THE INDUCED DECOMPOSITION

OF DIETHYL ETHER

by

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The purpose of this research has been to establish the existence or non-existence of long reaction chains involving free radicals, in the normal pyrolysis of diethyl ether - by attempting to induce such chains at a much lower temperature than the normal decomposition requires, with radicals produced from another source (azomethane) and further, determining the length and nature of such chains (if any) by a detailed study of the factors such as temperature and concentration, affecting them.   The relation of such an investigation to current theories in the field of Reaction Kinetics, is related in the following paragraphs.

Introduction

One of the first studies made on the thermal decomposition of diethyl ether, was by Berthelot in 1863[1]. The first modern investigation however was that of Nef[2] (1901), who showed that below 500°C the ether is relatively stable, but decomposes vigorously at 550° to give large amounts of acetaldehyde, together with ethylene, ethane, methane, carbon monoxide and hydrogen[3].

A few years later, Nef attempted to explain the pyrolysis mechanism[4] on the basis of his theories concerning divalent carbon. This mechanism involved the preliminary dissociation of the ether into water and free ethylidene radicals CH_3CH--

which then interacted to give ethane, acetaldehyde and ethylene. As evidence for his theory, Nef quoted the fact[5] that ether decomposes quantitatively into ethylene when passed over P_2O_5 even below the dissociation temperature; further, ether burns very slowly at room temperature in dry oxygen, giving acetaldehyde - presumeably from the ethylidene radicals present in equilibrium.

The rate of thermal decomposition of diethyl ether was first studied by Hinshelwood[6] in 1927. His experiments, made in the temperature range 525-588°C, indicated that the reaction was homogeneous or nearly so, and first-order over a wide range of pressure, the specific rate however falling off in value at the lower pressures. Further, he noticed that this falling-off did not occur in the presence of excess hydrogen, altho other inert gases failed to maintain the rate. In order to explain his results, in view of gas analyses on the reaction products, Hinshelwood suggested the following mechanism:

$$(C_2H_5)_2O \longrightarrow CO + \begin{matrix} CH_5 \\ C_2H_5 \end{matrix}$$

$$\downarrow$$

$$2CH_4 + CH_2--$$

$$= CO + 2CH_4 + \tfrac{1}{2}C_2H_4$$
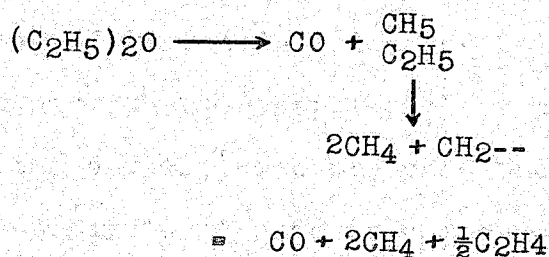
This it may be noted also involved a dissociation of the ether into free radicals, altho no evidence was given to support the idea. It was at this stage that Paneth and Hofeditz[7] announced the preparation of free methyl and later free ethyl radic-
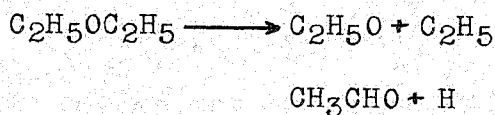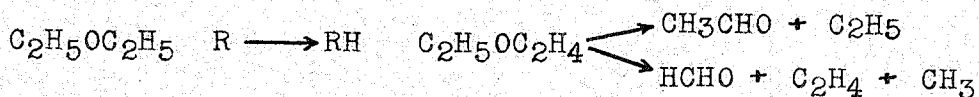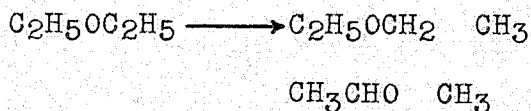
als, for the first time.[8]

Previous to this time, a not inconsiderable amount of physico-chemical (particularly photochemical) evidence had been accumulated which pointed to the momentary existence of free aliphatic radicals in chemical reactions.[9] Now however direct chemical evidence was available. Paneth's technique, in brief, consisted of sweeping metal alkyls at a very fast pumping speed thru a hot tube and then over a metallic mirror deposited in the cold part of the tube. The experiments established beyond doubt that the metal alkyls when heated, dissociate into metal atoms and free radicals; e.g. $ZnEt_2 = Zn + 2Et$. These radicals then unite with the cold mirror and the resulting products may be identified by chemical methods.

Two years later, the Paneth mirror technique was used by F.O.Rice and his co-workers to show that a great many organic compounds, when heated at $800-1000°C$ and a few mm pressure, dissociate into free methyl and ethyl radicals; among the compounds so tested was diethyl ether. On the basis of his experiments, and those of Paneth in which the half-life, temperature coefficient and other properties of free radicals were investigated in some detail, Rice proposed the theory[9],[10] that in general the pyrolysis of organic compounds proceeds thru a free radical mechanism, and not by internal rearrangements in the substrate molecule followed by the splitting off of product molecules as such. According to Rice, when an organic compound is heated it breaks up into radicals, the kind of radicals being determined by the nature of the compound and the rel-

ative strengths of its various bonds. A radical thus formed
may undergo either of two types of reaction; it may react with
a molecule of the original compound, forming a compound itself
and leaving a new (heavy) radical; or it may spontaneously de-
compose into a smaller radical and a new compound. In this
manner a reaction "chain" is set up, which is only broken when
two free radicals unite. Such mechanisms, Rice submits, form
a more reasonable picture now that the existence of free ethyl
and methyl is definitely established, than the somewhat fantas-
tic internal rearrangements which are the only alternative.
Unfortunæately however the Paneth technique cannot be used to
establish the presence of free radicals except at high temper-
atures and low pressures, as otherwise the life of the partic-
les is too short and their concentration too low for detection
by this method.

Rice has recently worked out in detail the free radical
mechanisms to be expected[9],[11] in the pyrolysis of many common
organic compounds such as the ethers, aldehydes, ketones and
hydrocarbons (aliphatic). These mechanisms were so chosen
that the activation energies assigned to the various steps
would result, in each case, in a correct value for the overall
rate, the temperature coefficient and the relative proportions
of products produced in the initial stages. The activation
energies in many cases were also correlated with thermochemic-
al estimates of the various bond strengths involved.

The mechanism proposed[9] by Rice for the normal pyrolysis
of diethyl ether, is as follows. Two chains are possible,

$$C_2H_5OC_2H_5 \longrightarrow C_2H_5OCH_2 \quad CH_3$$

$$CH_3CHO \quad CH_3$$

$$C_2H_5OC_2H_5 \quad R \longrightarrow RH \quad C_2H_5OC_2H_4 \diagdown \begin{array}{l} CH_3CHO + C_2H_5 \\ HCHO + C_2H_4 + CH_3 \end{array}$$

$$C_2H_5OC_2H_5 \longrightarrow C_2H_5O + C_2H_5$$

$$CH_3CHO + H$$

This is followed by a chain decomposition of the acetaldehyde formed, thus

$$CH_3CHO + R \longleftrightarrow RH + CH_3CO$$

$$CH_3 + CO$$

The formaldehyde probably decomposes directly into hydrogen and carbon monoxide. These chains account for all the observed products (as well as the observed intermediate aldehydes) and Rice has predicted the relative proportions in which they should be found in the initial stages of the reaction[9] but no data is available to check his prediction.

One of the first[12] experiments carried out to test directly for the presence of free radical reaction chains in a pyrogenic decomposition, was the work of Allen and Sickman[13] in 1934. According to these authors, the reaction R + M should have a lower activation energy than the dissociation M → radicals. Hence if free radicals from an extraneous source are

mixed with a compound, chemical decomposition of the compound should be induced at a temperature lower than the normal decomposition temperature. This prediction was tested by introducing methyl radicals from azomethane into acetaldehyde, at 300° C and lower. Chains were actually found to be produced under these conditions, lengths as long as 500 units being obtained. The experiments were highly satisfactory from the point of view of the chain theory since by mathematical treatment of the expected mechanism, these authors were able to correctly predict the manner in which the total reaction rate (in the initial stages) would vary with the aldehyde and azomethane pressures respectively; further, a determination of the temperature coefficient of the reaction gave a value which agreed very closely with the predicted value based on F.O.Rice's estimations of the various activation energies involved.

In the same year (1934) two other induced chain decompositions were reported. Frey[15] decomposed certain hydrocarbons in the presence of mercury alkides. Leermakers[16] released methyl radicals in dimethyl ether by the photolysis of acetone vapour at 270-400°C, and obtained large quantum yields. The high-temperature photolysis of acetone alone showed that methyl radicals do not, below 400°C, initiate chains in this compound. This conclusion was confirmed by an experiment of Rice in which[17] methyl radicals from dimethyl mercury were released in acetone at 350-400°. Only $CH_3COCH_2.CH_2COCH_3$ was obtained, equivalent to the $HgMe_2$ added. Above 400° however the chain

$$Me_2CO + Me \longrightarrow CH_4 + CH_3COCH_2 \longrightarrow Me + CH_2:CO$$
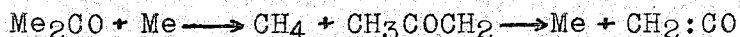
was initiated. Below 300° the acetone was not attacked by the radicals.

It was suggested by Allen[13] that since the chain-breaking step (the recombination of two radicals) is a wall reaction[9] by packing the reaction vessel it should be possible to produce a noticeable decrease in the rate of a reaction, provided it proceeds thru a free radical chain mechanism. This suggestion was first utilized by Hinshelwood, in a reinvestigation[18] of the normal pyrolysis of acetone[19]. The rate was very carefully determined in an empty silica bulb, then again with the bulb packed with silica spheres. The author reports a small but definite retardation of the rate in the latter case, indicating that short chains may be present (540-600°C).

Similar but more accurate experiments on acetone, at 460°, were carried out by Allen[20] who was able to reduce the measured initial rate to nearly half its normal value, by using a large reaction chamber packed with tubing. These results seemed to prove that acetone decomposes by a chain mechanism.

Experiments with packed bulbs were also made by Hinshelwood on acetaldehyde[21] at 526°C, but absolutely no retardation could be detected - indicating the absence of chains in the normal pyrolysis. However, F.O.Rice was able in the case of acetaldehyde to account on the basis of a chain mechanism, for the experimentally observed[22-25] order of 1.5, an order which cannot apparently be explained by any other mechanism.

A third method of testing for reaction chains was recently

developed[26] by Hinshelwood and his co-workers. It was found
that nitric oxide[33] reduces the quantum yield in the photo-
chemical decomposition of acetaldehyde from hundreds to unity
- hence NO appears to be a chain-breaker. As expected, when
NO was added to propaldehyde[32], the reaction was definitely
inhibited presumeably by shortening of the reaction chains.
For acetaldehyde[31] and acetone[27] however, no inhibition was
observed. Hinshelwood states in this paper that acetaldehyde
must be a non-chain reaction and that further the acceleration
by azomethane observed by Allen[13] may be explained by homogen-
eous catalysis.

A fourth and more direct method of testing for reaction-
chains has been used by Patat[30] and co-workers[29] in Germany.
By means of a deuterium exchange experiment, the hydrogen-atom
concentration present in various decomposing organic compounds
was estimated: the substances studied included ethane, acetone,
acetaldehyde and propaldehyde. Patat concludes from this work
that reaction chains do actually exist in these cases, but such
chains are far too few in number to account for the total de-
composition as required by the Rice theory.

Recently, the pyrolysis of ethylene oxide[12] has been the
subject of much research in this field. This substance decom-
poses[37] to give acetaldehyde and free methyl radicals, which
then induce a chain decomposition of the aldehyde. It has
therefore been used in the study of induced reactions[41], in
particular with gaseous paraffins[40], acetaldehyde[38,39] and

others[43].

The preceeding brief summary of the present status of the Rice-Herzfeld chain reaction theory, reveals much evidence which is seemingly contradictory and which certainly cannot be explained until much more experimental data concerning the nature of chain reactions, has accumulated. The results of the present investigation on diethyl ether together with the previous work on this compound, are discussed in a later paragraph.

EXPERIMENTAL PART

In the present experiments, the reaction rates were measured by following the pressure increase with time, when the gases were decomposed at constant volume. This method was supplemented by a series of analyses of the reaction products. The apparatus was designed to be capable of accurately measureing rates in the initial pressure range of from 1 to 25 cm. In this range the high-pressure rate of many gas reactions begins to exhibit the pronounced decrease which is of interest theoretically[25]. Further, the design was such that a variety of gaseous mixtures could be readily prepared and used for rate study.

General Description of the Apparatus

The pyrolysis chamber consisted of a 100 cc pyrex vessel (3.3 by 14 cm), which was connected thru thick capillary

VAC. LINE

E

S14

S12

M3

R

V

L2

S7

M2

H

S5

G

F

S4

C

S3

M1

S2

L1

S1

B

HVAC

APPARATUS

FIG. I.

M

S 13

To E

To A
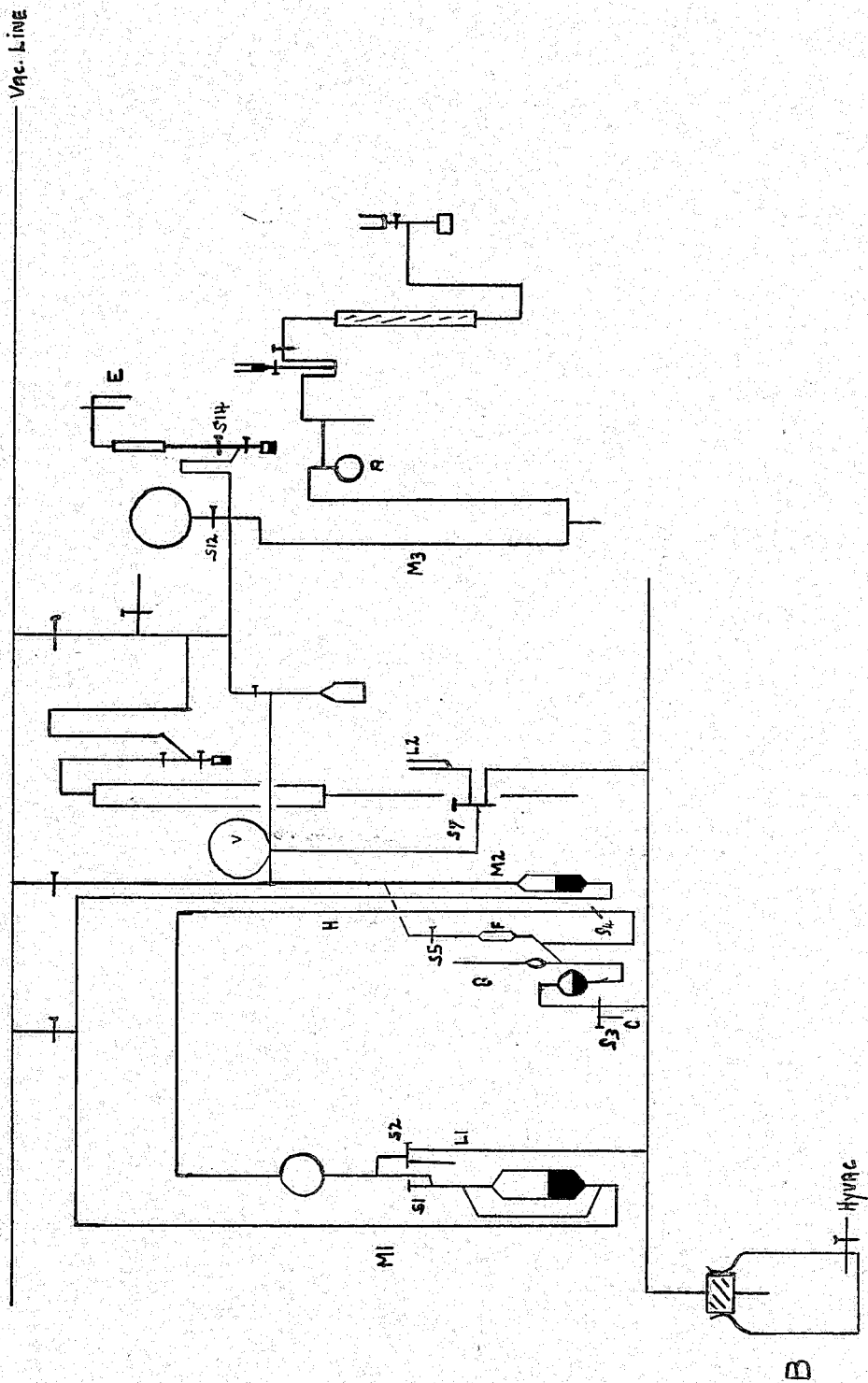
FIG. 2

tubing (2 mm bore) to a small capillary stopcock. The press-
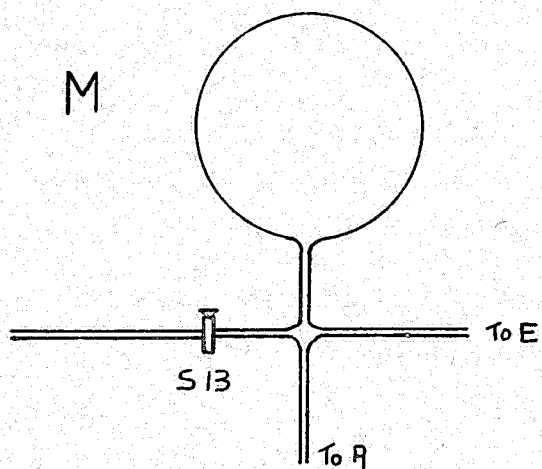ure in this chamber was measured by means of a glass-membrane
or "clicker" type of gage, functioning as a null-point instru-
ment. This gage was connected to the chamber thru a capillary
side-tube sealed in just below the stopcock. The total volume
of these connections outside the reaction chamber was probably
not greater than 4cc.

The balancing pressures outside the gage membrane were
obtained by admitting or withdrawing air as necessary thru a
single three-way stopcock (S7). Air was admitted slowly thru
a controlled leak (L2), and withdrawn by expansion into a large
previously-evacuated bottle. The volume of the system outside
the membrane was increased to nearly a litre, by introducing a
large bulb (v) between the gage and the controlling stopcock.
Air pressures were then more easily adjusted. These pressures
were measured either on an ordinary constant-level mercury
manometer (M2), or on a specially-designed type of McLeod Gage
$\int$ pressures of from 5 to 18 cm.

Azomethane was stored in a 250-ml bulb (A), connected to
the 500-ml mixing bulb thru a long mercury cut-off (M3) which
served also as a manometer for indicating azomethane pressures
and pressures of gas mixtures.

Liquid diethyl ether (about 5cc) was stored in a tube (E)
connected to the mixing bulb a mercury cut-off fitted with a
capillary stopcock.

Evacuation of the apparatus was carried out by a mercury
diffusion pump, backed by a Hyvac rotary oil pump. The high-

vacuum line was fitted with a McLeod Gage (all glass) which permitted estimation of gas pressures down to 10^{-5} mm. The vacuum side of the various manometers of the pressure gage, were connected to this vacuum line thru stopcocks.

The reaction-chamber stopcock was connected to the air-pressure side of the clicker gage thru the vacuum line, as the pressures on either side of the membrane could not differ greatly without danger of rupturing it; consequently both sides had to be evacuated simultaneously when pumping out from atmospheric pressure. This stopcock also led to a Topler Pump which formed part of a gas-analysis apparatus.

For the third series of experiments (Runs 30 et seq) the arrangement for storing the gas mixtures was altered somewhat. The 500cc mixing chamber (M) was provided with a single stopcock (S12): the stopcock (S13) leading from it to the reaction chamber was removed. A new chamber, consisting of a long cylindrical vessel (capacity 425 ml) was connected to the reaction chamber thru a mercury cut-off, also provided with a stopcock. This storage cylinder was fitted with a mercury leveling bulb, which permitted the gas pressure to be varied, within limits. The change was made to remedy two defects in the previous arrangement - the irreproducibility of a given initial pressure of gas mixture (the pressure in the storage chamber naturally fell as gas samples were withdrawn for each experiment) - and the impossibility of making an experiment with either ether or azomethane alone while a mixture was present in the storage bulb.

The Clicker Gage and
Pressure-compensated McLeod Gage

The glass-membrane or "clicker" gage[50] was constructed of 2-mm bore pyrex tubing, by blowing a bulb of moderate thickness and flattening the end in a hot flame, in such a manner that a "wrinkle" resulted on the flat surface.

The pressure difference on such a membrane necessary to produce a click sound is constant over a wide range of temperatures and pressures[51]; in general the accuracy of the device often exceeds 0.001 cm, if the zero-correction is small. The zero-correction for the membrane used (corresponding to the air pressure at which the membrane clicked out, when the reaction chamber was completely evacuated) was measured accurately with a cathetometer. The value of this click-constant was found to be nearly 7 cm. As it was desired to make rate measurements with initial pressures of from 20 cm down to one cm, a McLeod Gage was attached for use in this range. For higher pressures an ordinary mercury manometer (M2) could be used.

The McLeod Gage was constructed of widest-bore heavy capillary tubing; a series of bulbs gave magnifying ratios of about 5, 8, 10 and 30, the gage being used as a constant-ratio instrument. The mercury head necessary to give readings of suitable accuracy in the lowest range of pressures used, corresponded to nearly two atmospheres: to eliminate the necessity for such an unwieldly column of mercury, the usual form of McLeod gage was modified as shown in the figure (3). The air pressure to be measured was introduced thru a stopcock (S5)

and a mercury float valve (F) into the compression volume of the gage (G). The latter was provided with three paper marks, encircling the tube to avoid parallax errors: with a backgr- ound of black paper it was found that this arrangement gave by far the best visibility of the mercury meniscus, if strongly illuminated from high to one side.

Adjustment of the mercury level to the appropiate mark on the gage, was accomplished by manipulation of the three-way stopcock (S3) and the screw clip (C) by means of which the pressure over the mercury reservoir (R) could be varied from a few centimeters to two atmospheres. One arm of this stopcock was connected to a large evacuated bottle, and the other to an oxygen tank giving 15 lbs/ins^2 pressure. The resulting head of mercury was read from a tube (H) of the same bore and thick- ness as the gage itself, connected thru a large stopcock (S4) to one end of a mercury U-trap, the other end of which was sealed in between the float valve and compression volume. The top of the mercury-head tube (H) was connected to a 300cc bulb in which the air pressure could be varied up to one atmosphere by using the three-way stopcock (S2) attached. This pressure in turn could be read off the attached manometer (M1); the total head therefore was the sum of the pressures observed on this manometer and the other mercury column (H).

Calibration of the magnification ratios of the McLeod Gage was carried out with the cathetometer, the pressures be- ing read off the manometer (M2). Correction was made for cap- illary depression of the mercury level, by measureing this sep-

arately. The click constant, as already mentioned, was also determined with the cathetometer. To set the click pressure, the vacuum reservoir bottle (B) was used at a pressure not much less, so that the air in the volume outside the clicker was withdrawn very slowly. When the click was heard, the stopcock (S7) was immediately closed. The error involved here, calculated from the observed rate of pressure fall (on M2) was negligible as there was never more than one second delay in closing the stopcock; the settings, furthermore, were entirely reproducible.

Temperature Control and Measurement

The furnace used in these experiments consisted of an alundum tube, wound closely with heavy nichrome wire which was fixed in place with alundum cement. This was surrounded by a metal case filled with infusorial earth and wrapped on the outside with sheet asbestos paper. To decrease the temperature gradient, a somewhat smaller brass tube was placed inside the alundum one, and cemented into place. Further, the reaction chamber itself was wrapped closely with a thin sheet of aluminum foil, and the mouth of the furnace was closed with four inches of cement plug.

Inserted thru this plug, into the space beside the reaction chamber in the furnace tube, was the stem of a quartz platinum resistance thermometer. This was connected thru heavy copper wire to form one arm of a box bridge, for reading the resistance. A sensitive ballistic galvanometer was used - it was found by direct measurement that one centimeter on the
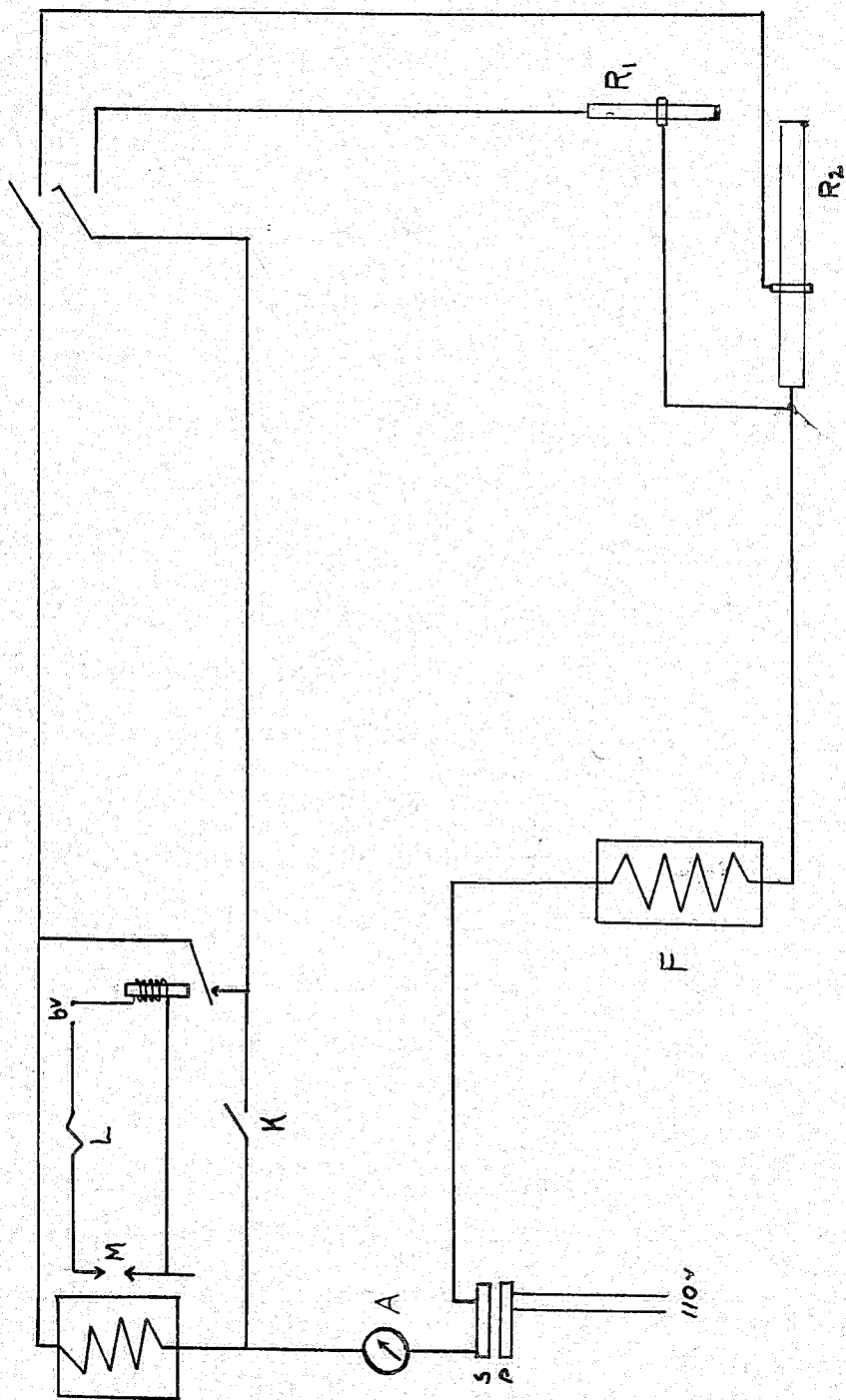
FIG. 4.

galvanometer scale corresponded to about $\frac{1}{4}$°C for all temperatures between zero and 500°C.

Calibration of the platinum resistance thermometer was made according to U.S. Bureau of Standards Methods[53]. As reference points, melting ice, boiling sulfur, freezing tin and freezing zinc were used; the cooling curves were readily reproduced. The results are expressed by the equation following:

$$R_T = 50.36(1 + 3.8749 \times 10^{-3} - 6.1086 \times 10^{-7} T^2)$$

In practice, temperatures were read off a large-scale graph of this equation (1mm graph = $\frac{1}{2}$°C).

The temperature of the furnace was closely adjusted by the use of a variable transformer ("Variac") utilizing the 110v line and giving secondary voltages of from zero to 130v. An ammeter indicated the current being used - about 2.7 amperes for a temperature of 300°C.

Owing to the large fluctuations in the line current supply it was found necessary to devise a scheme to keep the current effectively constant. This was accomplished with the circuit shown in figure (4). The furnace was connected in series with a heating coil of nichrome ribbon, which was wrapped around the long (pyrex) mercury reservoir of a thermoregulator. The latter was provided with another reservoir fitted with a stopcock for storing excess mercury resulting from expansion when the coil is first heated. The whole was mounted in a small wooden box, lined with asbestos paper, and provided with binding posts outside. A small hole in the top of this box, immediately over the capillary tube opening of the regulator, contained a tight-fitting cork supporting a length of tungsten wire acting as an

electrical contact with the mercury in the capillary. Adjustment of the height of the contact point could then be made by simply sliding this wire down thru the cork, to the required position. To protect the regulator as far as possible from room temperature changes, the box was placed in a large earthenware crock with a similar crock inverted over it.

The relay circuit of the thermoregulator consisted of an ordinary magnetic relay provided with silver contacts, whose action opened and closed a resistance circuit in parallel with a variable rheostat, which in turn was in series with the furnace. Current for operating the relay was obtained from a 6v D.C. source, which when used in series with a 40-w lamp acting as a resistance, was found completely satisfactory in regard to lack of serious sparking across the tungsten-mercury gap, and power to overcome any sticking tendency in the relay itself.

The working of the device depended upon the large temperature lag in the furnace, compared with the extremely low lag in the thermoregulator reaction. To obtain a constant average current thru the furnce, the parallel rheostats were so adjusted that when the relay contacts were closed the current was 0.25 amperes above, and when open 0.25 amperes below, the desired current. This spread was found ample to accommodate the fluctuations in line voltage in this laboratory.

In practice the arrangement was found to work very well (the usual variation during a three-hour run being 0.0 to 0.5°) provided the room temperature was kept quite constant. Wide fluctuations were found to occur however (up to ±10°) when this

was not the case, owing to temperature effects both on the furnace and the regulator oven itself. Further, for exact work the method of setting the device for a desired temperature (this is described under Experimental Procedure) was not sufficiently precise, depending as it did upon adjustment of the furnace to this temperature for a period of at least several hours, to establish proper thermal equilibrium in the oven.

Preparation and Purification of Azomethane

In these experiments some three samples of azomethane were used. The first (Runs 1-9) and the second (Runs 10-29) were prepared according to the method of Ramsperger[56] and of Thiele[57]. The third sample was generated using sym-hydrazomethane dihydrochloride prepared from the method of Hatt[58].

The latter preparation proceeded through sym-dibenzoyl hydrazine, from hydrazine sulfate and benzoyl chloride,

$$2C_6H_5COCl + N_2H_4 \cdot H_2SO_4 \longrightarrow (C_6H_5)_2C_2O_2N_2H_2$$
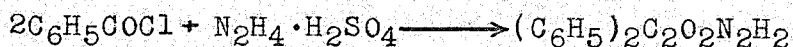
to dibenzoyldimethylhydrazine, using methyl sulfate as the methylating agent

$$(C_6H_5CO)_2N_2H_2 + 2Me_2SO_4 + 2NaOH = (C_6H_5CO)_2N_2Me_2 + 2MeSO_4Na + 2H_2O$$

which is then hydrolysed to give the desired product -

$$(C_6H_5CO)_2N_2Me_2 + 2HCl + 2H_2O \longrightarrow MeNHNHMe \cdot 2HCl + 2C_6H_5CO_2H$$
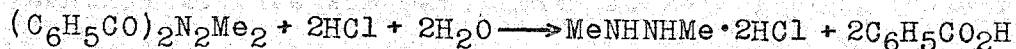
The benzoic acid was extracted with a 1:1 benzene-ether mixture. The yield obtained, using quantities stated in the reference, was about 7 grams of pure dry material.

The method of Thiele and of Ramsperger for preparing hydrazomethane was analogous to the above, but was found very unsat-

isfactory, owing to lack of sufficient detail in the references quoted. The starting product was sym-diformylhydrazine

$$2HCOONa + N_2H_4 \cdot H_2SO_4 \rightarrow HCO \cdot NHNH \cdot HCO + Na_2SO_4 + 2H_2O$$
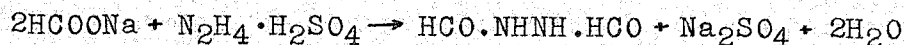
According to Beilstein, when hydrazine sulfate and sodium formate are heated together dry at $100^\circ C$, the above product is formed. The freezing point is given as $159-160^\circ$ and the solubility as small in alcohol, but soluble in water, insoluble in ether. No other data on the reaction could be found in the available journals.

In the preparation it was assumed that the equation above represents the main reaction; equivalent quantities of the two reactants were therefore heated together in a corked flask at 100° for 24 hours. The mixture was then of semi-fluid consistency, and gave off a strong sharp odour, not recognized. Attempts to purify the product were not successful, so the entire mass was used in the next step, assuming arbitrarily about 80% yield.

Dimethyl sulfate (96cc) and $2\frac{1}{2}N$ NaOH (400cc) were added slowly from separate dropping funnels, to 44g of diformyl hydrazine suspended in 125cc of water, with continuous stirring. The reaction mixture was maintained at 20° by gentle cooling in running water. The reagents were added in four separate portions over a period of eight hours, the reaction mixture being neutral before each new addition was made.

$$HCONHNHCHO + 2MeSO_4 \rightarrow (HCO)_2N_2Me_2 + MeHSO_4$$

After complete methylation the mixture (neutral) was evaporated strongly, then evaporated further as strongly as possible with

two volumes of concentrated hydrochloric acid almost to dry-
ness. The residue was taken up in a small amount of water and
vigorously steam-distilled with an excess of concentrated sod-
ium hydroxide solution (using a 12-litre flask) until the res-
idue no longer reacted alkaline. This distillate was collected
directly in one mol of dilute hydrochloric acid (2-litre flask)
thus $(HCO)_2N_2Me_2 + HCl + 2H_2O \longrightarrow 2HCOOH + MeNHNHMe.HCl$

The weakly acid liquid was evaporated just to dryness on the
water-bath and the residue taken up in absolute alcohol. This
solution was then completely saturated with dry hydrogen chlor-
ide gas, cooled, and the fine white crystals of dihydrochlor-
ide filtered. After washing with alcohol-HCl (anhydrous) and
then absolute ether, this product was dried completely on a
porous plate at 110°, in a vigorous stream of dry hydrogen chl-
oride gas. Yield, about two grams.

From sym-hydrazomethane dihydrochloride, azomethane was
prepared in each case by the following method.

The apparatus consisted first of a 100cc pyrex flask with
a tube, leading from a small dropping-funnel, sealed into the
neck. A side-tube from the neck led to two drying-tubes (in
series): the first contained pure anhydrous calcium chloride
and was about 25cm long; the second, containing calcium chlor-
ide and a central layer of soda-lime, was some 50cm long. The
tubes were of 2cm diameter. This purification train led to a
cooled trap (carbon dioxide-ether at -78°) from which it was
separated by a single right-angle stopcock, forming one arm of
a mercury cut-off. The trap was connected directly to the

250-ml azomethane storage bulb.

Azomethane was generated by oxidation of the hydrazomethane salt with a cold, saturated solution of neutral potassium chromate. For the third sample of azomethane generated, 10g of potassium chromate dissolved in 20cc of water were placed in the partly-evacuated generating-flask. In the dropping-funnel was placed 4g of sym-hydrazomethane dihydrochloride dissolved in 8-ml of water. The generator was cooled in an ice-bath and the pressure over the chromate solution reduced to 25 centimeters. With the carbon dioxide-ether freezing mixture in place, the solution in the dropping-funnel was added in very small portions over a period of five hours. After standing for two hours longer, the pressure in the system (which had risen considerably owing to the accumulation of a gas not condensed in the trap) was reduced extremely slowly (to permit complete drying of the gases in the purifying train) to about 3cm. After standing for five hours longer, the cut-off between the generator and the trap was raised, completing the preparation.

The product, on removing the freezing-mixture from the trap, was about 3cc of very light yellow liquid, which rapidly vapourized when allowed to reach room temperature. Dissolved gases (which were present in considerable amount) were removed by pumping off the re-frozen azomethane (liquid air on the trap) with a diffusion pump, then allowing it to vapourize completely by warming to room temperature with the cut-off (M3) raised, and refreezing and repumping further - the process being repeated (about 9-10 times) until no gas residue remained

after freezing. When this had been done the above quantities gave a yield of 51cm pressure in the storage apparatus described. The residual gas pressure over the frozen azomethane was 10^{-5}mm.

Azomethane is described by Thiele as a colorless explosive gas, or pale yellow liquid, boiling point 1.8° at 756mm. It explodes vigorously when heated in the absence of air. Its thermal and photochemical decomposition has been studied by Ramsperger[56,60], O.K.Rice and Sickman[59], Patat[61], Goldfinger[63] and Heidt & Forbes[62].

The first sample of azomethane prepared as described above was found to decompose slowly in the storage chamber. After one month, the sample was frozen with liquid air, but a pressure of 35cm of an uncondensed gas remained, the condensable residue being no more than 10cm. Furthermore, a rate determination showed that even this residue was not pure azomethane. The second sample was protected from sunlight by a black cardboard screen; no yellow oil appeared as had in the first case, even after two months storage. Some fine white lustrous needles were observed in the storage bulb however, the presence of which could not be explained. At the end of some six months, these had disappeared.

The third sample showed none of these effects.

The initial purity of the azomethane samples was tested by rate determinations (see Tables of Data) and found to be satisfactory in general. Sample 3 was further checked by an analysis of the reaction products for ethylene (using activated sul-

furic acid, q.v.): the result showed 1.7% in exact agreement
with Ramsperger's analysis[56].

Preparation of the Diethyl Ether Samples

All samples of ether used were prepared in essentially
the same manner from B.D.H. Aether Puriss. anaesthetic ether
of high purity. Sample I (Runs 1-10) and sample II (Runs 10-
29) were allowed to stand over sodium wire for three weeks,
after which several fractional distillations were carried out.
Sample III (Runs 30 &c) stood over sodium-potassium amalgam
(1:2 by weight) for one month before fractionation. Sample II
was also distilled several times over freshly-cut sodium.

In every case, it was found impossible to detect any ran-
ge of boiling-point during the fractionations, using a therm-
ometer reading to tenths of a degree. First and last runnings
from each distillation however were rejected. This was taken
as indicating a high degree of purity in the ether samples,
and no further chemical treatment was considered necessary.

Ether samples (about 5cc) were placed in the apparatus
thru the top of the storage tube (E) which was opened with a
blowtorch for the purpose. Immediately after the ether had
been added, it was frozen in the tube with liquid air. The
open top was then sealed over (with the blowtorch) just as
soon as the operation was deemed safe.

To remove dissolved air (which was always considerable)
the sample was repeatedly frozen back and forth between the
arms of the ether storage tubes, using liquid air for the pur-
pose, and pumping off the solid ether to a very low pressure

each time. When a negligible amount of residual gas remained after a recondensation of the ether (about 8 or 9 times) the system was completely evacuated and the mercury cut-off raised.

As diethyl ether is affected by sunlight, the liquid was stored always in the dark. A Dewar flask, containing cold water to prevent condensation in the connecting tubing, served this purpose. A short tube containing KOH pellets was inserted between the ether storage tube and the cut-off. This served to remove incidental water-vapour, arising from the blowtorch or other sources.

Rate determinations were also made on the ether alone, to check the purity of the samples.

Preparation of the Gas Mixtures

The procedure for preparing mixtures I to V inclusive was as follows. The azomethane gas was first frozen (liquid air) to permit lowering of the mercury cut-off (M3) connecting the azomethane storage bulb with the mixing chamber. After the desired amount of the gas had been admitted, by removing the liquid air, the cut-off was raised. The exact amount of azomethane admitted was then measured by reading with a cathetometer the difference in level between the two mercury columns comprising the cut-off, with the azomethane trap frozen. The vacuum over the frozen azomethane was always previously tested by comparing the two levels when the mixing chamber also was evacuated.

To admit ether to the mixing chamber, the mercury cut-off leading to the ether storage bulbs was lowered, with the stop-

cock, however, still closed. This stopcock (S14) was then op-
ened just enough to permit nearly all the mercury column above
it to pass through, when it was again closed. The mercury lev-
el below was then adjusted to a height of about 2cm above the
crutch of the cut-off. On again opening the stopcock, and per-
mitting the ether vapour to stream out slowly, this arrangement
functioned as a valve, allowing ether to pass into the mixing
chamber, but preventing the azomethane already present there
from diffusing back into the ether storage tubes. When about
the right amount of ether had been admitted in this manner, the
cut-off was raised above the stopcock (S14) by cooling the li-
quid ether in a cooling mixture.

To determine the proportion of ether in the mixing chamber
the new total pressure of both gases was read on the cathetom-
eter, care being taken to have the temperature the same as be-
fore. The volume of the manometer tubing (which of course was
increased after the ether was added) was neglected in the cal-
culation of percentage azomethane, as being negligible compared
with the total volume (500cc or more) or amount of gas present.

Experimental Procedure in
Making Rate Measurements

Before an experiment, the furnace was allowed to heat up
to about the right temperature, some 12 hours being required
to attain proper thermal equilibrium. The regulator oven was
then switched into the furnace circuit (by opening K) at the
same current, and allowed to heat for a further 12 hours. Be-
fore turning on the relay circuit of the regulator, the cur-
rent was kept at exactly the desired value, by manually adjust-

ing the transformer, for a period of thirty minutes. The stop-cock connecting the mercury reservoir on the regulator was then closed, the lid on the box being replaced as quickly as possible to avoid cooling the oven. The tungsten wire contact, fitting through the top of the box as described elsewhere, was then pushed down until the relay clicked, indicating contact with the mercury in the regulator. The current was then incr-eased to a value 0.25 amperes below the desired equilibrium value: then when the oven cooled and the relay circuit was broken, the current was automatically increased to 0.25 amps. above the equilibrium value, if the rheostats were adjusted to give a total current change of half an ampere. A greater or less total current change than this was found to give less ac-curate temperature control. After at least six hours on the regulator, the furnace equilibrium temperature was record-ed.

To completely evacuate the reaction chamber and connect-ions before a run, the diffusion pump was used for several hours while the chamber was hot. Usually the residual gas pre-ssure was less than 10^{-4} mm, as measured on the McLeod Gage.

Several methods of obtaining an initial gas pressure were used. If the pressure desired was small (1-10 cm) the connect-ing tubing was simply filled with the gas at a higher pressure, the storage chamber closed, and the reaction chamber then open-ed to the connections for a few seconds. Alternatively, if the air pressure outside the click gage was adjusted to correspond to the desired initial pressure (including of course the click constant) the reaction chamber could be opened carefully to

the storage chamber until the click was heard. Neither of these methods enabled a predetermined initial pressure to be obtained with any accuracy. For most of the experiments recorded in this thesis, the storage chamber was a 500cc bulb. For a high pressure run therefore (10-20cm), the gas pressure which happened to exist in the bulb at the time of the experiment, had to be used.

Time was measured on a large watch fitted with a seconds hand. This watch was checked, before using, against an electric clock of known accuracy. Time readings were probably accurate to ±2 seconds.

Before allowing the gas into the reaction chamber, the air pressure on the clicker gage was increased to such a point that the maximum possible pressure in the chamber would not exceed it by more than a few centimeters. The maximum air pressure ever used on the particular gage of these experiments, with the reaction chamber evacuated, was 20cm or slightly less. The maximum initial gas pressure it has been possible to use therefore, is about 20cm. When this adjustment had been made, the stopcock leading from the reaction chamber to the gas source was opened for just five seconds, then closed - the latter action marking "zero time". Using the controlled leak, the air pressure is then increased until a click is heard, indicating that the glass membrane has been pushed in, to its unstable position. This pressure is 2cm greater than the pressure at which the membrane "clicks out" to the stable position again; the pressure is therefore reduced to a value about 1mm greater than the click-out critical pressure. When the gas

pressure in the reaction chamber rises a millimeter, a click
is heard, and the time immediately noted.

The stopcock connecting in the McLeod Gage (S5) is left
open during these manipulations; the air pressure over the mer-
cury reservoir of this gage must be adjusted, using the three-
way stopcock (S3), so that when the critical click-pressure
has been set the mercury level rests just below the tee-joint
on the compression volume (G). If any dead-space is allowed
above this mercury level, the air pressure being measured will
be materially changed when the level is raised to take a read-
ing.

When time has been recorded, and the manometer (M2) also
read and recorded (this may be done before the click is heard)
the mercury in the McLeod Gage is allowed to rise quite slowly;
when the mercury level has passed the T-joint mentioned above,
the stopcock (S5) is closed. The level is never allowed to
rise rapidly, as the compression of the air must be completely
isothermal if serious errors are to be avoided. To obtain ac-
curate control of the rising mercury level, the screw clip (C)
was invariably used to regulate the flow of compressed air or
oxygen into the mercury reservoir (and not the stopcock).
When the latter is first opened the clip is kept tight, and us-
ually a sufficient pressure of air remains above the closed
clip to raise the mercury level above the T-joint as just des-
cribed. The stopcock (S3) on the reservoir is then opened ful-
ly, and further adjustment of the mercury level made with the
screw clip alone. Just before the rising mercury level reach-
es the mark (on the compression volume) to which adjustment is

being made, the large stopcock (S4) below the mercury-head scale is opened. The air pressure on this mercury head was usually kept at one atmosphere by leaving the stopcock (S2) open. When the mercury level in the compression volume reaches the mark (a reading-glass was always used for this observation) the stopcock on the reservoir is closed , the mercury-head tube tapped sharply, and the large stopcock (S4) closed, if the first mercury level has not then shifted from the mark. Otherwise, if the mercury level has fallen somewhat below the mark (as often happens) it may be raised by simply warming the compressed air above the mercury reservoir very slightly, with the hand: the tapping is then repeated, the mercury level re-checked and the large stopcock closed.

The mercury is now drawn into the reservoir (using S3, connected to the vacuum bottle) until the level is again just below the T-joint; the stopcock (S5) above the float valve is then opened, and the air pressure on the clicker readjusted to a critical value as before. While waiting for the click-out, the two manometer readings (M1 and H) are recorded.

The entire operation of measuring a pressure as described above, requires about five minutes time. During a two-hour experiment, a dozen experimental points were usually obtained, which is ample for graphing a smooth pressure-time curve.

Final pressures, taken as soon as the pressure in the reaction chamber no longer rose appreciably over a period of several hours, were measured with the cathetometer and manometer (M2)..

Treatment of Data

In order to calculate the pressure of gas in the reaction chamber from the McLeod Gage readings rescribed above, several factors had to be taken into account. First, the pressure obtained on the Gage included of course the "click constant": this therefore had to be subtracted. The head of mercury in the gage itself was read off an arbitrarily fixed scale, hence the scale reading corresponding to zero pressure in the Gage (called H_0 here) was subtracted from the observed reading (H). The pressures used on the second manometer (Ml) of the Gage, were various, hence a correction for corresponding changes in the lower mercury level of this manometer, was applied. This turned out to be 0.02 cm fall per centimeter rise above zero of the scale; the latter corresponded to exactly 25.40 cm pressure as measured with the cathetometer. The true mercury head, calculated with these corrections, could then be divided by a factor corresponding to the magnification ratio used in the experiment. Alternatively, a head of mercury corresponding to the value of the click-constant could be subtracted before dividing by the factor, the result then representing directly the gas pressure in the reaction chamber. Using the latter method, the formula for calculating gas pressures was -

$$P = \left[M(1.02) + (H-H_0) + 25.40 - 33.42 \right] \div 4.967$$
$$= \left[M(1.02) + (H-H_0) - 8.02 \right] \div 4.967$$

for magnification ratio I (March, 1937). Other calibrations used for the low pressure experiments are given in the Tables of Data. The Click Constant in this formula was 6.727 cm,

somewhat greater than the value used in earlier experiments[64], (6.700cm). Apparently the constant tends to increase very slowly but appreciably over a period of months. The value used however was always redetermined at the beginning and end of any series of experiments.

When the pressure values (for a run) were calculated, the results were graphed on a large scale (1mm scale = 10 secs and 0.01 cm pressure). A smooth curve was drawn thru the points by using a spline; this also permitted a fairly accurate extrapolation of the data back to "zero time", giving the initial pressure.

In order to determine the rate of decomposition of substrate molecules, from measurements of the rise of total pressure with time, it is necessary to know how many mols of product are being produced from a mol of substrate. If then it is assumed that this number is constant thruout a given experiment (i.e. if the products themselves are not decomposing at a measurable rate) then a simple calculation will give the number of mols of substrate, still undecomposed, at any time from the total pressure at that time, the initial pressure of the experiment and the final pressure. In the case of the present experiments it may be assumed (see discussion of results) that diethyl ether produces three mols of product from one of ether, while azomethane is simultaneously producing two mols. Hence at any time,

$$P = P_e + P_a + 3(P_o\beta - P_e) \quad 2(P_o\alpha - P_a)$$

$$P_e = \tfrac{1}{2}\left|P_o\left\{3-\alpha(1+e^{-k_o t})\right\} - P\right|$$

When $P_a \ll P_e$ then P_a may be neglected, and hence -

$$P = 3P_O - P_O\alpha - 2P_e$$

$$2P_e = P_O(3-\alpha) - P$$

and
$$-dP_e/dt = \tfrac{1}{2}dP/dt \tag{1}$$

In all calculations the correction of initial-final pressure ratios for deadspace outside the furnace, has been neglected. The value of the correction has been derived by Allen[65].

In the present experiments, the ether was never completely decomposed; the amount remaining depended on the percentage of azomethane added, the temperature and the total pressure. In order to determine the number of mols of ether disappearing per mol of azomethane added (i.e. the total chain-length λ) measurements of the initial-final pressure ratio were used. Thus

$$P = P_O(3-\alpha) - 2P_e - P_a$$

$$P_f = P_O(3-\alpha) - 2(P_e)_f$$

$$N = 3 - \alpha - 2(P_e)_f/P_O$$

$$= 3 - \alpha - 2(\beta - \alpha\lambda)$$

whence
$$\lambda = (N - 1 - \alpha)/2\alpha \tag{2}$$

This equation was used to calculate the chain-length values given in the Tables of Data.

The initial specific rate of decomposition of the diethyl ether may be calculated from the initial slopes of the pressure-time curves, if a first-order equation is assumed. Thus

$$dP/dt = -2dP_e/dt - dP_a/dt$$

At the very beginning of the reaction, the last term is given by $k_O P_O \alpha$ and the partial pressure of ether by $P_O(1-\alpha)$, and so $\dot{P}_e/P_e$ is readily found. These results are also included in

the Tables of Data.

In all cases where it has been necessary to use k_0, the specific reaction rate constant of azomethane, in the calculations, it has been assumed[25] that the cross-activational efficiency between the ether and the azomethane is unity. In view of the large excess of ether present, this seems a reasonable assumption. The values of k_0 have therefore been calculated on the basis of the total pressure of gas mixture; the data on values of k_∞/k_0 at various pressures was obtained from a paper by Kassel[66,67]. For k_∞ the equation[25]

$$k_\infty = 3.13 \times 10^{16} e^{-52440/RT}$$

was used.

THEORETICAL PART

The induction of decomposition in diethyl ether at low temperatures (300°C) by small amounts of azomethane was predicted, in this laboratory, on the basis of F.O.Rice and Herzfeld free radical theory. The mechanism of the normal ether decomposition as postulated by this author on the basis of his theory, has already been described (q.v.). The mechanism of the induced decomposition will be worked out on similar lines, and attempts made to correlate theoretical results with the experiments.

The Suggested Mechanism

The most reasonable mechanism, from consideration of the known properties of free radicals and their reactions with mol-

- ecules, has seemed to be the following:-

$$CH_3N:NCH_3 \longrightarrow 2Me + N_2 \qquad\qquad k_0$$

$$CH_3CH_2OCH_2CH_3 + Me \longrightarrow CH_4 + CH_3CH_2OC^H_{CH_3} \qquad k_1$$

$$\qquad\qquad k_2$$

$$Et + CH_3CHO$$

$$CH_3CH_2OCH_2CH_3 + Et \longrightarrow C_2H_6 + CH_3CH_2OC^H_{CH_3} \qquad k_3$$

$$CH_3CHO \; Me \longrightarrow CH_4 \quad CH_3CO \qquad\qquad k_4$$

$$Me + CO$$

$$2Me \longrightarrow C_2H_6 \qquad\qquad k_5$$

$$2Et \longrightarrow C_4H_{10} \qquad\qquad k_7$$

$$Et + Me \longrightarrow C_3H_8 \qquad\qquad k_6$$
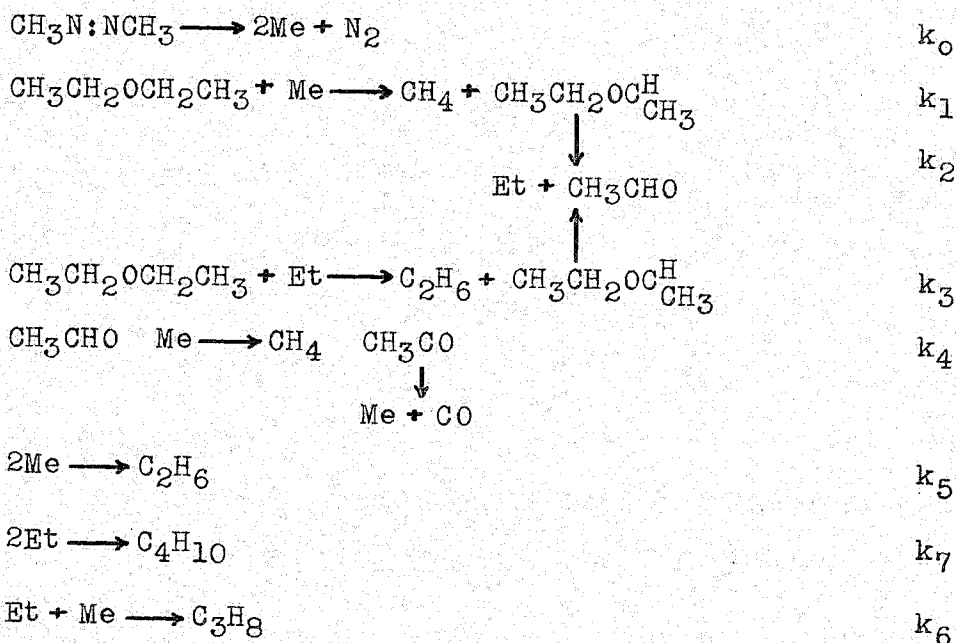
If k_0 &c refer to the respective specific reaction rates of the various steps of the mechanism; if further x_0 is the azomethane concentration, x_1 the ether concentration, x_2 that of methyl radicals, x_3 that of $CH_3CH_2OCHCH_3$ radicals, x_4 of ethyl radicals, then at the very beginning of the induced reaction, when a steady state of free radical concentration may be assumed, we have

$$dx_2/dt = 2k_0x_0 - k_1x_1x_2 - k_5x_2^2 - k_6x_2x_4 = 0 \qquad (1$$

$$dx_3/dt = k_1x_1x_2 + k_3x_1x_4 - k_2x_3 \qquad\qquad 0 \qquad (2$$

$$dx_4/dt = k_2x_3 - k_3x_1x_4 - k_6x_2x_4 - k_7x_4^2 \qquad 0 \qquad (3$$

$$- dx_1/dt = k_1x_1x_2 + k_3x_1x_4 \qquad\qquad (4$$

From equations (2) and (3) we obtain equation (5); then (6) at once follows from (1); subtraction of (5) and (6) gives (7):-

$$k_1x_1x_2 = k_6x_2x_4 + k_7x_4^2 \qquad\qquad (5$$

$$k_1x_1x_2 = 2k_0x_0 - k_5x_2^2 - k_6x_2x_4 \qquad\qquad (6$$

$$2k_0x_0 - k_5x_2{}^2 - k_6x_2x_4 - k_7x_4{}^2 = 0 \tag{7}$$

$$x_2 = k_7x_4{}^2/(k_1x_1 - k_6x_4) \tag{8}$$

The latter follows from equation (5). It shows that $x_2 \ll x_4$, which is to be expected from the fact that x_4 represents the concentration of the chain-carrier (ethyl) and hence it will be larger than x_2 (methyl concentration). Then, from (7)

$$2k_0x_0 - k_7x_4{}^2 = 0$$

$$x_4 = (2k_0x_0/k_7)^{\frac{1}{2}} \tag{9}$$

This value of x_4 may be substituted in equation (8) above; if then the result is combined with equations (9) and (4) we have

$$-dx_1/dt = k_3x_1x_0^{\frac{1}{2}}(2k_0/k_7)^{\frac{1}{2}} + 2k_1x_1k_0x_0(k_1x_1-X)^{-\frac{1}{2}} \tag{11}$$

where X is equal to $k_6(2k_0x_0/k_7)^{\frac{1}{2}}$; since this term may be neglected in comparison with k_1x_1, as described later, the final equation is

$$-dx_1/dt = k_3(2k_0/k_7)^{\frac{1}{2}}x_1x_0^{\frac{1}{2}} + 2k_0x_0 \tag{12}$$

Considering the concentration terms for the moment as pressure, equation 12 may be written in terms of the initial slope of the experimental pressure-time curve, by using a previous equn, page 31.

$$(dP/dt)_0 = 2K(2k_0)^{\frac{1}{2}}x_1x_0^{\frac{1}{2}} + 5k_0x_0 \tag{13}$$

At the very beginning of the reaction, where this relation should hold, we may place

$$x_0 = P_0\alpha$$

$$x_1 \quad P_0(1-\alpha) \tag{14}$$

In equation 13 therefore all the quantities with the exception

of K, are known or can be measured directly. At low pressures however, in the region of 15-20 cm or lower, the value of k_0 begins to drop off, in accordance with the accepted theory of unimolecular reactions. This means that in the pressure range in which the present experiments were carried out, the specific azomethane rate k_0 is a function of the pressure. If equn 13 is to be tested therefore, this must be taken into account.

According to the experimental results of Ramsperger on azomethane at low pressures, the relationship of log k_∞/k_0 to log P - where k_∞ is the limiting high-pressure rate constant at a given temperature, k_0 the rate constant at a lower pressure P - is roughly linear up to about 100 mm. Hence in this range we may write

$$- \log k_0 = - \log k_\infty - C_1 \log P \quad \log C_2$$

$$1/k_0 = C/Pk_\infty$$

$$k_0 = \text{Constant} \cdot P \tag{15}$$

This constant is of course a function of the temperature. If this is applied to equation 13,

$$\dot{P}_0 = 5CP_0^2 \alpha + 2(C\alpha)^{\frac{1}{2}}\beta P_0^2 K$$

$$= \text{Constant} \times P_0^2 \tag{16}$$

It therefore follows that the variation of initial slope with initial pressure for a given mixture is such that

$$\dot{P}_0 / P_0^2 = \text{constant}$$

for all initial pressures less than 10cm. At pressures greater than this, but less than 200 mm, no such simple relationship can be deduced.

For experiments 25 and 26 respectively, the calculated values of the above quotient are 1.05×10^{-6} and 1.00×10^{-6}

mm sec^{-1} mm^{-2}. More data is needed to check this agreement.

Activation Energies of Elementary Reactions

The suggested mechanism for the induced reaction, if shown to be correct, may be used to determine experimentally the activation energies of the various reactions between free radicals and molecules which are involved[9]. The estimation of such energies, as already mentioned, is extremely important from the point of view of the Rice-Herzfeld theory (qv) as the nature of the free radical chains in other decompositions may be predicted from these values.

The theoretical equation may be written as follows

$$-\dot{x}_1 = Kk_0^{\frac{1}{2}}A + Bk_0$$

where A and B are constants independent of temperature. By logarizing after making the substitutions $k_0 = Ce^{-E_1/RT}$ and $K = C_1e^{-E_2/RT}$, we obtain

$$\ln(-\dot{x}_1-Bk_0) = -E_1/2RT -E_2/RT -C_3$$

By differentiating with respect to 1/T it is seen that the value of E_2 may be obtained by a plot of the experimental data.

Discussion of the Suggested Mechanism

The thermal decomposition of azomethane has been known for some time as a straight dissociation into free methyl radicals and nitrogen[25]. This simultaneous splitting of two bonds is explained by the formation of the enormously stable nitrogen molecule. The first step of the suggested mechanism, therefore seems secure.

The second step is based on F.O.Rice's mechanism for the normal pyrolysis of the ether. The alternative step,

$$CH_3CH_2OCH_2CH_3 + Me \longrightarrow CH_4 + CH_3CH_2OCH_2CH_2$$

would give

$$C_2H_4 + HCHO + Me$$

and

$$HCHO \longrightarrow H_2 + CO$$
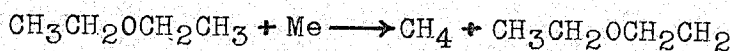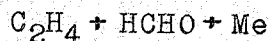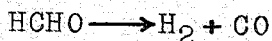
so that equivalent amounts of hydrogen and carbon monoxide would be formed. To determine if this step took place, an analysis of the final products of Run 15, and also of Run 28, was made. In both cases, negligible amounts of hydrogen were found. Ethylene, which should also be formed here in equimolar amounts with the carbon monoxide, was similarly shown to be absent. With this evidence, it was assumed that the reaction of a methyl radical with the a-carbon atom of the ether molecule, requires a sensibly higher activation energy than the reaction with a b-carbon atom, and hence could be neglected.

The third step, the spontaneous decomposition of the heavy radical EtOCHMe into acetaldehyde and free ethyl, follows from the known instability of heavy radicals.

An assumption has been made in the derivation of equation 12 that the chain decomposition of the acetaldehyde is fast compared with the other rate-determining steps. This assumption is based on the results of Allen and Sickman[13] who studied the decomposition of acetaldehyde with azomethane, and obtained long chain-lengths in the temperature range of the present experiments. In the presence of an excess of azomethane and hence free methyl radicals, the acetaldehyde would not therefore be expected to appreciably accumulate.

Further stages in the proposed mechanism consist of the chain decomposition of the diethyl ether, with ethyl radicals

as the chain-carrier. These chains are ultimately broken, probably at the walls, by the recombination of two free radicals to form a saturated hydrocarbon.

In the mathematical treatment of these processes, it was assumed that $k_1 x_1 >> k_6 (2k_0 x_0 / k_7)^{\frac{1}{2}}$. Now the values of the specific rate constants for various types of reactions involving free radicals, may be estimated if the activation energies are known. By semi-empirical methods, F.O.Rice and co-workers have assigned values to these activation energies, which fit satisfactorily many of the reactions thus far studied from the free-radical point of view. If we represent a light free radical by "R" and a heavy radical by "R_1" the various simple types of interaction of these with molecules (M) are as follows:

$$R + M \longrightarrow RH + R_1 \qquad\qquad E = 15 \text{ Cal}$$
$$R + R' \longrightarrow RR' \qquad\qquad\qquad 8$$
$$R_1 \longrightarrow R + M \qquad\qquad\qquad 25-50$$
$$R_1 + M \longrightarrow R_1 H + R_1' \qquad\qquad 15-25$$

Now in general it may be written very approximately for second-order processes, that $k'' = 10^9 e^{-E/RT}$; for unimolecular processes the constant is 10^5, in units of mols per 24 litres. When k_1, k_6 and k_7 were calculated from this data, it was found that the inequality stated above, was justified.

Final Products of the Reaction

If the final products resulting from the suggested mechanism of the reaction are considered, it is seen that for the various chain-lengths we may write, for example,

$$Me_2 N_2 + Et_2 O \longrightarrow 2CH_4 + C_3 H_8 + CO + N_2$$

$$Me_2 N_2 + 2Et_2 O \longrightarrow 3CH_4 + C_3 H_8 + 2CO + N_2 + C_2 H_6$$

$$Me_2N_2 + 5Et_2O \longrightarrow 6CH_4 + C_3H_8 + 5CO + N_2 + 4C_2H_6$$
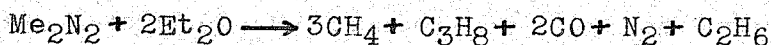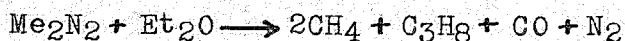
Then for each extra molecule of ether consumed, the final products should be increased by three mols - and by subtraction of the equations, these three mols are C_2H_6, CO and CH_4. Hence in effect, the induced decomposition is proceeding thus

$$C_2H_5OC_2H_5 \longrightarrow CH_4 + C_2H_6 + CO$$

This leaves the azomethane effectively producing two mols of products, per mol of azomethane decomposed. This is the basis of equations used in a previous section (qv).
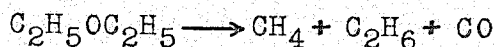
To test these conclusions, the gas analysis of Run 15 may be considered. According to the above mechanism, one mol of CO should be produced per mol of ether decomposed. Further, each mol of ether should produce three mols of products. The confirmation of the required absence of hydrogen and ethylene in appreciable amounts, has already been mentioned. In Experiment 15, the initial pressure of ether was 61.35 mm, and of azomethane was 7.7 mm. The residual ether pressure in the products was measured and found to be 21.05 mm (14.1% of the total final pressure). Hence the chain length in this case was = 40.30/7.7 = 5.2 units. The carbon monoxide found was 85% of the decomposed ether. The measured residue of unabsorbed nitrogen and saturated hydrocarbons was 187% of the decomposed ether plus azomethane (theoretically 200%). Further, if it is assumed that azomethane produces two mols of products, then

total pressure of products	128.2 mm
azomethane products	15.4
ether products	112.8 mm

Hence one mol of ether produced 112.8/40.3 = 2.8 mols of

products. The agreement is seen to be good.

The Effect of Various Factors on the Chain-Length

The chain-length of this induced reaction is given by the ratio $\dot{x}_1/\dot{x}_0$ hence from equation 12,

$$\lambda_o = K(2/k_0)^{\frac{1}{2}}x_1/x_0^{\frac{1}{2}} + 2$$

gives the theoretical initial chain-length. The minimum value is apparently two. This equation may be written

$$\lambda_o = K(2/k_0)^{\frac{1}{2}}P_0^{\frac{1}{2}}(1-\alpha)/\alpha^{\frac{1}{2}} + 2$$

It is seen that the chain-length should, qualitatively at least i) increase with initial pressure ii) decrease with increasing percent of azomethane in the mixture iii) decrease with temperature. Chain-length results quoted in the Tables show that this is true in the present experiments.

An estimation of the actual value of the initial chain-length, may be made from the experimental initial P-t slopes. Thus if we call k_e the specific rate constant of the induced ether decomposition, then $\lambda_o = dx_1/dx_0 = k_e x_1/k_0 x_0 = k_e \beta/k_0 \alpha$. The values of k_e have been calculated as already described, so the following table was obtained

Expt	λ_o	λ
19	0.8	5.5
26	1.2	12.3
27	1.6	8.4
28	2.5	36.7

In this table, is the total chain-length, calculated from N. It is seen from these examples, that i) the initial "chains" are seemingly less than two units long ii) there is no apparent connection between the total and initial chain-lengths, at least when calculated in this manner.

Further Discussion of Results

In addition to the classic work of Hinshelwood[6] on diethyl ether, this compound has been studied by O.K.Rice and Sickman[44] Steacie[45,46,47], Kassel[48], Newitt and Vernon[49], Fletcher[42]. These authors were interested in the ether decomposition reaction as an experimental example of the current theory of unimolecular reactions[25], which predicts a falling-off in specific rate of such reactions, at low pressures. When the Rice-Herzfeld theory of chain reactions was proposed however, it became apparent[13] that here was another explanation of the effect of pressure on rate - i.e. the effect on the reaction chains. It therefore became of very great importance to determine whether or not this reaction (and others similarly) involves a chain mechanism, and if so whether the chains are of sufficient importance in the reaction to account for the observed dropping-off in rate, with pressure.

The various methods of testing for reaction chains have already been described. Of these, one has recently been applied by Hinshelwood[28,71], who mixed diethyl ether with nitric oxide and redetermined the rate. He found a definite inhibition, but calculated from his results that the chain decomposition represented only a small part of the total reaction. About the same time however Steacie[45], investigating the normal ether decomposition at pressures up to 20,000 cm, concluded qualitatively that the high pressure reaction (observed order 1.4) agrees with the free radical theory.

The very recent work of Fletcher[42,43] has shown that a chain decomposition of acetaldehyde is induced (490-550°C)

when this compound is heated with diethyl ether; presumably these chains originate with free radicals from the ether.

In the present investigation, it has been shown that methyl radicals, produced thermally from azomethane, initiate decomposition of the ether at as low as 300°C.

The possibility that the azomethane in this reaction is merely acting as a homogeneous catalyst (see page 8) does not seem likely in view of the experimental results. An experiment was carried out in which the ether-azomethane mixture was heated to 230°C for about 24 hours; the total pressure however remained unchanged. At this temperature the azomethane does not decompose, hence there are no methyl radicals present to act on the ether and in the absence of homogeneous catalysis, no decomposition would be expected.

The calculations of total and initial chain-lengths, described above, reveal that the induced chains are very short, even 10% of azomethane failing to decompose all the ether. Furthermore, the chains become shorter as the temperature is raised, and longer as the pressure is raised. Steacie's conclusions on the high pressure ether decomposition have just been mentioned; the present results are thus in agreement with his ideas. The shortening of the chains with temperature is however more significant: it seems only reasonable to suppose that at the high temperature of the normal pyrolysis (and all ordinary pressures) the chains must be so short as to form only a very small and unimportant part of the total decomposition reaction.

PART   II

A NEW METHOD OF SEMI-MICRO GAS ANALYSIS

AN APPARATUS FOR SEMI-MICRO GAS ANALYSIS

In the study of the mechanism of gas reactions by the reaction rate method, it is apparent that an accurate method of gas analysis, which may be used when only moderately small quantities are available, and which is particularly suited to the determination of those constituents usually found in the products of organic pyrolyses, is very necessary. The methods at present available are in general far from satisfactory from the point of view of accuracy and speed; further, many substances which it is of great importance[9] in reaction kinetics to be able to estimate accurately, cannot be determined at all in the mixtures usually found in such cases.

The work about to be described, forms the first stage of what is hoped will form a comprehensive study of this problem, to be undertaken by this laboratory. Perhaps the most important part in the solution of the problem, is the development of a suitable apparatus; this consequently was undertaken first, as part of a separate research by the present writer.

Preliminary Results

The first apparatus design to be considered, was based on the well-known arrangement of Bone and Wheeler[70]. The arrangement is shown in the accompanying sketch.

The gases to be analyzed were pushed into the constant-volume buret (B) by means of the attached Topler Pump. The connection between the pump and the buret was a length of quite fine capillary tubing, attached to the buret some distance

M

TOPLER

B

P

C
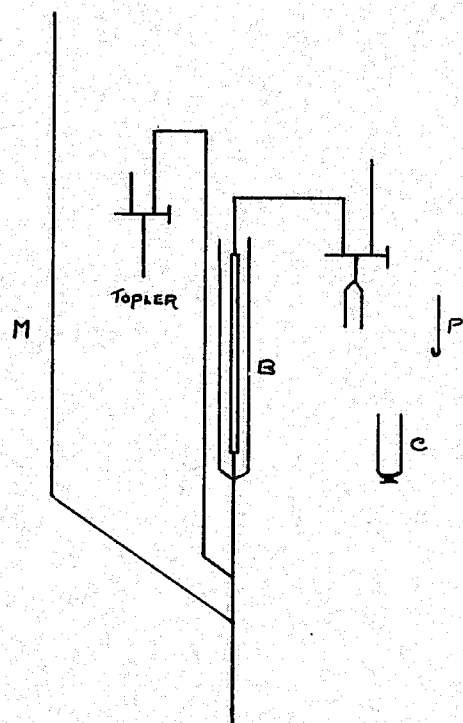
v. P. 43

below the reading marks. The buret itself was provided with volumes of about 5, 15 and 35 ml; the exact ratio between the volumes could be readily determined by experiment. The confining liquid used was of course, mercury; this was introduced into the buret and the attached manometer-tube side arm (M) by means of a leveling bulb. Behind the tube M (of wide-bore but heavy capillary tubing) a millimeter scale was permanently fixed. The top end of the buret comprised one arm of a three-way stopcock thru which the gases could be introduced into the gas pipet (G) when the mercury reservoir (C) was in place. Trapped air could be previously removed from the pipet by attaching a Bunsen Pump to the other arm of the three-way stopcock, and cautiously allowing the mercury to rise from the reservoir. Reagents were introduced into the gas pipet by means of a curved delivery pipet (P) of 5 ml volume.

This apparatus was used in the analysis of Experiment 15 (Part I of this thesis). After some considerable use however the design was finally rejected, for the following reasons:

1) The method of introducing the gas from the Topler into the buret, was awkward and hard to control; further, the reverse operation was not possible.

2) Since the reagent had to be partly drawn into the buret after an absorption, the buret itself quickly became dirty with an accumulated mixture of reagents on the walls. The vapour-pressure of these reagents was then a source of error, as it was not possible to keep a drop of standard acid in the buret to correct for this.

3) The buret stopcock soon froze in contact with the re-

agents used as absorbents. This was liable to cause air leaks during an analysis.

4) Cleaning and drying the absorption pipet after each absorption, occupied a very long time, owing to the awkward shape of the pipet.

5) It was also necessary to clean some 200cc of mercury for each new reagent used, as well as the glass container. This greatly increased the time necessary for an analysis.

Several attempts were made to carry out a slow combustion of hydrocarbons with a platinum spiral heated electrically inserted in the gas pipet. Explosions of serious proportions resulted, however.

A New Apparatus

In order to eliminate entirely any necessity for manipulation of the reagents, which is the source of most of the disadvantages of the above apparatus and many others described in the literature, the arrangement in figure (5) was devised.

Gas samples were introduced into the constant-volume gas buret, fitted with mercury leveling bulb and side-tube for measuring pressures as before, thru the Topler Pump. To withdraw a sample from the buret, the mercury in the latter was usually raised to a point just above the top of the water-jacket, then held in place by clamping the rubber leveling-tube and pumping on the small dead-space remaining, with the Topler. This allowed the buret to contain permanently about 0.2 ml of 6N sulfuric acid, thereby maintaining a constant water vapour pressure during all experiments.

From the Topler, the gas sample could be pushed, thru two three-way stopcocks, into the absorption pipet attached at P (diagram) by a ground-glass joint. The pipet itself was merely a 10cc glass bulb, sealed to one half of the ground-glass joint. After absorption had taken place (using 5 ml of reagent in each case) the residual gas was replaced in the buret by pumping with the Topler (usually three strokes were ample, as the volume of the Topler was at least 200cc). To evacuate the pipet of air after a reagent had been inserted, the Topler pump was also used, and the air pushed out thru Q (figure).

It is seen that in this arrangement an important change has been made from orthodox practice with liquid reagents, i.e. the gas is removed from the pipet by pumping. In this manner, the reagent has no opportunity of contaminating the measuring portion of the apparatus, as it only comes in contact with the gas sample itself. Actually of course the liquid reagents are not "pumped off" in the usual meaning of the term, but instead the amount of gas or air above the reagent is successively reduced by partition with the Topler volume. The space above the reagent is then always at the partial pressure of the reagent itself (at least), hence there is no cause for it to boil at ordinary temperatures.

Other advantages of the arrangement are apparent from the figure. The pipet, being detachable, can be readily cleaned and refilled with another reagent. The shape of the pipet permits the contents during absorption to be cooled in a Dewar flask, as is required for example in the absorption of ethers. A mercury trough and small test-tube seated over the outlet at

P

Q

W

FIG. 5

EL '36
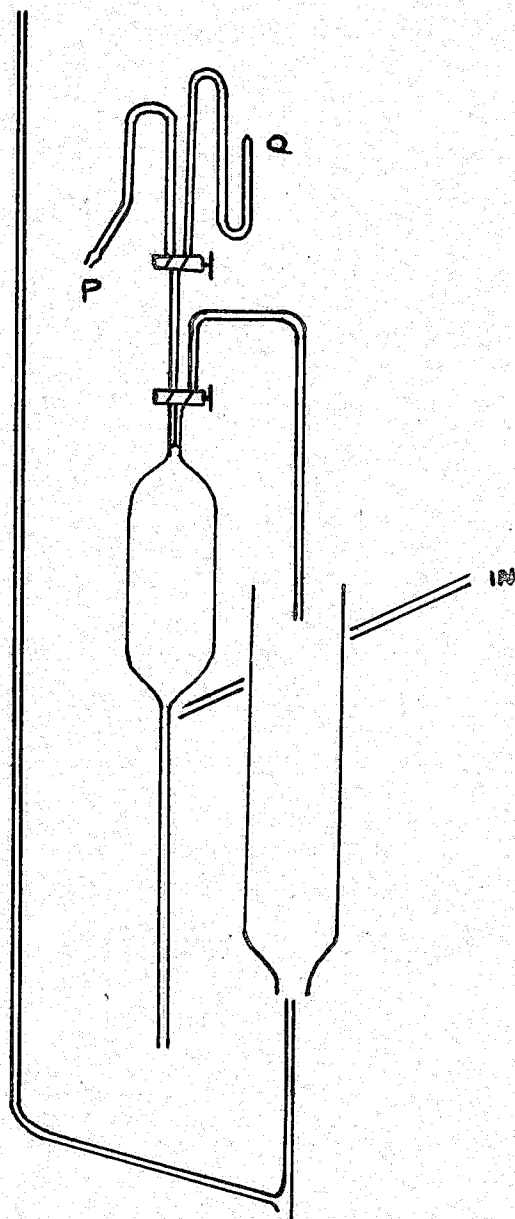
Q permits gas samples to be stored if necessary. An explosion pipet may be attached thru a rubber connection at P. As the reagents do not come in contact with mercury, solutions such as palladous chloride which are attacked by mercury, may be used. The important feature however is the ease and simplicity of manipulation. The entire process of measuring, absorbing and remeasuring the gas sample, is carried out merely by raising and lowering a mercury leveling bulb and turning two stopcocks. This reduces the possible sources of error, involved when more complex manipulations are necessary, and also increases the speed of operation.

The disadvantages of the arrangement may be mentioned. Since the gases are removed from the pipet by successively reducing their partial pressure, reagents which depend on physical absorption (Henry's Law solution) cannot be used; however these are very seldom met. Also, it is difficult with the type of pipet used, to have a sufficient surface of reagent available to the gas to permit rapid absorption. This is a more serious problem.

Experiments with the Apparatus

Preliminary experiments on the apparatus (July, 1936) included a determination of the oxygen in an air sample (sodium hyposulphite reagent), the absorption of a sample of pure hydrogen by palladous chloride reagent (at room temperature), and the analysis of Experiment 28 (Part I of thesis). The first determination gave just 20.0% by volume; the second showed that 5 ml $PdCl_2$ reagent was capable of absorbing 3cc of pure hydrogen (1 atm). All three experiments demonstrated that

none of the common reagents used in gas analysis, show any permanent tendency to boil, when used in the new apparatus.

SUMMARY

(1) The decomposition of diethyl ether has been induced at temperatures between 300-340°C, by introducing a few percent of azomethane.

(2) A chain mechanism for the process has been postulated, and evidence presented to support it.

(3) The experiments indicate that the chains are very short; the normal ether decomposition has been discussed in view of these results.

(4) An apparatus for accurate reaction rate measurements has been described.

(5) An apparatus for the exact determination of small quantities of gases has been designed.

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TABLE I

Summary of All Experiments

Expt	%azo	P_o mm	N	T	$\dot{P}_o$ mm/sec
5	9.6	22.20	1.97	313.0	4.1×10^{-3}
6	9.6	20.45	1.62	329.0	4.8
7	1.2	49.70	1.38	306.8	1.4
8	1.2	47.95	-	317.5	2.0
13	11.2	27.60	2.29	307.2	2.2
14	11.2	16.70	-	307.4	1.2
15	11.2	69.05	2.16	307.7	8.3
17	11.2	29.60	-	299.5	1.6
18	11.2	28.45	1.83	326.2	8.0
19	6.34	32.75	1.76	309.6	2.1
20	1.13	21.90	-	309.5	0.2
21	1.13	71.15	1.35	310.0	2.0
22	1.13	30.95	1.14	325.9	1.2
23	1.13	54.35	1.24	343.9	11.0
24	1.13	33.90	-	324.4	1.4
25	1.13	30.85	-	322.2	1.0
26	1.13	57.50	1.29	322.2	2.5
27	1.13	53.65	1.20	321.5	2.5
28	1.13	161.05	1.84	321.8	13.5
31	1.24	181.50	1.59	325.5	15.0
32	1.24	150.15	-	313.0	5.0

TABLE II

$10^5 k_e$	Expt	$10^4 k_o$
2.48	13	3.15
2.26	14	2.82
1.14	25	8.75
1.34	26	9.85
7.65	23	45.0
1.15	21	4.66
1.96	17	1.71
8.10	18	11.8
4.32	15	3.88
2.11	19	3.88
1.79	27	9.85
3.48	28	13.2

TABLE III

Total Chain-Lengths

λ	Expt
15.33	7
5.21	13
8.36	27
36.68	28
4.68	15
12.33	26
3.20	18
5.70	22
4.55	5
2.72	6
10.12	23
14.98	21
5.49	19

TABLE IV

Constituent	Scale Reading	Pressure	Temperature
sample	49.68	46.40	24.9°
ether	43.15	39.87	25.0
ethylene	42.85	39.57	26.4
oxygen	42.40	39.12	25.3
carbon monoxide	31.67	28.39	24.8
hydrogen	31.63	28.35	24.8

Run 15

Constituent	Reagent	% vol
ether	cold conc H_2SO_4	14.1
ethylene	activated H_2SO_4	1.2
oxygen	sod. hyposulf.	0.9
CO	amm. CuCl	23.1
hydrogen	$PdCl_2$ @ 20°C	0.0
residue		60.6

TABLE V

Pure Azomethane Sample (I)

(Experiment 4)

TIME sec	PRESSURE
zero	22.70 mm
1000	29.35
2000	30.65
2500	31.80
3000	32.95
3500	34.05
4000	35.15
4500	36.20
5000	37.10
5500	37.90
6000	38.60
6500	39.25
7000	39.90
	44.45

Temperature $307.4^\circ C$
P_f/P_o 1.95

TABLE VI

Pure Ether Sample (I)

(Experiment 3)

TIME sec	PRESSURE
zero	23.65 mm
250	23.95
500	24.25
1000	24.85
1500	25.40
2000	26.00
2500	26.60
3000	27.10
6000	30.20
6500	30.65
7000	31.05

Resistance 136.5
P_f/P_o 4.59

dP/dt initially 1.2×10^{-3} mm/sec

Experiment 12

Pure Ether Sample (II)

TIME sec	PRESSURE
zero	68.45 mm
185	72.73
672	74.52
1087	78.01
1490	81.27
1902	84.47
3185	94.52
infinity	264.4

Temperature (139.3 ohms)
P_f/P_o 3.86

TABLE VII

TIME sec	RUN 5	RUN 6	RUN 7	RUN 8	RUN 13
zero	22.20	20.45	49.70	47.95	27.60
250	23.30	21.60	50.00	48.45	28.15
500	24.25	22.80	50.35	48.90	28.65
1500	25.90	24.90	51.05	49.80	29.70
1000	27.20	26.90	51.75	50.65	30.70
2000	28.35	28.60	52.45	51.40	31.60
2500	29.50	29.90	53.05	52.10	32.55
3000	30.65	30.80	53.55	52.80	33.50
3500	31.75	31.40	54.05	53.50	34.50
4000	32.65	32.00	54.55		35.50
4500	33.50				36.45
5000	34.25				37.35
5500	34.95				38.10
6000	35.70				38.85
infinity	43.80	33.15	68.90		53.15

This table gives total pressures in millimeters

TABLE VIII

TIME sec	RUN 14	RUN 15	RUN 17	RUN 18	RUN 19
zero	16.70	69.05	29.60	28.45	32.75
250	17.05	71.15	30.00	30.35	33.25
500	17.30	73.20	30.40	32.10	33.80
1000	17.85	77.35	31.25	35.35	34.85
1500	18.35	81.50	32.05	37.85	35.90
2000	18.85	85.55	32.85	39.95	36.90
2500	19.30	89.45	33.65	41.65	37.90
3000	19.80	93.15	34.45	43.15	38.85
3500	20.20	96.85	35.25	44.45	39.75
4000	20.65	100.20	36.00	45.55	40.70
4500	21.10	103.35	36.75	46.40	41.60
5000	21.55	106.25	37.45	47.15	42.45
5500	21.95	109.05	38.20	47.75	43.25
6000	22.30	111.60	39.00	48.25	43.95
infinity		149.25		52.10	57.60

TABLE IX

TIME sec	RUN 21	RUN 22	RUN 23	RUN 24	RUN 25
zero	71.15	30.95	54.35	33.90	30.85
250	71.65	31.25	56.80	34.25	31.15
500	72.15	31.55	58.55	34.60	31.40
1000	73.10	32.15	60.80	35.25	31.95
1500	74.05	32.70	62.15	35.90	32.50
2000	75.05	33.15	63.00	36.35	32.85
2500	76.00	33.50	63.50	36.75	33.15
3000	76.90	33.85	63.90	37.15	33.50
3500	77.85	34.20	64.25	37.50	33.85
4000	78.70	34.55	64.55	37.90	34.20
4500	79.40	34.80	64.80	38.25	34.50
5000	80.10	35.00	65.05	38.45	34.80
5500		35.10	65.25	38.70	
6000		35.20		38.95	
Infinity	81.91	35.25	67.85		

TABLE X

TIME secs	RUN 26	RUN 27	RUN 28
zero	57.50	53.65	161.00
250	58.15	54.30	164.35
500	58.80	54.95	167.55
1000	60.00	56.05	173.65
1500	61.25	56.90	179.15
2000	62.35	57.70	183.95
25000	63.45	58.40	188.35
3000	64.35	59.00	192.25
3500	65.10	59.55	195.40
4000	65.90	60.05	198.00
4500	66.60	60.50	200.15
5000	67.25	60.90	202.15
5500	67.80	61.20	204.00
6000	68.30	61.50	
infinity	73.95	64.45	297.7

EXPERIMENT 30

Pure Azomethane (III)

TIME sec	PRESSURE	
zero	107.30	mm
370	136.12	
705	156.78	
1219	177.78	
1695	190.26	
2160	197.99	
2978	206.83	
6000		
infinity	224.2	

Temperature $326^{\circ}C$

P_f/P_o = 2.09

Graphical half-life, 885 seconds

ACKNOWLEDGEMENT