THE PYROLYSIS OF DIPHENYLMETHANE AND FLUORENE

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PYROLYSIS
OF
DIPHENYLMETHANE AND FLUORENE

being a Thesis

presented by

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DECLARATION

I hereby declare the following Thesis to be a record of results of experiments carried out by me and furthermore that the Thesis is my own composition and has not been previously presented in application for a Higher Degree.

The investigations were carried out in the Chemical Research Laboratories of the United College, St. Andrews, under the direction of Doctor Charles Horrex.

[redacted]

[redacted]

UNIVERSITY CAREER

I entered the United College of the University of St. Andrews in October 1946 and graduated with First Class Honours in Chemistry on the 30th June, 1950.

The research described in this Thesis was carried out in the United College under the direction of Dr. Charles Horrex within the period July 13th 1950 to 22nd September 1952.

CERTIFICATE

I hereby certify that Mr. James Osborne McCrae has spent nine terms at research work under my direction, and that he has fulfilled the condition of Ordinance No.16 (St. Andrews) and that he is qualified to submit the accompanying Thesis in application for the Degree of Doctor of Philosophy.

Director of Research.

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DISCUSSION

ABBREVIATIONS AND SYMBOLS.

The following are employed throughout the thesis unless otherwise stated.

^{o}C	Degrees centigrade
^{o}K	Degrees Kelvin
E_a	Energy of activation
D	Bond dissociation energy
ϵ	Molecular extinction coefficient
k	Rate constant
log.	Logarithm to base 10
ln	Logarithm to base e
λ	Wavelength
O.D.	Optical Density
c	Concentration
Q_f	Heat of formation
t	Contact time
α	Resonance exchange integral
A	Appearance potential
e	Charge
m	Mass
V	Voltage
H	Magnetic field strength
D.P.M.	Diphenylmethane
T.P.E.	Tetraphenylethane

SUMMARY

This thesis is divided into four main sections.

In the 'Introduction' an attempt has been made to give, by a historical approach, a brief account of some of the advances which have been made towards a solution of the general problem of evaluating the energy associated with chemical bonds in the undisturbed molecule and also that required to disrupt the molecule into two fragments.

A detailed review of the many experimental methods available for the determination of bond dissociation energies has not been given since there are now good accounts[1] available in the literature, but attention has been focussed on those techniques which are of interest in connection with the present investigation.

The 'Present Investigation' deals with all the experimental work which has been carried out in the examination of diphenylmethane, fluorene, diphenylmethyl bromide, tetraphenylethane and toluene. Discussion in this section has been confined mainly to experimental points.

In the third section, the 'Discussion', the results are dealt with, not in the chronological order in which they were obtained, but in a sequence which permits a more satisfactory treatment. As the information obtained from the studies on fluorene is required in the discussion of the diphenylmethane results it is considered first. Then an examination is made of data from other investigations

in order to assess what products might have been expected from the pyrolysis of diphenylmethane, and this is followed by a consideration of the results of the present work carried out on this compound.

Bond dissociation energies have been derived for the methylenic C-H bond in fluorene and in diphenylmethane, also for the central C-C bond in tetraphenylethane. A mechanism is proposed for the decomposition of diphenylmethyl bromide but the limited experimental data does not permit a definite conclusion to be reached.

An account of the method of analysis of the ultra-violet absorption curves of the toluene pyrolysis products precedes a brief resume of the limitations of the method of analysis by ultra-violet spectrophotometric examination of the mixtures resulting from hydrocarbon pyrolyses.

The section is concluded with a short account concerning the existence of unsaturated dimer analogues in the thermal decomposition products of hydrocarbons.

In the 'Appendix' details are given of thermochemical and kinetic calculations, the results of which are used in the 'Discussion' section.

INTRODUCTION

Modern Free Radical Chemistry can be regarded as having originated from the classic triphenylmethyl researches of the Gomberg[2] school early in the present century.

This and much of the work which subsequently followed in the field was of an essentially empirical nature involving largely the techniques of organic reactions in solution.

About the same time as Gomberg was carrying out his experiments, Wegscheider[3] proposed that chemical reactions go in steps involving unstable intermediates and that the reason was because in this way free energy changes were gradual. He further suggested that compared to the concentrations of the reactants, the concentrations of these intermediates are negligibly small and that the rates of the successive steps are equal. This was known as the principle of "Equality of Partial Velocities".

However, it was not until 1929 that Paneth and Hofeditz[4] widened the field of knowledge considerably by demonstrating the existence of alkyl free radicals as unstable intermediates in gaseous reactions. This work has initiated a great number of researches in which methods of physical chemistry have been applied to the investigation of free radicals.

Through these researches, it has become recognised that many apparently complex chemical reactions take place in a series of simple steps in which the active agents are free radicals. It is therefore inevitable since these intermediates are formed by the rupture of a chemical bond that attention should have become directed towards a study of the energetics of the dissociation process and of the fragments thereby formed. F.O. and K.K. Rice[5] were early workers in this field and used essentially the same metal mirror techniques as Paneth and Hofeditz.

Unfortunately some confusion has existed in the literature dealing with the nomenclature in this field of study and it is therefore proposed to give a brief account of

(1) The two main concepts concerning the energy associated with chemical bonds i.e.
  (a) Average Bond Energy[6] (previously bond energy[7], bond energy term[8], mean bond energy[9])
  (b) Bond Dissociation Energy[10] (previously bond energy)

(2) Theoretical calculation of the energy and reactivity of free radicals.

Consideration will then be given to experimental methods used to determine bond dissociation energies.

Average Bond Energy

The expression "Bond Energy" was introduced by Fajans[11] in 1920 and a method devised by him for calculating from thermochemical data the bond energies in organic molecules. This was based on the observation that heats of combustion and hence heats of formation of isomeric compounds are almost the same and that in a homologous series the increase in heat of formation is almost constant for each $-CH_2-$ group added. He therefore as an initial simplification assumed that the energy contribution of each bond was a definite and fixed amount, completely independent of the nature of the molecular environment.

This method was developed by other workers, chiefly Winberg[12] Huckel[13], Thiel[14] and more recently by Pauling[15].

The last named has from the field of quantum mechanics[16] derived evidence which he claims is in support of Fajans initial assumption and proceeds to his postulate of the additive nature of normal covalent bonds. Using this in conjunction with spectroscopic data on diatomic molecules and thermochemical data on molecules containing only one type of bond he has drawn up tables of bond energies.

The general procedure adopted has been, in the case of molecules containing only one type of bond to divide the molecular heat of formation from atoms equally between each of the bonds e.g.

$$q = \frac{Q_f^a}{n}$$

Q_f^a = heat of formation of the molecule from atoms.

q = Average bond energy

n = number of bonds in the molecule.

Such a process is unequivocal in molecules containing only one type of bond as there is no doubt about partitioning the heat of formation amoung the 'n' identical bonds. The value of q obtained by this method is obviously an average value.

For molecules containing more than one kind of bond, it was necessary to know the energies of all types except one from other data and to obtain the remaining bond energy as a residuum. Take for example CH_3Cl.

$$q(C - Cl) = Q_f^a(CH_3 - Cl) - 3q(C - H)$$

the value of $q(C-H)$ having been previously derived from $Q_f^a\ (CH_4)$. This method of course involves the assumption that $q(C - H)$ in chloromethane is the same as in methane.

By making such assumptions it is possible in principle to determine the average bond energies of bonds involving carbon; a practical difficulty arises, however, over the latent heat of sublimation of carbon which is not yet known with certainty. This figure is necessary to calculate the heat of formation of a molecule from its atoms as shown below.

$$\begin{tikzcd}
n\,C_{solid} \arrow[d, "-nL"] & + (n + 1)\,H_2 \arrow[d, "-(n+1)x102"] \arrow[r] & C_nH_{2n+2} + Q_f^o \\
n\,C\ \text{gas} & + (2n + 2)H \arrow[r] & C_nH_{2n} + {}_2 + Q_f^a
\end{tikzcd}$$

$$Q_f^a = Q_f^o + 102n + 102 + nL.$$

Q_f^a and Q_f^o are the heats of formation from atoms and from the elements in their standard states. L is the latent heat of vaporisation of carbon.

Regarding the magnitude of L the position has been reviewed in 1950 by Springall[17] who as unable to reach a definite conclusion from all the available data. Since then Marshall and Norton[18], from mass spectrometric measurements of the appearance potentials of CH_4^+ CH_3^+ CH_2^+ CH_1^+ and C^+ have derived a value for the heat of sublimation of carbon which checks satisfactorily with the experimental results of Brewer, Gillies and Jenkins[19] and of Simpson Thorn and Winslow[20]. However, using this value to calculate average bond energies in hydrocarbons, Glockler[21] has shown that the difficulties associated with L have not yet been resolved.

Recently Szwarc and Evans[6] have given a new definition of average bond energy as being "the work done in separating two atoms in a molecule in a process during which all the other bonds are independently and simultaneously stretched in such a way that the molecule as a whole swells infinitely whilst preserving its original geometric form."

In a molecule of type AB_n this definition leads to the same expression $q = \frac{Q_f^a}{n}$ but by a rigorous mathematical treatment they produce a method by means of which it is possible in principle to partition the energy of atomisation between the different bonds of a molecule for each and every molecule without reference to any other molecule. Their method depends on the knowledge of the potential energy of the molecule as a function of all the interatomic distances and angles but unfortunately such experimental data are not yet available.

Although average bond energies cannot be determined by direct experimental measurement, attempts have been made to conceive relationships between this quantity and certain other bond properties which can be measured, for example, force constants and bond lengths[22,23]. Szwarc[24] however states that in view of the uncertainty of the numerical values of stretching force constants, any average bond energies derived from them should be discarded. He points out that bond lengths provide a more satisfactory basis but that it is first of all necessary to prove that the average bond energy is independent of molecular environment and is determined solely by the length of the bond.

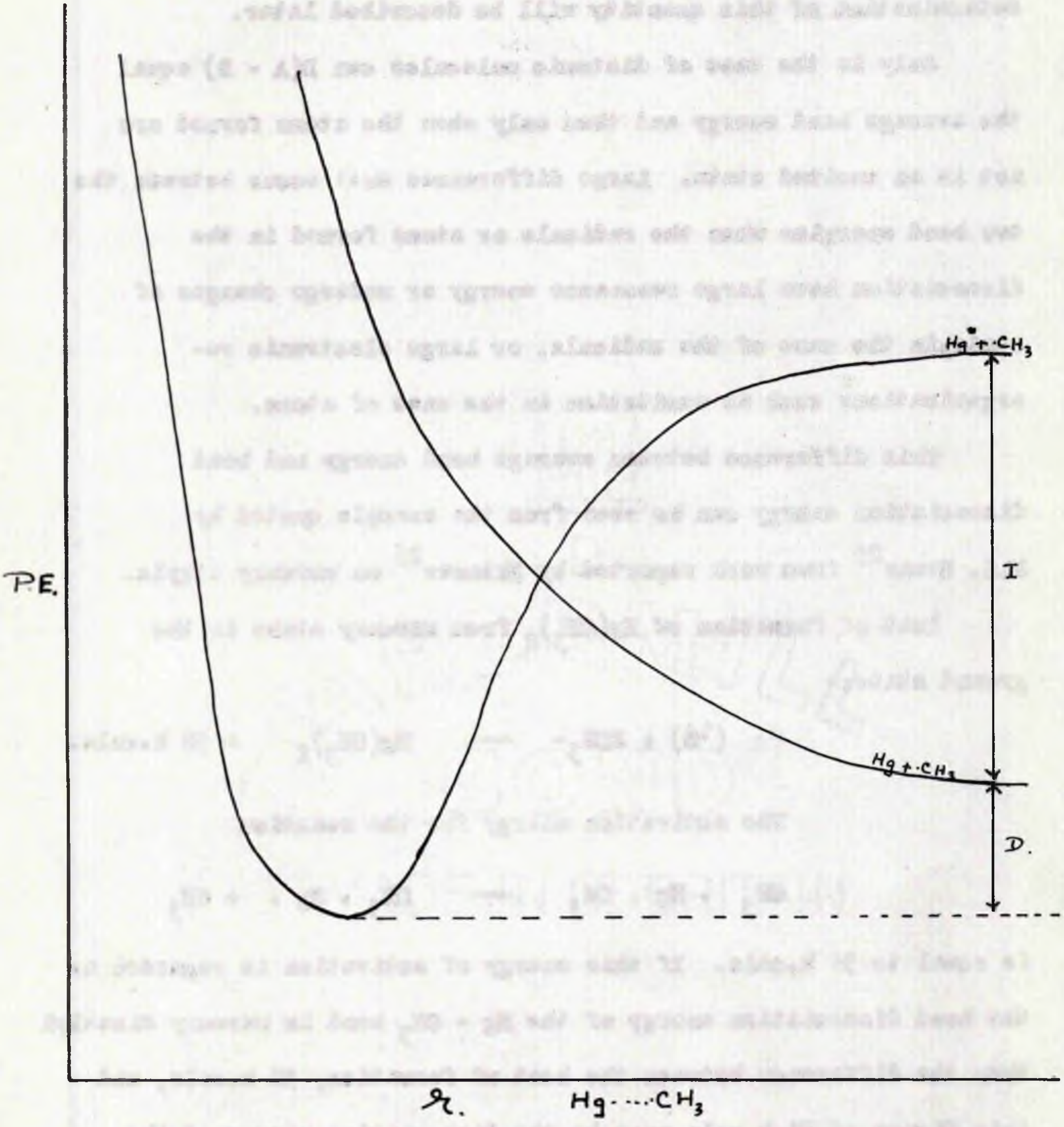
The average bond energy can therefore be regarded as that portion of the total energy of atomisation of the molecule ascribed to the bond as it exists in the molecule. A knowledge of the magnitude of this energy is necessary to calculate the 'resonance energy' of molecules, i.e. the difference between the actual energy of the molecule and that of some standard reference system.

Bond Dissociation Energy.

Fortunately, the problems connected with the evaluation of average bond energies do not arise in the determination of bond dissociation energies as the latter can in many cases be measured directly as the endothermicity of the reaction in which AB is dissociated into two fragments

$$AB \longrightarrow A\cdot + B\cdot \qquad -D(A-B)$$

Fig. 1



I. Energy to get Hg to excited state.

D. Measured dissociation energy.

D.+I. True dissociation energy.

Some of the experimental methods available for the determination of this quantity will be described later.

Only in the case of diatomic molecules can D(A - B) equal the average bond energy and then only when the atoms formed are not in an excited state. Large differences must occur between the two bond energies when the radicals or atoms formed in the dissociation have large resonance energy or undergo changes of state, in the case of the radicals, or large electronic reorganisations such as excitation in the case of atoms.

This difference between average bond energy and bond dissociation energy can be seen from the example quoted by M.G. Evans[25] from work reported by Skinner[26] on mercury alkyls.

Heat of formation of $Hg(CH_3)_2$ from mercury atoms in the ground state;-

$$Hg\ (^1S) + 2CH_3- \longrightarrow Hg(CH_3)_2 \quad + 58 \text{ k.cals.}$$

The activation energy for the reaction

$$CH_3 \cdot Hg \cdot CH_3 \longrightarrow CH_3 \cdot Hg \cdot + CH_3$$

is equal to 51 k.cals. If this energy of activation is regarded as the bond dissociation energy of the $Hg - CH_3$ bond in mercury dimethyl then the difference between the heat of formation, 58 k.cals, and this figure of 51 k.cals must be the dissociation energy of the $Hg - CH_3$ bond in the radical, i.e. 7 k.cals.

Skinner states that mercury cannot form bonds when in its (^1S) ground state, but must be in an electronically excited state.

Table I

Compound	D (C - Br)
CH_3 - Br	67
Ph.Br	69
Ph. CH_2 Br	50.5
CH_2 = CH - CH_2 Br	48
CF_3 - Br	64
C Cl_3 - Br	48

Then when the Hg - CH_3 bond is ruptured the mercury atom reverts to its ground state and the dissociation energy of the bond is reduced by the energy of change of the electronic state of the atom.

This can be represented graphically as in fig.1.

The dissociation energy of a number of bonds has now been determined and an examination of the tables of values given by Szwarc [1,24,28] and Roberts and Skinner[27] shows that for any particular type of bond the dissociation energy is not constant. The values determined for a number of C - Br bonds are given in table I.

It is not surprising that such variations should occur when the differences of reactivity exhibited by compounds containing a characteristic link are considered. An example of this is the gradation in reactivity of the compounds in the homologous series[29]. Another example is provided by the values (Table II) of the energy of activation derived by Polanyi[30] and his co-workers for the reaction

$$Na + R.Cl \longrightarrow NaCl + R-$$

In this reaction the bond formed is independent of R, and any variations in the energy of activation are attributed to the bond broken and hence to the effect of R on the bond in the molecule or to the stability of R- as a free radical. It is not generally possible to disentangle the factors affecting the radicals and molecules so the procedure adopted by Szwarc[24], based on theory of Baugham, Evans and Polanyi[24a], has been to take as standard the

Table II

Chloride	Activation energy k. cals.
Methyl	10.0
Ethyl	9.4
n. Propyl	9.2
iso-Propyl	8.6
n-Butyl	8.6
sec.Butyl	8.4
tert.Butyl	7.8
Vinyl	10.4
Allyl	6.0
Benzyl	2.9
Phenyl	10.4
Acetyl	5.0
Benzoyl	0
Acetonyl	2.0

C-H bond in methane (102 k.cals) and the C-C bond in ethane (85 k.cals) and then to assume that the difference between the C-H bond dissociation energy in a molecule and in methane is due to the resonance energy of the radical. Similarly for the C-C bond. This treatment however is by no means complete as it has become necessary to introduce further qualifying assumptions. Consider, for the sake of example, the benzyl radical.

From the pyrolysis of toluene, Szwarc[31] derived the value of 77.5 k.cals for the dissociation energy of the C-H bond. The resonance energy of the benzyl radical by the above definition is therefore 24.5 k.cals from which it immediately follows that the C-C bond dissociation energy in dibenzyl is 85 - 49 k.cals = 36 k.cals.

However, from a calculation involving the heats of formation of toluene and dibenzyl and the figure of 77.5 k.cals. for the toluene C-H bond energy, the value of 47 k.cals was obtained for the same quantity. The difference of 11 k.cals has been attributed to a strengthening of the C-C bond through shortening[32]. It is of interest to note that experimental determination of the dissociation energy of the C-C bond in dibenzyl[33] gave a value of 48 k.cals. which agrees very closely with the second of the calculated figures.

It is now also becoming useful to refer to the heat of formation of a radical. This idea originates from the method devised by Butler and Polanyi[34] for assessing bond dissociation energies from thermochemical data in conjunction with other measured dissociation energies.

The dissociation energies are given by the equations:

$$D(R - X) = Qf(RX) - Qf(R) - Qf(X)$$

and

$$D(R - Y) = Qf(RY) - Qf(R) - Qf(Y)$$

all being in the gaseous state.

Suppose D(R-X) is known, then if data are available for the heats of formation of RX, RY, X and Y it is possible to calculate D(R-Y).

Sufficient accurate thermochemical information would therefore allow a whole series of dissociation energies to be obtained from one measured value. The method also permits calculation of the dissociation energy of bonds which cannot be readily measured directly. As an example of this, consider the work carried out on the pyrolysis of n.propyl-benzene by Leigh and Szwarc[35]. They estimated that $D(C_6H_5.CH_2 - CH_2.CH_3)$ was equal to 57.5 k.cals/mol. The heat of formation of benzyl radicals was already known from the investigation on toluene [31] to be 37.5 k.cals/mol. and from thermochemical measurements the heat of formation of n.propyl-benzene is 1.9 k.cals. By substitution of these values in the equation:

$$D(C_6H_5.CH_2 - CH_2.CH_3) = Qf(C_6H_5.CH_2.CH_2CH_3) - Qf(C_6H_5.CH_2-) - Qf(-CH_2.CH_3)$$

they calculate the heat of formation of ethyl radicals to be 22 k.cals/mol ± 4 k.cals.

Having this heat of formation they proceed to derive:

$$D(-CH_2.CH_2 - H) = 41.5 \pm 4 \text{ k.cals/mol.}$$

$$D(C_2H_5 - H) = 94 \pm 4 \text{ k.cals/mol.}$$

these being dissociation energies which cannot be measured directly by other than the electron impact method. The energy of activation of $C_2H_5 \longrightarrow C_2H_4 + H$ has been calculated by Bawn[36] who obtained for this reaction the value of 48 k.cals/mol.

This combination of thermochemical and kinetic data also permits a cross check to be made between experimental determination of different bonds. This was not possible to any great extent in the present work because of the dearth of thermochemical measurements on systems involving diphenylmethane and fluorene, but in an appendix calculations are made from the data available.

Theoretical Calculation of Radical Properties.

By the generally accepted definition of a free radical as "any chemical entity which carries an unpaired valence electron", we must include not only organic free radicals but also free atoms of elements such as hydrogen, sodium, potassium, chlorine etc. and even relatively stable molecules such as oxygen and nitric oxide.

As a result of this electronic idea of a free radical it has been possible for a theoretical approach to be made to the understanding of such radical properties as energy, structure and reactivity.[36a]

It would not be possible to give a detailed description of these various theoretical approaches within a reasonable space, hence this account will be of a more general nature.

Where the free radical has a simple structure such as the hydrogen atom or even a methyl radical, the locus of the odd electron is fairly clearly defined and it has to be regarded as being in rather close association with a particular atom of the radical.

It is not yet possible to apply wave-mechanical methods rigidly to the solution of these systems but progress has been made with the aid of two separate treatments which involve approximations.

1) The Valence Bond Method.

2) The Molecular Orbital Method.

By both these treatments the same general results are obtained.

Out of the valence bond method has arisen the Resonance Theory which is an intuitive generalization requiring for its practical application two assumptions in addition to those already implied in the valence bond method[37].

a) The wave function of a molecule can be represented as a linear combination of the wave functions for the unexcited canonical structures.

b) If there are two or more canonical structures the molecule will have an intermediate reactivity, and the greater the number of canonical structures possible, then the greater is the stability of the molecule, i.e. it has a larger resonance energy.

Dewar and Longuet-Higgins[38] have pointed out that there is no theoretical justification for these two assumptions and that indeed there is no sound reason for neglecting excited canonical forms on the ground that the contribution made by a particular unexcited canonical form may be much greater than that of one excited canonical structure since there may be a greater number of the latter. Furthermore, that the stability of a molecule does not depend only on the number of canonical forms but also on interactions between them.

In spite of these observations the resonance theory has been quite successful - a success which Dewar and Longuet-Higgins attribute to a certain "correspondence principle" between it and the method of molecular orbitals.

The most interesting results obtained have been in connection with certain free aryl radicals. For example, the phenylmethyl radical can be dealt with on the basis of five canonical structures (neglecting excited states).

1

2

3

4

5

A relatively simple wave function[39] can be set up for this system by assuming equivalence of structures 1 and 2 and for 3,4 and 5.

$$\phi = a(\phi 1 + \phi 2) + b(\phi 3 + \phi 4 + \phi 5)$$

The energy difference between the system 1 or 2 alone, which are the Kekule structures, and that of the whole system 1 ⟶ 5 is regarded as being the resonance energy of the free radical.

The greater the complexity of the radical, the more possible canonical forms and hence the greater the resultant resonance energy, i.e. the more stable is the radical. For diphenylmethyl there are 16 canonical structures, therefore it would be anticipated that this radical is more stable than the benzyl radical. This is in agreement with the experimental results of this investigation.

Quantitatively however, there is not a good fit between the calculated and the experimental resonance energies of the phenyl methyl and diphenylmethyl radicals. The treatment of Pauling and Wheland[40] leads to values of 0.51α and 0.84α respectively for the two radicals. They maintain that there is considerable evidence for taking α (the single exchange integrals involving adjacent atoms) as 32.2 k.cals so leading to resonance energies of 16 k.cals for the benzyl radical and 27 k.cals for the benzhydryl radical. The latter value is in quite good agreement with the experimental quantity of 30 k.cals derived in the present study but the benzyl values differ widely. Szwarc[41] has proposed that Sklar's α value of 44.2 k.cals is more reliable and should therefore be used. This of course brings the calculated resonance energy for the phenylmethyl radical more into line with his experimental results.

Similarly the resonance energies of phenylmethyl and diphenylmethyl calculated by the method of molecular orbitals is in resonable agreement with the experimental value for the latter, but is much too low in the case of the former. By this treatment the results obtained are for (a) phenylmethyl :- 15 k.cals.

(b)diphenylmethyl :- 28 k.cals.

Determination of Bond Dissociation Energies.

In a recent review dealing with the methods of determining bond dissociation energies, Dr.M.Szwarc[1] has pointed out that the experimental determination of these quantities requires the investigation of one of two processes.

(a) The process of formation of a bond by association of the respective radicals or atoms.

(b) The process of breaking a bond resulting in the formation of the respective radicals or atoms.

The first of these methods is difficult to carry out experimentally and therefore, in contrast to the second method has not been extensively used.

Depending on how the energy required for the dissociation is supplied, the bond breaking method can be divided into three groups:

(1) The photochemical method where the energy is supplied by radiation.

(2) The electron impact method where the kinetic energy of an electron beam is used.

(3) The equilibrium method and the kinetic method where the bond splitting energy is thermal energy.

It is proposed to consider here only the kinetic and the electron impact methods. The former because it was employed in the present work, and the latter as it involves an application of a mass spectrometer quite different from that developed in this investigation.

Kinetic Method.

In chemical reactions the original molecules, the reactants, disappear and in their place are formed new molecules, the products. The final state differs from the initial state in that some of the original bonds are broken and other ones have been formed. Associated with these changes is an energy factor, termed the Energy of Activation, which is a function of the dissociation energy both of the bond broken and the bond formed.

Since chemical kinetics is concerned with the mechanism of chemical reactions and the speed at which they occur, it follows that the relationship of energies of activation and bond dissociation energies is an object of studies in this field.

From the point of view of bond dissociation energy determinations the simplest reaction to consider would be a simple bond rupture:

$$AB \longrightarrow A- \quad + \quad -B$$

which if it took place as a unimolecular process would have a velocity constant:

$$k = \frac{2.303}{t} \log. \frac{a}{a - x}$$

where t is in seconds (or other units of time) a is the initial concentration of AB and x the amount decomposed at time t. If the products of such a unimolecular decomposition were stable or underwent one exclusive and quite definite subsequent reaction it would be possible in principle to find the extent of the decomposition by suitable methods of analysis. Values of k derived for various temperatures would permit the energy of activation for the decomposition to be determined by use of the Arrhenius expression:

$$\log.k = \log.A - \frac{E}{4.57T}$$

It is known in some cases and conjectured for most that there is no energy of activation for the reverse association reaction:

$$A- + B- \longrightarrow AB$$

Since the heat absorbed equals $E_{forward} - E_{reverse}$ the assumption that the latter term is zero means that the energy of activation for the dissociation process would equal the required heat of dissociation.

The problem however is not so simple because in fact the free radicals and atoms formed in the dissociation are very reactive and undergo rapid reaction with other species present. The task therefore becomes one of either "arresting" these radicals as fast as they are produced or by arranging the experimental conditions so that reaction occurs exclusively between the radicals and the parent molecule. An alternative method would be the determination of the concentration of the radicals as they are produced, A number of experiments in this direction have been carried out by Eltenton,(50) but which will be considered later.

In the opening paragraphs of this introduction, reference was made to the metal mirror experiments of Paneth and Hofedits to detect free radicals in the gas phase. This technique was subsequently developed by F.O. Rice and his colleagues[42-46] in investigations into the thermal decomposition of hydrocarbons and also of oxygen and nitrogen containing compounds. They employed very low partial pressures of reactant in the presence of an excess of a condensible carrier gas and to keep the percentage decomposition to a low value they maintained a very fast flow through the reaction vessel. The radicals produced were 'captured' by the metallic mirror before chain reactions could develop.

Although using this method Rice and Dooley[46] obtained a value of $D(CH_3 - H) = 100 \pm 6$ k.cals/mol. which is in good agreement with the accepted value of 101 k.cals/mol., the technique can seldom be employed to determine bond dissociation energies with accuracy.

The extent to which free radical chain reactions may account for all the products resulting from the thermal decomposition of organic molecules when using the gas flow method without metal mirrors was demonstrated by Rice and Herzfeld.[47]

They give three examples showing how the experimental facts observed in the pyrolysis of ethane, acetone and acetaldehyde can be explained on the basis of such free radical chains. Their calculations showed that the first order nature of the overall reaction could be maintained under the correct conditions and estimated reaction rates and activation energies which were in accord with the known facts.

The general scheme for the decomposition proposed by them is represented by:

$$M_1 \longrightarrow R_1 + M_2 \qquad (1)$$

$$R_1 + M_1 \longrightarrow R_1H + R_2 \qquad (2)$$

$$R_2 \longrightarrow R_1 + M_3 \qquad (3)$$

$$R_1 + M_1 \longrightarrow R_1H + R_2 \text{ etc.} \qquad (2)$$

$$R_1 + R_1 \longrightarrow M_4$$

where the R's are radicals and the M's are molecules.

The radical formed in the primary reaction abstracts a hydrogen atom from another of the original molecules forming a hydrocarbon and another radical. This second radical decomposes giving a new molecule and reforms another of the first type of radical which is then ready to act as in (2). The chain is stopped however when two radicals combine as in (4).

From this scheme, assuming the rate of (1) to be the slowest step and the concentrations of the free radicals involved reach a limiting low value within a short time after the commencement of reaction, also that the chains terminated by dimerisations of R_1, Rice and Herzfeld obtained a first order constant for the reaction. It is important to note that their reaction proceeded to a very limited extent (5-10% decomposition) and hence there was always an excess of reactant present.

The expression found was:

$$- \frac{d\,[M_1]}{dt} = [M_1] \sqrt{\frac{k_1 k_2 k_3}{2k_4}}$$

$$= {}^{k}\,\mathrm{exp}\ [M]$$

The rate at which molecules disappear is determined by two factors - the rate of the primary reaction $k_1\ [M_1]$ and the rate of the chain reaction $k_2\ [R_1]\ [M_1]$. The chain cannot start until the primary reaction takes place, but for each molecule which decomposes by the primary reaction there are many which disappear by the chain mechanism. The ratio of the two gives the chain length:

$$= \frac{k_2\ [R_1]\ [M_1]}{k_1\ [M_1]}$$

$$= \sqrt{\frac{k_2 k_3}{2k_1 k_4}}$$

The energy of activation of the overall reaction can be determined from the slope of the line obtained by plotting k_{exp} against the reciprocal of the absolute temperature.

The temperature variation of k_{exp} gives E_{exp} but as k_{exp} is composite the experimental energy of activation must be given by:

$$E_{exp} = \tfrac{1}{2}\ [E_1 + E_2 + E_3 - E_4]$$

In any reaction system where fully developed chain sequences of the type considered are occurring, the experimental activation neergy is clearly a composite quantity and therefore the deduction of a bond dissociation energy from the results is very uncertain if not well nigh impossible.

The next advance in the kinetic flow method of determining bond dissociation energies was made by Butler and Polanyi[48] in connection with their study of the thermal decomposition of organic iodides. The condensible carrier gas used by Rice and ~~company~~ colleagues ~~were~~ was replaced by nitrogen circulated in a closed system by means of a mercury diffusion pump. The reactant was introduced through a narrow capillary into the nitrogen stream which carried it through the reaction vessel, the products and unchanged material being frozen out at the reaction vessel exit.

By maintaining very small partial pressures of reactant and keeping the percentage decomposition to a low level the chances of secondary radical reactions were assumed to be very little. These were considered to be further suppressed by the brief duration of the reaction which lasted less than a second, this being the time for the gas to pass through the reaction chamber. The rate of flow was calculated from a determination of the pressure drop across a capillary inserted in the nitrogen stream.

The iodine formed in experiments carried out at different temperatures was estimated by titration and the result used to calculate a first order velocity constant and hence a value for the energy of activation which was then equated to the energy

D(R - I), it being assumed that the energy of activation for the recombination process of the free radicals was aero.

Although there is little experimental data from which to calculate the activation energy associated with the recombination of free radicals, the available evidence[49,50] suggests that it is negligible. Furthermore, the self-consistent nature of the pyrolytic results and the good agreement with results obtained by other methods are in support of the validity of the assumption. There is of course the notable exception of recombination of triphenylmethyl which Zeigler[51] has shown to have an activation energy of 8 k.cals/mol. but Butler and Polanyi[48] state that the deviation of E_a = D for hexaphenylethane does not necessitate any serious reservation in the identification of these two magnitudes for bonds of a more "normal character". If the recombination process does have a finite energy of activation, then the value of the dissociation energy obtained by the kinetic method will be too high and will represent the upper limit of the true value.

The kinetics of the thermal decomposition of organic iodides has since been shown to be more complex[52,53] than assumed by Butler and Polanyi and that their adjustment of experimental conditions to reduce subsequent radical reactions had not been entirely successful.

Toluene Carrier Gas Technique.

M. Szwarc[31] in a study of the pyrolysis of toluene by the Butler-Polanyi method found that the velocity constant of the primary reaction

$$C_6H_5\cdot CH_3 \longrightarrow C_6H_5\cdot CH_2 + H$$

was first order and could be represented by:

$$k = 10^{13} e^{\frac{-77,500}{RT}} \text{ sec.}^{-1}$$

The activation energy he associated with the C-H bond dissociation energy in toluene.

A subsequent study of the pyrolysis of ethylbenzene[54] was complicated by the formation of polystyrene at the furnace exit. This result was explained on the basis of a chain reaction involving the methyl radicals formed by the initial decomposition:

$$C_6H_5 \cdot CH_2 \cdot CH_3 \longrightarrow C_6H_5CH_2\text{-} + CH_3\text{-}$$

It had earlier been demonstrated by H.S. Taylor and J.O. Smith[55] that the methyl radical reacts very rapidly with toluene

$$C_6H_5 \cdot CH_3 + CH_3 \cdot \longrightarrow C_6H_5 \cdot CH_2 + CH_4$$

producing methane and benzyl radicals which are comparatively inert and only dimerise to dibenzyl. Szwarc made use of this fact by carrying out the pyrolysis in a stream of toluene vapour which acted as a radical accepter for the very reactive fragments formed by the decomposition of whichever organic compound was being studied. In every case the benzyl radicals formed were assumed to undergo no reaction other than that of dimerization.

(This assumption was shown to be substantially correct in the present investigation by subjecting the pyrolytic products of toluene to Ultra Violet spectrophotometric examination.)

The toluene carrier technique was first tried out on a repeat of the decomposition of ethylbenzene. The results obtained were found to be reproducible and independent of the partial pressure of toluene. The experimental energy of activation and probability factor were estimated at 63.2 ± 1.5 k.cals/mol. and 1×10^{13} sec^{-1}.

The method has since been applied by Szwarc to a number of pyrolyses including those of benzyl bromide[56], hydrazine[57], propylene[58], allyl bromide[56], substituted bromomethanes[59], substituted benzyl bromide[60] and acetic anhydride[61].

In spite of the apparent very wide application of this method it is important to note that it does have its limitations. It cannot be used when determining the dissociation energy of:-

(1) Bonds stronger than the C-H bond in toluene because at the high temperatures necessary, the toluene itself decomposes.

(2) Weak Bonds. In these cases the energy of activation of the reaction:

$$R + C_6H_5 \cdot CH_3 \longrightarrow C_6H_5 \cdot CH_2- + RH$$

may be sufficiently large to make it a very slow process at the required low reaction temperatures.

(3) R-I bonds because of the unreactivity of the iodine atom. For example, it would not be suitable to study benzyl iodide decomposition in the presence of toluene as iodine and toluene will certainly not react as well as bromine and toluene.

(4) When the molecule being studied decomposes, not to free radicals but directly into two molecules. The use of toluene in these instances could however give valuable information

as to the decomposition mechanism since if there was no reaction with toluene it could be presumed that no free radicals were formed.

In addition to these shortcomings of the toluene method there is another isolated investigation of interest in which toluene cannot be used as a radical acceptor and that is the pyrolysis of dibenzyl. The decomposition of this compound has been studied by C. Horrex and S.E. Miles[33] who obtained a value for the first order velocity constant, based on the primary dissociation of the molecule into two benzyl radicals, which could be represented by:

$$k = 9.29 - \frac{48 \times 10^3}{2.3\ RT} \ \text{secs}^{-1}$$

The energy of activation is in agreement with the figure predicted from consideration of the heat of formation of the benzyl radical (from toluene decomposition) and the heat of formation of dibenzyl, but the pre-exponential factor of 9.29 is much lower than the figure of 13 usually associated with first order reactions. The products, toluene, stilbene, benzene, and styrene were accounted for by the attack of the benzyl radicals on the parent molecule giving rise to toluene and another free radical which could then decompose by various routes to give the other three hydrocarbons.

These complicating secondary steps could be avoided by the use of a suitable acceptor for benzyl radicals and one of the reasons for the present study of the pyrolysis of diphenylmethane was to ascertain the possibility of using it in a re-investigation of dibenzyl. The possibility of its use in the study of organic iodides was also envisaged. One drawback to this use of diphenylmethane is that its low vapour pressure prevents it being employed also as the carrier gas and an inert gas must be used in conjunction to serve the latter purpose. Another, but more serious drawback is the complicated mechanism of its own decomposition. From this last point of view fluorene would be of more value as a radical acceptor.

Treatment of Experimental Data.

It is relevant to consider briefly, exactly what information is required from this type of experiment and the various methods of treating these data.

The first essential is the identification of all the products and a determination of the amounts of each formed. From this it should be possible to write down an equation representing the overall reaction. The next step is to draw up a mechanism which will account for all the products and which agrees with the stoichiometry of the previous equation, Very often more than one such mechanism is possible and it is then necessary to design further experiments to enable the correct reaction mechanism to be deduced. If theevidence suggests that the rate determining step is the rupture of some bond it is then permissible to calculate the rate of disappearance of the reactant from measurements of the rate of formation of one of the products with a view to identifying the energy of activation with the dissociation energy of the bond which split in the original molecule.

It is appreciated that this procedure cannot always be observed but it is obviously unsound to continue to a study of the energetics of a reaction before all the complicating factors have been satisfactorily unravelled, except in those cases where it is still necessary to have such information in order to decide between two or more mechanisms. Even then an unequivocal conclusion is not always possible.

Such a process is time consuming but it should be carried out as it may reveal the existence of complexity where simplicity had been assumed.

When a seemingly satisfactory conclusion regarding the mechanism has been reached, the velocity constant k is calculated from the first order equation:

$$k = \frac{2.303}{t} \log. \frac{a}{a - x}$$

where t is time of contact and x is the percentage decomposition of the reactant over a range of the experimental variables, partial pressure of reactant, time of contact, partial pressure of carrier gas and furnace temperature. If k is found to be independent of these, except of course temperature, it can be taken that the decomposition of the reactant is a unimolecular process.

The variation of k with temperature is then considered.

Early in the history of chemical kinetics, Arrhenius proposed an empirical formula for describing the effect of temperature on the rate of a chemical reaction.

It may be expressed as:

$$k = Ae^{\frac{-E}{RT}}$$

where T is the absolute temperature, R is the gas constant and A and E are constant for the reaction.

Concerning these last two quantities a great deal has been written which it is not possible to consider here. As a first approximation however, A has been related to a collision frequency and a steric factor in the case of bimolecular reactions. In the case of unimolecular decompositions the interpretation of A is more difficult. Collisions are required to maintain a supply of energised molecules and a proportion of the latter concentrate sufficient energy in the vital link to permit decomposition to occur. These conceptions[62] lead to an A of 10^{13} sec.$^{-1}$, a value of the same order as the vibration frequency of single bonds.

La Mer[63] has pointed out that E probably changes with temperature but the experimental methods are not sufficiently accurate to distinguish the difference. ~~If E does depend on temperature an entropy of activation must exist which may arise from certain steric factors~~.

The energy of activation, E, can be determined from the temperature coefficient of the reaction rate either by direct substitution into the Arrhenius equation of the value of k at two different temperatures, or by plotting log k against the reciprocal of the absolute temperature and multiplying the slope by 2.303 R. For this purpose the absolute values of k need not be determined, but to obtain accurate values of E and A the data for k must be of high quality and extend over a considerable range of temperature. A range of at least 50°C is very desirable and due to practical difficulties few researches cover more than 100°C. In the case of fluorene, reported in this thesis, the range studied was actually 160°C.

Finally, in a study of a series of substituted compounds to determine the effect of the substituent on the dissociation energy of a particular bond, Szwarc[59] has assumed a constant probability factor of 10^{13} for each of the unimolecular decomposition processes. Then if D_1 denotes the bond dissociation energy in the reference molecule and

$$k_1 = A_1 e^{\frac{-D_1}{RT}} \sec^{-1},$$

D_2 denotes the bond dissociation energy of the substituted molecule and

$$k_2 = A_2 e^{\frac{-D_2}{RT}} \sec^{-1} .$$

Since A_1 is assumed to equal A_2 it follows that

$$D_1 - D_2 = RT \ln k_2/k_1 .$$

As the assumption of a constant value for A throughout a series has not yet been shown to be valid it would probably be more satisfactory to make a complete detailed investigation and calculate D and A independently for each compound.

The Mass Spectrometer.

General Theory.

As the technique of determining dissociation energies by electron impact, and also part of the present investigation involve the use of a mass spectrometer, the basic principle of this instrument will first be considered.

It consists essentially of a device for separating atoms or molecules of a gaseous mixture according to their absolute mass. This is effected by ionising them by means of a beam of high energy electrons and accelerating the ions through a high voltage field where they will attain velocities related to their masses. They then pass into a magnetic field where they are analysed, the particles of different velocities and masses being deflected to different extents. By the adjustment of either the accelerating potential or the magnetic field strength, ions of any desired mass can be directed through a slit, after passing through the magnetic field, on to a collector plate. The very small electrical current produced is then amplified and made to operate some recording device.

The mode of operation is made quite clear from the following:

If an ion of charge e, of zero kinetic energy and mass m enters a voltage field V, then on passing across the potential gradient it will have had imparted to it an energy:

$$V_e = \tfrac{1}{2} mv^2$$

Furthermore when a particle of mass m and charge e moves with a velocity v in a magnetic field of strength H, the particle will be deflected in a circular path whose radius will be such that

$$Hev = \frac{mv^2}{r}$$

From these two equations, the expression

$$\frac{e}{m} = \frac{2V}{H^2r^2}$$

can be readily obtained. 'r' has a definite value being a function of the instrument and defined by the relative positions of the ionisation chamber, the magnetic field and the collector slit. Only those ions having a definite value of r can pass through the collector slit. The $\frac{m}{e}$ values for the particular particles having a path of this radius is fixed by V and H. It is normal in operation to maintain either V or H at a constant value and to vary the other while automatically recording the ion current of each $\frac{m}{e}$ present. For a given electron bombarding voltage the relative magnitudes of these are constant for any given compound and are hence referred to as the mass spectrum of that compound. This is as characteristic as the ultraviolet or infra-red spectrum and is about as difficult to interpret as the latter.

The usual method of recording the mass spectra is to cause the amplified ion current to deflect a movable pen over the surface of a strip of paper moving at a constant speed at right angles to the direction of motion of the pen. In this way a series of peaks are drawn out and as the deflection of the pen is proportional to the ion current the heights of the peaks are a measure of the relative amounts of each $\frac{m}{e}$ species. These are now referred to as mass peaks.

A gas such as CO_2 gives not only a mass 44 peak due to CO_2^+ ions but also smaller peaks at 28, 16 and 12. These are due to the fragment ions CO^+, O^+ and C^+ which are produced simultaneously with the parent peak by rupture of the various bonds in the molecule. In addition there will possibly be peaks at 22, 14, 8 and 6 resulting from the doubly ionised particles CO_2^{++}, CO^{++}, O^{++}, C^{++}.

A further complication arises through different fragments having the same mass. An example is given by $C^{12}\,O_2^{16}$ and $C_3^{12}\,H_8^{1}$ whose respective masses are 44.004 and 44.065. Unless the instrument has a resolving power of 1 in 1000 at this mass range it is not possible to distinguish between these two.

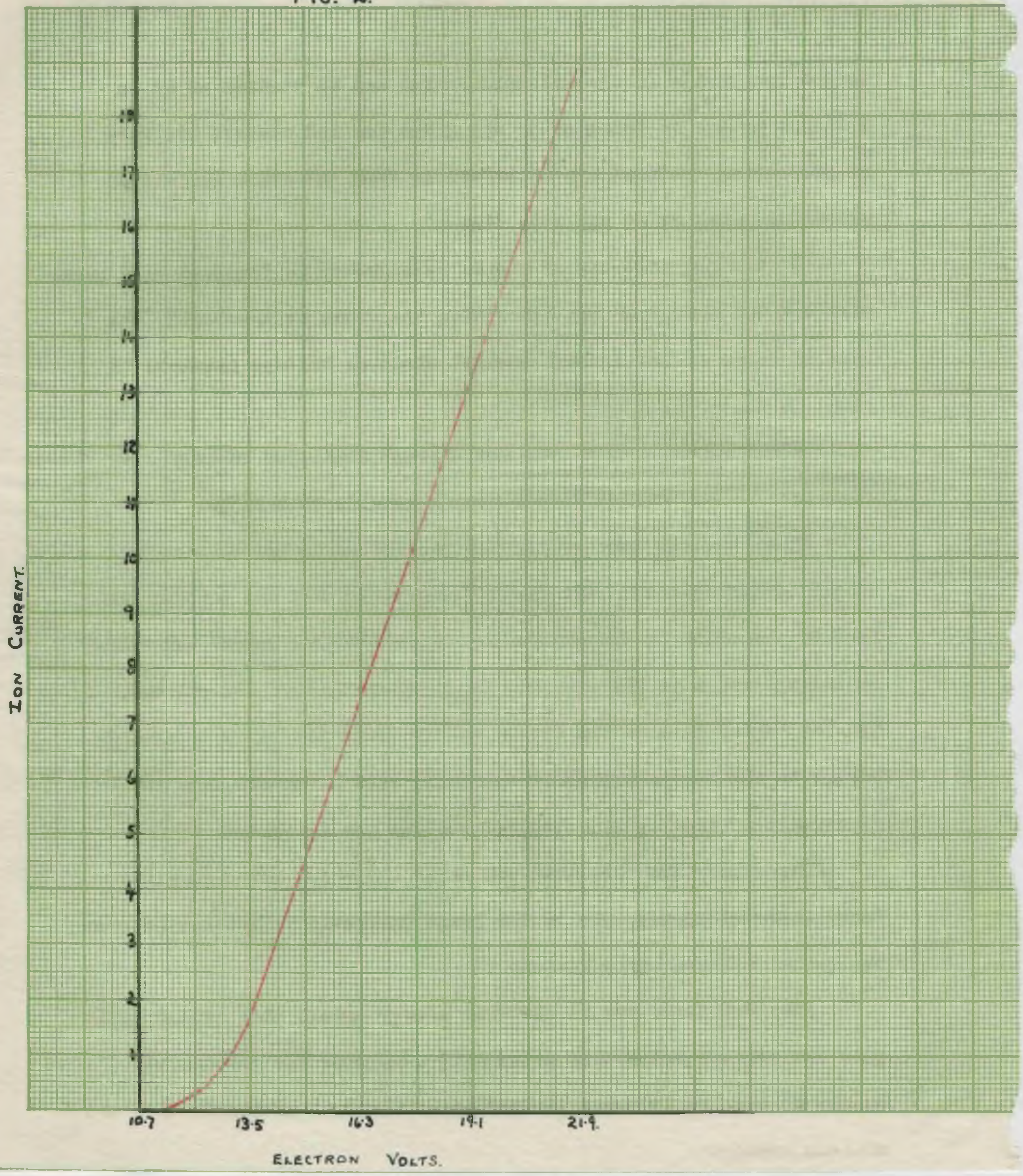
Owing to its ability to measure the abundance of various molecular masses present in a vapour, the mass spectrometer provides a useful method of carrying out quantitative analysis of unknown mixtures. This is the particular application which was made of a mass spectrometer in this work to determine the partial pressure of fluorene and the amount of hydrogen resulting from its thermal decomposition. Although this investigation was carried out with a view to measuring the dissociation energy of the methylenic C-H group in fluorene this particular use of a mass spectrometer is quite distinct from the electron impact methods of determining bond dissociation energies, which will now be considered.

Ionisation and Dissociation by Electron Impact.

The method of electron impact has been used for some time to determine ionisation potentials and electron affinities[64].

The instrument used is similar to the ordinary ionisation gauge and only simple molecules can be studied as there is no means of separating the ions produced by different processes. The mass spectrometer provides an answer to this difficulty. There is no limit

FIG. 2.



ION CURRENT.
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
10·7
13·5
16·3
19·1
21·9.
ELECTRON VOLTS.

to the complexity of the molecules which can be studied as it is a simple matter to focus on to any given ion and observe its rate of production, without any interference from the other ionisation processes going on at the same time.

If the ion detector of a mass spectometer is focussed on a given mass and the energy of the bombarding electrons is increased, the type of curve of ion current against electron voltage obtained is shown in figure 2.

After initial onset, the ion current increases rapidly over about a volt and then is linear over a considerable range.

There are two main schools of thought as to how these data should be interpreted. The first[65] maintains that the tail at the foot of the curve is due solely to electron energy spread and takes an extrapolation of the straight line region to zero ion current. The fitting of an electron energy filter would therefore apparently result in the disappearance of the tail, with an unambiguous sudden appearance of ions as the electron voltage was increased.

The other idea[65] is that the point where ion ~~and~~ current is first observed corresponds to the least energetic transition between the ground and the ionic states.

Provided there was no electron energy spread this method would give the correct ionisation potential, otherwise the possibility exists of a molecule being ionised by an electron of higher than the minimum energy.

The voltages at which ions appear, termed the Appearance

Potentials, are used in computing the relevant bond dissociation energies.

The commonest method, in addition to the appearance potential requires a knowledge of the ionisation potential of the fragments studied. For example, if the bombardment of a molecule AB causes the decomposition

$$AB + e \longrightarrow A^{+} + B + 2e$$

then the appearance potential of the ion A^{+} is given by

$$V(A^{+}) = D(A-B) + I(A) + E(A^{+}) - E(AB) + KE(A^{+}) + KE(B) - KE(AB) + E(B)$$

I(A) is the ionisation potential of A, E's are internal energies above the ground state and KE's are kinetic energies of the particles. The most reliable ionisation potentials are derived from spectroscopic data but unfortunately these are not always available and recourse must be made to the much less certain values derived by use of the mass spectrometer. The uncertainty of the latter measurements arises from the undeterminable "excess energies" of the various fragments. Douglas and Herzberg[66] found evidence which indicated the mass spectrometer ionisation potential for the ion CH^{+} produced from HCN included 99.5 k.cals "excess energy".

In spite of these difficulties, Stevenson[67] obtained the following results which are in good agreement with values obtained by other methods.

$D(CH_3 - H)$ = 101 ± 4.5 k.cals/mol.
$D(C_2H_5-H)$ = 96.7 ± 4.5 " "
$D(CH_3-CH_3)$ = 82.6 ± 9 " "
$D(C_2H_5-C_2H_5)$ = 77.6 ± 9 " "

A different technique takes into account thermochemical heats of reaction. Stevenson and Hipple[67a] by measuring the appearance potential of the $CH_3 - C^+ = CH_2$ ion from both propylene and isobutylene and assuming the heat of hydrogenation of the latter, calculated the dissociation energy of $CH_3 - H$ to be 103 ± 2k.cals/mol.

Application to Kinetic Studies.

(1) Analysis for radicals produced.

In this method, which was introduced by Eltenton[68], the reaction is carried out in a chamber separated from the ionisation chamber of a mass spectrometer by a suitable 'leak' through which passes a stream of the reaction mixture under conditions which permit the radicals to reach the electron beam. The effectiveness of the method depends on the fact that the appearance potential for a specific radical ion produced directly from a parent molecule is always greater than the ionisation potential of the radical itself.

Eltenton has applied the techniques to a study of a number of pyrolyses and oxidations involving hydrocarbons and has obtained valuable data concerning their mechanisms. To take one example, the thermal decomposition of methane has been of interest, particularly in its relation to the general problem of hydrocarbon synthesis and decomposition. The products of a methane reaction is a complex mixture of olefinic substances, carbon and hydrogen. From mirror-method studies of the free radicals[69] evidence was obtained for both the primary processes:

$$CH_4 \longrightarrow CH_2 + H_2$$

$$CH_4 \longrightarrow CH_3 + H$$

Eltenton was able to obtain ample indication of the presence of free methyl in the reaction mixture and was also able to determine the temperature coefficient of their production with considerable accuracy. None of his efforts to detect CH_2: succeeded, notwithstanding the favourable conditions for mass spectrometer detection of this radical. The Appearance potential for CH_2^+: from CH_4 is 15.7 volts while the ionisation potential of free CH_2: is only 12 volts.

(2) Continuous Analysis of Stable Products.

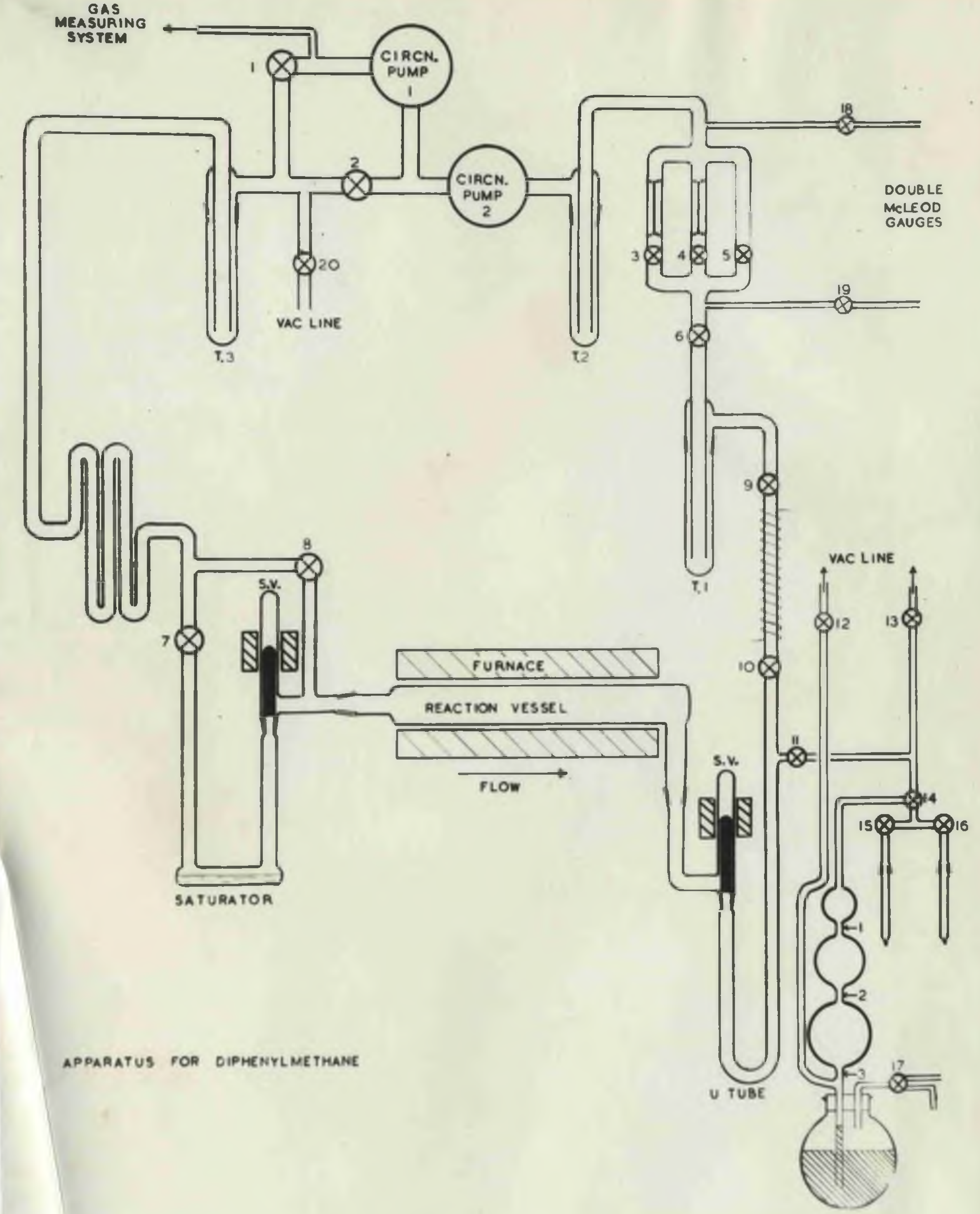
In the flow method of studying chemical decompositions a great deal of time has to be spent preparing the apparatus for each experiment which itself may only be of from 10 to 30 minutes duration. The products have then to be removed and analysed by some suitable method. Even with the most favourable conditions, i.e. freedom from leaks and other experimental mishaps it is only possible to complete about one experiment per day when studying compounds such as diphenylmethane and fluorene.

Any means of analysing the products continuously as they are formed would appreciably speed up the rate of obtaining experimental data as it would not then be necessary to open up the system between runs in order to remove the products. A further advantage which would be gained from such procedures would be the maintenance of steady surface conditions during a series of runs. In the present work there was no surface reaction but in the pyrolysis of iodides[52,53] it was noted when using a triplicate collecting system that differences existed between the first and the remaining samples in a set of three supposedly identical experiments done in a closed system. It seems reasonable to suppose from the evidence presented in those researches that the surface attained a uniform state after pyrolysis had been proceeding for a few minutes. Such a steady state could be maintained while a great number of experiments was performed if a method of continuous analysis was utilised.

The mass spectrometer is an instrument admirably suited to this purpose and although it has been used to determine the composition of isolated samples of the products of kinetic reactions[70b] there has not been much application of it to continuous direct analysis in academic researches. It has been used for monitoring process units in the petroleum and atomic energy fields[70], and Urey[70a] made an application of it to the kinetics of decomposition of dimethyl ether in a static system some years ago. The application made in the present research did not make full use of the capabilities of the method for following the fate of several components simultaneously since the decomposition of fluorene yielded only two products, but as far as it is known this is the first time that a mass spectrometer has been employed to analyse the stable pyrolytic products when studying the kinetics of thermal decomposition of organic compounds in a flow system.

THE PRESENT INVESTIGATION

1. DIPHENYLMETHANE



APPARATUS FOR DIPHENYLMETHANE

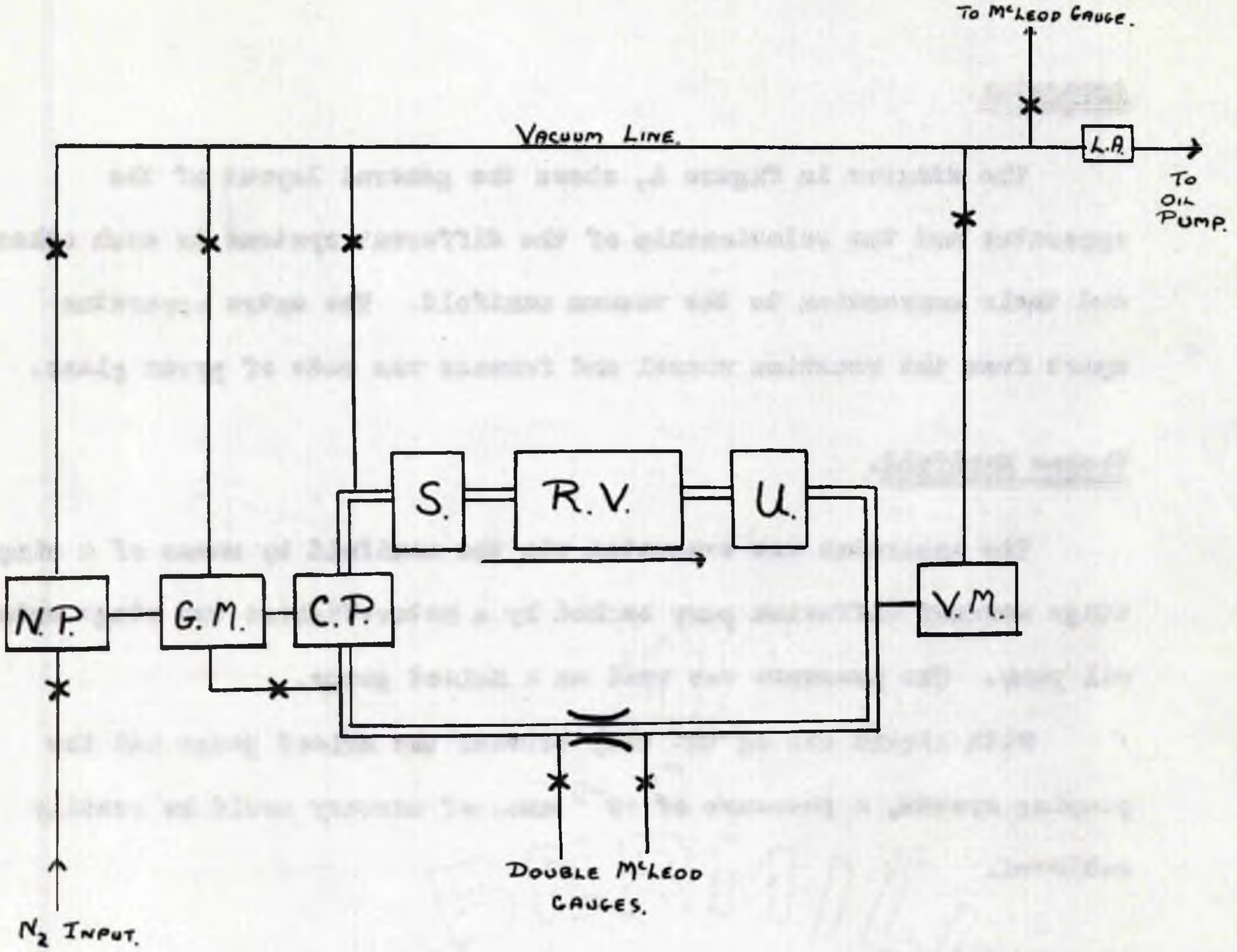
FIG. 3

Although Graebe[71] reported fluorene, hydrogen, benzene and toluene to be formed by passing diphenylmethane repeatedly through a red hot tube, it was felt that in view of the different experimental conditions employed in this work the first step should be the identification of the products. For this purpose a comparatively simple apparatus was used initially, then as the investigation progressed the apparatus was modified and extended to enable a quantitative assay of the products to be made.

The following report of the work carried out commences with a description of the complete equipment as shown in figs. 3 and 5, and includes for the sake of clarity a very brief description of the experimental results which led to the development of the original simpler apparatus. A full account of all the results is given in a later section.

The experimental technique chiefly employed in the pyrolysis of diphenylmethane was in principle the same as that used by Butler and Polanyi[72] in their investigations into the thermal decomposition of organic iodides, and which has since been adopted in many other studies of the pyrolysis of organic compounds. Several experiments were carried out without a carrier gas, similar to the method used by M. Szwarc with toluene.

FIG. 4



L.A.	**Liquid Air Trap**
N.P.	**Nitrogen Purifying and Storage System**
G.M.	**Measuring System for Gaseous Products**
V.M.	**Measuring System for Volatile Products**
S	**Saturator**
R.V.	**Reaction Vessel**
U	**U-Tube**

Flow System in double lines.

Arrow denotes direction of flow.

Apparatus.

The diagram in figure 4, shows the general layout of the apparatus and the relationship of the different systems to each other and their connection to the vacuum manifold. The entre apparatus apart from the reaction vessel and furnace was made of pyrex glass.

Vacuum Manifold.

The apparatus was evacuated via the manifold by means of a single stage mercury diffusion pump backed by a Metro-Vickers two stage rotary oil pump. The pressure was read on a McLeod gauge.

With liquid air on the trap between the McLeod gauge and the pumping system, a pressure of 10^{-5} mms. of mercury could be readily achieved.

Flow System.

Reaction Vessel.

The reaction vessel was constructed from a quartz tube, 72 cms. in length and with an internal diameter of 2.9 cms. One end was tapered down and fitted with a B.19 standard cone. The other end was closed off and fitted with a similar cone sealed in at right angles to the main tube.

Surrounding a portion of the reaction vessel was a furnace consisting of a 62 cms. length of steel tube, 5 cms. diameter, covered with asbestos paper, then with a layer of alundum cement and finally with a winding of nichrome tape. Four tappings made on the winding divided it into five sections. The turns of tape in the two end sections were placed ½ cm. apart and in the three inside sections, 1 cm. apart. Although care was taken in the construction to ensure even spacing of the individual turns it was found necessary to place shunts in the form of rheostats across each of the sections and adjust them to obtain a uniform temperature along the length of the furnace. The windings were covered with a layer of alundum cement and further insulated by enclosing in a 1½" thick asbestos lagging.

The voltage across the windings was controlled by means of a Variac auto-transformer supplied from the mains via a constant voltage transformer. The latter smoothed out the mains fluctuations but it was still necessary to keep a check on the furnace current and to maintain it steady by adjusting the Variac as the extent of load shedding at that time was outside the limits of compensation by the constant voltage transformer.

The temperature of the reaction vessel was measured by a chromel-alumel thermocouple enclosed in a narrow bore quartz tube lying along side the reaction vessel within the furnace. The electromotive force was measured by means of a direct reading potentiometer and the corresponding temperature obtained from a graph plotted from data given by Roeser, Dahl, and Gowens. Bur. Standards. J. Res. 14, 239 (1935) for chromel-alumel thermocouple and reproduced in "Handbook of Chemistry and Physics" - (Chemical Rubber Publishing Co.)

Saturator.

The saturator was connected to the reaction vessel through a standard ground glass core and socket sealed with polythene to give a vacuum tight joint. Polythene was used for this purpose as the apparatus between the saturator and the reaction vessel had to be heated to over 100°C to prevent the diphenylmethane from condensing out and it was found to be the most durable of several materials tested.

A solenoid type valve was employed to control the introduction of the diphenylmethane as lack of a suitable lubricant prevented the use of a conventional type glass tap. The valve and inlet tube were heated by means of a winding of nichrome tape (not shown in diagram).

Tap 7 prevented the back diffusion of diphenylmethane when the nitrogen stream was directed through tap 8 which served as a by-pass to the saturator.

U-Tube.

The unchanged diphenylmethane and the products of pyrolysis were frozen out in a U-tube immersed in a Dewar vessel of liquid air.

Considerable difficulty was experienced before a satisfactory method was evolved for the complete collection of these condensible materials.

Among the products were tetrphenylethane and tetraphenylethylene which condensed out immediately at the exit of the reaction vessel and could only be driven down into the U-tube by being heated to about 180°C. At this temperature the polythene on the ground glass joint between the U-tube and the reaction vessel tended to oxidise, a process which was greatly accelerated by unsealing of the joint to remove the U-tube after each run for the recovery of the condensed solids. The oxidised polythene was quite insoluble and had to be burned off the ground surfaces before the connection could be remade. After being heated a few times the pyrex socket invariably became deformed and a vacuum tight seal could not be obtained. There was also a very great danger of fracturing the silica core.

It was found to be more satisfactory to leave the polythene joint intact and to remove the U-tube by cutting the pyrex tube below the connection. After washing out the products the U-tube was glass blown back into position.

Another of the products, fluorene, tended to pass through the U-tube and condense out in trap T 1. This was overcome by using a double U-tube and heating to 200°C, by means of a nichrome winding, the portion between the two bends immersed in liquid air. The double U-tube is not shown in the diagram as it was very similar in form to the device for removing mercury from the N_2 carrier gas.

Circulating Pump.

The nitrogen was circulated by a mercury vapour pump (circulating pump 2) heated by a Wood's Metal Bath. The latter consisted of an insulated iron vessel heated electrically and maintained at a constant temperature (± 1°C) by means of a Sunvic Energy Regulator.

In experiments without carrier gas the pump was used to remove the gaseous products which were formed as the diphenylmethane was distilled under high vacuum from the saturator at 70°C, through the reaction vessel into the U-tube at -80°C. In order to maintain the flow of hydrocarbon the non-condensible gases had to be pumped away as fast as they were produced.

They were extracted from the exit of the reaction vessel, through tap 5 and the by pass to the flow capillaries and stored in the portion of the apparatus between the pump and taps 7 and 8 which were closed. It was found that as the back pressure built up, the pump was unable to maintain a good vacuum in the reaction vessel so a second mercury diffusion pump was installed in series. With this arrangement a pressure of 10^{-4} mms. of mercury could be readily obtained in the reaction vessel, while the pressure in the backing volume was 6 mms.

A tap (2) was placed in parallel with the second diffusion pump (no.1) so that the flow of carrier gas in subsequent experiments using nitrogen would not be impeded by having to pass through the pump jets.

At a later date, in the quantitative work, the two pumps were used to transfer the nitrogen and gaseous products from the flow system to the gas measuring system.

Flow Capillaries.

The nitrogen carrier gas could be directed through either of the two capillaries arranged in parallel by opening taps 3 or 4 and the pressure drop across it measured by means of the double McLeod gauges.

By applying Meyer's modification of Poisseuille's Law, the rate of flow of nitrogen was determined:

$$\text{Rate of flow (mols/sec)} = \frac{\pi r^4 (p_1^{\,2} - p_2^{\,2})}{16 \eta \, l \, RT}$$

r = radius of capillary in cms.

l = length of capillary in cms.

p_1 and p_2 = pressure before and after the capillary

η = viscosity of nitrogen in Poises

R = gas constant

T = absolute temperature.

The two capillaries were of quite different dimensions so that a wide range of flow rates could be obtained.

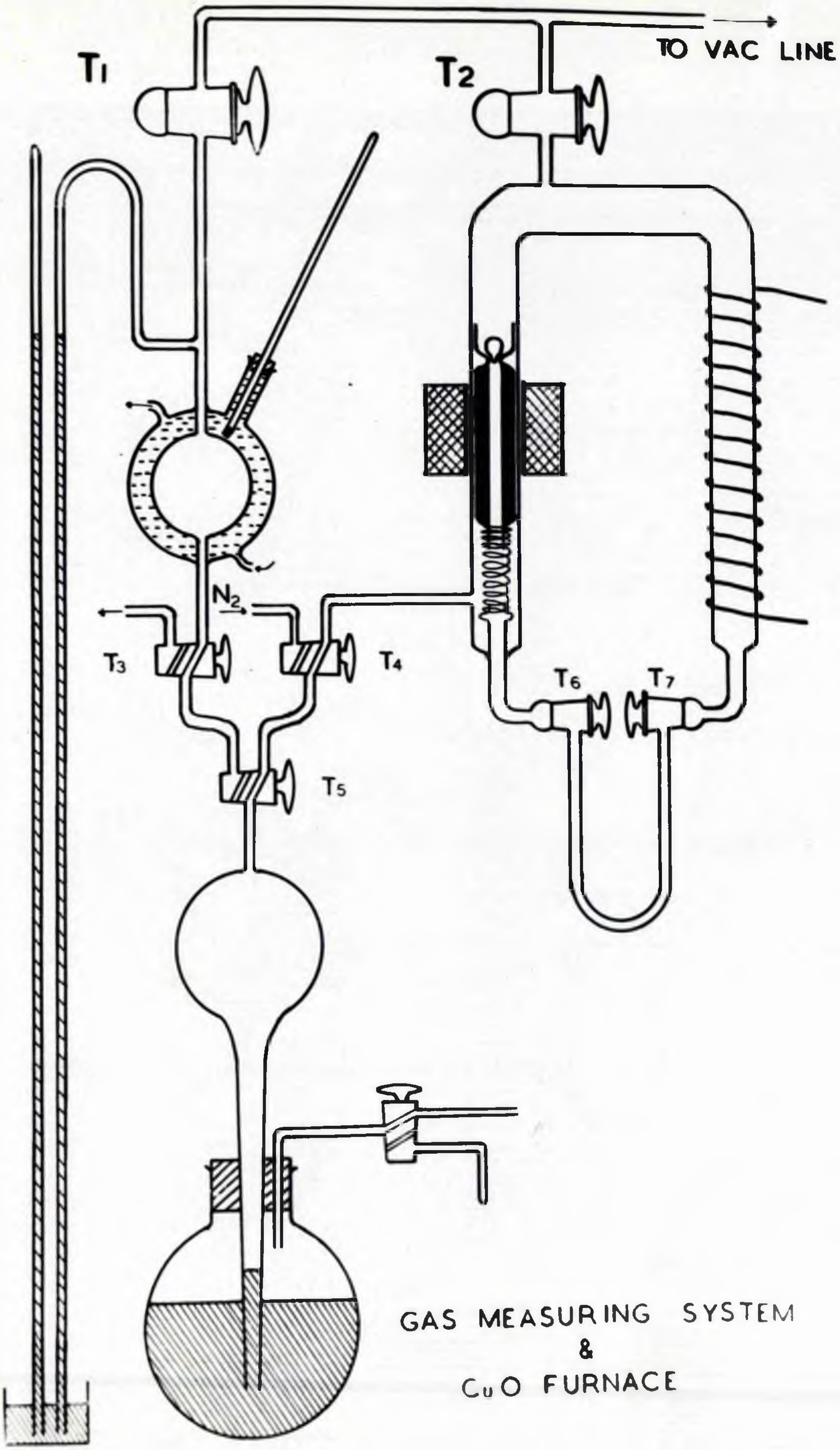
Nitrogen Purifying and Storage System.

The nitrogen carrier gas was cleared of condensible impurities and oxygen by passing slowly through a liquid air trap and then in turn through two sodium traps heated to 300°C before being stored in three 3-litre flasks.

The nitrogen used was supplied by B.O.C.

Measuring System for Gaseous Products.

It was not possible to determine with any degree of accuracy the amount of hydrogen formed in a run by measuring the increase of pressure in the flow system, as it only amounted to about 0.05 → ·3 mms. and



GAS MEASURING SYSTEM
&
CuO FURNACE

FIG. 5

the high pressure McLeod gauges were not very sensitive to such small differences in a total pressure of about 6 mm.

The mass spectrometer which was later used in the work on fluorene was not available at this stage so an alternative method was devised and an apparatus constructed (fig.5).

This apparatus consisted of a Toepler type pump with three two-way solid key taps arranged in such a manner that the gas could be transferred as required to either the water jacketed bulb of known volume or to the small copper oxide furnace which comprised the rest of the system. Connection was also made through these taps to the nitrogen storage flasks and to the flow system at a point between tap 1 and circulation pump 1 (fig.3).

The pressure in the jacketed bulb was determined by measuring the difference in height of the column of mercury in the simple barometer and that in the manometer.

The barometer and manometer were constructed from tubing of the same diameter to eliminate effects of capillarity and as both tubes had a common reservoir, changes of level of the mercury in the latter could be ignored when making the pressure determinations.

In the CuO furnace the gas was circulated by means of an electromagnetic pump, through a short column of hot copper oxide and a U-tube immersed in liquid air.

The pump was operated by automatically switching on and off the current through the solenoid. The hollow soft iron piston was pulled down while the current was flowing and returned to its original position by the action of the spring when the current was off. The piston was enclosed in a glass envelope and fitted at the top with a small glass valve.

The bulb and the CuO furnace could be independently evacuated through taps T1 and T2.

Operation.

The system was first of all completely pumped out and taps T1 and T2 then closed.

An amount of nitrogen was admitted into the Toepler pump via T4 and T5 and then forced up into the jacketed bulb through taps T5 and T3 until the pressure in the bulb was about 250 - 260 mms. Any surplus nitrogen was returned to the storage flasks.

The nitrogen was kept in the bulb for at least half an hour to allow thermal equilibrium with the water circulating through the jacket to be established before the pressure was noted.

The nitrogen could then be transferred to the pyrolysis system when it was required for a run.

On completion of the run, circulation pump 1 was started up, taps 1 and 2 (fig.3) closed and T3 and T4 (fig.5) adjusted so that the nitrogen and hydrogen were pumped by the mercury diffusion pumps acting in cascade, from the main apparatus into the Toepler pump. When the diffusion pumps had built up their maximum backing pressure, T3 and T5 were set to direct the gases into the calibrated bulb when the mercury was raised in the Toepler pump. This sequence of events was repeated until the pressure in the main circulating system was down to 10^{-4} mms. of mercury.

Again after waiting for the gases in the calibrated bulb to reach the same temperature as the jacket, the pressure and temperature were noted.

The gases were then transferred to the CuO furnace, liquid air placed round the U-tube, the copper oxide heated to dull red heat and the electromagnetic pump started. The hydrogen was thus oxidised and the water condensed out in the U-tube. After circulating for about 5 - 10 minutes the nitrogen was returned to the bulb and the temperature and pressure again recorded.

The pressures corresponding to 0°C were calculated.

The values of the 1st and 3rd observations should be the same if the gases formed were entirely oxidised in the CuO furnace, while the difference between these two and the second observation was due to the gases produced in the pyrolysis.

The volume of the pyrolysis system was about 40 times greater than the volume of the calibrated bulb so a pressure increment of say 0.2 mms. in the former became 8 mms. when the gases were compressed in the latter, This increase over the 240 mms. pressure of nitrogen in the bulb could be determined quite accurately.

Measuring System for Volatile Products.

In the initial experiments, the presence of benzene and toluene was detected in the products by means of a U.V. spectrophotometer and an attempt made using this instrument to determine the amount of these two substances formed. This was not successful as deterioration of the hydrogen lamp (the source of the U.V. radiation) rendered the instrument very insensitive. The same difficulty was encountered by C.B. Cowan[73] when he tried to analyse a mixture of toluene and benzene.

The apparatus as shown on the righthand side of fig.3 was then constructed and joined to the U-tube through tap 11.

Description of Apparatus.

Three bulbs of different sizes were connected one above the other by two short lengths of capillary tubing. From the bottom of the largest bulb a third piece of tube led through a rubber stopper tightly fitted into the mouth of a bolt-necked flask and dipped into a reservoir of mercury contained in the flask. Horizontal lines were etched on the glass at positions 1, 2 and 3.

A long length of tube of the same bore was arranged parallel to the bulbs and connected with them below position 3.

From the top of the smallest bulb connection was made through the two way tap 14 to two smaller detachable product tubes, each of which could be isolated by taps 15 or 16. The volume of each of the bulbs between the marks, also of the product tubes with their connecting tubes and taps was known.

The pressure in the bolt necked flask and hence the level of mercury in the apparatus when evacuated was controlled by means of the two way tap 17 which could be turned to either the atmosphere or a rough vacuum provided by a water pump. The height of the mercury in the two limbs was measured by means of a cathetometer, the difference being a measure of the pressure exerted by the material in the detachable tube.

Operation of the Apparatus.

During an experiment tap 11 was closed, the system evacuated through taps 12 and 13 and the mercury level adjusted to a point above the smallest bulb.

When the run was completed the carrier gas was pumped away and the U-tube isolated by closing tap 10 and the solenoid valve at the furnace exit. Any gases which were trapped in the products were released by removing the liquid air bath from round the U-tube and gently warming with a small gas flame until the evolution of bubbles ceased. The cold bath was then replaced and after allowing time for the materials to condense, the solenoid valve and tap 10 were opened and pumping out continued till a pressure of 10^{-4} mms. had been achieved.

The U-tube was again isolated and the liquid air bath transferred to the right hand product tube where the volatile materials condensed out after distilling through taps 11, 14 and 16 from the U-tube.

On completion of the distillation, tap 14 was turned to connect the product tube to the system of bulbs, now filled with mercury, and the liquid air bath replaced by one of CO_2 and acetone.

The mercury level usually fell, showing the presence of some material more volatile than benzene or toluene. This material was isolated in the other product tube by freezing down with liquid air and then closing tap 15.

The pressure exerted by the products remaining in the tube was determined at 0°C and 20°C. As long as liquid remained in the tube these values would have represented the vapour pressure of a mixture of benzene and toluene at these two temperatures (assuming a binary mixture of these two) and hence allowed the relative amount of each present to be calculated.

The total amount of material was determined by expansion into the bulbs and measuring the pressure at each of the three marks. Then, if no liquid was present in the detachable tube,

$$P_1V_1 = P_2(V_1 + V_2) = P_3(V_1 + V_2 + V_3)$$

and as V_1, V_2 and V_3 were known, the actual number of moles. present could be calculated.

The Purification of Hydrocarbons and Preparation of Standard Absorption Curves.

In addition to obtaining the diphenylmethane in a high state of purity before it was pyrolysed, it was necessary to purify a sample of each of the hydrocarbon products so that standard U.V. absorption data could be prepared; this data to be subsequently used in a quantitative analysis of the pyrolytic products.

Diphenylmethane.

When a study is made of the kinetics of the thermal decomposition of any substance the results obtained are very often not reproducible unless the material used is in a very pure state. This was found to be the case in the present investigation when the diphenylmethane had been purified by distillation under reduced pressure followed by two recrystallisations from ethyl alcohol of the fraction which came over between 184°C and 185°C under a pressure of 20 mms. of mercury. Not only did the amount of certain of the products vary from run to run

Table III

λ	Prepared by distillation and recrystallisation	Purified by fractional freezing
m μ	log. ε	log. ε
270	2.53	2.52
272	2.02	1.99
274	1.74	1.48
276	1.62	1.08
278	1.52	0.12
280	1.44	
286	1.24	
290	1.17	
298	1.04	
310	0.88	
330	0.65	
350	0.54	

carried out under the same experimental conditions, but it was difficult to understand how one of these products could be formed from diphenylmethane.

There was a considerable improvement in the reproducibility of the results when the diphenylmethane was purified by the following method.

The fraction collected between 184°C - 185°C was contained in a conical flask and raised above its melting point till all the diphenylmethane was liquid. The mouth of the flask was loosely corked and the vessel placed in a thermostat at 23.5°C. After six hours, the material which had not crystallised was poured off and the residual solid again heated till entirely molten. The flask and contents were then replaced in the thermostat, which was now adjusted to 24°C, for a further period of six hours. This procedure was repeated at 24.5°C, 25°C and 25.3°C. The diphenylmethane which solidified at this last temperature after 24 hours was then stored in a brown glass, tightly stoppered bottle till required for an experiment.

The ultra-violet absorption spectrum of diphenylmethane purified only by distillation and recrystallisation showed a sharp decrease in absorption between 270 and 276 m μ but then very gradually fell away and still absorbed at wavelengths greater than 350 m μ. This was in agreement with the data given in American Petroleum Institute Research Project 44 but not with that given elsewhere in the literature[74]. Further distillation and crystallisation had no effect in reducing the absorption at the longer wavelengths.

When purified however, by the method of fractional freezing, the diphenylmethane did not absorb at wavelengths above 280 m μ (Table III)

Fluorene.

In 1935 Askew[75] showed that fluorene could not be completely purified by fractional crystallisation and that the previously published absorption curves all of which showed bands above 310 m μ were wrong, the bands in that region being due to impurities.

Several attempts were made to purify fluorene by the method described by Askew but no pure hydrocarbon was obtained.

A sample of 10 gms. of commercial fluorene which had been thrice recrystallised from glacial acetic acid was then oxidised to fluorenone by the action of sodium dichromate in glacial acetic acid and 5 gms. of the fluorenone reduced to fluorene[76] by heating to 150°C for 20 hours in a sealed tube with hydriodic acid and amorphous phosphorus. After vacuum distillation and two recrystallisations from glacial acetic acid, 2.2 gms of fluorene (M.P. and 115°C) which did not absorb at wavelengths longer than 310 m μ were obtained.

This spectroscopically pure fluorene still had a very marked blue fluorescence when exposed to U.V. radiations. This is not in agreement with the statement by N. Campbell[77] that the fluorescence is due to impurities in the fluorene.

Tetraphenylethylene.

As tetraphenylethylene and tetraphenylethane were not available commercially, samples of these two compounds had to be prepared.[78]

A mixture of 12 gms. of benzophenone and 10 gms. of phosphorus pentachloride were heated to 150°C for 35 minutes and then poured into ice cold water. The resulting dark brown oil was extracted with ether which was then evaporated off and the benzophenone chloride distilled under reduced pressure with collection of the fraction which came over at 190°C under 31 mms. pressure.

4 gms. of the benzophenone chloride and 2.5 gms. of diphenylmethane were heated under reflux for as long as HCl was given off (about 8 hrs.). The mixture was then cooled and filtered and the solid washed on the filter with chilled ether until the crystals were almost colourless. After two recrystallisations from alcohol the solid melted sharply at 222°C.

<u>Tetraphenyl Ethane</u>.

The method of preparation was that described by Norris, Thomas and Brown[79].

7 ccs. of bromine were slowly added with vigorous stirring to 20 gms. of diphenylmethane maintained at 150°C. The resulting diphenylmethylbromide was distilled under reduced pressure.

3 gms. of the fraction collected at 183°C under 23 mms. pressure was dissolved in 15 ccs. of dry ethyl alcohol and 6 gms. of granulated zinc added to the solution. After allowing to stand overnight, the liquid was poured off, washed with water and then dried with fused potassium sulphate. The solid tetraphenyl ethane obtained by evaporating off the ethyl acetate was recrystallised from ethyl alcohol.

The U.V. absorption curve showed the product contained about 4 - 6% of tetraphenyl ethylene. This was reduced with sodium and alcohol after an unsuccessful attempt had been made in which a solution in glacial acetic acid of the material prepared was shaken with Adams

Table IV

Substanse	Conc. of soln. mol./litre.
Diphenylmethane	$1.5 - 2 \times 10^{-3}$
Fluorene	$5 - 6 \times 10^{-5}$
Tetraphenylethane	$4 - 5 \times 10^{-4}$
Tetraphenylethylene	$8 - 9 \times 10^{-5}$
Benzene	$5.5 - 6.5 \times 10^{-3}$
Toluene	$3.5 - 4.5 \times 10^{-3}$

catalyst in an atmosphere of hydrogen for a period of 24 hrs.

Benzene and Toluene.

These were purified by shaking with concentrated sulphuric acid at 0°C, washing successively with dilute sodium carbonate solution and water then dried over sodium and distilled from sodium using a Fenske fractionating column with a reflux ratio of 7:1.

Preparation of Standard U.V. Data.

In the preparation of standard solutions of each of these hydrocarbons and the examination of them by means of a 'Unicam' Quartz Single Beam Spectrophotometer the following procedure was always adopted.

1. The solvent used in preparation of the solutions was magnesium-dried methyl alcohol.
2. The hydrocarbon was accurately weighed using a micro balance.
3. At least five standard solutions of each hydrocarbon were prepared and examined.
4. The cell thickness was 1 cm.
5. Instrument slit width .3 mms.
6. Observations made every 2 m μ.

Table IV shows the concentrations of the solutions studied.

Absorption curves constructed from the experimental data by plotting log. ϵ against wavelength (m μ) are shown in graphs I, II and III for the above compounds.

Description of an Experiment.

Before an experiment the furnace was heated to approximately the operating temperature and the whole apparatus with the exception of the nitrogen storage bulbs, pumped out.

During this evacuation the diphenylmethane was outgassed by removing the surrounding bath of CO_2 and acetone from the saturator after closing tap 7 and the solenoid valve (fig.3) and gently heating until the diphenylmethane was entirely molten. The cold bath was then replaced and the released air pumped away from the saturator. To ensure complete removal of the dissolved air this process was repeated three times.

When a pressure of 10^{-5} mms. of mercury had been attained, and the apparatus found to be free from leaks, the U-tube, traps T1, T2 and T3 were immersed in liquid air and the taps to the vacuum line then closed.

The required pressure of nitrogen was admitted via the gas measuring system. The mercury diffusion pump 2 was started up and the cold bath round the saturator replaced by one of boiling water. When the rate of flow of nitrogen was steady, the diphenylmethane was admitted to the reaction vessel by opening tap 7 and the solenoid valve and at the same time closing tap 8.

The time of commencement of the experiment was noted. Pressure readings on the double McLeod gauges were taken every few minutes.

When sufficient solid had collected in the U-tube the run was stopped by opening tap 8 and then closing the solenoid valve and tap 7. In this way the flow of nitrogen through the reaction vessel was never interrupted and diphenylmethane was not allowed to remain in the vessel for a longer period than the calculated time of contact.

The carrier gas and non-condensible products were tansferred to the gas measuring system and analysed in the manner already described. When volatile substances were formed in the run they were distilled from the U-tube into the system for measuring their vapour pressure.

After letting air into the flow system, the U-tube was cut off and the solids washed out with magnesium dried methanol and made up to known volume for spectrophotometric analysis.

Analysis of Solid Products.

Optical density measurements of the solutions were made over the range of wavelengths 230 m μ $\longrightarrow$ 350 m μ, then from the standard absorption data previously obtained for the hydrocarbon components, the concentration of each in the solution was determined by making use of the relationship:

$$\text{O.D.} = \epsilon_1 C_1 + \epsilon_2 C_2 + \epsilon_3 C_3$$

where O.D. = Optical density of the solution at a given wavelength.

$\epsilon_1 \epsilon_2 \epsilon_3$ are the molecular extinction coefficients of the hydrocarbons 1, 2, 3.

$C_1 C_2 C_3$ are the concentrations in mols/litre.

In order to calculate the concentrations the O.D. need only be determined at as many different wavelengths as there are hydrocarbons in the solution. However, in many of the experiments the optical density was measured every 2 m μ over the whole range of wavelengths in which the solution showed any appreciable absorption so that when the concentration of each of the components had been calculated an absorption curve could be constructed using these values and the agreement between it and the experimental curve then checked.

This was intended to act as a test of the accuracy of the values determined for the concentrations but, as will be shown later, the contribution of tetraphenyl ethane to the optical density of the solution at most of the wavelengths was less than the variation between the calculated and experimental values of the O.D.

As can be seen from the graphs I and II, all four of the hydrocarbons absorb in the region 230 ⟶ 280 mμ but from 280 ⟶ 320 mμ only fluorene and tetraphenyl ethylene absorb and above 320 mμ the absorption is entirely due to tetraphenyl ethylene.

It was therefore possible to calculate the concentrations by the following method and so avoid the solution of four simultaneous equations.

Concentration of tetraphenyl ethylene

$$= \frac{\text{O.D. of soln. at a wavelength above 320}}{\epsilon \text{ for tetraphenyl ethylene at same wavelength}}$$

$$= C_1$$

$$\text{Concentration of fluorene} = \frac{\text{O.D.} - \epsilon_1 C_1}{\epsilon_2}$$

where the values of O.D., ϵ_1 and ϵ_2 are those at 292 mμ.

The concentration of diphenylmethane and tetraphenyl ethane could then be determined by subtracting at any two wavelengths between 230 and 270 mμ the absorption at these wavelengths of the fluorene

Table V

λ	O.D. due to T.P.E.	O.D. due to D.P.M.	O.D of soln.	% of O.D. due to T.P.E.
270	0.008	0.404	0.412	2
266	0.011	0.360	0.371	3
264	0.012	0.411	0.423	2.8
260	0.012	0.456	0.468	2.6
258	0.012	0.410	0.422	2.8
256	0.011	0.390	0.401	2.7
250	0.010	0.295	0.305	2.5
248	0.009	0.246	0.255	3.5
244	0.011	0.184	0.195	5.6
240	0.017	0.143	0.160	10
238	0.023	0.136	0.159	15
236	0.035	0.152	0.187	18.5
234	0.050	0.194	0.244	20
230	0.108	0.544	0.652	20

and tetraphenyl ethylene and solving the two simultaneous equations:-

$$\text{O.D.} - (\epsilon_1 C_1 + \epsilon_2 C_2) = \epsilon_3 C_3 + \epsilon_4 C_4 \quad \text{(values at 234 m}\mu\text{)}$$

$$\text{O.D.} - (\epsilon_1 C_1 + \epsilon_2 C_2) = \epsilon_3 C_3 + \epsilon_4 C_4 \quad \text{(values at 260 m}\mu\text{)}$$

The wavelengths 234 mμ and 260 mμ were chosen because at the former the difference between the degree of absorption of tetraphenyl ethane and of diphenylmethane is greater than at any other wavelength while at 260 mμ they are most alike.

However, this method of analysis did not allow a very accurate determination of the tetraphenyl ethane concentration to be made as it was present in very much smaller amount than the similarly absorbing diphenylmethane.

For the purpose of illustrating the difficulties let us suppose that in an experiment the percentage decomposition was 1%; so in the solution there will be 100 times more diphenylmethane than tetraphenyl ethane.

Let the concentration of D.P.M. = 0.001 mol/litre

then the " " T.P.E. = 0.00001 mol/litre.

Table V shows the calculated O.D. of a solution of these two in those concentrations.

An error of 2% in the O.D. at 260 mμ led to a difference of 24% in the value for the concentration calculated for tetraphenyl ethane from the two linear equations while a similar error at 234 mμ varied the result by 26%.

Although the experimental error in the O.D. measurements is normally less than 2% the actual values used in the simultaneous equations were obtained by subtracting from the O.D. of the mixture at 234 m µ and 260 m µ the calculated absorption due to tetraphenylethylene and fluorene, the concentrations of which were themselves subject to some error. Furthermore at 234 m µ the rate of change of absorption with wavelengths for both diphenylmethane and tetraphenylethane is quite considerable, calling for very careful manipulation of the spectrophotometer in order to obtain the greatest accuracy. A series of O.D. measurements made on a solution of diphenylmethane at 230 m µ did show a random variation of about 1.5% even after muchpractice in the use of the instrument.

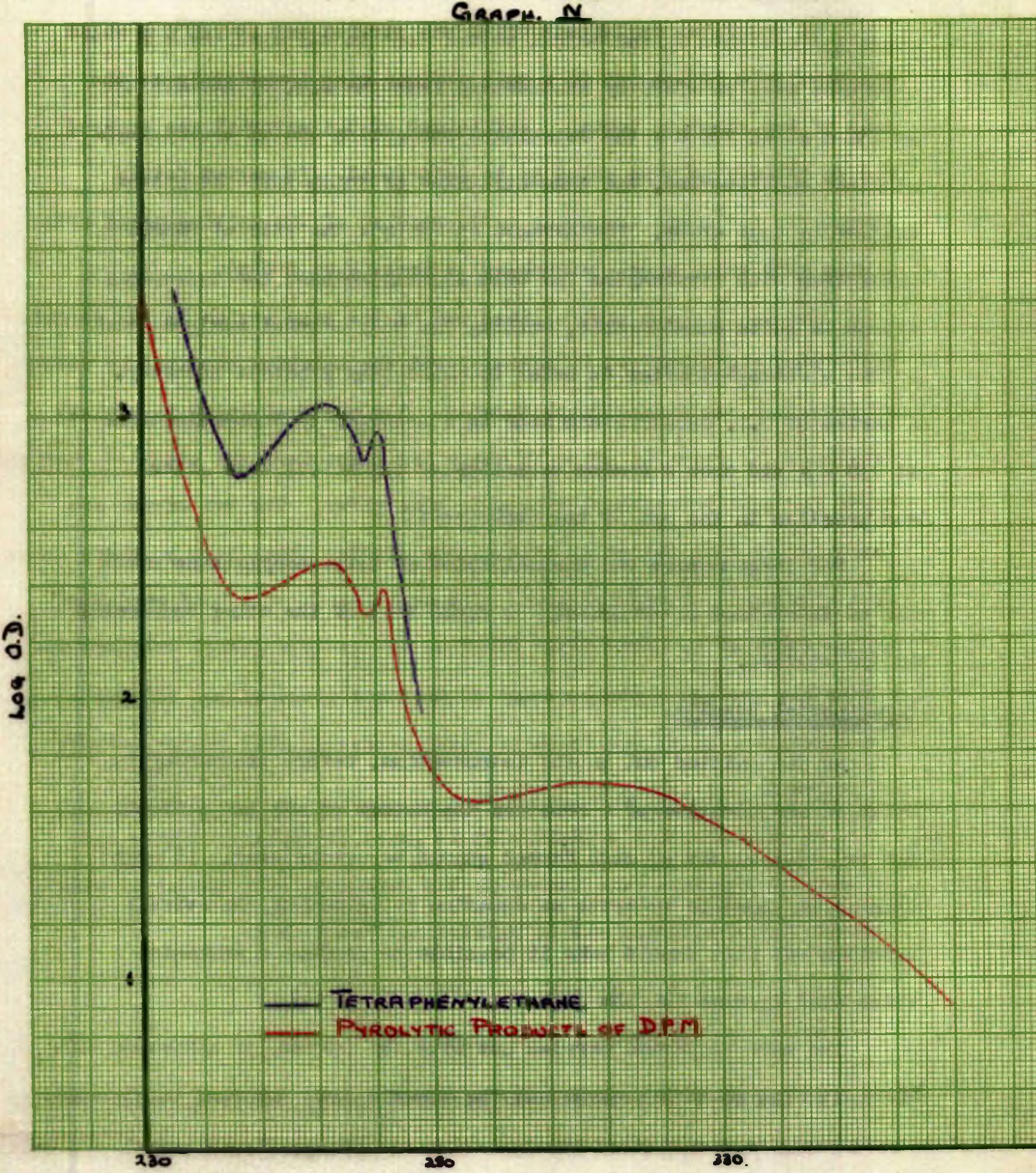
For these reasons the concentration of tetraphenylethane could not be determined as accurately as could that of the other components in the mixture.

Experimental Results.

As was pointed out in the introduction, before proceeding to a study of the kinetics of a reaction the nature of all the products and the relative amount of each formed should be established. It ought then to be possible to write an equation representing the overall reaction and this should make it possible to produce a mechanism which will account for the products.

The work which was carried out with the purpose of achieving this is dealt with in this section and the kinetic data recorded in the next.

GRAPH. IV



Log O.D.
3
2
1
230
280
330.
mμ.
Tetraphenylethane
Pyrolytic Products of D.P.M.

In the first experiment, which was carried out at 720°C, a solid was seen to condense out in a well defined ring immediately at the exit of the reaction vessel. Sufficient of the material was scraped out to allow a melting point to be determined. It melted fairly sharply at 209°C and there was no depression of the melting point after mixing with symmetrical tetraphenyl ethane (M.Pt.210°C).

The solid which crystallised out in the same region in the second experiment was dissolved in methanol and the solution examined by means of the ultra violet spectrophotometer. The curve of log.O.D. against wavelength is shown in graph IV where for comparison the standard absorption curve for pure tetraphenyl ethane is also given. The two curves are identical in form except at wavelengths greater than 274 m μ where there is a very broad absorption band. The position of this band suggested the presence of an unsaturated material and as tetraphenyl ethylene was a possible product a small amount of this was prepared and examined. Its absorption curve was found to match perfectly that of the unknown substance in the pyrolytic products.

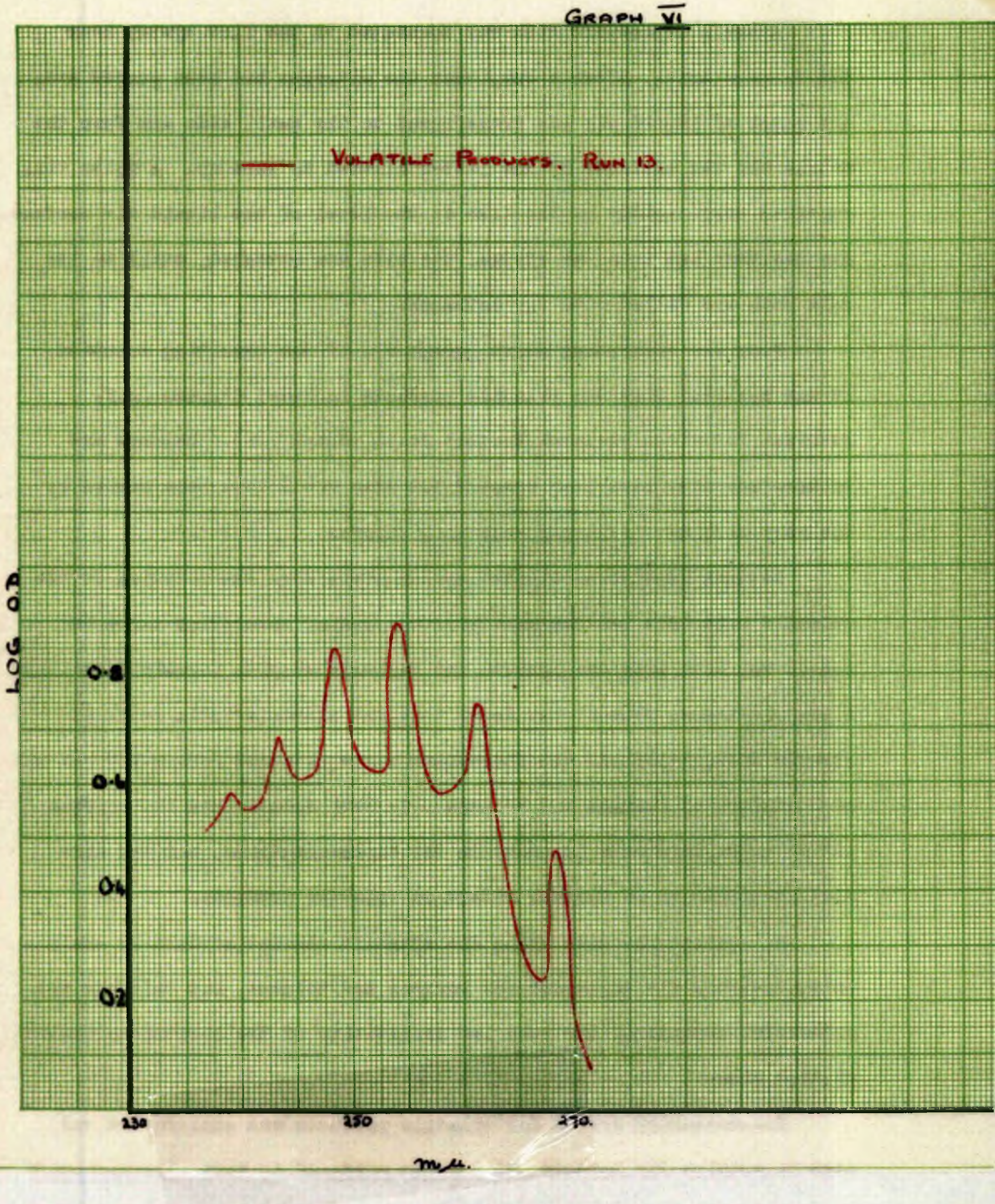
It thus appeared evident that at least tetraphenyl ethane and tetraphenyl ethylene were formed in the reaction. The amount of each present in the solution was calculated and found to be:

T.P. Ethylene - 4.25×10^{-7} mols.
T.P. Ethane - 1.82×10^{-5} mols.

No increase in pressure was observed during the runs, which had there been would have indicated the formation of hydrogen, so a search was made for benzene and toluene (volatiles) in the contents of the U-tube.

GRAPH V

GRAPH VI



A small detachable limb was connected to the flow system near the furnace exit. After a run, when the nitrogen had been pumped away the batch of liquid air was transferred to the small side arm from the U-tube and the contents of the latter allowed to warm up. A white ring appeared very rapidly in the limb at the level of the liquid air surface. Air was then let into the system, the side arm detached, still in its cold bath and filled with dry methanol.

From the absorption curve (graph V), of the resulting solution, it was apparent that the volatile products included Styrene (c.f. American Petroleum Research Project No.44, Graph 168). Benzene and toluene may also have been present but they would have been masked by the very much more strongly absorbing styrene.

Several runs were repeated and in every case the solution of the volatile materials had the same general type of absorption curve but after run 12 the saturator was removed and replenished with freshly distilled diphenylmethane, when it was found that the characteristic peaks of styrene disappeared and the absorption curve obtained (graph VI) was that of a mixture of benzene and toluene. It thus seemed that the styrene had resulted from some impurity in the diphenylmethane, but two more distillations had no further effect on volatile products.

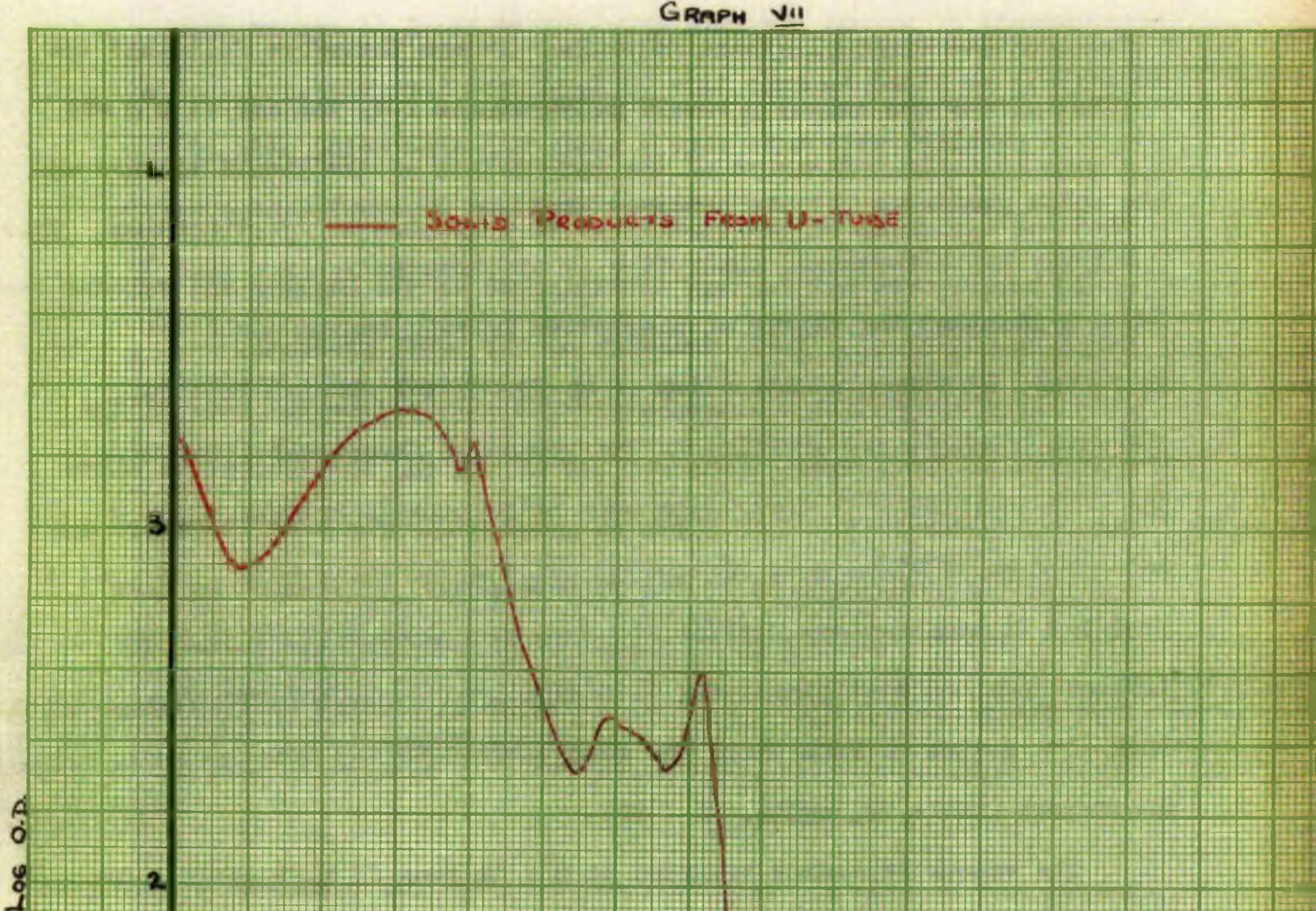
An attempt was made using the standard absorption data to analyse quantitatively the solutions for benzene and toluene, but this was not successful because of the very low sensitivity of the spectrophotometer at that time.

The measuring system for volatile products was constructed and used to examine the benzene and toluene produced in several experiments

Table VI

Run	Pressure at - 78°C	Pressure at 0°C	Pressure at 20°C	Total Mols - 10^{-5}
14	0.67	1.27	1.61	3.2
15	1.40	2.60	3.15	4.8
16	1.17	1.91	2.70	4.2
17	1.02	1.41	2.62	2.2
18	0.81	2.20	3.22	3.1
19	3.73	1.40	2.65	1.9
20	4.00	1.38	3.35	3.3
21	0.38	2.12	4.82	0.5
22	0.36	2.08	5.11	0.62
23	0.32	2.04	4.98	0.74
24	0.22	2.21	5.17	0.58
25	0.34	2.15	5.02	0.52

GRAPH VII



carried out under identical conditions. From the results of the measurements of vapour pressure shown in table VI it can be seen that those obtained in runs 14 - 20 were most irregular.

In parallel with this work a study was also being made of the solid products. It was observed that the diphenylmethane before pyrolysis had a continued absorption at wavelengths greater than 280 m μ and that the degree of absorption in this region could not be reduced by vacuum distillation or by fractional crystallisation, but when a sample was purified by the method of fractional freezing, described earlier, the absorption band ended sharply between 270 m μ and 278 m μ. Furthermore, the thermal decomposition of this purified diphenylmethane yielded not only very much less benzene and toluene than had been previously obtained, but the amount produced in each of a series of runs under the same conditions was much more consistent (table VI, expts. 21 - 25).

The vapour pressures recorded at 0°C in runs 21 - 25 corresponds to amixture of about 65% of benzene and 35% of toluene, but the values obtained at 20°C approximates more to the vapour pressure of a 50-50 mixture of benzene and toluene at that temperature.

Although an equal number of benzyl and phenyl radicals are produced by the breaking of a C-C bond in diphenylmethane, it should be remembered that the benzyl radicals are more stable under these experimental conditions than are the phenyl radicals and that some of them will exist as such until they reach the cold zone when they will unite with other radicals. The phenyl radical however, will be more likely to form a molecule of benzene by the abstraction of a hydrogen atom from another diphenylmethane molecule. It was therefore felt that the first of the two vapour pressure measurements i.e. the one at 0°C was a more reliable indication of the composition of the liquid mixture and that the low value of the reading at 20°C was due to fractionation. This point however was not further investigated as the benzene and toluene were found to represent a small fraction of the total products.

When a complete spectrophotometric examination was made of the contents of the U-tube, condensed out in run 14, the absorption curve was found to have the form shown in graph VII. The band above 310 m μ had already been shown to be due to tetraphenyl ethylene. Between 230 m μ and 274 m μ the great excess of diphenylmethane masked the tetraphenyl ethane which was also known to be present and the shape of the curve between these two wavelengths was very similar to that of the former.

The cause of the bands with maxima at 301 m μ and 290 m μ was not known, but as Graebe[71] recorded that fluorene was produced by pyrolysis of diphenylmethane a sample was purified and its absorption curve obtained (graph I). The bands between 280 mμ and 308 m μ coincided perfectly with those in the solid product absorption curve. It is of interest to note in passing that the fluorene produced by the thermal decomposition of D.P.M. was spectroscopically pure in that it did not absorb above 310 mμ but it did have a marked blue fluorescence.

As all the features of the U.V. absorption curve of the solid fraction had been accounted for, a start was made to determine how much of each compound was present. (Table VII).

Table VII

Run	D.P.M. gm.mols. x 10^{-3}	T.P. Ethylene gm.mols. x 10^{-6}	T.P. Ethane gm.mols. x 10^{-5}	Fluorene gm.mols. x 10^{-5}
23	1.89	1	2.5	3.93
24	1.61	1.2	2.1	3.72
25	1.65	0.93	1.8	3.81

The total number of molecules of solid products formed in each run was about ten times greater than the amount of benzene and toluene produced. No hydrogen had yet been detected but as the amount would be in the order of 5×10^{-5} mols. the comparatively large bulk of nitrogen made the detection of non-condensible products very difficult.

The apparatus was therefore modified to enable experiments to be performed without using a carrier gas. A second mercury diffusion pump was fitted, which, when used in cascade with the one normally employed for circulating the carrier gas could maintain a vacuum of 10^{-5} mms. of mercury in the reaction vessel against a back pressure of 6 mms. The backing pressure was measured by making a connection from one of the double McLeod gauges to that portion of the apparatus into which the gases were to be pumped, i.e. between the pumps and taps 7 and 8. A rough determination of the volume of this portion of the apparatus was made by admitting a known amount of air into the flow system from a small calibrated bulb temporarily fitted by means of a ground glass joint, and operating the pumps until the pressure in the reaction vessel was 10^{-5} mms. From the value of the pressure built up by the pumps it was possible to calculate the unknown volume.

Runs 26 - 33 were carried out without a carrier gas. A bath of ice and water was round the U-tube and the saturator immersed in a bath of water kept between 70°C and 75°C. By means of the double McLeod gauges, simultaneous observations were made of the pressures in the reaction vessel and in the backing volume. That in the reaction vessel stayed at 10^{-3} mms. while the backing pressure was directly proportioned to time

GRAPH VIII

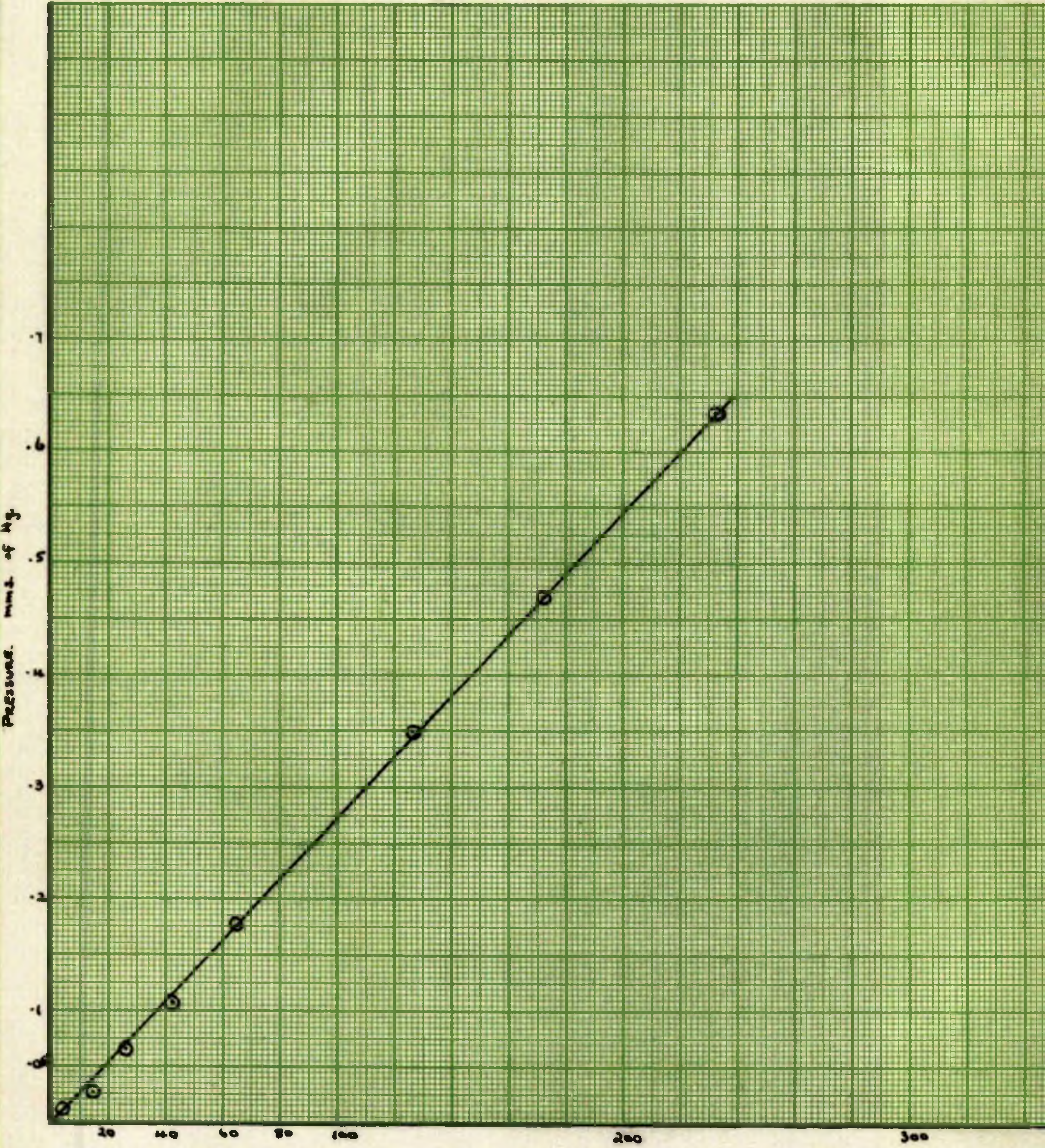


Table VIII

Run	Temp.	% Decomp.	T.P. Ethylene $\times 10^{-5}$	T.P. Ethane $\times 10^{-5}$	Fluorene $\times 10^{-5}$	H_2 $\times 10^{-5}$	Benzene $\times 10^{-5}$	Toluene $\times 10^{-5}$
28	796	0.7	0.9	27.8	14.2	47	3.2	2.2
29	760	0.18	0.1	11.2	3.1	16.2	1	0.8
30	Leak	Developed						
31	750	0.18	0.06	8.4	2.4	8.7	0.4	0.25
32	Leak	Developed						
33	710	0.08	0.04	3.3	0.5	3.2	lost	lost

of run (graph VIII). The gas formed was identified as hydrogen by circulating over a small nickel boat containing copper oxide inserted between taps 9 and 10 (fig.3) and heated by means of a coil of nichrome tape wound round the apparatus between the two taps. The heating coil was kept at a dull cherry red during the circulation of the gaseous products. At that temperature the copper oxide could be reduced by hydrogen but not by methane which was a possible product.

From the results shown in table VIII of the runs carried out without N_2 carrier gas over a temperature range of 86°C the following points emerge:

(a) The number of molecules of hydrogen produced in any run although not exactly equivalent to the total number of molecules of solid products is of the same order and is within the error of the U.V. absorption analysis.

(b) The ratio, mols of T.P.E./mols of fluorene decreases with increase in temperature.

(c) Benzene and toluene are formed in very much less amounts than hydrogen.

Kinetic Data.

Kinetic Data.

The production of tetraphenyl ethane suggests the intermediate formation of a benzhydryl radical by reaction (1)

$$Ph_2CH_2 \longrightarrow Ph_2CH- + H \qquad (1)$$

followed probably by:

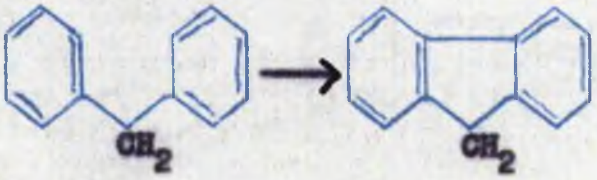
$$H + Ph_2CH_2 \longrightarrow Ph_2CH- + H_2 \qquad (2)$$

and

$$2Ph_2CH- \longrightarrow Ph_2CH-CHPh_2 \qquad (3)$$

Had hydrogen and tetraphenylethane been the sole products, the evaluation of the first order constant for reaction (1) would have been obtained simply by determining the rate of formation of H_2, this being taken as a measure of the initially formed radicals.

Since fluorene was also a product of the decomposition of diphenylmethane, increasing in importance as the temperature of the reaction rose, there is one fundamental point about the mechanism which has to be considered before calculating velocity constants for (1), and that is the mode of formation of fluorene. It is possible that it is formed by an entirely independent reaction:



$+ H_2$ (4)

or from some of the benzhydryl radicals formed in (1) and (2). The details of this can be left for discussion later but the influence of these alternatives on the calculation of velocity constants can be shown by considering the following:

A. <u>Separate Formation of Fluorene by (4)</u>

$$Ph_2CH_2 \longrightarrow Ph_2CH- + -H \qquad (1)$$

x mols. x x

$$Ph_2CH_2 + H \longrightarrow Ph_2CH- + H_2 \qquad (2)$$

x x x x

$$\begin{array}{lcll} Ph_2CH- & \longrightarrow & Ph_2CH - CHPh_2 & (3) \\ 2x & & x & \end{array}$$

$$\begin{array}{lclll} Ph_2CH_2 & \longrightarrow & \text{Fluorene} & + \; H_2 & (4) \\ 2y & & 2y & \;\;\; 2y & \end{array}$$

$$\%\ \text{Decomposition by primary step} = \frac{x}{\text{Total mols. of D.P.M.}} \times 100$$

$$= \frac{(x + 2y) - 2y}{\text{mols. of D.P.M.}} \times 100$$

$$= \frac{\text{Total mols. of } H_2 - \text{mols of fluorene}}{\text{Mols. of D.P.M.}} \times 100$$

B. <u>Formation of Fluorene via Benzhydryl Radical</u>.

$$\begin{array}{lclll} Ph_2\,CH_2 & \longrightarrow & Ph_2CH- & + \; H & (1) \\ (x + y)\text{mols.} & & (x + y) & (x + y) & \end{array}$$

$$\begin{array}{llclll} H & + \; Ph_2CH_2 & \longrightarrow & Ph_2CH- & + \; H_2 & (2) \\ (x + y) & (x + y) & & (x + y) & (x + y) & \end{array}$$

$$\begin{array}{lcll} Ph_2CH- & \xrightarrow{2x} & Ph_2CH\text{-}CHPh_2 & (3) \\ 2(x + y) & & x & \\ & \searrow\xrightarrow{2y} & \text{Fluorene} \; + \; H_2 & (5) \\ & & 2y \;\;\; + \; y & \end{array}$$

% Decomposition by primary step

$$= \frac{x + y}{\text{Total mols. of D.P.M.}} \times 100$$

$$= \frac{(x + 2y) - y}{\text{Total mols. of D.P.M.}} \times 100$$

$$= \frac{(\text{Total mols. } H_2 - \frac{1}{2} \text{ mols. of fluorene}}{\text{Total mols. of D.P.M.}} \times 100$$

The numerical values resulting from the expressions produced in A and B diverged to an increasing extent as the temperature of experiment rose, because the proportion of fluorene increased at higher temperatures.

In order to determine which mechanism was correct, tetraphenyl ethane was pyrolysed at 750°C, 710°C, 705°C and 635°C under the same conditions as for diphenylmethane.

Fluorene and hydrogen were produced at each temperature and in amounts approximately in accordance with:-

$$Ph_2CH\text{-}CHPh_2 \longrightarrow 2\text{Fluorene} + H_2 \qquad (6)$$

There are strong reasons for believing that in tetraphenyl ethane the weakest bond will be the central C-C link and hence that the benzhydryl radicals will be the first products of decomposition. This supports the view that the fluorene is formed from this radical and that the calculation of velocity constants for diphenylmethane decomposition should be made by the expression for % decomposition in (B) above.

Table IX

	Method A	Method B
k.at 744°C (Run 85)	0.0056	0.00846
k.at 804°C (Run 118)	0.0043	0.0619

Table X

Run	Temp.	% Dec.	T. of C.	k	
39	752	0.64	0.64	0.010	P
41	752	0.65	0.6	0.0113	
42	752	0.89	0.8	0.0112	
40	799	2.2	0.34	0.0655	P
43	799	2.3	0.38	0.0625	
44	799	1.2	0.26	0.0461	

The results obtained by this procedure seem a further point in its favour. As indicated later, the temperature variation of the velocity constants for the primary decomposition calculated on this basis seem very reasonable since the temperature independent factor for the reaction has a value near to 10^{13} and the energy of activation is in accord with expectations based on the known values of this quantity for toluene.

If calculations were based on assumption (A) the temperature variation of (1) would be very low. In table IX are given calculated values of k_1 for two runs chosen at random.

The values of the velocity constant valculated from data obtained from runs 39 and 40 which were carried out with the reaction vessel packed with silica wool are compared in table X with runs carried out at the same temperature without packing. It will be seen that increasing the surface/volume ratio by a factor of 11.7 had no effect on the reaction rate.

Variation of;

(1) Partial pressure of diphenylmethane,

(2) time of contact,

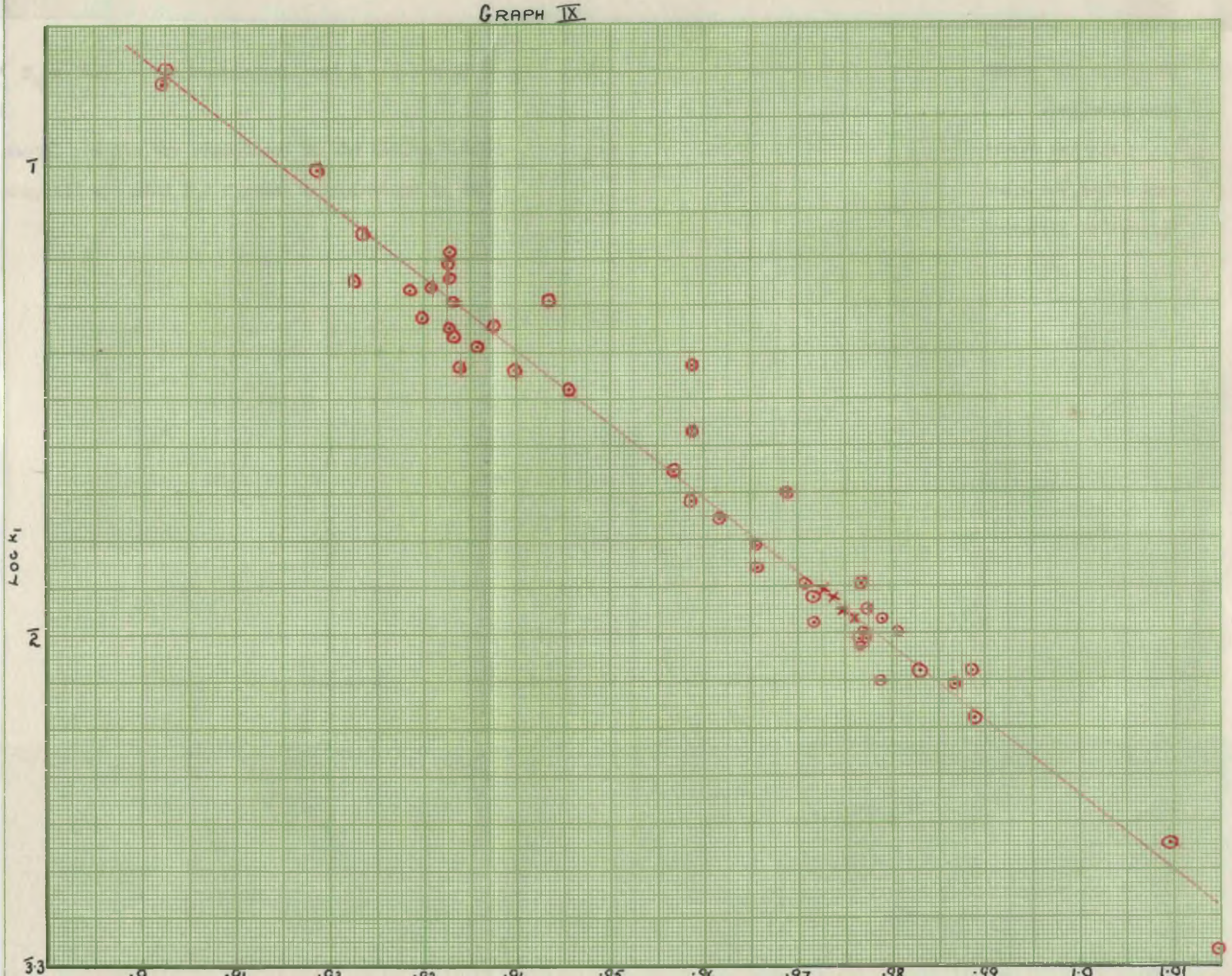
(3) nitrogen pressure had no effect on the value of the calculated first order constant. (See table XI).

The data for $\log.k_2$ obtained from a number of experiments carried out over the temperature range 712°C ⟶ 835°C are plotted against $1/T$ in graph IX. The best straight line through these points was determined by the method of least mean squares and from the slope of

Table XI.

Run	Temp.	% Dec.	T of C secs.	P.Press. of D.P.M. mms.	P.Press. of N_2 mms.	k $secs.^{-1}$
73	753	0.74	0.65	0.041	6.0	0.0106
75	753	0.74	0.58	0.95	6.0	0.0128
62	795	1.26	0.24	0.21	6.8	0.0528
61	795	3.2	0.75	0.6	6.6	0.0435
92	753	0.73	0.65	0.65	3.0	0.0111
100	753	0.6	0.56	0.35	10.8	0.0101

GRAPH IX



this line the values $E_A = 71.9 \pm 1.6$ k.cals/mol. and $A = 3.7 \times 10^{13}$ were obtained.

All the experimental results are reproduced in the tables which come after the Appendix, and are used for further calculations in the discussion section.

2. FLUORENE.

Apparatus and Experimental Technique.

The apparatus and technique used in the initial experiments on fluorene differed only from those employed in the investigation of the kinetics of pyrolysis of diphenylmethane in

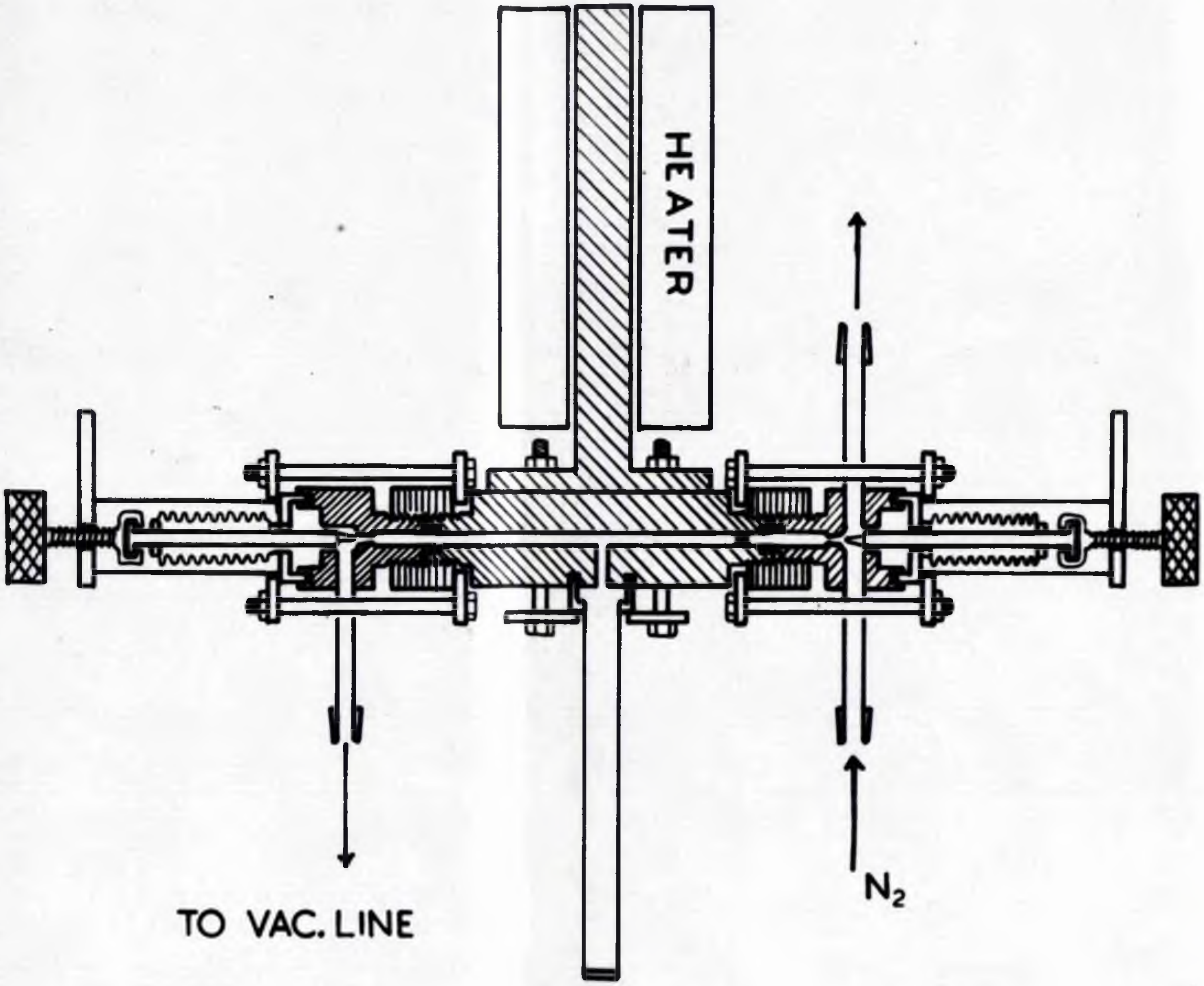
(a) the method of introducing the organic material into the nitrogen stream and

(b) the separation of the solid products of pyrolysis from the unchanged fluorene before analysis.

Later a mass spectrometer became available and a new technique was developed using it to determine the partial pressure of fluorene during each run and also the amount of hydrogen formed. In this way data was obtained very much more quickly.

The 'saturator' method of introducing the hydrocarbon into the carrier stream was considered to be unsuitable for the work on fluorene, chiefly because of the irreproducibility of partial pressures given by the method. It was essential to devise some system of introduction which would give reproducible partial pressures of fluorene in the carrier stream so that the relationship between mass spectrometer output voltage of $\frac{m}{e} = 166$ and partial pressure of fluorene could be proved.

Another shortcoming of the saturator method was the lack of positive control over the introduction of the hydrocarbon into the reaction vessel. The solenoid valve and bypass arrangement used in the work on diphenylmethane was not very reliable because of the tendency of the valve to stick. The shape of the valve prevented its



INJECTOR UNIT

FIG. 6

being heated efficiently by nichrome winding which often resulted in the condensation of considerable amounts of hydrocarbon within the valve.

With a view to overcoming the drawbacks, an all metal injector unit was constructed.

The Injector Unit.

The main features of the unit as finally developed are shown in the diagram (fig.6) opposite. It consists essentially of a central body and container and two Edwards type needle valves modified to enable them to be operated up to 200°C and remain vacuum tight. One of the valves controls the introduction of the material while the other allows the unit to be evacuated without having to pump through the injector orifice. The container was made as light as was consistent with strength so that by weight differences the determination of material used per run could be made as accurately as possible. Polytetrafluoroethylene sheeting was cut and used for gaskets to give vacuum tight joints, but later they were replaced by lead because of the tendency to flake and block up the jet.

The body was made from a 4" length of 1" square brass stock turned to circular section of $\frac{5}{8}$" diameter for a distance of $\frac{1}{2}$" from each end. A hole of 3/32" diameter was drilled lengthwise through its centre from end to end. Centrally placed on one of the faces a 3/32" hole was drilled to meet the longitudinal through passage at rightangles. Concentric with this second hole a circular slot of $\frac{1}{2}$" internal diameter, 11/16" outer diameter by 1/10" deep was turned.

A $\frac{3}{8}$" British Standards brass thread was cut on both turned down ends of the stock. This particular thread was chosen as it was the form of screw used on the commercial needle valves.

Two 1" long bushes were turned out of 1" diameter brass and internally threaded $\frac{3}{8}$" British Standard brass thread. These bushes were screwed one on to each end of the stock and silver soldered into position to make a vacuum tight joint. A Primus stove jet of 0.012" bore was fitted into one end of the longitudinal passage.

The Edwards needle valves were modified as follows to adapt them to the present purpose. All soft solder joints were changed to silver solder. The main assembly locking nut was dispensed with and the barrel and stem of the valve then held together by means of two clamping plates and four $\frac{1}{4}$" B.S.F. nuts and bolts. The rubber gasket between these two portions was replaced by a lead washer. When sufficient pressure was applied by the clamping plates and bolts to the lead washer a vacuum tight joint was obtained.

The threaded connector fitted at rightangles to the original needle-valve stem was removed from each and replaced by a cone turned in brass to fit a standard B 14 glass socket. In one of the valves only, a second brass cone was fitted in the stem at rightangles to the first one.

When the modified valves were tested it was found that on heating them up to 200°C the needle became so firmly seated that the retractor spring was too weak to withdraw it. To overcome this difficulty, a special rotating bush was turned from steel stock and fitted as shown in the diagram.

The modified valves were screwed into the threaded bushes fixed at each end of the body. The valve with the two standard brass cones being fitted to the end of the body in which the jet was fixed. A lead washer was fitted between the mating faces of each needle valve and the body in order to obtain vacuum tight joints.

A container for the hydrocarbon was constructed from a ⅜" diameter nickel silver tube 4" long. The tube was plugged at one end by a brass insert and brazed. On the other end was silver soldered a brass collar turned to fit the annular slot turned in the body. A polytetrafluoroethylene gasket was cut from 1/16" sheet to provide a vacuum tight seat for the collar of the container when clamped into position.

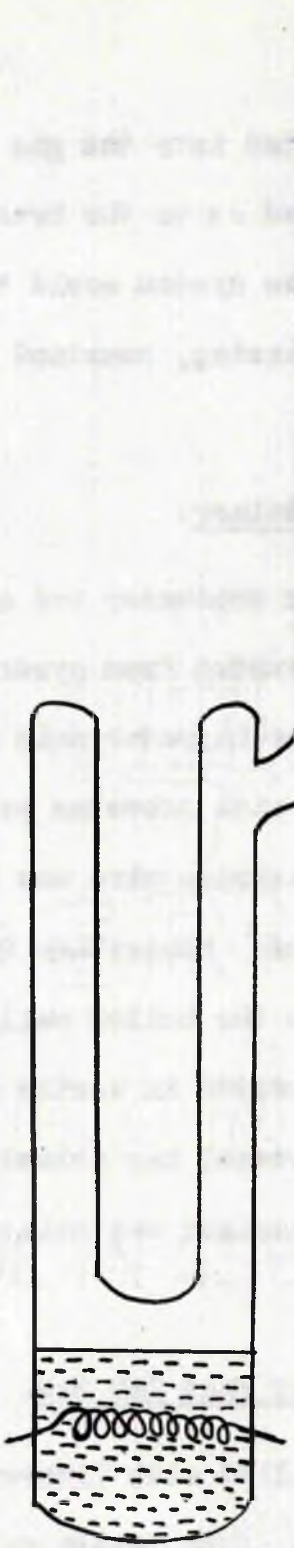
A heating plate was fitted to the opposite face of the body and fixed in position by the container retaining plate bolts.

The temperature of the unit could be determined by placing either a thermometer or thermocouple into the pocket which was drilled through the heating plate into the body (not shown in diagram).

The valve barrels were covered with asbestos paper wound with half a metre of nichrome tape, 3.5 ohms per yard, giving 7 complete turns on each. These two windings were joined in parellel and connected in series with the heater windings for the body.

The entire unit except for the container was wrapped in asbestos wool. With this arrangement a current of 3.5 amps. gave a temperature of 195°C. Manual control of the current by means of a rheostat was sufficient to maintain the temperature steady within ± 2°C.

FIG. 7



CONTAINER HEATER.

The unit was connected into the gas flow system by means of B14 standard sockets fitted on to the brass cones using polythene as a seal for the joints. The system could then be pumped down to 10^{-5} mms. of mercury, and after degassing, remained at this pressure when heated to 190°C.

Thermostat Heater for Container.

A boiler with reflux condenser and central thimble as shown in the diagram (fig.7) was constructed from pyrex glass, the thimble being large enough to enclose the injector unit container. The outer surface of the boiler was wrapped with asbestos paper and wound with nichrome tape. A small heating coil of nichrome wire was fitted inside the boiler to promote constant ebullition. Connection to this coil was made through tungsten wires sealed into the boiler wall. The internal coil and outer heating windings were connected in series with a variable resistance.

By boiling in this vessel any selected suitable organic compound, the temperature of the container was maintained constant at the boiling point of the compound.

Preparation of the Injector Unit for Use.

The container was filled with fluorene and after being weighed, was clamped into position. Both needle valves were opened and the unit pumped out. During the evacuation the container was immersed in liquid air and the unit heated up. When the temperature reached the operating value of 190°C the valves were closed and the liquid air removed from round the container which was then heated by means of a small gas flame to release air dissolved in the fluorene. After the liquid air had been replaced and sufficient time allowed to elapse to ensure complete cooling of the fluorene, the needle valve to the vacuum line was opened and any released air pumped away. Three repetitions of the freezing-pumping-warming cycle were usually sifficient to ensure complete outgassing of the hydrocarbon.

When the outgassing was completed, the needle valve was closed and the container surrounded by the boiler half filled with an organic compound whose boiling point was close to the temperature calculated to give the desired partial pressure of fluorene. In order to allow the fluorene to reach the bath temperature no runs were done for at least 30 minutes after starting to heat the container.

When the system had attained equilibrium the fluorene could be introduced into the nitrogen stream as required by opening the needle valve.

Test of Injector Unit for Reproducibility.

When in operation the container of the injector unit was surrounded by a constant temperature bath and therefore the amount of fluorene delivered into the N_2 stream per fixed period of time should also be constant. To test this, four separate runs each of five minutes duration were carried out with mesitylene (B.Pt.164°C) in the boiler and the furnace just sufficiently hot to prevent the fluorene from condensing out. After each run the fluorene in the trap was dissolved in 100 ccs. of dry methanol and the optical density of the solution measured at certain wavelengths.
There was good agreement between the results, thus

Table XII

Run No.	1	2	3	4
O.D. at 294	43	42.6	44	43.4
O.D. at 292	43.9	43.5	45	44.5
O.D. at 284	31.8	31.6	32	32
Mols.of fluorene	9.35×10^{-4}	9.28×10^{-4}	9.56×10^{-4}	9.47×10^{-4}

showing that the unit did inject a substantially constant stream of hydrocarbon (table XII).

Purification of Fluorene.

In this section an account is given of the work carried out in the attempt to obtain pure fluorene. Askew states that fluorene does not absorb at wavelengths longer than 310 m μ and that in all previous published ultra violet absorption curves, the peaks shown in the region 310 - 370 m μ were due to impurities. It was therefore decided to use the absorption of the processed samples in that region as a criterion of purity.

Commercial fluorene (B.D.H.) which was brown and tarry in appearance was dissolved in benzene and shaken in turn with dilute alkali and acid. After being washed with water, the benzene was evaporated off and the fluorene distilled under high vacuum. The thus partially purified material was used in the following attempts to obtain completely pure fluorene.

(1) 4.2 gms. of fluorene and 1 gm. of sodamide[80] were heated together up to 150°C. When ammonia ceased to be given off, the mixture was cooled and extracted with dry benzene to remove unchanged fluorene. The application of water to the residue did not yield fluorene. The experiment was repeated several times but no pure fluorene was obtained.

(2) Sublimation Method.

Fluorene in a bolt necked flask was heated in an oil bath and allowed to sublime onto a round bottomed flask filled with cold water placed immediately above the mouth of the bolt necked flask.

The sublimed fluorene absorbed strongly above 310 m μ.

(3) Oxidation to Fluorenone followed by Reduction.

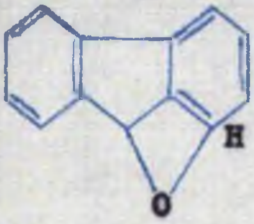
It was then decided to oxidise fluorene to fluorenone, purify the latter by several fractional crystallisations and then reduce the purified fluorenone to fluorene.

75 gms. of fluorene were oxidised by sodium dichromate in glacial acetic acid to yield 58 gms. of fluorenone.

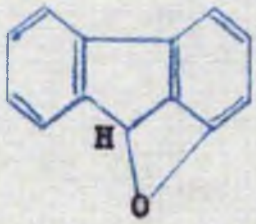
(3a) Clemmensens Reduction of the Fluorenone.

5 gms. of the fluorene and 72 ccs. of 50% HCl were heated under reflux with 12.4 gms. of amalgamated zinc for 3½ hours with the addition of 3.5 gms. of concentrated HCl at the end of every full hour. The reaction product, which was red in colour, solidified on cooling. It was purified by distillation under reduced pressure. (Mt.Pt. 62°C). On repeating the experiment, the same result was obtained.

The nature of the red material was not investigated, but attention is drawn to Kemp[81] and to Stoebl[82] who report the existence of a pseudo form of fluorene which is dark red in colour and to which they give the formulae



and



(3b) Hydrogen Iodide and Amorphous Phosphorus

According to Graebe[83], fluorene is reduced to fluorenone by heating in a sealed tube with hydriodic acid and amorphous phosphorus. 5 gms. of fluorene were reduced by this method to yield, after vacuum distillation and two recrystallisations ex. glacial acetic acid, 2.2 gms. of fluorene (Mt.Pt.115°C) which did not absorb at wavelengths longer than 310 mμ.

The experiment was repeated using double the above quantity but no fluorene could be isolated from the black tar-like product. After two more failures the method was given up.

(3c) Modified Wolff-Kishner Method[84] of Reduction.

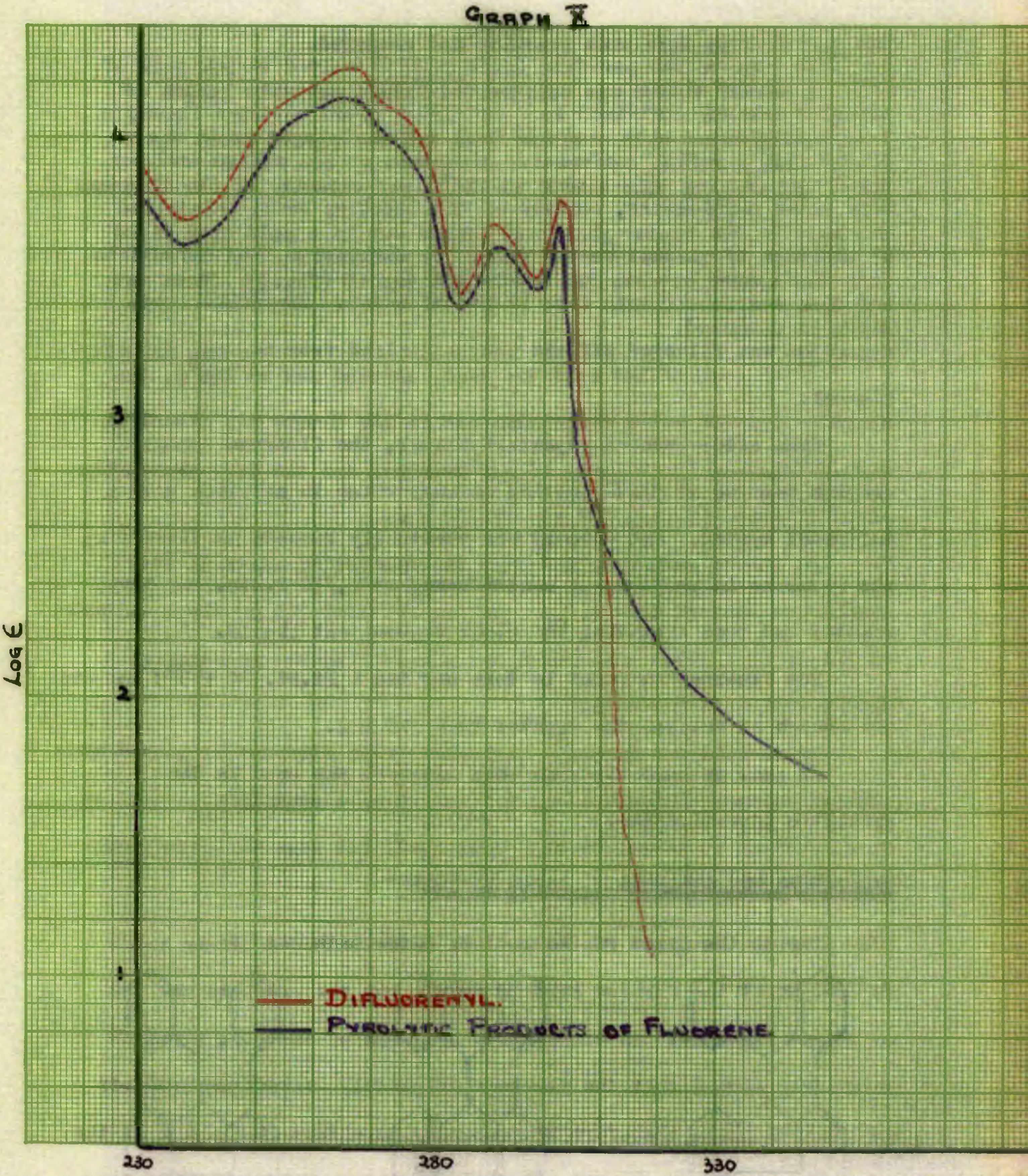
A mixture of 18.2 gms. of fluorene, 7 gms. NaOH, 93 gms. triethylene glycol and 10 ccs. of 100% hydrazine hydrate was refluxed for 1½ hours. The temperature was then raised to 195°C and maintained for 4 hours, after which time the mixture was cooled, acidified and extracted with benzene. The triethylene glycol was removed and the remaining solid product recrystallised from benzene. Melting Point of the solid >245°C Yield 6.6 gms.

The U.V. absorption curve showed the material to be difluorenyl. The experiment was not repeated but it is of interest since the production of difluorenyl shows the immediate formation of fluorenyl radicals.

(3d) Reduction by Sodium Amalgam[85]

13 gms. of fluorenone were converted to the oxime by refluxing for ½ hour with 32.5 gms. of hydroxylamine hydrochloride in 260 ccs. of 5% sodium hydroxide solution. The 9 isonitrosofluorene was recrystallised from ethyl alcohol (Mt.Pt.190°C) Yield 10.5 gms.

GRAPH X


4
3
2
1
LOG E
230
280
330
mμ.
DIFLUORENYL.
PYROLYTIC PRODUCTS OF FLUORENE

10 gms. of the purified oxime were dissolved in 500 ccs. of absolute alcohol contained in a one litre round bottomed flask, fitted with a reflux condenser. 1000 gms. of 2½% sodium amalgam were added portionwise, acidity of the solution being maintained by addition of glacial acetic acid. On completion, the colourless solution was poured into four litres of water. The solid which separated was filtered off and recrystallised from benzene and ethyl alcohol.

Even after several crystallisations, the fluorene appeared greyish because of contaminating mercury which in solution gave a colloidal system. The mercury was eventually removed by dissolving the fluorene in benzene and centrifuging at 2,750 r.p.m. for three minutes and then decanting the clear supernatant liquid.

The fluorene obtained in this way had a Mt.Pt. of 115°C and did not absorb at wavelengths greater than 310 m μ.

72 gms. of pure fluorene were prepared and used in the pyrolytic investigation.

Collection and Analysis of Solid Products.

During the first run an ice and water bath was placed round the U-tube at the furnace exit to freeze out the products and the unchanged fluorene. An examination by means of the U.V. spectrophotometer showed that the fluorene completely masked the products and that it would therefore be necessary to effect separation of the products from the unchanged material. Hydrogen was produced during the run showing that some reaction had occurred.

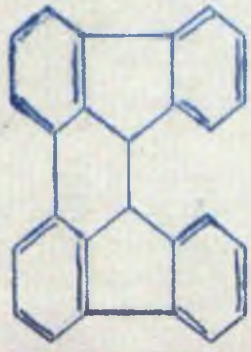
A heater sleeve was constructed from a suitable length of iron tubing wound with nichrome tape and was placed round the U-tube. By keeping this sleeve at 125°C the majority of the fluorene was kept in the vapour phase and frozen out in a cold trap fixed into the system between the U-tube and tap 10 (fig.3). (Trap not shown in diagram).

After each of the next two runs, carried out at 740°C, the slightly reddish solid which came out in the U-tube was dissolved with difficulty in 100 ccs. of dry methanol and the U.V. absorption curve obtained between 380 mμ and 230 mμ.

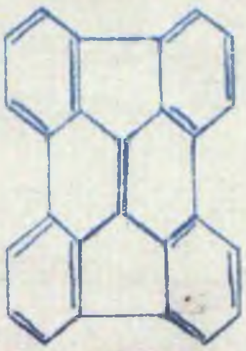
As can be seen from graph X, the absorption curve is very similar to that of pure difluorenyl except that the products continue to absorb in a broad band above 312 mμ showing the presence of a more unsaturated material.

Dziewonski and Suszko[86] claim that when fluorene is passed at reduced pressure through a red hot quartz tube containing a coil of wire, most of it passes through unchanged, but some difluorenylene, rubicene and dihydrorubicene are formed.

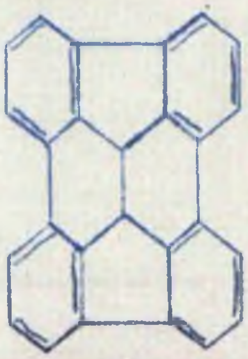
They give the formulae of these three hydrocarbons as:-



Difluorenylene

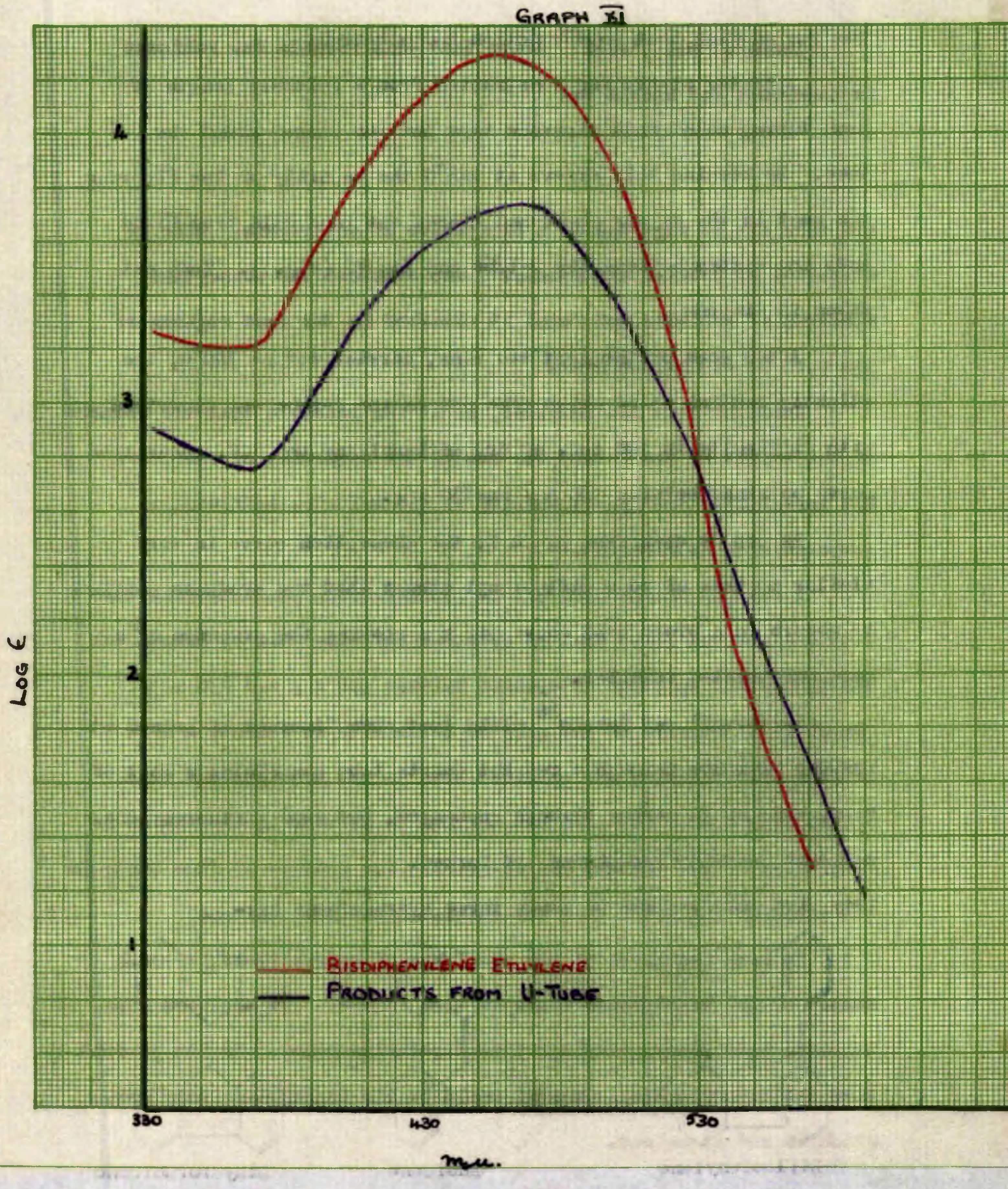


Rubicene

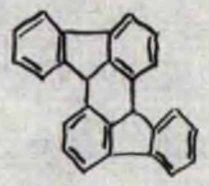


Dihydrorubicene

GRAPH XI


Log ε
4
3
2
1
330
430
530
mμ.
Bisdiphenylene Ethylene
Products from U-Tube

Pummerer and Ulrich[87] state that this formula for rubicene is incorrect and should be:



and this can be regarded as a derivative of anthracene. This is supported by Setkina and Fedorov[88] who examined the absorption spectrum of rubicene and found it absorbed in the same regions of the U.V. as anthracene does.

Rubicene is a red compound, so it was possible that the redness of the solids in the U-tube was due to the formation of rubicene. The exceedingly sparing solubility in alcohol also indicates a compound such as rubicene.

A run (4) was carried out at 790°C and the products from the U-tube dissolved in 10 ccs. of spectroscopically pure n. hexane and the absorption spectrum determined between 590 m μ and 230 m μ, (graph XI). Because of the greater solubility in hexane, a more concentrated solution was obtained than in the previous two runs so enabling a more detailed examination to be made in the region of absorption of the unknown red material. The absence of fine bands in the spectrum indicated that the substance was not rubicene.

In many instances of the pyrolysis of hydrocarbons, a small amount of the unsaturated dimer is also formed. (Ex. stilbene from toluene, tetraphenyl ethylene from diphenylmethane). In the present case the corresponding compound would be bis diphenylene ethylene, which is red in colour.

A small amount of bis diphenylene ethylene was prepared[89] by treating 9:9 dichlorofluorene with alcoholic K_2S. The red product was extracted with CS_2 then evaporated to dryness. The residue was dissolved in the least possible quantity of benzene and mixed with a concentrated solution of picric acid in benzene. The red crystals which separated were decomposed by ammonia and the resulting red solid recrystallised from a mixture of alcohol and chloroform. (Mt.Pt. 187 - 188°). The standard absorption curve of bis diphenylene ethylene was prepared between 590 mμ and 370 mμ (graph XI). The broad absorption band in that region agrees very closely with the absorption of the pyrolysis products.

Thus the products of pyrolysis of fluorene appear to be difluorenyl, bis diphenylene ethylene and hydrogen. Two runs were then carried out to determine the amount of each product formed. The hydrogen was measured by means of the gas measuring system as in the work on diphenylmethane. The solids which condensed out in the U-tube were dissolved in 100 ccs. of dry methanol and the optical density of the solution measured accurately at several wavelengths.

The bis diphenylene ethylene was determined quite readily as it was the only component of the mixture which absorbed in the visible region.

Then from the optical density at 282 and 303 mμ, by the method of simultaneous equations, the concentrations of fluorene and difluorenyl were calculated using the molecular absorption coefficient values obtained from the standard curves.

Table XIII

λ	Calculated O.D.	Measured O.D.
302	8.58	8.7
301	8.16	8.6
300	7.03	7.45
298	5.75	5.84
296	6.12	6.18
294	7.21	7.22
292	7.84	7.82
290	7.18	7.22
288	6.23	6.4
286	5.78	6
284	6.53	6.58

$$8.83 = 11{,}560\,C_D + 3{,}760\,C_P \qquad (\lambda = 282\ \mathrm{m}\mu)$$

$$\underline{8.7 = 11{,}600\,C_D + 3{,}423\,C_P} \qquad (\lambda = 303\ \mathrm{m}\mu)$$

$$32{,}712 = 43{,}616{,}000\,C_D$$

$$\underline{30{,}225 = 39{,}569{,}900\,C_D}$$

$$2{,}487 = 4{,}046{,}100\,C_D$$

$$\therefore C_D = 6.15 \times 10^{-4}\ \text{mol/litre}$$

$$\text{Actual No. of mols.} = \underline{6.15 \times 10^{-5}\ \text{mols}}.$$

$$\therefore C_P = \frac{8.83 - (6.15 \times 11{,}560)}{3{,}760}$$

$$= 4.57 \times 10^{-4}\ \text{mol/litre.}$$

$$\text{Actual mols.} = \underline{4.57 \times 10^{-5}\ \text{mols}}.$$

The result was checked by calculating at several wavelengths what the optical density of a solution of these concentrations would be and comparing with the measured values. As seen from Table XIII very good agreement was obtained.

The results of analysis of the gaseous and solid products for several experiments are given in Table XIV.

Table XIV

Expt.	Hydrogen mols. x 10^{-5}	Difluorenyl mols. x 10^{-5}	Bisdiphenylene ethylene mols. x 10^{-5}
5	6.9	6.15	0.27
6	4.8	4.1	0.18
7	4.9	4.1	0.3
8	5.1	4.4	0.21
9	11.7	9.64	0.49
10	12.8	10.4	0.6

The amount of hydrogen is not exactly balanced by the solids, but it is unlikely that the latter condensed out completely in the U-tube and because of lack of data on the vapour pressures of these compounds, it was not possible to calculate how much passed over into the trap, but it is very probable that the hydrogen/solid ratio = 1:1. This result can be satisfactorily explained by the following mechanism:

Fluorene ⟶ Fluorenyl radical + H (1)

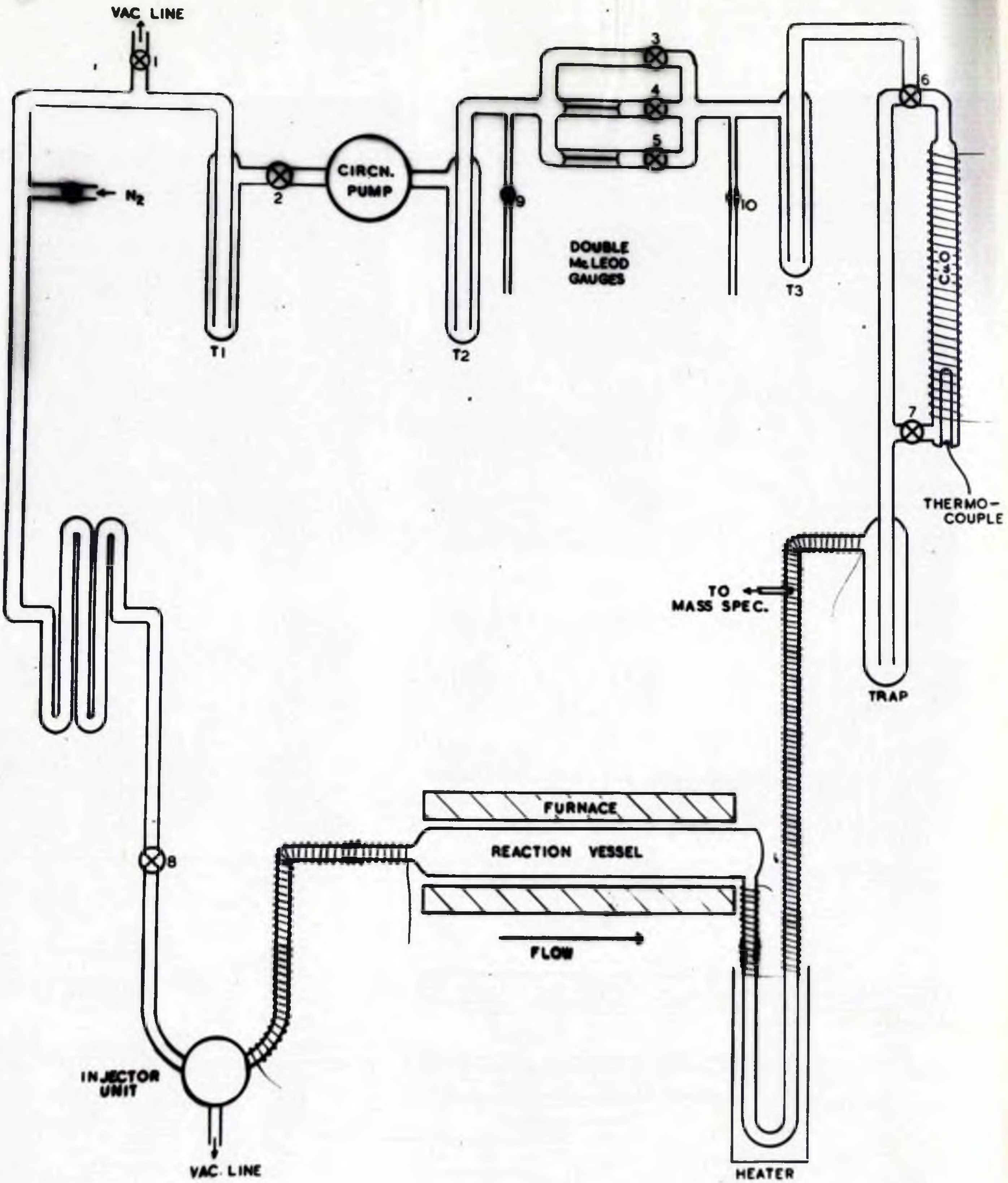
H + Fluorene ⟶ Fluorenyl radical + H_2 (2)

2 Fluorenyl radicals ⟶ Difluorenyl (3)

The primary step in the reaction is the fission of one of the C-H bonds in the methylenic group of a molecule of fluorene with the formation of a hydrogen atom and a fluorenyl radical. The hydrogen atom then attacks a second molecule of fluorene removing one of its methylenic hydrogens to form a molecule of hydrogen and a second fluorenyl radical. The radicals dimerise on leaving the furnace to form a molecule of difluorenyl. The method of formation of the bis diphenylene ethylene is not unambiguous and is discussed later, but since it represents about 5% of the total solid products, the rate of the primary dissociation can be measured by the rate of formation of hydrogen.

Several runs were carried out which indicated that the formation of hydrogen followed a first order law and was independent of surface/volume ratio.

The rate of hydrogen production was calculated from the expression:-



APPARATUS FOR FLUORENE

FIG. 8

$$k = \frac{2.303}{t} \log. \frac{100}{100 - \%\ \text{Dec.}}$$

t = time of contact $= \frac{V \times P \times 273}{\text{Mols. } N_2/\text{sec.} \times 22{,}400 \times 760 \times T}$

V = vol. of heated portion of reaction vessel.

P = average N_2 Pressure in reaction vessel.

T = temperature of the reaction vessel in degrees absolute

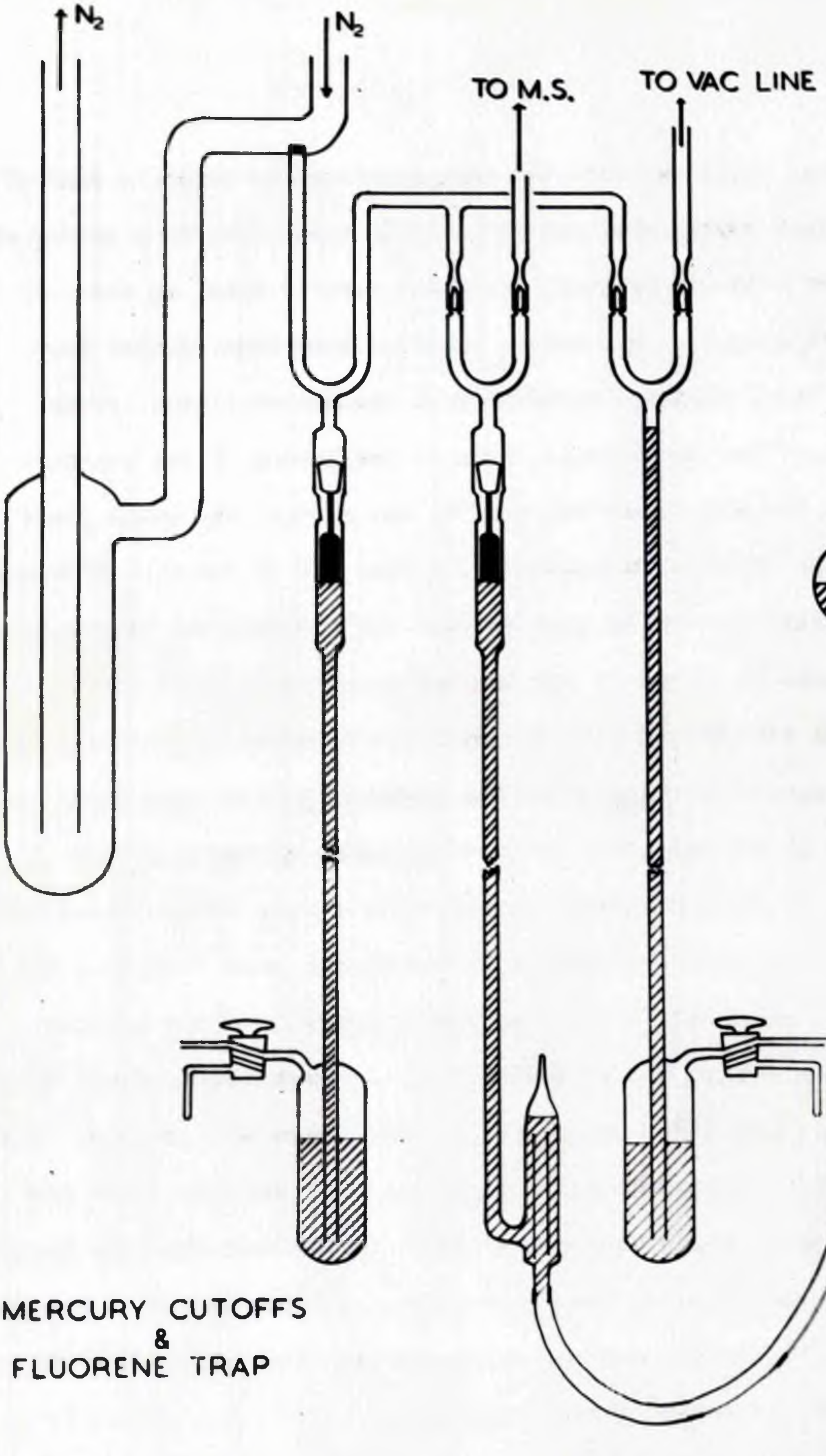
$$\%\ \text{Dec} = \frac{\text{Mols. of } H_2 \text{ formed in run} \times 100}{\text{Mols. of Fluorene passed through reaction vessel}}$$

Application of the Mass Spectrometer.

At this stage a mass spectrometer which was built in the department was completed and became available for use. Part of the work to apply it to the quantitative determination of the parent material and one of the products of thermal decomposition of fluorene was carried out in collaboration with Mr. W.F. Volume who constructed the instrument.

Inlet System and Fluorene Trap.

The flow system (fig.8) was connected via a 4 mm. thick plug of 4F metrosil through mercury cut offs to the ionisation chamber of the mass spectrometer. It had previously been found that a leak of that composition and dimensions was suitable for the pressure range, e.g. 5 - 7 mms., under which it was desired to operate. It was also shown that the rate of flow of nitrogen through the plug was proportional to the pressure difference across it.



MERCURY CUTOFFS
&
FLUORENE TRAP

FIG. 9

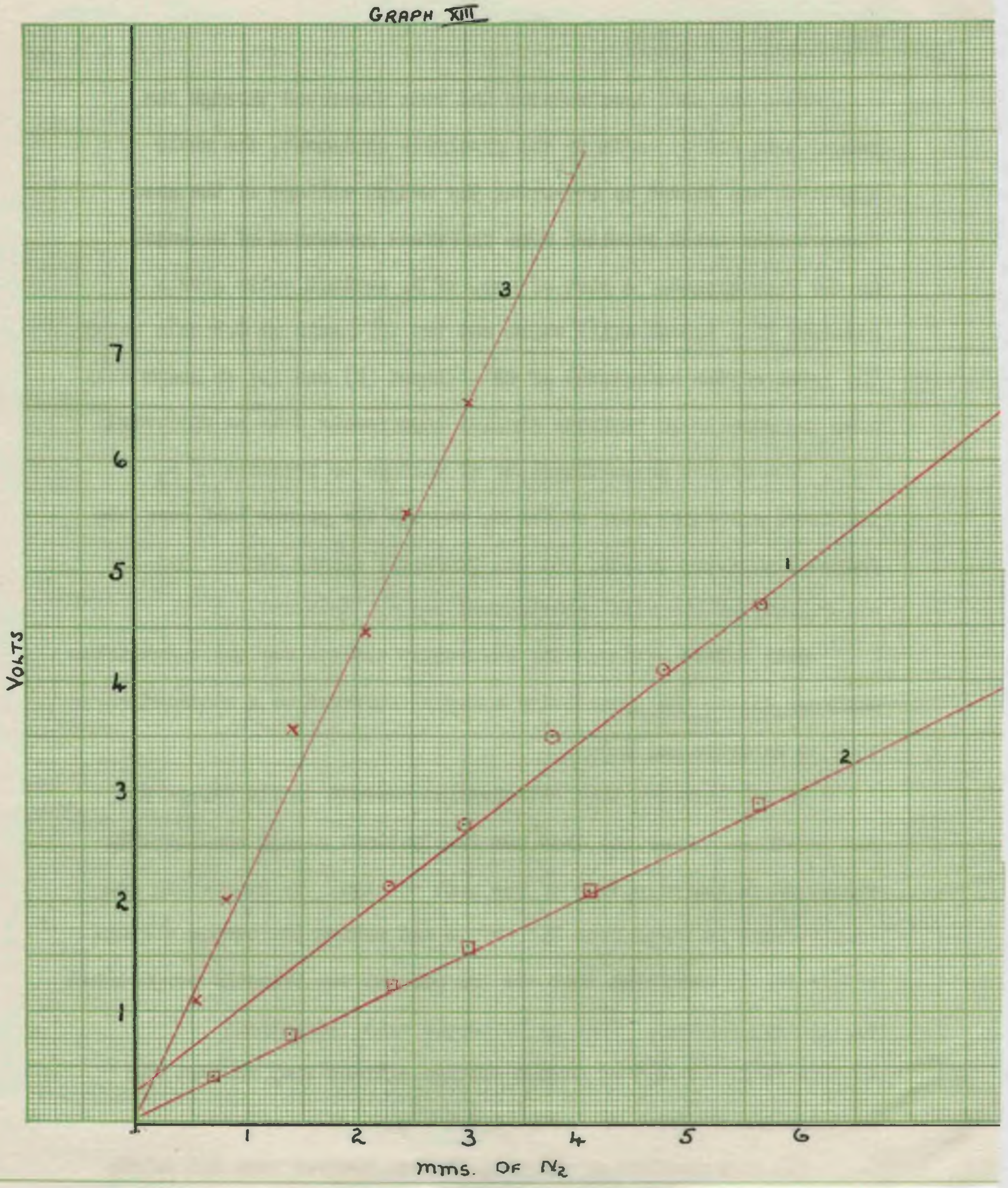
It was essential that the mass spectrometer could be shut off from the flow system when not actually in operation, so a system of mercury cut offs was devised, the final form of which is shown in the diagram (fig.9). The heater windings have been omitted for clarity. These windings extended from the metrosil leak, round each of the first two U-bends, down to the bottom of the standard sockets on the main limbs and over to the seat of the small glass float in the third of the cut-offs. Thus all of the system through which the fluorene had to pass between the metrosil and the ionisation chamber could be raised to any desired temperature. The first experiments carried out with the mass spectrometer in this work (and which are described fully under the heading "Test of Apparatus") had shown that it was essential to heat the inlet system to reduce adsorption of the hydrocarbon on the walls of the tubes. The original cut-offs had no float valves fitted but it was found that when the system was heated the fairly high vapour pressure of the mercury considerably reduced the sensitivity of the instrument. Small float valves were constructed out of B14 standard cones and sockets. The float fixed to the underside of each cone kept the valve open until all the mercury had drained out of the U-tube. Then when the mercury column was lowered below the float level, the cone became seated in the socket, completely separating the mercury from the ionisation chamber. The permanent circulating gas was freed from fluorene by passing through a large trap surrounded by a liquid air bath. The trap was made sufficiently large to remove the possibility of the condensed fluorene causing a blockage to the gas flow.

Copper Oxide Furnace.

The hydrogen formed in the reaction could be oxidised when required by adjusting taps 6 and 7 to direct the gases through the tube of copper oxide which was heated to 450°C. The original idea was that the circulating gas should always pass through the copper oxide furnace so that the H_2 would be oxidised as fast as it was formed and not be allowed to accumulate in the system. Then the percentage decomposition could have been quickly obtained by using the mass spectrometer to determine the partial pressure of fluorene and of H_2 coming from the exit of the reaction vessel. However, it was found that even by increasing the length of the copper oxide furnace to $1\frac{1}{2}$ metres and packing the oxide as tightly as was possible without impeding the flow of gas, the hydrogen was produced more rapidly than it could be oxidised. This was shown very clearly by focussing the mass spectrometer to $\frac{m}{e} = 2$ and observing the increase in the magnitude of the peak while fluorene was passing through the reaction vessel and the carrier gas and hydrogen through the copper oxide furnace. It thus became necessary to modify the proposed method of operation.

A by-pass was then fitted to the copper oxide furnace so that during a run the hydrogen would be allowed to accumulate as it was produced and the amount formed determined from the increase in the height of the $\frac{m}{e} = 2$ peak. The gases were only directed through the copper oxide furnace when it became desirable to reduce the partial pressure of hydrogen in the system.

GRAPH XIII



Test of the Apparatus.

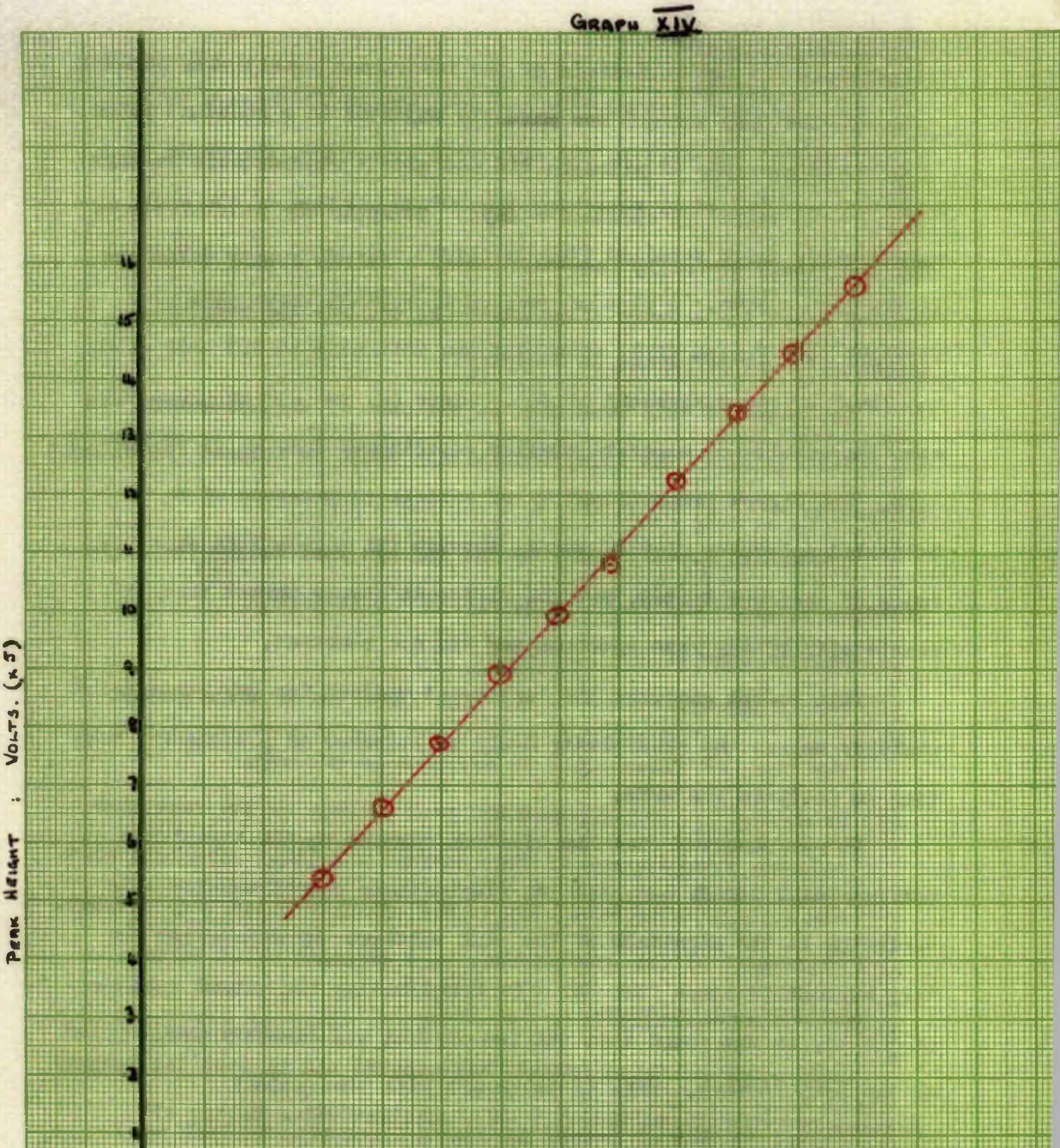
When the mass spectrometer had been connected through the porous leak and cut-offs to the pyrolysis equipment, the whole apparatus was tested by observing the output voltage of the mass spectrometer which resulted from different pressures of nitrogen in the flow system. A plot of mms. of N_2 against volts gave a straight line (graph XIII) which cut the volt axis at 0.3 this being the level of the background of 28^+. Lines (2) and (3) on graph XIII show the results of separate similar experiments done on different days. The direct proportionality of voltage to pressure of N_2 indicated molecular flow of the N_2 through the porous leak over the range of pressure tested, but the different slopes showed that the sensitivity of the mass spectrometer was not constant.

This defect rendered the instrument useless for any quantitative analyses unless the sensitivity could be referred to a standard every time an analysis was made.

It was observed that the electron current to the 'trap' was not remaining steady and that the flustuations caused considerable variation in the magnitude of the peak voltage. By decreasing the trap current in steps from 24 ⟶ 6 and noting the output voltage of $\frac{m}{e} = 28$, it was found that the ion current was directly proportional to the trap current. This is in accord with theoretical expectations. A plot of output voltage against trap current was prepared and is shown in graph XIV.

The flustuations of the trap current however were not solely

GRAPH XIV


PEAK HEIGHT : VOLTS. (x 5)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
2
4
6
8
10
12
14
16
18
20
22
24
METER READING : SCALE DIVISIONS.

responsible for the variations of the instrument sensitivity because although the trap current was manually adjusted to a constant value, a definite pressure of nitrogen did not give a reproducible voltage output when tested on successive days. Everyday the sensitivity of the instrument gradually increased until a fairly steady value was reached about 3 - 4 hours after switching on, but the eventual sensitivity was different on everyday.

The cause of this behaviour on the part of the instrument was not investigated as the irreproducibility could be allowed for without difficulty.

The day to day variation of the voltage peak height for a given nitrogen pressure was known to be due to two factors:-

(1) Fluctuations of trap current.

(2) Day to day variations in the mass spectrometer sensitivity.

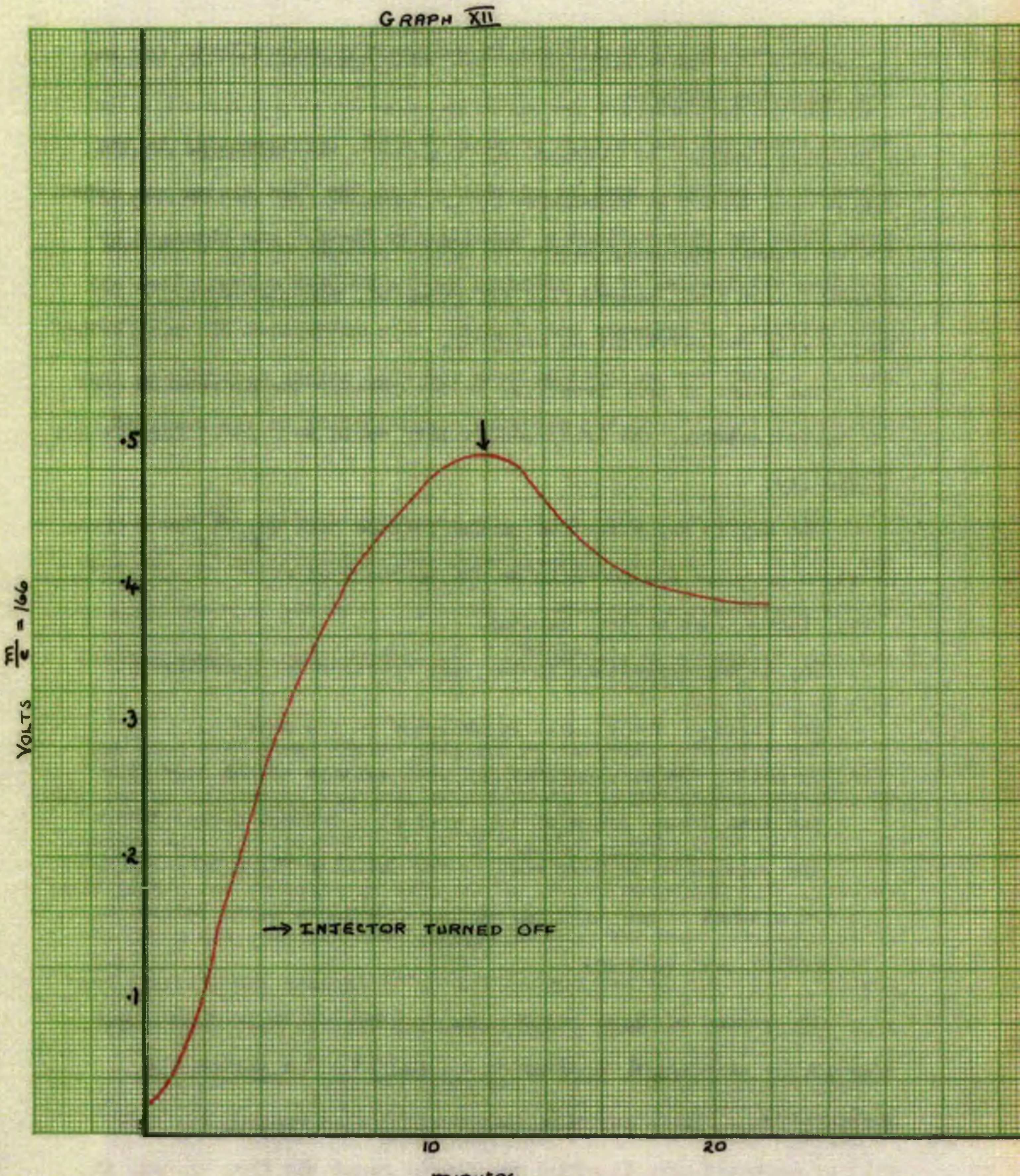
The first of these could be overcome in two ways:

(a) By noting the trap current and peak voltage at the same time and then from a graph of trap current v voltage calculate what the voltage would have been at any definite fixed trap current.

(b) Adjustment of the trap current to a definite value before noting peak voltage.

The second of these methods was adopted and in fact the trap current was maintained manually at a constant value during all operations.

GRAPH XII



The day to day variations in sensitivity were allowed for in the following manner:-

Before every run the voltage of peak $\frac{m}{e} = 28$ corresponding to the pressure of nitrogen used as carrier gas in the flow system was noted. From these two observations a "sensitivity factor" was obtained by dividing millimetres of N_2 pressure by $\frac{m}{e} = 28$ peak volts. Then all peak voltages of hydrogen and fluorene were multiplied by this factor when obtaining the calibration data and also before determining from the calibration graphs the pressure corresponding to the recorded voltage.

The first attempts to use the mass spectrometer to determine the partial pressure of fluorene were not successful as the response of the instrument to the opening and closing of the injector unit was very sluggish. A plot of $\frac{m}{e} = 166$ peak voltage is shown against time in graph XII.

The very slow decrease of the peak height could have been due to fluorene condensing out somewhere in the flow system and so maintaining a fairly high vapour pressure after the injector unit was closed. However, this was shown not to be the case by stopping the circulation of carrier gas, when the peak voltage did not decrease any more rapidly; but when the mercury was run up to isolate the metrosil and flow system from the mass spectrometer the voltage fell very rapidly. This seemed to indicate that the hydrocarbon was adsorbed in the metrosil leak. The adsorption theory would also explain the slow voltage increase when fluorene was passed round the flow system, the maximum not being reached till equilibrium was attained. To test the effect of temperature on the porous leak, a piece of 4F metrosil 4 mms. thick was sealed into the middle of a short piece of pyrex tube which was then connected between the flow and inlet systems in such a way as to bypass the leak already in position. A small electrical heating jacket was placed round the metrosil and the temperature measured by means of a thermocouple and pyrometer.

On heating the leak, there was no marked difference in the rate of increase of the $\frac{m}{e} = 166$ peak height over a range of 300°C. Thus the theory of metrosil adsorption did not appear to be valid. It was then observed that warming of the inlet tubes with a gas flame considerably speeded the response of the mass spectrometer to fluorene so the tubes were wound with nichrome tape and heated to 70°C. This did cause the output voltage for the fluorene peak to reach a maximum more quickly, but if the heaters were switched off after a maximum value had been obtained the voltage <u>rose</u> very rapidly to a much higher level before starting to fall.

Experiments with N_2 and H_2 showed that the maximum voltage recorded for a given partial pressure of gas was reduced as the inlet system was heated but rose again to the original value when cooled. In all these tests the level of the mercury in the cut-offs had been adjusted to just below the bottom of the heater windings and had not been moved during any of the experiments. Subsequent work showed that if the mercury was allowed to get even very slightly above room temperature there was complete lack of resolution and <u>loss of</u> sensitivity of the mass spectrometer.

Table XV

	1	2	3	4	5	6	7
Maximum on opening valve	3.6	3.6	3.65	3.65	3.65	3.8	3.7
After being open for 2 mins.	3.6	3.55	3.6	3.5	3.65	3.65	3.65
After being closed for 2 mins.	2.2	2.4	2.4	2.35	2.35	2.3	2.3

It was concluded that the greater rate of increase of the fluorene voltage was due to reduction of adsorption on the heated walls of the inlet systems, but the higher vapour pressure of mercury in the system as a result of the heating caused a decrease in the sensitivity of the instrument. Thus the overall effect of the heating was a quick build up of the output voltage to a much lower maximum than would have been eventually reached with a cold inlet.

Gallium has been used as a substitute for mercury in mass spectrometer cut-offs which have to be heated, but as this element was not available it became necessary to either:

(a) modify the existing cut-offs to isolate the mercury from the instrument during operation, or

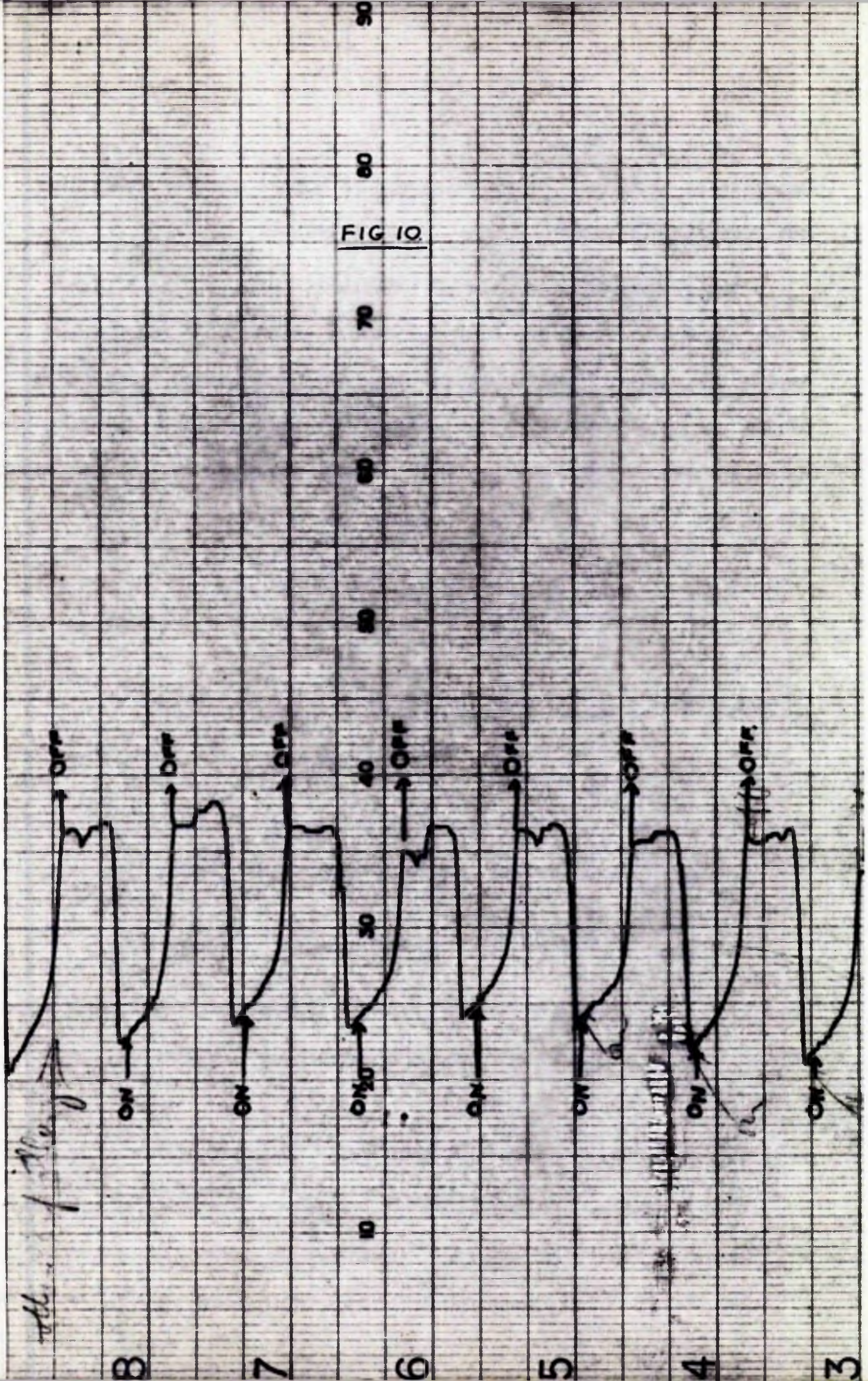
(b) devise a system of metal valves to replace the mercury cut-offs.

It was decided to try initially the first of these two alternatives so ~~that~~ the float valves as already described were made and fitted into the limbs of the cut-offs. The mercury being effectively sealed off, it was possible to operate the inlet tubes at a higher temperature without loss of sensitivity.

With the system at 100°C the voltage rose very quickly to a steady value when the injector was opened and fell only a little less rapidly when the fluorene was shut off.

Table XV shows the degree of reproducibility of the output voltage on repeatedly opening and closing the injector unit while all other experimental conditions were kept constant.

FIG 10.



90
80
70
60
50
40
30
20
10
OFF
OFF
OFF
OFF
OFF
OFF
OFF
ON
ON
ON
ON
ON
ON
ON
8
7
6
5
4
3

Opposite is shown a photographic copy of a part of the automatic pen recording from which Table XV was compiled.

The number of molecules of hydrocarbon admitted in a given time into the carrier gas depended on the pressure of hydrocarbon inside the injector unit which in turn depended on the temperature of the container bath; but the partial pressure of hydrocarbon in the N_2 stream was affected by the rate of flow and pressure of the carrier gas in the manner shown by the expression:

$$\frac{\text{mols. of } N_2/\text{sec.}}{\text{pressure of } N_2} = \frac{\text{mols. of hydrocarbon/sec.}}{\text{pressure of hydrocarbon}}$$

$$\therefore \text{Mols. of } N_2/\text{sec.} \times \text{partial pressure of hydrocarbon} = \text{Mols. of hydrocarbon/sec.} \times \text{pressure of } N_2.$$

The pressure of N_2 at the injector could be determined by means of the double McLeod gauges and was found to remain fairly steady so therefore

$$\text{Mols. } N_2/\text{sec.} \times \text{p.pressure of hydrocarbon} = \text{Constant.}$$

Thus if the voltage recorded by the mass spectrometer were proportional to the partial pressure of fluorene, the product of rate of flow of N_2 and the output voltage should be constant.

As is shown in table XVI this was found to be so.

These results indicated that the mass spectrometer was capable of determining with a fair degree of accuracy the partial pressure of fluorene in the circulating system, so it was decided to calibrate the

Table XVI

Rate of Flow mols/sec.	Voltage $\frac{m}{e} = 166$	Rate of flow x voltage
2.32×10^{-5}	8.4	1.95×10^{-4}
2.52×10^{-5}	7.65	1.93×10^{-4}
3.1×10^{-5}	6.2	1.92×10^{-4}
3.67×10^{-5}	5.25	1.92×10^{-4}

instrument for fluorene and for hydrogen and to prepare for each a pressure v voltage graph.

Calibration of Mass Spectrometer for Hydrogen.

In all work with the mass spectrometer, the $\frac{m}{e} = 28$ voltage was determined with the less sensitive grid leak in position as the 5 - 7 mms. pressure of nitrogen was outside the range of the instrument when the higher grid leak was used. All other $\frac{m}{e}$ observations were made on the more sensitive range.

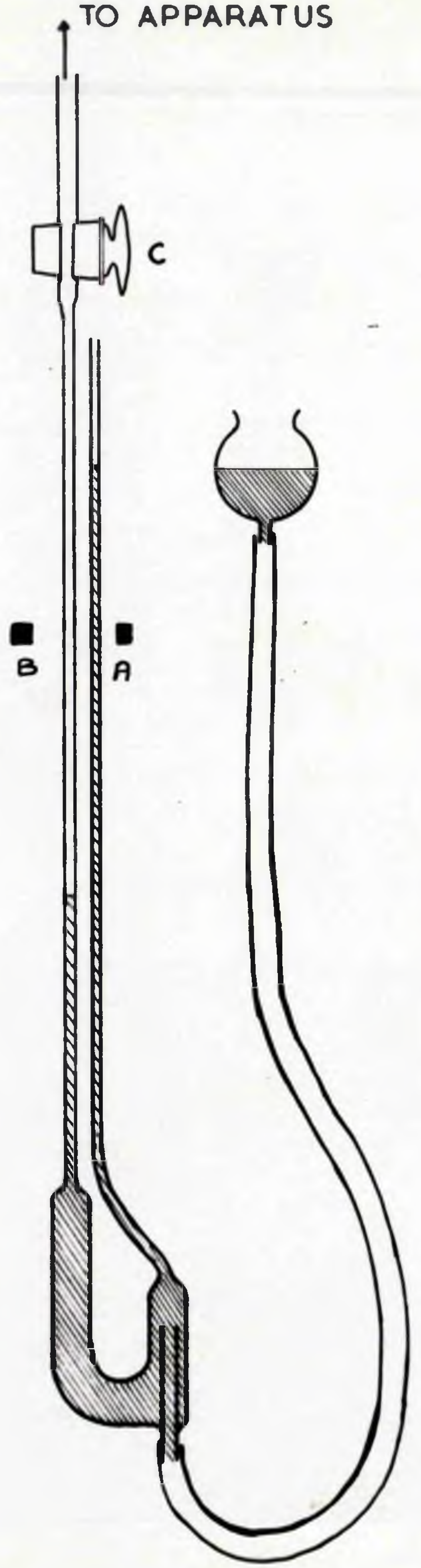
(a) Apparatus.

A gas burette, as shown in fig.11 was constructed from two pieces of glass tubing A and B of the same bore in order to annul capillary depression errors. A solid key tap was glass blown to one end of limb B which was then calibrated before it was incorporated in the burette.

Since the end of the limb next to the tap was of uneven bore, because of the glass blowing, the volume of this space was determined separately and found to be 0.66 ccs.

The data was used to prepare a graph of ccs. against cms. From the slope of the resulting straight line, it was found that 1 cc. of volume = 13.6 cms. of length of tube over the whole tube, except for the small portion adjacent to the tap.

The burette was then assembled and fitted into the apparatus between the U-tube and the metrosil leak (fig.8). A metre stick was used as a scale.



GAS BURETTE

FIG. 11

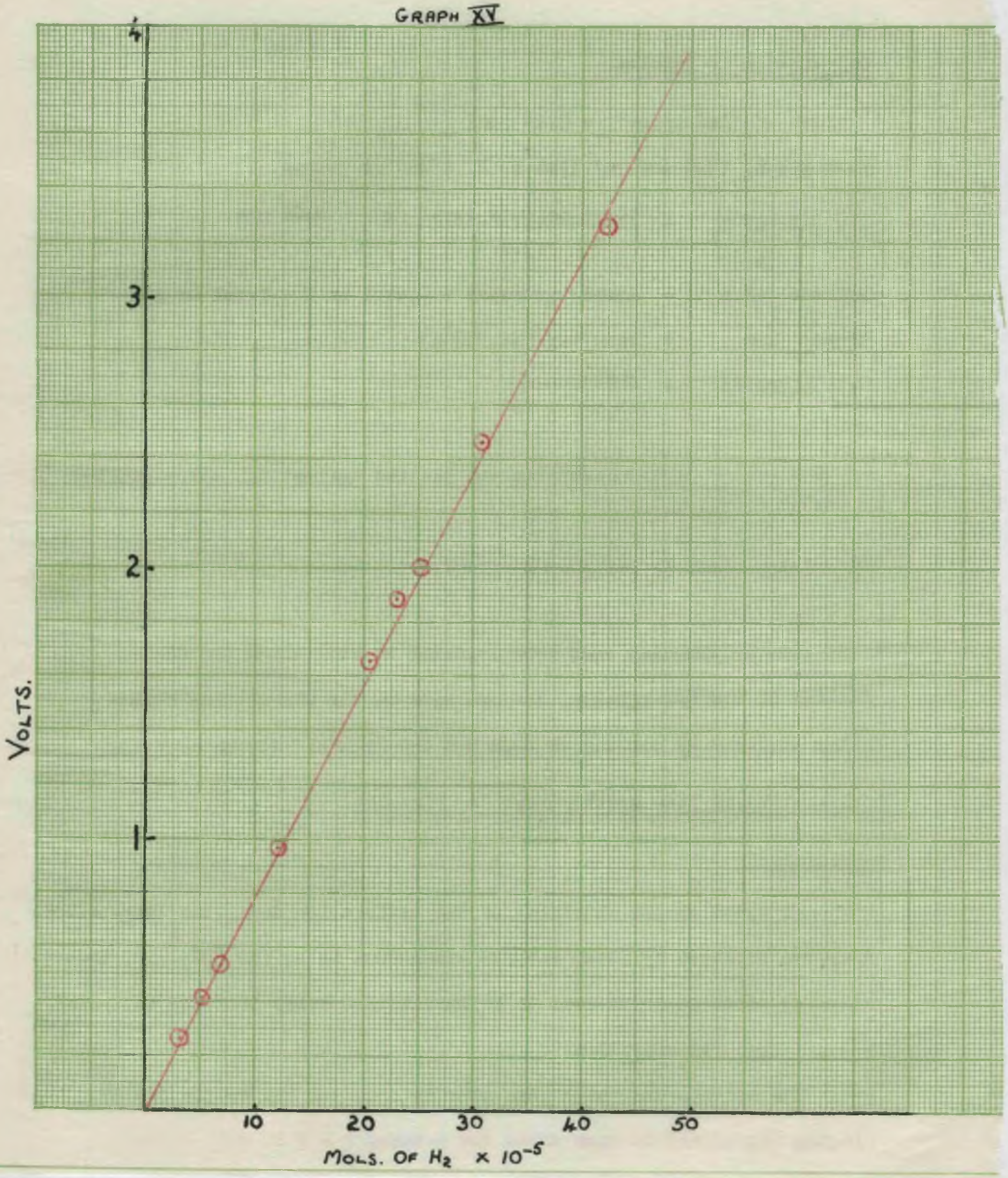
Method of Operation.

The complete apparatus was pumped out with the burette tap open and the reservoir adjusted until the mercury in tube B was just at the tap. When a good vacuum had been obtained, evacuation was stopped and hydrogen admitted from a cylinder into the apparatus until the level in B had fallen about 60 cms. Tap C was then closed and the hydrogen pumped out of the rest of the system.

About 6 mms. of nitrogen was then put into the system from the nitrogen reservoirs and the circulating pump started. The apparatus was set so that conditions were exactly the same as would exist when pyrolytic runs were being carried out, i.e. all heaters and the reaction vessel were at their operating temperature and liquid air was around all traps. The cut-offs were lowered and the nitrogen pressure and $\frac{m}{e} = 28$ voltage were noted with the trap current at 16 (arbitrary units). The mass spectrometer was then focussed to $\frac{m}{e} = 2$ and the peak height observed. This reading represented the hydrogen background.

Barometric pressure and the mercury levels in limbs A and B were recorded. The burette tap was opened very slightly to allow a small amount of hydrogen to enter the nitrogen stream. While the hydrogen was becoming thoroughly mixed in the gas stream the levels in A and B were again noted. When the mass 2 voltage was quite steady, its value was taken and immediately followed by an observation of the nitrogen pressure and voltage. The hydrogen was admitted to the gas stream in a series of small amounts and the above sequence of operations repeated after each admission.

GRAPH XV



Calculation of Results.

Volume of "end space" = 0.66 ccs.

From graph, 13.6 cms. of limb B = 1 cc. of volume.

$$\therefore \text{vol. of } H_2 = \frac{100 - \text{mercury level (B)}}{13.6} + 0.66 \text{ ccs.}$$

Pressure of H_2 = Atmos. pressure - (level in B - level in A)

Temperature = room tap (ca. 20°C)

$$\text{Mols injected} = \frac{\Delta pV}{24{,}000 \times 76}$$

$\Sigma \dfrac{\Delta pV}{24{,}000 \times 76}$ after each step was plotted against the corresponding

H_2 voltage minus H_2 background (graph XV)

The calibration runs were repeated several times for each filling of the gas burette, the hydrogen in the circulating system being oxidised by passing through the CuO furnace between each run.

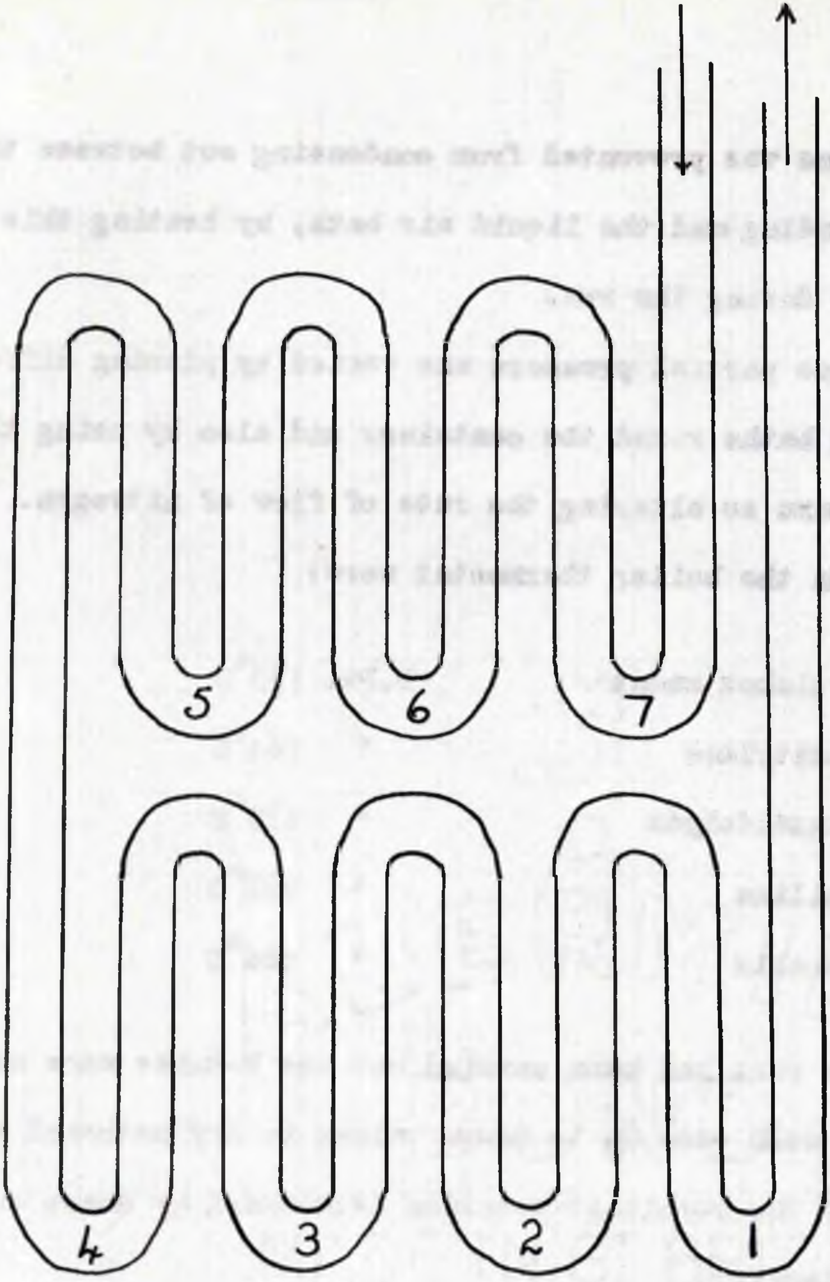
Calibration of Mass Spectrometer for Fluorene.

Apparatus.

To speed up the obtaining of the calibration data, the large single trap was replaced by seven U-tubes connection in series (fig.12), thus allowing seven separate runs to be carried out every time the equipment was prepared for operation.

The hydrocarbon which came over in each run was frozen out by placing liquid air in turn round the U-tubes 1 - 7 in that order.

Fig. 12



System Of U-Tubes Used In Calibration Of Mass Spectrometer.

The fluorene was prevented from condensing out between the end of the heater winding and the liquid air bath, by heating this portion with a gas flame during the run.

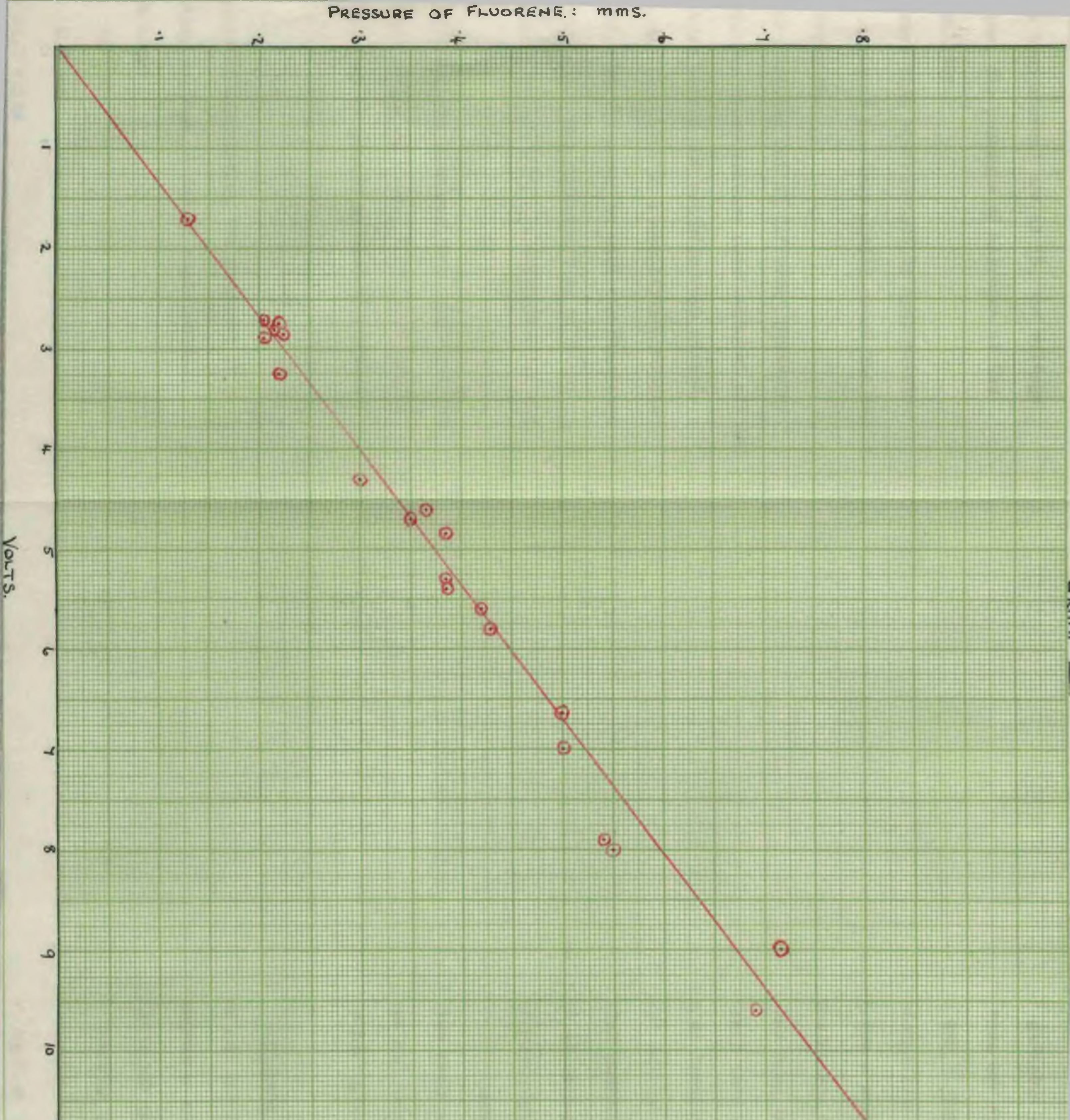
The fluorene partial pressure was varied by placing different constant boiling baths round the container and also by using the two capillaries in turn so altering the rate of flow of nitrogen. The materials used in the boiler thermostat were:

Cyclohexanone	B.Pt.	155°C
Mesitylene	"	164°C
Benzaldehyde	"	179°C
Aniline	"	182°C
Decalin	"	186°C

When seven runs had been carried out the U-tubes were cut off, the contents of each made up to known volume in dry methanol and the concentration of the resultant solution determined by means of the U.V. spectrophotometer.

Operation.

As a preliminary to a group of seven calibration runs, the apparatus (fig.8) was evacuated for at least two hours through tap 1. During this time the injector unit was heating up and also being evacuated through its connection to the vacuum line, a Dewar of liquid air being round the container to prevent the fluorene from volatilizing. When the fluorene had been outgassed the boiler containing cyclohenanone was placed round the container and heated



GRAPH XVI

until refluxing was steady. The reaction vessel and its inlet and outlet connections were heated to about 220°C. The out-offs to the mass spectrometer were then opened and its inlet system heated to 100°C.

After these operations had been completed, tap 1 was closed and about 6 mms. of nitrogen admitted to the apparatus from the storage bulbs through the tap indicated. The pressure of nitrogen was read directly on one of the double McLeod gauges.

The filament of the mass spectrometer was switched fully on and the instrument focussed to $\frac{m}{e}$ = 28 and the voltage recorded.

The circulating pump was then started up and one of the flow capillaries brought into the system by opening either of taps 4 or 5. Taps 6 and 7 were also set so that the gas would bypass the copper oxide furnace. Liquid air was placed round U-tube 1.

The mass spectrometer accelerating volts and magnet current were adjusted to bring $\frac{m}{e}$ = 166 on to the collector slit and trap current set to 16. The automatic recorder chart drive was switched on and the pen lowered on to the paper.

After ensuring that the rate of flow of nitrogen was constant the needle valve was opened to allow a stream of fluorene to be injected into the carrier gas for a period of exactly 3 minutes. During this time the trap current was maintained at a value of 16 (arbitrary units).

At the end of the run the recorder chart drive was stopped and the pen lifted from the chart. $\frac{m}{e}$ = 28 was immediately brought into focus and again ensuring the trap current was at 16, the voltage was noted and at the same time, the pressure of nitrogen at the high pressure end of the capillary.

The flow capillaries were then interchanged by appropriate adjustment of taps 4 and 5, a liquid air trap placed round the U-tube 2 and the operations repeated.

When seven runs had been carried out at different pressures of fluorene the mass spectrometer input heaters were switched off and a little time allowed to elapse before the cut offs were raised.

Air was admitted into the apparatus to atmospheric pressure and the seven U-tubes cut off. The fluorene in each was dissolved in dry MeOH and made up to 100 ccs. The concentration of each solution was determined by means of the U.V. spectrophotometer and the standard data.

The glass tubes were glass-blown into position again and the equipment prepared for another series of runs. Three such series were carried out giving a total of 21 points on the calibration graph (XVI).

Calculation of Results.

To illustrate the method of calculating the pressure of fluorene and the corresponding voltage, a set of experimental observations are dealt with here:

Trap current - 16

Nitrogen pressure - 6.8 mms.

voltage - 11.7 volts

This measures the excess of silver nitrate present. Hence calculate the amount of silver nitrate which reacted with the chloride ions present in the HCl-HNO$_3$ mixture to form silver chloride. This in turn enables the concentration of hydrochloric acid in the acid mixture to be calculated.

Then determine the total acid strength. Titrate 20 cc. of standard sodium hydroxide solution with the acid, using bromothymol blue as indicator. Hence calculate the normality of the total acid.

(Equation for the reaction between ammonium thiocyanate and silver nitrate is:-

$NH_4CNS + AgNO_3 \longrightarrow$ N [illegible] $AgCNS\downarrow$

or $CNS^- + Ag^+ \longrightarrow AgCNS\downarrow$.

$\therefore$ Sensitivity = $\frac{6.8}{11.7}$ = 0.58 mm./volt.

Recorded voltage of fluorene = 4.75 volts

Corrected voltage = 4.75 x 0.58 volts

= 2.76 volts.

McLeod recordings P_1 3.4; 3.4; 3.4 mms.

P_2 6.8; 6.8; 6.8 mms.

$P_2^2 - P_1^2$ = 46.2 - 11.6 mm^2

= 34.6 mm^2

Capillary Constant for N_2 = 2.6991×10^{-6}

$\therefore$ Rate of flow = 9.4×10^{-5} mols/sec.

Duration of run = 180 seconds.

$\therefore$ No. of mols. of N_2 flowed past the leak

= 1.69×10^{-2} mols.

No. of mols. of fluorene by U.V. spectrophotometer

= 5.2×10^{-4} mols.

Partial pressure of fluorene = $\frac{\text{Mols. of fluorene x pressure of } N_2}{\text{Mols of } N_2}$

= $\frac{5.2 \times 6.8 \times 10^{-2}}{1.69}$

= $\frac{0.352}{1.69}$ = 0.21 mms.

Voltage corresponding to $\frac{m}{e}$ = 166 peak = 2.76 volts

Partial pressure of fluorene = 0.21 mms.

The results of the 21 runs are plotted in graph XVI. This calibration graph was used in all the runs to obtain the partial pressure of fluorene from the corrected value of the recorded voltage. When the calibrations had been completed work was commenced on the investigation of the kinetics of the thermal decomposition of fluorene.

Description of a Series of Runs.

Each day before a series of runs was commenced, the apparatus was subjected to hard vacuum for several hours with the reaction vessel hot and liquid air on all traps. Meanwhile the mass spectrometer was switched on and allowed to warm up.

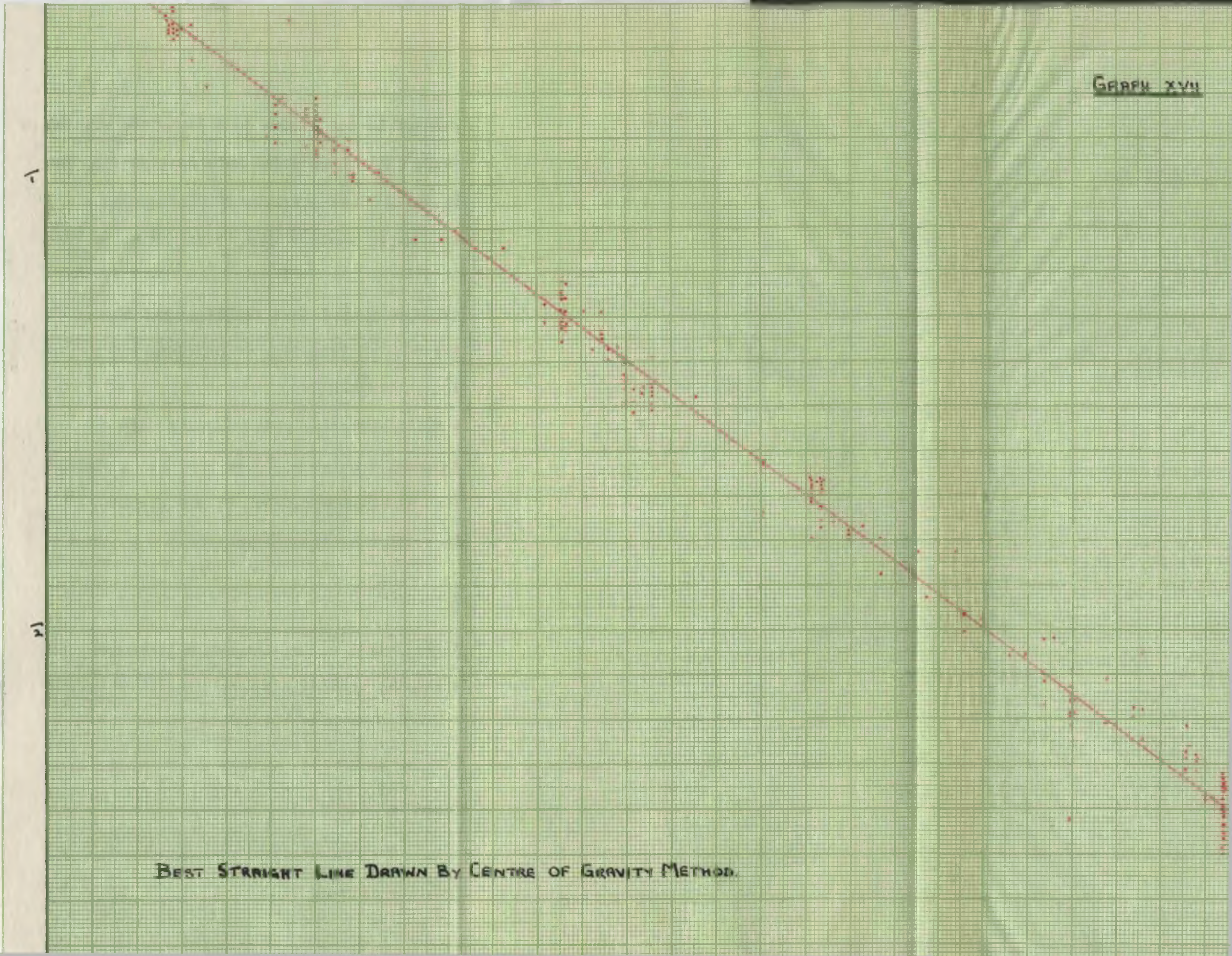
Fluorene was filled into the container which was then bolted on to the injector unit and outgassed in the manner already described. The boiler containing one of the organic materials was placed round the container and heated to reflux steadily.

Nitrogen to the required pressure was let in to the system and the circulating pump started. When the gas was circulating steadily the mass spectrometer was focussed to $\frac{m}{e} = 2$ and the voltage noted. This observation was immediately followed by recording both the height of $\frac{m}{e} = 28$ peak and the nitrogen pressure at the high pressure end of the flow capillary. From these data the sensitivity of the mass spectrometer could be determined and used to give the corrected voltage of the hydrogen peak as already described.
Peak $\frac{m}{e} = 166$ was then brought into focus, the pen lowered on to the

Table XVII

Run	Temp. $^{\circ}$K.	Time of contact secs.	Partial pressure of fluorene mms.	% Dec.	k sec.^{-1}
66	1050	0.34	0.43	1.5	0.0445
261	1050	0.38	0.13	1.8	0.0480
239	1026	0.33	0.13	0.72	0.0218
243	1026	0.68	0.58	1.7	0.0240
5	1041	0.45	0.32	1.56	0.0348
9	1041	0.1	0.3	1.4	0.0325

GRAPH XVII



BEST STRAIGHT LINE DRAWN BY CENTRE OF GRAVITY METHOD.

chart and the driving mechanism started. The needle valve was then opened to allow fluorene to be injected into the carrier gas. The time and the furnace temperature were noted.

During a run the pressure readings were taken on the double McLeods once every minute and a check kept on the value of the trap current to ensure that any variation was corrected immediately. The pressure of nitrogen at the injector was also noted and the value taken as being the pressure in the reaction vessel for purposes of calculating the time of contact.

The duration of each run depended on the temperature of the reaction vessel, being longer at low temperatures to allow a measurable amount of hydrogen to be produced. When it was desired to stop the run the needle valve was screwed in, the recorder chart drive was stopped and the pen lifted from the paper before $\frac{m}{e} = 28$ voltage and N_2 pressure was again observed. The hydrogen voltage was then noted and corrected by the use of the sensitivity factor, the increase over the previous $\frac{m}{e} = 2$ value being due to the hydrogen formed in the run.

Then one of the variables, furnace temperature, rate of flow of carrier gas or partial pressure of fluorene was adjusted to a new value and another run carried out as just described. The homogeneity of the reaction had been tested by packing the reaction vessel with silica wool to increase the surface/volume ratio by a factor of 6 in the experiments before the mass spectrometer was used. There was no increase in the first order rate constant.

By using the apparatus in the manner just described a total of 270 runs were carried out. The first order rate constant was not affected by a change in the partial pressure of fluorene by a factor of $4\frac{1}{2}$ and of the time of contact by a factor of up to 5. (Table XVII).

Thus, it was considered proved that the decomposition of fluorene measured by the rate of formation of hydrogen was a homogeneous first order gas reaction.

The variation of the first order rate constant was determined over the temperature range 943°K to 1101°K. A plot of the log velocity constant against reciprocal of the absolute temperature resulted in a straight line (graph XVII).

Calculation of Results

As an example of the method of calculation of the rate constant from the experimental results a set of results is worked out below.

Run No.238.

Temperature of furnace = 747°C

$$= 1020^{\circ}K$$

$$\therefore \frac{10^3}{T} = 0.9804$$

Flow Capillary used - Fast flow.

Capillary constant for N_2 = 5.310×10^{-6}

N_2 pressure at capillary = 7 mms.

$\frac{m}{e}$ = 28 voltage = 16.8 volts.

$\therefore$ Sensitivity = 0.416 mm/volt.

Volts of H_2 before run = 0.057

Corrected for sensitivity = 0.024 volts

Volts of H_2 after run = 0.29 volts

Corrected for sensitivity = 0.121 volts

$\therefore$ Increase in H_2 volts = 0.121 - 0.024

= 0.097 volts

From calibration graph No. of mols. = 1.28×10^{-5}

From recorder, voltage of fluorene = 4.15 volts

Corrected for sensitivity = 1.73 volts

From calibration graph pressure = 0.13 mms.

McLeod Reading 4.6; 4.5; 4.4; 4.6; 4.6; 4.5; 4.6 mms.

7; 7; 7; 7; 7; 7; 7 mms.

$\Delta p^2 = 49 - 19.9$ = 29.1

Rate of flow of gas = $29.1 \times 5.310 \times 10^{-6}$ mols/sec.

= 1.54×10^{-4} mols/sec.

Duration of run = 540 secs.

∴ No. of mols of N_2 which passed round the system

$$= 540 \times 1.54 \times 10^{-4}$$

$$= 8.35 \times 10^{-2} \text{ mols.}$$

∴ No. of mols of fluorene $= \dfrac{8.35 \times 10^{-2} \times 0.13}{7}$

$$= 1.49 \times 10^{-3} \text{ mols.}$$

∴ % Dec. $= \dfrac{1.28 \times 10^{-5} \times 10^{2}}{1.49 \times 10^{-3}} = 0.86\%.$

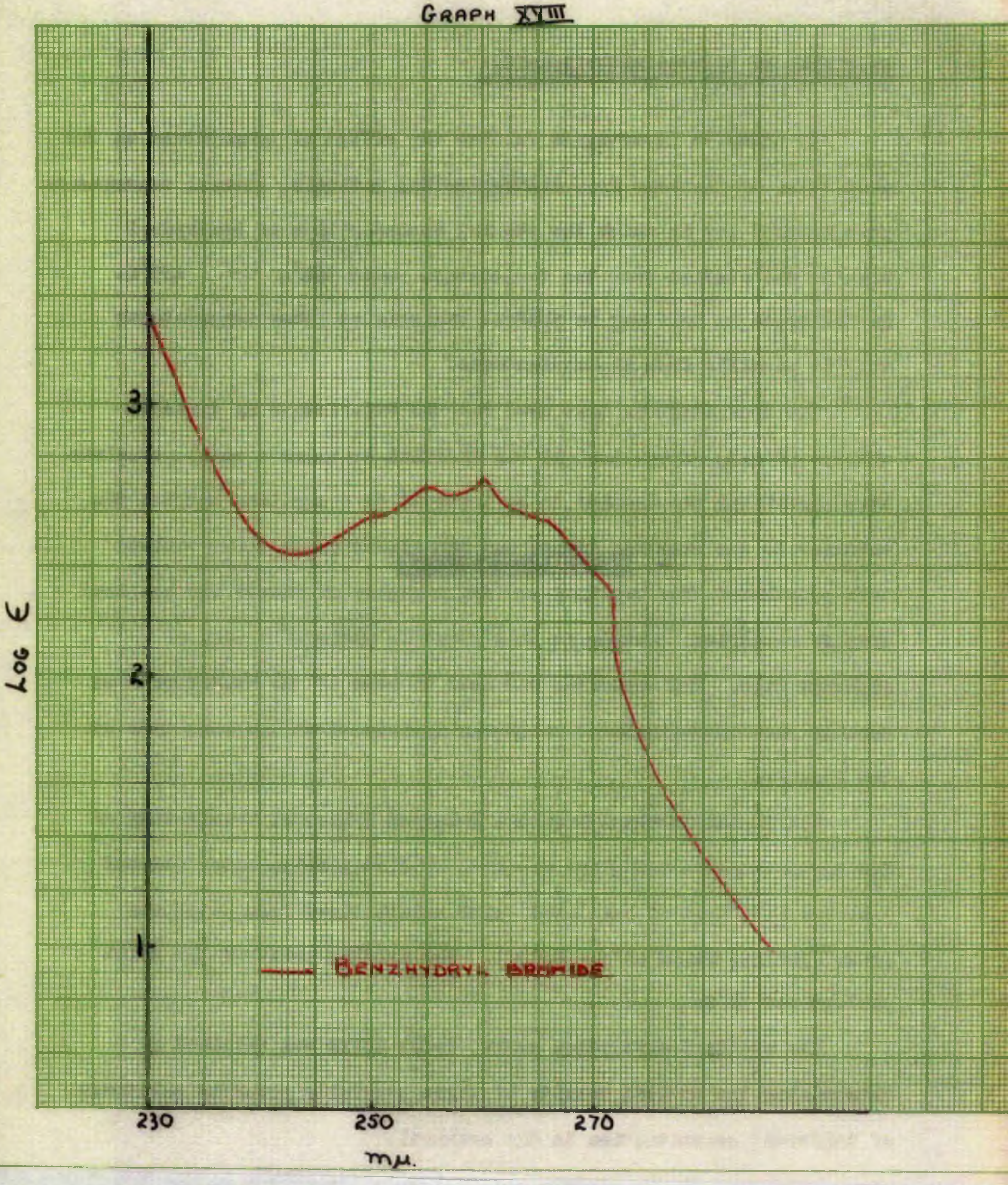
From the percentage decomposition the first order rate constant was calculated using the expression:-

$$k = \frac{2.303}{t} \log. \frac{100}{100 - \% \text{ Dec.}}$$

Tables of all the experimental results are given after the Appendix.

3. DIPHENYLBROMOMETHANE

GRAPH XVIII



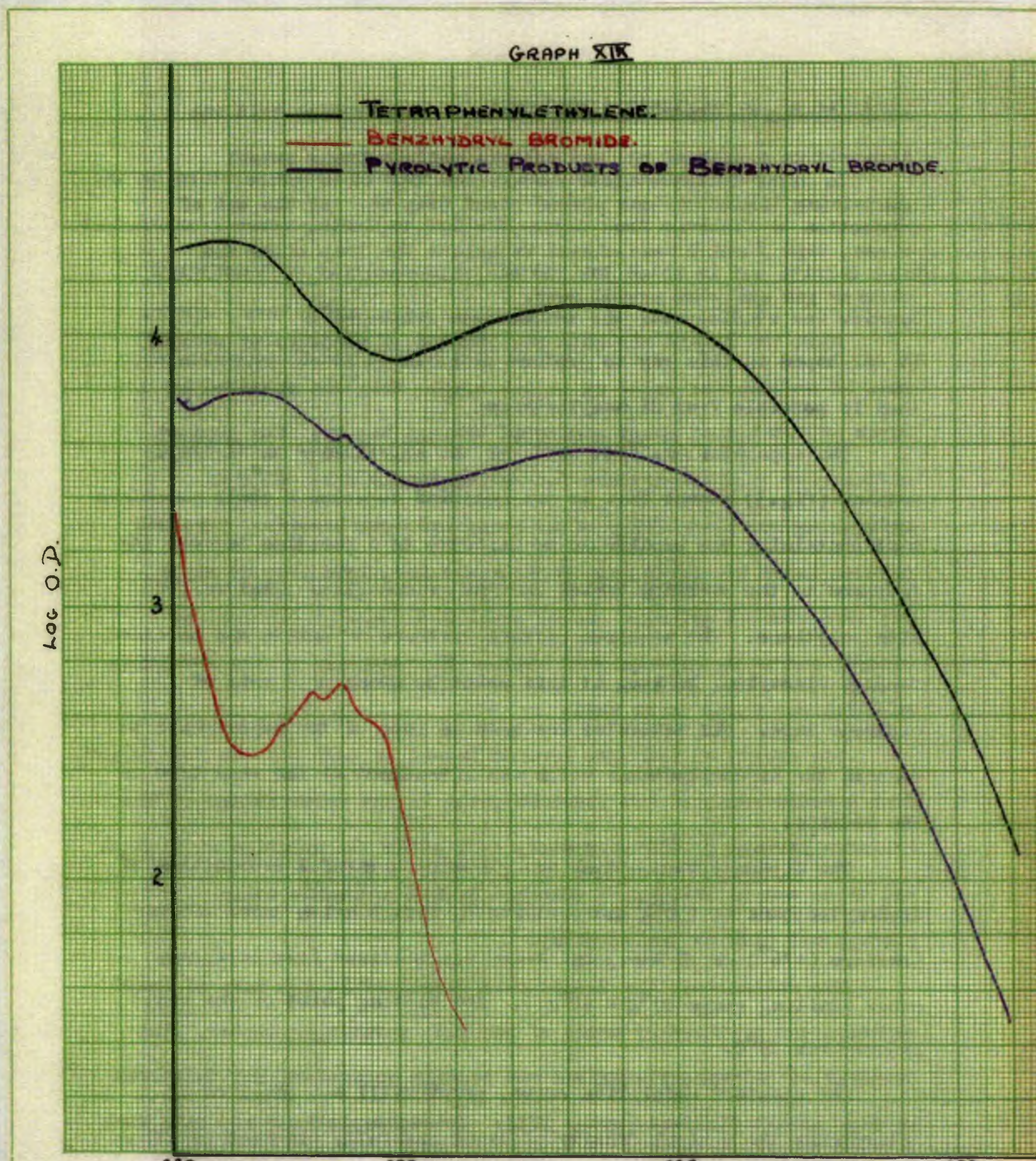
Pyrolysis of Diphenylmethylbromide.

In order to investigate further the effect of temperature on the production of fluorene from diphenylmethyl radicals, several experiments were carried out in which the thermal decomposition of benzhydryl bromide was studied over the temperature range 368°C ⟶ 435°C. It was hoped in this way to produce radicals at lower temperatures than is possible from diphenylmethane.

The apparatus was that used for the experiments on diphenylmethane (fig.3) except that it was modified to allow a small porcelain boat containing the bromide to be inserted to a position between the entrance to the reaction vessel and the ground glass joint sealed with polythene. The required partial pressure of halide was obtained through electrical heating at this point by means of a coil of nichrome tape. The saturator was used in some of the experiments to contain the diphenylmethane which was introduced at the same time as the bromide.

The diphenylbromomethane was prepared by careful bromination of diphenylmethane at 150°C and purified by distillation under reduced pressure (176°C at 10 mm.) and twice crystallised from petroleum ether (Boiling range 40°C - 60°C). The melting point of the solid product was 39°C.

The standard absorption curve, graph XVIII was obtained by determining the optical density of three carefully prepared solutions of different concentration in dry methanol.


GRAPH XIX
TETRAPHENYLETHYLENE.
BENZHYDRYL BROMIDE.
PYROLYTIC PRODUCTS OF BENZHYDRYL BROMIDE.
LOG O.D.
4
3
2
230
280
330
380
mμ

During an experiment the U-tube at the furnace exit was immersed in a bath of CO_2 and acetone while a Dewar vessel containing liquid air was placed round trap T1. At the end of a run, taps 3 and 9 were closed to isolate the trap after the carrier gas had been pumped away.

When the liquid air bath was removed, a pressure of several mms. of mercury was built up in the trap. This was measured by means of the McLeod gauge connected through tap 19. The product giving rise to this pressure was not condensible at -80°C so indicating the possibility of it being hydrogen bromide. This was substantiated by refreezing, with liquid air, into trap T1 which was then removed and kept cooled until a mixture of 100 ccs. of ethanol and water were quickly added. The reaction of the resulting solution was found to be acid.

The amount of hydrogen bromide formed in each run was determined from a measurement of the pressure given in the known volume of the isolated portion of the apparatus; as a check the solution in alcohol and water was titrated with standard sodium hydroxide using bromophenol blue as an indicator.

The solids from the U-tube were dissolved in 250 ccs. of dried methanol and examined by means of the U.V. spectrophotometer. The presence of tetraphenylethylene was readily recognised but there was no sign of any fluorene (graph XIX). Tetraphenylethane may have been present but would have been masked by the more strongly absorbing tetraphenylethylene.

Table XVIII

Run	Temp. °C	H.Br. mols x 10^{-4}	Tetraphenyl ethylene mols x 10^{-4}	Benzhydryl bromide mols x 10^{-4}	k. to H.Br. $sec.^{-1}$	k. to Tetraphenyl ethylene $sec.^{-1}$
1	435	36.2	15.3	12.5	0.352	0.138
2	328	2.3	0.87	15.9	0.017	0.006
3	368	3.9	1.46	14.5	0.0366	0.014
4	368	5.5	1.55	16.7	0.0477	0.012
5	368	1.43	0.39	7.2	0.028	0.0078
6	368	very little	0.48	9.0	-	0.0072
7	368	3.2	1.1	11	0.042	0.0138
8	369	1.9	0.54	10.1	0.026	0.0082
9	368	1.6	0.29	6.3	0.039	0.0075
10	368	very little	0.28	6.4	-	0.0049
11	435	12.7	2.8	6.6	0.362	0.0734

In runs 5, 6, 8, 9, 10 and 11, diphenylmethane was introduced to the reaction vessel simultaneously with the benzhydryl bromide.

In one of the experiments (run 11) with added diphenylmethane, tetraphenylethane was definitely shown to be present by reducing the volume of the solution of the products, after U.V. examination, and filtering off the first crystals to be deposited on cooling. These were examined spectrophotometrically and found to be a mixture of tetraphenylethane and tetraphenylethylene, present in the ratio 4:1.

Unfortunately, this was not done for those experiments without diphenylmethane so the formation of tetraphenylethane under this condition cannot be completely discounted.

The data obtained were analysed on a first order basis, assuming firstly that tetraphenylethylene and secondly that hydrogen bromide was a measure of the initially formed radicals (Table XVIII). Although it appeared that the formation of tetraphenylethane was considerably reduced by the addition of diphenylmethane, while the hydrogen bromide was affected to a much less degree, the results were not very consistent and lack of time prevented a full investigation from being made.

The results will be discussed in a later section in conjunction with the other experimental data.

DISCUSSION

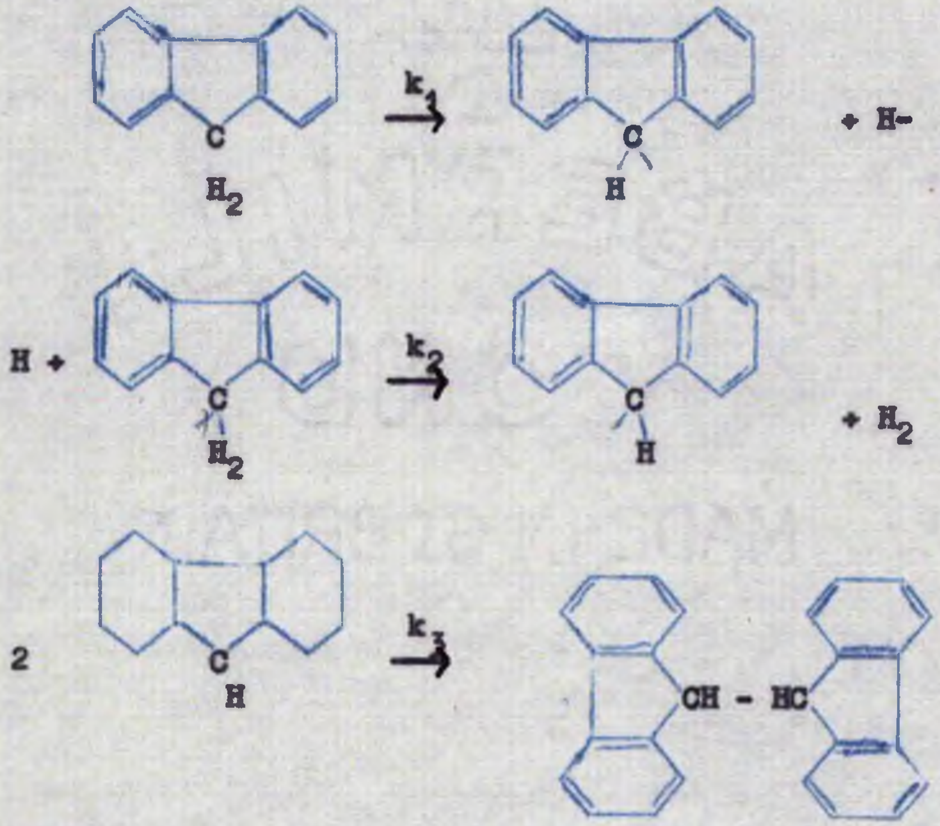
As stated in the 'Introduction', the original purpose of this work was an investigation of the pyrolysis of diphenylmethane to establish first of all the decomposition mechanism and then to study the reaction kinetics under conditions which might lead to the determination of the energy of activation with a view to attributing this quantity to the dissociation energy of that bond which underwent initial rupture.

The experimental work began with the pyrolysis of diphenylmethane. As fluorene and tetraphenylethane were found to be produced it was felt that the decomposition proceeded by formation of a benzhydryl radical and hydrogen atom. It was clearly necessary to have some idea of the thermal stability of fluorene and tetraphenylethane and since the former provided the most clear cut case from the kinetic point of view, it is proposed to take its discussion first, although chronologically the experiments were not done in this order.

Pyrolysis of Fluorene.

The main products of the fluorene decomposition were hydrogen and difluorenyl in equimolecular amounts. Bisdiphenylene ethylene was also formed in the reaction but in amounts so much less than the two main products that it could be safely ignored without affecting the value of the first order velocity constant calculated on the basis of hydrogen produced.

Unlike the diphenylmethyl radicals, the fluorenyl radicals have no alternative to dimerising and the formation of equal amounts of hydrogen and difluorenyl indicates the absence of any other complicating factor in the reaction which can therefore be represented by the scheme.



(1)

(2)

(3)

From this:

$$\frac{d\,[H_2]}{dt} = k_2\,[H]\,[FH]$$

$$\frac{d\,[H]}{dt} = k_1\,[FH] - k_2\,[H]\,[FH]$$

Assuming a steady state is reached, i.e. infinitesimal concentration of hydrogen is ~~ever~~ built up:

$$\frac{d\,[H]}{dt} = 0$$

$$\therefore \quad \frac{d\,[H_2]}{dt} = k_1\,[FH] = -\frac{d\,[FH]}{dt}$$

i.e. the rate of decomposition of fluorene is proportional to the first power of its concentration. Using the production of hydrogen as a measure of the free radicals formed in the initial step, the first order velocity constant of the reaction was calculated.

The results obtained can be expressed by the equation:

$$k = 10^{12.9} \quad e^{\frac{-68,500}{RT}}$$

The energy of activation of the reaction, - 68.5 k.cals is considered to be the dissociation energy of the methylenic C-H bond in fluorene. The value of $10^{12.9}$ for the pre-exponential term is in excellent agreement with the figure expected from theoretical considerations and supports the other experimental evidence that the thermal decomposition of fluorene is a unimolecular process.

Application of the Mass Spectrometer.

In view of the simplicity of the kinetics of the decomposition of fluorene it was regarded as being a particularly suitable substance to study in assessing the possibility and practicability of using a mass spectrometer as a continuous analytical instrument in this type of investigation.

The principle and the practice of the method adopted have been fully described in an earlier section (The Present Investigation: Fluorene) so it is only necessary to consider now to what extent the method has been successful.

The most obvious advantage was the great rapidity with which experiments could be carried out. Although the low vapour pressure of fluorene caused considerable initial experimental difficulties, when these had been overcome and the apparatus calibrated it was found to be possible to complete 250 separate runs in fourteen days. This is roughly equivalent to one years work using any other analytical method which could have been applied to this investigation. It is acknowledged that the individual results obtained by alternative methods would probably have been subject to less experimental error but the very large number of experiments more than counter the possible lower accuracy of each individual velocity constant calculated from the data obtained by the use of the mass spectrometer.

It was also possible to carry out the whole series of experiments without letting air into the flow system, except for two occasions when leaks developed. This prevented oxygen which may have been adsorbed on the apparatus walls and in the tap grease from affecting the experimental results.

Support for the soundness of the method can be derived from the fact that the theoretically predicted value of 10^{13} was obtained for the probability factor of a reaction which from other tests was known to be unimolecular.

This technique with refinements and slight modification is capable of application to a wide number of varied studies where it is necessary to have information concerning reactions occurring in the gas phase within an enclosed system.

The Methylenic C-H Bond in Fluorene.

Discussion of the conformity of the value of 68.5 k.cals to what may be expected for the dissociation energy must be very limited because of the little work which has been done on fluorene or its derivatives. Such work as has been carried out has chiefly been concerned with the relative reactivity of hydrocarbons towards free radicals. These investigations do show that in the series toluene, diphenylmethane, triphenylmethane, fluorene, we may expect a decreasing methylenic C-H bond dissociation energy but it is not possible to determine the exact relative magnitude of each.

In a study of the efficiency of several different hydrocarbons as chain transfer agents in the polymerisation of styrene, Gregg and Mayo[90] found that toluene, diphenylmethane, triphenylmethane and fluorene showed an increasing activity in chain transfer. They also pointed out that the acidities of these hydrocarbons determined by Conant and Wheland[91] and by McEwen[92] are in the same order as the transfer constants.

More recently, Kooyman[93] in an investigation of the reactivity of α methylenic groups towards active free radicals has observed once again the same order of reactivity towards free radicals in the series:-

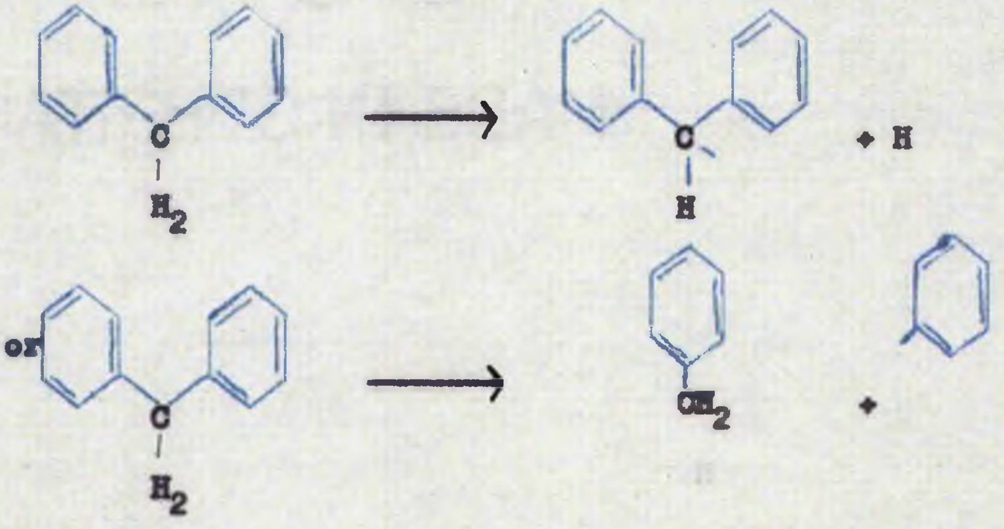
Toluene, Diphenylmethane, Triphenylmethane, Fluorene.

Although Wheland[94] has calculated the resonance energies of several phenyl substituted ethanes, the results obtained are not of much value in this instance as he assumed coplanarity for triphenylmethyl and so derived a much enhanced stability for it, compared with say the benzyl radical[95].

The above considerations are of no help in deciding the accuracy of the value 68.5 k.cals for the C-H dissociation energy in fluorene but they do indicate that it is at least in the correct order of magnitude.

Pyrolysis of Diphenylmethane.

Before proceeding to a discussion of the results obtained it is of interest to consider briefly, from the experimental evidence available at the onset of this work, which of the obvious possible primary reactions would be more likely to occur i.e.



(1)

(2)

Taking these in turn:

(1) M. Szwarc[31] has derived a value of 77.5 k.cals/gm. mol. for the dissociation energy of a C-H bond in the methyl group of toluene,

so it would be anticipated in view of the greater resonance possibilities of the benzhydryl radical that the dissociation energy of a C-H bond in the methylenic group of diphenylmethane would be less than 77.5 k.cals.

A.Pullman[96] has deduced by the method of molecular diagrams[97] that there is a steady decrease in the free valence number of the methyl group on the addition of a new phenyl group in the series:- Phenylmethyl, Diphenylmethyl, Triphenylmethyl. Calculated resonance energies of these radicals by the methods of Molecular Orbitals and of Valence Bonds are also in that order[98].

In a study of the photobromination of phenylmethanes, Magee and Daniels[99] found that the lengths of the chains were 50 for toluene, 250 for diphenylmethane and 1000 for triphenylmethane. It is probable that the chains are ended by the dimerisation of the radicals and thus a shorter chain implies lower radical stability.

These three examples chosen from the work which has been carried out on the phenylmethanes indicate that the C-H bond dissociation energy in diphenylmethane should be intermediate to that in toluene and in triphenylmethane.

Unfortunately, no study has been made of the thermal decomposition of triphenylmethane in the gas phase but Zeigler[100] and his colleagues have amassed a large amount of data on the energy of activation of the dissociation of hexaphenylethane in solution. From their results the dissociation energy of the Ph_3C-H bond in triphenylmethane has been calculated at about 75 k.cals[1]. In view of the very different experimental conditions however, and some discrepancies between E_{Act} and ΔH for the dissociation of hexaphenylethane, it seems reasonable to require further data directly on the Ph_3C-H bond. It was therefore considered likely that the probable value of the Ph_2C-H bond dissociation energy would be less than 77.5 k.cals but that the grounds for limiting it between 77.5 k.cals and 75 k.cals were not strong.

(2) Regarding the second of the possible primary reactions, J.S. Roberts and H.A. Skinner[101] have calculated from thermochemical and kinetic data that the dissociation energy of the $Ph - CH_2Ph$ bond in diphenylmethane is 74 k.cals.

The equation used in their calculations was that introduced by Polanyi[34] and is in its general form.

$$D(R-X) = Qf(RX) - Qf(R) - Qf(X)$$

where Qf is the heat of formation. By inserting in this expression values for the heats of formation of RX, R- and X-, the dissociation energy of R-X can be calculated. The accuracy of the result depends of course on the accuracy of the inserted heat of formation values. It is on this point that calculations involving a knowledge of the heat of formation of the phenyl radical are weakest because of the very great uncertainty regarding the actual magnitude of this quantity.

The value employed by Roberts and Skinner was that of -69.8 k.cals calculated by Laidler[102] based on the experimental work of Taylor[103]. C.B. Cowan[104] however quotes seven different literature values which when considered in conjunction with his figure of

Table XIX.

Qf (Ph-)	-60.2	-63.9	-65.5	-66.4	-70.1	-71.7	-78.6	k.cals/mol.
D(Ph-CH$_2$Ph)	64.5	68.2	69.8	70.7	74.4	76	82.9	k.cals/mol.

61 k.cals for the C-I dissociation energy in phenyl iodide give that number of possible values for the heat of formation of the phenyl radical.

These are reproduced along with the corresponding calculated Ph-CH_2Ph bond dissociation energy in diphenylmethane. (Table XIX)

The very great variation in the derived heats of formation of the phenyl radical is due to the uncertainty involved in the experimental measurements of heats of combustion of organic halides. Unfortunately other suitable D(Ph-x) values are not available but it was realised that if the thermal decomposition of diphenylmethane proceeded by the initial rupture of the Ph-CH_2Ph bond, the determination of its dissociation energy would give a heat of formation of the phenyl radical. This route would not require organic halide combustion data but would employ the more accurate data on the heat of combustion of diphenylmethane.

Consideration of these possible primary reaction steps has revealed that the dissociation energy of the C-H bond should have some value less than 77.5 k.cals while that of the C-C bond may be expected to be between 64.5 and 82.9 k.cals. If both happened to be of comparable magnitude, then the two reactions would occur simultaneously and at similar rates assuming the temperature independent factors to be the same. It is perhaps worthy of note that the pyrolysis of dibenzyl[33] has the anticipated low value of E for the central C-C bond but the temperature independent factor is 10^9 instead of 10^{13}. Such discrepancies, at present unexplained, can invalidate arguments based on dissociation energy values only.

Even if both reactions did occur it would still be possible to determine the energy of activation of each since the products of the two reactions are different. It was obvious however that the kinetic study would have to be preceded by a complete investigation of all the products so that the nature of the primary reaction (s) could be determined.

Since all the possible products(with the exception of hydrogen) are hydrocarbons, some of them involatile, there was a limited number of methods suitable for such an investigation. Fortunately an ultra-violet spectrophotometer was available and was used to examine the solutions of the hydrocarbons which condensed out in each experiment. This technique has serious limitations in this application for reasons which will be discussed in a later paragraph.

Experimental Results.

The products which resulted from the pyrolysis of diphenylmethane under the experimental conditions employed, were tetraphenylethane, fluorene, hydrogen and a comparatively small amount of tetraphenylethylene. Very little benzene and toluene were detected showing that the C-C bond was not decomposing to any great extent and hence, on the basis of Cowans value of 61 k.cals for the C-I bond dissociation energy in phenyl iodide, only the two highest quoted (Table XIX) heats of formation of the phenyl radical are in accord with these experimental results.

It has already been pointed out in this thesis (Kinetic Data Diphenylmethane) that the production of tetraphenylethane suggests the intermediate formation of a benzhydryl radical by

$$Ph_2CH_2 \longrightarrow Ph_2CH- + H \qquad (1)$$

If it is assumed for the moment that the fluorene formation follows (1) it is merely necessary to allow for the hydrogen produced by

$$2Ph_2CH- \longrightarrow 2 \text{ fluorene} + H_2$$

and calculate the first order velocity constant k_1 for the primary step (1).

The constants calculated in this way were found to be independent of time, partial pressure of diphenylmethane and the surface/volume ratio in the reaction vessel. The energy of activation and the temperature independent factor computed from the slope of the plot of log.velocity constant against the reciprocal of the absolute temperature (graph IX) had the values:

$$E_A = 71.9 \pm 1.6 \text{ k.cals/mol. and } A = 3.7 \times 10^{13}$$

In the rest of the discussion E_A is rounded off to 72 k.cals.

As in the case of fluorene, very little work has been done on diphenylmethane which can be used to check the E_A value of 72 k.cals. From a consideration however, of the reactivity of diphenylmethane as a chain transfer agent in polymerisation reactions, etc. (see section 'The methylenic C-H bond in fluorene' page 116) it would be expected that its Ph_2CH-H bond dissociation energy would have a value somewhere between that of toluene and of fluorene. This was found to be so.

The pre-exponential factor of 3.7×10^{13} is in very good agreement with the theoretically predicted value for uni-molecular decompositions and hence gives considerable support to the accuracy of this method of treating the experimental data.

This treatment, while it gives reasonable results does not go into the fine detail of the reaction and how in particular fluorene arises. On this last point the ground is more debatable. However reasonable the conclusions reached by the above technique of computing the energy of activation and pre-exponential factor may be, they are overthrown if the benzhydryl radical does not serve as an intermediate in the formation of fluorene.

In this connection the two main possible routes,

(1) Formation of fluorene direct from diphenylmethane molecule,

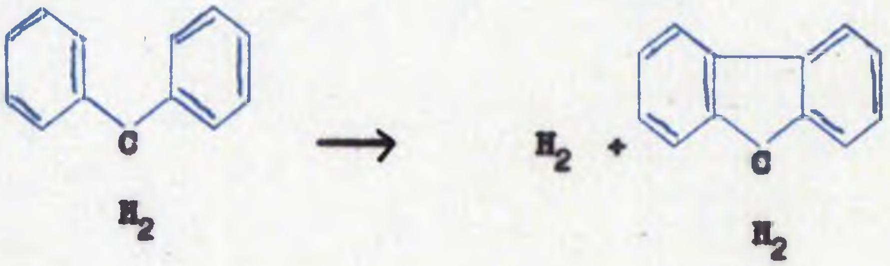
(2) Formation of fluorene from benzhydryl radical,

will therefore now be considered in turn.

(1) <u>Formation of Fluorene from Diphenylmethane Molecule</u>.

The production of fluorene by thermal decomposition of diphenylmethane was reported by Graebe[71] many years before the recognition of the existence of free radicals and the part played by them in chemical reactions, the mechanism proposed by him to explain his results did not include the intermediate formation of these entities. Instead, he suggested that the fluorene was formed directly from the diphenylmethane molecule and that some of the hydrogen thus produced reduced other diphenylmethane molecules to benzene and toluene which were also among the products he isolated.

If Graebe's reaction is correct, the primary step in the pyrolysis of diphenylmethane is neither of those considered in the opening paragraphs of this section, but is



(4)

(The system of numbering equations from here on is the same as far as possible as that used in the experimental section dealing with diphenylmethane).

The endothermicity of reaction (4) calculated from the known heats of formation of fluorene and diphenylmethane is 4.3 k.cals (see appendix). This endothermicity can be regarded as the energy difference between the bonds made and those ruptured in the overall reaction.

i.e. Bonds broken = 2 C-H ortho bonds of diphenylmethane

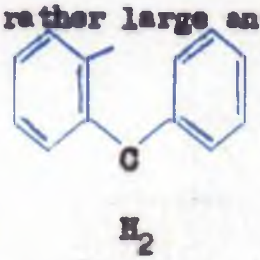
Bonds made = 1 C-C bond between ortho positions and
1 H-H bond in H_2 (102 k.cals)

$\therefore$ 2(C-H)- 1(C-C) = 97.7 k.cals.

The dissociation energy of the C-C bond formed between the two phenyl groups in this reaction may be of the same order of magnitude as the bond between the two groups in diphenyl i.e., in the most probable range of values for the latter, 110-116 k.cals. This would lead to a value of between 104 and 107 k.cals for the dissociation energy of the ortho C-H bond in question, which is very much greater than the highest value possible for the methylenic C-H bond in diphenylmethane. On these grounds alone it is very unlikely that this first step in the decomposition will be the rupture of an ortho C-H bond.

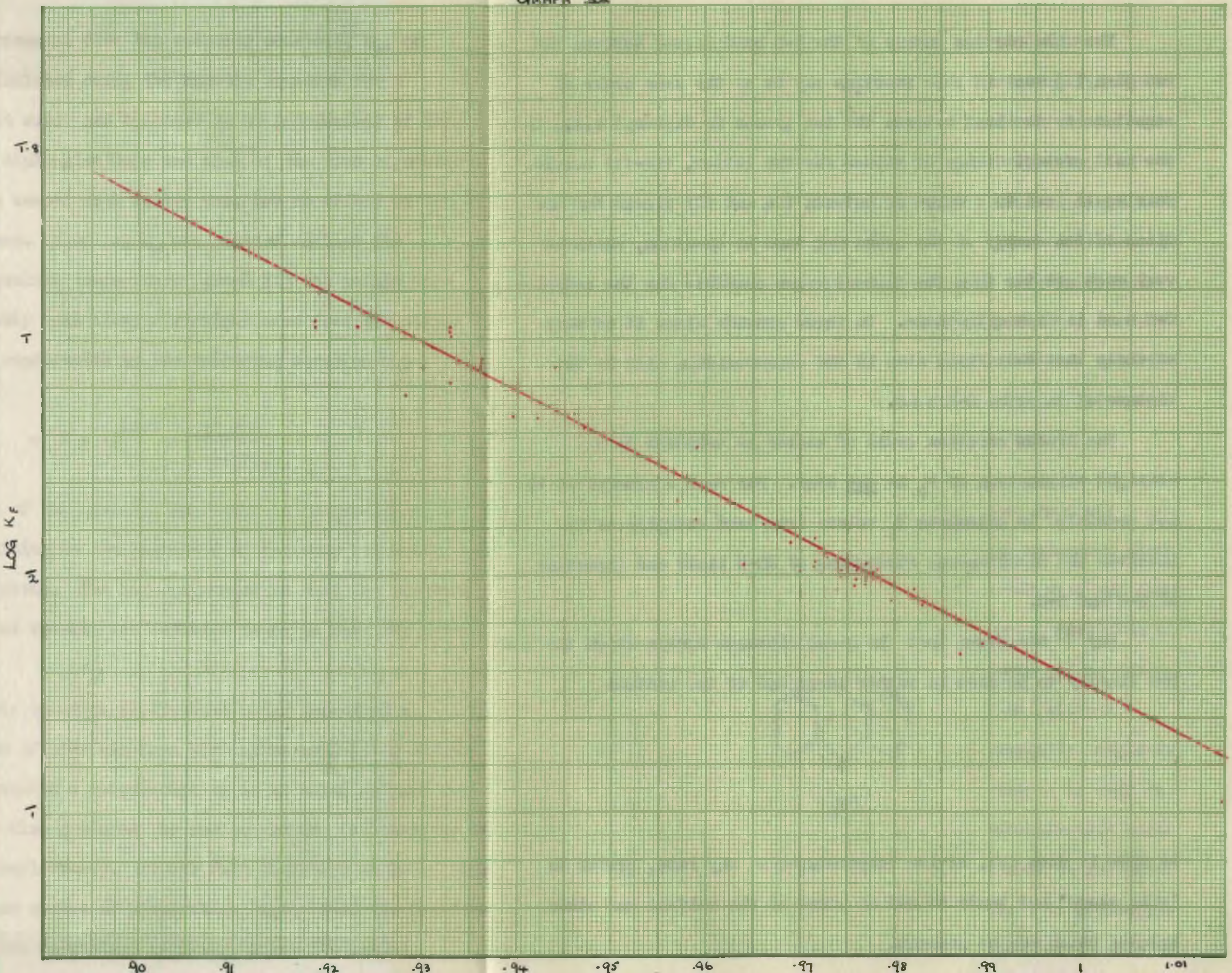
The Graebe reaction could of course be achieved as a straight elimination of H_2 in <u>one</u> step. For such a process it is not possible to calculate E_A values from bond energies as it involves the simultaneous stretching of 2C-H links and formation of H-H and C-C.

Hey[105] has shown that the C---C distance across which the link has finally to be made is rather large and if the radical



is made it does not, at low temperatures at any rate, prefer to 'ring close' but tends to add on parts of the solvent and other species which may be present.

GRAPH $\overline{XX}$



From the experimental data the velocity constant, k_F, of reaction (4) was calculated using the kinetic equation for a reaction of the first order and appeared to be independent of the partial pressure of diphenylmethane and also of the time of contact. Packing the reaction vessel with silica wool had no effect on the value of this constant. When log k_F was plotted against the reciprocal of the absolute temperature (graph XX) the points were found to lie reasonably well along a straight line from the slope of which the result represented by the following equation was obtained.

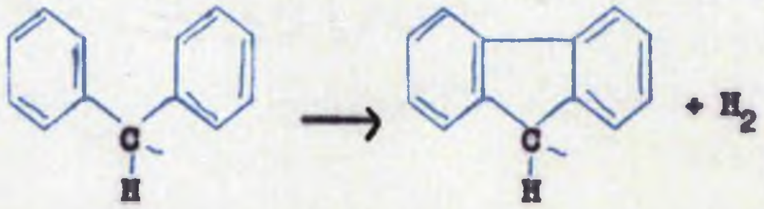
$$\log. k_F = 2 \times 10^{18} - \frac{95,000}{4.57T.}$$

The high value of the probability factor is suggestive of a chain mechanism resulting in the formation of fluorene but E is much too high for a chain. The best inference is that the reaction is not first order and reasons are advanced later to show why this cannot be the case.

Finally, on this question of fluorene being formed as a straight elimination of hydrogen from diphenylmethane it is rather odd that it should require a temperature to do it which we know from these investigations also produces the radical Ph_2CH- (as shown by the formation of tetraphenylethane). It was felt therefore to be at least suggestive of a common method of preparation, i.e. that the fluorene is also formed from the benshydryl radical. This will now be considered.

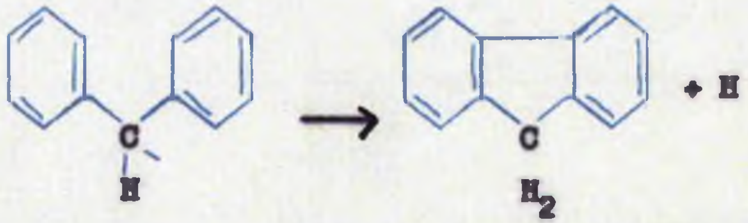
(2) Formation of Fluorene from the Benzhydryl Radical.

It has been shown[106] from a consideration of the magnitude of molecular dimensions that it is not possible for the triphenylmethyl radical to assume the planar configuration required by the trigonal hybridisation of the carbon atom with the free valence, but that the phenyl groups are inclined at an angle after the fashion of the blades of a propeller. It is probable that the same steric factors will prevent the two phenyl groups of the benzhydryl radical from lying in the same plane. This will result in the bringing of two ortho hydrogen atoms into close proximity, so permitting a ready elimination of H_2 as in (6)



(6)

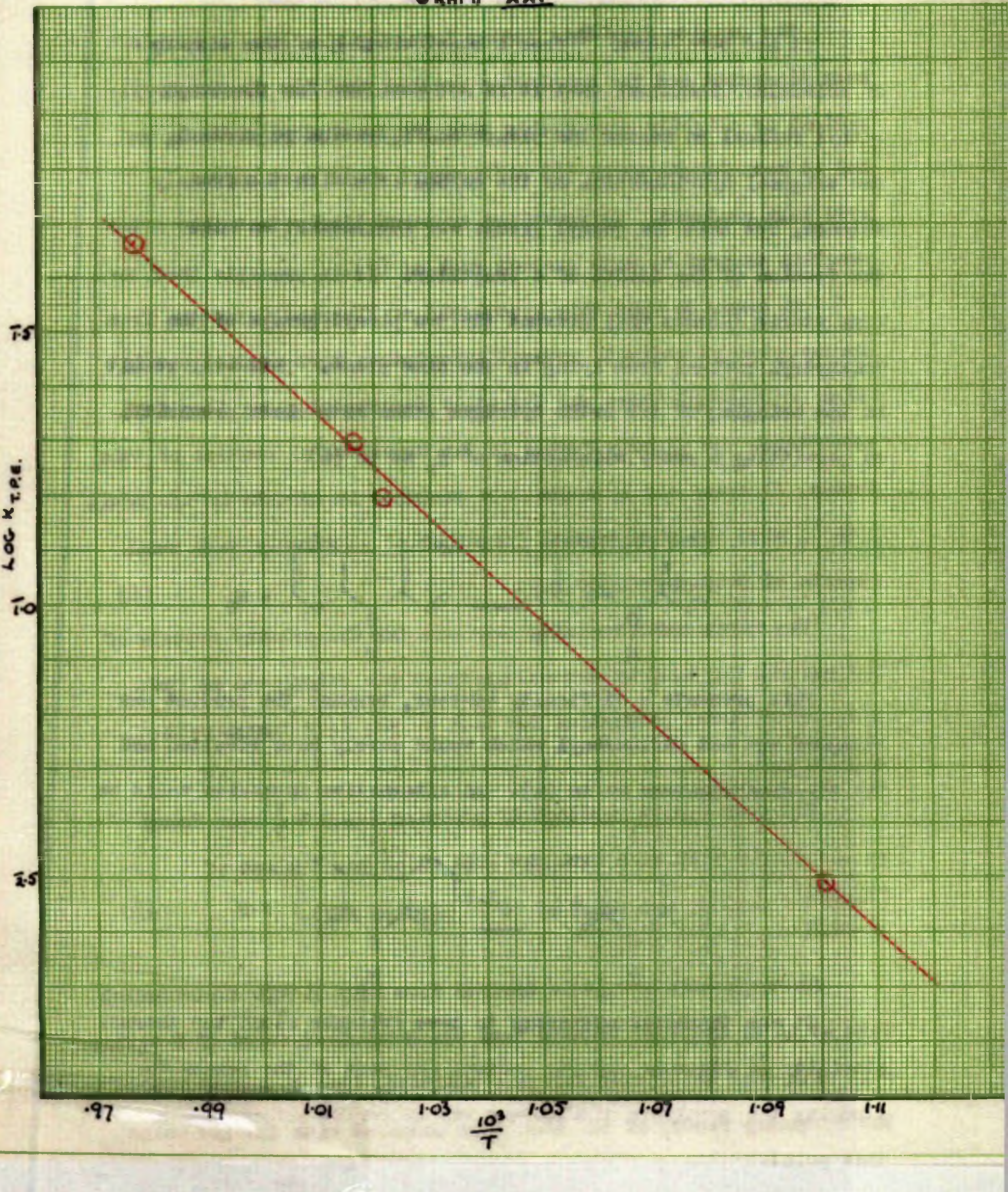
This presents a difficulty however, because the product was fluorene and not difluorenyl which would surely have resulted had the reaction occurred as in (6). An alternative mechanism would be



(7)

It was therefore necessary to have evidence about the thermal stability of fluorene and its radical and part of the reason for studying the pyrolysis of fluorene was to derive information on this point.

GRAPH XXI



LOG K T.P.E.
$\bar{1}$·5
$\bar{1}$·0
$\bar{2}$·5
·97
·99
1·01
1·03
1·05
1·07
1·09
1·11
$\frac{10^3}{T}$

The results from this latter investigation have already been discussed and the conclusion reached that the fluorenyl radical is slightly more stable than the benzhydryl radical, so had it been formed as in (6) difluorenyl would most certainly have been produced. It therefore appeared likely that the reaction occured by some process such as (7).

In order to test this hypothesis of fluorene formation from the benzyhydryl radical, several experiments were carried out in which tetraphenylethane was thermally decomposed under identical conditions. As already stated in the experimental section of this thesis, fluorene and hydrogen were produced in amounts in the ratio 2 to 1, with the simultaneous formation of relatively very small amounts of tetraphenylethylene.

The first order velocity constant for the primary rupture of the central C-C bond in tetrapheylethane was calculated on the basis of fluorene production for each of the four experiments carried out.

The four points obtained by plotting log.k V $\frac{1}{T}$ were found to lie fairly well on a straight line which has a slope of $\frac{-43,500}{2.303R}$ and an intercept of $10^{9.1}$ (graph XXI).

Although this result is derived from very little experimental data it is of interest to note that the determined value of E agrees well with that calculated for this reaction. (See Appendix). Also the frequency factor of 10^9 should be compared with the low value obtained by Horrex and Miles in their study of the pyrolysis of dibenzyl.

It is reasonable to assume that the carbon - carbon ethane bond is the weakest in the tetraphenylethane molecule and that therefore it will break most readily giving two diphenylmethyl radicals. The radicals so formed then might undergo any of the following reactions.

(a) Dimerise to give tetraphenylethane, which is the reverse of the initial reaction.

(b) Undergo a re-arrangement to form a molecule of fluorene and an atom of hydrogen.

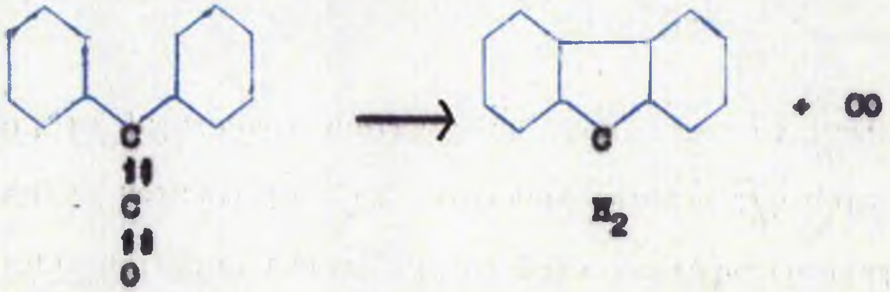
(c) React to yield a fluorenyl radical and a molecule of hydrogen.

(d) Disproportionate to a molecule of diphenylmethane and a molecule of fluorene.

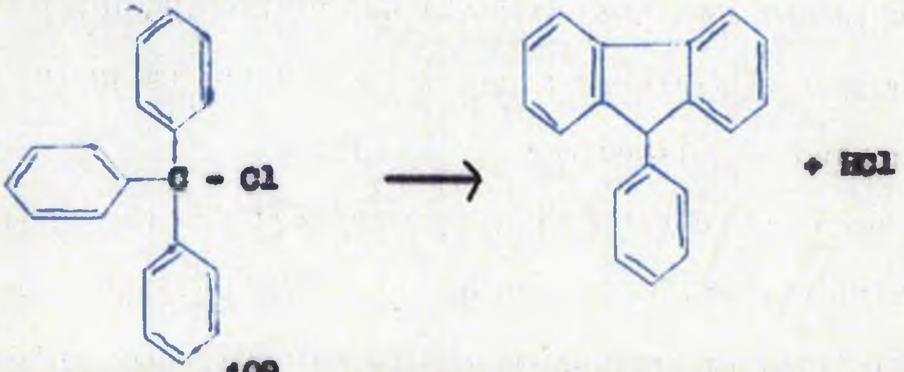
The parallel production of hydrogen excluded the possibility of fluorene arising by (d) and as there was no doubt about the product being fluorene and not difluorenyl, the third alternative (c) must also be discounted.

It thus appeared that the radicals react as in (b) and that fluorene is produced from diphenylmethane via the intermediate formation of the benzhydryl radical which ratifies the assumption made in the method of computing the first order velocity constant for the primary step in the decomposition of diphenylmethane. What has still to be considered is the actual detailed mechanism of the second step but before proceeding to a discussion of that point it is of interest to note other observations concerning similar radical rearrangements which have been reported in world literature.

Staudinger and Endle[107] found that by slowly passing diphenyl Ketene methane over a silver spiral at 600°C - 700°C, fluorene was formed in substantial amounts. Presumably the other product was carbon monoxide in which case the reaction equation is:

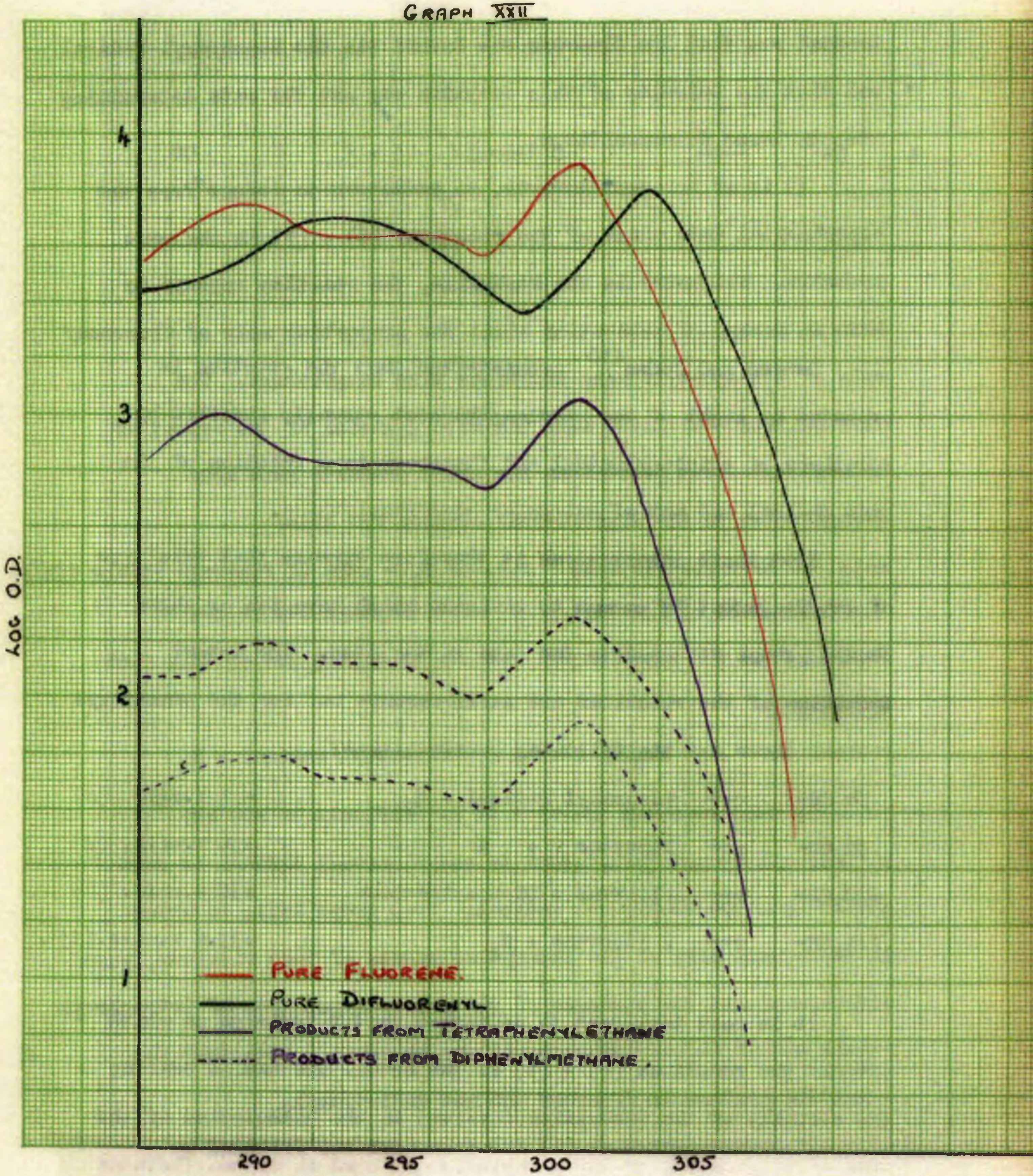


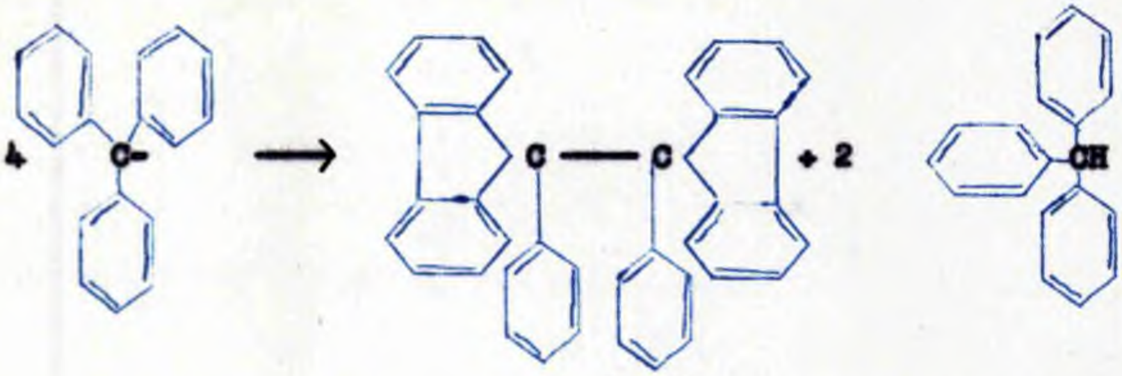
In this example both hydrogen atoms appear to migrate. Triphenylchloromethane[108] undergoes pyrolysis at 200°C to form 9 phenylfluorene and HCl.



Garcia-Banus[109] showed that a yellow solution of triphenylmethyl was decolourised on exposure to sunlight with the production of diphenyl bisdiphenylene-ethane, a substance which dissociates to a less extent than does hexaphenylethane. Free hydrogen was not formed but reacted with triphenylmethyl to give triphenylmethane.

GRAPH XXII


4
3
2
1
Log O.D.
290
295
300
305
mμ
Pure Fluorene.
Pure Difluorenyl
Products from Tetraphenylethane
Products from Diphenylmethane.



Bowden and Jones[110] demonstrated that the reaction is promoted by light of the wavelengths most strongly absorbed by solutions of triphenylmethyl and therefore is a reaction of the free radical and not of molecular hexaphenylethane.

From these observations it therefore appears that this type of rearrangement is common to radicals which have two or three phenyl groups attached to the same carbon atom. The actual mechanism of the reactions are still obscure but for the benzhydryl radical there are the following possibilities:

Ph_2CH-	⟶	Fluorenyl radical + H_2	- 1 k.cal. (6)
Ph_2CH-	⟶	Fluorene + H	-34 k.cals. (7)
$2Ph_2CH-$	⟶	Fluorene + Diphenylmethane	+38 k.cals. (8)
$2Ph_2CH-$	⟶	2 Fluorene + H_2	+33.2 k.cals.(9)

It is most important to emphasize that a decision on which one of the reactions (6) - (9) is the actual one has no bearing on the validity of the assumption involved in the calculation of the dissociation energy of the methylenic C-H bond in diphenylmethane and of the central C-C bond in tetraphenylethane. All that was assumed was that the fluorene was formed via the benzhydryl radical and that the velocity of this reaction was not the rate determining step in these decompositions.

It is of interest however, to endeavour to deduce from the experimental data which of the reactions (6) - (9) is the most probable. Whichever is the mechanism, the reaction appears to have an energy of activation since the proportion, mols of fluorene/ mols of tetraphenylethane increases with temperature. The difficulties associated with the determination of the amount of tetraphenylethane present in the solid products have been demonstrated in the experimental section but since

mols. of tetraphenylethane = mols of H_2 - mols of fluorene (table VIII)

the ratio, mols of fluorene/mols. of tetraphenylethane can be derived from the experimental results by making use of this fact.

Reaction 6.

$$Ph_2CH- \longrightarrow \text{fluorenyl radical} + H_2$$

If this reaction operates it is difficult to see why difluorenyl is not the product as the fluorenyl radical is more stable than the benzhydryl radical. From graph XXII, in which is reproduced part of the absorption curves of pure fluorene, pure difluorenyl and the products of thermal decomposition of tetraphenyl ethane and of diphenylmethane, it can be readily seen that the pyrolytic product is fluorene and not difluorenyl.

If however reaction (6) did occur but was followed by

$$\text{fluorenyl radical} + H \longrightarrow \text{fluorene} \qquad (6a)$$

the problem is then to consider where the hydrogen atom comes from.

Suppose:

fluorenyl radical + H_2 → fluorene + H - 33.5 k.cals (6b)

This is very endothermic and is also bimolecular which at the low experimental pressures of reactant and small percentage decomposition makes the reaction (6b) very unlikely.

It is easier to concede (6c) on thermal and collision frequency grounds.

fluorenyl + Ph_2CH_2 → fluorene + Ph_2CH- - 3.5 k.cals (6c)

This would mean that the concentration of benzhydryl radicals would not be reduced if reaction (6) was followed by (6c) because for each molecule of fluorene formed another benzhydryl radical is produced and a chain reaction would result.

The effect of nitric oxide on the reaction was not studied since there is evidence that it has no effect on resonance stabilised molecules. C. Horrex and M. Szwarc[111] found that benzyl iodide decomposed at the same rate in the presence of a great excess of nitric oxide as in nitrogen although they had already shown that the reaction

Benzyl + I → Benzyliodide

or Benzyl + I_2 → Benzyliodide + I

was occuring to a great extent.

Indirect evidence obtained from the pyrolysis of tetraphenylethane indicates that the chain mechanism 6 - 6c does not operate. Under these conditions the fluorenyl radical would have to abstract a hydrogen atom from one of the central carbon atoms of a tetraphenylethane molecule, a reaction which, although exothermic would be sterically difficult. Had this reaction occurred a considerable amount of tetraphenylethylene should have been formed by the thermal decomposition of tetraphenylethane as shown in the following scheme:

Tetraphenylethane ⟶ 2 Benzhydryl radicals (6d)

2 Benzhydryl radicals ⟶ 2 Fluorenyl radicals + $2H_2$ (6e)

2 Fluorenyl radicals + 2 tetraphenylethane — 2 fluorene + $2Ph_2\underset{\bullet}{C} - CH\,Ph_2$ (6f)

$$2Ph_2\underset{\bullet}{C} - CH\,Ph_2 \longrightarrow 2\,Ph_2C = C\,Ph_2 + 2H \qquad (6g)$$

$$2H + 2Ph_2CH\cdot CH\,Ph_2 \longrightarrow 2Ph_2\underset{\bullet}{C} - CH\,Ph_2 + 2H_2 \qquad (6h)$$

(6g) and (6h) again constitute a chain sequence which would have resulted in the production of a large amount of tetraphenylethylene while in actual fact very little was formed.

<u>Reaction 7</u>.

$$Ph_2\,CH\text{-} \longrightarrow \text{Fluorene} + H$$

In this case a molecule of fluorene and an atom of hydrogen would be formed directly from the benzhydryl radical. It is difficult to understand the apparent transfer of one of the ortho hydrogen atoms to the free valence on the methylenic carbon instead of the formation of a molecule with the other ortho hydrogen atom which was split~~t~~ off.

If reaction (7) occurred it would most certainly be followed by:

$$H + Ph_2CH_2 \longrightarrow H_2 + Ph_2CH- \quad + 30 \text{ k.cals.} \quad (7a)$$

and a radical chain would occur as with (6) and (6C).

Apart from the endothermicity of (7) which would be a deterrent to such a chain mechanism the non-production of tetraphenylethylene by the thermal decomposition of tetraphenylethane indicates that free hydrogen atoms are not formed in the presence of the last named hydrocarbon.

Reaction 8.

$$2Ph_2CH- \longrightarrow \text{fluorene} + \text{diphenylmethane}.$$

Although thermodynamically very favourable, this reaction has to be discounted as a possible means of formation of fluorene from the benzhydryl radical since it does not allow for production of hydrogen as was observed in the pyrolysis of tetraphenylethane.

Reaction 9.

$$2Ph_2CH- \longrightarrow 2 \text{ fluorene} + H_2$$

This reaction is also favourable from the point of view of thermodynamics and since it is similar to dimerisation in that it requires the encounter of two radicals it is possible if it has a low energy of activation that it could compete with dimerisation. There is no possibility of reaction chains since both products are stable molecules.

Table XX

Run	Temp.	Mols of Fluorene
	°C	Mols. of Tetraphenylethane
45	712	0.72
37	717	0.59
113	738	1.65
82	751	1.67
101	751	1.62
39	752	1.66
41	752	1.56
100	753	1.58
88	756	1.95
109	762	3.02
67	772	1.62
61	795	2.9
44	799	4.3
117	802	6.6
119	809	8.2
54	814	8.9

If it is assumed for the sake of argument that the radicals are stable in the hot zone of the reaction vessel and only disappear at the exit by either rearrangement as (9) or by dimerisation, then, if both processes have a zero activation energy there is statistically an equal probability of either reaction taking place and the number of mols. of fluorene produced should be twice the number of mols. of tetraphenylethane.

However, from the experimental results (table XX) it is observed that the ratio, mols of fluorene/mols of tetraphenylethane does not have a constant value of 2 but increases with temperature. The ratio is subject to a considerable degree of variation which arises from inaccuracies in the quantitative analyses, but there is no doubt that relatively much more fluorene than tetraphenylethane is produced at the higher temperatures.

These observations show that the assumption of equal probability for the two reactions, rearrangement and dimerisation, is not correct and furthermore in view of the temperature dependence of the ratio, the reactions cannot be occurring at the reaction vessel exit.

The results can however be accounted for in either of the two following ways:

(1) The rearrangement reaction has a finite energy of activation and is taking place within the reaction vessel while dimerisation of the unchanged radicals occurs at the exit. As the temperature is increased so will the rate of formation of fluorene increase and a proportionally smaller concentration of radicals will be available

for dimerisation at the exit.

(2) Both reactions occur inside the reaction vessel but rearrangement is more favourable than dimerisation at the higher temperatures.

If the first of these alternatives is correct then the concentration of fluorene should increase with time of contact and also with the square of the radical concentration and therefore the proportion fluorene/tetraphenylethane should depend on these two variables in the following way.

After time "t" secs.

Concentration of benshydryl radicals $= 2k_1 t \ [DPM]$

Concentration of fluorene at exit $= k_8 t \ [Rad]^2$

$$= 4k_1^2 k_8 t^3 [DPM]^2$$

$\therefore$ Conc. of radicals undecomposed at exit $= 2k_1 t \ [DPM] - 4k_1^2 k_8 t^3 [DPM]^2$

$\therefore$ Conc. of tetraphenylethane resulting by dimerisation

$$= k_1 t \ [DPM] - 2k_1^2 k_8 t^3 [DPM]^2$$

$$\therefore \frac{\text{Mols of fluorene}}{\text{Mols of tetraphenylethane}} = \frac{4k_1^2 k_8 t^3 [DPM]^2}{k_1 t \ [DPM] - 2k_1^2 k_8 t^3 [DPM]^2}$$

$$= \frac{4k_1 k_8 t^2 [DPM]}{1 - 2 k_1 k_8 t^2 [DPM]}$$

In experiments carried out at the same temperature a variation of partial pressure of diphenylmethane by a factor of 20

Table XXI

Run	Temp. °C	% Dec.	T.of C secs.	P.Press. of D.P.M. mms.	$\frac{\text{Mols.of Fluorene}}{\text{Mols.of Tetraphenylethane}}$
73	753	0.74	0.65	0.041	1.56
75	753	0.74	0.58	0.95	1.2
61	795	3.2	0.75	0.6	2.9
62	795	1.26	0.24	0.21	3.3

at constant percentage decomposition had no apparent effect on the ratio of the solid products nor had a threefold variation in time of contact. (Table XXI). The experimental variation may of course hide any real change in the ratio.

If now the second alternative is considered i.e. both rearrangement and dimerisation occurring within the reaction vessel, it is possible to represent the overall reaction by the scheme:-

$$Ph_2CH_2 \longrightarrow Ph_2CH- + H \qquad (1)$$

$$H + Ph_2CH_2 \longrightarrow Ph_2CH- + H_2 \qquad (2)$$

$$2Ph_2CH- \longrightarrow 2\ \text{Fluorene} + H_2 \qquad (9)$$

$$2Ph_2CH- \longrightarrow Ph_2CH\text{-}CHPh_2 \qquad (3)$$

The disappearance of hydrogen atoms by

$$H + H \longrightarrow H_2$$

is not considered to be important because of their low concentration and the great excess of diphenylmethane.

Then:

$$\frac{d\ [\text{Fluorene}]}{dt} = k_9\ [Ph_2CH-]^2$$

$$\frac{d\ [Ph_2CH-]}{dt} = k_1\ [Ph_2CH_2] + k_2[H]\ [Ph_2CH_2] - k_3[Ph_2CH-]^2 - k_9[Ph_2CH-]^2$$

If a steady state is assumed, i.e. the concentration of Ph_2CH- never rises above an infinitesimally low value

$$\frac{[d\ Ph_2CH-]}{dt} = 0$$

$$\therefore k_1\ [Ph_2CH_2] + k_2\ [H]\ [Ph_2CH_2] - k_3\ [Ph_2CH-]^2 - k_9\ [Ph_2CH-]^2 = 0$$

Table XXII

$\frac{10^3}{T}$	$2\,k_1$	k_r	$\frac{2k_1}{k_r}$
0.9	0.34	0.347	0.98
0.91	0.24	0.21	1.14
0.92	0.166	0.13	1.43
0.93	0.116	0.081	1.43
0.94	0.08	0.051	1.57
0.95	0.56	0.032	1.75
0.96	0.04	0.02	2
0.97	0.27	0.126	2.14
0.98	0.019	0.00776	2.44
0.99	0.013	0.00478	2.72
1	0.009	0.00288	3.12

$$\therefore\ k_3\,[Ph_2CH\text{-}]^2 + k_9\,[Ph_2CH\text{-}]^2 = k_1[Ph_2CH_2] + k_2[H][Ph_2CH_2]$$

$$\therefore\ [Ph_2CH\text{-}]^2 = \frac{k_1\,[Ph_2CH_2] + k_2\,[H]\,[Ph_2CH_2]}{k_3 + k_9}$$

$$\frac{d\,[H]}{dt} = k_1\,[Ph_2CH_2] - k_2\,[H]\,[Ph_2CH_2] = 0$$

$$\therefore\ [H] = \frac{k_1}{k_2}$$

$$\therefore\ \frac{d\,[\mathrm{Fluorene}]}{dt} = \frac{2k_1k_9\,[Ph_2CH_2]}{k_3 + k_9}$$

i.e. the rate of formation of fluorene would be first order with respect to diphenylmethane which is in accord with the experimental results for the total reaction

$$Ph_2CH_2 \xrightarrow{k_f} \mathrm{Fluorene}$$

k_f then equals $\dfrac{2\,k_1k_9}{k_3 + k_9}$

$$\therefore\ \frac{2k_1}{k_f} = 1 + \frac{k_3}{k_9}$$

The ratio $2k_1/k_f$ is inversely proportional to temperature as shown in table XXII, therefore k_3/k_9 is also inversely proportional to temperature, i.e, radical disappearance by rearrangement becomes more prominent than by dimerisation as the temperature is increased.

This is quite understandable since at higher temperatures tetraphenylethane would be decomposed to a greater degree.

If dimerisation does occur to a certain extent in the reaction vessel the formation of the small amounts of tetraphenylethylene could be explained on the basis of radical or hydrogen atom attack on the dimer formed. This point will be considered later.

The Apparent First Order Conversion of Diphenylmethane to Fluorene.

The association of a frequency factor of 10^{18} with an energy of activation of 95,000 cals. is most irregular. With the somewhat narrow range of experimental variables possible with the flow technique it is easy to fall into error when testing the order of a reaction and so to overlook a dependence of the velocity constant on the factors, time of contact and partial pressure of reactant and it is possible that this may have occurred in this investigation.

However it has been established that fluorene is formed from diphenylmethane and from tetraphenylethane via the benzhydryl radical and that it is fast compared with the primary step in the decomposition of diphenylmethane since it occurs quite readily at 635°C (the lowest temperature at which tetraphenylethane was pyrolysed).

Fluorene is not the only organic product derived from the two radicals, the other being tetraphenylethane, the ratio of these two hydrocarbons varying by about a factor of ten over the range of temperature studied. The formation of fluorene is substantially the sole reaction at the high temperatures but accounts for the disappearence of only about half the radicals at the lowest temperatures. Consider now the effect of this on the constant k_f.

At the high temperatures $k_f = 2k_1$ while at the lowest temperatures where there is about twice as much tetraphenylethane as there is fluorene, i.e. only one in three radicals go to fluorene k_f should be lower than $2k_1$ by about a factor of three. This is indeed the case. This alteration at lower temperatures is enough to displace the log. k_f v. $\frac{1}{T}$ graph to an extent which gives a slope of $-\frac{95,000}{4.57}$ and an intercept of 10^{18}. Quite apart from this agreement it is of course invalid to treat

$$\begin{tikzcd}
 & & C \\
A \arrow[r] & B \arrow[ur] \arrow[dr] & \\
 & & D
\end{tikzcd}$$

by a first order constant which only deals with A and C and ignores D especially when it has reached substantial amounts.

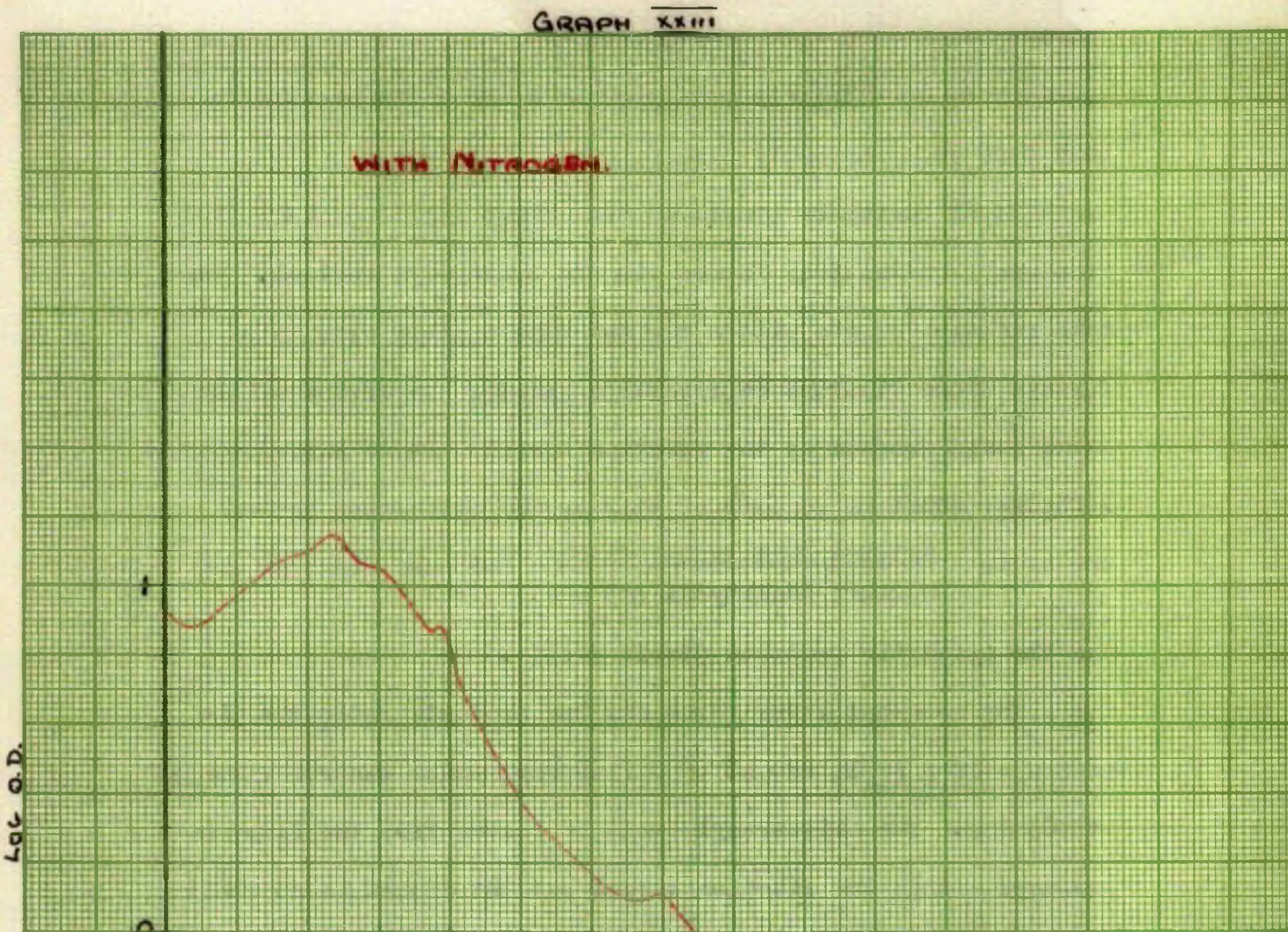
The difficulty of deciding upon the first order nature of the reaction by judging the k values when reaction parameters cannot be varied widely has already been commented upon. This has also been noted by Lapage[52] when dealing with the decomposition of methyl iodide under conditions where there was a back reaction $CH_3 + I_2 \longrightarrow CH_3I + I$. When this reaction was ignored in the original kinetic scheme, the constants of the first order mechanism

Table XXIII

	$\frac{\text{O.D. at 301 m}\mu}{\text{O.D. at 303 m}\mu}$
Pure fluorene	3.26 3.4 3.35
Products from tetraphenylethane	2.7 2.8 2.5
Products from diphenylmethane	2.5 2.1 2.6

These figures are obtained from three separate absorption curves of pure fluorene and from three experimental runs on diphenylmethane and tetraphenylethane.

GRAPH $\overline{\text{XXIII}}$



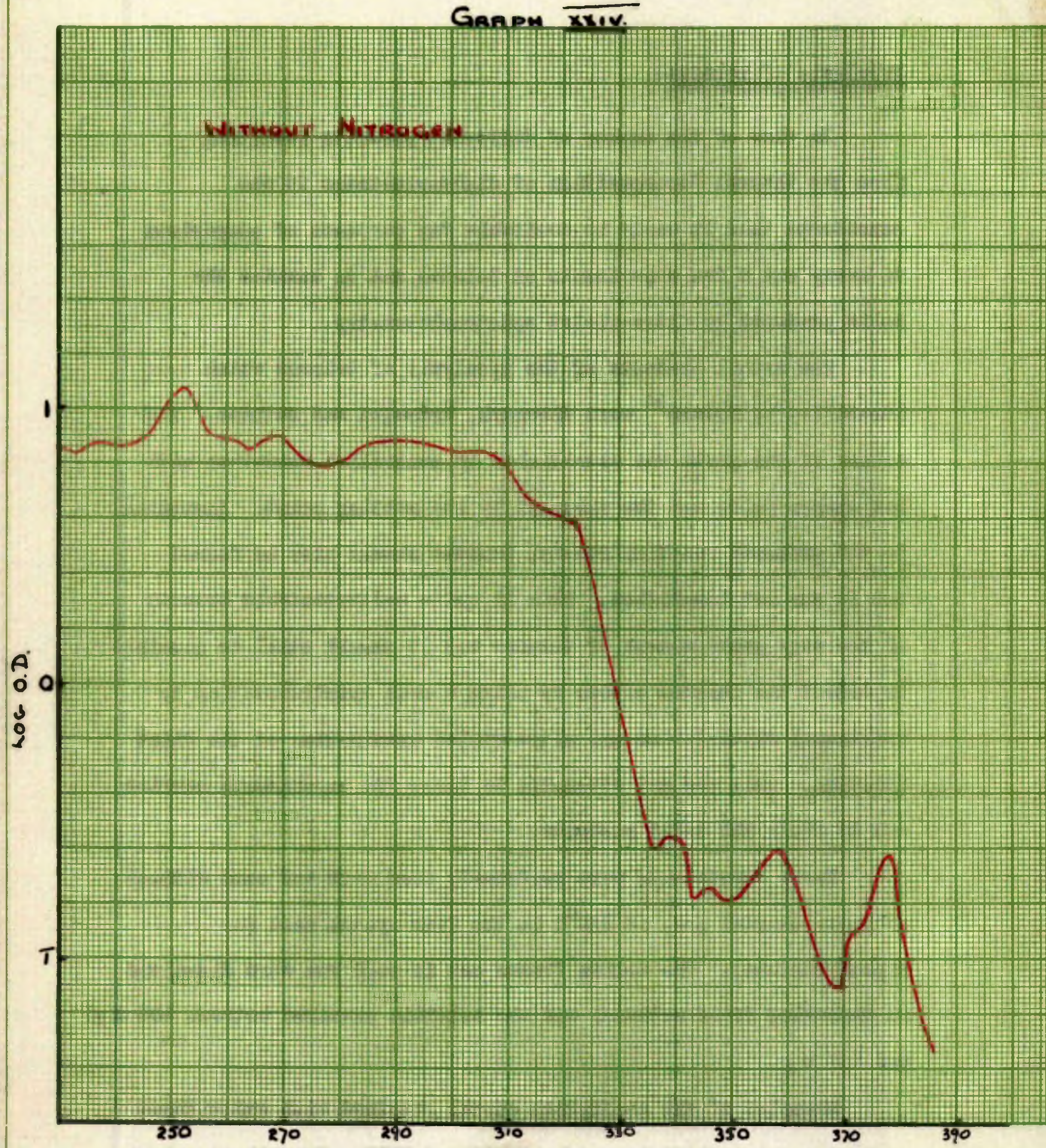
appeared to be extremely good but the A and E values as with this case were obviously absurd.

It is therefore concluded from these considerations that fluorene is definitely formed via the benzhydryl radical. That this reaction occurs within the hot zone appears also to be certain since fluorene represents a greater proportion of the total solid product as the reaction temperature is increased. A further point in support of this is the difference between the ratio $\frac{\text{Optical Density at 301 m}\mu}{\text{Optical Density at 303 m}\mu}$ for pure fluorene and for the pyrolytic products (table XXIII).

The somewhat lower value for the products indicates the presence of a small amount of difluorenyl which absorbs strongly at 303 m μ. The difluorenyl could be formed from the fluorene produced within the reaction vessel but the amount is so small that it could not readily be detected in the presence of the excess of fluorene. The data is not accurate enough to permit a quantitative determination being made.

The idea of radical disappearance by dimerising in the hot zone is not so satisfactory as tetraphenylethane would be decomposed to a considerable extent at the reaction temperatures involved but some further evidence in support of radical dimerisation in the furnace is given in the last section of this discussion.

GRAPH $\overline{XXIV}$.



GRAPH XXV


Curve I
Curve II
Curve III
1
0
$\bar{1}$
Log O.D.
250
270
290
310
330
350
370
mμ

Pyrolysis of Toluene.

In view of the number of different products resulting from the thermal decomposition of diphenylmethane it was considered that it would be desirable for purposes of comparison to carry out a few experiments on toluene and to examine the solid products by ultra-violet spectrophotometry.

The actual products of the pyrolysis of toluene which were identified by Szwarc[31] were dibenzyl, hydrogen and methane. The nature of the gases was established by controlled oxidation with hot copper oxide and the dibenzyl by its melting point. According to the proposed reaction scheme, benzene should also be formed but it was not identified. This is quite understandable because of the very great excess of toluene but it should still be possible to detect the benzene either by using a mass spectrometer or by fractional distillation and ultra-violet examination of the first fraction. This was not attempted in these few experiments carried out to study the solid products.

These experiments were performed, some with and some without nitrogen carrier gas, at 850°C in the flow system used for diphenylmethane. The solids frozen out in each run were dissolved in magnesium-dried methanol and the solution examined between 400 mμ and 200 mμ.

Examples of the absorption curves obtained with and without carrier gas are shown in graphs XXIII and XXIV. From these graphs it is at once obvious that more than dibenzyl was present in the solid products.

Although at first sight these two absorption curves seem to be very dissimilar there is really only one significant difference between them and that is the presence of a peak at 300 m μ in the "N_2 present" curve. The other apparent dissimilarities are caused by the absorbing components being present in different proportions in the two mixtures.

A search through the recorded ultra-violet spectra of hydrocarbons compiled by the American Petroleum Institute (Research Project 44) revealed that anthracene was responsible for the absorption bands with maxima at 377, 372.5, 358, 350, 346, 340 and 252 m μ. The large wide band between 330 and 270 m μ was readily recognised as being due to stilbene.

As both these compounds have very high extinction coefficients, small amounts of them can completely obscure the presence of relatively much larger concentrations of a substance such as dibenzyl which absorbs less strongly. When this happens the existence of the latter can be demonstrated by the following sort of 'process of elimination' as applied to this particular case.

From a knowledge of the anthracene concentration, derived from the absorption between 340 mμ and 380 m μ, it was possible to deduce the contribution made by it to the measured optical density at each wavelength over the whole range of wavelengths. examined. By subtracting the calculated anthracene contribution at each wavelength from the experimentally determined optical density of the mixture, curve II (graph XXV) which is due to the other components was obtained. This procedure was repeated for stilbene and resulted eventually in the production of curve III which is the absorption curve of dibenzyl.

The amounts of dibenzyl, stilbene and anthracene produced in this particular experiment were in the ratio 380:7:1. A similar calculation on the "N_2 present" curve did not give such a clear result because of the presence of a fourth material with an absorption maximum at about 301 m μ.

This peak was at first attributed to fluorene resulting from traces of diphenylmethane left in the system from the previous experiments, but it persisted in the absorption curves of the products obtained after every tap had been cleaned and regreased and the whole apparatus between the saturator and furnace entrance had been heated for several hours under hard vacuum.

When using toluene as a radical acceptor for phenyl radicals, C.B. Cowan[53] noted the presence of a band with a maximum about 301 m μ in the absorption curve of some of his products.

It is by no means certain that the substance giving rise to this peak is fluorene, but if it is, it would appear that phenyl and benzyl radicals can react under these experimental conditions to give fluorene - perhaps through the intermediate formation of diphenylmethane.

Incidentally, the above results show that Szwarc was substantially correct in his assumption that the benzyl radicals produced from toluene in his investigation only disappeared by dimerisation.

Pyrolysis of Diphenylbromomethane.

The purpose of these experiments was to produce diphenylmethyl radicals at lower temperatures than is possible from diphenylmethane in order to observe whether any fluorene was produced from the radicals at these lower temperatures.

It was expected that the initial step in the decomposition would be the breaking of the C - Br bond so giving rise to the desired radical which would dimerise to tetraphenylethane or perhaps rearrange to fluorene.

Contrary to expectations however, the products were hydrogen bromide and tetraphenylethylene in the ratio of roughly 2:1 and no free bromine was formed. An obvious interpretation of the results was that decomposition was proceeding by the direct formation of a molecule of HBr and a diphenylmethylene radical and that diphenylmethyl radicals were not formed at all. In order to test this, a few experiments were carried out in which an excess of diphenylmethane was introduced concurrently with the halide into the reaction vessel. Unfortunately there was not much time for these experiments and the technique adopted for simultaneous introduction was not very satisfactory. The results obtained were not very consistent but it did appear that the presence of diphenylmethane suppressed the rate of formation of both tetraphenylethylene and HBr.

Tetraphenylethane was definitely formed when diphenylmethane was used as a "bromine acceptor" but its non formation in the absence of diphenylmethane was not proved.

A great deal more work would have to be carried out before a reaction scheme which was absolutely certain could be drawn up but a tentative mechanism is presented from the results obtained. In this reaction:

$$\mathrm{Ph_2CHBr} \longrightarrow \mathrm{Ph_2CH}\text{-} + \mathrm{Br} \qquad (1)$$

is the most favoured initial single step.

The absence of Br_2 shows that (1) is not followed by

$$\mathrm{Ph_2CHBr} + \mathrm{Br} \longrightarrow \mathrm{Ph_2CH}\text{-} + \mathrm{Br_2} \qquad (2)$$

and that therefore

$$\mathrm{Ph_2CHBr} + \mathrm{Br} \longrightarrow \mathrm{Ph_2CBr}\text{-} + \mathrm{HBr} \qquad (3)$$

is most probably the second step.

If (3) is followed by dimerisation as in (4)

$$\mathrm{Ph_2CH}\text{-} + \mathrm{Ph_2CBr}\text{-} \longrightarrow \mathrm{Ph_2CH\text{-}BrCPh_2} \qquad (4)$$

the tertiary C - Br bond in the product would be very weak and readily decompose to HBr and tetraphenylethylene (5)

$$\mathrm{Ph_2CH\text{-}\ BrCPh_2} \longrightarrow \mathrm{Ph_2C = CPh_2} + \mathrm{HBr} \qquad (5)$$

In the presence of excess diphenylmethane the primary step (1) could be followed by

$$\mathrm{Br} + \mathrm{Ph_2CH_2} \longrightarrow \mathrm{Ph_2CH}\text{-} + \mathrm{HBr} \qquad (6)$$

the benzhydryl radicals then dimerising to tetraphenylethane. This would result in less tetraphenylethylene and HBr being formed since reaction (3) and hence (4) and (5) would not be occurring to the same extent.

No fluorene was produced in any of these experiments, so if it is accepted that diphenylmethyl radicals are produced by thermal decomposition of benzhydryl bromide, then at these low temperatures the radicals only disappear by dimerisation. This is what would be expected since the ratio, mols of fluorene/mols of tetraphenylethane fell rapidly with temperature.

Ultra Violet Spectrophotometry - Application in this Work.

In this research, attempts have been made to establish more completely the nature of all the products than has been the case in previous works of the same general nature reported in the literature.

Apart from tetraphenylethane which crystallised out above the U-tube in the initial experiments on diphenylmethane and was first recognised by its melting point, all the solid products were identified in the presence of other compounds by ultra-violet spectrophotometric examination of a solution of the mixture.

This method is particularly successful when the unknown material possesses some very prominent absorption band or bands in a region of the spectrum where the other compounds do not absorb. Examples of this which have been met with in the course of this work are

(1) Fluorene in a mixture of diphenylmethane, tetraphenylethane and tetraphenylethylene.

(2) Bis diphenylene-ethylene in the presence of fluorene and difluorenyl.

(3) Anthracene mixed with stilbene and dibenzyl.

The method was also of value for detecting impurities present in the materials before the kinetics of decomposition were studied.

However, when the 'unknown' has an absorption spectrum similar to that of a component present in excess in the mixture and does not have a very much greater extinction coefficient, the problem is more difficult. This will obviously be the case when the structures of the two compounds are alike, i.e. monomer and dimer. For example, tetraphenylethane in excess of diphenylmethane, difluorenyl in excess of fluorene.

It is in this respect that ultra-violet analysis of the mixtures of parent material and pyrolytic products is of least value because the former is always present in such excess that the existence of the dimer cannot be detected.

Although experimental conditions can be arranged, as in the work on fluorene, so that the dimer, being less volatile will condense out before the unchanged parent material, a reliable quantitative assay of the product still cannot be made by ultraviolet spectrophotometry or any other method unless information on its vapour pressure is available. Probably infra-red analysis of this type of mixture would be more fruitful but at the time of the investigation no instrument was available.

In spite of its limitations the method of ultra-violet spectrophotometric analysis has been of very great value in this research, indeed it is doubtful whether the work on diphenylmethane could have been completed without it.

Mechanism of Formation of Unsaturated Dimer Analogue.

It has already noted on page 84 of this thesis that the dimerisation of free radicals formed in the gas phase was very often accompanied by the simultaneous formation of the unsaturated analogue of the dimer. This phenomenon is not confined to the gas phase but also occurs with radicals in solution.

Waters and Bickel[112] found that benzyl radicals prepared by decomposing w,w azotoluene in boiling decalin solution at 200°C did not just recombine to form dibenzyl but also gave rise to stilbene. They ascribed the formation of this latter compound to disproportionation of the benzyl radicals i.e.

$$2\ \mathrm{Ph-CH_2^{\cdot}} \longrightarrow \mathrm{Ph\,CH_3} + \mathrm{Ph.CH:} \qquad (1)$$

followed by dimerisation of the phenylmethylene radicals.

Szwarc[113] points out that the activation energy of the disproportionation reaction would have to be less than 5 k.cals/mol. if it is to compete successfully with dimerisation and he goes on to deduce from thermochemical and kinetic data that a probable value for the energy of activation of (1) is about 25 k.cals/gm.mol.

In addition it has been pointed out by Dr.C. Horrex[114] that if benzyl radicals disproportionate it would be expected that the reaction would be very rapid at the temperatures of toluene pyrolysis and so a great deal of stilbene should be produced.

Ultra-violet examination of the solid products from toluene pyrolysis have shown them to contain a negligible amount of stilbene and that the predominating reaction of the benzyl radicals under these conditions was therefore dimerisation.

An alternative mechanism which has been proposed is that the benzyl radicals first dimerise to dibenzyl but as the concentration of the latter increases it becomes more possible for benzyl radicals to attack it with the formation of toluene and stilbene.

The very small amount of stilbene in the products of thermal decomposition in the gas phase is in accord with this idea because the temperature at which the benzyl radicals are produced is so high that dibenzyl itself would be rapidly decomposed.

Further support of this mechanism comes from the production of large amounts of stilbene in experiments carried out by Dr. R. Lapage[52] and Dr. C.B. Cowan[53] in which they used toluene as an acceptor for methyl and phenyl radicals. Under these conditions the benzyl radicals were produced at temperatures at which the rate of decomposition of dibenzyl is very slow. Finally, in a study of the thermal decomposition of dibenzyl itself, Dr. C. Horrex and Dr.S.E. Miles[33] found that stilbene was one of the major products.

These results support the idea of radical dimerisation within the furnace because if the dimer were only formed at the exit there would be very little opportunity for radical attack on the molecules formed.

Conclusions.

(1) The decomposition of fluorene proceeds by a uni-molecular mechanism with the production of a free fluorenyl radical and an atom of hydrogen. The radicals disappear entirely by dimerisation. The rate of formation of hydrogen is given by

$$k = 10^{12.9} \cdot e^{\frac{-68,500}{RT}} \text{ secs}^{-1}$$

This energy of activation is regarded as being the dissociation energy of the methylenic C-H bond in fluorene.

(2) In the decomposition of diphenylmethane the primary dissociation gives rise to a free benzhydryl radical and a hydrogen atom. The hypothesis that fluorene is produced from the benzhydryl radical gives very reasonable values for the velocity constant of the initial step in the decomposition of diphenylmethane in the respect that $A = 10^{13.57}$ which is theoretically expected, and that $E = 72$ k.cals/mol, which as anticipated is intermediate to the energies of activation for the decomposition of toluene and fluorene. The calculation of the velocity constant k_1 (diphenylmethane $\rightarrow$ benzhydryl radical) only requires that fluorene is produced via the radical and is independent of the mechanism of this second stage.

(3) The idea of fluorene formation from the benzhydryl radical is supported by the conversion of tetraphenylethane to fluorene under the same experimental conditions. Curiously enough the velocity

constant for this reaction is given by:

$$k = 10^{9} \cdot e^{\frac{-44,000}{RT}} \ \text{secs}^{-1}$$

which bears a strong resemblance to the case of dibenzyl ($A=10^{9}$) and has an energy of activation which is equal to the value calculated on the basis of the heat of formation of the benzhydryl radical. The data are very scanty but seem to point to this being true.

Appendix

Thermochemical Calculations.

(1) Heat of formation of Diphenylmethane.

Heat of combustion[1] in gaseous state = 1666 k.cals/mol.

Since:

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O_1 \quad + 68.3 \text{ k.cals}$$

and

$$C_s + O_2 \longrightarrow CO_2 \quad + 94.05 \text{ k.cals}$$

$$13C_s + 6H_2 + 16O_2 \longrightarrow 13CO_2 + 6H_2O_1 \quad + 1631.4 \text{ k.cals.}$$

$$C_{13}H_{12} + 16O_2 \longrightarrow 13CO_2 + 6H_2O_1 \quad + 1666 \text{ k.cals.}$$

$$\therefore 13\,C_s + 6H_{2(g)} \longrightarrow C_{13}H_{12(g)} \quad \overset{-}{+}\ 3\overset{4}{3}.6 \text{ k.cals.}$$

BH

Heat of formation of diphenylmethane = $- 3\overset{4}{3}.6$ k.cals/mol.

(2) Heat of formation of Fluorene.

$$13C_s + 5H_2 + 15\tfrac{1}{2}\,O_2 \longrightarrow 13CO_2 + 5H_2O_1 \quad + 1564.1 \text{ k.cals.}$$

$$C_{13}H_{10} + 15\tfrac{1}{2} \longrightarrow 13CO_2 + 5H_2O1 \quad + 1602 \text{ k.cals}$$

$$\therefore 13C_s + 5H_{2(g)} \longrightarrow C_{13}H_{10(g)} \quad \overset{-}{+}\ 37.9 \text{ k.cals.}$$

Heat of formation of fluorene = -37.9 k.cals.

Ft.Note.

[1] Heats of combustion for diphenylmethane and fluorene quoted by Wheland ("Theory of Resonance" 1945 p.69) from compl$\overset{?}{i}$mation by

Kharasch and Brown, with correction to gas phase by use of data from Landholt-Bornstein.

(3) Heat of Formation of Benzhydryl Radical.

$$D(Ph_2CH-H) = Qf(Ph_2CH_2) - Qf(Ph_2CH-) - Qf(H)$$

$$72 = -33.6 - Qf(Ph_2CH-) + 51$$

$$\therefore Qf(Ph_2CH-) = -54.6 \text{ k.cals/mol.}$$

(4) Heat of Formation of fluorenyl radical (F)

$$D(F-H) = Qf(FH) - Qf(F) - Qf(H)$$

$$68.5 = -38 - Qf(F) + 51$$

$$\therefore Qf(F) = -55.5 \text{ k.cals/mol.}$$

(5) Heat of dissociation of Tetraphenylethane.

Heat of combustion of solid tetraphenylethane = 3248 cals/mol.

(Coops, Mulder, Dienske and Smittenberg. Rec.Trav.Chim.1946.65.128)

The latent heat of sublimation, λ, is not known.

∴ Let heat of combustion of gaseous tetraphenylethane

= (3248 + λ) k.cals

i.e. $C_{26}H_{22} + 31\frac{1}{2}O_2 \longrightarrow 26CO_2 + 11\,H_2O + (3248 + \lambda)$k.cals.

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ 68.3 k.cals.

$C_{26}H_{22} + H_2 + 32O_2 \longrightarrow 26CO_2 + 12H_2O + (3316.3 + \lambda)$k.cals.

but $2C_{13}H_{12} + 32O_2 \longrightarrow 26CO_2 + 12H_2O + (3332\ \ )$k.cals.

$$\therefore \; C_{26}H_{22} + H_2 \longrightarrow 2C_{13}H_{12} \qquad + (15.7 - \lambda)\text{k.cals.}$$

$$H_2 \longrightarrow H + H \qquad - 102 \quad \text{k.cals.}$$

$$2\,C_{13}H_{12} \longrightarrow 2C_{13}H_{11} + 2H \qquad - 144 \quad \text{k.cals.}$$

$$\therefore \; C_{26}H_{22} \longrightarrow 2C_{13}H_{12} - H - H \qquad + (117.7_{\lambda})\text{k.cals.}$$

$$\text{and} \; C_{26}H_{22} \longrightarrow 2C_{13}H_{1\bar{1}} \qquad - (26.3 + \lambda)\text{k.cals.}$$

A reasonable value for λ would be between 15 and 20 k.cals.

∴ Dissociation energy of central C-C bond in tetraphenylethane = 40 to 45 k.cals/mol.

Experiments on Diphenylmethane

Calculation of k_1

Run	Temp °C	TofC Secs	P.P.of D.P.M. mms.	Pres. of N_2 mms.	% Dec.	D.P.M. mols.x10^{-3}	Fluorene mols.x10^{-5}	H_2 mols.x10^{-5}	k Sec^{-1}
45	712	.52	.258	6.8	.11	15.14	.88	2.1	.00209
37	717	.68	.4	6.6	.24	12.8	1.37	3.8	.00359
48	737	.78	.248	6.6	.57	3.92	1.66	3.08	.00837
113	738	.6	.71	3.4	.42	6.1	2.3	3.7	.00670
57	740	.47	.36	6.6	.37	10.5	2.3	5.08	.00789
35	744	.37	.31	6.7	.31	17.2	4.76	7.77	.00846
53	746	.52	.39	6.3	.53	3.89	1.78	2.96	.0101
49	748	.52	.171	6.8	.55	2.9	1.42	2.3	.0107
55	748	.53	.095	6.4	.42	3.11	1.19	1.9	.00794
107	750	.71	.3	3.4	.82	1.61	1.07	1.83	.0114
108	750	.61	.55	2.9	.79	1.89	1.31	2.14	.00968
82	751	.61	.42	6.0	.61	2.81	1.57	2.51	.0101
95	751	.62	.47	3.3	.85	4.4	2.47	5.0	.0135
101	751	.72	.43	10.8	.71	2.09	1.33	2.15	.00968
102	751	.66	.29	10.0	.56	2.6	1.97	2.45	.00837
39	752	.64	.61	2.9	.64	5.52	3.18	5.1	.0100
41	752	.6	.3	5.2	.68	2.25	1.28	2.1	.0113
42	752	.8	.17	2.9	.87	1.645	1.27	2.1	.01120
56	752	.62	.16	6.4	.83	3.539	2.4	4.14	.0132
60	752	.56	.305	6.6	.53	4.88	2.38	3.76	.00927
93	752	.7	.388	3.0	.7	2.13	1.4	2.2	.0100

Run	Temp $^{\circ}C$	TofC Secs.	P.P.of D.P.M. mms.	Pres. of N_2 mms.	% Dec.	D.P.M. mols.x10^{-3}	Fluorene mols.x10^{-5}	H_2 mols.x10^{-5}	k Sec^{-1}
94	752	.67	.26	3.6	.7	1.77	1.09	1.8	.0104
96	752	.71	.35	2.8	.77	3.15	2.16	3.5	.0109
72	753	.71	.539	6.0	.78	2.95	2.15	3.38	.0110
73	753	.65	.041	6.0	.72	1.65	1.03	1.69	.0106
75	753	.58	.95	6.0	.74	2.41	1.35	2.47	.0128
76	753	.60	.33	6.1	.7	3.05	2.03	3.15	.0116
90	753	.71	.44	2.9	.56	3.57	1.93	3.0	.00783
92	753	.65	.65	3.0	.73	4.2	2.70	4.5	.0111
100	753	.56	.35	10.8	.6	3.83	2.02	3.3	.0101
104	753	.63	.196	10.1	.76	2.8	1.53	2.9	.0121
105	753	.6	.22	10.2	.85	1.43	.85	1.64	.0142
112	753	.7	.32	3.2	.92	2.7	1.90	3.43	.0133
59	754	.56	.26	6.4	.71	4.4	2.20	4.23	.0128
89	754	.79	.49	2.7	1.14	3.53	2.48	5.4	.0146
103	754	.68	.33	9.8	.81	1.93	1.37	2.25	.0120
110	754	.58	.3	5.2	.67	1.81	1.12	1.80	.0116
111	754	.67	.29	3.8	.64	1.83	1.31	1.85	.00973
98	755	.64	.27	8.7	.8	2.43	1.75	2.8	.0124
99	755	.8	.27	10.0	1.0	1.9	1.79	2.8	.0125
86	756	.48	.36	7.7	.78	2.7	1.79	3.0	.0161
87	756	.46	.52	7.7	.56	4.07	2.06	3.3	.0122
88	756	.63	.32	4.5	.67	2.69	1.79	2.71	.0107
115	757	.51	.16	6.5	.65	1.9	.65	1.57	.0131
85	759	.49	.25	6.6	.97	2.6	1.7	3.4	.0203

Run	Temp °C	T of C Secs.	P.P. of D.P.M. mms.	Pres of N_2 mms.	% Dec.	D.P.M. mols.x10^{-3}	Fluorene mols.x10^{-5}	H_2 mols.x10^{-5}	k Sec^{-1}
66	762	.38	.2	6.7	.58	5.2	1.84	4.0	.0155
109	762	.69	.25	3.2	.95	2.04	2.33	3.1	.0138
47	767	.47	.25	6.6	.82	3.8	3.8	5.1	.0176
38	770	.31	.41	6.8	1.15	6.35	6.7	10.6	.0373
69	770	.43	.31	6.8	.82	5.35	3.8	6.3	.0193
67	772	.35	.3	6.8	.77	4.9	3.4	5.5	.0223
116	784	.37	.14	6.7	1.24	2.2	3.8	4.65	.0336
50	786	.32	.31	7.0	1.18	6.0	14.6	14.4	.0374
121	792	.55	.17	6.8	2.00	1.25	3.06	4.0	.037
65	793	.39	.34	6.7	1.75	5.00	10.6	14.0	.0455
52	795	.34	.2	6.8	1.4	2.5	6.5	6.7	.0414
61	795	.75	.6	6.6	3.3	2.3	9.0	12.1	.0450
62	795	.24	.21	6.8	1.26	2.1	3.3	4.3	.0528
40	799	.34	.33	6.8	2.2	6.1	21.9	24.3	.0655
43	799	.38	.2	6.5	2.34	2.84	10.74	12.0	.0625
44	799	.26	.37	6.3	1.17	5.1	8.1	10.0	.0451
51	799	.44	.2	6.4	2.46	2.83	11.46	12.7	.0579
46	801	.37	.21	6.8	2.0	3.7	13.0	13.8	.0547
117	802	.4	.17	7.5	1.87	1.85	5.3	6.1	.0472
68	804	.38	.4	7.2	2.0	2.9	10.8	11.2	.0545
119	809	.34	.16	8.8	2.4	2.3	8.9	10.0	.0717
120	810	.33	.26	9.6	1.7	3.2	13.1	12.0	.0565
54	814	.34	.18	6.8	3.2	3.1	16.0	17.8	.0979
63	835	.36	.19	6.6	6.0	1.9	27.2	25.4	.172
64	835	.38	.173	6.8	6.0	1.15	15.8	14.4	.153

Experiments on Diphenylmethane. Calculation of k_F.

Run	Temp. °C	Fluorene mols.x10^{-5}	D.P.M. mols.x10^{-3}	% Dec.	T.of C Secs.	k_F Sec.$^{-1}$
45	712	.88	1.5	.06	.53	.0011
37	717	1.37	12.8	.105	.68	.0016
48	737	1.66	3.9	.43	.78	.0056
113	738	2.3	6.1	.37	.6	.00615
57	740	2.3	10.5	.22	.48	.0045
35	744	4.76	17.2	.27	.37	.0073
53	746	1.8	3.9	.46	.53	.0086
49	748	1.4	2.9	.47	.52	.0091
55	748	1.2	3.1	.39	.53	.0076
107	750	1.07	1.6	.66	.7	.0096
82	751	1.6	2.8	.56	.61	.0092
95	751	2.5	4.4	.56	.6	.0094
101	751	1.3	2.1	.64	.7	.0097
102	751	1.97	2.6	.75	.7	.0107
39	752	3.2	5.5	.58	.64	.009
41	752	1.3	2.2	59	.6	.0095
42	752	1.27	1.65	.77	.8	.0098
56	752	2.4	3.5	.67	.63	.0107
60	752	2.4	4.9	.47	.56	.0084
93	752	1.4	2.1	.65	.7	.0096
94	752	1.1	1.8	.62	.67	.0092
96	752	2.16	3.15	.69	.72	.011

Run	Temp. °C	Fluorene mols.x 10^{-5}	D.P.M. mols.x10^{-3}	% Dec.	T.of C Secs.	k_p Sec.$^{-1}$
72	753	2½15	3.0	.72	.71	.0103
73	753	1.03	1.6	.65	.65	.0101
75	753	1.35	2.4	.56	.58	.0098
76	753	2.03	3.1	.66	.6	.0107
90	753	1.9	3.6	.55	.71	.008
92	753	2.7	4.2	.63	.65	.0099
100	753	2.0	3.8	.53	.56	.0103
104	753	1.5	2.8	.53	.63	.0084
105	753	.85	1.4	.6	.6	.010
112	753	1.90	2.7	.71	.7	.0102
59	754	2.2	4.4	.49	.56	.0088
89	754	2.48	3.5	.71	.8	.0090
103	754	1.4	1.9	.71	.68	.0105
110	754	1.12	1.8	.62	.58	.0107
111	754	1.31	1.8	.74	.67	.0110
98	755	1.75	2.4	.72	.64	.011
99	755	1.8	1.9	.94	.8	.0118
86	756	1.79	2.7	.66	.48	.0138
87	756	2.06	4.1	.51	.46	.011
88	756	1.79	2.7	.66	.63	.0106
115	757	.65	1.9	.34	.51	.00634
85	759	1.7	2.6	.65	.49	.0136
66	762	1.84	5.2	.36	.38	.0095
109	762	2.33	2.0	1.14	.69	.0166

Run	Temp. °C	Fluorene mols.x 10^{-5}	D.P.M. mols.x10^{-5}	% Dec.	T.of C. Secs.	k_F Sec.$^{-1}$
47	767	3.8	3.8	1.0	.47	.0210
38	770	6.7	6.4	1.05	.31	.034
69	770	3.8	5.4	.7	.43	.0166
67	772	3.4	4.9	.69	.35	.0199
116	784	3.8	2.2	1.7	.37	.0465
50	786	14.6	.6	2.4	.32	.0735
121	792	3.06	1.25	2.45	.55	.0453
65	793	10.6	5.00	2.2	.39	.056
52	795	6.5	2.5	2.6	.24	.0764
61	795	9.0	2.3	4.0	.7	.061
62	795	3.3	2.1	1.6	.24	.078
40	799	22.0	6.1	3.3	.34	.0995
43	799	10.7	2.8	3.8	.38	.103
44	799	8.1	5.1	1.5	.21	.075
51	799	11.5	2.8	4.1	.4	.105
46	801	13.0	3.5	3.35	.370	.090
117	802	5.3	1.8	2.9	.39	.0755
68	804	10.8	2.9	3.7	.38	.099
119	809	8.9	2.3	3.9	.34	.116
120	810	13.1	3.2	4.2	.34	.11
54	814	16.0	3.1	5.2	.34	.156
63	835	27.2	1.9	14.6	.36	.439
64	835	15.8	1.2	13.4	.38	.376

Experiments on Fluorene

Run	Temp °K	Durn. mins	T.of C secs.	P.Press. Fluorene mms.	H_2 mols.x10^{-5}	Fluorene mols.x10^{-3}	% Dec.	k $secs^{-1}$
245	943	23.5	1.28	.33	.6	2.84	.211	.00164
246	943	20	165	.34	.47	2.24	.21	.00139
250	943	21	1.44	.35	.45	2.24	.20	.00139
251	943	25	1.35	.34	.58	2.8	.206	.00151
147	944	6	1.46	.78	.17	.78	.218	.00155
148	944	12	1.33	.82	.34	1.9	.18	.00133
149	944	12	1.33	.8	.36	1.9	.19	.00144
150	944	12	1.33	.81	.4	1.9	.21	.00157
151	944	12	1.33	.83	.41	2,16	.19	.00144
152	944	15	1.43	.7	.47	2.36	.20	.00141
247	952	12	1.25	.33	.3	1.5	.20	.00161
248	952	25	1.24	.31	.77	2.76	.28	.00224
249	952	20	1.24	.33	.5	2.34	.214	.0017
142	953	6	.95	.88	.32	1.53	.212	.00222
143	953	7	.95	.83	.32	1.66	.196	.00206
144	953	9	.95	.82	.4	2.08	.193	.00204
145	953	10	.95	.83	.32	2.36	.14	.00147
146	953	12	.95	.73	.47	2.24	.21	.00221
44	954	4	.74	.87	.36	2.2	.16	.00224
45	955	4.5	.71	.85	.42	2.3	.18	.00252
141	955	6	.95	.87	.42	1.5	.28	.00327

Run	Temp °K	Durn. mins	T.of C secs	P.Press. Fluorene mms	H_2 mols.x 10^{-5}	Fluorene mols.x10^{-3}	% Dec.	k secs.$^{-1}$
140	956	6	.97	.81	.25	1.35	.185	.00193
139	957	6	.95	.68	.275	1.3	.21	.0022
77	959	3	.72	.3	.25	.55	.46	.00645
80	959	4	.75	.34	.25	.79	.32	.00425
81	959	3.5	.75	.34	.15	.72	.21	.0025
79	961	4	.77	.33	.23	.73	.31	.00388
18	962	5	.34	.39	.35	2.7	.13	.00378
116	963	10	.725	.38	.53	2.3	.23	.0031
117	963	9	.725	.38	.44	2.0	.22	.00298
118	963	9	.725	.37	.5	2	.25	.00326
119	963	8½	.72	.36	.45	1.89	.24	.0033
46	964	4½	.69	.78	.38	2.18	.175	.00254
82	965	4	.74	.33	.25	.83	.30	.00403
109	965	9	.73	.4	.52	2.2	.24	.00324
110	965	7	.71	.38	.5	1.65	.30	.00425
111	965	9½	.73	.39	.65	2.2	.29	.004
112	965	9	.76	.39	.48	2	.24	.00318
113	965	9	.73	.38	.43	2	.21	.0029
114	965	9	.68	.38	.53	2.2	.24	.00296
115	965	9	.73	.38	.5	2.0	.25	.00306
47	966	4½	.69	.86	.5	2.4	.21	.00308
19	969	4	.36	.38	.33	2	.16	.00448

Run	Temp °K	Durn. mins	T.of C secs	P.Press. Fluorene mms	H_2 mols.x10^{-5}	Fluorene mols.x10^{-3}	% Dec.	k secs^{-1}
196	969	8	.73	.4	.48	1.9	.25	.00337
197	969	8	.78	.4	.53	1.9	.28	.00366
198	969	11	.73	.36	.62	2.6	.24	.00324
199	969	6	.76	.31	.25	1.1	.23	.0031
201	970	7	.78	.4	.20	1.6	.26	.0033
210	970	8	1.0	.34	.5	1.2	.41	.0042
211	970	8	.9	.34	.45	1.3	.34	.00386
212	970	8	.9	.34	.35	1.3	.27	.0030
213	970	8	.96	.34	.4	1.3	.32	.0033
214	970	10	.96	.35	.58	1.9	.31	.00324
215	970	6	1	.36	.32	.87	.37	.00375
216	970	6	1	.36	.32	.87	.37	.0037
217	970	8	.97	.37	.45	1.35	.34	.00346
218	970	8	.97	.37	.45	1.35	.34	.00346
219	970	15	.97	.37	.85	2.5	.34	.00346
83	971	5	.74	.35	.33	1.01	.325	.00436
17	971	5	.34	.36	.35	2.47	.14	.00418
20	972	4	.58	.59	.52	1.75	.3	.0052
21	972	3	.58	.6	.41	1.4	.29	.00504
185	972	6	.72	.4	.4	1.45	.27	.00381
186	972	6	.69	.42	.45	1.66	.27	.00394
187	972	8	.67	.42	.73	2.18	.33	.00495

Run	Temp °K	Durn. mins	T.of C secs	P.Press. Fluorene mms	H_2 molsx10^{-5}	Fluorene mols.x10^{-3}	% Dec.	k secs^{-1}
85	973	8	.7	.36	.37	1.08	.35	.00496
106	974	6	.75	.37	.45	1.3	.35	.00465
107	974	9	.76	.43	.75	2.1	.34	.00445
108	974	9	.74	.41	.70	2.2	.32	.00440
188	974	8	.67	.42	.52	2.18	.24	.00415
189	974	8	.67	.42	.65	2.18	.298	.0044
190	974	8	.67	.42	.47	2.18	.22	.0032
191	974	6	.78	.42	.52	1.4	.37	.00476
192	974	6	.78	.41	.32	1.4	.24	.00312
193	974	8	.78	.42	.46	1.9	.25	.00352
194	974	8	.75	.4	.53	1.9	.28	.0038
195	974	8	.72	.4	.55	1.9	.29	.0041
200	974	15	.72	.28	.73	2.5	.29	.00405
208	976	7	1.0	.32	.5	1.17	.43	.00426
209	976	8	1	.34	.5	1.21	.41	.00416
22	977	3	.5	.58	.4	1.45	.27	.00524
173	977	8	.8	.59	1.02	2.41	.43	.0051
184	977	8	.77	.31	.52	1.43	.37	.0048
202	977	10	.78	.28	.67	1.52	.43	.0055
203	977	11	.78	.25	.72	1.53	.47	.0061
204	977	14	.78	.28	.9	2.14	.42	.0054
205	977	10	.72	.31	.65	1.86	.35	.00483
206	977	6	1.0	.3	.4	.78	.52	.00515

Run	Temp. °K	Durn. mins	T.of C secs.	P.Press. Fluorene mms	H_2 mols.x10^{-5}	Fluorene mols.x10^{-3}	% Dec.	k $secs^{-1}$
207	977	6	1	.3	.43	.88	.49	.00486
86	982	5	.7	.37	.53	1.13	.47	.0066
87	982	5	.7	.35	.53	1.13	.47	.0066
88	982	3½	.72	.38	.3	.75	.40	.00565
89	983	4	.7	.38	.41	.92	.45	.00635
90	983	3½	.7	.38	.4	.81	.46	.0066
23	986	4	.66	.6	.65	1.53	.43	.00616
48	986	4½	.55	.67	1.025	2.4	.43	.00776
49	990	5	.48	.59	.78	2.54	.31	.00645
174	990	8	.83	.38	.9	1.57	.57	.00695
175	990	9	.83	.35	.93	1.6	.57	.00695
176	990	10	.83	.30	.8	1.54	.52	.00633
177	990	10	.83	.32	1.0	1.83	.55	.00662
178	990	10	.83	.31	.93	1.61	.57	.00695
179	990	9	.83	.30	.78	1.43	.54	.00656
180	990	10	.77	.33	.98	1.77	.55	.00717
181	990	9	.77	.32	.73	1.55	.47	.00609
182	990	5	.77	.25	.43	.75	.57	.00744
183	990	6	.77	.25	.44	.87	.5	.00655
24	992	3	.8	.73	.95	1.25	.76	.00955
91	993	3	.75	.37	.45	.63	.715	.0096
92	993	3	.75	.38	.4	.66	.61	.00798
93	993	3	.75	.38	.4	.68	.59	.00765

Run	Temp. °K	Durn. mins.	T.of C secs.	P.Press. Fluorene mms	H_2 mols.x10^{-5}	Fluorene mols.x10^{-3}	% Dec.	k secs^{-1}
94	995	3	.7	.38	.43	.68	.62	.00885
50	997	4	.5	.45	.65	1.51	.43	.0087
24a	1000	4½	.55	.51	1.00	1.75	.58	.0106
95	1000	6	.7	.38	1.05	1.41	.75	.0106
25	1003	4	.42	.32	.75	1.22	.62	.0149
51	1002	4	.47	.46	.75	1.63	.46	.00995
52	1002	3	.48	.43	.58	1.12	.52	.0108
26	1005	4	.42	.28	.65	1.06	.61	.0146
53	1007	4	.48	.43	.82	1.49	.56	.0118
54	1008	3	.48	.40	.73	1.02	.71	.0150
27	1009	4	.42	.27	.58	1.02	.57	.0136
28	1012	4	.41	.27	.53	1.04	.51	.0126
55	1012	3	.46	.38	.75	1.01	.74	.0160
56	1014	3	.46	.37	.83	.99	.84	.0173
29	1016	4	.52	.27	.70	.98	.72	.0162
57	1016	3	.46	.37	.73	.99	.73	.0159
220	1016	3	.48	.40	1.15	1.44	.8	.0168
58	1018	3	.44	.37	.76	1.02	.76	.0174
59	1019	3½	.44	.37	.90	1.17	.77	.0176
221	1019	4	.47	.31	1.17	1.16	1.01	.0214
222	1019	4	.47	.38	1.45	1.4	1.03	.0214
223	1019	4	.46	.39	1.37	1.5	.95	.0208
224	1019	4	.46	.3	1.13	1.1	1.03	.0218

Run	Temp. °K	Durn. mins.	T.of C secs.	P.Press. Fluorene mms	H_2 mols.x10^{-5}	Fluorene mols.x10^{-3}	% Dec.	k secs^{-1}
225	1019	4	.46	.385	1.4	1.4	1.0	.0218
226	1019	4	.46	.25	.88	.89	.99	.0216
227	1019	3	.46	.23	.68	.68	1.0	.0218
228	1019	3	.46	.22	.48	.61	.78	.0170
229	1019	5	.46	.21	.85	.98	.87	.0190
60	1020	3	.44	.36	.9	.99	.91	.0208
230	1020	3	.5	.20	.53	.52	1.02	.0204
231	1020	3	.5	.2	.53	.58	.91	.0185
232	1020	5	.48	.28	1.33	1.28	1.03	.0216
233	1020	3	.48	.2	.53	.55	.96	.020
234	1020	3	.48	.2	.55	.55	1	.0209
235	1020	3	.48	.2	.55	.55	1	.0209
236	1020	4	.49	.2	.55	.74	.75	.0159
237	1020	6	.47	.2	1.025	1.11	.92	.0196
238	1020	9	.37	.13	1.28	1.49	.85	.0230
239	1026	9	.33	.13	1.02	1.43	.72	.0218
240	1026	3	.67	.26	.87	.47	1.86	.0242
241	1026	3	.62	.27	.55	.50	1.10	.0183
242	1026	3	.62	.28	.58	.52	1.10	0.183
243	1026	3	.68	.58	1.93	1.1	1.70	.0240
30	1034	5	.43	.26	1.7	1.2	1.40	.0335
8	1039	13¼	.12	.28	1.4	.98	1.43	.0353
12	1039	4	.29	.18	1.05	1.06	1.10	.0344

Run	Temp. °K	Durn. mins.	T.of C. secs.	P.Press. Fluorene mms.	H_2 mols.x10^{-5}	Fluorene mols.x10^{-3}	% Dec.	k secs^{-1}
14	1039	5	.44	.29	2.0	1.35	1.54	.0339
15	1039	5	.44	.28	2	1.27	1.58	.0360
16	1039	5	.32	.18	1.3	1.3	1.00	.0312
31	1039	4	.41	.24	1.23	.95	1.30	.0318
61	1039	3½	.34	.18	1.1	.79	1.39	.0410
6	1040	5	.44	.30	2.1	1.37	1.55	.0352
7	1040	4	.43	.30	1.2	1.05	1.09	.0249
11	1040	4	.29	.19	1.05	1.06	1.00	.0344
12	1040	4	.29	.18	1.05	1.06	1.00	.0344
5	1041	5	.45	.32	2.2	1.41	1.56	.0348
9	1041	17	.10	.30	1.6	1.1	1.45	.0325
10	1041	6½	.22	.21	1.2	1.4	.87	.0380
1	1042	5	.33	.34	2.9	2.2	1.34	.0407
2	1042	5	.33	.34	2.3	2.0	1.15	.0348
3	1042	5	.31	.31	1.9	1.86	1.00	.0324
4	1042	5	.33	.31	2.3	1.83	1.23	.0374
62	1042	3½	.34	.18	1.08	.79	1.36	.0398
252	1043	3	.35	.19	1.06	.71	1.50	.0430
32	1044	4	.40	.23	1.5	.92	1.63	.0414
63	1044	4½	.34	.18	1.47	1.01	1.45	.0425
253	1045	5	.38	.2	1.96	1.09	1.80	.0472
254	1045	5	.35	.19	1.68	1.1	1.53	.044
255	1045	5	.36	.19	1.75	1.08	1.62	.045
256	1045	5	.37	.21	2.2	1.16	1.90	.0515

Run	Temp. °K	Durn. mins.	T.of C. secs.	P.Press. Fluorene mms	H_2 mols.x10^{-5}	Fluorene mols.x10^{-3}	% Dec.	k $secs^{-1}$
64	1046	3½	.34	.18	1.2	.79	1.45	.0425
257	1047	8	.38	.21	3.6	1.81	2.00	.052
258	1049	5	.38	.20	2.5	1.14	2.19	.060
259	1049	6	.38	.16	2.3	1.07	2.12	.056
260	1049	6	.38	.16	1.88	1.06	1.77	.047
265	1049	4	.65	.27	2.2	.66	3.30	.0519
266	1049	4	.83	.3	1.8	.58	3.02	.0485
267	1049	5	.83	.3	2	.69	2.90	.0478
33	1050	3½	.28	.15	1.18	.75	1.57	.057
66	1050	4	.34	.43	3.18	2.1	1.55	.0445
261	1050	6	.38	.13	1.5	.83	1.81	.0480
262	1050	7	.38	.15	2.3	1.18	1.97	.0522
263	1050	4	.42	.19	1.68	.7	2.40	.0577
264	1050	3	.42	.18	1.27	.5	2.5	.0605
268	1050	4	1.74	.32	2.58	.281	9.2	.0554
269	1050	4	1.37	.43	3.05	.48	6.4	.0480
270	1050	5	1.37	.4	3.25	.52	6.3	.0475
65	1052	4	.38	.48	4.3	2.18	2.0	.0540
67	1052	7	.31	.48	6	4.05	1.5	.0490
34	1057	3½	.3	.15	1.63	.75	2.16	.0726
68	1060	4½	.37	.28	3.25	1.4	2.32	.0630
69	1063	9	.37	.23	6.75	2.34	2.88	.0786
35	1065	4	.3	.15	1.83	.82	2.23	.0755

Run	Temp. °K	Durn. mins.	T.of C. secs.	P.Press. Fluorene mms	H_2 mols.x10^{-5}	Fluorene mols.x10^{-3}	% Dec.	k secs^{-1}
36	1068	4	.31	.15	1.85	.82	2.26	.0755
70	1073	7	.36	.2	6	1.58	3.8	.107
71	1074	4	.34	.18	2.65	.86	3.08	.093
38	1076	3	.31	.15	1.9	.58	3.3	.109
39	1076	3	.31	.15	1.8	.58	3.12	.103
72	1076	4	.35	.18	2.83	.86	3.3	.096
73	1076	4	.35	.17	2.83	. 8	3.54	.103
74	1077	3	.35	.16	2.25	.55	4.1	.119
75	1077	5	.35	.16	3.95	.93	4.25	.126
40	1078	3	.31	.15	1.8	.59	3.05	.105
41	1078	3	.29	.16	2.1	.64	3.24	.112
42	1078	3½	.38	.15	2.4	.5	4.8	.128
96	1081	7	.32	.12	5.1	1.1	4.6	.141
99	1081	11	.31	.11	7.8	1.75	4.5	.149
100	1081	6	.31	.12	4.5	1.02	4.5	.146
101	1081	7	.31	.12	4.4	1.2	3.68	.111
102	1081	8	.33	.11	5.9	1.1	5.2	.155
103	1081	6	.33	.12	3.9	.89	4.4	.138
104	1081	8	.33	.11	5.2	1.2	4.5	.142
121	1081	5	.33	.23	6.1	1.47	4.2	.120
122	1081	5	.33	.20	4.9	1.21	4.05	.118
123	1081	6	.34	.16	5.2	1.13	4.5	.133
124	1081	5	.33	.18	4.3	1.07	4.0	.124
125	1081	6	.33	.18	4.9	1.34	3.7	.118

Run	Temp. °K	Durn. mins.	T.of C. secs.	P.Press. Fluorene mms.	H_2 mols.x10^{-5}	Fluorene mols.x10^{-3}	% Dec.	k secs^{-1}
126	1081	6	.37	.17	5.5	1.11	4.95	.135
127	1081	6	.38	.17	4.9	1.06	4.6	.126
128	1082	6	.31	.14	4.6	1.03	4.45	.147
129	1082	6	.32	.14	3.9	1.03	3.8	.122
136	1082	6	.34	.09	2.8	.59	4.7	.143
97	1084	5	.31	.1	5.2	.69	7.5	.234
135	1085	6	.32	.075	2.9	.57	5.1	.155
130	1086	6	.32	.125	4.1	.96	4.25	.144
131	1086	6	.32	.15	4.6	1.1	4.23	.133
132	1086	6	.33	.11	3.95	.81	4.85	.151
133	1086	8	.32	.1	3.88	.99	3.93	.123
134	1087	7	.33	.09	3.13	.75	4.2	.125
172	1095	6	.28	.1	4.03	.9	4.5	.164
171	1097	3	.28	.09	2.2	.41	5.35	.196
169	1098	3	.29	.096	2.6	.4	6.5	.228
170	1098	3	.29	.095	2.0	.37	5.4	.188
154	1099	3	.26	.1	2.7	.43	6.25	.256
155	1099	3	.26	.16	3.6	.04	5.6	.222
156	1099	3	.26	.1	2.33	.43	5.4	.224
157	1099	3	.26	.1	2.33	.43	5.4	.214
158	1099	3	.26	.1	2.98	.44	6.75	.268
159	1099	4	.26	.1	3.55	.57	6.3	.251
160	1099	3	.27	.1	2.2	.44	5.0	.193
161	1099	3	.26	.1	2.15	.42	5.1	.214
162	1099	3	.26	.1	2.25	.42	5.4	.222

Run	Temp. °K	Durn. mins.	T.of C. secs.	P.Press. Fluorene mms.	H_2 mols.x10^{-5}	Fluorene mols.x10^{-3}	% Dec.	k secs.$^{-1}$
165	1099	3	.26	.1	2.33	.43	5.4	.215
166	1099	3	.26	.09	2.2	.40	5.5	.226
167	1099	3	.26	.11	2.8	.46	6.1	.245
168	1099	5	.26	.11	4.8	.78	6.2	.246
163	1101	5	.28	.1	4.7	.72	6.5	.238
164	1101	3	.29	.095	2.6	.39	6.6	.234

Experiments on Tetraphenylethane

Run	Temp. °C	T.ofC. secs.	Tetraphenyl ethylene mols x 10^{-5}	Fluorene mols x 10^{-5}	Tetraphenyl ethane mols x 10^{-5}	% Dec.	k
1	750	0.7	1.1	27.2	47.2	29	.468
2	705	0.66	0.24	21	107	10	.159
3	710	0.55	0.33	53	256	10.3	.198
4	635	0.7	0.06	4.5	101	2.2	.0314

Note: The percentage decomposition is calculated by:

$$\frac{\frac{1}{2}\text{ No. of mols. of fluorene}}{\text{No. of mols. of tetraphenylethane.}}$$

since in the decompostion of each molecule of tetraphenylethane two benzhydryl radicals are formed.

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