THE THERMAL DECOMPOSITION OF ESTERS, POLYESTERS, AND RELATED SUBSTANCES.

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award of the degree of Doctor of Philosophy.

by

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SUMMARY

In the first section of the thesis a study was made of the vapour-phase decomposition of the ester cyclohexyl benzoate. The ester was pyrolysed in a flow reactor system at temperatures between 300° and 500°.

Thermal breakdown of the ester was also studied in a static system by an empirical method in which the breakdown rate was followed by measuring pressure changes in a system containing the vapourised ester with a quantity of liquid reflux. From the study using the flow reactor system it was found that the ester decomposed by an exclusive alkyl-oxygen scission to give benzoic acid and cyclohexene only, over the range of temperatures employed. In the presence of small amounts of metal catalysts, breakdown of the ester was more complex and several competitive scissions were detected. From studies with the static reactor system it was found that the exclusive alkyl-oxygen scission of the ester was a homogeneous reaction.

In the second part of the thesis, the thermal decomposition routes of three esters were studied using

a flow system at 500°. The first ester, vinyl benzoate, was investigated as part of a study of the decomposition of the polyester 'Terylene'. The main pyrolysis route was re-examined in greater detail and a new minor competitive scission established, by which the ester produced keten and benzaldehyde.

Two other related enol carboxylates, isopropenyl benzoate, and α-phenylvinyl benzoate were pyrolysed and the products examined. Decomposition of each ester took place by several competitive scissions including thermal rearrangement to a β-diketone, previously reported to be the exclusive breakdown product for this group of esters.

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PART I

Competitive Routes in the Pyrolysis of Cyclohexyl Benzoate

PART 1

1. INTRODUCTION

1.1. General

Pyrolysis, or the effect of heat on organic compounds, has been a notable field of research for a number of years. Structural changes in, and breakdown products from, materials subjected to heat stresses have been determined for many groups of compounds[1]. In spite of the complex nature of many degradations, the general routes by which a variety of compounds decompose are well established.

1.2. The Pyrolysis of Esters and Polyesters

The thermal degradation of carboxylic esters has been studied widely. Esters of the general formula $R.CO_2.CH_2.CH_2.R'$ have been found to undergo pyrolysis according to the general scheme[2,3]:

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

Ester pyrolysis was recognised as a method for preparing olefins, and for a considerable period esters were thought to pyrolyse smoothly by one route, producing an olefin and acid only. Early workers frequently failed to seek other competing routes, but it was later realised that although this was often the major route, others could compete, and in some cases, actually predominate.

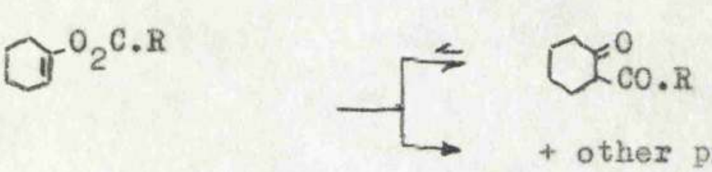
With the advent of better analytical techniques, competing routes were detected which could not have been recognised by the methods available to earlier workers. Methods used to investigate the breakdown products from several acetates, work completed as recently as 1956[4,5], have been shown to be in error[6] with the advent of improved analytical techniques.

Many examples of ester pyrolysis in the literature now appear to be of questionable value owing to the fact that no attempt was made to detect compounds which could arise from competing routes; in some cases products were found which could only have arisen from secondary decomposition of primary fragments. For example, Chitwood[7] identified benzoic acid and vinyl benzoate in the pyrolysate from ethylene dibenzoate, but failed to detect acetophenone, found later by Allan and Ritchie,[8] as the main product from secondary breakdown of vinyl benzoate:

$$\mathrm{Ph.CO_2.CH_2.CH_2.O_2C.Ph} \rightarrow \mathrm{Ph.CO_2H} + \mathrm{Ph.CO_2.CH{:}CH_2}$$

$$\mathrm{Ph.CO_2.CH{:}CH_2} \rightarrow \mathrm{(Ph.CO.CH_2.CHO)} \rightarrow \mathrm{Ph.CO.CH_3} + \mathrm{CO}$$

In some cases an ester whose main pyrolysis route has been established, has been re-investigated and other routes found. For example, it has been claimed[9] that enol carboxylates undergo thermal rearrangement to β-diketones. Ritchie *et al.*[10] confirmed this, but were also able to detect several other competing routes:



+ other products(*cf.* p.15 *et seq.*)

The way in which any ester breaks down depends ultimately on many factors. The extent and variety of competitive scissions is affected by points of weakness in the molecule, structural and substituent groupings, lability of hydrogen atoms and steric effects; in addition, temperature, pyrolytic techniques, in the gas or liquid phase, static or flow systems must all be considered.

Much recent detailed work on ester pyrolysis has been published as a result of studies of the thermal stability of organic polymers and polyesters. The behaviour of the polyester, poly(ethylene terephthalate) or 'Terylene'(I.C.I. Ltd., Fibres Division) has been of interest. Degradation of this material has been studied by two methods, the first of which involves an examination of the polymer itself. Using this technique, Pohl[11] measured the rate of gas evolution from the polymer at 300° and suggested that random main-chain scission was occurring. The polymer was found to evolve water, carbon dioxide, carbon monoxide, and in the pyrolysate, anhydride and carboxyl functional groupings were detected. Pohl suggested that the methylene groups β- to the ester groups were the weak points in the molecule. Marshall and Todd,[12] studying changes in the melt viscosity of the polymer at 300°, concluded also that random main-chain scission was occurring, and suggested a possible free-radical mechanism.

Traces of unwanted colour in the polyester have been shown to be caused by slight thermal degradation during the manufacturing process. Small amounts of polyene groups and poly-substituted benzene nuclei were produced, and small quantities of coloured material were isolated by Goodings.[13] This worker also demonstrated that the presence of acetaldehyde, from degraded material in the polymer, increased the rate of decomposition.

The second method devised for the study of the degradation of 'Terylene' involved the choice of a model compound representing a segment of the polyester chain, or a pyrolysis product from the segment. The choice was made by examination of the polymer chain, and the compounds studied contained the same end groupings or other linkages as the polymer:

$$\sim\sim O_2C.Ph.CO_2.CH_2.CH_2.O_2C.Ph.CO_2.CH_2.CH_2.O_2C.Ph.CO_2 \sim\sim$$

This technique was devised by Ritchie,[8] and it led to the publication of much work on the pyrolysis of alkyl esters of aromatic acids.[14-17] Kinetic studies and identification of the reaction products were greatly simplified by this method. The importance of ester pyrolysis was apparent from these studies, as was the variety of decomposition routes. A nomenclature system has been suggested by Ritchie[14] to cover various routes for ester breakdown, and is described in the following section.

1.2.1. Alkyl- and alkenyl-oxygen scission: Routes A^1 and A^2

$$\underset{\text{I}}{R.CO_2.CH_2.CH_2.R'} \rightarrow R.CO_2H + CH_2{:}CH.R' \qquad ...A^1$$

$$\underset{\text{II}}{R.CO_2.CH{:}CH.R'} \rightarrow R.CO_2H + CH{\vdots}CR' \qquad ...A^2$$

This, the classical route in ester pyrolysis, involves the rupture of a carbon-oxygen bond and transfer of a proton. The scission requires the presence of a β-hydrogen atom in the alkyl group of the molecule. At some point in the process the proton of the alkyl grouping becomes attached to the carbonyl oxygen of the ester group. Rupture of the bond between the ether oxygen of the ester group and the α-carbon of the alkyl portion takes place, and the products are an acid and an unsaturated hydrocarbon molecule. The route is designated A^1 or A^2 depending on the degree of unsaturation of the hydrocarbon produced.

Typical compounds decomposing by the A^1 route to give the corresponding acid and olefin are ethyl benzoate[3](I; R=Ph, R'=H) and ethyl acetate[2](I; R=CH_3, R'=H). Vinyl acetate(II; R=CH_3, R'=H), and vinyl benzoate[14](II; R=Ph, R'=H) both decompose by several routes, one of which is an A^2 scission.

Variations in the alkyl portion of the ester have been shown to affect the pyrolysis temperature and decomposition routes. Hurd and Blunck,[18] in a study of n-, s-, and t-alkyl acetates, found that the stability of the ester increased as the number of available β-hydrogen atoms decreased, but that with increased thermal stability greater complexity of the pyrolysis routes occurred. For ethyl, isopropyl, and t-butyl acetates, Maccoll[19] showed that the decomposition rates were in a ratio of 1:26:515 at 400°. The corresponding formates gave a decomposition rate ratio of the same order, indicating that changes in the acid group of the ester molecule have a relatively small effect on its thermal stability.

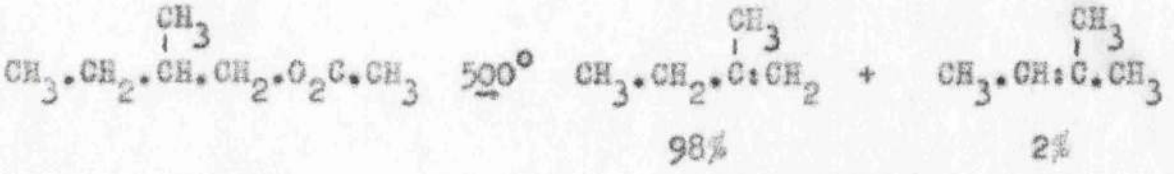
The relative thermal stability of esters was confirmed by van Pelt and Wibaut,[20,21] and other workers[22]. In the ester pyrolyses studied by van Pelt and Wibaut, it was also claimed that there was no evidence for competing breakdown routes, and that the olefins underwent no displacement of the double bond or change in the carbon skeleton. Several examples of single-route decomposition were given:

Acetate of:	Olefin produced:
butan-1-ol	but-1-ene
pentan-3-ol	pent-2-ene
hexan-1-ol	hex-1-ene
heptan-1-ol	hept-1-ene
2-ethylbutan-1-ol	2-ethylbut-1-ene
menthol	menth-3-ene

Pyrolysis temperatures for primary acetates were shown to be in the region 500-525°, on the basis of the results obtained from the esters examined.

This work was disputed by Houtman *et al.*[23], who claimed that temperatures in the region of 625° were required for the pyrolysis of primary alkyl acetates, and that decomposition occurred at 500° only if the reactor had been carbonised by previous pyrolyses. For two of the primary acetates examined, small amounts of double bond shift were detected in the olefins produced:

$$\mathrm{CH_3.CH_2.CH_2.CH_2.O_2C.CH_3} \xrightarrow{490^\circ} \underset{98.5\%}{\mathrm{CH_3.CH_2.CH{:}CH_2}} + \underset{1.5\%}{\mathrm{CH_3.CH{:}CH.CH_3}}$$

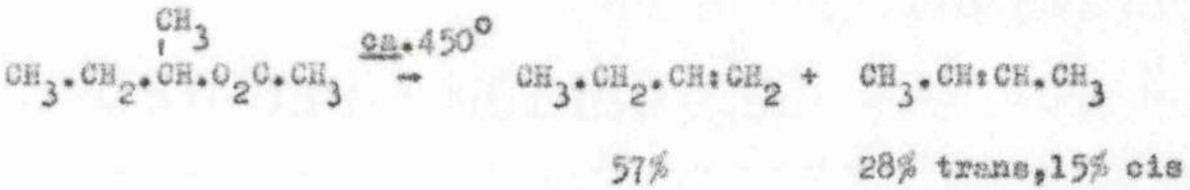


$$CH_3.CH_2.\overset{CH_3}{CH}.CH_2.O_2C.CH_3 \xrightarrow{500^\circ} \underset{98\%}{CH_3.CH_2.\overset{CH_3}{C}{:}CH_2} + \underset{2\%}{CH_3.CH{:}\overset{CH_3}{C}.CH_3}$$

This shift was concluded to be a secondary reaction brought about by increased contact times in the reactor.

1.2.2. Alkyl-oxygen scission: Direction of elimination.

An ester with an alkyl group which consists of an unsymmetrical branched carbon chain may theoretically produce a mixture of isomeric olefins by A^1 route scission.[24] Pyrolytic elimination from *s*-butyl acetate gives the following mixture of isomers:[23,25]



$$CH_3.CH_2.\overset{CH_3}{CH}.O_2C.CH_3 \xrightarrow{\underline{ca}.450^\circ} \underset{57\%}{CH_3.CH_2.CH{:}CH_2} + \underset{28\%\ \text{trans},15\%\ \text{cis}}{CH_3.CH{:}CH.CH_3}$$

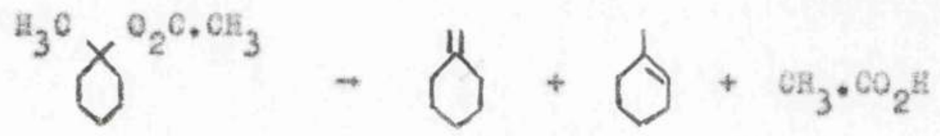
Selectivity in the direction of elimination from esters has been the subject of much controversy. It may be governed by two rules, suggested by Saytzeff and by Hofmann.

Saytzeff,[26,27] from a study of the decomposition of secondary and tertiary alkyl bromides, deduced that the olefin formed preferentially on elimination would be the one bearing the largest number of attached alkyl groups. Production of the predominating olefin is governed by the fact that the eliminated proton comes from the β-carbon atom bearing the smallest number of hydrogen atoms.

Elimination from a quaternary ammonium hydroxide containing different primary alkyl groups was investigated by Hofmann.[27,28] He found that preferential elimination occurred to give the olefin containing the smallest number of alkyl substituents.

Primary esters with an unsymmetrical carbon chain normally give <u>one</u> olefin on pyrolysis, and not an isomeric mixture, so that the rules do not apply. However, olefin elimination from a series of unsymmetrical secondary and tertiary acetates was studied by Bailey and co-workers.[29,30] The olefin produced exclusively in all the cases studied was that bearing the least number of alkyl substituents.
It was concluded that elimination from acetates in the gas phase was governed by the Hofmann rule.[31] Control of the pyrolysis conditions to prevent carbonisation was thought to be the factor responsible for the production of a single olefin.[32,33]

Studies of the pyrolytic behaviour of several acetates by a number of workers[6,25,34] have since shown that Bailey's work was in error. In the eliminations studied, isomeric mixtures of olefins were found, and in a reappraisal of previous work, Bailey and Hale[35] were unable to reproduce the selectivity reported earlier. They studied the effect of temperature variation on the direction of elimination from *t*-amyl acetate and 1-methylcyclohexyl acetate. The Saytzeff product was found to be favoured as the temperature was lowered, but even this has recently been questioned.[6] Results from the pyrolysis of 1-methylcyclohexyl acetate are of interest. The ester decomposes as follows:



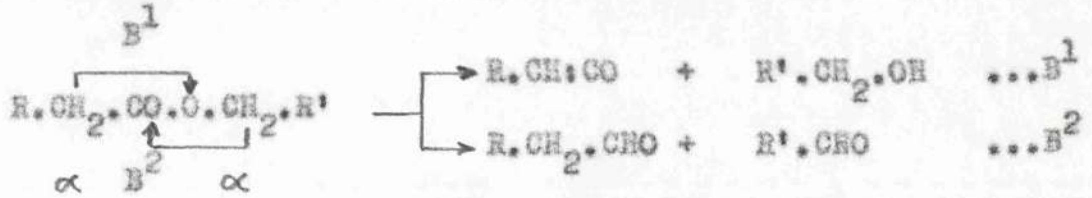
III IV V

Source	Temp.	Composition of olefin mixture	
		IV	V
Bailey *et al.*[30]	450°	100%	nil
Eglinton and Rodger[36]	450°	18%	82%
Froemsdorf *et al.*[25]	450°	24%	76%
Bailey and Hale[35]	300°	15%	85%
	450°	26%	74%
DePuy *et al.*[6]	400-500°	27%	73%

Ingold[40,41] has pointed out that in any one reaction, both rules may govern elimination simultaneously, independently of each other. In elimination from cyclic esters such as acetates and benzoates, the Saytzeff product predominates[6,35,37-39] but is not the exclusive olefin. With non-cyclic acetates, steric and statistical factors favour elimination to give the least substituted olefin, and the predominating olefin is that apparently predicted by the Hofmann rule.

It appears that none of the secondary or tertiary acetates studied gives one specific olefin, and that, in fact elimination occurs in a random fashion governed solely by thermodynamic, steric, and statistical factors inherent in the molecule. The reaction is possibly even less selective than pyrolytic elimination from unsymmetrical amine oxides, shown by Cope *et al.*[42,43] to produce olefinic mixtures.

1.2.3. Acyl-oxygen scission: Routes B^1 and B^2.



$$\overset{\alpha}{R.CH_2}.CO.O.\overset{\alpha}{CH_2}.R' \longrightarrow \begin{cases} R.CH{:}CO + R'.CH_2.OH & \ldots B^1 \\ R.CH_2.CHO + R'.CHO & \ldots B^2 \end{cases}$$

In common with routes A^1 and A^2, acyl-oxygen scission involves rupture of a carbon-oxygen bond and proton transfer. With this route, hydrogen atom transfer occurs from one of the carbon atoms in the α-position to the ester group as shown above, and not the β-position from which transfer takes place in the A^1 and A^2 routes. If the proton migrates from the acyl grouping, the products are a keten and a hydroxyl compound, and the route is designated B^1. Transfer of the proton from the alkyl group, the B^2 route, produces two carbonyl compounds. In general, this route is only common with esters which do not have a β-hydrogen atom in the alkyl portion of the molecule, thus precluding the

A^1 route, and it normally requires higher temperatures than does alkyl-oxygen scission, although a recent investigation[129] suggested that this might not be so. A compound decomposing by two routes, one of which is the B^1 route, is acetyl bromide:[44]

$$CH_3.CO.Br \xrightarrow{600^\circ} CH_2{:}CO + HBr \qquad ....B^1$$

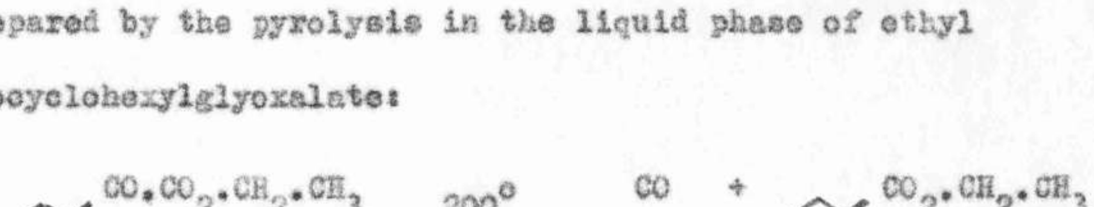
At 1100°, methyl acetate[45] decomposes by several routes, among which is a B^2 scission:

$$CH_3.CO_2.CH_3 \rightarrow \underset{\substack{\downarrow \\ \text{further decomposition}}}{CH_3.CHO} + H.CHO \qquad ....B^2$$

1.2.4. <u>Decarbonylation and decarboxylation: Routes C^1 and C^2.</u>

Loss of carbon monoxide from an ester molecule (route C^1) is relatively uncommon, but this decomposition route has been recorded for phenyl formate.[50] This route has been found to be a characteristic decomposition route for ketones and aldehydes, which yield carbon monoxide and the appropriate hydrocarbon.[46]

Pyrolytic decarbonylation has been used as a synthetic method. For example, in the preparation of pimelic acid from cyclohexanone,[47] the intermediate ethyl 2-ketohexahydrobenzoate is prepared by the pyrolysis in the liquid phase of ethyl 2-ketocyclohexylglyoxalate:



The ester molecule which is decarbonylated may contain a ketonic or aldehydic grouping, but elimination from the molecule of the carbon and oxygen atoms from these functional groups does not necessarily occur, and may in fact take place from the esterified carboxyl group. For instance, Calvin and Lemmon[48] studied the loss of carbon monoxide from ethyl pyruvate by using tracer techniques, and found that the carbon monoxide produced came from the ester group and not the α-carbonyl group:

$$CH_3.C^{14}O.CO_2.CH_2.CH_3 \xrightarrow{110-130^\circ} CO\ (90\%) \qquad ....C^1$$

+ all the radioactive
material in other by-products

A similar technique has been employed to study diphenyltriketone, and it was shown that the central carbonyl grouping was eliminated on pyrolysis.[49]

That it is not always necessary for the ester molecule to contain a ketonic carbonyl grouping to undergo decarbonylation is shown by phenyl formate[50]:

$$H.CO_2.Ph \rightarrow CO + Ph.OH \qquad ....C^1$$

Decarboxylation (route C^2) is well established as a pyrolysis route for carboxylic acids, but has recently been shown to occur during the decomposition of several esters such as vinyl benzoate[14], cyclohex-1-enyl benzoate[10], phenyl acrylate, and phenyl methacrylate.[53] Also, this route has been found to be general for the aryl esters of cinnamic acid[51]:

$$\mathrm{Ph.CH{:}CH.CO_2.Ar} \rightarrow \mathrm{CO_2} + \mathrm{Ph.CH{:}CH.Ar} \qquad \ldots\ldots\ldots C^2$$

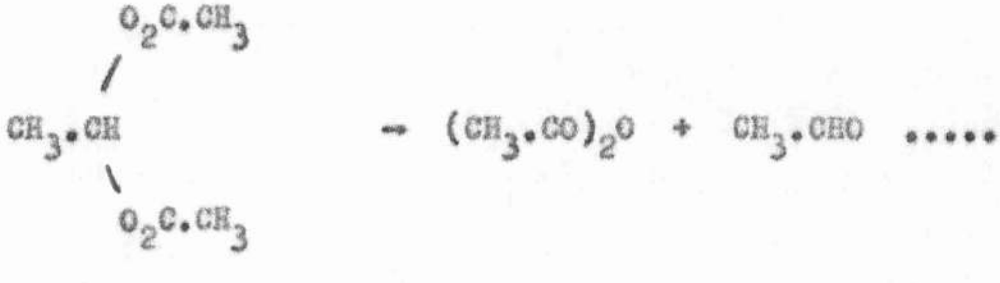
Esters known to undergo decarboxylation (cinnamates, maleates;[52] acrylates;[53] and enol carboxylates[10]) show either olefinic or benzenoid unsaturation, which may be a prerequisite for this route.

1.2.5. Disproportionation: Route D.

In many instances when an ester pyrolyses by the disproportionation route, an apparently intermolecular reaction is involved. For example, the pyrolysis of 2-hydroxyethyl benzoate occurs as follows:

$$2\ \mathrm{Ph.CO_2.CH_2.CH_2.OH} \rightarrow \mathrm{Ph.CO_2.CH_2.CH_2.O_2C.Ph} + \mathrm{HO.CH_2.CH_2.OH}$$

Compounds produced by this route are generally more symmetrical than the original ester. In contrast to the above reaction, ethylidene diacetate produces acetic anhydride and acetaldehyde by a disproportionation reaction.[55] The mechanism suggested was apparently intramolecular, requiring the participation of only one ester molecule:



$$\mathrm{CH_3.CH(O_2C.CH_3)_2} \rightarrow \mathrm{(CH_3.CO)_2O} + \mathrm{CH_3.CHO} \qquad \ldots\ldots\ldots D$$

Many disproportionation reactions have been investigated which occur in the gas phase and involve the transfer of a hydrogen atom.[69] There is a good deal of evidence that the reaction involves a free radical mechanism.[76]

1.2.6. Rearrangement: Route R.

Esters are known to undergo molecular rearrangement in several ways according to a variety of schemes. Rearrangement may or may not require a catalyst, or the reaction may involve a shift or scission of the ester grouping of the molecule in a number of ways. Each rearrangement requires careful examination, and early workers had difficulty studying the phenomenon with esters owing to the transient nature of some of the products. A clue to one type of ester rearrangement, 'keto-enol' tautomerism, was found by Claisen in an investigation of acetyldibenzoylmethane and tribenzoylmethane.[56] He found that each compound could be isolated in two solid forms, true examples of tautomeric systems:

$$\mathrm{Ph.CO.CH(CO.Ph)_2} \rightleftharpoons \mathrm{Ph.C(OH){:}C(CO.Ph)_2} \quad \ldots\ldots\mathrm{R}$$

Later, separate, easily interconvertible isomeric forms of β-ketonic esters and β-aldo-esters were isolated.[57]

Most rearrangements require the application of heat or the presence of a catalyst. A Claisen rearrangement (common to allyl ethers of phenols) brought about by either agency is the conversion of ethyl α-allyloxycrotonate to ethyl α-allylacetoacetate, first reported to require an ammonium chloride catalyst[58] and later found to rearrange by purely thermal means:[59]

$$\begin{array}{l} O.CH_2.CH{:}CH_2 \\ | \\ CH_3.C{:}CH.CO_2.CH_2.CH_3 \end{array} \rightarrow \begin{array}{l} O\ \ CH_2.CH{:}CH_2 \\ \|\ \ \ | \\ CH_3.C.CH.CO_2.CH_2.CH_3 \end{array} \quad ......R$$

Wislicenus[60] studied the rearrangement of methyl formylphenyl acetate and found that it gave two isomers, only one of which would produce a coloured iron complex. Later studies with unsaturated systems, in particular enol carboxylates[61], led the same worker to record their conversion to β-diketones by thermal means:

$$R.CO_2.CR'{:}CHR'' \rightarrow R.CO.CHR''.CO.R' \quad ......R$$

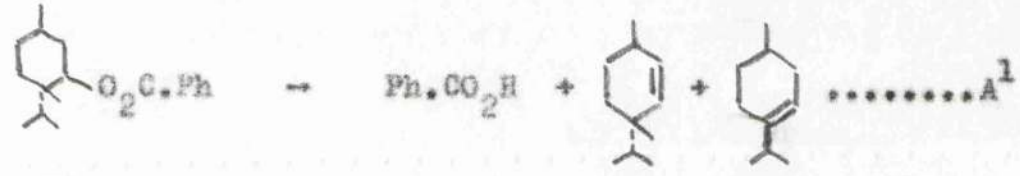
This reaction, found to be common to a number of enol carboxylates,[9,62] both acetates and benzoates, occurred by thermal means and also with a boron trifluoride catalyst at lower temperatures. For isopropenyl acetate, the reaction was originally described[62] as:

$$\begin{array}{l} O_2C.CH_3 \\ | \\ CH_3.C{:}CH_2 \end{array} \xrightarrow{500^\circ} CH_3.CO.CH_2.CO.CH_3 \quad ....R$$

A later study of this reaction by Ritchie *et al.*[10] showed that it was reversible, pyrolysis of the diketone yielding small amounts of the corresponding ester. Pyrolysis of several enol esters and their related diketones showed that equilibrium was far towards the diketone side, and that several minor competing routes were also taking place, not recorded by earlier workers.[62]

1.3. The Pyrolysis of (-)-Menthyl Benzoate.

An outstanding paper by Barton, Head, and Williams[39] showed that (-)-menthyl benzoate(VI) undergoes alkyl-oxygen scission exclusively by the A^1 route at temperatures up to 400° in both static and dynamic systems, to give benzoic acid and a mixture of the olefins (+)-p-menth-2-ene(VII) and (+)-p-menth-3-ene(VIII):

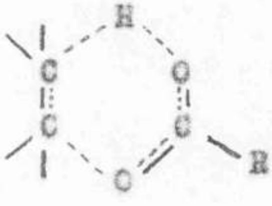


VI VII VIII

From the kinetic study it was found that the ester displayed first order kinetics to greater than 50% decomposition. No induction periods were detected in pyrolyses at lower temperatures in packed reactors, nor was the rate lowered in the presence of propylene or nitric oxide. It was concluded that the reaction was homogeneous and unimolecular, with no evidence for pyrolysis by radical or free-radical chain mechanisms.

Analysis of the pyrolysate revealed that approximately twice as much of VIII as VII was present after decomposition. On the basis of this result, Barton claimed that his postulate[63] on the relationship between cis-elimination and a unimolecular mechanism was correct.

A decomposition mechanism for esters was suggested by Hurd and Blunck,[18] which involved a six-membered transition state shown below; Barton agreed with this mechanism, so that for the menthyl ester, with a unimolecular mechanism established, _cis_-stereospecificity would follow.[63-65]



IX

The related ester, (-)-menthyl acetate(IX; R=Me), has been studied by several workers[37,38] and _cis_-elimination established by product analysis, but no attempt was made to study the reaction mechanism.

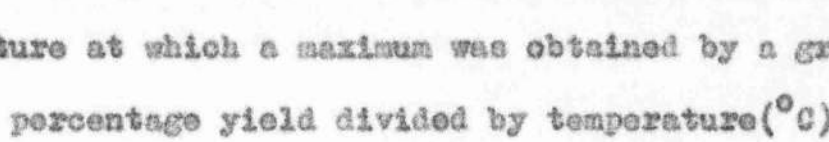
Chemical stoichiometry was established by confirming that the pyrolysis products from (-)-menthyl benzoate were stable under the reaction conditions, and also by careful analysis of the pyrolysate, with the benzoic acid and (-)-menthyl benzoate determined, found to correspond exactly with that expected from a known amount of pyrolysand. In this way it was confirmed that only one breakdown route was occurring under the reaction conditions employed.

1.4. <u>The Pyrolysis of Cyclohexyl Benzoate.</u>

In a study of the effect of molecular size and structure on the pyrolysis of esters, Smith and Wetzel[66] examined a series of cyclohexyl esters from the formate to the octadecanoate which included the benzoate and found that the pyrolysis temperature decreased as the molecular weight of the ester increased.

It was not found possible to correlate the results obtained by comparing the ester structure and size with the pyrolysis temperature which yielded a maximum amount of acid and olefin. Success in this direction came with the concept of 'characteristic temperature'. This was defined as the temperature at which a maximum was obtained by a graphical plot of percentage yield divided by temperature(°C) <u>vs</u>. the temperature(°C). The characteristic temperature was thus the temperature at which the most efficient pyrolysis occurred if the flow rate for all the esters was constant.

Cyclohexyl benzoate was claimed to decompose smoothly at temperatures up to 465°C by a smooth A^1 alkyl-oxygen scission to give benzoic acid and cyclohexene as the only products:



....A^1

Substituted cyclohexyl benzoate esters were shown to pyrolyse more readily than the ester itself. Those esters with electronegative groups in the m- and p- positions were found to break down more readily than those with substituents in the o- , as shown below:

Ester	Characteristic temperature(°C)	Acid yield(%)
Cyclohexyl Benzoate	465	98
Cyclohexyl o-chlorobenzoate	457	99
Cyclohexyl m-chlorobenzoate	444	94
Cyclohexyl p-chlorobenzoate	448	95

1.5. Physical Studies of Ester Pyrolysis.

Degradation of an ester may take place during pyrolysis in the liquid or gas phase, or in both simultaneously. Several experimental methods have been employed to bring about thermal decomposition. The material may be heated in a sealed tube at elevated temperatures,[67] refluxed in an inert atmosphere,[68] or pyrolysed in a flow system.[14] The products are analysed by chemical means, often supplemented by such physical methods as infrared and ultraviolet spectrometry, nuclear magnetic resonance, mass spectrometry, and gas chromatography. Most accurate information about reaction rates and decomposition mechanisms has been obtained from gas phase studies.[69] In this phase, the simplest reactions take place, uncomplicated by solution and adsorption effects found in liquids and at surfaces.

Gas phase studies are carried out either in a flow or a static system. In the flow system, the reactant in gaseous form is passed through the heated reactor, and the pyrolysate collected and analysed. Liquids are studied using this method by pre-heating, followed by decomposition of a quantity of the vapour, although for best results this technique is limited to gases and liquids with high vapour pressure. Product analysis and the various physical factors involved are correlated mathematically to give the required kinetic information.[70-72,78]

The reactant may be transported through the system by pressure difference across the reactor or by transport in a stream of inert gas, or in a vapour(e.g., nitric oxide, toluene, or propylene) known to suppress an unwanted minor competing radical mechanism.[44]

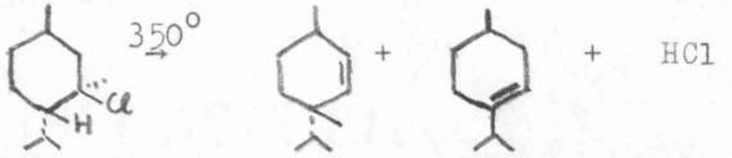
The second physical method used to study a gas phase system is the static technique. A measured amount of the material to be decomposed is allowed to flow in the vapour phase into an evacuated reactor of known volume which is heated at a uniform temperature. Pressure plots against time are obtained under different conditions of temperature and concentration. Pressure changes in the system are most commonly used to detect decomposition, but in some cases variations in thermal conductivity of the gas, or mirror techniques[73,77] have been employed, in several ingenious methods depending on the system under examination. Reaction kinetics are then deduced for the system by correlating the various factors, but confirmation is often obtained, by direct chemical analysis if possible, of the reaction products and unchanged starting material.

1.5.1. The kinetic study of ester pyrolysis.

After establishing the pyrolysis products and breakdown routes for any ester, there remains the task of elucidating the reaction kinetics, which are the factors governing the decomposition rate and the mechanism by which the reaction occurs. Several difficulties arise in the study of a decomposition; breakdown may take place in the gas phase in a completely homogeneous manner, but this main reaction may be accompanied by a heterogeneous one at the walls of the reaction vessel. The presence of radicals or a radical chain mechanism, if undetected, may give rise to errors in the kinetic interpretation. Kinetic studies establish the reaction order, and reactions involving more than three molecules are not known to occur in the gas phase.

Many gas phase decompositions have been found to be homogeneous unimolecular eliminations, either proceeding by a single route or such that any competing routes were small enough to be ignored. Before the possibility of radical mechanisms was realised, many early workers assumed that all thermal decompositions proceeded by molecular elimination, with the result that no attempts were made to look for possible radical mechanisms in the reactions studied.

Contemporary workers apply tests in each reaction investigated, to determine the type of mechanism by which the compound decomposes. For instance, Barton, Head, and Williams[79] found that (-)-menthyl chloride pyrolysed to give hydrogen chloride and a menthene mixture by a true homogeneous unimolecular mechanism:



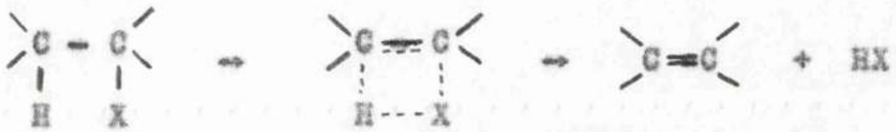
$.....A^1$

The activation energy for the reaction was 45 k.cal./mole. It was found that in clean glass reactors, a much faster heterogeneous decomposition reaction predominated

Using a toluene-inhibition technique to suppress other minor mechanisms, it has been shown[75] that ethyl and isopropyl formate, and ethyl and isopropyl acetate undergo unimolecular homogeneous decomposition. The activation energies for the reactions were all between 44 and 48 k.cal./mole.

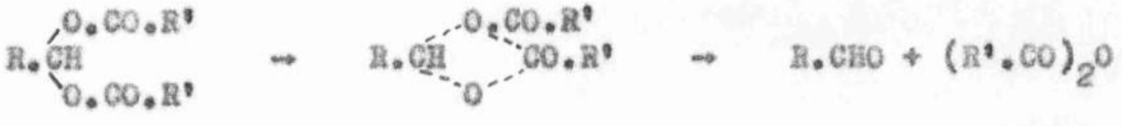
1.5.2. Mechanisms in ester pyrolysis.

Esters which decompose by true molecular elimination are thought to do so by an intermediate activated complex, to give two or more molecules. The mechanism postulated for many non-carboxylic esters of halogen acids(for example, ethyl chloride, isopropyl chloride, and t-butyl chloride), where HX is eliminated,[80-82] involves a four-membered ring in the transition complex(X=Cl,Br):



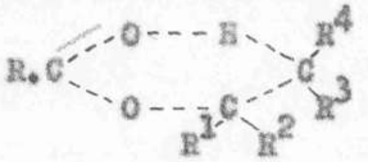
Barton[63] found that where cis- elimination of HX from chlorohydrocarbons was occurring, the homolytic bond dissociation energies decreased in order from the primary to the secondary to the tertiary compound.

Carboxylic esters decomposing by a molecular elimination mechanism are also thought to do so by an activated complex involving a multi-atom intermediate. With some of the compounds studied, a four-membered activated ring has been suggested:



Examples of esters for which this mechanism has been suggested are dimethyl malonate, diethyl malonate,[83] and ethylidene diacetate.[84]

However, for monocarboxylic esters which decompose by A^1 alkyl-oxygen scission, Hurd and Blunck[18] suggested a six-membered ring for the activated complex:

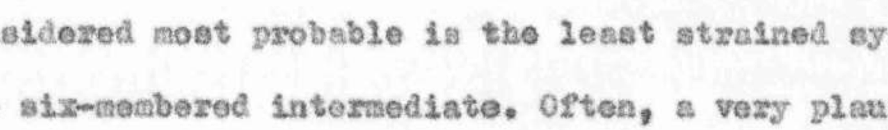


Apart from this mechanism, and a four-membered intermediate for the rearrangement of enol carboxylates to β-diketones suggested by Young et al.[62], there are no generally accepted mechanisms for the other known routes, although radical mechanisms have been suggested for the breakdown of some esters.

In ester eliminations, it is often possible to envisage activated rings with three, four, five or six members; the one normally considered most probable is the least strained system, that is, the six-membered intermediate. Often, a very plausible radical mechanism is also possible, which must be rejected because of lack of evidence for its participation. For instance, vinyl benzoate could decompose by a radical mechanism, but experimental evidence has suggested that pyrolysis occurs mainly by a molecular mechanism.[85] For vinyl benzoate, a hypothetical radical mechanism would be as follows:[129]

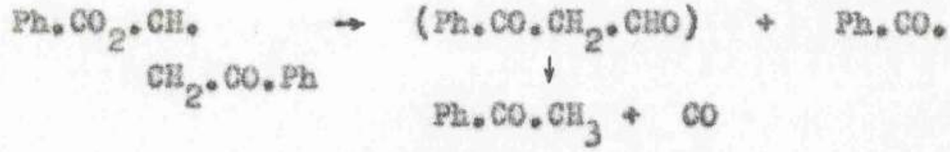
Initiation: $\mathrm{Ph.CO_2.CH{:}CH_2 \rightarrow Ph.CO. + .O.CH{:}CH_2}$

Propagation:



$$\mathrm{Ph.CO_2.CH{:}CH_2 + Ph.CO. \rightarrow Ph.CO_2.\underset{CH_2.CO.Ph}{CH.}}$$

Propagation continued:



$$\underset{\text{CH}_2\text{.CO.Ph}}{\text{Ph.CO}_2\text{.CH.}} \rightarrow \underset{\substack{\downarrow \\ \text{Ph.CO.CH}_3\ +\ \text{CO}}}{(\text{Ph.CO.CH}_2\text{.CHO})} + \text{Ph.CO.}$$

With no general mechanisms for molecular eliminations, the compounds under consideration in this present work will be considered individually at appropriate stages of the discussion.

1.5.3. <u>Catalytic decomposition of esters.</u>

The rate of thermal decomposition of monocarboxylic esters has been found to be increased by the presence of metal and metal oxide catalysts.[86] Senderens[87] pyrolysed ethyl acetate, ethyl propionate, and ethyl butyrate, alone and also in the presence of an alumina or thoria catalyst. In the experiments where the ester pyrolysed over a catalyst, increased breakdown was recorded when compared with the same ester pyrolysed in an all-glass system.

The catalytic effect of metal oxides derived from amphoteric hydroxides on the thermal breakdown of esters was studied by Sabatier and Mailhe.[88] These workers found that the catalyst promoted competitive breakdown routes, and suggested that the decomposition was facilitated by the action of the catalyst on the primary breakdown products, the acid and olefin. In this way the equilibrium concentration of the reactant and primary products would be disturbed during pyrolysis, and increased breakdown could result. Secondary pyrolysis products were detected by analysis:

$$2\ R.CO_2.C_nH_{2n+1} \xrightarrow[catalyst]{heat} 2\ C_nH_{2n} + \underbrace{CO_2 + H_2O + R.CO.R}_{\text{products from pyrolysis of the acid}}$$

Analysis of the pyrolysate from the methyl ester showed that dimethyl ether was present, but water was not detected.

With some of the esters examined, the catalyst acted preferentially towards one of the primary breakdown products, and the complexity of the reaction scheme was increased:

$$4\ R.CO_2.C_nH_{2n+1} \xrightarrow[\text{on the acid}]{\text{catalyst acts}} 2\ R.CO.R + 2\ CO_2 + 2\ C_nH_n + 2\ C_nH_{2n+1}.OH$$

Where the catalyst was not active towards the acid, the predominating reaction was alkyl-oxygen scission of the ester to an acid-olefin mixture.

In comparison with their decomposition in an all-glass system, formates were found to give increased breakdown in the presence of finely divided metal catalysts such as nickel, copper, and platinum.[86] Although stable at 400° in a flow system in the gas phase, formates broke down at temperatures between 220° and 350° in the presence of the above metals. Several competing routes participated; the pyrolysate contained an ether (or water and an olefin), an alcohol, an aldehyde, formic acid, carbon monoxide and carbon dioxide. These results contrasted with the work of Steacie[89] who investigated the pyrolysis of methyl formate and found that the predominating route was decarbonylation:

$$H.CO_2.CH_3 \quad \rightarrow \quad CH_3.OH \ + \ CO \qquad ....C^1$$

Examples have been recorded of other esters which decomposed by several competing routes at increased rates by the action of metallic zinc,[90] nickel,[91] anhydrous zinc chloride, rare earth hydroxides, alumina, and traces of sulphuric acid.[92]

The mechanisms by which catalysed reactions occur are extremely complex, and only partially understood. Three theories exist which attempt to account for catalytic activity and explain possible mechanisms. These are the stoichiometric, the adsorption, and the radiation theories. According to the stoichiometric or chemical theory, there occurs during the reaction, alternate formation and decomposition of a complex formed by the catalyst and the reactant. The intermediate produced is considered to be sufficiently labile to decompose during the course of the reaction to produce the final products and the catalyst in an unchanged state.[93]

According to the adsorption theory, a reaction takes place between unsaturated atoms on the surface of the catalyst and the reacting molecules. The reacting molecule and the catalyst are considered to come together initially by physical or chemical means, after which the reacting molecule, in an excited state, decomposes.[94]

The radiation theory of catalytic activity postulates that the catalyst emits radiation of wavelength suitable to activate one or more of the reactants. Each of the theories has been used to account for results obtained in specific examples studied.

PART 1

2. OBJECT

Competitive routes in the pyrolysis of cyclohexyl benzoate

It was decided to study the thermal decomposition of cyclohexyl benzoate over a range of temperatures (300-500°C) in search of routes other than the exclusive alkyl-oxygen scission reported for menthyl esters over the same temperature range. An attempt was also made to elucidate the kinetics and mechanisms involved. The pyrolysis of (-)-menthyl benzoate was an interesting example of one route thermal breakdown , and cyclohexyl benzoate was chosen as a simpler model based on this ester. It was thought that the pyrolysate from the model compound could be more readily examined than that from (-)-menthyl benzoate, which gave benzoic acid and an olefinic mixture of stereoisomers; a simple mixture of benzoic acid and cyclohexene from the cyclohexyl ester would be expected up to moderately high temperatures(400°), based on the results from the menthyl ester.

PART 1

3. EXPERIMENTAL

3.1. Preparation of Compounds

3.1.1. Cyclohexyl benzoate

The ester may be prepared by direct combination of cyclohexene with benzoic acid in the presence of an acid catalyst,[95] but better yields were reported with freshly distilled benzoyl chloride, pyridine, and cyclohexanol.[96] Accordingly, cyclohexanol (200g.) and pyridine(175g.) were mixed together in a flask cooled in an ice bath. Benzoyl chloride(140g.) was added slowly, and when completed, the mixture was heated and refluxed gently for one hour. After cooling, pyridine hydrochloride was removed from the mixture by washing several times with water. Ether was added to the oily layer and traces of benzoic acid were removed from it with sodium hydrogen carbonate solution. After shaking with water, the ether extract was dried over anhydrous magnesium sulphate and the pure ester obtained from it by fractional distillation under vacuum. The ester was obtained as a colourless liquid(280g.,63%), b.p. 160-165°/45 mm., n_D^{20} 1.525

(lit.[96], b.p. 170°/50 mm., n_D^{20} 1.523) (Found: C, 76.2; H, 8.1 . Calc. for $C_{13}H_{16}O_2$: C, 76.5; H, 7.9%).

3.1.2. Cyclohexene

This compound was prepared by the pyrolysis of cyclohexyl benzoate in the vapour phase in a flow reactor under nitrogen at 400°. The ester(65g.) yielded a white slurry from which benzoic acid(24g.) was removed by filtration. The filtrate was distilled and three fractions obtained (i) b.p. 75-83°, (ii) b.p. 115-132°/36 mm., (iii) a dark residue b.p. $>$150°. Fraction (i) on redistillation yielded only cyclohexene(12.9g.,65%), b.p. 80-82°(lit.[99], b.p. 83°); fraction (ii) contained undecomposed ester(18g.), n_D^{20} 1.514; fraction (iii), a dark tarry residue, gave a small amount of benzoic acid(ca. 3g.) which had remained dissolved in the ester.

3.1.3. Cyclohexylbenzene

Alkylation of benzene(40g.) with cyclohexene(40g.) by a Friedel-Crafts reaction using a hydrofluoric acid catalyst(2ml.) was carried out in a polyethylene receiver cooled in an ice bath. The hydrocarbon separated as a cloudy liquid and was taken up in ether. The aqueous layer was run off and the ether extract was shaken with dilute sodium hydrogen carbonate solution followed by several washings with water. The ether layer was dried and the pure product obtained as a colourless liquid by distillation under reduced pressure. The cyclohexylbenzene

(37g.,45%) as obtained had b.p. 180-188°/20 mm.(lit.,^{100} b.p. 235°, m.p. 8°).

3.1.4. Other compounds

Compounds used for comparative identification by gas chromatography, such as diphenyl, dicyclohexyl, benzaldehyde, cyclohexanone, etc., were obtained from commercial sources.

3.1.5. Purity of prepared samples

The purity of prepared samples was tested by comparing the physical constants obtained with the literature values (refractive indices, densities and boiling points for liquids; melting points for solids). With new compounds, microanalysis was used. In all examples, unless otherwise noted, literature values are given in brackets after experimentally obtained constants. Wherever possible, gas-liquid chromatography was employed to ensure that only one compound was present in a sample. The apparatus was heated by refluxing vapour(I.C.I. design,^{97} Nobel Division, Stevenson, Ayrshire), and the chromatography column was 4mm. bore, 4ft. in length, with a 'Celite 545'/20% Apiezon'M' packing.

3.2. Apparatus for Ester Pyrolysis

A flow reactor system was used to investigate the nature of the decomposition of cyclohexyl benzoate, related compounds, and the enol carboxylates described later in the work.

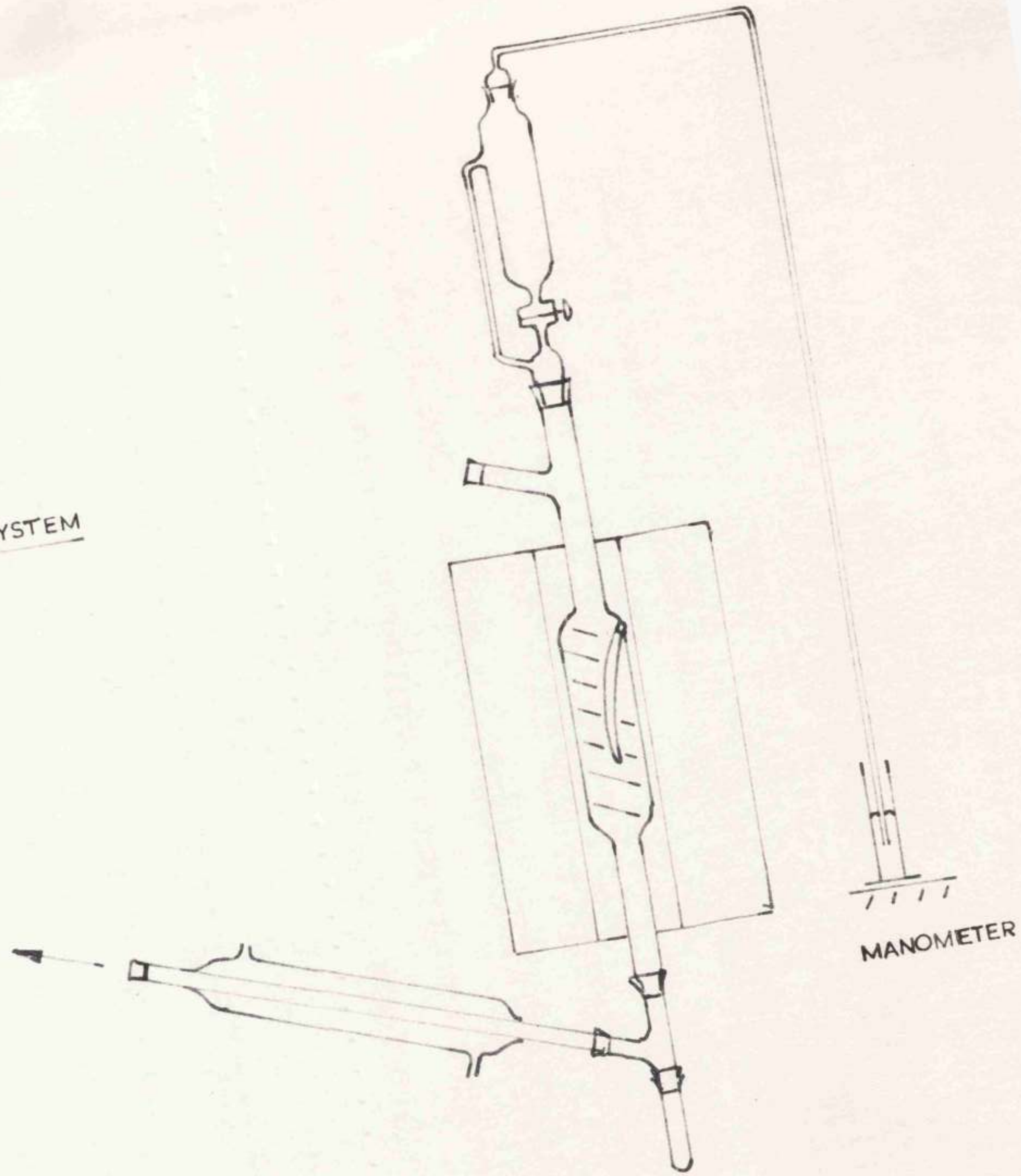
A flow system did not lend itself to a mechanistic study, and a static system was employed for cyclohexyl benzoate. The chief difficulty with this system was the low volatility of the ester concerned, when the gas phase studies were involved, but the problem was approached by an empirical method.

3.2.1. Flow reactor system

The apparatus used is shown in Figure 1. The system was based on that used by Ritchie *et al.*[14] for ester pyrolysis, but glass was employed throughout. Pyrolysis occurred in a Pyrex reactor, a 70cm. tube with a central chamber, 25cm. long, 3cm. diam., heated by an electric furnace, to temperatures up to 550°. For higher temperatures, a silica or quartz reactor was required. Liquids were fed into the reactor by gravity feed from a dropping funnel with a pressure-equalising side arm. The reactor was connected to a condenser, traps, and gas receiver; all joints were made with 'Quickfit' ground glass fittings. Air was removed from the system by an oil pump to a pressure *ca.* 10^{-1}mm., and liquids were degassed at the same time. Pyrolysis took place in the reactor packed with Pyrex glass helices under oxygen-free nitrogen from a 5-litre reservoir on the line, or from a cylinder connected to it. Pyrolysates were collected below the reactor in a receiver

FIGURE 1.

FLOW REACTOR SYSTEM



and fractionated under vacuum on the line or removed from it and fractionally distilled. The reactor temperatures, regulated with a 'Variac' controller, were measured by a chromel-alumel thermocouple.

3.2.2. Static reactor system

The classical static technique for the gas phase study of ester decomposition under various physical conditions could not be used due to the low volatility of the compound concerned, cyclohexyl benzoate.

A means of following the decomposition of a relatively involatile ester by a static method where pressure changes in a closed system were followed manometrically was devised by Steedman,[85] who investigated the kinetics and mechanisms involved in the pyrolysis of vinyl benzoate. The system employed is shown in Figure 2. With this reactor, used without modification for the studies on cyclohexyl benzoate, decomposition took place in a heated U-tube attached to a vacuum line. Pressure changes were measured on a mercury manometer, and the reactor was fitted with a coiled air condenser and splash head at the pump side. Circulation of hot vapours between the two limbs of the reactor was aided by an open bridge near the top; the joint at the bridge also gave rigidity to the unit. Access to each limb was by stoppered 'Quickfit' joints at the top. The reactor

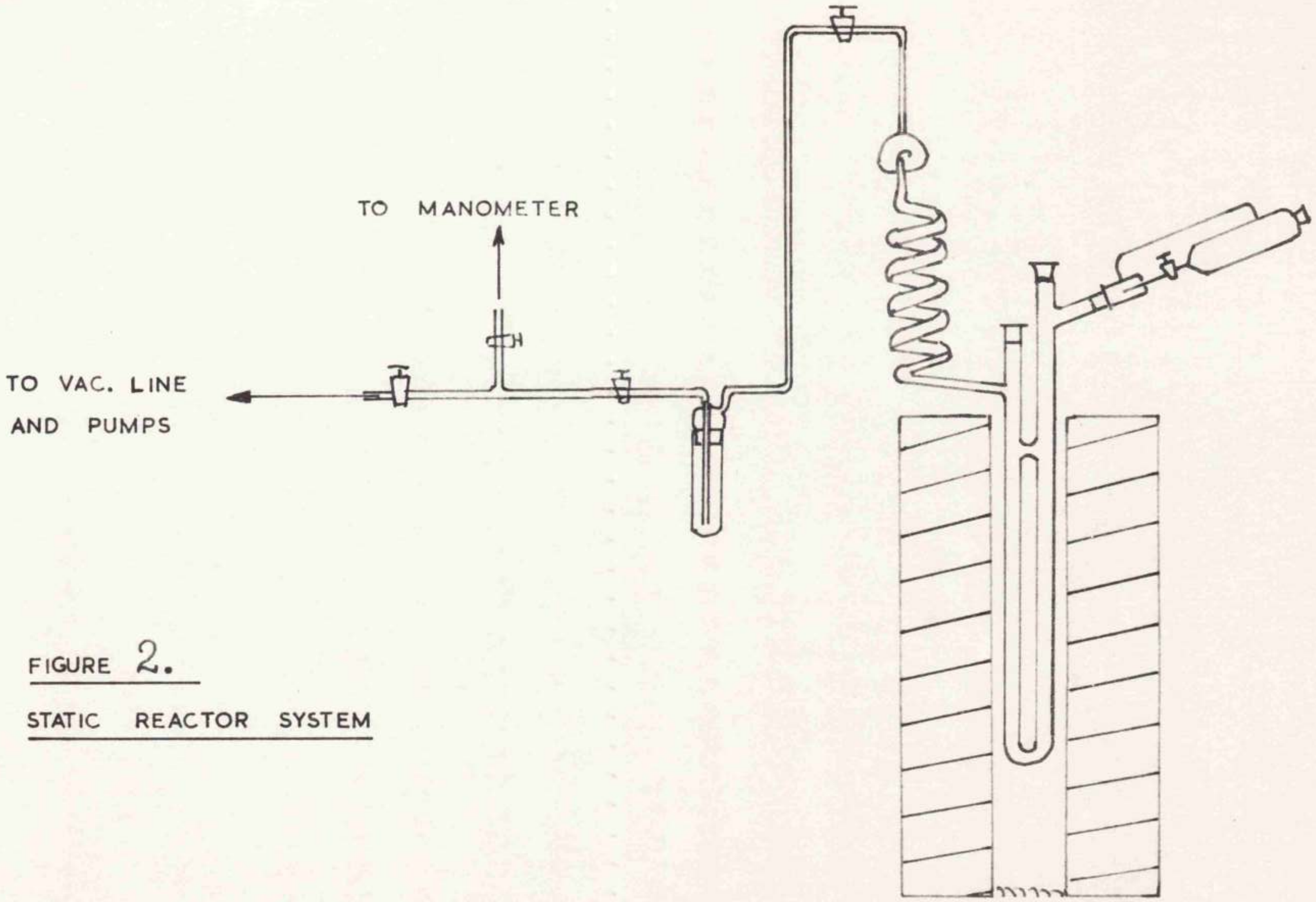


FIGURE 2.

STATIC REACTOR SYSTEM

length to the bridge was 43cm., diameter 12mm., volume 65ml., and the volume to the tap above the splash head was 130ml. The total volume of the system including the trap and adjacent leads was 390ml. The reactor was heated in the furnace used for the flow studies, temperatures being measured by the chromel-alumel thermocouple attached to the outside of the reactor by asbestos string. A plug at the furnace base prevented convection currents and ensured a steady thermal gradient in the inside of the furnace. The ester was introduced into the reactor by a dropping funnel with a pressure equalising side arm.

The system was operated by measuring a volume of ester (normally 2ml.) into the container followed by evacuation and de-gassing. This was continued while the furnace temperature was allowed to settle. The system was closed to the pump and the run started by dropping the ester(2ml. required ca.5 seconds) into the reactor. Pressure changes were followed at regular intervals(1-2 minutes) on the manometer until no variation occurred in consecutive pressure readings.

Where gases were used, for instance nitrogen for the pressure dependence studies and nitric oxide for inhibition, each was stored in a bulb attached to the vacuum line and tapped as required. Solid and liquid initiators and inhibitors were dissolved in the ester before pyrolysis. During the investigation of reaction homogeneity, the reactor was packed with glass wool or fused quartz fibre. Silicone grease was used for joints above the reactor where resistance to heat was important; on other seals, 'Apiezon M' grease was employed. After each reaction the decomposition products were removed with an acetone-benzene mixture, and the surface of the reactor was cleaned by passing a stream of air through the reactor while it was maintained at 450° in the furnace.

Temperature distribution: Furnace temperatures were measured with a chromel-alumel thermocouple inserted in a glass pocket of the flow reactor, and at the surface of the static reactor on the outside wall. The furnace had a slight hot spot, and the temperature distribution curve is shown in Figure 3. Readings from a 25 mV. meter calibrated for the thermocouple against a standard potentiometer, gave temperatures with an estimated accuracy of ±3°.

Reproducibility of reaction rates: Successive pyrolyses of the ester in carbonised reactors which were not cleaned after each run showed a marked fall in reaction rate. Successive runs deposited a surface layer of carbon, and the fall in rates was most noticeable in a new glass reactor. Runs in a cleaned reactor gave reproducible rates over short time periods, and the cleaning technique described above was used throughout; each run was compared with a blank carried out at the same time.

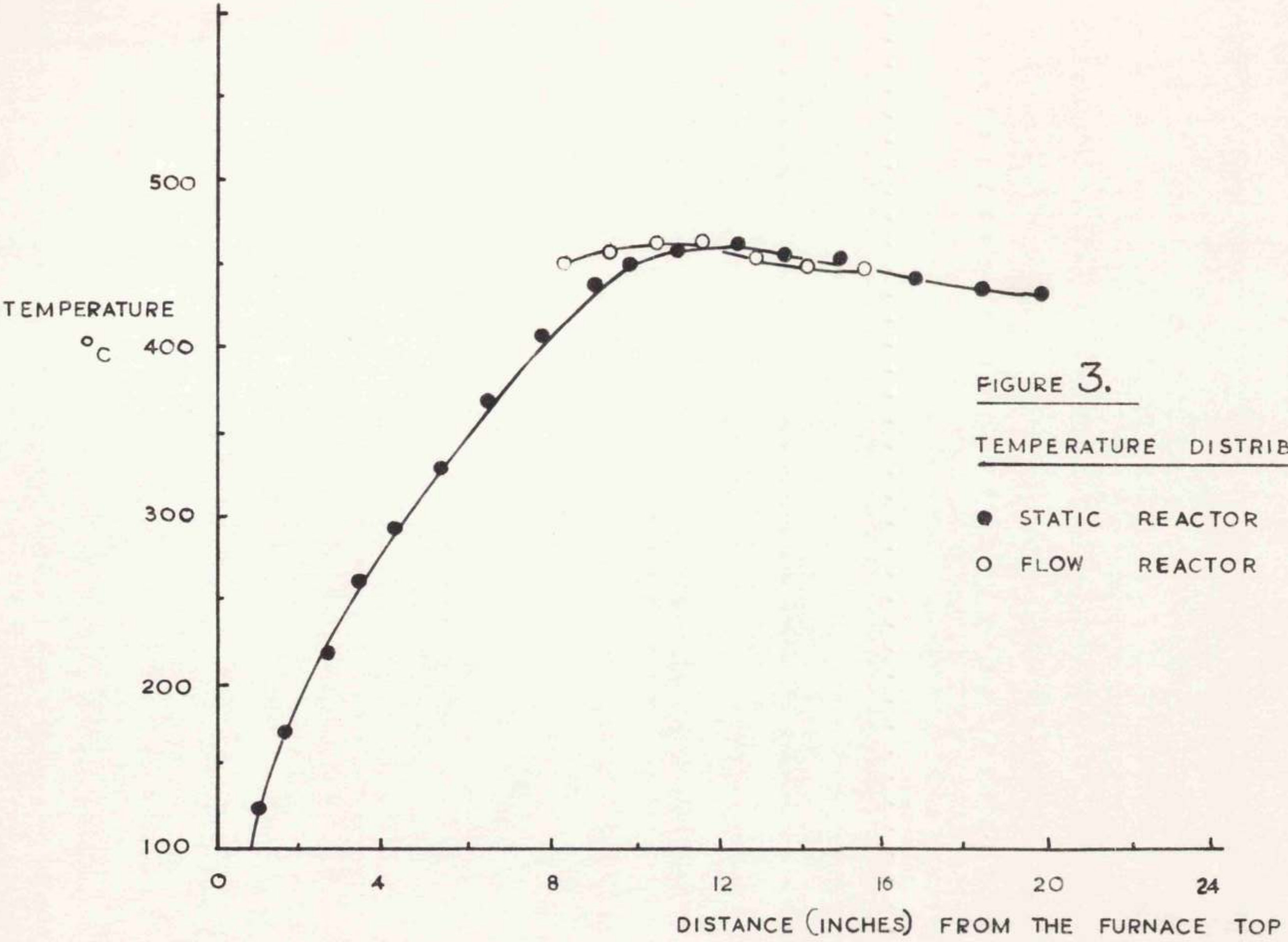


FIGURE 3.

TEMPERATURE DISTRIBUTION AT 475°

3.2.3. Analytical gas chromatography unit

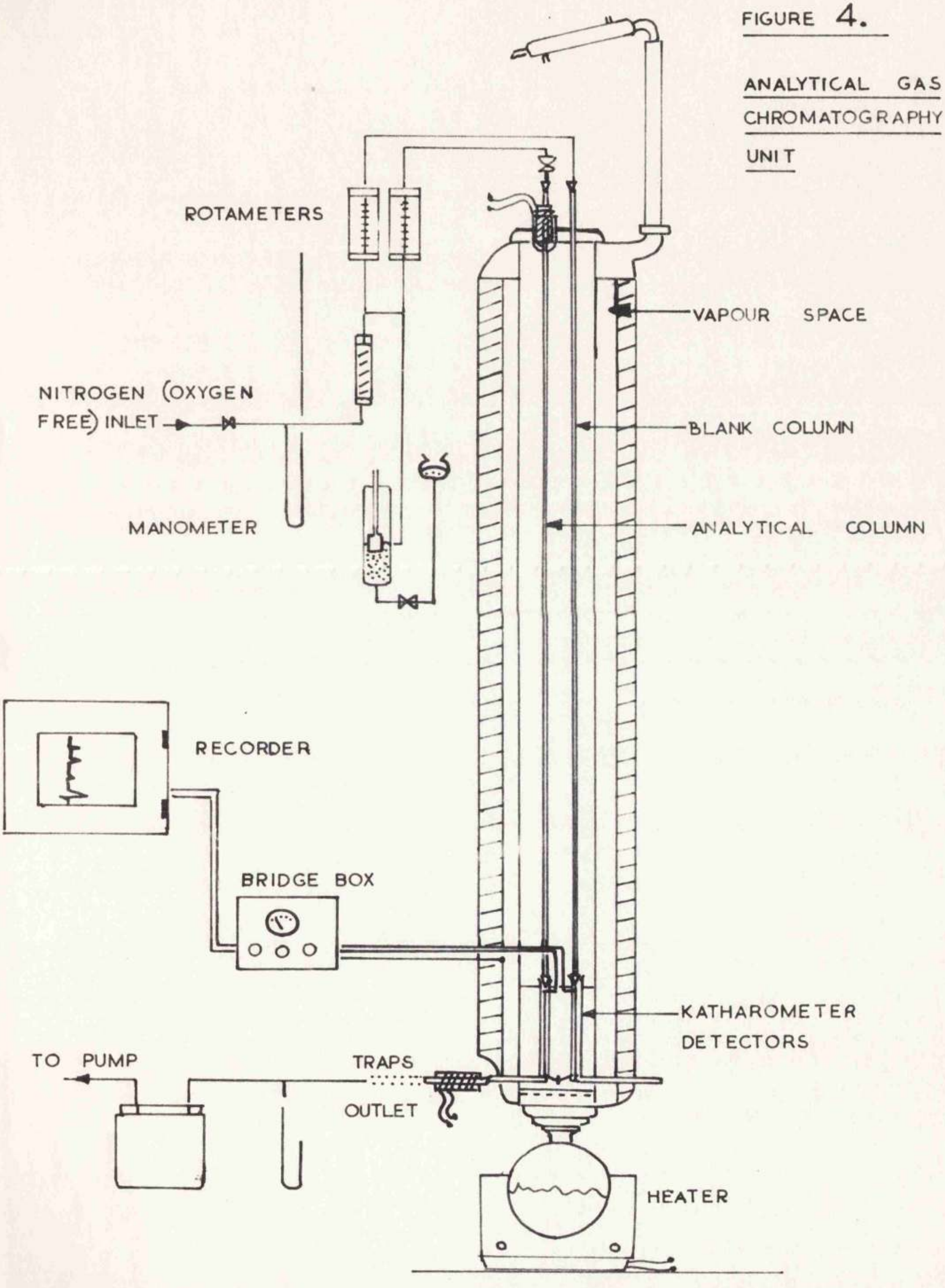
Analysis of ester decomposition products by gas-liquid partition chromatography is a well established technique.[6,34] In the present work, it was used to supplement chemical analysis in a search for small amounts of compounds produced by minor competing routes, and also in the purity tests and synthetic work on vinyl benzoate.

The unit is shown in Figure 4. It contained two chromatographic columns, 120cm. in length, 4mm. diameter, packed with a stationary liquid phase on 'Celite 545', one of which was operational, the other a blank column. The carrier gas, nitrogen, flowed through each column via a constant pressure device. Compounds, vapourised by a heater at the column entrance, passed through and were detected at the column exit by katharometer wires in a bridge circuit; differences in conductivity were recorded on a Honeywell-Brown 'Electronik' unit. The chromatographic tubes and glass cells of the detector were kept at uniform temperature by refluxing vapours from liquids of known boiling points, selected for the required analysis. The system was lagged with 'Fibreglass' sheeting.

In operation, steady conditions were obtained with a known nitrogen flow. The gas flow was stopped, and the material injected into the column by an 'Agla' micrometer syringe. Liquids were added directly, solids in a suitable solvent. Simultaneously,

FIGURE 4.

ANALYTICAL GAS CHROMATOGRAPHY UNIT



a small slug of air was added, which served as a marker from which other retention times were measured, since it produced an opposite deflection from the sample. The 'retention time', the interval between the air peak and the peak for the compound being analysed, was used to identify the sample under the conditions obtaining at the time. For quantitative work, the method of direct calibration of peak area against sample size was used; in a few examples, the 'internal normalisation' technique was used.[98]

PART 1

4. RESULTS

4.1. The Pyrolysis of Cyclohexyl Benzoate: Flow System

The ester was pyrolysed at atmospheric pressure in a glass system using nitrogen as the inert gas. Over the heated area, the reactor was packed with Pyrex helices. In a run in an evacuated system at 450°, only slight pyrolysis occurred. Pyrolysis was carried out at temperatures between 300° and 500° at 50° intervals. Competing routes, if any, were expected at the higher temperatures, and accordingly, the high temperature pyrolysates were examined in the preliminary study.

4.1.1. Pyrolysis at various temperatures

Pyrolysis 1(400°): Decomposition of the ester(42g.) gave a white slurry(37.5g.). This was filtered and the solid obtained(9g.) recrystallised(from light petroleum b.p.60-80°) and identified as benzoic acid with m.p. 120°(mixed m.p. with an authentic sample gave m.p.120-122°). Distillation of the remaining liquid yielded four fractions(i-iv) and a residue(v). Fraction (i) (b.p. 67-92°), redistilled, gave a clear liquid(8g.), b.p. 80-85°, containing only cyclohexene(gas chromatographic analysis and positive unsaturation test; oxidation with alkaline potassium permanganate solution produced adipic acid(2.2g.), m.p. 152° (lit.,[101] m.p. 152°)). Fraction (ii)(b.p. 95-155°/20mm.) contained unchanged ester(7g.), n_D^{20} 1.518(lit.,[96] b.p. 170°/50mm.,n_D^{20} 1.523: confirmed by infrared). Fraction (iii)(6g.; b.p. 150-172°/15mm.) consisted of ester contaminated with benzoic acid(chromatographic analysis). Fraction(iv)(b.p. 165-200°/3mm.), a pale yellow liquid (2.5g.), solidified in the condenser and was identified as benzoic acid,by m.p. and mixed m.p.(m.p. 116-120°). Fraction(v) (*ca.* 2g.) was a high boiling residue. The pyrolysis gas(0.9 l.) contained displaced nitrogen and a trace of olefin(infrared), possibly ethylene or cyclohexene vapour.

Pyrolysis 2(450°): The ester(35g.) gave a yellow pyrolysate(28g.) from which suspended benzoic acid(7g.) was filtered. The filtrate, distilled, gave three fractions(i-iii) and a residue(iv). Fraction(i)(5g.; b.p. 72-85°) was mainly cyclohexene, n_D^{20} 1.433 (lit.,[99] n_D^{22} 1.445), with a little benzene(*ca.*5%), demonstrated by a two peak chromatogram. Fraction(ii)(10.5g.; b.p. 115-160°/28 mm.) was undecomposed ester(confirmed by alkaline hydrolysis to benzoic acid and cyclohexanol). Fraction (iii) was a trace of benzoic acid, and fraction(iv) was a high boiling residue.

The pyrolysis gas(1.7 l.) contained displaced nitrogen(10%), carbon dioxide(7%), and unsaturated hydrocarbons(83%), the last-named mainly ethylene(infrared).

Pyrolysis 3(500°): The ester(40g.) gave a pyrolysate(34g.) which was a distinct pink colour owing to incomplete removal of pyridine used in the preparation of the ester. On standing for 24 hours the colour disappeared and did not interfere with subsequent analysis. Benzoic acid(13g.) was filtered off and three fractions(i-iii) obtained by distilling the filtrate. Fraction(i)(12g.; b.p. 75-85°) contained cyclohexene and benzene. Fraction(ii)(3g.; b.p. 110-135°/18mm.) was unpyrolysed ester. Fraction(iii)(4g. b.p. 162-195°/7mm.) was benzoic acid. Each fraction was chromatographed on the unit described previously (p. 33 *et seq.*). The pyrolysis gas(3.4 l.) contained CO_2 31%, CO 7%, and unsaturated hydrocarbons 61%, mainly ethylene(infrared).

Pyrolyses 4,5, and 6(300°, 350°, and 530° respectively): These runs all used 15g. of ester. The pyrolysates were analysed and previous results confirmed. In the run at 530° the pyrolysate was brown and there was carbon in the reactor, but in the other runs, only carbon traces were found, and the pyrolysates were light coloured.

Detection of carbonyl compounds: Fractions(i) and(ii) from pyrolyses 1,2,3, and 6 were tested with semicarbazide hydrochloride and 2:4-dinitrophenylhydrazine in solution in an attempt to isolate carbonyl derivatives, but even after heating and prolonged standing there was no precipitate from any of the samples, confirming that carbonyl compounds were absent.

4.1.2. Pyrolysis in the presence of metals

An automatic feed system to give accurate ester flow rates for pyrolysis was devised which used a hypodermic syringe above the reactor with its plunger driven by a geared electric motor. During a series of runs, cyclohexyl benzoate in the syringe was found to be grey in colour from contamination with a very fine suspension of metal from a seal or the plunger of the syringe. More complex pyrolysates and increased gas production resulted at the various pyrolysis temperatures. Carbonaceous deposits were also noted in the reactor, but the presence of nickel traces or an alloy of lead, tin, and bismuth were suspected as the cause.

Accordingly cyclohexyl benzoate(10g.) was pyrolysed within the range 350-550° in a packed reactor containing Wood's metal (3g.) on a layer of glass wool above the reactor packing in the heated zone. The metal was finely divided.

Pyrolysis	Decomposition	Temperature	Pyrolysis gas
7	10-20%	350°	0.7 l.
8	70-80%	450°	2.15 l.
9	*ca.*100%	550°	2.6 l.

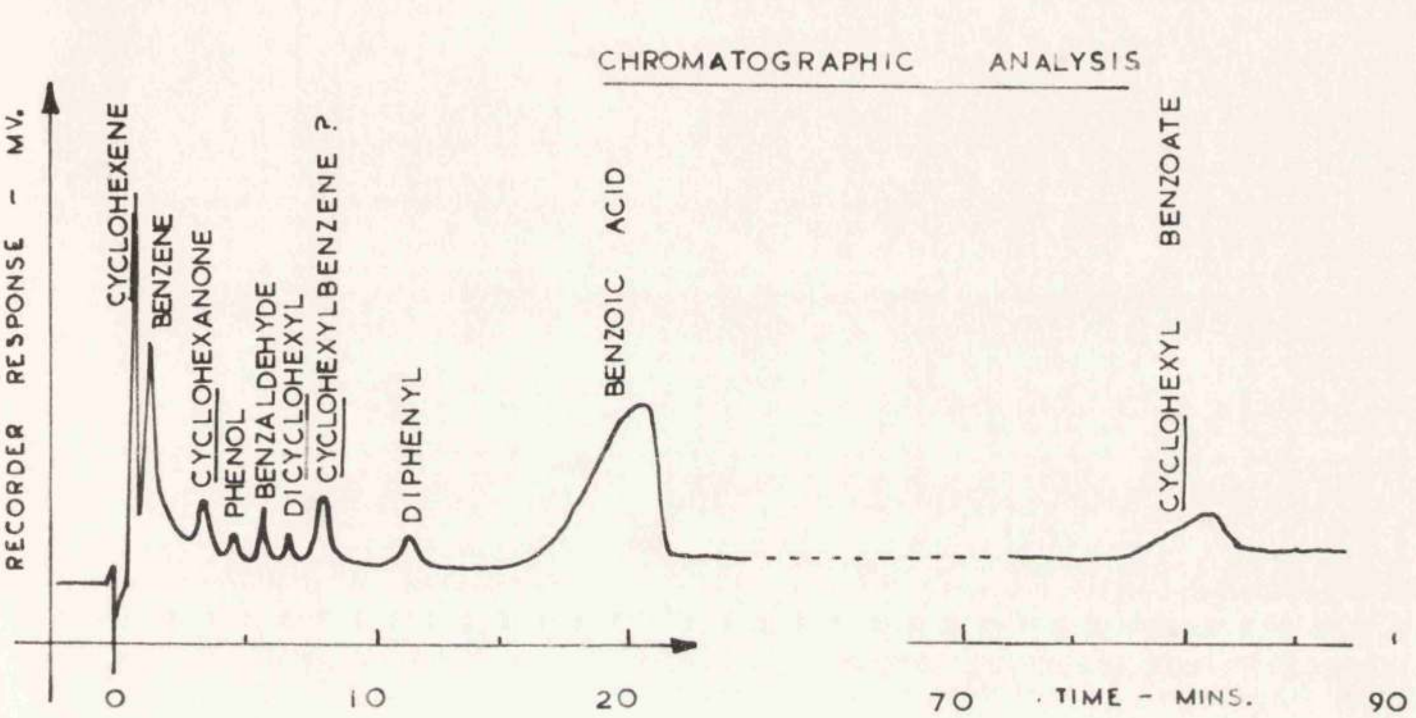
The gas pyrolysate from run no.7 consisted of CO_2(52%), CO(11%), saturated hydrocarbons(37%; mainly ethylene: infrared), while pyrolysis 8 gave a gaseous mixture of CO_2(57%), CO(17%), and unsaturated hydrocarbons(26%). Pyrolysis 9 gave CO_2(32%), CO(13%), and unsaturated hydrocarbons(55%). The metal catalysed pyrolysate from run no.8 was chromatographed at 197° and the results are shown in Figure 5.

Decomposition in the presence of pure metals(Pyrolyses 10,11,12):

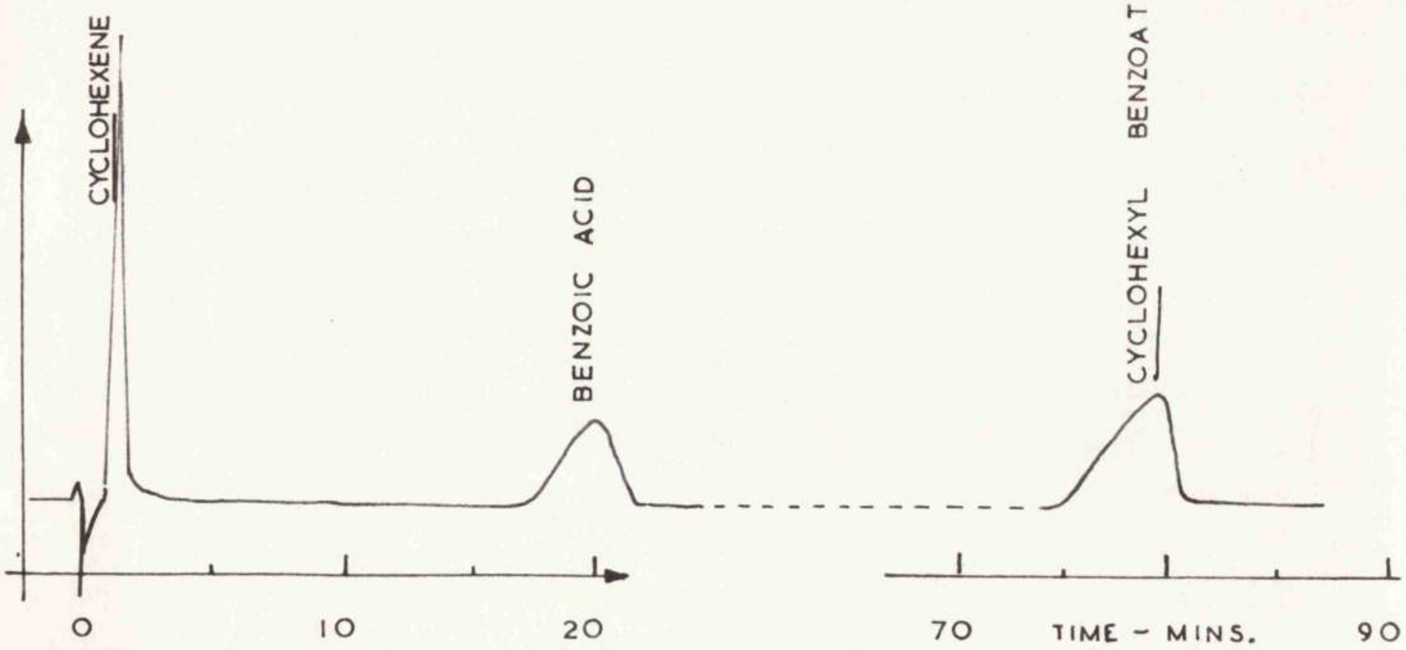
The catalytic activity of metals in the pyrolysis of the ester was confirmed by repeating the procedure described above using a catalyst of tin, lead, and bismuth(1g. of each) in each of three runs at 450°. Tin was found to be an active catalyst, producing a pyrolysate containing cyclohexanone, cyclohexene, benzoic acid, and benzene(chromatographic analysis); benzaldehyde was not identified. No activity was shown by bismuth or lead, only benzoic acid and cyclohexene being produced(A^1scission). In the run with lead, a fine yellow film was deposited over the hot surfaces of the reactor.

Several runs with varying amounts of tin in the reactor confirmed the activity, but in several of the pyrolyses there was almost no evidence for competing routes. This was found to be caused by the particle size of the tin, catalytic activity being shown only by the finest particles obtained by attrition of the metal. Pure nickel was not tested for activity.

FIGURE 5.



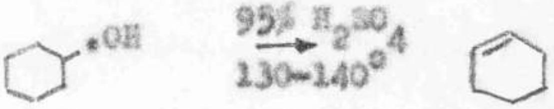
(a.) CYCLOHEXYL BENZOATE DECOMPOSITION IN PRESENCE OF WOOD'S METAL. AT 450°.



(b.) ESTER DECOMPOSITION ALONE AT 450°.

4.2. The Pyrolysis of Cyclohexene

Cyclohexene from commercial sources is normally prepared by dehydration of cyclohexanol in yields up to 80%:



Although the main reaction is the removal of the elements of water from the molecule, several competing intermolecular reactions are possible, and unreacted cyclohexanol is also a possible contaminant of the olefinic product. A commercial sample of the hydrocarbon, chromatographed, contained seven compounds. After careful distillation it was still impure, but a pure sample for pyrolysis was obtained from cyclohexyl benzoate by the method described previously(section 3.1.2.).

Pyrolysis 13(450°): Cyclohexene(10g.), pyrolysed in a flow reactor under nitrogen, gave 2.5g. of liquid pyrolysate. A slight condensate in the acetone/'Drikold' trap was unchanged material only. The gas evolved(1.7 l.), consisted of acetylene(6%), other unsaturated hydrocarbons(86%; mainly ethylene), and saturated hydrocarbons(8%). The main component of the saturated hydrocarbon gas was methane(infrared).

4.3. The Pyrolysis of Cyclohexyl Benzoate: Static System

The ester was subjected to pyrolysis in the gas phase using the apparatus described in section 3.2.2. at 475° under various conditions, and time-pressure plots obtained for each run using a 2ml. sample of ester.

4.3.1. Pyrolysis in a carbonised reactor

Typical time-pressure plots for the ester are shown in Figure 6. In a dirty reactor(i.e. one in which decomposition products were allowed to accumulate from run to run), the breakdown rate fell markedly with successive pyrolyses, and reproducible rates could not be obtained. Over the linear part of the decomposition curve, the rate fell from 0.74mm./min. to 0.12mm./min. in 8 successive runs.

4.3.2. Pyrolysis in a clean reactor

Reasonably reproducible rates were only obtained using a reactor from which breakdown products were removed after each run by a combination of washing with mixed solvents, followed by heating in a stream of air at 400°. Fluctuations did occur, but blank runs were always made where rates were being compared. It was never found possible to reproduce the rates obtained in new glass reactors after a number of runs, despite the most stringent cleaning precautions. In a seasoned reactor, any rate variations were small and easily detected during pyrolysis.

4.3.3. The effect of nitrogen

The effect of adding different amounts of nitrogen to the system is shown in Figure 6. Pyrolysis of the ester in the system, to which nitrogen to a pressure of 40mm. had been

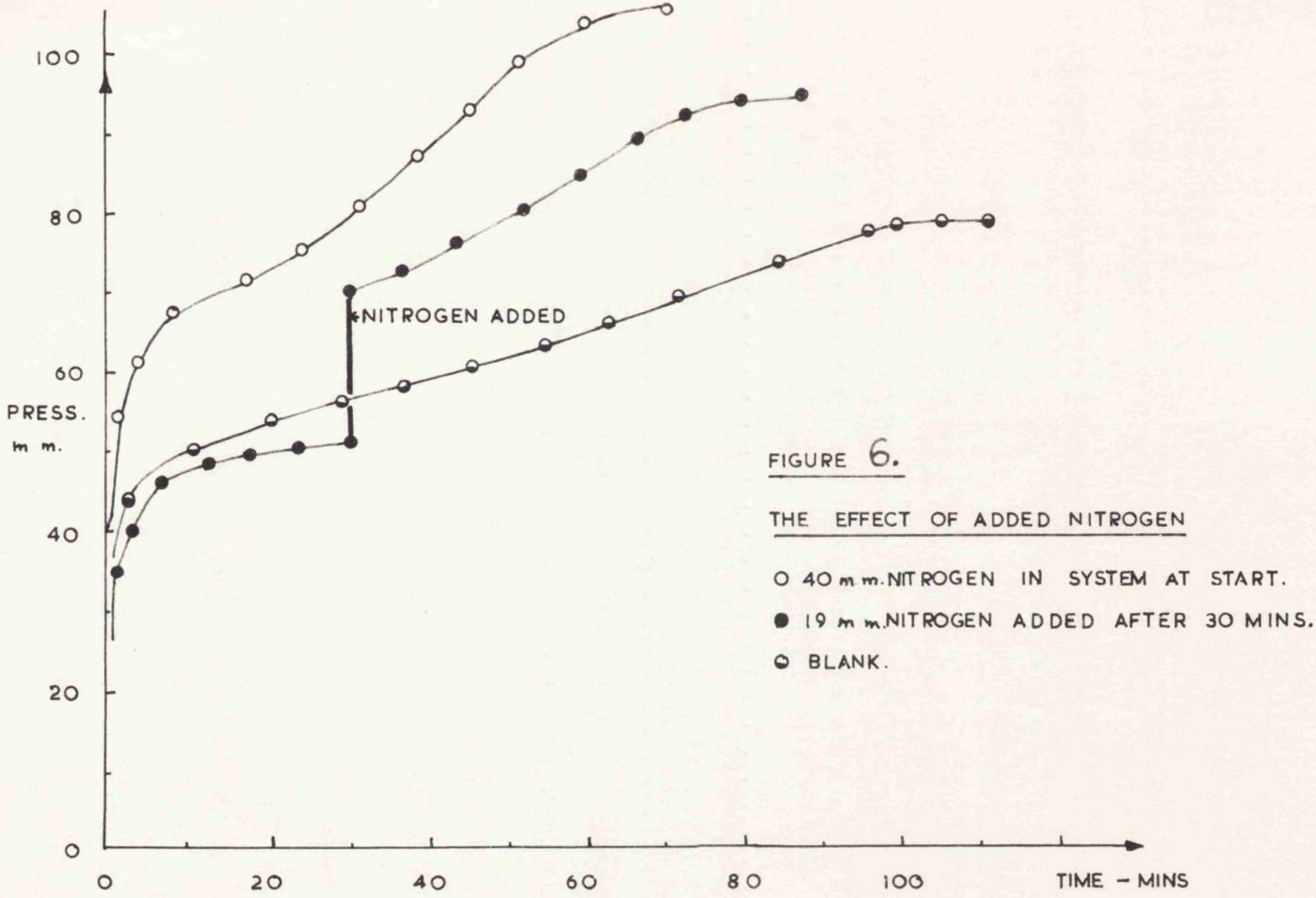


FIGURE 6.

THE EFFECT OF ADDED NITROGEN

added before the start, gave a rate of 0.7mm./min. compared with 0.3mm./min. in the blank run. The reaction also appeared to go to completion much faster. Where 18mm. of nitrogen was added after the reaction had run for 30min., the rate increased from 0.2 mm./min. to 0.4mm./min., and the reaction went to completion before the blank.

4.3.4. Co-pyrolysis with benzoic acid and cyclohexene

Pyrolysis of the ester with its own degradation products, each added separately, gave the following results:

Cyclohexene addition: A small amount of cyclohexene vapour was introduced into the reactor during an early run in a new glass reactor and decomposition stopped immediately. In a later run, with the reactor surface in a 'seasoned' condition, the addition of this compound had no effect whatever, a result confirmed by repeating the run several times, indicating a different mechanism.

Benzoic acid addition: Addition of 0.25g. of acid to the 2ml. sample of ester before the run produced a fall in the rate from 0.36mm./min. for the blank run to 0.23mm./min. for the co-pyrolysis. Degradation products such as benzaldehyde and cyclohexanone were not tested for possible effect on the decomposition rate.

4.3.5. The effect of free-radical inhibitors and initiators

Known free-radical initiators were tested for a possible effect on the breakdown rate of the ester in a clean reactor with an 'aged' surface. The initiators were added prior to each run in the following concentrations:

	Concentration
di-*t*-butyl peroxide	1.2%
1:1'-azobiscyclohexanecarbonitrile	0.5%
benzoyl peroxide	1.0%

None of the additives used had a detectable effect on the decomposition rate.

The following free-radical inhibitors were also tested. Nitric oxide was added during the run, but each of the other compounds was added before commencing.

	Concentration
hydroquinone	2.0%
toluene	0.5%
p-toluquinone	0.5%
nitric oxide	30mm.

None of the compounds caused a significant rate change compared with the blank run. Nitric oxide was introduced during the run after 40min. had elapsed, but the rate before addition, 0.52mm./min. rose to 0.61mm./min. afterwards.

4.3.6. Surface effects

The effect of artificially increasing the available surface area in the reactor was investigated by packing each limb loosely

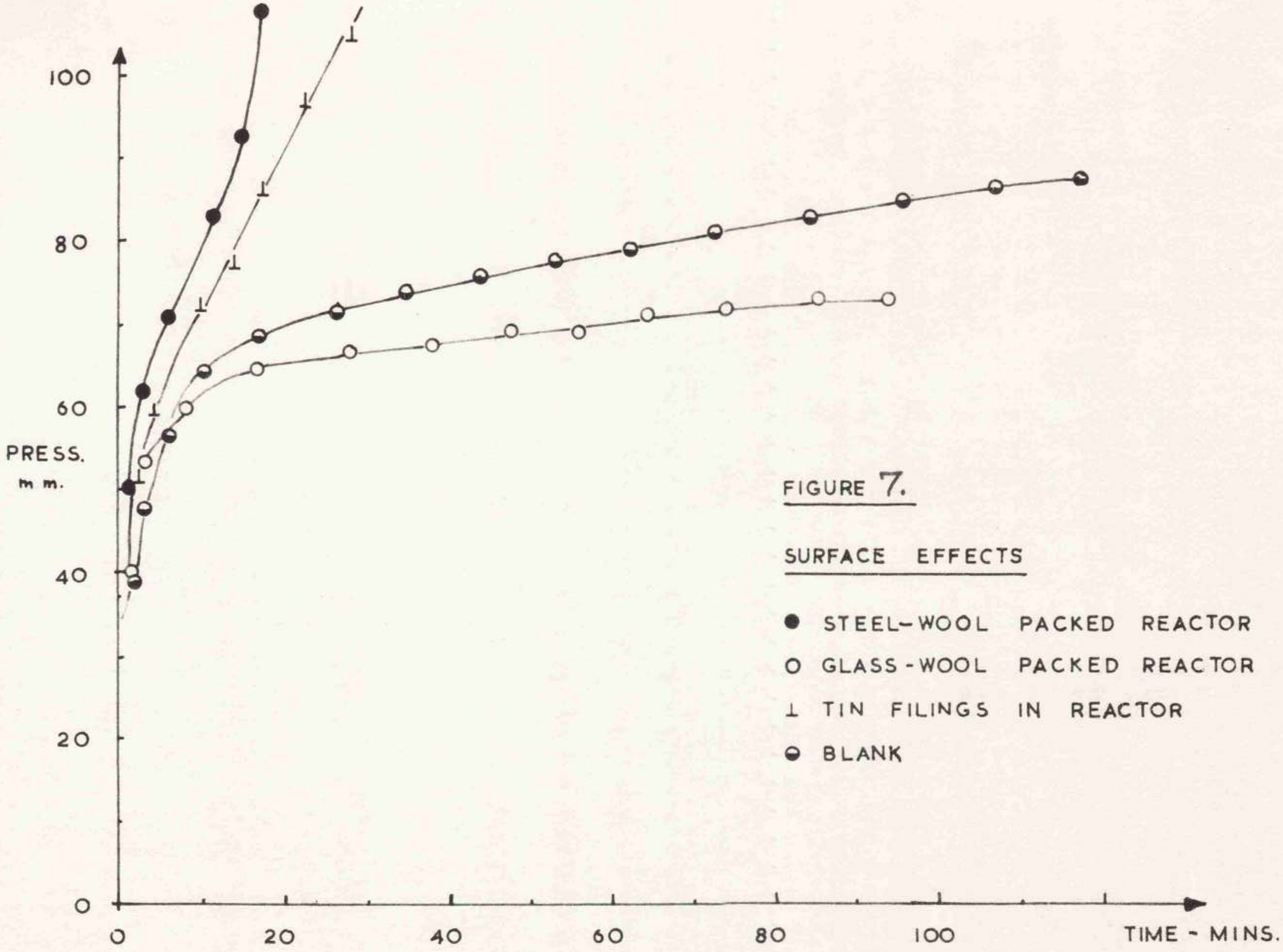


FIGURE 7.

SURFACE EFFECTS

with glass wool(8g.), over the bottom six inches of the hot zone, and in one run with fused quartz fibre(3g.). In the quartz run a small increase in rate took place, from 0.22mm./min. for the blank, to 0.38mm./min. for the packed run. The glass wool packing caused a fall in rate to 0.1mm./min., and the reaction proceeded to completion at this low rate, taking considerably longer than the blank run, although normal reflux of the hot ester was observed in the coil of the air condenser.

The surface provided by steel wool was tested for its effect on the decomposition rate. Before use, the wool was cleaned and degreased by washing with benzene, then acetone, and finally dried in an oven at 110°. The wool(2.6g.) was placed in the reactor before the run; a rate increase was detected, from 0.22mm./min. for the blank run to 3mm./min. for the packed run. The pressure rose to 215mm. after 50 min., then ceased completely; blank runs required 100min. for completion. Tin filings(0.2g.) in the reactor gave a similar effect, with a rate of 1.9mm./min., and heavy carbon deposition. Decomposition in each run was observed by a film of benzoic acid from the ester on cool parts of the reactor.

4.3.7. Temperature variations

An increase in the decomposition rate was evident(see Figure 8) when the pyrolysis temperature was increased, with a four-fold rate increase for a temperature rise of 60°.

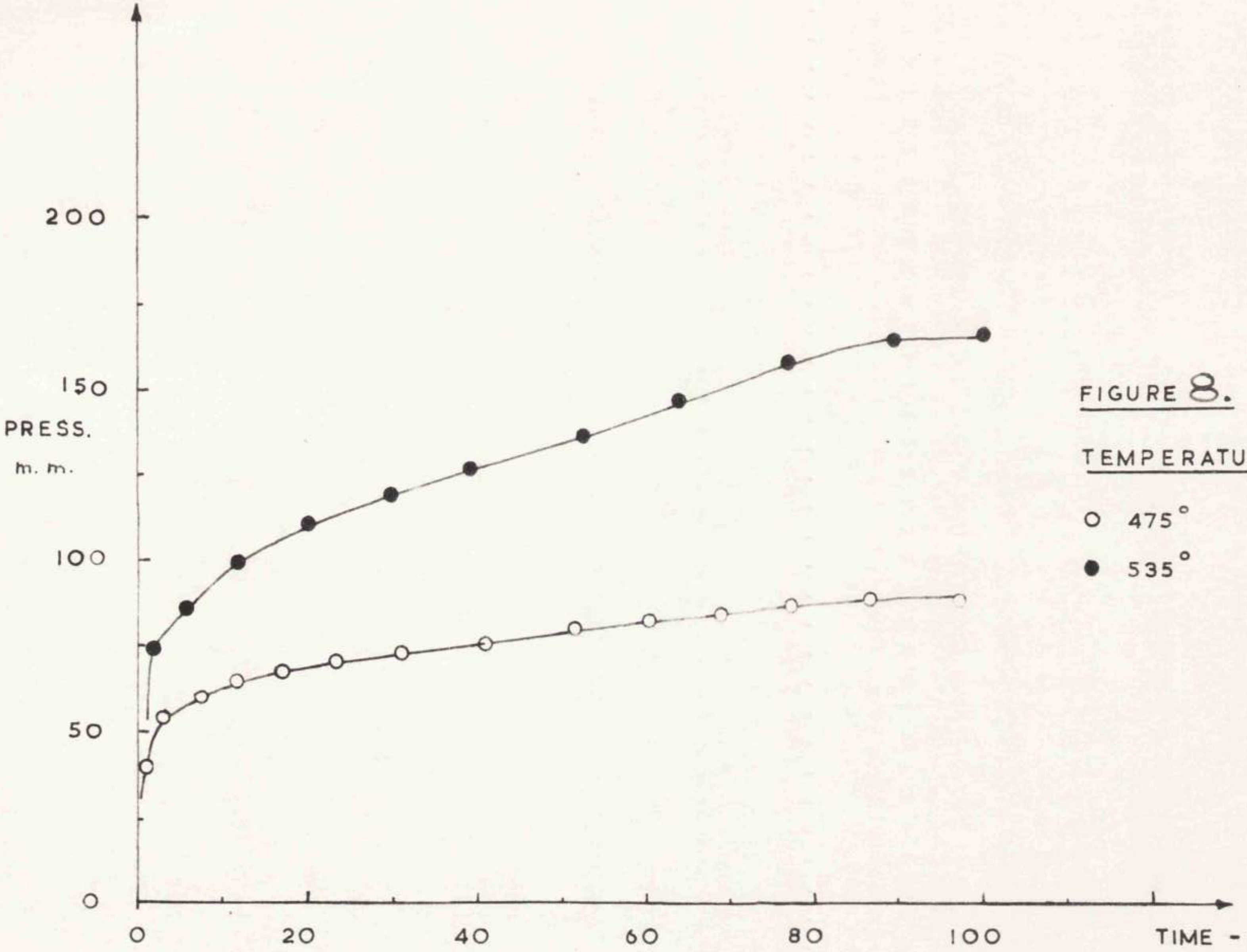


FIGURE 8.

TEMPERATURE VARIATION

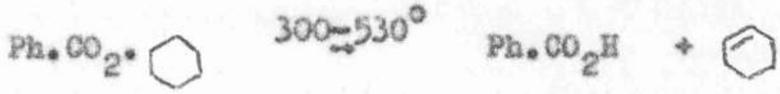
PART 1

5. DISCUSSION

5.1. The Pyrolysis of Cyclohexyl Benzoate: Flow System

5.1.1. The reaction scheme

Cyclohexyl benzoate was found to decompose at temperatures between 300-530°C. by an exclusive A^1 alkyl-oxygen scission, to give benzoic acid and cyclohexene as products:



......A^1

Compounds which could arise from other competing routes were sought. Acyl-oxygen scission of the ester by the B^2 route would give cyclohexanone and benzaldehyde, but neither compound was found in the pyrolysate fractions concerned, using tests for carbonyl compounds. This result was confirmed by gas chromatography; products from routes competing with the main A^1 scission could not be detected, but compounds from the secondary breakdown of benzoic acid and cyclohexene(benzene, carbon dioxide, methane, ethylene, and acetylene) were readily identified.

Examination of high-boiling fractions from the pyrolysates gave no positive evidence for possible condensation or rearrangement products, although the isomeric ester phenyl cyclohexanecarboxylate, undergoes thermal rearrangement to cyclohexyl _o_-hydroxyphenyl ketone:[67]

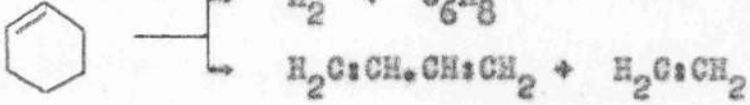
........R

Alkyl-oxygen scission of cyclohexyl benzoate at temperatures up to 400° was expected on the basis of results obtained from the pyrolysis of (-)-menthyl benzoate(_cf._ p.17) over the same temperature range. With the menthyl ester, exclusive alkyl-oxygen scission was established, and on the basis of a homogeneous unimolecular mechanism, _cis_-elimination in a carboxylic ester was first demonstrated by the presence of (+)-_p_-menth-3-ene in the pyrolysate. The pyrolysis of cyclohexyl benzoate could not produce an olefinic mixture of stereoisomers, and the question of _cis_-elimination did not arise, but it was possible to establish whether or not the reaction was homogeneous and unimolecular, and this was done to the extent permitted by the experimental techniques(_cf._ p.60 and p. 61).

5.1.2. Secondary decomposition

Above 400°, with the detection of benzene and various gases in the pyrolysate, it was evident that secondary breakdown of benzoic acid and cyclohexene, the primary scission products, was taking place.

Cyclohexene: Rice and Teller[102,106] showed that cyclohexene pyrolysed according to the following scheme:

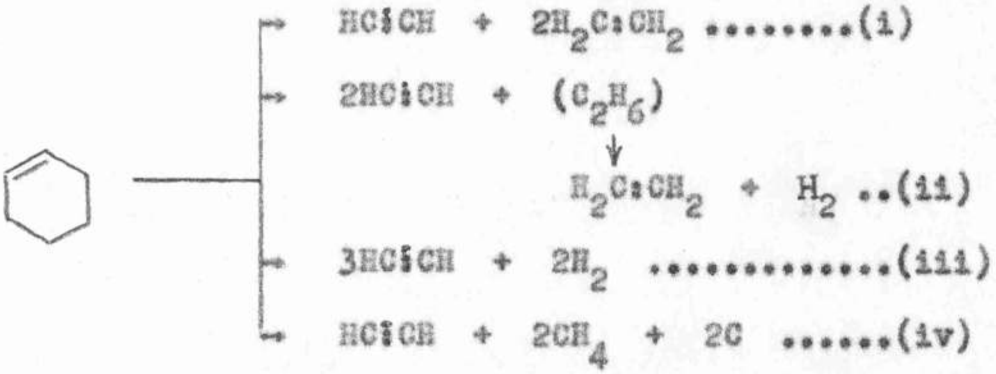


$H_2 + C_6H_8$

$H_2C{:}CH.CH{:}CH_2 + H_2C{:}CH_2$

Butadiene and ethylene were the main products, but small amounts of hydrogen and higher olefins were also found. This work was confirmed by a later study of substituted cyclohexenes,[103] where the pyrolysate was found to contain mainly substituted butadienes.

Decomposition of cyclohexene by secondary decomposition from cyclohexyl benzoate was confirmed by pyrolysing a pure sample of the hydrocarbon at 450° in a flow reactor. The pyrolysate was a gaseous mixture containing acetylene, ethylene, saturated hydrocarbons(mainly methane), and small amounts of hydrogen. One possible reaction scheme would be as follows:



$HC{\vdots}CH + 2H_2C{:}CH_2$ ....(i)

$2HC{\vdots}CH + (C_2H_6)$

$\downarrow$

$H_2C{:}CH_2 + H_2$ ..(ii)

$3HC{\vdots}CH + 2H_2$ ....(iii)

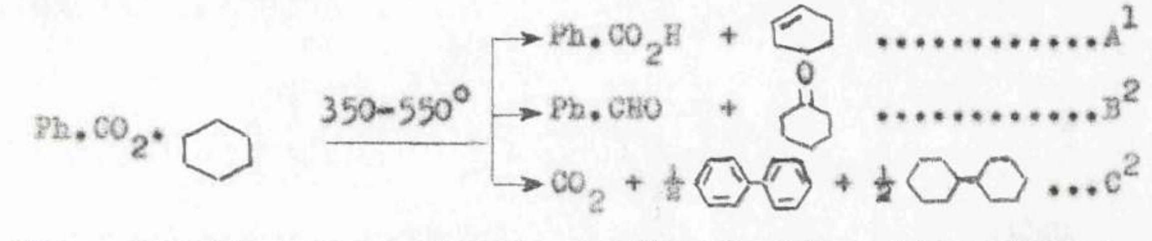
$HC{\vdots}CH + 2CH_4 + 2C$ ......(iv)

With regard to the major constituent of the pyrolysis gas, ethylene, route(i) of the reaction scheme would appear to predominate, although acetylene was not found present to the extent predicted by this route. Other routes participated in in the decomposition, as shown by the methane and hydrogen traces found. These results would account for the quantities of ethylene in the gaseous pyrolysate from cyclohexyl benzoate. Benzoic acid: Benzene and carbon dioxide in the pyrolysate from the ester above 400° were derived from decomposition of benzoic acid, which has been studied by earlier workers. Meyer and Hofmann[104] detected benzene in the pyrolysate from benzoic acid at temperatures above 450°. Moser[105] found that the acid broke down by a heterogeneous mechanism in a glass system around 370° by a major decarboxylation to benzene and carbon dioxide accompanied by a minor competitive route yielding phenol and carbon monoxide to a maximum of 8% of the total breakdown. At an acid concentration of 0.164moles/l., the half-life was found to be 4.75 hours.

Above 400° benzene, carbon dioxide, and carbon monoxide were detected in the pyrolysate from cyclohexyl benzoate, but phenol was not found even at temperatures up to 530°in the glass system with no catalyst present; it could have undergone further decomposition or was present in amounts too small to be identified, but this problem was not investigatedd further.

5.1.3. Metal catalysed decomposition

Routes competing with the exclusive alkyl-oxygen scission found for cyclohexyl benzoate in the glass system were detected when small amounts of finely divided metals were introduced into the reactor at temperatures from 350° to 550°. The greatest activity was found with a mixture of lead, tin, bismuth, and a trace of nickel. The compounds found to be present in the pyrolysate are shown in the following reaction scheme:



These results were partially confirmed with a tin catalyst used alone in the reactor at 450°, when the A^1 and B^2 routes (see above) were again detected. However, with only tin in the reactor, the C^2 route was not confirmed. Extensive carbonisation accompanied the breakdown, which was apparently surface catalysed and heterogeneous in nature, as the activity of the metal was found to depend on its particle size. In some of the runs, when the metal was not placed in the reactor in a finely divided state, only A^1 scission was found. Identification of diphenyl, dicyclohexyl, and (tentatively) cyclohexylbenzene in the mixed metal catalysed pyrolysis indicated that a radical mechanism might have participated in the C^2 route.

It has been suggested[86] that in any decomposition reaction, a catalyst does not introduce new reactions; rather does it act by increasing the rate at which a reaction occurs which under normal conditions would take place to a very minor extent. In view of this, results obtained from the pyrolysis of ethyl benzoate were of interest. Bilger and Hibbert[3] pyrolysed this ester and found only ethylene and benzoic acid from A^1 scission. These workers made a careful search for carbonyl compounds in the pyrolysate with 2:4-dinitrophenylhydrazine in acetic acid, but found no trace of acetaldehyde or benzaldehyde, resulting from a possible B^2 scission. Ethyl benzoate was pyrolysed during the present investigation in a reactor containing a Wood's metal catalyst, at 450°, and acetaldehyde was readily identified in the pyrolysate by the isolation of its 2:4-dinitrophenylhydrazone derivative.

5.2. The Pyrolysis of Cyclohexyl Benzoate: Static System

The empirical approach used to study ester decomposition rates in the present work was subject to the limitations imposed by the experimental techniques, and accordingly, results obtained were interpretated with caution.

A typical pressure-time curve for the decomposition of the ester showed a sharp pressure rise in the initial minutes of the run, followed by a steady linear pressure rise at a much lower rate. The sharp initial rise was thought to be evaporation of the liquid in the hot zone of the reactor, followed by pyrolysis at a steady rate as shown by the pressure rise over the linear portion of the curve until completion of the reaction. The curves were reproducible over short time periods, with regard to both curve shape and reaction rate during the linear portion of the curve, provided that a clean reactor with a 'seasoned' surface was employed. 'Steady' rates(during the linear part of the curve) between 0.25 and 0.5mm./min. were obtained with the 'seasoned' reactor during a series of blank runs, while rate variations between runs of ±0.1mm./min. were taken as limits of reproducibility.

Another limitation of the technique was the problem of decomposition temperature; a range of 20° existed over the hot zone of the reactor at a nominal 475°C, measured at the furnace hot-spot. In addition, the ester concentration during pyrolysis, the contact time in the reactor, and the effective reactor volume were all unknown. With these factors to be considered in any interpretation, the importance of comparative rate measurement was amply demonstrated.

5.2.1. Decomposition in 'clean' and carbonised reactors

Preliminary studies showed that the decomposition rates fell steadily with successive runs if breakdown products were allowed to accumulate in the reactor; reproducible rates were not obtained, and the rate fell from *ca.* 1mm./min. to 0.11mm./min. after 12 runs. This rate drop in carbonised reactors has been recorded in many pyrolytic reactions.[39,79] Generally, it has been found that reproducible rates are only obtainable in reactors whose surfaces have been 'seasoned' by a number of runs.

The number required for the 'seasoning' effect has been shown to vary greatly among different compounds. Barton and Howlett[80] found that over one hundred runs were necessary before 1:2-dichloroethane gave reproducible decomposition rates, whereas Brearly _et al._[107] obtained reproducible results after only ten runs in a study of the pyrolysis of _t_-butyl and _t_-amyl chlorides. In the present investigation, the limiting decomposition rate of cyclohexyl benzoate in a carbonised reactor was very low, and reaction conditions differed from those obtaining in the above mentioned systems; the present study used much higher ester concentrations, with correspondingly increased carbon deposits. Falling decomposition rates with the cyclohexyl ester may have been caused by three factors, a fall in the surface activity of the reactor by an 'ageing' process, the presence of heavy carbon deposits, and to a smaller extent, the presence of benzoic acid. Barton[79] has suggested that the rate fall in 'seasoned' vessels is due to elimination of heterogeneous decomposition on the glass surface. Certainly this effect was evident in early runs with the cyclohexyl ester, when a large excess of cyclohexene stopped the reaction. In later runs with a clean 'seasoned' reactor, the activity of the glass surface had decreased, and the effect of cyclohexene could not be reproduced.

Carbon deposits normally produce positive catalytic results in decomposition rate studies, and not the fall in rates found in this series of experiments. The observed rate fall was greater than that directly attributable to 'seasoning of the reactor surface alone, and carbon deposits together with the presence of breakdown products undoubtedly played some part.

In heterogeneous reactions, decomposition rates have been observed to fall in the presence of reaction products due to preferential adsorption of the products on reaction sites at a surface.[81] The decomposition of cyclohexyl benzoate was a homogeneous reaction, but if heterogeneous breakdown did take place at a carbon surface, the main homogeneous reaction would be expected to maintain at least a steady rate, and coupled with any heterogeneous reaction, should give an overall rate increase. In fact, no rate increase took place.

The slight fall in rate associated with the addition of small amounts of benzoic acid to the ester for co-pyrolysis may have been due to inhibition. A more plausible explanation arose from the observation of reactors after a pyrolysis. Benzoic acid produced by the pyrolysis, condensed on the cool surfaces of the reactor above the furnace, absorbed quantities of the ester and prevented some decomposition. In runs with acid added, more ester could be absorbed, resulting in lower breakdown rates.

Decomposition in new glass reactors gave high rates of a heterogeneous nature. In later runs in clean, 'seasoned' reactors, the high rates could be approached but not equalled by careful surface cleaning. From the results obtained in runs with initiators and inhibitors, it was apparent that decomposition of the ester in a clean, 'seasoned' reactor was a homogeneous reaction.

5.2.2. Decomposition by free-radical chain processes

The production of a free-radical in a reacting system requires a higher energy of activation than that required for a molecular reaction giving the same end products. However, the chain process which the radical can initiate requires only a small amount of energy, with regeneration of the radical, which may then initiate further decomposition. Accordingly, many reactions may occur by a combination of both processes, and may even do so by a predominantly radical-chain process.

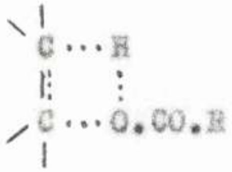
The inhibition of cyclohexyl benzoate decomposition in a new glass reactor illustrated the presence of a radical process in early runs. It is also probable that radicals or a radical-chain process participated in the breakdown in both the static and flow systems where metals were present(*cf.* p.54). The results obtained in clean, 'seasoned' reactors demonstrated that radical processes were not participating to a significant extent. Free-radical initiators, benzoyl peroxide and 1:1'-azobiscyclohexane-carbonitrile, did not affect rates significantly. Neither was the rate depressed by quinones, toluene, or nitric oxide. The latter gas was added during the course of a reaction, and a small rate increase observed, consistent with the pressure effect observed when inert gas was added. Nitrogen added to the system during a run with the ester caused an increase in the decomposition rate; the reaction was pressure dependent, which would account for the result with nitric oxide, but there was no rate fall indicating radical inhibition by this gas. Alkyl-oxygen scission of 1-methylcyclohexyl acetate has recently been shown[35] to be unaffected by azo- and peroxide catalysts. t-Butyl formate also decomposes by alkyl-oxygen scission[108], and the reaction is unaffected by cyclohexene, a known free-radical inhibitor.

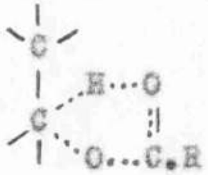
5.2.3. Reaction homogeneity

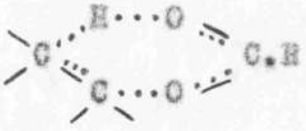
Comparison was made between the decomposition rates of cyclohexyl benzoate in packed and unpacked reactors. In a reactor packed with glass wool, the rate was 0.1mm./min. compared to 0.22mm./min. for the blank. Quartz fibre packing increased the rate to 0.38mm./min. The rate increase was not considered great enough to be positive evidence for a heterogeneous reaction, and rate variations were thought to be caused by packing effects. In the absence of other evidence, the reaction in a clean, 'seasoned' reactor was considered to be homogeneous. Reactors containing steel wool and tin filings showed high rates, thought to be indicative of heterogeneous decomposition on the metal surfaces.

5.2.4. Reaction mechanisms

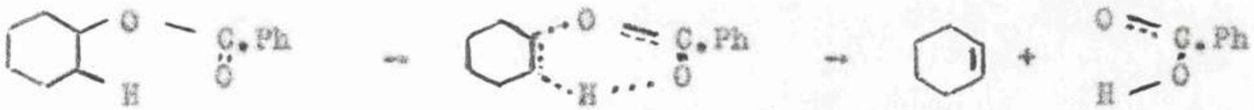
In view of the absence of a free-radical or radical chain process, a molecular mechanism appeared to be the most plausible one for the alkyl-oxygen scission of cyclohexyl benzoate. A unimolecular mechanism would proceed through a multi-membered cyclic intermediate involving four, five, or six atoms:







Steric and other factors favoyr the six-membered system, and a mechanism of this type involving a chelate ring system was proposed by Hurd and Blunck[18] to account for A-type ester scissions. With cyclohexyl benzoate, the mechanism would be as follows:



The cyclic transition state mechanism has been agreed on as the method by which many compounds decompose. Arnold, Smith, and Dodson[109] concluded that <u>cis</u>- and <u>trans</u>-methylcyclohexyl acetates decomposed by this mechanism, and it has also been used to explain the breakdown mechanism for xanthate esters[68].

PART 1

6. CONCLUSIONS

1. Cyclohexyl benzoate undergoes thermal decomposition in the vapour phase by an exclusive alkyl-oxygen scission to give benzoic acid and cyclohexene only, at temperatures up to 500°. There was no evidence for participation of radical or radical chain mechanisms in the decomposition, and it was concluded that the reaction occurs by a homogeneous unimolecular mechanism.
2. In presence of metal catalysts, the ester decomposes by different heterogeneous mechanisms involving competing routes. Dicyclohexyl, diphenyl, and possibly cyclohexylbenzene from one of the competing routes, a decarboxylation, suggested that breakdown could occur by a free-radical process.
3. In the static system, retardation of the decomposition rate of the ester by benzoic acid takes place by a physical action and not by chemical interaction.

PART II

Competitive Routes in the Pyrolysis of Enol Carboxylates

PART 11

7. INTRODUCTION (LITERATURE SURVEY)

7.1. The Thermal Rearrangement of Enol Carboxylates

The formation of β-diketones from enol carboxylates was first recorded by Wislicenus in 1905:[61]

$$\mathrm{R.CO_2.CR':CHR''} \rightarrow \mathrm{R.CO.CHR''.CO.CR'} \qquad \ldots\ldots\ldots\ldots R$$

X XI

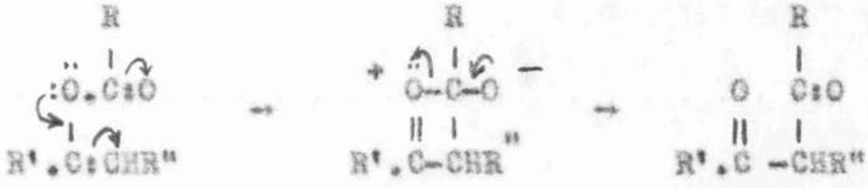
This rearrangement has been employed commercially for the preparation of β-diketones[9]. For instance, acetylacetone (XI; $R=R'=CH_3$: $R''=H$) was prepared from isopropenyl acetate (X; $R=R'=CH_3$: $R''=H$) by a thermal rearrangement at 500° in yields up to 85% [62](<u>cf.</u> p.15 <u>et seq.</u>).

Conversion of enol esters to β-diketones has also been shown to occur at much lower temperatures in the presence of a boron trifluoride catalyst, first recorded by Kastner[110] in 1948 after a study of the conversion of cyclohex-1-enyl acetate (XII; $R=CH_3$) to 2-acetylcyclohexanone(XIII; $R=CH_3$):

........R

XII XIII

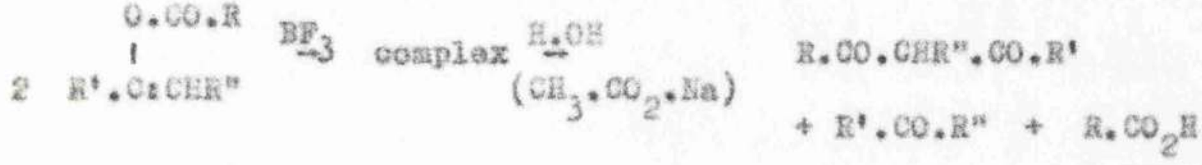
The general nature of enol carboxylate rearrangements was not realised until Young *et al.*[62] found that several ketone enol esters(acetates and benzoates) were converted to β-diketones by thermal rearrangement and also by a boron trifluoride catalyst at lower temperatures. The latter workers concluded that thermal rearrangement of enol carboxylates was an intramolecular reaction involving a four-membered intermediate for the transition state with an α, γ-shift occurring:



........R

Young co-workers also investigated the rearrangement of enol esters to β-diketones under the influence of boron trifluoride. Several esters were treated with boron trifluoride at temperatures between 0° and 20°. The mixture was hydrolysed with aqueous sodium acetate. Conversions of the ester to the corresponding β-diketone in yields of 22% for isopropenyl acetate and 45% for α-benzyl vinyl benzoate were recorded. Some side reactions also occurred, and benzoic acid and the parent ketone(from benzoate esters) were found in the reaction mixture. Blank runs showed that the ketone and acid were not formed by hydrolysis (of the ketone enol ester) nor by cleavage of the β-diketone, but were in fact by-products from the boron trifluoride reaction.

In contrast to their suggested mechanism for thermal rearrangements, Young *et al.* postulated that the boron trifluoride catalysed reaction was an intermolecular acylation of one molecule by another, with the following mechanism:

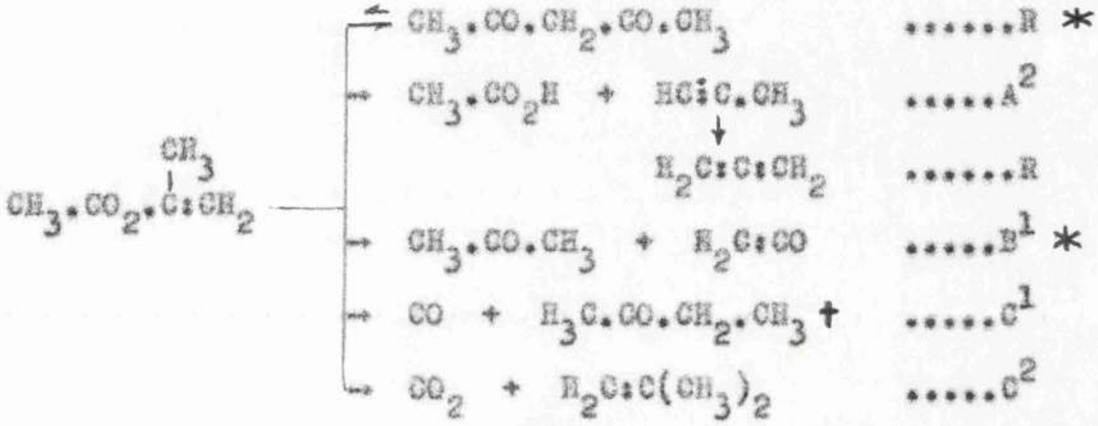


$$2\ \overset{\overset{\displaystyle O.CO.R}{|}}{R'.C:CHR''} \xrightarrow{BF_3} \text{complex} \xrightarrow[(CH_3.CO_2.Na)]{H.OH} R.CO.CHR''.CO.R' + R'.CO.R'' + R.CO_2H$$

7.2. Competing Routes in the Pyrolysis of Enol Carboxylates

Allan, McGee, and Ritchie[10] examined the thermal rearrangement of enol carboxylates(other than vinyl esters, X; R'=R"=H) to β-diketones and showed that the reaction was reversible. Pyrolysis of three enol carboxylates, isopropenyl acetate, cyclohex-1-enyl acetate, and cyclohex-1-enyl benzoate(X; R=R'=CH_3, R"=H, XII; R=CH_3 and Ph respectively) and of two of the corresponding β-diketones(XI; R=R'=CH_3, R"=H, XIII; R=Ph) in the vapour phase at *ca.* 500° revealed that the rearrangement was a reversible reaction with the equilibrium far over to the β-diketone side. Pyrolysates from the pure β-diketones, acetylacetone and 2-benzoylcyclohexanone were found to contain small amounts of the enol carboxylates, isopropenyl acetate and cyclohex-1-enyl benzoate respectively.

Young and co-workers[62] did not record any products from competing routes in their investigation of enol carboxylates. Allan, McGee, and Ritchie[10] found that, in general, enol carboxylates decomposed by a complex series of competitive scissions according to a reaction scheme suggested earlier for vinyl carboxylates(X; R'=R"=H) by Allan, Forman, and Ritchie.[14] Isopropenyl acetate, an enol ester, was found to pyrolyse according to the proposed scheme which is outlined below:



$CH_3.CO_2.\overset{CH_3}{C}:CH_2 \rightarrow$

$\rightleftharpoons CH_3.CO.CH_2.CO.CH_3$ ......R *

$\rightarrow CH_3.CO_2H + HC\vdots C.CH_3 \downarrow H_2C:C:CH_2$ .....A^2 ......R

$\rightarrow CH_3.CO.CH_3 + H_2C:CO$ .....B^1 *

$\rightarrow CO + H_3C.CO.CH_2.CH_3$ † .....C^1

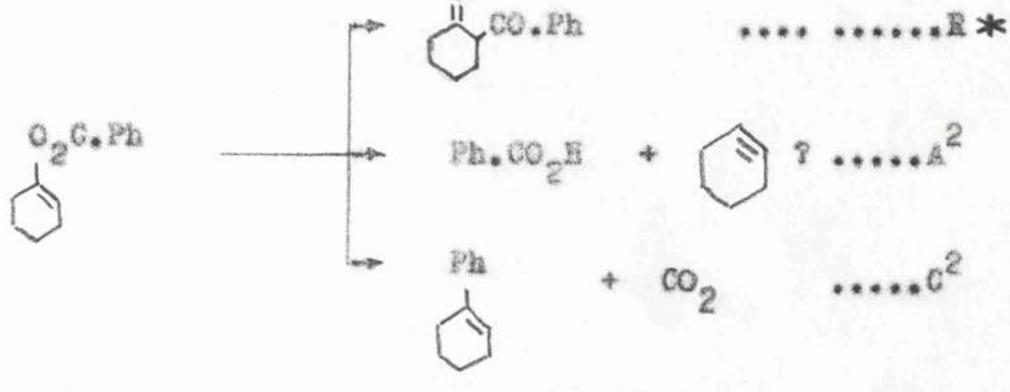
$\rightarrow CO_2 + H_2C:C(CH_3)_2$ .....C^2

+ traces of $(CH_3.CO)_2O$, CH_4, and $H_2C:CH_2$

* indicates a major route

† a product identified only in the ester pyrolysate and not in that from the β-diketone

Allan, McGee, and Ritchie found that the enol benzoate, cyclohex-1-enyl benzoate, pyrolysed by fewer routes as follows:

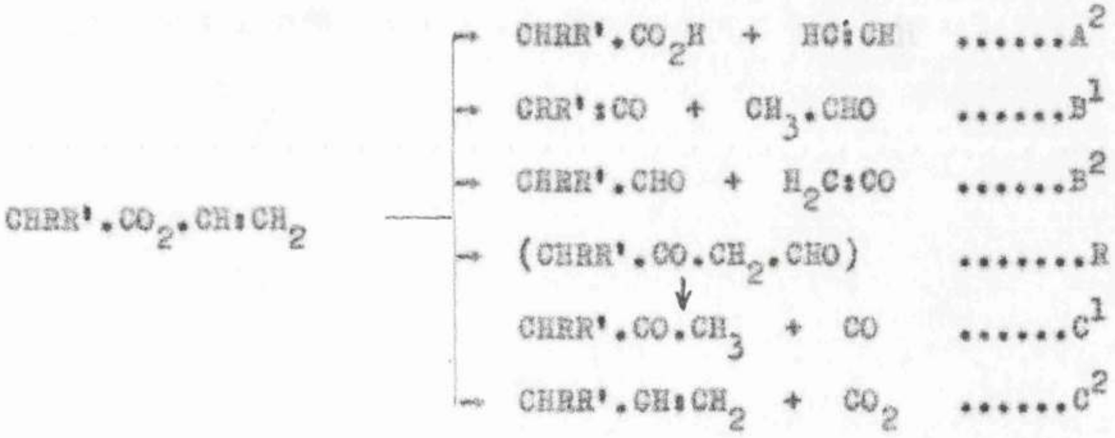


+ traces of CO, $H_2C:CH_2$, benzene, and cyclohexanone

In each ester pyrolysis investigated, the β-diketone was the major product, and in agreement with this, from pyrolysis of the β-diketone, it was found that the diketone was more thermostable than its parent ester.

7.3. The Pyrolysis of Vinyl Benzoate

Ritchie et al.[14] suggested the following reaction scheme for the pyrolysis of aliphatic vinyl carboxylates:



$CHRR'.CO_2.CH{:}CH_2$ →

$\rightarrow CHRR'.CO_2H + HC{:}CH$ ......A^2

$\rightarrow CRR'{:}CO + CH_3.CHO$ ......B^1

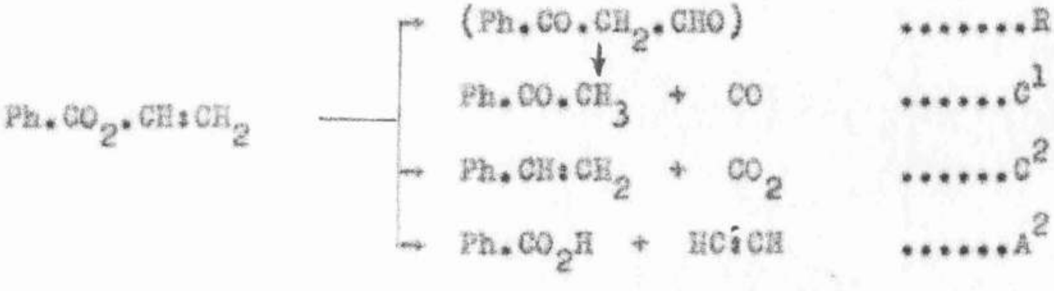
$\rightarrow CHRR'.CHO + H_2C{:}CO$ ......B^2

$\rightarrow (CHRR'.CO.CH_2.CHO)$ ....R

$\downarrow$ $CHRR'.CO.CH_3 + CO$ ......C^1

$\rightarrow CHRR'.CH{:}CH_2 + CO_2$ ......C^2

The same workers found that the aromatic vinyl ester, vinyl benzoate pyrolysed by three routes between 350° and 500°, and that this ester was less stable than the aliphatic esters. The scheme is shown below:



$Ph.CO_2.CH{:}CH_2$ →

$\rightarrow (Ph.CO.CH_2.CHO)$ ....R

$\downarrow$ $Ph.CO.CH_3 + CO$ ......C^1

$\rightarrow Ph.CH{:}CH_2 + CO_2$ ......C^2

$\rightarrow Ph.CO_2H + HC{:}CH$ ......A^2

From an examination of the pyrolysis gas, Steedman[85] estimated that for vinyl benzoate decomposition, route R/C^1, the major route, accounted for 70–80% of total breakdown, route C^2 for 10–20% of the total, and route A^2 for 5–10%. Steedman concluded that the vapour-phase pyrolysis of vinyl benzoate was predominantly homogeneous, routes R/C^1 and A^2 being completely homogeneous, while route C^2 was partially heterogeneous. No positive evidence was found in the first two routes for participation by radical or radical-chain processes.

7.4. The Pyrolysis of Isopropenyl Benzoate

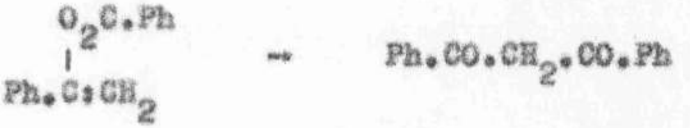
It has been shown[62] that isopropenyl benzoate, in common with other enol carboxylates, undergoes thermal rearrangement and rearrangement in presence of a boron trifluoride catalyst to the β-diketone, benzoylacetone:

$$\mathrm{CH_3.\overset{O_2C.Ph}{\overset{|}{C}}{:}CH_2} \rightarrow \mathrm{Ph.CO.CH_2.CO.CH_3} \qquad .....\mathrm{R}$$

No other products from pyrolysis of the ester were reported[62] which could have arisen from competing routes. When the ester rearranged to benzoylacetone under the influence of the boron catalyst, the reaction mixture was also found to contain acetone and benzoic acid(*cf.* p. 66).

7.5. The Pyrolysis of α-Phenylvinyl Benzoate

α-Phenylvinyl benzoate(X; R=R'=Ph; R"=H) was also investigated by Young *et al.*[62] and found to rearrange to the β-diketone dibenzoylmethane by thermal rearrangement and also in the presence of boron trifluoride at room temperature:



$$\underset{\text{Ph.C:CH}_2}{\overset{\text{O}_2\text{C.Ph}}{|}} \quad \rightarrow \quad \text{Ph.CO.CH}_2\text{.CO.Ph} \qquad \text{......R}$$

In common with the results reported for the pyrolysis of isopropenyl benzoate, products from competing reactions were not detected in the pyrolysate from α-phenylvinyl benzoate.

PART II

8. OBJECT

Competitive routes in the pyrolysis of enol carboxylates

The enol benzoate of acetaldehyde, vinyl benzoate, has been shown to pyrolyse by several competing routes. The main route produced acetophenone and carbon monoxide, and it was suggested by earlier workers[14] that these compounds arose through a postulated intermediate, benzoylacetaldehyde, which then decomposed. Benzoylacetaldehyde was not isolated from the ester pyrolysate in any of the previous studies. Vinyl benzoate was selected for pyrolysis in the hope of isolating or identifying the labile intermediate; it was also intended that a careful search be made for compounds from decomposition routes other than those previously recorded for the ester.

Two related esters, isopropenyl benzoate and α-phenylvinyl benzoate, were also selected for pyrolysis. It was decided that the pyrolysates from these esters should be examined for products from routes competing with the exclusive thermal rearrangement to a β-diketone previously reported for each ester.[62]

PART II

9. EXPERIMENTAL

9.1. Preparation of Compounds

9.1.1. Vinyl benzoate

A survey of the literature revealed several preparations for this ester, and in the present study, three of these were used in an attempt to obtain a highly pure sample. Ritchie *et al.*[14] were unable to prepare a pure sample of vinyl benzoate in an earlier investigation because it was found that the ester decomposed to give acetophenone around 190°. It was obvious that methods involving high temperatures for the preparation should be avoided. Direct combination of acetylene with benzoic acid in the vapour phase at 350° over a mixed chromite catalyst[111]; and pyrolysis of ethylene dibenzoate[7], two preparative methods requiring temperatures above 200°, were thus discarded.

Adelman[112] recorded a method for preparing a pure sample of vinyl benzoate by a 'vinyl interchange' reaction. The conditions were mild and it was claimed that by-products could be excluded by careful choice of the reaction conditions.

A sample of the ester was prepared by a method similar to that used by Adelman:

(a) <u>Vinyl benzoate from the 'vinyl interchange' reaction</u>

Benzoic acid(120g.) was dissolved in vinyl acetate(330g.), previously distilled. The acid dissolved under vigorous stirring. Mercuric acetate(3.8g.) and sulphuric acid(1ml., s.g.1.84) were added to the reaction mixture to produce the mercuric sulphate catalyst <u>in situ</u>. The mixture was refluxed for varying periods. After cooling, sodium acetate(anhydrous) was added to neutralise any unreacted acid. The ester was obtained by fractional distillation from the mixture through a two-foot spiral column under vacuum. According to Adelman,[112] copper acetate was added to the reaction mixture to prevent polymerisation of the reactants and product, but the inhibitor may reduce the yield[85], and was not used in the present study. Yields were increased, and only a small amount of polymerisation of the product took place during distillation. The following reactions were carried out:

Reaction	Reflux temp.	Reaction time(hrs.)	Yield
1[+]	35°	77	67%
2[‡]	55°	42	51%
3[⊕]	75°	5	23%

[+] no diacetate esters present

[‡] traces of both diacetates present

[⊕] both diacetates present, ethylidene diester predominating

By-products in the reaction were found by gas chromatographic analysis of aliquot samples taken from the reaction mixture at intervals. Physical constants for the product are listed(p.77).

Sladkov and Petrov[113], in a paper on the reaction of acetaldehyde with acid chlorides in a basic medium, described a preparation for vinyl benzoate where acetaldehyde reacted as (enolic) vinyl alcohol with benzoyl chloride:

$$CH_3.CHO \overset{base}{\rightleftharpoons} CH_2:CH.OH + Ph.CO.Cl \rightarrow Ph.CO_2CH:CH_2$$

Three bases were used. Pyridine gave highest yields; in some preparations quinoline reacted violently with the acid chloride and caused resinification of the acetaldehyde. Dimethylaniline was found to be difficult to separate from the vinyl ester produced. The preparation of vinyl benzoate was thus attempted:

(b) Benzoylation of (enolic) acetaldehyde

Acetaldehyde and the base were mixed in a flask cooled in an ice-bath. Benzoyl chloride was added carefully while the mixture was stirred over a two hour period. The acid chloride was redistilled before use. After adding the acid chloride, the mixture was heated to 60° for one hour, then poured into ice-water. An oily layer did not separate as described in in the original paper, but the mixture was extracted several times with ether. The extract was dried(anhydrous Na_2SO_4) and distilled. No ester was produced in any of the reactions. Each reagent was carefully distilled before use and dried.

Pyridine was purified by adding the amine to a concentrated solution of zinc chloride followed by hydrochloric acid. A copious precipitate of pyridine hydrochloride resulted which was purified by recrystallisation from absolute ethanol. Sodium hydroxide released the pyridine, which was then dried over sodium hydroxide pellets, distilled, and the fraction collected with b.p. 114-115°. Dimethylaniline, a brown liquid(L.Light & Co.), was dried over calcium chloride and distilled from a flask containing zinc dust. It gave a clear liquid with b.p. 60-62°/3mm. The following reactions were carried out:

Reaction	Base	reactants base	 acid chloride	acetal- dehyde	Yield
1	pyridine	200g.	140g.	88g.	nil
2	pyridine	260g.	112g.	88g.	nil
3	pyridine	460g.	140g.	88g.	nil
4	dimethyl- aniline	365g.	140g.	88g.	nil

In the first three reactions, the ether extract contained only some benzoic acid, and traces of reactants, but no ester. Reaction 4, on extraction, contained no product.

It was not found possible to prepare vinyl benzoate by this method in the present investigation, and it may be significant that although Sladkov and Petrov claimed high yields for the seven vinyl esters(benzoate, maleate, fumarate, phthalate, β-naphthoate, adipate, and sebacate), physical constants for these esters were not listed.

The preparation of monohalomercuriketones and aldehydes and their reactions was studied by Nesmeyanov *et al.*[114,115] These workers described a preparation for vinyl benzoate by reacting chloromercuriacetaldehyde with benzoyl chloride. The ester was prepared in the present study accordingly:

(c) *Vinyl benzoate by benzoylation of chloromercuriacetaldehyde*

Chloromercuriacetaldehyde, $Cl.Hg.CH_2.CHO$, was prepared by adding vinyl acetate(86g.) to an aqueous solution of mercuric acetate(320g. in 1.5 l.) with vigorous shaking. The precipitate of mercury salts was filtered off, and potassium chloride(75g.) added to the solution. A crystalline precipitate of chloromercuriacetaldehyde(196g., 71%) was obtained as colourless plates m.p. 132-133°(lit.,[115] yield 100%, m.p. 129-130°). On standing, the reaction mixture gave another precipitate(23g., m.p. 160-162°) which was not examined further. The mercury complex was ground finely and suspended in sodium-dried xylene (200ml.). Benzoyl chloride(100g.) was slowly added to the mixture, after which it was heated to 50° for six hours. After cooling, mercuric chloride was filtered off and the crude ester obtained by fractionation *in vacuo*. The ester product persistently contained traces of benzoyl chloride which were removed by treatment with pyridine, dilute acid(3% v./v.), sodium hydrogen carbonate solution, and washed finally with water. The ester was dried and redistilled(23g., 15%) and shown to be pure by chromatographic analysis. Constants obtained for the ester from the literature and from prepared samples are listed below:

Physical Constants for Vinyl Benzoate

(a) Reported in the literature

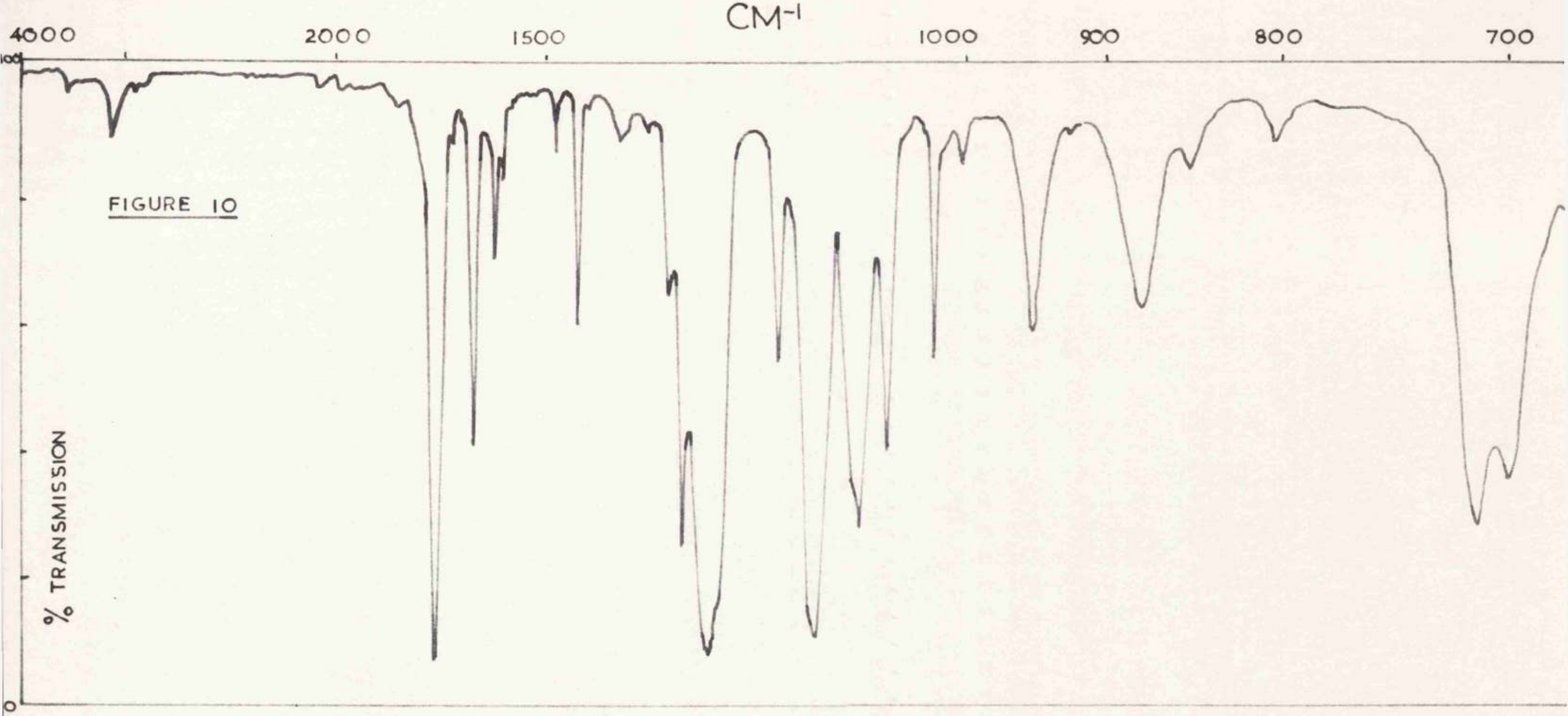
Reference	b.p.	n_D^t	Analysis C	Analysis H	d_4^{20}	Yield
Burnett and Wright[116]	96°/20mm.	$n_D^{24.5}$ 1.5130	-	-	1.067	-
Sladkov and Petrov[113]	75°/4mm.	-	-	-	-	89%
Adelman[112]	72-74°/3mm.	$n_D^{21.5}$ 1.5259	-	-	1.0706	71%
Nesmeyanov *et al.*[115]	72-73°/3mm.	n_D^{20} 1.5279	-	-	1.068	65%

(b) Present work

	b.p.	n_D^t	C	H	d_4^{20}	Yield
(i) from the method of Adelman	71-73°/3mm.	n_D^{20} 1.5263	73.2	5.6	1.070	67%
(ii) from the method of Nesmeyanov *et al.*	78-80°/5mm.	n_D^{20} 1.5283	73.3	5.5	1.071	15%

Calculated for $C_9H_8O_2$: C, 73.0; H, 5.4%.

FIGURE 10



SPECTRUM OF VINYL BENZOATE (NESMEYANOV PREPARATION.[115])

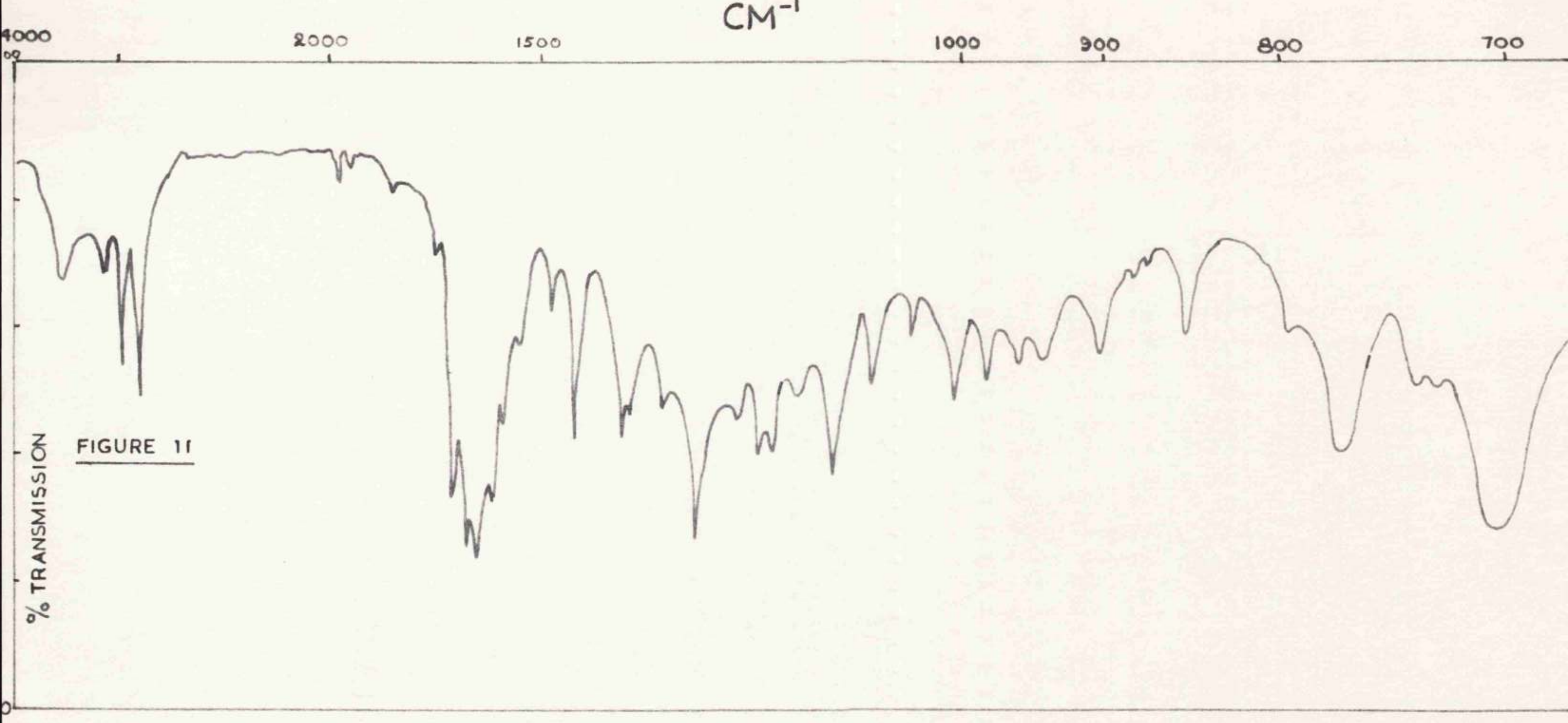


FIGURE 11

SPECTRUM OF BENZOYLACETALDEHYDE.

9.1.2. Ethylene diacetate

Acetic anhydride(112g.), ethylene glycol(62g.), and sulphuric acid(2ml.,s.g.1.84) were mixed together. After refluxing for three hours at 130°, the mixture was cooled and extracted with ether. Traces of ethylene glycol were removed from the extract by several washings with water. The product was obtained by fractionating the extract, as a colourless liquid(45g., 31%) and had b.p. 180-185°(lit.,[117] b.p.186°).

9.1.3. Benzoylacetaldehyde[118]

Acetophenone(120g.), ethyl formate(110g.), and sodium ethoxide(34g.) were mixed together in anhydrous ether(110ml.). The mixture was cooled in an ice-bath, and the sodium salt of benzoylacetaldehyde precipitated out. This sodium complex was converted to the copper salt(with copper acetate) which had m.p. 202-206°. Hydrolysis with dilute mineral acid gave benzoylacetaldehyde as a yellow liquid(yield 30%). Some product decomposed during hydrolysis(product gave a 3-peak chromatogram) and could not be distilled; the material was not characterised by C, H analysis(Allan, Forman, and Ritchie[14] also prepared this compound and were unable to obtain it pure. Analysis for their sample was unsatisfactory). In another preparation, the sodium salt of benzoylacetaldehyde was converted to the nickel complex(saturated nickel acetate solution) as a dark green solid(m.p. 340-344°). Hydrolysis of the nickel complex with dilute mineral acid gave a purer product(found: C, 75.1; H, 4.8) Calc. for $C_9H_8O_2$: C, 73.0; H, 5.4%) but the analysis was still outside accepted limits. Benzoylacetaldehyde gave a characteristic red colouration for(enolic) $-CO.CH_2-$ groupings with an alcoholic solution of ferric chloride.[56]

9.1.4. Compounds related to vinyl benzoate

Materials for the pyrolysis studies connected with vinyl benzoate: ethylidene diacetate, acetophenone, styrene, benzaldehyde, phenylacetylene, *etc.*, were obtained from commercial sources.

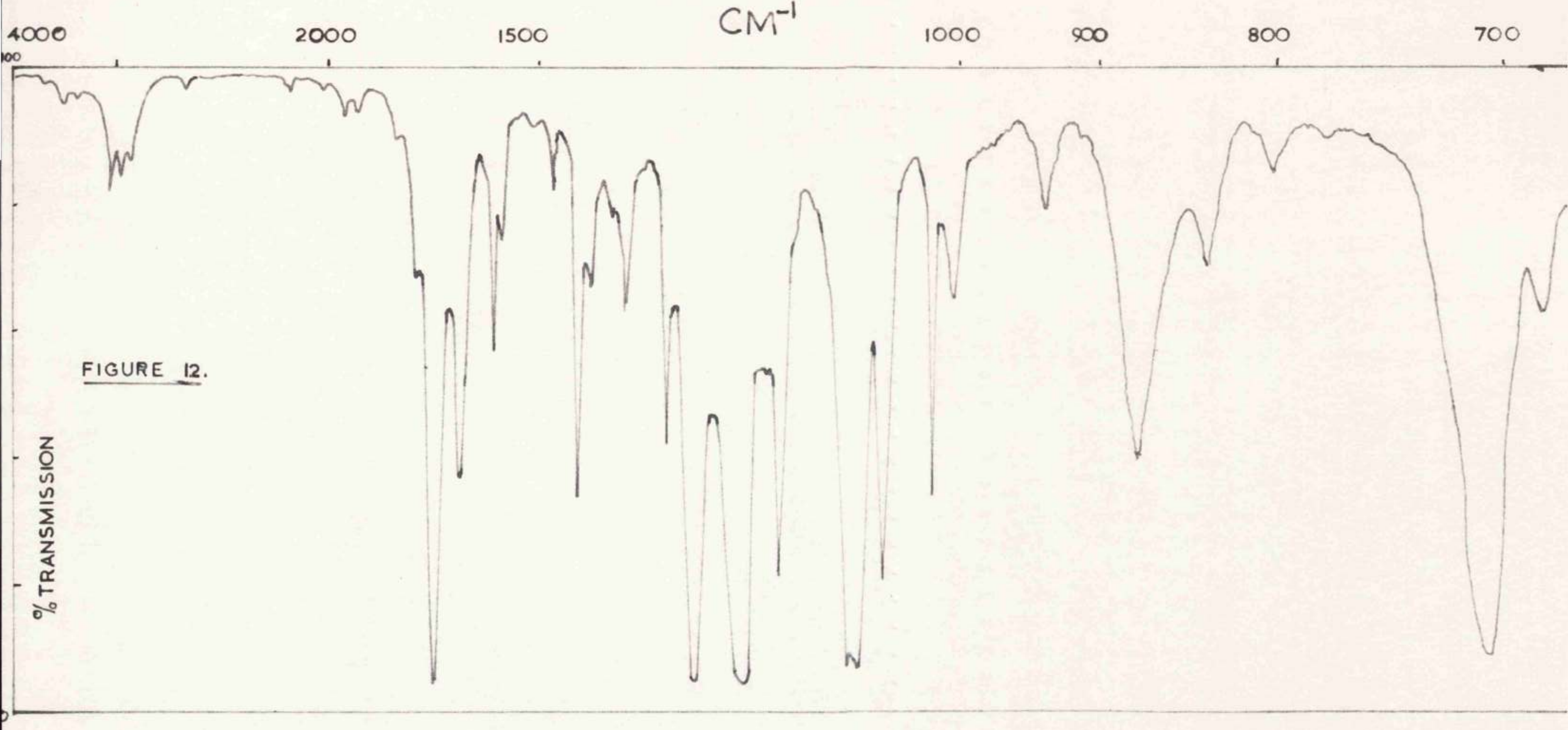
9.2. Isopropenyl Benzoate

Two methods have been described previously for preparing this ester. In an apparatus similar to that described by Young *et al.*[62], the following reaction was carried out:

Isopropenyl acetate(300g.) and a sulphuric acid catalyst(1ml.,s.g. 1.84) were refluxed gently under an efficient column while benzoyl chloride(140g.) was added over a five hour period. During this time, a low-boiling fraction was distilled out. The reaction mixture was fractionated under reduced pressure, but produced only benzoic acid and starting materials. It was not found possible to prepare the ester by this method.

It was eventually prepared by a method similar to the one used for vinyl benzoate(p.76) described by Nesmeyanov *et al.*[115]

FIGURE 12.



SPECTRUM OF ISOPROPENYL BENZOATE

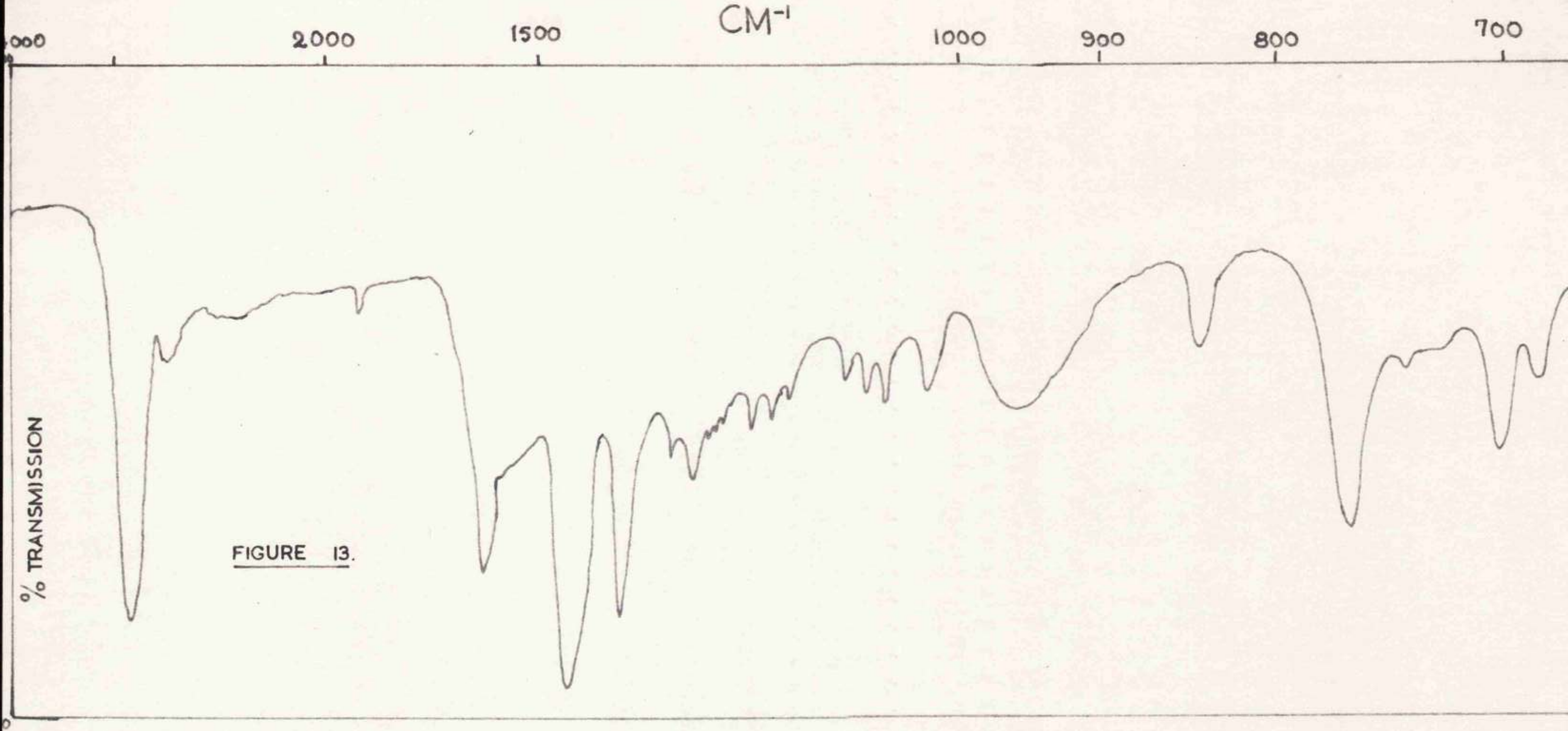
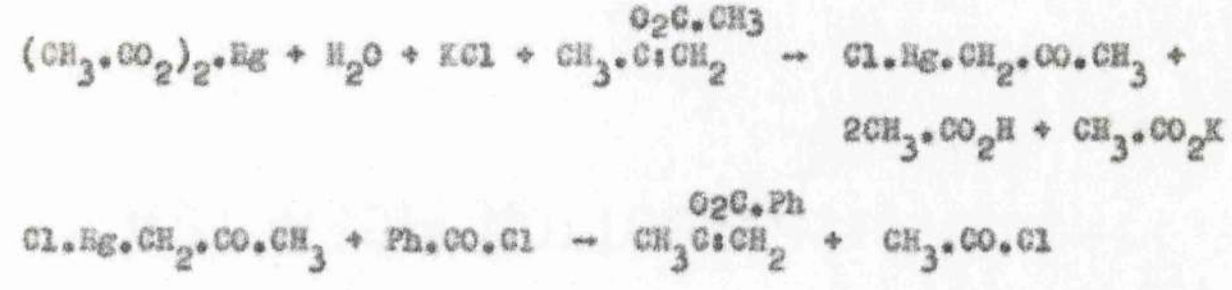


FIGURE 13.

SPECTRUM OF BENZOYLACETONE



$$(CH_3.CO_2)_2.Hg + H_2O + KCl + CH_3.\overset{O_2C.CH_3}{C}{:}CH_2 \rightarrow Cl.Hg.CH_2.CO.CH_3 + 2CH_3.CO_2H + CH_3.CO_2K$$

$$Cl.Hg.CH_2.CO.CH_3 + Ph.CO.Cl \rightarrow CH_3\overset{O_2C.Ph}{C}{:}CH_2 + CH_3.CO.Cl$$

Chloromercuriacetone(166g.,57%) with m.p. 102-103°(lit.,[115] 75%, m.p. 103-104°) was prepared by mixing isopropenyl acetate(100g.) with mercuric acetate(320g.) in water(1.5 l.) and adding potassium chloride(75g.). Benzoyl chloride(140g.) was added to the mercury complex suspended in dry xylene(250ml; rigorous drying with sodium metal increased the yield of ester greatly[10]) and the mixture was heated to 50° for six hours. The crude ester was obtained by fractioning the mixture.under reduced pressure. Traces of mercury salts were removed with dilute ammonia(benzoyl chloride was removed with pyridine in another prepmration), after which the ester was dried and redistilled. The product was a colourless liquid(71g., 44%) with b.p. 62°/2mm., n_D^{20} 1.516, d_4^{20} 1.045(lit.,[115] 63%, b.p. 87°/7mm., n_D^{20} 1.517, d_4^{20} 1.047)(Found: C, 74.08; H, 6.27. Calc. for $C_{10}H_{10}O_2$: C, 74.1; H, 6.2%).

9.2.1. Allylbenzene

Allyl bromide(60g.) reacted with a Grignard reagent prepared from bromobenzene(80g.), magnesium(20g.), and anhydrous ether(350ml.) gave on hydrolysis, allylbenzene(41g.,73%) with b.p. 150-153°(lit.,[121] 82%, b.p.153-154°).

9.2.2. Propenylbenzene[123]

Allylbenzene was passed through a flow reactor at 250° packed with Pyrex helices coated with Fe_2O_3 and a conversion of *ca.* 45% to propenylbenzene obtained. The product was not isolated, but conversion was measured by chromatographic analysis.

9.2.3. Compounds related to isopropenyl benzoate

Compounds used in the work connected with isopropenyl benzoate, benzoylacetone, α-methylstyrene, propiophenone, acetone, *etc.*, were obtained from commercial sources.

9.3. α-Phenylvinyl Benzoate

Acetophenone(120g.) and benzoyl chloride(140g.) were refluxed together for ten hours as described by Lees[120]. The ester was obtained as a pale yellow liquid with b.p. 140-144°/4mm., n_D^{20} 1.589(lit.,[120] b.p. 200-204°/11mm.)(Found: C,80.7; H,5.6. Calc. for $C_{15}H_{12}O_2$: C,80.5; H,5.4%). The yield was 92g. or 41%. Young[62] also prepared this ester in 30-35% yield and recorded b.p. 186-189°/9mm. In one preparation, Young claimed to have obtained the ester as a solid, m.p. 37-38°, recrystallised from methanol. In the present work, a methanol-soluble, colourless material was isolated from the reaction mixture which proved to be not the ester product, but benzoic anhydride, m.p. 38-40°, confirmed by mixed m.p. and infrared.

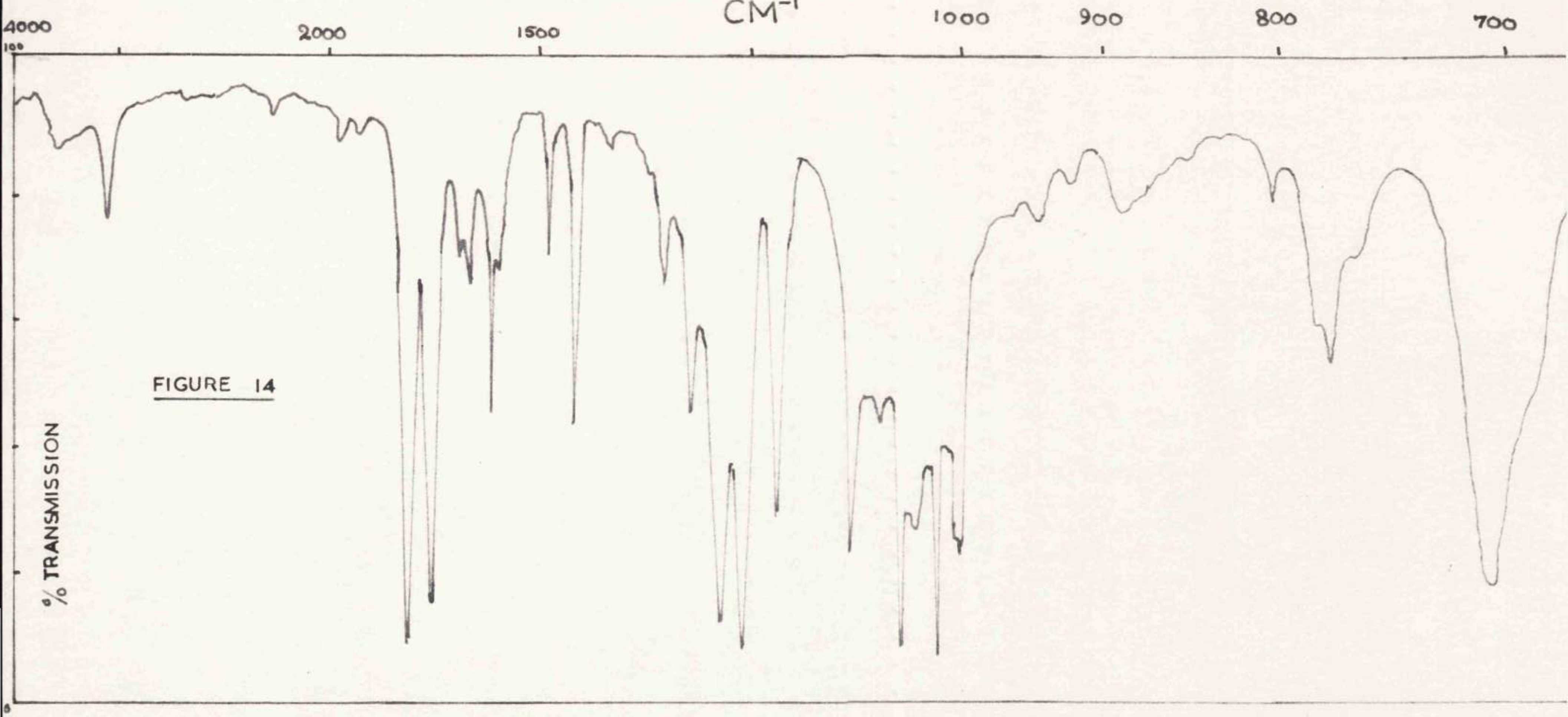


FIGURE 14

SPECTRUM OF ACETOPHENONE ENOL BENZOATE

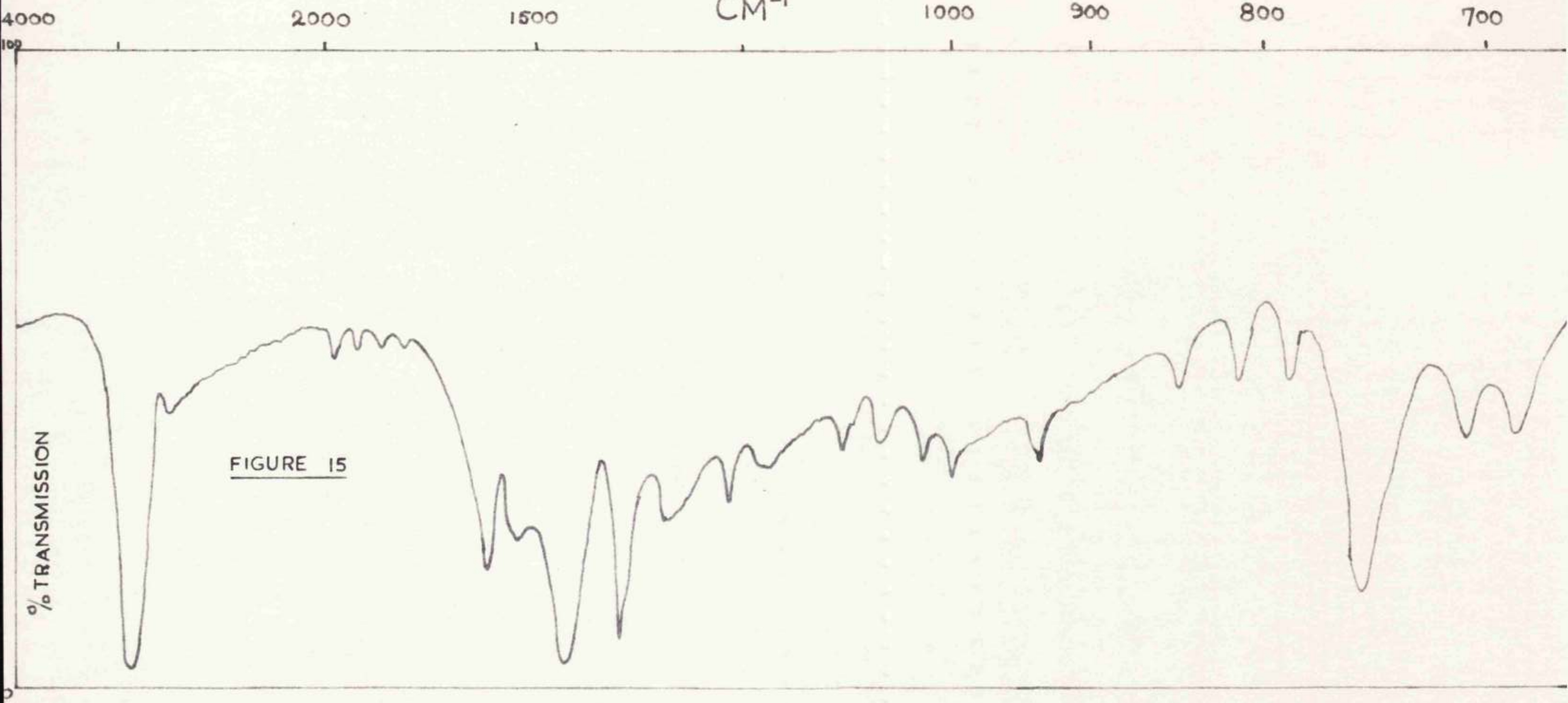


FIGURE 15

SPECTRUM OF DIBENZOYLMETHANE

9.3.1. Compounds related to α-phenylvinyl benzoate

Compounds used in the work connected with α-phenylvinyl benzoate, such as dibenzoylmethane, diphenylmethane, phenyl benzyl ketone, 1:1'-diphenylethylene, *etc.*, were obtained from commercial sources.

PART II

10. RESULTS

10.1. Examination of Preparative Methods

10.1.1. Vinyl benzoate

Adelman[112] claimed that vinyl benzoate could be obtained in a pure state by the 'vinyl interchange' reaction. The conditions were mild, and the ester was not contaminated with its own pyrolysis products as happened in other preparations.[7,111] In the 'vinyl interchange' reaction, benzoic acid reacts with vinyl acetate in the presence of a mercuric sulphate catalyst. Although termed a catalyst by Adelman, it is possible that the mercuric sulphate forms an intermediate of a type similar to that isolated by Nesmeyanov *et al*[115] during their preparation of vinyl benzoate(*cf.* p.76). Possible reactions in the 'vinyl interchange' reaction are:

(i) $Ph.CO_2H + CH_3.CO_2.CH{:}CH_2 \xrightarrow{HgSO_4} Ph.CO_2.CH{:}CH_2 + CH_3.CO_2H$

(ii) $CH_3.CO_2H + CH_3.CO_2.CH{:}CH_2 \xrightarrow{H_2SO_4} CH_3.CH.(O_2C.CH_3)_2$

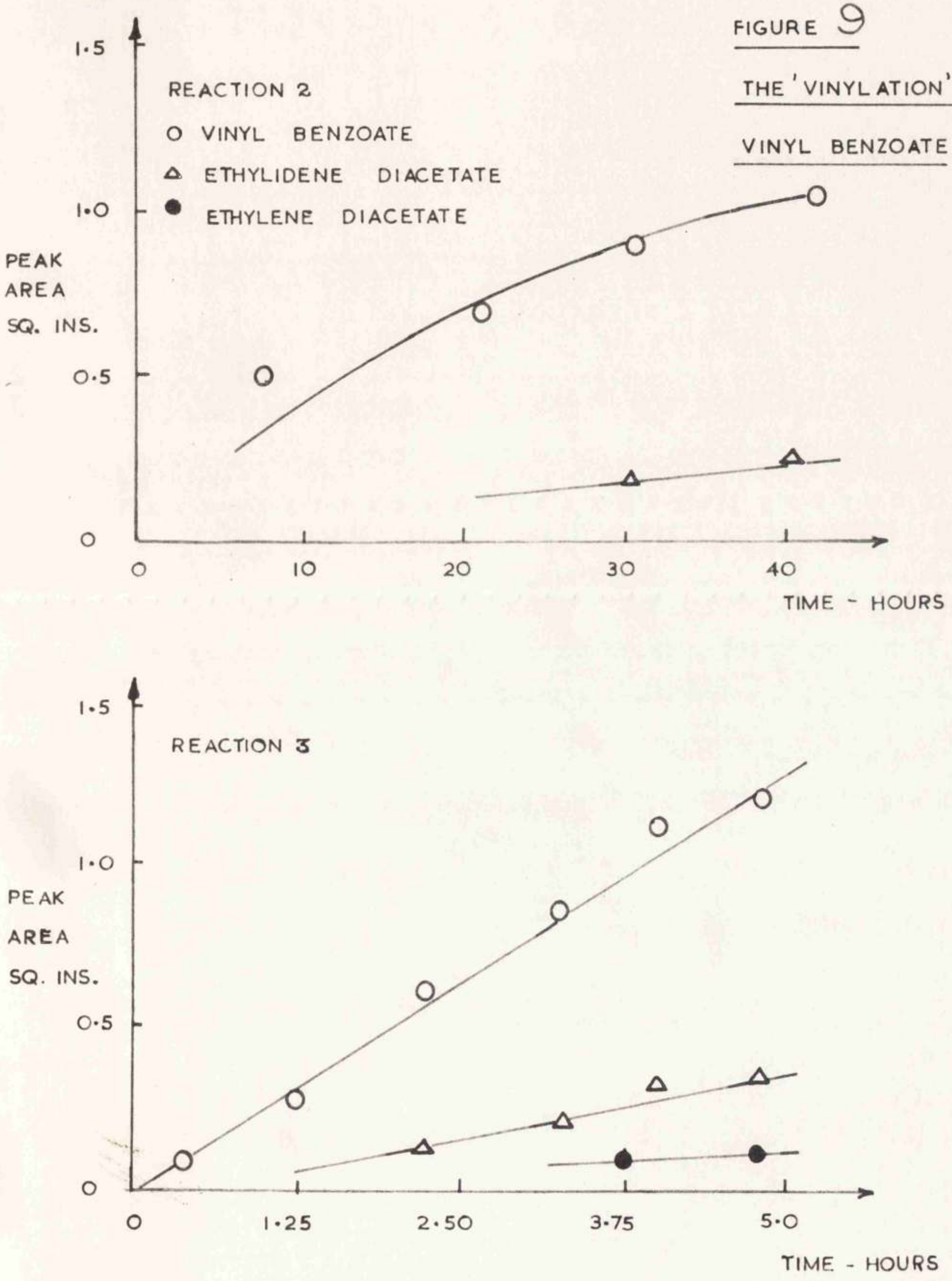
(iii) $CH_3.CO_2H + CH_3.CO_2.CH{:}CH_2 \xrightarrow{H_2SO_4} CH_3.CO_2.CH_2.CH_2.O_2C.CH_3$

Adelman detected ethylidene diacetate, the main by-product(ii), but failed to detect ethylene diacetate(iii), found in the present work by chromatographic analysis. The ethylene diester appeared as a by-product when the reaction mixture was heated above 50°. Adelman found that the yield of vinyl benzoate was increased by lowering the reaction temperature from 75° to 30° and raising the reflux time from 6 to 75 hours. Burnett and Wright[116] prepared vinyl benzoate for polymerisation by the 'vinyl interchange' reaction, but claimed that the yield did not vary despite the use of a wide range of reaction temperatures and times.The last workers did not mention contamination of the benzoate ester by other products, but inhibition periods were reported in the polymerisation experiments, indicative of impurities in the ester. In view of these conflicting results, the ester was prepared by a series of 'vinylation' reactions(p.73) and the course of two reactions followed by analysing aliquot samples removed from the reaction mixture at intervals. These are shown in Figure 9. For the analysis, samples(1μl. from an 'Agla' micrometer syringe) were chromatographed and each peak-area measured. In early stages of each reaction, ethylidene diacetate could not be determined on account of blocking by the vinyl acetate peak. The unknown peak was identified by comparing its retention time at different temperatures with that of a pure sample of ethylene diacetate. The reaction mixture gave peaks for vinyl acetate, acetic acid, benzoic acid, and those shown

FIGURE 9

THE 'VINYLATION' REACTION

VINYL BENZOATE



below:

Peak	Retention time(minutes)
1	9.1
ethylidene diacetate	9.0
2	14.7
ethylene diacetate	14.6
3	29.1
vinyl benzoate	27.8-30.2 *

* depending on sample size

Vinyl benzoate sample was prepared by the method of Nesmeyanov *et al*[115]. Ethylidene diacetate was an Eastman Kodak chemical, reagent grade. Of the three methods used in the present study to prepare vinyl benzoate, that proposed by Nesmeyanov[115] gave the purest samples, which were used for pyrolysis studies.

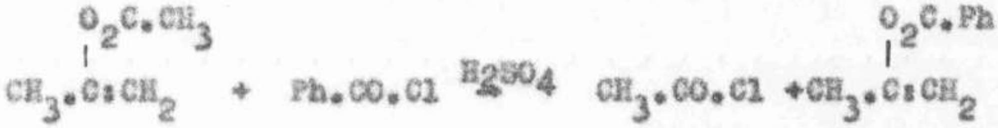
10.1.2. Isopropenyl benzoate

Attempts to prepare this ester by benzoylation of (enolic) acetone in pyridine were unsuccessful:

$$CH_3.CO.CH_3 \rightleftharpoons CH_3.\overset{OH}{C}:CH_2 + Ph.CO.Cl \not\rightarrow Ph.CO_2.\overset{CH_3}{C}:CH_2$$

Instead, a quantitive yield of benzoic anhydride was obtained. In another preparation, molar quantities of acetone and benzoyl chloride were refluxed together, but no ester was produced. This reaction failed on account of the low enol content of acetone in the liquid phase, reported[119] to be as low as $2.5 \times 10^{-4}\%$, although Lees[120] was able to prepare a series of ketone enol benzoates from higher molecular weight ketones by direct interaction between benzoyl chloride and the corresponding ketone. The scope of this reaction was investigated, and the results are included in the appendix to this thesis.

Young et al.[62] prepared isopropenyl benzoate by refluxing benzoyl chloride with isopropenyl acetate in the presence of an acid catalyst, acetyl chloride produced during the reaction being removed by distillation through a column:



$$\overset{O_2C.CH_3}{\overset{|}{CH_3.C:CH_2}} + Ph.CO.Cl \xrightarrow{H_2SO_4} CH_3.CO.Cl + \overset{O_2C.Ph}{\overset{|}{CH_3.C:CH_2}}$$

It was not found possible to prepare the ester by this method during the present work, and the use of alternative catalysts, mercuric sulphate and quinoline, also proved unsatisfactory for preparing the ester. In each reaction, the main product was benzoic acid. The ester was eventually prepared *via* the monohalomercuriketone complex.[115]

10.2. The Pyrolysis of Vinyl Benzoate

Pyrolysis 14(500°): The ester used for pyrolysis was the product obtained by the method of Nesmeyanov *et al.*[115] Decomposition of the ester(21.5g.) gave a dark liquid pyrolysate(16.8g.) and a trace of clear liquid(*ca.* 0.5g.) in the cold trap. Distillation of the liquid pyrolysate gave four fractions(i–iv) and a residue(v).

Fraction(i)(ca.1g.,b.p. 45-94°) contained benzene(infrared). Fraction(ii)(3.2g.,b.p. 95-150°) contained benzene, toluene, and styrene(infrared and chromatographic analysis). Fraction(iii) (6.5g.,b.p. 72-110°/10mm.) contained styrene, benzaldehyde(trace), and acetophenone, identified by its 2:4-dinitrophenylhydrazone derivative, m.p. 235-237°(lit.,[122] 239-242°), and by mixed m.p. with an authentic sample. Fraction(iv)(5g.,b.p. 77-152°/4mm.) was unchanged vinyl benzoate with some dissolved benzoic acid. There was no evidence for benzoylacetaldehyde in appreciable amounts in this fraction. A portion of the undistilled pyrolysate gave a positive dark red colouration with an alcoholic solution of ferric chloride, indicative of the presence of an(enolic) $-CO.CH_2-$ grouping of the type present in the benzoylacetaldehyde molecule.[56] A sample of the pyrolysate was also tested for anhydride groupings with the Davidson-Newman reagent,[130] in a search for benzoic anhydride, and there was a slight positive reaction. The liquid in the cold-trap was benzene(infrared). Acetaldehyde was possibly present in the gaseous pyrolysate (shown by a yellow precipitate when the gas was passed through 2:4-dinitrophenylhydrazine/HCl reagent), but there was no evidence for keten in the gas(aniline-ether trap). The main gas pyrolysate(1.1 l.) contained acetylene(6.9%), carbon dioxide(9.4%) olefins(1.6%), and carbon monoxide(82.1%).

The pyrolysate and each fraction of the distillate was chromatographed in an attempt to find the number of products:

Peak	Standard	Retention time(min.)	Remarks
1	-	0.5	dissolved gases,
2	-	0.8	or acetaldehyde.
3	-	1.2	
4	-	2.2	
-	benzene	2.1	
5	-	3.8	
-	toluene	3.8	
6	-	6.6	phenol or phenylacetylene
7	-	7.5	
-	styrene	7.4	
8	-	11.2	
-	benzaldehyde	11.3	
9	-	17.3	
-	acetophenone	17.0	
10	-	32.1	
-	vinyl benzoate	29.2-33.4	depending on the sample size injected

Analyses were carried out on a column containing 20% Apiezon 'N' on 'Celite 545'.

10.3. The Pyrolysis of Isopropenyl Benzoate

Pyrolysis 15(500°): Decomposition of the ester(14.7g.) gave a dark pyrolysate(11.8g.) containing carbon which settled out.

Carbon was filtered out, and on standing, the pyrolysate precipitated out a solid(4g.) which was removed and recrystallised several times from ethanol; it was identified as benzoylacetone, m.p. 58-60°(lit.,[124] m.p. 60-61°), by mixed m.p. and infrared. The liquid pyrolysate was distilled into three fractions(i-iii). Fraction(i)(2g.,b.p. 33-39°/40mm.) contained acetone, benzene, α-methylstyrene or an isomer, and possibly ethylbenzene(chromatographic analysis). Fraction(ii)(1.5g.,b.p. 80-155°/28mm.) contained propiophenone and undecomposed ester. Fraction(iii) (2g.,b.p. 84-125°/3mm.) was unchanged ester and a little benzoic acid; the ester was further characterised by alkaline hydrolysis to acetone and benzoic acid. The pyrolysate, and fraction(iii) were tested for acid anhydride,[130] but gave a negative reaction. The pyrolysate gas from isopropenyl benzoate(0.8 l.) contained a trace of methylacetylene(*ca*.1%), confirmed by infrared, carbon monoxide(85%), olefins(mainly ethylene; 7%), and carbon dioxide (8%). There was also a trace of methane present(infrared).

The pyrolysate and distillate fractions were chromatographed to determine the products:

Peak	Standard	Retention time(min.)	Remarks
1	-	0.9	trace present
2	-	1.1	" "
3	-	1.6	
-	acetone	1.6	

continued overleaf

chromatographic results for isopropenyl benzoate, continued:

Peak	Standard	Retention time(min.)	Remarks
4	-	2.0	
-	benzene	2.1	
5	-	3.0	trace component
6	-	3.5	" "
7	-	5.0	" "
8	-	7.4	" "
-	ethylbenzene	7.7	
9	-	10.0	
10	-	10.2	
-	α-methylstyrene	10.1	
-	β-methylstyrene	10.1	
-	allylbenzene	10.2	
11	-	22.5	trace component
12	-	29.8	
-	propiophenone	30.1	
13	-	38.5	
-	isopropenyl benzoate	38-41	depending on the sample size injected
14	-	56	

All the analyses were carried out on a column containing 20% Silicone grease on 'Celite 545'.

10.4. The Pyrolysis of α-Phenylvinyl Benzoate

An exploratory run with the ester(24g.) gave a dark slurry (17g.) from which solid material was removed by filtering. Recrystallised several times from benzene, the material(3.5g.) was a yellow solid, m.p. 75-77°, which proved to be dibenzoylmethane(lit.,[131] m.p. 77-78°) by mixed m.p. and infrared. Distillation of the liquid pyrolysate gave four fractions(i-iv) and a carbonaceous residue. Fraction(i)(a few drops, b.p.40-95°) contained benzene(infrared) and two other compounds(chromatographic analysis). Fraction(ii)(7g.,b.p.85-130°/3mm.) was acetophenone, phenylacetylene, and undecomposed ester(chromatographic analysis). Fraction(iii)(2.5g.,b.p.130-175°/3mm.) contained ester and benzoic acid, the latter characterised by m.p. and mixed m.p. Fraction(iv)(4g.,b.p.130-180°/1mm.) was a heavy yellow oil containing several compounds. Treated with 2:4-dinitrophenylhydrazine/HCl reagent, fraction(iv) gave the 2:4-dinitrophenylhydrazone derivative of phenyl benzyl ketone, with m.p. 199-203° (lit.,[125] m.p. 204°). The cold trap contained a clear liquid(3g.) which was not characterised. It boiled slightly above room temperature, and its infrared spectrum showed the following peaks: 3800w, 3600w, 2400s, 2200m, 2100m, 1320m, 950w, 740m, 720m, and 675s $cm.^{-1}$

The pyrolysate gas(1.36 l.) contained carbon dioxide(26%), carbon monoxide(69%), olefins(5%) possibly ethylene(infrared), and a trace of methane(infrared). The pyrolysate and distillate fractions were chromatographed to determine the products:

Peak	Standard	Retention time(min.)	Remarks
1	-	2.0	
-	benzene	2.1	
2	-	2.5	trace component
3	-	3.4	trace component
4	-	7.2	
5	phenylacetylene	7.2	
5	-	8.5	
6	-	20.5	
-	acetophenone	20.2	trace component
7	-	53	
-	benzoic acid	54	
8	-	76	trace component, poor resolution
9	-	82	
10	∝-phenylvinyl benzoate	80-84	depending on sample size injected

For identification, retention times for unknown peaks were compared with times for known samples chromatographed under identical conditions.

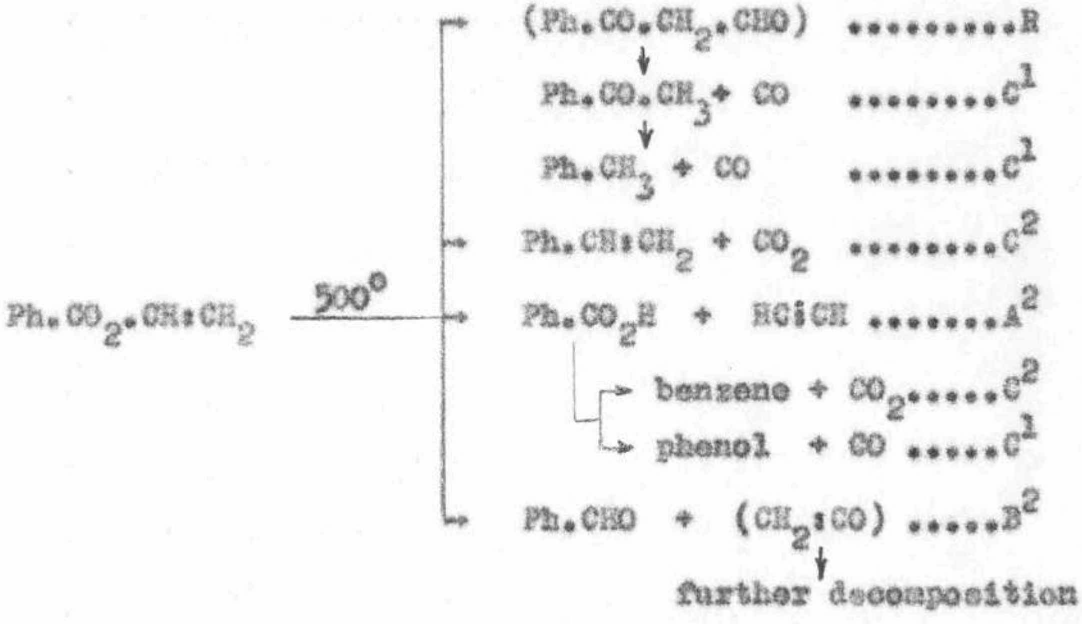
PART II

11. DISCUSSION

11.1. The Pyrolysis of Vinyl Benzoate

11.1.1. The reaction scheme

From the work described in the previous section, the decomposition of vinyl benzoate appears to be as follows:



In common with the results obtained from the pyrolysis of vinyl benzoate in earlier work,[14] the three routes, R/C^1, C^2, and A^2 predominated in that respective order. The postulated intermediate for the thermal rearrangement of the ester, benzoylacetaldehyde has been shown to decompose to acetophenone and carbon monoxide,[8] the main pyrolysis products from vinyl benzoate itself. The thermal instability of the β-ketoaldehyde was also noted by earlier workers,[14,126] and for this reason it was possibly not isolated from the ester pyrolysate, although its presence was indicated by the ferric chloride colour test. A sample of benzoylacetaldehyde, chromatographed at 117°, gave with difficulty a three-peak chromatogram, mainly acetophenone and a small amount of the ketoaldehyde. The benzoylacetaldehyde retention time was similar to that for an authentic sample of vinyl benzoate, and it is doubtful whether the two compounds were separable by gas chromatography. The chromatographic and distillation techniques employed in the attempts to isolate benzoylacetaldehyde from the ester pyrolysate were probably sufficient to cause complete decomposition to carbon monoxide and acetophenone as found previously.[14,85,126]

The two other primary routes for vinyl benzoate pyrolysis (routes C^2 and A^2) were also confirmed in the present study by chemical and chromatographic means, but were of much less importance in the reaction scheme than the R/C^1 route.

A previous investigation of the pyrolysis of(aliphatic) vinyl esters[14] showed that those esters decomposing by the B route do so by the B^1 route to a keten and a hydroxyl compound.

A new primary decomposition route for vinyl benzoate was found in the present investigation. Pyrolysis of the ester by the B^2 route to benzaldehyde and keten occurred to a very minor extent. Benzaldehyde was identified by chromatographic analysis of the pyrolysate fractions. The B^2 route was recently found to compete in the decomposition of three other aromatic vinyl esters, vinyl *o*-, *m*-, and *p*-chlorobenzoate.[127] The corresponding chlorobenzaldehyde isomer was found in the pyrolysate from each ester in the relative ratio of 4:2:1 for the *o*-, *m*-, and *p*- isomer respectively. Keten, the other product from B^2 scission of vinyl benzoate, was not isolated from the gas pyrolysate, although products from keten breakdown, ethylene, carbon dioxide, and carbon monoxide were present. Young[128] pyrolysed keten at temperatures between 510° and 570° in a static system with an initial vapour concentration of keten of up to 300mm. His suggested decomposition sbheme was as follows:

$$2\ H_2C{:}CO \rightarrow H_2C{:}C{:}CH_2 + CO_2$$

$$H_2C{:}C{:}CH_2 \rightarrow {:}CH_2 + HC\vdots CH$$

$${:}CH_2 + H_2C{:}CO \rightarrow {\cdot}CH_3 + {\cdot}HC{:}CO$$

Young proposed that the reaction would continue by attack of the methyl radical and the $CH\vdots$ group(from decomposition of $\cdot HC{:}CO$) on the keten molecule. A radical chain mechanism was suggested, the chain-length increasing with temperature, a process thought to overwhelm the bimolecular decomposition at higher temperatures. In a run at 511°, keten gave the following mixture: hydrogen, carbon monoxide(40% of total), methane, ethylene, ethane, carbon dioxide(26%), and allene. These products varied with the pyrolysis temperature, but were mainly carbon monoxide, carbon dioxide, and ethylene. Of the three gases, carbon monoxide and carbon dioxide arose mainly from routes R/C^1 and C^2 breakdown of the ester, with some contribution from secondary pyrolysis of keten present. Ethylene would only be explained in the ester pyrolysate by keten breakdown, although it was not found possible to isolate keten from the vinyl benzoate pyrolysate with an aniline-ether trap.

11.1.2. Secondary breakdown routes in the pyrolysis of vinyl benzoate

Decomposition of several of the primary products from pyrolysis of the ester would account for small amounts of ethylene, methane, benzene, and toluene found in the pyrolysate. Ethylene, as previously mentioned would arise from keten breakdown; benzene is a known decarboxylation product of benzoic acid[105]; decarbonylation of acetophenone would account for toluene in the pyrolysate. A similar decarbonylation reaction by a free-radical mechanism was shown to occur in the pyrolysis of methyl *n*-butyl ketone[132] between 430° and 500°, when carbon monoxide and several hydrocarbons were produced.

Methane would arise from pyrolysis of acetaldehyde, produced during pyrolysis by interaction between benzoic acid and vinyl benzoate, known to give ethylidene dibenzoate[16] which then gives the acid anhydride and acetaldehyde:

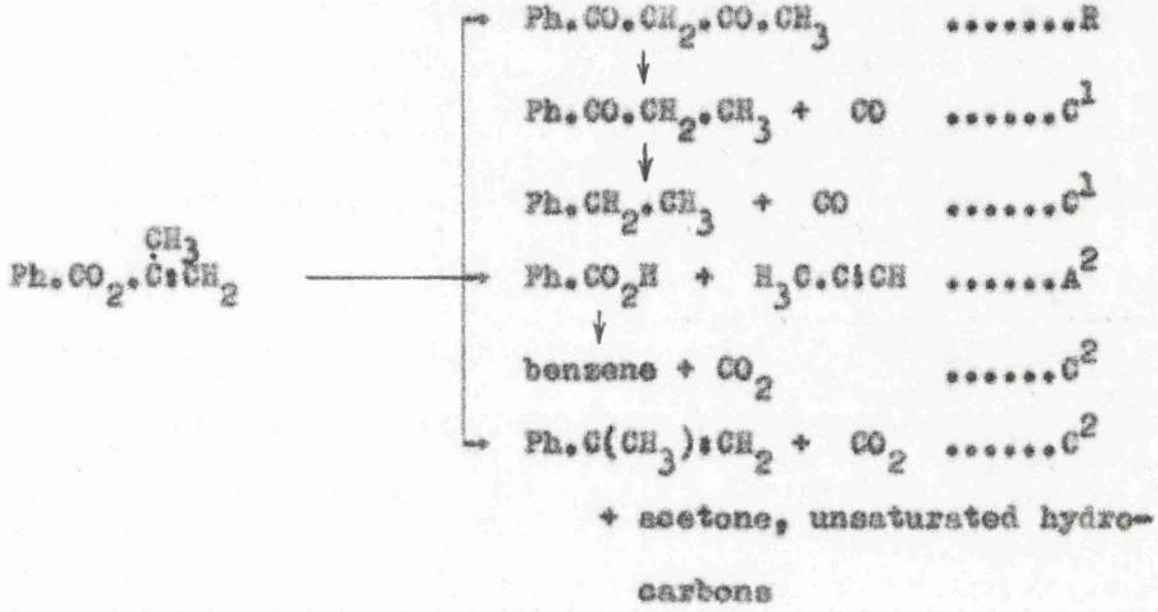
$$\begin{array}{l} \mathrm{Ph.CO_2CH{:}CH_2 \;+\; Ph.CO_2H \;\rightarrow\; (Ph.CO_2)_2.CH.CH_3} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad\;\; \downarrow \\ \qquad\qquad\qquad\qquad\qquad \mathrm{(Ph.CO)_2.O \;+\; CH_3.CHO} \;\ldots\mathrm{.D} \end{array}$$

In the chromatographic analysis of the ester pyrolysate(p.92), peak no.4 was of particular interest. Its retention time(7.2min.) did not correspond to any previously recorded breakdown product from the ester. Phenol(8.1 min.) was considered, but its retention time was outside accepted limits. On the assumption that the unknown compound was a hydrocarbon, a graph of molecular weight vs. retention time was drawn for the unknown and for three other compounds, benzene, toluene, and styrene. The molecular weight obtained by this graphical method for the unknown compound, between 100 and 104, indicated phenylacetylene, confirmed by chromatographic analysis, but the mechanism by which this compound arose is obscure, if it was indeed present.

11.2. The Pyrolysis of Isopropenyl Benzoate

11.2.1. The reaction scheme

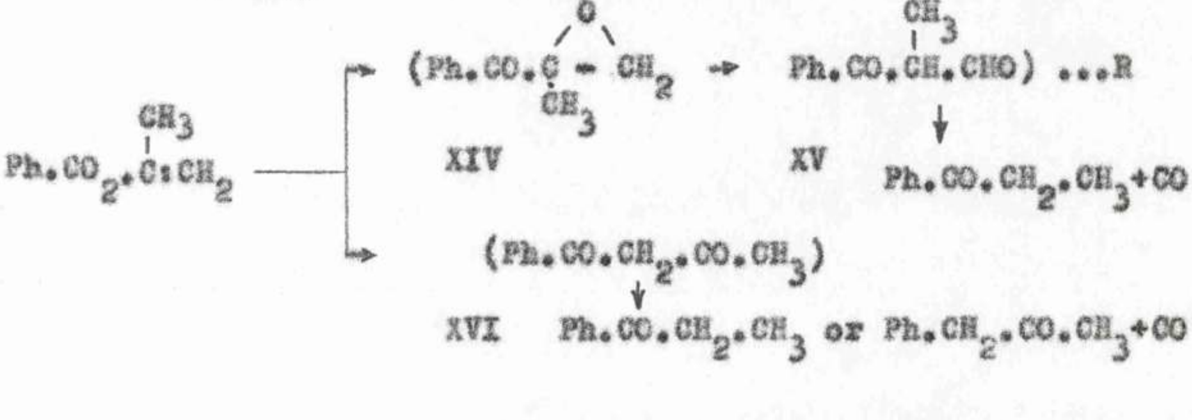
In addition to the thermal rearrangement of this ester to benzoylacetone earlier recorded,[62] isopropenyl benzoate pyrolysed as follows:



$$\mathrm{Ph.CO_2.\overset{CH_3}{C}{:}CH_2} \longrightarrow \begin{cases} \mathrm{Ph.CO.CH_2.CO.CH_3} & \ldots\ldots\ldots R \\ \quad\downarrow & \\ \mathrm{Ph.CO.CH_2.CH_3 + CO} & \ldots\ldots\ldots C^1 \\ \quad\downarrow & \\ \mathrm{Ph.CH_2.CH_3 + CO} & \ldots\ldots\ldots C^1 \\ \mathrm{Ph.CO_2H + H_3C.C{:}CH} & \ldots\ldots\ldots A^2 \\ \quad\downarrow & \\ \mathrm{benzene + CO_2} & \ldots\ldots\ldots C^2 \\ \mathrm{Ph.C(CH_3){:}CH_2 + CO_2} & \ldots\ldots\ldots C^2 \\ \quad\text{+ acetone, unsaturated hydrocarbons} & \end{cases}$$

Route R

The main reaction, as recorded previously,[62] was rearrangement of the ester to benzoylacetone. Propiophenone was also identified in the pyrolysate and may have arisen from secondary decarbonylation of the β-diketone (*cf.* decarbonylation of dibenzoylmethane during the pyrolysis of α-phenyl vinyl benzoate), or alternatively, *via* the intermediates XIV and XV shown below:



$$\mathrm{Ph.CO_2.\overset{CH_3}{C}{:}CH_2} \longrightarrow \begin{cases} \underset{\text{XIV}}{(\mathrm{Ph.CO.\underset{CH_3}{C}\overset{O}{-}CH_2}} \rightarrow \underset{\text{XV}}{\mathrm{Ph.CO.\overset{CH_3}{CH}.CHO})} \ldots R \\ \qquad\qquad\qquad\downarrow \\ \qquad\qquad\qquad \mathrm{Ph.CO.CH_2.CH_3 + CO} \\ \underset{\text{XVI}}{(\mathrm{Ph.CO.CH_2.CO.CH_3})} \\ \qquad\downarrow \\ \mathrm{Ph.CO.CH_2.CH_3 \text{ or } Ph.CH_2.CO.CH_3 + CO} \end{cases}$$

The only intermediate isolated from the pyrolysate was XVI, benzoylacetone. Ethylbenzene, the final decarbonylation product expected from benzoylacetone was also identified in the pyrolysate. There was no positive evidence for the presence of the other possible decarbonylation product, phenylacetone.

Route A^2

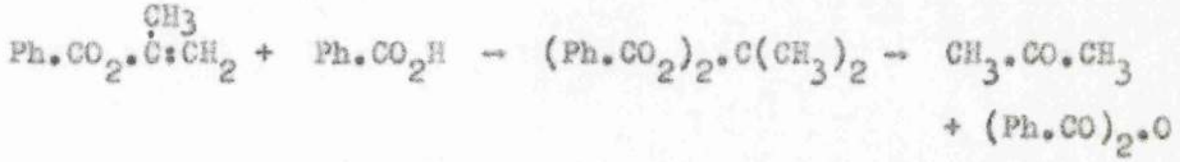
This route was the smallest of the three main competing routes in the pyrolysis and took place to the extent of about 4-6% based on the benzoic acid recovered from the pyrolysate. Methylacetylene was also produced by this scission, but its isomer, allene, was not confirmed, although it has been shown that isopropenyl acetate pyrolyses at 500° by the A^2 route to give acetic acid, allene, and methylacetylene. Secondary breakdown of benzoic acid produced by this route was noted by the isolation of benzene.

Route C^2

Decarboxylation of isopropenyl benzoate produced carbon dioxide and α-methylstyrene, but it was not found possible to identify its isomers, and allylbenzene and propenylbenzene may also have been present. α-Methylstyrene was present in the pyrolysate(infrared) but chromatographic analysis failed to produce peaks for the two other compounds.

Other Routes

Secondary decomposition of benzoylacetone, the thermal rearrangement product from the ester, would account for propiophenone and ethylbenzene. There was also a small amount of acetone in the pyrolysate, and this was considered unlikely to have arisen by hydrolysis of the ester during pyrolysis, since the ester had been dried rigorously before decomposition. It could have arisen by the following reaction:



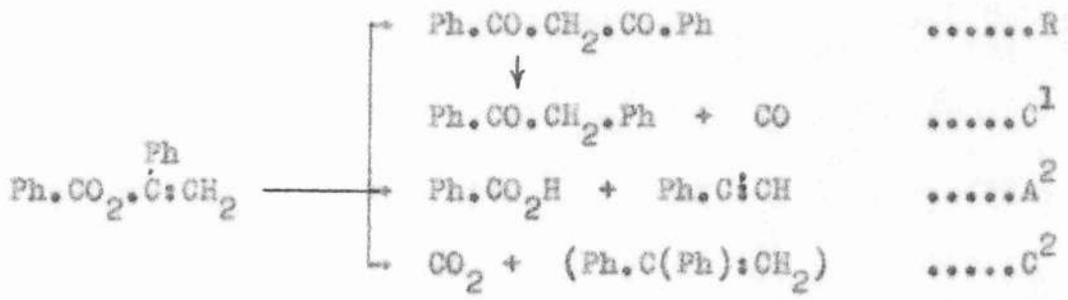
$$Ph.CO_2.\overset{CH_3}{C}{:}CH_2 + Ph.CO_2H \rightarrow (Ph.CO_2)_2.C(CH_3)_2 \rightarrow CH_3.CO.CH_3 + (Ph.CO)_2.O$$

The presence of ethylene in the pyrolysis gas was only explained by possible decomposition of ∝-methylstyrene or its isomers.

11.3. The Pyrolysis of ∝-Phenyl Vinyl Benzoate

11.3.1. The reaction scheme

Evidence was obtained for decomposition of the ester by the following scheme:



$$Ph.CO_2.\overset{Ph}{C}{:}CH_2 \longrightarrow \begin{cases} Ph.CO.CH_2.CO.Ph & \text{......R} \\ \downarrow & \\ Ph.CO.CH_2.Ph + CO & \text{.....}C^1 \\ Ph.CO_2H + Ph.C{\vdots}CH & \text{.....}A^2 \\ CO_2 + (Ph.C(Ph){:}CH_2) & \text{.....}C^2 \end{cases}$$

This ester was more thermostable at 500° than either of the previous esters studied. In addition to the pyrolysis products shown above, there were also small amounts of acetophenone, ethylene, and methane.

Route R

In common with the result from isopropenyl benzoate, the main reaction was rearrangement of this ester to dibenzoylmethane but further decomposition by C^1 decarbonylation did not occur to a large extent, and although phenyl benzyl ketone was present, there was no evidence for diphenylmethane. In this pyrolysis it was not evident which carbonyl grouping was lost from the β-diketone, whereas the carbonyl β- to the phenyl group was eliminated from benzoylacetone during the pyrolysis of isopropenyl benzoate.

Other routes

α-Phenyl vinyl benzoate pyrolysed by the A^2 route to benzoic acid and phenylacetylene, and is another addition to the group of esters previously reported to decompose by this route.[53] The gas pyrolysate from α-phenyl vinyl benzoate contained appreciable amounts of carbon dioxide(26%), and accordingly, C^2 scission was expected, but the other product, 1:1-diphenylethylene was not identified; it may have undergone rearrangement or further breakdown. Methane and olefinic gases in the pyrolysate were also unexplained, as was the small amount of acetophenone and the unknown liquid from the cold-trap whose infrared spectrum was recorded.

Since thermal rearrangement of enol benzoates to β-diketones was shown to be reversible,[10] it is difficult to ascertain from which side of the system products arose, or whether they were produced by pyrolysis of one or both compounds.

11.4. Reaction Mechanisms

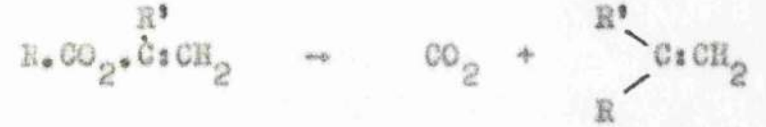
The thermal rearrangement of enol benzoate esters studied in this work, vinyl benzoate, isopropenyl benzoate, and ∝-phenyl vinyl benzoate, produced β-diketones by a mechanism best explained by Young *et al.*[62] in an earlier paper in which a four centre transition mechanism was proposed(XVII):

XVII

The above rearrangement, originally suggested for enol esters, led to the proposal for the analogous rearrangement of vinyl benzoate[8] to account for the main pyrolysis products, carbon monoxide and acetophenone, arising *via* the intermediate benzoylacetaldehyde. The present work has confirmed this suggestion.

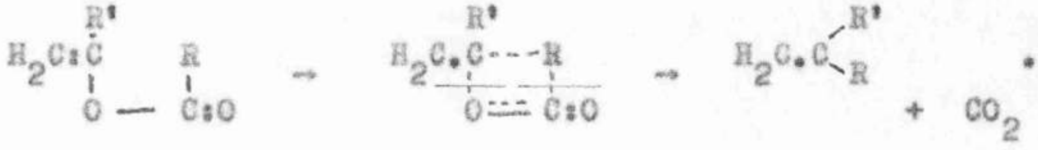
Decarbonylation of the β-diketones produced by the above rearrangement probably takes place by several mechanisms, among which will be a radical mechanism. Previously recorded ketone decarbonylations,[76,132,133] some photochemically induced, have been shown to occur by dissociation into free radicals yielding carbon monoxide and other products. It has also been noted that the amount of carbon monoxide produced by ketone pyrolysis varies markedly with temperature.[134]

Route C^2, next in importance for this group of esters, gave an acid and an alkene:



$$\mathrm{R.CO_2.\overset{R'}{C}{:}CH_2 \rightarrow CO_2 + \begin{matrix}R'\\ R\end{matrix}\!\!>C{:}CH_2}$$ ....C^2

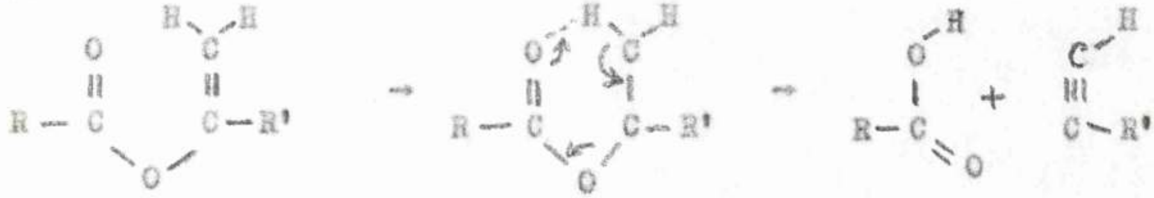
No generally accepted mechanism has been established for this route, but on the basis of a gas-phase pyrolysis of one enol benzoate, vinyl benzoate which decomposed to the extent of 10-20% by this route,[85] it was proposed that the C^2 decarboxylation to styrene and carbon dioxide was a partially heterogeneous reaction. A radical or intermolecular mechanism may participate, or the reaction could proceed by an intramolecular mechanism via a four-membered intermediate. This appears unlikely since it would involve some such system as that depicted below:



$$\mathrm{\begin{matrix}H_2C{:}\overset{R'}{C} & R\\ | & |\\ O\,— & C{:}O\end{matrix} \rightarrow \begin{matrix}H_2C.\overset{R'}{C}\cdots R\\ \vdots\qquad\vdots\\ O\cdots C{:}O\end{matrix} \rightarrow H_2C.C\begin{matrix}R'\\ R\end{matrix} + CO_2}$$ ...C^2

It is probable that several mechanisms participate in C^2 decarboxylation of enol benzoate esters.

The smallest of the primary decomposition routes, A^2 scission of the ester to benzoic acid and an alkyne may have occurred by a mechanism similar to that proposed for A^1 alkyl-oxygen scission of saturated esters[18]:



PART II

12. CONCLUSIONS

1. Vinyl benzoate pyrolyses in the vapour phase at *ca.* 500° by the three major routes previously recorded, and in addition, by a fourth minor scission to keten and benzaldehyde: the last-named compound was identified in the pyrolysate, whereas keten was not, and was presumed to have undergone further breakdown. Direct evidence was found for the postulated intermediate benzoylacetaldehyde by which *ca.* 80% of the total decomposition takes place. The ketoaldehyde was not isolated, on account of its thermal instability, but was identified by chemical means.

2. Two other enol benzoate esters, isopropenyl benzoate, and α-phenyl vinyl benzoate, previously reported to undergo exclusive thermal rearrangement to the corresponding β-diketone, were found to decompose by several minor competing scissions in addition to the previously reported major rearrangement. The β-diketone produced from the ester was found to undergo subsequent decarbonylation.

13. APPENDIX

13.1. Gas Analysis

The gaseous pyrolysates were analysed in an absorption apparatus using the following solutions:

Acetylene: Alkaline potassium iodomercurate solution was prepared from mercuric chloride(40g.), potassium iodide(100g.), and sodium hydroxide(8g.), dissolved in water and made up to 220ml.[135]

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

Unsaturated hydrocarbons: Bromine(60g.) 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(40g.), 150ml. of (30%) ammonium chloride solution, and concentrated ammonia(30ml.).

13.2. Preparation of Enol Benzoate Esters by Lees' Method[120]

During the work for this thesis, a simple method for preparing enol carboxylates was sought. Lees[120] showed that various ketone enol benzoates could be prepared by refluxing together equimolar quantities of the ketone and the acid chloride, benzoyl chloride. An attempt to prepare the enol benzoate of acetone, isopropenyl benzoate, by this method failed. Lees claimed that methyl n-propyl ketone was the lowest ketone in the series which would react with benzoyl chloride to give the enol ester. During the present study, a new enol benzoate ester, α-ethyl vinyl benzoate was synthesised by refluxing together methyl ethyl ketone(2 moles) with benzoyl chloride(1 mole) at 125° for 24 hours. The ester was obtained after careful distillation as a clear liquid(58g., or 34% based on the weight of ketone consumed) with b.p. 126°/16mm., n_D^{20} 1.5170. This method was also used successfully to prepare the enol benzoate of acetophenone, α-phenyl vinyl benzoate in good yield. Lees used this method to synthesis several higher weight enol benzoate esters such as the ketone enol esters of methyl n-heptyl ketone, methyl s-hexyl ketone, and acetophenone.

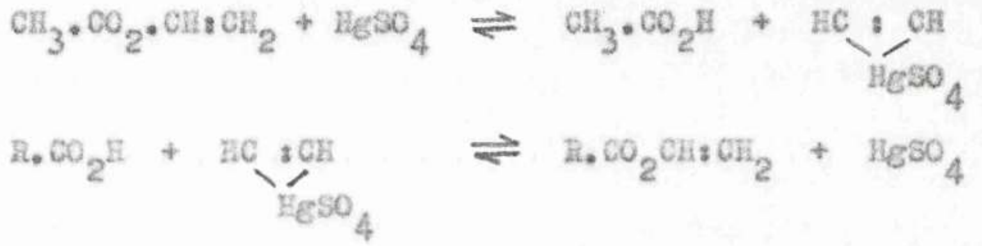
13.3. Determination of Physical Constants of Pure Esters

Density: The D_4^{20} values quoted throughout were measured by the pyknometer method using a Towson and Mercer thermostated water bath, type X27. Bath temperatures were regulated to within ±0.01°C.

Refractive Index: Refractive indices were obtained from a Hilger & Watts Refractometer. The prisms were maintained at 20° for n_D^{20} values by circulating water from a pump attached to the thermostat bath described above.

13.4. The 'Vinyl Interchange' Reaction

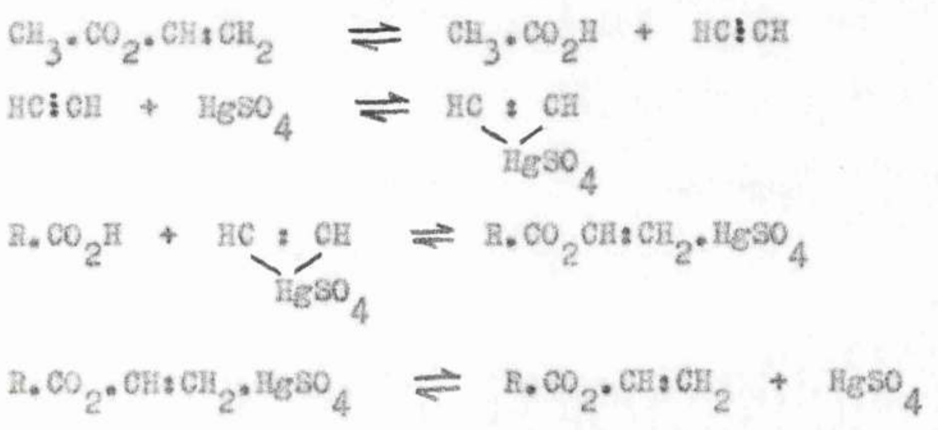
Adelman[112] prepared vinyl benzoate from vinyl acetate and benzoic acid by a reaction he termed the 'vinyl interchange' reaction in which a catalyst, mercuric sulphate, was employed. It was proposed that the process involved dissociation of the vinyl acetate into a n acetylene-mercury complex, and acetic acid. The acetylene-mercury complex was then thought to react with the various acids present to form the vinyl derivatives:



(a) $CH_3.CO_2.CH:CH_2 + HgSO_4 \rightleftharpoons CH_3.CO_2H + \underset{HgSO_4}{HC:CH}$

(b) $R.CO_2H + \underset{HgSO_4}{HC:CH} \rightleftharpoons R.CO_2CH:CH_2 + HgSO_4$

Suggested intermediate steps were:



(a_1) $CH_3.CO_2.CH:CH_2 \rightleftharpoons CH_3.CO_2H + HC{\vdots}CH$

(a_2) $HC{\vdots}CH + HgSO_4 \rightleftharpoons \underset{HgSO_4}{HC:CH}$

(b_1) $R.CO_2H + \underset{HgSO_4}{HC:CH} \rightleftharpoons R.CO_2CH:CH_2.HgSO_4$

(b_2) $R.CO_2.CH:CH_2.HgSO_4 \rightleftharpoons R.CO_2.CH:CH_2 + HgSO_4$

The $HgSO_4$ catalyst was prepared <u>in situ</u> during the reaction by adding mercuric acetate and sulphuric acid to the reaction mixture. In each reaction, the $HgSO_4$ concentration did not exceed 0.5g. per mole of vinyl acetate, and in the preparation of vinyl trimethyl acetate, the reaction proceeded at the rate of 3%

conversion per five minutes when trimethyl acetic acid was reacted with an excess of vinyl acetate.

This reaction closely resembled the process used by Nesmeyanov <u>et al</u>.[115] (p.76) to prepare vinyl benzoate, but the reaction was carried out in an aqueous medium, and the complex from vinyl acetate and mercuric acetate was isolated by adding KCl to precipitate chloromercuriacetaldehyde, $\mathrm{ClHg.CH_2.CHO}$, which was obtained in a pure crystalline form. Adelman was unable to isolate any of the proposed intermediates or acetylene from his reaction scheme, although several attempts were made to do this.

Accordingly, vinyl benzoate may be produced in the 'vinyl interchange' reaction by a much simpler mechanism than Adelman's, as outlined below:

$$\mathrm{CH_3.CO_2.CH{:}CH_2 + (CH_3.CO_2)_2.Hg + H_2O}$$

$$\downarrow$$

$$\mathrm{(CH_3.CO_2).Hg.CH_2.CHO + 2CH_3.CO_2H}$$

$$\Big\downarrow \mathrm{+Ph.CO_2H + H_2SO_4}$$

$$\mathrm{Ph.CO_2.CH{:}CH_2 + HgSO_4 + CH_3CO_2H + H_2O}$$

Any mechanistic scheme, must however, be regarded with suspicion unless the intermediates can be isolated and characterised, but the above scheme appears to be attractive on account of its simplicity.

13.5. Pyrolysis Data

Pyrolysand	p	p	p	p	p	p	p	p
Run No.	1	2	3	4	5	6	7^a	8^a
Temp.	400°	450°	500°	300°	350°	530°	350°	450°
Feed-rate(g./min.)	0.44	0.57	0.61	0.35	0.30	0.50	0.47	0.28
Contact time(sec.)	30	22	19	44	47	23	30	44
Wt. pyrolysed(g.)	42	35	40	15	15	15	10	10
Pyrolysate recovered:								
1. In cold trap(ml.)	3	4	2	nil	1.5	1	<u>ca</u>.0.5	1
2. In main receiver(g.)	37.5	28	34	13.5	12.5	11.5	8.5	7
3. Gaseous pyrolysate(l.)	0.9	1.7	3.4	-	-	-	0.7	2.15
Composition(%) of 3.								
CO	-	-	7	-	-	-	11	17
CO_2	-	8	31	-	-	-	52	57
Unsat. hydrocarbons	trace	92	61	-	-	-	37	26
CH_4	-	-	-	-	-	-	trace	-

a:Reactor contained Wood's Metal.

p: Cyclohexyl benzoate pyrolysand.

Pyrolysis Data(continued)

Pyrolysand	p	p	p	p	q	r	s	t
Run No.	9^a	10^b	11^c	12^d	13	14	15	16
Temp.	550°	450°	450°	450°	450°	500°	500°	510°
Feed-rate(g./min.)	0.45	0.50	0.40	0.23	0.15	0.30	0.50	0.20
Contact time(sec.)	24	25	31	54	33	28	18	63
Wt. pyrolysed(g.)	10	10	10	10	10	21.5	14.7	24
Pyrolysate recovered:								
1. In cold trap(ml.)	ca.0.5	1	trace	1	2	ca.0.5	1	3
2. In main receiver(g.)	6.1	7.8	7.4	8.5	2.5	16.8	11.8	17
3. Gaseous pyrolysate(l.)	2.6	-	-	-	1.7	1.1	0.8	1.36
Composition(%) of 3.								
CO	13	-	-	-	-	82.1	85	69
CO_2	32	-	-	-	-	9.4	8	26
Unsat. hydrocarbons	55	-	-	-	86^v	1.6^w	7	5
CH_4	-	-	-	-	8	trace	trace	tr.

a: Reactor contained Wood's Metal.

b: " " tin.

c: " " lead.

d: " " bismuth.

q: Cyclohexene.

r: Vinyl Benzoate.

s: Isopropenyl Benzoate.

t: ∝-Phenylvinyl Benzoate.

v: plus 6% acetylene.

w: plus 7% acetylene.

14. BIBLIOGRAPHY

1. Hurd, 'The Pyrolysis of Carbon Compounds', Chemical Catalog Co., New York, 1929.
2. Oppenheim and Precht, *Ber.*, 1876, *9*, 325.
3. Bilger and Hibbert, *J.Amer.Chem.Soc.*, 1936, *58*, 823.
4. Bailey and Nicholas, *J.Org.Chem.*, 1956, *21*, 648.
5. Traynham and Pascual, *ibid.*, 1956, *21*, 1362.
6. DePuy, King, and Froemsdorf, *Tetrahedron*, 1959, *7*, 123.
7. Chitwood, U.S.P. 2,251,983/1941.
8. Allan and Ritchie, *Chem.and Ind.*, 1953, 747.
9. Boese and Young, U.S.P. 2,395,800/1946.
10. Allan, McGee, and Ritchie, *J.Chem.Soc.*, 1957, 4700.
11. Pohl, *J.Amer.Chem.Soc.*, 1951, *73*, 5660.
12. Marshall and Todd, *Trans.Faraday Soc.*, 1953, *49*, 67.
13. Goodings, 'The Thermal Degradation of Polyethylene Terephthalate,' Symposium on High Temperature Resistance and Thermal Degradation of Polymers, Society of Chemical Industry, 1960, in press.
14. Allan, Forman, and Ritchie, *J.Chem.Soc.*, 1955, 2717.
15. Iengar and Ritchie, *ibid.*, 1956, 3563.
16. Allan, Jones, and Ritchie, *ibid.*, 1957, 524.
17. Iengar and Ritchie, *ibid.*, 1957, 2556.
18. Hurd and Blunck, *J.Amer.Chem.Soc.*, 1938, *60*, 2419.

19. Maccoll, *J.Chem.Soc.*, 1958, 3398.

20. van Pelt and Wibaut, *Rec.Trav.chim.*, 1938, *57*, 1055

21. van Pelt and Wibaut, *ibid.*, 1941, *60*, 65.

22. Rehburg and Fisher, *J.Amer.Chem.Soc.*, 1945, *67*, 56.

23. Houtman, van Steenis, and Heertjes, *Rec.Trav.chim.*,1946, 65,781.

24. Alexander, 'Principles of Ionic Organic Reactions', Wiley, New York, 1950, p.113.

25. Froemsdorf, Collins, Hammond, and DePuy, *J.Amer.Chem.Soc.*, 1959, *81*, 643.

26. Saytzeff, *Annalen*, 1875, *179*, 296.

27. Ingold, 'Structure and Mechanisms in Organic Chemistry', Bell, London, 1953, p.443.

28. Hofmann, *Annalen*, 1851, *78*, 253; *ibid.*, 1852, *79*, 11.

29. Bailey and King, *J.Amer.Chem.Soc.*, 1955, *77*, 75.

30. Bailey, Hewitt, and King, *ibid.*, 1955, *77*, 357.

31. Bailey and King, *J.Org.Chem.*, 1956, *21*, 858.

32. Bailey, Rosenberg, and Young, *J.Amer.Chem.Soc.*,1954, *76*, 2251.

33. Bailey and Rosenberg, *ibid.*, 1955, *77*, 73.

34. Royals, *J.Org.Chem.*, 1958, *23*, 1822.

35. Bailey and Hale, *J.Amer.Chem.Soc.*, 1959, *81*, 647.

36. Eglinton and Rodgers, *Chem.and Ind.*, 1959, 256.

37. Wibaut, Beyerman, and van Leeuwen, *Rec.Trav.chim.*,1952,*71*,1027.

38. McNiven and Read, *J.Chem.Soc.*, 1952, 2067.

39. Barton, Head, and Williams, *ibid.*, 1953, 1715.

40. Ingold et al., J.Chem.Soc., 1948, 2097.

41. Ingold, Proc.Chem.Soc., 1957, 279.

42. Cope et al., J.Amer.Chem.Soc., 1957, 79, 4720.

43. Idem, ibid., 1957, 79, 4729.

44. Szwarc and Murawski, Trans.Faraday Soc., 1951, 47, 269.

45. Peytral, Bull.Soc.chim.France, 1922, 31, 118

46. Nef, Annalen, 1901, 318, 198.

47. Blatt, 'Organic Syntheses' Vol.II, Wiley, New York, 1943, p.531.

48. Calvin and Lemmon, J.Amer.Chem.Soc., 1947, 69, 1232.

49. Roberts, Smith, and Lee, ibid., 1951, 73, 618.

50. Adickes, Brunnert, and Lücker, J.pr.Chem., 1931, 130, 163.

51. Anschütz, Ber., 1927, 60, 1320.

52. Anschütz, ibid., 1885, 18, 1945.

53. Mackinnon and Ritchie, J.Chem.Soc., 1957, 2564.

54. Cretcher and Pittenger, J.Amer.Chem.Soc., 1925, 47, 2560.

55. Geuther, Annalen, 1858, 106, 249.

56. Claisen, ibid., 1896, 291, 25.

57. Knorr, Rothe, and Averbeck, Ber., 1911, 44, 1138.

58. Claisen, ibid., 1912, 45, 3157.

59. Lauer and Kilburn, J.Amer.Chem.Soc., 1937, 59, 2586.

60. Wislicenus, Annalen, 1896, 291, 147.

61. Wislicenus, Ber., 1905, 38, 546.

62. Young, Frostick, Sanderson, and Hauser, J.Amer.Chem.Soc., 1950, 72, 3635.

63. Barton, <u>J.Chem.Soc.</u>, 1949, 2174.

64. Barton and Rosenfelder, <u>ibid.</u>, 1949, 2459.

65. Alexander and Mudrak, <u>J.Amer.Chem.Soc.</u>, 1950, <u>72</u>, 1810.

66. Smith and Wetzel, <u>ibid.</u>, 1957, <u>79</u>, 875.

67. Skraup and Beifuss, <u>Ber.</u>, 1927, <u>60</u>, 1070.

68. O'Connor and Nace, <u>J.Amer.Chem.Soc.</u>, 1952, <u>74</u>, 5454.

69. Trotman-Dickenson, 'Gas Kinetics', Butterworths, London, 1955.

70. Hurd, <u>Ind.Eng.Chem.</u>, 1934, <u>26</u>, 50.

71. Fisher, <u>ibid.</u>, 1942, <u>34</u>, 473.

72. Barton, <u>J.Chem.Soc.</u>, 1949, 148.

73. Rice and Johnson, <u>J.Amer.Chem.Soc.</u>, 1934, <u>56</u>, 214.

74. Farkas and Melville, 'Experimental Methods in Gas Reactions', Macmillan, London, 1939.

75. Blades, <u>Canad.J.Chem.</u>, 1954, <u>32</u>, 366.

76. Steacie, 'Atomic and Free-Radical Reactions', Reinhold, New York, 1946.

77. Paneth, Hofeditz, and Wunsch, <u>J.Chem.Soc.</u>, 1935, 372.

78. Friess and Weissberger, 'The Investigation of Rates and Mechanisms of Reactions', Interscience, New York, 1953.

79. Barton, Head, and Williams, <u>J.Chem.Soc.</u>, 1952, 453.

80. Barton and Howlett, <u>ibid.</u>, 1949, 165.

81. Barton and Onyon, <u>Trans.Faraday Soc.</u>, 1949, <u>45</u>, 725.

82. Sherman, Quimby, and Sutherland, <u>J.Chem.Physics</u>, 1936, <u>4</u>, 732.

83. Coffin and Beazley, *Canad.J.Res.*, 1937, *15B*, 229.

84. Coffin, *ibid.*, 1931, *5B*, 636.

85. Steedman, Ph.D. Thesis, Glasgow, 1959.

86. Sabatier, 'Catalysis in Organic Chemistry', Library Press, London, 1922.

87. Senderens, *Bull.Soc.chim.France*, 1909, *5*, 482.

88. Sabatier and Mailhe, *Compt.rend.*, 1912, *152*, 669.

89. Steacie, *Proc.Roy.Soc.*, 1930, *A127*, 314.

90. G.P. 284,996/1914.

91. Pearce and Wing, *J.Physical Chem.*, 1932, *36*, 703.

92. Berkman, Morrell, and Egloff, 'Catalysis', Reinhold, New York, 1946.

933 Squibb, *J.Amer.Chem.Soc.*, 1895, *17*, 187.

94. Langmuir, *ibid.*, 1915, *37*, 1139.

95. Brunel, *Bull.Soc.chim.France*, 1923, (3), *33*, 273.

96. Brunel, *Ann.Chim.Phys.*, 1905, *6*, 217.

97. Williams, 'Symposium on Gas Chromatography', Butterworths, London, 1956, p.281.

98. Hendriks, Soemantri, and Waterman, *J.Inst.Petroleum*,1957,*43*,288.

99. Waterman and van Westen, *Rec.Trav.chim.*, 1929, *48*, 637.

100. Case, *J.Amer.Chem.Soc.*, 1934, *56*, 716.

101. Blatt,'Organic Syntheses' Vol.II, Wiley, New York, 1941, p.18.

102. Rice and Teller, *J.Chem.Physics*, 1938, *6*, 489.

103. Rice and Murphy, *J.Amer.Chem.Soc.*, 1944, *66*, 765.

104. Meyer and Hofmann, *Monatsh.*, 1916, *37*, 681.

105. Moser, *Helv.Chim.Acta.*, 1931, *14*, 971.

106. Rice, Ruoff, and Rodowskas, *J.Amer.Chem.Soc.*, 1938, *60*, 955.

107. Brearly, Kistiakowsky, and Stauffer, *ibid.*, 1936, *58*, 43.

108. Gordon, Price, and Trotman-Dickenson, *J.Chem.Soc.*, 1957, 2813.

109. Arnold, Smith, and Dodson, *J.Org.Chem.*, 1950, *15*, 1256.

110. Kastner, 'Newer Methods of Preparative Organic Chemistry', Interscience, New York, 1948, p.289.

111. B.P. 581,501/1946.

112. Adelman, *J.Org.Chem.*, 1949, *14*, 1057.

113. Sladkov and Petrov, *J.Gen.Chem.U.S.S.R.*, 1954, 459.

114. Nesmeyanov and Lutsenko, *Proc.Acad.Sci.U.S.S.R.*, 1948, *59*, 707.

115. Nesmeyanov, Lutsenko, and Tumanova, *Izvest.Akad.Nauk.S.S.S.R., Otdel.Khim.Nauk.*, 1949, 601.

116. Burnett and Wright, *Trans.Faraday Soc.*, 1953, *49*, 1108.

117. Davidson, *Ind.Eng.Chem.*, 1926, *18*, 672.

118. Bülow and von Sicherer, *Ber.*, 1901, *34*, 3889.

119. Schwarzenbach and Wittwer, *Helv.Chim.Acta.*, 1947, *30*, 669.

120. Lees, *J.Chem.Soc.*, 1903, *83*, 145.

121. Hershberg, *Helv.Chim.Acta.*, 1934, *17*, 352.

122. Allen, *J.Amer.Chem.Soc.*, 1930, *52*, 2957.

123. Levina, *J.Gen.Chem.U.S.S.R.*, 1939, *9*, 2287.

124. Beyer and Claisen, *Ber.*, 1887, *20*, 2178.

125. Vogel, 'Practical Organic Chemistry', Longmans Green, London, 1948, p.707.

126. Claisen and Fischer, *Ber.*, 1887, *20*, 2191.

127. Reininger and Ritchie, unpublished observations, Glasgow, 1958.

128. Young, *J.Chem.Soc.*, 1958, 2909.

129. suggestion by Dr.W.I.Bengough.

130. Davidson and Newman, *J.Amer.Chem.Soc.*, 1952, *74*, 1515.

131. Wislicenus, *Annalen*, 1898, *308*, 229.

132. Walters and Barry, *J.Amer.Chem.Soc.*, 1957, *79*, 2101.

133. Ausloos and Steacie, *Canad.J.Chem.*, 1955, *33*, 1062.

134. Noyes and Brunet, *Bull.Soc.chim.France*, 1958, 121.

135. Hurd and Spence, *J.Amer.Chem.Soc.*, 1929, *51*, 3353.