STUDIES IN PYROLYSIS

PART I

Kinetics and Mechanism in the Pyrolysis of Vinyl Benzoate

PART II

Mechanism of Pyrolytic Production of Benzaldehyde from 2-Phenoxyethyl Acetate

A thesis submitted to the University of Glasgow in accordance with the regulations governing the award of the degree of Doctor of Philosophy

by

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SUMMARY

Part I

A study has been made of the vapour phase pyrolysis of vinyl benzoate. Vinyl benzoate is a model compound for the study of end-groups formed during the pyrolysis of Terylene, poly(ethylene terephthalate).

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The catalytic decomposition of vinyl benzoate in the

presence of metals (Sn, Pb, Cd, Bi) has been studied. An apparatus has been designed by means of which low-melting metals were fed dropwise into the flow reactor at a desired feed-rate, simultaneously with the liquid ester. In general the metal increased the pyrolysis in the following order:

$$Sn > Pb > Cd > Bi$$

Sn is the most effective, increasing the total pyrolysis by ca. 4%.

Part II

In the second part of the thesis evidence has been sought to explain the known unexpected formation of benzaldehyde on pyrolysis of 2-phenoxyethyl acetate. A model compound 1,2-diphenoxyethane has been pyrolysed and a reaction scheme devised which adequately accounts for the products. A free radical mechanism for the production of benzaldehyde is postulated.

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Mechanism of Thermal Decarbonylation of Vinyl Carboxylates (P.D. Ritchie and A.H.K. Yousufzai)

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CONTENTS

Preface Page

PART I

PART II

PART I

Kinetics and Mechanism in the Pyrolysis of Vinyl Benzoate

PART I

1. INTRODUCTION

Within the last twenty years polymeric materials have assumed an ever-increasing commercial importance. The most serious disadvantage of organic polymers as constructional materials is their inability to withstand quite moderate service temperatures. Most of these materials have a ceiling operating temperature in the region of 250°C. It is thus extremely important to study the thermal breakdown of polymers with a view to elucidation of the pyrolysis mechanism. If this mechanism were known, an attempt might be made to modify the structure of the polymer in such a way as to increase its thermal stability, or to inhibit decomposition by the incorporation of stabilisers.

Pyrolysis of organic compounds has been a notable field of research for a number of years, and the qualitative nature of the degradation process of many substances is now well established [1]. In these laboratories Ritchie *et al.* [2,3] have made a systematic study of the thermal decomposition of poly(ethylene fumarate) and its cross-linked derivatives, and also of the commercially important polyester terylene, poly(ethylene terephthalate). It was soon realised that the pyrolysis of these compounds led to complex results, owing to the diversity of the products obtained. It was decided, therefore, to investigate the pyrolysis of various model compounds which could be regarded as representing fragments of the original polymer chain, or products of its primary degradation. Hence the investigations have been concerned in the main with simple esters, rather than the polyesters. The pyrolysis of the simple esters themselves led to a diversity of results. A brief summary of the most important ester breakdown routes is given below.

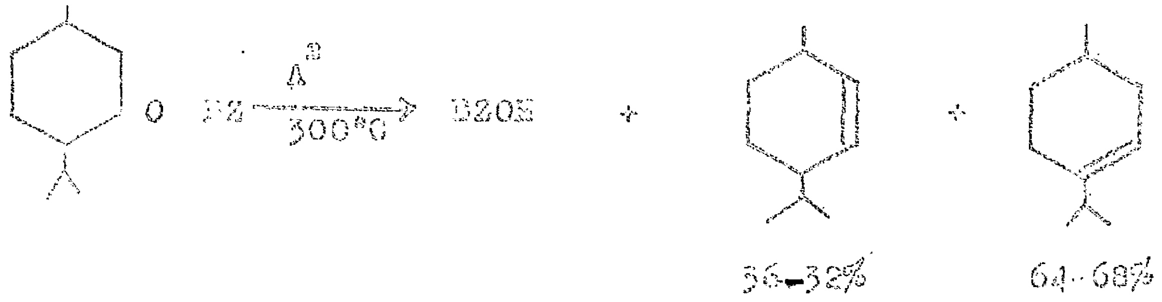
1.1. The Pyrolysis of Esters.

It is known that alkyl esters pyrolyse to give an acid and an olefin [4]. This route may be represented by the following scheme.

$$\underset{\text{ester}}{R.CO_2.CH_2.CH_2.R'} \longrightarrow \underset{\text{acid}}{R.CO_2H} + \underset{\text{olefin}}{CH_2{:}CHR'}$$

It was originally thought that ester-breakdown occurred by one route only, and in fact ester pyrolysis was recognised as a method of olefin preparation. It was not realised at first that this route could be accompanied by other competing routes. However, with the advent of better analytical techniques, notably gas chromatography, it has been shown that esters may breakdown by a number of routes, and although the above equation represents a reaction of primary importance it need not be the major route in any particular case, and may sometime, in fact, be structurally precluded.

Several examples are now known of esters which breakdown by more than one route: for example, allyl acetate decomposes by at least two primary routes [5], phenyl acrylate by four [6], and isopropenyl acetate by five [7]. Moreover, there are examples in the literature of esters decomposing by one route only. Barton [8] has shown that (−)-menthyl benzoate pyrolyses by one route only, though here two isomeric olefins are formed along with free carboxylic acid.



Nair [9] found that under similar conditions cyclohexyl benzoate pyrolyses to give benzoic acid and cyclohexene only: but in the presence of Wood's metal and its components, as catalysts, it also gives several other compounds including diphenyl, benzaldehyde, and cyclohexanone.

In addition to these primary routes, secondary and even tertiary breakdown of the original primary products can occur. The number of routes, and the extent to which each occurs, will depend on a large number of independent factors, such as polarity of substituents, number of available point of scission, weak points in the molecule, and steric factors. Increase in temperature and catalysis may also alter the reaction scheme. Carbonisation was at one time thought to affect the pyrolysis [10], though more recent work by Bailey [11] and Royals [12] has shown that this has very little effect. However, in the present work, the reactor was decarbonised before each run in order to eliminate any possible effects of this variable. As a result of extensive work on pyrolysis of esters, Ritchie _et al._ [2, 3, 13] have classified the general modes of thermal breakdown, and a nomenclature has been developed. A brief description is given below.

1.1.1. Alkyl-oxygen and Alkenyl-oxygen Scission. Route A

This general reaction involves rupture of the bond between oxygen and the alkyl or alkenyl group. The alkyl-oxygen type may be subdivided depending upon the presence or absence of β-hydrogen atom in the alkyl group thus:

$$R.CO_2.CH< \longrightarrow R.CO_2H + \tfrac{1}{2}\ >C{:}C< \qquad \ldots\ldots\ldots\ldots A^0$$

$$R.CO_2\ C.CH< \longrightarrow R.CO_2H + >C{:}C< \qquad \ldots\ldots\ldots\ldots A^1$$

Methyl acetate lacking a β-hydrogen atom breaks down in part by A° scission to give acetic acid and ethylene [14].

$$CH_3.CO_2CH_3 \longrightarrow CH_3.CO_2H + \tfrac{1}{2}\ CH_2{:}CH_2 \qquad \ldots\ldots\ldots\ldots\ A^{\circ}$$

Ethyl acetate, on the other hand, breaks down mainly to give acetic acid and ethylene by A¹ scission [4,16].

$$CH_3.CO_2C_2H_5 \longrightarrow CH_3.CO_2H + CH_2{:}CH_2 \qquad \ldots\ldots\ldots\ldots\ A^{1}$$

The alkenyl-oxygen type occurs as follows:

$$R.CO_2.\overset{|}{C}{:}\overset{|}{C}H \longrightarrow R.CO_2H + -C{\vdots}C- \qquad \ldots\ldots\ldots\ldots\ A^{2}$$

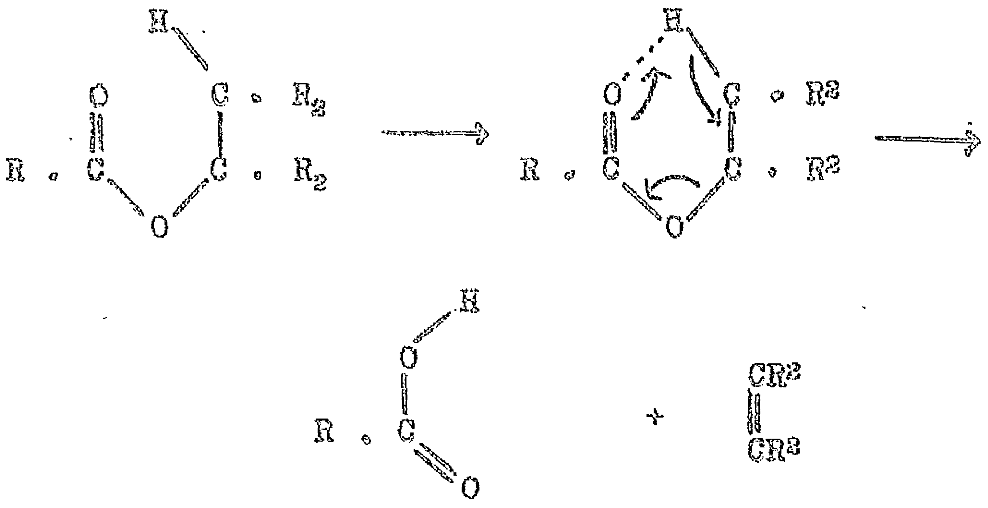
Thus, vinyl benzoate can breakdown by A² scission to give benzoic acid and acetylene [3].

$$C_6H_5.CO_2.CH{:}CH_2 \longrightarrow C_6H_5.CO_2H + CH{\vdots}CH \qquad \ldots\ldots\ldots\ldots\ A^{2}$$

A¹ scission in esters is the most important single classical route. It involves the rupture of the carbon-oxygen bond and proton transfer. The scission requires the presence of a β-hydrogen in the alkyl group of the molecule.

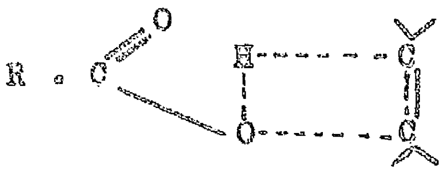
The reaction was first reported by Heintz [15](for ethyl acetate), and later by Oppenheim and Precht [4]. Still later, Hurd and Blunck [16] studied the A¹ scission process in detail in tertiary alkyl formates and acetates, and proposed a scheme of esters breakdown involving hydrogen bridges.

Esters possessing a β-hydrogen atom would undergo a chelate type of 6-atom ring closure, *via* a hydrogen bridge. Electron rearrangement would lead to acid and olefin, as follows:



They rejected, however, a radical chain mechanism, because this called for more products than were found experimentally.

Several other mechanisms have been put forward notably one by Warrick and Fugassi [17], who proposed that the transition state could be regarded as a pseudo four-centre system of the type:



Blades [18] did not find any evidence of a free radical process on pyrolysing various esters using the toluene flow-technique.

However, the six-membered ring intermediate proposed by Hurd and Blunck [16] is now fairly generally accepted.

It is known that two rules govern elimination reactions in general. The Hofmann rule [19] states that the elimination of olefin from a quaternary ammonium hydroxide will lead to preferential formation of that olefin carrying the smallest number of attached alkyl groups, while the Seytzeff rule [20] states that elimination will lead to the preferential formation of that olefin carrying the largest number of attached alkyl group. This rule has been found to apply to elimination reactions of secondary and tertiary alkyl bromides [20].

For an unsymmetrical branched-chain ester, two different olefins can be produced by A^1 scission. Houtman, Van Steenis, and Heertjes [10] found that on pyrolysis of *S*-butyl acetate two olefins were produced thus:

$$\mathrm{AcO{\cdot}CHMe.CH_2.CH_3} \xrightarrow{500^\circ\mathrm{C}} \mathrm{AcOH} + \tfrac{1}{2}\ \underset{56\%}{\mathrm{CH_3.CH_2.CH{:}CH_2}}$$

$$+ \tfrac{1}{2}.\ \underset{44\%}{\mathrm{CH_3.CH{:}CH.CH_3}}$$

Bailey and King [22] concluded that gas-phase eliminations in general are governed by the Hofmann rule. However, later workers [12, 33, 24] showed that Bailey's work was in error, and subsequently Bailey and Hale [11] themselves could not reproduce their own previous results.

Maccoll [18], in a discussion of published results, showed that A^1 elimination reactions could be thought of as quasi-heterolytic, and compared the reaction with the E_2 mechanisms operating in solutions. He also showed that the relative rates of decomposition to acid and olefin for ethyl, isopropyl, and t-butyl acetates are in the ratio of 1:26:515, and 1:20:720 for the corresponding formates which indicates that the thermal stability of alkyl esters is not strongly dependent upon the nature of the parent carboxylic acid. Maccoll concludes that the reaction is best considered as a nucleophilic attack of the oxygen on the β-hydrogen atom, and that it is the forming of the O-H bond which determines the rate and not the breaking of the alkyl-oxygen bond. Although Maccoll upholds the Hofmann theory, which Ingold has shown to imply inductive control of the reaction, several more recent papers have questioned the specificity of direction of eliminations.

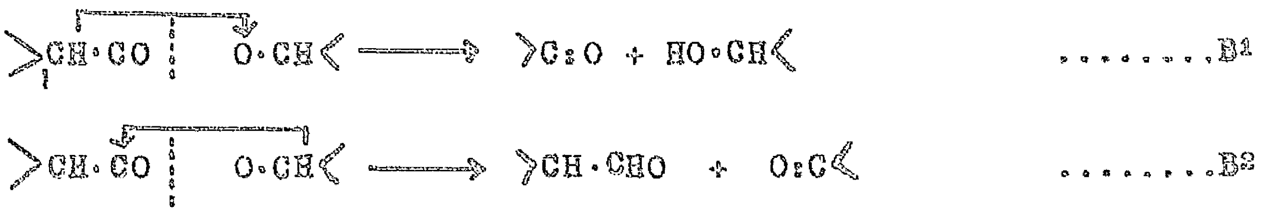
In view of these conflicting results no firm conclusions have been drawn here regarding this specificity.

Where no β-hydrogen is available, A° scission occurs, to a minor extent. High temperatures are required for such reactions which probably occurs by a radical mechanism. Hurd [16] suggests that the stability of methyl esters is due to their inability to form a six-membered cyclic transition state.

A^2 type scission may be compared with alkyl-oxygen scission of saturated esters (A^2). It is probable that the mechanism suggested by Hurd and Blunck for A' scission applies also to A^2 scission.

1.1.2. Acyl-oxygen Scission. - Route B.

This class of reaction can be subdivided into two categories, B^1 and B^2, since a hydrogen atom can migrate from either of two sites leading to two different pairs of products, as shown below:



$$>CH\cdot CO \;\vdots\; O\cdot CH< \;\longrightarrow\; >C{:}O + HO\cdot CH< \qquad \ldots\ldots\ldots B^1$$

$$>CH\cdot CO \;\vdots\; O\cdot CH< \;\longrightarrow\; >CH\cdot CHO + O{:}C< \qquad \ldots\ldots\ldots B^2$$

In the absence of a β-hydrogen atom, alkyl-oxygen scission is precluded, and a route B is normally predominant, yielding either two carbonyl compounds or an alcohol and a keton. The latter is normally a very minor route.

An example of B^1 scission is provided by the decomposition of phenyl acetate [16], thus:

$$CH_3.CO_2Ph \xrightarrow{625^\circ C} CH_2{:}CO + PhOH \qquad \ldots\ldots\ldots B^1$$

Methyl acetate decomposes at 1100°C by B^2 scission to give the following products [14]:

$$CH_3.CO_2CH_3 \xrightarrow{1100^\circ C} [\underset{\substack{\downarrow \\ \text{Secondary products}}}{CH_3.CHO} + H.CHO]$$

Benzyl benzoate breaks down by B^2 scission to give benzaldehyde thus [25]:

$$BzO.CH_2.Ph \longrightarrow 2\ Ph.CHO \qquad \ldots\ldots\ldots B^3$$

Generally, however, an ester must be subjected to higher temperatures before acyl-oxygen scission can be induced.

1.1.3. Decarbonylation: Route C^1

Loss of carbon monoxide (i.e. decarbonylation), is normally a reaction more characteristic of aldehydes and ketones than of esters. However, there are examples of ester decarbonylation in the literature. These have involved either esters containing an aldehydic or ketonic group, or esters undergoing decarbonylation as a secondary reaction, having first undergone primary rearrangement to a labile aldehydic or ketonic intermediate.

Phenyl formate [26] provides a simple example of ester decarbonylation. The formation of carbon monoxide and phenol from phenyl acrylate [6] depends on primary formation of phenyl formate, which then breaks down as mentioned above:

$$CH_2{:}CH.CO_2Ph \longrightarrow CH{\vdots}CH + \underset{\displaystyle CO + PhOH}{\underset{\Downarrow}{[H.CO_2Ph]}}$$

Ritchie et al. [2] have shown that in the case of vinyl esters, the decarbonylation proceeds by way of primary rearrangement to a β-keto-aldehyde, which then predictably loses carbon monoxide. Decarbonylation of an α-keto-ester has been studied by Calvin and Lemmon [68], who pyrolysed a ^{14}C-labelled ethyl pyruvate (^{14}C α-carbonyl group) and established the surprising result that the eliminated carbon monoxide originated in the ester grouping and not the α-keto-group thus:

$$CH_3.^{14}CO.CO_2Et \longrightarrow CO + {}^{14}C\text{-products}$$

No mechanism has yet been proposed to account for this unexpected mode of breakdown.

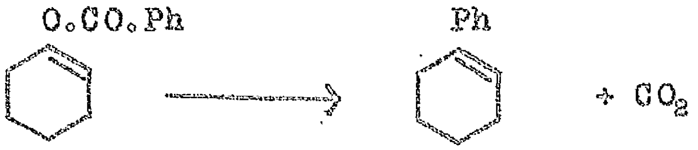
1.1.4. Decarboxylation: Route C^2

Though the thermal decarboxylation of acids is common, ester decarboxylation was until recently an infrequently recorded mode of thermal decomposition.

Anschütz [67] observed this reaction as early as 1885 during the pyrolysis of phenyl maleate (or fumarate):

$$PhO_2C.CH:CH.CO_2Ph \longrightarrow Ph.CH:CH.Ph + CO_2 \qquad ....C2$$

Allan, McGee and Ritchie [7] found that decarboxylation (ca. 10%) competes in the complex pyrolysis of cyclohex-1-enyl benzoate at 500°C



..........C2

Similarly, phenyl acrylate [6] yields styrene and carbon monoxide among other competing reactions:

$$CH_2:CH.CO_2Ph \xrightarrow{500°C} CO_2 + CH_2:CHPh$$

Vinyl benzoate, which is isomeric with phenyl acrylate, also yields similar products among other competing reactions [2].

In general, decarboxylation reaction occurs only in an ester $R.CO_2R'$ where R and or R' show either aliphatic or aromatic unsaturation. A complex example was noted by Bennett, Jones, and Ritchie [28], who found that α:α'-dicyanobenzyl benzoate undergoes decarboxylation (ca. 20%) in competition with other modes of breakdown.

This has been explained as due to the influence of the unsaturated $C\vdots N$ group:

$$\mathrm{PhCO_2.CPh.(CN)_2 \longrightarrow CPh_2(CN)_2 + CO_2 \quad \ldots\ldots\ldots\ldots C^2}$$

$$+ \text{ other competing routes}$$

1.1.5. <u>Disproportionation:</u> <u>Route D</u>

This is most commonly found in unsymmetrical esters, and leads to compounds of greater symmetry. Cretcher and Pittenger [29] demonstrated this phenomenon for a half-ester of ethylene glycol. The reaction may be written down as:

$$\mathrm{2\ Ar.CO_2.CH_2.CH_2.OH \longrightarrow Ar.CO_2.CH_2.CH_2.CO_2Ar}$$

$$\mathrm{+\ HO.CH_2.CH_2.OH \quad \ldots\ldots\ldots\ldots D}$$

Another example has been recorded in these laboratories [5] in the pyrolysis of methylene dibenzoate:

$$\mathrm{BzO.CH_2.OBz \longrightarrow Bz_2O + CH_2O \quad \ldots\ldots\ldots\ldots D}$$

1.1.6. <u>Rearrangement:</u> <u>Route R.</u>

From the point of view of the present work, the most important example is the thermal rearrangement of αβ-unsaturated esters to their isomeric β-diketones, first reported by Wislicenius[30] in 1905.

It may be represented thus:

$$\mathrm{RCO_2.\ CR':CHR'' \longrightarrow R.CO.CHR''.CO.R'}$$

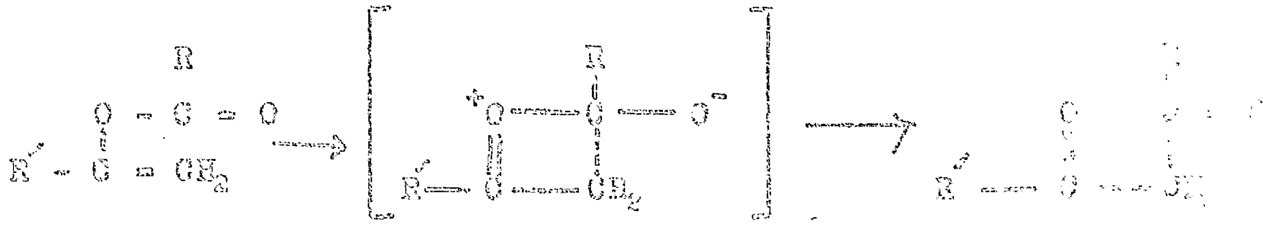
This was confirmed by Young *et al.* [30]

They also demonstrated that the enol benzoate of aceton

can be converted to benzoyl acetone, as follows:

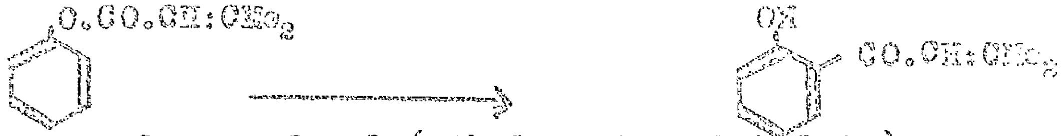
$$Ph.CO_2.CMe{:}CH_2 \xrightarrow{500°C} Ph.CO.CH_2.CO.CH_3 \quad ....$$

They postulated a mechanism involving a four-centred cyclic transition state:



This concept has been applied [2] to the case of vinyl benzoate and is discussed later. Other ester rearrangements are known, e.g. the Fries rearrangement brou about by a catalyst.

A similar purely thermal rearrangement has been described by Skraup and Beng [32].



1.2 The Pyrolysis of Poly(ethylene terephthalate).

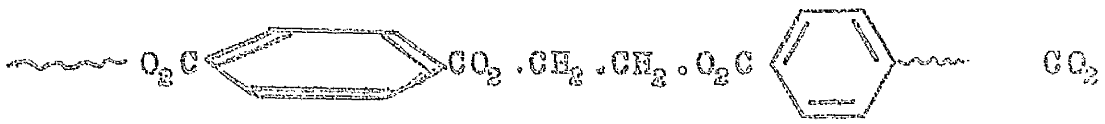
Pohl [25] studied the thermal degradation of poly(ethylene terephthalate) by measuring the rate of gas-evolution from the polymer at 300°C and concluded that random chain scission was occurring, with progressive reduction in molecular weight. The pyrolysate contained acetaldehyde, water, and carbon monoxide; and in addition carboxyl and anhydride groupings were detected. Pohl suggested that the β-methylene groups were the weak points in the molecule.

Marshall and Todd [34] studied the degradation kinetics of poly(ethylene terephthalate) by following the change in melt-viscosity of the polymer around 300°C; and they also deduced that random chain-scission was occurring, probably at the ester linkages, producing one carboxyl group per scission. They found that the overall activation energy is 32 K.cal mole and that pyrolysis is accelerated by oxygen. They found acetaldehyde carbon monoxide, carbon dioxide, terephthalic acid in the pyrolysate together with an unidentified solid thought to be a mono-alkyl ester or an acid dimer. They tentatively postulated a free radical mechanism.

Goodings [35] isolated small amounts of coloured material from the pyrolysate of poly(ethylene terephthalate) in an attempt to explain the unwanted colour produced during the manufacture of terylene at or above 250°C and demonstrated that the presence of acetaldehyde increased the rate of decomposition. He selected ethylene dibenzoate as a model compound for the pyrolysis of poly(ethylene terephthalate).

The same model was amongst those previously selected by Ritchie et al. [2, 3, 36] in a systematic study of the pyrolysis of poly (ethylene terephthalate). Preliminary work in these laboratories showed that pyrolysis of the polymer itself leads to great diversity of products. To simplify the problem, attention was therefore turned to model compounds representing a segment of the intact polyester chain, or a primary pyrolysis product. This method proved very successful in explaining the general nature of the pyrolysis of terylene [2, 3, 36, 37].

Model compounds were selected by consideration of the structure of the polymer:



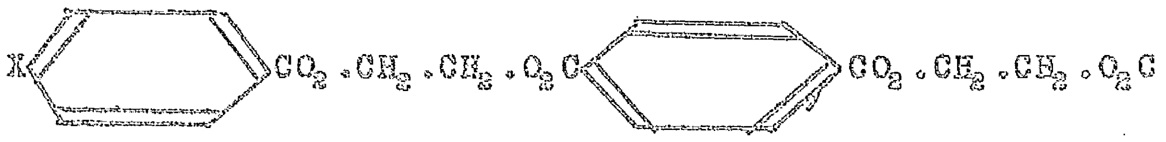
It was thought probable that the known A^1 scission of simple alkyl esters would also occur in this polyester, with the formation of vinyl ester end-groupings. Preliminary work failed, however, to reveal such end-groupings in the pyrolysate: and later studies with molten polyester [38] at 340° and 450-475°C showed that carbon monoxide, acetaldehyde, and terephthalic acid were the major products of pyrolysis, with smaller amounts of anhydrides, benzoic acid, *p*-acetylbenzoic acid, acetophenone, vinyl benzoate, an uncharacterised ketonic substance, water, methane, ethylene, and acetylene. To assist the interpretation of these complex results attention was turned to the following model compounds:

$BzO.CH_2.CH_2.OBz$

(I)

$BzO.CH_2.CH_2.O.CH_2.CH_2.OBz$

(II)



(III; X = H or Cl)

$BzO.CH_2.CH_2.OH$

(IV)

$BzO.CH{:}CH_2$

(V)

Models I and III clearly represent simple repeat-segments from within the intact polyester chain. Model II was selected because of the known unavoidable incorporation of occasional ether-linkages into the chain during poly condensation by way of ethylene glycol units. Model IV represents an end-group containing a half-esterified ethylene glycol molecule, while model V represents the vinyl ester end-group which would be formed by primary A¹ scission of the chain.

The pyrolysis of ethylene dibenzoate (model I) at 360–425°C can be represented by [39, 40]:

$$\mathrm{Ph.CO_2.CH_2.CH_2.O_2C.Ph}$$

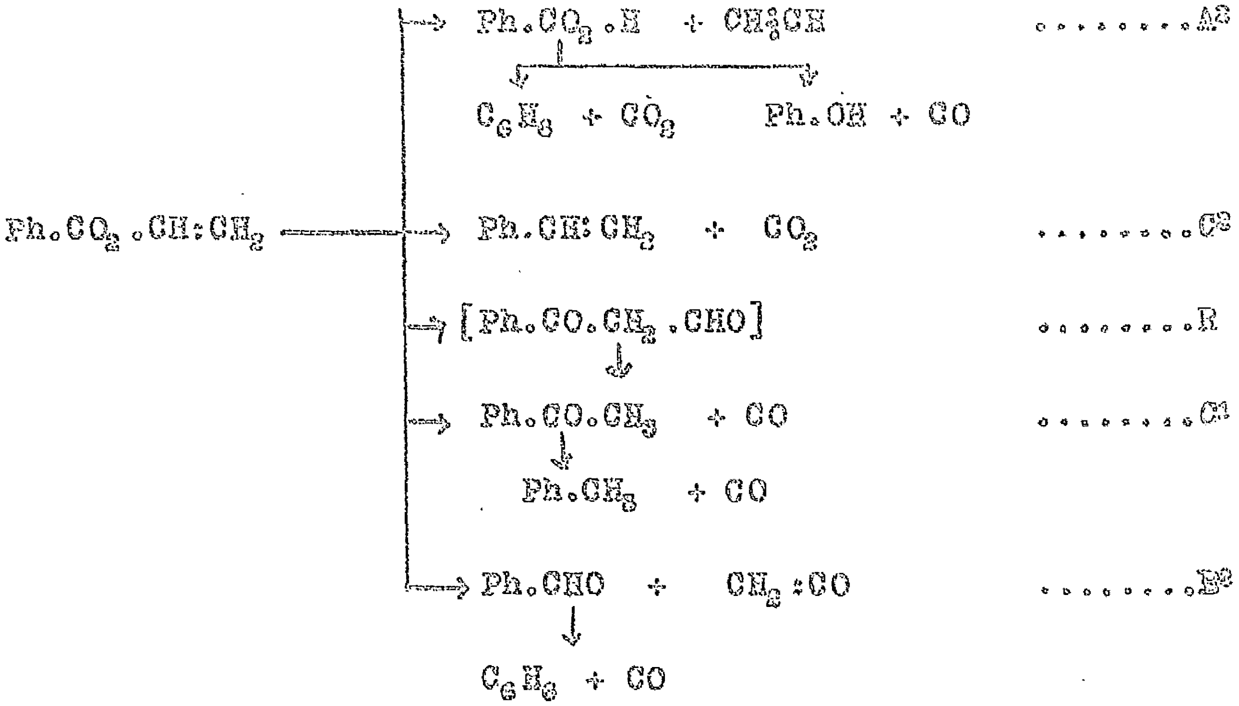
$$\Big\downarrow A^1$$

$$\mathrm{Ph.CO_2H \quad + \quad Ph.CO_2.CH{:}CH_2}$$

It is clear that the vinyl benzoate produced on A¹ scission from model I suitably represents the vinyl ester end-group expected on A¹ scission of the polyester itself. This suggests that a study of the pyrolysis of vinyl benzoate should prove a major tool in interpreting the complex pyrolysis of terylene. Previous work on pyrolysis of vinyl benzoate is discussed below. Details of the pyrolysis of other model compounds is given [3] by Ritchie *et al.*

1.3. Pyrolysis of Vinyl Benzoate

Allan, Forman, and Ritchie [2] have shown that vinyl benzoate pyrolyses by three competing routes in the temperature range of 350–450°C. Later, Muir and Ritchie [41] detected a very minor fourth route (B^2) at the same temperatures. These routes are formulated in the following overall scheme, together with the secondary decompositions previously established.

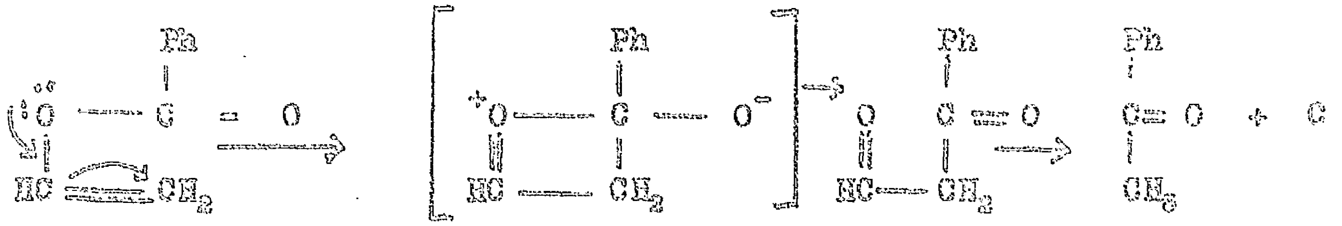


On the basis of analyses of exit gases from the pyrolysis of vinyl benzoate, Bengough, Steedman and Ritchie [42] concluded that at 510°C, route R/C^1 constitutes 76% of the decomposition, route C^2 15%, and route A^2 6%; and the balance may be accounted for by uncharacterised side-reaction leading to ethylene. The above authors have also shown that the overall pyrolysis of vinyl benzoate is a homogeneous reaction and that free radicals play no appreciable part in the pyrolysis of vinyl benzoate.

1.3.1. Primary Routes in the Pyrolysis of Vinyl Benzoate

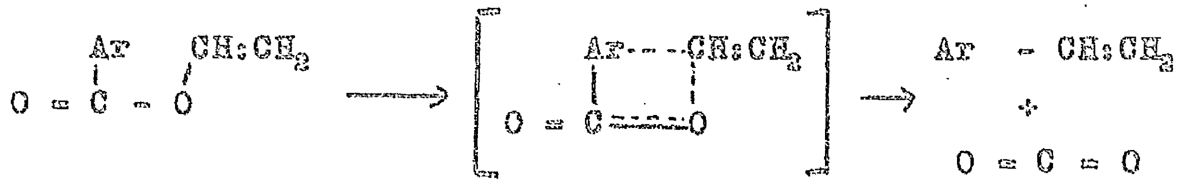
(i) Route R/C^1 is the major mode of breakdown. It has been postulated that vinyl benzoate rearranges to benzoylacetaldehyde as suggested for the analogous rearrangement of enol carboxylates [43, 31] [see Section 1.1.5]. This labile β-ketoaldehyde could not be positively detected in the pyrolysate: Pyrolysis of vinyl benzoate gave acetophenone and carbon monoxide. However, the instability of the β-keto aldehyde is well known [44]. Allan, Forman and Ritchie [2] pyrolysed benzoylacetaldehyde at 500°C and reported that only 15% remained undecomposed. Muir [9] repeated the pyrolysis of benzoylacetaldehyde and found it to decompose exclusively to carbon monoxide and acetophenone.

An intramolecular mechanism involving a cyclic transition state as suggested by Young et al. [31] has been applied [2] to this reaction of vinyl benzoate. This labile intermediate decomposes further by the known aldehyde reaction at high temperatures to give carbon monoxide and acetophenone.

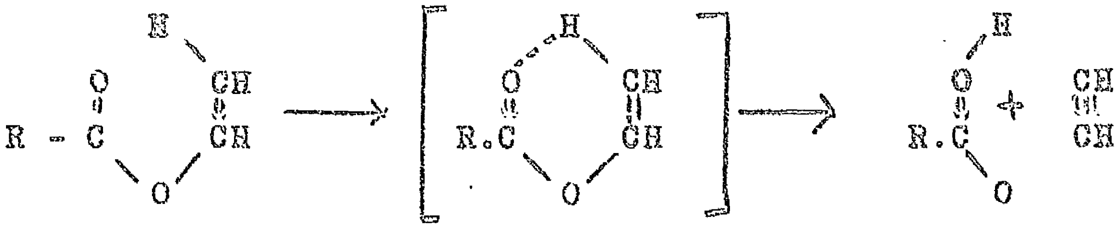


(ii) The decarboxylation reaction (route C^{a}) of vinyl benzoate provided the first of a series of unexpected ester decarboxylations. Bengough, Ritchie and Steedman [42] showed by means of gas analyses that this reaction is mainly homogeneous but also occurs in part at the walls of reaction vessel. This suggests that there may be two types of mechanisms operating in this reaction.

In order to elucidate the reaction mechanism, Reminger and Ritchie [45] pyrolysed vinyl o-, m- and p-chlorobenzoates. If decarboxylation occurs by a free radical mechanism, chlorophenyl and vinyl radicals should combine to give chlorostyrenes with new orientations. However, it was found that in all of these cases almost the whole of the resulting chlorostyrene had the same orientation as the parent ester. With the help of gas chromatography they were able to detect a very minor amount of differently substituted (orientated) chlorostyrene in the pyrolysate. Hence, with all this evidence and the fact that decarboxylation is not effected by inhibitors [42], Reminger and Ritchie have proposed an intramolecular mechanism such that the aryl grouping is at no stage wholly detached from an adjacent carbon atom, so that there is no opportunity for change of orientation, thus:



(iii) It has been suggested [45] that the mechanism for A^2 scission of vinyl esters is similar to that proposed by Hurd and Blunck [16] for A^1 elimination from saturated esters, again involving a six-membered ring, as follows:



1.3.2. Secondary Routes in the Pyrolysis of Vinyl Benzoate

Several secondary products have been detected toluene, from acetophenone; benzene, from the decomposition of benzoic acid; and methane, from the decomposition product of acetaldehyde, the latter being produced in the following way [45]:

$$Ph.CO_2.CH{:}CH_2 + Ph.CO_2H \longrightarrow (Ph.CO_2)_2CHMe \longrightarrow (Ph.CO_2)_2O + Me.CHO \quad ....D$$

1.4. Catalysed Thermal Decomposition of Esters

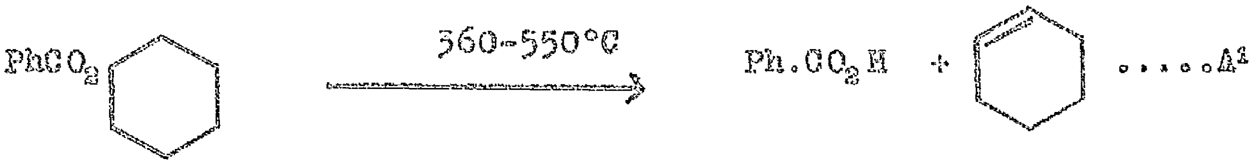
Though there are not many recorded examples of the catalytic decomposition of esters, it is recognised [46] that catalysts do effect the rate of degradation and can produce more products than the simple thermal reactions. Sabatier and Mailhe [47] have shown that formic esters break down by two competitive routes on pyrolysis in presence of certain metals (Ni, Pt, Cu):

$$(1)\quad 2\ H.CO_2.C_nH_{2n+1} \longrightarrow CH_2O + CO_2 + (C_nH_{2n+1})_2O$$

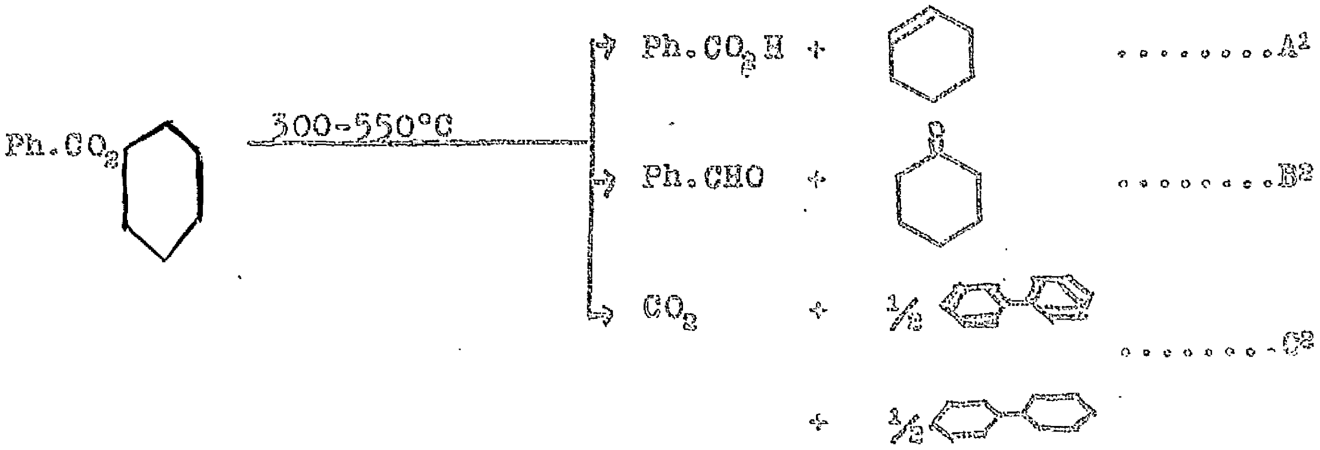
$$\longrightarrow CH_2O + CO_2 + H_2O + 2\ C_nH_{2n}$$

$$(2)\quad H.CO_2.C_nH_{2n+1} \longrightarrow (C_nH_{2n+1}OH)$$

The second route is the normal predominant A^1 scission of aliphatic esters. The ether from the first reaction was not detected in the pyrolysate, but decomposed further to water and olefins. Formic esters were found to be stable when pyrolysed above at 400°C under vacuum in glass tubes, but decomposed at lower temperature when pyrolysed over metals. The formates started to decompose above 220°C with nickel as catalyst, with platinum at 270°C, and with copper at 350°C. Other catalysts have also been tried. Senderens [48] has pyrolysed ethyl acetate and ethyl butyrate over alumina and thoria, and increased breakdown was observed as compared to the all-glass system. Other esters have been recorded which breakdown by several competitive routes, and with increased thermal breakdown Catalysts other than metals have been used, and increased breakdown was observed. For example, Pearce and Wing [49] have pyrolysed esters over anhydrous zinc chloride, rare earth hydroxides, alumina, and traces of sulphuric acid over pumice, Muir [9] pyrolysed cyclohexyl benzoate in an all-glass system, and also over Wood's metal. In the former system it breaks down exclusively by A^1 scission to benzoic acid and cyclohexene:



In the presence of Wood's metal, however, the breakdown was much more complicated:



Of all the Wood's metal components (tin, lead, bismuth, cadmium) tin was found most effective.

1.3. Kinetic Studies on Ester Pyrolysis

Much work has been done on the kinetics and mechanism of the thermal decomposition of a variety of esters [50, 51]. Makens and Eversole [52] have shown that the thermal breakdown of ethyl formate into formic acid and ethylene is homogeneous and of the first order, having an activation energy of 40 k.cal/mole. Blades [53] later found, by means of a toluene flow-technique, that the activation energy of the inhibited reaction was 44 K.cal/mole. Dibenzyl could not be detected in the reaction products, and there was thus no evidence of any free radical reaction.

Other similar studies have dealt with n-propyl formate [54], (-)-menthyl benzoate [8], t-butyl propionate [56], and t-butyl acetate [55]. All these decompositions are homogeneous and of the first order, with activation energies ranging from 30-50 K.cal/mole. In all these reactions only alkyl-oxygen scission was followed; other primary and secondary routes occurred to an extent small enouth to be ignored. No intensive search was made for free radical reactions. However, Blades [53] could not inhibit pyrolysis of ethyl formate by means of toluene. Similarly, Gordon, Price, and Trotman-Dickenson [57] reported that cyclohexene, a free radical inhibitor, had no effect on the pyrolysis of t-butyl formate.

Coffin [58] reported the disproportionation of ethylidene diacetate to acetic anhydride and acetaldehyde and found that the decomposition was homogeneous and of the first order.

2. OBJECT OF WORK

In view of the work described in Section 1 of this thesis, it was decided to study the pyrolysis of vinyl benzoate, which is a model compound for the end-groups formed during the pyrolysis of terylene.

Previous work on this ester had given a full qualitative picture to explain all the observed products; but no accurate quantitative study was then made, because of the difficulty of analysing the very complex pyrolysate.

In the present work, it was planned to study the pyrolysis of vinyl benzoate quantitatively, in the hope of determining the kinetics and mechanism of each competing reaction and the effect of catalysis by metals on each preliminary route.

Gas chromatography appeared to be the most promising analytical tool; and preliminary work was done in order to assess its accuracy for the above system.

3. EXPERIMENTAL

3.1 Preparation of Compounds.

3.1.1 Vinyl Benzoate.

Vinyl benzoate was prepared by the following two methods:

(a) Adelman's method [59]; ester interchange

(b) Nesmeyanov's method [60]; benzoylation of chloromercuriacetaldehyde.

(a) Vinyl Interchange method.

120 g. of Analar benzoic acid were dissolved in 320 g. of vinyl acetate by vigorous shaking. 4g. of mercuric acetate and 1 ml. of concentrated sulphuric acid were added to produce mercuric sulphate *in situ*. The mixture was refluxed for 80 hr. at 35°C, then was cooled, and anhydrous sodium acetate was added to neutralise any acetic acid formed. It was then fractionally distilled through a 2 foot column. The ester was collected at 71-73°C/3 mm. Yield 65%.

The ester was found to contain impurities, by gas chromatographic analysis. These were ethylidine diacetate and ethylene diacetate. Muir [9] suggested the following reaction scheme to account for these impurities.

$$\mathrm{Ph.CO_2H + CH_3.CO_2.CH{:}CH_2 \xrightarrow{HgSO_4} Ph.CO_2.CH{:}CH_2 + CH_3.CO_2H}$$

$$\mathrm{CH_3.CO_2H + CH_3.CO_2.CH{:}CH_2 \xrightarrow{HgSO_4} \begin{array}{c}(CH_3.CO_2)_2CH.CH_3 \\ + \\ CH_3.CO_2.CH_2.CH_2.O_2C.CH_3\end{array}}$$

(b) Nesmeyanov Method.

Nesmeyanov prepared a series of vinyl esters by reacting the complex chloromercuriacetaldehyde with the corresponding acid chloride:

$$\mathrm{ClHg.CH_2.CHO + C_6H_5.COCl \longrightarrow C_6H_5.CO_2.CH{:}CH_2 + HgCl_2}$$

The complex $\mathrm{ClHg.CH_2.CHO}$ was prepared by adding 86 g. of vinyl acetate to an aqueous solution of mercuric acetate (320 g. in 1.5 l. distilled water) with vigorous shaking. Any precipitate of mercuric salt was filtered off, and 75 g. potassium chloride were added to the solution. A crystalline precipitate of chloromercuriacetaldehyde was obtained as colourless plates (196 g.: 71% yield), m.p. 132-133°C (lit. m.p. 129-130°C: yield 100%).

The mercury complex was finely ground and suspended in sodium-dried xylene (200 ml.), 100 g. of benzoyl chloride were slowly added to the mixture, which was then heated at 50°C for 8 hr., with constant stirring. Mercuric chloride was filtered off. The ester (crude) was then treated successively with pyridine, dilute acid, sodium hydrogen carbonate solution, and finally with water. The ester was dried overnight over calcium chloride and redistilled.

Yield 35 g. (25%) (lit.: yield 60%)

Physical Constants

	Present work	lit.(Nesmeyanov)
b.p.	71°C/3 mm	71°C/3 mm
d_{3}^{20}	1.060	1.068
n_{D}^{20}	1.520	1.525

3.1.2 Benzoylacetaldehyde [61]

A mixture of 60 g. of acetophenone and 40 g. of ethyl formate was added, with cooling, to 35 g. of sodium ethoxide suspended in water-free ether. This yielded the sodium salt of benzoylacetaldehyde, which was converted to a sparingly soluble copper salt by adding concentrated copper acetate solution in water. This was filtered off and washed with water and ether. Cautious acidification with cold mineral acid gave benzoylacetaldehyde.

The product gave a three-peaked chromatogram, the main impurity being acetophenone, which could not be removed because it had the same boiling point as benzoylacetaldehyde (b.p. 200°C/760 mm.).

3.1.3 2-Phenyl-1:3-butadiene [62]

$$\mathrm{Ph.CO.Me} \xrightarrow[\text{(2)}\ \mathrm{H_2O}]{\text{(1)}\ \mathrm{CH{:}CHMgBr}} \mathrm{HO.CMePh.CH{:}CH_2}$$

$$\xrightarrow{\mathrm{Ph.NH_2\ HBr}} \mathrm{CH_2{:}CPh.CH{:}CH_2}$$

(a) Vinyl Magnesium Bromide [63]

61 g. (0.61 mole) of vinyl bromide were added to 14.6 g. (0.61 g. atom.) of magnesium turnings in 500 ml. of tetrahydrofuran. The tetrahydrofuran was distilled from lithium aluminium chloride to remove water and peroxide. A dry-ice condenser was used, and a few drops of methyl iodide were added to start the reaction. When the reaction was over the condenser at -78°C was replaced by water condenser.

Vinyl magnesium bromide was recovered.

(b) Methyl Phenyl Vinyl Carbinol

200 g. of acetophenone (1.67 mole), dissolved in 500 ml. tetrahydrofuran, were added to vinyl magnesium bromide solution at a rate which maintained a gentle reflux. The mixture was constantly stirred during addition, and for 1 hr. after addition. 500 ml. of saturated ammonium chloride solution in water were added to hydrolyse the complex.

The organic layer was separated in a separating funnel, the tetrahydrofuran was removed on a steam bath, and the residue distilled through a 12 inch Vigreux column to yield 180 g. (75%) of methyl phenyl carbinol, as a colourless liquid, b.p. 73-74°C 1 mm.

(c) Dehydration of Methyl Phenyl Vinyl Carbinol.

40 g. of methyl phenyl vinyl carbinol (0.27 mole), 4 g. of aniline hydrobromide, and 0.5 g. hydroquinone were mixed in a 100 ml. round-bottomed flask connected to a 6 inch Vigreux column, with distillation take-off. The pressure was reduced to 13 mm. and the flask was heated on an oil bath to 100°C and ultimately to 150°C. The receiver was cooled in an ice-salt bath.

2-Phenyl-1,3-butadiene was collected as a colourless liquid at 58-63°C/13 mm., and dried over calcium chloride. (lit. b.p. 57-63°C/13 mm.)

3.2. Analytical Techniques.

Quantitative analyses of the pyrolysed products were carried out using gas-chromatography for liquids and solids, and gas absorption analysis for the pyrolysate gases. A brief description of the former is given below.

The instrument used was the Pye argon chromatograph.

It uses a 122 cm. 4 mm. Pyrex column, packed with Celite 545 with a suitable stationary phase. The apparatus uses a β-ray ionisation detector with Sr^{90} as a β-ray source, first developed by Lovelock [64]. This instrument is highly sensitive and capable of detecting organic vapours of the order of 2×10^{-12} g. in argon, the latter being used as a carrier gas.

One of the chief advantages of this instrument is that the argon flow-rate has no effect on the base line, because it is based on the measurement of electrical conductivity of partially ionised gases. The conductivity is altered by the appearance of an eluted vapour in the originally pure gas. By contrast to this, with a detector dependent on measurement of gas properties such as thermal conductivity, density, heats of combustion, etc., small changes in the conditions of flow of the carrier gas, or fluctuations in temperature measurement, can produce signals comparable in size of those of the eluted vapours.

The carrier-gas was dried by passing through molecular sieve 5A°, was previously dried at 400°C with argon passing through it for 2 hr. The detector source (Sr^{90}) was renewed every 6 months.

3.2.1 Preparation of the Columns.

A number of columns were made in order to fulfil the needs of various experimental conditions. The column, 122 cm. in length and 4 mm. in diameter, was made of Pyrex glass, with B-7 joints at top and bottom. It was filled with Celite 545 using a suitable stationary phase. The celite 545 (mesh size 30-80) was obtained from Hopkins and Williams, and was made specially for gas chromatography. A brief description of the preparation of the column packing is given below.

3.2.1(i) Column with Apiezon L as Stationary Phase.

2 g. of Apiezon grease were dissolved in ether, the solution filtered to remove any impurities, and then added to 8 g. of Celite 545 in a round-bottomed flask. The ether was slowly evaporated off on a water bath, the solution being continuously shaken, and the residue was then dried under vacuum at 100°C for 2 hr.

3.2.1(ii) Packing the Column.

A piece of glass fibre was placed in the bottom of the column to support the packing, and the column was then clamped vertically, standing on a soft pad. The packing was then slowly introduced from the top, with constant tapping of the column with a piece of hard rubber tubing. Before use the columns were heated to 50°C higher than the required working temperature, with argon passing through, for at least 24 hr.

3.2.2 Introduction of the Sample

The usual way of introducing the sample in the Pye argon chromatograph was to stop the gas-flow and wait till the pressure inside the column reached atmospheric. The liquids were then introduced into the column by micropipettes, devised by Tenny & Harris[65] which consist of fine tubing connected to a calibrated capillary. The method has the disadvantage that it introduces some air into the column, which might oxidise some of the substances under investigation. Styrene, for example, one of the compounds estimated, is susceptible to oxidation around 150°C, the normal working temperature of the column [39].

The system was modified slightly to prevent air entering when the sample was introduced, the sample being introduced by means of a calibrated capillary attached to a steel rod.

3.3. Quantitative Analysis.

The liquids were analysed quantitatively by gas chromatography, and the gases by the Hempel gas absorption unit. In the Pye argon chromatograph the sample size was of the order of $0.02\,\mu\ell$ which was extremely difficult to measure accurately. However there are a number of methods available in which the sample size need not be known. A brief description is given below (see section 3.3.2).

The quantitative interpretation of a chromatogram is based on the peak height or peak area. The latter is the more satisfactory, and the areas of peaks can be measured by the following methods.

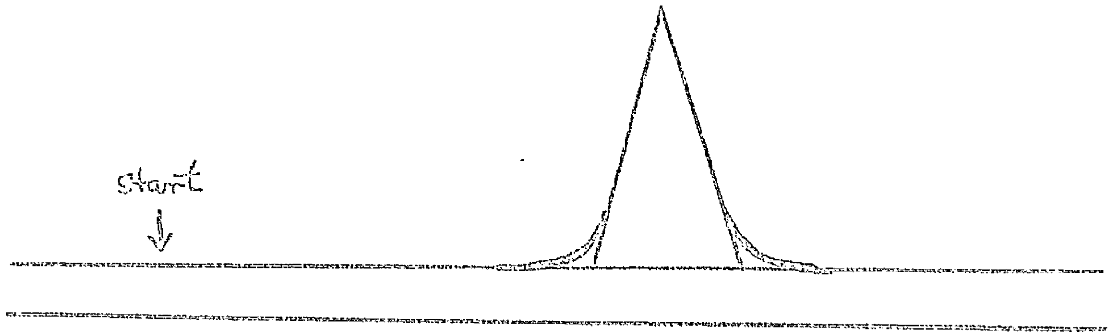
(1) By cutting the peaks out from the charts, and weighing them. This method is rather tedious and requires more time.

(2) By means of a planimeter.

(3) By employing some automatic integrating.

(4) By multiplying the peak height by the width at half-height.

(5) By approximating the triangles. Tangents are drawn at the point of inflection, and form a triangle with the base line.



The area of triangle is given by ½ base x altitude.

Method (5) was used for measuring the areas, being found more satisfactory in estimating the relative percentage composition of a mixture. The following methods available for quantitative analysis do not require that the amount of sample should be known.

3.3.1. The Internal Marker Method

A suitable pure substance in known amount (the 'marker') is added to the mixture. Supposing the mixture had only two components A and B, then several synthetic samples are made of A and marker, and the ratio of percentage composition is plotted against the ratio of areas of A and the marker. A straight line is usually obtained, and similar plots are obtained for B and the same marker. A chromatogram of the mixture plus a known amount of marker is then obtained, and the amounts of A and B are calculated thus. This method becomes complicated when more than two components are present. Lee and Oliver [66] have suggested the use of two or more internal markers in some circumstances.

3.3.2. The Method of Internal Normalisation

In this method, it has to be assumed that the area under each peak is directly proportional to the amount of the responsible component. Then the amount of each component can be determined by adding together all the peak areas and finding the proportion of each area to this total. This method is not applicable to all detectors and mixture containing compounds having a wide range of boiling points.

3.3.3. Bracketing Technique.

In this technique an approximate composition of the sample is calculated without applying calibration factors from the total peak area. A synthetic mixture of this composition is then prepared and analysed under the same conditions. The peak areas are compared with the original sample, and figures for analysis are adjusted accordingly.

In the present work a modified bracketing technique was used. The areas of peaks were measured by triangulation method. At least three synthetic mixtures (unless otherwise stated) were prepared and chromatographed under identical condition. The percentage composition of the unknown was then measured by comparing the areas of the peaks of the known mixtures to the unknown. The percentage composition of the unknown was adjusted accordingly.

3.4. Pyrolysis of Vinyl Benzoate

Earlier studies on the pyrolysis of vinyl benzoate [2,3] concentrated on qualitative identification of the pyrolysis products. The technique used was pyrolysis of vinyl benzoate at 450-550°C in a flow reactor, and the results helped to elucidate the general nature of the pyrolysis of vinyl benzoate. At that stage it could only be deduced that route B/C^1 was a major reaction and route B^2 a trace reaction and so on.

A detailed study was done by Bengough, Steedman and Ritchie[42], who followed the rate degradation of the ester empirically by measuring the rate of gas evolution from a system containing the refluxing ester and its vapour. They used a static reactor connected to a mercury manometer, and the gases were collected in a flask connected to a high vacuum line.

In the present work the pyrolysis of vinyl benzoate was studied by using a flow system whereby liquid vinyl benzoate was dropped into the top of the reactor at a controlled feed-rate.

One of the chief advantages of the flow reactor is system is that it minimises secondary breakdown reactions and reaction between the pyrolysand and the products of pyrolysis. This method also ensures that sufficient material can be collected for analysis.

The main disadvantages are that the reaction time and the reaction temperature cannot readily be defined exactly (see section 3.4.2). The reaction time is calculated from the rate of flow of the reactants through the system and the length of the reactor zone; but this, of course, assumes that the gas comes to the reactor temperature immediately, on entering the reactor zone, and is quenched immediately on leaving the zone.

3.4.1 The Flow System.

The all-glass flow system consisted of the following parts:

(1) The feeder (Fig. 1).

(2) The reactor (Fig. 2).

(3) Constant pressure gas collection device.

(1) The Feeder

The feeder was designed so that the feed-rate of the ester could be varied and the pyrolysis carried out at different residence times. It consisted of a 6 inch pyrex tube of 1 inch diameter, with a B-19 socket at the top through which pressure on the liquid could be varied if desired by means of nitrogen. A stopcock was joined to the bottom and the stopcock outlet was connected to 2 inch of 1 mm. capillary, which had a B-7 cone at the bottom. Capillaries of various sizes were fitted to the feeder using this cone, and the feed rate of the pyrolysand could thus be altered.

Fig. No.1

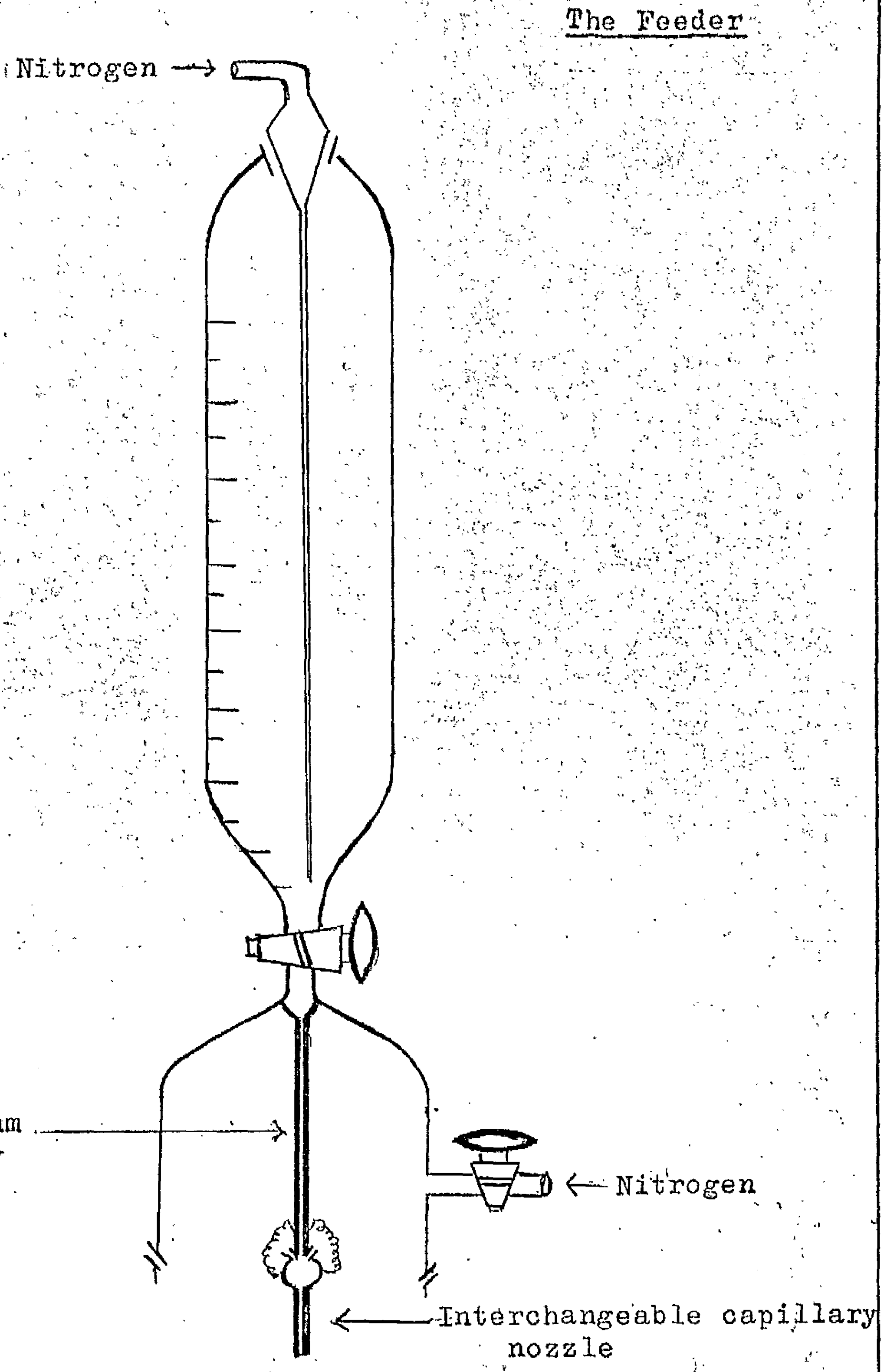

The Feeder
Nitrogen
5 cm of 1 mm capillary
Nitrogen
Interchangeable capillary nozzle

Fig. No.2

The Reactor

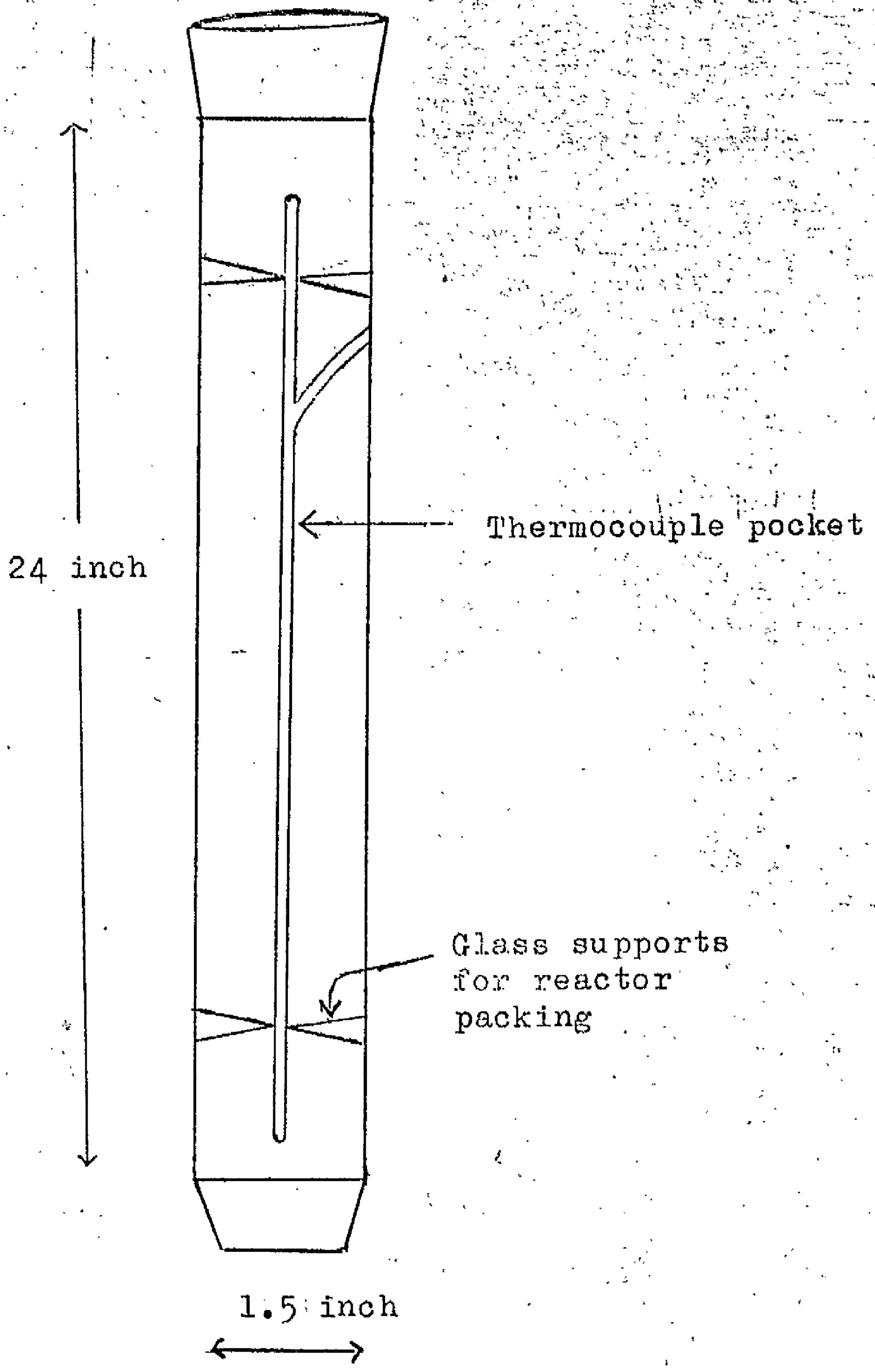
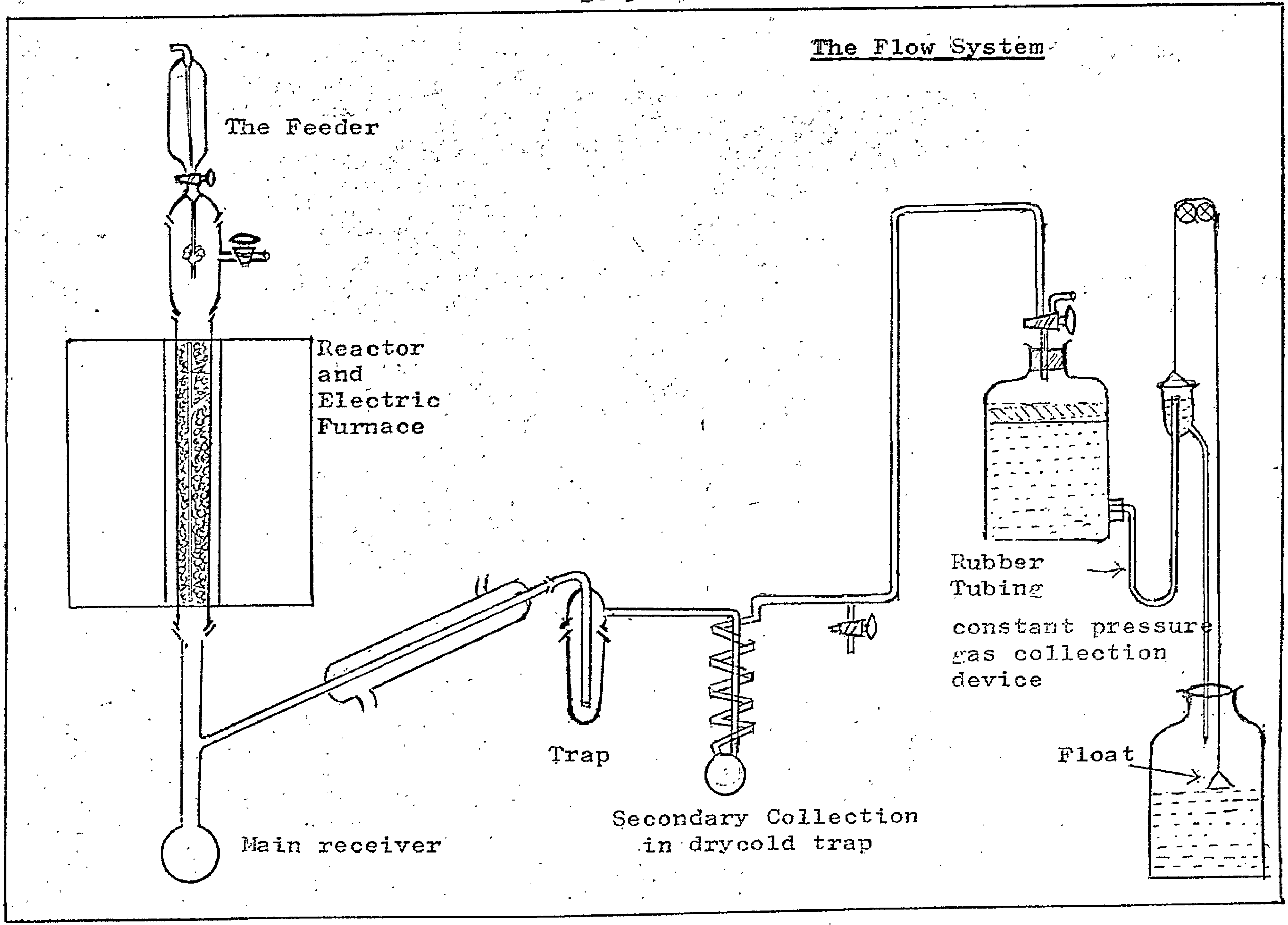


Fig. 3



The Flow System

3.4.2. The Reactor

The reactor consisted of a Pyrex tube of about 1.5 inch diameter and 24 inch length. It contained a thermocouple pocket, which ran the length of the reactor and allowed the thermocouple to be placed at any point along the length. The reactor was packed with glass Raschig rings, or glass helices, the volume of unpacked space being about 0.21 litre. The dimensions given above varied slightly for the different reactors used. The temperature inside the reactor was measured by a chromel-alumel thermocouple. The temperature of the furnace was controlled manually by a 'Sunvic' thermostat. The thermocouple readings were taken from an 0-50 millivoltmeter. The accuracy of the temperature measurement was ± 5°C.

The temperature distribution inside the reactor was measured by moving the thermocouple along the length of the reactor and measuring the temperature at various points. Fig. 4. Shows a typical temperature distribution. The hottest spot indicated by this curve is taken as the effective temperature of the reactor.

3.4.3. Constant Pressure Gas Collection Device

Since all pyrolyses were carried out at atmospheric pressure, the exit gases were collected at constant atmospheric pressure to avoid altering the pressure in the reactor during a run. In this system two aspirators were

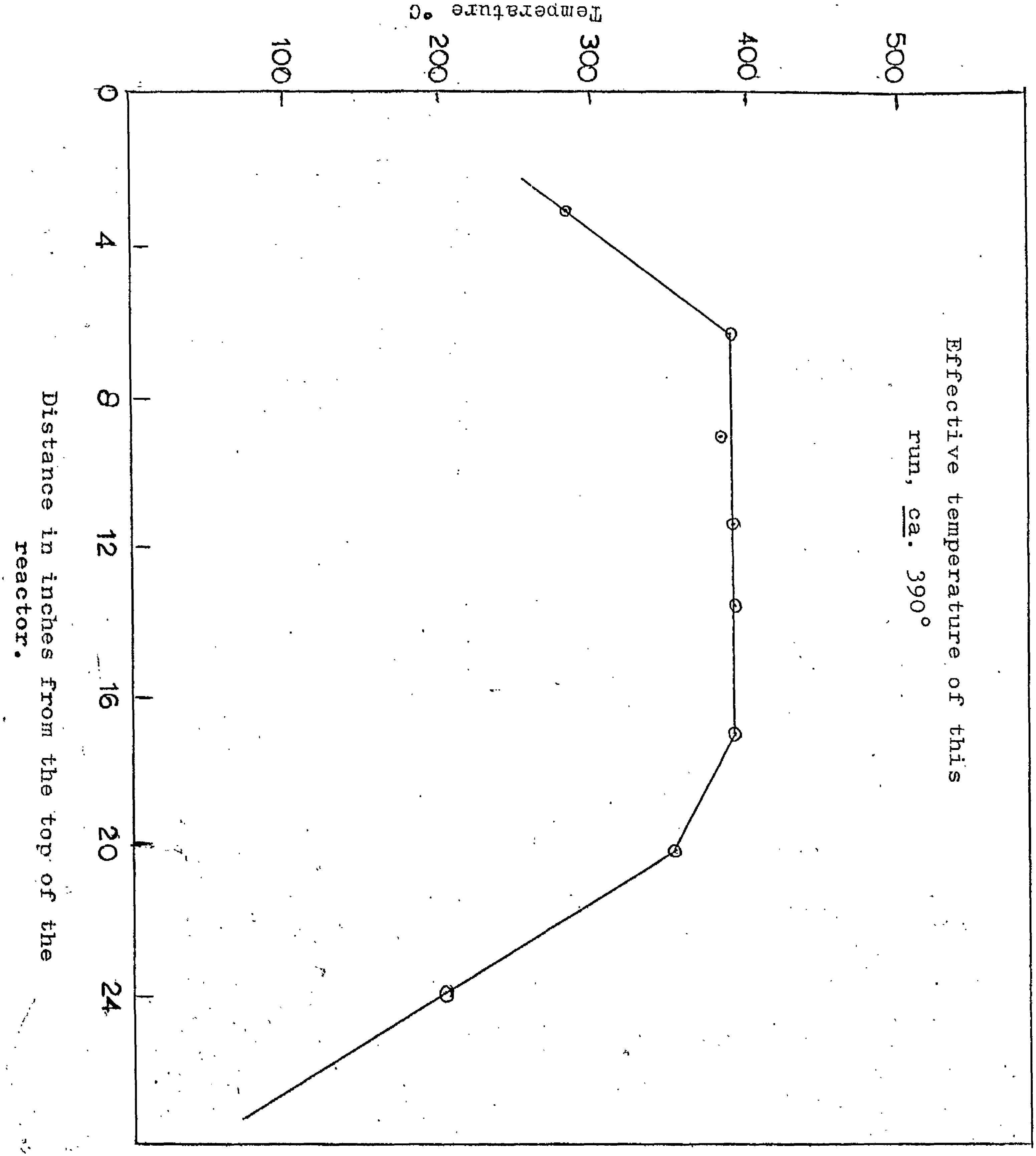


Fig. 4. Distribution of temperature along the reactor

used. One of them filled with water with a surface layer of paraffin, was connected to the flow system. The outlet from this aspirator is connected to a small reservoir level of which is maintained at the same position as that of the aspirator by means of a pulley-and-float system. There is an outlet from the reservoir to a second aspirator which must be at a lower level. The reservoir is suspended by means of a string through a pulley and is counterbalanced by a float on the surface of the water in the second aspirator. Any change in the pressure in the system due to pyrolysis will cause water to flow from the first aspirator into the second through the reservoir. The level of the float will be raised and thus the reservoir will be lowered and its level will be adjusted to that of the first aspirator.

3.4.4. Decarbonisation of the Reactor

Before each new run condensed reaction products were removed from the reactor by washing with mixed solvents, and the reactor was then decarbonised by heating for 2 hr. at 550°C with air passing through it.

3.5. Pyrolysis of Vinyl Benzoate over Wood's Metal Components

Muir [9] studied the pyrolysis of cyclohexy benzoate in the presence of Wood's metal and its components, using a static reactor. In the present study, the object was to extend this work by comparing the flow pyrolysis of vinyl benzoate alone with the pyrolysis in presence of the components of Wood's metal alloy, and examine any catalytic effects.

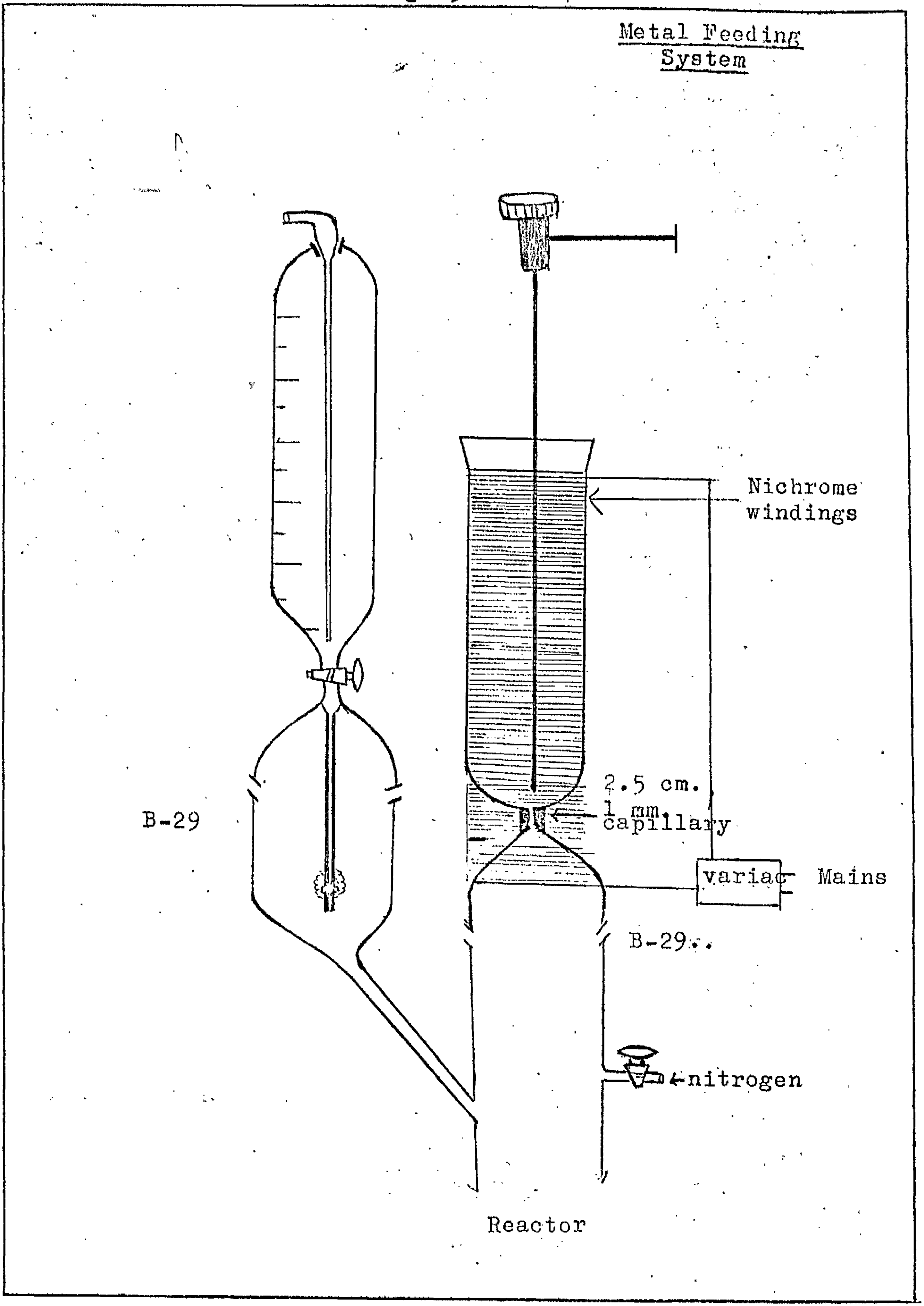
Initially there were a number of experimental difficulties. The component of Wood's metal (Sn, Pb, cd, Bi) all melt below 350°C, so that if the reactor is simply packed with pieces of metal, these melt and run away during a run at 400-550°C. As an alternative Pyrex glass was vacuum coated with a tin mirror, and broken up to act as packing for the reaction but again the metal simply melted and run away at 400-550°C.

The method finally adopted was to melt the metals at the top of the reactor and allow them to run into the reactor at a rate which ensured good contact between the metals and vapourized pyrolysand. About 100-150 g. of metal was used for 3-4 g. of liquids pyrolysed.

3.5.1. The Apparatus

The apparatus as shown in the figure 5 is essentially a small furnace capable of giving temperatures up to 400°C It consists of two Pyrex tubes, one 6 inch by 1 inch and the other 1 inch by 1 inch, joined together by a 2.5 cm. capillary of 1 mm. diameter. This was covered with asbestos paper

Fig. 5.


Metal Feeding System
Nichrome windings
2.5 cm.
1 mm. capillary
B-29
variac
Mains
B-29
nitrogen
Reactor

and nichromewire (24 gauge) was wound round it. The nichrome winding was again covered with asbestos. The winding had a resistance of 46 ohms , and 30-40 volts potential difference was necessary to raise the temperature to 300-340°C.

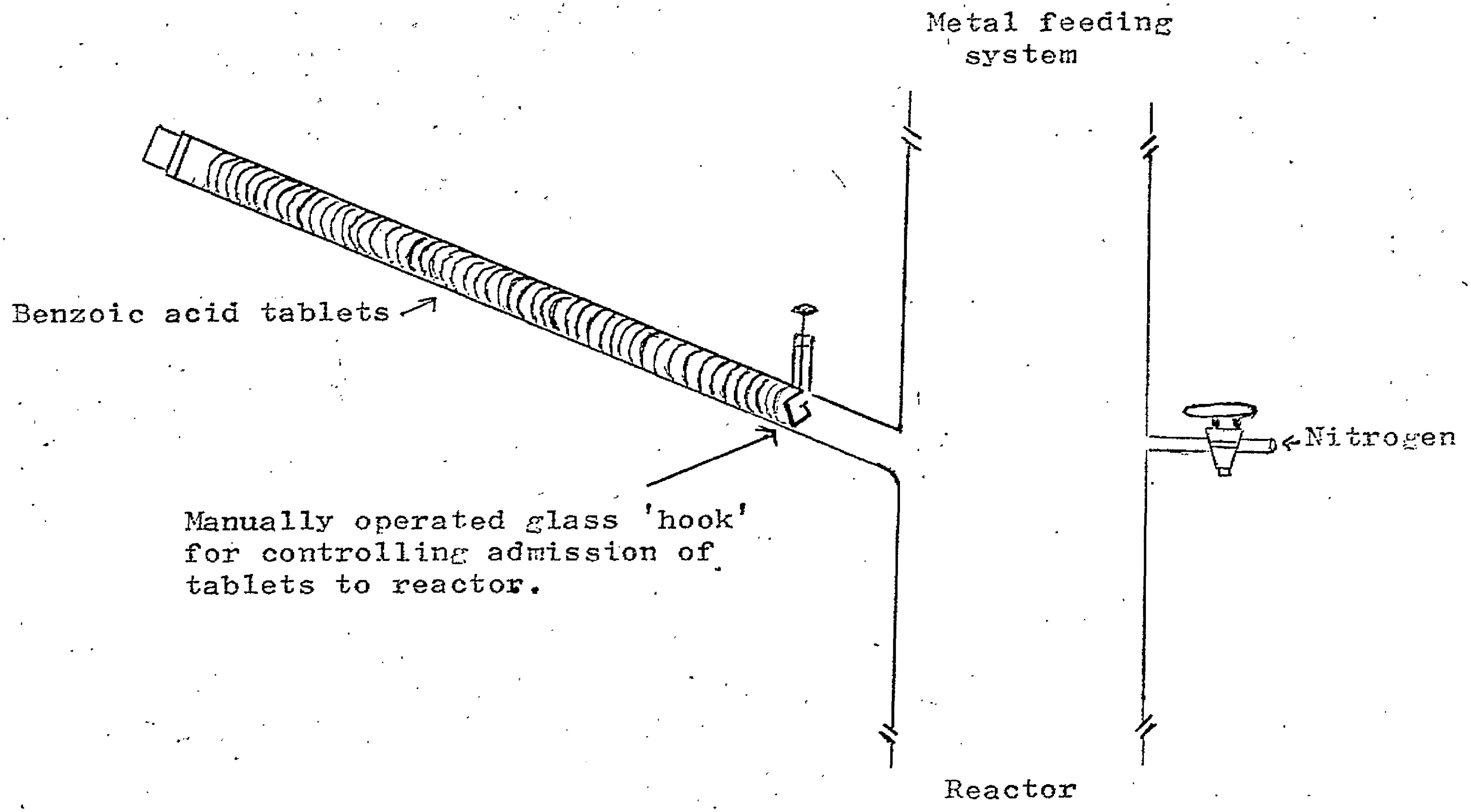
In order to control the flow of metals through the apparatus, a glass rod fitted to a screw drive, and with a ground end, was inserted into the metal feed-tube. The ground end of the glass rod fitted over the capillary tubing, so that by adjusting the screw, the feed-rate could be controlled.

3.6. Pyrolysis of Benzoic Acid

Since benzoic acid is a solid of fairly high m.p. it was dropped into the reactor in the form of tablets, while tin was introduced into the reactor by melting it at the top of the reactor and dropping it in as described in section 3.5.1. Each tablet contained about 0.26 g. of benzoic acid and was dropped into the reactor by means of an 8 inch long side-tube with diameter slightly greater than that of the tablet (Figure 5). The tablets were dropped into the reactor at a steady rate being released one at a time by a manually operated glass 'hook' (see Figure 5).

Fig. 6

Apparatus for pyrolysis of benzoic acid.



4. RESULTS

4.1 Purity of Vinyl Benzoate

Vinyl benzoate, prepared by the vinyl interchange method and by the Nesmeyanov method, was chromatographed at 150°C on a column of 10% Silicone grease on Celite 545. A three-peaked chromatogram was obtained from the vinyl benzoate prepared by former method, the two minor peaks being due to ethylene diacetate and ethylidene diacetate. Their occurrence has been accounted for in Chapter 3. An attempt was made to remove these impurities by fractional distillation, but without success. Vinyl benzoate prepared by the Nesmeyanov method gave a single sharp peak indicating very high purity, and by this method of preparation was therefore used in the present work.

The initial yields of ester were rather low (25%; lit. 60%). However they were increased to 35% by constant stirring of the reaction mixture, raising the reaction temperature from 50°C to 80°C, and increasing the time of heating from 6 to 10 hr.

4.1.2 The Validity of Quantitative Analyses.

The pyrolysed products were analysed quantitatively by gas chromatography and Hempel gas analysis. Initially a number of difficulties were encountered in the gas chromatographic analysis owing to the high sensitivity of the instrument, and to there being no satisfactory available method of

The samples were introduced into the column by a capillary attached to a stout rod, as described in Chapter 3. The best method of introduction, however, is through a serum cap by means of a hypodermic needle. However, at the time the experimental work was done, the smallest hypodermic needle available had a capacity of 10 ul, whereas the sample required for good resolution was 0.02 ul, anything in excess of this causing the recorder needle to run off the chart. A hypodermic needle of 1 µl capacity divided into 100 parts, is now available, though this can be used only for clear homogeneous mixtures or liquids.

A number of runs were done to find a suitable temperature at which all components from the vinyl benzoate pyrolysate could be resolved. This was found to be 150°C. The compounds estimated were: benzene (b.p. 80°C), toluene (b.p. 110°C), styrene (b.p. 146°C), acetophenone (b.p. 200°C), and vinyl benzoate (b.p. 203°C). Four synthetic mixtures of these, with varying known compositions, were chromatographed at 150°C under identical conditions and percentage composition of one of them was estimated by the remaining three samples. The following conditions were used.

Column : 20% High vacuum silicone grease on Celite 545 mesh (80-100)

Column temp. : 150°C

Argon flow rate : 25 ml min.

Detector voltage and sensitivity : 1250 v. x 10

Sample size : 0.02 µl

It is seen from table 1 that percentage error of analyses is within ± 5%.

4.1.3 Pyrolysis of Vinyl Benzoate.

Vinyl benzoate was pyrolysed at four temperatures (450°C, 500°C, 525°C and 550°C) in a flow reactor, with different residence times at each temperature. The residence time was varied by changing the capillaries of the feeder, as described in chapter 3. For each temperature, three runs were made, one with each of the three different capillaries. The pyrolysed products were collected; liquids and solids were analysed by gas-chromatography, and gases by Hempel gas analysis. The detailed results are given in the following pages. The results of the quantitative analyses were from chromatograms, [illegible] under the following conditions (unless otherwise stated). The only variable was gas flow-rate, which, since it was the same at a particular run for both synthetic mixtures and pyrolysed

TABLE I

No.	Compounds	Original % Comp. of Mix.	% Comp. Calc. by Mix. I	%Comp. Calc. by Mix. II	% Comp. Calc. by Mix. III	Mean % Cpmp.	% error
1	Benzene	5.2	5.0	5.0	5.1	5.63	-3.1
2	Toluene	3.2	3.1	3.1	3.0	3.15	-4.3
3	Styrene	12.6	12.7	12.8	12.8	12.76	+1.5
4	Acetophenone	40.2	40.2	41.2	42.2	41.2	+2.5
5	Vinyl benzoate	38.8	38.1	37.2	37.0	37.1	-2.7

products, is not given here except where retention time is stated.

Column : 20% Silicone grease (Edwards High Vacuum) on Celite 545 (mesh 80-120)

Column temp. : 150°C

Detector voltage and sensitivity : 1250 x 10

Argon flow-rate : 20-30 ml. min

Sample size : about 0.02 µl

In each of Tables 2-5, result 1 shows the amount of initial vinyl benzoate destroyed in each run. Results 5-9 re represent the analysis of non-gaseous pyrolysate (excluding benzoic acid, and small traces of diphenyl and benzaldehyde). Results 10-13 represent the analyses of total gaseous pyrolysate (percentage composition by volume).

Table 2

PYROLYSIS OF VINYL BENZOATE AT 450°C

No.	Residence Time (sec.)	42.2	167	310
1	% pyrolysis	10.7	14.3	16.8
2	Amt.-pyrolysed (g.)	5.25	4.50	4.64
3	Amt. recovered (g.)	4.75	4.03	4.04
4	Gas collected (ml.)	82	97	135
5	Benzene (%)	0.03	0.04	0.11
6	Toluene (%)	0.005	0.007	0.02
7	Styrene (%)	0.5	0.6	1.1
8	Acetophenone (%)	1.1	1.3	2.5
9	Vinyl benzoate (%)	98.3	98.1	96.2
10	CO (%)	75.2	75	75.4
11	CO_2 (%)	18.4	16.4	15.6
12	CH:CH (%)	5.5	6.8	7.0
13	Unsat.Hydrocarbon (%)	0.9	1.8	2.0

Table 3

PYROLYSIS OF VINYL BENZOATE AT 500°C

No.	Residence Time	34	125	270
1	% Pyrolysis	23.5	27.2	50.8
2	Amt.pyrolysed (g.)	3.58	3.78	4.75
3	Amt.recovered (g.)	3.00	3.05	3.65
4	Amt. of Gases (ml.)	120.0	205	387
5	Benzene (%)	0.4	0.9	1.8
6	Toluene (%)	0.1	0.5	0.8
7	Styrene (%)	1.5	3.6	5.4
8	Acetophenone (%)	4.8	14.9	24.6
9	Vinyl Benzoate (%)	43.3	80.2	67.4
10	CO (%)	75.8	76.1	76.3
11	CO_2 (%)	14.8	14.7	13.6
12	CH;CH (%)	7.2	7.9	7.9
13	Unsat.Hydrocarbons	2.2	2.1	2.2

Table 4

PYROLYSIS OF VINYL BENZOATE AT 525°C

No.	Residence Time	49.3	128	252
1	% pyrolysis	37.5	51.6	60.5
2	Amt. pyrolysed (g.)	5.20	4.90	4.96
3	Amt. Recovered (g.)	4.20	3.76	3.76
4	Amt. of Gas Collected (ml.)	235	382	475
5	Benzene (%)	1.48	1.42	1.63
6	Toluene (%)	0.6	0.8	0.6
7	Styrene (%)	2.9	3.2	6.4
8	Acetophenone (%)	14.9	27.6	36.2
9	Vinyl Benzoate (%)	79.9	66.9	55.6
10	CO (%)	76.6	76.6	77.0
11	CO_2 (%)	13.1	12.6	10.8
12	CH:CH (%)	7.8	8.2	8.2
13	Unsat. Hydrocarbon (%)	2.5	2.6	3.2

Table 5.

PYROLYSIS OF VINYL BENZOATE AT 550°C

No.	Residence Time	25	74	237
1	% pyrolysis	51.5	61.9	87.6
2	Amt. pyrolysed (g.)	6.10	5.27	5.10
3	Amt. recovered (g.)	4.70	3.85	3.56
4	Gas collected (ml.)	404	510	660
5	Benzene (%)	2.1	2.2	4.3
6	Toluene (%)	0.9	0.9	1.4
7	Styrene (%)	5.5	7.2	12.0
8	Acetophenone (%)	26.2	36.2	63.9
9	Vinyl benzoate (%)	65.0	54.2	18.2
10	CO (%)	76.1	76.6	77.8
11	CO_2 (%)	13.2	12.8	10.8
12	CH ; CH (%)	8.2	8.2	8.2
13	Unsat. Hydrocarbon (%)	2.5	2.6	3.2

4.1.4 Detection of Benzaldehyde and Diphenyl

Gas-chromatograms did not show any new products in the pyrolysate (benzene, toluene, styrene, and acetophenone all having been previously established). It was thought likely that some components might be present in the pyrolysate which would not show in the chromatograph, either being present in too minute quantities, or having high boiling points and not showing up at low column temperatures. The pyrolysate (vinyl benzoate, residence time 237 seconds) was chromatographed and the retention times are given below:

Column : 10% Apiezon L on celite 545 (mesh 80-60)
Column temp. : 150°C
Argon gas flow-rate : 25 ml min.
Sample size : 1 µl
Detector voltage and sensitivity : 1250 x 10

Table 6

Retention Time in Minutes

No.	Compounds	Pyrolysate	Standard
1	Benzene	1.4	1.4
2	Toluene	1.7	1.8
3	Styrene	3.2	3.2
4	Benzaldehyde	3.8	3.8
5	Acetophenone	6.9	6.9
6	Vinyl benzoate	8.8	8.8
7	Diphenyl	20.5	20.3

Two new peaks appeared on the chromatogram when a larger sample was used. These peaks were shown (Table 6: No. 4 and 7) to correspond to the peaks produced by benzaldehyde and diphenyl. Chromatographic analysis at 200°C also confirmed these two compounds in the pyrolysate.

An attempt to analyse them quantitatively proved rather difficult, since when the sample was large enough to produce measurable peaks for diphenyl and benzaldehyde, the peaks for other compounds present could not be recorded on the chart.

It was concluded, however, that benzaldehyde and diphenyl are present in the pyrolysate of the vinyl benzoate as minute traces (i.e. of the order of 1-2%).

4.1.5 Detection of 1,3-Butadiene in the Pyrolysate from Vinyl Benzoate.

An attempt was made to detect certain components not previously identified. 1,3-Butadiene was formally possible (see Section 5 Part I), though present only in minute traces, and the following procedure was adopted.

Vinyl benzoate (50 g.) was pyrolysed in a flow-reactor so that enough pyrolysate gases were produced and butadiene could be collected in sufficient quantity for analysis.

About 8 litres of gases, produced during pyrolysis were passed through successive traps. The first was kept at 0°C to collect any volatile products; the next contained anhydrone to absorb water; and butadiene was finally condensed in a third trap at -78°C (dry ice). This last trap was transferred to a high vacuum line, where it was further 'degassed' in a trap under liquid nitrogen at -195°C, and finally transferred to an infrared gas cell. The following infrared absorption frequencies were observed:

3000, 1800, 1597, 1360, 1000, and 900 cm.$^{-1}$

Barnes et al. (68) have given a number of examples of absorption near 1600 cm.$^{-1}$ arising from conjugated C=C system, (1,3-butadiene 1597 cm.$^{-1}$). Rao [69] quotes infrared spectra of various gases, and in the list reproduced from [70] gives the infrared absorption of 1,3-butadiene as:

3000, 1820, 1600, 1360, 1030 and 900 cm.$^{-1}$

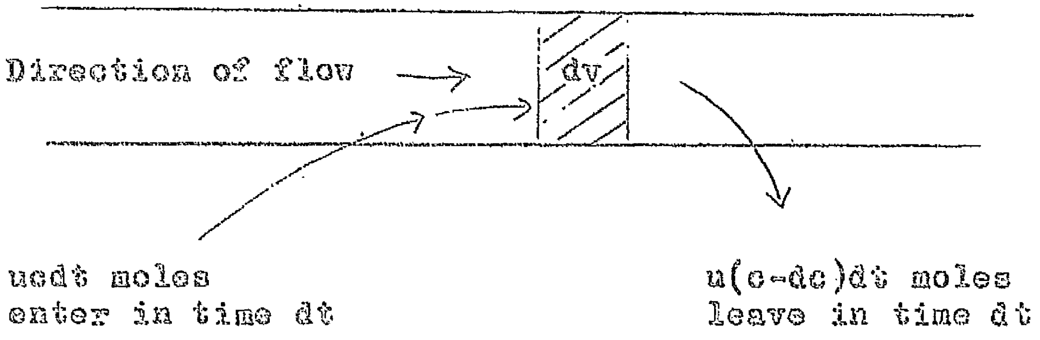
Hence the infrared absorption suggests that 1,3-butadiene is in fact present in the gases. A further confirmation was provided by the ultraviolet absorption spectrum of the pyrolysate gases (dissolved in n-hexane). A value of $\lambda_{max.}$ = 220 mμ was obtained (lit., 217 mu, in n-hexane [71], 217 mu in ethanol [72]). This further confirms the presence of butadiene in the gases. The slight discrepancy (3 mμ) may be due to impurities.

4.1.6 Rate Constants and Activation Energies.

From the results on pages (7-10), information on the pyrolysis kinetics of vinyl benzoate was obtained. A flow-reactor was used for the pyrolysis, and a brief description is given below of the calculations involved, as described by Laidler [73].

If the reaction mixture or reactant pass through a reactor at a volume rate of flow u (expressed as mole sec litre), consider a slab of volume dv in the reactor.

Kc dv dt moles disappear by chemical reaction in time dt, where C = concentration



For a first order reaction, the rate of disappearance of the substance is given by:

$$v = -\frac{dc}{dt} = Kc \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The number of moles disappearing in unit time in volume dv is therefore Kcdv.

After the reaction has proceeded for a sufficient time, a steady state is established. This means that there is no change with time in the concentration of the reactantsin the slab of volume dv. Three processes actually contribute to the steady state.

(a) Molecules of reactant enter the slab by the left face, the number of moles entering in time dt being ucdt

(b) Molecules leave the slab by the right face, the number of moles leaving in time dt being U(c + dc)dt.

(c) Molecules disappear by chemical reactions for the first order case, the number of moles disappearing in time dt being Kcdvdt.

The steady-state relationship for the slab is obtained by equating the rates of entry of reactant into the slab (by process *a*) to the sum of the rates of removal (by processes *b* and *c*). The result is:

$$ucdt = u(c + dc)dt + Kcdvdt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

This reduces to:

$$-\frac{dc}{c} = \frac{K}{v}\, dv \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

This must be integrated over the whole volume of the reactor v_o. At the entrance of the reactor $v = o$ and $c = c$ (the initial concentration), while at the exit, $v = v_o$ and $c = c_f$ (the final concentration of the reactant). Therefore

$$- \int_{c_i}^{c_f} \frac{dc}{c} = \frac{K}{u} \int_{o}^{v_o} dv \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

therefore

$$\ln \frac{c_f}{c_i} = K \frac{v_o}{u} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$\frac{v_o}{u}$ is equal to the t of the static system and is called residence time, the average time taken by a molécule to pass through the reactor. The residence times were calculated by the following equations.

$$t = \frac{v_o}{u} = \frac{273\ pv}{22.4\ \ TN} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

where t = residence time (seconds)

p = pressure (atmospheres)

v = free unpacked space in the reactor (litres)

T = temperature (absolute degrees °K)

N = feed rate (mole sec)

where p = 1 am., expression (6) can be simplified to:

$$t = \frac{12.2\ v}{TN} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

It is seen from equation (5) that if a log c_f/c_t is plotted against residence time, the value of K is given by the slope of the curve.

Plotted in this way, the results (Fig. 9) for the overall breakdown of vinyl benzoate show the linear relationship required by equation (5) for a first order reaction. The value for K for the overall reaction is given in Table 7.

Table 7

No.	Temperature °C	K sec.$^{-1}$ (overall reaction)
1	450	1.04×10^{-4}
2	500	8.91×10^{-4}
3	525	1.62×10^{-3}
4	550	2.80×10^{-3}

Figs 8 and 7 show the relationship between breakdown (%) and residence time at 550°C and 500°C respectively.

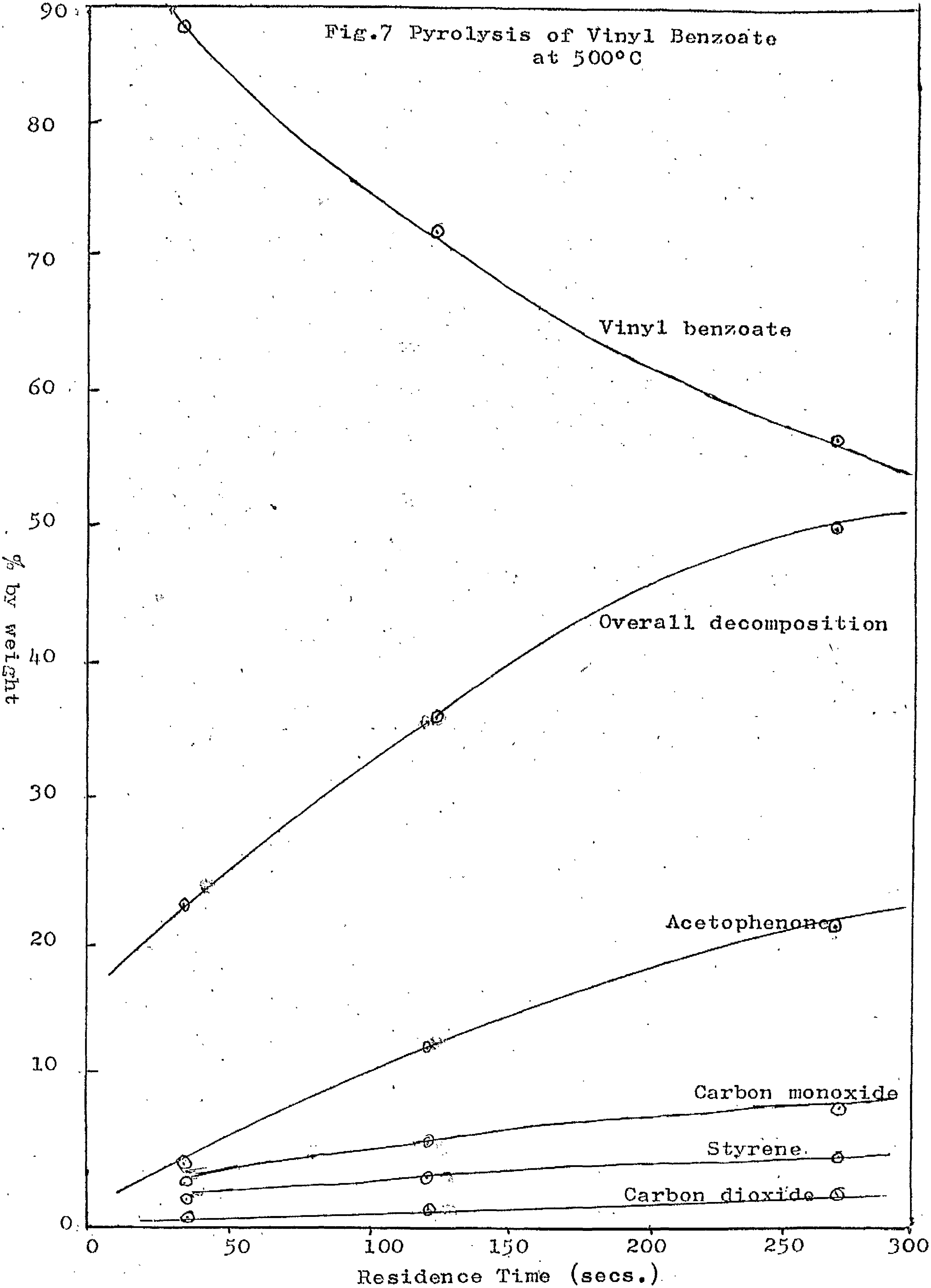


Fig.7 Pyrolysis of Vinyl Benzoate at 500°C

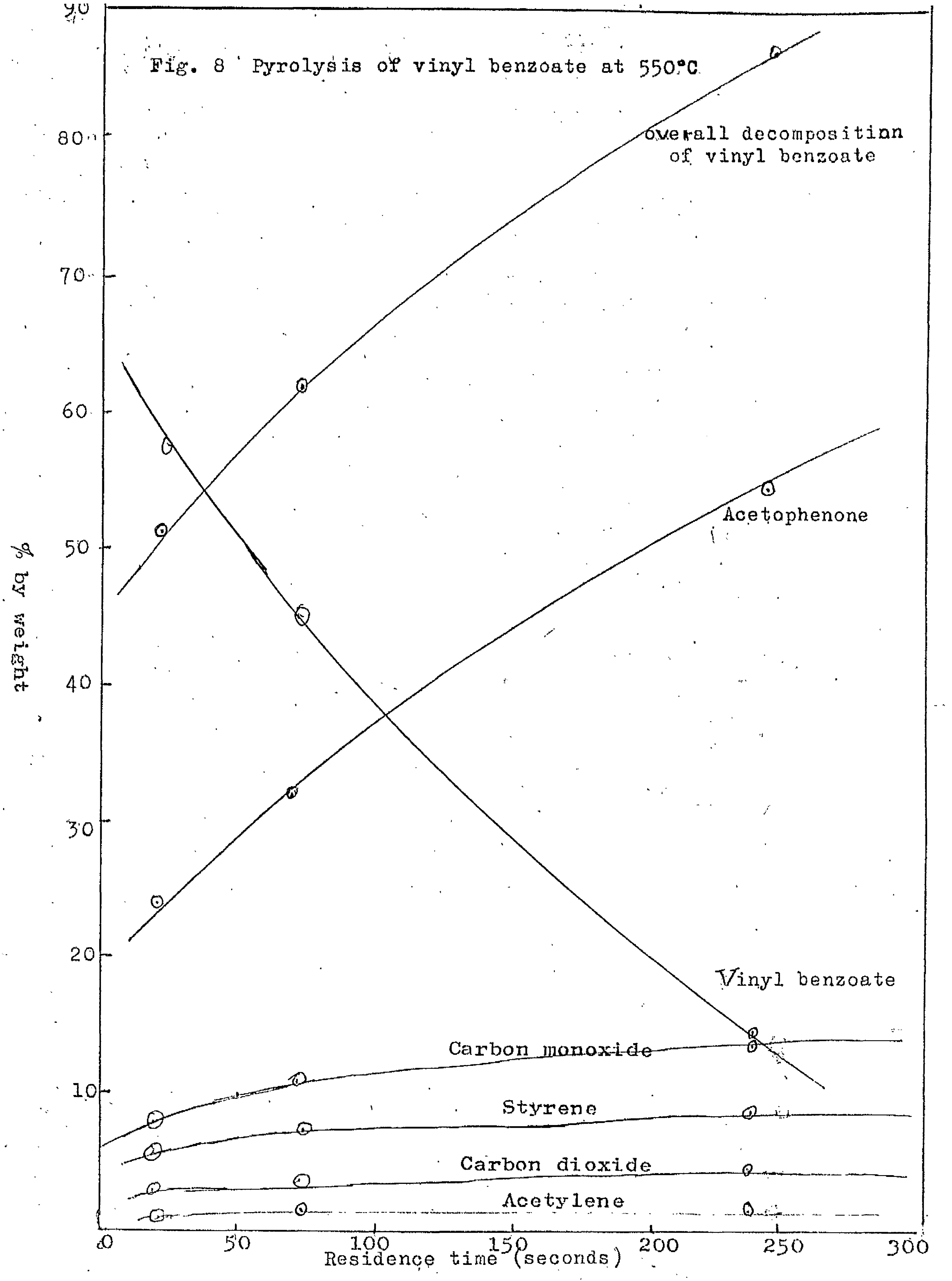


Fig. 8 Pyrolysis of vinyl benzoate at 550°C

4.1.6(i) Determination of the Rate Constant and the Activation Energies for the Primary Reactions in the Pyrolysis of Vinyl Benzoate.

In the pyrolysis of vinyl benzoate a considerable amount of material is lost as tar, etc., retained in the reactor (see tables 2 - 5). The amount lost varies with temperature and residence time. There are two ways by which the rate constant can be calculated. In the first, the calculations were done on the basis of the initial amount of vinyl benzoate used, on the assumption that no secondary decomposition of primary products (eg. acetophenone from R/C' reaction) took place.

Method A.

Initial amounts of vinyl benzoate pyrolysed and the amounts of acetophenone (for R C' reaction) formed were converted into moles and log

$$\left[\frac{\text{moles of vinyl benzoate} - \text{moles of acetophenone}}{\text{moles of vinyl benzoate}}\right]$$

was plotted against residence time, the slope giving K the rate constant.

Similar calculations were done for C² reaction.

Method B

The calculations were done in a similar way as above except the total weight recovered after the pyrolysis was considered as initial concentration and was converted as moles of vinyl benzoate.

Fig 11,12 shows the plots by two methods, and the rate constant so obtained were used to determine the activation energy of the reaction.

In the second method, the total weight of materials recovered (not including the loss by hold-up) was taken as the initial weight of ester. It was assumed that the ratio of primary product to vinyl benzoate was the same in the collected product as in the fraction lost by hold-up

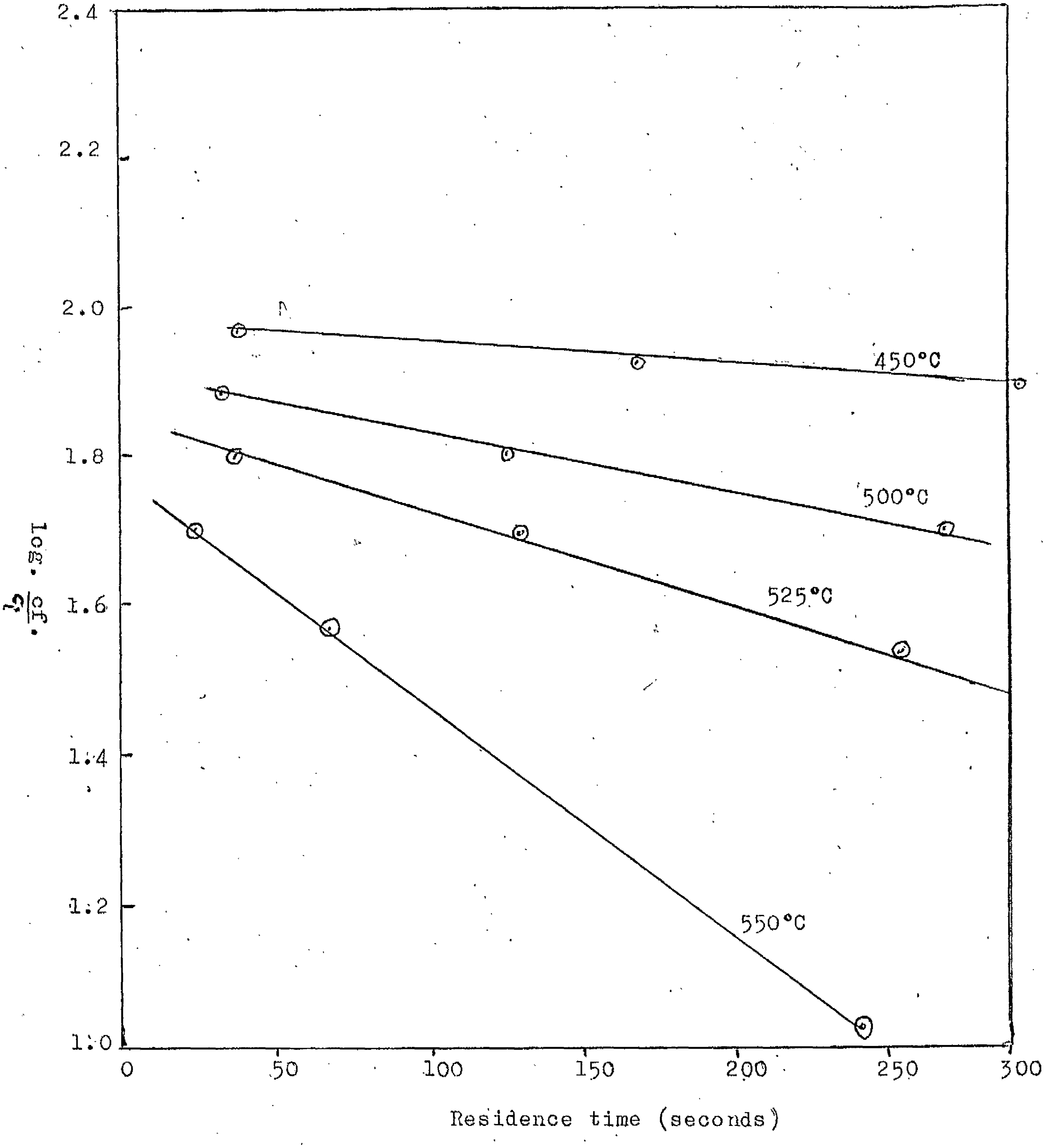


Fig. 9 Plot of log c_f/c_i vs Residence time for the pyrolysis of vinyl benzoate.

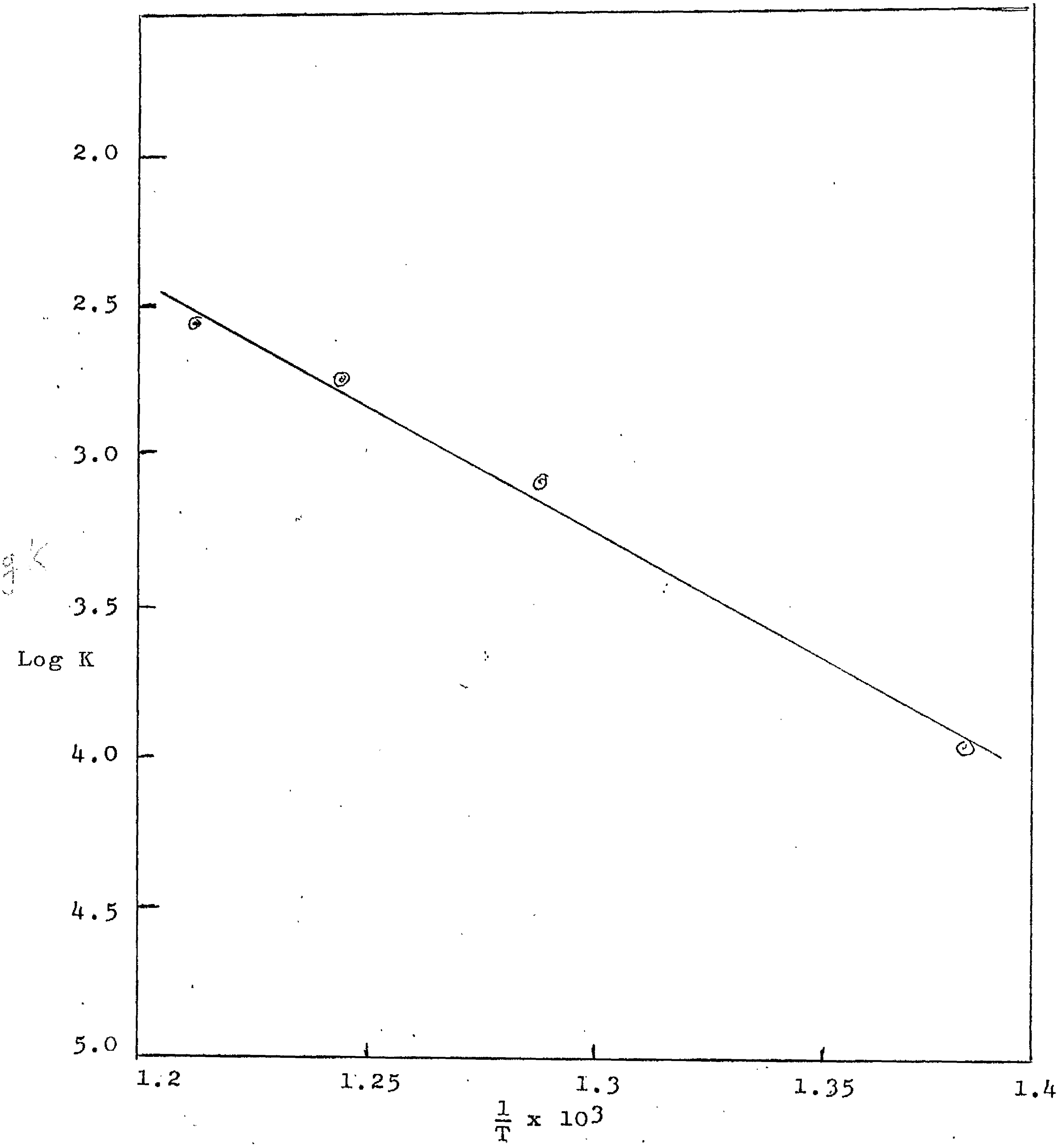


Fig.10. Arrhenius plots for the overall decomposition of vinyl benzoate.

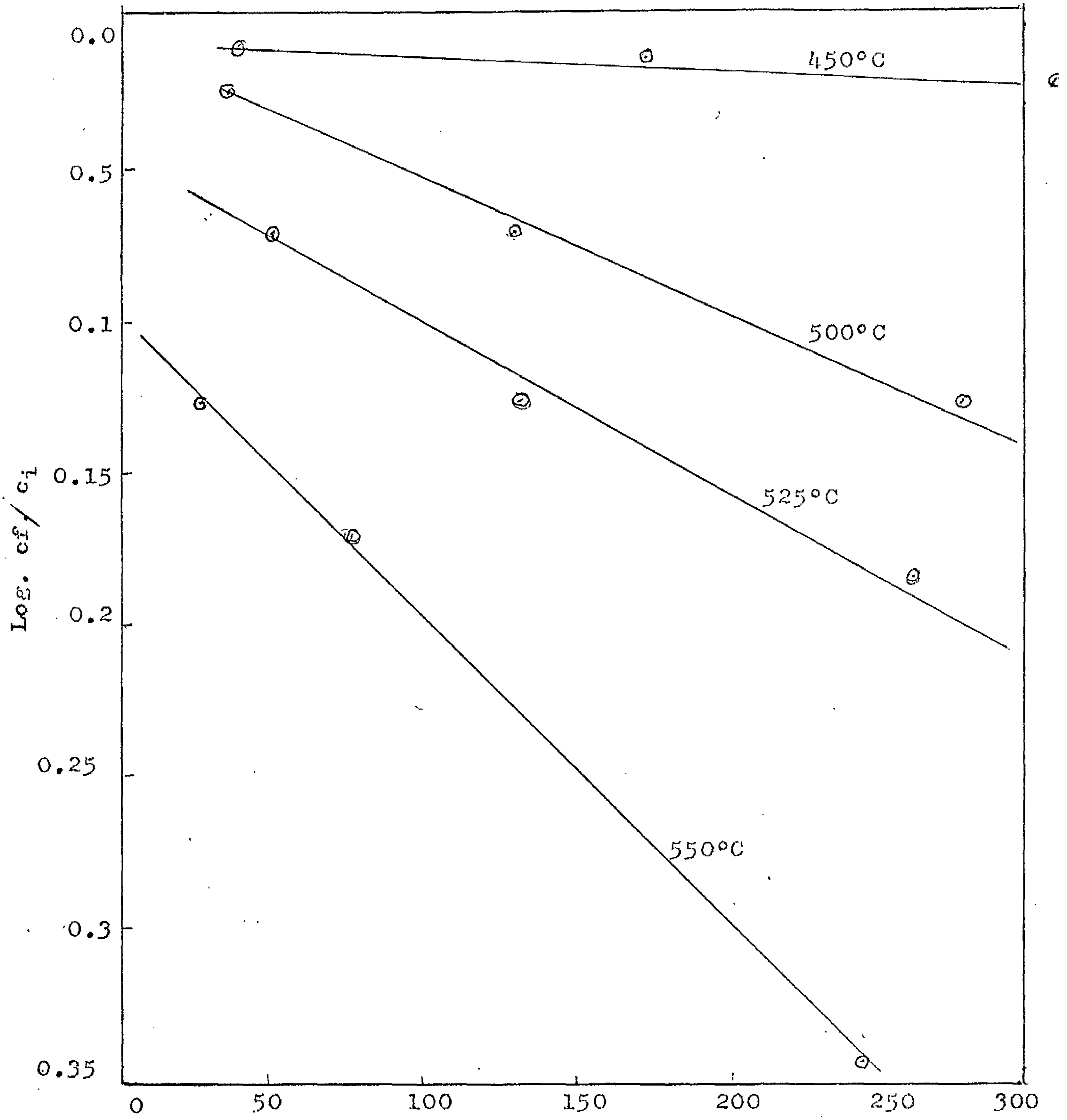


Fig.11. Plot of log c_f/c_i VS Residence time for the production of acetophenone from vinyl benzoate (Method A)

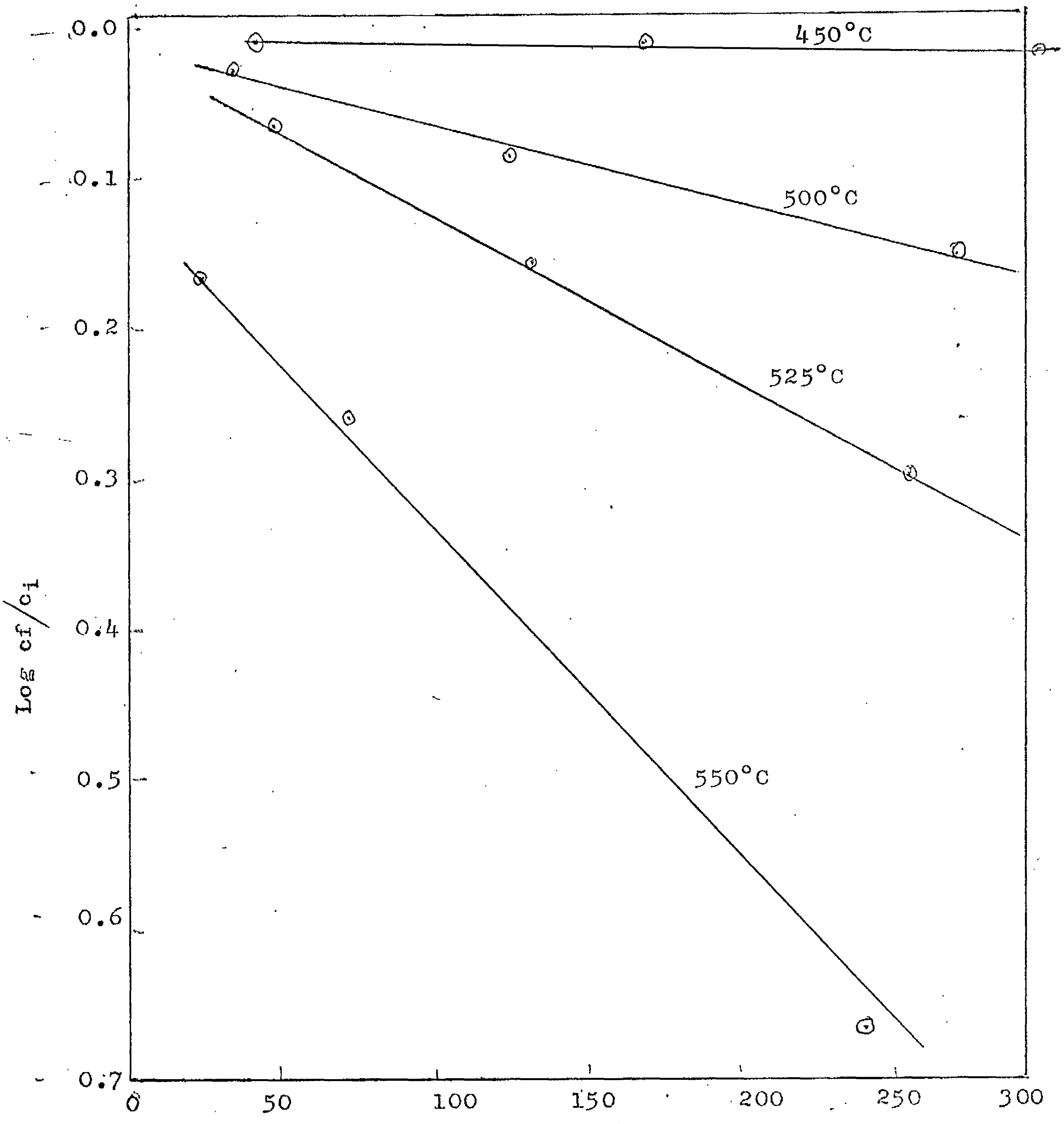


Fig. 12. Plot of log cf/c_i Vs Residence time for the acetophenone formation (Method B).

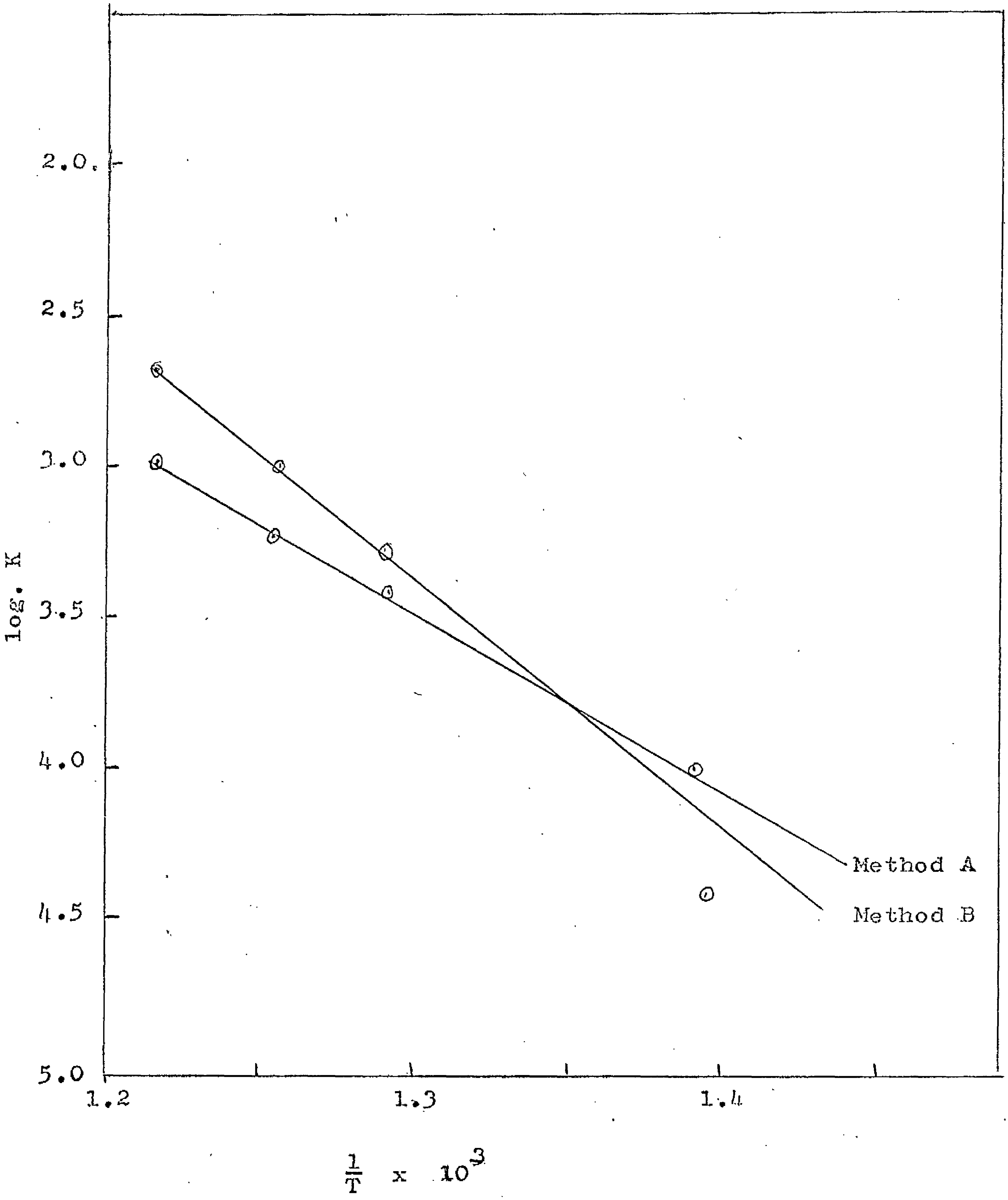


Fig. 13. Arrhenius plots for acetophenone formation,

4.1.6(ii) Activation Energies

Activation energies were calculated by the Arrhenius equation.

$$K = A e^{-E/RT} \qquad \ldots\ldots\ldots\ldots\ldots(8)$$

where K = rate constant

A = frequency factor

E = activation energy

R = gas constant (1.986 cal/degree/mole)

T = absolute temperature (°K)

Plots of log K vs T^{-1} were drawn, and the activation energies calculated (slope = $-E/2.303R$). The following values were obtained for the overall reaction and the R/C^1 reaction

Table 8

Activation energy for the overall decomposition	38.7 k.cal/mole	
Activation energy for acetophenone formation	31.02 37.6	Method A Method B
Activation energy for styrene formation	14.6 16.2	Method A Method B
Activation energy for carbon monoxide	28	K.cal/mol.

4.1.7 Mass-balance

An attempt was made to complete a mass-balance by washing out the reactor with mixed solvents, evaporating the solvents and weighing the residue. Tar adhering to the walls was combusted at high temperature, with oxygen passing through the reactor, and the carbon dioxide and water given off were estimated by absorption in soda lime and magnesium perchlorate respectively. This method, however, did not work well, since a large amount of water condensed and fell into the receiver at the bottom of the reactor and could not be estimated.

The only alternative was to weigh the reactor before and after each run, and this was done.

Vinyl benzoate was pyrolysed at 550°C, with residence time 237 seconds.

Details

Amount pyrolysed	5.100 g.
Amount recovered	3.564 g.
Amount of gases collected	660 ml.

Quantitative analysis of the recovered liquid by gas chromatography is given in Table 9.

Table 9

No.	Compounds	% Composition	Weight gm.
1	Benzene	4.3	0.15
2	Toluene	1.4	0.05
3	Styrene	12.0	0.44
4	Acetophenone	63.9	2.26
5	Vinyl benzoate	18.2	0.66

Gas analyses = Total gas collected ≈ 660 ml.

Table 10

No.	Compounds	% Composition	Weight gm.
1	Carbon monoxide	77.8	0.63
2	Carbon dioxide	10.8	0.139
3	Acetylene	8.2	0.056
4	Unstd. hydrocarbon	3.2	-
		Total ≈	0.825

Adding all the weights together, we thus have:

Amount recovered (liquid-solid pyrolysate)	3.56 g.
Gases	0.83
Solvent extract	0.46
Weight difference of the reactor before and after pyrolysis	0.18
Total	5.03 g.

5.10 g. was pyrolysed and 5.03 g. was accounted for which is 98% of the initial vinyl benzoate. This discrepancy is within the experimental error.

4.2 Pyrolysis of Benzoylacetaldehyde

Benzoylacetaldehyde was pyrolysed at 500°C, with residence time 100 sec. (The aldehyde contained up to 10% of acetophenone, arising during its preparation; (See section 3.1.2) 5 g. of the aldehyde was pyrolysed, and, as expected, broke down exclusively by C^1 scission to give acetophenone and carbon monoxide.

4.3 Pyrolysis of Vinyl Benzoate over Wood's Metal Components.

The pyrolysis of vinyl benzoate over the low-melting metals, tin, lead, cadmium, and bismuth, was studied by and dropping the molten metals into the reactor along with the vinyl benzoate. The vaporised ester and the molten metals come into contact as they pass down over the glass helices which comprise the packing of the reactor.

A difficulty encountered was that at the lower temperatures at the bottom of the reactor, the metal solidified and prevents liquid pyrolysate from flowing down into the system. The difficulty was overcome by removing the glass helices from the last 2 inches of the reactor, so that the metals will either fall down into the receiver or solidify on the walls.

Detailed analyses are given inthe Tables 11-15, where results 6-10 show the analysis of the liquid pyrolysate, and results 11-14 the analysis of the pyrolysate gases.

From these tabulated results it appears that Wood's metal components increase the overall decomposition (see Fig. 1) shows a plot of percentage pyrolysis against residence time in presence of these metals, and also alone in an all-glass system. It can be seen that the order of the effect of Wood's metals on the pyrolysis of vinyl benzoate is as follows:

$$\mathrm{Sn} > \mathrm{Pb} > \mathrm{Cd} > \mathrm{Bi}$$

The yield of diphenyl is also increased from 2 to 4% and of benzaldehyde from a mere trace up to 2%.

The only pyrolysis products which are appreciably affected by the presence of metals are carbon dioxide and benzene. The amount of carbon dioxide given off is approximately

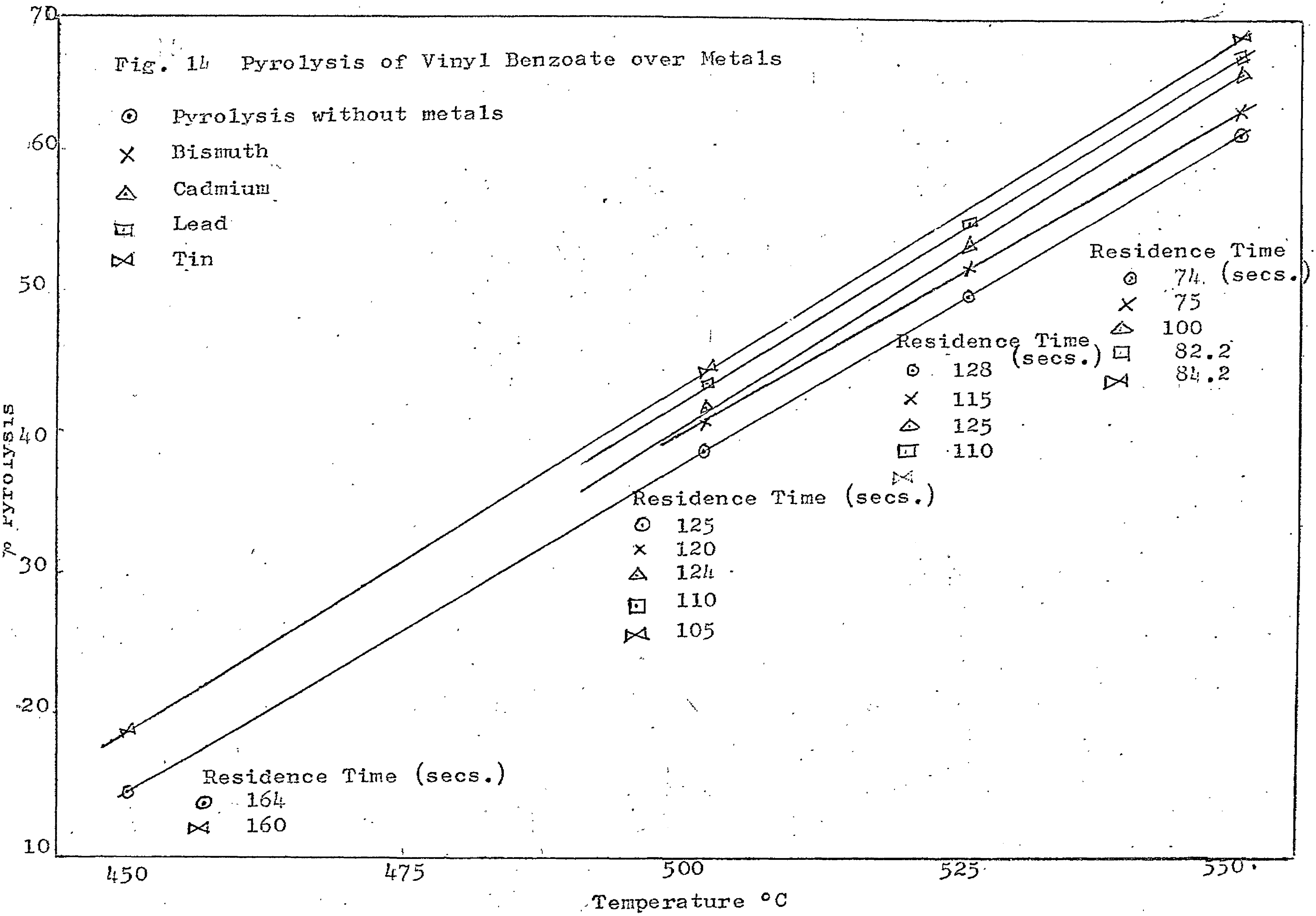


Fig. 14 Pyrolysis of Vinyl Benzoate over Metals

Table No. 11

PYROLYSIS OF VINYL BENZOATE OVER METALS

No.	Temp.	450°C	500°C			
1	Metal	Sn	Sn	Pb	Cd	Bi
2	Residence Time (sec.)	160	105.9	110.4	124	120
3	% pyrolysis	18.5	41.3	41.0	40.0	39.1
4	Amt. pyrolysed (g.)	4.20	5.20	4.10	3.00	2.00
5	Amt. recovered (g.)	3.54	3.76	3.26	2.36	1.59
6	Amt. Gas collected (ml.)	174	399	290	220	130
7	Benzene (%)	0.5	2.3	2.1	1.9	1.8
8	Toluene (%)	2.0	0.5	0.6	0.6	0.5
9	Styrene (%)	1.1	5.4	4.4	4.2	3.9
10	Acetophenone (%)	3.3	16.8	17.2	16.2	16.0
11	Vinyl benzoate (%)	94.8	75.8	76.2	77.2	78.2
12	CO (%)	47.5	59.0	59.0	59.0	58.2
13	CO_2 (%)	40.3	29.3	30.2	30.2	31.0
14	CH; CH (%)	9.5	10.4	8.2	8.6	8.6
15	Unsat. Hydrocarbon (%)	2.7	1.4	2.6	2.2	2.2

Table 12

PYROLYSIS OF VINYL BENZOATE AT 525°C OVER METALS

No.	Metals	Lead	Bi	Cd
1	Residence Time (sec.)	110	115	125
2	% pyrolysis	54	52.6	52
3	Amt. pyrolysed (g.)	4.0	3.6	2.9
4	Amt. recovered (g.)	3.22	2.76	2.22
5	Gas collected (ml.)	390	366	
6	Benzene (%)	2.4	2.3	2.8
7	Toluene (%)	0.84	0.82	0.88
8	Styrene (%)	5.4	4.8	4.9
9	Acetophenone (%)	25.8	25.6	26.8
10	Vinyl benzoate (%)	67.8	68.7	67.7
11	CO (%)	58.9	59	56.6
12	CO_2 (%)	29.21	30.0	32.2
13	CH:CH (%)	9.44	8.2	7.9
14	Unsat. Hydrocarbon (%)	2.4	2.6	3.2

Table 13

PYROLYSIS OF VINYL BENZOATE AT 550°C OVER METALS

No.	Metals	Sn	Pb	Bi	Cd
1	Residence Time (sec.)	84.2	82	75	100
2	% pyrolysis	68.9	67.8	63.5	66.2
3	Amt. pyrolysed (g.)	4.6	3.9	2.62	3.04
4	Amt. recovered (g.)	3.42	2.92	1.54	2.3
5	Gas collected (ml.)	620	529	375	480
6	Benzene (%)	5.2	6.5	5.31	5.45
7	Toluene (%)	1.4	1.17	1.29	0.98
8	Styrene (%)	10.5	8.95	6.73	6.2
9	Acetophenone (%)	30.3	39.53	35.37	41.9
10	Vinyl benzoate (%)	43.6	43.86	51.44	45.4
11	CO (%)	59.0	60.0	65.0	60.0
12	CO_2 (%)	29.6	28.0	24.0	28.7
13	$CH \vdots CH$ (%)	8.4	7.9	8.5	8.2
14	Unsat. Hydrocarbon (%)	3.1	3.1	3.0	3.1

doubled in the presence of metals, under the same condition of pyrolysis (e.g. at 500°C in the presence of metal the products of the pyrolysis contain 30% of carbon dioxide compared with 14.4% without metal and with about the same residence time). This is probably due to secondary decomposition of benzoic acid to carbon dioxide and benzene (the well-known thermal decarboxylation is accompanied [56] by a minor amount of decarbonylation to phenol: see Table 14). To confirm this idea benzoic acid itself was pyrolysed in presence and absence of tin. The benzoic acid was extracted by ethanol and titrated by standard N 10 sodium hydroxide in ethanol.

4.4. Pyrolysis of Benzoic Acid

Benzoic acid was pyrolysed in the form of tablets (see Section 3.6). The detailed results are given in the following Table 14.

Table 14

PYROLYSIS OF BENZOIC ACID AT 550°C

No.	Particulars	Pyrolysis Alone	Pyrolysis in presence of tin
1	Amt. pyrolysed	12 tablets ≃ 3.12 g.	14 tablets ≃ 3.64 g.
2	Amt. recovered	2.78	2.80
3	% pyrolysis	11.0%	22.2%
4	Amt. of gases	170 ml.	250 ml.
5	Residence time	10 sec.	11 sec.
6	Carbon dioxide	90%	80%
7	Carbon monoxide	9.2%	17.8%
8	Benzene	90%	80%
9	Phenol	10%	20%

Note: Result 3 is based upon the amount of benzoic acid recovered unchanged

Results 6-7 show composition of exit gases (by volume)

Results 8-9 show composition of non-gaseous pyrolysate (by weight)

4.5 Radioactive Tracer Work

4.5.1 Preparation of Labelled Vinyl Benzoate

Vinyl benzoate, labelled with ^{14}C in the carboxyl group, was prepared from radioactive [$^{14}CO_2H$]-benzoic acid by the Adelman [89] vinyl interchange method. The labelled benzoic acid was obtained from the U.K. Atomic Energy Commission Radiochemical Centre, Buckinghamshire, England.

5 mg. of 0.1 mc. benzoic acid were dissolved in boiling distilled water (2 l.), and 50 g. of Analar (inactive) benzoic acid were then further dissolved in the same solution, which was thoroughly stirred and allowed to cool. The recrystallised acid was dried under vacuum. 5 g. of the dried material (0.01 ml or 10 µc) were then further diluted with 50 g. of inactive Analar benzoic acid in order to make up to a suitable concentration for measurement with the liquid scintillation counter. 50 g. of this benzoic acid (10 µc) were dissolved in 120 g. of vinyl acetate with shaking. 2 g. of mercuric acetate and 1 ml. of concentrated sulphuric acid was added to form the catalyst mercuric sulphate in situ. The mixture was refluxed for 77 hr. at 35°C cooled, treated with anhydrous sodium acetate, and fractionally distilled through a 2 ft. column. The product had b.p. 71°C 3 mm. (Yield 20 g.: 50%).

4.5.2 Activity Measurements

The activity of the liquid and solid products was measured using a liquid scintillation-counter, while that of the gases was measured using an end-window geiger counter, which had been previously calibrated.

The scintillation-counting technique, as well as other methods for measuring radioactivity, rests on the interaction of nuclear radiations with matter. The effect of these interactions offers a unique way of detecting single nuclear events. In gas counters and ionisation chambers use is made of ionised particles produced in the counting gas. These charged particles are collected at the electrodes, giving rise to a small electrical current or voltage variation, either of which may be recorded after suitable amplification.

In scintillation counting, use is made of the photons created when a suitable luminescent material is excited by nuclear radiations. These photons are collected at the cathode of a photocell, which converts them into electrons. Multiplication of these electrons in the photomultiplier tube will give rise to the electrical pulses which may be recorded in the usual way.

The Nuclear Enterprise (Edinburgh) Scintillation Counter was made. It was calibrated by the standard ^{60}Co (γ-ray) 1 μc source. The following conditions were used for the activity measurements.

Constant voltage EHT	750 v.
Coarse gain	20
Fine gain	0.55
Pulse height	0.25

Using 512-channel analyser.

The scintillator (NE 213) consisted of a mixture of 3 g. litre^{-1} of 2,5-diphenyloxazole (P.P.O), and 0.1 g. litre^{-1} of 1,4-bis[2-(5-phenyloxazole)]-benzene (P.O.P.O.P), in toluene.

4.5.3 Background Corrections

Because of cosmic radiations and other factors a background radiation is always counted by the counter. This was corrected as usual by subtracting the background counts from the original counts. Where possible attempts were made to minimise the background counts by using lead sheets, especially in counting with the end-window Geiger counter.

4.5.4 Initial Activity of Labelled Vinyl Benzoate

5 mg. (100 µc) of benzoic were diluted to 50 g. acid . 5 g. of this mixture (10 µc) was used for preparation of the ester. The yield of ester was 15 ml. (50%).

0.1 ml. of this 15 ml. of ester was diluted with 'unlabelled' ester to 1 ml., and 0.1 ml. of this diluted product was used for measurement. It was added to 4 ml. of scintillation solution (NE 213), gave 80 c.p.s. (counts/sec) with background corrections.

Since 3.7×10^{10} d.p.s = 1C

The initial activity of vinyl benzoate

$$= \frac{80}{37} \text{ m}\mu\text{c}$$

$$= 2.16 \text{ m}\mu\text{c}$$

Total activity in 15 ml. = 2.16 x 150 x 10 = 3.25 μc

4.5.5 Pyrolysis of Labelled Vinyl Benzoate

7.5 g. (1.625 μc) of labelled vinyl benzoate was pyrolysed at 500°C in a flow-reactor, with a residence time of 50 seconds. 6.5 g. of non-gaseous pyrolysate and 340 ml. of gases were collected. The former product was distilled, in order to get a colourless liquid for scintillation counting, and also to permit the making of a colourless and pure derivative of acetophenone. Acetophenone was isolated as its semicarbazone derivative, which was recrystallised from methanol (m.p. 198°C ; lit., m.p. 198-201°C). The activities of all these products were measured separately.

4.5.6 Activity of Overall Non-gaseous Pyrolysate

0.1 ml. of the distillate from the non-gaseous pyrolysate (6.5 g.) was diluted to 1 ml., and 0.1 ml. of this solution was added to 4 ml. of scintillator solution. After background correction, this solution gave 72 c.p.s.

$\therefore$ Activity of Solution $= \frac{72}{37}$ mμc

$= \underline{1.95 \text{ mμc}}$

$\therefore$ Total activity in pyrolysed products collected (6.5 g.)

$= 1.95 \times 65 \times 10 = 1.27$ μc

Initial activity in vinyl benzoate	= 1.625 μc
Activity in the pyrolysed products	= 1.27 μc
% Activity in the pyrolysed	= 78.5% of the initial value.

4.5.7 Activity of Acetophenone

A similar pyrolysis of unlabelled- vinyl benzoate (550°C; residence time 74 seconds; section 4.1.3) yielded about 40% of acetophenone. It was therefore assumed that 40% acetophenone i also produced in the 'labelled' reaction.

Total mass of pyrolysate	= 6.5 g.
Percentage of acetophenone assumed in pyrolysate	= 40%

$\therefore$ Mass of acetophenone in pyrolysate = 2.6 g.

$\therefore$ Theoretical weight of semicarbazone derivative of acetophenone in pyrolysate = 3.6 g.

60 mg. of semicarbazone was dissolved in 10 ml. of acetone, 0.1 ml. of this (containing 0.6 mg.) was used for

measuring. After background corrections it gave 4 c.p.s.

$\therefore$ The activity in 0.6 mg. $= \frac{4}{37}$ muc = 0.108 mμc

activity in 60 mg. = 10.8 muc

$\therefore$ Activity in 3.6 g. of semicarbazone $= \frac{3600 \times 10.8}{60}$

= 650 mμc

Initial activity in vinyl benzoate (7.5 g.) = 650 mμc

Activity in pyrolysate (liquids) (6.5 g.) = 1.27 μc

= 78.8% of the initial

Activity in acetophenone (2.6 g. 40%) = 650 mμc

= 47% of total original activity.

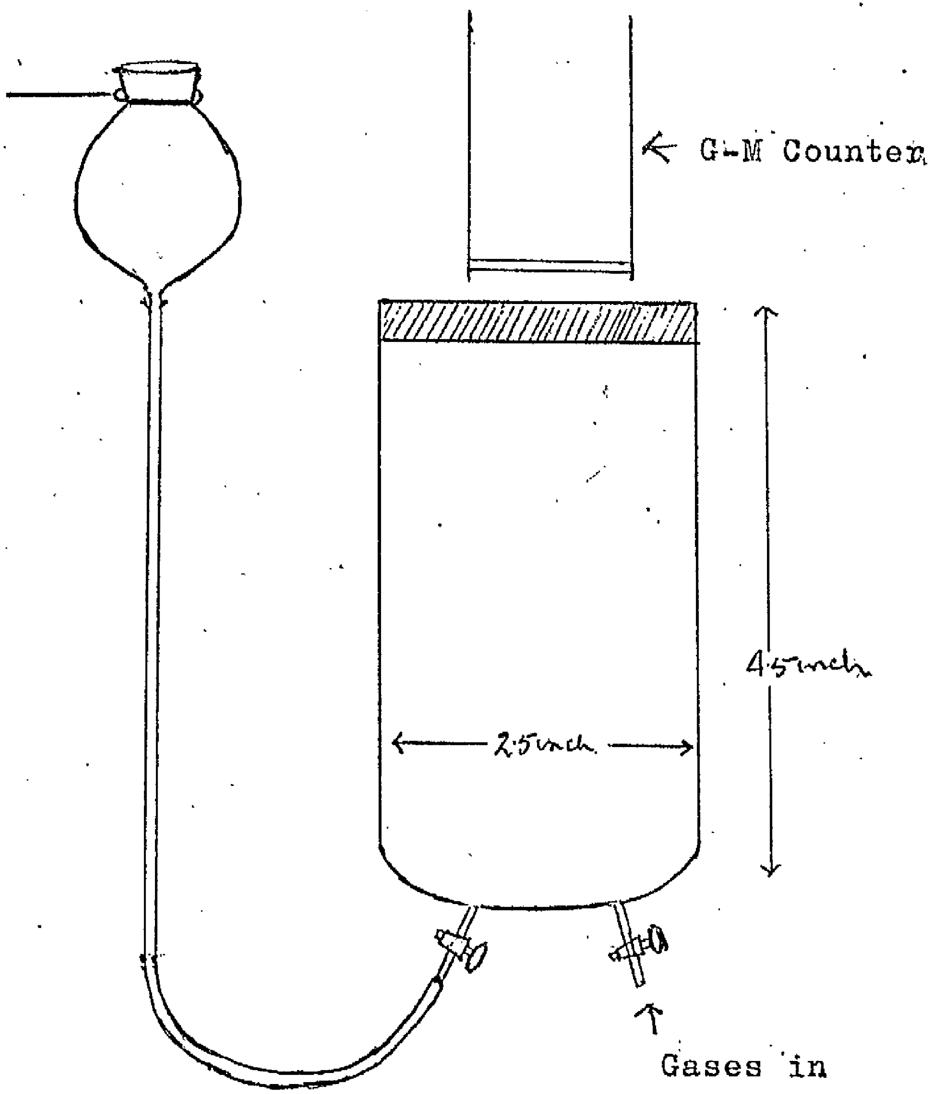
4.5.8 Activity of Gaseous Pyrolysate

The activity of the gases was measured by the end-window Geiger counter.

A simple apparatus was designed to enable the counter to be brought near the gases, and their activities to be measured in a standardised manner. This consisted of a gas sampling tube with an open end covered with a polythene window [Fig. 15]. The bottom of the tube contained two stopcocks, one connected to a thistle funnel through which the tube could be filled with

Fig. No.15

Apparatus for measurement of activity in gases



acidified water, and the other for introduction of the gas sample.

The counter was calibrated by injecting an aqueous solution of standard radioactive sodium carbonate ($Na_2{}^{14}CO_3 5\mu c$) and a 10% sulphuric acid solution into the sample bottle through the polythene film by means of a syringe. The puncture in the polythene film was immediately sealed with a piece of Sellotape and the radioactive carbon dioxide evolved was counted by bringing the window of the counter to approximately less than 0.5 cm. from the polythene window.

500 c.p.s. were recorded, and, therefore, it can be deduced that if vinyl benzoate of 2 μc is pyrolysed, and pyrolysis goes to the extent of 65% at 550°C, approximately 50% of the activity will be in the carbon monoxide, if the proposed mechanism is incorrect (see Chapter 5), and a count of 100 c.p.s., which is easily detectable, would be recorded.

The pyrolysed gases, after background corrections, gave 10 c.p.s. = 0.1 μc (6.2% of the initial activity of the vinyl benzoate). However, when these gases were treated with alkali (to absorb carbon dioxide), the residual gases gave only 2 c.p.s after background correction, which is equal to only 1.2% of the initial activity of the vinyl benzoate. Hence, the liberated carbon monoxide is virtually inactive, within the limits of accuracy of the counting technique: the activity of the gas clearly resides in the carbon dioxide.

5. DISCUSSION

5.1 Original Aims of the Work

The work was begun with one clear intention though a second intention emerged as it proceeded.

Previous studies on the pyrolysis of vinyl benzoate [2, 41, 42] had given a good general picture of the reactions contributing to total breakdown: but there had been no systematic quantitative study of changes in composition of the complex pyrolysate brought about by changes in temperature, residence time in the reactor, and the presence or absence of catalysts. It was hoped that by using a range of these variables, it would be possible to produce significant changes in the relative amounts of the breakdown products, and accurate quantitative analysis of the total pyrolysate for each choice of variable might then shed some light on the nature of the mechanism of each competing route. It might, for example, prove possible to determine the reaction order of each and to calculate their activation energies; and if only some of the routes were effected by the presence of metallic catalysts it might be possible to divide them into clearly different categories, and perhaps to distinguish between molecular, ionic, and free radical reactions. The results have been presented in section 3.

As the work proceeded, it was also decided to study one of the main breakdown routes (R/C^1) by means of isotope-labelling and to use model compounds to elucidate the mechanism of breakdown of some related esters previously examined in these laboratories by other workers. These results have been presented to Part II.

5.2. Limitations of Analytical and Experimental Techniques

It was first of all necessary to develop sufficiently accurate methods of quantitative analysis. Gas-chromatographic methods calibrated by synthetic samples were mainly relied upon: these have been described in Section 3.3 Part I) and their limits of reproducibility assessed, but the following points may be emphasised here.

Of the compounds to be estimated, benzoic acid (formed by A^2 scission) was one which could not be determined by this method, since it is very strongly adsorbed by the column packing, and the chromatograms always gave a 'tailing' effect. A similar poor separation of certain fatty acids was observed by Martin and James [21], though they were able to eliminate this 'tailing' effect by using a column containing 10% w/w stearic acid, Silicone oil (DC 550), with 10% orthophosphoric acid. A similar type of column containing orthophosphoric acid was tried in the present work, but without success, and it was decided to use determination of acetylene rather than of benzoic acid as the measure of the primary A^2 route.

Another limitation of experimental accuracy has also to be considered here. The temperature of the reaction was considered to be the highest temperature within the furnace: moreover, as described in Section 3. It was assumed that the liquids entering the furnace acquires that temperature immediately and lose it on leaving. Temperature fluctuations were not more than ± 5°C during each run, since most of the runs were done at a fairly slow feed-rate.

5.3. General Nature of Quantitative Results.

One disappointing fact soon became apparent during the work, namely, that in general the variables studied had surprisingly little effect on the ratio of the competing breakdown routes. This meant that part of the original intention could not be achieved. Also, though the main non-gaseous product (acetophenone) was formed in sufficient amount to be determined quite accurately, within the limits of experimental error, most of the others (such as styrene, toluene, and benzene) were formed in such relatively small amounts that the unavoidable experimental error was here fairly serious. Reliable calculations could be based on the amount of acetophenone, and of undecomposed ester; but calculations based upon other minor materials were obviously less reliable. The fraction of ester breaking down to acetophenone by the R/C^1 route was ca. 75% under most conditions, and the characteristics of this particular reaction could be separately assessed with some confidence.

The overall breakdown of vinyl benzoate could also be measured quite accurately (based upon undecomposed ester): but its apparently simple nature must be regarded with some reserve. It is clearly dominated and determined by the major R/C^1 reaction: and it must not be assumed that all the other competing reactions are also simple and of the first order. It is well known that many vapour-phase reactions which appear to be simple and give good first order plots are in fact the sum of several complicated contributing concurrent reactions.[89].

The activation energy of the overall pyrolysis is 38.7 k.cal/mole. The activation energy of the R/C^1 reaction is between approximately 31.0 and 37.6 k.cal/mole (the limits as estimated by two different methods: see Section 4 Part I). That of the C^2 reaction has been calculated from the styrene content of the total pyrolysate and appears to be between approximately 14.2 and 16.6 k cal./mole (again the limiting values from two methods of estimation). These latter figures are surprisingly low, and even though determination of the small styrene content is less accurate than that of the large acetophenone content, it is unlikely that the calculated activation energy of the C^2 reaction is entirely wrong. This large difference between the R/C^1 and C^2 activation energies is nevertheless consistent with previous tentative conclusions (summarised in Section 1 Part I), that there is a marked difference between the mechanisms of these two breakdown routes.

5.4. Reaction Mechanisms

5.4.1 The R/C^1 Route

In the light of the present evidence, coupled with the evidence of previous workers [2, 41, 42], this reaction is best considered as proceeding by a molecular mechanism. A four centre cyclic transition - state for the vapour-phase rearrangement of vinyl benzoate to its isomeric β-ketoaldehyde was suggested by Allan, Forman, and Ritchie [2] (see Section 1]. The intermediate benzoylacetaldehyde then decomposes further to give acetophenone and carbon monoxide. Benzoylacetaldehyde is extremely unstable and was never isolated from the pyrolysate. In the present work benzoylacetaldehyde was prepared and pyrolysed at 400°C, giving almost exclusively acetophenone and carbon monoxide.

There was, however, no clear proof of the above picture, and the possibility of some other mechanism could not be excluded (see Section 1.1.3)

Confirmation has now been obtained by pyrolysing isotope labelled vinyl benzoate (550°C; residence time 50 sec.), prepared by the known ester interchange [59] method, from vinyl acetate and [$^{14}CO_2H$]-benzoic acid. If the postulated mechanism (see Section 1 Part 1) is correct, none of the original radioactivity should appear in the eliminated carbon monoxide from the proposed transient benzoylacetaldehyde, whereas it cannot be correct if the acetophenone is inactive and the carbon monoxide active.

The results were completely in agreement with the original postulate. Some 79% of the original activity appeared in the liquid pyrolysate, and acetophenone (separated as semicarbazone) showed some 47% of the initial activity. 6% of the original activity appeared in the gases; but when these were later treated with alkali (30% KOH) to remove carbon dioxide, the residual gases had only a mere trace (1-2%) of the original activity, which is within the experimental error of the counting techniques. Hence, it is confirmed that carbon monoxide is in fact produced by the thermal decarbonylation of the CHO group of the intermediate benzoylacetaldehyde.

5.4.2 Decarboxylation

It has been found by various workers that duality in the mechanism occurs in the decarboxylation of vinyl carboxylates. Bengough, Ritchie and Steedman [72] deduced that the overall decarboxylation is mainly homogeneous, but also occurs in part at the walls of the reaction vessel. Similarly, Reininger and Ritchie [45] found that pyrolysis of vinyl *o*-, *m*- and *p*-chlorobenzoate yielded chlorostyrene having very largely the orientation of the parent ester; but critical examination of the pyrolysate by infrared and gas-chromatography revealed a very minor amount of differently substituted (orientated) chlorostyrenes. This again suggests that there is duality in the mechanism, the major one preventing change of orientation and the minor leading to a change.

Another example of this dual nature of mechanism is provided by Reininger, Ritchie and Ferguson [78]. They copyrolysed an equimolar mixture of phenyl fumarate and 4-chlorophenyl maleate, which gave a mixture of *trans*-4,4'-dichlorostilbene (49%), *trans*-stilbene (22%), and *trans*-4-chlorostilbene (1%).

Phenyl fumarate and 4-chlorophenyl maleate, when pyrolysed separately, gave *trans*-stilbene and 4,4'-dichlorostilbene respectively. It was thought that if the decarboxylation occurs by a free radical mechanism, in which each CO.O group is completely detached from its flanking groups before recombination of the later as free radicals, then a good deal of symmetrical trans-stilbene should be obtained. They were able to find very little unsymmetrical stilbene.

The present work also supports the view expressed above. The activation energy for this reaction has been found to be 14-16 k.cal/mol., which is rather low for a free radical reaction. However, a minor amount of diphenyl and 1,3-butadiene has also been detected in the pyrolysate. This can be best explained by postulating that the major decarboxylation (C^2) of vinyl benzoate is a molecular reaction, as suggested by Reininger and Ritchie [45] (see Section 1.3.1, part I), and that the minor one probably proceeds by a free radical mechanism, as follows:

$$\mathrm{Ph.CO_2.CH{:}CH_2} \longrightarrow \mathrm{Ph.} + \mathrm{.CO_2.CH{:}CH_2} \qquad \ldots\ldots\ldots(1)$$

$$\mathrm{.CO_2.CH{:}CH_2} \longrightarrow \mathrm{CO_2} + \mathrm{.CH{:}CH_2} \qquad \ldots\ldots\ldots(2)$$

$$\mathrm{Ph.} + \mathrm{.CH{:}CH_2} \longrightarrow \mathrm{Ph.CH{:}CH_2} \qquad \ldots\ldots\ldots(3)$$

$$\mathrm{Ph.} + \mathrm{.Ph} \longrightarrow \mathrm{Ph.Ph} \qquad \ldots\ldots\ldots(4)$$

$$\mathrm{.CH{:}CH_2} + \mathrm{.CH{:}CH_2} \longrightarrow \mathrm{CH_2{:}CH.CH{:}CH_2} \qquad \ldots\ldots\ldots(5)$$

5.4.3 The A^2 Reaction

It has been mentioned (Section 5.2. Part I) that the benzoic acid produced by this reaction could not readily be measured. Hence, the content of acetylene in the pyrolysate was preferred as a measure of the A_2 reaction; but since there was not much variation in the amount of acetylene, no new evidence for this reaction is presented here.

Very little is known about the A^2 scission, though a lot of work has been done on A^1 scission (see Section 1 Part I). It seems likely, however, that the six-membered cyclic intermediate proposed by Hurd and Blunck [16] for the A^1 reaction also operates for the A^2 reaction. Reininger and Ritchie, in a study of the pyrolysis of the vinyl chlorobenzoates, found that the onset temperatures $T(CH{\vdots}CH)$ for A^2 scission and $T(CH_3.CHO)$ for A^1 scission (of polymer) are similarly and markedly dependent upon the dissociation constant of the parent acid, whereas $T(CO)$ and $T(CO_2)$ form a less dependent pair. Later, Ramsay [74] repeated their results, and found that metal catalysts markedly depress $T(CH{\vdots}CH)$ and $T(CH_3CHO)$, but does not effect $T(CO)$ and $T(CO_2)$. This again suggests that A^1 and A^2 scission have a similar class of mechanism, but different from that of R/C^1 and C^2 scission.

5.5 The Pyrolysis of Vinyl Benzoate over Metals.

In general, all the metals employed as catalysts increased the overall composite pyrolysis. Increased amounts of gases were collected. The order of catalytic activity is as follows:

$$Sn > Pb > Bi > Cd$$

However, the most effective metal (tin) increased the pyrolysis by only 4%. The pyrolysis is thus not strongly catalysed, and the small increase in overall pyrolysis may be due to a difference in the effective packing of the reactor, rather than to catalysis. These results, therefore, do not of themselves exclude the possibility of that the overall reaction may be homogeneous rather than the heterogeneous.

Once again, the gas-chromatograms did not reveal any new compounds, though the yields of benzaldehyde and diphenyl were increased. Benzaldehyde occurred in the non-catalysed reactions to only a minute extent, while in the presence of metallic catalysts the yield increased to about 2%. Similarly, the yield of diphenyl increased from 2% to 4% (approx.). The yields of secondary products (benzene and toluene) also increased to a great extent. The yield of benzene increased to almost double the amount formed during pyrolysis without metals.

5.5.1 Origin of Carbon Dioxide

The gaseous pyrolysate from the metal-catalysed reactions showed a marked increase in the amount of carbon dioxide present (almost double the amount with an all-glass system).

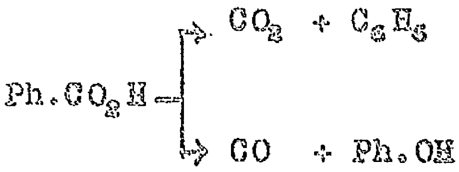
Table 15

Amount of CO_2: Tin as Catalyst

Temperature	450°C		500°C		550°C	
Reactor	all-glass	Sn	all-glass	Sn	all-glass	Sn
Residence Times (sec)	160	167	125	124	75	74
% Carbon dioxide (vol.)	16.9	40.2	14.7	30.2	12.8	29.6
% Benzene (wt.)	0.64	0.5	0.9	1.9	2.2	5.2

However, gas-chromatographic analysis did not show any corresponding increase in the amount of styrene; but increase in the amount of benzene was noted, again roughly double the amount from non-catalysed reactions. This suggests that a secondary decomposition of benzoic acid is taking place in the presence of metals, since decomposition of bensoic acid is a well known heterogeneous reaction. Moser [56] pyrolysed benzoic acid in presence of copper and reported a nine-fold increase in the breakdown.

To check this idea, benzoic acid was pyrolysed alone and in the presence of tin as catalyst. It was found that the pyrolysis indeed increased two-fold under the experimental conditions. This may explain the large increase in the amount of carbon dioxide. In addition to benzene and carbon dioxide, phenol (10%) and carbon monoxide were also detected in the pyrolysate from benzoic acid. Moser [56] had previously recorded this little-known pair of competitive scissions:



$$Ph.CO_2H \rightarrow \begin{cases} CO_2 + C_6H_6 \\ CO + Ph.OH \end{cases}$$

5.5.2 The Acyl-oxygen Scission

The presence of benzaldehyde in the pyrolysate confirms the very minor acyl-oxygen scission (B^2). This is increased by metal catalyst in the reactor and high temperature is required for this route, which suggests that it might be free radical in nature.

Vinyl benzoate can react thus to a small extent, because of the presence of a β-hydrogen atom. Where there is no β-hydrogen atom in the hydrocarbon group of an ester, route B^2 predominates [77].

In the molecule of vinyl benzoate, the electron-attracting property of the carbonyl group, the nucleophilic character of the phenyl group, and the electron repulsion of the vinyl group may counterbalance each other and scission across the C–O bond would probably be free radical. Since the bond energy of the C–O bond is 85 k.cal .

However, on the above evidence, it is possible that the initial scission produces two free-radicals, which then disproportionate, thus:

$$\begin{tikzcd}
\mathrm{Ph.CO.O.CH{:}CH_2} \arrow[r] & \mathrm{Ph.CO.} \arrow[d, "+H"] & + & \mathrm{O.CH{:}CH_2} \arrow[d, "-H"] \\
 & \mathrm{Ph.CHO} & & \mathrm{O{:}C{:}CH_3}
\end{tikzcd}$$

Keten, which should accompany benzaldehyde in this reaction, was not detected in the pyrolysate which is not surprising since it is a known unstable gas [75]. Young [75] pyrolysed keten and found it to decompose at 510°C into carbon monoxide, carbon dioxide, methane, ethylene, and hydrogen

5.6 2-Phenyl-1,3-butadiene.

Zwanenburg [76] has studied the pyrolysis of 1-ethoxyvinyl carboxylates (R' = OEt, in scheme below), and has obtained evidence for the following sequence of reactions:

Rearrangement: $\mathrm{R.CO_2.CR'{:}CH_2 \longrightarrow R.CO.CH_2.CO.R'}$

Enolisation: $\mathrm{R.CO.CH_2.CO.R' \longrightarrow R.C(OH){:}CH.CO.R'}$

Acylation: $\mathrm{R.C(OH){:}CH.CO.R' + R.CO_2.CR'{:}CH_2}$

$\mathrm{\longrightarrow R.CO_2.CR{:}CH.CO.R' + Me.CO.R'}$

If this idea is applied to vinyl benzoate (where R = Ph and

R' = H), it appears that in addition to the pyrolysis products already noted there might be a minor reaction sequence of the above type, leading to $Ph.CO_2.CPh:CH.CHO$, which would breakdown further by decarbonylation to $Ph.CO_2.CPh:CH_2$. Now, since it has been shown (Section 4.1.4 and 4.1.5, Part I) that pyrolysis of vinyl benzoate alone yields _inter alia_ small quantities of diphenyl and 1,3-butadiene (consistent with the idea of a minor free radical component of C^8 scission), its pyrolysis in the presence of some $Ph.CO_2.CPh:CH_2$ might correspondingly be expected to yield _inter alia_ a mixture of 1,3-butadiene, 2,3-diphenyl-1,3-butadiene, and 2-phenyl-1,3-butadiene (with the last named predominating). To check this idea 2-phenyl-1,3-butadiene was prepared; its infrared absorption and chromatographic retention times were determined, and its presence was sought in the pyrolysate from vinyl benzoate. The results were, however, negative. Either the Zwanenburg pyrolytic sequence is not followed if R' = H, or decarboxylation (C^8) does not occur in measurable amount by way of a free radical mechanism: there is insufficient evidence here to distinguish between these two alternatives.

PART II

Mechanism of Pyrolytic Production of Benzaldehyde from 2-Phenoxyethyl Acetate

PART 2

Mechanism of pyrolytic production of benzaldehyde from 2-phenoxyethyl acetate.

6. INTRODUCTION

Iongar and Ritchie [38], while studying the pyrolysis of the model compound 2-hydroxyethyl benzoate for the pyrolysis of poly(ethylene terephthalate), found that its analogue 2-phenoxyethyl acetate breaks down thermally at 500–550°C in the following way:

$$\mathrm{AcO.CH_2.CH_2.OPh} \longrightarrow \left\{\begin{array}{ll}
\rightarrow \mathrm{Ac.OH + CH_2{:}CH.OPh} & \ldots\ldots\ldots A^1 \\
\rightarrow \mathrm{Me.CHO} + [\mathrm{PhO.CH_2.CHO}] & \ldots\ldots\ldots B^1 \\
\qquad\qquad\qquad \downarrow & \\
\qquad\qquad \mathrm{CO + Ph.O.CH_3} & \ldots\ldots\ldots C^1 \\
\rightarrow \mathrm{Ph.OH + AcO.CH{:}CH_2} & \ldots\ldots\ldots A^1 \\
\qquad\qquad\quad \downarrow & \\
\qquad\qquad \mathrm{CO + COMe_2} & \ldots\ldots\ldots B/C^1 \\
\rightarrow \mathrm{Ph.CHO}\ (+\ \text{unknown products}) &
\end{array}\right.$$

The ester breaks down predominantly by A¹ scission to give acetic acid (33%) and phenyl vinyl ether, with a little acyl-oxygen scission to acetaldehyde and phenoxyacetaldehyde. Phenoxyacetaldehyde could not be identified in the products; but its predictable decarbonylation (C^1) products were identified (anisole and carbon monoxide). Similarly acetone, a major predictable product from vinyl acetate, was also identified.

On the whole the pyrolysis of the ester follows the known breakdown modes, except for the very surprising formation of benzaldehyde. Knights and Cooper [79] also independently found benzaldehyde (17%), on the pyrolysis of the same ester at 600°C in a flow reactor. The aim of the present work was to elucidate the reaction mechanism by which benzaldehyde is produced.

The formation of benzaldehyde at first sight entails a step where phenoxy group is ruptured at the very stable phenyl-oxygen bond. It was thought unlikely that such a primary scission occurs, but it is perhaps possible that some homolytic scission takes place at the $-CH_2-CH_2-$ grouping of the molecule, in which case the following stages may occur:

$$\begin{array}{ccc} \text{AcO} - CH_2 & \vdots & CH_2.\text{O.Ph} \\ & \downarrow & \\ [\text{AcO}.CH_2.] & + & [.CH_2.\text{OPh}] \\ \downarrow{+H} & & {-H}\downarrow \\ \text{AcOMe} & & \text{Ph.CHO} \\ & & (\text{rearrangement}) \end{array}$$

The two free radicals may disproportionate, with transfer of hydrogen, and with rearrangement of the $-C-O-Ph$ skeleton to $-O-C-Ph$, yielding benzaldehyde.

The tentative suggestion that breakdown occurs by the above mechanism can be studied by labelling the C atoms of the $-CH_2-CH_2-$ linkage with C^{14} and following the activity in the decomposed products. If radioactivity appears in the benzaldehyde, this would agree with the mechanism proposed above. However such a study might be difficult, because benzaldehyde is produced to the extent of only 10-15% in the reaction, with the further possibility of the known C^1 scission at higher temperatures to benzene and carbon monoxide. Hence, only very little benzaldehyde may survive in the pyrolysate which will require the use of higher active initial ester so as to detect positively the active benzaldehyde. Eventually it was decided to study the above reaction by means of a modified and symmetrical model compound:

$$PhO.CH_2.CH_2.OPh$$

The advantages of this compound are as follows:

(1) It eliminates complications due to the acetyl grouping in the ester first considered.

(2) It has two symmetrically disposed phenoxy groups, so that if scission occurs within the $-CH_2-CH_2-$ grouping, it will give rise to two identical radicals $[PhO.CH_2.]$, one of which may lose hydrogen and rearrange to give benzaldehyde. At the same time, the other should give anisole.

The literature was first of all surveyed, in a search for known radical rearrangement of the type R-O-C. → R-C-O.

Radical Rearrangements

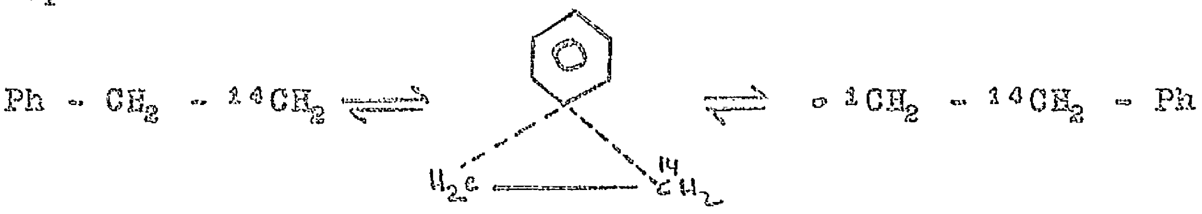
The reactions of organic molecules in the gas phase and in non-polar solvents often involve free-radical intermediates Several further reactions of such intermediates can take place, including recombination, disproportionation, etc. Recent work has established that a further important reaction of the free radicals produced in such a system is intramolecular rearrangement or isomerisation. Detailed reviews of this topic are given by Fish [80] and Reutov [81].

Radical rearrangements can be represented as an attack by the free valency of the radical on some other bond in the radical. These reactions occur by intramolecular transfer of an atom or group, usually the hydrogen atom.

Urry and Kharasch[82] were the first to observe a skeletal rearrangement, while studying the reactions between phenyl magnesium bromide and neophyl chloride in the presence of cobalt chloride, thus:

$$Ph - CMe_2 - CH_2 . \xrightarrow{\text{Rearrangement}} .CMe_2 - CH_2 - Ph$$

Later, a similar type of skeletal rearrangement was revealed in cobalt chloride catalysed reactions between organomagnesium compounds and halogen derivatives [83], in particular, rearrangement with 1,2 migration of the aryl group



No references to the phenoxymethylene radical Ph.O.CH$_2$. could be traced, though the two following results are of some relevance. Razuvaev and Terman [84] found that dibenzylperoxydicarbonate decomposes in solution in the following way:

$$Ph.CH_2.OC.O.OC.O.CH_2.Ph$$

$$\Big\downarrow -2CO_2$$

$$2[Ph.CH_2.O]$$

$$\Big\downarrow \text{H from solvent (benzene and isopropyl alcohol)}$$

$$PhCHO \;+\; PhCH_2OH$$

Furthermore, Porter et al. [85] irradiated anisole, and found that it breaks down to give a radical of the type Ph.O. and not Ph.O-CH$_2$.

7. EXPERIMENTAL

7.1 Preparation of Ethylene Glycol Diphenyl Ether (1,2-diphenoxyethane)[86].

$$2NaOPh + Br.CH_2.CH_2.Br \xrightarrow{\text{Cu as catalyst}} Ph.O.CH_2.CH_2.O.Ph + 2NaBr$$

Sodium phenolate was prepared by dissolving phenol in concentrated sodium hydroxide in water. It was filtered and washed with ether on the Buchner funnel to remove any unreacted phenol and also sodium hydroxide. It was dried under vacuum (Yield 100%; m.p. 61°C).

Equimolar quantities of sodium phenolate (232 g.) and ethylene dibromide (94 g.) were mixed in xylene in 500 ml. R.B. flask. Some copper bronze was added to the mixture as catalyst. It was then heated for 2 hr. at 140°C xylene was distilled off, the residue was washed with water to remove unreacted sodium phenate, and extracted with ether. The desired ether was obtained (Yield 60°, m.p. 97°C. Literature m.p. 97°C)

7.2 Pyrolysis of 1,2-Diphenoxyethane

7.2.I Pyrolysis in Flow Reactor

The ether was pyrolysed in the flow reactor at 550°C (residence time 150 sec.) by the method described in Section The feed rate was controlled roughly. 4g. of the ether was used, but at this temperature almost all of it was recovered as solid, and only 50 ml. of gases were collected. The solid pyrolysate was dissolved in chloroform and a vapour-phase chromatograph was taken (Apiezon L column: 150°C). Traces of phenol and anisole were readily detected, and there was also a very small peak corresponding to the retention time of benzaldehyde. However, in view of the very slight amount of breakdown, it was decided to confirm these products by means of a static pyrolysis.

7.2.II Pyrolysis in Static Reactor

The static reactor (Fig. 16) consisted essentially of a tube 9 inch long an 1.5 inch diameter, with a thermocouple pocket. The exit gases and liquids were passed through a coil where unreacted pyrolysand was condensed and returned to the reactor. The gases were collected as previously described for flow reactor. Nitrogen was passed through the apparatus for about 2 hr. before pyrolysis. The ether was melted and dropped in the reactor; it was pyrolysed at 550°C for about 1 hr.

Much tar was produced and 200 ml. of gases, and all the material, both from cold trap and from reactor, was collected in a single sample bottle and gas chromatographed at 150°C. Four products were identified and measured, as shown in the table below.

Fig. 16

Static Reactor

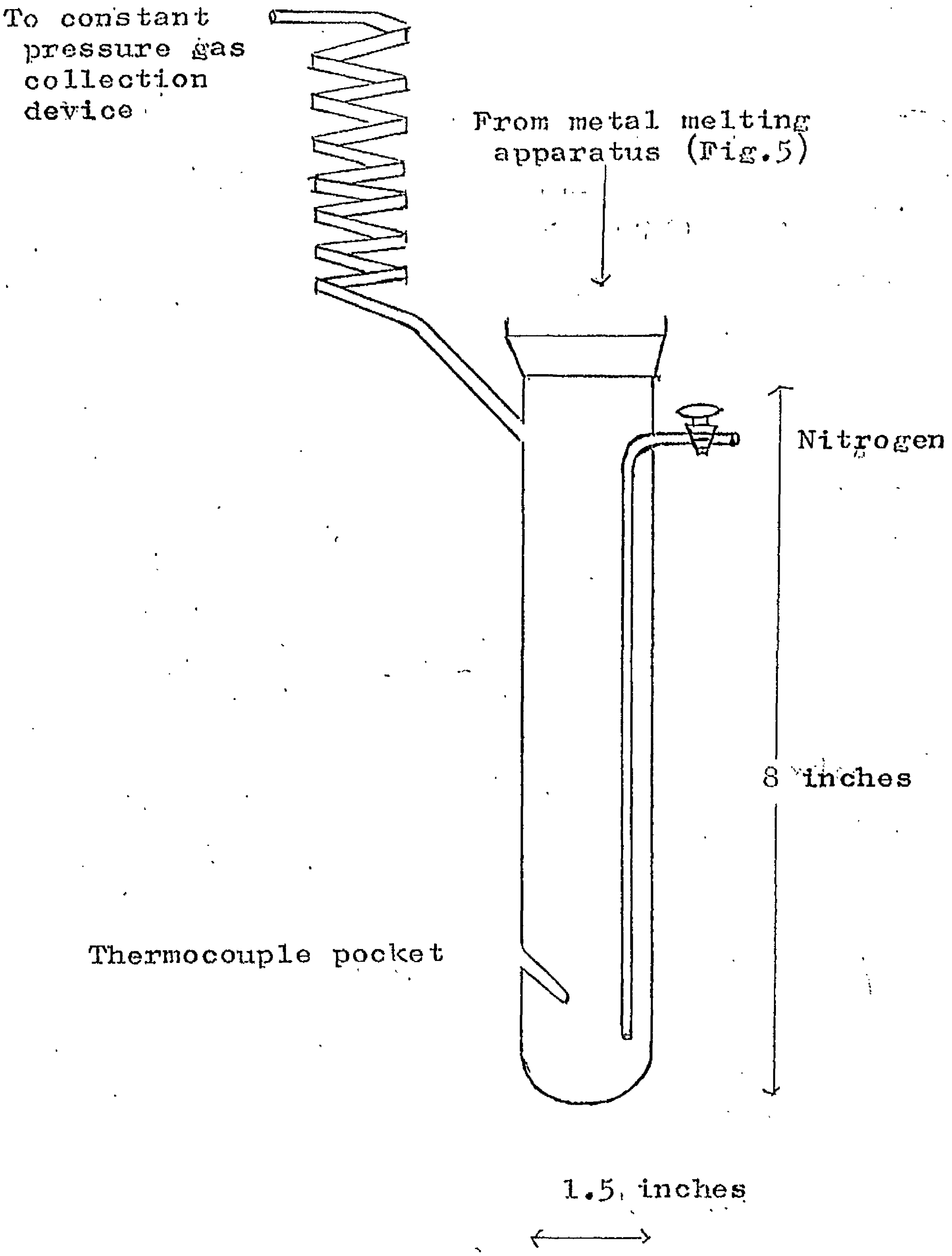


Table 16

Retention times (sec.) for two duplicate runs

Compounds	Pyr. I	Pyr. II	Control	Relative Amounts
Benzene	81	77	77	10%
Toluene	115	120	120	2%
Anisole	217	210	212	23%
Phenol	340	360	350	65%

Chromatographic conditions:

Column: Apeizon L on Celite 545

Temp.: 150°C

Gas flow rate: 20 ml minute

Sensitivity: X10

Detector Voltage: 1250 volts.

7.2.III Analysis of Exit Gases:

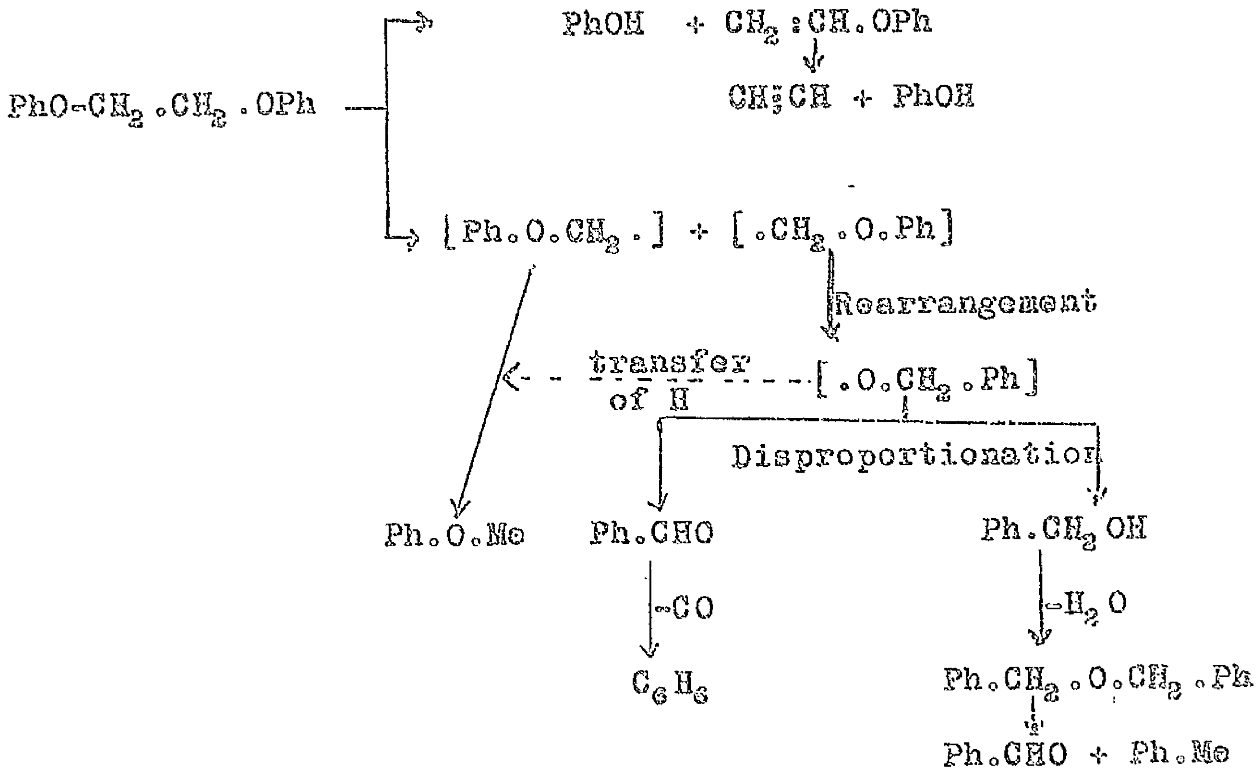
$CO = 78\%$

$CH\vdots CH = 18\%$

Unsat. hydrocarbon = 4%

8 DISCUSSION

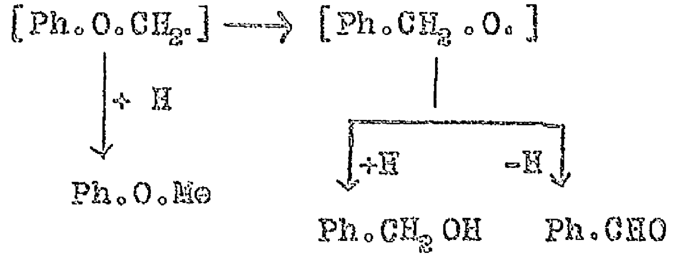
The products detected in the pyrolysate can be tentatively accounted for by the following scheme



1,2-Diphenoxyethane is extremely stable, but at high temperatures it breaks down mainly by A^2- scission to phenol (65%). Phenyl vinyl ether, which should accompany this, was not present in the pyrolysate but it is known [38] to break down readily to phenol and acetylene (detected). Benzaldehyde was not detectable in the pyrolysed products but its expected decarbonylation products, benzene (10%) and carbon monoxide, were observed. As would be expected, benzaldehyde will not survive at 550°C in a static reactor for 1 hr. Nevertheless it is possible that benzaldehyde is in fact produced during pyrolysis of 1,2-diphenoxyethane as shown on p.98

There ideas can be applied to the earlier pyrolysis of 2-phenoxyethyl acetate. It is possible that a similar mechanism operates in the pyrolytic production of benzaldehyde as suggested on page

Among other products detected in the pyrolysate from 1,2-diphenoxyethane were anisole (23%) and toluene (2%). The production of toluene is interesting. It seems likely that it is yet another product from the phenoxymethylene radical. The phenoxymethylene radical can form two isomeric products, anisole and benzyl alcohol with the gain of hydrogen :



9. Pyrolysis of Benzyl Alcohol

Benzyl alcohol was pyrolysed in a flow reactor. The following compounds were identified in the pyrolysate by gas-chromatography by means of their retention times, as in the following table.

Table 17

Retention Time (sec.)

Compounds	Pyrolysate	Control
Benzene	51	50
Toluene	69	70
Benzaldehyde	120	120
Diphenylmethane	149	150
Dibenzyl	170	172
Dibenzyl ether	240	245

Chromatographic conditions:

Column: 10% Silicone high vacuum grease on Celite 545, mesh 80-120

Column Temperature: 200°C

Gas Flow Rate: 25 ml min.

Detector voltage: 1250 v. x 10 sensitivity.

This confirms the view that toluene is in fact produced amongst other substances by the further decomposition of benzyl alcohol. It is known from previous work [87] that dibenzyl ether yields toluene and benzaldehyde on pyrolysis.

Proposed direct study of the phenoxymethylene radical

To confirm these ideas fully, it is obviously desirable to study the behaviour of the phenoxymethylene radical, in solution or in gas-phase. This radical should be produced by phenoxyacetyl peroxide:

$$PhO\cdot CH_2.CO.O.O.OC.CH_2.OPh$$

With the loss of carbon dioxide, it should yield two phenoxymethylene radicals, whose behaviour could then be studied. This peroxide does not appear to be known, but Mr. A. Pajaczkowski [88] kindly attempted to prepare it, and to evaluate its stability. He tried six preparations by various methods, but without success, though there was some indication by infrared spectrometry of a transient peroxide group at one stage, which was stable only in the refrigerator. Due to the lack of time, this interesting idea could not be pursued further, but it is hoped that some future worker may complete the study.

10. APPENDIX

Gas Analysis

The gaseous pyrolysates were analysed in Hempel's absorption apparatus using the following solutions.

Acetylene: Alkaline potassium iodomercuric solution was prepared from mercuric chloride (40 g.), potassium iodide (100 g.), and sodium hydroxide (8 g.), dissolved in water and made up to 220 ml. [90].

Carbon Dioxide: The solution employed was prepared by dissolving potassium hydroxide (60 g.) in water which was then made up to 200 ml.

Unsaturated Hydrocarbons: Bromine (60 g.) was dissolved in an aqueous solution of potassium bromide (10%) for this reagent.

Carbon Monoxide: An ammoniacal solution of cuprous chloride was prepared from cuprous chloride (40 g.), 150 ml. of (30%) ammonium chloride solution, and concentrated ammonia (30 ml.).

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