THE DEGRADATION OF POLYMERS AND RELATED MODEL COMPOUNDS

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by

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SUMMARY

This work describes the investigation of the physico-chemical aspects of the thermal degradation of PVC and related short-chain compounds (telomers).

The latter, made with a chain transfer agent such as bromotrichloromethane, consist of either one or two molecules of vinyl chloride joined to a molecule of bromotrichloromethane e.g. $Cl_3C-CH_2-CHCl-CH_2-CHClBr$

A system has been devised whereby the rates of degradation of these polymers and telomers can be followed empirically by titrating the quantity of acid evolved against standard alkali.

The major processes occurring in the degradation of PVC are dehydrochlorination and cross-linking, found to be first and second order processes respectively. Cross-linking is thought to be a random process of condensation between molecules, the rate at which it proceeds being dependent on such variables as polymer concentration and chain length. Dehydrochlorination is believed to commence at the chain ends, "zipper" down the chain and terminate at a cross-link. It is dependent on polymer concentration but not on chain length. Of the two processes, it is energetically easier for cross-linking to occur. There is

no evidence to suggest that the degradation of the polymer is free radical in nature as is believed by some workers.

In a parallel study on model compounds of PVC, the major factor influencing the pyrolysis was the reactivity of the $-CCl_3-$ group. Due to this reactivity no true comparison could be made between these compounds and the high polymer although breakdown rates for the telomers are of the same order as those for the cross-linking of PVC, indicating that intermolecular condensation is occurring between telomer molecules. The latter is thought to cause polymer formation.

There is no reason to suppose that the decomposition of these compounds is free radical, although the breakdown may be partially ionic in character.

CONTENTS

Page

Effect of Additives

Effect of Additives

CHAPTER I.

Introduction.

With the rise of the plastics industry, much research has been concentrated on the thermal breakdown of synthetic high polymers. In recent years, work has been carried out on polymers such as polyethylene, polyacrylonitrile, polystyrene and polyvinyl chloride which have become available to a wide public.

In particular, the pyrolysis of polyvinyl chloride (PVC) has been studied extensively, because this polymer breaks down very easily indeed under comparatively mild thermal conditions such as those encountered in its manufacture and fabrication. There is, however, a great diversity of opinion as to the interpretation of the results of this study, so complex is the breakdown of the polymer.

In this study of the breakdown of PVC, the approach adopted was to prepare model compounds possessing the basic structure contained in the high polymer. It was hoped that the pyrolysis of these compounds would throw some light on the degradation of the high polymer. Model compounds were chosen because they are chemically simpler then the high polymer. They do not contain such structural defects as chain branching which may encourage side reactions to occur, thus obscuring the true nature of the pyrolysis. Furthermore if the compounds are of very low molecular weight, degradation cannot proceed by the so-called "zipper" mechanism although some type of chain mechanism is possible. On the other hand, it is not always possible to say just how much of the information obtained is applicable to the high polymer.

Unfortunately the use of model compounds did not prove as fruitful as hoped. It was not possible to isolate compounds in the intermediate molecular weight range, i.e. of degree of polymerisation greater than 2 but less than 100 in a pure state. The problem was therefore attacked from another angle, and it was decided to study the breakdown of the high polymer. Pyrolysis of the latter was carried out in solution because observations could be made regarding cross-linking and gelation. Rate dependences on polymer concentration could also be determined for low conversions. Degradation in solution also eliminates possible difficulties such as diffusion control of the reactions, and poor heat transfer to the polymer.

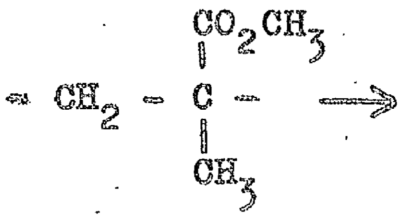
Literature Survey.

A general study of the thermal degradation of high polymers reveals that there are various reactions which can occur and these may be classified as follows:

Chain Scission Reactions	1. Depolymerisation 2. Random Chain Scission
Non, Chain Scission Reactions	3. Side Group Elimination 4. Cross-Linking and Molecular Rearrangement.

1. Depolymerisation

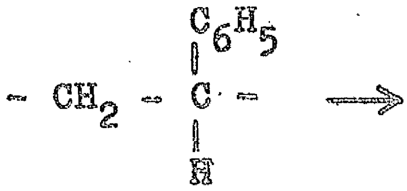
This process is the reverse of polymerisation, polymer being degraded to the monomer. Depolymerisation is regarded as a radical process, involving initiation, depropagation and termination. The yield of monomer obtained from the polymer varies greatly with the structure of the latter e.g. for polymethyl methacrylate



$$-CH_2-\overset{\overset{\displaystyle CO_2CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}- \longrightarrow$$

Monomer yield greater than 90%

Polystyrene produces a complex mixture of molecules of intermediate size:



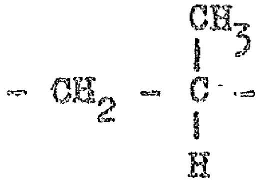
$$-CH_2-\overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}- \longrightarrow$$

Monomer yield greater than 65% plus a mixture of dimer, trimer and tetramer, etc.

2. Random Chain Scission.

The main difference between depolymerisation and random chain scission is that in the former the main product is monomer, whilst in the latter the polymer is split up into chain fragments which are many times bigger than the monomer. A very small quantity of monomer is usually present in random chain scissions.

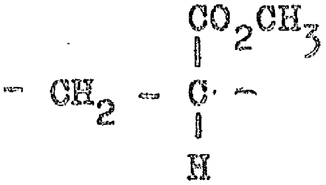
e.g. polypropylene



$$-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}- \longrightarrow$$

Mixture of large chain fragments with a minute quantity of monomer.

and in the case of polymethyl acrylate



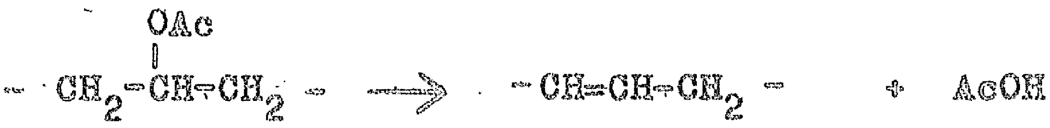
$$-CH_2-\overset{\overset{\displaystyle CO_2CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}- \longrightarrow$$

Monomer yield of 1% and larger chain fragments.

Whether a polymer will yield mainly monomer or an assortment of chain fragments depends upon factors such as the heat of polymerisation, steric hindrance, etc.

3. Side Group Elimination.

There are a few polymers in which the main polymer backbone remains unbroken during pyrolysis. The polymer, however, loses side groups in the form of acids. Thus polyvinyl acetate loses acetic acid, simultaneously forming a double bond in the polymer molecule

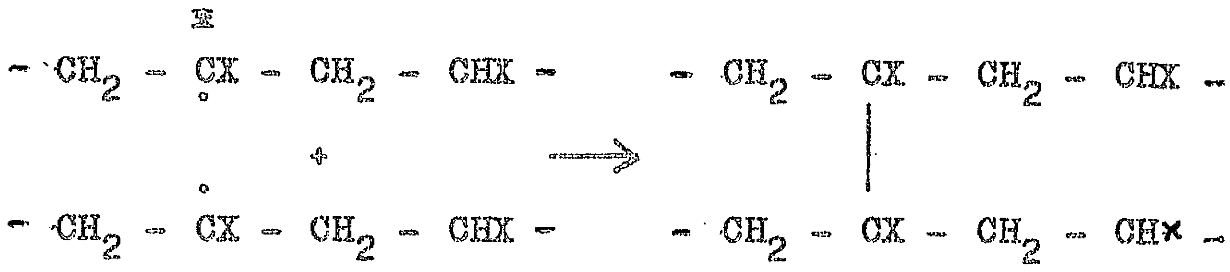


$$-CH_2-\overset{\overset{\displaystyle OAc}{|}}{CH}-CH_2- \longrightarrow -CH{=}CH-CH_2- \quad + \quad AcOH$$

This type of reaction can take place at temperatures as low as 160°C, and the ability of the reaction to occur so readily is a function of the polymer structure.

4. Cross-Linking and Molecular Rearrangement.

Here two molecules of the polymer combine to give a larger molecule which, in turn, can combine with other molecules eventually yielding a polymer network. In a radical reaction involving a vinyl polymer, the following type of mechanism has been suggested by Grassie(1)



$$\begin{array}{c} -CH_2-\overset{x}{\underset{\cdot}{C}}X-CH_2-CHX- \\ + \\ -CH_2-\overset{\cdot}{C}X-CH_2-CHX- \end{array} \longrightarrow \begin{array}{c} -CH_2-CX-CH_2-CHX- \\ | \\ -CH_2-CX-CH_2-CHX- \end{array}$$

Having examined the possible reactions which can occur in thermal degradations, attention may now be focussed on the particular study of PVC. Detailed research has shown that the pyrolysis of the polymer proceeds through the stages of side group elimination or dehydrochlorination[xx], cross-linking and random chain scission. It is convenient at this point to survey past studies of these reactions according as they were carried out in an atmosphere of nitrogen or oxygen.

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[x] The dot above, below or at the side of any atom denotes the free radical state.

[xx] The process of removing HCl from a molecule such that a double bond is produced therein i.e.

$$-CH_2-CHCl-CH_2-CHCl- \longrightarrow -CH{=}CH-CH_2-CHCl- + HCl$$

Dehydrochlorination in Nitrogen

Early work on the dehydrochlorination of PVC noted that HCl was evolved and the polymer coloured, becoming yellow initially, then reddish brown, dark brown and finally black.

Lewis and Calvin(2) were among the first to suggest that the colouring of the polymer results from the formation of conjugated double bonds. They claimed that a minimum of seven double bonds is necessary for colour formation, and such a sequence implies the removal of the HCl present in a systematic fashion. Hauser(3) compared the colour intensities of samples of degraded PVC with those of the diphenyl polyenes and pointed out the similarity between them.

The expulsion of HCl from the polymer may be thought of as a sort of chain reaction, involving no free radicals.(4) The initiation process consists in the removal of a molecule of HCl from the saturated polymer molecule:

$$-CH_2-CHCl-CH_2-CHCl-CH_2-CHCl- \longrightarrow HCl$$
$$+ -CH{=}CH-CH_2-CHCl-CH_2-CHCl-$$

This produces an allyl-type structure which is reported to exert an activating influence on the rest of the molecule(5,6). The removal of further acid from this allylic structure is taken to be the propagation step, the "zipper" reaction.

$$\mathrm{-\,CH{=}CH - CH_2 - CHCl - CH_2 - CHCl—} \longrightarrow \mathrm{HCl}$$
$$+ \quad \mathrm{-\,CH{=}CH - CH{=}CH - CH_2 - CHCl—}$$

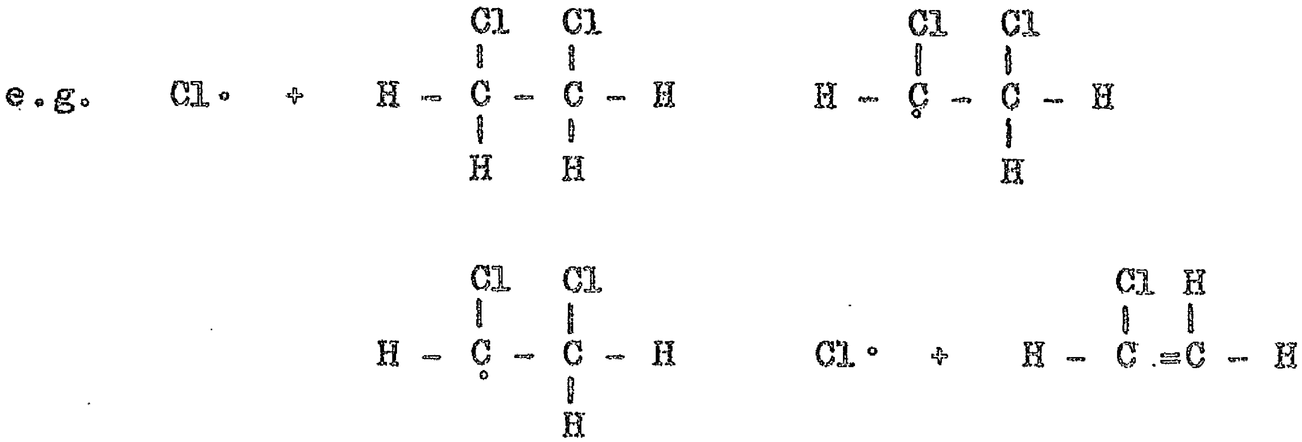
$$\mathrm{-\,CH{=}CH - CH{=}CH - CH_2 - CHCl—} \longrightarrow \mathrm{HCl}$$
$$+ \mathrm{—CH{=}CH - CH{=}CH - CH{=}CH -} \quad \text{etc.}$$

It is by no means certain, however, that the reaction does not involve free radicals. Experimental evidence, favouring the theory that the removal of HCl is a free radical process, was obtained by Arlman(7). In measuring the rate of evolution of HCl he showed that the rate increases with the addition of recognised free radical chain initiators such as benzoyl peroxide and diazoaminobenzene. Arlman postulated that an end group could be removed from the polymer, thereby forming a free radical:

$$\mathrm{R{-}CH_2{-}CHCl{-}CH_2{-}CHCl{-}CH_2{-}} \longrightarrow \mathrm{R\cdot + \cdot CH_2{-}CHCl{-}CH_2{-}CHCl{-}CH_2{-}}$$
$$\mathrm{\cdot CH_2{-}CHCl{-}CH_2{-}CHCl{-}CH_2{-}} \longrightarrow \mathrm{HCl + \cdot CH_2{-}CH{=}CH{-}CHCl{-}CH_2{-}}$$
$$\mathrm{\cdot CH_2{-}CH{=}CH{-}CHCl{-}CH_2{-}} \rightleftharpoons \mathrm{CH_2{=}CH{-}\overset{\circ}{C}H{-}CHCl{-}CH_2{-}} + \mathrm{HCl}$$
$$\mathrm{CH_2{=}CH{-}\overset{\circ}{C}H{-}CHCl{-}CH_2{-}} \longrightarrow \mathrm{CH_2{=}CH{-}\overset{\circ}{C}H{-}CH{=}CH{-}}$$
$$\mathrm{CH_2{=}CH{-}\overset{\circ}{C}H{-}CH{=}CH{-}} \longrightarrow \mathrm{CH_2{=}CH{-}CH{=}\overset{\circ}{C}H{-}CH{-}}$$

Chlorine atoms would thus be successively activated and this would result in their removal from the polymer.

Barton and Howlett's(8) work supports a free radical theory. It was shown that 1:2-dichloroethane decomposes in the temperature range 362-485°C by a first order process. Propylene is a powerful inhibitor of the decomposition and this and other facts led Barton and Howlett to believe that the decomposition proceeds by a free radical mechanism

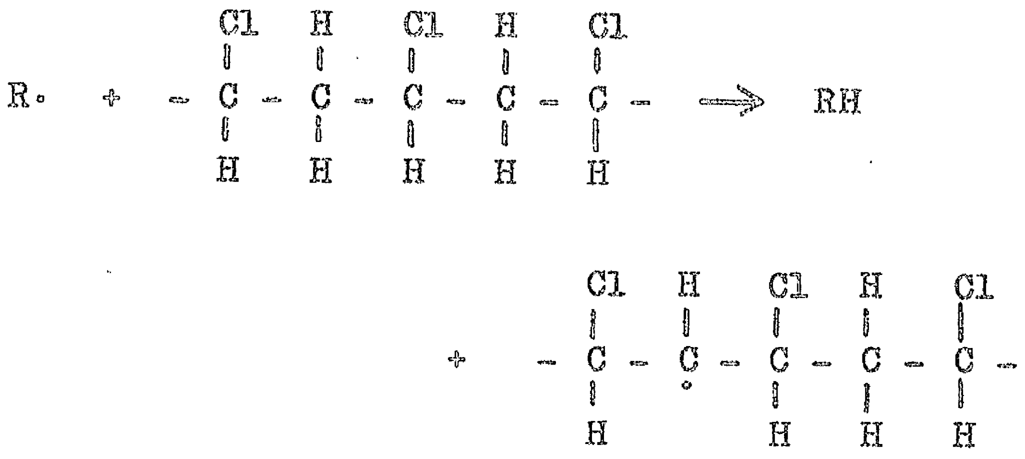


$$\text{e.g.}\quad Cl\circ + H-\underset{H}{\overset{Cl}{C}}-\underset{H}{\overset{Cl}{C}}-H \qquad H-\underset{\circ}{\overset{Cl}{C}}-\underset{H}{\overset{Cl}{C}}-H$$

$$H-\underset{\circ}{\overset{Cl}{C}}-\underset{H}{\overset{Cl}{C}}-H \qquad Cl\circ + H-\overset{Cl}{C}=\overset{H}{C}-H$$

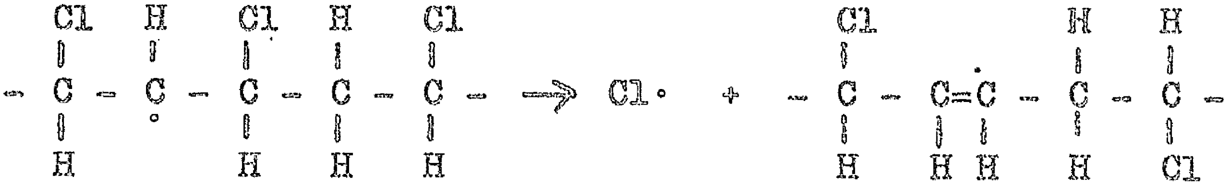
In 1957, Fuchs and Louis(9) suggested that the methylene groups in PVC are liable to attack by free radicals. These workers chlorinated the polymer, thus removing the methylene groups, i.e. the product consisted of a chain with one chlorine atom attached to each carbon atom. It is known that chlorination is a free radical process in light of wavelength less than 5460 Å(10). The indication was that methylene groups are prone to attack by free radicals.

Combining the work of Barton and Howlett and Fuchs and Louis, Winkler(11), in a review paper, deduced the following mechanism:



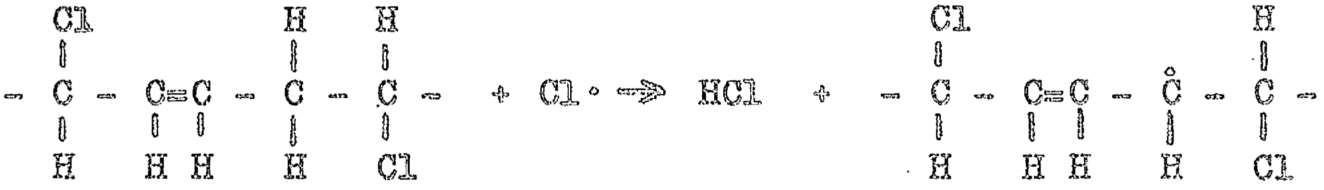
$$R\cdot + -\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}- \longrightarrow RH + -\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{\circ}{C}}-\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-$$

A given radical attacks the methylene hydrogen preferentially$^{(9)}$ and this induces lability in an adjacent chlorine atom.



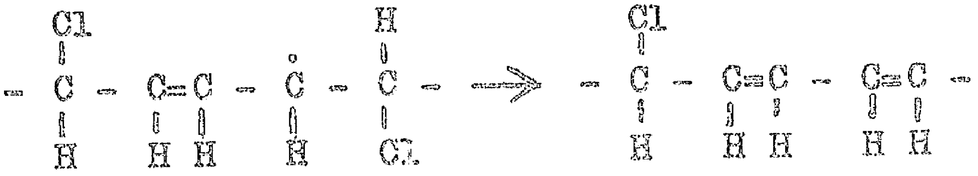
$$-\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{\circ}{C}}-\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}- \longrightarrow Cl\cdot + -\overset{Cl}{\underset{H}{C}}-\underset{H}{C}=\overset{\cdot}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-$$

The labile chlorine atom thus produced in a ß position would be released to stabilise the molecule



$$-\overset{Cl}{\underset{H}{C}}-\underset{H}{C}=\underset{H}{C}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}- + Cl\cdot \longrightarrow HCl + -\overset{Cl}{\underset{H}{C}}-\underset{H}{C}=\underset{H}{C}-\overset{\circ}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-$$

The probability is that the free chlorine atom would abstract a hydrogen atom from one of the nearest methylene groups. Since the nearest one in the chain is also an allylic hydrogen atom its abstraction would be highly favoured



$$-\overset{Cl}{\underset{H}{C}}-\underset{H}{C}=\underset{H}{C}-\overset{\circ}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}- \longrightarrow -\overset{Cl}{\underset{H}{C}}-\underset{H}{C}=\underset{H}{C}-\underset{H}{C}=\underset{H}{C}-$$

Thus a chain reaction is started and perpetuated which could lead to a sufficient number of double bonds to impart colour.

Several mechanisms have been proposed for the initiation of dehydrochlorination, but little is known of the termination reaction. It is possible that defects in the polymer chain e.g. branching could prevent the continuation of the reaction. Druesedow and Gibbs(12) have suggested a number of ways in which branching could occur. These include co-polymerisation between polymers containing polyene segments, chain transfer between a polyene segment and a molecule of PVC, and a type of Diels-Alder reaction between polyene segments.

Dehydrochlorination in Oxygen.

Several workers(7,12) found that the rate decreases with time in nitrogen or in a vacuum. This is consistent with initiation proceeding from activated structures present in the polymer.

In oxygen, however, the reaction rate is greater than in nitrogen(7,12-15) and it accelerates as the degradation proceeds. This effect was ascribed to the production of reactive sites by free radicals. There is some doubt, however, whether oxygen reacts with saturated or unsaturated structures. Oxygen apparently does not affect the reaction until a certain minimum amount of dehydrochlorination has occurred(13). Furthermore, PVC degraded in oxygen is less coloured than when degraded in its absence(7,12). Taken in conjunction, these observations suggest that oxygen reacts with unsaturated in preference to saturated molecules. Bersch and co-workers(16), however, suggested that both saturated and unsaturated structures are subject to oxidation. There has been much speculation as to how oxygen accelerates the rate, but it was believed that oxidative initiation commences within the polymer chain as opposed to thermal initiation at the chain ends(7). Campbell and Rauscher(17) followed up Arlman's work by proposing that oxygen was capable of forming peroxide radicals. Abstraction of the polymer's hydrogen by these radicals would produce peroxides that eventually degrade to carbonyl-containing products, the presence of which has been established(5,18). PVC exposed to oxygen under thermal degradation is unstable when subjected to UV irradiation(5,12,14), presumably because any carbonyl groups present absorb energy very strongly indeed at 2,730 Å. The importance of hydroperoxides as a source of free radicals can be seen from the following scheme

$$\begin{array}{lll} \mathrm{RH} + \mathrm{O_2} \longrightarrow \mathrm{R\cdot} + \mathrm{OOH\cdot} & & \\ \mathrm{R\cdot} + \mathrm{O_2} + \mathrm{RH} \longrightarrow \mathrm{RO_2\cdot} + \mathrm{RH} & & \underline{\text{Initiation}} \\ \mathrm{RO_2\cdot} + \mathrm{RH} \longrightarrow \mathrm{RO_2H} + \mathrm{R\cdot} & & \underline{\text{Chain Transfer}} \end{array}$$

$$RO_2H + R\cdot \longrightarrow RO\cdot + OH\cdot + R\cdot$$ Propagation

where	RH	represents	a	polymer	molecule
	$R\cdot$	"	"	"	radical
	$RO_2\cdot$	"	"	"	peroxy radical
	RO_2H	"	"	"	hydroperoxide
	$RO\cdot$	"	"	"	alkoxy radical

Hence if peroxide is present, a large number of free radicals may be available to initiate dehydrochlorination.

The remaining major reactions occurring during pyrolysis of PVC are cross-linking and chain scission, and these reactions will be conveniently reviewed together since one could almost be described as the reverse of the other; in addition, they often occur simultaneously.

Cross-Linking and Chain Scission in Nitrogen

That part of the degraded PVC which is soluble displays a progressive increase in its intrinsic viscosity with increase in pyrolysis time(7,12). This is attributed to cross-linking(12). There is lack of agreement on what happens to the PVC in the early stages of decomposition. Results have been obtained which are in direct conflict with the work of Arlman and Druesedow. It has been found that the intrinsic viscosity of the soluble polymer fraction decreases with time(19,20) which indicates chain scission. Taylor(21) has demonstrated very effectively that cross-linking and chain-scission occur simultaneously by determining the solubilities and intrinsic viscosities of samples of degraded PVC.

Table 1. Extent of Cross-Linking and Chain Scission in Thermally Degraded PVC

Thermal Ageing at 160°C(min.)	Cross-Linking (%)	Intrinsic Viscosity of Uncross-Linked Sample
0	0	0.61
376	0.31	0.53
436	0.46	0.51
608	0.64	0.48
739	0.70	0.42
980	1.36	0.38
1030	2.72	0.32
2200	4.81	0.30

These results indicate that although cross-linking increases gradually, the intrinsic viscosity tends to approach a constant value. Chain-scission probably predominates in the early stages with cross-linking becoming the major reaction later.

Cross-Linking and Chain Scission in Oxygen

It was claimed that the intrinsic viscosity decreases in the early stages, but begins to increase later(12). This might be expected, for the oxidation of unsaturated polymer would form unstable peroxides as described elsewhere. The polymer would then be more liable to undergo chain scission.

There are a number of factors which contribute towards the way in which the polymer decomposes. Many pyrolyses, for instance, are run at atmospheric pressure so that the degradation products, if involatile, are allowed to remain in contact with the polymer and may catalyse its breakdown.

The structure of the polymer is important, for such characteristics as the polarity of side groups, branched chains, unsaturation and oxidised structures all affect the kinetics of degradation. The phase in which pyrolysis is carried out, and the pyrolysis temperature will mean that the decomposition proceeds by a selected route dependent on these physical conditions. Indeed an increase in temperature often gives rise to a completely new breakdown route. The influence of these factors on the degradation of PVC will now be considered in more detail.

Autocatalysis

The question has been posed, does the liberation of HCl during pyrolysis of PVC catalyse the further removal of acid from the polymer. Fox et al.(5) found that HCl does catalyse breakdown in nitrogen, whilst others(12,13,14) established that autocatalysis occurs only in oxygen.

Arlman(22) carried out an interesting series of experiments in which he pyrolysed PVC in a stream of hydrogen chloride gas. He used gas streams consisting of a mixture of nitrogen and hydrogen chloride, and of oxygen and hydrogen chloride. Despite variations in polymer type, reaction phase, temperature and carrier medium, the conclusion was that autocatalysis does not occur and this was subsequently confirmed(23).

Earlier work(4) had indicated that the presence of oxygen and/or liberated acid is not necessary for the reaction to proceed autocatalytically. Under high vacuum, and in the temperature range, 208°C to 223°C, Grassie found that the degradation of PVC progressed autocatalytically. The decomposition of polyvinyl acetate under similar conditions revealed a similar acceleration in the rate(24,25). This decomposition would appear to be analogous to that of PVC because only acetic acid is evolved at the temperatures quoted, and the polymer colours very quickly.

Nature of the Polymer.

PVC can possess either a "head-to-tail" or a "head-to-head" structure. The former would be expected owing to the polar nature of the double bond, $\overset{-}{C}H_2=\overset{+}{C}H \longrightarrow Cl$

and this proved to be the case(26). If head-to-head were the structure, then the attainment of polyene chains would not be possible.

It is believed that the thermal stability of a polymer molecule decreases as the extent of chain branching increases(27). During the polymerisation of vinyl chloride, particular molecular groups(28) may be introduced into the polymer molecule. These groups, e.g. tertiary chlorides tend to evolve HCl more easily than the linear polymer. Using the technique of reductive hydrogenation, Cotman(29) converted PVC to a hydrocarbon and demonstrated by infra-red methods that tertiary chlorides are,in fact,present. Kenyon(30) showed that such structures lost HCl readily and it was pointed out(15) that HCl may be lost in three directions from a tertiary chloride.

Unsaturation is also a source of weakness in the polymer. PVC containing double bonds breaks down much more easily than the saturated polymer. This was effectively shown by Telamini and Pezzin(31) who introduced 5% carbon-carbon double bonds into PVC at 200°C. The polymer evolved acid at more than fifty times its normal rate. After the initial acceleration, however, the rate soon returned to its normal value. Terminal double bonds in PVC were reported to be largely responsible for initiating dehydrochlorination at 180°C; Baum and colleagues(15) chlorinated PVC vary slightly and this lowered the rate of degradation. They therefore assumed that initiation begins at the chain ends. It was felt that the double bonds responsible were probably introduced into the polymer during polymerisation, mainly by chain transfer with monomer, and also by disproportionation.

The effect of oxygen on the decomposition has been dealt with above, but if oxygen finds its way into the polymer structure, it may prove equally offensive *in situ*. It was suggested that oxygen incorporated into the polymer(16) could initiate active centres which would be prone to undergo dehydrochlorination.

There are a number of ways in which oxygen can be inserted into the polymer.

1. The polymer may be oxidised during polymerisation e.g. in emulsion polymerisation the reaction occurs in the presence of small amounts of oxygen.
2. The initiator fragments derived from e.g. benzoyl peroxide may be chemically combined with the polymer at its ends.
3. Oxidation of the polymer by such initiator fragments, e.g. $C_6H_5COO\cdot$, which may happen during decomposition.

Oxidation by these means may be prevented by the use of the appropriate free radical initiator and by making sure that no oxygen is present during polymerisation.

Temperature of Degradation

Much of the work on PVC has been carried out in the temperature range 100-200°C due to the commercial interest, but some work has been completed at much higher temperatures. Stromberg and co-workers(23) prepared samples of γ-initiated and free radical-initiated PVC and removed all the available HCl in approximately thirty minutes at 300°C. The resulting polymer residues were pyrolysed for an additional thirty minutes. The principal products of this secondary pyrolysis as determined by mass spectrographic analysis were low molecular weight saturated and unsaturated aliphatic hydrocarbons, benzene and toluene. With regard to the aromatics, cyclisation of one end of the polyene chains formed initially would probably yield these products. When PVC is pyrolysed at 400°C, appreciable quantities of polycyclics are present(32) and at 800°C, Winslow and Matreyek(33) had to deploy X-ray and infra-red analytical techniques to identify the constituents in a complex mixture of alkenes and alkanes.

Reaction Phase

Most of the research has centred on the bulk degradation of the polymer. There are, however, two big disadvantages associated with bulk degradation.

The rate of diffusion of HCl from the polymer depends upon the latter's thickness, which may become rate-controlling. Diffusion rates also depend upon particle size, and this in turn depends upon whether the polymer is made by suspension or emulsion polymerisation. If diffusion troubles are to be eliminated the thickness of the polymer layer must be minimised, and this reduces the quantity of polymer available for pyrolysis.

A second difficulty is the heating of the PVC, for it has a low thermal conductivity. The evolution of HCl also abstracts heat from the polymer mass due to the heat of evaporation. Thus there may be a temperature difference between the surface and the centre of the polymer mass. The addition of powdered silver to the polymer is reported to improve heat transfer(34).

PVC does not become liquid when heated, but remains as a semi-molten mass which soon becomes hard and infusible. Thus the problems of eliminating diffusion control of HCl from the polymer and heating the latter adequately are serious ones. Degradation in solution rules out many difficulties because particle size is unimportant and the polymer solution can be uniformly heated. If the polymer solution stays mobile there should be no difficulty in removing HCl during pyrolysis.

In addition to pyrolysis, PVC has been degraded by photochemical and electronic irradiation and a brief résumé of the work done in these fields is included, since it has been claimed to support the free radical mechanism of degradation.

The Photo-Degradation of PVC

PVC stored in the dark at room temperature remains stable for years, but if exposed to sunlight it slowly degrades. On exposure to high frequency UV irradiation, however, the polymer degrades quickly, although compared with thermal degradation it is still slow. The higher efficiency of UV light is attributed to the fact that more than 95% of solar light incident on the earth possesses wavelengths longer than 3000 Å.

It is difficult to assess the individual influences of UV light and oxygen on the decomposition of PVC, but both factors appear to be inter-dependent. Holman *et al.*(35) have shown that UV light has a catalytic effect on the oxidation of polyene systems, and PVC definitely absorbs oxygen in UV light(12). Coloured polymer is also bleached under these conditions which indicates oxidative attack. The alleged catalytic effect of oxygen has received support from Kenyon(30) who studied the irradiation of UV light on sec-butyl chloride and on PVC and showed the catalytic effects of reagents containing carbonyl groups on the breakdown of these compounds. Some workers(13,14) believe that oxidative attack depends mainly on initial dehydrochlorination to provide points in the chain susceptible to oxidation. With increased exposure to UV light, samples of PVC absorb more strongly in the longer wavelengths of the UV absorption spectrum, until eventually absorption occurs in the visible region when the polymer appears yellow(13). Similar results were obtained with the saturated and unsaturated alkyl halides.

Recently Taylor(21) has shown that exposure of PVC to UV light at room temperature results in simultaneous chain scission and cross-linking, with the former predominating.

Although prolonged exposure of PVC to UV light results in the evolution of only a small quantity of HCl, the important factor would appear to be the sensitisation of the polymer to thermal breakdown. All PVC samples exposed to sunlight or UV irradiation decompose much more readily than the unexposed polymer on thermal degradation.

The Electronic Irradiation of PVC

The exposure of PVC to a beam of high-energy electrons at low temperatures produces visible colour changes similar to those observed in the thermal degradation of the polymer. It has been suggested that the colour is due to a mixture of frozen free radicals and a polyene structure(36). Miller(37) reported that there is a quantitative relationship between colour and free radical concentration at −196°C in vacuo. Post-irradiation changes in the polymer were followed visually and by electron spin resonance (ESR), which was also used by Atchison(38) in support of Chapiro's(36) postulations. From a kinetic analysis of the ESR spectrum, Atchison deduced that there are three species of radicals which decay exponentially at room temperature; a conclusion in agreement with Loy's(39) work.

According to Millar(37) the main chemical processes participating during irradiation involve the formation of the free radicals, $-CH_2-\overset{\circ}{C}H-$ + $Cl^{\cdot}$, leading to the system, $-CH{=}CH-$ + HCl. The development of conjugated unsaturation is believed to involve the unstable radical $-\overset{\circ}{C}H-CHCl-$ in a free radical chain dehydrochlorination process, a mechanism similar to that of Winkler(11).

With respect to the degradation processes described above, it is pertinent to ask what were the consequences of these theories in the field of stabilisation.

Stabilisation of PVC

Apart from a reduction in the temperature of degradation, the obvious method of stabilisation was the removal of HCl because of the alleged catalytic effect of the acid. Compounds capable of combining with the HCl liberated during pyrolysis retard the breakdown, although probably not for the reason indicated, since it has been shown that the acid does not catalyse the decomposition.(12,22,23) However such HCl-acceptor compounds are still in general use, and an enormous variety have been tried(40).

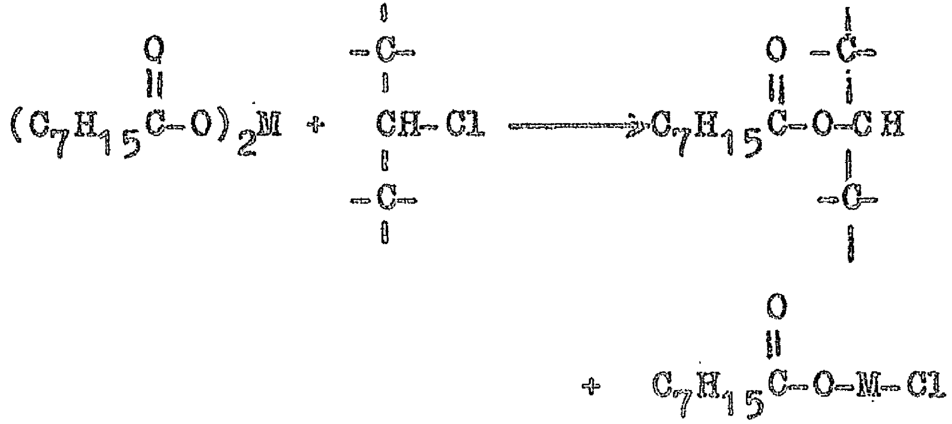
Evidence has been presented in support of the theory that stabilisers act as free radical acceptors(11,30), thereby disrupting free radical processes. Kenyon(30) observed that PVC in the presence of carbon 14-butyl-labelled dibutyl tin diacetate showed an increase in retained β-activity when irradiated with light of wavelength greater than 2700 Å, with increase in time of irradiation. The stabiliser was then extracted repeatedly until the retained β-activity was constant. A similar experiment was carried out with the same stabiliser possessing only a labelled acetate group. In this case there was no change in retained β-activity with time of irradiation. This indicated that the butyl and not the acetate group had been incorporated into the PVC, and it was proposed that radicals already present had reacted with the butyl group of the stabiliser.

$$\mathrm{R\cdot} + (\mathrm{C_4H_9})_2\mathrm{Sn(OAc)_2} \longrightarrow \mathrm{RC_4H_9} + \mathrm{C_4H_9}\overset{\circ}{\mathrm{Sn}}\mathrm{(OAc)_2}$$

It was also suggested that the addition of the butyl group to the polymer radical prevented oxidation taking place.

For heat stabilisation of PVC, the cadmium, zinc and barium salts of fatty acids have proved very effective(11). Such compounds are usually used in combination with other stabilising additives such as organic phosphites. To obtain an insight into the way these compounds retard degradation, the infra-red spectra of a series of PVC films with and without admixed, barium, cadmium and zinc 2-ethyl hexanoate were studied after various heat treatments(41). The spectra of these mixtures revealed a band at 5.75μ, which was absent from the spectra of the unmixed components. The intensity of this band varies with the salt, temperature, and length of heat treatment, and it was attributed to the carbonyl-stretching frequency of an aliphatic ester. The spectra of vinyl acetate - vinyl chloride (1:19) copolymers also display a band at 5.75μ. It was therefore inferred that these 2-ethyl hexanoate salts stabilise PVC by interchanging certain of its chlorine atoms with 2-ethyl hexanoate groups:

i.e.



$$(C_7H_{15}\overset{O}{\overset{\|}{C}}-O)_2M + \begin{array}{c} | \\ -C- \\ | \\ CH-Cl \\ | \\ -C- \\ | \end{array} \longrightarrow C_7H_{15}\overset{O}{\overset{\|}{C}}-O-\begin{array}{c} | \\ -C- \\ | \\ CH \\ | \\ -C- \\ | \end{array}$$

$$+ \; C_7H_{15}\overset{O}{\overset{\|}{C}}-O-M-Cl$$

Since there is reason to believe that expulsion of the carboxylic acid from the esterified polymer requires a greater activation energy than the expulsion of HCl, the above reaction would stabilise the PVC.

The above theory has recently been verified (42). PVC films into which had been incorporated the barium, cadmium and zinc salts of 2-ethyl-hexanoic-1-C-14 acids retained their radioactivity even after repeated dissolution and precipitation, showing that the carboxy group was chemically combined with the polymer. Furthermore the extent of retained radioactivity varies with the temperature and length of heat treatment; qualitatively it parallels the variation in intensity of the 5.75 μ band observed in the infra-red studies.

There has also been support for the belief that stabilisers act as antioxidants (5,43,44), capable of absorbing oxygen and hence precluding the formation of peroxides. This is tied up with the ability of the stabiliser to act as a selective absorber of UV irradiation (5).

The current tendency is to employ compounds capable of functioning as free radical stoppers and antioxidants. The stability of PVC may, however, be improved by the simple expediences of removing the lowest molecular weight fraction with acetone (45) or by washing the polymer free from extraneous foreign materials e.g. ionic impurities, which are usually left in the polymer during polymerisation.

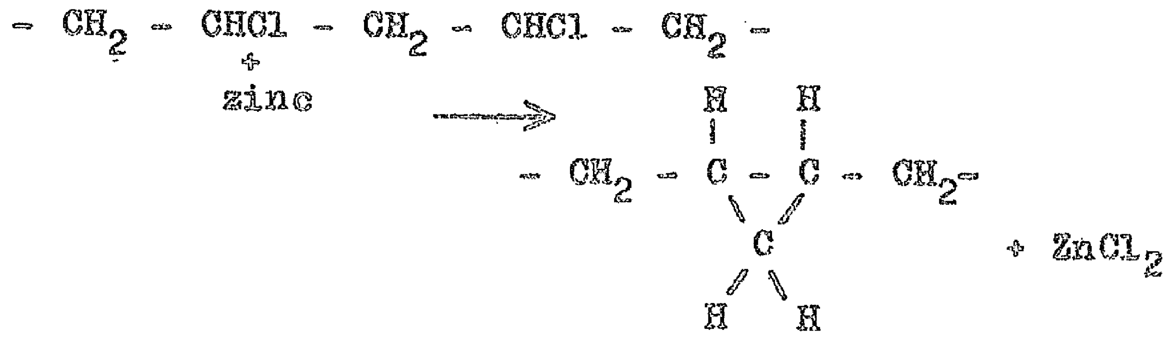
CHAPTER II

EXPERIMENTAL

Materials for Telomerisation[x] and Polymerisation

For certain experiments branched PVC was required. Branching was achieved by the introduction of cyclopropane rings into the polymer structure(26).

i.e.



8g. of chloride-free, activated zinc were transferred to a large flask containing 500 c.c. of peroxide-free dioxan and 1g. of polymer. The contents were refluxed for 8 hours; the PVC was precipitated in methanol and filtered off. The filtrate contained zinc chloride which was estimated by titration against standard silver nitrate. Thus the amount of chlorine removed was obtained and this gave an indication of the number of cyclopropane units incorporated into the polymer chain.

Vinyl chloride (VC), a gas at room temperature, was found to be free from acetylenic impurities. From a cylinder

---

[x] The process whereby short-chain compounds or telomers are prepared.

the monomer was passed into a cold trap on the vacuum line, distilled and degassed for one hour. The monomer was allowed to vapourise and the vapour collected in two 5-litre bulbs attached to the line.

Bromotrichloromethane (BTCM) - from Eastman Kodak, Ltd. It was washed with 5% sodium carbonate solution, then with water. The BTCM was dried over calcium chloride and finally distilled under reduced pressure.

1:1′Azobisisobutyronitrile (AIBN) - from Eastman Kodak, Ltd. It was purified by recrystallisation from absolute alcohol. A known weight was dissolved in 100 c.c. chloroform just before use.

Benzoyl peroxide (BP) - from B.D.H., Ltd. The BP was dissolved in chloroform and reprecipitated in absolute alcohol. This initiator was also made up in chloroform.

Solvents. Cyclohexanone and dioxan - from Eastman Kodak, Ltd. - were distilled before use. Benzene - from B.D.H. Ltd. - molecular weight grade used in addition to the AR grades of acetone, chloroform, toluol and methanol.

Materials for Pyrolysis

Heating Media. The main liquids used were nitrobenzene (212°C), ethylene glycol (198°C) decalin (192°C) and p-cymene (178°C). Others included water, bromobenzene, chlorobenzene, etc.

Inhibitors and Commercial Stabilisers - AR grade of hydroquinone (HQ) from May and Baker, Ltd. - and the AR grades of anthracene, α-naphthol, catechol, naphthalene, phenanthrene, stilbene, phenol - all from B.D.H.,Ltd.

α-Phenylindole and Stanclere 70 were kindly supplied by Distiller's Co., Ltd. Stanclere 70 is a mixture of plasticiser, diethyl tin dilaurate and diethyl tin dimaleate.

Analytical Reagents.- Sodium hydroxide, supplied by B.D.H. in concentrated volumetric solutions in polythene ampoules.

AR grades of sodium bromide, sodium chloride, silver nitrate, fuming nitric acid, sodium bicarbonate, hydrazine sulphate - all from B.D.H.,Ltd.

Solvents. These included ethyl benzoate (B.D.H.,Ltd.), o-dichlorobenzene (Eastman Kodak,Ltd.) and nitrobenzene (B.D.H.,Ltd.)

Apparatus

Apparatus used in Telomerisations and Polymerisations

Vacuum Line. This was built in Pyrex glass. It included two 5 litre bulbs and a series of taps and traps, etc.

The pumping system consisted of a three-stage mercury vapour diffusion pump backed by a rotary vacuum oil pump. A vacuum of ca. 10^{-4} m.m. mercury could be obtained, estimated by testing the line with a high voltage discharge coil.

Taps were lubricated with Apiezon-M grease and the cold traps contained drikold-acetone mixture or liquid nitrogen. The traps were placed immediately before and after the diffusion pump to prevent the escape of volatile contaminants into the pumping system.

Dilatometers. These varied in volume from 20 to 80 c.c. in capacity, and were constructed in Pyrex glass, or from Carius tubing when required for thermal polymerisation. For the latter, the dilatometer bulb was sheathed in a cylindrical brass casing. This served as a protection against the higher vapour pressure developed. Table 2 shows how the vapour pressure of vinyl chloride increases with temperature.

Table 2. The Vapour Pressure of Vinyl Chloride

Temperature (°C)	Pressure (cm. mercury)
-23.02	51.30
-13.61	76.75
- 1.570	122.4
5.530	158.2
25.72	302.7
39.72	449.2
46.80	543.4
54.87	667.6
60.34	758.6

Thermostat. It consisted of a circular Pyrex glass tank contained in a copper jacket. The annulus between the copper and the glass was insulated with fibre-glass. The required temperature was held to within ± 0.01°C by a heater operated by a relay circuit which was actuated by a mercury-toluene regulator.

UV Lamp. A 125 watt Osira mercury vapour lamp provided UV irradiation which was filtered through a Chance OX1 filter. The lamp was connected to a choke and capacitor to eliminate variations in the applied current.

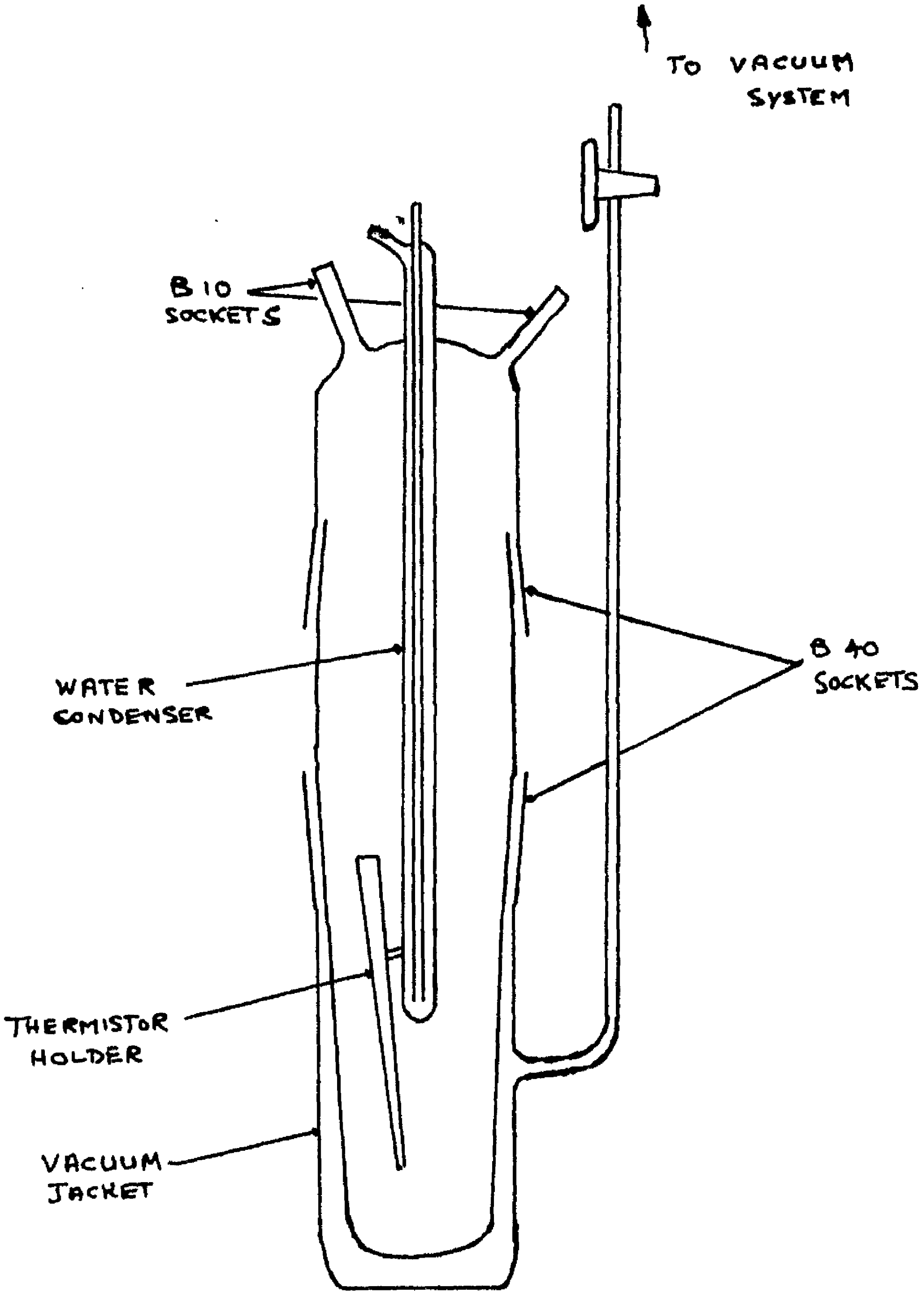
Cryoscopic Cell. The cell was a modification of that used by Vofsi and Katchalsky(46) in molecular weight determinations. It was a vacuum-jacketed tube socket into which could be fitted a B40 Quickfit cone. The latter incorporated a simple water condenser to which was attached a holder for a thermistor (fig.1).

The temperature-measuring element was a thermistor of ca. 220 ohms resistance at 20°C. The thermistor formed one arm of a conventional Wheatstone bridge, with a pair of resistance boxes as the ratio arms, and a precision decade box as the balancing arm. A sensitive mirror galvanometer was used as a detector.

In operation, solution was introduced into the cell, the thermistor was connected up to the Wheatstone circuit and placed in its holder. The cell was immersed in an

FIG. 1

CRYOSCOPIC CELL



ice-bath, thus cooling the solution, which was stirred by a magnetic follower. The latter was activated by a magnetic stirrer on which the cell and ice-bath were placed. Temperature change was indicated in terms of resistance on the decade box.

The main advantages of the cryoscopic cell over the Beckmann apparatus are

1. The method is more rapid and the apparatus more robust.
2. Smaller quantities of solute can be used.
3. The stirring of the solution is more efficient.
4. Cooling takes place much more slowly.

Apparatus used in Pyrolyses

The pyrolysis unit is shown in fig.2. Each section will be described in turn.

The Heater Unit.

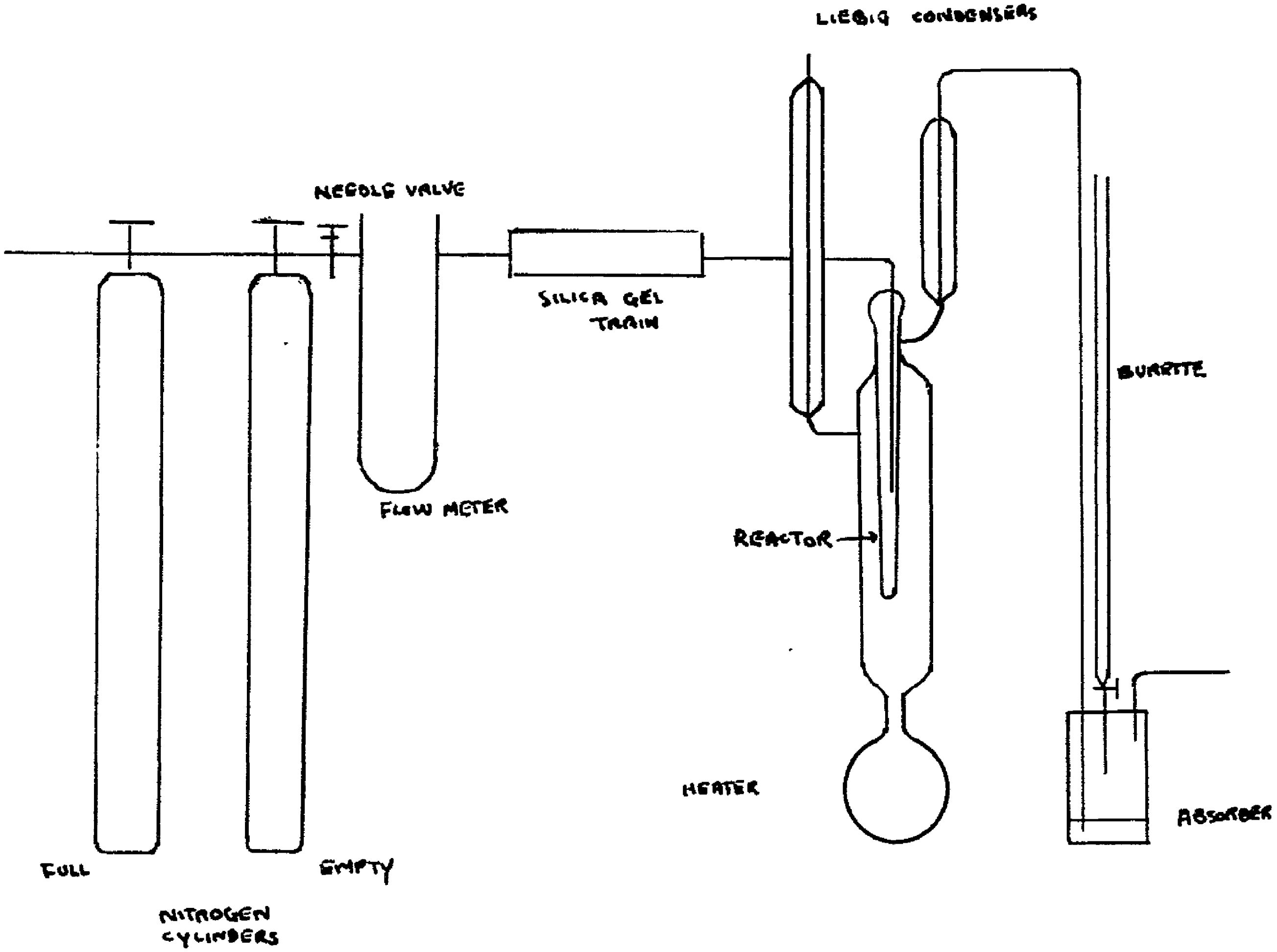
The main points governing its construction were

1. Good temperature control and easy adjustment of temperature.
2. Ability to observe the progress of the pyrolysis.
3. Whether the pyrolysand can be uniformly heated.
4. Easy access to the reactor for cleaning purposes.
5. A means whereby distillation in the reactor could be prevented or at least reduced.

The apparatus which satisfied these requirements is

FIG. 2

PYROLYSIS SET-UP



that shown in fig.3. It was a unit constructed entirely of Pyrex glass of which the two main parts were the reactor and still-head and the heater.

The reactor was a Pyrex glass tube, 28 cm. in length, internal diameter 1.7 cm. The upper part consisted of a B24 Quickfit cone joined to a B24 socket.

The still-head was simply a Drechsel head attached to a water condenser. The Drechsel head fitted into the B24 socket of the reactor, so that the latter was easily detachable from the former.

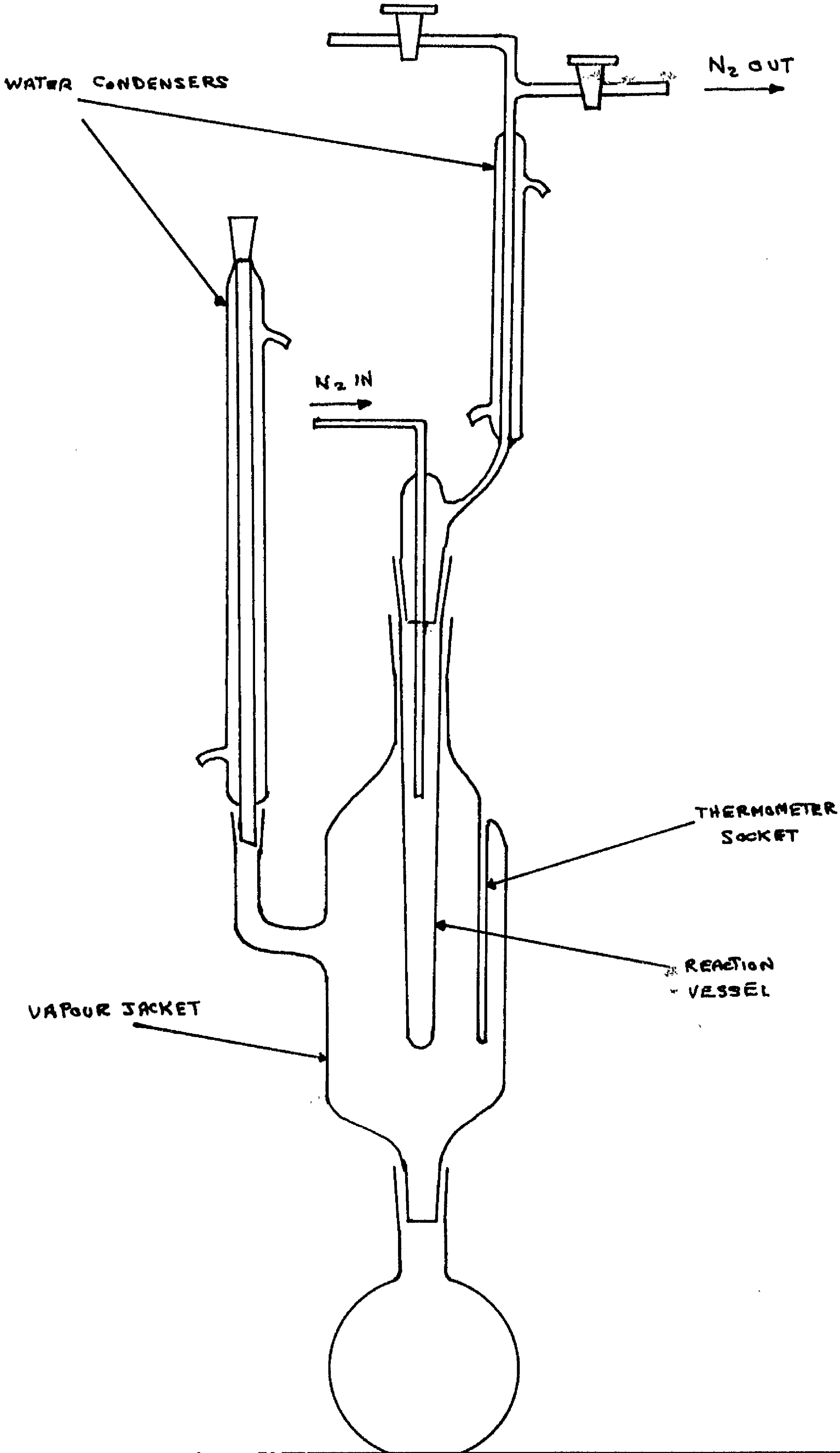
The heater comprised a cylindrical body with a side arm to receive a water condenser; it also contained a thermometer socket. The body tapered to a B24 cone at one end and a B24 socket at the other end. The latter held the reactor, whilst the former fitted into a vessel which contained the heating medium e.g. ethylene glycol.

Since the main product evolved from PVC compounds is HCl the unit was designed so that the evolution of acid could be easily recorded. Acid evolved was collected by sweeping it out from the reactor with an inert gas,such as nitrogen, into an absorber.

The Flow System.

A stream of oxygen-free nitrogen was passed through a flow-meter and a tube loosely packed with silica gel.

THE HEATER UNIT AND REACTOR



The gas then entered the reactor and passed out through the condenser into the absorber and out to the atmosphere.

The flow of nitrogen was controlled by connecting an empty cylinder to a full one. By charging the former at a low pressure and bleeding off at a needle valve the required flow rate was obtained.

The Recording System.

Acid evolved during pyrolysis was swept into a glass cell containing distilled water and indicator. The reaction was tracked by titrating the acid evolved against either N/10 or N/100 sodium hydroxide. For more dilute solutions, conductivity and potentiometric(47) methods are desirable. The efficiency of absorption was tested by coupling up the absorber in series with a second absorber. No acid was detected in the latter.

With the apparatus set up as in fig.2., it was later decided to heat the carrier gas, prior to its entering the reactor, as it was thought that this might have some bearing on the pyrolyses of the model compounds (telomers).

Preheating the Gas Stream.

The heating of the gas proved to be extremely difficult due to its low flow rate and low thermal conductivity. The conventional type of heating coil was of no use, and it became necessary to investigate the heat transfer conditions.

The general equation for heat transfer is $Q = UA\Delta t$.

where Q = Quantity of heat passing per unit time (B.Th.U./ft.hr.)

U = Overall heat transfer coefficient (B.Th.U./hr.ft^3.°F.)

A = Cross-sectional area of the tube (Ft.^{2})

Δt = Temperature gradient (°F)

It can be shown that U is dependent on the thickness of the gas film formed(48), at the walls of the heater, which in turn is dependent on the gas velocity.

For good heat transfer from the walls of the heater to the flowing gas, there should be turbulent flow. The type of flow can be gauged by the value of the Reynolds Number (Re), a dimensionless quantity:

$$Re = \frac{V.D.\rho.}{\eta}$$

where V = Velocity of gas flow (ft./sec.)

D = Diameter of the tube (ft.)

ρ = Gas density (lb./ft.^{3})

η = Gas viscosity (lb./ft.sec.)

The condition for turbulent flow is that $Re > 2,100$. If less than this value, the flow is streamline. The required Re could only be attained by reaching a compromise between the gas velocity and the diameter of the heating tube. As the heater temperature rises so does the viscosity of the nitrogen and hence the gas velocity decreases. Thus at higher temperatures there is a more pronounced film effect tending to yield streamline rather than turbulent flow. It was evident that the gas could only be heated to the required temperature of 200°C if the gas flow were very high. Only under these conditions would there be increased turbulence.

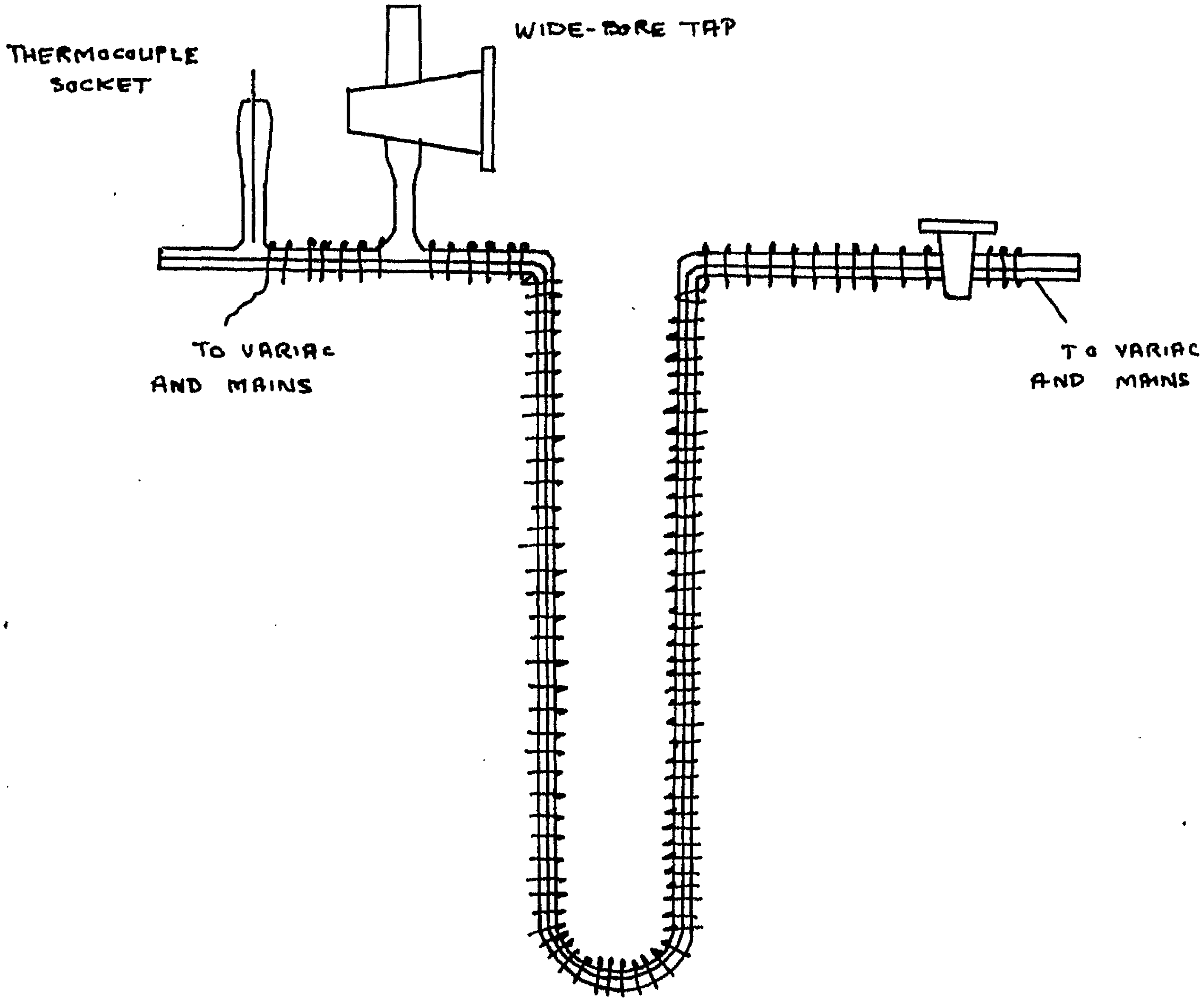
The most suitable type of heater is that shown in fig.4. Nitrogen was forced through an electrically-heated capillary at high velocity. The greater part of the hot gas was diverted at a wide-bore tap just before it entered the reactor. A thermocouple inserted between the tap and the reactor recorded the temperature. The heating element was connected to a variac by means of which it was possible to alter the heat input to the U-tube.

Separation of Chloride from Bromide.

During certain pyrolyses large volumes of HCl and HBr were evolved and absorbed in water. These halide mixtures could be analysed only if the chloride was separated from the bromide. The separation was effected by using a modified version of the apparatus used by Gilchrist and co-workers(49). It works on the principle that bromide can

FIG. 4

NITROGEN PREHEATER



be quantitatively oxidised to bromine in presence of chloride, the latter being unaffected by the oxidant. Referring to fig.5., the halide mixture was placed in flask A where the bromide was oxidised to bromine which was then distilled into flask B. Any bromine which escaped flask B was trapped in flask C. Drechsel bottles D and E contained silver nitrate and mercury respectively. The nitrate removed halide impurities from the air in the apparatus which was drawn in through E. The mercury was used as an indication of the vacuum obtained.

Procedure

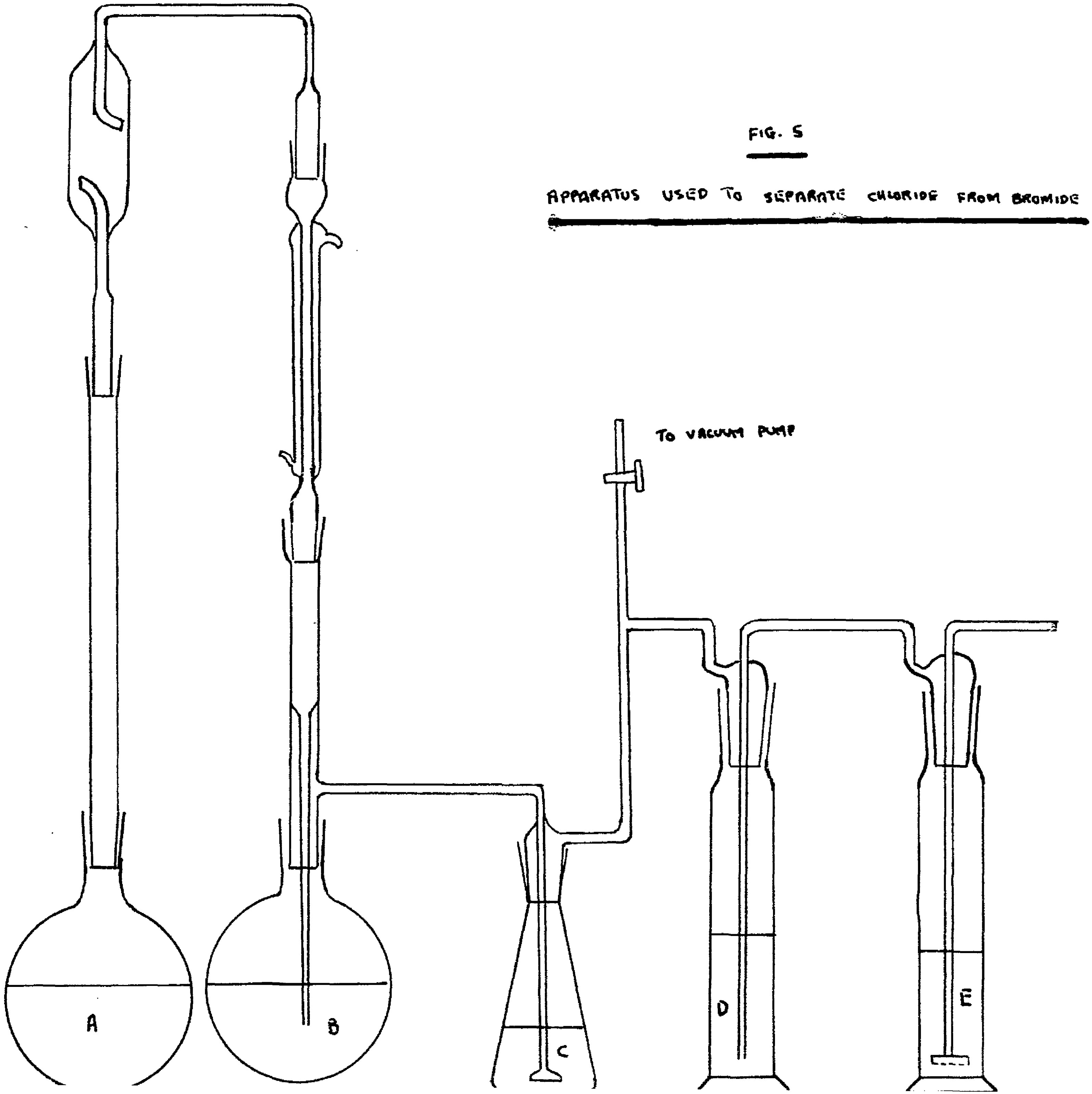
Telomerisation and Polymerisation

Calibration of Vacuum Line. Given the volume of one of the bulbs on the line, it was possible to determine the volume of any part of the line. This was done by simply allowing the volume of air in the bulb to be shared with that part of the line and noting the pressure drop. Volumes were calculated using Boyle's Law, always assuming that air behaves like a perfect gas.

The Filling of Dilatometers. These were cleaned with chromic acid, water, acetone and then dried. The dilatometers were calibrated at 25°C by filling them with known volumes of acetone.

FIG. 5

APPARATUS USED TO SEPARATE CHLORIDE FROM BROMIDE



Vinyl chloride, free from oxygen, was introduced into the 5-litre storage bulbs as described previously.

The calculated quantity of BTCM was introduced into the dilatometer which was transferred to the vacuum line. The BTCM was frozen, the dilatometer evacuated, and the BTCM allowed to warm up. This cycle of operations was repeated until the BTCM had been thoroughly degassed. The bulb of the dilatometer was immersed in liquid nitrogen, and on opening the vinyl chloride reservoir bulb the vapour rapidly distilled into the dilatometer. The volume of monomer condensed corresponded to the pressure drop on the calibrated manometer. Thus, knowing the densities of the monomer liquid and its vapour, it was possible to calculate the exact weight of vinyl chloride added. Filled with the required quantities of the reactants, the dilatometer was sealed off and stored in freezing mixture until required.

In some instances it was necessary to add initiator to the reactants. The appropriate volume of initiator solution was then introduced and the solvent pumped off. Where BTCM was needed in addition to the initiator, then the procedure was that described above.

Rate Determinations. Sealed dilatometers were submerged in a thermostat at 25°C. When thermal equilibrium was reached, UV light of 3650 Å was shone on the bulb of the vessel. The rate of contraction of the polymerising or telomerising system was followed in calibrated, narrow-stemmed dilatometers by a cathetometer.

Isolation of Products. When the required amount of contraction had occurred the dilatometer bulbs were immersed in liquid nitrogen and the stem broken open. The reaction mixture was poured into a beaker and gently warmed to expel the unreacted vinyl chloride.

The residual liquid was placed in the bulb of a molecular still. The still was attached to the vacuum line, and the bulb was jacketed with a beaker of warm water. Any unreacted BTCM was pumped off, leaving behind the liquid telomer.

In polymerisations, the polymer produced was insoluble in the monomer and precipitated out . Unreacted vinyl chloride was allowed to vapourise, and the polymer was dissolved in cyclohexanone. A dilute solution of the polymer was slowly poured into a large volume of methanol whilst stirring. The precipitated polymer was dried.

Identification and Characterisation of Products.

The molecular weights of telomers were determined cryoscopically in benzene. The Beckmann apparatus was used initially but most molecular weights were determined rapidly and accurately in the cryoscopic cell specially devised for the present work.

Exactly 10 c.c. of pure benzene were pipetted into the cell which was immersed in an ice-bath. A freezing curve was recorded for the pure solvent (fig.6) in terms of electrical resistance. The solvent was thawed out and a known weight of a known pure compound, diphenyl phthalate, was introduced; a second curve was obtained. The solution was successively diluted. Thus for given concentrations of a known pure solute, temperature differences could be calculated. These were plotted against thermistor resistance to give the calibration curve shown in fig.7. Thus it was possible to find the molecular weights of various solutes.

The molecular weights of high polymers were determined viscosimetrically. The viscosity of PVC-cyclohexanone solutions was measured in a modified Ubbelohde viscometer at 25°C. In these viscometers, the concentration can be altered *in situ* by adding successive, known volumes of solvent and thoroughly mixing the solution. The flow times between two marks on the viscometer stem were noted for the pure solvent and the polymer solutions. These recordings furnished the relative and hence the intrinsic viscosities of the solutions.

Other physical properties of the telomers which were measured included refractive index and density. The

FIG. 6

TYPICAL COOLING CURVES OBTAINED IN THE DETERMINATION OF MOLECULAR WEIGHTS. (ORIGIN SHIFTED TO AVOID SUPERPOSITION)

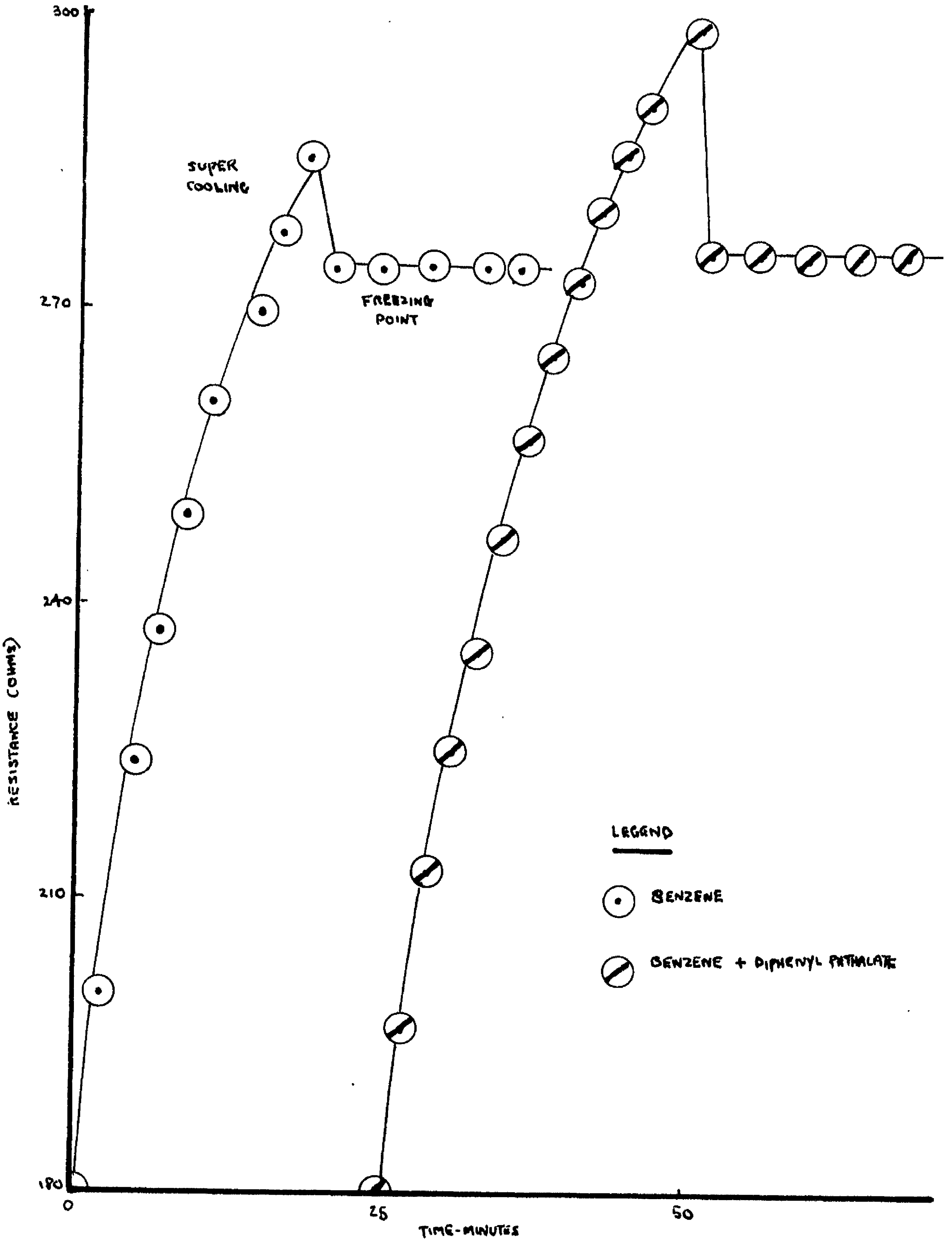
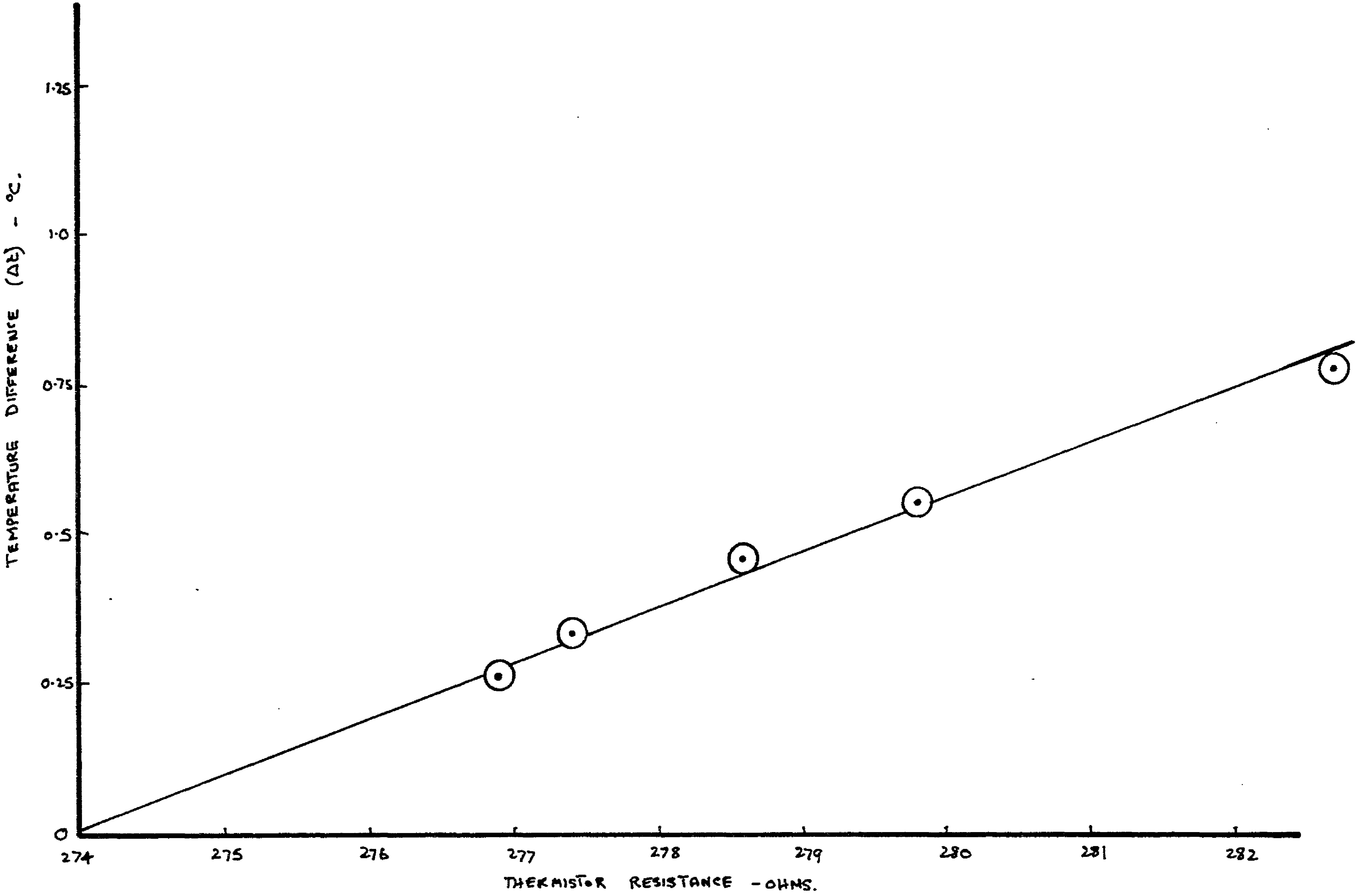


FIG. 7

CALIBRATION GRAPH (THERMISTOR RESISTANCE v TEMPERATURE DIFFERENCE)



latter was determined with a 1 c.c. pyknometer calibrated with water at 25°C whilst the refractive index was determined in an Abbé refractometer. Infra-red absorption spectra, vapour phase chromatograms (fig.8) and microanalyses were also performed in these laboratories.

Pyrolysis.

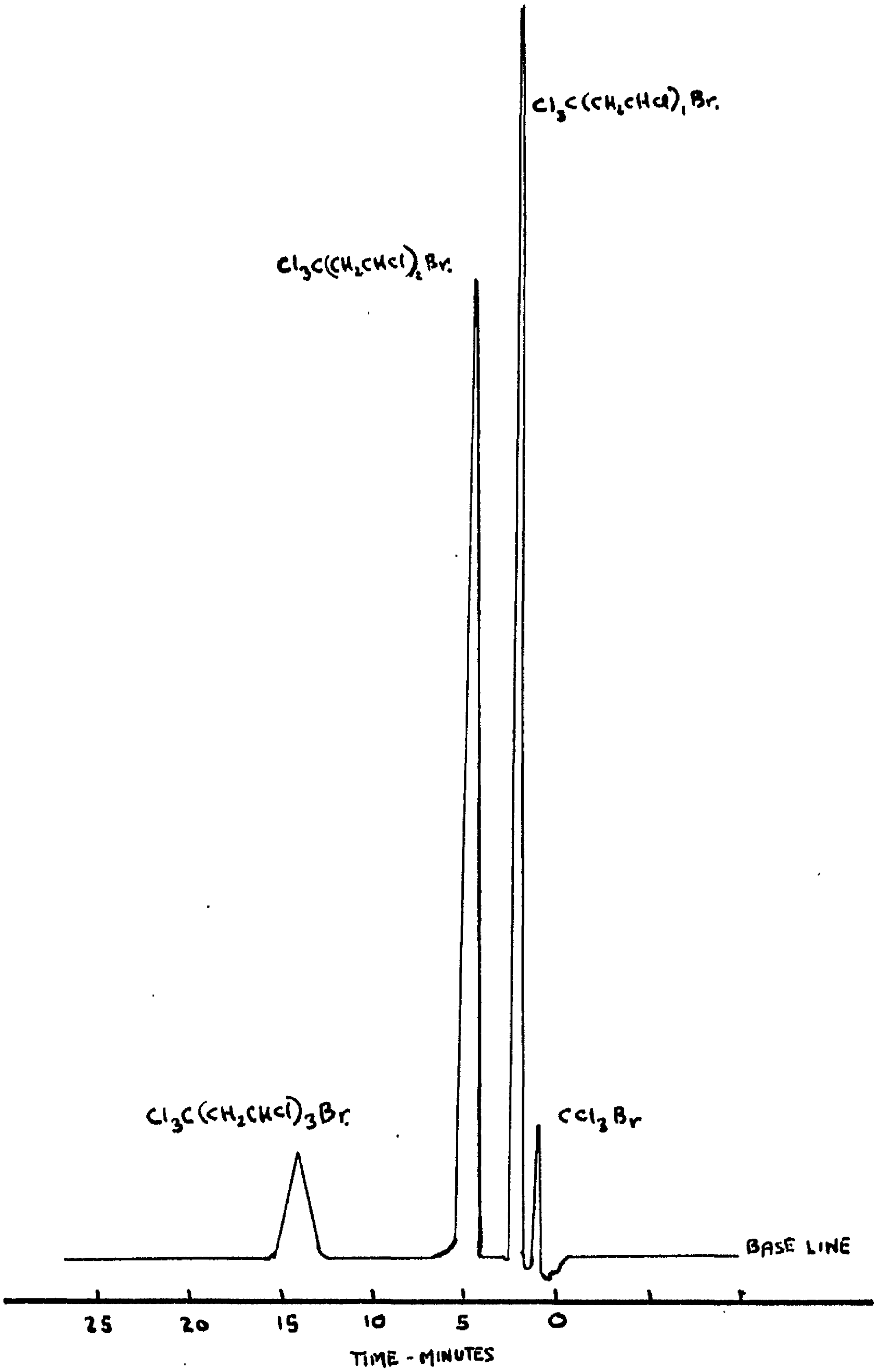
Using the static set-up shown in fig.2., many pyrolyses were carried out at 198°C, but when other temperatures were required the heater was thoroughly cleansed with benzene, then acetone and finally dried. The liquid of required b.pt. was then introduced into the heater. Initially the nitrogen preheater was included, but since it was found not to affect decomposition rates it was later omitted from the apparatus.

At the start of a typical pyrolysis the heater was switched on. When thermal equilibrium had been attained the weighed sample in the reactor was inserted into the heater and the flow of gas commenced. The progress of the reaction was followed volumetrically. If the volume of acid evolved was small, readings were taken over longer intervals. For pyrolyses over long periods, say a week, the heater was switched off and a slow stream of nitrogen was allowed to flow over the pyrolysand at night.

Where initiators and inhibitors were required, they were usually introduced with the pyrolysand at the

FIG. 8

TYPICAL CHROMATOGRAM OF A MIXTURE OF TELOMERS



commencement of the pyrolysis. In certain cases, the initiators were introduced into the reactor during the later stages of pyrolysis.

Isolation of Products Evolved during Pyrolysis.

Reference has already been made to the apparatus used in separating HCl from HBr (page 35). The procedure will now be described for the separation of the components of a mixture containing known quantities of sodium bromide and sodium chloride.

A standard mixture of sodium chloride and sodium bromide was placed in flask A (fig.5.); 150 c.c. distilled water and 30 c.c. of AR fuming nitric acid were added. The mixture was heated, and air withdrawn from the set-up. After 1½ hours the solution was cooled. It was assumed that all the bromide had been oxidised to bromine which had distilled into flask B, the latter containing a 0.5% solution of hydrazine sulphate as absorbent. The solutions in flasks A and B were then ready for the analysis of chloride and bromide respectively.

The liquid in flask A had its pH adjusted by the addition of AR sodium bicarbonate. Blanks were carried out to determine the chloride content of the bicarbonate. The chloride content of the sample was estimated volumetrically by the method of Volhard(50). Unfortunately no reliable method could be found for the determination of bromide, which was obtained by difference. Analysis of a wide range of these standards (varying from low bromide/high chloride to high bromide/low chloride mixtures) showed that the method employed was suitable and it was therefore adopted for the mixtures of halides resulting from the pyrolysis of telomers.

Table 3. The Analyses of Standard Mixtures of Chloride and Bromide.

Standard	Actual Quantities Present (moles) x 10^3			Measured Quantities Present (moles) x 10^3		
	Total Halide	Chloride	Bromide	Total Halide	Chloride	Bromide
A	3.570	1.970	1.600	3.640	1.970	1.670
B	4.262	3.940	0.322	4.202	3.860	0.342
C	3.614	0.394	3.220	3.620	0.380	3.240
D	0.716	0.394	0.322	0.800	0.425	0.375
E	4.262	3.940	0.322	4.350	4.000	0.351

Infra-red, UV spectra, molecular weight determinations and microanalyses carried out on pyrolysands helped to reveal their structural characteristics.

CHAPTER III

RESULTS

Chain Transfer

To vary the chain lengths of polymers in free radical polymerisations, it is necessary to use compounds which react with the polymer radical at an early stage in its growth to produce a new chain. Such compounds are called chain transfer agents. In the bulk polymerisation of a monomer it is possible for the growing radical (R·) to remove an atom from a molecule of unreacted monomer (M). The latter then becomes an 'active' centre or radical itself (M·).

$$R\cdot + M \longrightarrow P + M\cdot \qquad \underline{\text{Monomer transfer}}$$

where R· is the initiating radical

P is a dead polymer molecule

Flory(51) deduced that in polymerisation in the presence of solvents, transfer to the latter could take place:

i.e. $$R\cdot + S \longrightarrow P + S\cdot \qquad \underline{\text{Solvent transfer}}$$

where S is a solvent molecule from which, say, a halogen atom may be abstracted. The solvent radical may then propagate further:

$$\left.\begin{array}{l} S\cdot + M \longrightarrow R_1\cdot \\ R_1\cdot + M \longrightarrow R_2\cdot \end{array}\right\} \qquad \underline{\text{Propagation}}$$

$$2\,R_1\cdot \longrightarrow R_1 - R_1 \qquad \underline{\text{Termination}}$$

and the result is that fragments of the solvent are incorporated into the polymer chain as terminal groups.

In this work, the solvent chosen was bromotrichloromethane (BTCM), which is easily decomposed into free radicals, i.e.

$$CCl_3Br \xrightarrow[3650\mathring{A}]{h\nu} CCl_3\cdot + Br\cdot$$

BTCM was used to prepare telomers and polymers whose molecular weights were determined by cryoscopic and viscosimetric methods respectively.

Cryoscopic Determination of Degree of Polymerisation ($\bar{r}$)

When a telomer is dissolved in a suitable solvent e.g. benzene, the vapour pressure of the benzene is lowered. Since the vapour pressure of the solution is lower than that of pure benzene, then freezing occurs at a lower temperature. This depression in freezing point can be related to molecular weight according to the equation

$$\Delta t = \frac{Kw_1 \cdot 100}{x \cdot w_2}$$

where Δt = freezing point depression ($^{\circ}C$)

w_1 = weight of telomer (g.)

w_2 = weight of benzene (g.)

x = molecular weight of the telomer

K = depression constant (for benzene, $K=51.2^{\circ}C/100g.$)

Viscosimetric Determination of ($\bar{\bar{r}}$).

Any polymer solution possesses a higher viscosity than the pure solvent and it was Staudinger(52) who first proposed that this change in viscosity be used as a measure of the molecular weight of the polymer.

The specific viscosity (η_{sp}) of any polymer solution was defined as $\dfrac{\eta - \eta_o}{\eta_o}$

where η = viscosity of the polymer solution

η_o = viscosity of the pure solvent.

$$\text{i.e. } \eta_{sp} = \eta_R - 1$$

where $\eta/\eta_o = \eta_R$ = relative viscosity

Staudinger postulated that the specific viscosity was proportional both to the molecular weight of the polymer ($\bar{\bar{r}}_w$) and to its concentration $[c]$

$$\text{i.e. } \eta_{sp} = K\,\bar{\bar{r}}_w[c] \text{ where K is a constant.}$$

The above equation was, however, a very rough approximation and it became clear that other factors were involved, such as the dependence of viscosity on the rate of shear. Most of the factors exerted their influence in concentrated solutions, and this was overcome by extrapolation to infinite dilution. The molecular weights of polymers may therefore be estimated by measuring their intrinsic or limiting viscosities $[\eta]$ in a suitable solvent. The intrinsic viscosity $\lim_{c \to 0} \eta_{sp}/[c]$ can be obtained from the plot of $\eta_{sp}/[c]$ vs $[c]$.

The equation $[\eta] = K \bar{r}_w$ does not hold for all polymers and subsequent work by Flory(53) showed that the equation $[\eta] = K \bar{r}_w^{\alpha}$, where K and α are constants for a given solute-solvent system was generally applicable. For the system PVC-cyclohexanone, Mead and Fuoss(54) worked out the following relationship

$$[\eta] = 7 \times 10^{-5} \times \bar{r}_w \quad (\alpha = 1)$$

with $[\eta]$ in units of 100 c.c./g. and $[c]$ = g./100 c.c.

In this relationship, which was used in the present work, $\bar{r}_w$ is a weight average molecular weight. Since number average molecular weights were required, these were obtained by assuming that in a typical vinyl distribution

$$\bar{r}_w = 2\,\bar{r}$$

where $\bar{r}_w$ = weight average degree of polymerisation

$\bar{r}$ = number average degree of polymerisation.

It is convenient at this stage to make brief mention of the mechanism of the reaction between BTCM and vinyl chloride (VC).

The Photochemical Addition of BTCM to Vinyl Chloride at 25°C

Kharasch and co-workers(55-57) were the first to study the photochemical addition of halogen hydrocarbons to olefins. In studying the photolysis of BTCM(58) they showed that trichloromethyl radicals were formed. Later work by Melville <u>et al.</u>(59) on the photolysis of BTCM in presence of vinyl acetate led these workers to postulate a kinetic scheme involving such radicals. Bengough and Thomson(60) studied the photochemical addition of BTCM to vinyl chloride at 25°C and postulated a scheme analogous to that put forward by Melville:

$$\begin{array}{llll}
1. & CCl_3Br & \longrightarrow CCl_3\cdot & \underline{\text{Initiation}} \\
2. & CCl_3\cdot + M & \longrightarrow CCl_3M\cdot & \left.\begin{array}{l} \\ \\ \\ \end{array}\right\} \\
3. & CCl_3M\cdot + M & \longrightarrow CCl_3(M)_2\cdot & \underline{\text{Propagation}} \\
4. & CCl_3(M)\cdot + (n-1)M & \longrightarrow CCl_3(M)\ \cdot & \\
5. & CCl_3(M)_n^{\cdot} + CCl_3Br & \longrightarrow CCl_3(M)_nBr + CCl_3\cdot & \underline{\text{Chain}} \\
 & & & \underline{\text{Transfer}} \\
6. & 2CCl_3\cdot & \longrightarrow C_2Cl_6 &
\end{array}$$

Various types of termination, e.g. cross-terminations, may also occur but these will not appreciably affect the major products of these reactions provided the kinetic chains are long. It should be possible to prepare compounds of the following type,

$$\left.\begin{array}{r} CCl_3 - CH_2 - CHClBr\ (1:1\ \text{Adduct}) \\ CCl_3 - CH_2 - CHCl - CH_2 - CHClBr\ (2:1\ \text{Adduct}) \end{array}\right\}\quad \text{Telomers.}$$

provided the rate constant for the chain transfer reaction is sufficiently high.

The Preparation of Telomers.

These were prepared photochemically at 25°C, using the appropriate quantities of BTCM and VC: the initial mole ratio of BTCM to VC ranged from 1:5 to 1:25

Table 4. Physical Properties of the Reactants

	Bromotrichloromethane	Vinyl Chloride
Molecular Weight	198	62.5
Density at 25°C g/c.c.	2.006(61)	0.905(62)
Boiling Pt. at 760 m.m.	104°C	-13.9°C

Most of the telomerisations were taken to approximately 10% conversion as estimated by contraction measurements in the dilatometers. On the assumption that 1:1 adduct alone is produced, it is possible to calculate the absolute rate of reaction between BTCM and vinyl chloride. The reaction may be represented as:

$$\begin{array}{llcll} & CCl_3Br & \overset{h\nu}{+} & VC & \longrightarrow CCl_3(VC)_1Br \\ \text{Mol. Wgt.} & 198 & + & 62.5 & \longrightarrow 260.5 \\ \text{Density (g./c.c.)} & 2.006 & + & 0.905 & \qquad\;\; 1.825 \\ \text{No. of c.c./mole} & 99.0 & + & 69.1 & \longrightarrow 143.0 \end{array}$$

i.e. Contraction = 168.1 - 143 = 25.1 c.c./mole 1:1 adduct.

This contraction is independent of the concentration of the reactants, always provided that there is at least one mole of each reactant present.

Let V = total volume of the reaction mixture and

x = contraction after t seconds

$\therefore$ Contraction per unit time = x/t c.c. per sec.

The theoretical contraction for one mole of 1:1 adduct

is 25.1 c.c./mole

Thus rate of formation of 1:1 adduct $= \dfrac{x}{t \times 25.1}$ moles sec^{-1}

i.e. Rate of reaction in absolute units

$$= \frac{x \cdot 1000}{t \times 25.1 \times V} \text{ moles sec}^{-1}\text{litres}^{-1}$$

$$\text{and Fractional Conversion Per Second} = \frac{\text{Percentage Contraction/Sec.}}{\text{Percentage Contraction in the Formation of 1 mole of Adduct}}$$

The above reasoning is based on the assumption that the rate of formation of 1:1 adduct, and the rate of removal of vinyl chloride and BTCM are equal.

Having estimated the extent of reaction in the reaction vessel, the excess vinyl chloride was allowed to vapourise and the unreacted BTCM removed. Molecular weights were determined cryoscopically for the telomers resulting from various reaction mixtures and the variation in $\bar{r}$ with BTCM concentration is set out in table 5.

Table 5. The Variation in $\bar{\bar{r}}$ with Decreasing Concentration of BTCM for the Photochemical Telomerisation of Vinyl Chloride at 25°C.

Initial Mole Ratio (BTCM/VC)x 10^4	Molecular Weight	$\bar{\bar{r}}$
10,000	260	1.00
2,000	282	1.35
700	309	1.77
480	326	2.05
350	305	2.67

The infra-red absorption spectra for the 1:1 and 2:1 adducts displayed peaks at the following wave numbers.

Table 6. Absorption Peaks for the Infra-red Spectra of the 1:1 and 2:1 Adducts

1:1 Adduct (Wave Number. Cm.$^{-1}$)	2:1 Adduct (Wave Number. Cm.$^{-1}$)
	708
728	
	762
819	810
	895
	930
969	968
1020	1030
1060	1055
	1090
1170	1175
1205	
	1240
	1320
1340	
1410	1420

It was also important to find the effect of extent of reaction on the molecular weight of the telomers in order that maximum yields could be obtained. An initial mole ratio of 10:1 for VC:BTCM was therefore taken to various stages of conversion and the molecular weights of the products determined cryoscopically. Above a conversion of 10% the telomer mixture became cloudy and gelled on standing at room temperature.

An attempt was also made to prepare solid telomers by decreasing the initial concentration of BTCM in the reactant mixture. Initial mole ratios of 60:1, 80:1, and 100:1 for VC:BTCM were taken to ca. 10% conversion and there resulted a mixture of high and low molecular weight material. The solid was separated from the liquid, taken up in toluol, precipitated by petroleum ether and dried.

Unfortunately the molecular weights of these compounds could not be determined cryoscopically for they were only partially soluble in various solvents. Neither was it possible to use viscosimetric methods since the molecular weight lay outwith the required range.

The Preparation of Polymers.

These were prepared a) thermally with the initiators 1:1′azobisisobutyronitrile (AIBN) or benzoyl peroxide (BP) at various temperatures b) photochemically at 25°C with

BTCM and/or AIBN as photosensitiser.

The $\bar{r}$ of polymers may be varied by altering the polymerisation temperature$^{(63)}$. Increase in the temperature of polymerisation produces PVC having a lower $\bar{r}$. This method was limited, however, since it was not practicable to carry out polymerisations above 70°C due to the higher pressures developed in the dilatometer (see table 2).

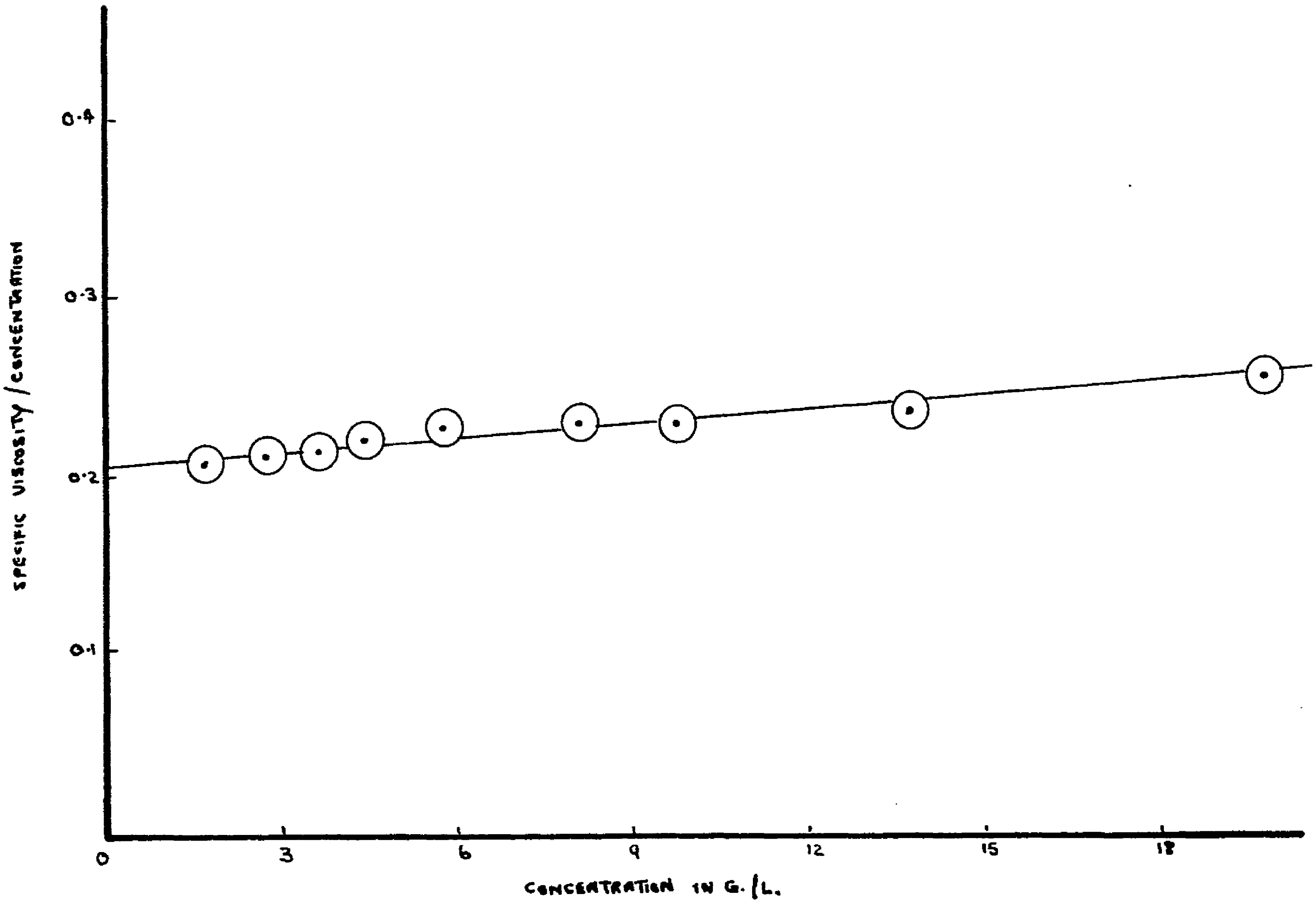
The photochemical preparation of these polymers lent itself much more to the study of variation in $\bar{r}$ with, say initiator or transfer agent concentration. At 25°C the system BTCM-VC photosensitised with BP was investigated. The concentrations of the peroxide and vinyl chloride were kept constant, whilst the BTCM concentration was altered. The molecular weight of the solid PVC obtained was estimated viscosimetrically (fig.9.). Table 7 shows how the $\bar{r}$ of the polymer changed with the decreasing concentration of BTCM.

Table 7. The Variation in $\bar{r}$ with Decreasing Concentration of BTCM for the Photosensitised Polymerisation of Vinyl Chloride at 25°C.

Initiator (moles/l.) Benzoyl peroxide $\times 10^3$	Initial Mole Ratio (BTCM/VC) $\times 10^4$	Intrinsic Viscosity in 100 c.c./g.	$\bar{r}$
1.000	2.000	0.209	145
0.973	1.330	0.290	206
1.000	1.000	0.460	325
0.962	0	0.960	685

FIG. 9

TYPICAL INTRINSIC VISCOSITY DETERMINATION



Density determinations were carried out on samples of PVC and also on the telomers, pyknometers being used for the latter. There appeared to be a trend in relationship between density and chain length as can be seen from table 8.

Table 8. Properties of the Compound Resulting from the Photolysis of Vinyl Chloride and BTCM at 25°C.

Initial Mole Ratio (BTCM/VC) x 10^4	$\bar{r}$	Density (g/c.c.)
20	1.47	1.399
756	1.76	1.770
6,650	1.00	1.825

A rough idea of the differences in rates of contraction between polymerisation and telomerisation may be gauged from table 9.

Table 9. An Approximate Comparison of the Reaction Rates for the Photochemical Telomerisation and Polymerisation of Vinyl Chloride at 25°C.

Initiator Benzoyl Peroxide (moles/l.)	Initial Mole Ratio (BTCM/VC) x 10^4	Percentage Contraction Per Hour
0	10,000	1.00
0	1,000	0.646
0	400	0.455
0	100	0.346
10^{-3}	20	0.087
10^{-3}	1	0.158
10^{-3}	0	0.158

Since products of widely varying $\bar{r}$ were formed under the conditions quoted in table 9, the comparison was approximate. The appreciable differences in density among the various products would mean ipso facto differences in rates of contraction.

In many polymerisations the rate of reaction was linear for both heterogeneous and homogeneous systems (fig.10). Similar results were obtained by Breitenbach and Schindler(64) for the system vinyl chloride-tetrabromomethane.

Preliminary to Pyrolysis of Telomers

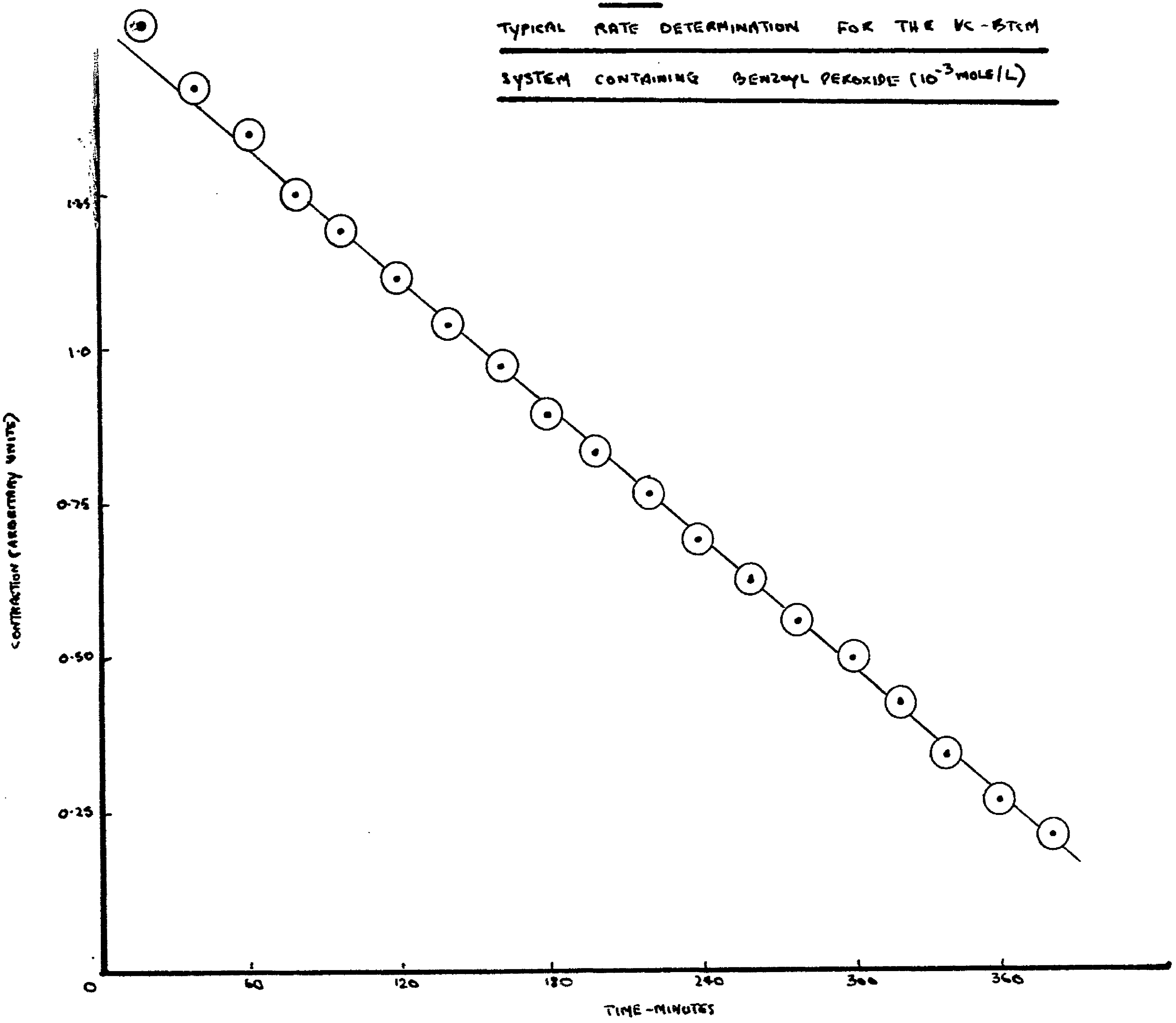
The effects of heating the carrier gas and varying its flow rate were investigated. The effect of the quantity of telomer used on the rate of evolution of acid was also studied.

Variation in Flow Rate.

The direct method was to alter the volume of nitrogen passing over the pyrolysand in a given time. A second method consisted in maintaining a steady flow rate, stopping the flow completely for a short period, then resuming the original flow rate. Variation in the time taken for

FIG. 10

TYPICAL RATE DETERMINATION FOR THE VC-BTCM SYSTEM CONTAINING BENZOYL PEROXIDE (10^{-3} MOLE/L)



stopping meant a variation in the gas flow rate. Using this second method, it was possible to estimate whether or not the pyrolysis was autocatalytic with respect to the evolution of acid during pyrolysis. Stoppage of the flow allowed the evolved acid to remain in contact with the pyrolysand. This did not affect the rate at which acid was evolved from the telomer (fig.11.).

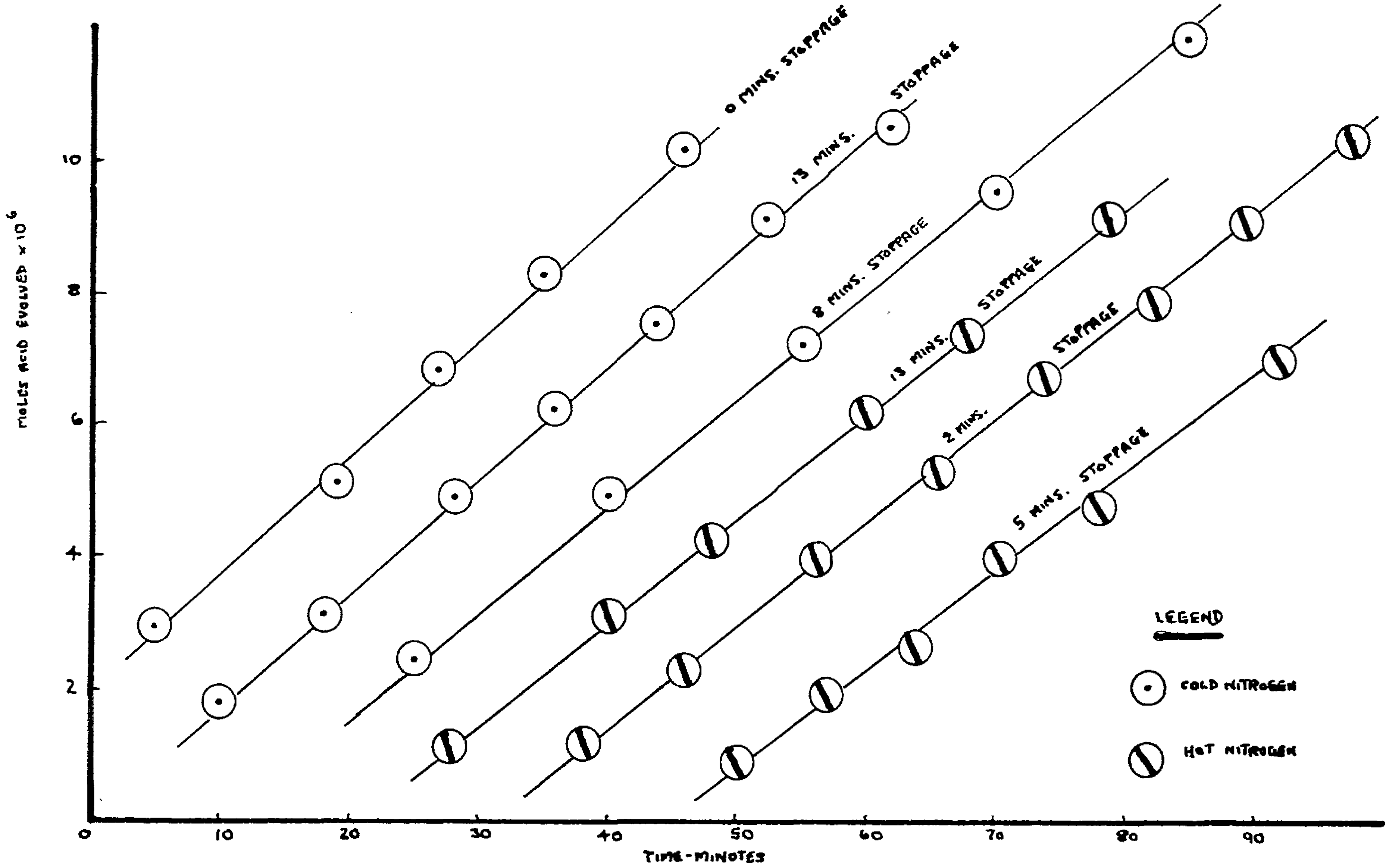
The rate of evolution of acid (hereafter referred to as the rate) from the 1:1 adduct was independent of the gas flow rate below 12 litres per hour. This was in good agreement with the work of Telamini and Pezzin(31) for a similar type of system. The most suitable flow rate was 3 to 4 litres per hour, because higher flow rates tended to sweep over a little pyrolysand into the absorber.

Preheating the Nitrogen.

It was thought that the cold gas flowing over the surface of the pyrolysand might cool the latter. Thus if breakdown were taking place mainly in the vapour phase it would be affected by the temperature of the carrier gas. When allowance was made for the expansion of the hot gas, by applying Charles' Law, it was found that for the same gas flow rate, hot gas was no more efficient than cold gas in carrying over the acid into the absorber. The hot gas entrained the pyrolysand more efficiently than the

FIG. 11

THE EFFECT OF VARIATION OF FLOW RATE ON THE RATE OF EVOLUTION OF ACID AT 198°C FROM 2.56g. OF 1:1 ADDUCT



cold gas, judging by the relative amounts of condensation on the walls of the condenser. Hot gas flow rates of the order of 3 to 4 litres per hour did not appear to entrain the pyrolysand.

Since the 2:1 adduct has a much higher b.pt.(265°C) than the 1:1 adduct (220°C), it was not necessary to duplicate the above experiments for the former. In the event of either of the adducts being swept over into the absorber during pyrolysis, a simple test was performed. Both adducts were allowed to stand in water for several days. There was no evidence of any hydrolysis to acid materials.

Quantity of Adduct.

Different amounts of the 1:1 adduct were pyrolysed at 198°C. The volume of acid evolved was directly proportional to the weight of adduct taken for pyrolysis.

Table 10. The Proportionality between Weight Pyrolysed and Acid Evolved from the 1:1 Adduct at 198°C

Relative Weight of 1:1 Adduct	Relative Rate
2.79	3.05
1.67	1.62
1.00	1.00

Pyrolysis of Telomers in Solution and in Bulk.

Variation in Concentration.

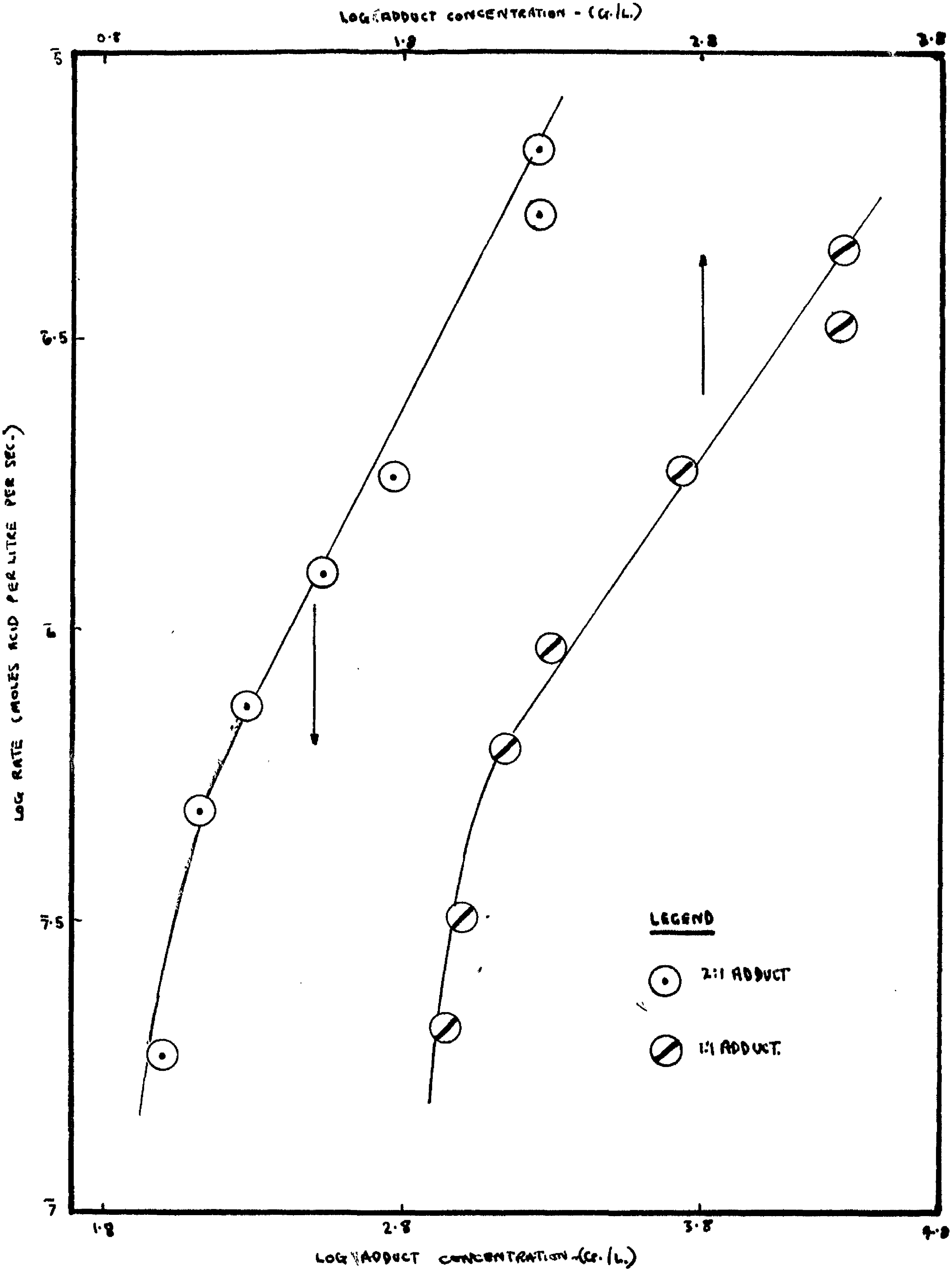
All pyrolyses mentioned in this section were conducted at 198°C except where specific mention is made of other temperatures. To obtain a dependence on telomer concentration, pyrolyses of the 1:1 and 2:1 adducts were carried out in ethyl benzoate solution. The amount of telomer was kept constant, but the volume of solvent and hence the concentration was altered. The plot of log rate against log adduct concentration (fig.12.) showed a rate dependence of 1.1 on the 2:1 adduct, and 0.76 on the 1:1 adduct, which indicated a first order dependence on these telomers. The fall-off in rate at the lower telomer concentrations was attributed to dilution effects.

Variation in Temperature.

The rates for the 1:1 and 2:1 adducts in bulk and in ethyl benzoate were measured for a series of temperatures. Fig.13 shows the variation in rate with temperature for the bulk pyrolysis of 1.98 g. of 1:1 adduct. For the latter, rate determinations were not carried out until the rate had reached the 'steady state' (i.e. the rate of evolution of acid per unit time was linear) because in the initial stages the rate changed continuously. Activation energies for the breakdown of both adducts were evaluated

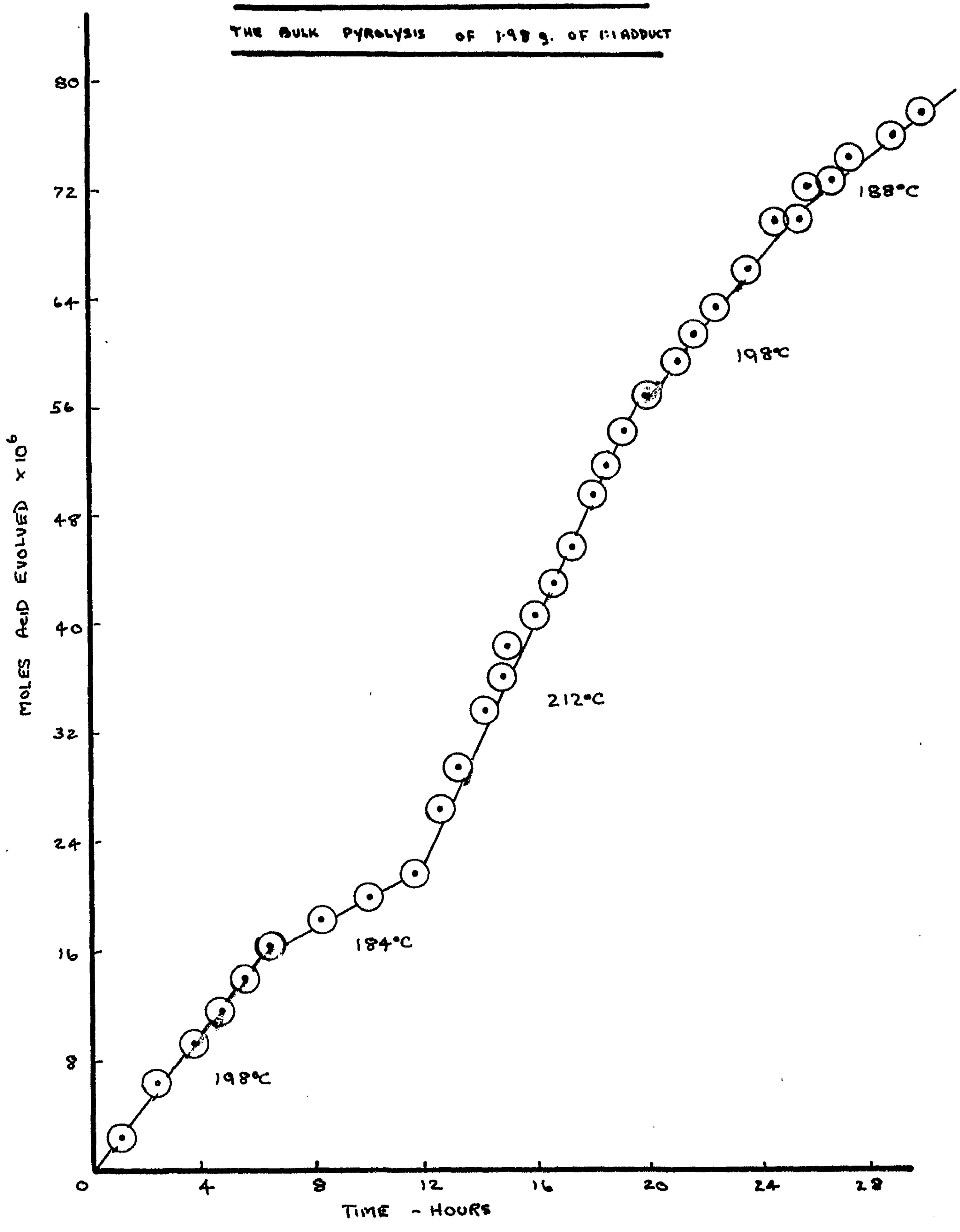
FIG. 12

RATE DEPENDENCES OBTAINED IN THE SOLUTION PYROLYSES OF THE 1:1 AND 2:1 ADDUCTS



VARIATION IN RATE WITH TEMPERATURE FOR

THE BULK PYROLYSIS OF 1·98 g. OF 1:1 ADDUCT



from the plot of log rate versus reciprocal of absolute temperature. Fig.14 is a typical Arrhenius plot for the bulk pyrolysis of the 1:1 adduct. As can be seen from table 11, there was no great difference between the activation energies for telomers pyrolysed in bulk and in ethyl benzoate solution.

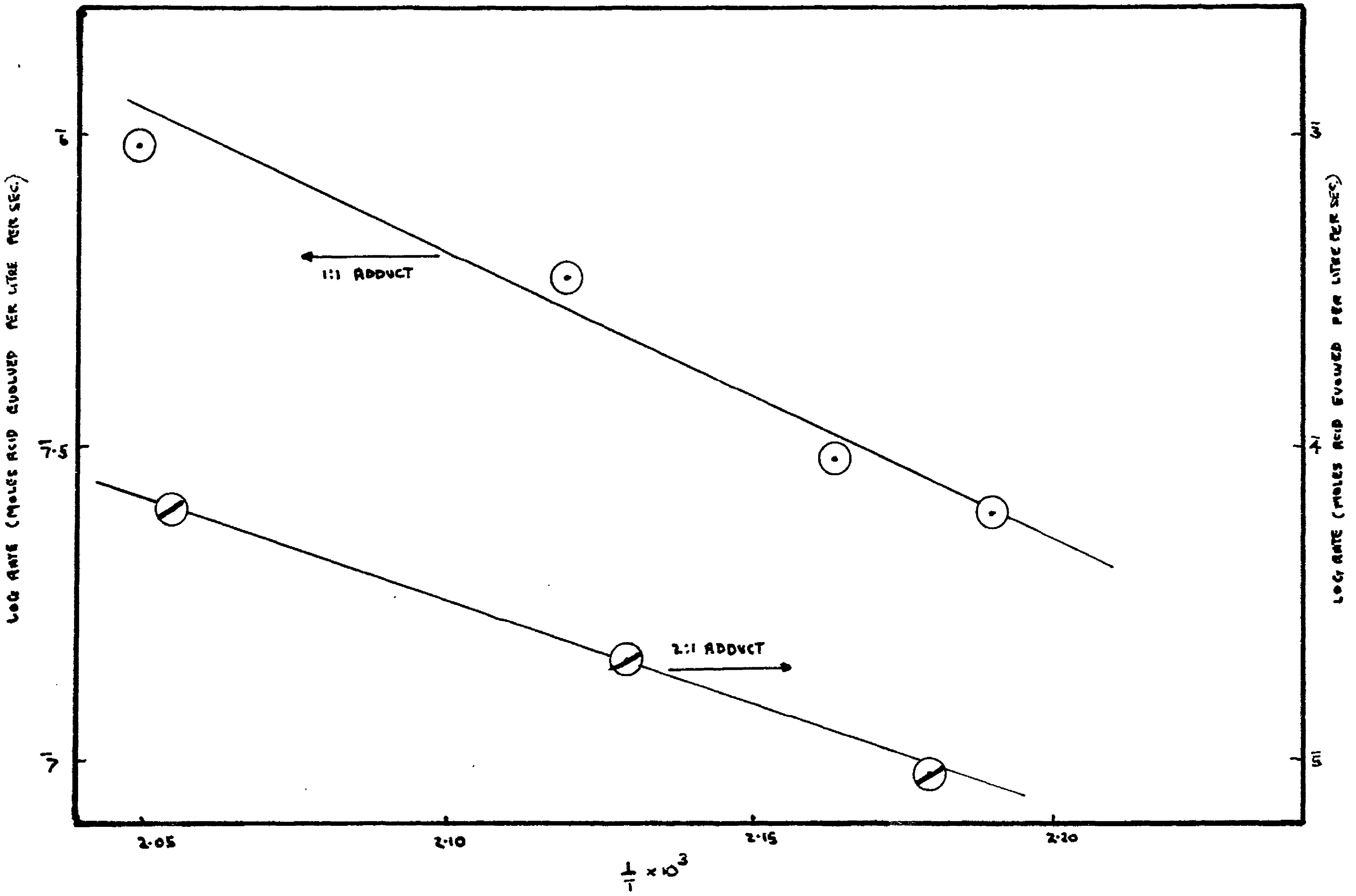
Table 11. Activation Energies for the Pyrolysis of the 1:1 and 2:1 Adducts in Bulk and in Ethyl Benzoate Solution

Adduct	Medium	Activation Energy (k.cal./mole)
1:1	Bulk	21.3
1:1	Ethyl Benzoate	22.1
2:1	Bulk	29.0
2:1	Ethyl Benzoate	28.0

In order to compare these activation energies with those obtained in the decomposition of similar compounds, a number of halogenated hydrocarbons were pyrolysed under similar conditions. These compounds included 1-bromooctane, 1:4-dibromobutane, 1:5-dibromopentane, 1-chlorodecane. Unfortunately none of these compounds evolved measurable yields of acid and it was not possible to obtain their activation energies in the temperature range 170 to 220°C.

FIG. 14

ARRHENIUS PLOTS FOR THE DEGRADATION OF THE 1:1 AND 2:1 ADDUCTS IN BULK.



The comparatively high stability of these halogenated compounds prompted a more detailed investigation into the bulk breakdown of the telomers.

Bulk Pyrolysis.

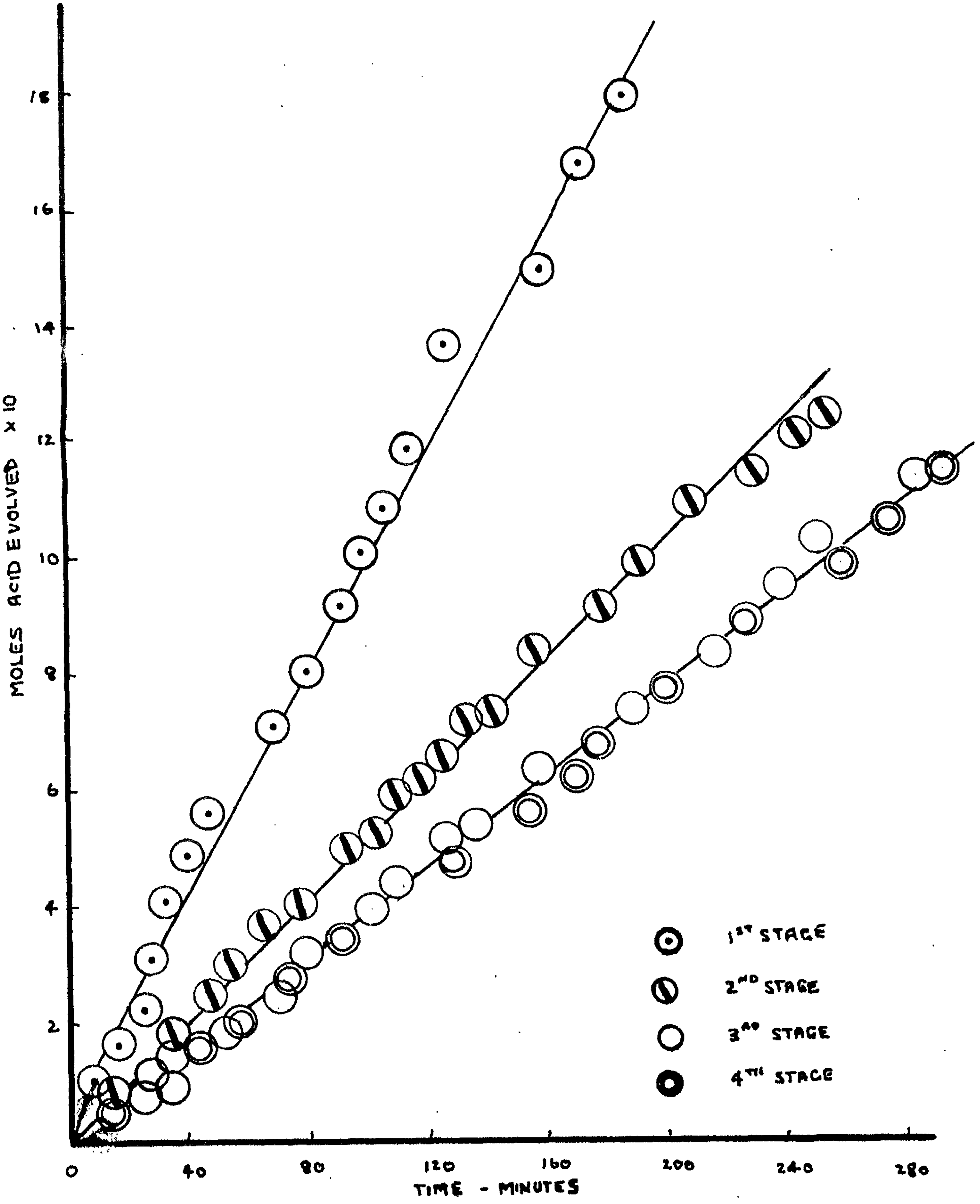
(1) 1:1 Adduct ($Cl_3C - CH_2 - CHClBr$)

The 1:1 adduct coloured very rapidly on pyrolysis and evolved acid at a comparatively fast rate for a halogen compound. When 2.56 g. of 1:1 adduct was pyrolysed for 33 hours the yield in acid amounted to 10^{-4} moles. Assuming the total available quantity of acid was 3 moles per mole of 1:1 adduct, then 10^{-4} moles of acid represented only 0.3% breakdown. The initial stages of this pyrolysis are shown in fig.15.

Evolution of acid probably produced a double bond in the molecule, and it was decided to prepare 1:1 adduct containing a double bond. It was hoped that pyrolysis of this compound would give some indication of the mechanism of decomposition.

The 1:1 adduct was treated with methanolic caustic potash, dried, and distilled under reduced pressure. The compound thus obtained did not hydrolyse when added to water. The presence of the double bond in the molecule was confirmed by the usual tests and also from infra-red spectra. The molecular weight of the compound was 202

THE INITIAL STAGES IN THE BULK PYROLYSIS OF 2·56 g. OF 1:1 ADDUCT AT 198°C



which corresponded to a 50-50 mixture of the unsaturates $Cl_3C - CH = CHCl$, $Cl_2C = CH - CHBrCl$. It was not possible, however, to carry out pyrolyses on the mixture because it had a b.pt. of ca.126°C. If the pyrolysis of this mixture were carried out at a much lower temperature, say 110°C, then the results could not be justifiably compared with those obtained at 198°C.

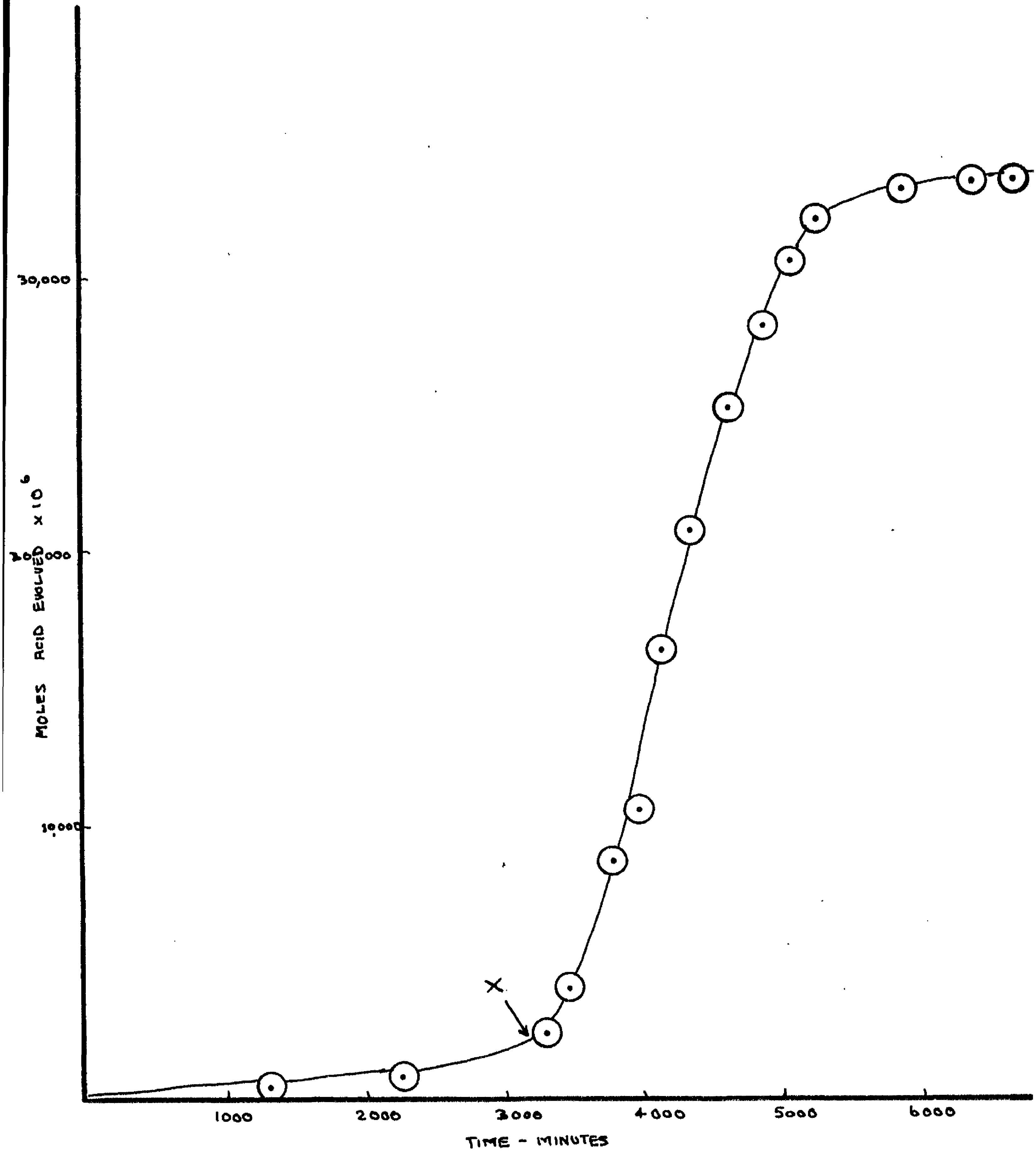
(2) 2:1 Adduct ($Cl_3C - CH_2 - CHCl - CH_2 - CHClBr$)

As with the 1:1 adduct, the 2:1 adduct coloured very quickly on pyrolysis, but 2.83 g. of 2:1 adduct yielded 8×10^{-4} moles of acid after 33 hours. Hence, disregarding the initial stages, the 2:1 adduct decomposed at a much faster average rate than the 1:1 adduct for the same time. Assuming there were 6 available moles of acid per mole of 2:1 adduct, 8×10^{-4} moles of acid corresponded to 1.50% degradation.

Because the 2:1 adduct evolved acid at a much faster average rate, its pyrolysis could be taken to completion, i.e. until no more acid was evolved. This made it possible to analyse the relative amounts of HBr and HCl being evolved and absorbed at various stages in the pyrolysis. The overall pyrolysis is depicted in fig.16.

Acid evolved was absorbed in distilled water and

THE OVERALL PYROLYSIS OF 2·83 g. OF 2:1 ADDUCT AT 198°C.



samples were drawn off as required for analysis. These were analysed qualitatively for bromide(65), then quantitatively for chloride as described in the section on Experimental. The bromide content was obtained by difference.

Table 12. The Relative Quantities of Hydrogen Chloride and Hydrogen Bromide Liberated during the Pyrolysis of 2:1 Adduct at 198°C.

Period of Pyrolysis (Hours)	Ratio of Cl^-/Br^- (moles)	Nature of the Pyrolysand
0 - 21.9	0.68/1[x]	Mobile, dark brown liquid
21.9 - 36.8	4.70/1	
36.8 - 54.6	6.04/1	
54.6 - 57.5	8.55/1	Extremely viscous, black liquid
57.5 - 62.8	6.51/1	Begins to solidify
62.8 - 65.9	6.25/1	
65.9 - 68.2	5.26/1	Cracked, hard, shiny material
68.2 - 72.0	4.92/1	
72.0 - 76.1	5.15/1	Small shiny lumps.
76.1 - 79.7	6.39/1	
79.7 - 83.0	6.15/1	
83.0 - 96.3	5.30/1	

[x] This value is doubtful since there was insufficient material for accurate analysis.

At point X in fig.16 the infra-red spectrum of the pyrolysand revealed the presence of an isolated double bond (fig.17.) at a wavelength of 6.25 microns. This was confirmed in the UV spectrum ($\varepsilon_{max(ethanol)} = 2,970$).

The end-product of the pyrolysis was a hard, shiny, crystalline black solid insoluble in all the common laboratory solvents. For this compound there were no identifiable peaks in its infra-red spectrum. Although its insolubility prevented a molecular weight determination, a microanalysis of the compound showed that its empirical formula was C_4H_2Cl.

Knowing the initial and final weights of the adduct, the quantity of acid evolved, the initial and final empirical formulae, it was possible to draw up a mass balance on the hydrogen participating in the degradation.

Mass Balance on Hydrogen.

Initial weight of the 2:1 adduct = 2.830 g.
Final " " " " " = 0.897 g.
$\therefore$ Weight of the 2:1 adduct used = 1.933 g.
Molecular Weight of 2:1 adduct = 323

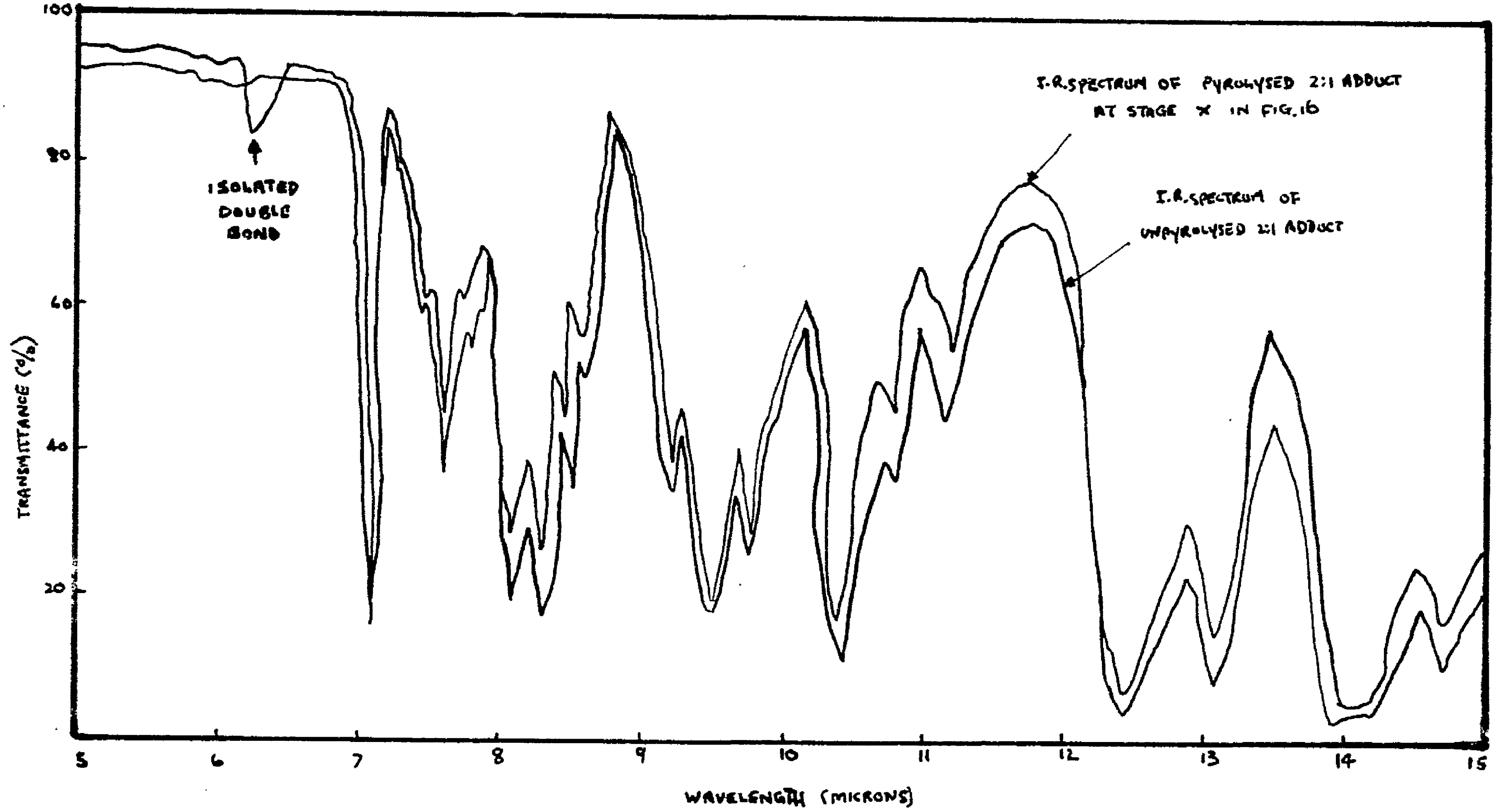
1 molecule of $Cl_3C - CH_2 - CHCl - CH_2 - CHClBr$ contained 6 g. atoms of hydrogen.

So that 2.83 g. adduct contained $\frac{2.83}{323} \times \frac{6}{1}$ g. atoms hydrogen

$\therefore$ Total available hydrogen = 52.6×10^{-3} g. atoms hydrogen.

FIG. 17

THE I.R. SPECTRA OF THE 2:1-ADDUCT AND ITS PYROLYSAND



Total acid evolved in the pyrolysis = 29.13×10^{-3} moles.

Each mole of acid contained 1 g. atom of hydrogen

.°. 29.13 moles of acid contained 29.13×10^{-3} g.atoms hydrogen.

.°. Total hydrogen evolved = 29.13×10^{-3} g. atoms.

Microanalysis yielded 4C 2H 1Cl

Final weight of adduct = 0.8970 g.

.°. Weight of hydrogen remaining = $\frac{2}{85.5} \times 0.8970$ g.atoms hydrogen.

= 21×10^{-3} g.atoms hydrogen

.°. Weight of hydrogen remaining + weight of hydrogen evolved

= $(21 \times 10^{-3} + 29.13 \times 10^{-3})$ g. atoms

= 50.13 g. atoms hydrogen.

This compared with the total available hydrogen,

i.e. 52.6×10^{-3} g. atoms.

According to fig.16 the inclusion of a double bond in the 2:1 adduct increased the rate. This stage in the pyrolysis was simulated by the artificial insertion of a double bond into the saturated molecule. Treatment of the adduct with methanolic caustic potash yielded an unstable, unsaturated, yellow, oily liquid of b.pt. 230°C.

The pyrolysis of 2.13 g. of this unsaturated compound produced an end-product similar in many respects to that of the 2:1 adduct. Furthermore the initial breakdown of this compound was of the same order as the breakdown of the 2:1 adduct at stage X in fig.16.

Table 13. Comparison of Rates for the 2:1 Adduct and Unsaturated 2:1 Adduct at 198°C.

Compound	Weight (moles) x 10^3	Rate of Evolution of Acid (moles acid/1/sec) x 10^7
2:1 Adduct	8.75	56
2:1 Adduct at Stage X in fig.16	8.65	664
Unsaturated 2:1 Adduct	8.90	615

From the data in table 13 it might be inferred that the presence of the double bond exerted a powerful influence on the rate of decomposition of the 2:1 adduct.

Thus far there has been no real indication of the mechanism of breakdown of these adducts. However in polymer chemistry one of the best indirect proofs of the nature of a polymerisation or degradation may be obtained by the addition of so-called free radical chain initiators or inhibitors to the reacting system.

Effect of Additives on Telomers.

(1) Free Radical Initiators.

The 1:1 and 2:1 adducts were pyrolysed in the presence of 2% (w/w) AIBN at various temperatures.

Table 14. Addition of AIBN to the 1:1 and 2:1 Adducts Pyrolysed in Ethyl Benzoate Solution

Adduct	Temperature of Pyrolysis (°C)	Effects observed
1:1	100	No increase in rate
1:1	130	" " " "
1:1	157	Fourfold increase
2:1	100	No increase in rate
2:1	130	" " " "
2:1	157	Fourfold increase

Larger quantities of AIBN tended to give even bigger increases in rates, but only at or above 157°C. Similar results were obtained when 2% benzoyl peroxide was used. With BP, however, it was necessary to carry out blank runs in ethyl benzoate due to the liberation of carbon dioxide from this initiator.

Samples of 1:1 and 2:1 adduct were also pyrolysed in bulk at 198°C in the presence of initiators. For a better assessment of the effect of initiator on rate, samples of 'pre-pyrolysed' 1:1 adduct only were used for these experiments. In pre-pyrolysis, samples of the 1:1 adduct were pyrolysed until the rate of evolution of acid per unit time was linear, so that even a small increase in rate on addition of initiator would be readily observed. When BP and AIBN were added to such samples of 1:1 adduct both were found to increase the rate. AIBN (0.6% w/w) was added to 1:1 adduct at 198°C with a resultant considerable increase in rate (fig.18.). Similar results were obtained with the 2:1 adduct and AIBN.

The number of free radicals associated with one molecule of HCl was estimated as follows:

Weight of 1:1 Adduct = 2.56 g.
Weight of AIBN = 0.0149 g.
Molecular Weight of AIBN = 164.

The increase in the quantity of HCl evolved was 7.5×10^{-6} moles in 40 minutes; all the AIBN was assumed to have decomposed in this time at 198°C.

i.e. $\frac{0.0149}{164}$ moles AIBN yielded 7.5×10^{-6} moles HCl

i.e. 18.12×10^{-5} AIBN radicals yielded 7.5×10^{-6} moles HCl

or 24 radicals were associated with 1 molecule of HCl

Bawn and Mellish$^{(66)}$ reported that the decomposition of AIBN was a first order reaction, with

$$k = 10^{15}\ e^{-30,700/RT}\ \text{sec.}^{-1}$$

But $$k = \frac{2.303}{t} \log_{10} a/a-x \quad \text{sec}^{-1}.$$

where a = original concentration of initiator (moles/l.)
a-x = concentration of initiator at time t (")
k = rate constant (sec.$^{-1}$)

For pyrolysis at $198^{\circ}C$, $k = 6.166\ sec.^{-1}$ Thus the time taken for 95% decomposition of AIBN should be 29 minutes as compared with the initial period of acceleration of 75 minutes (fig.18).

Oxygen may act indirectly as a free radical initiator by forming peroxides which decompose into free radicals. Several pyrolyses in bulk were run on the 1:1 and 2:1 adducts in an oxygen atmosphere. Compared with bulk pyrolysis rates in nitrogen, those in oxygen were much faster (fig.19).

(2) Radical Polymerisation Inhibitors.

These were completely ineffective in retarding or inhibiting rates. Indeed both adducts evolved much greater amounts of acid when pyrolysed in the presence of small quantities of these so-called inhibitors; table 15 quotes values for the 2:1 adduct.

THE EFFECT OF ADDING 0·6% AIBN (w/w) TO 2·56 g. 1:1 ADDUCT AT 198°C.

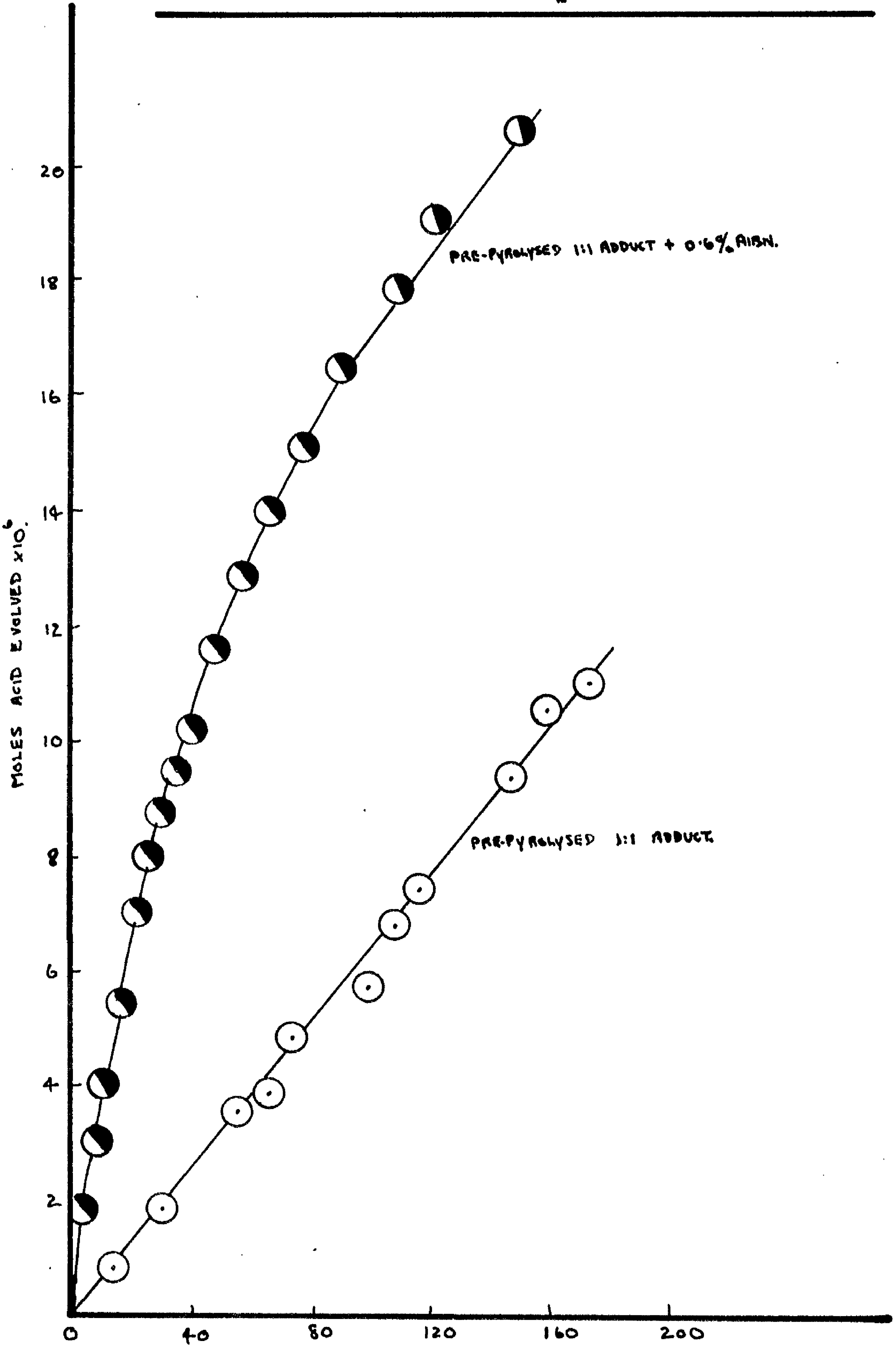


FIG. 19

TYPICAL PYROLYSES OF THE 2:1 ADDUCT (1·1g)
IN a) OXYGEN b) NITROGEN AT 198°C.

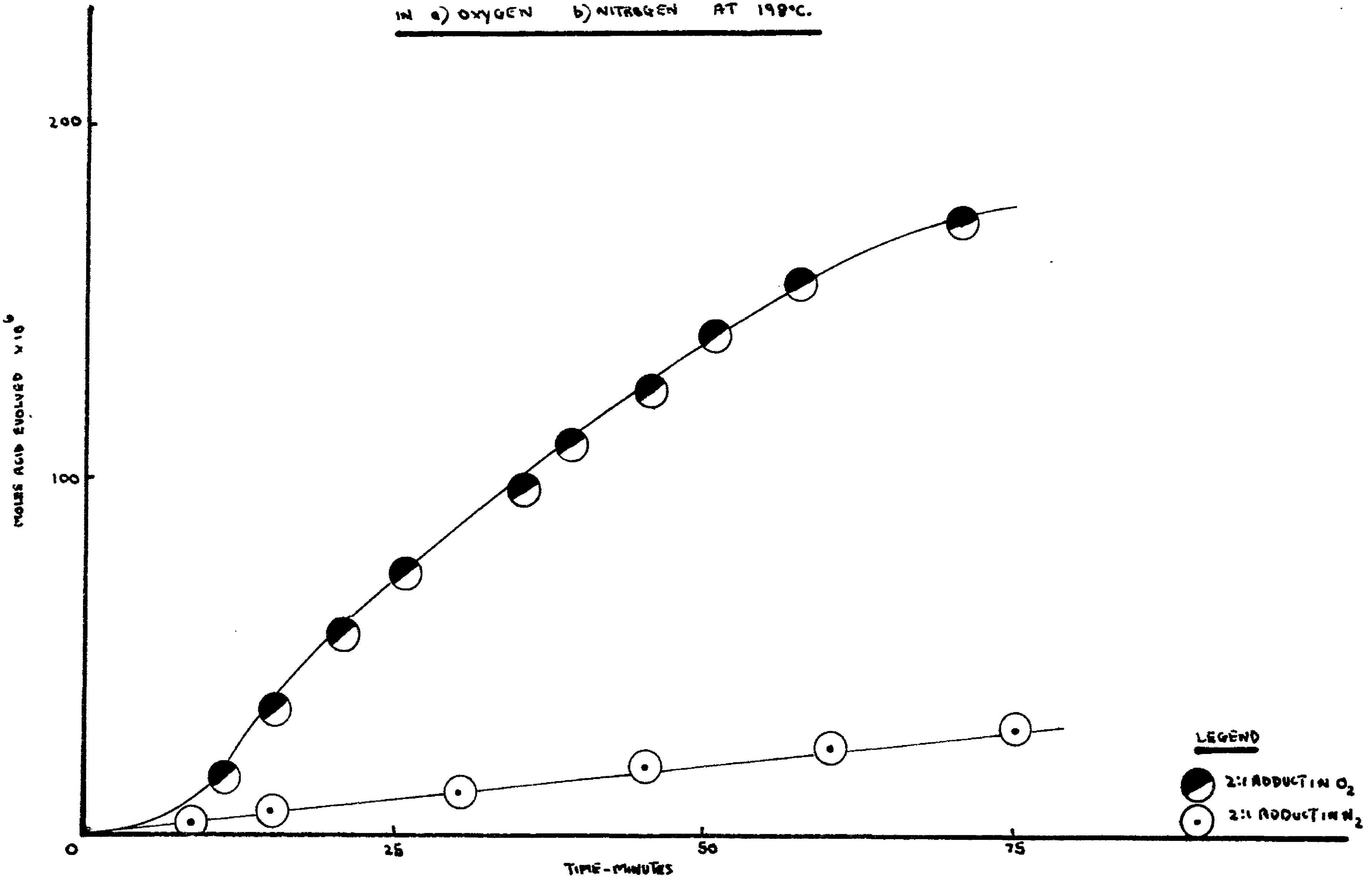


Table 15. The Effect of Various Radical Polymerisation Inhibitors on the Rate of Evolution of Acid from 1.86 g. 2:1 Adduct at 198°C.

Inhibitor	Percentage Inhibitor (w/w)	$\frac{\text{moles inhibitor}}{\text{moles 2:1 adduct}}$	Rate of Evolution of Acid (moles acid/hr) x 10^6
-	-	-	20.2 (Bulk 2:1)
α-Naphthol	6.05	0.136	740
Hydroquinone	5.58	0.164	335
Anthracene	6.20	0.113	332
Catechol	6.02	0.117	126
Naphthalene	6.06	0.154	98
Phenanthrene	6.06	0.110	46
Stilbene	6.50	0.117	33
Phenol	6.75	0.232	18

It was decided to study the reaction between these radical polymerisation inhibitors and the telomers. Hydroquinone (HQ) accelerated the decompositions of both adducts very markedly e.g. for 1:1 adduct containing 4% (w/w) HQ, the initial rate was ten times as fast as for the adduct alone. Furthermore HQ has been classed as a definite radical polymerisation inhibitor(67). It is easily obtainable in a high state of purity and is stable at high temperatures. It was thus a suitable choice for further co-pyrolysis studies.

The Action of HQ on Telomers

HQ protonises (pKa = 10) and it was just possible that it might be contributing to the total acid content in the absorber. To determine if HQ was a source of acid, blanks were run on HQ at 198°C and also on HQ in diphenyl as solvent at 240°C. No acid was evolved in either case. Finally in a pyrolysis of the system HQ – 1:1 adduct, the total acid evolved was titrated against

a) standard sodium hydroxide solution

b) standard silver nitrate solution.

The hydrogen ion concentration was identical with the halide ion concentration, so the HQ did not contribute to the hydrogen ions collected in the absorber.

The system HQ – adduct was pyrolysed at 198°C with a) adduct in excess b) HQ in excess.

The System Excess Adduct – HQ at 198°C

A series of pyrolyses on samples of 2:1 adduct containing different quantities of HQ revealed that the rate increased very markedly with increase in the HQ concentration (fig.20.). The dependence of initial rate on HQ concentration for the systems excess 1:1 adduct – HQ, excess 2:1 adduct – HQ is shown in fig.21. There appeared to be a sharp change in rate above a concentration of 4% HQ.

The log – log plots constructed for these systems

FIG. 20

THE RATES OF EVOLUTION OF ACID FROM THE SYSTEM HQ-EXCESS 2:1 ADDUCT (1·1 G IN EACH CASE) AT 198°C.

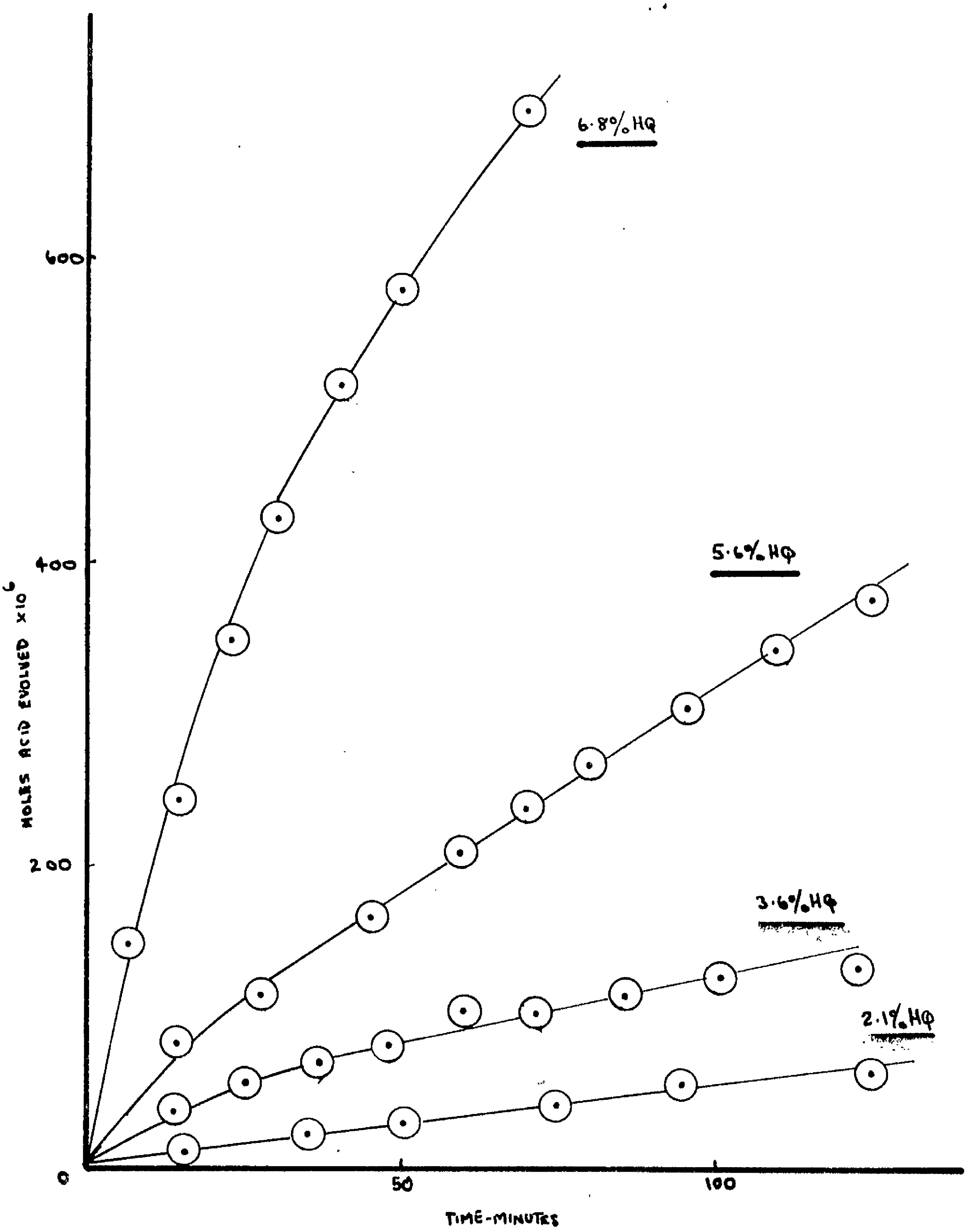
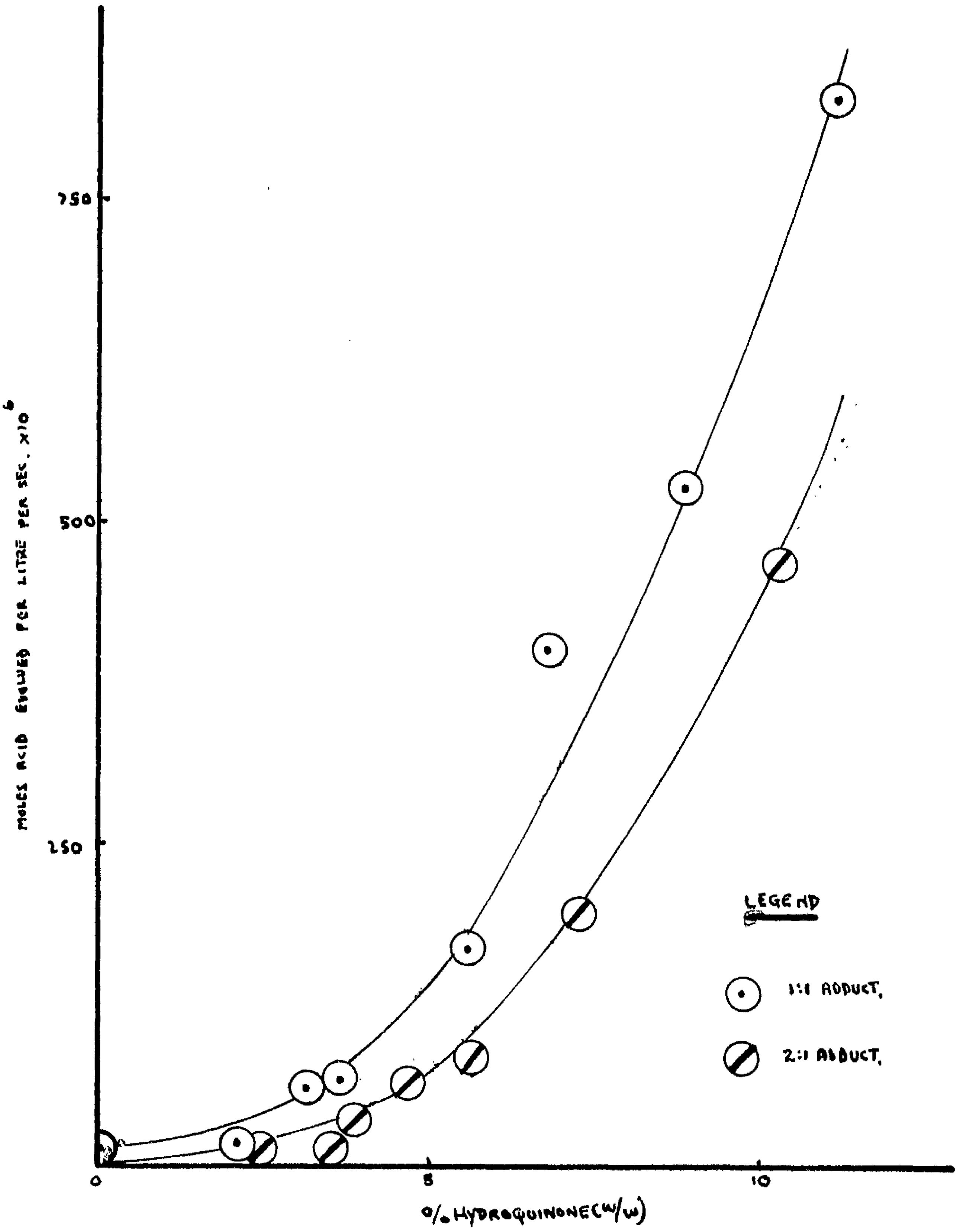


FIG. 21

THE EFFECT OF INCREASING HQ CONCENTRATION ON THE RATE OF EVOLUTION OF ACID FROM THE 1:1 AND 2:1 ADDUCTS AT 19.8°C.



gave the rate dependences on HQ concentration (fig.22.). Dependences on the catechol concentration were also obtained for the analogous systems excess 2:1 adduct - catechol, excess 1:1 adduct - catechol. The catechol system was very similar to that of HQ , but rates were somewhat lower.

Table 16. Rate Dependences for the System Excess Adduct - Radical Polymerisation Inhibitor at 198°C.

Excess Adduct	Radical Polymerisation Inhibitor	Dependence on Inhibitor Concentration
1:1	HQ	2.8
1:1	Catechol	2.3
2:1	HQ	2.3
2:1	Catechol	3.0

The System Excess HQ - Adduct at 198°C.

Samples of HQ containing various amounts of 2:1 adduct were pyrolysed and the acid evolved yielded a sigmoid type of curve (fig.23.). Similar curves were obtained for the system excess HQ - 1:1 adduct. All these curves were characterised by an initial surge of acid which gradually diminished. The plot of initial rate versus adduct concentration revealed a definite trend in that the former increased with increase in the adduct concentration (fig.24.). Fig.25 is the plot of total acid evolved up to the turning point on

FIG. 22

RATE DEPENDENCE ON HQ CONCENTRATION IN THE PYROLYSIS OF THE SYSTEM HQ-EXCESS ADDUCT AT 198°C.

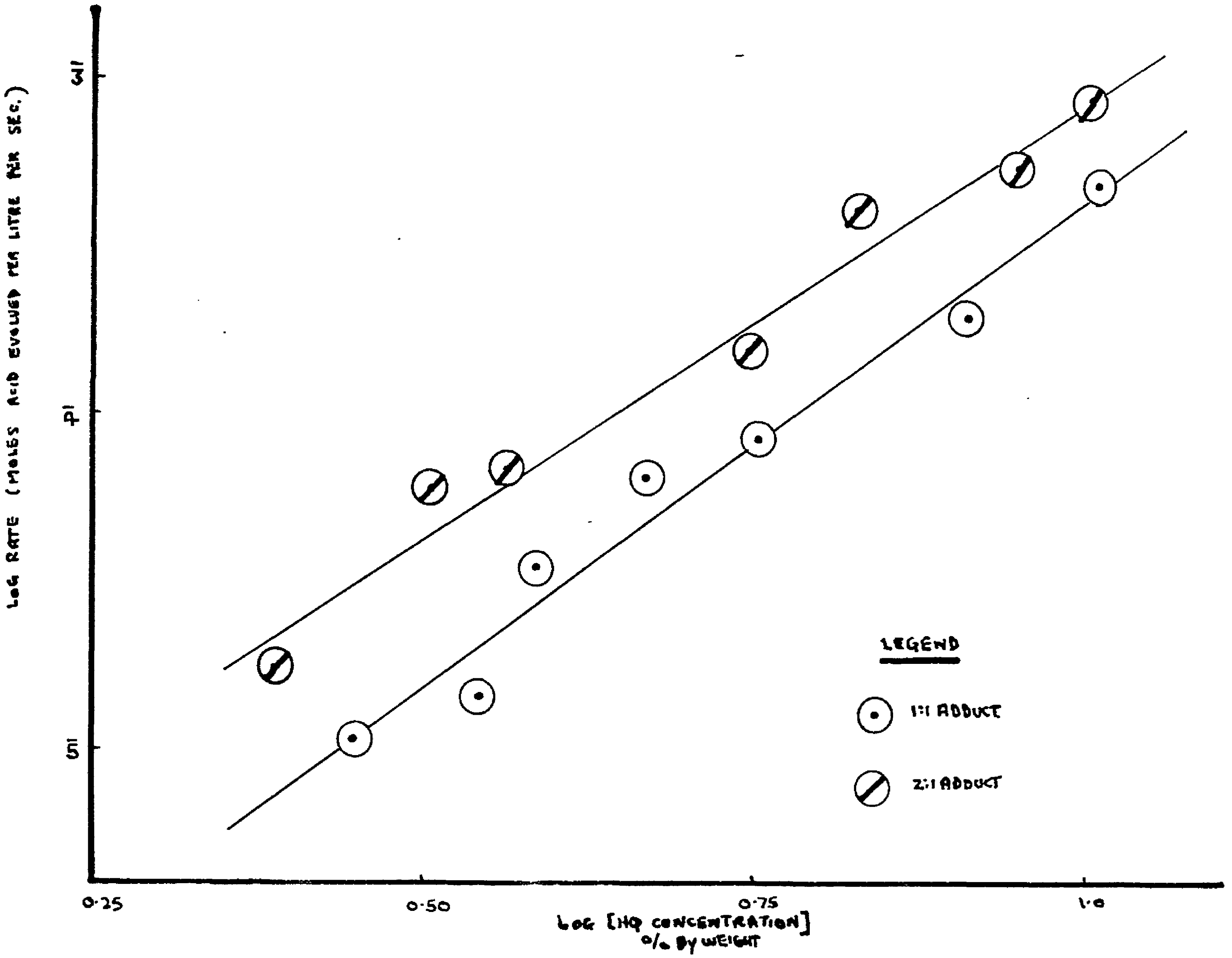


FIG. 23

TYPICAL CURVES FOR THE REACTION BETWEEN 2:1 ADDUCT AND EXCESS HCl (2·30 g.) AT 198°C.

(THE ORIGIN HAS BEEN SHIFTED TO AVOID SUPERPOSITION)

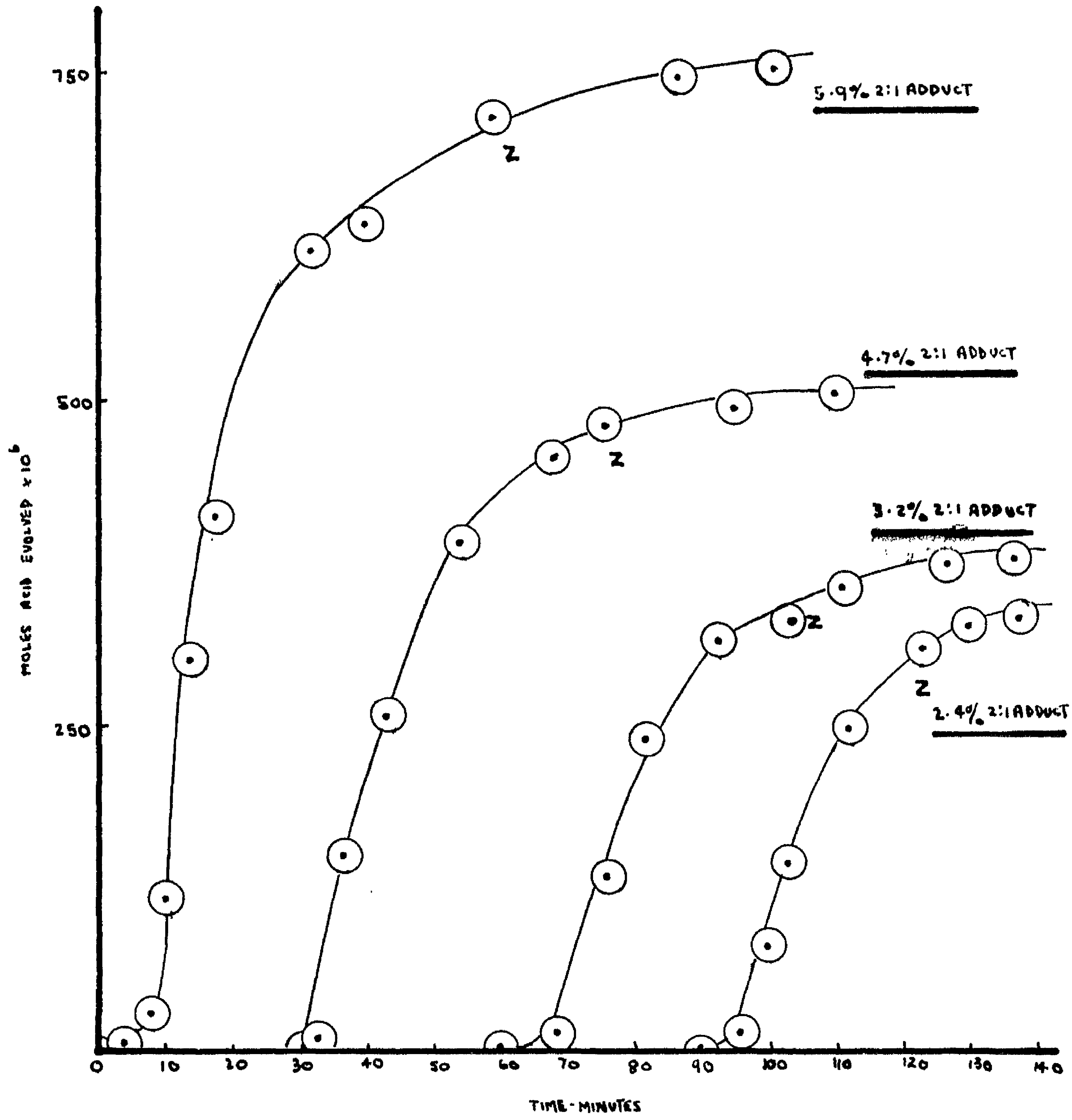


FIG. 24

VARIATION OF RATE WITH ADDUCT CONCENTRATION

FOR THE SYSTEM 2:1-ADDUCT-EXCESS HQ (2·3g.) AT 198°C

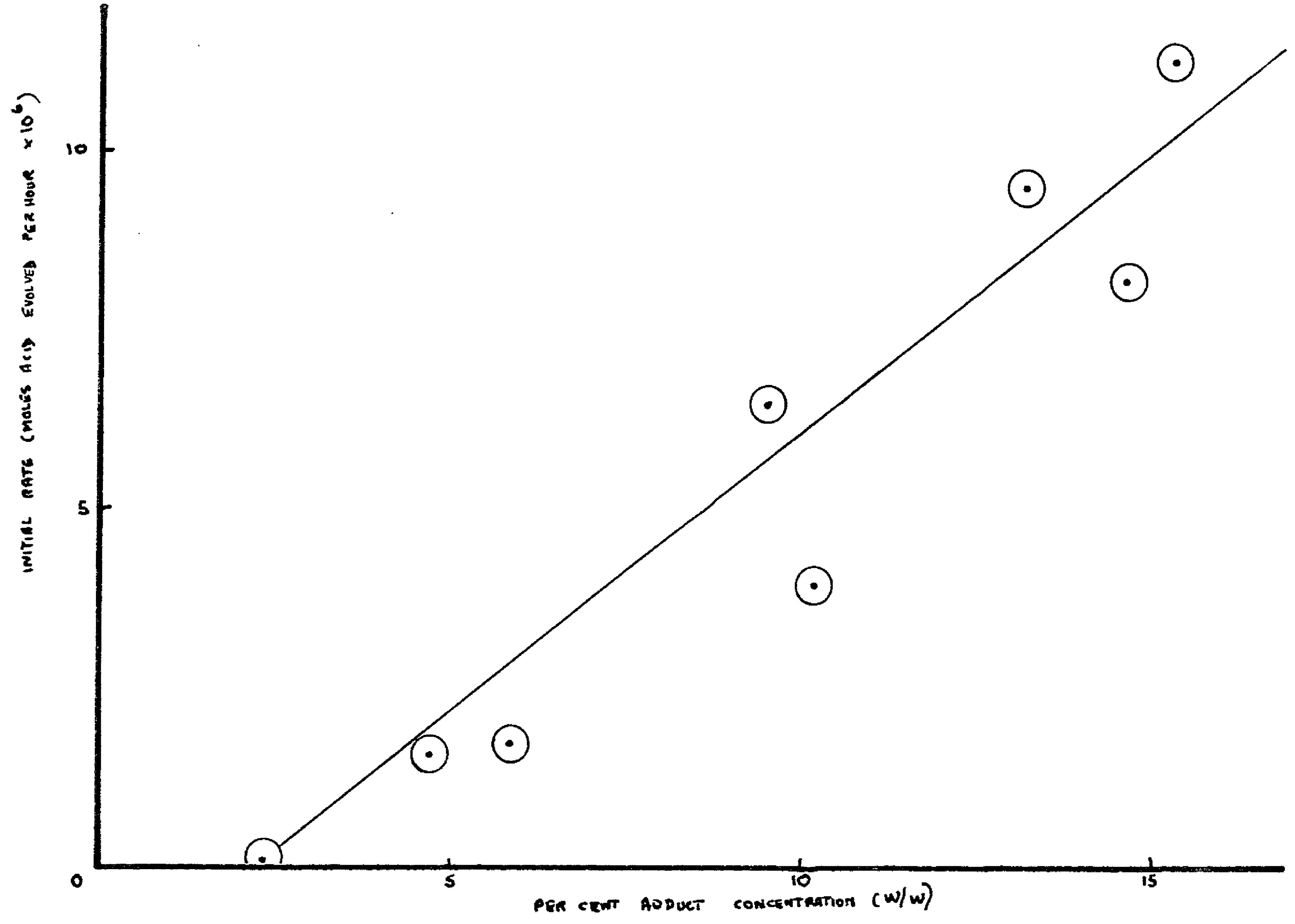
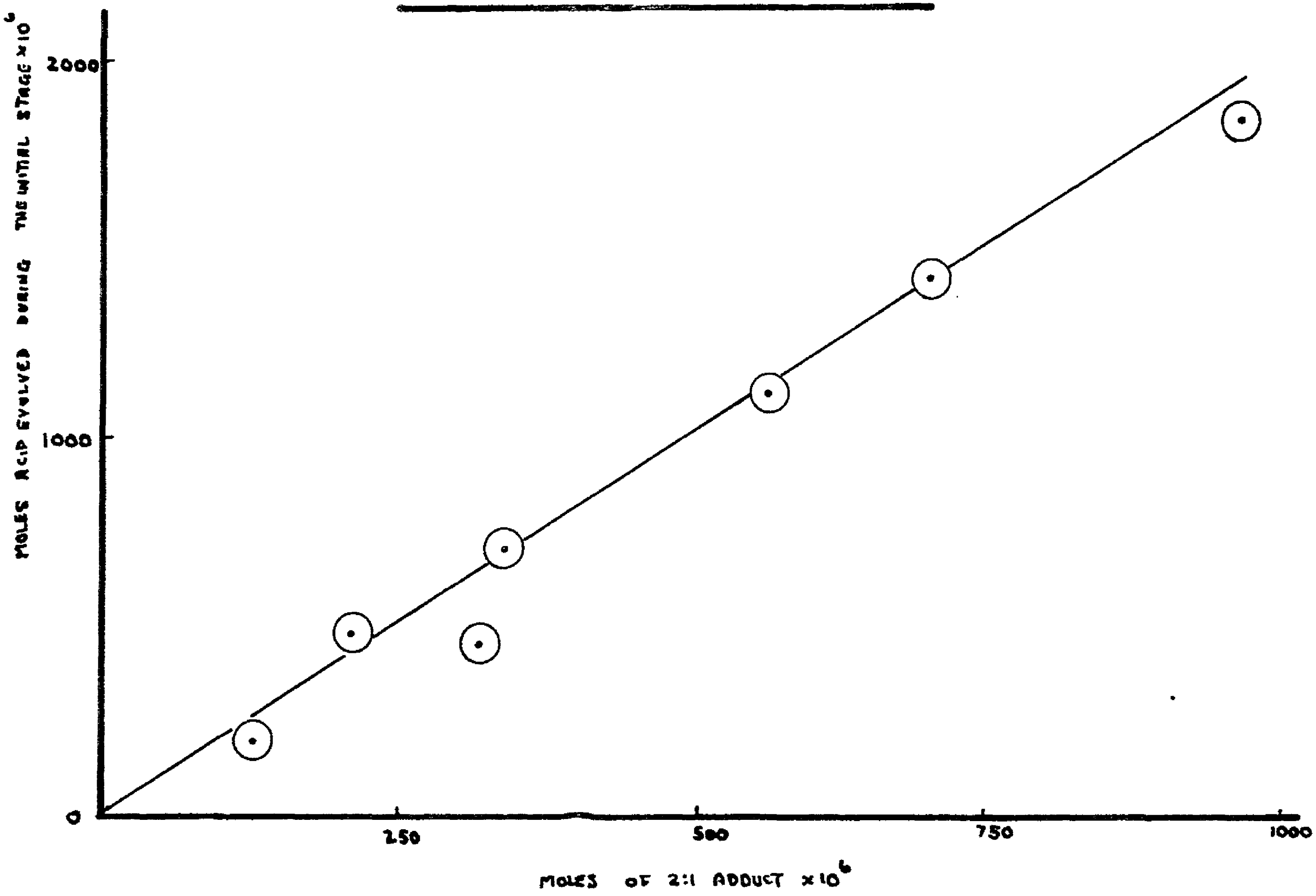


FIG. 25

ACID EVOLVED AT 198°C DURING THE INITIAL STAGE IN THE PYROLYSIS OF THE SYSTEM 2:1 ADDUCT - EXCESS HQ.



the sigmoid curve (Z on fig.23.) against adduct concentration. It was found that 1 mole of 2:1 adduct evolved 2 moles of acid up to point Z.

Since acid was liberated readily from both these systems it might be expected that the activation energies for the reactions would be fairly low. Before these were evaluated, however, it was important to find the solubility of the HQ in the telomer, and vice versa, so that runs could be carried out in a homogeneous system.

Solubilities.

These were gauged by the minimum quantity of constituent necessary to form a two-layer system.

Table 17. Solubility Data for the 2:1 Adduct - HQ System at 198°C.

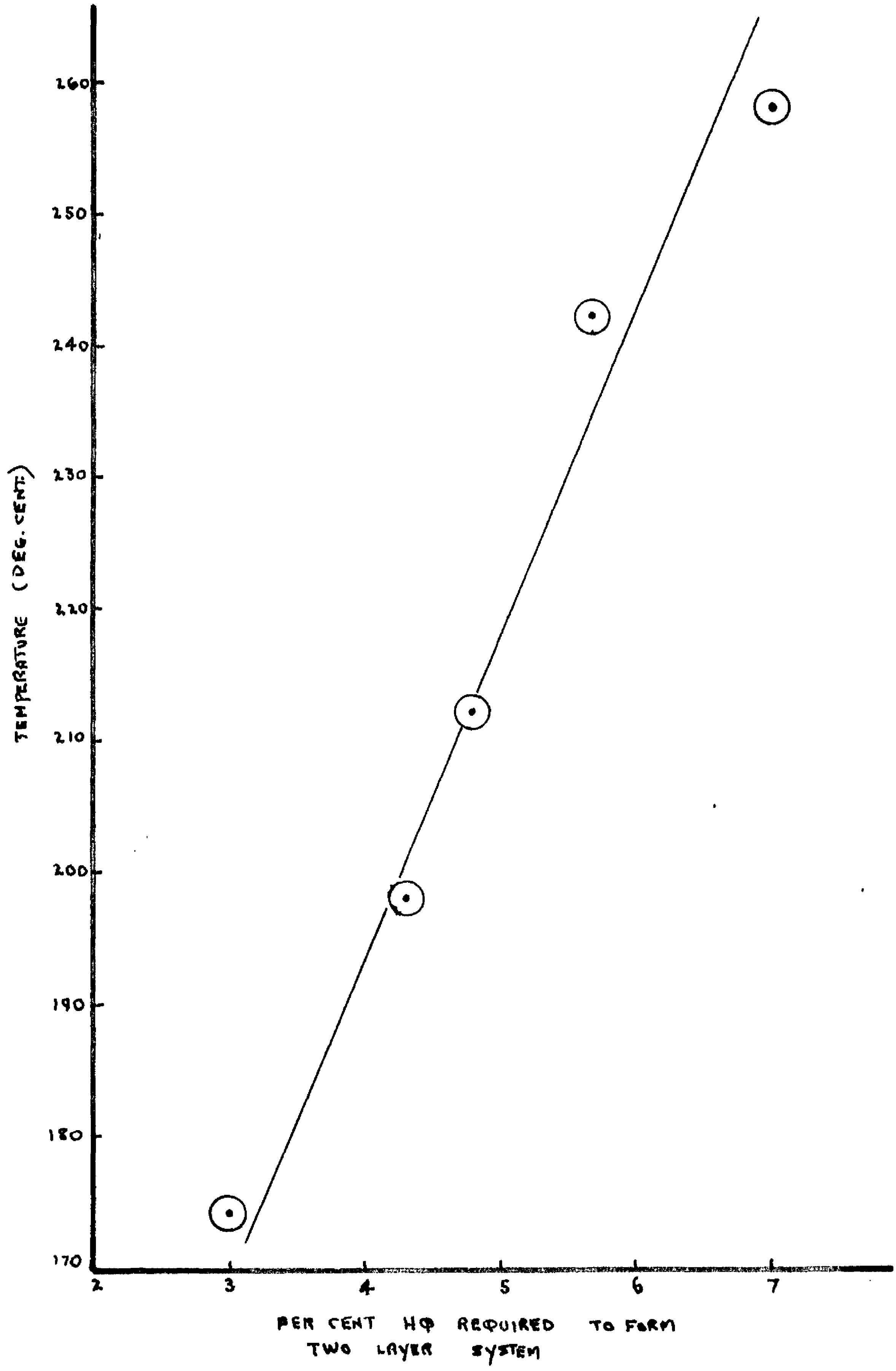
Excess 2:1 Adduct + HQ	Solubility of HQ in 2:1 Adduct	w/w 4.3%
Excess HQ +2:1 Adduct	Solubility of 2:1 Adduct in HQ	22.0%

The solubility of HQ in excess 1:1 adduct was ca.4% (w/w) at 198°C, i.e. more than 4% by weight would produce a two layer system.

The solubility of HQ in 2:1 adduct over the range 170-260°C was determined (fig.26.) so that rates could be followed in one phase. It was not necessary to determine

FIG. 26

THE SOLUBILITY OF HQ IN 2:1 ADDUCT AT TEMPERATURES ABOVE ITS MELTING POINT



the solubilities of the 1:1 or the 2:1 adducts in excess HQ for the above temperature range since the adducts were much more soluble in HQ.

Due to the comparatively low solubility of HQ in the telomers, the rate dependences on the HQ, and presumably the catechol, will be invalidated since rate determinations were carried out on adduct samples containing more than 4% HQ.

Activation Energies.

Rates were recorded at various temperatures for the systems excess 2:1 adduct - HQ, excess 1:1 adduct - HQ and excess HQ - 2:1 adduct. In each case the composition of the single phase system was held constant.

Table 18. Activation Energies for the Pyrolysis of the Adduct - HQ System.

System	Activation Energy (k.cal./mole)
1:1 Adduct alone	21.3
Excess 1:1 Adduct + HQ	21.0
2:1 Adduct alone	29.0
Excess 2:1 Adduct + HQ	31.8
Excess HQ + 2:1 Adduct	14.7

As can be observed, HQ only affected the activation energy of the system when present in excess. In such a system (excess HQ - 2:1 adduct) it was noted that two moles of acid were evolved for each mole of adduct. To postulate a reaction mechanism it was important to know the relative quantities of HBr and HCl evolved during the various stages of pyrolysis.

Halide Analysis.

The acid evolved during several different co-pyrolyses of 2:1 adduct and excess HQ was absorbed in water and the solution analysed for its halide content. The samples were collected at various times for it was thought that the ratio of chloride to bromide would be unity and therefore independent of time and initial adduct concentration.

Table 19. Analysis of Halide Evolved from Various Mixtures of Excess HQ - 2:1 Adduct Pyrolysed at 198°C

Sample	Time of Pyrolysis (minutes)	Chloride (moles) x 10^3	Bromide (moles) x 10^3	$\frac{\text{Chloride}}{\text{Bromide}}$
1	10	7.62	0.38	20.0/1
2	14	5.90	0.30	19.7/1
3	25	2.34	0.26	9.00/1
4	39	3.13	0.31	10.0/1
5	43	1.83	0.20	9.20/1

Table 19 shows that the ratio of chloride to bromide was much greater than unity. As a check on these results, a larger quantity of 2:1 adduct (3.81 g.) was pyrolysed in excess HQ, and samples of acid again collected for analysis, but this time at successive stages in this single pyrolysis.

Table 20. Analysis of the Halide Evolved at Successive Stages in the Pyrolysis of 3.81 g. of 2:1 Adduct in Excess HQ at 198°C.

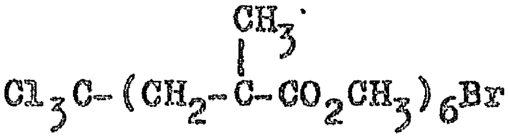
Time after commencement of pyrolysis (minutes)	Chloride (moles) x 10^3	Bromide (moles) x 10^3	Chloride / Bromide
4.0	6.80	0.34	20.0/1
8.0	4.85	0.14	34.7/1
13.0	3.28	0.05	65.6/1
19.5	2.58	0.16	16.6/1
27.5	1.41	0.02	70.5/1
41.5	1.55	0.08	19.4/1

From these results it appeared that HCl was preferentially liberated to HBr. This was rather surprising as the -CHClBr bond should be weaker than say the $-CH_2-CHCl$ bond. The probability was that the trichloromethyl group was providing the HCl evolved. This possibility was explored by pyrolysing various halogen hydrocarbons containing the trichloromethyl group in excess HQ at 198°C.

Pyrolysis of Halogen Compounds.

The pyrolysis of various halogen compounds showed that those containing the $-CCl_3-$ group evolved a large quantity of acid initially, whilst the others did not.

Table 21. Pyrolysis of Various Halogen Compounds in Excess HQ at 198°C.

Compound	Formula	Evolution of Acid During Initial Period
1-Bromooctane	$C_8H_{17}Br$	None
1-Chlorodecane	$C_{10}H_{21}Cl$	None
1:4-Dibromobutane	$C_4H_8Br_2$	Very slight
Hexachloroethane	C_2Cl_6	Great
Benzotrichloride	$C_6H_5CCl_3$	Great
Methyl methacrylate Telomer ($\bar{x}$ = 6)	 $Cl_3C-(CH_2-\overset{CH_3}{\overset{\vert}{C}}-CO_2CH_3)_6Br$	Great

Since 1-bromooctane, 1-chlorodecane, 1:4-dibromobutane did not yield any acid on co-pyrolysis with HQ this emphasised the unreactive nature of lone halogens attached to carbon atoms in these compounds. Previous work also supported these results when it was found that pyrolysis of these compounds in the absence of HQ did not yield any acid.

Blanks were run on all the halogen compounds employed and only benzotrichloride evolved a little HCl (there is usually some HCl in benzotrichloride due to hydrolysis). Benzotrichloride, in which there is only one source of halogen, also has the convenient b.pt. of 214°C. It was therefore suitable for further pyrolysis experiments.

Pyrolysis of Benzotrichloride.

Benzotrichloride (0.25 g.) was pyrolysed in excess HQ at 198°C. The course of the reaction is shown in fig.27; as indicated two atoms of chlorine were removed initially. The plot was very similar to those in fig.23 in which it was also shown that two atoms of chlorine were removed initially.

The large quantity of acid evolved in this reaction indicated that the HQ might be supplying the hydrogen. The implication was that some type of condensation compound had been formed, one perhaps in which the HQ condensed with the benzotrichloride, HCl being eliminated.

A mixture of HQ and benzotrichloride in the ratio 4 moles to 1 mole was pyrolysed at 198°C for two hours. The reaction mixture was allowed to cool, washed with water several times to remove any unreacted HQ and finally dried. The properties of the product were then examined.

FIG. 27

THE REACTION BETWEEN 0·25g. BENZOTRICHLORIDE AND EXCESS HΦ AT 198°C.

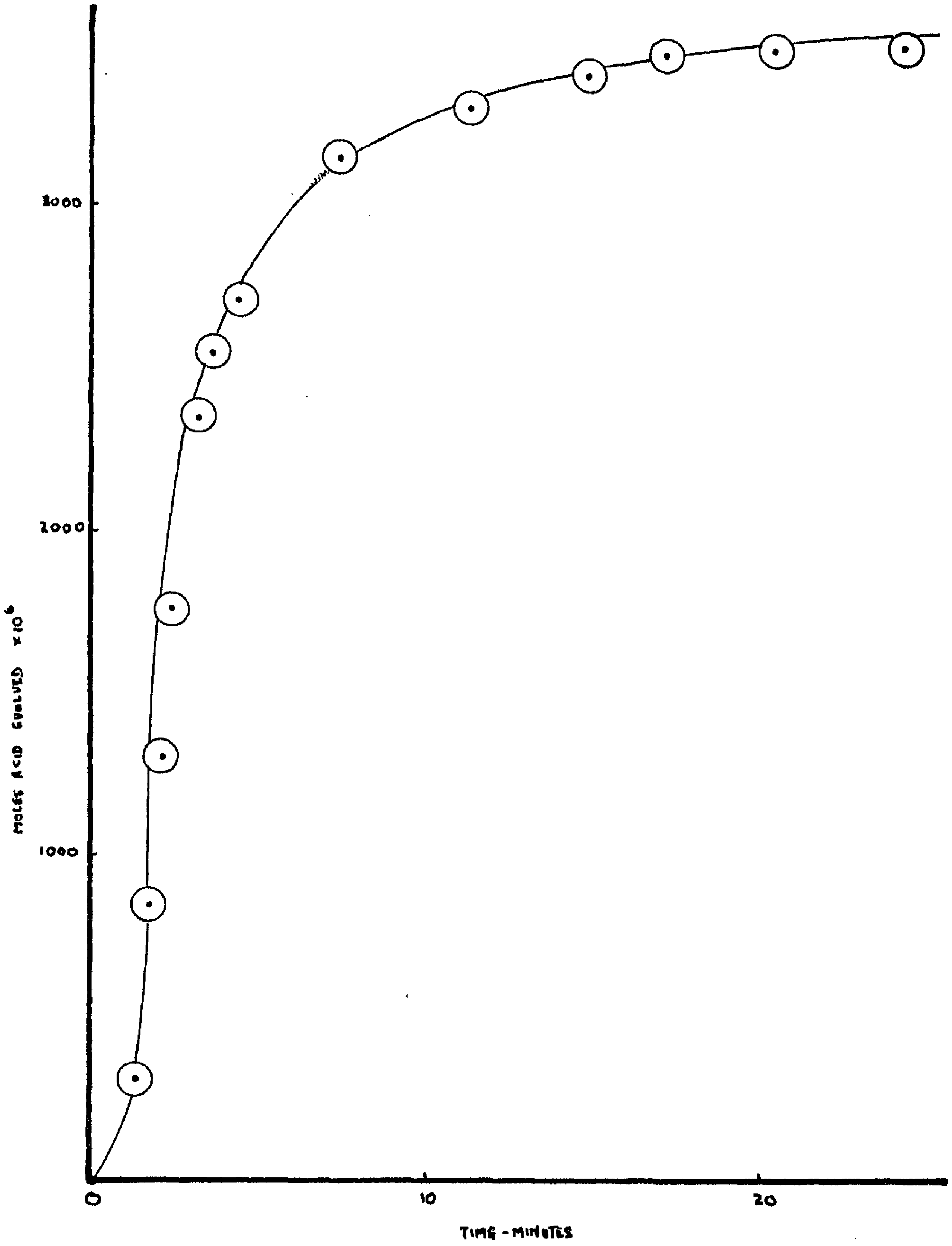
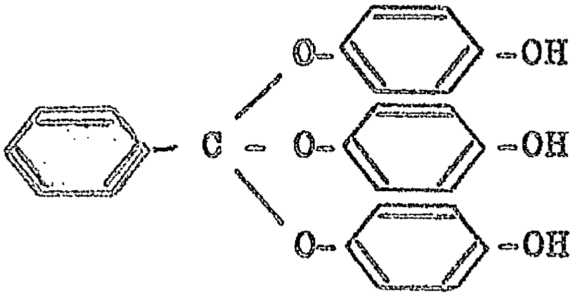


Table 22. Properties of the Compound Formed in the Reaction between HQ and Benzotrichloride at 198°C.

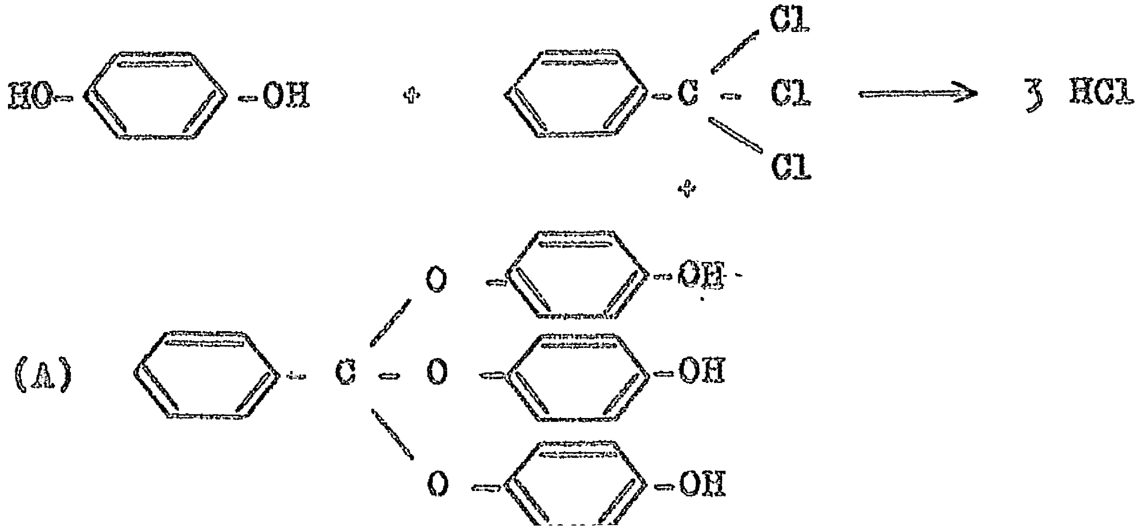
	% Carbon	% Hydrogen	% Oxygen	% Chlorine
Observed	68.1	4.80	27.1	–
Calculated for $C_{25}H_{20}O_6$	72.0	4.90	23.1	–
	Molecular Weight			
Observed	388			
Calculated for $C_{25}H_{20}O_6$	416			

The observed values were in fair agreement with the theoretical values which were worked out for the following compound.



This compound could result from the condensation between benzotrichloride and HQ:

i.e.



It seemed reasonable to conclude from the above data that (A) was produced in the reaction. Thus the indication was that the $-CCl_3-$ group was responsible for the large quantities of acid evolved during the pyrolysis of the 1:1 and 2:1 adducts in excess HQ.

Having investigated the effect of HQ on these telomers and noted the reactivity of the $-CCl_3-$group, it was felt that some work should be completed on the reaction between the adducts and substituted phenols. More information might thus be obtained of the mechanism of reaction between HQ-type compounds and the adducts.

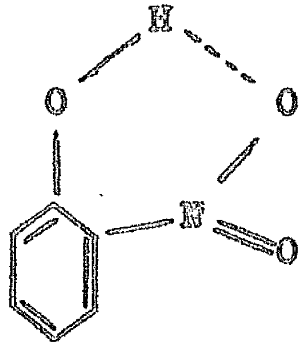
Substituted Phenols.

It was proposed to examine the effect of the position of the substituted group in the phenol, i.e. how o, m, or p-substitution influenced the reaction between a particular phenol and the 2:1 adduct. A series of related phenols was pyrolysed in the presence of a fixed weight of 2:1 adduct (1.1 g. in each pyrolysis), the phenol being in excess.

Table 23. Relative Rates in the Pyrolysis of the System 2:1 Adduct - Excess Substituted Phenol at 198°C.

1.1 g. of 2:1 Adduct + Excess Phenolic Compound	Relative Rates
Phenol x	1.59
o-methoxyphenol	No reaction
o-methylphenol	1.05
o-aminophenol xx	No reaction
o-hydroxyphenol	3.93
m-hydroxyphenol	4.85
p-hydroxyphenol /	10.39
o-chlorophenol	1.00
m-chlorophenol	3.11
p-chlorophenol	3.64
o-nitrophenol //	No reaction
m-nitrophenol	5.33
p-nitrophenol	10.39
x Boils at 181°C / Boils at 176°C	// Exists as chelate compound xx Dissolved in nitrobenzene

There was a trend in that *p*- were more reactive than *m*- , which, in turn, were more reactive than *o*-substituted phenols towards the 2:1 adduct. In addition those groups which have a tendency to withdraw electrons from the phenolic OH appeared to exert the greatest influence by yielding the fastest rates. It was interesting to note that o-nitrophenol did not react with the adduct. This compound exists in a chelate form, and the hydrogen of the hydroxyl group is thus not available for reaction with the halogen of the $-CCl_3-$ group in the 2:1 adduct.



Pyrolysis of High Polymers.

The pyrolysis of the 1:1 and 2:1 adducts was fairly informative so it was decided to apply similar techniques to telomers containing say, ten or fifteen vinyl chloride units in the molecule, i.e. of $\bar{\bar{r}}$ 10 or $\bar{\bar{r}}$ 15. The proposal was to obtain a comprehensive range of telomers of $\bar{\bar{r}}$ 10, 20, 30, 40 etc. and to study and compare their decomposition rates. Unfortunately compounds intermediate between the 1:1 and 2:1 adducts and the high polymer could not be satisfactorily prepared or easily defined. High polymer could, however, be easily prepared and its molecular weight readily obtained. It was therefore possible to study the effect of chain length on the breakdown of the high polymer. Moreover the degradation of PVC in solution would enable cross-linking to be studied. This was of particular interest as little work has been done on this aspect of PVC degradation.

A series of high polymers was prepared thermally with AIBN as initiator at different temperatures. Preliminary rate investigations were carried out on these polymers dissolved in o-dichlorobenzene (b.pt.182°C) and in ethyl benzoate (b.pt.215°C). Rates of dehydrochlorination were independent of the flow rate of the carrier gas below about 12 litres/hour. Furthermore liberated HCl allowed to remain in contact with the PVC solution did not affect the rate.

Experiments on PVC dissolved in o-dichlorobenzene and ethyl benzoate revealed that the hot polymer solution rapidly gelled on cooling to room temperature; the gel again became a solution on warming. If pyrolysed at temperatures of the order of 180°C the PVC solution rapidly became an irreversible gel. It was also found that the gel time[x] (time taken for gelation to occur) varied markedly with the polymer concentration as did the rate of dehydrochlorination. The results of these experiments are shown in table 24.

---

[x] The time during which polymer molecules cross-link to form a three dimensional polymer network.

Table 24. Comparison of Gel Times and Dehydrochlorination Rates at 178°C for PVC ($\bar{F}$ 405) in Ethyl Benzoate and o-Dichlorobenzene

		Concentration (g./l.)		
		212	150	115
Rate of Dehydrochlorination (moles HCl/l./sec.) $\times 10^6$	Ethyl Benzoate	~~6~~6.66	3.95	2.25
	o-Dichlorobenzene	4.24	2.49	1.85
Gel Time (Secs.) x 10^{-3}	Ethyl Benzoate	13.74	24.00	29.10
	o-Dichlorobenzene	13.26	21.00	27.90

Gel times were slightly faster in o-dichlorobenzene than in ethyl benzoate, although dehydrochlorination proceeded at a much faster rate in the latter.

Other solvents which were tried included the 1:1 adduct and nitrobenzene. Both these liquids attacked the polymer vigorously (fig.28) at low and high temperatures and were therefore unsuitable as solvents. Ethyl benzoate, with its high b.pt., was the most convenient solvent and all other work on PVC has been carried out in this solvent over a wide range of temperatures and concentrations.

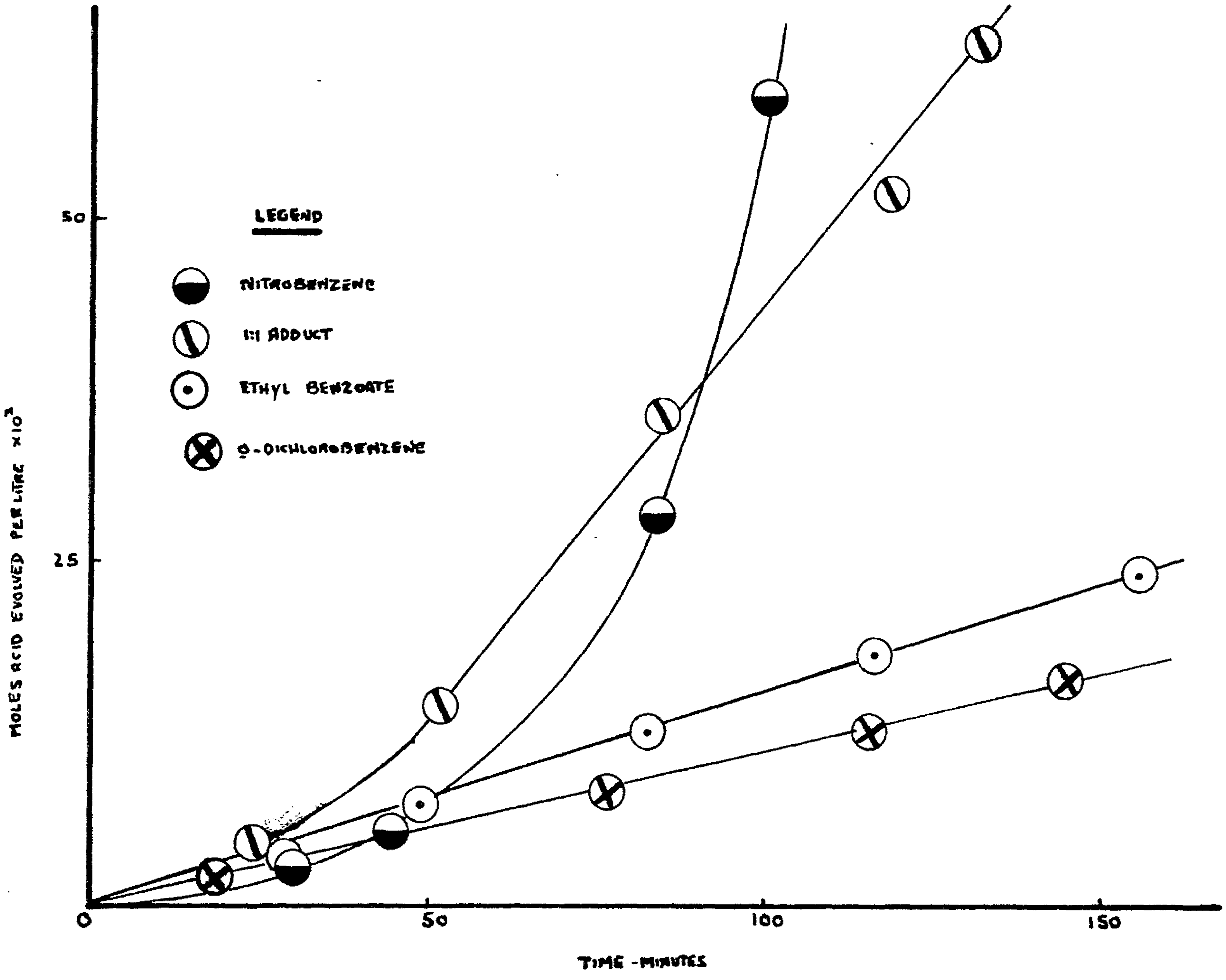
The Cross-Linking Reaction in Ethyl Benzoate.

Variation in Concentration.

Different weights of polymer ($\bar{F}$ 905)

FIG. 28

THE EFFECT OF VARIOUS SOLVENTS ON THE DEGRADATION OF PVC AT 178°C.



were pyrolysed at 212°C and the gel time was found to vary greatly with the concentration (table 25). In several samples, once the gel point had been reached, fresh ethyl benzoate was added to the gel. These did not mix and no swelling was observed. The rate of evolution of acid was not affected.

Table 25. Dependence of the Gel Time on the Polymer Concentration for the Pyrolysis of PVC ($\bar{F}$ 905) in Ethyl Benzoate at 212°C.

Gel Time (t_g) (Sec.) x 10^{-3}	Polymer Concentration (g./l.)	c x (t_g) x 10^{-3}
2.82	149	420
4.62	106	490
6.72	86	579
8.64	73	630

The product of the gel time and polymer concentration was reasonably constant indicating that the concentration was directly proportional to the reciprocal of the gel time.

Variation in Chain Length.

Gel times were recorded for a fixed weight of various polymers at 198°C.

Table 26. Dependence of the Gel Time on the $\bar{r}$ of the PVC for a Solution of Fixed Weight Pyrolysed in Ethyl Benzoate at 198°C.

$\bar{r}$	Gel Time (t_g) (Sec.) x 10^{-3}	(t_g x $\bar{r}$) x 10^{-3}
905	4.98	4,525
553	5.62	3,110
367	9.00	3,305
192	17.2	3,295

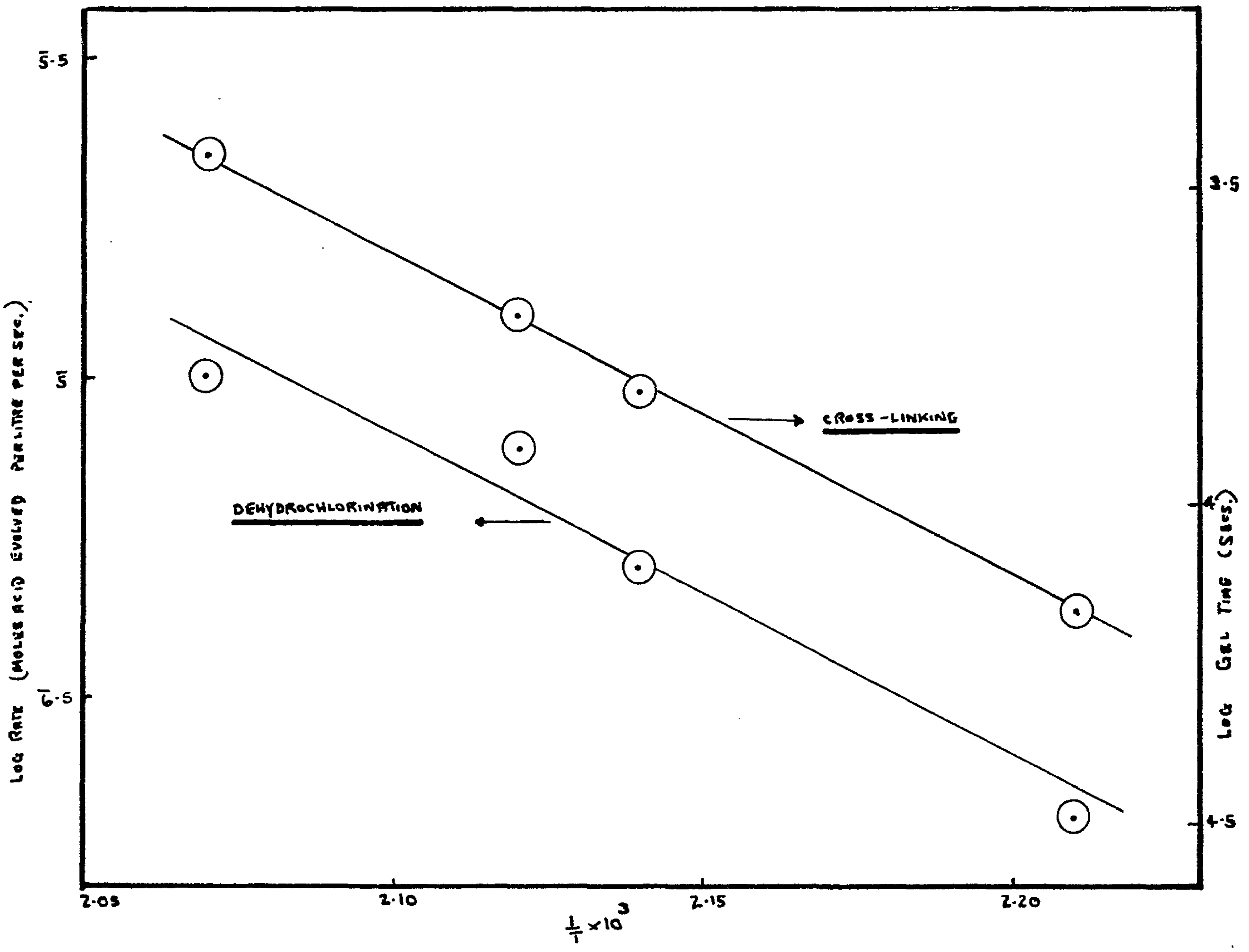
The gel theory of Flory(68) is based on 0.5 cross-linked units per polymer molecule for a number average distribution at the gel point. Thus if polymers of different $\bar{r}$ are used, a very big difference in gel times should be observed. This was found to be the case, the lower $\bar{r}$ polymers being very slow to gel even at fairly high concentrations. Furthermore the gel point was much more sudden with polymers of low $\bar{r}$. The product of gel time and $\bar{r}$ was relatively constant, indicating that $\bar{r}$ was inversely proportional to the gel time.

Variation in Temperature.

There was little variation in activation energy with chain length, the average value for cross-linking being 23.7 k.cal./mole. Fig.29 is a typical Arrhenius plot for

FIG. 29

TYPICAL ARRHENIUS PLOTS FOR THE DEGRADATION OF PVC ($\bar{r}$ 90S)



cross-linking.

Table 27. Activation Energies for Cross-Linking.

$\overline{r}$	Activation Energy (k.cal./mole)
905	22.8
553	25.3
367	22.5
192	24.3

Cross-Linking in Bulk.

This could be estimated by extrapolation of the plot of reciprocal concentration against acid evolved per monomole of polymer (fig.30), the concentration of bulk PVC being 1.4 g./c.c. The variation in the percentage of total acid liberated at the gel point with $\overline{r}$ for bulk pyrolysis was also obtained by extrapolation (fig.31). This did not vary greatly for polymers of high $\overline{r}$.

From the results quoted so far cross-linking could be a free radical process or otherwise. It was felt that the addition of free radical initiators and inhibitors to PVC solutions might give some indication as to what was happening during cross-linking.

FIG. 30

THE ACID EVOLVED AT THE GEL POINT FROM PVC ($\bar{r}$ 905) AT 212°C.

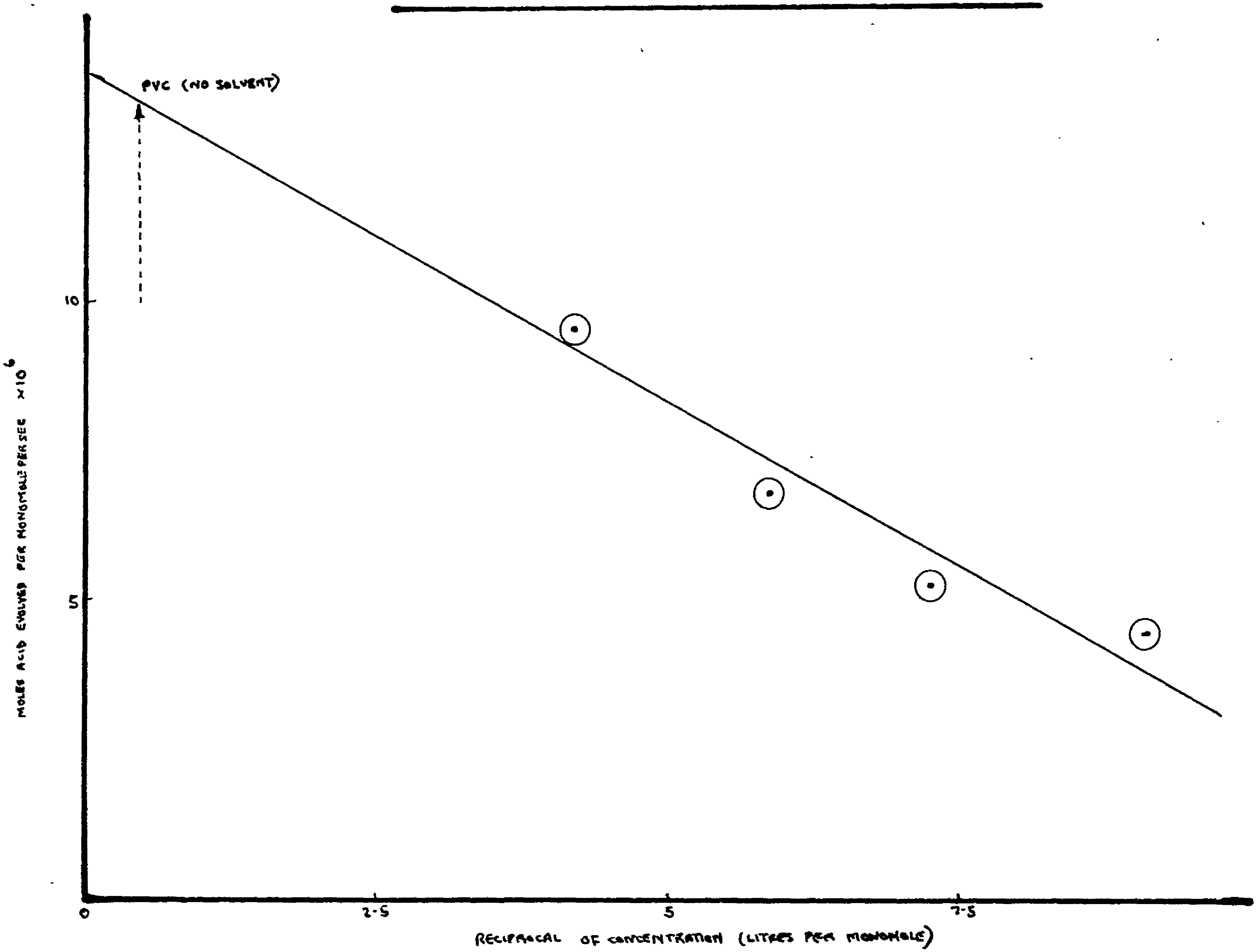
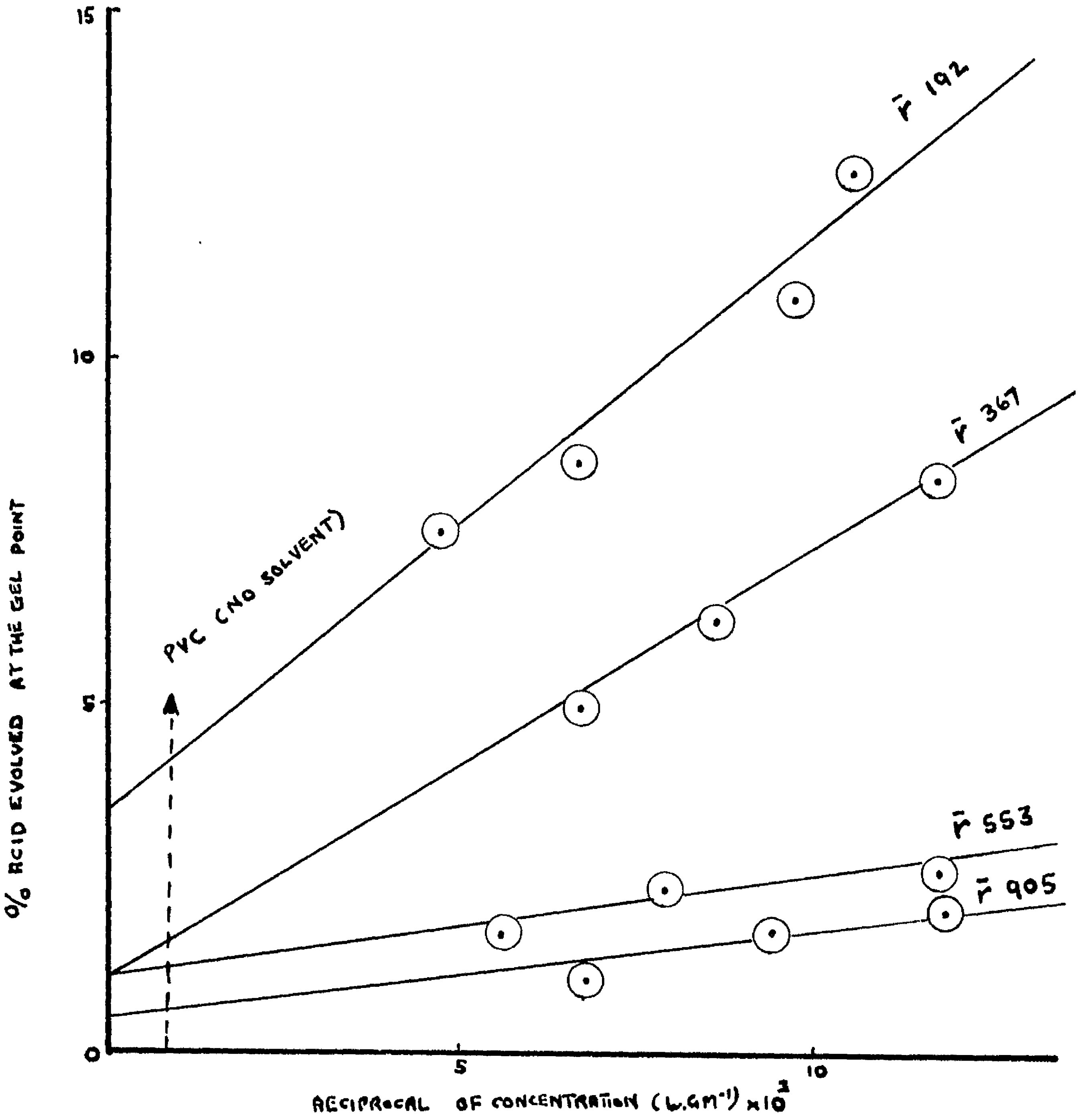


FIG. 31

THE ACID EVOLVED AT THE GEL POINT FROM VARIOUS SAMPLES OF PVC AT 212°C.



(1) Free Radical Chain Initiators.

In this section on the effect of additives, the experiments were carried out on PVC ($\bar{r}$ 905) mainly at 212°C. Table 28 shows that small quantities of AIBN have no effect on the gel time. This was also true for BP. More than 10% AIBN, however, delayed the gel time appreciably.

Table 28. Effect of Addition of AIBN to PVC ($\bar{r}$ 905) on the Gel Time at 212°C.

Weight % AIBN	Gel Time (t_g) (Secs.) x 10^{-3}
0	2.82
3.5	2.88
3.8	2.82
10.4	3.72
24.9	4.20
32.3	4.32

(2) Action of Iron Compounds.

A few pyrolyses were carried out in the presence of

a) 2% ferric chloride
b) 2% iron filings
c) a steel ball-bearing

all in ethyl benzoate solution.

In the first two cases, the result was the almost instantaneous formation of a black gel, rendering it impossible to measure rates. This unusual and rapid gel formation was also found by Bevington and Norrish(69). The ball-bearing did not affect the gel time.

(3) Free Radical Chain Inhibitors and Oxygen.

Grassie(70) showed that 1:4-diaminoanthraquinone was an effective inhibitor in the depolymerisation of methyl methacrylate: 2% of this inhibitor had no effect on gel time. A similar quantity of tetrachloro-o-benzoquinone reduced the gel time very slightly.

Some commercial stabilisers were also tried. These were Stanclere 70 and α-phenylindole. The latter delayed the gel time considerably as can be seen from table 29.

Table 29. Effect of Addition of α-phenylindole to PVC ($\overline{P}$ 905) on the Gel Time at 212°C.

Weight % α-Phenylindole	Gel Time (Sec.) x 10^{-3}
0	2.82
1.36	4.75
3.70	6.30
4.03	7.74

Stanclere 70 affected gel times only when large quantities were added.

Table 30. Effect of Addition of Stanclere 70 to PVC ($\bar{r}$ 905) on the Gel Time at 212°C.

Weight % Stanclere 70	Gel Time (Sec.) x 10^{-3}
0	2.82
3.18	3.06
7.80	3.90
16.3	4.14

In the presence of oxygen there was a very long delay in gel formation at temperatures ranging from 157°C to 212°C. Hence oxygen was the most effective 'inhibitor' of cross-linking.

The Dehydrochlorination Reaction in Ethyl Benzoate

Variation in Concentration.

Various weights of polymer ($\bar{r}$ 905) were pyrolysed at 212°C. Table 31 shows that the yield of HCl per gram per second was constant.

Table 31. Dependence of the Rate of Dehydrochlorination on the Polymer Concentration for the Pyrolysis of PVC ($\bar{r}$ 905) in Ethyl Benzoate at 212°C.

$\frac{d[HCl]}{dt}$ (moles acid/l./sec.) x 10^6	Polymer Concentration (g./l.)	$\frac{d[HCl]}{dt}$ (moles acid/g./sec.) x 10^8
90.0 (Bulk)	1400	6.44
9.55	149	6.42
6.82	106	6.47
5.34	86	6;26
4.70	73	6.44

The rates were proportional to the polymer concentration (fig.32).

Variation in Chain Length.

The effect of change in $\bar{r}$ on the rate of dehydrochlorination was studied. Fig.33 shows the variation in rate per fixed weight of polymers of different $\bar{r}$ at 178°C. The rate for a fixed weight was apparently much faster for polymers of lower $\bar{r}$. When the rate per mole of polymer was calculated it was found to be relatively constant. Some idea of the constancy of the rate per polymer chain may be obtained from fig.34.

FIG. 32 THE VARIATION IN RATE WITH CONCENTRATION FOR PVC ($\bar{v}$ 905) AT 212°C.

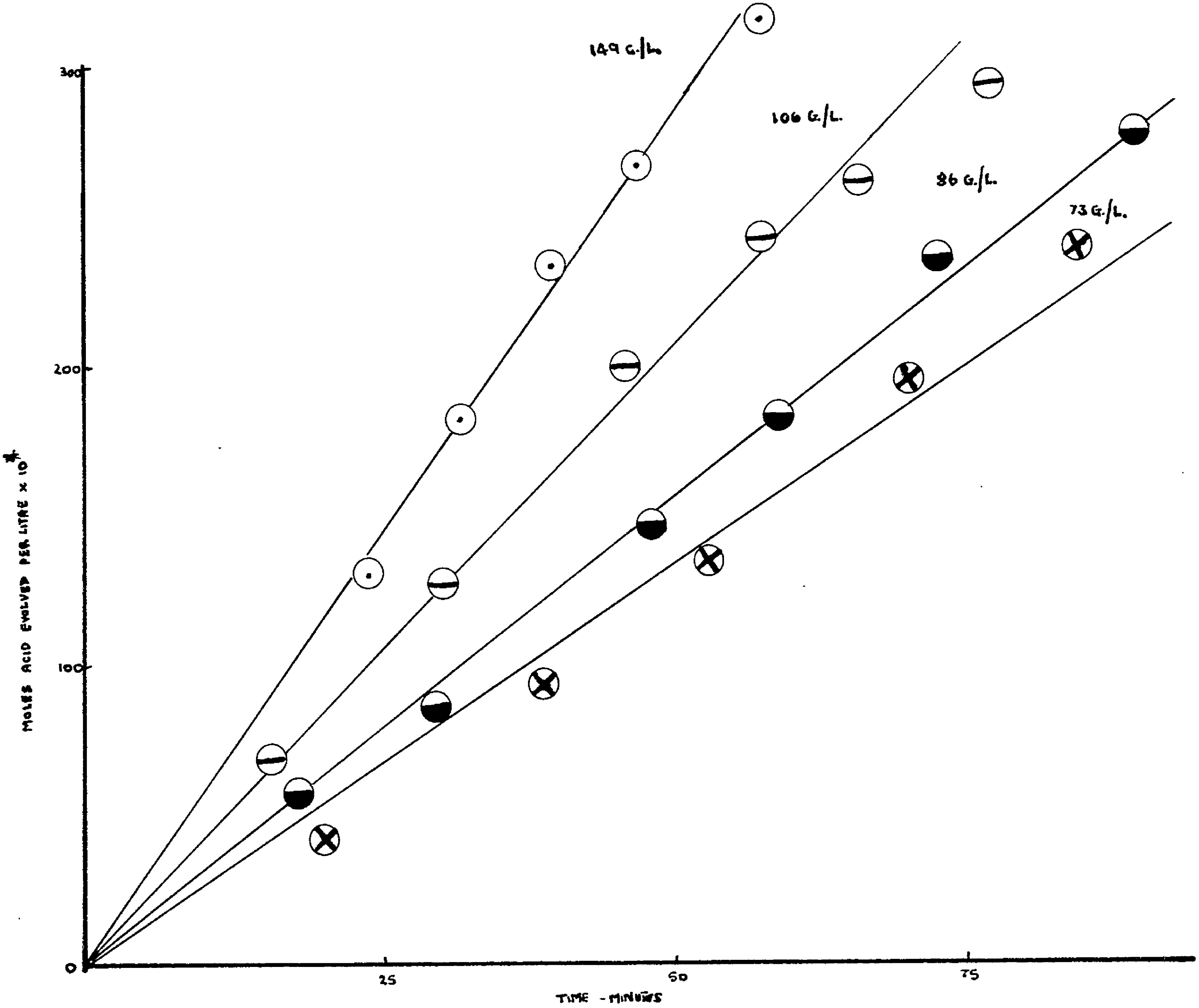


FIG. 33

THE EFFECT OF CHAIN LENGTH ON THE RATE OF EVOLUTION OF ACID AT 178°C.

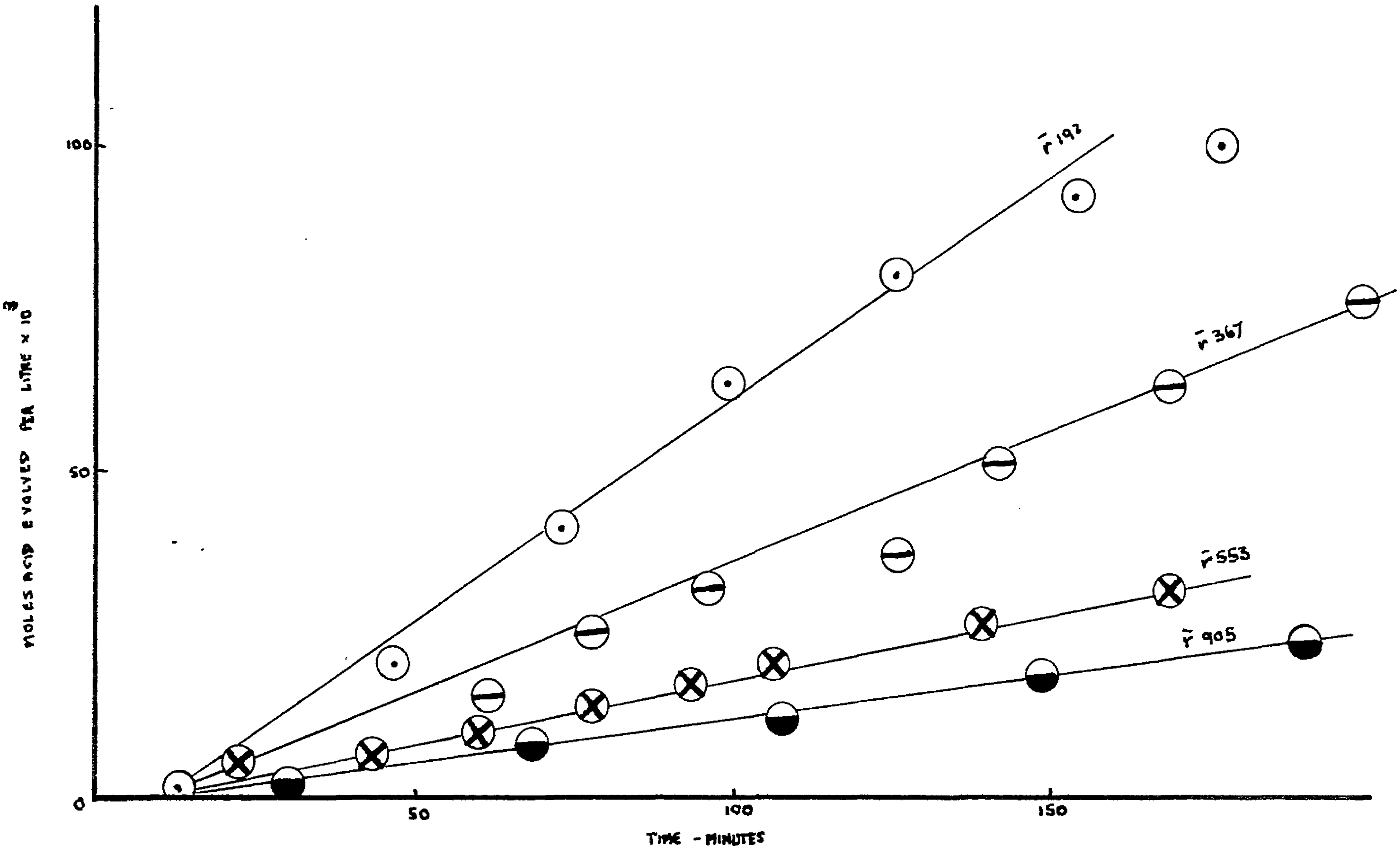
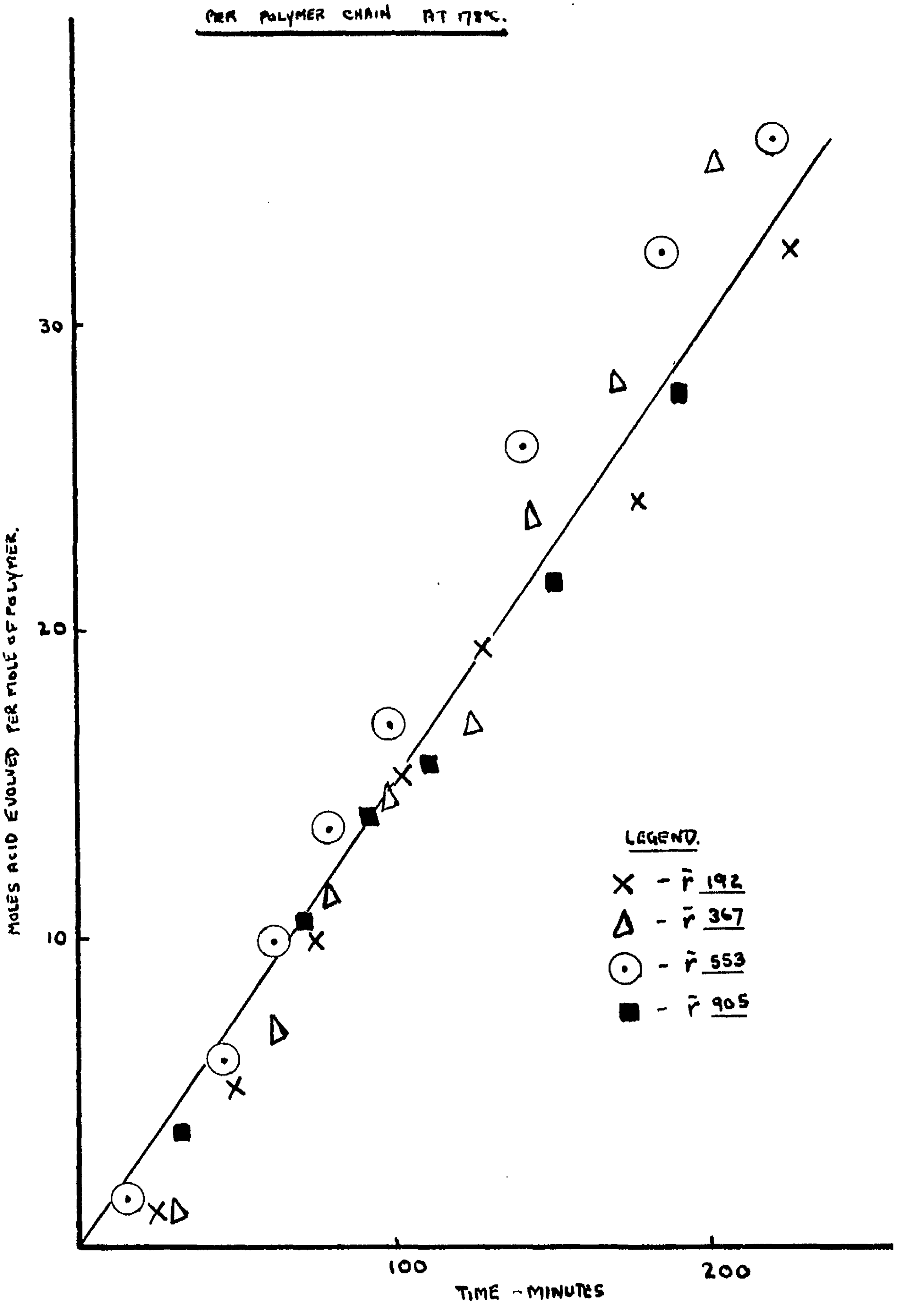


FIG. 34.

THE CONSTANT NATURE OF THE RATE PER POLYMER CHAIN AT 178°C.



Variation in Temperature.

Rates were determined at four temperatures and a typical Arrhenius plot is shown in fig.29. The activation energy for dehydrochlorination was constant for polymers of different chain length, the average value being 23.2 k.cal./mole.

Table 32. Activation Energies for Dehydrochlorination

$\bar{r}$	Activation Energy (k.cal./mole)
905	22.8
553	22.8
367	24.0
192	23.3

The effect of additives, such as free radical initiators, on the dehydrochlorination was investigated. This was because the chief support for a free radical mechanism stems from Arlman's(7) work, in which the addition of free radical initiators to PVC increased the rate of dehydrochlorination. This was checked using AIBN and BP as the initiators.

(1) Free Radical Chain Initiators.

Many of the experiments were carried out on PVC ($\bar{r}$ 905) at 212°C, except where specific mention is made of other temperatures.

When 2% AIBN (w/w) was added to a solution of PVC at 100°C, 130°C, 157°C there was virtually no change in the rate of dehydrochlorination which was very low at these temperatures.

At 212°C, however, the addition of 4% AIBN (w/w) to the polymer solution doubled the rate of dehydrochlorination (fig.35). Larger quantities of AIBN gave somewhat higher rates. The number of molecules of HCl evolved associated with one free radical was estimated as follows:

Weight of PVC = 0.1000 g.
Weight of AIBN = 0.0040 g.
Molecular Weight of AIBN = 164

The increase in the quantity of HCl evolved was 175×10^{-6} moles in 30 minutes. All the AIBN was assumed to have decomposed in this period

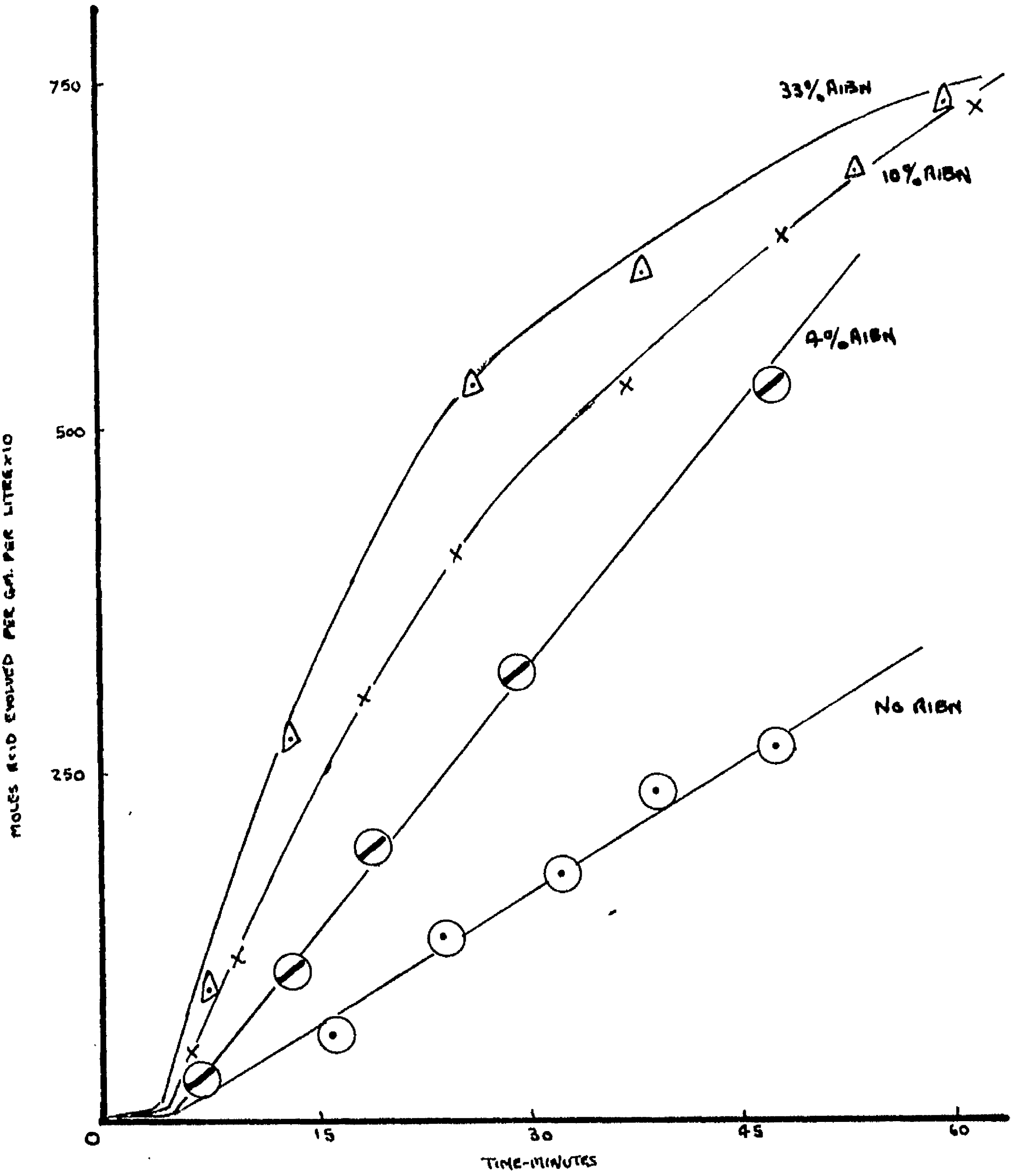
i.e. $\frac{0.0040}{164}$ moles AIBN produced 175×10^{-6} moles HCl

i.e. 1 free radical was associated with 4 molecules of HCl.

Two per cent BP added to PVC solution at temperatures below 160°C did not produce any increase in dehydrochlorination. At 100°C, BP coloured PVC solution yellow, although there was no measurable HCl after two hours pyrolysis. However a blank of BP in ethyl benzoate at 100°C also produced colour. Subjected to UV light (3650 Å) at 50°C for two hours, a BP-initiated solution of PVC yielded no

FIG.36

THE EFFECT OF ADDED INITIATOR ON THE DEHYDROCHLORINATION OF PVC ($\bar{r}$ 905) AT 212°C



measurable HCl, but again became yellow. These findings were in agreement with the work of Achhammer(23).

Dehydrochlorination in Oxygen.

Solution pyrolyses were carried out in nitrogen and in oxygen for a given weight of polymer ($\bar{r}$ 553) at 157°C and 212°C. There was no appreciable difference in yield of acid per unit time between the two runs (fig.36). The polymer solution darkened much more quickly in oxygen.

In the bulk pyrolysis of PVC oxygen promotes a greater rate of dehydrochlorination than in nitrogen. The rate also accelerated with time (fig.37). Bulk PVC, however, darkened more rapidly in nitrogen than in oxygen. The results for bulk PVC were in complete accord with those obtained by Druesedow and Gibbs(12) for bulk PVC.

2) Free Radical Chain Inhibitors and Commercial Stabilisers.

Pyrolyses carried out in the presence of 2% 1:4-diaminoanthraquinone, tetrachloro-o-benzoquinone and HQ showed that only the last two compounds affected the rate of dehydrochlorination by increasing it slightly. This was not altogether surprising for HQ which has been reported to catalyse the degradation of PVC(21). As described

FIG. 36

THE SOLUTION PYROLYSIS OF PVC ($\bar{P}$ 553) AT
212°C IN a) OXYGEN b) NITROGEN

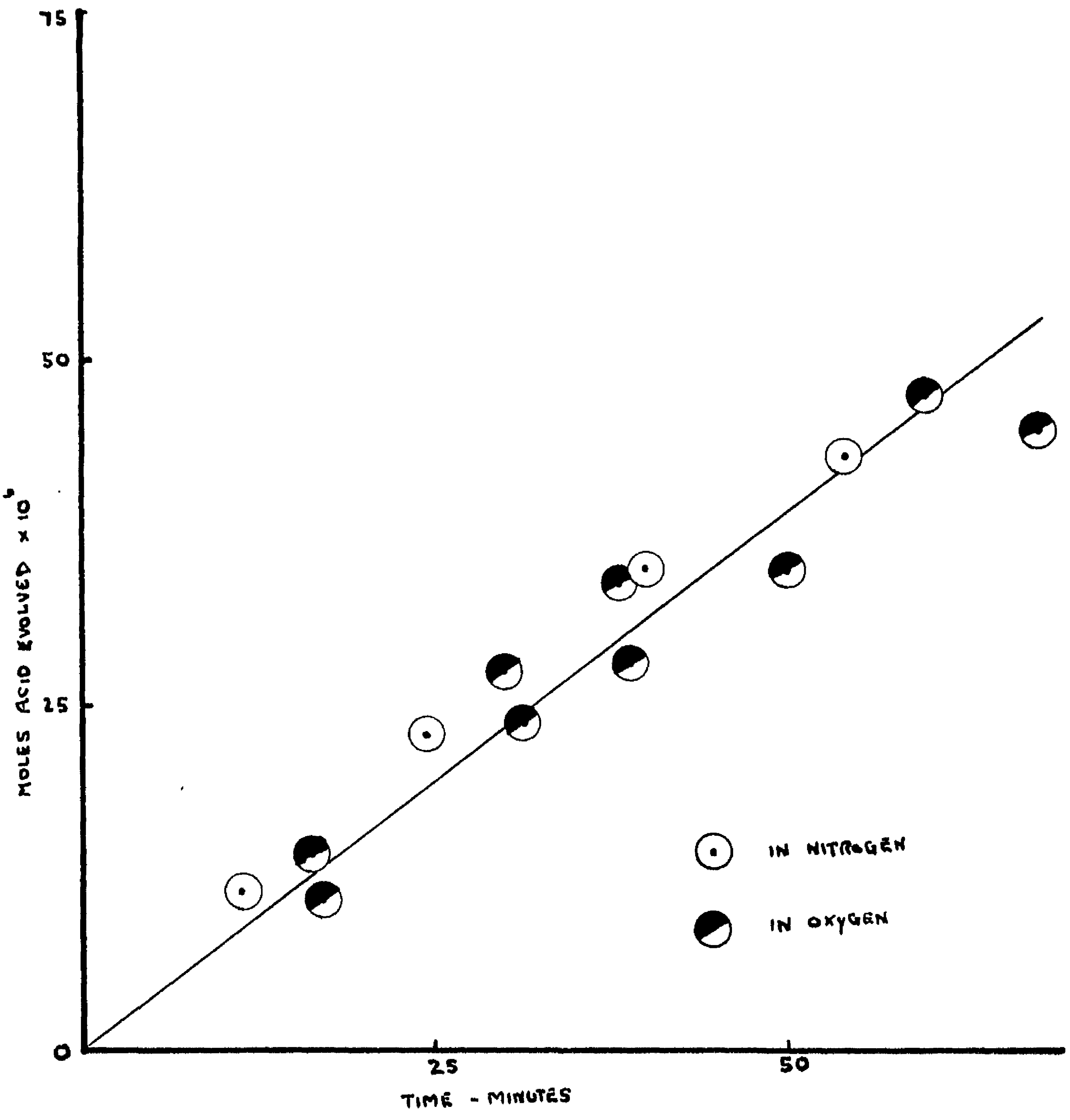
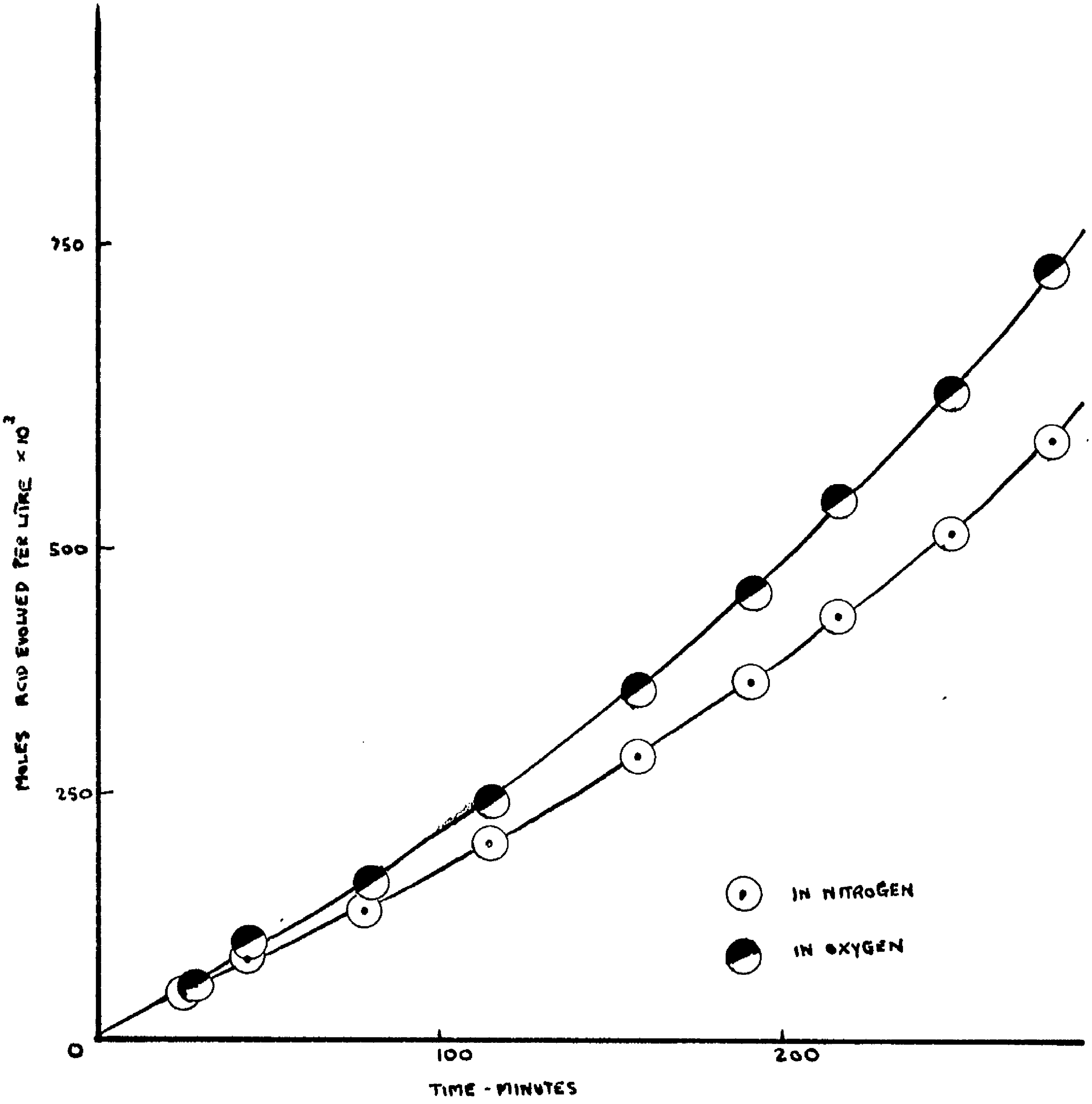


FIG. 37

THE BULK PYROLYSIS OF PVC ($\bar{F}$ 553) AT 178°C

IN a) OXYGEN b) NITROGEN



earlier, HQ definitely promoted the decomposition of the 1:1 and 2:1 adducts.

Of the commercial stabilisers used, α-phenylindole had no effect, but Stanclere 70 cut down the rate of dehydrochlorination very considerably. Comparatively small amounts retarded the rate of dehydrochlorination (fig.38). The duration of the retarded rate was directly proportional to the quantity of Stanclere 70 added (table 33). ~~when~~ When all the stabiliser had been used, the nominal rate was resumed as fig.38 shows. Stanclere 70 also retarded colouring of the polymer solution.

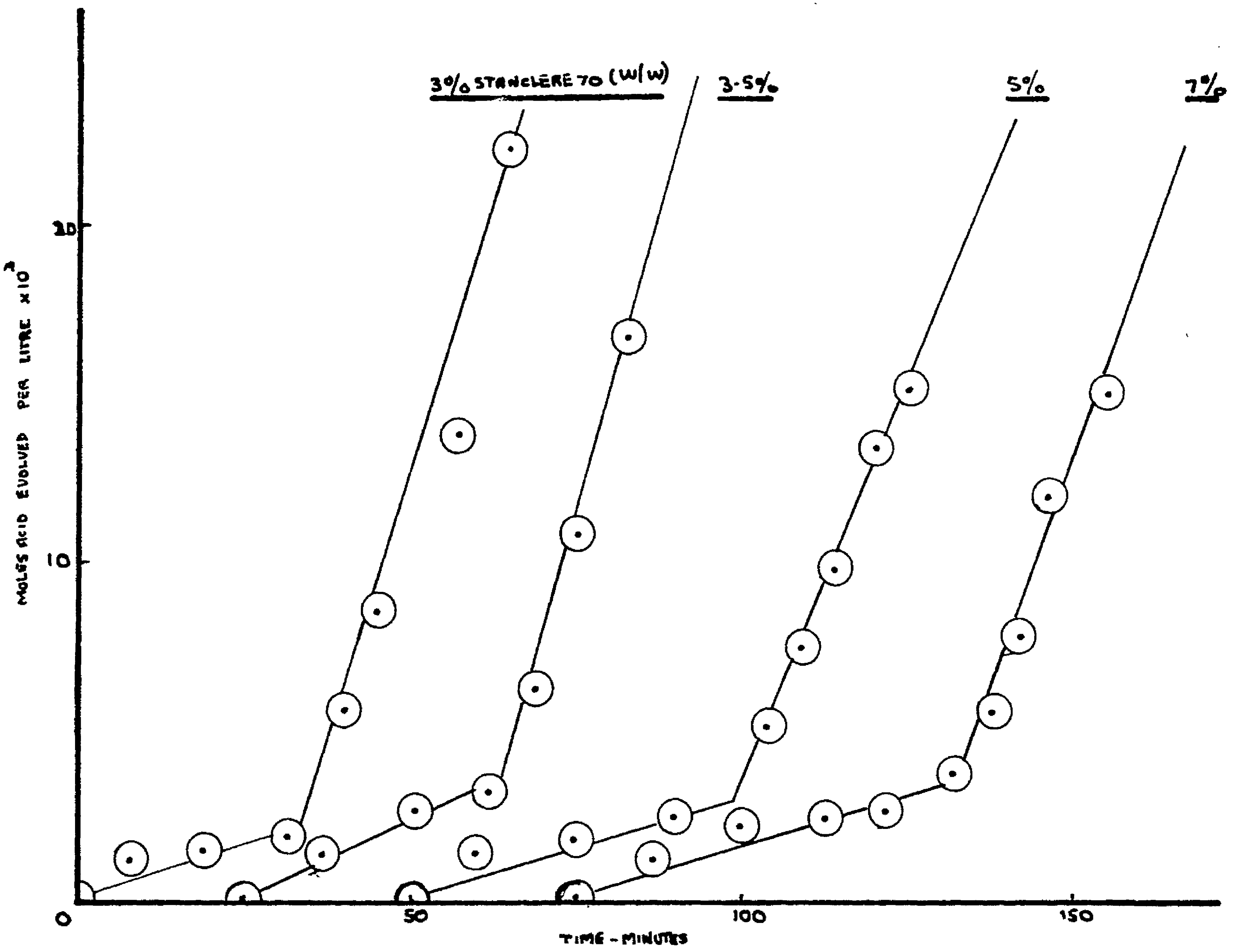
Table 33. Effect of Addition of Stanclere 70 to PVC ($\bar{r}$ 905) on the Rate of Dehydrochlorination at 212°C

Weight % Stanclere 70	Period of retarded rate (minutes)
3.0	34.0
3.5	40.0
5.0	50.0
7.0	59.5

Although several theories have been put forward for the initiation process, few have been postulated for termination of the reaction. The latter could be brought about by interruption of the "zipper" by branches, which are known to be present(71).

FIG.38

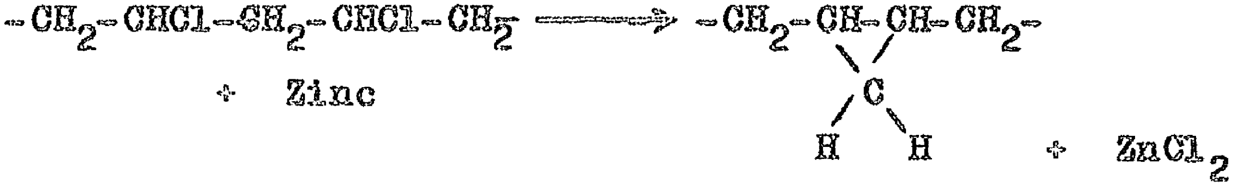
THE EFFECT OF THE ADDITION OF STANCLERE 70 TO PVC ($\bar{P}$ 905) AT 212°C (THE ORIGIN HAS BEEN SHIFTED TO AVOID SUPERPOSITION)



Effects of Branching.

A group equivalent to a branched point, and capable of terminating the "zipper", was introduced into PVC molecules. Such a group is the cyclopropane ring found in PVC when a mole of chlorine has been abstracted from a mole of polymer. Marvel, Sample and Roy(26) first employed this technique to produce "branched" PVC.

i.e.



PVC having 7.5% of its chlorine removed was pyrolysed in ethyl benzoate at 198°C. Compared with the untreated PVC, the rate of dehydrochlorination was doubled and the rate at which gelling occurred increased five-fold. The latter result was attributed to an increase in molecular weight which could happen if the reaction between the zinc and polymer molecules were inter- rather than intramolecular. Since the reaction was in dilute solution this appeared to be unlikely. Furthermore the $\bar{r}$ of the cyclopropane PVC proved to be identical with that of the original polymer so that the acceleration of gelling was certainly not due to an increase in molecular weight.

CHAPTER IV

Discussion.

Preparation of Telomers and Polymers.

Nature of the Chain Transfer Agent.

A number of chain transfer agents are available for the preparation of vinyl chloride compounds e.g. mercaptans, tetrabromomethane and bromotrichloromethane. Of these BTCM was the most suitable for the present work. Its excitation wavelength is from 3300 to 3900 Å and since the C–Br bond is weaker than the C–Cl bond in BTCM it follows that photolysis would yield equal quantities of bromine and trichloromethyl radicals. BTCM is also easily purified, attacks mercury only very slowly and because of its volatility can be easily removed from a reaction mixture. The use of this transfer agent ensures that the end groups of vinyl compounds polymerised in its presence will be halogen in character, and if necessary a comparison could be made between these compounds and say, halogen hydrocarbons.

Limitations in the Preparation of Telomers and Polymers.

Prior to an assessment of the factors involved in the preparation of these compounds, some mention will be made of the difficulties encountered.

Continuous changes in the initial mole ratio of a telomerising or polymerising BTCM-VC system limit the extent of conversion quite severely. If the amount of BTCM is small compared with VC, then there will be a large deviation from the original concentration of the reactants as shown in table 34.

Table 34. Concentration Changes in the System BTCM-VC During Photochemical Telomerisation.

Quantities of BTCM and VC reacting (moles)	BTCM (moles)	VC (moles)	VC / BTCM
0	1.00	20.00	20.0/1
0.25 moles BTCM 0.25 " VC	0.75	19.25	26.4/1
0.50 " BTCM 0.50 " VC	0.50	19.50	39.0/1

Telomers possessing more than two vinyl chloride units could not be isolated in a reasonably pure state. One of the difficulties here lay in the plasticising effect of the telomer on the high polymer. These telomers usually consisted of one main product e.g. 2:1 adduct, with very small quantities of other adducts present as would be expected from polymerisation theory. The removal of these adducts proved to be impossible and they remained as impurities.

One of the main reasons for preparing polymers was commercial samples invariably contain peroxides and other extraneous impurities, a fact which seems to have been overlooked by a number of investigators$^{(7,12,13)}$. Laboratory preparation had its disadvantages also, for the polymer precipitated out in the reaction vessel, and if exposed to UV irradiation was liable to undergo slight photochemical degradation. The precipitation of PVC made the reaction vessel opaque to irradiation which lowered the rate of reaction. Furthermore the $\bar{\bar{r}}$ of the PVC cannot be effectively controlled by simply varying the initiator concentration. This is because $\bar{\bar{r}}$ is independent of initiator concentration for values of up to 2% of the latter$^{(63,72)}$. If both BTCM and initiator are present, however, the $\bar{\bar{r}}$ can be controlled since BTCM acts as a very efficient chain transfer agent.

The advantages of thermal polymerisation are that precipitated polymer is not exposed to irradiation, and a greater ease in the control of $\bar{\bar{r}}$. The kinetics for the polymerisation of vinyl chloride have been worked out and to a first approximation

$$\bar{\bar{r}} \approx k_p/k_{tr}$$

where k_p = rate constant for propagation

k_{tr} = rate constant for chain transfer with monomer.

Since the activation energy for chain transfer is greater than that for propagation, k_{tr} will increase much more than k_p with increase in temperature and thus the $\bar{r}$ will decrease.

In the characterisation of these telomers and polymers, it was important to determine their molecular weights. For telomers, these were determined mainly in the cryoscopic cell mentioned previously. Alternatively the composition of a telomer mixture could be obtained by passing the mixture through a vapour phase chromatographic column which separated the various species (fig.8).

The $\bar{r}$ of high polymers was determined viscosimetrically in cyclohexanone. Nitrobenzene is claimed to be a suitable solvent for this work(73). It was, however, an undesirable solvent because it attacked PVC very vigorously and rapidly at 198°C (fig.28). At this temperature, nitrobenzene is believed to function as an oxidising agent(74), and it may cause extensive chain scission resulting in an increased rate of breakdown of the PVC. This solvent also attacked the telomers, although more slowly than the PVC. Nevertheless it is not to be recommended as a solvent in the determination of the molecular weights of telomers by boiling point methods.

Criteria for the Preparation of Telomers and Polymers.

As can be seen from table 8 the density of polymers and telomers tends to increase with decreasing chain length. This might be expected because of the influence of the weighty trichloromethyl group on the molecule.

The results showed that telomers ranging in $\bar{r}$ from 1 to 3 could be prepared for a sixfold change in the concentration of BTCM, provided the extent of conversion does not greatly exceed 10%. Only the 1:1 and 2:1 adducts could be obtained in a reasonably pure state however. A second provision was that the initial mole ratio of VC to BTCM should not be greater than 30 to 1 if appreciable quantities of telomer were required.

High polymers may be prepared photochemically with a transfer agent, or thermally with an initiator such as AIBN or BP.

Preliminary to Pyrolysis of Telomers.

In telomer pyrolyses the rate of evolution of acid was independent of the nitrogen flow rate below 12 litres per hour, which indicated breakdown in the liquid phase. The rate was also proportional to the quantity of telomer pyrolysed as might be expected if breakdown were taking place mainly in the liquid phase.

When acid was allowed to remain in contact with the telomers during pyrolysis there was no increase in rate. Thus it appeared that the reaction was not autocatalytic with respect to liberated acid.

Pyrolysis of Telomers.

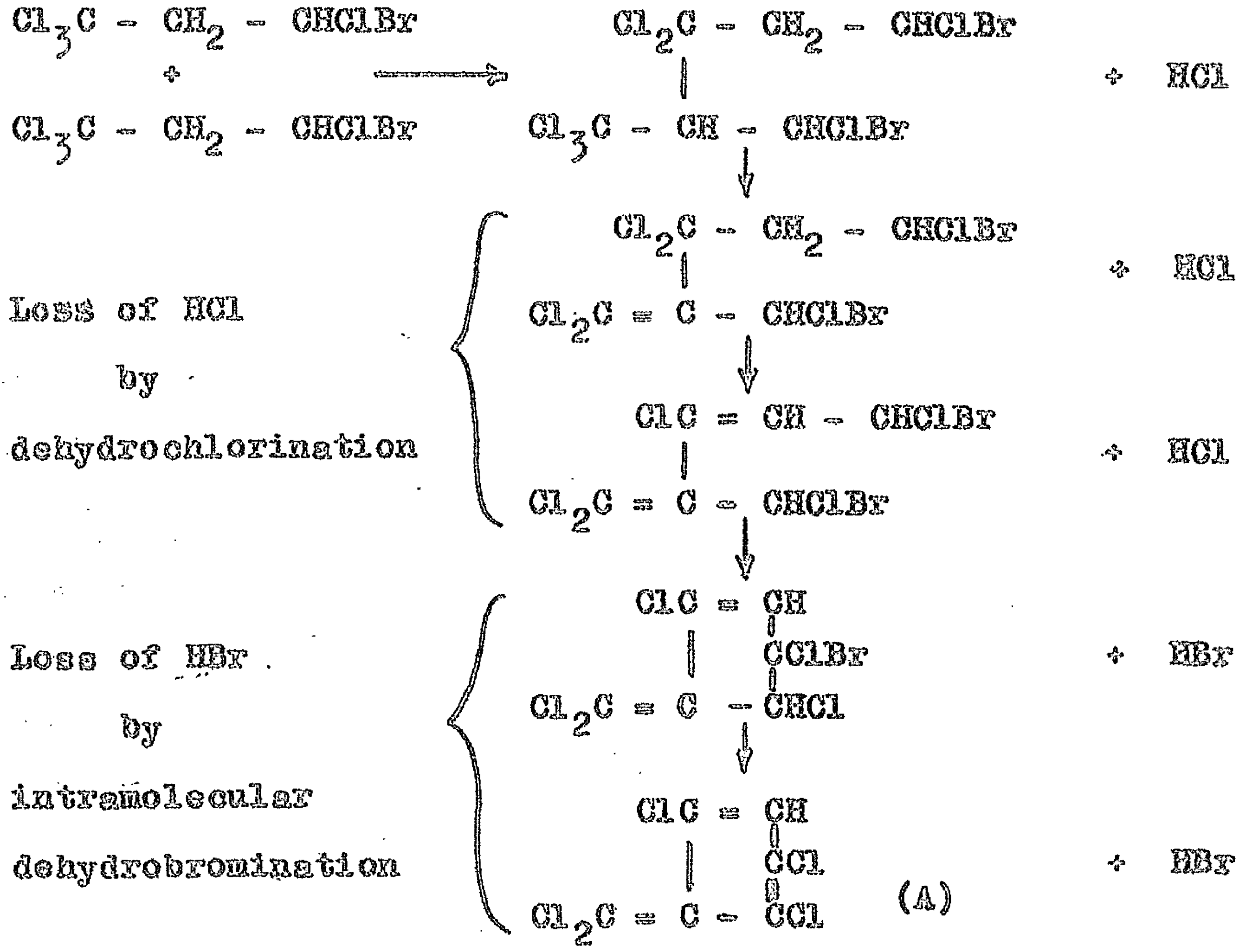
There was a number of characteristics common to the breakdown of the adducts. Both appeared to decompose by a first order process involving low activation energies. They coloured very rapidly in bulk and evolved acid at a very fast rate as compared with similar halogen compounds such as 1-chlorodecane etc.

Other features of the 2:1 adduct, whose pyrolysis was studied in greater detail, were the effect of the double bond on the rate, the apparent formation of high polymer and HCl being liberated in preference to HBr.

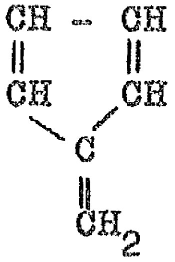
In view of this last fact and the unsuccessful attemp to decompose compounds such as 1:4-dibromobutane, 1:5-dibrom pentane, 1-chlorodecane, etc. under conditions similar to those of the telomers, it could be inferred that the $-CCl_3-$ group might be providing some of the acid evolved. Subsequent work with HQ revealed that the $-CCl_3-$ group did posses unusual reactivity in these telomers.

The formation of colour in these adducts was difficul to understand. It could scarcely be ascribed to the liberation of HBr since the acid would be swept out of the pyrolysand. Since it is similar to that found in the degradation of high polymers, the colour may be due to the formation of chromophores. The latter would have to be very efficient because colour was produced at 130°C, when the breakdown rate was very low.

Owing to the reactivity of the $-CCl_3-$ group it is conceivable that reaction could take place between adduct molecules, e.g. in the case of the 1:1 adduct.

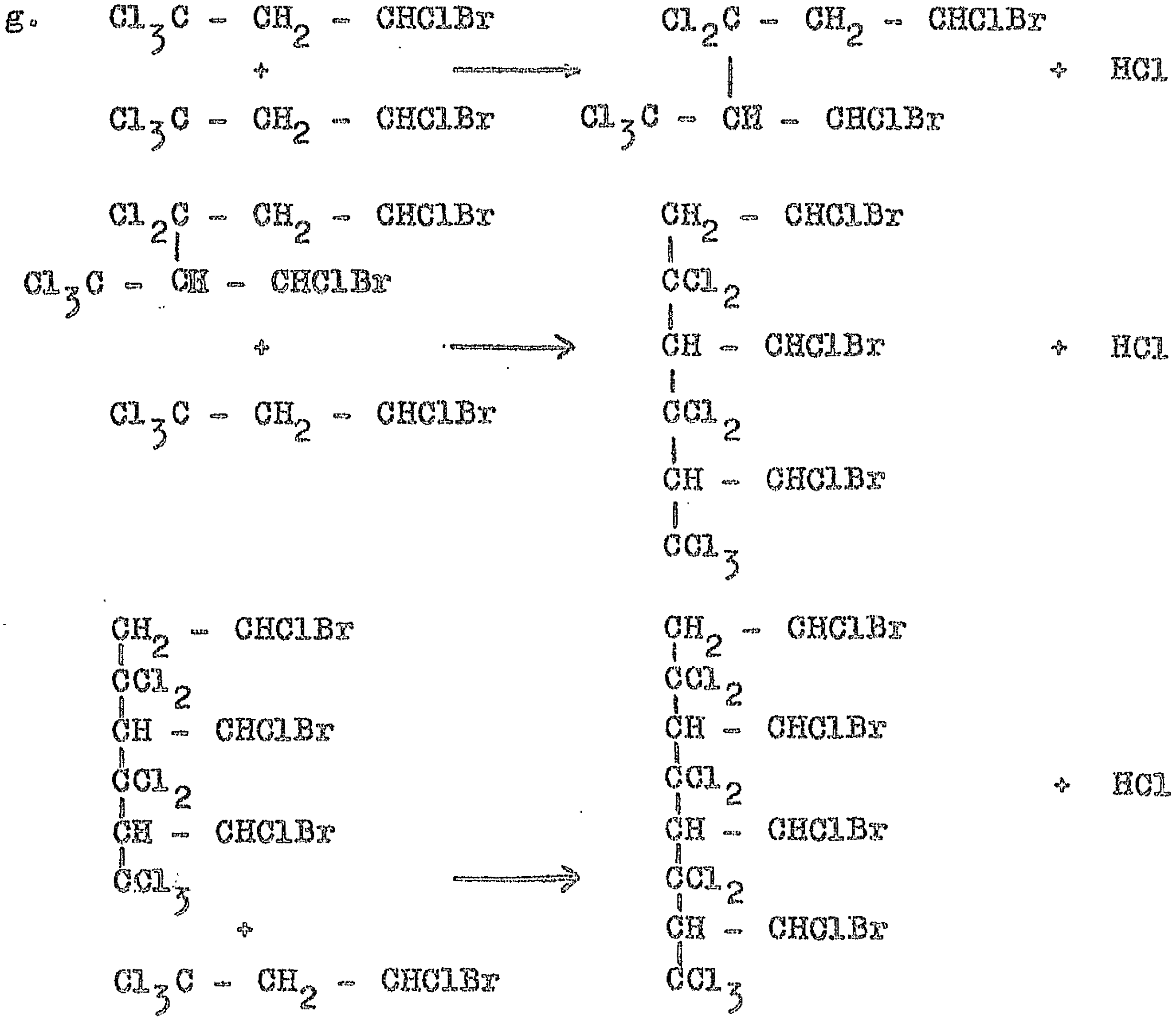


(A) would presumably be highly coloured since fulvene,


is a deep yellow$^{(75)}$.

An alternative explanation is the development of conjugated polyene chains. Seven conjugated double bonds could be formed if the adduct formed a polymer by intermolecular condensation. If the $-\mathrm{CCl_3}-$ group reacted with say, the $-\mathrm{CH_2}-$ groups of other adduct molecules

e.g.

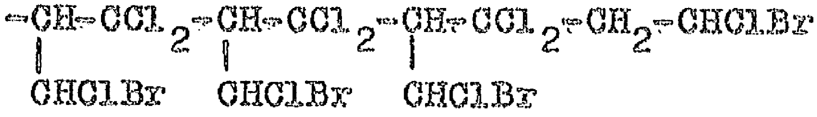


$$\begin{array}{l}\mathrm{Cl_3C-CH_2-CHClBr}\\ \quad + \\ \mathrm{Cl_3C-CH_2-CHClBr}\end{array} \longrightarrow \begin{array}{l}\mathrm{Cl_2C-CH_2-CHClBr}\\ \quad | \\ \mathrm{Cl_3C-CH-CHClBr}\end{array} + \mathrm{HCl}$$

$$\begin{array}{l}\mathrm{Cl_2C-CH_2-CHClBr}\\ \quad | \\ \mathrm{Cl_3C-CH-CHClBr}\\ \quad + \\ \mathrm{Cl_3C-CH_2-CHClBr}\end{array} \longrightarrow \begin{array}{l}\mathrm{CH_2-CHClBr}\\ | \\ \mathrm{CCl_2}\\ | \\ \mathrm{CH-CHClBr}\\ | \\ \mathrm{CCl_2}\\ | \\ \mathrm{CH-CHClBr}\\ | \\ \mathrm{CCl_3}\end{array} + \mathrm{HCl}$$

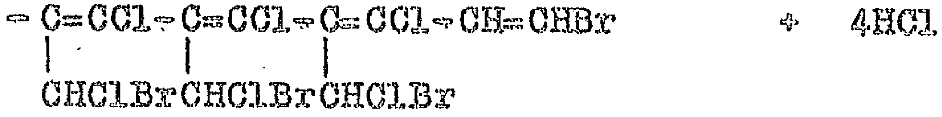
$$\begin{array}{l}\mathrm{CH_2-CHClBr}\\ | \\ \mathrm{CCl_2}\\ | \\ \mathrm{CH-CHClBr}\\ | \\ \mathrm{CCl_2}\\ | \\ \mathrm{CH-CHClBr}\\ | \\ \mathrm{CCl_3}\\ \quad + \\ \mathrm{Cl_3C-CH_2-CHClBr}\end{array} \longrightarrow \begin{array}{l}\mathrm{CH_2-CHClBr}\\ | \\ \mathrm{CCl_2}\\ | \\ \mathrm{CH-CHClBr}\\ | \\ \mathrm{CCl_2}\\ | \\ \mathrm{CH-CHClBr}\\ | \\ \mathrm{CCl_2}\\ | \\ \mathrm{CH-CHClBr}\\ | \\ \mathrm{CCl_3}\end{array} + \mathrm{HCl}$$

Thus the type of polymer formed would be



$$-\underset{\mathrm{CHClBr}}{\underset{|}{\mathrm{CH}}}-\mathrm{CCl_2}-\underset{\mathrm{CHClBr}}{\underset{|}{\mathrm{CH}}}-\mathrm{CCl_2}-\underset{\mathrm{CHClBr}}{\underset{|}{\mathrm{CH}}}-\mathrm{CCl_2}-\mathrm{CH_2}-\mathrm{CHClBr}$$

which, on losing HCl, would yield



$$-\underset{\mathrm{CHClBr}}{\underset{|}{\mathrm{C}}}=\mathrm{CCl}-\underset{\mathrm{CHClBr}}{\underset{|}{\mathrm{C}}}=\mathrm{CCl}-\underset{\mathrm{CHClBr}}{\underset{|}{\mathrm{C}}}=\mathrm{CCl}-\mathrm{CH}=\mathrm{CHBr} \qquad + \quad 4\mathrm{HCl}$$

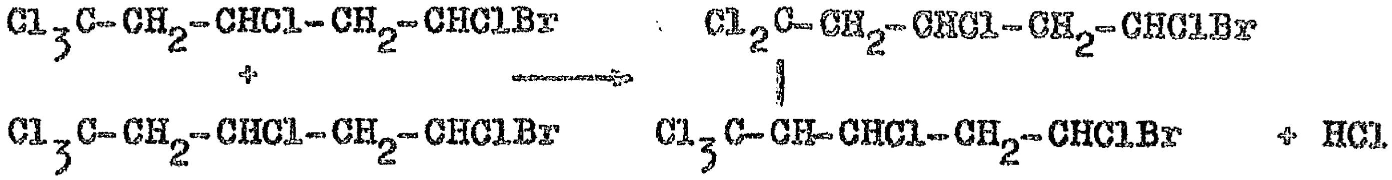
Similar types of polymer could be formed from the 2:1 adduct. The $-\mathrm{CCl_3}-$ group need not necessarily combine with the methylene groups, for polymers could just as easily be formed with reaction occurring between the $-\mathrm{CCl_3}-$ and say, the $-\mathrm{CHBrCl}-$groups.

Of the two possibilities quoted above, the formation of fulvene-type structures was thought to be the most probable as it is a simpler process. Intermolecular condensation was also supported by the telomers colouring much more slowly when diluted with ethyl benzoate. This may, however, be a general dilution effect involving all chromophores and not confined to those obtained in the reactions proposed above.

It is appropriate at this point to discuss the breakdown of the telomers in bulk. As can be seen from fig.15 the pyrolysis of the 1:1 adduct proceeded at a fast rate initially and then gradually diminished. It may be that the products of the breakdown are capable of inhibiting the pyrolysis. The drop in the rate was so marked, however, that it was not possible to take the reaction to completion (i.e. when all the available acid in the telomer had been liberated).

The pyrolysis of the 2:1 adduct was able to be taken to completion, and fig.16 shows that there were three distinct stages in its decomposition. In the first stage the processes occurring would probably be mainly intermolecular condensation rather than dehydrochlorination as the former is favoured energetically.

Consider the heat of condensation for reactions involving the $-CCl_3-$ group



$$\begin{matrix} Cl_3C-CH_2-CHCl-CH_2-CHClBr & & Cl_2C-CH_2-CHCl-CH_2-CHClBr \\ + & \longrightarrow & | \\ Cl_3C-CH_2-CHCl-CH_2-CHClBr & & Cl_3C-CH-CHCl-CH_2-CHClBr \quad + HCl \end{matrix}$$

Loss in bonds will be 1 C-H bond, 1 C-Cl bond (from $-CCl_3-$)

$= 101 + 63 = 164$ k.cal./mole.

Gain in bonds will be 1 H-Cl bond, 1 C-C bond

$= 102.2 + 82.6 = 184.8$ k.cal./mole.

∴ Nett Gain $= + 20.8$ k.cal./mole.

Dehydrohalogenation should occur with greatest ease at the ends of the molecule such that either $Cl_2C{=}CH-CHCl-CH_2-CHClBr$ or $Cl_3C-CH_2-CHCl-CH{=}CHCl$, or a mixture of both might result. As reliable bond energy values were not available for the removal of Br or Cl from a $-CH_2-CHBrCl$ group, values were worked out for the $-CCl_3$ group, i.e. for the compound $Cl_2C=CH-CHCl-CH_2-CHClBr$

Loss in bonds will be 1 C-H bond, C-Cl bond, 1 C-C bond (from $-CCl_3-$)

$$= 101 + 63 + 82.6 = 246.6 \text{ k.cal./mole.}$$

Gain in bonds will be 1 C=C bond, 1 H-Cl bond

$$= 145.8 + 102.2 = 248 \text{ k.cal./mole.}$$

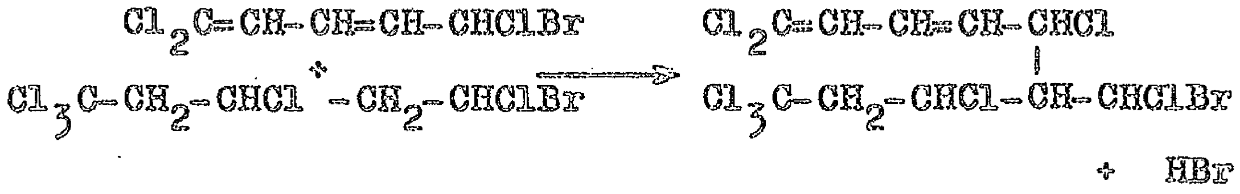
$$\therefore \text{ Nett Gain} = + 1.4 \text{ k.cal./mole.}$$

(All the above bond energy values have been taken from Cottrell[76]).

If dehydrobromination did occur then less energy would probably be required to break the C-Br bond; however this would be offset by the lower energy associated with the formation of an H-Br bond (86.5 k.cal./mole.). This would also apply to intermolecular condensation involving HBr. Since the value of C-Br in $CH_2-CHClBr$ is unknown it is not possible to say whether condensation or dehydrohalogenation resulting from the breakage of this bond are more or less exothermic than those quoted above. Unless the C-Br bond requires much less than 47.3 k.cal./mole. for dissociation, which is unlikely, condensation involving the $-CCl_3-$ group is almost certainly the most exothermic reaction which can occur and of the possible reactions it should be favoured. This is supported by the analytical results.

As the concentration of unsaturates increases so will the yield of HCl from the insertion of a second double bond in the molecule since the first double bond will activate the molecule. That is the adjacent double bond should lower the bond energy of the -C-Cl bond in $Cl_2C{=}CH{-}CHCl{-}$. This is consistent with the fast rates obtained in the pyrolysis of unsaturated derivatives of the 2:1 adduct such as $Cl_2C{=}CH{-}CHCl{-}CH_2{-}CHClBr$.

At later stages double bonds will be formed in the large molecules produced by the condensation of telomers. For example, the -CHBrCl group should be activated by the adjacent double bond in $Cl_2C{=}CH{-}CH{=}CH{-}CHClBr$ thus facilitati condensation with other molecules of adduct.



$$\begin{array}{l} Cl_2C{=}CH{-}CH{=}CH{-}CHClBr \\ \qquad\qquad + \\ Cl_3C{-}CH_2{-}CHCl{-}CH_2{-}CHClBr \end{array} \longrightarrow \begin{array}{l} Cl_2C{=}CH{-}CH{=}CH{-}CHCl \\ \qquad\qquad\qquad\qquad\quad | \\ Cl_3C{-}CH_2{-}CHCl{-}CH{-}CHClBr \\ \qquad\qquad\qquad\qquad + \quad HBr \end{array}$$

Subsequent "zipping" of HCl may increase the overall rate. Thus the accelerating rate is ascribed to the cumulative effect of a number of processes occurring simultaneously to produce acid.

The final stage might be associated with the more difficult decomposition of the products now devoid of many hydrogen and chlorine atoms in suitable positions for the elimination of HCl. Hence the rate should decrease gradually as shown. When no further acid could be obtained from the 2:1 adduct, an insoluble, coal-like material remained which had a high carbon content. Usually when a purely aliphatic compound is pyrolysed there is no residue. These facts pointed to the formation of some sort of polymer lending support to the above theory of condensation among telomer molecules. Considering the number of possible reactions which can occur, it does not seem unreasonable to postulate polymer formation.

The mechanism of decomposition of these telomers deserves some consideration. When 2% AIBN or BP was added to both telomers at 157°C the rate increased fourfold. This favours a free radical mechanism. However since a comparatively large quantity of initiator was required this suggests that if decomposition is free radical the kinetic chain length is short. On the other hand, the free radical may merely produce compounds containing carbon-carbon double bonds which increase the rate of breakdown.

The overall activation energy (E_o) for a free radical process involving mutual termination is of the form

$$E_o = \tfrac{1}{2} E_i + E_p - \tfrac{1}{2} E_t$$

where E_i = Activation energy for initiation

E_p = " " " propagation

E_t = " " " termination.

In accounting for the overall activation energy, it is likely that the activation energy for initiation requires the breakage of a C-Cl bond from say the $-CCl_3$ or a -C-Br bond from -CHBrCl groups. The values for both those groups are lower than the 81 k.cal.(8,76) necessary for the breakage of the -C-Cl bond in the $-CH_2-CHCl$ group.

It is also likely that the propagation process requires a fairly high activation energy because the free radical initiators used were ineffective at low temperatures. A high E_p is not unreasonable since Barton and Howlett(8) found that the main propagation step in the decomposition of 1:2-dichloroethane needed 22.0 k.cal./mole for activation. If a high E_p were involved, then the activation energy for termination would also have to be high to give the low overall activation energies of 28 and 21 k.cal./mole for the 2:1 and 1:1 adducts respectively. This seems unlikely.

It is interesting to compare these activation energies with those obtained for related compounds by other workers. Baum and Wartman(15) quoted an E_o of 22.5 k.cal./mole for 4 chlorohexene-2, $CH_3-CH_2-CHCl-CH=CH-CH_3$ over the temperature range 110°C to 140°C, whereas 1:2-dichloroethane decomposes with an E_o of 47 k.cal./mole by a first-order, free radical mechanism over the range 362-485°C as mentioned in the Introduction. Barton and Onyon(77) subsequently showed that 1:1:1-trichloroethane decomposes by a unimolecular (E_o = 48 k.cal./mole) and a radical chain mechanism (E_o = 54 k.cal./mole) over the range 362-427°C; the decomposition being a first-order process in the initial stages. The first order dependences obtained in the decomposition of these chlorinated hydrocarbons are in agreement with those found for the 1:1 and 2:1 adducts. Although the E_o values obtained by Barton and co-workers are high, Barton, in an earlier paper, had quoted much lower values over similar temperature ranges (table 35).

Table 35. Activation Energies for Various Chlorinated Hydrocarbons

Compound	Overall Activation Energy (k.cal./mole.)
Ethyl Chloride	32.0
1:2-Dichloroethane	27.1
1:1-Dichloroethane	33.9
1:1:2-Trichloroethane	38.0
Pentachloroethane	29.2
1:2-Dichloropropane	34.2
2:3-Dichlorobutane	30.4

The E_o values listed in table 35 are of course inconsistent with the more recent values obtained by Barton and colleagues.

A point in favour of a free radical mechanism for the telomers is the acceleration in rate in oxygen. The latter promotes the decomposition of 1:2-dichloroethane, 1:1:2-trichloroethane, and 1:1:2:2-tetrachloroethane(78), all of which are alleged to decompose by a radical chain mechanism.

On the other hand, the pyrolyses of these telomers may be non-free radical. The comparatively fast rates and rapid colouration suggested a condensation type of reaction. Furthermore the low activation energies were not consistent with a free radical mechanism, whilst radical polymerisation inhibitors did not retard or inhibit the reaction. There was, however, a likely explanation for this in that the inhibitors probably reacted exclusively with the reactive $-CCl_3-$ group as was the case for HQ and the telomers.

Because radical polymerisation inhibitors accelerated the decomposition of the telomers very markedly, their effect on the latter has been examined in some detail, particularly the reaction between HQ and 2:1 adduct.

The Reaction between 2:1 Adduct and HQ.

With regard to the heterogeneous system 10% HQ - excess 2:1 adduct, in addition to the thermal degradation of the adduct, there may be reaction between the HQ and the latter in either or both of the phases. Each phase will now be considered separately.

Excess 2:1 Adduct-HQ.

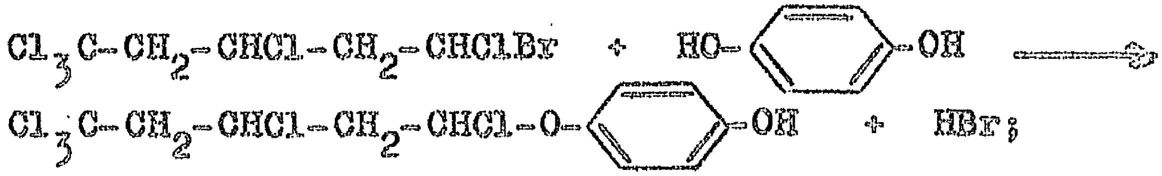
In fig.21., below 3% HQ the latter had only a slight catalytic effect, but in the concentration range 4-5% HQ the rate increased sharply. This change in rate could be associated with the formation of a second phase known to occur at about 4% HQ from solubility measurements. For it had been shown that the reaction proceeded rapidly in the HQ-rich phase. The reaction may also be influenced by the change in dielectric constant, in which case it may be partially ionic at least. The slight increase in rate up to 3% HQ may be due either to the reaction between HQ and the adduct or to an increase in dielectric constant.

Excess HQ-2:1 Adduct.

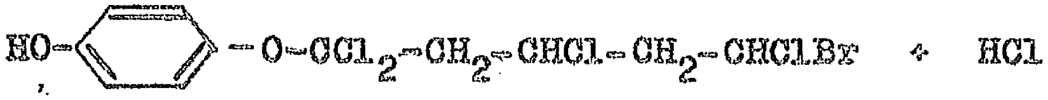
In a series of co-pyrolyses of excess HQ and 2:1 adduct two features were revealed; an initial surge of acid followed by a gradual fall-off in rate (fig.23), and the liberation of two moles of acid per mole of adduct initially.

The large volumes of acid evolved in a short time suggested an ionic type of reaction, possibly a condensation between the hydroxyl group of the HQ and a halogen atom from the 2:1 adduct

e.g.

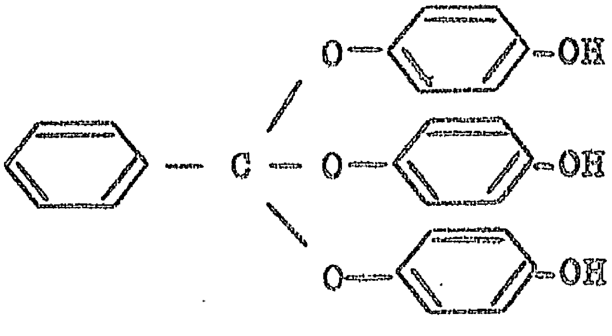


or perhaps the formation of

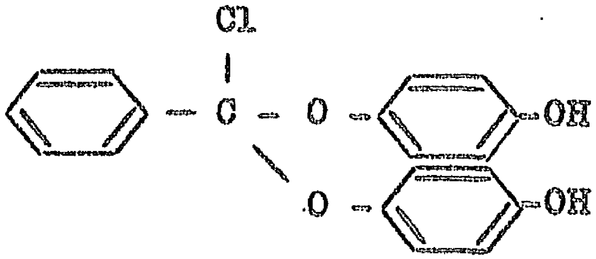


The Br atom was expected to react in preference to the Cl atoms present in the molecule because the C–Br bond is usually weaker than the C–Cl bond in a similar type of structure. Accordingly an excess of HBr would be expected. The major product evolved was HCl, however, in agreement with previous data on the decomposition of the adduct. Since bond energy considerations ruled out the possibility of HQ attacking the chain chlorines preferentially, the $-CCl_3-$ group appeared to be the source of the acid.

To investigate the nature of the $-CCl_3-$ group, benzotrichloride was pyrolysed in excess HQ. Two chlorine atoms were removed initially and the fall-off in rate (fig.27) reflected the greater difficulty in removing the third chlorine atom. The analysis of the product formed in this co-pyrolysis confirmed it to be

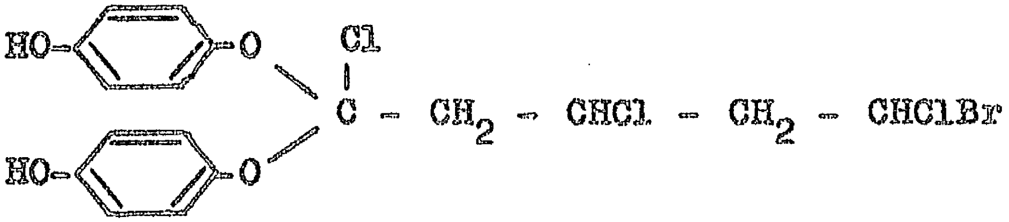


which would be expected if the chlorine atoms reacted with the OH groups of the HQ. The compound

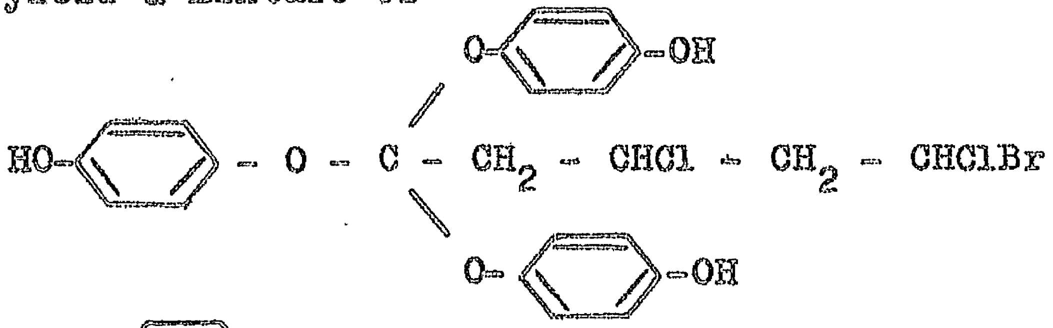


would be formed with ease initially, although the two bulky HQ groups probably hinder the approach of a third molecule of HQ. The third chlorine may also possess a higher bond energy due to the structural change in the molecule.

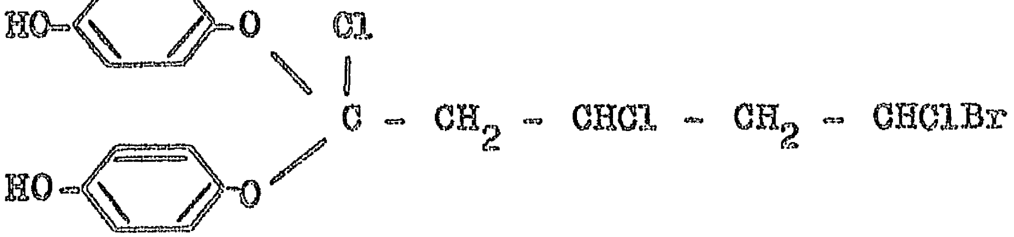
Returning to the analogous system excess HQ - 2:1 adduct, there is no reason to suppose that the $-CCl_3-$ group in the telomers should not be as reactive as that found in benzotrichloride. Hence the compound



is throught to be formed initially. Further reaction might yield a mixture of



and



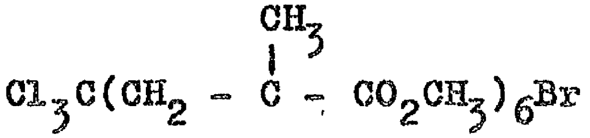
with the latter favoured sterically.

Activation Energies.

The addition of a small quantity of HQ to both telomers did not appreciably affect their activation energies (table 18). With HQ in excess, however, the activation energy for the breakdown of the 2:1 adduct dropped to half its nominal value. This is in agreement with reaction taking place much more easily in the HQ-rich phase (fig.21). In view of the reactivity of the $-CCl_3-$ group what was probably being measured was the activation energy of condensation between the HQ and the 2:1 adduct. The very low values of these activation energies implied that reaction occurred very readily indeed.

Other phenols, such as the chlorophenols, when pyrolysed with the 2:1 adduct also produced results similar to those obtained in the systems excess HQ - 2:1 adduct and excess HQ - benzotrichloride. Moreover the inability of o-nitrophenol to react with the 2:1 adduct was to be expected because of hydrogen bonding between the molecule's OH and nitro groups. There also appeared to be a trend between increase in dielectric constant of the phenol - adduct system and an increase in rate. These facts are additional support for the theory that the reaction between HQ and the adducts is ionic in nature.

Graphs obtained in the co-pyrolyses of phenols and compounds containing the $-CCl_3-$ group were so characteristi that they could be used in the identification of this group It was also possible to determine the approximate molecular weights of compounds such as the methyl methacrylate telomers and polymers prepared with BTCM, i.e.



$$Cl_3C(CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}-CO_2CH_3)_6Br$$

. When pyrolysed in excess HQ, they yielded the amount of HCl per weight of compound. Henc speedy approximation of the number average molecular weight of the telomer or polymer could be determined if these were linear.

Summing up, the pyrolysis of these telomers is very complex and it may be that both free and non-free radical processes are involved, the latter in view of the apparent reactivity of the $-CCl_3-$group.

Pyrolysis of High Polymers

General Considerations.

Liberated HCl allowed to remain in contact with the pyrolysand did not affect the rate, indicating that the reaction was not autocatalytic with respect to HCl evolved, in agreement with Arlman(22) and Stromberg *et al.*(23). Since others(12-14) found autocatalysis occurring only in oxygen this may mean that the gas oxidises the HCl evolved to chlorine free radicals which could initiate decompositio

Initial use of various solvents showed that only two of the ones tried were suitable, *o*-dichlorobenzene and ethy benzoate, the ester being the most suitable because of its wider temperature range. The rate of dehydrochlorination was faster in ethyl benzoate. This may be due to polymer solvent interaction. The faster gel times obtained in *o*-dichlorobenzene at 178°C may be due to distillation effects which would alter the concentration of PVC in this solvent (b.pt. 182°C), thus reducing the gel time.

Cross-linking and dehydrochlorination in ethyl benzoate were studied as the two main aspects of PVC degradation. Dehydrochlorination followed by chain "zipping" probably provides most of the acid evolved during pyrolysis. However even a small amount of cross-linking will enhance intra-condensation between cross-linked polyme chains, which must be reckoned as a subsidiary source of aci The usual contribution of acid from cross-linking processes is some 1 to 5% before the solution gels, but it becomes greater at high temperatures and concentrations, for under these conditions gelation occurs much more quickly.

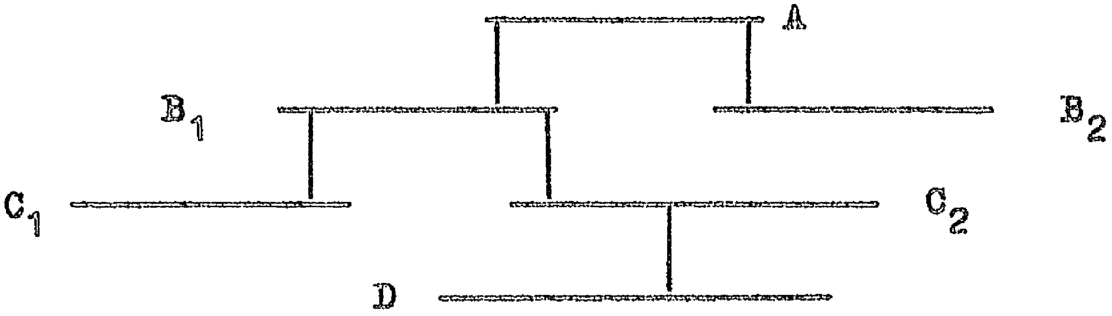
In order to avoid submerging the two main reactions in a mass of detail, each will be discussed in turn.

The Cross-Linking of PVC in Ethyl Benzoate.

The kinetics of cross-linking may be considered in the light of Flory's(68) theory of gelation.

Consider a cross-linked polymer molecule.

Let A be a primary chain which has become part of an infinite network, and let it be linked to a second primary chain B_1 as shown



The condition that there will be additional cross-links to say, B_1 is given by $q = \chi(r - 1)$ ......(1)

where q = additional number of cross-links,

χ = probability that any unit of the primar chains has entered into cross-linking,

r = degree of polymerisation of the primary chains.

Now $(r - 1)$ monomer units will remain after the firs cross-link, it being assumed that all the chains are the same length.

When $q < 1$, the network cannot be maintained and infinite network formation cannot occur. For $q > 1$, the network will be maintained and it can become infinite.

Thus $q = 1$ is the critical condition and hence from equation (1) the critical probability will be

$$\chi_c = \frac{1}{(r-1)}$$

Thus for high polymer $\chi_c = \frac{1}{r}$ approximately ...(2

In the text above it has been assumed that all chain are the same length. In practice, however, the initial primary chains are not uniform in length and equation (1) must be changed to

$$q = \chi \sum_{r=1}^{\infty} w_r (r-1)$$

$$= \chi (\bar{r}_w - 1) \qquad \ldots\ldots\ldots\ldots\ldots(3)$$

where w_r = weight fraction of r-mer.

$\bar{r}_w$ = weight average chain length.

Thus equation (1) becomes

$$\chi_c = \frac{1}{(\bar{r}_w - 1)} = \frac{1}{\bar{r}_w} \text{ approximately}..(4)$$

since the critical condition $q = 1$ is considered to hold at the gel point.

Thus incipient gel formation can occur when relative few cross-links have been formed. According to equation (when the initial chains are long, incipient gel formation corresponds to an average of only one cross-linked unit per primary chain initially present (or an average of one cross link between any two primary chains). The number of cross linked units per primary chain is called the cross-linking index, .

$$\gamma = \chi \bar{\bar{r}}_w$$

For a homogeneous primary polymer, $\gamma = 1$.

In a typical vinyl distribution, $\bar{\bar{r}}_w = 2\,\bar{\bar{r}}$, with $\bar{\bar{r}}$ the number average degree of polymerisation

$\therefore\ \gamma = 0.5$ for a number average chain length.

The above theory has assumed that intramolecular cross-linking processes do not occur. This will hold for finite chains. In the final gel, however, there will be many intramolecular links to produce an infinite network. If $\bar{\bar{r}}$, $\bar{\bar{r}}_w$ and the gel point are known, then an expressio can be deduced for the rate of formation of cross-links.

For the system PVC - solvent, let it be assumed tha there are y cross-links formed in time t_g, the gel time. The number of cross-links formed per unit time will be y/t i.e. $y/n/t_g$ cross-links per polymer molecule per unit time where n = number of polymer molecules.

In a system of volume V containing w g. of polymer of number average degree of polymerisation, $\bar{r}$ the rate of formation of cross-links will be:

$$\frac{(y/n) \times w}{t_g \times V \times \bar{r} \times M}$$

where M = molecular weight of the monomer.

Now at the gel point, y/n = 0.5 if the distribution is such that $\bar{r}_w = 2\bar{r}$.

$\therefore$ Rate of formation of cross-links $= \frac{0.5}{\bar{r}} \times \frac{w}{V \times t_g \times M}$

If it is assumed that the cross-linking reaction is second order (two molecules combine with each other to form one cross-link) then the rate of formation of cross-links $= k''c^2$ and

$$\frac{0.5 \times w}{\bar{r} \times V \times t_g \times M} = k''c^2$$

where c = polymer concentration in moles per litre

$$= \frac{w}{V \times M \times \bar{r}}$$

$$\therefore k'' = \frac{0.5 \times V \times M \times \bar{r}}{w \times t_g} = \frac{1}{2ct_g}$$

Order of the Reaction

From the theory, $k'' = \frac{1}{2ct_g}$ so that the concentration should be proportional to the reciprocal of the gel time. This was the case as can be seen from table 36.

The rate of cross-linking was also proportional to the square of the concentration.

Table 36. Calculated Second Order Rate Constant (k'') for the Cross-Linking of PVC ($\bar{r}$ 905) at 212°C in Ethyl Benzoate

Gel Time (Sec) x 10^{-3}	(Polymer Concentration)^2 (moles^2/litre^2) x 10^7	k'' (l./mole/sec) x 10^2
2.82	70.0	6.70
4.62	35.6	5.75
6.72	23.2	4.87
8.64	16.4	4.52

The k'' values listed appeared to fit in reasonably well with the idea that cross-linking is a second order process.

Dependence on Chain Length.

The rate constant dropped with decreasing $\bar{r}$ (table 37) and this was in agreement with Flory's concept of the size of the polymer molecule influencing the rate at which cross-linking occurs. Table 37 shows that whilst the rate was constant for a fixed weight it was not for a molar concentration. Thus the indication was that cross-linking may simply be random condensation between polymer molecules.

Table 37. Dependence of a) Rate Constant for Cross-Linking b) Rate of Cross-Linking for a Solution of Fixed Weight on the $\bar{r}$ of the PVC at 198°C.

$\bar{r}$	k'' (l./mole/sec) x 10^2	Relative rate per fixed weight
905	3.30	1.00
553	1.80	1.40
367	0.65	1.20
192	0.20	1.35

Energy of Activation.

No previous work has been done on the evaluation of activation energies for the cross-linking of PVC. It was not therefore possible to make any comparisons. From the low average value of 23.7 k.cal./mole the A factor was calculated to be $10^{9.8}$ which is of the correct order for bimolecular reactions.

Effect of Additives.

(1) Free Radical Chain Initiators.

Only very large quantities affected the rate of cross-linking, perhaps by causing chain scission. Cross-linking did not appear to be a free radical process, but it was certainly accelerated by catalysts such as ferric chloride which could then function as a Friedel-Crafts catalyst.

(2) Free Radical Chain Inhibitors and Oxygen.

Free radical chain inhibitors increased the rate of cross-linking slightly, although α-phenylindole used as a commercial stabiliser was found to prevent gelation quite efficiently. Pyrolysis in oxygen prevented gelation occurring and this may be due to extensive chain scission which would mean a much slower rate of cross-linking.

The Dehydrochlorination of PVC in Ethyl Benzoate.

As mentioned previously both the 1:1 and 2:1 adducts and 1:2-dichloroethane(8) appeared to decompose by a first order process. It was thought that this might also be true for the high polymer, especially since only one molecule is involved in the "zipping" process. However if the process were free radical - initiated the order mkght be expected to be 3/2(23).

In this work the rate of dehydrochlorination has bee calculated as moles of acid evolved per litre per second.

Assuming dehydrochlorination is a first order process, then

$$\frac{\text{moles acid evolved}}{\text{litres x seconds}} = k'c$$

where c = monomoles/litre

k' = rate constant (sec.$^{-1}$)

i.e. $c = \frac{w}{V \times M}$

where M = molecular weight of the monomer

V = total volume (litres)

w = weight of polymer (g.)

$\therefore \quad k' = \frac{\text{Rate}}{\text{monomoles/litre}}$

Order of the Reaction.

On the grounds that dehydrochlorination is a first order reaction, rate constants have been calculated.

Table 38. Calculated First Order Rate Constants (k') for the Dehydrochlorination of PVC ($\bar{F}$ 905) at 212°C in Ethyl Benzoate.

$\frac{d[HCl]}{dt}$ (mole/l/sec.) x 10^6	Polymer Concentration (monomole/l.)	k' (sec^{-1}) x 10^6
90.0 (Bulk)	22.4	4.03
9.55	2.38	4.01
6.82	1.70	4.05
5.34	1.37	3.90
4.70	1.17	4.01

The k' values fitted in quite well with a first order reaction. It was noteworthy that the rate constant for bulk PVC was the same as for PVC in solution, indicati that in the initial stages at least there was no diffusion control of the acid escaping from the polymer mass.

Dependence on Chain Length.

The rate varied markedly with the $\bar{r}_w$ of the polymer, those of lower $\bar{r}_w$ evolving acid at faster rates. On a weight average basis, in any given weight of polymer there will be more molecules in a polymer of low $\bar{r}_w$ than for one of high $\bar{r}_w$. Thus for a polymer of low $\bar{r}_w$ there would be more end groups, and if initiation began at the ends of the molecule, this would result in a faster rate of dehydrochlorination. Baum and Wartman(15) have also suggested that terminal double bonds were the main cause of chain initiation.

Table 39 shows that the rate constant increased with decrease in $\bar{r}_w$, but the rate per polymer molecule was fairly constant. This favours end-group initiation and the "zipper" since above a certain minimum chain length the "zipper" ought to be independent of $\bar{r}_w$.

Table 39. Dependence of the Rate Constant on the $\bar{r}_w$ of the Polymer for Dehydrochlorination at 212°C in Ethyl Benzoate

$\bar{r}_w$	k' at 212°C $(\text{sec}^{-1})\times 10^6$	Rate/Polymer,molecule (i.e. $k \times \bar{r}_w$)
1810	4.01	1.0
1106	6.70	1.0
734	15.6	1.6
384	11.4	0.61

Energy of Activation.

The average value of 23.2 k.cal./mole was in agreement with Baum and Wartman's(15) value for PVC over a similar temperature range.

The values for the activation energy reported in the literature for the range 160-200°C vary enormously from the doubtful value of 7.1 k.cal./mole obtained by Imoto and Otsu(73) to 39 k.cal./mole evaluated by Hartman(79). Other investigators(23,24,22) found intermediate values of 26, 33, and 34 k.cal./mole respectively for similar temperature ranges.

Since the $\bar{r}$ of PVC is controlled by chain transfer with monomer(63) there will be terminal carbon-carbon doubl bonds present in most of the polymer molecules. Thus previous investigators probably evaluated the activation energy for chain "zipping". Hence the large difference in activation energy cannot be attributed to the different energy requirements in producing the first double bond and the "zipper" which might require much more activation.

It is not unreasonable that the activation energies for cross-linking and dehydrochlorination are very similar. The overall heat of reaction for the two processes is similar if a value of 19 k.cal./mole is assumed for the resonanc stabilisation of the allyl radical.

For cross-linking,

$$\begin{array}{l} -CH_2-CHCl- \\ \quad + \\ -CH_2-CHCl-CH_2- \end{array} \longrightarrow \begin{array}{c} -CH-CHCl- \\ | \\ -CH_2-CH-CH_2- \end{array} + HCl$$

Loss in bonds will be 1 C-H bond, 1 C-Cl bond

$= 101 + 81 = 182$ k.cal./mole

Gain in bonds will be 1 H-Cl bond, 1 C-C bond

$= 102.2 + 82.6 = 184.8$ k.cal./mole

$\therefore$ Nett Gain $= + 2.8$ k.cal./mole

In dehydrochlorination,

$$CH_2=CH-CH_2-CHCl \longrightarrow CH_2=CH-CH=CH- \quad + HCl$$

Assuming the polymer molecules are in the form of allyl free radicals the C-H bond will now be 19 k.cal./mole weaker and 2.4 k.cal./mole will be evolved

$$\text{i.e.} \sim CH_2=CH-CH_2-CHCl \longrightarrow \begin{array}{c} -CH_2-\overset{\circ}{C}H-CH_2-CHCl- \\ \Big\downarrow \\ -CH_2-\overset{\circ}{C}H-CH=CH- \; +H \end{array}$$

Loss in bonds will be 1 C-H bond, 1 C-Cl bond, 1 C-C bond

$= 82 + 81 + 82.6 = 245.6$ k.cal./mole

Gain in bonds will be 1 C=C bond, 1 H-Cl bond

$= 145.8 + 102.2 = 248$ k.cal./mole

$\therefore$ Nett Gain $= + 2.4$ k.cal./mole

(All bond energies have been taken from Cottrell$^{(76)}$)

According to these values cross-linking and dehydrochlorination are competitive reactions. Dehydrochlorinatio proceeds at a much faster rate and since both processes require the same activation energy, the difference in rate is presumably due to the difference in the A factors for these reactions. If there were no terminal double bonds present initially in the PVC, cross-linking would probably predominate for an energy absorption of 16.6 k.cal./mole would be necessary for the insertion of the first double bond.

Effect of Additives.

(1) Free Radical Chain Initiators.

So far there has been no real evidence to indicate whether the reaction is free radical initiated. It was true that addition of 4% AIBN to PVC doubled the rate, but calculation showed there was only one free radical for every four molecules of HCl liberated; this could not justifiably be called a chain process. Possibly the catalytic effect of the free radicals was due to their use in forming double bonds in the polymer by disproportionatio

e.g. $- \overset{\circ}{C}H - CHCl - \quad + \quad - \overset{\circ}{C}H - CHCl- \longrightarrow$

$$- CH = CCl- \quad + \quad - CH_2 - CHCl -$$

Double bonds activate the molecule. To double the rate it would be necessary to double the number of double bonds. Hence this would be a very mild catalytic effect as observed. The alternative reaction

$$-\overset{\circ}{\mathrm{C}}\mathrm{H}-\mathrm{CHCl}-\mathrm{CH}_2 \longrightarrow -\overset{\circ}{\mathrm{C}}\mathrm{H}-\mathrm{CH}=\mathrm{CH}- \quad + \mathrm{HCl}$$

is also possible.

Winkler$^{(11)}$ suggested that a chlorine atom could act as a chain carrier during dehydrochlorination. He postulated the following reaction mechanism

$$\begin{array}{lll} -\overset{\circ}{\mathrm{C}}\mathrm{H}-\mathrm{CHCl} \longrightarrow & -\mathrm{CH}=\mathrm{CH}- & + \ \mathrm{Cl}^{\circ} \\ & \quad\ \downarrow & \\ & -\mathrm{CH}=\mathrm{CH}-\overset{\circ}{\mathrm{C}}\mathrm{H}-\mathrm{CHCl}- & + \ \mathrm{HCl} \\ & \quad\ \downarrow & \\ & -\mathrm{CH}=\mathrm{CH}-\mathrm{CH}=\mathrm{CH}- & + \ \mathrm{Cl}^{\circ} \end{array}$$

which has been more fully dealt with in the Introduction. It is difficult to see why Cl°, if free, does not abstract a H atom from another PVC chain rather than run along the same chain for, say 15 $-\mathrm{C}=\mathrm{C}-$ groups, particularly for reactions carried out in solution.

At 100 and 130°C when the rate of dehydrochlorinatio was very low, addition of 2% AIBN exerted no effect. This tends to disfavour a free radical theory. Benzoyl peroxid dissolved in ethyl benzoate coloured the solution, and the reported colouration of PVC compounds by BP may be entirely due to the latter, and not to any polymer degradation process.

(2) <u>Free Radical Chain Inhibitors and Commercial Stabilisers.</u>

Free radical chain inhibitors such as 1:4-diaminoanthraquinone and tetrachloro-o-benzoquinone had very littl effect on the decomposition of PVC. They did not inhibit the reaction.

However the commercial stabiliser, Stanclere 70 was a useful inhibitor in the sense that it greatly reduced the rate and extent of colouration in the initial stages. The mechanism of stabilisation may be analogous to that propose by Kenyon(30) in which compounds similar in nature to Stanclere 70 acted as free radical scavengers. (Introduction, page 23). The duration of the slow rate was directly proportional to the amount of Stanclere 70 added to the PVC. The slow rate was ca. two to three times that obtained in cross-linking for the same PVC concentration. Thus dehydrchlorination may be a mixture of free and non-free radical processes.

In the presence of oxygen the bulk pyrolysis of PVC was accelerated as opposed to its solution degradation bein unaffected. Probably too little oxygen was dissolved in the hot polymer solution to cause oxidation, whereas oxygen can be more readily adsorbed on to the surface of the unsaturated polymer.

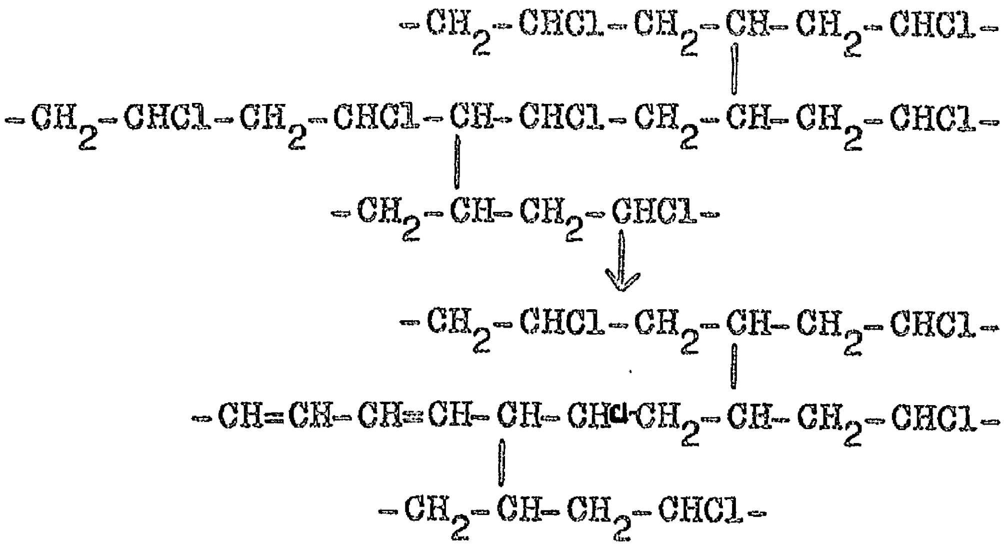
Summing Up.

One of the points in favour of a free radical mechanism was the ability of Stanclere 70 to retard the rate of dehydrochlorination. The latter was accelerated on additi of free radical initiators at high temperatures although similar to the telomers the activation energy for propagati is probably high. Further support was the acceleration of PVC in bulk in oxygen.

On the debit side, the variation in rates of dehydrochlorination and cross-linking in ethyl benzoate and o-dichlorobenzene did not favour a free radical mechanism. The effects of initiators and inhibitors generally, the low activation energies and the first order dependence for dehydrochlorination also did little to support this mechani

If in fact initiators do catalyse the formation of double bonds this would explain the increase in rate. Doub bonds, whether introduced at the ends of a PVC molecule by disproportionation and monomer transfer(15) during polymerisation or artificially into the dead polymer(31), have a profound effect on the degradation of the polymer. Druesedo and Gibbs(12) postulated that double bonds activate the molecule thus enhancing the opportunities for cross-linking This is not in agreement with the present work for initiato such as AIBN and BP did not affect the rate of cross-linkin

For the mode of termination, branching was believed to terminate the "zipper" in PVC. i.e.



The experimental evidence did not support this, however.

The comparison between the initial decomposition rates of telomers and the rates of dehydrochlorination and cross-linking found in high polymers in ethyl benzoate is of some interest.

Table 40. Comparison of Rates for a Fixed Weight of Telomers and High Polymers in Ethyl Benzoate at 198°C.

$\bar{\bar{r}}$	Rate of Dehydrochlorination (moles./l./sec.) x 10^7	Rate of Cross-linking (moles./l./sec.) x 10^7
905	54.4	1.36
192	117.	2.78
2	4.92	-
1	5.62	-

The acid evolved during the pyrolysis of telomers is believed to be due to the condensation and dehydrohalogenation reactions. As can be seen, the telomer rates compare very favourably with the cross-linking rates of the high polymer, whilst the rates for the dehydrochlorination of the polymer are much faster. This lends support to the reaction types postulated.

In conclusion, this work could be extended by using polymers initiated with different transfer agents. It would be interesting to study the effect of these various end-groups on the rate of dehydrochlorination in a suitable solvent over a very wide temperature range. A more detail picture of the cross-linking process would emerge if polyme were fractionated before pyrolysis, so that all measurement could be carried out on the various fractions of one particular polymer.

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