4 + \text{CO}_2$$
The most common decomposition is the following:

\[ \text{C}_2\text{H}_5\text{CO}_2\text{Cl} \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{CO}_2 \]

The stability of the chlorocarbonates varies quite widely with structure, certain of the aryl compounds being reported as unstable at room temperature (3).

Important ideas as to the structure of the chloroformates and carbonates have been gained from dipole measurements (39, 69).
THE STATIC METHOD

A static method of investigation was used by Frediani in the original investigation of the decomposition of ethyl chlorocarbonate. This method has distinct advantages of speed and accuracy. Moreover, since this original investigation has been the basis of comparative effects from a number of standpoints, its methods have been continued for certain experiments. Thus, errors of comparison were minimized. The method was used for two purposes: the extension of the low pressure data, and for a quite complete investigation of the effects of foreign materials. The first of these has been amplified slightly by dynamic work.

Experimental:–

The experimental method has been described in detail in the first publication of the ethyl chlorocarbonate series (6). Few alterations were made in the experimental unit. The thermostat was essentially the same: a platinum resistance thermometer, optical lever, and vacuum tube photoelectric cell which gave a temperature regulation to 0.01°. Dynamic balancing based on the all glass manometer of Daniels was used for pressure control, and for low pressures a Fisher micro-manometer with an accuracy of 0.05 mm. of mercury, and an inclined arm manometer were employed. Experiments made with ground glass joints in the pressure system added something in the way of convenience. Slight modifications of the cell construction sufficed to
lend greater accuracy to the low pressure measurements. Here the body of the reaction cell was made somewhat larger than the conventional type to accommodate a glass diaphragm of increased diameter. By reducing the diaphragm thickness until it could withstand a pressure difference of only 50 to 60 mm, satisfactory operation was observed over the range from 5-20 mm.

While the method has been thoroughly described in other sources it might be advisable here to review the general procedure as applied to a rate determination. It will be recognized that the low pressure work was carried out using the same general procedure, though that described here may be taken as referring specifically to a reaction measured in the presence of a foreign gas.

Before the first run with any gas each reaction cell was thoroughly cleaned and flamed. A small bulb containing ethyl chlorocarbonate was first sealed into the cell and the foreign gas supply attached to the cell through a small side arm. The cell was then alternately evacuated and rinsed with the gas to displace absorbed molecules of air and water vapor. The gas was next admitted to the desired pressure and the reaction vessel sealed. The vessel was finally brought to the temperature of the bath and the reactant bulb broken with the glass enclosed hammer.

When liquids of high vapor pressure were used as foreign materials a similar procedure was followed. However, when the vapor pressure was too low for the effective
utilization of this method solutions of the liquid in ethyl chloroformate were prepared. These solutions were chosen by composition to give approximately the desired partial pressure of each component, introduced into bulbs, and discharged in the cell in the usual way. The substances were tested thoroughly for chemical interaction before this procedure was employed.

In some cases the foreign substance was admitted at room temperature and the gas laws used to predict its partial pressure at reaction temperature. In other cases the foreign gas was allowed to come to temperature equilibrium before breaking the reactant bulb. Checks between the two methods showed the error to be negligible.

Oxygen, carbon dioxide, hydrogen and nitrogen were purified in conventional washing procedures for certain runs. They were not refractionated, however. Commercial carbon tetrachloride, hexane and benzene were subjected to careful fractionation. Nitric oxide was prepared according to the method of Johnston and Giauque (29) and stored in a five liter container. Because of the difficulty of separating nitric oxide from certain other oxides of nitrogen, particularly nitrous oxide, the effect of the latter compound on the reaction was investigated. For this purpose a cylinder of the commercial product was used without further purification.

Experimental Results:— Since the rate at 175° is of a
convenient magnitude and approximately in the middle of the measurable range, this temperature was used for the greater number of runs on foreign gas effects. The other temperatures used were 165° and 185°. The effects of foreign materials on the rate were catalogued by comparison with the values for the specific rate constant k obtained in the previous research, and checked by controls during the present investigation. In view of the effect of initial pressure upon the rate constant at values below 200 mm, most of the runs reported here were made in the high pressure region. Where low pressure runs were made this effect was taken into account in tabulating the effect of foreign materials.

Carbon dioxide was first investigated as a foreign gas. This was done for the purpose of testing the reaction for reversibility. No measurable equilibrium effect could be detected, indicating that excess carbon dioxide does not affect the reaction chemically. However, the carbon dioxide molecules seemed quite effective in maintaining the frequency factor and hence the rate. No appreciable decrease in the value of k was detected as long as the total initial pressure remained above 150 mm.

Nitrogen and oxygen were likewise found to have no effect other than to serve quite effectively in maintaining the high pressure energy distribution. Curves showing typical rates of decomposition in the presence of these gases are shown in Fig. 1 and 2. The decomposition of a
sample of the pure substance is shown for reference. Curves have also been included to show the effects of benzene, carbon tetrachloride and hexane. As may be seen from Table I and from Fig. 2, hexane is effective in maintaining the rate, raising it slightly above its normal value. Benzene and carbon tetrachloride, on the other hand, are not so effective. These substances, however, give easily reproducible results of such a nature that they may be regarded as inert.

Hydrogen is usually most effective in maintaining the rate at low pressures of reactant. However, in the case of ethyl chlorocarbonate hydrogen fails to fulfil this usual function. It is less effective than the above mentioned gases.

Chlorine exhibits a positive catalytic effect as shown in Fig. 3. The catalytic effect does not seem to vary with the amount of chlorine present over the range of investigated pressures. Analyses of the products checked the theoretical within experimental error.

Ethyl chlorocarbonate is known to undergo both ammonolysis and hydrolysis. In the liquid state these reactions take place at the phase boundary, the reaction with aqueous ammonia proceeding rapidly and that with water at a much slower rate. At 175° the hydrolysis proceeds quite rapidly and the products of hydrolysis slightly catalyze the thermal decomposition of any ethyl chlorocarbonate in excess. The presence of simultaneous reactions,
one the more rapid, is apparent. The initial stages of the reaction follow neither a first nor second order rate. If the matter were more thoroughly investigated one might expect a definite dependence of rate upon the concentration of water vapor. In view of the difficulty of separating these reactions the calculations of rate give at best a rough picture of the process, and were included as a qualitative estimate of the final effect of the bimolecular products upon the unimolecular reaction. At the end of a reaction hydrogen chloride, ethyl chloride, ethyl alcohol and carbon dioxide were determined analytically as the products.

Inhibition by nitric oxide has been widely used as a test for one type of chain mechanism. Hinshelwood (61) has found low partial pressures of this gas quite effective in suppressing the rates of a number of reactions which are known to proceed through aliphatic free radical mechanisms. Pressures of nitric oxide of the order of one or two mm., suggested as being sufficient to seriously alter the reaction rate, were found to have no effect in the present case. As the partial pressure of nitric oxide was increased, however, a period of induction was observed. The length of the induction period varied with the pressure of the nitric oxide (Fig. 5 and 6). At the end of the initial inhibition the reaction proceeded with a velocity greater than normal. Rate constant values obtained for this region showed a consistent increase over normal
values (Table I).

In view of the difficulty of obtaining nitric oxide free from traces of nitrous oxide several runs were made with nitrous oxide to determine its effect on the reaction. Smooth curves were the result, with rates slightly depressed.
Figure 2

Graph showing the log concentration over time for various compounds: 
- CO₂
- O₂
- N₂
- C₆H₆
- CCl₄
- N₂O
- C₆H₄

Time (min.)
Figure 4

![Graph showing log C against time (min.) with three curves. The x-axis represents time in minutes, ranging from 0 to 40, and the y-axis represents log C. The curves depict different trends and are labeled as G1p, G2p, and G3p.](image)
Figure 5

- NC -  30 ○
- 50 □
- 71 ■
- 95 ▲
Figure 5

NO-16 mm. •
NO-30 mm. ●
-50 mm. ●
-71 mm. □
-95 mm. ▲
Table I
(Temperature 175°)

<table>
<thead>
<tr>
<th>P&lt;sub&gt;total&lt;/sub&gt;</th>
<th>P&lt;sub&gt;foreign gas&lt;/sub&gt;</th>
<th>k&lt;sub&gt;observe&lt;/sub&gt;</th>
<th>k&lt;sub&gt;pure reactant&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>124</td>
<td>30</td>
<td>0.040</td>
<td>0.034</td>
</tr>
<tr>
<td>148</td>
<td>120</td>
<td>0.043</td>
<td>0.037</td>
</tr>
<tr>
<td>200</td>
<td>65</td>
<td>0.047</td>
<td>0.044</td>
</tr>
<tr>
<td>236</td>
<td>51</td>
<td>0.0403</td>
<td>0.045</td>
</tr>
<tr>
<td>402</td>
<td>284</td>
<td>0.0501</td>
<td>0.045</td>
</tr>
<tr>
<td>Oxygen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>15</td>
<td>0.0153</td>
<td>0.015</td>
</tr>
<tr>
<td>228</td>
<td>115</td>
<td>0.0373</td>
<td>0.045</td>
</tr>
<tr>
<td>280</td>
<td>251</td>
<td>0.0404</td>
<td>0.045</td>
</tr>
<tr>
<td>322</td>
<td>80</td>
<td>0.0478</td>
<td>0.045</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>45</td>
<td>0.0301</td>
<td>0.030</td>
</tr>
<tr>
<td>201</td>
<td>71</td>
<td>0.0309</td>
<td>0.044</td>
</tr>
<tr>
<td>286</td>
<td>206</td>
<td>0.0481</td>
<td>0.045</td>
</tr>
<tr>
<td>285</td>
<td>178</td>
<td>0.052</td>
<td>0.045</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>386</td>
<td>327</td>
<td>0.0234</td>
<td>0.045</td>
</tr>
<tr>
<td>337</td>
<td>294</td>
<td>0.0162</td>
<td>0.045</td>
</tr>
<tr>
<td>146</td>
<td>98</td>
<td>0.0221</td>
<td>0.037</td>
</tr>
<tr>
<td>131</td>
<td>57</td>
<td>0.0398</td>
<td>0.036</td>
</tr>
<tr>
<td>Chlorine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>50</td>
<td>0.114</td>
<td>0.045</td>
</tr>
<tr>
<td>301</td>
<td>144</td>
<td>0.099</td>
<td>0.045</td>
</tr>
<tr>
<td>350</td>
<td>155</td>
<td>0.106</td>
<td>0.045</td>
</tr>
<tr>
<td>527</td>
<td>342</td>
<td>0.177</td>
<td>0.045</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>136</td>
<td>70</td>
<td>0.0816</td>
<td>0.036</td>
</tr>
<tr>
<td>151</td>
<td>14</td>
<td>0.0781</td>
<td>0.038</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>50</td>
<td>0.0193</td>
<td>0.026</td>
</tr>
<tr>
<td>125</td>
<td>60</td>
<td>0.0174</td>
<td>0.033</td>
</tr>
<tr>
<td>168</td>
<td>35</td>
<td>0.0168</td>
<td>0.039</td>
</tr>
<tr>
<td>225</td>
<td>111</td>
<td>0.0224</td>
<td>0.045</td>
</tr>
<tr>
<td>268*</td>
<td>101</td>
<td>0.0628</td>
<td>0.089</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td><strong>Benzene</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>104</td>
<td>0.0295</td>
<td>0.044</td>
</tr>
<tr>
<td>493</td>
<td>133</td>
<td>0.0357</td>
<td>0.045</td>
</tr>
<tr>
<td><strong>Hexane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>108</td>
<td>54</td>
<td>0.0523</td>
<td>0.031</td>
</tr>
<tr>
<td>164</td>
<td>82</td>
<td>0.0532</td>
<td>0.039</td>
</tr>
<tr>
<td><strong>Carbon Tetrachloride</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>256</td>
<td>192</td>
<td>0.0334</td>
<td>0.045</td>
</tr>
<tr>
<td>260</td>
<td>130</td>
<td>0.0388</td>
<td>0.045</td>
</tr>
<tr>
<td>308</td>
<td>231</td>
<td>0.0356</td>
<td>0.045</td>
</tr>
<tr>
<td><strong>Nitric Oxide</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>155*</td>
<td>30</td>
<td>0.0986</td>
<td>0.089</td>
</tr>
<tr>
<td>236</td>
<td>72</td>
<td>0.0659</td>
<td>0.045</td>
</tr>
<tr>
<td>281</td>
<td>50</td>
<td>0.0571</td>
<td>0.045</td>
</tr>
<tr>
<td>320</td>
<td>45</td>
<td>0.0555</td>
<td>0.045</td>
</tr>
<tr>
<td>319</td>
<td>16</td>
<td>0.0466</td>
<td>0.045</td>
</tr>
<tr>
<td>350</td>
<td>30</td>
<td>0.0650</td>
<td>0.045</td>
</tr>
</tbody>
</table>

* Temperature 185°
A rate decrease can be observed at fairly high pressures and was easily detected without further refining techniques. The low pressure data have been extended, however, in prospect of determining the type of curve finally approached. Table II may be used to supplement this graph of rate against pressure. A few successful dynamic experiments have been included in this group to show their consistent behavior. They will be discussed in more detail in the following pages.

Figure 8, in which the low pressure approach to a second order rate is clearly shown, is also of interest. Here the reciprocal of reactant concentration against time is found to conform at low initial pressures to the straight line function. This conformity continues through 30 min. at \( p_0 \) values of the order of 10 mm. Such plots are indicative of second order reaction.
Table II

<table>
<thead>
<tr>
<th>$P_1$(mm)</th>
<th>$k_s$ (min.)</th>
<th>$k/k_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>212</td>
<td>0.044</td>
<td>0.99</td>
</tr>
<tr>
<td>152</td>
<td>0.035</td>
<td>0.77</td>
</tr>
<tr>
<td>126</td>
<td>0.034</td>
<td>0.76</td>
</tr>
<tr>
<td>102</td>
<td>0.030</td>
<td>0.68</td>
</tr>
<tr>
<td>85</td>
<td>0.028</td>
<td>0.61</td>
</tr>
<tr>
<td>45</td>
<td>0.026</td>
<td>0.58</td>
</tr>
<tr>
<td>37</td>
<td>0.021</td>
<td>0.45</td>
</tr>
<tr>
<td>24</td>
<td>0.013</td>
<td>0.29</td>
</tr>
<tr>
<td>18</td>
<td>0.015</td>
<td>0.37</td>
</tr>
</tbody>
</table>
Figure 8

[Graph showing data points and lines on a log-log scale with time (min.) on the x-axis and a function of 1/(x+y) on the y-axis.]
Figure 9

Pressure (mm.)

$k \times 10^2$

50 100 150 200
DISCUSSION OF RESULTS (I)

Let us first consider the results of the static experiments involving foreign gases. For this purpose occasional reference to Table I and Figs. 1-7 will be helpful. For the sake of clarity these results will be very briefly recounted.

In the absence of a measurable equilibrium value for the reaction, carbon dioxide would be expected to aid in maintaining the rate. Oxygen and nitrogen fulfil a similar function, and other inert materials show slight influences. Benzene, carbon tetrachloride and nitrous oxide are not so effective in rate maintenance, but their effect is not so great as to be remarkable. Hexane raises the rate constant slightly above its high pressure value. There appears to be nothing chemically specific in the action of these substances.

The rate at low pressures is not appreciable picked up by the addition of hydrogen, increasing only as the pressure of the reactant is increased. Similar results have been observed in other cases (25, 68), but no satisfactory explanation has been forthcoming.

Perhaps the most striking foreign gas effect is the apparent catalysis by chlorine. It will be noted from Table I that the specific rate constant is doubled by the addition of moderate amounts of chlorine. However, the increase in rate does not vary markedly with changing partial pressures of chlorine. In the presence of chlorine
the reaction definitely does not follow a first order rate over the first ten minutes. During this period the rate was more nearly second order with respect to the reactant. However, no good agreement for either first or second order reaction velocities was obtained over appreciable periods of time. As a point of interest in this connection it might be mentioned again that ethyl chlorocarbonate was found to decompose rapidly at room temperature in the presence of aluminum chloride and more slowly in the presence of zinc chloride. Other salts of these metals were without effect. It is entirely possible that the mechanism of this catalysis is similar in nature to that of chlorine in the gas phase. If the gas catalysis takes place at the walls with absorbed chlorine atoms acting as active centers a condition of saturated adsorption might govern the extent of catalytic action. Varying the partial pressure of chlorine in the cell would then have little effect on the rate. Rather the extent of catalysis would depend on the amount of chlorine open to contact with the reactant molecules at the walls. To fully exploit this possibility would require extensive variation of the wall surface under different conditions of chlorine saturation.

The use of nitric oxide as a test for the aliphatic free radicals has become a well established kinetic procedure. While the low decomposition temperature and the comparatively slight influence of wall effects in the
present case render the presence of such radicals extremely unlikely, the effect of nitric oxide was investigated as being of possible interest in other connections. At low partial pressures the gas was found to be without effect on the reaction. As its partial pressure was increased a slight and transient inhibitory effect was observed. This effect became more pronounced with increasing partial pressures until at values of 100 mm an induction period of twenty minutes was observed. The rate of pressure increase following this period was greater than the normal rate, and values of k calculated on the basis of this portion of the curve were higher than normal values. There remains the possibility of some transient chemical interaction between the gas and the reactant, or of some specialized wall effect to which later reference will be made. A catalytic effect of large partial pressures of nitric oxide has been observed in the decomposition of a number of compounds (14, 59, 60). Its mechanism has not been postulated.

Another point which will be of value in our subsequent discussion deals with the coating effect of the walls. Brearley, Kistiakowsky and Stauffer (4) observed that in experiments with t-butyl chloride much more reproducible results were obtained with coated walls. This means simply the use of reaction vessels whose walls have been for an appreciable time in contact with reactant and products at the temperature of reaction. A similar effect has been
reported by Daniels (14) in the decomposition of ethyl bromide. In view of the negligible effect of packing upon the decomposition of ethyl chlorocarbonate no appreciable surface catalysis was expected. However, pressure measurements of decomposition in clean vessels were observed to fluctuate slightly in the initial stages of reaction. Also, after several runs with the same vessel a very thin film of carbon was found on the walls, indicating that at least some small part of the reaction proceeded through disruption and degradation on the walls.

The low pressure runs require little further comment. It may be stated, however, that the rate decrease with lowering pressure is in good agreement with quasi-unimolecular theory. The continually changing order throughout this region is the clearly expected course of action.
THE DYNAMIC METHOD

Experimental: -

The suggestion has previously been made that this reaction might have greater velocities in the early stages. Such a suggestion was hard to verify using the static method because of the difficulty of distinguishing between temperature and reaction effects in this region. The dynamic method offered the most reasonable solution to this problem. Here the reaction time may be vastly decreased and the partial pressure of the reactant likewise lowered indefinitely. Admittedly this method is not capable of as great accuracy as the static type, but its results are not inaccurate enough to lose their value. Experimental procedures are more exacting and tedious and the work is much slower.

In order to measure significant reaction velocities during the initial minutes it was necessary to work with total pressures well above the point at which the rate decrease begins to occur. Such a pressure was conveniently attained by using nitrogen as a carrier gas for the reactant. The total pressure was then atmospheric plus the pressure resistance in the system. In the low pressure experiments no carrier gas was allowed and the pressure was regulated by controlling the temperature of the reactant.

Essentially the experiments consisted in streaming the reactant through a thermostated reaction chamber at a
constant rate of flow and under a constant pressure. The decomposition products were collected and analyzed after passing through the reaction zone.

The thermostat in this case was a filtercell insulated earthenware vessel of three gallons capacity. Heating was done with a 250 watt ring type immersion heater, and regulation was accomplished using a precision relay, mercury regulator and a 100 watt light bulb. The specially constructed mercury regulator was capable of an accuracy greater than 0.1°C. at 177°C.

Two sets of experiments were run using the dynamic method. In the first of these nitrogen was passed through a pressure regulator, then through a calibrated flow meter. Following this the gas was bubbled through ethyl chloro-carbonate. The reactant was placed in a semi micro bubbler immersed in a constant temperature mixture, and the vapor pressure kept constant. Following this operation the mixture of gases passed into the reaction zone consisting of a glass coil 6 mm. in diameter and about 150 cm. in length. Immediately following the reaction zone the products were collected for analysis. The bubbler was constructed with a small capacity to allow frequent replacement of reactant and thus to eliminate chances of contamination.

For experiments in which no carrier gas was used the system was much the same. However, an all glass needle valve (22) was interposed in the line to facilitate control.
The valve was solenoid operated, and functioned successfully in changing the rate of flow over a range of 15 cc. per min. for a pressure difference not greater than 50 mm. Pressures in this case were taken on a Zimmerli gauge to 0.1 mm. The manometer was attached to the system through a trap and stopcock for instantaneous readings at any pressure up to 100 mm. The train was evacuated with a Cenco pump, buffered with a 3 l. flask. The vapor of ethyl chlorocarbonate was allowed to stream through the reaction zone and samples were collected in a vessel immersed in a condensing medium. For higher rates of flow a double trap was used, with the pump in continuous operation.

The flow meter used in this work was of the Venturi type, and equipped with interchangeable capillary orifices. It was filled with n-butyl phthallate and calibrated with commercial nitrogen at atmospheric pressure in cc. per min. of gas. The calibration curves are shown in Fig. 11.

The ethyl chlorocarbonate was kept at constant temperature by immersion in ice-water or dry ice-bromobenzene mixtures contained in a two liter vacuum bottle. These mixtures were not immune to slow temperature changes, but for periods of an hour or more the change was usually less than 0.1°C.

Several methods of analysis were tried with varying success. The essential problem was obviously to find some chemical method of determining the decomposed portion of
the products as well as the total amount of reactant passing through the tube. The latter quantity was determined by the rate of flow and the vapor pressure. However, it was found more convenient to employ a simultaneous chemical determination of reactants and products, and to use the former method as a check. At atmospheric pressure this analysis was carried out continuously by passing the gases through an alcohol-water solution of silver nitrate, then through a drying tube and over ascarite. The carbon dioxide was determined directly by the increase in weight of the ascarite.

The ethyl chloride and ethyl chlorocarbonate were determined together as silver chloride by use of the Volhard method. The precipitation of silver chloride from ethyl chlorocarbonate solutions was catalyzed by the presence of ammonium ions. The extent of catalysis was not determined quantitatively but it has been estimated roughly that by making the precipitating solution about 1 normal in ammonium nitrate the time of complete precipitation of the silver chloride was reduced by half.

The silver nitrate solution was kept at a temperature about -15 or -20°C. to insure condensation of the reactants as the gases were passed through. Thus, even though the reaction was rather slow, there was no loss through evaporation. The lowered temperature also decreased the vapor pressure of the solution to an extent that made the error due to the possible carrying over of alcohol quite
negligible. There was no absorption of gaseous carbon dioxide if three or four drops of nitric acid were added to the silver nitrate solution, and there was no evolution of carbon dioxide from the ethyl chlorocarbonate reaction until fairly high acid concentrations were reached. This fact was attested by passing a current of nitrogen and pure ethyl chlorocarbonate through the precipitating solution, and thence into a solution of \( \text{BaCl}_2 \). Only after an hour or more at room temperature was there any darkening of the \( \text{AgCl} \) precipitate or any measurable evolution of carbon dioxide. The quantitative yield was checked by introducing weighed amounts of ethyl chlorocarbonate into the solution described above and determining the \( \text{AgCl} \) yield. There was no interference due to the \( \text{CO}_2 \). In this check, as in treating the kinetic data, the Volhard method was used to determine the excess \( \text{AgNO}_3 \). Typical data are shown below.

<table>
<thead>
<tr>
<th>( \text{EtClCO}_2 \text{(g.)} )</th>
<th>( \text{Cl(calcd.)} )</th>
<th>( \text{Cl(found)} )</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1801</td>
<td>0.0587</td>
<td>0.0583</td>
<td>0.68</td>
</tr>
<tr>
<td>0.1071</td>
<td>0.0351</td>
<td>0.0349</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Several variations of the above method were used at one time or another. Among the more successful of these, and of value in determining the chlorocarbonate alone, involved the use of ammonia. The chlorocarbonates react instantaneously with an excess of ammonia according to the following reaction:

\[
\text{ROCOCl} + \text{NH}_3 \rightarrow \text{ROCONH}_2 + \text{NH}_4\text{Cl}
\]
Obviously this leaves the chloride in an easily determined form. Accordingly, the CO₂, C₂H₅Cl, C₂H₅CO₂Cl mixture was passed through acidified alcohol at a temperature of -40 to -50°C to remove condensables. The CO₂ passed through the solution and was determined in the usual manner. The alcoholic solution of C₂H₅Cl and C₂H₅CO₂Cl was removed from the train and alcoholic ammonia added to insure rapid conversion of the chloride. The solution was then allowed to rise to room temperature and the chloride determined in the usual way.

In the experiments in which pure ethyl chlorocarbonate was used with no carrier the total mixture of gases was frozen in liquid nitrogen. Two small spiral condensers were employed for this purpose. After the flow of gases was interrupted the condensers were removed from the train. Nitrogen gas was passed slowly through and the temperature allowed to rise gradually by evaporating the surrounding liquid nitrogen. The carrier gas took the products through the alcoholic silver nitrate solution previously described, and the carbon dioxide was again determined in ascarite. An alternative and less satisfactory procedure was to allow the temperature to rise slowly to the sublimation point of CO₂, collect this fraction and determine the EtCl and EtCO₂Cl using ammonia.

By the use of the method outlined above the vapor pressures of ethyl chlorocarbonate and its heat of vaporization were determined over the range 0° to 35°C.
the carrier gas method was employed. The vapor pressure-temperature relationship is shown in Fig. 12.
Figure 10

A- pressure regulator; B- flowmeter; C- bubbler; D- glass needle valve;
E- to reaction tube; F- manometer; G- condenser; H- CO₂ absorption tube.
Figure 11

Tip 1

Tip 2

cc./min. (N₂)
Results:

The kinetic results of this work may well be preceded by a few words on the vapor pressure data collected in the course of the experiments. Many of the features of the well known "gas saturation method" are apparent in the preceding description. In view of the obvious advantages of a knowledge of the general vapor pressure trend in the low pressure region, these experiments were undertaken before the actual dynamic measurement of rate constants.

The pressures are easily calculated from an application of the gas laws, and no further discussion is required. Representative points are summarized in the following table:

<table>
<thead>
<tr>
<th>Temp. °C.</th>
<th>Vap. Press. mm.</th>
<th>1/T x 10⁴</th>
<th>Log p</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.45</td>
<td>34.5</td>
<td>33.8</td>
<td>1.538</td>
</tr>
<tr>
<td>18.1</td>
<td>29.3</td>
<td>34.4</td>
<td>1.468</td>
</tr>
<tr>
<td>16.55</td>
<td>25.5</td>
<td>34.52</td>
<td>1.407</td>
</tr>
<tr>
<td>14.0</td>
<td>23.7</td>
<td>34.8</td>
<td>1.374</td>
</tr>
<tr>
<td>12.7</td>
<td>23.25</td>
<td>35.0</td>
<td>1.367</td>
</tr>
<tr>
<td>5.8</td>
<td>14.01</td>
<td>35.8</td>
<td>1.148</td>
</tr>
<tr>
<td>4.4</td>
<td>12.32</td>
<td>36.0</td>
<td>1.091</td>
</tr>
<tr>
<td>2.0</td>
<td>10.4</td>
<td>36.4</td>
<td>1.020</td>
</tr>
<tr>
<td>0.13</td>
<td>9.84</td>
<td>36.6</td>
<td>0.993</td>
</tr>
</tbody>
</table>

A plot of 1/T vs. log p is shown in Fig. 12. An approximate heat of vaporization was calculated from these values by multiplying - slope x 2.303 x 1.987. This value
was found to be 88.5 cal./g.

A sample tabulation of the data by which one of the above values was calculated is given below:

<table>
<thead>
<tr>
<th>Temperature of EtClCO₂</th>
<th>285.7 Abs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate of flow of nitrogen</td>
<td>16.2 cc/min.</td>
</tr>
<tr>
<td>Time of flow</td>
<td>23.0 min.</td>
</tr>
<tr>
<td>Total volume of gas</td>
<td>372.5 cc.</td>
</tr>
<tr>
<td>Vol. AgNO₃(0.0998N)</td>
<td>10.00 ml.</td>
</tr>
<tr>
<td>Vol. KCNS(0.1131N)</td>
<td>4.40 ml.</td>
</tr>
<tr>
<td>Vapor pressure EtClCO₂</td>
<td>23.25 mm.</td>
</tr>
</tbody>
</table>

The calculations of reaction rate as measured by the flow method were carried through according to the method of Benton (2). This method can be given the following simple treatment:

Let the volume of the reaction space be $V_b$ and $V'$ be the volume of gas entering the space in unit time. In treating a reaction of the type $A \rightarrow vB$, then the time of contact is $V_b/V'$ if $v = 1$. However, the volume undergoes a change which we may represent by placing $n'_A$ equal to the number of mols of $A$ entering the reaction space in unit time, and $n_A$ equal to the number passing any given point per second. The volume changes from $V' = \frac{RT}{P} n'_A$ to $V = \frac{RT}{P} (n_A + n_B)$

$n_A + n_B = v n' - (v - 1) n_A$

and $V = \frac{RT}{P} [v n' - (v - 1) n_A] = V' \left[ v - (v - 1) \frac{n_A}{n'_A} \right]$
Now \( t = \frac{V_b}{V} \) and treating \( V_b \) as a variable,

\[
\frac{dV_b}{dt} = V' = V' \left[ v - (v - 1) \frac{n_A}{n_A'} \right]
\]

From the fundamental first order rate equation, we have:

\[
-\frac{dn_A}{dt} = k_1 n_A
\]

and

\[
-V' \left[ v - (v - 1) \frac{n_A}{n_A'} \right] \, dn_A = k_1 n_A dV_b
\]

On integration,

\[
k_1 V_b/V' = v \ln \frac{n_A'}{n_A} - (v - 1) \left( 1 - \frac{n_A}{n_A'} \right)
\]

If \( F \) represents the fraction of \( A \) which reacts, then

\[
k \frac{V_b}{V'} = v \ln \frac{1}{1 - F} - (v - 1) F
\]

where \( F = 1 - \frac{n_A}{n_A'} \)

An example of the data employed in a calculation using this method is given below:

<table>
<thead>
<tr>
<th>Reaction temperature</th>
<th>177(^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtClCO(_2) temperature</td>
<td>30.5(^\circ)</td>
</tr>
<tr>
<td>( V' ) (cc/min)</td>
<td>7.91</td>
</tr>
<tr>
<td>( V_b ) (cc)</td>
<td>43.4</td>
</tr>
<tr>
<td>EtClCO(_2) (equivalents/1000)</td>
<td>0.353</td>
</tr>
<tr>
<td>( F )</td>
<td>0.232</td>
</tr>
<tr>
<td>( k )</td>
<td>0.122</td>
</tr>
</tbody>
</table>
Other results of this method are given in tabular form in Table IV.

An increased rate during the first minutes was to be expected, though the results of Table IV seem to be abnormally high. However, they are reproducible, and serve to demonstrate the consistent trends that will be discussed later. There is the possibility of some inherent error which occurred consistently and which remains undefined, but as will be seen in subsequent discussions, such an explanation is hardly necessary.

As regards the dynamic runs made with pure ethyl chlorocarbonate, the results reported may be considered typical of the low pressure region.
Table IV

<table>
<thead>
<tr>
<th>( k )</th>
<th>Part. press. ( \text{EtClCO}_2 ) (mm.)</th>
<th>Reac. time</th>
<th>Temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.151</td>
<td>8.2</td>
<td>2.35</td>
<td>177</td>
</tr>
<tr>
<td>0.152</td>
<td>12.5</td>
<td>2.41</td>
<td>177</td>
</tr>
<tr>
<td>0.13</td>
<td>49.0</td>
<td>2.6</td>
<td>177</td>
</tr>
<tr>
<td>0.101</td>
<td>10.0</td>
<td>2.6</td>
<td>177</td>
</tr>
<tr>
<td>0.062</td>
<td>14.4</td>
<td>3.85</td>
<td>177</td>
</tr>
<tr>
<td>0.059</td>
<td>8.8</td>
<td>3.92</td>
<td>177</td>
</tr>
<tr>
<td>0.043</td>
<td>20.4</td>
<td>6.51</td>
<td>175</td>
</tr>
</tbody>
</table>

Without carrier gas:

| 0.0087 | 2.7         | 0.43 | 175 |
| 0.0099 | 4.5         | 0.67 | 175 |

\( k_0, 175^\circ \) 0.045

\( k_0, 177^\circ \) 0.047
DISCUSSION OF RESULTS (II)

As has been previously stated, a principal reason for undertaking the dynamic experiments was to investigate the first minutes of reaction. We have seen that at fairly low pressures of ethyl chlorocarbonate static experiments show an approach to a second order rate. However, it appears from Table IV that the second order theory is not needed to explain the increased rate during the initial reaction times. Fairly constant values of k were obtained for varying initial pressures, confirming the order condition. However, these values were quite high, in some cases more than twice the normal rate constants for reaction times of the order of one minute. It is improbable that this increase is related to the high pressure second order effect sometimes found in quasi-unimolecular reactions. The low pressures used in these experiments obviates this fact. However, some specialized wall action might well be involved. It has already been noted that a slight coating effect was present in the static experiments. The present experiments might indicate that appreciable coating takes place during the initial minutes. In this case the walls would be contributing to activation until rendered inactive by sufficient adsorption. The fact that the same phenomenon was observed in successive experiments using the same reaction tube may be explained by stating that the tube
remained at fairly high temperatures for long periods of time between runs. It was in contact with the atmosphere during these periods, and a considerable outgassing could well have taken place, destroying the earlier coating effect.

Dynamic experiments at low pressures bore out the appreciable rate decrease in this region, coinciding with the trend indicated in Fig. 9.

These experiments indicate that some very small percentage of the reaction may proceed by a rather complex mechanism. Indeed, such a possibility might be expected as a corollary of Hinshelwood's suggestion (61) that many organic compounds require both short chains and an internal rearrangement to explain the observed reaction rates. While the effect of nitric oxide is not completely clear, this hypothesis fits the observed effect very well. It will be seen from Fig. 6 that no rate increase is present during the initial minutes in the presence of nitric oxide, even at partial pressures too low to show an induction period.

However, the indications remain strong that the overwhelming percentage of the reaction is simple in nature. If our reasoning has been correct this reaction contains the essential elements for a collision theory treatment since its low pressure rate decrease cannot be satisfactorily explained on the basis of a complex mechanism.
ANALYTICAL PROCEDURES

Several methods of approach were followed. The first of these were repetitions of earlier work, with the exception of the gas analysis equipment used. In this method a weighed amount of ethyl chlorocarbonate was introduced by means of a small glass bulb into a large flask. The substance was allowed to decompose and the products were analyzed for C₂H₅Cl and CO₂. Typical data are given below:

<table>
<thead>
<tr>
<th>Sample (g.)</th>
<th>CО₂ (cc.)</th>
<th>AgCl (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>found</td>
<td>calcd.</td>
</tr>
<tr>
<td>0.4311</td>
<td>90.1</td>
<td>89.4</td>
</tr>
<tr>
<td>0.2104</td>
<td>44.2</td>
<td>43.6</td>
</tr>
<tr>
<td>0.1071</td>
<td>22.0</td>
<td>22.2</td>
</tr>
</tbody>
</table>

Clearly, if other products are formed the amounts are small and qualitative information as to their presence would be valuable. Certain possible modes of decomposition have been mentioned previously. With these as a key a number of qualitative tests were undertaken.

Ethyl chlorocarbonate was passed through a heated tube so that the average time of contact was about five minutes and the extent of decomposition greater than 50%. These products were passed continuously through bromine water and potassium permanganate solution, but no evidence of unsaturated compounds was obtained. Nor could a test for chlorine be obtained using a KI-starch solution.
Also thought to be of value was the work on the

catalytic decomposition reported by Underwood and Baril
(70). According to their data ethyl chlorocarbonate
decomposes at room temperature in the presence of ZnCl₂
to form ethyl chloride, carbon dioxide and small amounts
of ethylene and hydrogen chloride. Experiments in this
laboratory showed that AlCl₃ is capable of similar if
more violent behavior. However, in the latter case the
production of ethylene seems to be quite limited.

Spectrographic investigations of the products were
attempted. Ethyl chlorocarbonate alone gives absorption
in a continuum beginning at about 2500 Å. In no case
was any other absorption found. Of the possible products
phosgene or unsaturates would have given easily defined
absorption in the ultra violet. C. H. Smith (57)
investigated the substance spectrographically while it
was undergoing decomposition. Again the results showed
no absorption which could be distinguished from the normal
ethyl chlorocarbonate continuum beginning at 2500 Å.

In addition to the above indications, samples of the
products were frozen in liquid air and subsequently
distilled. In these cases very small amounts of a non
volatile substance remained above the boiling point of
ethyl chlorocarbonate. The amount was never more than a
film, which has been mentioned as probably having an
effect in deactivating the walls during reaction.
THE CALCULATION OF ACTIVATION ENERGY

Work has been initiated on the construction of a potential surface for the ethyl chlorocarbonate decomposition, and the theoretical determination of its activation energy. The semi-empirical method of Nyiring (19) has been followed in these calculations. The decomposition has been treated as a four electron problem and the equation developed by Slater (56) for such a problem, and subsequently used by Sherman (55) and others, has been employed.

This method is admittedly not absolute in its quantitative predictions but still is of great value to the chemist. The force constants of the bonds involved are probably a major source of error in these calculations. A great deal of uncertainty and discrepancy as to the proper value of a given bond may be noticed in the literature. Certain simplifying assumptions are also necessary; some of these are undoubtedly not quite valid, and hence add to the inherent error of the method.

At the suggestion of Dr. George Jaffe the problem was treated as being analogous to the ethylene bromide reaction with which Sherman and Sun (55) have recently dealt. Two methods of approach were tried in the preliminary calculations which will be mentioned here. In one of these a symmetrical approach of the C - Cl bond was used. The calculations bore out the rather obvious fact that this does not represent the system of lowest
energy, because of the difference in bond lengths between
C - Cl and C - O. A second method of treatment assumed
the oxygen bonding angles to be about ninety degrees,
with the other angles describing the system taken as
functions of the interatomic distances involved. This
system gave activation energies of a lower order,
indicating that it is more nearly the correct configuration.

The total energy was assumed to be 14% coulombic and
86% interchange. Since the Morse relation gives fairly
good values for total energy it was employed in the cal-
culations. The general equation for the total energy of
an interacting system involving four electrons is given
by:

\[ J = Q + K = \text{coulombic energy} + \text{exchange energy} \]

\[ J = (A_1 + A_2 + B_1 + B_2 + C_1 + C_2) \]
\[ \sqrt{\frac{1}{2} \left( (a_1 + a_2 - b_1 - b_2)^2 + (a_1 + a_2 - c_1 - c_2)^2 + (b_1 + b_2 - c_1 - c_2)^2 \right)} \]

Upon introducing the total energy with the fixed per-
centages indicated above this expression becomes:

\[ J = 0.14 \left[ (A_1 + A_2 + B_1 + B_2 + C_1 + C_2) \right] \]
\[ + 0.86 \left[ (A_1 + A_2 + B_1 + B_2 + C_1 + C_2) \right] \]
\[ + \left( A_1 + A_2 + B_1 + B_2 + C_1 + C_2 \right) \]
\[ + \left( A_1 + A_2 + B_1 + B_2 + C_1 + C_2 \right) \]

In the above expression the capital letters are taken
as representing the coulombic and the small letters the
exchange binding for any atom pair. The value \( J \) is the total
energy of the system referred to the four atoms completely
separated in space as zero energy. However, our energy of
activation must be referred to the stable ethyl chloro-
carbonate molecule; hence, the value of J for different configurations is subtracted from the sum of the bond energies of the stable C-O and the C-Cl linkages. A configuration of the following nature was assumed:

![Molecule Diagram]

The energy of the C-O, C=O bond was taken as constant at 94 kcal., with no better authority than the work of Sherman and Sun (55) on similar compounds.

The Morse constants used in the calculations are given below:

<table>
<thead>
<tr>
<th></th>
<th>D</th>
<th>r₀</th>
<th>w₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Cl</td>
<td>79</td>
<td>1.85</td>
<td>660</td>
</tr>
<tr>
<td>C=O</td>
<td>188</td>
<td>1.28</td>
<td>1720</td>
</tr>
<tr>
<td>C-O</td>
<td>82</td>
<td>1.43</td>
<td>1030</td>
</tr>
<tr>
<td>C-C</td>
<td>77</td>
<td>1.54</td>
<td>990</td>
</tr>
<tr>
<td>Cl-O</td>
<td>49.3</td>
<td>1.85</td>
<td></td>
</tr>
</tbody>
</table>

These values were obtained from tabulations of Daniels (12) and Pauling (41) with the exception of the Cl-O constants, which were estimated from a relation proposed by Badger (2).

Table V shows typical calculations for the parallel approach, Table VI for the more correct unsymmetrical approach. The value of 23.3 kcal. is quite low for the activation of ethyl chlorocarbonate (experimental value
Table V

$r_{ab}$ 2.00; symmetrical arrangement

$r_l$ distance between C-O, C-Cl bonds

<table>
<thead>
<tr>
<th>$r_l$</th>
<th>$r_{ac-bd}$</th>
<th>$r_{ad-bc}$</th>
<th>$-\theta$</th>
<th>$-\alpha$</th>
<th>$-\beta$</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>1.18</td>
<td>2.01</td>
<td>72.5</td>
<td>84.2</td>
<td>136.7</td>
<td>24.3</td>
</tr>
<tr>
<td>1.3</td>
<td>1.54</td>
<td>2.08</td>
<td>72.6</td>
<td>48.4</td>
<td>121.0</td>
<td>40.0</td>
</tr>
<tr>
<td>1.5</td>
<td>1.54</td>
<td>2.21</td>
<td>75.0</td>
<td>53.8</td>
<td>128.8</td>
<td>32.2</td>
</tr>
<tr>
<td>1.7</td>
<td>1.74</td>
<td>2.35</td>
<td>83.6</td>
<td>52.6</td>
<td>136.2</td>
<td>24.8</td>
</tr>
<tr>
<td>1.9</td>
<td>1.93</td>
<td>2.48</td>
<td>91.0</td>
<td>49.3</td>
<td>140.3</td>
<td>20.7</td>
</tr>
</tbody>
</table>

Table VI

$r_{ab}$ 1.85; normal arrangement

<table>
<thead>
<tr>
<th>$r_{ac}$</th>
<th>$r_{bd}$</th>
<th>$r_{ad}$</th>
<th>$r_{bc}$</th>
<th>$-\theta$</th>
<th>$-\alpha$</th>
<th>$-\beta$</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.85</td>
<td>1.43</td>
<td>2.75</td>
<td>1.96</td>
<td>83.0</td>
<td>54.7</td>
<td>140.4</td>
<td>19.6</td>
</tr>
<tr>
<td>2.02</td>
<td>1.60</td>
<td>2.69</td>
<td>2.07</td>
<td>86.0</td>
<td>54.0</td>
<td>140.0</td>
<td>21.0</td>
</tr>
<tr>
<td>2.12</td>
<td>1.70</td>
<td>2.74</td>
<td>2.17</td>
<td>87.0</td>
<td>51.8</td>
<td>138.8</td>
<td>22.2</td>
</tr>
<tr>
<td>2.22</td>
<td>1.80</td>
<td>2.78</td>
<td>2.24</td>
<td>88.1</td>
<td>49.6</td>
<td>137.7</td>
<td>23.3</td>
</tr>
<tr>
<td>2.32</td>
<td>1.90</td>
<td>2.89</td>
<td>2.33</td>
<td>93.9</td>
<td>46.7</td>
<td>140.6</td>
<td>20.4</td>
</tr>
<tr>
<td>2.42</td>
<td>2.00</td>
<td>2.96</td>
<td>2.41</td>
<td>98.1</td>
<td>44.0</td>
<td>142.0</td>
<td>19.0</td>
</tr>
<tr>
<td>2.62</td>
<td>2.20</td>
<td>3.09</td>
<td>2.57</td>
<td>110.0</td>
<td>39.0</td>
<td>149.0</td>
<td>12.0</td>
</tr>
</tbody>
</table>
29,410 cal.), but is within the accuracy reported for similar problems in the literature. The uncertainty of the constants involved, and the doubtful nature of certain of the operating assumptions leads one to believe that this value is not out of agreement with the predictions of the method. It will be noted from the tables mentioned that with distending bond lengths of the chlorocarbonate molecule the energy of the system reaches a maximum, then decreases again. It is this maximum which indicates the activation level.

This problem is being more extensively and accurately investigated at the present time. The construction of a complete energy surface will indicate much more clearly the shape of the barrier at its lowest point, though there is reason to believe that no value much lower than 23 kcal. will be found. It is possible that by correcting certain of the constants to more recent data this value may be raised to better agreement with experiment.
CONCLUSION

The observations previously cited indicate a mechanism of extreme simplicity. This conclusion was first strongly implied by the quantitative decomposition of ethyl chlorocarbonate to carbon dioxide and ethyl chloride. As mentioned before, chemical analyses of these products have been further supported by spectrographic investigations (57). No evidence of chlorine or phosgene could be obtained. Furthermore, ethyl chlorocarbonate does not absorb in the visible and the first appreciable ultraviolet absorption occurs with a continuum beginning in the region of 2500 A. Thus, there are apparently no side reactions contributing to the products.

The temperature at which decomposition takes place and the low energy of activation preclude the possibility of a purely thermal disruption into unstable fragments or radicals since the activation energy is lower by at least 40,000 cel. than the minimum bonding energies that might be involved. In addition to this the wall effects are inappreciable except perhaps for a very minor portion of the reaction. The reaction proceeds smoothly over a rather wide range of pressures and there is no marked effect of inert gases. It seems impossible on the basis of these facts to postulate any mechanism other than a rearrangement occurring internally with the elimination of carbon dioxide. The structure of ethyl chlorocarbonate as established by dipole measurements is in accord with
such a mechanism (39, 73). The following resonating structures have been proposed by earlier investigators:

$$\text{OCl} \quad \text{Cl}_2\text{O}$$

$$\text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \quad \rightarrow \quad \text{CO}_2 + \text{C}_2\text{H}_5\text{Cl}$$

Calculations of the activation energy have been carried far enough to indicate that the second of the forms above should decompose by rearrangement as indicated by the experimental evidence.

The complicating effects have been reduced to a minimum and the reaction seems firmly established as an excellent example of unimolecular decomposition.
The gas phase decomposition of ethyl chlorocarbonate was found to be homogeneous and unimolecular by Frediani, and thus to warrant extensive kinetic study. Several clear cut lines of investigation were indicated. One of these was the study of the low pressure region through which the rate constant decreases in value. This was especially important because this decomposition appears to be quasi-unimolecular in character; i.e., it appears to fit the ideas of the elaborated collision theory rather well. Such low pressure work has shown a definite approach to a second order rate in this region, following the pattern of other kinetic studies of organic decompositions.

Another of the more obvious lines of approach lay in the study of the effects of foreign materials upon the reaction. These effects are important in determining a mechanism, efficient in showing up complex phases of reaction and valuable in describing the general characteristics of the kinetic study. The effects of foreign materials have been extensively investigated. Carbon dioxide, nitrogen, and oxygen serve to maintain the rate constant at its high pressure level and may be considered normal. Carbon tetrachloride, benzene and nitrous oxide cause slight rate depressions. In the case of hydrogen an unexpected depression has been observed. This effect is not without parallel in the field, but seems to be a minority case, since hydrogen is usually quite effective.
in rate maintenance.

Water reacts with ethyl chlorocarbonate in the gas phase and the products catalyze the reaction slightly. Hexane increases the rate slightly and chlorine is markedly catalytic in effect. In the presence of nitric oxide there is an initial period of induction followed by an increased rate.

Where the foreign gas effects are slight no chemical explanation is needed. In the case of chlorine, however, the effect is so marked as to indicate specific interaction. It may be possible to explain this as an adsorption effect, perhaps bearing some analogy to the catalytic decomposition of ethyl chlorocarbonate on the surface of aluminum chloride.

Nitric oxide is ordinarily used as a test for the aliphatic free radicals. If they are present as the active fragments of a chain the reaction is inhibited by nitric oxide which attaches itself to the radicals engaged in chain propagation. This inhibition is complete for the chain carried reaction, extending over the whole time of decomposition. In the case of ethyl chlorocarbonate it has quite a different effect, which seems to be more complex in character; here one must rely on some rather obscure chemical interaction to explain the induction period at the beginning.

Coating of the walls of the reaction vessel with the products has been observed to have some effect on the decomposition, but this effect must be considered very
slight.

A higher rate during the initial minutes of the reaction was indicated by certain static runs. The dynamic method of investigation afforded an easy approach to the study of this region, since the reaction time was easily variable down to very small values. The rate was found to be definitely higher in the initial minutes. An explanation of this phenomenon has been based on the possibility of the walls being initially active, and subsequently deactivated by the adsorption of reaction products in a very short period of time. This idea is substantiated by the initial inhibitory effect of nitric oxide.

Certain of these experiments were also used to extend the low pressure data. The results were in agreement with the static experiments in this region.

Preliminary analyses indicated that the principal products of the reaction were carbon dioxide and ethyl chloride. Further chemical analyses strengthened this assertion considerably. Spectrographic work was employed as a supplementary procedure. It may be concluded on the basis of these results that other products than carbon dioxide and ethyl chloride are negligible at temperatures below 200°C. This fact contributes strongly to the proposal that the reaction can be adequately described by a single decomposition mechanism.

This mechanism, on the basis of the experimental work summarized above seems to be most accurately described as an internal rearrangement proceeding through a complex
of higher energy. This hypothesis does not eliminate the probability that some very small percentage of the total reaction proceeds through disruption and molecular fragments.

A theoretical calculation of the activation energy has been carried far enough to support the type of mechanism mentioned above. This calculation has followed the semi-empirical method developed by Eyring. It demonstrates the existence of a well defined energy barrier in the internal rearrangement scheme; the activation values seem rather low, but might be improved by refinement of certain of the calculations.
BIBLIOGRAPHY

1. Badger, R. W.
   The relation between the internuclear distances and force constants of molecules.

2. Benton, H. F.
   Kinetics of gas reactions at constant pressure.
   J. Am. Chem. Soc. 53: 2984-90 (1931)

3. Bowden, S. T.
   Thermal stability of the chloroformates and carbonates.
   J. Chem. Soc. 310 (1939)

   Thermal decomposition of t-butyl and t-amyl chlorides.
   J. Am. Chem. Soc. 55: 214 (1933)

5. Christiansen, J. A.
   Velocity of gas reactions.
   Proc. Cambridge Phil. Soc. 23: 438 (1926)

   Homogeneous decomposition of ethyl chlorocarbonate.
   J. Am. Chem. Soc. 61: 3176-80 (1939)

7. Coffin, C. C.
   Homogeneous first order gas reactions (I): decomposition of ethylidene dicarbonate.
   Can. J. Research 5: 635 (1931)

8. Coffin, C. C.
   (II): Decomposition of butylidene dicarbonate.
   Can. J. Research 6: 417 (1932)
9. Coffin, C. C.
   (III): Decomposition of paraaldehyde.
   Can. J. Research 7: 75 (1932)

10. Coffin, C. C.
   (IV): Decomposition of parabutyraldehyde and paraisobutyraldehyde.
   Can. J. Research 9: 603 (1933)

11. Coolidge, A. S. and James, H. M.
    Approximations involved in the calculation of atomic interaction and activation energy.
    J. Chem. Phys. 2: 811 (1934)

12. Daniels, F.
    "Chemical Kinetics."

13. Daniels, F. and Vernon, E. L.
    Kinetics of the dissociation of gaseous ethyl bromide.
    J. Am. Chem. Soc. 55: 922 (1933)

14. Daniels, F. and Veltman
    Decomposition of ethyl bromide.
    J. Chem. Phys. 7: 756 (1939)

15. Echols, L. S. and Pease, R. N.
    Inhibition of the thermal decomposition of n-butane by nitric oxide.
    J. Am. Chem. Soc. 59: 766 (1937)

16. Echols, L. S. and Pease, R. N.
    Thermal decomposition of n-butane.
    J. Am. Chem. Soc. 60: 1701 (1938)
17. Egloff, G. and Parrish, C. I.
   Thermal stability of paraffinic and oleofinic hydrocarbons.
   Chem. Rev. 19: 145 (1936)

18. Eyring, H. and Iolanyi, M.
   The calculation of heat of activation.
   Z. physik Chem. B 12: 279 (1931)

19. Eyring, H.
   Quantum mechanics and chemical reaction.
   Chem. Rev. 10: 105 (1932)

20. Eyring, H.
   The activated complex and the absolute rate of chemical reactions.

21. Eyring, H.
   The activated complex and chemical reactions.

22. Farkas, A and Melville, H. W.
   "Experimental Methods in Gas Reactions."
   London, Macmillan Co., Ltd., 1939; p. 64.

23. Frediani, H. A.
   "A Unimolecular, Homogeneous, Gas Reaction."
   Louisiana State University, Ph.D. Dissertation, 1937, p. 18.

24. Fugassi, F. and Daniels, F.
   A study of the decomposition of gaseous ethyl bromide.
   J. Am. Chem. Soc. 60: 771 (1938)
25. Glass, J. V. S. and Hinshelwood, C. N.

Unimolecular decomposition of some ethers in the gaseous state.
J. Chem. Soc. 1084 (1929)

26. Hinshelwood, C. N.

"Kinetics of Chemical Change in Gaseous Systems."

27. Hinshelwood, C. N.

Transition state method in chemical kinetics.
J. Chem. Soc. 635 (1937)

28. Hunt, J. K. and Daniels, F.

Rate of decomposition of nitrogen pentoxide at low concentrations.
J. Am. Chem. Soc. 47: 1602 (1925)

29. Johnston, H. L. and Giauque, W. F.

Heat capacity of nitric oxide etc.
J. Am. Chem. Soc. 51: 3194 (1929)

30. Kassel, L. S.

"Kinetics of Homogeneous Gas Reactions."
New York, Chemical Catalog Co., 1932; p. 93.

31. LaMer, V. K.

Temperature dependence of the energy of activation.
J. Chem. Phys. 1: 269 (1933)

32. Langmuir, I.

Radiation as a factor in chemical action.
J. Am. Chem. Soc. 42: 2190 (1920)
33. Leermakers, J. A.

Thermal decomposition of ethyl azide.


34. Leermakers, J. A.

Thermal decomposition of methyl azide.


35. Lessig, E. T.

Decomposition of ethyl bromide in the gas phase.

*J. Phys. Chem.* 36: 2325 (1932)

36. Lewis, W. C. McC.

The calculation in absolute measure of velocity constants.


37. Lindemann, R. A.


38. London, F.

Quantum theory of homopolar valence.

*L. Phys.* 46: 455 (1928)


Quantum mechanical resonance and internal rotation.


40. Ogg, R. A.

Kinetics of the thermal reaction of gaseous alkyl iodides with hydrogen iodide.


41. Pauling, L.

"Nature of the Chemical Bond."

*Ithaca, N. Y., Cornell University Press, 1939; p. 150."
42. Pease, R. N. and Morton

The thermal decomposition of the saturated hydrocarbons.
J. Am. Chem. Soc. 55: 3190 (1933)

43. Pease, R. N.

The theory of quasi-unimolecular reactions.
J. Chem. Phys. 7: 749 (1939)

44. Pelzer and Wigner

Velocity coefficients of interchange reactions.

45. Polanyi, M.

The transition state in chemical reactions.
J. Chem. Soc. 629 (1937)

46. Ramsperger, H. C.

Thermal decomposition of methyl isopropyl diimide.
J. Am. Chem. Soc. 51: 2134 (1929)

47. Ramsperger, H. C.

Decomposition of azoisopropyl.
J. Am. Chem. Soc. 50: 714 (1928)

48. Ramsperger, H. C. and Waddington, G.

Kinetics of the thermal decomposition of tri-
chloromethyl chloroformate.
J. Am. Chem. Soc. 55: 214 (1933)

49. Ramsperger, H. C. and Leermakers, J. A.

Thermal decomposition of dimethyl triazene.
J. Am. Chem. Soc. 53: 2061 (1931)
50. Rice, O. K. and Ramsperger, H. C.

Unimolecular gas reactions at low pressures.
J. Am. Chem. Soc. 49: 1617 (1927)
ibid. 50: 617 (1928)

51. Rice, F. O. and Rice, O. K.

"The Aliphatic Free Radicals."

52. Rice, F. O. and Polly, O. L.

Inhibition of homogeneous organic decompositions.

53. Rodebush, W. E.

The absolute rate of chemical reactions.
J. Chem. Phys. 1: 440 (1933)
ibid. 4: 744 (1936)

54. Schultz, R. F. and Kistiakowsky, G. B.

Thermal decomposition of t-butyl and t-amyl alcohols.
J. Am. Chem. Soc. 56: 395 (1934)

55. Sherman, Albert and Sun, C. E.

Calculations of the activation energies of some reactions between the halogens and the ethylene double bond.
J. Am. Chem. Soc. 56: 1096 (1934)

56. Slater, J. E.

Phys. Rev. 38: 1109 (1931)

57. Smith, C. H.

Unpublished results.
Louisiana State University, 1940.
58. Staveley, L. A. K.

Inhibition by nitric oxide of the decomposition of ethane.

59. Staveley, L. A. K. and Hinshelwood, C. N.

Detection of reaction chains by small amounts of nitric oxide.
J. Chem. Soc. 812 (1936)

60. Staveley, L. A. K. and Hinshelwood, C. N.

Catalysis and inhibition of a homogeneous gas reaction.

61. Staveley, L. A. K. and Hinshelwood, C. N.

Reaction chains in the decomposition of organic compounds.
J. Chem. Soc. 1568 (1935)

62. Staveley, L. A. K. and Hinshelwood, C. N.

Inhibition by nitric oxide of the decomposition of ethers.

63. Steacie, E. W. R. and Shaw, G. T.

Decomposition of alkyl nitrites (methyl nitrite)

64. Steacie, E. W. R. and Shaw, G. T.

Decomposition of alkyl nitrites (propyl nitrite)
65. Steacie, E. W. R. and Shaw, G. T.
   Decomposition of isopropyl nitrite.

   Decomposition of ethyl nitrite.
   J. Chem. Phys. 4: 345 (1936)

67. Steacie, E. W. R. and Smith, McF.
   Gaseous decomposition of butyl nitrite.
   J. Chem. Phys. 4: 504 (1936)

68. Taylor, K. A. and Achilles, H. E.
   Thermal decomposition of propylamine.
   J. Phys. Chem. 35: 2658 (1931)

69. Thomson
   Dipole moments and molecular structure of methyl
   and ethyl carbonates.
   J. Chem. Soc. 1118 (1939)

70. Underwood, H. W. and Baril, O. L.
   Catalysis in organic chemistry.
   J. Am. Chem. Soc. 53: 2200 (1931)

71. Williams, G. and Lawrence, A. S. C.
   Kinetics of the decomposition of benzalazine vapor.

72. Winkler, C. A. and Hinshelwood, C. N.
   Thermal decomposition of acetone vapor.

73. Wood, R. E.
   "The Dielectric Polarization of Ethyl Chlorocarbonate."
   Louisiana State University, Masters Thesis, 1939.
VITA

George Francis Kirby, Jr. was born in Cheneyville, Louisiana on December 7, 1916. Elementary education was completed in the grammar schools of Long Leaf and Glenmora, Louisiana. He graduated from Glenmora High School in May, 1932.

The following September he entered Louisiana College, remaining four years, and graduating with a B. A. degree.

In September, 1936, he entered the Louisiana State University with an appointment as teaching fellow in the Department of Chemistry. He received the M. S. degree in 1938.

He has remained in the department, continuing work on this investigation until the present time.
EXAMINATION AND THESIS REPORT

Candidate: George F. Kirby, Jr.
Major Field: Chemistry

Approved:

[Signatures]

Major Professor and Chairman
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination: May 1, 1940