A Study of the Pyrolysis of Linear Polyesters

by Means of Model Systems

A   Thesis

submitted to the University of Glasgow in fulfilment
of the regulations governing the award of the

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in the Faculty of Science.

by

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7. 6. 58.   Robert L. Forman

Publications

Part of the work described in this thesis has been published in the following paper:

"Studies in Pyrolysis. Part IV. Model Systems for the Pyrolysis of Poly(ethylene Terephthalate) and Allied Polyesters." R.J.P.Allan, R.L.Forman, and P.D.Ritchie, J., 1955, 2717-2725.

Another paper is being prepared for publication:

"Studies in Pyrolysis. Part XIII. Model Systems for the Pyrolysis of Poly(ethylene Fumarate)." R.L.Forman, H.M.Mackinnon, and P.D.Ritchie.

I N D E X

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Summary

A factor which frequently restricts the practical range of usefulness of an industrial high polymer is its pyrolytic breakdown during service at quite moderate temperatures, of the order of $300°$ and upwards. Before any modifications can be made with a view to improving the thermal stability of the material, and hence its range of usefulness, it is necessary to know in detail the mechanism of thermal breakdown; and this information is available, as yet, for only a few polymeric substances.

The present work is concentrated on poly(ethylene fumarate). Experiments with the polyester itself led to complex results, not easy to interpret, and this direct approach was therefore abandoned in favour of a study of model compounds representing (a) specific segments from within the intact polyester chain, (b) terminal segments from the intact chain, and (c) terminal segments of the pyrolysed chain, bearing new end-groups which might be predicted a priori.

No quantitative study of the breakdown kinetics has yet been made, as it was considered necessary that a full qualitative study of the breakdown products should precede detailed kinetic measurements.

C H A P T E R   I.

INTRODUCTION

CHAPTER   I

Introduction

1.1: The Pyrolysis of Esters

The pyrolysis of model compounds representing units of the linear poly(ethylene fumarate) chain has been found to include examples of almost every known type of ester thermal decomposition.   In order, therefore, to exemplify the relation between these known examples, and the present results, a detailed survey of all the known pyrolytic breakdown routes of carboxylic esters is given below.

The pyrolysis of an ester can give rise to a number of products as a result of (a) competitive primary decomposition routes, and (b) secondary and tertiary decomposition routes. A survey of the literature indicates that in many cases observers have a natural tendency to concentrate on the major products of pyrolysis, without seeking, or at least recording minor and less readily detectable by-products.

Formation of a wide range of products during a pyrolysis does not of itself, of course, imply primary scission by more than one route, for it is often possible to account for some of them as secondary rather than primary products.   Neverthe-less, in cases where minor as well as major products have been fully recorded, it is usually necessary to postulate two or more concurrent primary routes to interpret the results satisfactorily.   In general the pyrolytic breakdown routes of

an ester, $R.CO_2.R'$, will depend upon the composition and structure of the molecule, the relative polarities and steric effects of R and R', the presence or absence of α- and β-hydrogen atoms, and the presence or absence of unsaturated groups.

A good survey of the earlier literature, up to about 1929[1], has been presented by Hurd, although it offers a rather confusing picture of unrelated and to some extent conflicting results.   Using the existing knowledge and the many reported examples of ester pyrolysis, it is possible to produce a classification, which will cover the very great majority of the breakdown routes observed during the pyrolysis of carboxylic esters.   These are summarised, using a nomenclature developed in recent papers on this topic[2-11] :-

(i) A^o - Alkyl-oxygen scission (α-hydrogen type).

(ii) A^1 - Alkyl-oxygen scission (β-hydrogen type).

(iii) A^2 - Alkenyl-oxygen scission.

(iv) B^1 - Acyl-oxygen scission (acyl ⟶ alkoxyl type).

(v) B^2 - Acyl-oxygen scission (acyl ⟵ alkoxyl type).

(vi) C^1 - Decarbonylation.

(vii) C^2 - Decarboxylation.

(viii)   D - Disproportionation.

(ix)   IA - Intra-acyl scission.

(x)   R - Rearrangement.

These various types of ester scission are exemplified below under their respective headings.

1.1.1: Alkyl-oxygen scission (α-hydrogen type), type A^O.

In this scission the split occurs between the alkyl group (which contains no ß-hydrogen atom) and the ether oxygen of the ester group; the α-hydrogen atom migrates to the carboxyl group to form an acid and an alkene:-

$$R.CO_2 \cdot CH \diagdown \longrightarrow R.CO_2H + \tfrac{1}{2} \diagup C = C \diagdown \quad - - - - - - \quad A^O$$
$$\text{(acid)} \qquad \text{(alkene)}$$

e.g. $Ph.CO_2.CHPh.CN \longrightarrow Ph.CO_2H + \tfrac{1}{2}CPh(CN) = CPh(CN)$ - - A^O
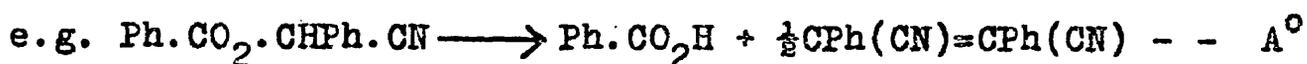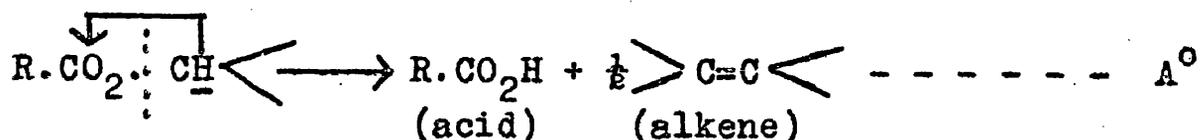
This scission requires high temperatures, of the order of 500° [12]. The mechanism of this breakdown is obscure, but is probably free-radical in type. It should be noted that the substituents on the α-carbon have a controlling influence on the breakdown. In the above case, the substituents are the phenyl and nitrile groups, whose electron-withdrawing properties probably facilitate radical formation. However, the pyrolysis of esters with unsubstituted methyl groups by Forman, Mackinnon, and Ritchie[11] showed no A^O scission at 500°. The esters examined (methyl maleate, fumarate, acrylate, methacrylate, and formate) were found to be very thermostable at 500°. Pyrolysing at the more drastic temperature of 1100°, Peytral[22] found, amongst other products, evidence for the A^O scission in the pyrolysis of methyl acetate, which has an unsubstituted methyl group:-

$$CH_3.CO_2.CH_3 \xrightarrow{\ 1100°\ } CH_3.CO_2H + \tfrac{1}{2}CH_2 = CH_2 \quad - - - - - - - \quad A^O$$
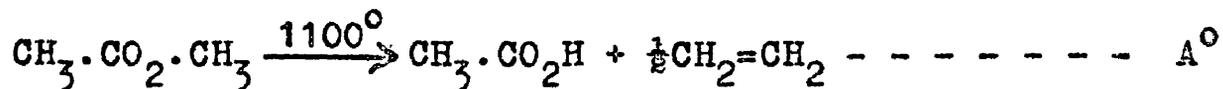
This reaction probably takes place via a transient diradical $(CH_2 \diagdown)$.

1.1.2: Alkyl-oxygen scission (ß-hydrogen type), type A^1.

In this scission the split occurs between the alkyl group (which contains a ß-hydrogen atom) and the ether oxygen of the ester group; the ß-hydrogen atom migrates to the carboxyl group to form an acid and an alkene:-

$$R.CO_2 \vdots C. \ CH< \longrightarrow R.CO_2H + >C=C< \ - \ - \ - \ - \ - \ - \ - \ A^1$$
$$\text{(acid)} \quad \text{(alkene)}$$

e.g. $CH_3.CO_2CH_2.CH_3 \longrightarrow CH_3.CO_2H + CH_2=CH_2 \ - \ - \ - \ - \ - \ - \ A^1$

The above pyrolysis of ethyl acetate was reported by Oppenheimer and Precht[13] to yield ethylene and acetic acid, and a great number of similar reactions have been reported since then, such as[14]. The A^1 scission, as a means of synthesis of unsaturated compounds, is now well established. A comparative study of tertiary, secondary, and normal alkyl carboxylates by Hurd and Blunck[18] has shown that the stability of the esters decreases as the number of available ß-hydrogen atoms increases. However, as the stability of the esters in a homologous series increases, so does the complexity of the pyrolysis, and the number of competing routes. Thus tert. butyl acetate pyrolyses simply, and at relatively low temperature, to acetic acid and isobutene, whereas, isopropyl acetate and ethyl acetate require higher temperatures and give more complex products, thus:-

$$CH_3.CO_2.CMe_3 \xrightarrow{360^o} CH_3.CO_2H + CH_2=CMe_2 \text{ (sole products)} - A^1$$

$$CH_3.CO_2.CHMe_2 \xrightarrow{430-460^o} CH_3.CO_2H + CH_2=CHMe \text{ (main products)} - A^1$$

$$+ CH_3.CHO + CH_3.CO.CH_3 + CO \text{ (by-products)}$$

$$CH_3.CO_2.Et \xrightarrow{525-530^\circ} CH_3.CO_2H + CH_2=CH_2 \text{ (main products)} - A^1$$

$$+ CH_3.CHO + H.CHO + (CH_3.CO)_2O$$

$$+ CH_4 + H_2 + CO + CH_2=CO \text{ (by-products)}$$

It has been stated above[18] that alkyl-oxygen scission is dependent on the presence of ß-hydrogen atoms, and by way of explaining this pyrolytic route, Hurd and Blunck[18] have postulated a hydrogen-bonded six-membered chelate ring thus:-
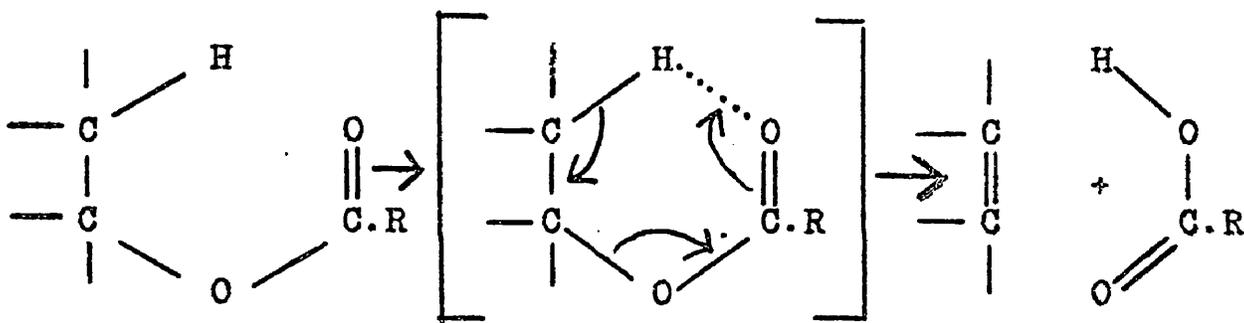
The type of hydrogen bonding implicit in this transition stage has been adversely criticised by Houtmann et al.[15], who preferred simply to call the bonding "mutual interaction". Certain other workers, Smith et al.[16] have preferred a simpler planar four-centre transition state, of the type later discussed by Barton[17], though this is open to the same kind of criticism as the six-membered ring:-
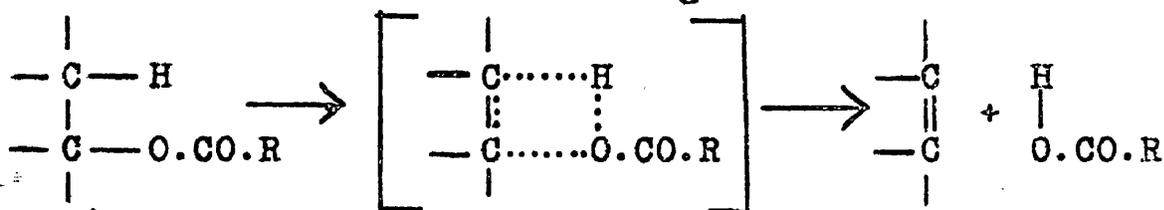
A[1] scission can take place at quite moderate temperatures (ca.360°) and it is frequently the predominant pyrolytic route for alkyl carboxylates with a ß-hydrogen atom[18].

1.1.3: Alkenyl-oxygen scission, type A^2.

In this scission the split occurs between the alkenyl group (which contains a ß-hydrogen atom) and the ether oxygen of the ester group; the ß-hydrogen atom migrates to the carboxyl group to form an acid and an alkyne:-

$$R.CO_2 \colon C=CH- \longrightarrow R.CO_2H + -C\equiv C- \quad ----- A^2$$
$$\qquad\qquad\qquad\qquad \text{(acid)} \quad \text{(alkyne)}$$

e.g. $CH_3.CO_2.CH=CH_2 \longrightarrow CH_3.CO_2H + CH\equiv CH \quad ----- A^2$
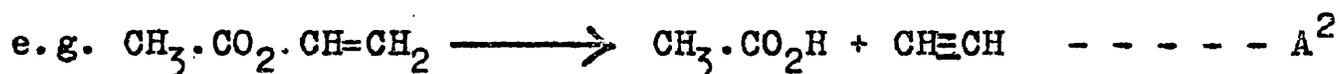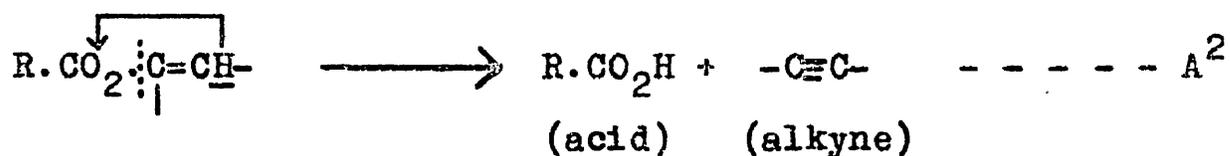
A^2 scission requires high temperatures (ca.500°), and it is usually a minor reaction in a complex competitive breakdown, as was found by Allan, Forman, and Ritchie[2] in the pyrolysis of vinyl esters. Examples of type A^2 scission are far fewer than type A^1.

1.1.4: Acyl-oxygen scission (acyl⟶ alkoxyl type), type B^1.

In this scission the split occurs between the carbonyl group and the ether oxygen of the ester group, with the migration of a hydrogen atom from the acyl to the alkoxyl group:-

$$>CH.CO.CH< \longrightarrow >C=CO + HO.CH< \quad ------- B^1$$
$$\qquad\qquad\qquad \text{(keten)} \quad \text{(hydroxy compound)}$$
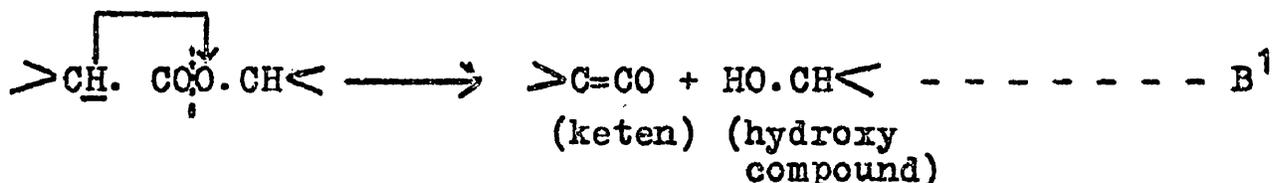
A good example of this scission was shown by Hurd and Blunck[18] in the pyrolysis of phenyl acetate:-

$$CH_3.COO.Ph \longrightarrow CH_2=CO + PhOH \quad ------- B^1$$
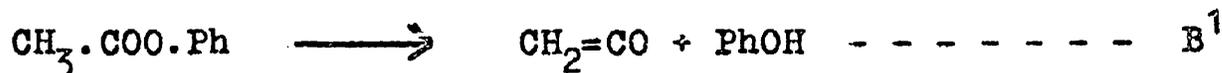
The hydroxy compound may be stable (as shown above, when phenol is formed), or a labile enol which will rearrange to an aldehyde, as was found in the pyrolysis of vinyl acetate[2]:-

$$CH_3.COO.CH=CH_2 \longrightarrow CH_2=CO + (HO.CH=CH_2 \longrightarrow CH_3.CHO) -B^1$$
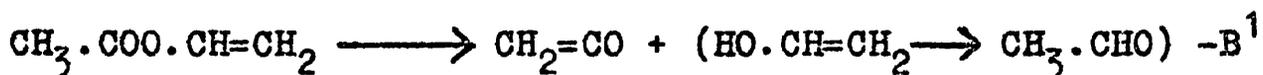
This type of scission requires high temperatures of the order of 500°.

1.1.5: Acyl-oxygen scission (acyl $\longleftarrow$ alkoxyl type), type B^2.

In this scission the split occurs between the carbonyl group and the ether oxygen of the ester group, with the migration of a hydrogen atom from the alkoxyl to the acyl group:-

$$>CH.COO.CH< \longrightarrow >CH.CHO + O=C< \quad -------- B^2$$
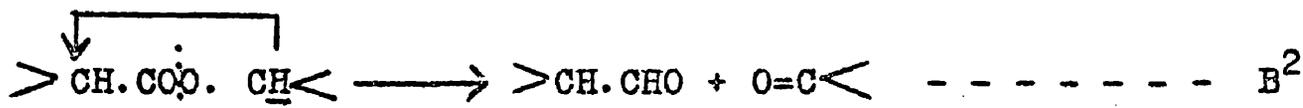
The formation of two carbonyl molecules from an ester constitutes a formal reversal of the Tischenko reaction[20]. B^2 scission is often observed with esters lacking a ß-hydrogen atom, as shown by Peytral[21] in the pyrolysis of methyl formate:-

$$H.COOCH_3 \xrightarrow{\quad 1150^\circ \quad} 2 H.CHO \quad ------------- B^2$$

Small amounts of methanol were recorded but no pyrolytic route was assigned. Re-investigation of this work[11] confirmed that at 500°, B^2 scission was a minor route and that the methanol was formed by a major route involving decarbonylation (see C^1 below):-

$$H.COO.CH_3 \longrightarrow CO + CH_3OH \quad ------------- C^1$$
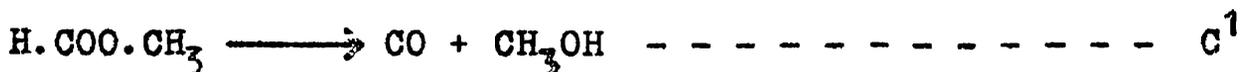
In addition minor decarboxylation was observed (see C^2 below):-

$$H.COO.CH_3 \longrightarrow CO_2 + CH_4 \quad\text{-- -- -- -- -- -- -- -- -- --}\quad C^2$$
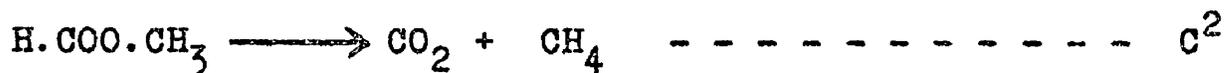
The C^1 decomposition route of methyl formate, given above, is further justified by the pyrolysis of phenyl formate[9], which gives phenol and carbon monoxide almost quantitatively:-

$$H.COO.Ph \longrightarrow CO + PhOH \quad\text{-- -- -- -- -- -- -- --}\quad C^1$$

When a ß-hydrogen atom is present, B^2 scission rarely predominates and only traces of it are observed as in the pyrolysis of ethyl maleate[11]. This type of scission requires temperatures of at least 500°.

1.1.6: Decarbonylation, type C^1.

This type of scission consists in the elimination of carbon monoxide from the ester, as found in a re-investigation[11] of Peytral's work[21]:-

$$H.COO.CH_3 \longrightarrow CO + CH_3OH$$
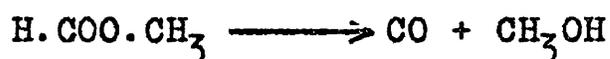
The decarbonylation of unsaturated acids has also been reported in addition to the general decarboxylation[1], as was found in the pyrolysis of methacrylic acid[11]:-

$$CH_2{=}\underset{\underset{CH_3}{|}}{C}.COOH \xrightarrow{\ C^1\ } CO + (CH_2{=}\underset{\underset{CH_3}{|}}{C}.OH \longrightarrow CH_3.CO.CH_3)$$
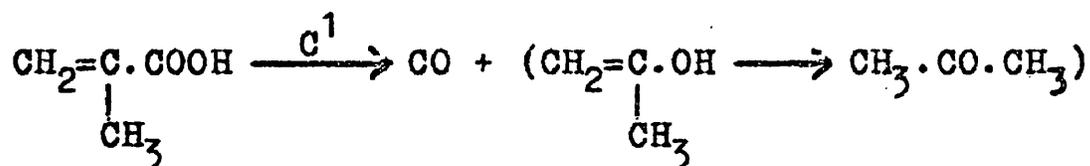
C^1 scission is commonly found in aldehydes or compounds containing an aldehydic group. Thus, Nef[23] has found that acetaldehyde and propionaldehyde suffer primary decomposition to carbon monoxide and the appropriate hydrocarbon.

Decarbonylation of esters takes place at temperatures of ca.500°. This scission may occur as the secondary stage of

a rearrangement process (see R below) where an aldehydic compound is formed[2]:-

$$Ph.COO.CH=CH_2 \xrightarrow{R} \left[Ph.CO.CH_2.CHO \right] \xrightarrow{C^1} Ph.CO.CH_3 + CO$$
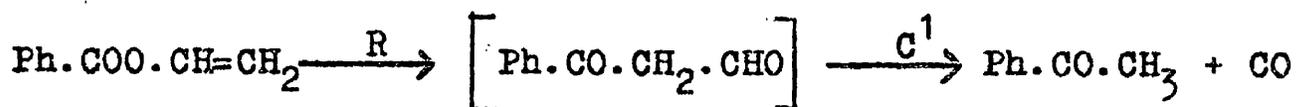
1.1.7: Decarboxylation, type C^2.

This type of scission consists in the elimination of carbon dioxide from the ester:-

$$R.CO_2.R' \longrightarrow CO_2 + RR' \; - \; - \; - \; - \; - \; - \; - \; - \; C^2$$
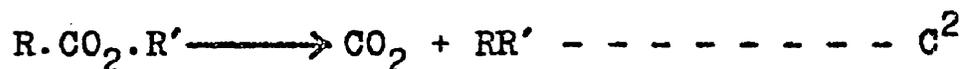
The thermal decarboxylation of carboxylic esters is a reaction which up till now has been reported only very rarely, although the decarboxylation of carboxylic acids[1] is a very general reaction. Several new examples of ester decarboxylation have been found in the present work and these are of considerable interest. The pyrolysis of vinyl acetate and vinyl benzoate[2], in addition to other pyrolytic routes, yielded C^2 scission to give propylene and styrene respectively:-

$$CH_3.CO_2.CH=CH_2 \longrightarrow CO_2 + CH_3.CH=CH_2 \; - \; - \; - \; - \; - \; - \; C^2$$

$$Ph.CO_2.CH=CH_2 \longrightarrow CO_2 + Ph.CH=CH_2 \; - \; - \; - \; - \; - \; - \; C^2$$
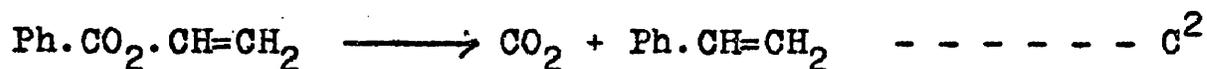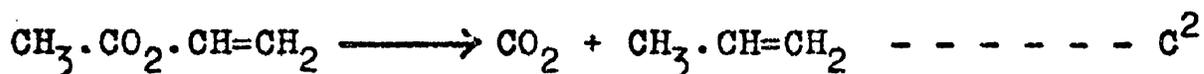
It is worth noting that the proximity of a double bond to the ester grouping greatly facilitates decarboxylation. For example, Hurd and Blunck[18] do not record decarboxylation in the pyrolysis of such saturated esters as phenyl acetate and ethyl acetate.

The pyrolysis of ethyl maleate[11] yielded, amongst other products, a most interesting example of double decarboxylation

to hex-3-ene:-

$$\underset{\substack{\text{CH.CO}_2.\text{Et} \\ \| \\ \text{CH.CO}_2.\text{Et}}}{} \quad \xrightarrow{2c^2} \quad 2CO_2 + Et.CH=CH.Et$$
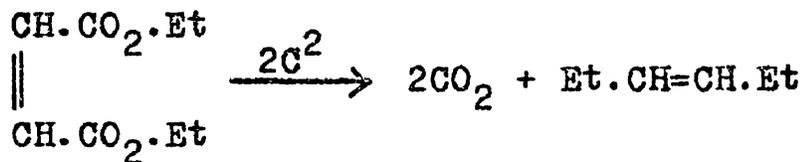
Brown and Ritchie[19] pyrolysed the analogous saturated ester, ethyl succinnate, and found no evidence for the occurrence of either primary or secondary decarboxylation of the ester, further verifying that c^2 scission is linked to the presence of an unsaturated grouping in the ester.

Formally, the c^2 reaction requires scission of the ester molecule at two points, with combination of the two terminal fragments; and it is difficult to visualise this as occurring except _via_ a free-radical mechanism. Mackinnon and Ritchie unsuccessfully attempted to inhibit the decarboxylation of phenyl acrylate[9], by the use of soluble inhibitors, although they successfully inhibited another free-radical intra-acyl scission (see IA below). For the present it is preferred not to suggest any detailed mechanism for decarboxylation.

Decarboxylation of esters requires a high temperature of _ca_.500°.

1.1.8: Disproportionation, type D.

Disproportionation is generally found in the breakdown of unsymmetrical esters to compounds of greater symmetry. Only a moderate temperature (_ca_.300°) is required. Thus, Cretcher and Pittenger[24] found that the monoaroyl esters of ethylene

glycol decompose into the diester and ethylene glycol:-

$$2Ph.CO_2.CH_2.CH_2OH \xrightarrow{300°} Ph.CO_2.CH_2.CH_2.O_2C.Ph + HOCH_2.CH_2OH \text{ --D}$$

The formation of acetaldehyde and benzoic anhydride in small quantities during the pyrolysis of ethylene dibenzoate is another case of disproportionation. It has been shown[6] to involve the intermediate formation of ethylidene dibenzoate:-

$$Ph.CO_2.CH_2.CH_2.O_2C.Ph \xrightarrow{A^1} Ph.CO_2H + CH_2=CH.O_2C.Ph$$

$$CH_3.CH(O_2C.Ph)_2$$

$$\downarrow D$$

$$CH_3CHO + (Ph.CO)_2O$$

1.1.9: Intra-acyl scission, type IA.

This type of scission is apparently very uncommon in ester pyrolysis and has not been hitherto recorded in the literature. Mackinnon and Ritchie[9] found that in the pyrolysis of an aromatic acrylate or substituted acrylate, migration of a hydrogen atom takes place within the acyl grouping to yield a formate and an alkyne:-

$$CH_2=CR{:}CO_2Ph \longrightarrow H.CO_2.Ph + CH{\equiv}CR \quad \text{------- -IA}$$
$$\text{(formate)} \quad \text{(alkyne)}$$

The formate undergoes further decarbonylation (C^1) to yield a phenol and carbon monoxide:-

$$H.CO_2.Ph \longrightarrow CO + PhOH \text{ ------------- } C^1$$

Examples of IA scission recorded by Mackinnon and Ritchie[9] are the pyrolyses of phenyl acrylate and phenyl methacrylate to yield carbon monoxide and phenol (via phenyl formate) and the corresponding acetylene and methyl acetylene:-

$$CH_2=CH.CO_2.Ph \longrightarrow H.CO_2.Ph + CH\equiv CH \quad \text{- - - - - - -} \quad IA$$

$$\downarrow$$

$$CO + PhOH \quad \text{- - - - - - - - - - - -} \quad C^1$$

$$CH_2=\underset{\underset{CH_3}{|}}{C}.CO_2.Ph \longrightarrow H.CO_2.Ph + CH\equiv C.CH_3 \quad \text{- - - - -} \quad IA$$

$$\downarrow$$

$$CO + PhOH \quad \text{- - - - - - - - - - - -} \quad C^1$$

IA scission is the major decomposition route of aromatic acrylates and takes place at high temperature (ca.550°). The reaction mechanism is thought to be free-radical in character and the IA scission has been entirely suppressed by adding 1% of quinol to the pyrolysand[9]. IA scission is peculiar only to aromatic acrylates or substituted acrylates as the pyrolysis of methyl acrylate and methyl methacrylate[11] in this work yielded no trace of a formate or its decomposition products.

1.1.10: Rearrangement, type R.

This category (R) includes the many known types of thermal isomerisation. These are often well known like the cis to trans rearrangements. One such rearrangement was found in the pyrolysis of ethyl maleate[11] where, amongst other products, ethyl fumarate was found:-

$$\begin{array}{c} \text{CH.CO}_2.\text{Et} \\ \| \\ \text{CH.CO}_2.\text{Et} \end{array} \longrightarrow \begin{array}{c} \text{Et.O}_2\text{C.C.H} \\ \| \\ \text{H.C.CO}_2.\text{Et} \end{array} \quad \text{- - - - -} \quad R$$

Of the more complex rearrangements in organic chemistry there are the well known examples of the classical Beckmann and Fries rearrangements. These, however, occur with the aid of a catalyst.

Of the purely thermal type of rearrangement it has been found by Boese and Young[25] that the esters of the enolic form of ketones rearrange to yield ß-diketones at temperatures of *ca*.500°. It is claimed by these authors that this rearrangement is undergone by enol esters of the form, $R.CO_2.CR' = C\big\langle$, where R and R' may be aliphatic or aromatic, or where R' together with the ethylenic carbon atoms may be part of an alicyclic ring. An example of this reaction is the rearrangement of *iso*propenyl acetate to acetylacetone:-

$$\begin{array}{c} \text{CH}_2= \underset{\underset{\text{CH}_3}{|}}{\text{C}}.\text{O}_2\text{C}.\text{CH}_3 \xrightarrow{\quad 500^{\circ} \quad} \text{CH}_3.\text{CO}.\text{CH}_2.\text{CO}.\text{CH}_3 \quad \text{- - - - -} \quad R \end{array}$$
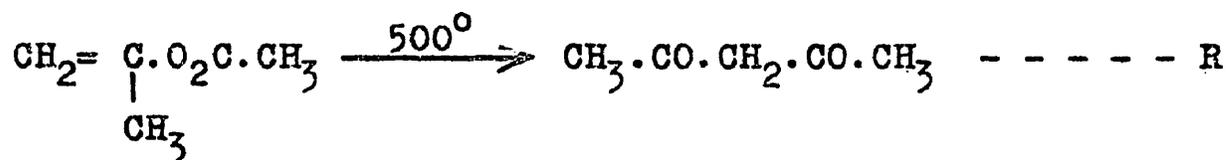
This series of rearrangements has been the subject of study by Young *et al.*[26], who have suggested that the reaction proceeds thermally by an intramolecular mechanism, involving a four-membered cyclic transition stage. Thus, for example, the pyrolysis of *iso*propenyl acetate would be predicted to proceed in the following manner:-

$$CH_3-C\overset{\overset{\displaystyle CH_3}{|}}{O}-C=O \quad \xrightarrow{500^o} \quad \left[CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_2}{||}}{C}}-\overset{+}{O}-\overset{|}{C}-O^- \right] \quad \longrightarrow \quad CH_3-\overset{O}{\underset{||}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_2}{|}}{C}}=O$$
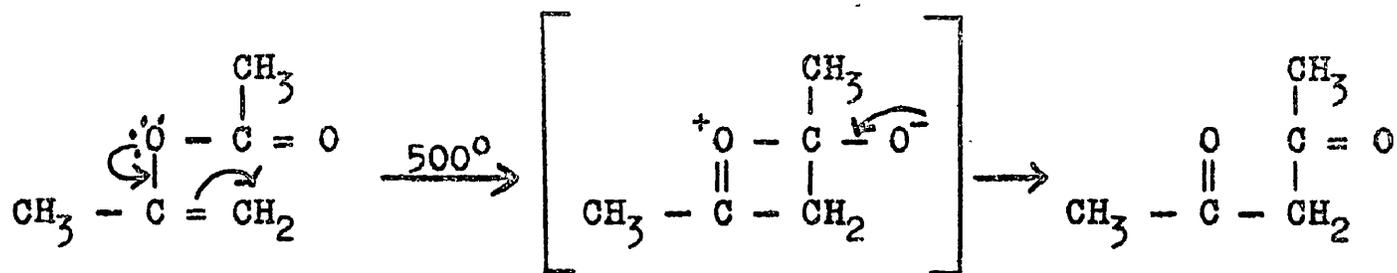
Young et al.[26] have also shown that the same rearrangement may
be effected at low temperature, using boron trifluoride as a
catalyst, and for this reaction they have postulated an inter-
molecular mechanism involving a complex addition compound as
the intermediate.

Another example of rearrangement occurs when the allyl
ether of a phenol or an enol is heated to about 200°. Hurd
and Pollack[27] have illustrated this reaction by the rearrange-
ment of allyl vinyl ether into allylacetaldehyde:-

$$CH_2=CH.CH_2.O.CH=CH_2 \quad \longrightarrow \quad CH_2=CH.CH_2.CH_2.CHO \ - \ - \ - \ R$$

1.2 The Pyrolysis of Polymers and Polyesters

1.2.1: General

The pyrolysis of pure polymers generally occurs at, and above, 300°, since at this temperature the thermal energy is sufficient to break the primary valence bonds between the carbon atoms. However, where traces of original catalyst or monomer are present, breakdown may take place at a lower temperature by other means, for example by chain transfer. Thus, in polyethylene the initial break occurs at the branches[29], and Grassie and Melville[30] have shown that the weak link in poly(methyl methacrylate) is actually at the chain end, and that consequently its susceptibility to rupture varies with the type of radical that initiated the chain, or the way in which it was terminated.

After initial scission at the weakest link, depolymerisation may then follow one of three courses of degradation, and these have been represented by Melville[31] in the diagram below:-

Molecular weight of remaining polymer

Type I

Type III

Type II

0   Conversion to monomer   100%
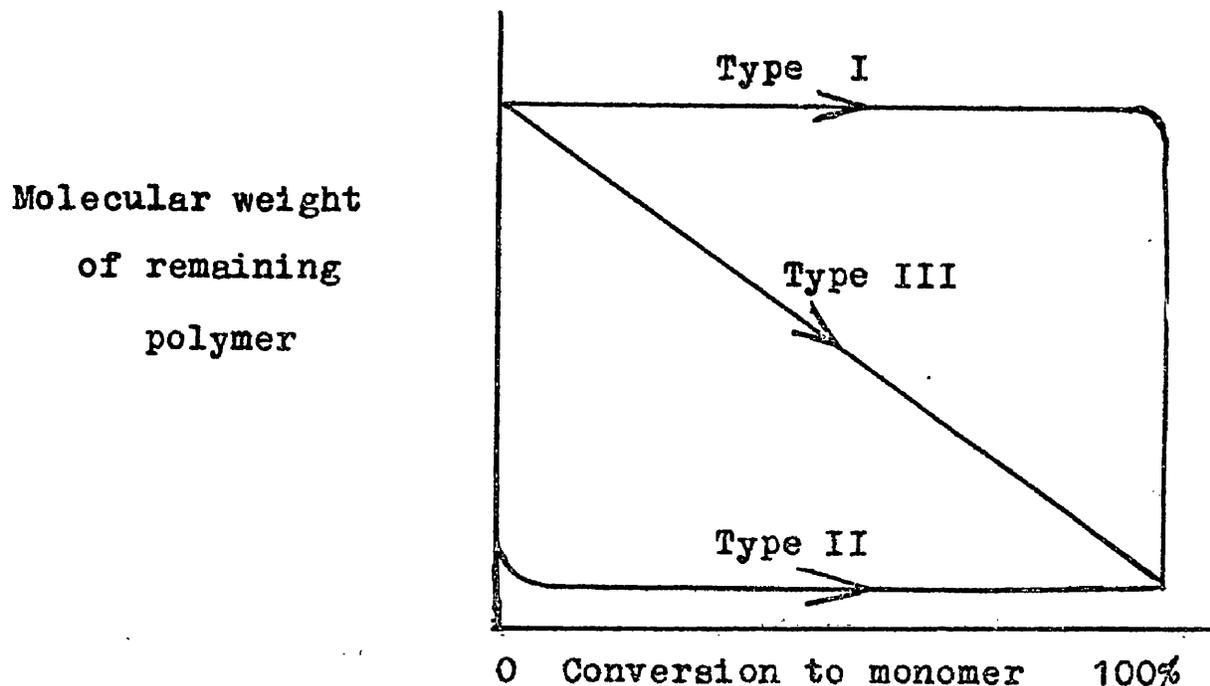
As an example of type I, Grassie and Melville[30] have shown that in poly(methyl methacrylate), molecular weight ca.50,000, the initial rupture is followed by complete depolymerisation of the polymer molecule. This is fairly typical of polymethacrylates generally except tertiary esters, such as poly(tert.-butyl methacrylate), which splits off iso-butene as a volatile fragment leaving behind isolated units of methacrylic acid in the chain[32]. Type II is a complete contrast, each chain scission occurring in a completely random manner, which results in a large drop in molecular weight. This is believed to be the manner in which condensation poly-esters degrade[33,34] and also polyethylene[35]. The third course is essentially a combination of I and II, and it is assumed that after initial random scission, depolymerisation proceeds rapidly, but in one direction only. This last course is characteristic of certain vinyl polymers[36,37,38], and also those polyesters and polyanhydrides which produce cyclic monomer at relatively low temperatures[39,40]. Generally speaking, polyesters which do not form cyclic monomers do not readily depolymerise to monomeric units, although poly(ethylene terephthalate), which can give a very small amount of cyclic trimer[41], has been induced to degrade thus by the addition of glycol[42].

It is of interest to note that poly(ethylene fumarate) has been estimated[43] to contain up to 8% of cyclic monomer, ethylene maleate, though this has not yet been isolated from

either the pure polyester or from its pyrolysis products.

1.2.2: Radical chain reactions in polymer pyrolysis.

For the thermal degradation of such polymers as poly(methyl methacrylate), polystyrene, and polyethylene it is possible to postulate a chain-reaction mechanism, which is essentially free radical polymerisation in reverse. This has been studied by Simha et al.[44,45], who have represented depolymerisation processes generally by the following reaction scheme. The initiation step is represented as scission of the main chain carbon-carbon bonds:-

Random initiation $\qquad M_n \longrightarrow P_j^{\cdot} + P_{n-j}^{\cdot}$

Terminal initiation $\qquad M_n \longrightarrow P_{n-1}^{\cdot} + P_1^{\cdot}$

Depropagation $\qquad P_i^{\cdot} \longrightarrow P_{i-1}^{\cdot} + M_1$

Transfer $\qquad P_i^{\cdot} + M_n \longrightarrow M_i + P_j^{\cdot} + M_{n-j}$

Termination $\qquad P_i^{\cdot} + P_j^{\cdot} \longrightarrow M_i + M_j$
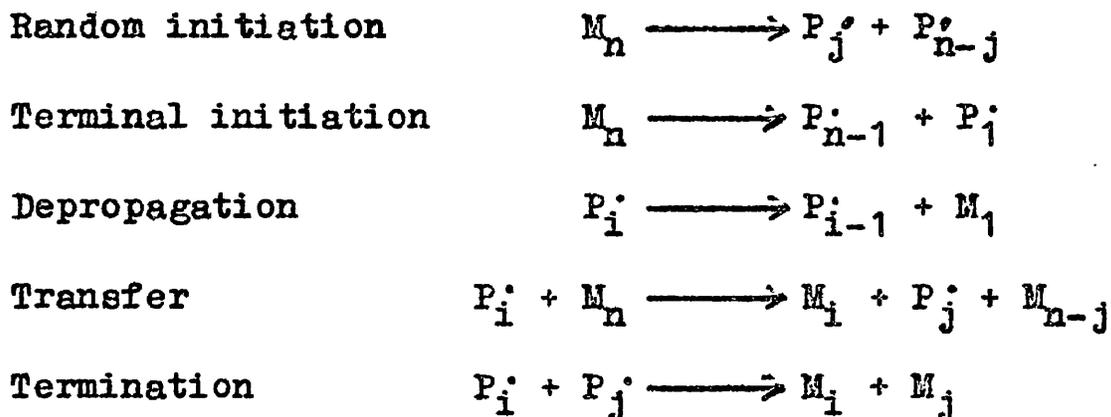
n is the chain length of the starting material and M_i, M_j, etc., represent dead polymer molecules, $P_i^{\cdot}$, $P_j^{\cdot}$, etc. represent long chain radicals. i, j, etc. represent the length of the units.

1.2.3: Radical reactions in polyester pyrolysis.

Condensation polyesters, unlike the addition polymers cannot possibly be reconverted into the original monomeric

material by physical agencies alone, since in their production
a molecule of water is lost at the formation of each ester
linkage.

Very little investigation into the pyrolysis of polyesters
has been reported with the exception of poly(ethylene-tere-
phthalate) or "Terylene". Pohl[46], one of the earlier investi-
gators, followed the degradation of the latter polyester by
measuring the rate of gas-evolution, and showed that at ca.300°
in the absence of oxygen the polyester undergoes random main-
chain scission, with progressive reduction in molecular weight.
Marshall and Todd[47] studied the kinetics of the degradation
(ca.$280-320^o$) by following changes in the viscosity of the
molten material. Like Pohl, they deduced random chain
scission, probably at the ester linkages, giving rise to one
carboxyl and one vinyl group per scission:-

$$\sim\hspace{-2pt}\bigcirc\hspace{-2pt}COO.CH_2.CH_2.OOC\hspace{-2pt}\bigcirc\hspace{-2pt}\sim$$
$$\downarrow$$
$$\sim\hspace{-2pt}\bigcirc\hspace{-2pt}COOH + CH_2=CH.OOC\hspace{-2pt}\bigcirc\hspace{-2pt}\sim$$
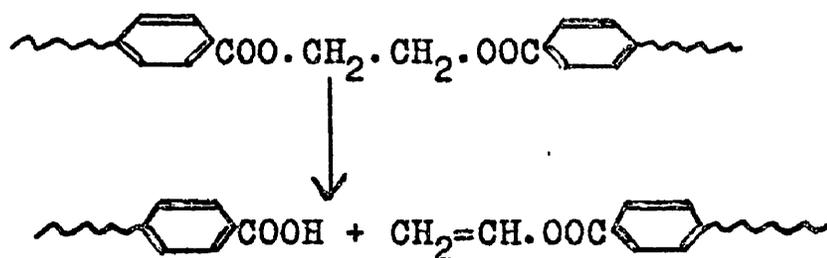
They concluded that degradation is essentially free-radical in
character, and outlined a tentative sequence of propagation
reactions.

Quantitative studies cannot, however, be fully interpreted
in the absence of a full qualitative identification of the
degradation products. Ritchie et al.[2,5,6,7,8], by studying

the pyrolysis of poly(ethylene terephthalate) and related
model esters, have produced a substantially qualitative
picture of the breakdown for this polyester.

1.3: Basic Plan of this Work (including some preliminary observations).

To elucidate the thermal breakdown of the resin obtained from the condensation of maleic anhydride and ethylene glycol, a sample of pure molten polyester (D.P.$_n$ ca. 2-9) was pyrolysed at 500° in a packed flow reactor. Two surprising results were obtained. Firstly the gaseous pyrolysate contained 65-70% of carbon dioxide and little carbon monoxide, which is quite the reverse of results[7] obtained from the pyrolysis of poly(ethylene terephthalate); secondly there were no signs of maleic acid or maleic anhydride in the pyrolysate, although they were expected to occur by A^1 and D scissions. The first result indicated that the ester had undergone extensive decarboxylation, and is discussed later. The explanation for the second result is now clear, though it was not known at the time this work was initiated – namely, that although unsaturated polyesters of this type are in practice normally made by poly- condensation of maleic anhydride (not fumaric acid) and ethyl- ene glycol, the resulting product is substantially poly(ethyl- ene fumarate). Several workers have shown[43,48,49] that there is a virtually complete cis $\longrightarrow$ trans inversion during the polycondensation, even in the absence of catalysts; and although there may be some residual cis units in the poly- ester[50], the final system is essentially trans in configuration. Another surprising feature was that no vinyl groups were detected in the pyrolysate, though, on the basis of previous

work[47], they would be expected to form by random A^1 scission at a ß-carbon atom:-

$$\sim\!\!\sim\!\!\sim CH_2.CH_2.OOC.CH=CH.COO.CH_2.CH_2.OOC.CH=CH \sim\!\!\sim\!\!\sim$$

Poly(ethylene fumarate)

$$\downarrow A^1$$

$$\sim\!\!\sim\!\!\sim CH_2.CH_2.OOC.CH=CH.COOH + CH_2=CH.OOC.CH=CH \sim\!\!\sim\!\!\sim$$

| Carboxylic end | Vinyl carboxylate |
| group | end group |

The complexity of the pyrolysis products indicated that model compounds should first be investigated. These models were selected to represent (a) specific segments from within the intact polyester chain, (b) terminal segments from the intact chain, and (c) terminal segments of the pyrolysed chain bearing new end groups which might be predicted a priori. The following models were selected:-

I $\quad CH_3.COO.CH=CH_2 \quad$ Vinyl acetate.

II $\quad \begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!>\!\!CH.COO.CH=CH_2 \quad$ Vinyl isobutyrate.

III $\quad \begin{array}{c} CH.COO.CH_2.CH_3 \\ \| \\ CH.COO.CH_2.CH_3 \end{array} \quad$ Ethyl Maleate

IV $\quad CH_2=\underset{\underset{CH_3}{|}}{C}.COO.CH_2.CH_2.OOC.\underset{\underset{CH_3}{|}}{C}=CH_2 \quad$ Ethylene dimethacrylate.
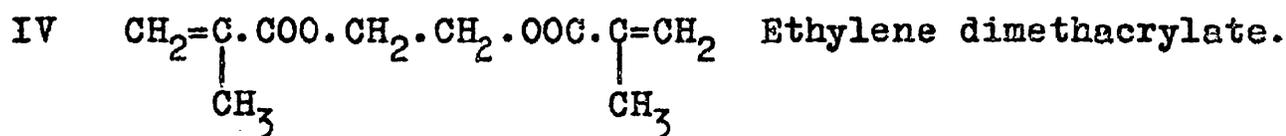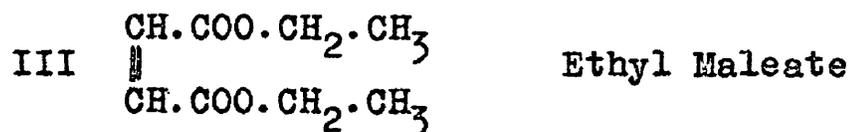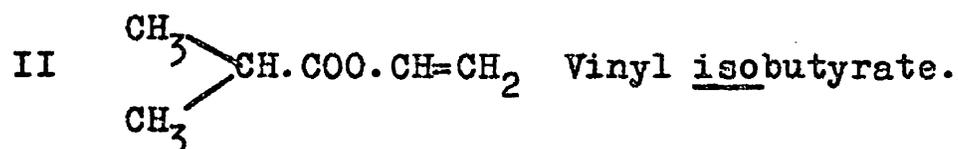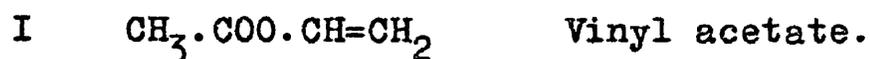
Vinyl acetate and vinyl isobutyrate, models I and II, were selected to investigate the thermal stability and breakdown of

vinyl carboxylates; and it was found that the results explained the absence of vinyl carboxylates from the pyrolysate of poly(ethylene fumarate). This work is later discussed in Chapter VI. The work on the above vinyl esters is discussed in Chapter II.

Ethyl maleate, model III, was an unfortunate original choice of model compound, as it was later found on discussion with co-workers[43] that the so-called "poly(ethylene maleate)" was actually poly(ethylene fumarate). This model was chosen to help investigate the absence of maleic anhydride and maleic acid in the pyrolysate of the polyester (discussed in Chapter VI). The model does, however, give a clear idea of the thermal stability and mode of breakdown of an unsaturated carboxylic residue with adjacent β-carbon atoms. This model is a fair representation of the following segment of the polyester chain:-

$$\sim\sim\sim CH_2 \cdot CH_2 \cdot OOC \cdot CH{=}CH \cdot COO \cdot CH_2 \cdot CH_2 \sim\sim\sim$$
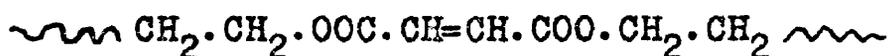
This work is discussed in Chapter III.

In the light of the present knowledge, it would have been more logical to study the pyrolysis of ethyl fumarate. One pyrolysis of ethyl fumarate was, in fact, carried out, but owing to the extreme dermatitic nature of maleates and fumarates and/or their breakdown products, the author was forced to abandon this section (see Appendix).

Ethylene dimethacrylate, model IV, was chosen as a complement to ethyl maleate, as the ethylene dimethacrylate

has an ethylene residue with adjacent unsaturated carboxylic groupings.   The ethylene dimethacrylate was also chosen for comparative work[28] with ethylene diacrylate, which is a fair model representation of the following segment of the polyester chain:-

$$\sim\!\sim\!\sim CH{=}CH.COO.CH_2.CH_2.OOC.CH{=}CH \sim\!\sim\!\sim$$
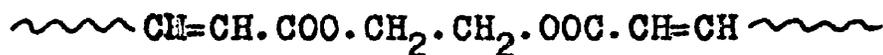
To assist in interpreting the pyrolytic breakdown of ethylene dimethacrylate, the following compounds were pyrolysed:-

$CH_2{=}C.COO.CH_3$
   $|$
   CH_3 Methyl methacrylate.

$CH_2{=}C.COO.CH_2.CH_3$
   $|$
   CH_3 Ethyl methacrylate.

$H.COO.CH_3$ Methyl formate.

$H.COO.CH_2.CH_3$ Ethyl formate.
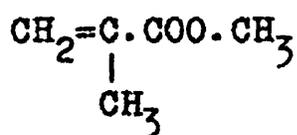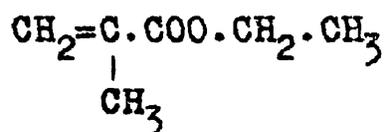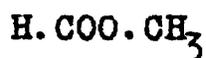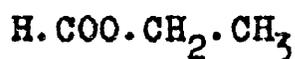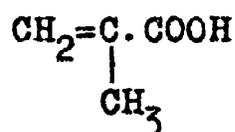
$CH_2{=}C.COOH$
      $|$
      CH_3 α-Methylacrylic acid.[x]
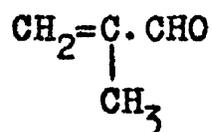
$CH_2{=}C.CHO$
      $|$
      CH_3 α-Methylacraldehyde.[x]

[x]   Later in the text the above compounds are referred

        to by their commoner names, i.e. Methacrylic acid

        and Methacrolein.

C H A P T E R   II

The Pyrolysis of Vinyl Acetate and Vinyl isoButyrate.

CHAPTER II

2.1: The Pyrolysis of Vinyl Acetate and Vinyl isoButyrate.

Vinyl acetate is stable up to $\underline{ca}.420^\circ$, while at 550° in a glass reactor $\underline{ca}.78\%$ of the ester is pyrolysed. A detailed pyrolysis, based on the ester broken down, is as follows:-

$$CH_3.CO_2.CH=CH_2 \xrightarrow{550^\circ}$$

$$\xrightarrow{3\%} CH_3.CO_2H + CH{\equiv}CH \quad -------- A^2$$

$$\xrightarrow{47\%} CH_2{=}CO + (HO.CH{=}CH_2 \rightleftharpoons CH_3.CHO) -- B^1$$

$$\xrightarrow{3\%} CH_3.CH{=}CH_2 + CO_2 \quad -------- C^2$$

$$\xrightarrow{47\%} \left[CH_3.CO.CH_2.CHO \right] \quad ------- R$$

$$\downarrow$$

$$CH_3.CO.CH_3 + CO \quad -------- C^1$$
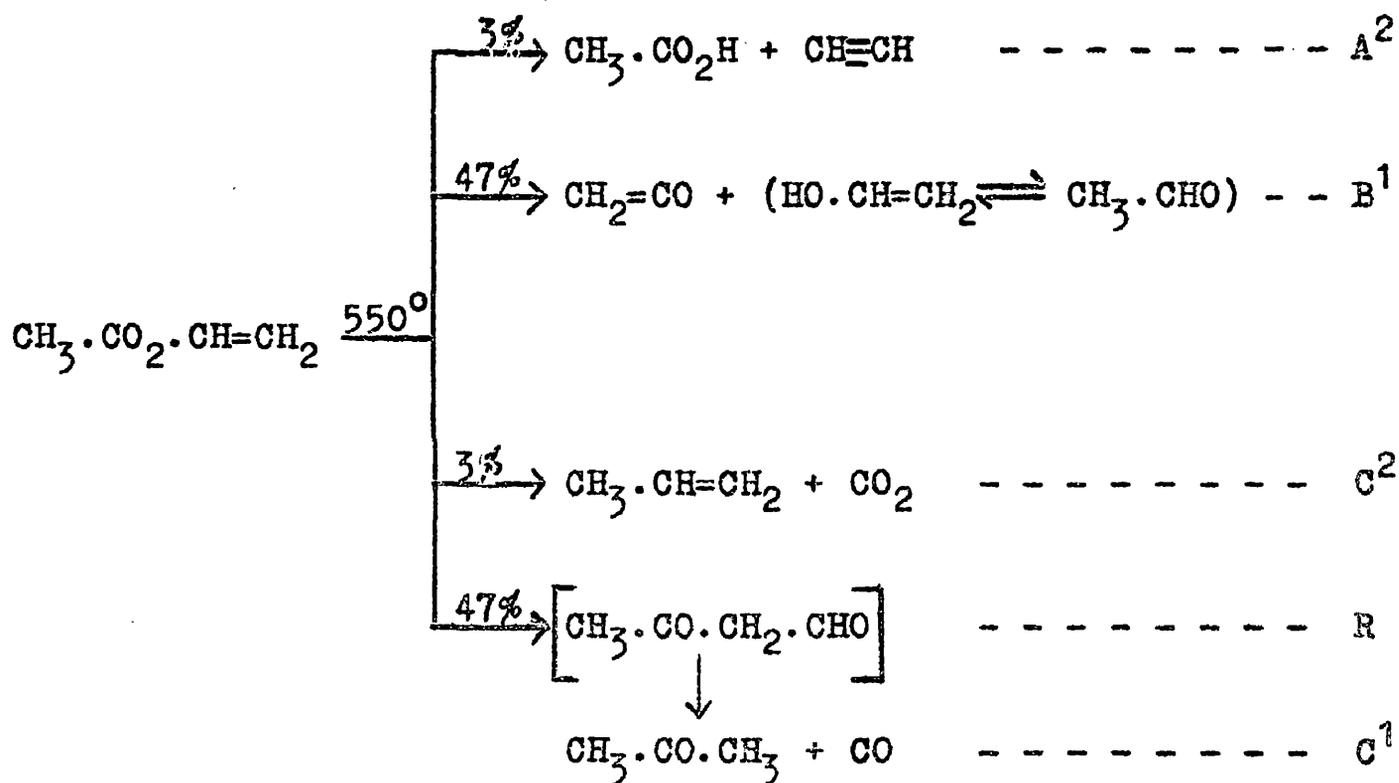
The quantitative estimation of the above pyrolysis and others given in this work were carried out by fractional distillation of the pyrolysate and cross-checking with the gas analyses. Although good agreement was obtained the figures should only be taken as approximate.

2.2: Discussion of Decomposition Routes.

Route A^2.   Alkenyl-oxygen scission of alkenyl carboxylates to an acetylene and a carboxylic acid does not seem to have been observed previous to this work[2], although alkyl-oxygen scission (A^1) is a well established major route (though not the only one) in the pyrolysis of alkyl carboxylates.   It is of interest that although monomeric vinyl acetate breaks down thermally by four competitive routes (A^2, B^1, $C\,^2_?$ and R/C^1), yet its polymer has been shown by Grassie[51] to break down <u>in vacuo</u> at <u>ca.</u>215-235° almost wholly by evolution of acetic acid, <u>via</u> a non-radical chain reaction.   Each successive step is the normal A^1 scission of an alkyl carboxylate, the olefinic product here being a polyacetylene, thus:-

$$\sim\!\!\sim CH_2.CH(OAc).CH_2.CH(OAc)\sim\!\!\sim \xrightarrow{-AcOH} \sim\!\!\sim CH=CH.CH=CH\sim\!\!\sim$$
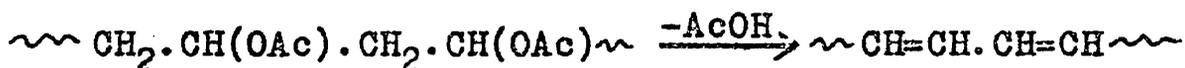
Route B^1.   There are two formally possible modes of acyl-oxygen scission for vinyl acetate, each yielding keten and acetaldehyde, thus:-

$$CH_3.CO\!:\!O.CH=CH_2 \longrightarrow CH_2=CO + (HO.CH=CH_2 \rightleftharpoons CH_3.CHO)\; -\;-\;B^1$$

$$CH_3.CO\!:\!O.CH=CH_2 \longrightarrow CH_3.CHO + CH_2=CO\; -\;-\;-\;-\;-\;-\;-\;-\;-\;B^2$$
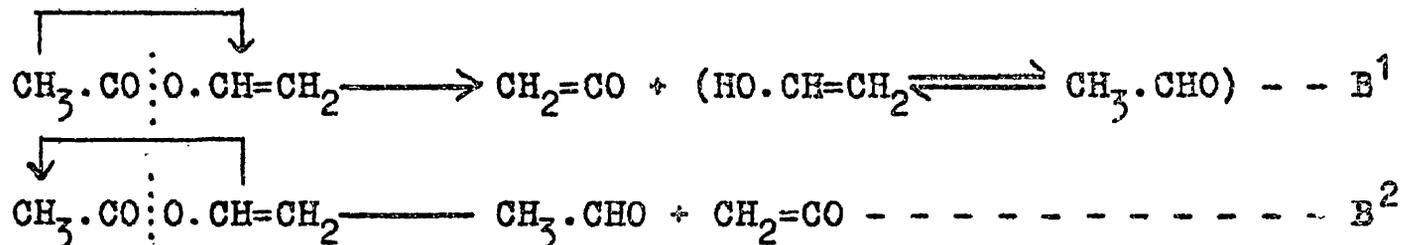
Since routes B^1 and B^2 both give keten and acetaldehyde (both found in the pyrolysate), it is not possible to say which route is followed from a study of vinyl acetate alone.   For aliphatic esters higher than the acetate, routes B^1 and B^2 are

no longer equivalent:-

$$(CH_3)_2.CH. CO.O.CH=CH_2 \longrightarrow (CH_3)_2C=CO + (HO.CH=CH_2 \rightleftharpoons CH_3.CHO) - B^1$$

Vinyl isobutyrate   Dimethyl-   Vinyl alcohol   acetalde-
                        keten   hyde

$$(CH_3)_2.CH.CO.O.CH=CH_2 \longrightarrow (CH_3)_2CH.CHO + CH_2=CO \quad ----- B^2$$

Vinyl isobutyrate   isoButyral-   Keten
                             dehyde

It was found that vinyl isobutyrate, when pyrolysed at 550° under similar conditions to vinyl acetate, yielded acetaldehyde and secondary products attributable to dimethylketen (Route B[1]), with no detectable quantity of isobutyraldehyde and keten (Route B[2]). The pyrolysis of vinyl isobutyrate was found to be analogous to the pyrolysis of vinyl acetate with ca.92% of the ester being pyrolysed. A detailed pyrolysis, based on the ester broken down, is as follows:-

$$(CH_3)_2.CH.CO_2.CH=CH_2 \xrightarrow{550^\circ}$$

Vinyl isoButyrate

x Unstable
    at
   550°

$\xrightarrow{6\%} (CH_3)_2.CH.CO_2H + CH\equiv CH \quad ------ A^2$
          isoButyric Acid   Acetylene

$\xrightarrow{30\%} (CH_3)_2.C=CO^x + (HO.CH=CH_2 \rightleftharpoons CH_3CHO) \; B^1$
          Dimethylketen   Vinyl   Acetalde-
                           Alcohol   hyde

$\xrightarrow{1\%} (CH_3)_2.CH.CH=CH_2^x + CO_2 \quad ----- C^2$
          3-Methylbut-1-ene   Carbon Dioxide

$\xrightarrow{63\%} \left[(CH_3)_2.CH.CO.CH_2.CHO\right] \quad ----- R$
          isoButyryl Acetaldehyde

$$\downarrow$$

$$(CH_3)_2.CH.CO.CH_3 + CO \quad ----- C^1$$
Methyl isoPropyl   Carbon Monoxide
       Ketone

Only one of the B^1 products from vinyl isobutyrate was identified directly (acetaldehyde); there was no direct evidence for the dimethylketen which should have accompanied it.   Presumably the latter failed to survive passage through the reactor at 550°; its transient existence is postulated by the identification of its breakdown products (see p. 32) and its accompanying acetaldehyde.

Vinyl benzoate was found on pyrolysis to break down by the same routes as vinyl acetate except that no acyl-oxygen scission was detected[2].   Of the two possible routes of this type of scission (B^1 and B^2), only B^2 could be obtained in the case of vinyl benzoate, since there is no available α-hydrogen atom on the phenyl group (necessary for B^1 scission):

$$\text{Ph.CO:O. CH=CH}_2 \longrightarrow \text{PhCHO} + \text{CH}_2\text{=CO} \quad - - - - - - B^2$$
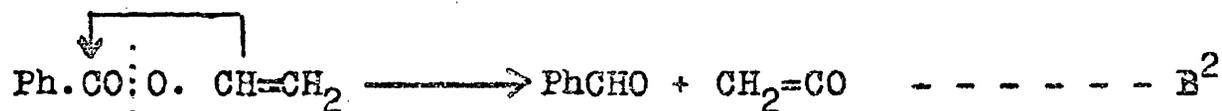
There was, however, no evidence of a B^2 scission taking place.

Further studies[2] have shown that vinyl esters which break down by acyl-oxygen scission do so by the B^1 route, and not by the B^2.

Route C^2[2].   In the pyrolysis of vinyl acetate, the route C^2 products (propylene and carbon dioxide) were readily identified.   However, vinyl isobutyrate by the C^2 route should have yielded 3-methylbut-1-ene and carbon dioxide.   Carbon dioxide, naturally, was readily identified, but 3-methylbut-1-ene was identified by its isomers.   This is further clarified in the section on side reactions (see page 32).

The direct decarboxylations of esters recorded in this work[2,11] are of considerable interest; for although thermal decarboxylation of acids is well established, only very few esters have been reported to show this behaviour[55].

Route R/C[1]. The mechanism of the unexpected conversion of vinyl carboxylates into carbon monoxide and a methyl ketone, which is the most important result emerging from the present work[2], is suggested by the fact that many enol carboxylates undergo intramolecular rearrangement at ca.500° to an isomeric ß-diketone[25,26], thus:

$$R.CO.O.C.CH_3=CHR' \longrightarrow CH_3.CO.CHR'.CO.R$$

(R is CH$_3$ or Ph, R'is H)
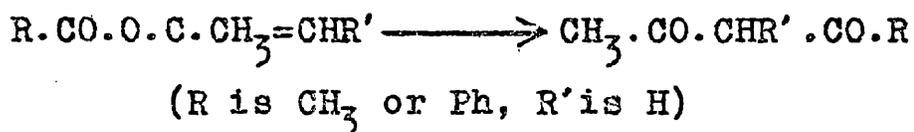
An analogous thermal rearrangement at 240° of the enol carboxylate, where R is CH$_3$ and R' is COO.C$_2$H$_5$, provides a further example in this category[56]. Allan and Ritchie[2] found that at ca.480° cyclohex-1-enyl benzoate rearranged similarly to 2-benzoylcyclohexanone, thus
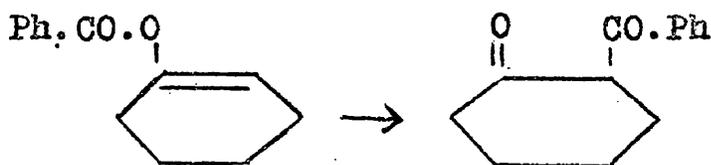
Young et al.[26] have suggested that the reaction proceeds thermally by intramolecular mechanism, involving a 4-membered cyclic transition stage. Thus the pyrolysis of vinyl acetate would be predicted to proceed in the following manner:-

.
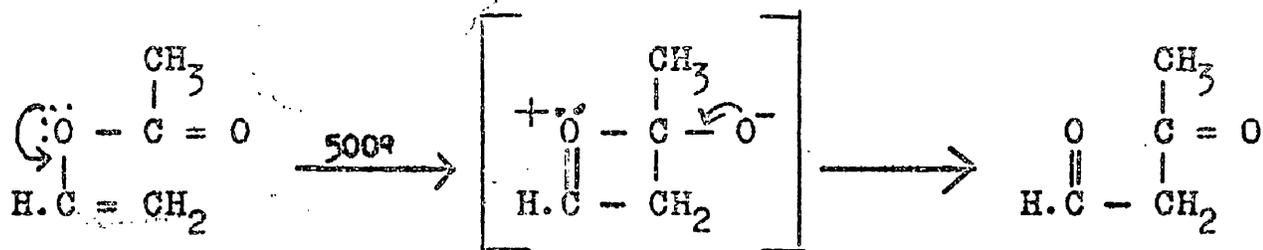
Vinyl Acetate   Acetoacetaldehyde

Young et al. have also shown that the same rearrangement may
be effected for enol carboxylates at low temperatures, using
boron trifluoride as a catalyst and for this they have postu-
lated an intermolecular mechanism involving a complex addition
compound as the intermediate.   As direct proof of the thermal
rearrangement of vinyl acetate to acetoacetaldehyde, an
attempt was made to rearrange vinyl esters using boron tri-
fluoride as a catalyst.   However, even at -40°, the boron
trifluoride acted as a polymerisation catalyst with explosive
violence.   Furthermore, the use of boron trifluoride etherate,
in an attempt to mitigate this effect, was equally unsuccess-
ful.   This property of boron trifluoride is, however, not
surprising in view of its known properties as a polymerisation
catalyst (e.g. for isobutene at -80°).

No direct evidence could be found for the R/C[1] route as
the intermediate ß-keto-aldehyde (acetoacetaldehyde) is
incapable of free existence, condensing spontaneously to
1:3:5-triacetylbenzene[57].   However, more direct evidence was
found by Allan and Ritchie[2] working on the pyrolysis of vinyl
benzoate.   They were able to synthesise the more stable
ß-keto-aldehyde (benzoylacetaldehyde) which underwent C[1]
pyrolysis to acetophenone and carbon monoxide:-

$$Ph.CO.CH_2.CHO \longrightarrow Ph.CO.CH_3 + CO \quad - - - - - - C^1$$
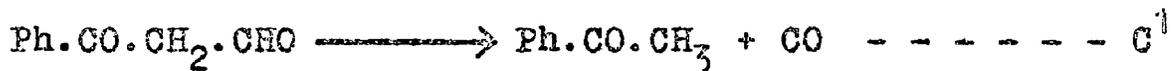
Nevertheless, the most convincing explanation of the observed acetone (from vinyl acetate) and methyl _iso_propyl ketone (from vinyl _iso_butyrate) is once again route R/C[1].

The previously unexplained by-products reported by Chitwood[58] in the pyrolysis of ethylene diacetate and di-propionate can now be readily accounted for on the basis of competing A[2], B[1], C[2], and R/C[1] scissions of vinyl carboxylates. For example, the formation of ethyl methyl ketone from ethyl-ene dipropionate can be attributed to secondary R/C[1] breakdown of vinyl propionate thus:-

$$C_2H_5.CO_2.CH=CH_2 \xrightarrow{R} C_2H_5.CO.CH_2.CHO \xrightarrow{C^1} C_2H_5.CO.CH_3 + CO$$
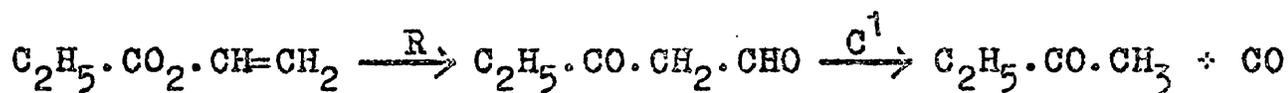
2.3. Secondary Pyrolytic Routes and Reactions in the

Pyrolysis of Vinyl Acetate and Vinyl isoButyrate.

Route A^2.   In addition to the various constituents detailed previously, the pyrolysate from vinyl acetate contained a small amount of acetic anhydride, whereas that from vinyl isobutyrate contained no acid anhydride.   The acetic anhydride may have arisen either by combination of acid (from A^2) with keten (from B^1), or by direct pyrolysis of the acid (cf.[54]).   The former explanation is favoured by the absence of isobutyric anhydride; for although keten itself largely survives passage through the reactor, the much less stable dimethylketen is represented by its breakdown products (see next paragraph), and would therefore not be expected to combine significantly with the free isobutyric acid to give the acid anhydride.

Route B^1.   In the pyrolysis of both vinyl acetate and vinyl isobutyrate readily measurable quantities of methane and carbon monoxide were noted.   Most of the carbon monoxide could be accounted for by the R/C^1 route and the remainder along with the methane (equal volumes) could be accounted for by the partial breakdown of the acetaldehyde thus:

$$CH_3.CHO \longrightarrow CH_4 + CO \quad - - - - - - - - C^1$$
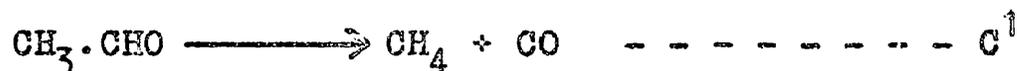
The acetaldehyde was the only one of the B^1 products from vinyl isobutyrate identified directly.   Presumably the

dimethylketen which should have accompanied it failed to survive passage through the reactor at 550°C., and it has in fact been shown to break down as follows at high temperatures[52,53], with the formation of a diradical:-

$$(CH_3)_2C=CO \xrightarrow{-CO} \left[(CH_3)_2C<\right] \longrightarrow \begin{cases} CH_3CH=CH_2 \quad \text{Propylene} \\ \tfrac{1}{2}(CH_3)_2.C=C.(CH_3)_2 \\ \text{2:3-Dimethylbut-2-ene.} \end{cases}$$
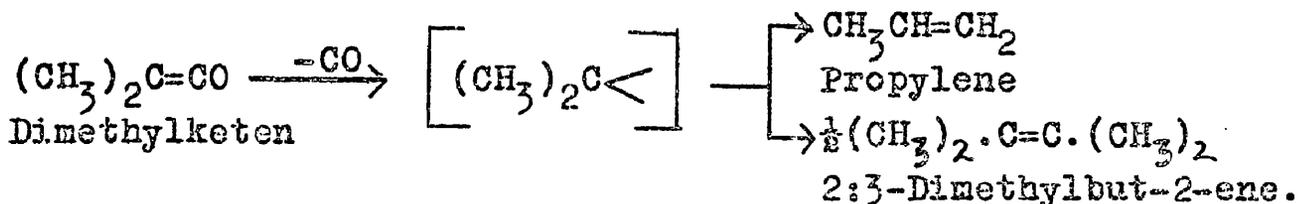
The gaseous pyrolysate from vinyl isobutyrate contained both propylene and 2:3-dimethylbut-2-ene (tetramethylethylene), which very strongly confirms that dimethylketen is a transient primary product in pyrolysis.

In the pyrolysis of vinyl acetate keten largely survives the pyrolysis at 500°C. apart from a possible small quantity reacting with acetic acid as described above. However, a small amount of ethylene was detected in the pyrolysis gases and this could be accounted for by a breakdown of keten analogous to dimethylketen:-

$$CH_2=CO \xrightarrow{-CO} \left[CH_2<\right] \longrightarrow \tfrac{1}{2}CH_2=CH_2$$
$$\text{Keten} \qquad\qquad\qquad \text{Ethylene}$$
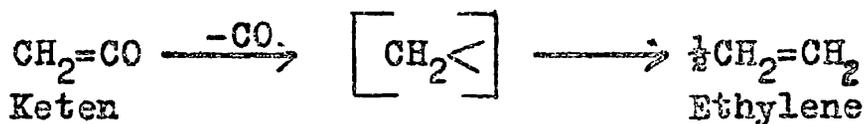
Route C^2. While the C^2 products were readily identified in the case of vinyl acetate, one of the C^2 products, 3-methylbut-1-ene, from vinyl isobutyrate could not be identified positively from the infra red spectrum of the gaseous pyrolysate, owing to masking effects; but two of its isomers were identified,

viz., 2 methylbut-1-ene (weak) and 2 methylbut-2-ene (strong),
and it is highly probable that these are due to thermal
isomerisation of the primary olefin to a mixture of isomeric
pentenes.

Route R/C[1].   In the cases of vinyl acetate and _isobutyrate_
no secondary decompositions or reactions were detected, after
decarbonylation.

Unassigned Route or Reaction.   In all the gaseous pyrolysates
from both vinyl acetate and _isobutyrate_, except when nitric
oxide was present, a strong band at 1140 cm.$^{-1}$ in the infra-red
spectrum was detected, and still remains unassigned.

2.4: The Catalytic Pyrolyses of Vinyl Acetate.

It may be noted that Deutsch and Hermann[59], who briefly described the breakdown of vinyl acetate at ca.470° over an activated carbon catalyst, recorded that, in addition to the constituents which have all now been observed in the uncatalysed thermal decomposition of the ester, the pyrolysate also contained "vinyläther". Translating this by old or modern German, this could be taken to mean either vinyl ester or ether. It should therefore be emphasised that no divinyl ether was observed, so that the disproportionation of vinyl acetate to acetic anhydride and divinyl ether is not one of the purely thermal competitive breakdown routes.

All the previously described pyrolyses took place in a Pyrex glass reactor, packed with Pyrex glass helices, and as most chemical reactions are carried out in glass vessels, it is generally recognised that if no other foreign material is present, the reaction is regarded as being uncatalysed.

The Pyrolysis of Vinyl Acetate in a Stainless Steel Reactor.

Vinyl acetate was pyrolysed at 500° in a stainless steel reactor packed with Pyrex glass chips, and a large volume of gas was obtained, containing 46% hydrogen. No hydrogen was found when a Pyrex glass reactor was used; and it would appear that the hydrogen formation is dependent on the catalysis by stainless steel. The products of pyrolysis from the stainless

steel reactor were the same as from a Pyrex glass reactor except for the large volume of hydrogen, a small quantity of water detected, and the complete absence of keten. It would therefore appear that the large volume of hydrogen was being catalytically produced from the keten. The absence of keten from a pyrolysis in a stainless steel reactor can be accounted for by the fact that keten decomposed to carbon and water[60] in an iron tube:-

$$CH_2=CO \xrightarrow[700^o]{Fe} 2C + H_2O$$

This was found to take place in a stainless steel tube at 500°. The carbon and water formed may undergo the "water gas reactions" to give hydrogen. Iron, chromium, and nickel, all present in the stainless steel reactor are known to catalyse the "water gas reactions" so that they take place in the region of $400-500^o$ [61]. The following "water gas reactions" are postulated to account for the formation of hydrogen:-

$$C + 2H_2O \rightleftharpoons CO_2 + 2H_2$$
$$C + H_2O \rightleftharpoons CO + H_2$$
$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$$
$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
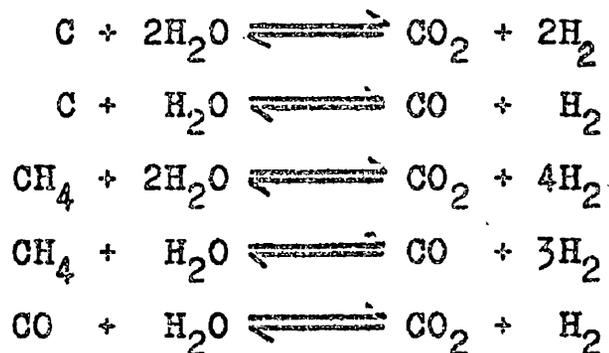
Acetone on pyrolysis at 700° is known to give methane and keten[60]. If this pyrolysis was carried out in a stainless steel reactor, the keten would further decompose to give water and carbon:-

$$CH_3 \cdot CO \cdot CH_3 \longrightarrow CH_4 + (CH_2=CO \longrightarrow 2C + H_2O),$$

thus giving all the necessary constituents for the above "water gas reactions", which should yield hydrogen. Acetone, on pyrolysis at 700° in a stainless steel reactor yielded a large volume of gas containing 65.9% hydrogen. This strongly confirms that the "water gas reactions" catalytically take place after the catalytic breakdown of keten in the pyrolysis of vinyl acetate in a stainless steel reactor.

The Pyrolysis of Vinyl Acetate in a Silica Reactor.

Vinyl acetate, when pyrolysed in a fused silica (Vitreo-sil) reactor, packed with coarse silica chips, was found to be qualitatively identical with the pyrolyses carried out in a Pyrex reactor. However, it was found that a higher percentage of the ester (94.5%) underwent pyrolysis at 550°. Of the ester which was pyrolysed it was found that the ratio of the pyrolytic routes was considerably altered (see table I on page 77).

The Pyrolysis of Vinyl Acetate in the Presence of Nitric Oxide.

In an attempt to inhibit radical breakdown routes in the pyrolysis of vinyl acetate, two pyrolyses were carried out in the presence of nitric oxide. However, there was no evidence that any of the decomposition routes were radical as distinct from molecular. The noteworthy features were that in both

cases more than 95% of the ester was pyrolysed at 550°, the ratio of the pyrolytic routes was considerably altered (see table 2 on page 78), and the unassigned 1140 cm.$^{-1}$ band in the infra-red spectrum of the gases was absent.

C H A P T E R   III

The Pyrolysis of Ethyl Maleate

Chapter III.

3.1 The Pyrolysis of Ethyl Maleate.

Ethyl maleate is stable[62] up to about 340° while at 500° in a silica flow reactor, 89% of the ester undergoes pyrolysis. A scheme for the pyrolytic breakdown routes with quantitative figures based on the pyrolysed ester is given below:-

(also a trace of acetylene)
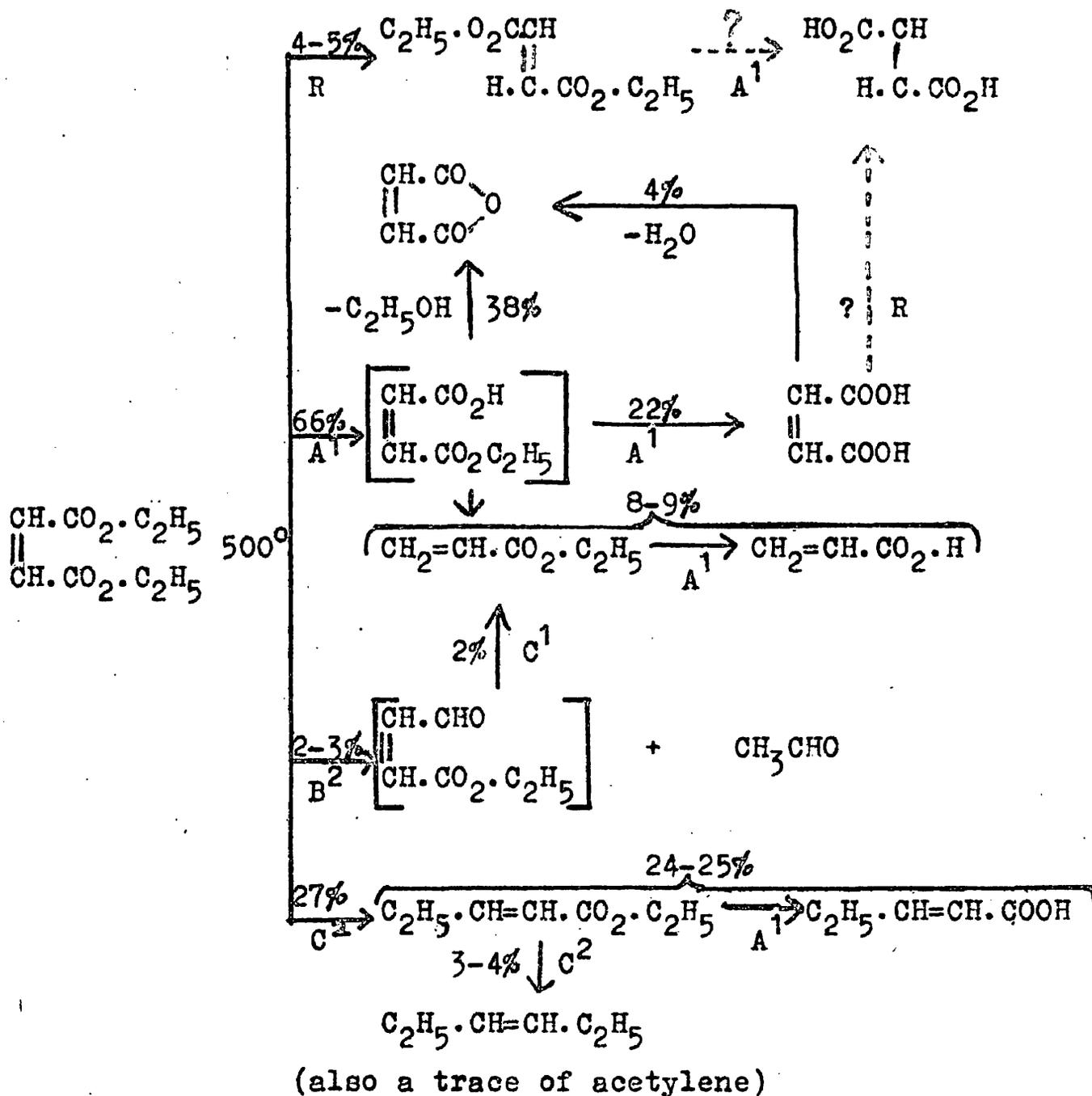
The scheme has been simplified by the omission of the ethylene and carbon dioxide formed $\underline{via}$ A^1 and C^2 scissions respectively. All the products shown (except those in square brackets) were actually identified; but the weight-percentage figures must be regarded as approximate only, since accurate quantitative analysis of the complex pyrolysate is almost impracticable. The broken arrows are explained in the following discussion of the four primary breadkdown routes.

3.2 Discussion of Decomposition Routes.

Rearrangement (R). The extent of the thermal $\underline{cis} \longrightarrow$ $\underline{trans}$ inversion is unknown, though it is certainly incomplete under the conditions used since both $\underline{cis}$ and $\underline{trans}$ compounds exist in the pyrolysate. This uncertainty causes difficulty in interpreting some of the results. For example, the fumaric acid observed ($\underline{ca}.4\%$) may have arisen by either or both of the routes indicated by the broken arrows; and the observed overall A^1, B^2, and C^2 scission products may formally have arisen from both the $\underline{cis}$ ester and its rearrangement product, ethyl fumarate. It is thus likely that primary $\underline{cis} \longrightarrow \underline{trans}$ inversion (R) occurs to an extent greater than the directly observed figure ($\underline{ca}.4\%$), an idea supported by the pyrolysis of methyl maleate[63] - the pyrolysis of methyl maleate at 500° yielded at least 60% of the more thermostable methyl fumarate.

A^1 __Route.__   Ethylene, the major gaseous product, arises by A^1 scission; and since maleic acid is produced, two such scissions must occur in succession, forming ethyl hydrogen maleate (or perhaps fumarate) as a transient intermediate. All endeavours to identify this somewhat unstable compound failed.   However, the presence of ethanol and maleic anhydride in the pyrolysate suggests that the half-ester undergoes ring closure, a reaction for which there is good precedent in the literature[64].   Part of the observed maleic anhydride presumably arises directly from the above mentioned maleic acid, since water also occurs in the pyrolysate.

B^2 __Route.__   The small amount of acetaldehyde identified in the pyrolysate can only be accounted for reasonably by assuming B^2 scission of ethyl maleate.   Further breakdown (C^1) of the two resultant aldehydic compounds accounts for the ratio of carbon monoxide to methane in the gaseous pyrolysate (see Table 3 on page 82).   Since the molar $CO:CH_4$ ratio is greater than unity, there must be some substance present, other than acetaldehyde, which is also decarbonylated under the conditions employed.   Theoretically, any or all of the ethyl esters present could supply acetaldehyde by B^2 scission, but other evidence permits some of these to be ruled out.   For example, B^2 scission of ethyl acrylate would yield acrolein and acetaldehyde; but, although it was carefully sought, acrolein could not be detected, whereas it has been

found[6] that at 500°, under similar conditions, acrolein is only partially destroyed. It is therefore suggested that B^2 scission of ethyl maleate (and/or fumarate?) yields acetaldehyde and the ester aldehyde shown in the foregoing scheme. No sign of this ester aldehyde could be detected: it is likely to become smoothly decarbonylated to ethyl acrylate as shown.

C^2 Route. The detection of hex-3-ene (a mixture of cis and trans) confirms the surprising fact that decarboxylation of an ester can occur even in competition with a simple classical A^1 scission. The configuration of the observed ß-ethylacrylic acid (and its ethyl ester) is not known.

The presence of traces of acetylene in the gaseous pyrolysate is accounted for by the fact that maleic anhydride undergoes pyrolysis at 500° to give acetylene, carbon monoxide, and carbon dioxide[65]:-

$$\begin{matrix} CH.CO \\ \| \qquad \searrow \\ \qquad \qquad O \xrightarrow{\ 500°\ } CH{\equiv}CH \ + \ CO_2 \ + \ CO \\ \| \qquad \nearrow \\ CH.CO \end{matrix}$$
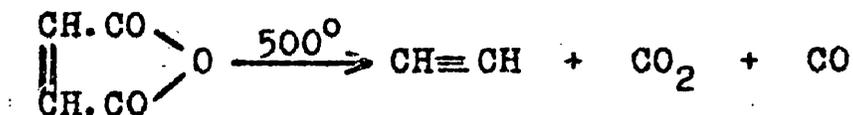
C H A P T E R   IV

Work Preceding the Pyrolysis of Ethylene Dimethacrylate

Chapter IV.

4.1 Work Preceding the Pyrolysis of Ethylene Dimethacrylate.

To assist in interpreting the pyrolytic breakdown routes of ethylene dimethacrylate, the following compounds were pyrolysed:-

$$CH_2=\underset{\underset{CH_3}{|}}{C}.COO.CH_3 \qquad \text{Methyl methacrylate.}$$

$$CH_2=\underset{\underset{CH_3}{|}}{C}.COO.C_2H_5 \qquad \text{Ethyl methacrylate.}$$

$$H.COO.CH_3 \qquad \text{Methyl formate.}$$

$$H.COO.C_2H_5 \qquad \text{Ethyl formate.}$$

$$CH_2=\underset{\underset{CH_3}{|}}{C}.COOH \qquad \text{Methacrylic acid.}$$

$$CH_2=\underset{\underset{CH_3}{|}}{C}.CHO \qquad \text{Methacrolein.}$$
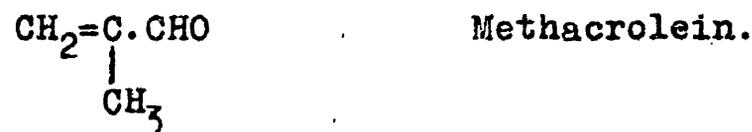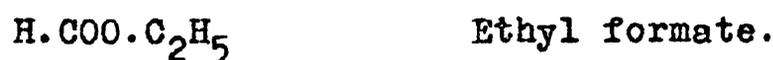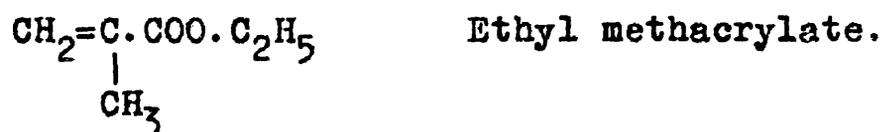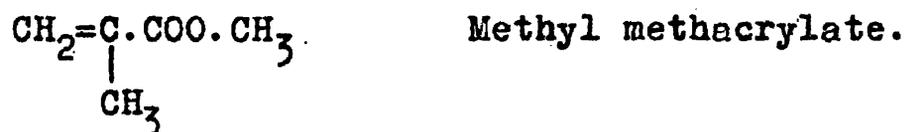
The first four compounds were chosen to investigate the possibility of aliphatic intra-acyl (IA) scissions. The pyrolyses of methacrylic acid and methacrolein were included in this preliminary investigation as they seemed likely primary products by the A^1 and B^2 scissions of ethylene dimethacrylate. Recent work by Mackinnon and Ritchie[9] has shown that aromatic acrylates and methacrylates on pyrolysis

undergo an IA scission to yield an acetylene and a formate.
It is a formal possibility that ethylene dimethacrylate might
undergo such a scission to yield methyl acetylene and ethylene
formate methacrylate:-

$$CH_2=C.CO_2.CH_2.CH_2.O_2C.C=CH_2 \xrightarrow{\quad ? \quad}$$
$$\qquad\quad | \qquad\qquad\qquad\qquad |$$
$$\qquad\quad CH_3 \qquad\qquad\qquad\qquad CH_3$$

$$CH\equiv C.CH_3 + H.CO_2.CH_2.CH_2.O_2C.C=CH_2 \quad \ldots\ldots\ldots \text{ IA}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad | $$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3$$
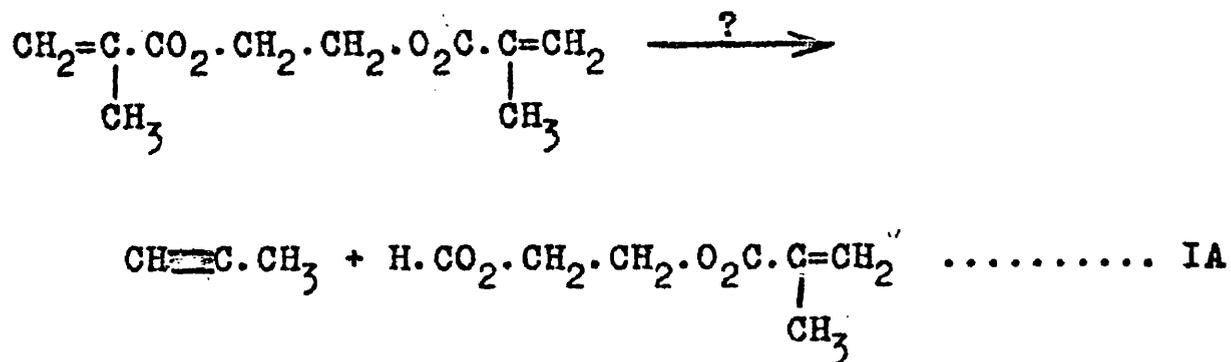
If this scission did take place along with competitive primary,
secondary, and tertiary breakdown routes it would lead to a
very complex analysis of the pyrolysate.   Consequently it was
decided to investigate first the pyrolyses of simple aliphatic
methacrylates to find if the IA scission is applicable to
aliphatic esters.   The simplest methacrylic esters, methyl and
ethyl methacrylate, were chosen for investigation and these
gave negative results.   If, however, these esters did undergo
IA scission, they should yield methyl and ethyl formate:-

$$CH_2=C.CO_2.CH_3 \xrightarrow{\quad ? \quad} CH\equiv C.CH_3 + H.CO_2.CH_3 \quad \ldots\ldots\ldots \text{ IA}$$
$$\qquad | $$
$$\qquad CH_3$$

$$CH_2=C.CO_2.C_2H_5 \xrightarrow{\quad ? \quad} CH\equiv C.CH_3 + H.CO_2.C_2H_5 \quad \ldots\ldots \text{ IA}$$
$$\qquad | $$
$$\qquad CH_3$$
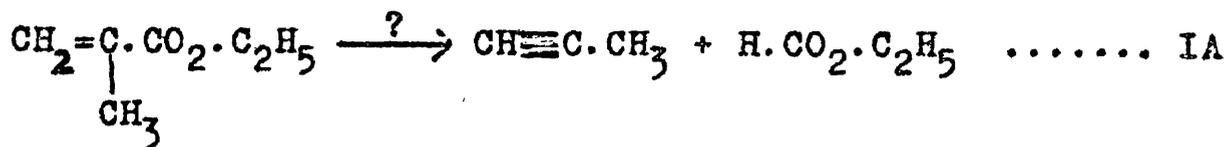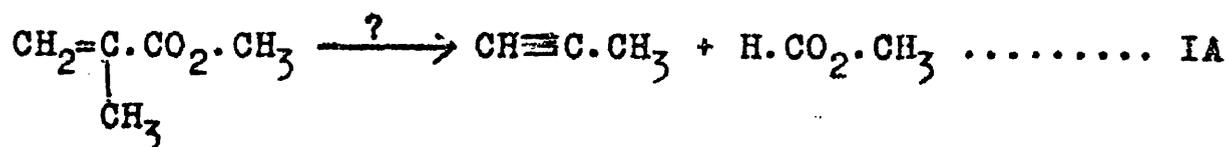
Although methyl and ethyl formate were not detected in the
above pyrolyses, it is possible that they may have undergone

rapid secondary decomposition.   Consequently methyl and
ethyl formate were pyrolysed to find their principal decom-
position products so that these could be sought in the
pyrolysate of methyl and ethyl methacrylate respectively.
Again negative results were obtained.   There was likewise no
evidence for IA scission of ethylene dimethacrylate, and it
appears that this scission is confined to aromatic acrylates.
Further, IA scission of phenyl acrylate[9] to acetylene and
phenyl formate is believed to be due to a high temperature
free-radical reaction in which the $.CO_2Ph$ radical plays a key
part.   This radical will be strongly stabilised by resonance;
but the corresponding radicals from aliphatic acrylates
$(.CO_2Alk)$ will not be resonance stabilised at high temperatures.

4.1.1 The Pyrolysis of Methyl Methacrylate.

Pyrolysing methyl methacrylate in a vitreosil flow
reactor at 500°, ca. 60-70% of the ester was unchanged while
the remainder broke down by a major B^2 scission and a minor
C^2 scission:-

$$
CH_2=\underset{CH_3}{\overset{}{C}}.CO_2.CH_3
\begin{cases}
\xrightarrow[\text{Major}]{B^2} \left[CH_2=\underset{CH_3}{\overset{}{C}}.CHO \right] + CH_2O \\
\xrightarrow[\text{Trace}]{C^2} CO_2 + CH_2=C.(CH_3)_2
\end{cases}
$$

$$\left[CH_2=\underset{CH_3}{\overset{}{C}}.CHO \right] \xrightarrow{C^1} CH_2=CH.CH_3 + CO$$

$$CH_2O \xrightarrow{C^1} H_2 + CO$$
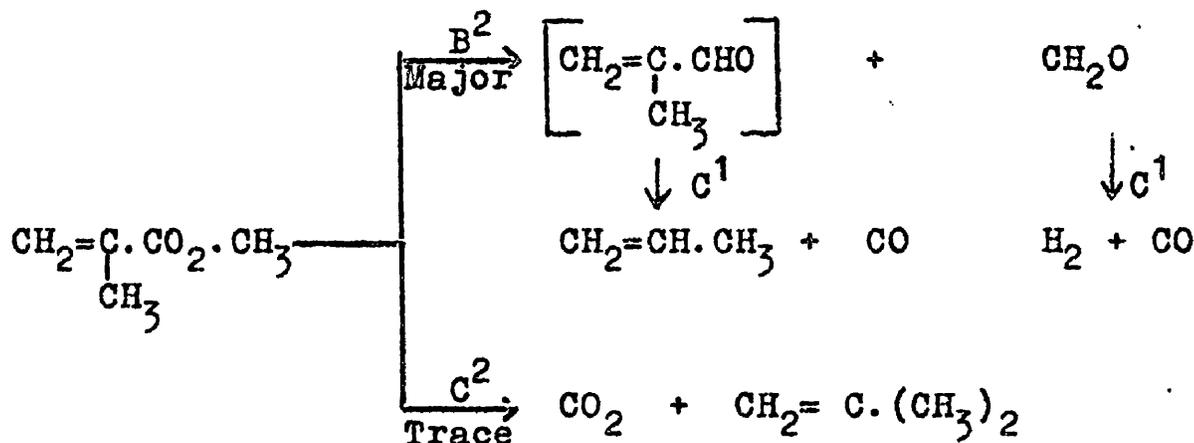
As stated above, there was no evidence for IA scission. One of the B^2 products, acrolein, was not identified directly but postulated by the presence of its C^1 products, propylene and carbon monoxide. The thermal stability of methyl methacrylate, like that of other methyl esters, is due to the absence of a ß-hydrogen atom in the alkoxy group, which precludes A^1 scission. Hence the pyrolysis of ethyl acrylate (see below), with a ß-hydrogen atom in the alkoxy group, yields only traces of unchanged ester when pyrolysed under the same conditions.

4.1.2: The Pyrolysis of Ethyl Methacrylate.

The thermal breakdown of ethyl methacrylate was mainly, as expected, by a classical A^1 scission to yield methacrylic acid and ethylene. The secondary pyrolysis of methacrylic acid is not shown in the scheme below, but is discussed on page 47 . B^2 and C^2 scissions of ethyl methacrylate compete on a very minor scale with the primary A^1 scission:-

$$CH_2=\underset{\underset{CH_3}{|}}{C}.CO_2.C_2H_5 \xrightarrow{500^\circ}$$

$$\xrightarrow[96\%]{A^1} CH_2=\underset{\underset{CH_3}{|}}{C}.COOH + CH_2=CH_2$$

$$\xrightarrow[\text{Trace}]{C^2} CO_2 + CH_2=\underset{\underset{CH_3}{|}}{C}.C_2H_5$$

$$\xrightarrow[3\%]{B^2} CH_2=\underset{\underset{CH_3}{|}}{C}.CHO + CH_3CHO$$

$$\downarrow C^1 \qquad\qquad \downarrow C^1$$

$$CH_2=CH.CH_3 + CO \qquad CH_4 + CO$$
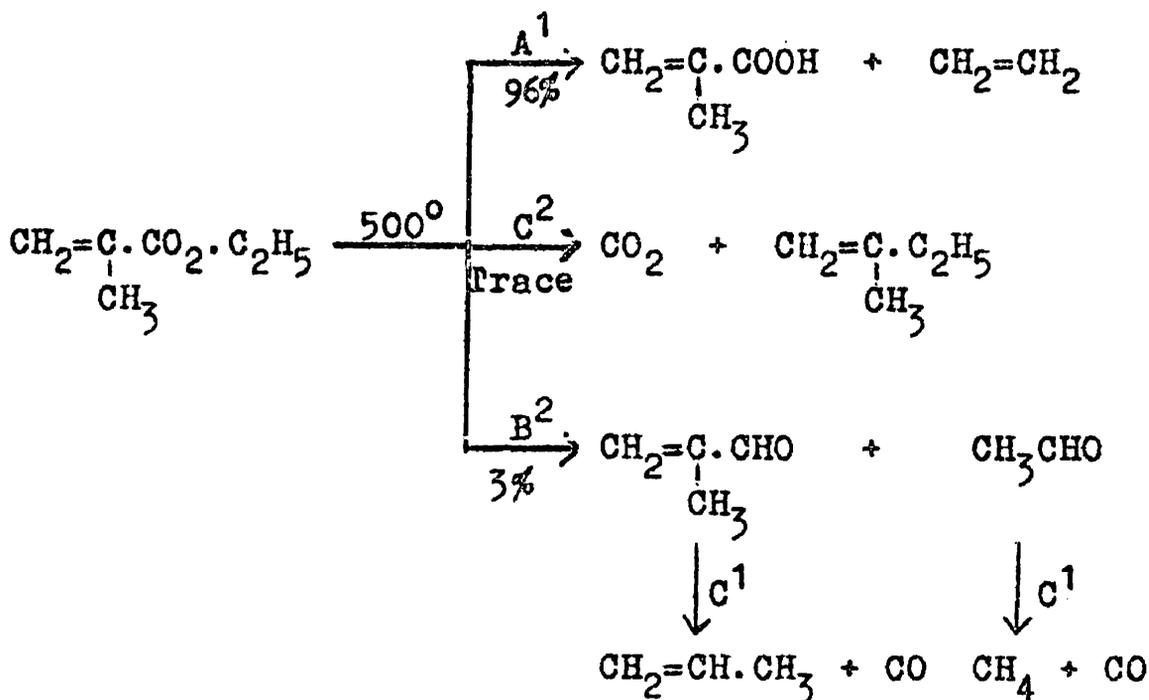
As previously stated, there was no evidence for IA scission.

4.1.3: The Pyrolysis of Methyl Formate.

Pyrolysing methyl formate in a vitreosil flow reactor at 500°, ca. 40% of the ester survived unchanged while the remainder broke down by a major C^1 route to yield carbon monoxide and methanol. A minor B^2 route competed to yield formaldehyde. Traces of decarboxylation were observed:-

$$H.COO.CH_3 \quad \xrightarrow{}
\begin{cases}
\xrightarrow[\text{Major}]{C^1} & CO \; + \; CH_3OH \\[1em]
\xrightarrow[\text{Minor}]{B^2} & 2H.CHO \xrightarrow{C^1} 2H_2 \; + \; 2CO \\[1em]
\xrightarrow[\text{Trace}]{C^2} & CO_2 \; + \; CH_4
\end{cases}$$
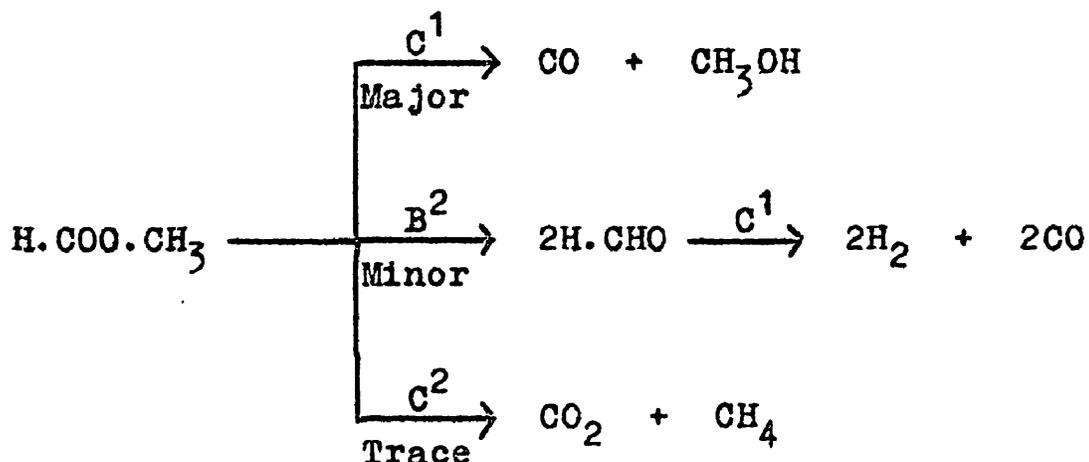
The pyrolysis of methyl formate has been investigated by Peytral[21], but the C^1 route was not recorded; instead of the C^1 route, Peytral postulated that methanol originated by the combination of carbon monoxide and hydrogen:-

$$CO \; + \; 2H_2 \longrightarrow CH_3OH$$

However, a mass balance indicated a large excess of carbon monoxide thus favouring the C^1 decomposition route.

4.1.4: The Pyrolysis of Ethyl Formate.

Ethyl formate was found to be very unstable on pyrolysis at 500°. No unchanged ester was recovered. The principal breakdown route was an A^1 scission to yield formic

acid and ethylene:-

$$H.COO.C_2H_5 \xrightarrow{500^o} H.COOH + CH_2=CH_2 \ldots\ldots\ldots A^1$$
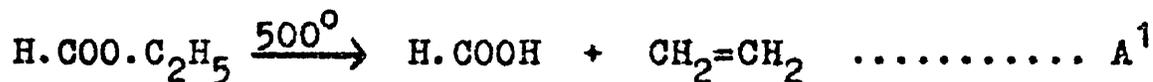
There was evidence for secondary decomposition of the formic acid by decarbonylation, decarboxylation and also disproportionation to yield such minor products as carbon monoxide, carbon dioxide, formaldehyde and water.   There was no evidence that the pyrolysis was other than that previously described by Makens and Eversole[66].

4.1.5: The Pyrolysis of Methacrylic Acid.

Pyrolysing methacrylic acid in a vitreosil flow reactor at 500°, _ca._ 81% of the acid survived pyrolysis, the remainder breaking down by a principal C^1 route to yield carbon monoxide and acetone _via_ an unstable enol.   A minor decarboxylation took place as well as an obscure reaction yielding water:-
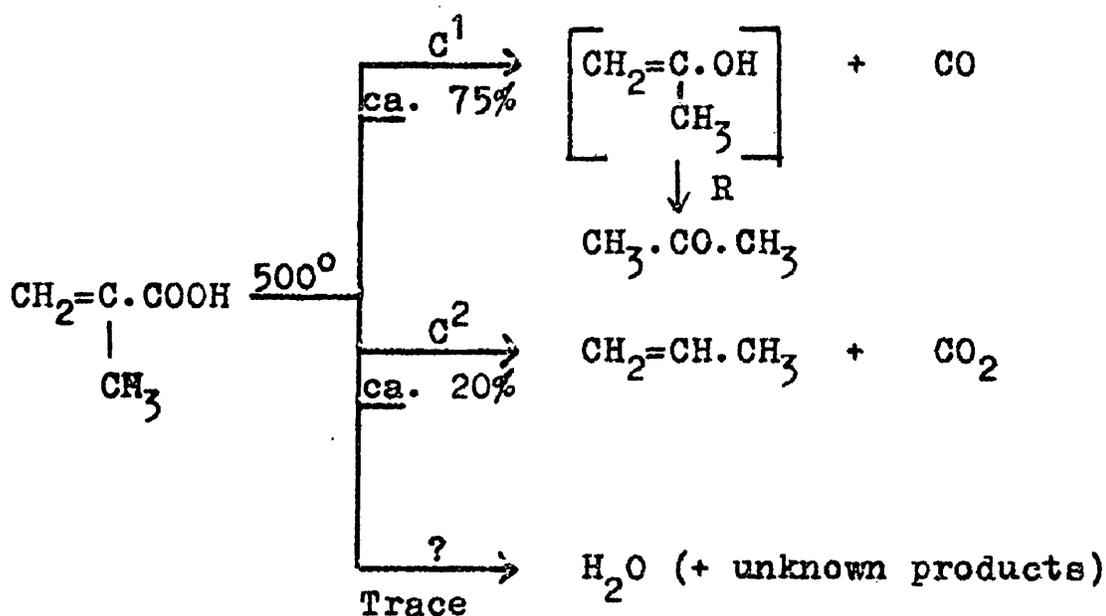
The C^1 reaction is interesting;   hitherto, the literature on

the pyrolysis of acids has made no mention of this (though of course the C^2 reaction is well known), except for the simple case of benzoic acid, which at ca. 370-400° breaks down by two competitive routes[67], thus:-

$$Ph.COOH \begin{cases} \xrightarrow[\text{ca. 95\%}]{C^2} CO_2 + C_6H_6 \\ \\ \xrightarrow[\text{ca. 5\%}]{C^1} CO + PhOH \end{cases}$$
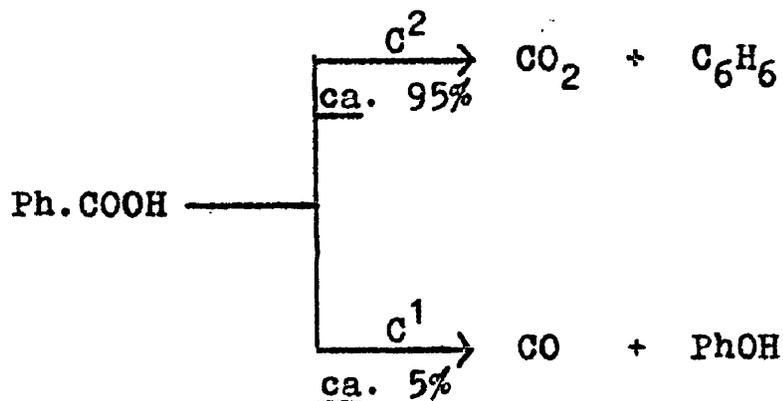
Here, the hydroxy compound formed on elimination of carbon monoxide is a stable one (phenol); in the case of methacrylic acid it is considered that the primary product on elimination of carbon monoxide is an unstable enol, which at once rearranges to acetone. This similarity in mechanism seems likely, for the benzenoid unsaturation of benzoic acid is in a sense comparable to the olefinic unsaturation of methacrylic acid. Carbon monoxide has been reported[66] in the pyrolysis of formic acid in the presence of ethyl formate but no specific decomposition route was postulated.

The formation of a trace of water from methacrylic acid poses a problem. Water has been detected in the pyrolysis of acrylic acid[68] but its proposed mode of formation is not comparable with methacrylic acid. It has been tentatively suggested[68] that the water arises from acrylic acid by a B^1

scission; the unstable methylene keten left after the elim-
ination of water would be expected to break down to acetylene
and carbon monoxide, two of the observed products:-

$$CH_2=CH.CO_2H \xrightarrow{\ B^1\ } [CH_2=C=CO] + H_2O$$

$$CH\equiv CH + CO$$
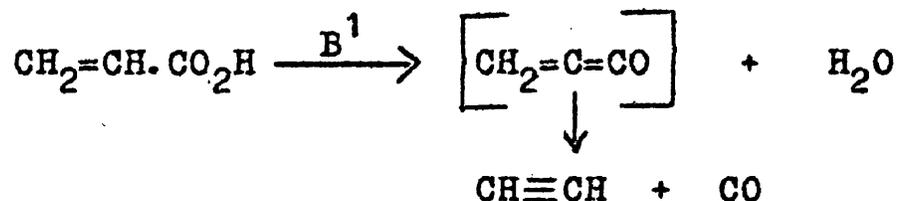
(C[1] and C[2] scissions of acrylic acid also take place).

The idea of thermal elimination of a keten from acrylic acid
is supported by the known thermal scission of acetic acid to
keten itself and water, in competition with a C[2] scission to
carbon dioxide and methane[69]. However, this mechanism cannot
apply to methacrylic acid, which lacks the α-hydrogen atom
necessary for a B[1] scission. For the present, therefore, it
is tentatively suggested that the two olefinic acids yield
water by two different mechanisms - a B[1] scission for acrylic
acid and some unspecified type of scission for methacrylic acid.

There is, however, a further possibility which avoids
the necessity to postulate two different mechanisms - namely,
that a minor primary reaction of each acid is the formation of
water and an acid anhydride, which is not unlikely in view of
the work of Davidson and Newman[54]. Little is known of the
thermal stability of unsaturated acid anhydrides, though there
is some evidence that they are unstable[65]. Brown and
Ritchie[65] have shown that saturated acid anhydrides
decarboxylate and decarbonylate on pyrolysis. Work in this

thesis, namely the pyrolysis of vinyl acetate, ethyl maleate, and ethylene dimethacrylate, has indicated that double bonds facilitate decarboxylation. Hence, one of the decomposition routes of an unsaturated anhydride would be expected to be decarboxylation and this has been observed in the case of maleic anhydride[65]. It is therefore postulated that traces of the methacrylic acid form water and methacrylic anhydride, which decarboxylates to form diisopropenyl ketone:-

$$2CH_2=C.COOH \xrightarrow{?} \left[CH_2=C.CO.O.OC.C=CH_2 \right] + H_2O$$
$$\quad\quad\ \ |\qquad\qquad\qquad |\qquad\qquad\quad |$$
$$\quad\quad\ \ CH_3\qquad\qquad\ \ CH_3\qquad\quad CH_3$$

$$C^2 \downarrow ?$$

$$CH_2=C.CO.C=CH_2 + CO_2$$
$$\quad\ \ |\qquad\quad |$$
$$\quad\ \ CH_3\quad\ \ CH_3$$

This postulation was partly borne out by the detection of an uncharacterised carbonyl compound in the pyrolysate.

4.1.6: The Pyrolysis of Methacrolein.

Methacrolein, redistilled to remove any polymerisation inhibitor, was pyrolysed at 500° in a vitreosil flow reactor. 21% of the aldehyde survived pyrolysis while 28% of the remainder decarbonylated to give propylene and carbon monoxide:-

$$CH_2=C.CHO \xrightarrow[28\%]{C^1} CH_2=CH.CH_3 + CO$$
$$\quad\ \ |$$
$$\quad\ \ CH_3$$

The above C^1 reaction was expected to be the major route
giving equimolar quantities of propylene and carbon monoxide.
However, the molar ratio of propylene to carbon monoxide was
approximately 1:3, indicating some other source of carbon
monoxide.   Similar results for the pyrolysis of acrolein have
been observed[6] with a high proportion of carbon monoxide in
the gaseous pyrolysate.

It is thought that in the cases of these two unsaturated
aldehydes, the polymer is being pyrolysed in competition with
the monomer.   There was some evidence for this in the case of
methacrolein as the aldehyde in the dropping funnel above the
hot reactor became cloudy during the course of the pyrolysis.
An unused sample was found to have polymerised overnight.
Stoner and McNulty[70] have produced evidence that methacrolein
can extensively dimerize even in the presence of the inhibitor
hydroquinone.   Other authors[71,72] have characterised this
dimer which shows little tendency for further polymerisation:-

$$H.C=O \atop | \atop CH_3.C=CH_2 \quad + \quad {CHO \atop | \atop C.CH_3 \atop || \atop CH_2} \longrightarrow {CHO \atop | \atop H.C - O - C.CH_3 \atop | \quad\quad | \atop CH_3.C - CH_2 - CH_2}$$
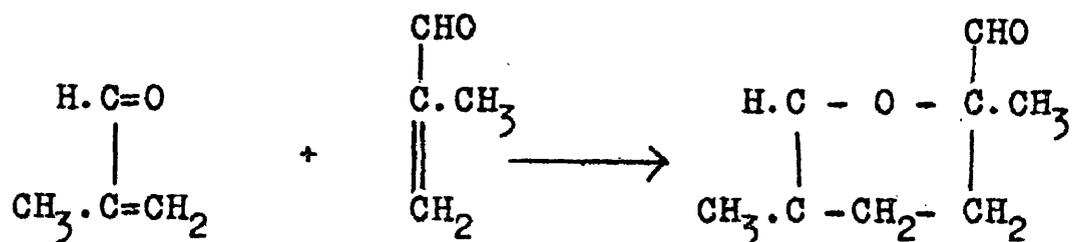
It is very possible that this dimer forms in the methacrolein,
free from inhibitor, in the dropping funnel above the reactor or
in the warm regions of the reactor before pyrolysis takes place.
Should this dimer form, one of its decomposition routes would
most likely be decarbonylation at the aldehydic grouping to give

carbon monoxide.   This would account for the high proportion
of carbon monoxide in the pyrolysis gases of methacrolein.

Chapter V.

5.1: The Pyrolysis of Ethylene Dimethacrylate.

The pyrolysis of ethylene dimethacrylate was found to be extremely complex. On pyrolysing the ester in a vitreosil flow reactor at 500°, ca. 90% of the ester decomposed. A scheme for the pyrolytic breakdown routes of ethylene dimethacrylate is given overleaf; the reaction scheme includes four products (shown in square brackets), which were not positively identified, but whose transient existence is strongly indicated by the identification of their predictable breakdown products.

5.2: Discussion of Decomposition Routes.

The well known A^1 scission[13,14,18] is one of the major decomposition routes to yield methacrylic acid and vinyl methacrylate. The vinyl methacrylate undergoes A^2, C^2, and R/C^1 scissions analogous to the pyrolysis of vinyl benzoate[2]; B^1 scission, which took place in the case of vinyl acetate[2], is precluded for vinyl methacrylate owing to the lack of an α-hydrogen atom in methacrylate grouping.

By analogy with the known thermal breakdown of ethylene diacetate and dibenzoate[6], the A^1/D sequence shown in the top left-hand portion of the breakdown scheme is to be expected. The identification of acetaldehyde confirms this idea, although the anhydride, detected in traces, was not specifically

Pyrolytic Breakdown Routes of Ethylene Dimethacrylate at 500°

$CH_2=C.CO_2.CH_2.CH_2.O_2C.C=CH_2$
   CH_3 CH_3

A^1 30–31% → $CH_2=C.CO_2H + CH_2=C.CO_2.CH=CH_2$
               CH_3 CH_3

A^1 ⇅ $[CH_2=C.CO_2.CH(CH_3).O_2C.C=CH_2]$
          CH_3 CH_3

D → $CH_3.CHO + (CH_2=C.CO)_2O$
                  CH_3

B^2 4–5% → $CH_2=C.CHO + [CH_3=C.CO_2.CH_2.CH_2.CHO]$
            CH_3 CH_3
C^1 ↓
$CH_2=CH.CH_3 + CO$

C^2 65% → $CO_2 + CH_2=C.CO_2.CH_2.CH_2.CH_2.C=CH_2$
                CH_3 CH_3

A^2 → $CH_3=C.CO_2H + CH\equiv CH$
         CH_3

C^2 → $CO_2 + CH_2=C.CH=CH_2$
             CH_3

R → $[CH_2=C.CO.CH_2.CHO]$
        CH_3
C^1 ↓
$CH_2=C.CO.CH_3 + CO$
   CH_3

A^1 → $CH_2=C.CH=CH_2 + CH_3=C.COOH$
         CH_3 CH_2

C^2 → $CO_2 + CH_2=C.CH_2.CH_2.CH_2.C=CH_2$
             CH_3 CH_3

B^2 → $CH_3=C.CHO + CH_2=C.CH_2.CHO$
         CH_3 CH_3
C^1 ↓ C^1 ↓
$CH_2=CH.CH_3 + CO$ C^1
$CH_2=C.(CH_3)_2$ +

characterised.   The fact that only traces of anhydride were detected may be an indication of the thermal instability of unsaturated acid anhydrides.

The minor primary B^2 scission is indicated by the detection of methacrolein in the pyrolysate.   Its accompanying product, α-methacrylyl oxyacetaldehyde, was not detected in the pyrolysate, the detection being hampered by the fact that this compound is not recorded in the literature and its thermostability is unknown.

The major primary decarboxylation of ethylene dimethacrylate is interesting as it is the first recorded ester pyrolysis where the C^2 reaction is greater than the classical A^1 scission, when both these scissions are competing.   The decarboxylation is believed, as in the case of ethyl maleate (see Chapter III), to be facilitated by the proximity of a double bond in the ester.   Like ethyl maleate, which double decarboxylates, ethylene dimethacrylate undergoes two C^2 scissions to yield 2.5 dimethyl hexa-1.5-diene.   Primary decarboxylation of ethylene dimethacrylate yields 2-methyl but-1-enyl methacrylate, which undergoes A^1, C^2, and B^2 scissions analogous to the thermal breakdown of ethyl methacrylate (see page 45).   One of the B^2 products, isopropenyl acetaldehyde, was not definitely characterised, but it seems a most likely product in view of the above analogy with ethyl methacrylate; in addition isobutene, the C^1 decomposition

product of isopropenyl acetaldehyde, was detected.

For the sake of simplicity, the secondary breakdown routes of methacrylic acid are not shown in the breakdown routes on page 54. These have been previously described on page 47.

CHAPTER VI

General Application of Results

Chapter VI.

6.1: General Application of Results.

In the preceding chapters the importance and relevance
of the individual results have been discussed as fully as
possible within the actual context.   In conclusion, therefore,
the information gained from the pyrolysis of model compounds
has been considered with its application to the thermal break-
down of poly(ethylene fumarate);   and this is discussed below.

6.2: Summary of Results for the Pyrolysis of Poly(ethylene fumarate).

Some of the observations on the pyrolysis of the polyester
have previously been referred to in the basic plan (pages 20-23).
The qualitative results, though incomplete as yet, combined with
a study of model compounds, give a good indication of the
principal breakdown routes of poly(ethylene fumarate).

A sample of the molten polyester ($D.P._n$ ca. 2-9) was
pyrolysed at 500° in a packed silica flow reactor.   The main
gaseous pyrolysate was carbon dioxide and to a lesser extent
carbon monoxide.   Small quantities of saturated and unsaturated
hydrocarbons (containing acetylene) were detected.   The liquid
pyrolysate was very complex, and on distillation yielded
fractions ranging from clear low boiling liquids to tar-like
resinous materials.   In the lower boiling fractions (b.p. up
to 105°) acetaldehyde and water were detected.   The higher

fractions contained unsaturated groupings and consisted of
acids, acid anhydrides, esters, and carbonyl compounds. These
could not be specifically characterised and it was considered
that many of these groupings were attached to polymer molecules
of low molecular weight. No vinyl groups were detected.
Mackinnon and Ritchie[73] pyrolysed the polyester in an unpacked
reactor and detected fumaric acid and lower molecular weight
polyester in the pyrolysate. It was because of the complexity
of these results that it was decided to study the pyrolysis of
the polyester by means of model compounds.

6.3: Pyrolytic Breakdown Routes of Poly(ethylene fumarate).

An interpretation of the pyrolytic breakdown routes of
poly(ethylene fumarate) is given in reaction scheme 2. The
main breakdown route of the polyester appears to be primary
decarboxylation as the gaseous pyrolysate contains ca. 65%
carbon dioxide. It seems unlikely that the major part of the
carbon dioxide arises via decarboxylation of unsaturated acid
end-groups formed in the pyrolysis, as the pyrolysis of an
unsaturated model, methacrylic acid, showed that this had a
greater tendency to undergo the C^1 reaction than the C^2 reaction
(see page 47). Primary decarboxylation of the polyester is
further indicated by the fact that the model esters ethyl
maleate (see page 38) and ethylene dimethacrylate (see page 54)
both undergo primary C^2 reactions; in the case of the latter
model ester, C^2 scission is the main decomposition route. It
is worth noting that the proximity of a double bond to the

Reaction Scheme 2 : Interpretation of the Pyrolysis of

Poly(ethylene Fumarate) or PEF at 500°

$\sim\!\!\sim\!\!CH_2.CH_2.CH=CH.CH_2.CH_2.CH=CH \sim\!\!\sim$

$\uparrow C^2$

$\sim\!\!\sim\!\!CH_2.CH_2.O_2C.CH=CH.CO_2.CH_2.CH_2.CH=CH\sim\!\!\sim$

Major $\uparrow C^2$

$\sim\!\!\sim\!\!CH_2.CH_2.O_2C.CH=CH.CO_2.CH_2.CH_2.O_2C.CH=CH \sim\!\!\sim$ (PEF)

Major $\downarrow A^1$ $\underset{\text{Minor}}{\overset{B^2}{\vert\longrightarrow}}$ $\sim\!\!\sim\!\!CH_2.CHO + OHC.CH=CH\sim\!\!\sim$

$\sim\!\!\sim\!\!CH_2.CH_2.O_2C.CH=CH.CO_2H + CH_2=CH.O_2C.CH=CH\sim\!\!\sim$

$\downarrow A^1$ $\overset{A^2}{\longrightarrow} CH\equiv CH + HO_2C.CH=CH\sim\!\!\sim$

$\sim\!\!\sim\!\!CH=CH_2 + H.C.CO_2H$ $\overset{C^2}{\longrightarrow} CO_2 + CH_2=CH.CH=CH\sim\!\!\sim$

$\underset{HO_2C.C.H}{\parallel}$ A^1 $\overset{R/C^1}{\longrightarrow} CO + CH_3.CO.CH=CH\sim\!\!\sim$

              $\overset{B^1}{\longrightarrow} CH_3CHO + O=C=C=CH\sim\!\!\sim$

$\sim\!\!\sim\!\!CO_2.CH(CH_3).O_2C\sim\!\!\sim$

D $\downarrow$

$\sim\!\!\sim CO.O.OC \sim\!\!\sim$

+

$OH_3.CHO$

$\sim\!\!\sim\!\!COOH + HOOC\sim\!\!\sim \overset{?}{\longrightarrow} \sim\!\!CO.O.OC\sim\!\!\sim + H_2O$

carboxyl grouping greatly facilitated decarboxylation. Brown and Ritchie[19] pyrolysed saturated model compounds, such as ethyl succinate, and found no evidence for the occurrence of either primary or secondary decarboxylation.

The breakdown route next in importance appears to be A^1 scission at the ß-methylene groups, to yield new carboxyl and vinyl ester end groups; and these react further by C^1 and C^2 reactions (cf. methacrylic acid, page 47) in addition to a possible minor dehydration reaction (shown at the bottom of page 59) to yield an anhydride and water. This would account for the presence of water in the pyrolysate, and is not unlikely in view of the work of Davidson and Newman[54]. The detection of fumaric acid[73], which would arise by a double A^1 scission, confirms that primary A^1 scission takes place. In addition to this evidence anhydride groupings and acetaldehyde were detected; and these would arise by the mutual interaction of carboxyl and vinyl ester end groups by the A^1/D sequence previously established by Allan, Jones, and Ritchie[6]. No vinyl ester end-groups were detected, and it is believed that these are broken down by the A^1/D sequence and by A^2, C^2, R/C^1, and B^1 reactions studied in the pyrolysis of vinyl acetate and vinyl isobutyrate (see Chapter II)[2].

In addition to the major primary C^2 and A^1 scissions it is postulated that a minor B^2 scission would take place to give aldehydic end-groups. This would be analogous to the minor B^2 scissions recorded for ethyl maleate (page 38) and ethylene

dimethacrylate (page 54).

6.4: Possible Practical Applications of Results.

To develop a more thermostable polyester of the poly(ethyl-
ene fumarate) type, the polymer should have a structure which
does not contain the two principal points of thermal weakness,
namely:-

> (1) Unsaturated groups adjacent to carboxyl groups, thus
> facilitating primary C^2 reactions.

> (2) ß-Methylene groups adjacent to carboxyl groups (viz.
> -COO.CH$_2$.CH$_2$-), which undergo A^1 scission.

(1) Unsaturated residues could be cut down by using a saturated
acid anhydride, such as succinic anhydride, for the poly-
condensation, with only the minimum of unsaturated maleic
anhydride to introduce double bonds for cross-linking purposes.

(2) The ß-methylene group could be eliminated entirely by using
a glycol without ß-methylene groups for the polycondensation.
Pohl[74], by using neopentylene glycol instead of ethylene glycol
in the polycondensation with terephthalic acid, produced a much
more thermostable polyester of the "Terylene" type without a
ß-methylene group:-
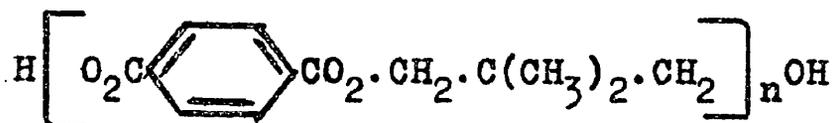
C H A P T E R   VII

Experimental Data

Chapter VII

7:   Experimental Data.

7.1: Apparatus (see page 65).

Four different flow reactors were used in the work – two
of Pyrex glass (P.1 and P.2), one of stainless steel (S), and
one of silica or Vitreosil (V).   The first three were packed
with Pyrex-glass helices, and the fourth with coarsely crushed
Vitreosil.   P.1, S, and V had approximately the same dimensions
(length 65 cm., bore 2 cm.).   P.2 had the same bore but was
only 30 cm. long.

Each reactor was supported vertically inside a cylindrical
electric furnace, which maintained the central section of the
reactor (about half its length) at a temperature controlled
($\pm 5^{o}$) by a Variac, and measured by a chromel-alumel thermocouple
in a pocket located axially within the reactor.   The pyrolysand
was run into the reactor from a dropping funnel fitted with a
side limb for equalising pressures above and below the feed-
liquid.   The feed system could be enclosed in a heating jacket
to melt solid materials (e.g. poly(ethylene fumarate)).   Liquid
and solid pyrolysates were collected in a first receiver, via
an inclined air-condenser and a vertical water-condenser;   the
exit gases were then passed to a receiver cooled in Drikold/
acetone;   the final uncondensed gases were then passed into an
aspirator filled with 20% magnesium chloride to avoid absorption
of any carbon dioxide.   This had an exterior overflow,

63.

SILICA THERMOCOUPLE POCKET

FURNACE

NITROGEN

SILICA TUBE

SILICA PACKING

RECEIVER

FIGURE I

DRIKOLD TRAP
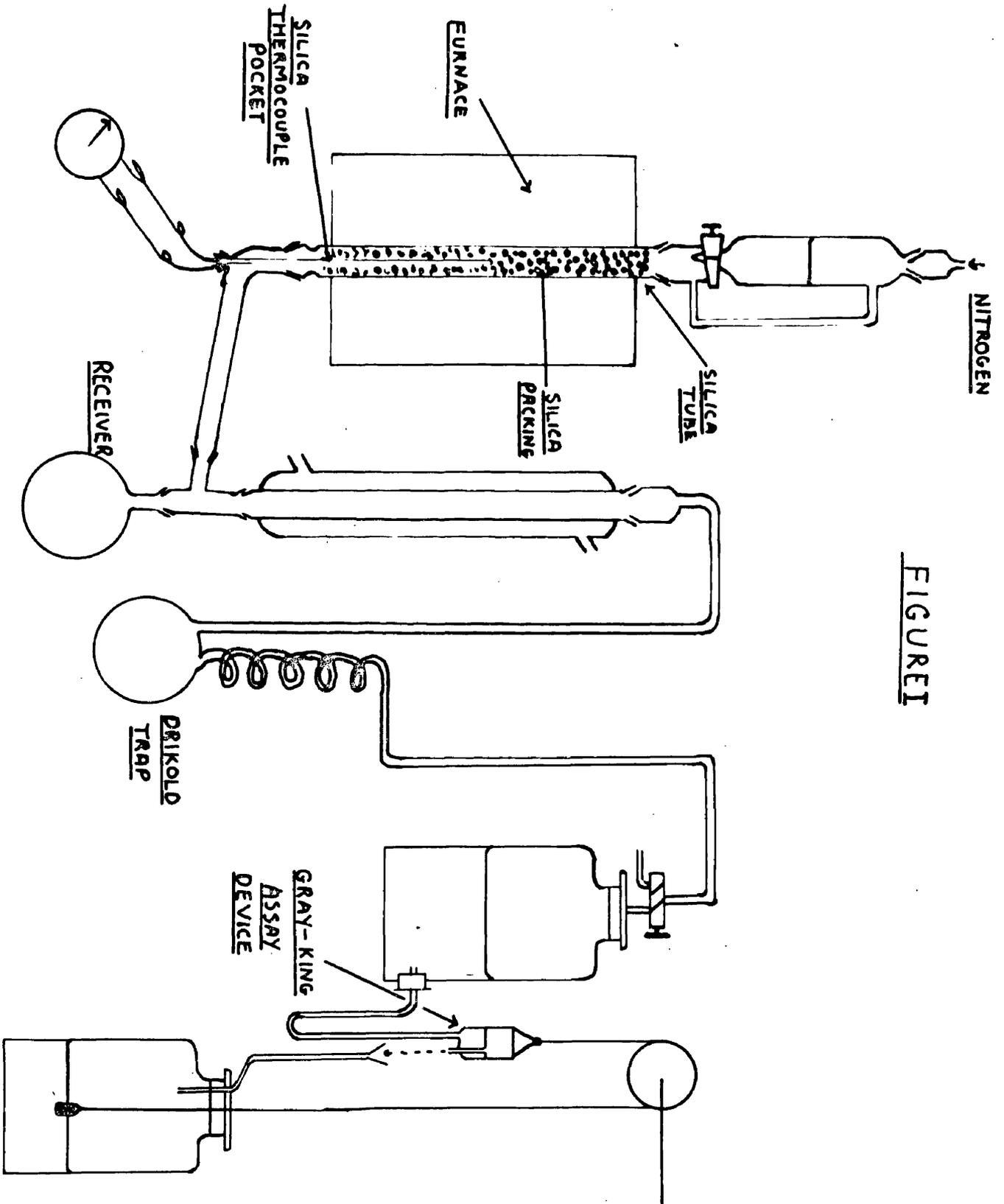
GRAY-KING ASSAY DEVICE

counterbalanced to effect automatic operation (Gray-King Assay Device), and to prevent any back pressure building up in the system.

7.2: Pyrolysis Procedure.

Before each pyrolysis the reactor system was several times evacuated and filled with nitrogen to avoid combustion or explosion of the vapours. The pyrolysand was introduced at a constant rate, generally 0.3 to 0.8 g./min. For materials giving a large volume of pyrolysis gas the drip feed had to be kept to the lower rate otherwise the gases generated forced unchanged material through the reactor and blew condensible vapour into the aspirator.

For the first fifteen minutes of each run the initial pyrolysis gases, with a high proportion of nitrogen, were burned off in a bunsen burner. They were then collected in the aspirator for the rest of the run. As the rate of flow of the material was constant throughout each run, the volume of gases which would have collected during the complete pyrolysis can be calculated by simple proportion. This technique assures that little nitrogen gets into the aspirator thus facilitating a more accurate gas analysis. In many cases appropriate chemical traps were placed between the first receiver and the aspirator. An aniline trap was used to detect keten _via_ the formation of acetanilide. Ammoniacal cuprous chloride solution was used to detect acetylene _via_ the formation of red cuprous

acetylide.

During two pyrolyses nitric oxide was introduced into the reactor-system. In the first case 800 ml. of nitric oxide were introduced from a constant pressure head into the top of the reactor <u>via</u> a side-limb during the pyrolysis of 100 g. of ester. In the second case 40 ml. of nitric oxide were dissolved in 103 g. of ester.

Mass balances were not carried out until at least six successive pyrolyses were carried out without cleaning the reactor. There were some quantitative discrepancies in the initial results and these were attributed to the degree of carbonisation in the reactor[75]. At the end of each investigation the reactor was cleaned simply by raising the temperature to the combustion point of carbon and drawing air through it.

7.3: Contact Time.

Contact times of the pyrolysand in the reactor, with due regard to the degree of carbonisation (mentioned above), were calculated by the abbreviated formula of Fischer[76]:-

$$\text{Contact Time (secs.)} = \frac{43.9 \times V_c}{N^r \times T}$$

V_c = Free space in reactor (ml.)

N^r = Moles Pyrolysand / hr.

T = Temperature $^\circ$Abs.

The free space (V_c) in the reactor was found by measuring the volume of water required to fill the packed reactor and subtracting 10%, assuming a 5% "dead space" or low temperature portion at either end of the reactor.

Free space in reactor P.1 —— 166 ml.

Free space in reactor P.2 —— 65 ml.

Free space in reactor S —— 154 ml.

Free space in reactor V —— 176 ml.

7.4: Methods of Analysis.

The pyrolysates collected in the receiver and the Drikold trap (Fig.I, page 63) were pooled together. There was little separation between the high and low boiling products; this was due to the fact that the pyrolysate came out of the reactor in the form of a gaseous colloid ^{AN AEROSOL} only broken down by the low temperature of the Drikold trap. Where possible, solid products were filtered off and recrystallised. The liquid pyrolysates were fractionally distilled in the presence of such polymerisation inhibitors as hydroquinone and cupric acetate (used for high vacuum distillation). Caution was necessary when using fractionating columns as some of the fractions showed a tendency to polymerise in the column on slow distillation. The knowledge gained from the boiling points was useful, in that some possible constituents could be eliminated straightaway. The examination of the various solid and liquid fractions obtained from a pyrolysis was done by established procedures.

The gaseous pyrolysate was analysed by the standard Hempel method. Ethylene, propylene, and acetylene in the unsaturated hydrocarbon fractions were estimated by a modified Orsat apparatus using specific reagents[77]. isoButene was estimated, after removal of carbon dioxide, by condensing it in a pipette maintained at -20°. The confining liquid in the pipette was a 25% solution of sodium acetate which does not solidify at this temperature.

The normal chemical examinations of pyrolysate fractions were in many cases supplemented by infra-red spectroscopy (described below).

7.5: The Use of Infra-Red Spectroscopy.

The normal chemical methods of examination of pyrolysate fractions were in many cases supplemented by infra-red spectroscopy. The infra-red analyses were done in a double beam spectrometer, described by Brownlie[78]. Solid samples were examined in a soft paraffin mull. Liquids were determined either in capillary films or in standard cells (for volatile liquids). Gases were examined in a 10 cm. long cell. The windows were all of sodium chloride. The identification of pyrolysate fractions involved comparison of their infra-red spectra with standard compounds. This method of proving the identity of a compound, viz., the obtaining of two identical spectra, one of the unknown and one of the known, is very accurate, and in many cases rapid. Infra-red spectroscopy is

particularly useful when standard chemical techniques fail –
for example differentiation between cis and trans esters.
Figure II (page 69) shows the infra-red spectra of ethyl
maleate and fumarate; the fumarate spectrum is distinct from
the maleate spectrum at 975 cm.$^{-1}$ where it shows a stronger
absorption band. When only a few drops of a material, often
impure, are available, infra-red spectrometry is of most
valuable assistance. An example of this is shown in Figure
III (page 70) in an analysis of a fraction found to be isoprene.

7.6: Syntheses

The syntheses of compounds relevant to this work are
described below. The gifts of two chemicals are gratefully
acknowledged – ethylene dimethacrylate by Imperial Chemical
Industries Ltd., and methyl isopropenyl ketone by British
Industrial Solvents Ltd. The ethylene dimethacrylate contained
1% hydroquinone and was washed with 10% sodium hydroxide solu-
tion to remove this inhibitor. A volume of ether equal to that
of the ester was added to assist partition of the ester and
alkali layers on washing. The ethereal ester solution was then
water washed, dried over calcium chloride, and distilled in
vacuo using ca. 2% cupric acetate as a polymerisation inhibitor.
The main fraction b.p.122-126°/15 mm. (cf. White[79]) was collected.
The pyrolysis of this model compound is described in Chapter V.
The methyl isopropenyl ketone (b.p.98-102°/760 mm.) was redis-
tilled using cupric acetate as a polymerisation inhibitor. The

FIG. II

ABSORPTION

ARBITRARY

ETHYL MALEATE

ETHYL FUMARATE

WAVE No. CM⁻¹
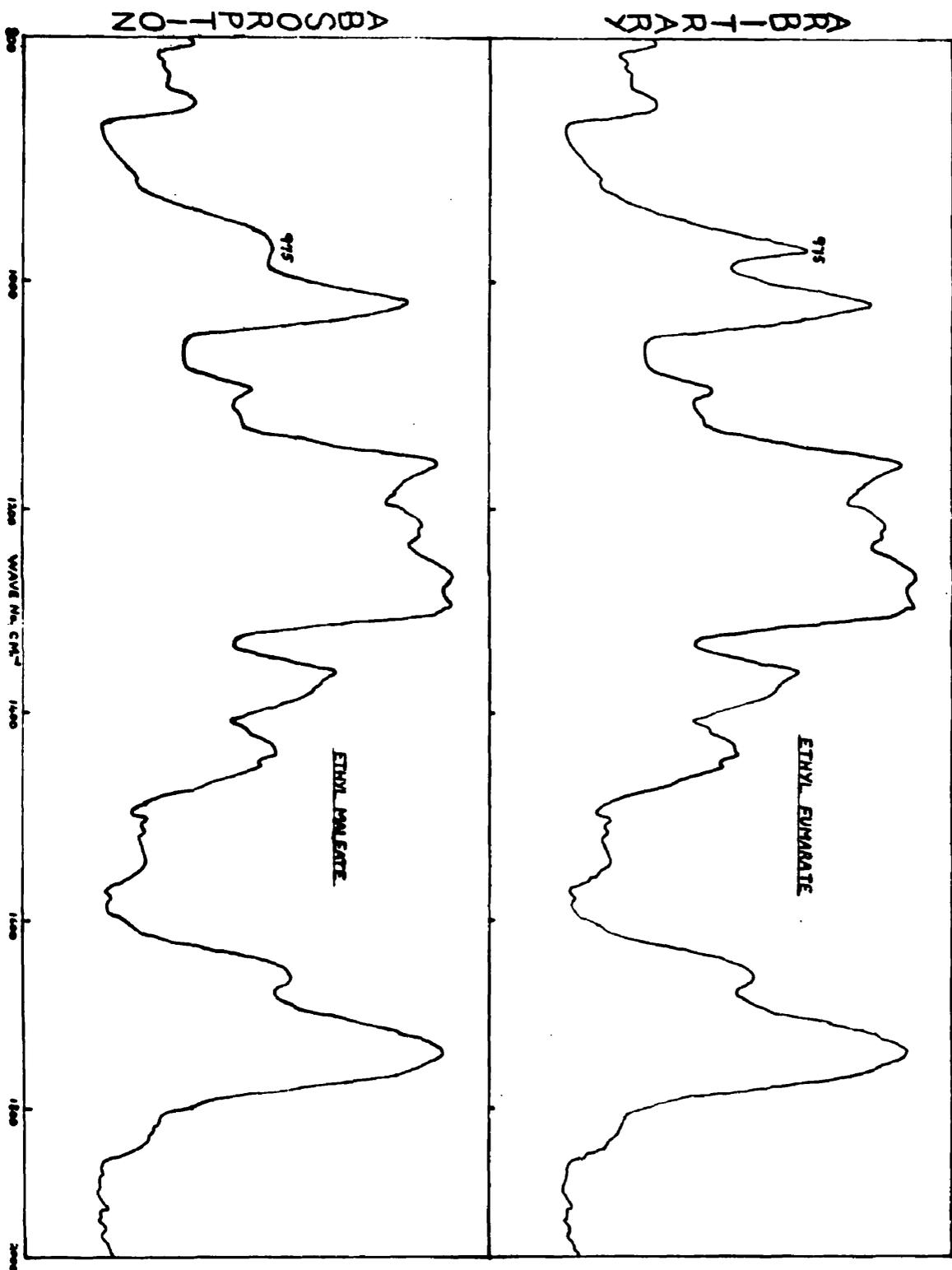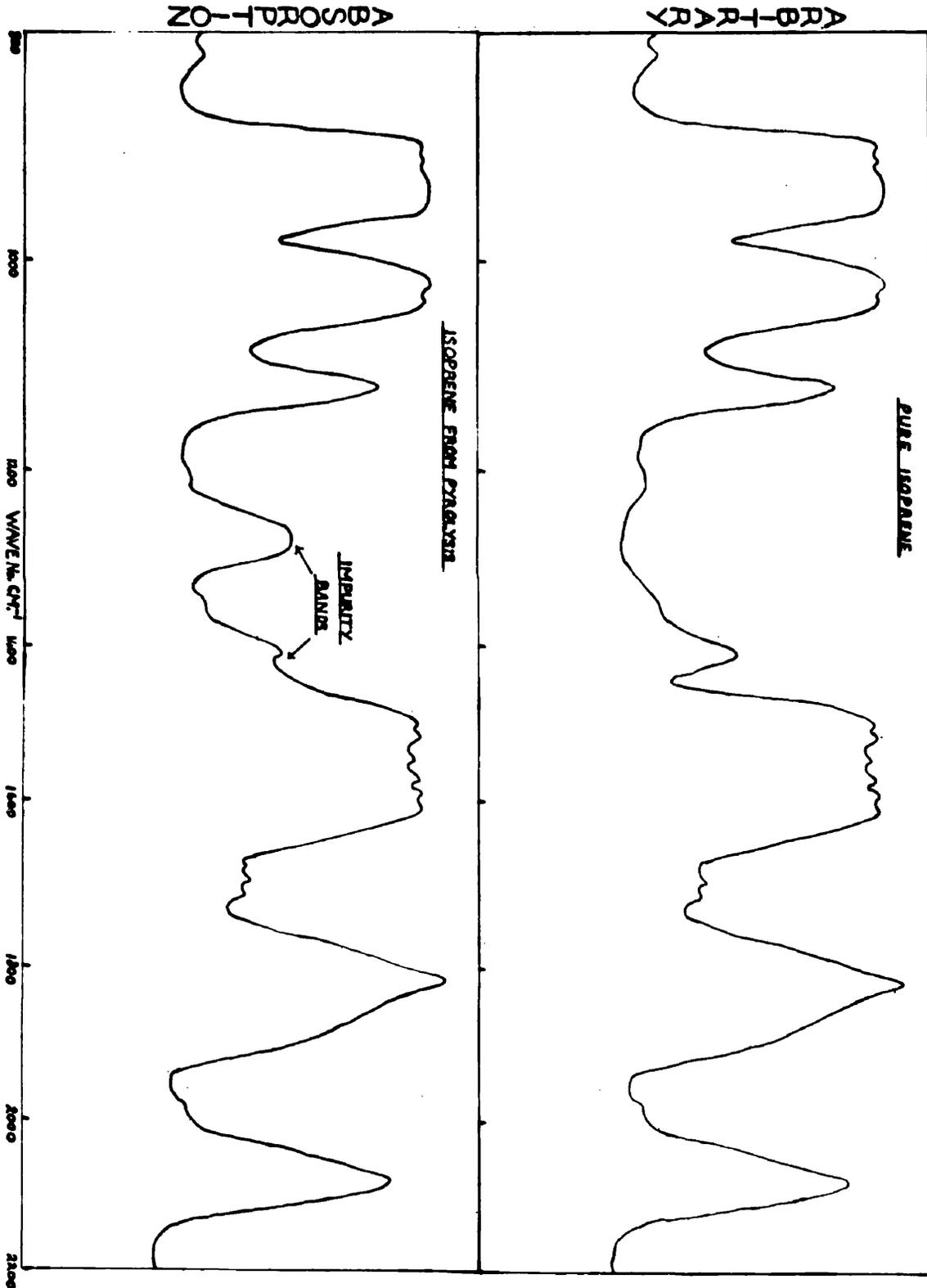
FIG.III

infra-red spectrum of this ketone was taken to help with the analysis of the pyrolysate of ethylene dimethacrylate.

(i) Vinyl isoButyrate.

This ester was prepared from vinyl acetate and iso-butyric acid via ester interchange (cf. Burnett and Wright[80]):-

$$CH_3.COO.CH{=}CH_2 + \underset{CH_3}{\overset{CH_3}{>}}CH.COOH \rightleftharpoons \underset{CH_3}{\overset{CH_3}{>}}CH.COO.CH{=}CH_2 + CH_3.COOH$$
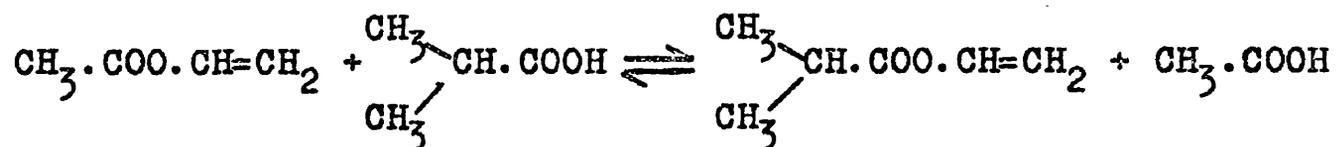
1 Mole of isobutyric acid was mixed with 3.5 moles of vinyl acetate; 0.1 g. of cupric acetate was added as an inhibitor to polymerisation. Ester interchange catalysts, mercuric acetate (3.5 g.) and conc. sulphuric acid (0.5 g.), were added slowly with moderate stirring. The whole was refluxed for three hours at 80°, then cooled and neutralised with excess sodium acetate. On distillation, after washing with dilute alkali to remove free acid, the vinyl isobutyrate was found to have a b.p. $105^o/760$ mm. This ester has been briefly described in patents[81], but no physical constants were quoted.

(ii) ß-Ethylacrylic Acid.

1 Mole of propionaldehyde, 1 mole of malonic acid, 0.75 mole of pyridine, and a trace of piperidine were heated on a water bath for 3 hours. The reaction is exothermic at first with the evolution of carbon dioxide:-

$$C_2H_5.CHO + CH_2\genfrac{}{}{0pt}{}{\diagup COOH}{\diagdown COOH} \longrightarrow C_2H_5.CHOH.CH\genfrac{}{}{0pt}{}{\diagup COOH}{\diagdown COOH}$$

$$-H_2O \Big\downarrow -CO_2$$

$$C_2H_5.CH=CH.COOH$$

ß-Ethylacrylic acid has been recorded in the literature to boil at 195-197° and 200-201°.   The mixture was distilled collecting fraction b.p. 195-201°.   This fraction was washed with dilute hydrochloric acid to remove remaining pyridine and was finally redistilled.   The boiling range of 195-201° is attributed to the ß-ethylacrylic acid being a mixture of _cis_ and _trans_ isomers.

(iii) ß-Ethyl Ethacrylate.

        This ester was prepared simply by esterifying part of the above ß-ethylacrylic acid.   5 g. of ß-ethylacrylic acid were refluxed with 5 g. of ethanol and 1.5 g. of conc. sulphuric acid for 4 hours:-

$$C_2H_5.CH=CH.COOH + C_2H_5OH \longrightarrow C_2H_5.CH=CH.COOC_2H_5 + H_2O$$

ß-Ethyl ethacrylate is recorded in the literature to have a b.p. 155-160°.   The products were dissolved in ether and washed with water to remove sulphuric acid.   The extract was dried over calcium chloride collecting fraction b.p. 155-160°.

(iv) Vinyl Methacrylate.

        Vinyl methacrylate was prepared by the same method

described above for vinyl isobutyrate except that methacrylic acid was used instead of isobutyric acid:-

$$CH_3.COO.CH=CH_2 + CH_2=\underset{\underset{CH_3}{|}}{C}.COOH \rightleftharpoons CH_2=\underset{\underset{CH_3}{|}}{C}.COO.CH=CH_2 + CH_3.COOH$$
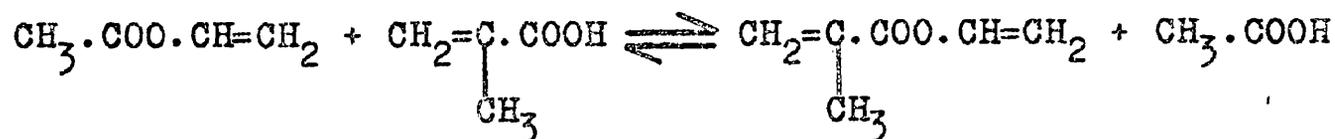
The vinyl methacrylate was found to have a sharp b.p. of $110^\circ/$ 760 mm., which is close to, but not quite in agreement with the work of Bauer and Kautter[82], who recorded a b.p. of $112^\circ/760$ mm.

(v) 2.5 Dimethyl Hexa-1.5-Diene.

This unsaturated hydrocarbon was prepared by a Wurtz reaction. 1 Mole of 3-chloro-2-methylpropene was added to a 5% molar excess of sodium wire suspended in dry ether. 2% ethyl acetate was added as a catalyst to the reaction:-

$$CH_2=\underset{\underset{CH_3}{|}}{C}.CH_2.Cl + 2Na + Cl.CH_2.\underset{\underset{CH_3}{|}}{C}=CH_2 \rightarrow CH_2=\underset{\underset{CH_3}{|}}{C}.CH_2.CH_2.\underset{\underset{CH_3}{|}}{C}=CH_2 + 2NaCl$$
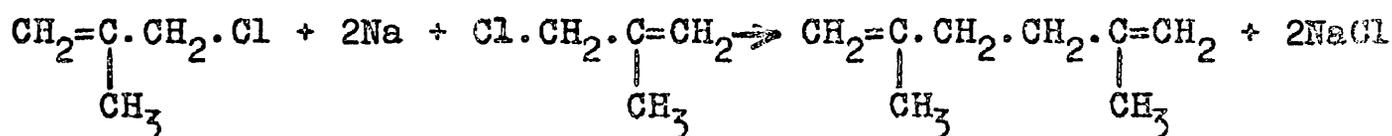
The mix was heated until reflux commenced, the heating being cut off at this point as the reaction proceeded exothermically. The mixture was allowed to cool overnight and the ether was distilled off. The liquor was then refluxed for a further hour. On cooling the liquor was decanted off and the excess sodium was dissolved in alcohol. The liquor was finally distilled using a long packed fractionating column and a high reflux ratio, collecting fraction b.p. $113-114^\circ/760$ mm. (n_D^{22} 1.4306). Literature reference quotes b.p. $113-114^\circ/760$ mm. (n_D^{20} 1.4309)

(vi) <u>2-Methyl-But-1-enal.</u>

This unsaturated alcohol was prepared by the following three stage synthesis from 3-chloro-2-methylpropene:-

$$CH_2=C.CH_2.Cl$$
$$\quad|$$
$$\quad CH_3$$
3-Chloro-2-methylpropene.

$$PhNO_2 \Big\Downarrow Cu_2(CN)_2$$

$$CH_2=C.CH_2.CN$$
$$\quad|$$
$$\quad CH_3$$
3-Cyano-2-methylpropene.

$$\Downarrow KOH/H_2O$$

$$\Downarrow H_2SO_4/H_2O$$

$$CH_2=C.CH_2.COOH$$
$$\quad|$$
$$\quad CH_3$$
<u>iso</u>Propenylacetic acid.

$$\Downarrow LiAlH_4$$

$$CH_2=C.CH_2.CH_2OH$$
$$\quad|$$
$$\quad CH_3$$
2-Methyl but-1-enal.
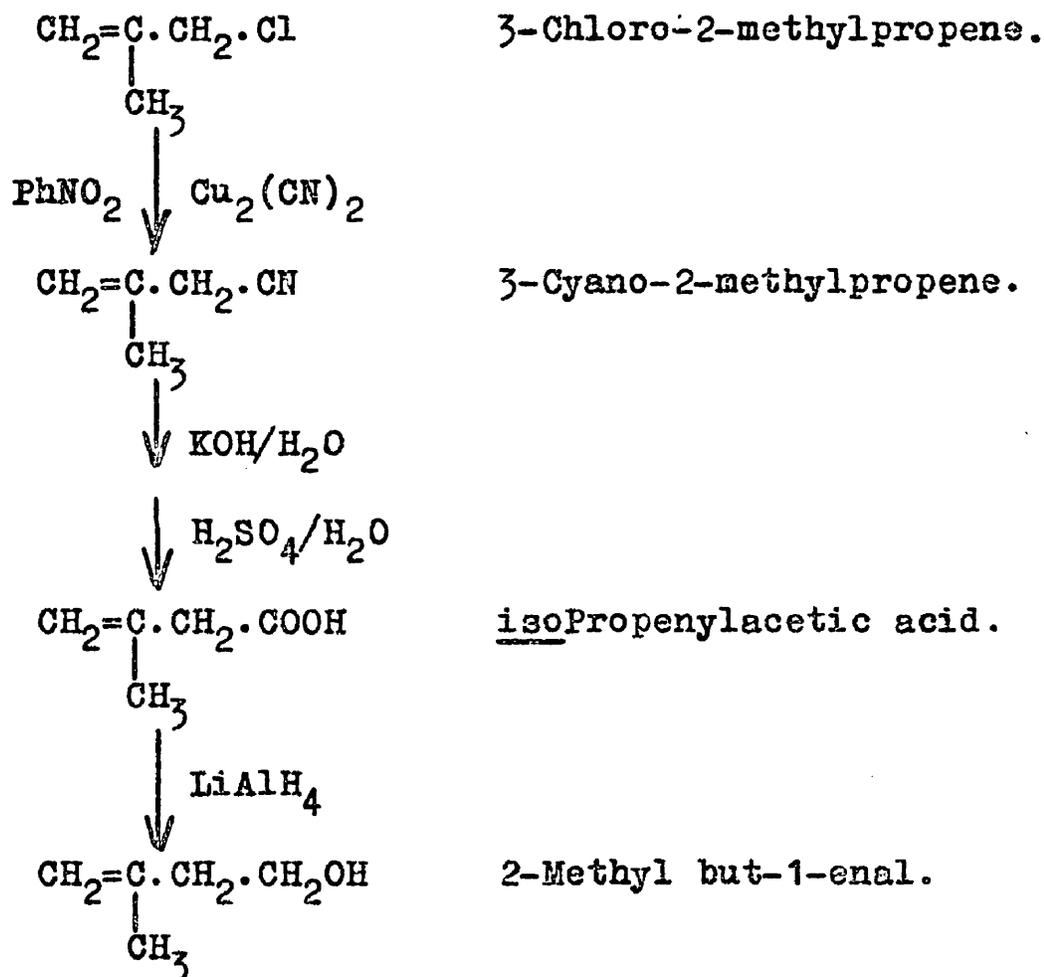
The first stage of the synthesis, the preparation of the nitrile intermediate, was the method used by Famele, Ott, Marple, and Hearne[83]. Three moles of cuprous cyanide were heated in 400 ml. nitrobenzene at 125-130°. Three moles of 3-chloro-2-methyl-propene were added slowly in portions of 25-30 ml. allowing time for the reaction to take place. The mixture was refluxed for 45 minutes, cooled, and the liquor filtered off. The liquor was then slowly distilled using a long packed column and collecting fraction b.p. 134.5 - 136.5°/760 mm.

The second stage, the preparation of the acid intermediate, was carried out by hydrolysing the nitrile with a 50% molar excess of water and potassium hydroxide.   This hydrolysis was carried out in a reflux medium of ethylene glycol to raise the reaction temperature.   The mixture was refluxed for 5 hours, cooled, and acidified with dilute sulphuric acid.   The iso-propenylacetic acid was ether extracted and redistilled collecting fraction b.p. 115-118°/25 mm.(literature ref.).

The final stage, the preparation of 2-methyl but-1-enal, was carried out by reducing the isopropenylacetic acid with lithium aluminium hydride using the method of Nystrom and Brown[84].   The alcohol was found to have a b.p. 130°/760 mm., C - 69.81, H - 11.62% (Calc. for $C_5H_{10}O$, C - 67.65, H - 11.94%).   The low overall yield did not permit further purification; however, infra-red evidence (see page 92) indicated that 2-methyl but-1-enal had been prepared by the above three stage synthesis.

(vii) Poly(ethylene Fumarate).

1 Mole of maleic anhydride was heated in nitrogen for nine hours at 200° with a 5% molar excess of ethylene glycol. The reaction was carried out in a four-neck Pyrex flask to allow for the following attachments - nitrogen inlet, stirrer, thermometer, and a stillhead attached to a condenser, which formed the nitrogen outlet and condensed off the water formed in the polyesterification:-

$$\begin{array}{c} \text{CH.CO} \\ \| \qquad \rangle \text{O} \\ \text{CH.CO} \end{array} \quad + \quad \begin{array}{c} \text{HO.CH}_2 \\ | \\ \text{HO.CH}_2 \end{array}$$

$$\downarrow$$

$$\text{HO} \left[\text{CH}_2 . \text{CH}_2 . \text{OOC} . \text{CH=CH} . \text{COO} \right]_n \text{H}$$
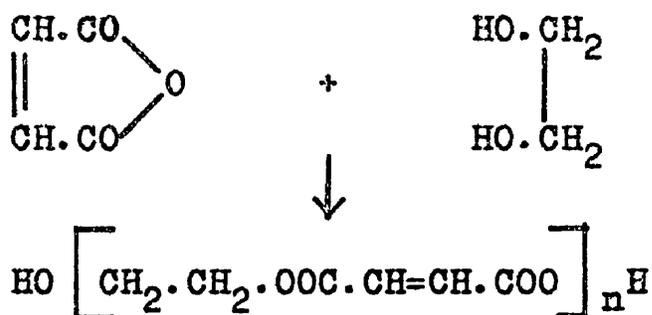
Cryoscopic determinations[85] on the polyester showed that it had a degree of polymerisation (D.P.$_n$) <u>ca</u>. 2-9. The configuration (as discussed on page 20) is essentially <u>trans</u>.[43,48,49]

7.7: Experimental Results for the Pyrolysis of Model Compounds.

7.7.1: Vinyl Acetate and Vinyl isoButyrate.

Table 1.

Pyrolysand	Vinyl Acetate							Vinyl iso-butyrate
Pyrolysis No.	1	2	3	4	5	6	7	8
Reactor	P.1	P.1	P.1	P.1	S	S	V	P.2
Temp.(^{o}C.)	550	550	550	550	500	500	550	550
Feed Rate (g./min.)	0.15	0.16	0.33	0.35	0.57	0.76	0.34	0.08
Contact Time (secs.)	83	79	38	36	22	16	40	82
Nitric Oxide Added (ml.)	nil	nil	800	40	nil	nil	nil	nil
Weight Pyrolysed (g.)	82	85.8	100	103	102	91.1	86	9.2
(a) Liquid Pyrolysate (g.)	49.5	60.6	49.3	45	13.9	13.8	54	5.6
(b) Gaseous Pyrolysate (L.)	10.2	13.4	27.2	43	94.5	58	25.6	2.1
% Composition of (b):								
Carbon Dioxide	4.1	3.3	3.6	4.0	2.6	7.5	3.2	2.4
Carbon Monoxide	86.2	88	75	67.2	39.4	36	81.7	67.5
Hydrogen	nil	nil	nil	nil	46.1	45	nil	nil
Methane	5.1	5	14.5	21.5	11.5	10	8.2	18.9
(c) Unsat.Hydrocarbons (total)	4.6	3.7	6.9	7.3	0.4	0.8	6.9	11.2
Approx. molar ratio of unsat. hydrocarbons in (c)								
Ethylene	0.61	–	0.68	0.61	–	–	.43	0.80
Propylene	0.09	–	0.06	0.14	–	–	.11	0.14
Acetylene	0.30	–	0.26	0.25	–	–	.46	0.06

Table 2.

Reaction-route Ratios in Pyrolysis of Vinyl Acetate and isoButyrate (550°).

Pyrolysis No.	Reactor	Ester	Additive	Route-ratio (molar)			
				A^2	B^1	C^2	R/C^1
1/2(av.)	P.1	Acetate	nil	0.03	0.47	0.03	0.47
3	P.1	"	NO (high)	0.02	0.32	0.01	0.65
4	P.1	"	NO (low)	0.12	0.34	0.02	0.52
7	V	"	nil	0.11	0.15	0.01	0.73
8	P.2	isoButyrate	nil	0.06	0.30	0.01	0.63

Pyrolysis at 420° and 700° (reactor P.1). Preliminary runs established the optimum temperature at ca. 550°, and showed that virtually no decomposition occurs at 420°, while at 700° strong secondary decompositions occur. For example, at 700°, propylene disappears from the pyrolysate and the methane content of (b) rises to ca. 25% owing to more complete breakdown of acetaldehyde, and, to a lesser extent, of propylene[86].

Pyrolyses 1 and 2 (reactor P.1). These two runs show that reasonably reproducible results can be obtained (Table 1). The two liquid pyrolysates were combined; distillation yielded:-

(i) Volatile fraction, b.p. 20°/660 mm.

(ii) Colourless liquid, b.p. 52-60°/760 mm.

(iii) Yellowish liquid, b.p. 62-87°/760 mm.

(iv) Cloudy yellow liquid, b.p. 97-114°/760 mm.

(i) Was mainly acetaldehyde; on bubbling the vapours through
a solution of 2:4-dinitrophenylhydrazine (D.N.P.), the
acetaldehyde derivative, m.p. 159° (mixed m.p. 158^{c}), was
obtained. (ii) Was mainly acetone; on continuous redistilla-
tion with ether, so that acetaldehyde would be removed by the
ether vapours, a sharp b.p. 56° was obtained and this gave the
acetone D.N.P. derivative, m.p. 126° (mixed m.p., 124°).
(iii) Was mainly unchanged vinyl acetate (ca. 22% of weight
pyrolysed); the fraction was unsaturated and polymerised on
heating with traces of benzoyl peroxide. (iv) Was mainly
acetic acid with traces of acetic anhydride: i.r. spectrum.
Keten was identified in the exit gases by passing these gases
into an aniline trap inserted in the gas line after the
Drikold trap. The products in the trap were acidified with
dilute hydrochloric acid. Excess aniline was dissolved as
aniline hydrochloride and the insoluble products were filtered
off. On recrystallisation from alcohol these products were
found to be acetanilide, m.p. 109° (mixed m.p. 109°). The
acetanilide establishes the presence of keten:

$$C_6H_5NH_2 + CH_2{=}C{=}O \longrightarrow C_6H_5NH.CO.CH_3.$$
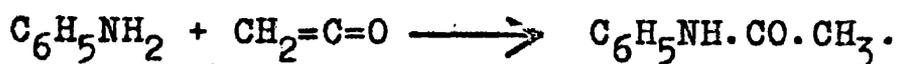
Ethylene, propylene, and acetylene were identified by i.r.
spectra. Acetylene was also characterized by bubbling the gases
through an ammoniacal solution of cuprous chloride; red cuprous
acetylide was deposited. No divinyl ether was detected in the

gases (i.r. spectrum).

Pyrolyses 3 and 4 (reactor P.1). In run 3 nitric oxide was progressively fed into the reactor along with the ester; in run 4, it was dissolved in the ester before feeding this into the reactor. The pyrolysates were qualitatively the same as in runs 1 and 2, but the reaction-route ratio was somewhat altered (Table 2, page 78). Less than 5% of unchanged ester was recovered in each run.

Pyrolyses 5 and 6 (reactor S). These duplicate runs again show reasonable reproducibility (Table 1, page 77). The liquid pyrolysates contained traces of water (anhydrous copper sulphate test); keten was absent from the gaseous pyrolysates.

Pyrolysis 7. Qualitatively, the results were the same as those of runs 1 and 2, but the reaction route ratio was somewhat altered (Table 2, page 78). High accuracy is not claimed for the ratios summarised in Table 2, but good approximations have been obtained by correlating the analyses of gas (b) with the weight of the fractions obtained from liquid (a).

Pyrolysis 8. The smallest reactor was used because of the small quantity of vinyl isobutyrate available; and the entire liquid pyrolysate was collected directly in the cold trap. Distillation of (a) yielded:-

(i)   Volatile fraction, b.p. $20^{\circ}/660$ mm.

(ii) Colourless liquid, b.p. $92-100^{\circ}/760$ mm.

(iii) Colourless liquid, b.p. $102-108^{\circ}/760$ mm.

(iv) Brownish liquid, b.p. $145-165^{\circ}/760$ mm.

(i) Was mainly acetaldehyde; on bubbling the vapours through a D.N.P. solution, the acetaldehyde derivative, m.p. 159° (mixed m.p. 158°), was obtained.   (ii) Was mainly methyl isopropyl ketone; D.N.P. derivative, m.p. and mixed m.p. 120°. (iii) Was mainly unchanged ester (ca. 7% of the weight pyrolysed); this was confirmed by the i.r. spectrum.   (iv) Was mainly iso-butyric acid, containing no isobutyric anhydride; this was confirmed by the i.r. spectrum.   In addition to the main compon-ents of the gaseous pyrolysate (b) listed in Table 1, page 77, the following three components were identified via the i.r. spectrum:- tetramethylethylene (2:3-dimethyl-but-2-ene) [bands at 1450 (s), 1390 (s), 1162 (s) cm.$^{-1}$] , 2-methylbut-1-ene [892 (w) cm.$^{-1}$] , and 2-methylbut-2-ene [804 (s) cm.$^{-1}$] . 3-Methylbut-1-ene could not be identified positively.

The gaseous pyrolysate (b) from runs 1, 2, 5, 6, 7, and 8 showed a strong band at 1140 cm.$^{-1}$ which still remains unassigned.

7.7.2: Ethyl Maleate.

Table 3.

Pyrolysis No.	9	10	11[x]
Reactor	V	V	V
Temperature	400°	450°	500°
Feed Rate (g./min.)	0.70	0.70	0.80
Contact Time (sec.)	41	41	47
Wt. Pyrolysed (g.)	77.5	100	172
Unchanged Pyrolysand	–	–	11
(a) Liquid pyrolysate (g.)	49	61	134.5
(b) Gaseous pyrolysate (L.)	11.8	24.9	27.0
% Composition of (b):			
CO	Trace	0.5	2.5
CO_2	14.3	15.7	17.6
CH_4	Trace	Trace	Trace
$CH_2=CH_2$	85.0	82.6	77.8
$CH_3 . CH=CH_2$	nil	nil	nil
$CH=CH$	0.5	1.0	2.0

x   Mass balance based on this run.

The first small crop of crystals from the liquid pyrolys-
ate (a) were filtered off and recrystallised from acetone/
petroleum ether.   These were found to be fumaric acid – sealed

tube m.p. 276-279° (mixed m.p. 279-281°). The liquid was fractionally distilled using a packed 6" fractionating column and cupric acetate as an inhibitor to polymerisation; the following fractions were yielded (i) b.p. 20°/660 mm., gaseous, (ii) b.p. 60-85°/760 mm., clear liquid, (iii) b.p. 95-105°/760 mm., clear liquid, (iv) b.p. 135-145°/760 mm., (v) b.p. 155-160°/760 mm., clear liquid, (vi) b.p. 190-205°/760 mm., clear liquid and white crystals, (vii) b.p. 205-220°/760 mm., clear liquid and white crystals, (viii) residual brown crystals.

(i) Was mainly acetaldehyde; on bubbling the vapour through a
   D.N.P. solution, the acetaldehyde derivative m.p. 154°
(mixed m.p. 155°) was obtained.

(ii) Was found to be <u>cis</u> and <u>trans</u> hex-3-ene and ethanol; the
   fraction was slowly redistilled under a high reflux ratio
using a 12" packed fractionating column; a few drops were taken
off at 67.5°, corresponding to the literature b.p. for hex-3-ene; refractive index was n_D^{20} 1.388 (lit. n_D^{20} 1.394) - the slight discrepancy n_D^{20} 0.006 could be attributed to traces of ethanol; the fraction was found to be unsaturated by bromine/carbon tetrachloride test. To confirm the presence of hex-3-ene the sample was subjected to infra-red analysis and compared with infra-red spectra of <u>cis</u> and <u>trans</u> hex-3-ene[87]. Corresponding peaks in the i.r. spectra were found at 1068 cm.$^{-1}$(m), 1149 cm.$^{-1}$(w), 1298 cm.$^{-1}$(m), 1325 cm.$^{-1}$(w), 1350 cm.$^{-1}$(w), 1406 cm.$^{-1}$(w), 1464 cm.$^{-1}$(m), and 1650 cm.$^{-1}$(m). The weak

bands at 1325 cm.$^{-1}$ and 1350 cm.$^{-1}$ were found in the reference
i.r. spectrum of _trans_ hex-3-ene but not in _cis_ hex-3-ene.
This would indicate the presence of _cis_ and _trans_ hex-3-ene in
the pyrolysate fraction.   The bulk of fraction (ii), however,
distilled at 76-80°/760 mm., and was identified as ethanol _via_
its 3:5 dinitrobenzoate derivative m.p. 86° (mixed m.p. 87°).

(iii) Was found to be water and ethyl acrylate.   Water was
detected by heating the fraction with phenyl _iso_cyanate
forming diphenyl urea m.p. and mixed m.p. 239°;   water was
further confirmed by the anhydrous copper sulphate test.   The
fraction was dried over calcium chloride and redistilled
collecting fraction b.p. 100-101°/760 mm.   This was found to
be ethyl acrylate (i.r. spectrum).

(iv)   Was redistilled collecting fraction b.p. 140°/760 mm.;
this was found to be acrylic acid (i.r. spectrum).

(v)   Was redistilled collecting fraction b.p. 155-160°/760 mm.;
this was found to be ß-ethyl ethacrylate (i.r. spectrum).

(vi)   The crystals were filtered off from this fraction and the
liquor was twice distilled collecting fraction b.p. 197-
201°/760 mm.;   this was found to be ß-ethylacrylic acid (i.r.
spectrum).

(vii) The crystals were filtered off from this fraction and the
liquor was washed with alkali, water, and dried over
calcium chloride.   Redistillation gave a fraction b.p. 210-214°/

760 mm. Infra-red analysis showed this to be unchanged ethyl maleate and ethyl fumarate (ca. 3:1 respectively). The absorption band corresponding to fumarate (975 cm.$^{-1}$) was quite distinct (cf. Fig.II page 69).

(viii) Was impure residual crystals and was pooled together with the crystals collected from (vi) and (vii). The combined crystal fractions were purified by sublimation in vacuo and were found to be maleic acid and maleic anhydride. The crystals were warmed in ether and cooled. The insoluble crystals were filtered off and the mother liquor was evaporated to dryness to yield a further crop of crystals. The crystals insoluble in ether were recrystallised from ether/benzene and were found to be maleic acid m.p. and mixed m.p. 135°. The crystals obtained from the ethereal mother liquor were further recrystallised from ether and were found to be maleic anhydride m.p. 52° (mixed m.p. 54°). The above analyses of maleic acid in maleic anhydride make use of the fact that maleic anhydride is slightly soluble in ether, while the acid is virtually insoluble in ether.

Methane could only be detected in the gaseous pyrolysate (b) by the i.r. spectrum.

7.7.3: Methyl Methacrylate (A), Ethyl Methacrylate (B), Methyl Formate (C), Ethyl Formate (D), Methacrylic Acid (E), and Methacrolein (F).

<u>Table 4.</u>

Pyrolysand	A	B	C	D	E	F
Run No.	12	13	14	15	16	17
Reactor	V	V	V	V	V	V
Temp. (^{o}C)	500	500	500	500	500	500
Feed Rate (g./min.)	0.22	0.29	0.32	0.33	0.31	0.21
Contact Time (secs.)	60	57	27	33	40	49
Weight Pyrolysed (g.)	63.1	60.0	46.0	33.0	60.0	33.0
% Unchanged Pyrolysand	<u>ca.</u>65	Traces	<u>ca.</u>40	nil	<u>ca.</u>81	<u>ca.</u>21
(a) Liquid Pyrolysate (g.)	47.8	41.6	25.0	3.9	55.3	18.2
(b) Gaseous Pyrolysate (L.)	8.1	15.1	15.0	25.6	4.4	9.5
% Composition of (b):						
CO	45.0	7.8	87.4	8.9	45.3	63.6
CO_2	17.5	6.1	4.3	26.5	35.8	0.0
$CH_2{=}CH_2$	–	83.3	nil	–	–	0.0
$CH_3.CH{=}CH_2$	–	2.2	nil	–	–	23.7
$CH{\equiv}CH$	–	0.5	nil	–	–	Trace
Total Unsats.	27.6	86.0	nil	45.2	18.9	23.7
H_2	0.0	0.0	2.9	11.5	0.0	0.0
Satd. Hydro-carbons	9.9	Trace	5.4	7.9	0.0	12.6

The liquid pyrolysate (a) of methyl methacrylate (A) was distilled using p-toluquinone as a polymerisation inhibitor; the vapours were passed through a D.N.P. solution. The formaldehyde derivative m.p. 162° (mixed m.p. 161°) was obtained. The pyrolysate appeared to be mainly formaldehyde and unchanged ester, the condenser blocking with paraformaldehyde. There was no trace of methacrolein; this was believed to have broken down at 500° to propylene and carbon monoxide :-

$$CH_2=C.CHO \longrightarrow CH_3.CH=CH_2 + CO$$
$$\underset{CH_3}{|}$$
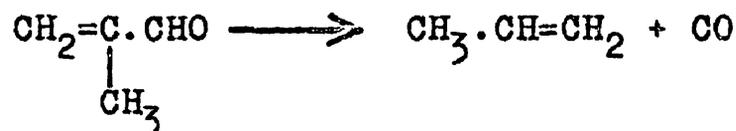
The i.r. spectrum of the gaseous pyrolysate (b) showed the presence of propylene and <u>iso</u>butene.

The liquid pyrolysate (a) of ethyl methacrylate (B) was distilled using p-toluquinone as a polymerisation inhibitor; the following fractions were collected:-

(i)   Volatile fraction, b.p. 20°/660 mm.
(ii)   Clear liquid, b.p. 27-38°/760 mm.
(iii)   Clear liquid, b.p. 50-60°/760 mm.
(iv)   Clear liquid, b.p. 60-76°/760 mm.
(v)   Clear liquid, b.p. 95-105°/760 mm.
(vi)   Clear liquid, b.p. 112-125°/760 mm.
(vii)   Clear liquid, b.p. 125-145°/760 mm.
(viii) Clear liquid, b.p. 155-165°/760 mm.

(i) Was mainly acetaldehyde; on bubbling the vapours through a D.N.P. trap, the acetaldehyde derivative, m.p. 159°(mixed m.p. 158°), was obtained.   (ii) Was found to be mainly 2-methylbut-1-ene; the vapours were evacuated into a sodium

chloride cell and were found to be 2-methylbut-1-ene on i.r. evidence. (iii) Was found to be mainly acetone on i.r. evidence. (iv) Was found to be mainly methacrolein; the fraction was redistilled collecting the major portion b.p. 66-70°/760 mm. This gave the methacrolein derivative with D.N.P., m.p. and mixed m.p. 190°. (v) Was found to be mainly water by the anhydrous copper sulphate test. (vi) Was found to be mainly unchanged ester on i.r. evidence. (vii) Was not definitely characterised, but gave a derivative with D.N.P. indicating the presence of a carbonyl compound, possibly diisopropenyl ketone. This same compound was found in the liquid pyrolysate (a) of methacrylic acid. (viii) Was the main fraction and was found to be mainly methacrylic acid on i.r. evidence. The i.r. spectrum of the gaseous pyrolysate (b) showed that the main gaseous product was ethylene, small quantities of propylene, traces of acetylene, and traces of methane.

The liquid pyrolysate (a) of methyl formate (C) was redistilled; the vapours were passed through a D.N.P. solution yielding the formaldehyde derivative m.p. 162° (mixed m.p. 162°). The liquid pyrolysate (a) was mainly unchanged ester and methanol; the 3.5 dinitrobenzoate of methanol, m.p. and mixed m.p. 108° was obtained.

Ethyl formate (D) was found to be very unstable on pyrolysis. There was no evidence to suggest that the pyrolysis was other than that previously described by Mackens and Eversole[66].

The liquid pyrolysate (a) of methacrylic acid (E) was

redistilled collecting the following fractions:-

(i)   Clear liquid, b.p. 50-60°/760 mm.

(ii)   Clear liquid, b.p. 95-105°/760 mm.

(iii) Clear liquid, b.p.125-145°/760 mm.

(iv)   Clear liquid, b.p.155-165°/760 mm.

(i)   Was found to be mainly acetone on i.r. evidence.
(ii) Was found to be mainly water by the anhydrous copper
sulphate test.   (iii) Was found to be the same carbonyl com-
pound, possibly diisopropenyl ketone, as was found in the
pyrolysate of ethyl methacrylate.   (iv) Was found to be
unchanged acid on i.r. evidence.   Anhydrides could not be
detected in the liquid pyrolysate (a).   The i.r. spectrum of
the gaseous pyrolysate (b) showed the presence of propylene
with traces of acetylene.

As previously described on page 50 the exact pyrolysis of
methacrolein (F) is somewhat obscure.   The i.r. spectrum of
the gaseous pyrolysate (b) showed that the unsaturated portion
was mainly propylene with traces of acetylene.

7.7.4: Ethylene Dimethacrylate.

Table 5.

Run No.	18	19	20[x]
Reactor	V	V	V
Temperature (°C)	500	500	500
Feed Rate (g./min.)	0.38	0.32	0.31
Contact Time (secs.)	75	90	93
Weight Pyrolysed (g.)	100	100	156
% Unchanged Pyrolysand	–	–	15
(a) Liquid Pyrolysate (g.)	63.6	61.9	97
(b) Gaseous Pyrolysate (L.)	25.8	22.6	35.3
% Composition of (b):			
CO	29.1	29.9	29.4
CO_2	36.5	35.5	36.6
$CH_2{=}CH_2$	nil	nil	nil
$CH{\equiv}CH$	2.1	2.4	2.2
$CH_2{=}C(CH_3)_2$	8.3	8.8	8.4
$CH_3CH{=}CH_2$	11.7	11.4	12.4
Total Unsats.	22.1	22.6	23.0
H_2	nil	nil	nil
Satd. Hydrocarbons	12.3	12.0	11.0

[x] Mass balance based on this run.

The liquid pyrolysate (a) was distilled using cupric acetate and hydroquinone as polymerisation inhibitors; the following fractions were collected:-

(i)   Volatile fraction, b.p. 20°/660 mm.

(ii)   Clear liquid, b.p. 30-40°/760 mm.

(iii) Clear liquid, b.p. 50-60°/760 mm.

(iv)   Clear liquid, b.p. 60-76°/760 mm.

(v)   Clear liquid, b.p. 95-105°/760 mm.

(vi)   Clear liquid, b.p.105-120°/760 mm.

(vii) Clear liquid, b.p.120-145°/760 mm.

(viii) Clear liquid, b.p.155-165°/760 mm.

(ix)   Clear liquid, b.p. 70-80°/20 mm.

(x)   Clear liquid, b.p.110-125°/13 mm.

(xi)   Yellow liquid,b.p. 80-100°/11 mm.

(This fraction polymerised on standing)

(i)   Was mainly acetaldehyde; on bubbling the vapours through a D.N.P. trap, the acetaldehyde derivative, m.p. and mixed m.p.159°, was obtained.   (ii) Was found to be mainly isoprene on i.r. evidence (see Fig.III page 70).   (iii) Was mainly acetone; the acetone D.N.P. derivative, m.p.126° (mixed m.p.125°) was obtained.   (iv) Was mainly methacrolein; this gave the methacrolein D.N.P. derivative, m.p. and mixed m.p. 190°.

(v)   Was mainly water and methyl isopropenyl ketone; water was detected by the anhydrous copper sulphate test and the remainder of the fraction was dried over calcium chloride.   On redistillation, using cupric acetate as a polymerisation inhibitor, this

fraction was found to have a boiling range 98-102°. This was found to be methyl isopropenyl ketone on i.r. evidence.

(vi) Was found to consist of vinyl methacrylate with traces of 2.5 dimethyl hexa-1.5-diene; the fraction was redistilled from cupric acetate collecting the main portion b.p. 110-114°. On i.r. evidence this was found to be vinyl methacrylate with impurity bands corresponding to 2.5 dimethyl hexa-1.5-diene.

(vii) Was not definitely characterised, but it appeared to be isopropenyl acetaldehyde as its D.N.P. indicated that it was a carbonyl compound. The presence of isopropenyl acetaldehyde is postulated as its C[1] breakdown compound isobutene was detected in the gaseous pyrolysate (b).   (viii) Was found to be methacrylic acid on i.r. evidence.   (ix) Was found to be 2-methylbut-1-enyl methacrylate; this fraction was washed with dilute alkali to remove any free acid, and was redistilled from cupric acetate.   This fraction gave a strong colour test for the presence of ester linkages[88].   The ester was then saponified by refluxing for one hour with 30% potassium hydroxide in the presence of cupric acetate.   An alcohol, immiscible with water, was distilled off and the alkaline residue was acidified with 50% sulphuric acid, ether extracted, dried over calcium chloride, and the ether distilled off.   The residual acid was found to be methacrylic acid on i.r. evidence.   The ester is therefore a methacrylate.   The alcoholic fraction was separated from water and dried over calcium chloride.   On redistillation this fraction gave a b.p. 130° and was found to be identical

(on i.r. evidence) to synthetic 2-methylbut-1-enal. This fraction therefore appears to be 2-methylbut-1-enyl methacrylate. (x) Was mainly unchanged ester on i.r. evidence. (xi) Was believed to consist partially of methacrylic anhydride; the polymeric material which settled out on standing gave a faint colour reaction for an anhydride[54].

The analysis of the gaseous pyrolysate (b) was supplemented by a special technique to characterise isobutene. The gaseous pyrolysate (b) from run 19 was passed through the following purifying traps - 30% potassium hydroxide to remove carbon dioxide, ammoniacal cuprous chloride to remove carbon monoxide, 35% sulphuric acid to remove ammonia, and powdered calcium chloride to dry the gases. A red precipitate of cuprous acetylide was obtained in the second trap confirming the presence of acetylene. The scrubbed gases were passed through a cold trap maintained at -40°, to condense out isobutene b.p. -6° and allow propylene b.p. -47.8° to pass on; ca. 2-3 mls. of condensate were obtained. Non-condensible gases were blown off in a stream of nitrogen and the condensate was then raised to 10° to boil off isobutene. The vapours were drawn into an evacuated cell and i.r. analysis showed them to be pure isobutene. The total gas analyses of (b) were carried out using the standard Hempel Burette and a modified Orsat unit[77] for measuring unsaturated gases. This gas analysis system was further modified by introducing a special pipette for the quantitative analysis of isobutene. After removal of acetylene, the isobutene was

condensed out in a pipette maintained at -20° in a freezing bath.   The confining liquid in this pipette was a 25% solution of sodium acetate, which does not solidify at this temperature.

The cursory investigation of the pyrolysate of poly(ethylene fumarate) is described in the basic plan (page 20).

A P P E N D I X E S

I. New Infrared Data.

II. The Dermatitic Nature of Maleates and
Fumarates and/or their Pyrolytic
Breakdown Products.

Appendix I.

New Infrared Data.   The spectra of the following substances were measured, and do not appear to have been previously recorded:

Vinyl Acetate: 850(w), 881(m), 954(m), 980(w), 1023(s),
1142(s), 1230(s), 1304(w), 1376(m), 1442(w), 1685(m),
and 1800(s) cm.$^{-1}$.

Vinyl isoButyrate: 942(w), 1095(m), 1145(s), 1190(m),
1240(w), 1295(w), 1370(m), 1395(m), 1450(w), 1475(m),
1665(m), 1725(s), and 1760(s) cm.$^{-1}$.

ß-Ethylacrylic Acid: 843(w), 968(m), 1120(w), 1216(s),
1291(s), 1429(s), and 1692(s) cm.$^{-1}$.

ß-Ethyl Ethacrylate: 843(w), 968(m), 1037(s), 1120(m),
1178(s), 1262(m), 1380(w), 1465(w), 1668(m), and
1732(s) cm.$^{-1}$.

Methacrylic Acid: 825(w), 962(s), 988(w), 1225(s), 1325(s),
1395(w), 1440(s), 1668(s), and 1725(s) cm.$^{-1}$.

Ethylene Dimethacrylate: 825(m), 864(w), 902(w), 960(s),
1022(m), 1080(m), 1194(s), 1270(w), 1324(s), 1352(s),
1392(w), 1422(w), 1460(m), 1668(m), and 1775(s) cm.$^{-1}$.

Vinyl Methacrylate: 810(m), 873(m), 915(w), 953(s), 1018(m),
1162(s), 1234(m), 1337(s), 1403(w), 1429(w), 1471(m),
1687(m), and 1800(s) cm.$^{-1}$.

Methyl isoPropenyl Ketone: 943(m), 1018(m), 1154(s), 1330(m),
1372(s), 1452(m) and 1750(s) cm.$^{-1}$.

2.5 Dimethyl Hexa-1.5-Diene: 880(s), 1314(w), 1396(m),
1453(s), 1694(m), and 1840(w) cm.$^{-1}$.

Appendix II

The Dermatitic Nature of Maleates and Fumarates and/or their Pyrolytic Breakdown Products.

Work on the pyrolysis of maleate and fumarate esters was greatly hindered by the onset of contact dermatitis. The irritant effect was particularly noticeable when working with ethereal solutions of fumarates. This is probably due to the dissolving of the natural skin oils in the ether leaving the skin unprotected from the fumarate ester. The author handled ethyl maleate and fumarate and their decomposition products for fully a year before any irritation began. Once the rash broke out, it spread rapidly from small pimples, barely visible, to large blisters filled with a watery fluid. On breaking, these blisters left a sore which was particularly slow in healing. The methyl maleate and fumarate esters appeared to be more dermatitic than the ethyl esters; one worker was troubled with a severe rash within several days of handling the methyl esters.

There has been some controversy as to whether the esters themselves or their breakdown products cause the irritation. The author observed that on handling the isolated breakdown products, the dermatitic attack was not noticeably fast; however, on handling the original maleate and fumarate esters, even the vapours had a powerful irritant effect.

Once dermatitis has been caused by maleates and fumarates,

the range of chemicals which the person handles must be greatly reduced as he becomes susceptible to contact dermatitis from a wide and unspecific range of chemicals. Even a hard water can then induce a mild form of dermatitis.

It must be emphasised that the dermatitic attack varies widely from person to person. For example, the author and a colleague were both susceptible to dermatitic rashes from maleates and fumarates, yet the author could handle acrylates with impunity while his colleague suffered an even more severe rash on handling acrylates.

As there is no specific form, observed as yet, for this type of dermatitis, there is consequently no specific cure short of not handling the materials in question. It was observed, however, that in one case "Rozalex" barrier cream (wet work grade) had a fair degree of curing power together with excellent barrier properties. It is best used after work, cleaning one's hands first with soap and water, followed by washing the hands with cotton wool soaked in ethanol.

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THE SYNTHESIS OF VINYL KETONES

by

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Summary.

A study has been made of some of the physical aspects of the vapour-phase pyrolysis of vinyl benzoate, which is known to undergo thermal degradation by three primary routes, viz. :-

$$Ph.CO.O.CH=CH_2 \longrightarrow \begin{cases} Ph.CO.OH + CH \equiv CH & - - - - A^2(c) \\ Ph.CH=CH_2 + CO_2 & - - - - - C^2(c) \\ (Ph.CO.CH_2.CHO) & - - - - - R \\ \qquad \downarrow \\ Ph.CO.CH_3 + CO & - - - - - C^1(c) \end{cases}$$
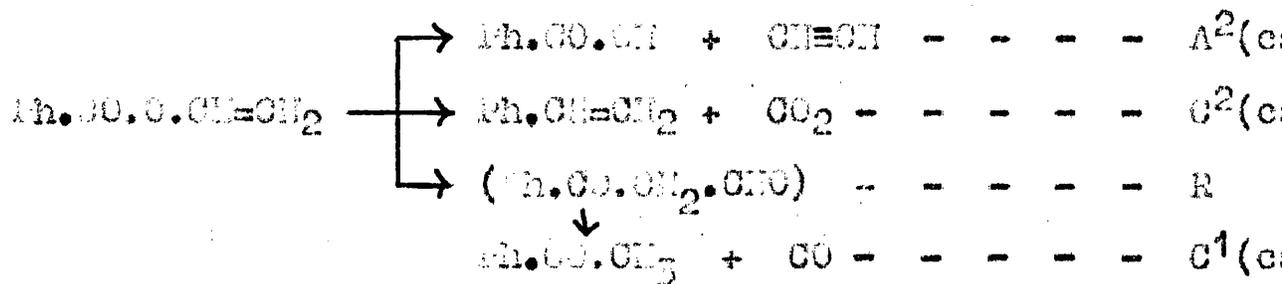
Because of the involatile nature of vinyl benzoate, a simple technique has been devised whereby the rate of degradation of the ester has been measured empirically by following the rate of gas evolution from a reactor containing the vapourised ester together with a quantity of liquid reflux. Rates under different conditions have been thus measured and compared against a standard rate. The reaction has also been examined by analysis of the pyrolysate gases. These investigations have been carried out at temperatures of about $520^{\circ}C$. An unsuccessful effort to isolate the intermediate benzoylacetaldehyde in route R by pyrolysis under mild conditions is reported.

The major findings of the investigation are :-

(i)　The vapour-phase pyrolysis of vinyl benzoate is
a predominately homogeneous reaction.　The major
route B/C^1 and the minor route A^2 are essentially
completely homogeneous.　The minor route C^2 is
mainly homogeneous, but exhibits some degree of
heterogeneous decomposition at a glass surface.

(ii)　Free-radical chain processes play no appreciable
part in the reaction scheme, and it is concluded that
all three routes proceed _via_ molecular mechanisms.
In particular, although no new evidence has been
found for the existence of benzoylacetaldehyde as
an intermediate in the major route, it is nevertheless
concluded that the ketoaldehyde is formed in the
course of the reaction, but in a labile state such
that it is incapable of free existence in these
present circumstances.

(iii)　The rate of degradation is severely checked
in a carbonised reactor, the retardation being partly
due to the carbonaceous deposits, and partly due to
the presence of one of the products of the reaction,
benzoic acid, which is found to have an anti-catalytic
effect upon the reaction.

(iv)　The pyrolysis of vinyl benzoate is mildly
catalysed by iodine.　The pyrolysis of the major
reaction product, acetophenone, is strongly catalysed

by iodine.

A short study of the vapour-phase pyrolysis of vinyl acetate has also been made, again by measuring the rate of gas evolution, at temperatures of between 625-920°C. The overall reaction is homogeneous in a silica reactor. No evidence has been found for the existence of free-radical chains in the reaction scheme.