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A THERMOGRAVIMETRIC STUDY OF
POLYPHOSPHAZENES
AND
HYDROCARBON CONDENSATION POLYMERS

A Thesis

presented for the degree of

DOCTOR OF PHILOSOPHY

in the Faculty of Science of the

University of St. Andrews

by

JOHN TANNER, B.Sc., A.R.I.C.

June 1969

United College of St. Salvator
and St. Leonard, St. Andrews.



Th 5641

DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself and that it has not been submitted in any previous application for a Higher Degree.

This thesis describes results of research carried out at the Chemistry Department, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Dr. J.R. MacCallum since the 1st of October 1966, the date of my admission as a research student.

JOHN TANNER

CERTIFICATE

I hereby certify that John Tanner has spent eleven terms of research work under my supervision, has fulfilled the conditions of Ordinance No. 16 (St. Andrews) and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

J.R. MacCALLUM,
Director of Research

ACKNOWLEDGEMENTS

I should like to record my gratitude to Dr. James R. MacCallum for his help and encouragement in all aspects of this work.

I am indebted to the Science Research Council for the award of a Research Studentship from 1966 to 1969 and to Professor J.I.G. Cadogan for research facilities during this period.

My thanks are also due to Professor G. Allen and Mr. S.M. Todd of Manchester University for some polyphosphazene samples, to Mr. James Rennie, Mr. Donald McGhee and Mr. Leslie Smith for their technical aid and finally to Miss Patricia Kirk who typed this thesis.

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SUMMARY

This thesis is presented as two separate yet interdependent parts. It was the original purpose of this work to study fully the degradation of various high polymeric phosphazenes and related compounds. Thus Part One of the thesis deals with the preparation and thermogravimetric degradation of some phosphazenes. However, once experimental work on the thermobalance had started, it became apparent that there were many unexplained problems both in the derivation and extraction of kinetic parameters from thermograms and in the lack of interlaboratory correlation between published results, even those given for the same compound.

It was therefore decided to curtail the phosphazene work somewhat and present a second part to the thesis dealing mainly with thermogravimetry. Thus Part Two of the thesis is an attempt to rationalise some of those aspects of thermogravimetry most in need of reappraisal. In carrying out this task, fully characterised organic polymers, copolymers and homopolymers, have been used since they present a more easily deciphered degradation pattern than do inorganic polymers.

Each part contains numbers in parenthesis which indicate bibliographic references. There are two separate bibliographies, each situated at the end of that part of the thesis to which they refer.

PUBLICATIONS

1. J.R. MacCallum and J. Tanner. The Preparation of Poly(diphenylphosphazene). *J. Polymer Sci. (A1)*, 6, 3163 (1968).
2. J.R. MacCallum and J. Tanner. Interpretation of the Kinetics of Thermogravimetric Analysis. *J. Phys. Chem.*, 73, 751 (1969).
3. J.R. MacCallum and J. Tanner. A Comparison of Methods of Analysis of Thermogravimetric Data. *I.U.P.A.C. Symposium*, Budapest August 1969.
4. J.R. MacCallum, D.H. Richards and J. Tanner. A Thermogravimetric Study of Hydrocarbon Condensation Copolymers. *I.U.P.A.C. Symposium*, Budapest August 1969.
5. J.R. MacCallum, J. Tanner and A. Werninck. Thermogravimetric Analysis of Some Phosphazenes. *Inorganic Polymer Symposium*, Northern Polytechnic, London April 1969.
6. J.R. MacCallum and J. Tanner. The Effect of Sulphur on the Polymerisation of Hexachlorocyclotriphosphazene. Submitted to *Polymer Letters*.

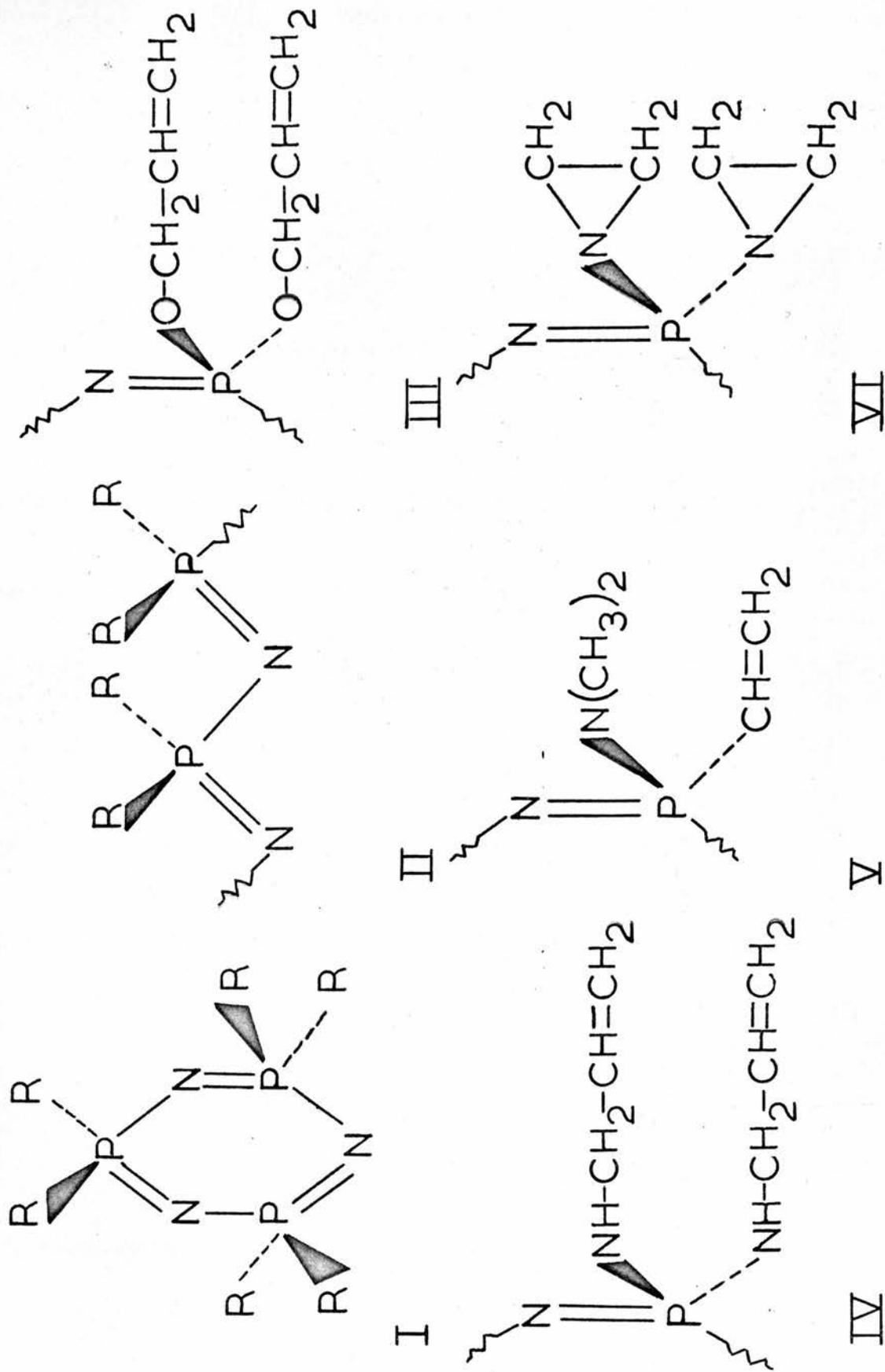
TO MY WIFE

PART ONECHAPTER 1. INTRODUCTIONA. General and Historical.

The phosphazenes have been well known for over a century but it is only within the last ten or fifteen years that research work has been heavily concentrated upon them particularly in the field of high polymeric species and small molecule substitution reactions. There is little doubt that the main reasons for this upsurge of interest were the high thermal stability and useful physical properties of some of the phosphazenes.

The phosphazenes, often known as phosphonitrilics, are inorganic phosphorous-nitrogen polymers formed from the repeat link $\text{-(R}_2\text{P=N)-}$, where R can be various inorganic and organic residues such as halide, pseudohalide, hydroxy, alkoxy, aryloxy, alkyl, aryl, amine or substituted amine, azide or mercapto groups. The polymers can take up two configurations, either rings [see figure 1 (I)] or chains [see figure 1 (II)]. Generally the ring compounds are of low molecular weight where the number of repeat units has been characterised from 3 to 17 for the halide series⁽¹⁾. Conversely the chain compounds are usually of much higher molecular

FIGURE 1. STRUCTURES OF SOME PHOSPHAZENES



weight and may be either linear or crosslinked. Low molecular weight chain compounds are known however and exist as oils.

This part of the thesis will be concerned primarily with long-chain polymers and no attempt, therefore, will be made to review the ring oligomers. Reviews by Audrieth et al.⁽²⁾, Shaw et al.⁽³⁾ and Paddock⁽⁴⁾ all fully cover this subject whilst a more general coverage has been given by Allcock^(5,6) and Gimblett⁽⁷⁾.

However, it is necessary to mention the preparation of hexachloro-cyclotriphosphazene [figure 1 (I) where R = Cl.] since this is the starting point for one of the most commonly used methods of preparing high phosphazenes.

Rose⁽⁸⁾ in 1834 described the reaction between phosphorous pentachloride and ammonia whilst in the same volume, Liebig, with an editorial comment, described a similar reaction performed with Wöhler⁽⁹⁾. The major product of this reaction was phospham together with a low yield of a stable white crystalline solid containing only phosphorous, nitrogen and chlorine. The formula was given incorrectly in both cases and it was left to Gerhardt^(10,11) and Laurent⁽¹²⁾ to establish the empirical formula and to Gladstone and Holmes⁽¹³⁾ and Wichelhaus⁽¹⁴⁾ to deduce the molecular formula. Several workers carried out substitution reactions on the chlorine

atoms though the actual cyclic nature of the trimer was not proposed until the last years of the century when Stokes performed a series of experiments which characterised the cyclic oligomers⁽¹⁵⁻²¹⁾. In 1924, Schenck and Römer modified the original synthesis and used a mixture of phosphorous pentachloride and ammonium chloride in a refluxing inert solvent such as sym.-tetrachloroethane. In so doing they produced a cheap, simple, high-yield synthesis which provided the original impetus for the phosphazene research of recent years. It is interesting to note that a good deal of recent patent literature has been concerned with modifications to the Schenck, Römer preparation⁽²²⁾.

B. Methods of Preparation

This section of the chapter deals with general and specific methods for the preparation of phosphazene polymers.

B1. Thermal Polymerisation of Ring Oligomers.

When hexachlorocyclotriphosphazene is heated in an evacuated, closed system at 250-350°C for some hours it partially polymerises to high molecular weight elastomeric and/or oily materials. This was first noticed by Stokes⁽¹⁸⁾ and has provided the most popular method of preparing the halogen-substituted high polymers. The bromo^(23,24) and fluoro^(25,26) phosphazenes react in a similar

fashion to give rubbery polymers. The isothiocyanato trimer was reported⁽²⁷⁾ to polymerise at about 150°C though it was not known whether the propagation was through the main chain, the side groups or both. Work done in this laboratory provides conclusive evidence for main chain polymerisation⁽²⁸⁾. However, except in very exceptional cases, it is not possible to thermally polymerise ring oligomers of organo-substituted phosphazenes to long-chain polymers.

B2. The Substitution Method

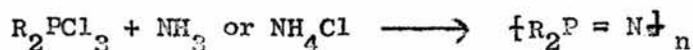
Whilst the long-chain halide polymers show much promise for industrial use, they have one important drawback. This is that the phosphorous-halide bond is hydrolytically unstable. For this reason a great deal of research has gone into attempting to produce a high molecular weight phosphazene where the halogen atoms have been replaced by other groups whose susceptibility to hydrolysis is low. The most favoured method of synthesis is to carry out nucleophilic substitution on the halogen (usually chlorine) atoms attached to the polymer backbone. Early work was performed on the crosslinked elastomer "dissolved" or, more correctly, solubilised in or blended with, the (dry) solvent⁽²⁹⁻³³⁾. The resultant polymers were incompletely substituted and insoluble

with only marginally improved hydrolytic stability⁽³⁴⁾. Recent work by Allcock⁽³⁵⁻³⁷⁾ and Rose⁽³⁸⁾ carried out the reaction on benzene-soluble linear dichlorophosphazene and achieved substantially complete substitution. This type of experiment has also been carried out in the Manchester University laboratories of Professor G. Allen and his associates.

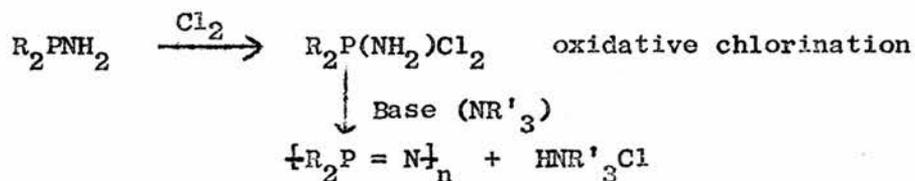
B3. The Substituted Phosphorane Synthesis

This and following methods will most probably be considered to be of general application in time, but for the present, insufficient research on what are certainly difficult chemical systems gives the impression that the methods are each specific for the production of a single polymer or a limited range of polymers.

This method itself is an extension of the classic Schenck and Römer preparation whereby a substituted five-valent phosphorous compound (a phosphorane or phosphonium compound) is heated with ammonia or ammonium chloride in an inert solvent to produce high polymeric and oligomeric species⁽³⁹⁻⁴²⁾.



A similar reaction involving the dehydrohalogenation of an aminodichloro phosphorane, was developed by Tesi and Douglas⁽⁴³⁾ and Tesi et al.⁽⁴⁴⁾

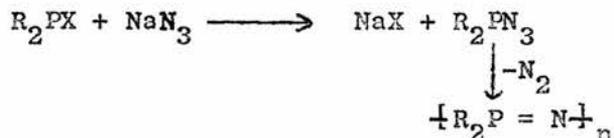


The preparation of $\text{---}(CH_3)_2P = N\text{---}_n$ has been achieved by the pyrolysis of diaminodimethylphosphonium chloride in the presence of ammonium chloride⁽⁴⁵⁾.

These methods tend to produce lower ring oligomers preferentially and in most cases the high polymeric residues have not been fully characterised.

B4. The Azide Method.

This synthesis was first carried out by Herring⁽⁴⁶⁾ who reacted a variety of trivalent phosphorous halides (of general formula PX_3 , RPX_2 , R_2PX ; where X = halide, R = alkyl or aryl) with sodium azide or lithium azide. The reaction appears to be quite general.



A hydrocarbon solvent can be used provided the decomposition temperature of the azidophosphine is below the boiling point of the solvent.

The products, according to Herring⁽⁴⁶⁾ are mainly polymeric. Tesi et al.⁽⁴⁷⁾ isolated the intermediate covalent azide as a yellow oil for the bisperfluoromethyl compound. They warned however of its explosive instability even at liquid nitrogen temperatures.

Using this synthesis, Reichle⁽⁴⁸⁾ prepared the first reported arsazene - the diphenyl tetrameric arsazene $\left[\text{Ph}_2\text{As} = \text{N} \right]_4$. Part of the author's work not reported⁽⁴⁹⁾ in this thesis was an attempted preparation of the dichloroarsazene from arsenous trichloride and sodium azide in various solvents. A presumed covalent azide intermediate was isolated on two occasions. The first was highly stabilised by solvent molecules and would not decompose even at high temperature (200°C). The second, using a different solvent system decomposed explosively at about 80°C. This work is to be continued.

B5. Side Group Linked Polymers

In these cases the high polymers are made up of discrete trimeric or tetrameric phosphazene ring units suitably substituted

and joined through the side groups.

1. Addition Polymerisation through the Side Group. After substitution of vinyl or allyl side groups on the hexachlorocyclo-triphosphazene, polymerisation may be induced through such side groups by treatment with suitable initiators or by heating. Two examples are hexa(allyloxy)cyclotriphosphazene [figure 1 (III)]^(50,51) and the analogous allylamino compound [figure 1 (IV)]⁽⁵²⁾. One vinyl phosphazene has been prepared [figure 1 (V)]⁽⁵³⁾ though no polymerisation data was given.
2. Side Group Rearrangement. The hexa(ethylenimino)cyclotriphosphazene [figure 1 (VI)] when heated, crosslinks through the side groups to give a hard colourless resin⁽⁵⁴⁾.
3. Condensation Polymers. Usually an unsubstituted or partially substituted hexachloro trimer is reacted with a di- or trifunctional linking agent such as a biphenol, often with the addition of some other crosslinking agent such as formaldehyde⁽⁵⁵⁾.

C. Polymerisation and Depolymerisation

C1. Polymerisation.

The reviews by Gimblett⁽⁷⁾ and Allcock⁽⁶⁾ have covered all aspects of polymerisation quite thoroughly. Since about 1950 the

bulk and solution polymerisation of the hexachlorocyclotriphosphazene has been studied extensively, though the results have been far from conclusive. A great deal of the controversy on these problems undoubtedly can be settled when due attention has been paid to methods of sample preparation and to the analysis of results. Gimblett⁽⁷⁾ has surveyed some of the effects of such variables as the type of glass used in the polymerisation vessel, trimer purity, the volume of trimer relative to the volume of the vessel and methods of analysing the extent of polymerisation.

Work by Schmitz-Dumont⁽⁵⁶⁾ involving sealed tube polymerisation at 600°C has led to the suggestion that the thermal bulk polymerisation is a true equilibrium set up between rings and chains. This is supported by the work of Van Wazer⁽⁵⁷⁾ and by Scülen and Silverman⁽⁵⁸⁾ who experimented on the effect of pressure on the polymerisation.

Kinetic studies have been carried out by Gimblett^(59,60) and MacCallum and Werninck⁽⁶¹⁾. The latter deduce that the experimental results could reasonably be fitted to zero, first and second order kinetics for the first 30% of polymerisation though the second order fit is marginally the best. Colclough and Gee⁽⁶²⁾ rigorously purified the chlorotrimer before use and found that there was a definite

catalytic effect of some impurity present. The impurity was not identified.

Solution polymerisation has been reviewed by Allcock⁽⁶⁾. Most of the work was carried out by Patat and co-workers. They used non-hydrogenated solvents to prevent the formation of hydrogen chloride at the elevated temperatures of polymerisation.

The actual mechanism of polymerisation and the effects of catalysts on the polymerisation reaction are closely connected and must be discussed together. The subject has been reviewed by Allcock and Best⁽⁶³⁾ and Allcock⁽⁶⁴⁾. In brief, the mechanisms of polymerisation can follow two main paths:-

1. via free radicals, suggested by Patat and co-workers to explain the catalytic effect of oxygen in solution polymerisation. The mechanism supposes the homolytic fission of the P-N bond, and, because of evidence from Allcock and Best⁽⁶³⁾, Eley and Willis⁽⁶⁵⁾ and Manley⁽⁶⁶⁾, has now fallen into abeyance in favour of an ionic mechanism:-

2. via ions, suggested first by Konecny et al.⁽⁶⁷⁾ to explain the effects of various catalysts. The mechanism usually involves the dissociation of a chloride ion (halide ion) followed either by a propagation step or by a ring scission and then propagation step.

Various catalysts were suggested by Konecny^(67,68) such as benzoic acid, ketones, ethers, alcohols, peroxides and metals such as zinc and sodium. They also noted that certain substances had no marked effect on the rate. One of these, sulphur, has been tested in this laboratory with the result that sulphur was found to be a good catalyst at 250°C and produced an interesting, black, very rubbery polymer⁽⁶⁹⁾. This leads to the possibility of at least some free radical initiation as sulphur is known to exist as an S₈ diradical at these temperatures⁽⁷⁾.

Finally, it has been noted earlier that non-halogeno or non-pseudohalogeno substituted ring oligomers do not in general ring open to produce long chain polymers. This has been discussed at length by Allcock⁽⁶⁾ and explained as partly being due to steric control of the ring-chain equilibrium and partly due to the obvious difficulty of a primary ionisation step.

C2. Degradation.

Very little work has been carried out on thermal degradation studies of the phosphazenes. Patat and Derst⁽⁷⁰⁾ found that the polymer, formed when the trimer was polymerised into quartz sand,

depolymerised by a first order process in an atmosphere of nitrogen. Gimblett⁽⁶⁰⁾ reported that attempted trimer polymerisation at 495°C resulted in a rapid polymerisation followed quickly by depolymerisation. MacCallum and Werninck^(71,71a) using vacuum thermogravimetric techniques confirm first order depolymerisation kinetics. Apart from this work on the dichloropolymer and some thermogravimetric work by Herring et al.⁽⁷²⁾, no systematic degradation studies have been reported to date, though occasionally some very qualitative attempts have been made to assess the thermal stability of individual phosphazenes.

The hydrolytic degradation of the dichloropolymer has been studied in some detail by Gimblett⁽⁷³⁾ carrying out the hydrolysis in 5% aqueous acetone. However the organophosphazenes tend to be much more stable, some withstanding boiling in acid or base for prolonged periods.

D. The Characterisation of the High Polymers.

The molecular weight of the high polymers has been variously reported. Unfortunately, the earlier workers in this field did not

realise that it was possible to produce uncrosslinked linear chloro polymer which was soluble in such solvents as aliphatic and halogenated aliphatic solvents. For this reason, it is only quite recently that solution molecular weight measurements have been attempted. Pornin and Parrod⁽⁷⁴⁾ found the molecular weight by light scattering was of the order 10^6 . Allcock et al.⁽³⁵⁻³⁷⁾ inferred that the molecular weight of the chloro polymer was of the order 7.5×10^5 from measurements performed on the organo substituted soluble polymers. They also made light scattering measurements. Using an expression for the molecular weight derived from the density and the elastic modulus, Specker⁽⁷⁵⁾ and Yokoyama⁽⁷⁶⁾ deduced the molecular weight of the chloroelastomer to be 3.7×10^4 to 7.8×10^4 and 1.75×10^5 to 2.1×10^5 respectively.

The glass-rubber transition temperatures for the polymers are of some interest (see Allcock⁽⁶⁾ and Lewis⁽⁷⁷⁾) and indicate the remarkable flexibility of the chain at low temperatures. The Tg of poly(dichloro)phosphazene is -64°C . Replacement of the chlorine groups by methoxy and ethoxy groups lowers the Tg to -76°C and -84°C respectively. The introduction of three fluorine

atoms into the β -carbon atom of the ethoxy groups raises the Tg from -84°C to -70°C . More bulky groups raise the transition point considerably. Thus the Tg of the diphenoxy polymer is -8°C and the phenylamino polymer 91°C .

X-ray investigations of the dichloro polymer indicate that the rubber is amorphous but that it is easily crystallised by stretching⁽⁷⁸⁾. Meyer et al.⁽⁷⁸⁾ suggested that the chain took up a regular helical structure on extension. However a later study by Giglio et al.⁽⁷⁹⁾ suggested that the conformation was close to a cis-trans planar structure.

There has been very little systematic published infrared work on the substituted polymers. Most of such data produced to date has been taken from the ring oligomers. Allcock⁽⁶⁾ summarises some of the most important peaks whilst papers reporting newly synthesised phosphazenes usually report at least the main frequencies. This subject will be continued in the next chapter.

There has been no published work on the ultraviolet spectra

of the high polymers.

To date the only thermogravimetric work published has been by Herring et al.⁽⁷²⁾ and Patat and Derst⁽⁷⁰⁾. MacCallum, Tanner and Werninck⁽⁸⁰⁾ have also surveyed the thermogravimetric degradation of various high phosphazenes.

CHAPTER 2. EXPERIMENTAL AND RESULTS

Introduction

This chapter will be subdivided into the following sections:-

- A - Methods of Preparation of Linear Polyphosphazenes
- B - Infrared Spectral Analysis
- C - Thermogravimetry
- D - Products of Degradation
- E - Molecular Weight Changes During Degradation.

Each of these five sections will contain a part on experimental procedures and a part on the results.

A. Methods of Preparation of Linear Polyphosphazenes.

In the previous chapter, various methods of preparing high molecular weight phosphazenes were described. The most commonly used method was given as that first introduced by Allcock et al.⁽³⁵⁻³⁷⁾ in 1965-66. This involved the substitution of organic substituents on the previously prepared phosphazene polymer backbone. The

remainder of this section (A) will describe in more detail the preparation, by this method, of those phosphazenes which were used for degradation studies.

A1. Poly(dichloro)phosphazene. $[\text{Cl}_2\text{P=N}]_n$

This polymer was prepared as a sample for degradation studies and as the precursor of other (substituted) polymeric systems.

Experimental. A weighed amount of hexachlorocyclotriphosphazene (from Albright and Wilson, Oldbury, Birmingham,) was resublimed in vacuum into prepared, dry, necked tubes and sealed under a pressure of approximately 10^{-3} torr. It was found by experience, that, for the samples of trimeric dichlorophosphazene used in this laboratory, an optimum yield (approximately 70%) of linear, benzene-soluble poly(dichloro)phosphazene was obtained by heating the samples at 250°C for 24 hours. Higher temperatures and/or longer times resulted in a crosslinked elastomer. Thermogravimetric experiments were performed on both the linear, soluble samples and also the crosslinked, insoluble elastomers. No significant difference was noticed between them.

For the preparation of samples for degradation studies, the

polymerisation was carried out in a flat-bottomed tube. The tube was opened about one centimetre from the flat end and excess, unpolymerised trimer was sublimed out in vacuum. This polymerisation tube was then used as the sample holder on the thermobalance.

A2. Poly(diphenyl)phosphazene. $[\text{Ph}_2\text{P}=\text{N}]_n$

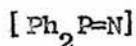
The preparation of this compound was first accomplished in this laboratory⁽⁸¹⁾. Previous attempts to prepare phosphorous-alkyl or phosphorous-aryl bonds in high polymers had led to uncharacterised, partially substituted compounds^(32,77). The method used was to carry out a nucleophilic substitution reaction on linear, benzene-soluble poly(dichloro)phosphazene using a solution of phenyl lithium.

Experimental. A 25g. portion of hexachlorocyclotriphosphazene (m.pt. 112.5 - 114°C) was evacuated in a clean dry tube to a pressure of 10^{-3} torr and sealed off at a constriction. The tube and its contents were then heated at 250°C for 24 hours, when 70% of the original trimer had been converted to polymer. After cooling and opening the tube, excess trimer was removed by vacuum sublimation. Soluble polymer

was dissolved in sodium-dried benzene and the solution carefully decanted from residual, insoluble gel (which comprised about 10% by weight of the original polymeric sample). A solution of phenyl lithium in sodium-dried diethyl ether stored under dry nitrogen was prepared in a twice-molar excess with respect to the replaceable chloride in the benzene solution. The benzene solution was then added drop by drop to the solution of phenyl lithium and thoroughly mixed. After refluxing the reaction mixture for 48 hours, during which time the solution deepened in colour from light buff to dark brown, the solvents were distilled off under reduced pressure and the residue thoroughly washed with water. The soluble portion of the polymer was further purified by precipitation from acetone solution by the addition of water and was then dried in high vacuum at 30°C for several hours. The overall yield of polymer was 22% relative to the starting material.

The infrared spectra was obtained and will be presented in section B of this chapter.

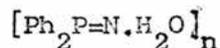
Elemental analysis was as follows:-



Calculated C, 72.36%; H, 5.02%, N, 7.03%; P, 15.59%.

Found C, 66.14%; H, 4.87%; N, 6.00%; P, 13.40%.

It was known that the phenyl polymer was sensitive to moisture and that the water appeared to be strongly enough bound to be removed only by heating in a high vacuum. For this reason it was suspected that the analyses were complicated by the presence of occluded water.



Calculated C, 66.36%; H, 5.53%; N, 6.45%; P, 14.29%

Found C, 66.14%; H, 4.87%; N, 6.03%; P, 13.40%

The above figures are quite close to the actual analysis and appear to be feasible. However, this department has recently obtained its own Perkin Elmer 240 Elemental Analyser and all the analyses were repeated, with substantially the same results. Nevertheless it was noted that, even at 950°C in a stream of oxygen (the pyrolysis conditions in the analyser), there was a residue of between 5% and 10%. This residue resisted further combustion, even when the polymer was mixed with tin to provide a higher pyrolysis temperature. Thus the analysis discrepancy was due to the formation of a refractory residue. A sample of polymer was heated in high vacuum for some hours to drive off all water. The sample was then sealed off, removed from the vacuum and

opened in a dry box. A nujol (sodium-dried nujol) mull was prepared and the infrared spectra showed no water peak. Then the analyser container (weighed) was filled with some of the dry polymer, sealed, reweighed and combusted. The analysis was little different from before but there was still an unanalysable refractory residue. This suggests that the presence of water was not necessary for the formation of the incombustible "ceramic" residue.

The hydrolytic stability of the diphenyl polymer was tested by refluxing for 48 hours finely divided samples of the polymer in 0.1M nitric acid and 0.1M sodium hydroxide solutions. The character of the polymer seemed unchanged after such treatment. Potentiometric titration of the resultant solutions with a silver nitrate standard solution suggested that no chloride was present on the polymer backbone, supporting the proposed complete substitution of the chloro groups by phenyl groups in the phosphazene polymer.

A3. Other Polymers

The following polymers were used for degradation purposes.
poly(diphenoxy)phosphazene, $[(\text{PhO})_2\text{P}=\text{N}]_n$

poly(bisparabiphenyloxy)phosphazene, $[\text{Ph-Ph-O}]_2\text{P=N}]_n$

poly(bistrifluoroethoxy)phosphazene, $[(\text{CF}_3\text{CH}_2\text{O})_2\text{P=N}]_n$

and poly(diisothiocyanato)phosphazene, $[(\text{NCS})_2\text{P=N}]_n$.

The first three were the gift of Professor G. Allen and Mr. S.M. Todd of Manchester University. They were prepared by the substitution method (see A2). The diisothiocyanato polymer was prepared thermally from a sample of hexaisothiocyanatocyclotriphosphazene [prepared by the method suggested by Tesi et al. (27,27a)] from this laboratory. The partially hydrolysed dichloropolymer was prepared by the thermal polymerisation of some partially hydrolysed hexachlorocyclotriphosphazene.

Hexaparabiphenyloxycyclotriphosphazene (m.pt. 205-206°C) was also a gift from the Manchester University group.

Hexaphenoxycyclotriphosphazene (m.pt. 111-112°C) was prepared by the method of Allcock and Best (66) by the author.

A sample of 4-hydroxybiphenyl was a gift from Professor J.I.G. Cadogan and his colleagues (m.pt. 164°C).

These last three compounds were required as authenticated standards in the degradation experiments.

B Infrared Spectral Analysis

There has been very little experimental and theoretical work done on the infrared of the high polymer phosphazenes. The work of Daasch and Smith^(82,83) represents the most important systematic study of the ring oligomers to date, whilst some authors have published limited spectra of new high polymers which they have prepared (see for instance Allcock et al.^(36,37)).

Experimental

1. $[\text{Cl}_2\text{P=N}]_n$ - the polymer was smeared when hot onto a potassium bromide plate. A film was cast from benzene solution onto an aluminium frame for another spectrum.

2. $[\text{Ph}_2\text{P=N}]_n$ - the polymer was intimately ground up with potassium bromide and a disc was prepared using a Wilkes Scientific "Mini-press". (75 mg. KBr: 1 mg. polymer.)

A similar method was used for $[(\text{PhPhO})_2\text{P=N}]_n$ and $[(\text{CF}_3\text{CH}_2\text{O})_2\text{P=N}]_n$. For the latter, because of repeated poor quality of the disc (probably due to the very low glass-rubber transition, T_g , of the polymer.) a nujol mull was also prepared.

3. $[(\text{PhO})_2\text{P=N}]_n$ - was supplied as strips of rubbery material (T_g . -8°C). For this reason spectra were prepared from an

TABLE 1

INFRARED SPECTRA OF SOME PHOSPHAZENES

- $[\text{Cl}_2\text{P=N}]_n$:- 1400-1200 (broad, v.s.); 950 (broad, wk.); 870 (broad, wk.);
740 (broad, m.); 550-610 (broad, s.); 510 (m.); 460 (m.);
360-400 (broad, wk.).
- $[\text{Ph}_2\text{P=N}]_n$:- 3050 (m.); 1584 (m.); 1475 (m.); 1434 (s.); 1200 (broad, v.s.);
1115 (s.); 1024 (m.); 995 (m.); 920 (broad, m.); 740 (s.);
720 (s.); 695 (s.); 540 (broad, v.s.).
- $[(\text{PhO})_2\text{P=N}]_n$:- 2936 (m.); 2363 (wk.); 1533 (s.); 1479 (s.);
Broad group between 1400 and 1100 - peaks centered at 1330 (m.),
1240 (s.), 1187 (v.s.) and 1150 (v.s.); 1069 (s.); 1024 (s.);
1005 (m.); 900 (broad, v.s.); 750 (broad, v.s.); 684 (s.);
620 (m.); 570 doublet (s.).
- $[(\text{Ph-Ph-O})_2\text{P=N}]_n$:- 3035, 3060 (doublet, wk.); 1590 (m.); 1502 (m.);
1474 (s.); 1441 (wk.); Broad group between 1400 and 1130 -
peaks centered at 1320 (m.), 1206 (v.s.) and 1160 (s.);
1100 (wk.); 1070 (wk.); 1035 (wk.); 1017 (m.); 1004 (wk.);
930 (broad multiplet, s.); 835 (s.); 735 (m.); 759 (s.);
715 (m.); 692 (s.); 633 (wk.); 590 (m.); 525 (broad, m.);
485 (broad, m.).
- $[(\text{CF}_3\text{CH}_2\text{O})_2\text{P=N}]_n$:- 2975 (wk.); Broad band between 1420 and 1240 - peaks
centered at 1420 (m.) and 1260 (s.); 1170 (s.); 1030 (s.);
970 (s.); 835 (broad, m.); 850 (m.); 670 (m.); 575 (broad, m.);
520 (m.); 510 (m.).

KEY Intensities:- s. - strong; m. - medium; wk. - weak

Units:- cm^{-1} .

internal reflectance unit having a KRS-5 crystal (A.T.R. unit TR-8, Research and Industrial Instruments Company).

The characteristic peaks in the infrared spectra of the polymers are given in Table 1. Similar methods have been used for the standard compounds and ring oligomers (KBr discs usually). Their spectra have not been tabulated except when certain frequencies have been employed for diagnostic purposes.

C. Thermogravimetry.

As was pointed out in the summary, the bulk of the thermogravimetry is to be found in Part Two of this thesis. This includes all the general experimental techniques, apparatus design and analytical methods and it is not intended to duplicate such work in this section.

Experimental. The modified Stanton Massflow Thermobalance was used and will be described fully in Part Two, Chapter 2.

A vacuum atmosphere of 10^{-5} torr was achieved throughout the apparatus. With the exception of the dichlorophosphazenes, sample sizes of 50 mg. were used. In the former case it was found to be impossible to gauge exactly the extent of polymerisation

FIGURE 2. FRACTIONAL WEIGHT REMAINING vs. TEMPERATURE FOR SOME POLYPHOSPHAZENES

1. $[(NCS)_2P=N]$ 2. $[Ph_2P=N]$ 3. $[Cl_2P=N]$ 4. $[Cl_2P=N]$
(partially hydrolysed)

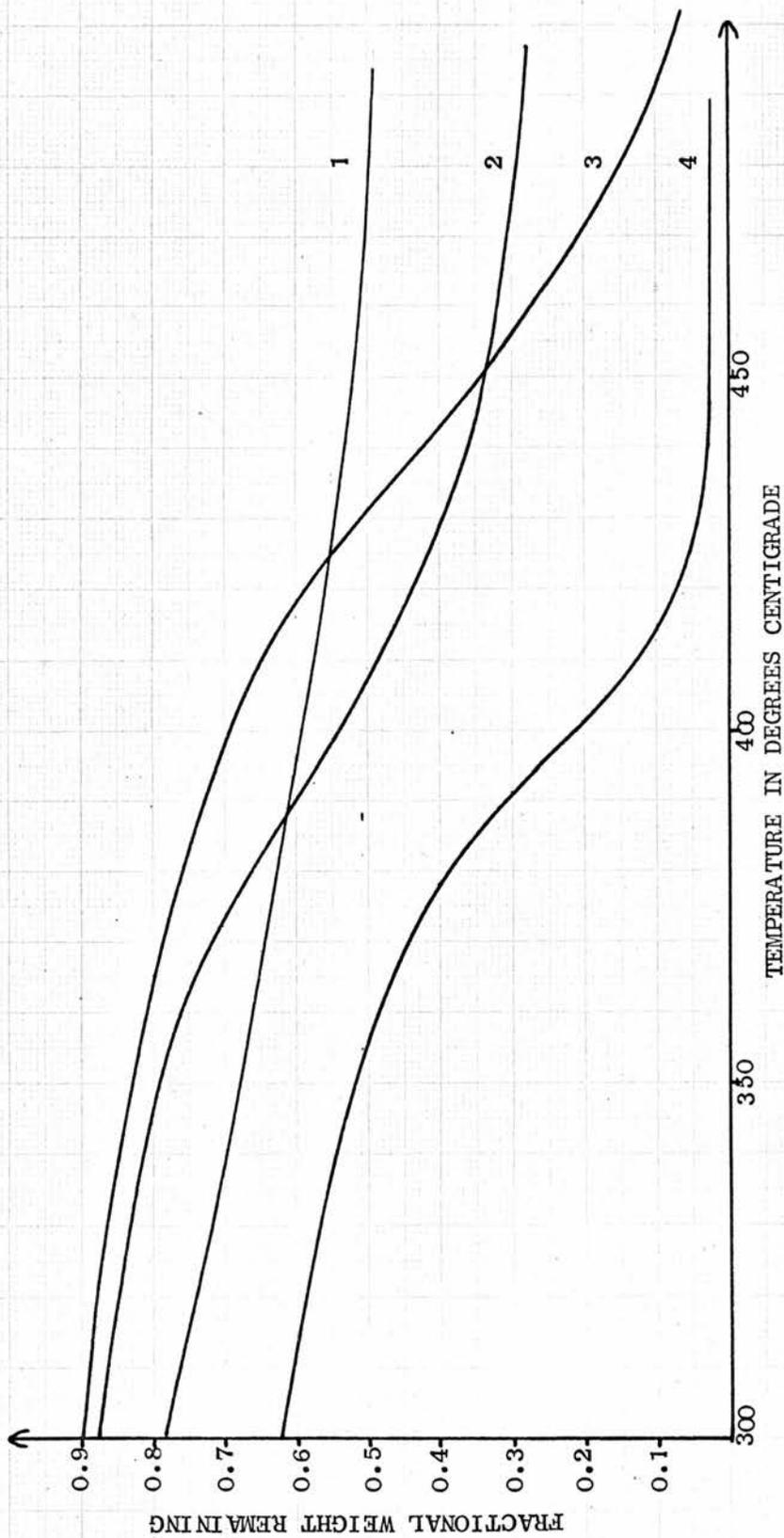
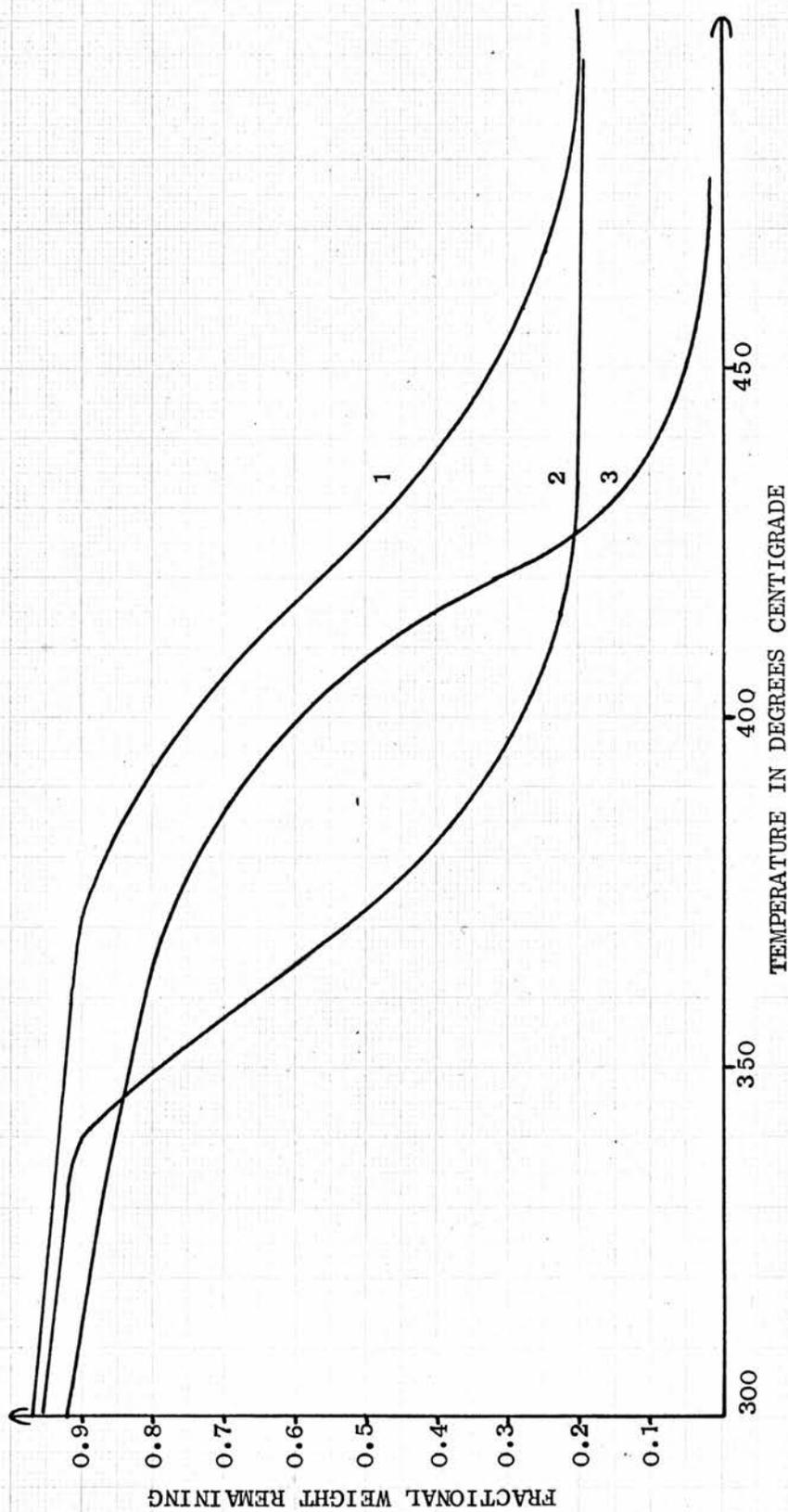


FIGURE 3. FRACTIONAL WEIGHT REMAINING vs. TEMPERATURE FOR SOME POLYPHOSPHAZENES

1. $[(\text{Ph-Pho})_2\text{P=N}]$ 2. $[(\text{Pho})_2\text{P=N}]$ 3. $[(\text{CF}_3\text{CH}_2\text{O})_2\text{P=N}]$



of the trimer, and therefore to gauge the exact amount of polymer itself. However it was found that 25, 50 and 75 mg. samples all gave the same thermogram in vacuo, so that small deviations from the 50 mg. norm introduced no error. The sample holders were made of glass. A programmed heating rate of 3°C/min. was employed for all the thermograms so that comparison could be made between the phosphazene results and the organic polymer results which come in Part Two.

Kinetic Analysis. The method of Fuoss et al. (see Part Two, Chapter 1) was used to deduce an energy of activation for the decomposition of each polymer such that:-

$$E_{\text{max.}} = nRT_{\text{max.}}^2 \cdot \left(\frac{dC}{dT} \right)_{\text{max.}} \cdot \left(\frac{1}{1-C} \right)_{\text{max.}}$$

An order of unity ($n = 1$) was assumed for each polymer degradation, an assumption that is certainly valid for the poly(dichloro)phosphazene sample (71, 71a).

Results. Figures 2 and 3 show the thermograms for each of the phosphazene polymers degraded. With the single exception of $[\text{Ph}_2\text{P=N}]_n$, none of the polymers were taken to temperatures beyond 500°C. The diphenyl polymer was actually, in one series of

experiments, degraded up to 900°C in a nitrogen atmosphere on a DuPont 950 Thermogravimetric Analyser in a platinum boat. At this temperature there was a 20-25% residue as against a 25-30% residue at 500°C in vacuo. At 900°C, the residue reacted with the platinum sample holder.

TABLE 2.

Polymer (Repeat Unit)	Activation Energy kcal mol ⁻¹	Temperature (°C) at which sample reaches fixed percentage decomposition		
		10%	30%	50%
[(Cl) ₂ P=N]	20.0	276	399	431
[(Cl) ₂ P=N] Impure trimer	40.0	-	196	353
[(Ph) ₂ P=N]	12.0	281	372	409
[(Ph-O) ₂ P=N]	15.5	339	359	372
[(Ph-Ph-O) ₂ P=N]	14.0	371	405	423
[(CF ₃ CH ₂ O) ₂ P=N]	53.5	314	387	402
[(NCS) ₂ P=N]	-	262	341	436
Styrene	-	335	394	392

Table 2 shows the activation energies for the degradation of each of the polymers as well as the temperatures of fixed degrees of

conversion ($T_{10\%}$, $T_{30\%}$ and $T_{50\%}$) in degrees centigrade. An anionically prepared sample of head to tail polystyrene is included as a "marker".

D. Products of Degradation.

A survey of the nature of the products of degradation was made by degrading some of the polymeric phosphazenes on a separate vacuum line.

Experimental. Figure 4 is a plan of the vacuum line used. The circled crosses indicate ground-glass taps, all of which were at least 6 mm. in bore.

A. A typical sample carrier and furnace system is shown in the inset (A1). The inner tube was placed in a horizontal position as some of the ring oligomer products of degradation tended simply to reflux if the tube was in a vertical position. In this way the products were able to leave the hot reaction zone and condense on the cold part of the tube. Volatiles moved further on and were condensed by liquid air traps in which they were stored.

The sample was heated by a circular block furnace which was either temperature programmed by a Pye 104 series Temperature

Controller or governed by an Ether Transitrol Indicating Temperature Controller.

B. Mercury manometer, calibrated roughly by a metre rule and provided with a tap.

C. Coned outlet for the gas cell. The gas cell was fitted with potassium bromide windows which were sealed with silicone grease and clamping flanges to hold a vacuum of 10^{-4} torr.

D. Ball-and-socket ground-glass joint to smooth any strain on the line.

E. Three-way tap.

F. Pumping system; rotary oil pump and mercury diffusion pump.

G. Pirani gauge (head).

H, H'. U-tubes for gas storage.

Results.

The product analysis of each polymer will be given in turn. Percentages given are by weight.

$[\text{Cl}_2\text{P=N}]_n$. The products were trimer, tetramer, higher ring oligomers and oily linear analogues^(71a). There was a very low yield (2-5%) of a black/grey porous residue of low chloride content.

$[\text{Ph}_2\text{P=N}]_n$. Volatile products were ammonia (1.5%), water,

benzene and a phosphine. The total volatile part was approximately 7%. The volatiles were identified by their gas spectra with the exception of the phosphine. This was in such low yield that infrared techniques were insensitive. In fact it was only detected by its smell and for this reason it was not known exactly which phosphine it was and its nature must remain speculative. The difference between the volatiles and a black residue (20-30%) was accounted for by unchanged polymer and low molecular weight cyclic and linear homologues. These latter were not positively identified from infrared data since no obvious ring frequencies were available for quantitative analysis. However the infrared spectrum of the products was similar to a spectrum of hexaphenylcyclotriphosphazene sent to us by Dr. D.L. Herring of the United States Navy Laboratories, Corona, California. The black residue had an infrared spectrum which was very diffuse and ill-defined but was a "shadow" of the starting material. When the degradation was repeated in vacuo in an electron spin resonance tube, the resultant resonance signal was consistent with a fairly high concentration of free electrons in the residue. This may have been due to the formation of carbon.

There appeared to be no drop in the signal intensity with time (over one month) again consistent with the behaviour of carbon.

$[(\text{PhO})_2\text{P=N}]_n$. The volatile products in this case were not fully characterised. A yield of phenol (approximately 5% by weight) was definitely collected along with a gas which was not identified. The gas spectrum was unidentified as was its mass spectrum. A black residue was formed (20%) together with ring oligomers and lower molecular weight polymer. Identification of the ring compounds was possible by comparison of the infrared spectrum of $[(\text{PhO})_2\text{P=N}]_3$ with that of the ring products. There was good correspondence.

$[(\text{Ph-Ph-O})_2\text{P=N}]_n$. No gas product was detected. However, at about 200°C a white sublimate (5-6.5%) condensed in the cool part of the tube. This was identified from its infrared spectrum and melting point (164°C) to be 4-hydroxybiphenyl. Comparison was made from an authenticated sample of the compound. Again a black residue was formed (20%) along with ring oligomers and linear polymer. Here infrared evidence was conclusive since it was possible to distinguish a ring frequency (doublet, 880 and 890 cm^{-1}) in the product. The high polymer showed no such ring frequency whilst a sample of $[(\text{Ph-Ph-O})_2\text{P=N}]_3$

showed an intense doublet in this position. The actual product of degradation showed a doublet in the 880-890 cm^{-1} position, but of diminished intensity compared with the trimer. This confirms a mixture of polymer, possibly of lower molecular weight, and ring oligomers.

These degradation products are summarised on Table 3.

TABLE 3

<u>Polymer Repeat Unit</u>	<u>Volatiles</u>	<u>Lower analogues</u>	<u>Residue</u>
$[\text{Cl}_2\text{P=N}]$	-	Trimer, tetramer and linear oils 95-98%	Grey/black residue 2-5%
$[\text{Ph}_2\text{P=N}]$	Ammonia (1.5%) Water, benzene (and a phosphine) Total yield: 7%	63-73% of ring oligomers and lower molecular weight analogues	20-30% of black residue
$[(\text{PhO})_2\text{P=N}]$	Trace unidentified gas, phenol Total yield: 5%	75% ring oligomers etc.	20% black residue
$[(\text{Ph-PhO})_2\text{P=N}]$	4-hydroxybiphenyl Yield: 6%	74% ring oligomers etc.	20% black residue
$[(\text{CF}_3\text{CH}_2\text{O})_2\text{P=N}]$	-	-	2% residue
$[(\text{NCS})_2\text{P=N}]$	-	-	50%

E. Molecular Weight Changes During Degradation

The only polymer studied which would dissolve freely in a solvent was the diphenoxy polymer. It was thus possible to follow the molecular weight changes of this polymer when heated using viscometric techniques.

Experimental. A known weight of polymer was heated at a fixed temperature ($T = 150^{\circ}\text{C}$) in high vacuum (on the vacuum line described in the previous section, figure 4.) Under these conditions the samples lost no weight. A known weight of the sample was then placed in a standard flask (0.1 g. in 50 ml. solvent) and dissolved up in redistilled cyclohexanone (reagent grade). The normal techniques of viscometry were then employed to deduce the specific viscosities ($\eta_{\text{sp.}}$) of the various solutions and finally the intrinsic viscosities $[\eta]$. The intrinsic viscosities were then plotted against the time of heating.

A suspended-level viscometer was used and the usual precautions for solvent purity, viscometer cleanliness and solution accuracy were taken. The viscometer bath was held at 30°C for all readings and the time of flow of the solvent was rechecked for each series of readings taken. The viscometer itself was chosen to give a

FIGURE 5. VISCOSITY MEASUREMENTS OF $[(\text{PhO})_2\text{P}=\text{N}]_n$
 (IN CYCLOHEXANONE AT 30°C)

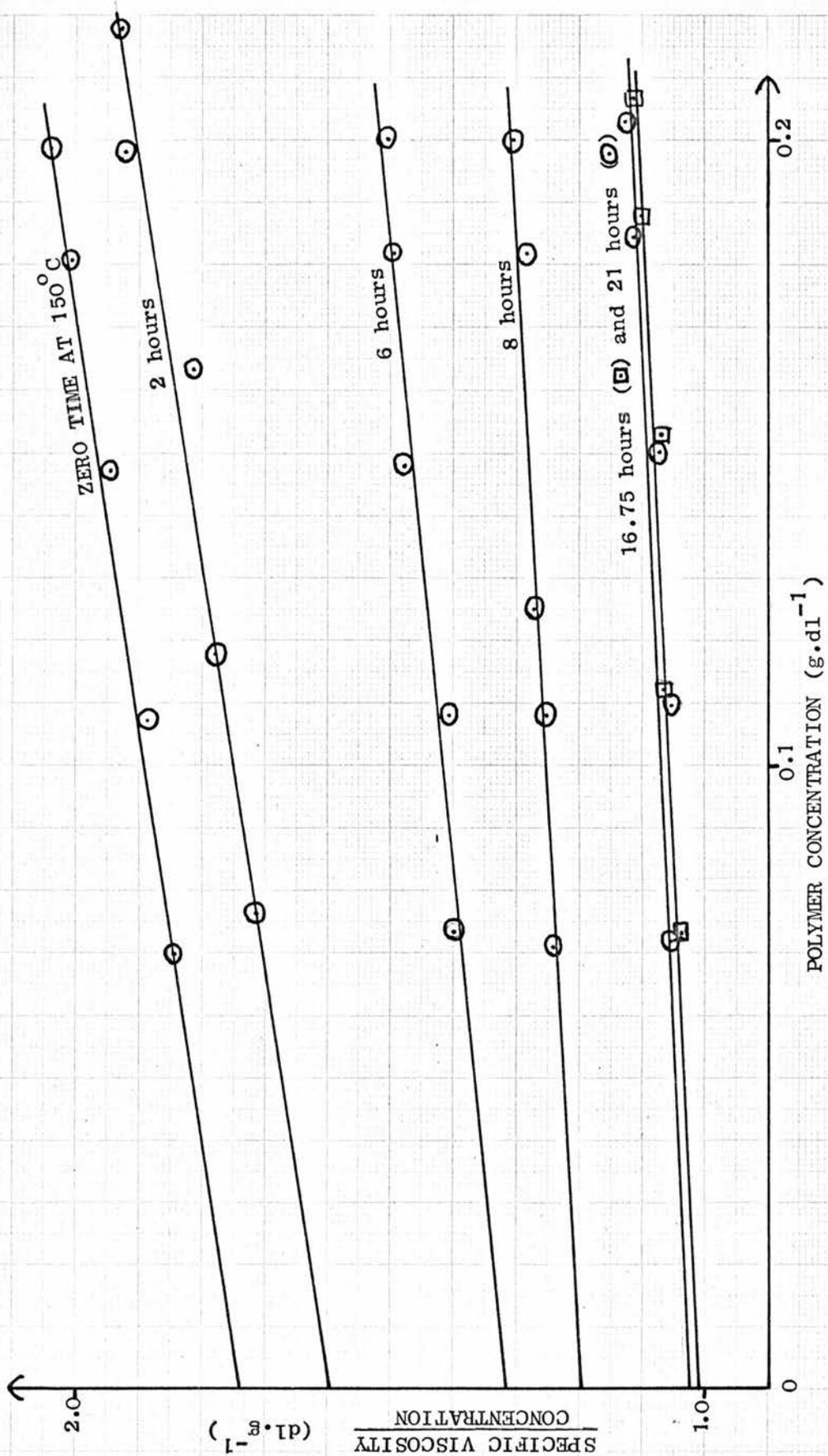
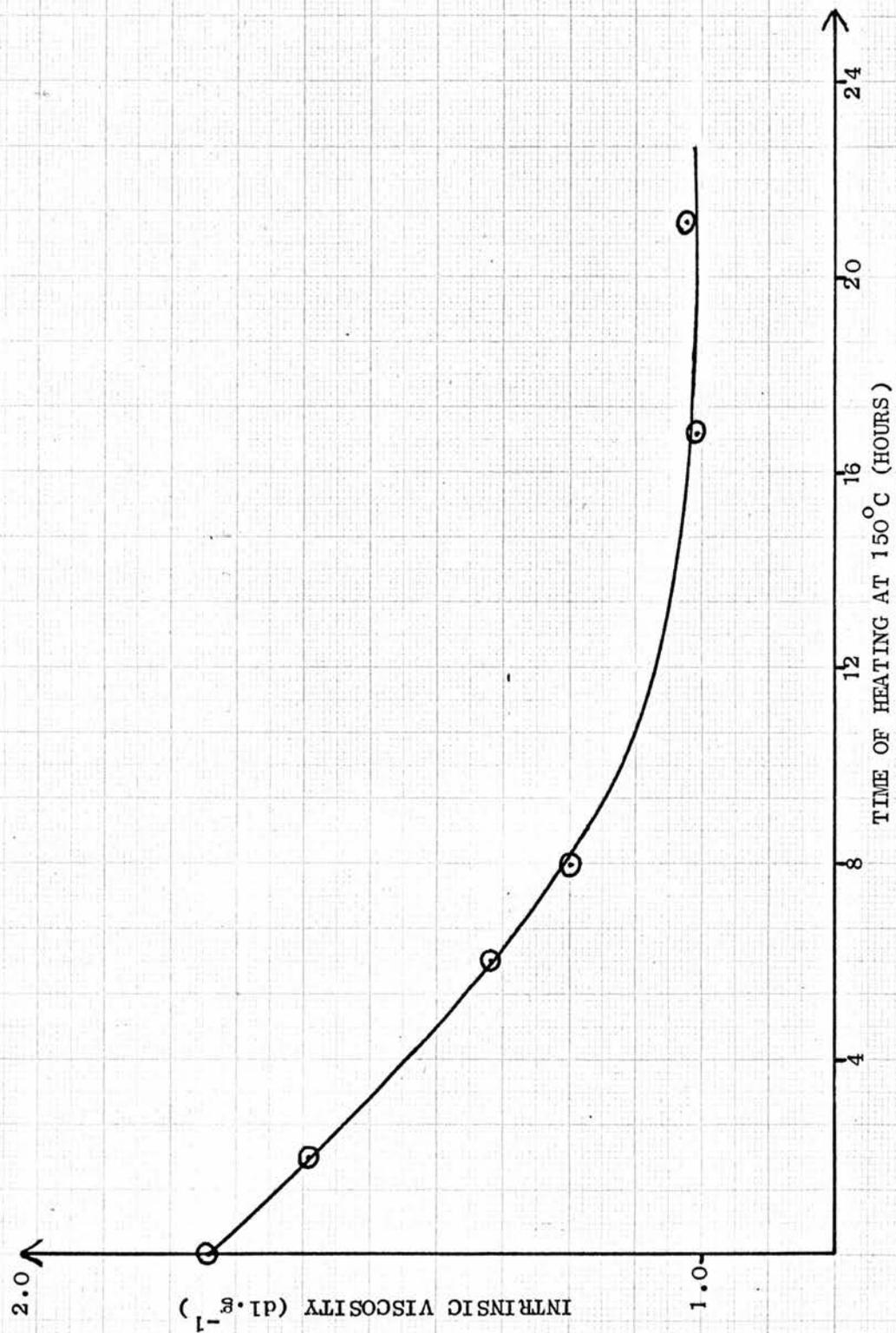


FIGURE 6. VARIATION OF THE INTRINSIC VISCOSITY OF $[(\text{PhO})_2\text{P=N}]_n$
WITH TIME OF HEATING AT 150°C .



reading of about 100-140 seconds flow time.

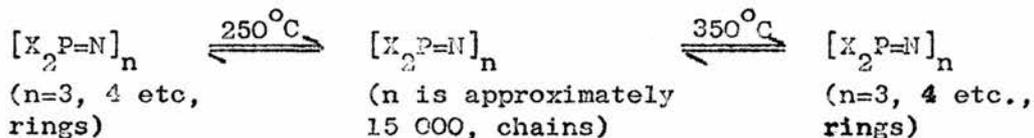
Results. The results have been plotted in figures 5 and 6.

Figure 5. A plot of η_{sp}/C , the reduced viscosity, versus C . C is the concentration in grams per decilitre, and $\eta_{sp} = \frac{t-t_0}{t_0}$, the specific viscosity where t and t_0 are flow times in seconds for solution and solvent respectively. The intercept on the vertical axis is the intrinsic viscosity $[\eta]$.

Figure 6. A plot of $[\eta]$, the intrinsic viscosity versus the time of heating in hours. Temperature of heating (in vacuo) was 150°C .

CHAPTER 3 - DISCUSSION

For the halophosphazenes it has been suggested⁽⁶⁾ that there is an equilibrium set up between rings and chains in the following manner:-



It is possible to describe the reversible reaction moving towards an equilibrium position by considering the free energy difference between the products (chains) and reactants (rings).

It can be shown that,

$$\Delta G = \Delta G_0 + RT \ln \frac{[\text{Products}]}{[\text{Reactants}]}$$

Where ΔG is the free energy change, ΔG_0 is the standard free energy change and where the concentrations of products and reactants should strictly be considered to be activities.

Letting $[\text{Products}]/[\text{Reactants}]$ be Q_a , it follows that at equilibrium where $\Delta G = 0$, Q_a equals K_a where K_a is the equilibrium constant. Thus $\Delta G = RT \ln (Q_a/K_a)$.

Now, provided that the temperature remains constant, K_a is a constant and the reversible reaction will move to give products (chains for polymerisation) where ΔG is negative.

The free energy change itself is linked to the enthalpy and entropy changes of the system by the expression, $\Delta G = \Delta H - T\Delta S$. Furthermore, if the volume change is small on polymerisation, then the enthalpy change may be directly linked to the internal energy change by the expression $\Delta H = \Delta U - p\Delta V$.

[H, enthalpy; S, entropy; U, internal energy; V, volume; p, pressure.]

It is usually considered that the entropy change is small compared with the enthalpy changes at low temperatures, though at higher temperatures the $T\Delta S$ factor can control the direction of the reaction. It is thus reasonable to assume that the lower temperature polymerisation reaction is controlled by internal energy changes (ΔU). These internal energy changes are particularly concerned with side group steric effects. Electronic effects and conjugation changes are usually considered to be of little significance in the case of phosphazene reactions⁽⁶⁴⁾.

The foregoing arguments have solely been concerned with

thermodynamic control of the reaction. However, no account has been taken of the kinetic or, more exactly, the mechanistic possibility of the polymerisation occurring.

For these reasons, the observed inability of the organo substituted ring oligomeric phosphazenes to polymerise can be readily rationalised⁽⁶⁴⁾. The groups tend to be bulky [see figure 1 (I and II where R is a large side group)] and since inter-group steric repulsions in the ring compounds are less than in the linear chains, there is a free energy increase on attempted polymerisation. Thus the extent of polymerisation is small or non-existent. In the case of the halogens [see figure 1 (I and II where R = F, Cl or Br)] there is little steric interaction and polymerisation can in fact occur. Over and above these thermodynamic arguments is the increased possibility of a phosphorous-halogen bond ionising to provide a mechanistic pathway for the reaction.

It was the purpose of this part of the thesis to compare, using thermogravimetry, the effects of various side groups on the "second" part of the reversible reaction - the depolymerisation of linear polymer to ring oligomers. If the preceding arguments are correct it would be expected that depolymerisation would be

favoured at lower temperatures for those polymers with organic (bulky) substituents as against those containing halogen groups.

It is the conclusion of this work, that the temperature-dependent reversible reaction which tends to an equilibrium position can only exist for the organic-substituted phosphazenes at temperatures below (very approximately) 200°C. This may well also be the case for the halogen phosphazenes and is certainly the case for the pseudohalogen phosphazenes.

The evidence for this statement will be given in the following paragraphs.

For the reversible reaction to exist, there must be dynamic side group and main chain bond interconversion. Since the "end-members" of the depolymerisation reaction must be chain polymer to start with and lower molecular weight species (especially rings) to end up with, the production of any compounds which are not phosphazenes of the same substitution pattern would entirely invalidate the notion of an exclusive reversible reaction occurring. This would not of course preclude the possibility of some other reaction being superimposed upon the ring-chain interconversion.

This is undoubtedly the situation with those organically substituted phosphazenes studied. $[\text{Ph}_2\text{P=N}]_n$, $[(\text{PhO})_2\text{P=N}]_n$,

$[(\text{Ph-Ph-O})_2\text{P=N}]_n$ and $[(\text{NCS})_2\text{P=N}]_n$ all produce degradation products other than ring oligomers when pyrolysed in vacuum. The first three give gaseous products and/or volatile species (see Table 3) and all, without exception, produce a black residue which so far has defied attempts at elemental analysis. There can therefore be no doubt that the originally supposed chain-ring interconversion is strongly perturbed by the effects of side reactions. Yet the depolymerisation reaction is not entirely destroyed since rings and presumably lower molecular weight chains are made in yields varying from 50% in the isothiocyanate case to nearly 100% with the trifluoroethoxy and chloro cases.

Nevertheless this is not the whole story. Allcock^(36,64) notes that his samples of $[(\text{PhO})_2\text{P=N}]_n$ and $[(\text{CF}_3\text{CH}_2\text{O})_2\text{P=N}]_n$ underwent intrinsic viscosity changes on being heated at 150°C for eight hours in vacuum, falling to one seventh and one half of their original values respectively. As is shown in figure 6, similar behaviour was observed for the sample of $[(\text{PhO})_2\text{P=N}]_n$ used in this work. This molecular weight change did not appear to coincide with any side group degradation. Figure 6 also shows that the intrinsic viscosity stopped falling after

about 20 hours of heating. This behaviour is consistent with the attainment of an equilibrium position at 150°C between chains and lower molecular weight species.

It therefore seems probable that the overall reaction is a chain-ring reversible interconversion with perturbations caused, at temperatures beyond about 200°C, by side group interaction. These perturbations, which can sometimes involve the main chain atoms as well as the side groups, may be more or less important according to the polymer, the conditions and the mode of degradation.

The nature of the side group reaction is difficult to discuss in general terms since each of the compounds appear to give different types of product. There are however one or two general points to consider.

The two aryloxy phosphazenes pyrolysed to give phenols. It is necessary to ask from where the extra hydrogen atoms came? Unless there was some unknown impurity as a hydrogen donor, the hydrogen atoms must have been extracted from the phenyl rings, thus causing crosslinking or the eventual production of carbon.

In the case of the diphenyl compound, the volatiles benzene and ammonia both require extra hydrogen atoms. It is noteworthy that in all these cases a high proportion of refractory black residue "ceramic" is produced. The partial elemental analysis which was carried out on the residues indicated the presence of carbon, hydrogen, nitrogen and phosphorous. It therefore seems possible that one of the main results of side group interaction is to help the production of the black residue by causing hydrogen abstraction from the aromatic rings. It is perhaps of note that there is only a very small amount of residue from the bistrifluoroethoxy phosphazene. This is perhaps because the β -carbon atoms are sterically the more attainable but contain the chemically less reactive carbon-fluorine bond, thus inhibiting side group interaction. However hydrogen abstraction is not a prerequisite of residue formation since the isothiocyanato phosphazene yields about 50% of a very hard orange/black solid at 500°C. This may well be due to crosslinking between the (NCS) groups.

The actual thermogravimetric analyses must now be considered in terms of relative thermal stabilities. It was the original

purpose in preparing organic linear phosphazenes rather than halogeno phosphazenes, to increase the hydrolytic stability of the polymers. This increase has certainly been achieved, except for the pseudohalogen polymer, but the overall thermal stability has, as predicted, fallen. There are two exceptions to this. The $[(\text{PhO})_2\text{P=H}]_n$ and $[(\text{CF}_3\text{CH}_2\text{O})_2\text{P=H}]_n$ polymers are slightly more stable than the dichloro polymer for the first 15% conversion, whilst the $[(\text{Ph-Ph-O})_2\text{P=N}]$ polymer is more stable for the first 30% conversion and of comparable stability from then on (see figures 2 and 3 and Table 2). It must be pointed out, though, that in all cases molecular weight changes are either known, or may be presumed, to have occurred before actual loss of weight. So in this sense all the polymers are less stable to heat than the dichlorophosphazene.

The high polymer dichlorophosphazene, prepared from trimeric dichlorophosphazene which had been very slightly hydrolysed, was very much less stable thermally than the pure chloro polymer. This underlines the need for the preparation of hydrolytically stable polyphosphazenes, since the introduction of hydroxyl groups does seem to lower the thermal stability.

The activation energy figures quoted in Table 2 are of

dubious worth (see Part Two) and it would be misleading to draw any conclusions from them.

Finally, it may be said that, whilst the organic phosphazenes show improved hydrolytic stability, they are in themselves of diminished thermal stability. However for very specialised uses, the pyrolytic residues may be of some benefit as refractories. The isothiocyanate polymer gives a residue which appears to be very hard, scratching case-hardened steel.

Suggestions for Future Work

(1) It is known that the phosphazenes on stretching can be aligned in a molecular sense⁽⁶⁾ as fibres, even in some cases crystallising. Controlled pyrolysis experiments on such a system would be of interest as the product could well retain some of its regularity and thus have useful properties.

(2) The thermogravimetric experiments could be carried out in different atmospheres. For instance an atmosphere of damp or dry air might well be considered to be more realistic as far as commercial exploitation of the phosphazenes is concerned.

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PART TWOCHAPTER I INTRODUCTION

Throughout the years there have been many attempts to follow the course of thermal reactions by the simultaneous measurement of the temperature of the reaction and such parameters as the colour, weight change, conductivity of the reaction. Some of the commoner methods used are:- Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TGA), Dynamic Electrothermal Analysis (ETA), Thermal Volatilisation Analysis (TVA) and most recently and potentially perhaps the most powerful, Mass Spectrometric Thermal Analysis (MTA). To date, DTA and TGA have been the most used and described in the literature. It is the latter, TGA, which is the subject of the second part of this thesis.

1. Scope of the Introduction.

Thermogravimetric analysis has become, particularly in the sixties, a very large subject in its own right and there have been quite a number of review articles and books devoted to it^(1-6, 47-49, 62). It is not the purpose of this introduction to cover exhaustively the whole field and therefore it will be restricted to those sections which have some bearing on the remainder of the thesis. An attempt will be made to point out the applicability of the technique to the field of

polymer degradation with particular reference to analysis of kinetic data. For this purpose TGA is considered to be a continuously recorded or frequently repeated measurement of the weight change of a sample, be it loss or gain, whilst that sample is subjected to a programmed rise or fall in temperature. The experiment may be carried out either in a controlled atmosphere or in a vacuum.

2. Apparatus

Much of the early work on thermogravimetry was carried out using home-made apparatus of various types. It is now possible to choose from a wide variety of thermobalances which are available commercially.

Perhaps the earliest mention in the literature of a study of the relationship between weight and temperature was as early as 1903 by Nernst⁽⁷⁾, though the first actual thermobalance was made by Honda⁽⁸⁾ in 1915. Between 1947 and 1950, Duval⁽⁹⁻¹⁰⁾ published a series of papers on inorganic filtrates and made the first study of a polymer decomposition by pyrolysing a filter-paper with what was then the only commercially available instrument - the Chevenard Thermobalance⁽¹¹⁾.

The thermobalances currently available may be described under two broad classifications, beam and non-beam balances.

Beam Balances

Beam balances are probably the more accurate for measuring percentage weight change as distinct from absolute weight change. There are various

types of beam balance and each will be discussed separately.

a. Null balance, where a weight is added or subtracted to one side of the beam to regain the null position when the sample weight changes and beam deflection occurs.

b. Restoring force null balance where the null position is regained by use of some restoring force, other than weights, either mechanical or electrical, which is itself proportional to the weight change.

c. Displacement measurement where the displacement of the beam is measured in some way usually optically or by following the change in some property such as capacitance, and then related electronically to the weight change.

Non-beam Balances

Non-beam balances, more accurate for the measurement of absolute weight change, consist of many different sorts, each one needing to be considered separately. Two examples will suffice here.

d. Torsion balances where the sample is suspended from a torsion wire. The measurement of weight change is either carried out using a restoring force method or by measuring the deflection.

e. Spring balances where the sample under examination is suspended from a spring and its weight change is measured directly from the extension or compression of the spring which is usually made of quartz.

There are many other types, strain gauge support, cantilever support,

magnetic support and hydrostatic support for example, but in general the beam balances are to be preferred since they have a linear, reproducible response, have fewer moving parts and rarely require major recalibration. They are also less susceptible to outside influences, a point of some importance where an instrument is to be used in an ordinary laboratory.

Differential thermogravimetric analysis has been carried out⁽¹⁹⁾ where two samples are heated in different furnaces, the temperature of one lagging behind the other by a small amount. The difference signal is plotted against time or temperature and is a measure of the rate of weight loss. Any of the previously described balance systems may be used for this experiment.

Garn⁽¹⁾ has reviewed apparatus and techniques applied to the simultaneous performance of Differential Thermal Analysis (DTA) and TGA. He concludes however that the general utility of the combination may not be worth the expenditure of time, equipment and energy.

It is not the purpose of this introduction to describe each and every thermobalance now manufactured. Gordon and Campbell⁽¹²⁾, Lewin⁽¹³⁾ and Garn⁽¹⁾ amongst others, have written comprehensive reviews of this subject. In the next chapter, the thermobalance used to take the readings for this thesis is described more fully.

3. Standardisation and Errors.

This topic is considered in more detail in the next chapter. Some work has been done on standardisation and error elimination in thermogravimetry and the results of this work go far to explain the discrepancies in thermogravimetric data presentation for a given compound in the literature. Newkirk and Simons⁽¹⁴⁾ have made suggestions for standardisation, as has Doyle⁽⁶³⁾, Newkirk⁽¹⁵⁾, Duval⁽¹⁶⁾, Lukaszewski and Redfern⁽¹⁷⁾, Lukaszewski⁽¹⁸⁾ and Doyle⁽⁶²⁾ have all investigated possible sources of error particularly with controlled atmosphere systems. Little work has been carried out on errors peculiar to vacuum systems.

4. The Uses of Thermogravimetry.

Thermogravimetric techniques have been put to many varied uses.

For example,

a. Polymer stability, the main concern in this laboratory^(21,22) and a subject which has involved a large proportion of the literature. Herring⁽²⁰⁾, Friedman⁽²³⁾, Flynn and Wall⁽²⁴⁾ and Doyle⁽⁶³⁾ have recently been active in America with Coats and Redfern⁽²⁵⁾ and a few others working in this country.

b. Inorganic compound stability. Historically the earliest uses of thermogravimetry were on the degradation of inorganic salts in a controlled atmosphere. Amongst many others Duval^(3,9,10) and Freeman and Carroll⁽²⁶⁾ have been active.

c. The kinetics of thermal degradation. Many attempts have been made in the degradation of polymers and inorganic compounds to abstract from thermograms kinetic parameters which have some absolute meaning. In spite of a great deal of work which has been done on this subject it is only during the last three years that doubt has arisen about some of the methods used and, indeed, upon the whole question of the abstraction of data which has any fundamental significance.

There have been many other uses but the foregoing undoubtedly represent the bulk of the work done using this technique. Further applications will be found in papers by Jen Chiu⁽²⁾, Friedman⁽²³⁾ and Gordon and Campbell⁽¹²⁾ as well as in the technical literature.

5. The Kinetics of Degradation from TGA.

Papers by Flynn and Wall⁽²⁷⁾ and Doyle⁽⁶²⁾ both published in 1966 represent the only comprehensive reviews of thermogravimetric analysis methods to date.

For the sake of clarity the widely varying symbols used in each paper will be standardised in this thesis. They are:-

n - the order of reaction

C - the degree of conversion such that $(1-C) = \frac{W}{W_0}$,
the fractional weight remaining.

E - the energy of activation of the decomposition
reaction (k.cal/mole)

A - the pre-exponential factor in the Arrhenius equation.

ln - \log_e

log - \log_{10}

T - the temperature in degrees Kelvin.

R - the gas constant, 1.937 cal/mole.

Any other symbols used will be defined at the time of introduction.

a. General Theory. It is widely assumed that for a reaction $B \longrightarrow$ Products, the rate of conversion of B to products is given by the equation:- $\frac{dC}{dt} = k \cdot f(C)$ for the isothermal case. In general terms, the rate of conversion $(dC/dt)_T$ is a linear function of a temperature-dependent rate constant (k) and a temperature-independent function of conversion (f(C)). When the temperature is varying linearly with time, such that $\beta = dT/dt$ is the heating rate, we can write:-

$$\frac{dC}{dT} = \frac{k}{\beta} \cdot f(C) \quad \dots [1]$$

The temperature dependence of k, the rate constant is usually assumed from the Arrhenius equation:-

$$k = A \cdot e^{-E/RT} \quad \dots [2]$$

so that equation [1] becomes

$$\frac{dC}{dT} = \frac{A}{\beta} \cdot f(C) \cdot e^{-E/RT} \quad \dots [3]$$

for a programmed temperature rise, or

$$\left(\frac{dC}{dt}\right)_T = A \cdot f(C) \cdot e^{-E/RT} \quad \dots [4]$$

for the isothermal case. Equation [3] upon integration becomes:-

$$F(C) = \int_0^1 \frac{dC}{f(C)} = \frac{A}{\beta} \int_{T_0}^T e^{-E/RT} \cdot dT = G(T) \quad \dots [5]$$

It is upon these five equations that the bulk of the methods of kinetic analysis are based.

The pre-exponential factor A, from the Arrhenius equation is usually considered to be a constant for the temperature ranges considered.

The various methods of handling data from thermogravimetric experiments will be considered under separate headings.

b. Integral Methods. The fundamental difficulty with this method has been the need for various limited-range approximations of the temperature integral, G(T), in equation [5] such that

$$\frac{A}{\beta} \int_{T_0}^T e^{-E/RT} \cdot dT = G(T) = \frac{AE}{\beta R} \left[\frac{-e^x}{x} + \int_{\infty}^x \frac{e^x}{x} \cdot dx \right] = \frac{AE}{\beta R} \cdot p(x)$$

Where p(x) includes the exponential integral and where $x = -E/RT$.

To date, the most commonly used solution for this integral is due to Doyle⁽³⁰⁾, where he has tabulated values for log p(x) for values of -x between 10 and 50, and again by Doyle⁽³¹⁾ to give the

approximation:-

$$\log p(x) \approx -2.315 - 0.457 E/RT \quad \dots [6]$$

where $x > 20$

Equation [6] has been the most used to establish $p(x)$ and only integral kinetic equations using it will be described in detail. Methods proposed by van Krevelen et al.⁽³²⁾, Farmer⁽³³⁾, Coats and Redfern^(25,34), Horowitz and Metzger⁽³⁵⁾, Turner and Schnitzer⁽³⁶⁾ and Haber⁽³⁷⁾ have entailed the use of different approximations of $p(x)$ all of which, with the exception of Coats and Redfern⁽²⁵⁾ are less accurate than Doyle^(30,31). (See Flynn and Wall⁽²⁷⁾ on Integral methods). Cameron and Fortune⁽³²⁾ have reviewed these methods and conclude that the method of Coats and Redfern⁽²⁵⁾ is the best when allied to the Horowitz and Metzger⁽³⁵⁾ method. However the method of Doyle⁽³⁰⁾ is not questioned in Cameron's article⁽³⁸⁾ though recent work by Zsakó⁽³⁹⁾ has refined Doyle's technique a little.

All the expressions described so far have come up against the problem of predetermination of n , the order of reaction. Coats and Redfern⁽⁴⁰⁾ and Flynn and Wall⁽⁴⁴⁾ have attempted to minimise this by using low conversion data ($C = 0.3$ or less). Reich and Levi⁽⁴¹⁾ have proposed a graphical method of estimating the order, whilst Reich⁽⁴²⁾ has obviated the use of n , the order, by using a simultaneous DTA and TGA trace or by assuming it to be unity ($n=1$)⁽⁴³⁾.

Undoubtedly the best method proposed, is that one due to Osawa⁽⁴⁵⁾

who uses Doyle's value of $\log p(x)^{(31)}$ to derive the equation:-

$$\log F(C) \stackrel{A}{=} \log \frac{AE}{R} - \log \beta - 2.313 - 0.457 \frac{E}{RT} \quad \dots [7]$$

Then, assuming $F(C)$ to be constant for a given degree of conversion (C), a plot of $\log \beta$ against $1/T$ will have a slope of $-0.457 E/R$. Some months later, Flynn and Wall⁽⁴⁶⁾ deduced equation [7] and, in the same way, used it to find the activation energy, E. They go further in that they suggest a technique of successive approximations to find E using Doyle's tables⁽³⁰⁾ to modify the first and subsequent values for E obtained. Osawa⁽⁴⁵⁾ also mentions a way of finding the pre-exponential factor, A, graphically by setting up theoretical master curves of (1-C) against $\log \left[\frac{AE}{\beta R} \cdot p(x) \right]$ and then comparing these curves with the experimental curves of (1-C) against $\log \left[\frac{E}{\beta R} \cdot p(x) \right]$. The lateral shift required to superimpose these curves will be $\log A$. The disadvantage is the use of a mean value for E in the theoretical curve as well as an assumption of the form that $f(C)$ will take together with the order of the reaction.

c. Differential Methods. These methods are based on a rate of weight loss versus temperature, (or inverse temperature) plot. The best of them are as good as the best integral methods but most suffer from the difficulty of abstracting accurate rates from thermograms with a consequent magnification of experimental scatter, as well as

the necessity for finding n , the order of reaction.

Van Krevelen et al.⁽³²⁾, Turner and Schnitzer⁽³⁶⁾ suggested differential methods whilst Kaesche-Krische and Heinrick⁽⁵⁰⁾ utilised the van Krevelen equations at various heating rates. In all these cases, the order of the reaction was assumed.

Starting from equation [4], Murray and White⁽⁵¹⁾ for the first order case and Kissinger⁽⁵²⁾ for the n th order case derived the following equation:-

$$\frac{E \cdot \beta}{RT_{\max}^2} = A \cdot n(1-C)_{\max}^{n-1} \cdot e^{-E/RT_{\max}} \quad \dots [3]$$

Kissinger⁽⁵²⁾, assuming $n(1-C)_{\max}^{n-1}$ to be almost invariant with heating rate and to be approximately equal to unity, took logarithms and differentiated equation [3] to obtain:-

$$\frac{d \ln(\beta/T_{\max}^2)}{d(1/T_{\max})} = - \frac{E}{R} \quad \dots [9]$$

a result he had earlier derived by another route⁽⁵³⁾.

Fuoss et al.⁽⁵⁴⁾, assuming first order kinetics derive the equation:-

$$E = -RT_{\max}^2 \cdot \left(\frac{dC}{dT} \right)_{\max} \cdot \frac{1}{(1-C)_{\max}} \quad \dots [10]$$

Where $(1-C)_{\max}$ is the fractional weight remaining at the

temperature (T_{\max}) of the maximum rate of weight loss. These authors attempt to extend this to the nth order case but make a mistake and succeed only in deriving the same equation [10]. The equation for the nth order case should be:-

$$E = -nRT_{\max}^2 \left(\frac{dC}{dT} \right)_{\max} \cdot \frac{1}{(1-C)_{\max}} \dots [11]$$

This method only relying on one set of data, has the disadvantages that the E value is only found for the conversion at which maximum rate of weight change occurs and that the order must be known or assumed.

One of the simplest differential methods is the use of the logarithm of the Arrhenius equation:-

$$\begin{aligned} \ln k &= \ln \left[\frac{\beta \cdot (dC/dT)}{(1-C)^n} \right] = \ln \beta \left[\frac{d \ln(1-C)}{dT} - (n-1) \ln(1-C) \right] \\ &= \ln A - \frac{E}{RT} \dots [12] \end{aligned}$$

When β is a constant equation [12] becomes:-

$$\ln \left[\frac{dC/dT}{(1-C)^n} \right] = \ln \left[\frac{A}{\beta} \right] - \frac{E}{RT} \dots [13]$$

Kofstand⁽⁵⁵⁾, Newkirk⁽¹⁵⁾, Barrer⁽⁵⁶⁾, Magnuson⁽⁵⁷⁾, whose paper also deals with the practical aspect of taking data from thermograms, and Coats and Redfern⁽³⁴⁾ have all used this method usually assuming first order kinetics.

The most useful differential method is that of Friedman⁽⁵³⁾ who derived the equation:-

$$\ln\left(\frac{dC}{dt}\right) = \ln A \cdot f(C) - E/RT \quad \dots [14]$$

so that values of $\ln(\text{rate})_c$ are plotted against $(1/T)_c$ at a fixed conversion for various heating rates. This has the virtue of finding E values for various values of conversion (compare with Osawa, equation [7]) and not assuming the order of the reaction.

Chatterjee⁽⁵⁹⁾ suggested that the order of the reaction might be expressed by the equation:-

$$n = \frac{\Delta \log dw/dt}{\Delta \log w}, \text{ where } w = \text{weight remaining}$$

This method supposes the use of two or more different initial weights. However the author assumes the pre-exponential factor A is invariant with the initial weight in his derivation which is not so. The fallacy in this method has recently been pointed out by Broido⁽²³⁾

d. Difference-Differential Methods. Freeman and Carrol⁽²⁶⁾ have described what is perhaps the most commonly used equation for the analysis of thermogravimetric data especially amongst those workers dealing with inorganic decomposition reactions.

They derive the relationship:-

$$-\frac{E}{R} \cdot \frac{\Delta(1/T)}{\Delta \ln(1-C)} = -n + \frac{\Delta \ln(dC/dt)}{\Delta \ln(1-C)} \quad \dots [15]$$

Anderson and Freeman^(60,61) have modified equation [15] slightly. Flynn and Wall⁽²⁷⁾, using a theoretical plot for a given value of E, have plotted $\frac{\Delta \ln(dC/dt)}{\Delta \ln(1-C)}$ versus $\frac{\Delta(1-T)}{\Delta \ln(1-C)}$ and have recalculated the E values from the graph so obtained. However they find that the graph, instead of being a straight line, is a curve and gives three areas, corresponding to three ranges of conversion, where the slope is, approximately, a constant. Only at low conversion does the calculated value of E approach the theoretical value. MacCallum and Tanner⁽²⁹⁾ have published a modification to the Freeman and Carrol equation.

d. Isothermal Methods. Historically these were the earliest methods used to derive kinetic data for degradation studies. Jellinek⁽⁶⁴⁾ and later Madorsky⁽⁶⁵⁾ both used isothermal thermogravimetry to study polymer pyrolysis with spring balances and may be regarded as the pioneers of this technique.

Taking logarithms of equation [4] gives:-

$$\ln(dC/dt) = \ln A + \ln f(C) - E/RT \quad \dots [16]$$

Thus at constant conversion, a plot of $\ln(dC/dt)$ against $1/T$ gives a straight line of slope $-E/R$.

Then assuming $f(C) = (1-C)^n$, equation [16] becomes:-

$$\ln(dC/dt) = \ln A - E/RT + n[\ln(1-C)]. \quad \dots [17]$$

Thus at constant temperature, a plot of $\ln(dC/dt)$ against $\ln(1-C)$

will have a slope of n , the order of the reaction. Furthermore when $(1-C)$ tends to unity, the intercept on the $\ln(dC/dt)$ axis will give the natural logarithms of the initial rates for each isotherm. A plot of these intercepts against $1/T$ will give a slope of $-E_0/R$ where E_0 is the initial activation energy.

CHAPTER 2 EXPERIMENTAL METHODS

This chapter is divided into four parts, the first three of which bear considerably upon one another. They are:-

1. Errors and Standardisation in Thermogravimetry
2. The Apparatus - the Stanton Massflow Balance.
3. Modifications to the Balance.
4. The Polymers Investigated.

1. Errors and Standardisation in Thermogravimetry

Newkirk⁽¹⁵⁾, Duval⁽¹⁶⁾, Lukaszewski and Redfern⁽¹⁷⁾, Lukaszewski⁽¹⁸⁾ and Doyle⁽⁶²⁾ have all investigated possible sources of error particularly with controlled atmosphere systems.

The various types of errors which can occur will be described in detail.

A. Errors Concerned with Weighing

A1. Explosive Loss of Sample. This is a common occurrence with thermobalances and can be very serious in terms of percentage weight loss. Effects vary from a less serious sputtering, through decrepitation to a virtually explosive reaction which can eject all sample from the weighing area.

This last effect has been experienced in these laboratories with the thermogram of sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4 \cdot \text{H}_2\text{O}$) in vacuum. However there is no explosion with this sample heated in one atmosphere of nitrogen⁽⁶⁶⁾. In general the effect, when not too violent, can be overcome by using a small sample and a container which is conical in section, wider at base than top. Container covers and covering layers of inert powder have also been used⁽⁶⁷⁾.

A2. Chemical Attack of sample, or sample degradation product, on the container can have an important effect, particularly in the formation of a spurious residue. This author, in early work performed for him on a DuPont Thermobalance in a nitrogen atmosphere, has found, for example, that poly(diphenylphosphazene) or one of its degradation products attacks platinum holders at about 900°C . Perhaps the best way to overcome such effects is to remove products as swiftly as possible using a vacuum system or to choose a sample holder impervious to attack.

A3. Buoyancy and Aerodynamic Effects. These are much more serious in controlled atmosphere systems. As a source of error they can vary greatly in magnitude of effect^(1,5,15,18,62) and

a great deal of work has been carried out in an attempt to minimise them. Many factors affect these errors such as turbulence at high temperatures, drag characteristics of gas flow, furnace pulsing effects and so on, but for this study these errors were overcome by the use of a vacuum system. A double furnace system with a blank in one furnace and the sample in another would also have gone far to minimise these errors.

A4. Mechanical and Electronic Effects. Such effects are largely a matter of bad design in the thermobalance under consideration and also bad maintenance. These errors were minimised in the present work by frequent cleaning of the weighing system and regular recalibration of the weight recording output. The vacuum system was frequently cleaned and an efficient liquid air trapping system was incorporated between the rotary pump and the oil diffusion pump to help the removal of undesirable vapours.

A5. Geometry of Sample Holder and Sample Size. Once again these effects are more important in controlled atmosphere systems. This author performed experiments under rigidly controlled conditions on three weights of sample (25 mg, 50 mg. and 75mg). There was no difference in the thermograms and so, for all

further runs a 50 mg sample was used. The shape of the sample holder used was slightly conical (see A1. to reduce loss by sputtering) but other shapes did not show any significant differences. (This is in contradiction to other workers' results from controlled atmosphere systems⁽⁶⁸⁾). The sample holder used was made of glass and was baked in a vacuum at 500°C for two hours before use.

A6. Condensation of Volatiles on the Weighing System. This can be the most serious sort of error for all types of thermogravimetry. The magnitude of the error will greatly depend on the type of sample used and the geometry of the heating and weighing system. Degradation products which are volatile at room temperature will not condense but some polymers which degrade to yield large molecular weight fractions, volatile at high temperature but involatile at ambient temperature, can easily cause condensation anywhere on the balance system. Soulen and Mockrin⁽⁶⁹⁾ have attempted to minimise this by enclosing the sample holder support (the rise-arm) in a metal sleeve. However this effect was not found to be significant in this work perhaps because of the use of a high vacuum (10^{-5} torr) As a further precaution a water jacket was placed around the

mullite tube between the furnace and the weight compartment to condense out any involatiles on to the side of the mullite.

B. Errors Concerned with Temperature.

B1. Due to the Atmosphere. As has been noted elsewhere turbulence due to high temperature and excessive or variable gas flow not only affects the balance mechanism but also the temperature read-out. Once again this was largely overcome by use of a vacuum.

B2. Due to Rate of Heating and the Thermocouple Position.

Doyle⁽⁶²⁾ notes that in modern thermobalances it is not usual to have the thermocouple within the sample and that the fact of this isolation from the seat of degradation causes difficulty in accurate temperature measurement. This effect was minimised on our Stanton thermobalance by placing a more accurate thermocouple just above the sample surface. Previous work in this laboratory⁽⁷⁰⁾ indicates that such a temperature read-out shows little measurable difference from that of a thermocouple placed in the sample holder in a dummy run. This does not take into account the heat of reaction. This could have caused temperature inconsistencies but was not thought to

be a significant factor for such a small sample (within the accuracy of the experiment).

Heating rate affects decomposition temperatures considerably. (The higher the heating rate, the higher the decomposition temperature for a given conversion). A rate of heating of $3^{\circ}\text{C}/\text{min}$. was taken as standard for comparative runs. This was found to be a suitable rate for convenient study of the compounds used in this thesis. Higher rates ($5^{\circ}\text{C}/\text{min}$ and above) were considered to be of dubious linearity and to cause too great a rate of weight loss for accurate measurement. For kinetic studies rates of between $1^{\circ}\text{C}/\text{min}$ and $4^{\circ}\text{C}/\text{min}$ were used. Accurate heating rates were calculated graphically.

B3. Due to Thermocouple Performance. Together with what has already been said about the positioning of the thermocouples must be added the fact that certain thermobalances are wide range instruments, supplied with thermocouples which read up to a high temperature (often beyond 1000°C .) The Stanton balance is no exception to this and uses a platinum/platinum - 13% rhodium couple where, from $0-500^{\circ}\text{C}$, the output is 4.2 millivolts. Over the same range the chromel/alumel thermocouple has an output of 20.7 millivolts. (See balance description.) This latter thermocouple was used to give more accurate temperature readings.

C. Errors Concerned with Timing

These are self-evident and were easily overcome.

- C1. Heating Rate. Accurate measurements of the rate were measured graphically. A check on the linearity was kept in this way.
- C2. Timing Marks. Every five minutes the Stanton balance shows a timing mark when the balance mechanism is momentarily set at rest off the beam knife-edges. This period was checked regularly.
- C3. Chart Speed. This was checked regularly.

D. Standardisation of Approach

One of the distinguishing features of thermogravimetric measurements in the past has been a certain lack of standardisation of approach both in experimental techniques and in methods of analysis. Only Newkirk and Simons⁽¹⁴⁾ and Doyle⁽⁸²⁾ have suggested methods of standardisation. The former workers⁽¹⁴⁾ suggest that the following pieces of information should accompany every thermogram.

1. Identification of the thermogram by the name and formula of the substance together with its source.
2. Sample weight.
3. Furnace heating rate.
4. Atmosphere and pressure (and gas flow).
5. Size, shape and material of sample container.
6. Methods used to identify intermediates and final products.
7. Identification of thermobalance and location of thermocouple.
8. Identification of temperature/time coordinate.

Doyle⁽⁶²⁾ draws attention to the need to standardise such parameters as sample size, preparation, type of sample holder and notes that the microstructure of the polymer may have effect on depolymerisation. He also makes the point that some of the physical factors are nullified by the fact that a polymer often softens before degradation and flows to assume the shape of the holder. The results quoted in this thesis have been standardised, though some of the chemical reactions in the polymer degradations have not as yet been fully studied.

2. The Apparatus - The Stanton Massflow Balance

The standard apparatus is a Stanton Massflow Thermobalance purchased from Stanton Instruments Ltd., Copper Mill Lane, London S.W.17. Model number MF-L5. The balance has the following specifications.

Sensitivity - 0.2 mg. per smallest chart division.

Chart range - 20 mg. full scale.

Maximum loading - 200 mg.

Maximum rate of weight change - 20 mg. per minute.

Capacity - 20 g.

Maximum temperature - 1000°C.

The vacuum equipment consists of a 5" water-cooled baffle valve N.G.N. three-stage oil diffusion pump backed by single stage air balasted N.G.N. rotary pump. There are electromagnetic air/gas admittance valves connected to a "no-volt" drop-out relay. There are also two pressure gauges, a thermocouple gauge for high pressures ($3.0 - 10^{-2}$ torr.) and a Penning ionisation gauge for lower pressures ($10^{-2} - 10^{-5}$ or 10^{-6} torr.).

The two figures (Figures 1 and 2) are described in the following sequence.

The areas in the figures enclosed by heavy black shading and crosshatched shading (Figure 1 only) are capable of being

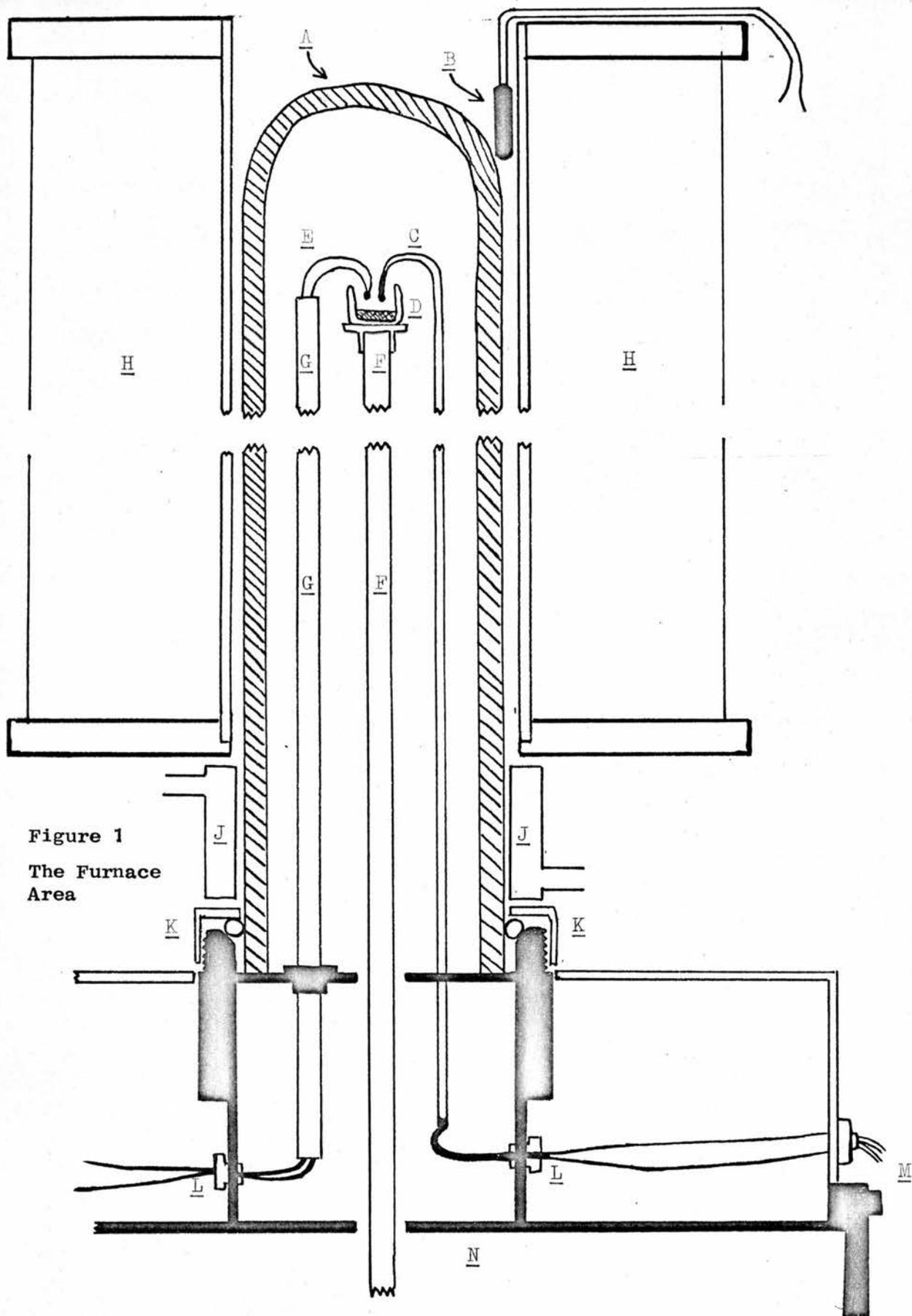


Figure 1
The Furnace
Area

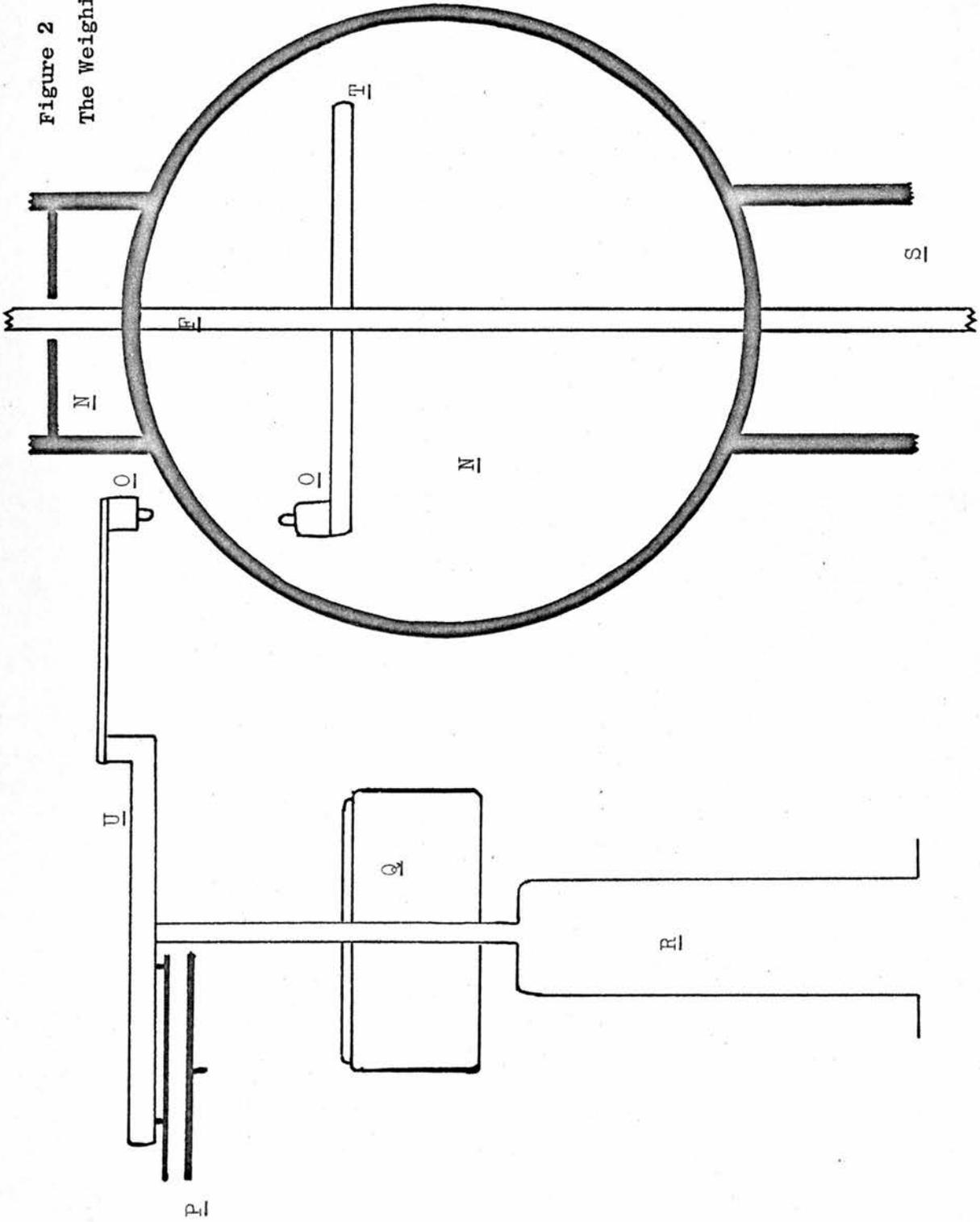
evacuated to a pressure of better than 10^{-5} torr. The figures show the standard apparatus with some of the modifications described in the next section (3).

Figure 1. Furnace and Thermocouple Assembly

This is a frontal view of the balance. The discontinuity near the centre of the diagram is to indicate foreshortening of the vertical scale.

- A. Mullite tube ("mullite" is a refractory material capable of withstanding high temperature under vacuum),
- B. platinum resistance thermometer - sensor for the Pye programmer,
- C. self-supporting platinum/platinum - 13% rhodium thermocouple,
- D. glass sample holder (with sample shaded in),
- E. chromel/alumel thermocouple,
- F. rise-arm supporting the sample and supported by the balance,
- G. twin-bore silica tube, insulating support for the chromel/alumel thermocouple,
- H. bifilar nichrome-wound furnace,
- J. water-jacket,

Figure 2
The Weighing Area



- K. vacuum seal assembly for mullite tube ("o"-ring shown),
- L. vacuum glands leading thermocouple wires from the vacuum to atmospheric pressure,
- M. Side-port bolt.

Figure 2 . Weight Change System.

This figure is a side view of the balance and is schematic only, not a detailed representation.

- N. Vacuum compartment (containing balance equipment),
- O. (two) pole-opposed magnet(s),
- P. variable capacitor connected to an R.F. bridge circuit; the bottom plate is connected to a servo-motor (not shown),
- Q. mechanical air damper,
- R. support columns,
- S. to vacuum pump equipment,
- T. inner beam,
- U. outer beam.

Since the Stanton temperature recording equipment is no longer used (see Chapter 2(1)B3.) only a description of the

balance system will be given here.

The balance is a beam-displacement type where the beam operates on a constant load mode.

The rise-arm [F] is carried on the stirrup above the knife-edge (not shown, synthetic sapphire corundum faceted) of the inner beam [T]. As the beam operates on a constant load mode, ring weights (20 mg. each) are added after every 20 mg. loss of weight (or one complete traverse of the chart scale). The end of the inner beam [T] carries a small magnet [O] which is in opposition to another magnet [O] of the same polarity on the outer beam [U]. The main vacuum chamber (heavy black line) comes between the two magnets but is made of copper and does not affect their operation. The beams are poised (not shown) to keep the magnetic link in compression.

The outer beam [U] carries one plate of a variable condenser [P] the other plate of which is connected via a rod to a servo-motor (neither are shown). The electronic chassis (not shown) carries an R.F. bridge circuit which is balanced when the capacitance between the two plates is equal to a pre-selected value. When there is a weight change the bridge circuit goes out of balance (through the magnetic link sequence),

energizes the servomotor which in turn restores capacitative balance through the rod and the lower capacitor plate [P]. Simultaneously the motor moves the recorder pen across the chart. When correct calibration is made the full scale movement is 20 mg. A micro-switch is attached to the rod and on full scale deflection, when the pen reaches the edge of the chart, another motor system is switched on which places a 20 mg. weight on the inner beam [T]. The cycle is then repeated.

3. Modifications to the Balance

Errors and possible modifications have been pointed out in the first part of this chapter. The modifications carried out on the balance were all performed in these laboratories. They will be described in two sections, weight and temperature modifications. As in the previous part reference will be made to the appropriate area of figures 1 and 2.

A. Weight Modifications.

A slightly conical glass container [D], baked out in vacuum, was used. The base of the container was ground down to a rough,

flat surface to provide frictional contact with the head of the balance rise-arm.

A brass water-jacket [J] was constructed to aid condensation of involatile degradation products on the inside of the mullite tube rather than on the balance rise arm or the weight system where it would be recorded as a weight gain.

Great care was taken to ensure that the ring weights were clean and hanging freely above the inner beam [T].

B. Temperature Modifications.

For the most useful methods of kinetic analysis (see Introduction) a variable rate of heating is required. However the standard Stanton thermobalance was not provided with a variable linear programmer. Indeed at the time of purchase of the balance, though not at present, the manufacturers were not able to provide a satisfactory means of varying heating rate. The balance was therefore modified to dispense with the Stanton heating system (which heated at a rate of about $5.5^{\circ}\text{C}/\text{min.}$) but to retain the platinum thermocouple read-out on to the chart as a guide for the more accurate thermocouple (described later). A variable heating rate was then supplied to the furnace by a Pye programmer-controller of the type fitted to the Pye gas chromatographs (series 104). This provided accurate

heating rates of nominal value 1.0, 1.5, 2.0, 3.0 and 4.0°C/min. (as well as higher but less accurate ones). The sensor for this device was a platinum resistance thermometer giving a range of 0-500°C. The controller could also provide isothermal conditions with control of $\pm 1^\circ\text{C}$.

The original platinum/platinum - 13% rhodium thermocouple supplied with the instrument [C] remained in use although accurate temperature readings were taken from the new chromel/alumel thermocouple [E]. This last was supported near the sample by a twin-bore silica tube [G] which also provided the necessary electrical insulation for the two wires. The wires were taken out of the vacuum chamber through a vacuum gland packed with "Araldite". This thermocouple, set against an ice-water cold junction at 0°C, was monitored by a Pye Universal Decade potentiometer and a solid-state battery galvanometer. This apparatus was able to record temperatures with a sensitivity of 0.2°C. Visual display of the thermocouple output was recorded on a Honeywell-Brown potentiometric recorder of 1 mV. full-scale deflection. A potentiometric back-off device was used to cut the thermocouple output to a suitable value for this recorder.

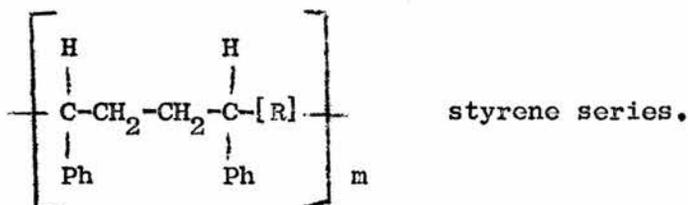
4. The Polymers Investigated.

It will be seen in the next chapter that the thermogravimetric study consisted of a survey of methods of analysis of kinetic data and a non-kinetic survey of a series of copolymers.

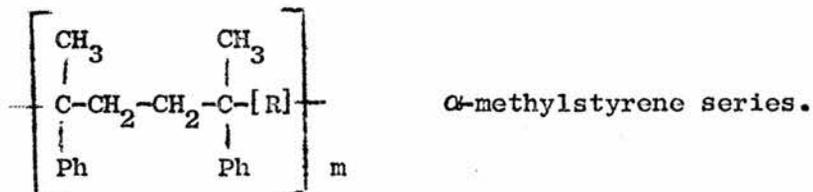
For the kinetic analysis, one of the copolymers was used as well as a sample of poly (α -methylstyrene) prepared using an anionic initiator system.

The copolymers have recently been developed at the Explosives Research and Development Establishment, Ministry of Technology, Waltham Abbey, Essex, by Dr. D.H. Richards and his co-workers. Dr. Richards kindly made this laboratory a gift of a range of copolymers for degradation purposes.

These copolymers take the following general form:-



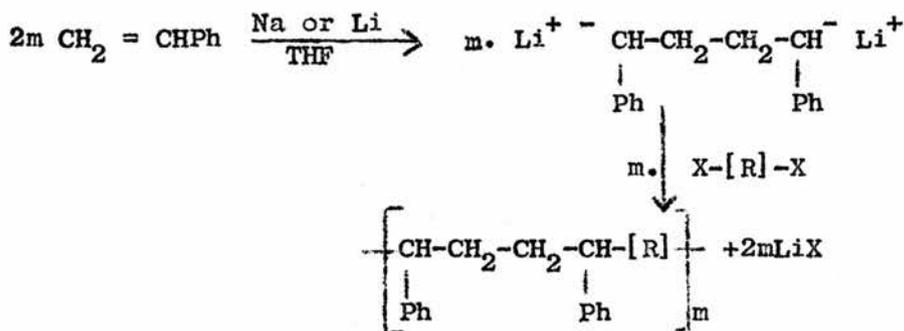
or



The two series were made by a novel preparation which has its basis in the anionic "living-polymer" system first observed by Swarc⁽⁷¹⁾.

The synthesis⁽⁷²⁾ requires that a suitable vinyl or diene monomer (in this case styrene or α -methyl styrene) is reacted with an alkali metal in tetrahydrofuran (THF). The dimeric dianion so formed normally reacts with more monomer to produce the living polymer until terminated. This method however, produces the dimeric dianion as described but allows this to terminate in the presence of a difunctional terminating agent X-[R]-X, where X is usually the halides, bromide or iodide.

This may be summarised as follows for styrene.



There seem to be few limitations to the nature of the difunctional linking agent X-[R]-X. In the work reported here, $\text{R} = \text{-(CH}_2\text{)}_n\text{-}$ and

$n = 0, 1, 3, 4, 5, 6$ and 10 for both series. Also for the α -methyl styrenes, R could also have been $[\text{Si}(\text{CH}_3)_2]$, $-\{\alpha, \alpha'\text{-orthoxylenel}-\}$, $-\{\alpha, \alpha'\text{-paraxylenel}-\}$.

All the compounds used had the same approximate molecular weight (10,000).

When a vicinal dihalide is used as the linking agent the expected product $[\text{CHPh-CH}_2\text{-CH}_2\text{-CHPh-(CH}_2)_2]$ is not synthesised. Instead, the head to head homopolymer is made in good yield. This provides a direct route to the preparation⁽⁷³⁾ of head to head polymers and such polymers prepared by this method have been used in this thesis.

CHAPTER 3 RESULTSIntroduction

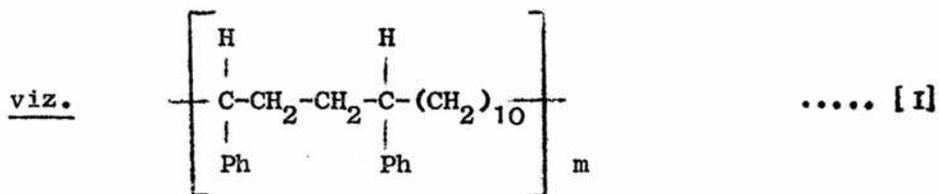
The aim of this thesis is twofold. Firstly, to carry out a survey of some of the better-known methods of kinetic analysis of thermogravimetric data and, secondly, to survey in a quantitative sense a range of copolymers of varying composition.

Part A, the kinetic analysis was considered necessary because of the number of differing values given in the literature for the activation energy of the decomposition of a specific compound. The value quoted varies according to the method of analysis used. The thermal degradation of polytetrafluoroethylene is a case in point. The literature activation energies vary between 60 and 80 k.cal/mole (see Doyle⁽³⁰⁾, Anderson⁽⁷⁴⁾, Cameron and Fortune⁽³⁸⁾, Fuoss et al.⁽⁵⁴⁾, and Wall and Florin⁽⁷⁵⁾ etc.,) using either isothermal or dynamic methods of data collection.

Part B, the copolymer survey, was attempted to obtain some idea of the scope of the TGA technique with particular reference to the investigation of a range of varying chemical structures.

A. The Kinetic Study

Originally it was intended to carry out this study on only one compound, the Richards-type copolymer (see chapter 2 part 4) formed from styrene and dibromodecane.

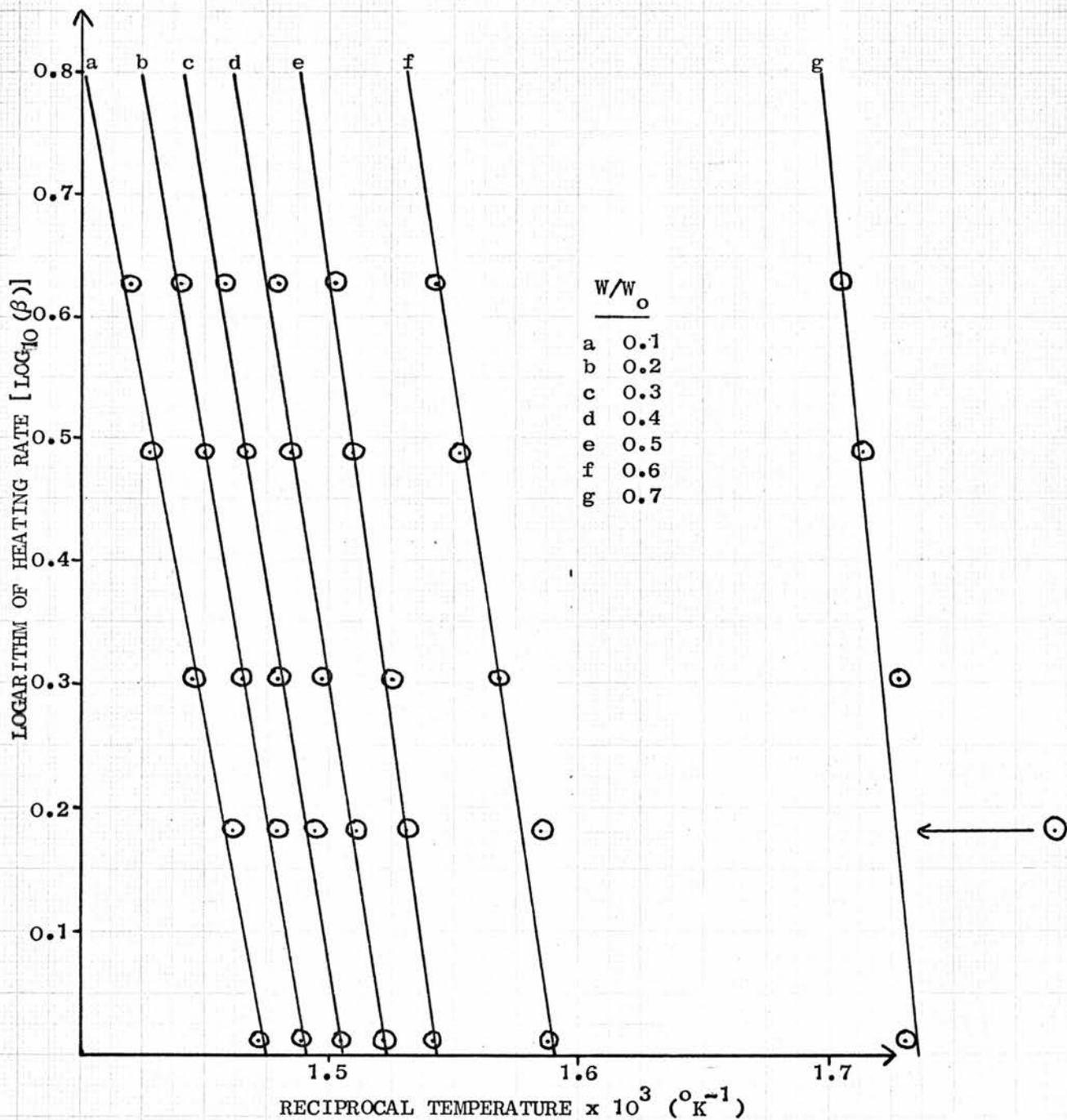


However, because of some anomalies in the early part of the kinetic analysis, particularly with the Osawa method, another compound was studied to help resolve these difficulties. This compound was anionically initiated poly(α -methylstyrene),



and was chosen because of its fairly well-documented thermal behaviour and its relatively simple method of chain degradation to produce monomer⁽⁷⁶⁾ as the only product within the temperature range studied (0-500°C) in a vacuum. Various workers have also calculated the energy of activation of decomposition by isothermal methods^(77,78,79,80), a study not attempted in this thesis.

FIGURE 3. OSAWA METHOD OF EVALUATING ACTIVATION ENERGY



The analytical methods used were:-

- | | | |
|-----|--------------------------------------|--------------------------------|
| (1) | The Osawa method ⁽⁴⁵⁾ | See Introduction, equation [7] |
| (2) | The Friedman method ⁽⁵⁸⁾ | " " " [14] |
| (3) | The Fuoss method ⁽⁵⁴⁾ | " " " [10] and [11] |
| (4) | The Kissinger method ⁽⁵²⁾ | " " " [9] |
| (5) | The Isothermal method | " " " [16] and [17] |

The analysis of compound [I] will be considered first.

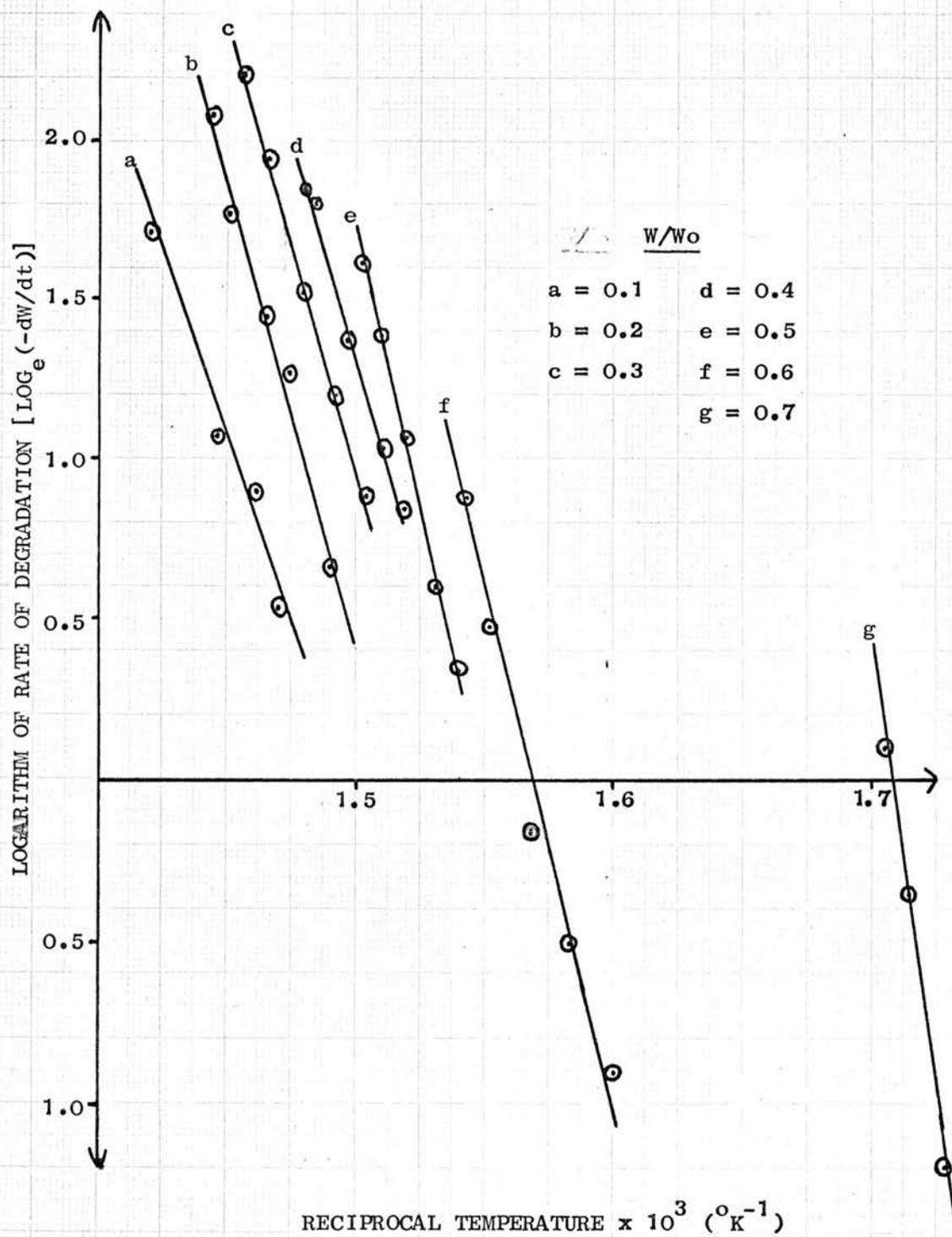
Method I. Osawa.

This is probably the most satisfactory method used.

$$\log F(C) \approx \log \frac{AE}{R} - \log \beta - 2.313 - 0.457 \cdot \frac{E}{RT} \quad \dots [7]$$

A plot of the logarithm of the heating rate ($\log \beta$) against reciprocal temperature gave a straight line for a given conversion, the slope of the line being $-0.457 E/R$, (see figure 3). However for low conversion the rate of degradation was slow and it was difficult to derive accurate I/T values for conversions less than about 25% (for this compound). It was chiefly for this reason that the degradation studies of poly(α -methylstyrene) were carried out. Here the degradation is a chain unzipping reaction with no possibility of chain transfer through a tertiary

FIGURE 4. FRIEDMAN METHOD OF EVALUATING ACTIVATION ENERGY



hydrogen atom (as in the case of styrene and its copolymers). Thus the reaction profile, by which is meant the plot of fractional weight remaining against temperature or time, is much steeper in form than is compound I. Early conversion results might therefore be expected to be rather more accurate.

Method 2. Friedman

This method is a differential technique where a rate parameter is derived from experimental data.

$$\ln \left(\frac{dC}{dt} \right) = \ln[A.f(C)] - \frac{E}{RT} \quad \dots [14]$$

In this case the natural logarithm of the rate of weight loss (or conversion) was plotted against reciprocal temperature for a given conversion. The different values were obtained by varying the heating rate, (see figure 4). The method is more laborious than the Osawa method though it uses exactly the same set of thermograms. Rates of weight loss must be extracted from the data and are liable to some error when the rates are very high and very low.

FIGURE 5.

RATE OF DEGRADATION vs.
TEMPERATURE AT VARIOUS
HEATING RATES

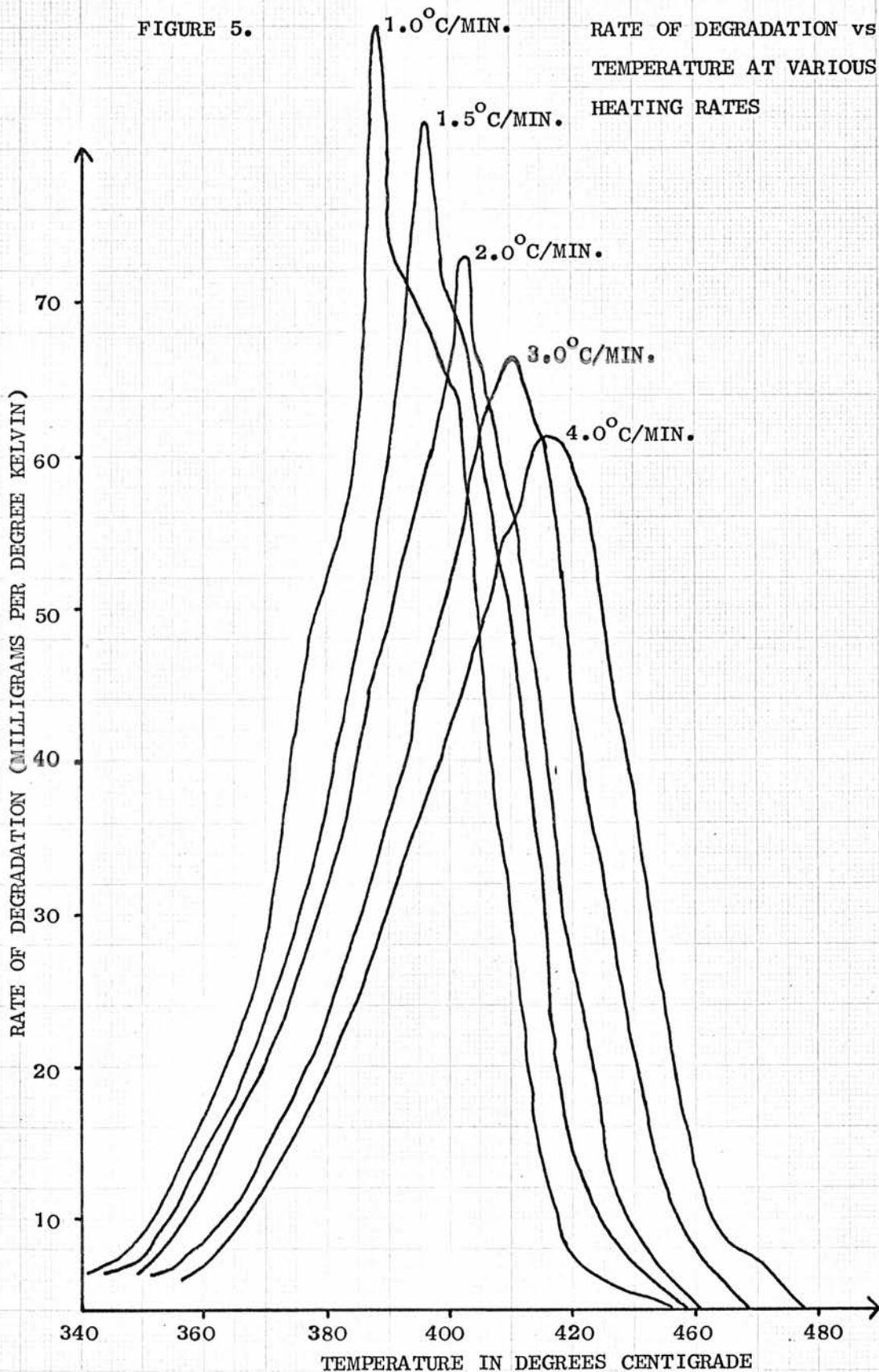
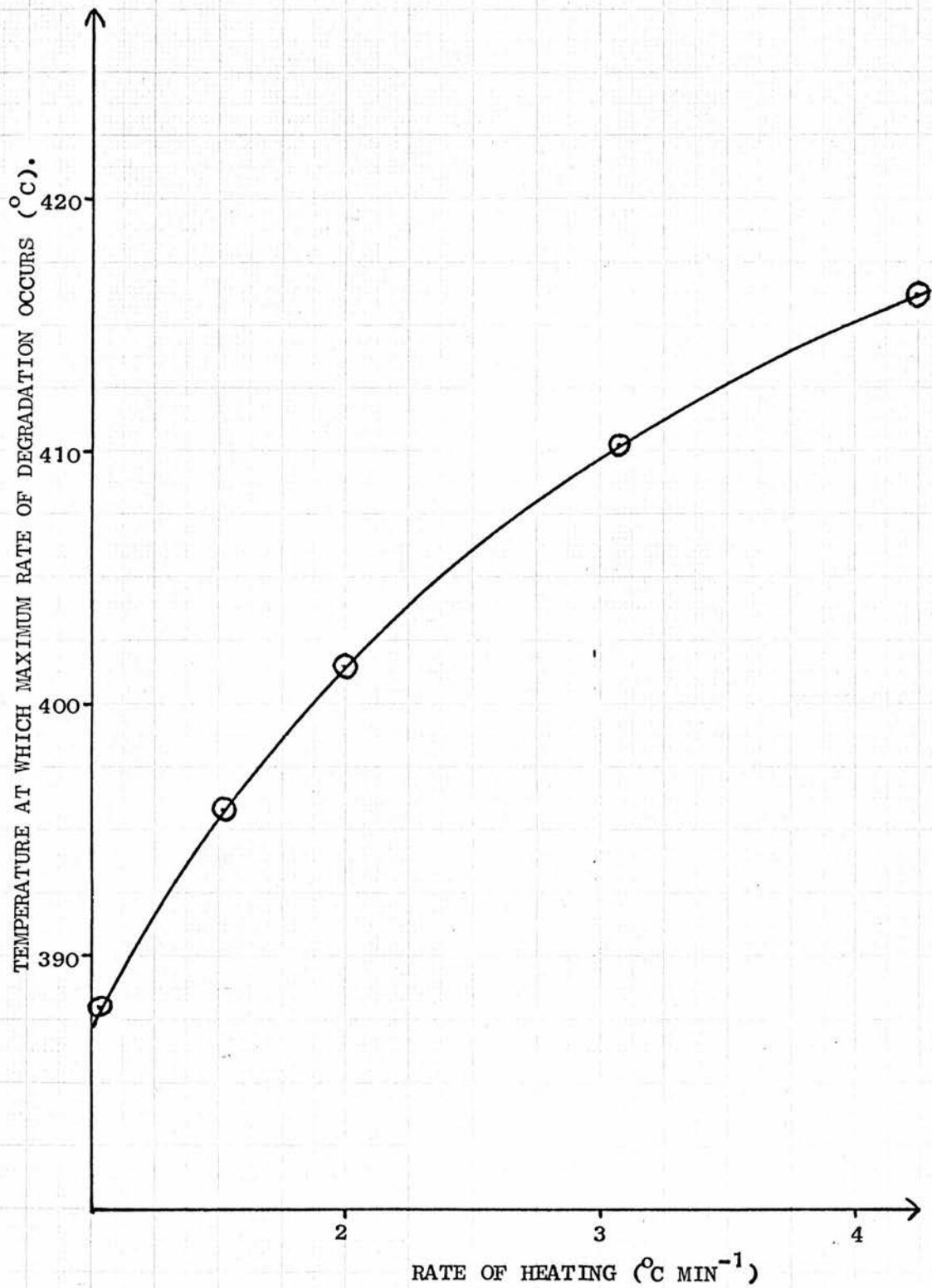


FIGURE 6. EFFECT OF HEATING RATE ON TEMPERATURE
AT WHICH MAXIMUM RATE OF DEGRADATION OCCURS



Method 3. Fuoss.

This method is of some interest since it relies on a knowledge or an assumption of the order of the reaction.

$$E = nRT_{\max}^2 \left(\frac{dC}{dT} \right)_{\max} \cdot \frac{1}{(1-C)_{\max}} \quad \dots [11]$$

For the slower heating rates the parameters are accurately and easily derived, but, with faster heating rates, the temperature of the maximum rate of weight loss (T_{\max}) can be equivocal as can the rate itself, $(dC/dT)_{\max}$ also affecting $(1-C)_{\max}$. In general, however, these criticisms are common to differential methods.

At this point some mention must be made of the effect on the thermograms of varying the heating rate, (see figures 5 and 6). From figure 5 it will be seen that the temperature of attainment of maximum rate of weight loss (T_{\max}) increases with increasing heating rate and that the differential curves show more detail for lower heating rates, a point of some importance. Figure 6 indicates the dependence of T_{\max} upon heating rate.

The Fuoss (and the Kissinger) method give energies of activation for a virtually fixed conversion which depends on the compound used. For compound I the conversion is at about 75%.

FIGURE 7. KISSINGER METHOD OF DETERMINING ACTIVATION ENERGY

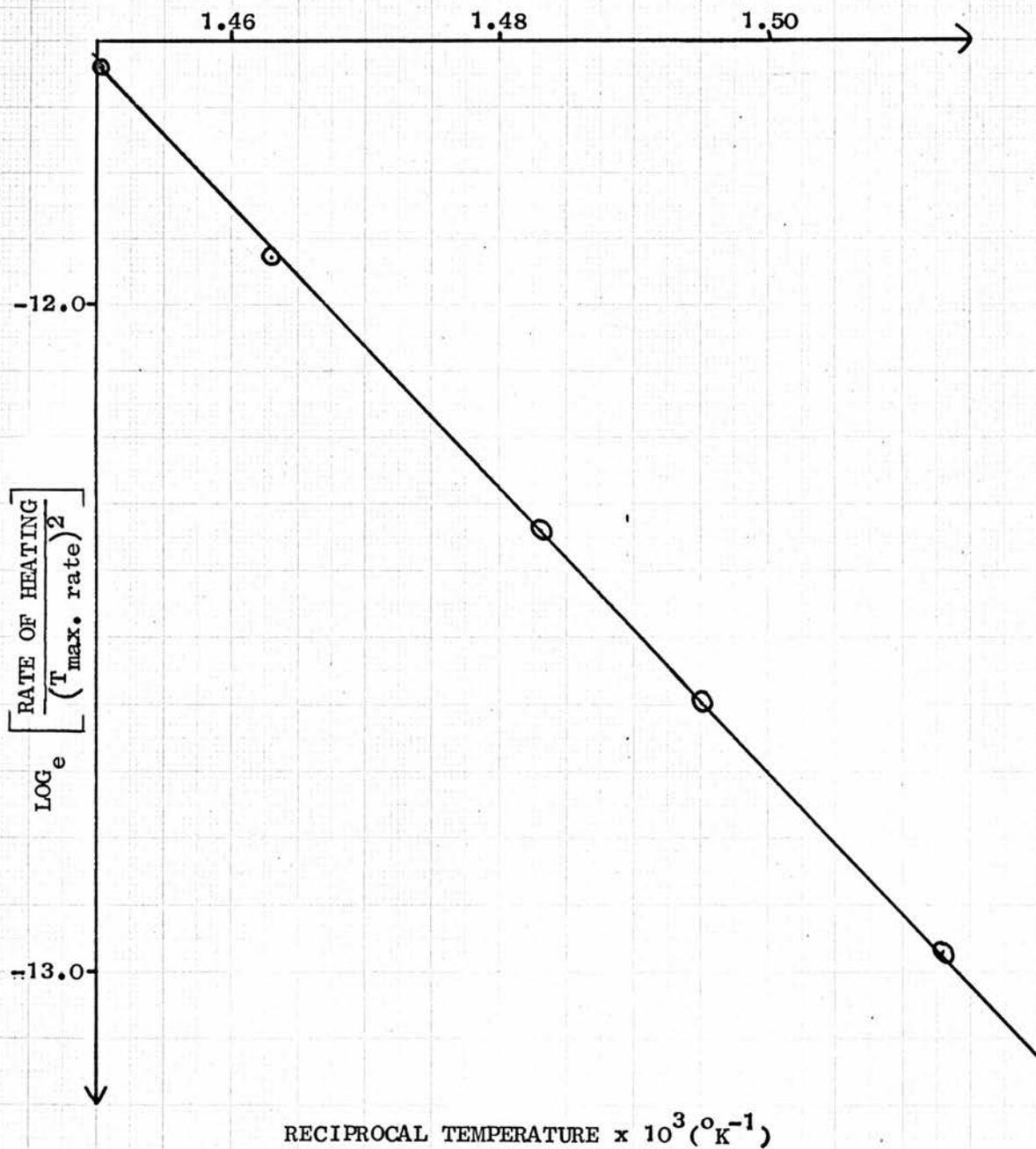


FIGURE 8A.

ARRHENIUS METHOD OF
DETERMINING ACTIVATION
ENERGY.

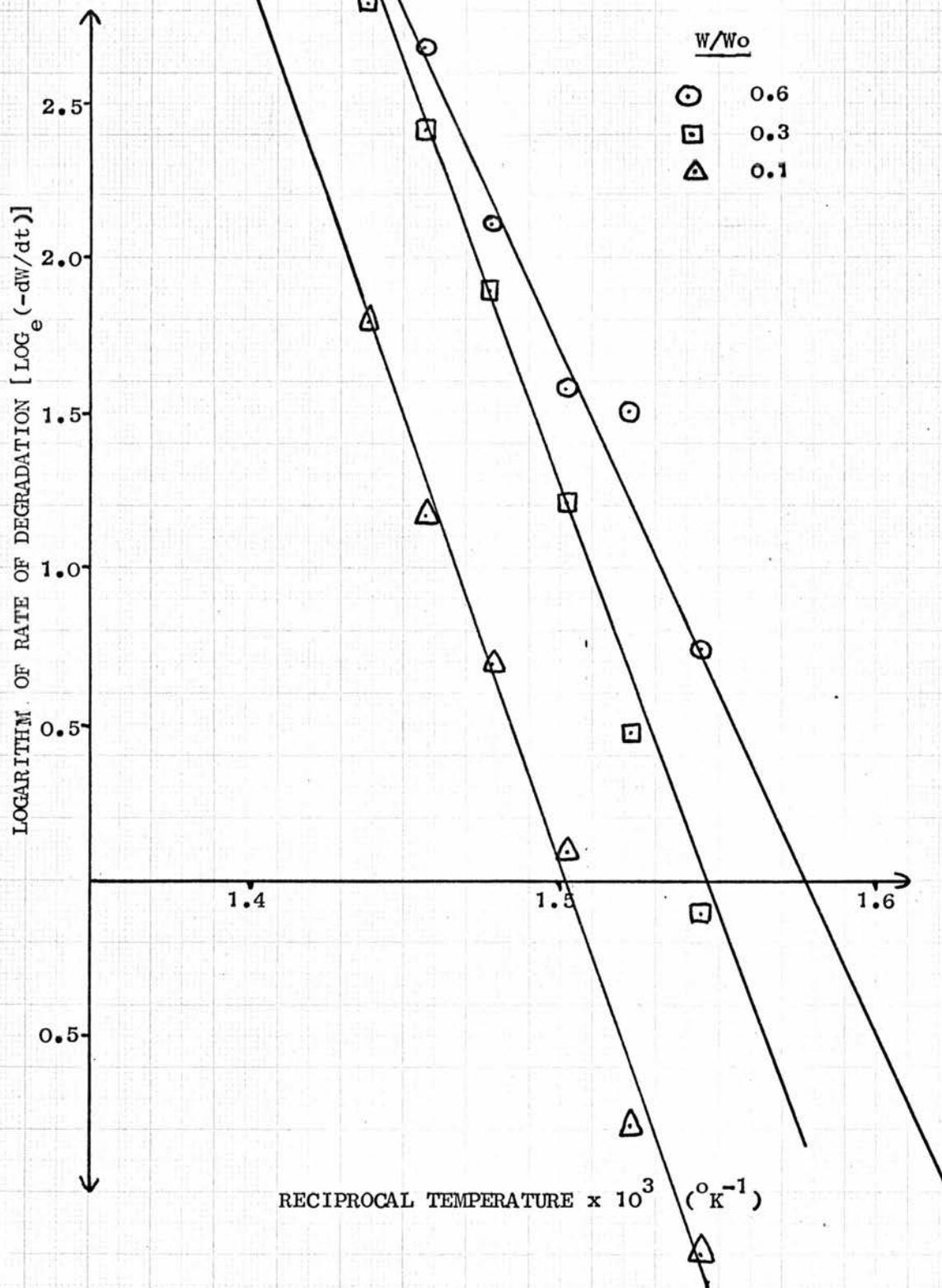
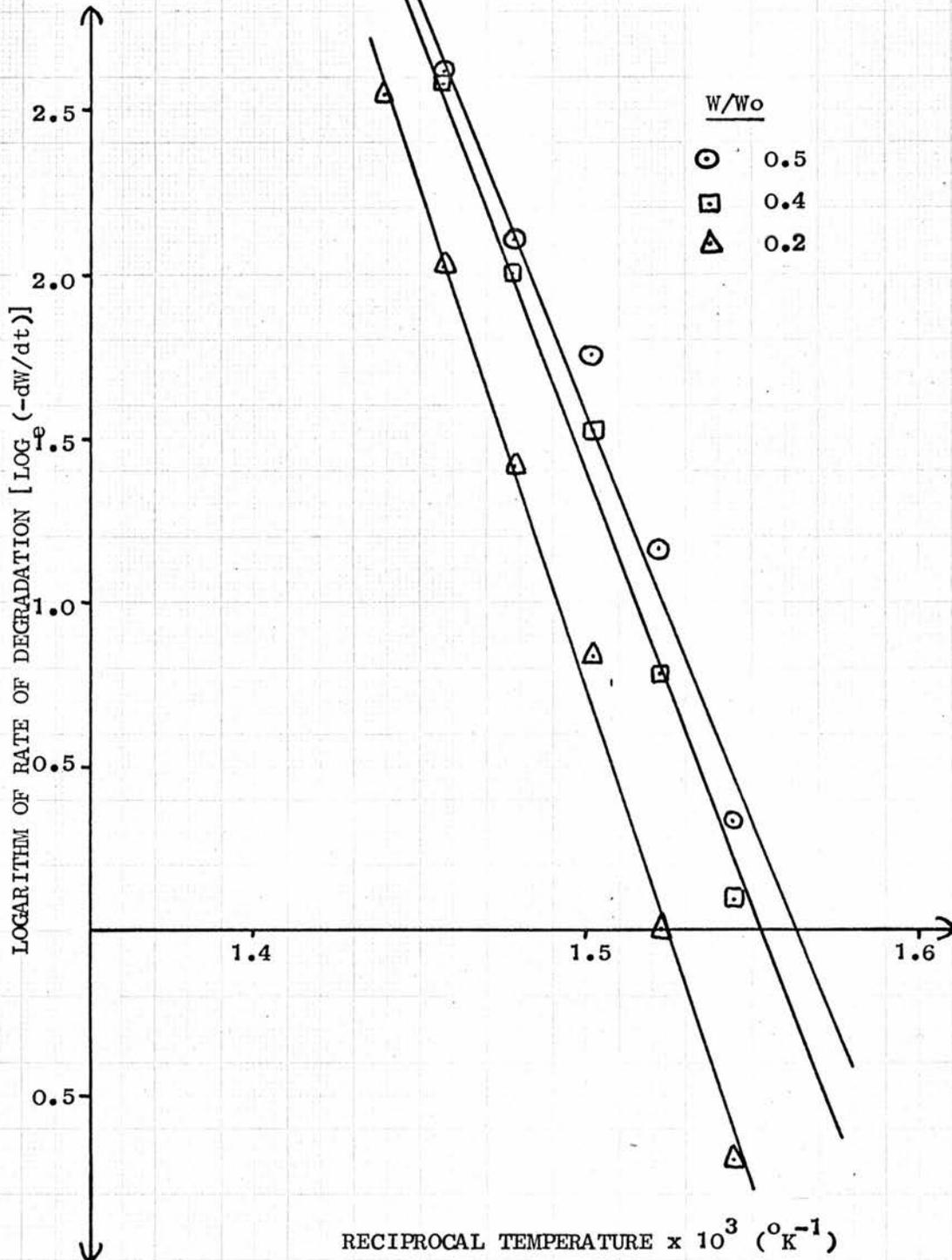


FIGURE 8B.

ARRHENIUS METHOD OF
DETERMINING ACTIVATION
ENERGY



Method 4. Kissinger.

This method uses exactly the same set of data as the Fuoss method.

$$\frac{d \ln (\beta/T_{\max}^2)}{d \ln (I/T_{\max})} = - \frac{E}{R} \quad \dots [9]$$

A plot of the natural logarithm of (β/T_{\max}^2) against (I/T_{\max}) gave a straight line of slope $-E/R$ yielding another value of the energy activation when the rate of conversion is a maximum, (see figure 7).

Method 5. Isothermal

Two equations are used for dealing with isothermal data, the second [17] being an extension of the first [16].

$$\ln \left(\frac{dC}{dt} \right) = \ln A + \ln f(C) - \frac{E}{RT} \quad \dots [16]$$

A plot of reciprocal temperature against the logarithm of the rate for a given conversion gave a straight line of slope $-E/R$, (see figures 8A and 8B. The data has been spread over two graphs for clarity).

However when equation [17] is used,

$$\ln \left(\frac{dC}{dt} \right) = \ln A - \frac{E}{RT} + n[\ln(I-C)] \quad \dots [17]$$

FIGURE 9.
ISOTHERMAL METHOD OF
DETERMINING ORDER OF
REACTION

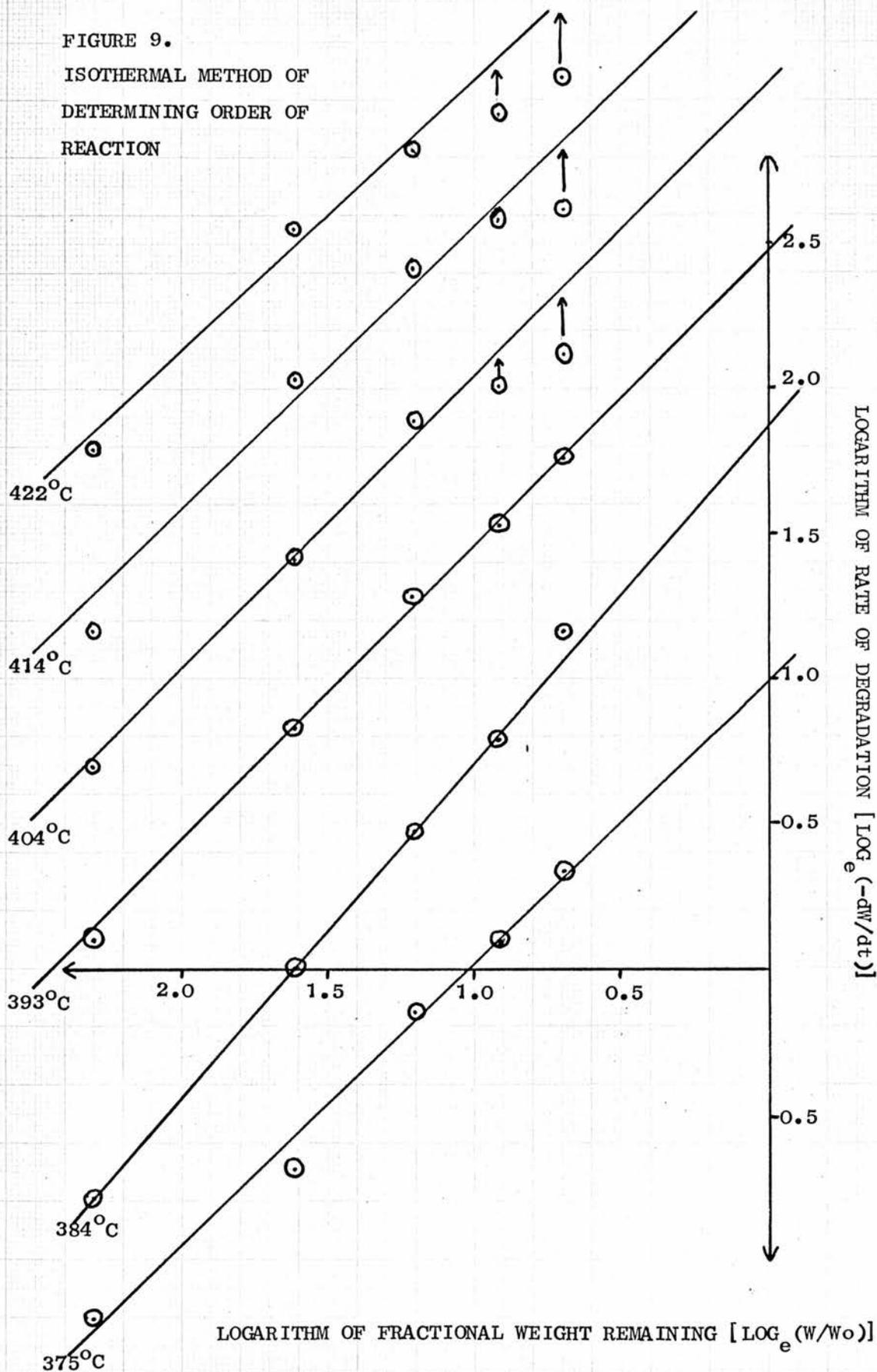
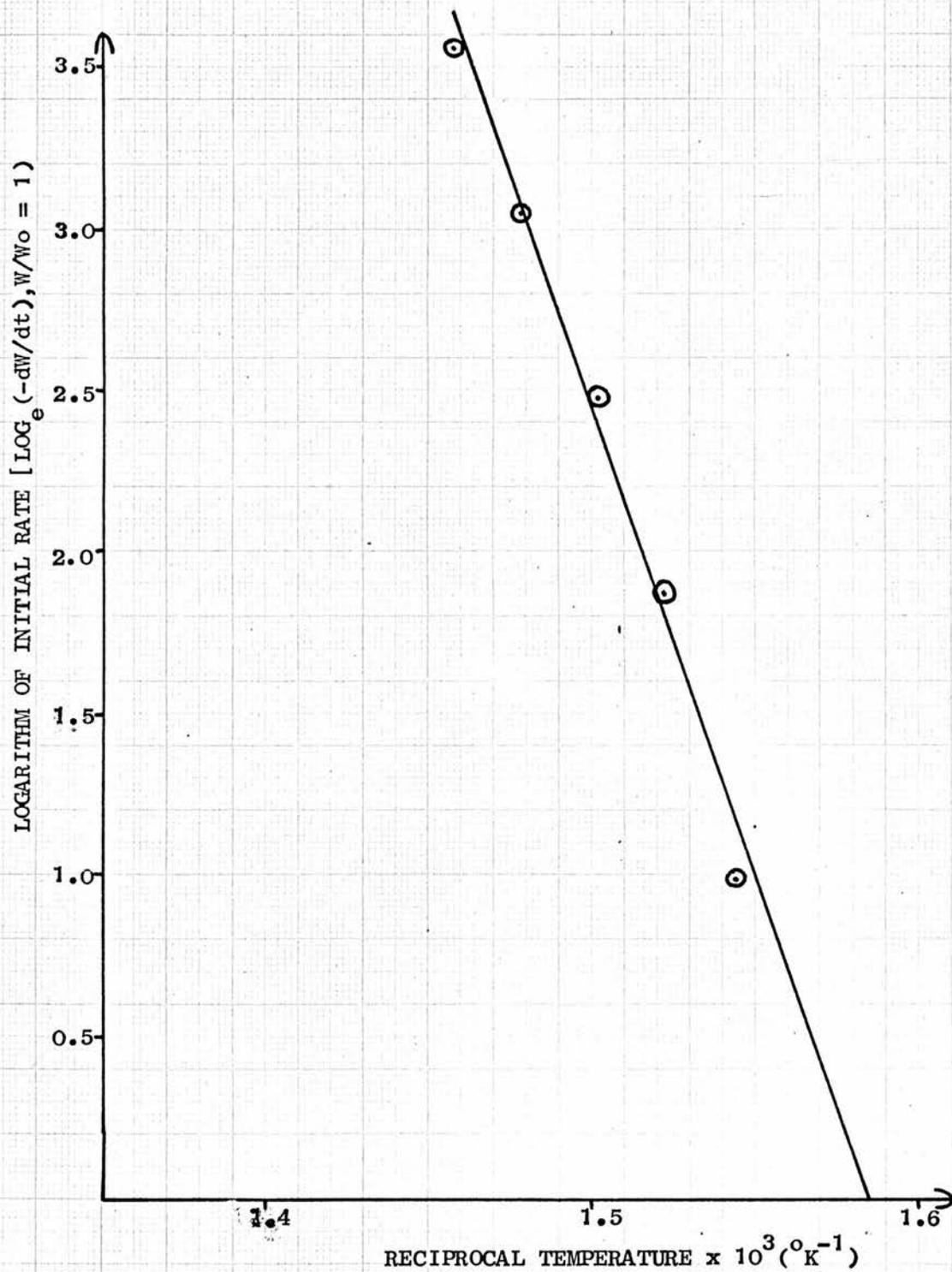


FIGURE 10. ESTIMATION OF ACTIVATION ENERGY USING INITIAL ISOTHERMAL RATES



an assumption of the exact form of $f(C)$ is made. In fact $(1-C)^n$ is substituted for $f(C)$ in equation [16] giving equation [17]. A plot of $\ln(dC/dt)$ against $\ln(1-C)$ for constant temperatures gave a slope of n , the order of the reaction, (see figure 9). Furthermore, a plot of the intercept on the $\ln(dC/dt)$ axis (where $\ln(1-C)$ tends to zero) against the reciprocal of the temperature $(1/T)$ gave a straight line of slope $-E/R$ where E in this case is the initial activation energy. The intercept on the vertical axis should be some function of A , the pre-exponential factor, (see figure 10).

All isothermal methods suffer from the disability that an exact knowledge of the temperature of the sample is not known for the early stages of the reaction. This is because it is necessary to bring the sample from ambient (or non-degrading) temperature to the temperature at which degradation is taking place isothermally. The Stanton Massflow Balance is particularly prone to such drawbacks because the large thermal inertia of the mullite tube, the furnace and the sample holder prevent rapid attainment of a constant temperature. Thus, by the time isothermal conditions were reached, some considerable degradation had occurred. For this reason no readings were taken before about 40% conversion.

TABLE 1

Activation Energy (k.cal.mole⁻¹) for the Thermal
Decomposition of $\text{-(CH(Ph)-CH}_2\text{-CH}_2\text{-CH(Ph)-(CH}_2\text{)}_{10}\text{-}$

(1) Graphical Determination

W/W ₀	Isothermal	Friedman	Osawa
0.6	44	66	61
0.5	50	68	64
0.4	53	56	57
0.3	56	59	55
0.2	60	58	52
0.1	57	45	47
Mean Value	53.6	59.1	56.3

(2) Least mean square Determination

0.6	41	56	58
0.5	49	46	67
0.4	53	51	60
0.3	56	46	50
0.2	62	50	55
0.1	57	(35)	49
	53.5	49.9	56.4

Fuoss $\beta = 1.0 \quad 1.5 \quad 2.0 \quad 3.0 \quad 4.0 \quad ^\circ\text{C/min.}$
 $E = 45.6 \quad 50.0 \quad 47.0 \quad 46.1 \quad 48.0 \quad \sim \text{Mean } 47.4$

Kissinger 43.0

Initial Isothermal 57.5

FIGURE 11. OSAWA METHOD OF EVALUATING ACTIVATION ENERGY

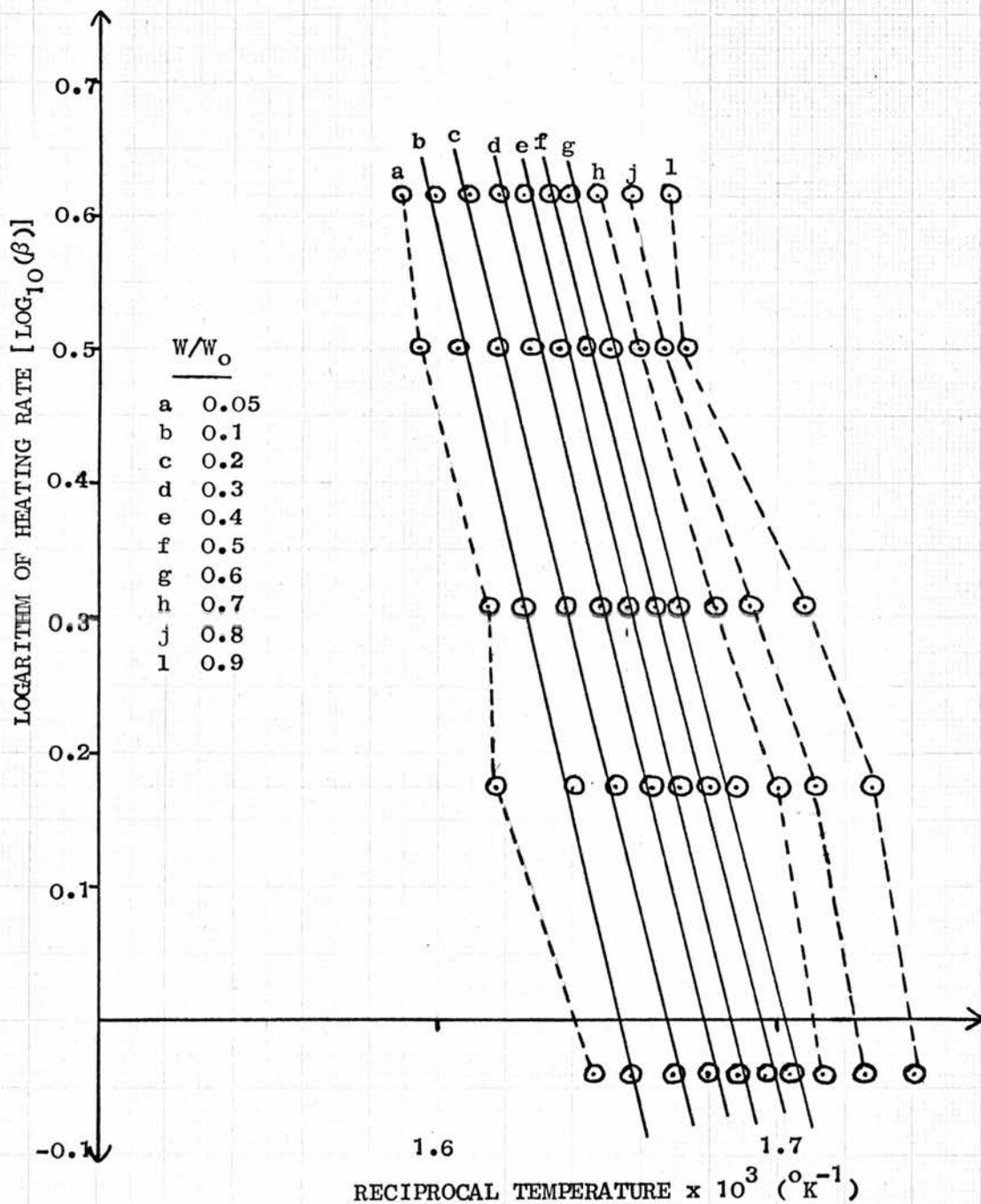
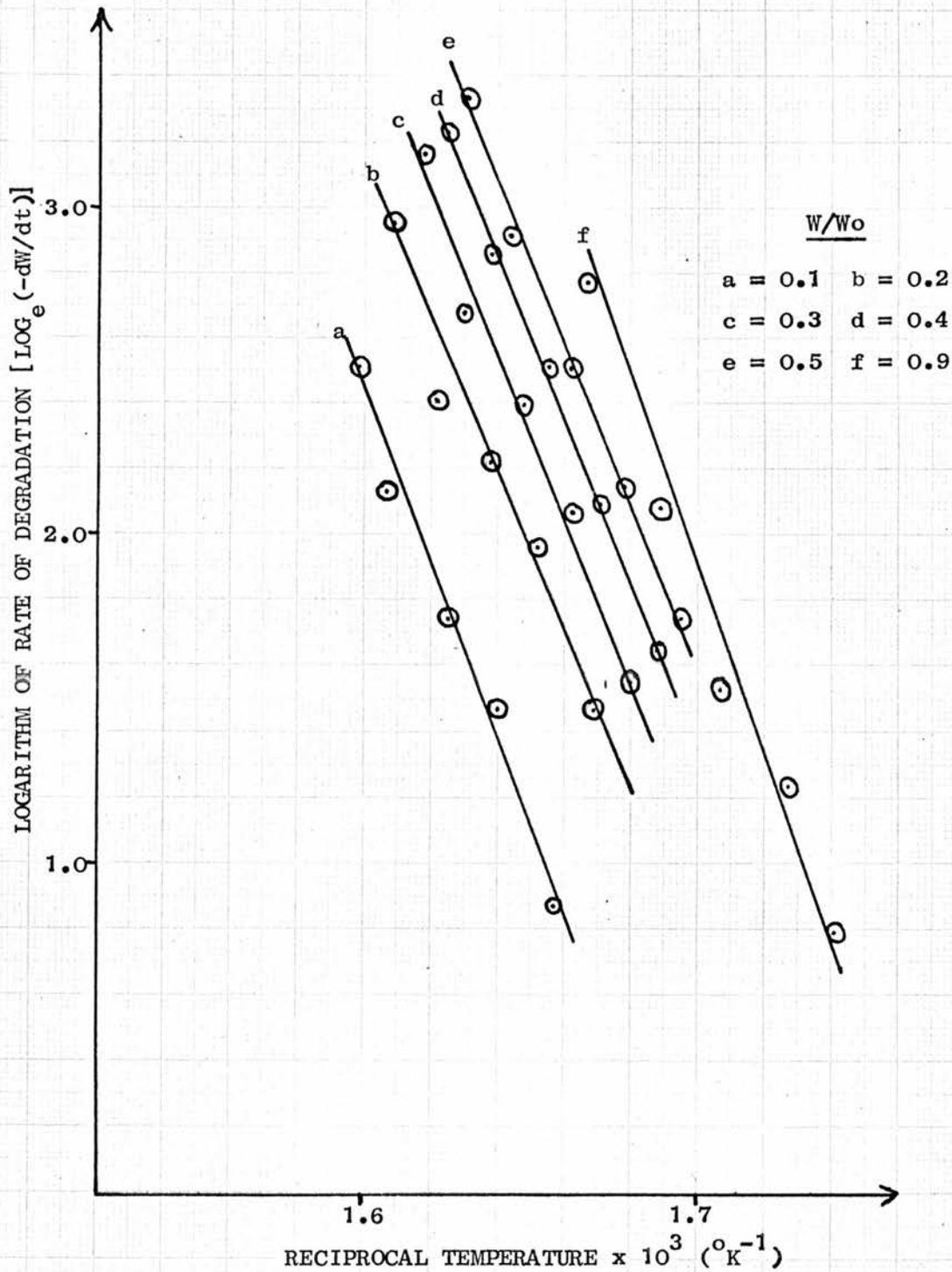


FIGURE 12. FRIEDMAN METHOD OF EVALUATING ACTIVATION ENERGY



Even at 40% conversion ($\frac{W}{W_0} = 0.6$) there was some dubiety in the readings particularly at the higher temperatures.

A table of results for styrene/dibromodecane, compound I, faces this on a separate page. (Table 1.)

The analysis of compound II - poly(α -methylstyrene) will now be considered.

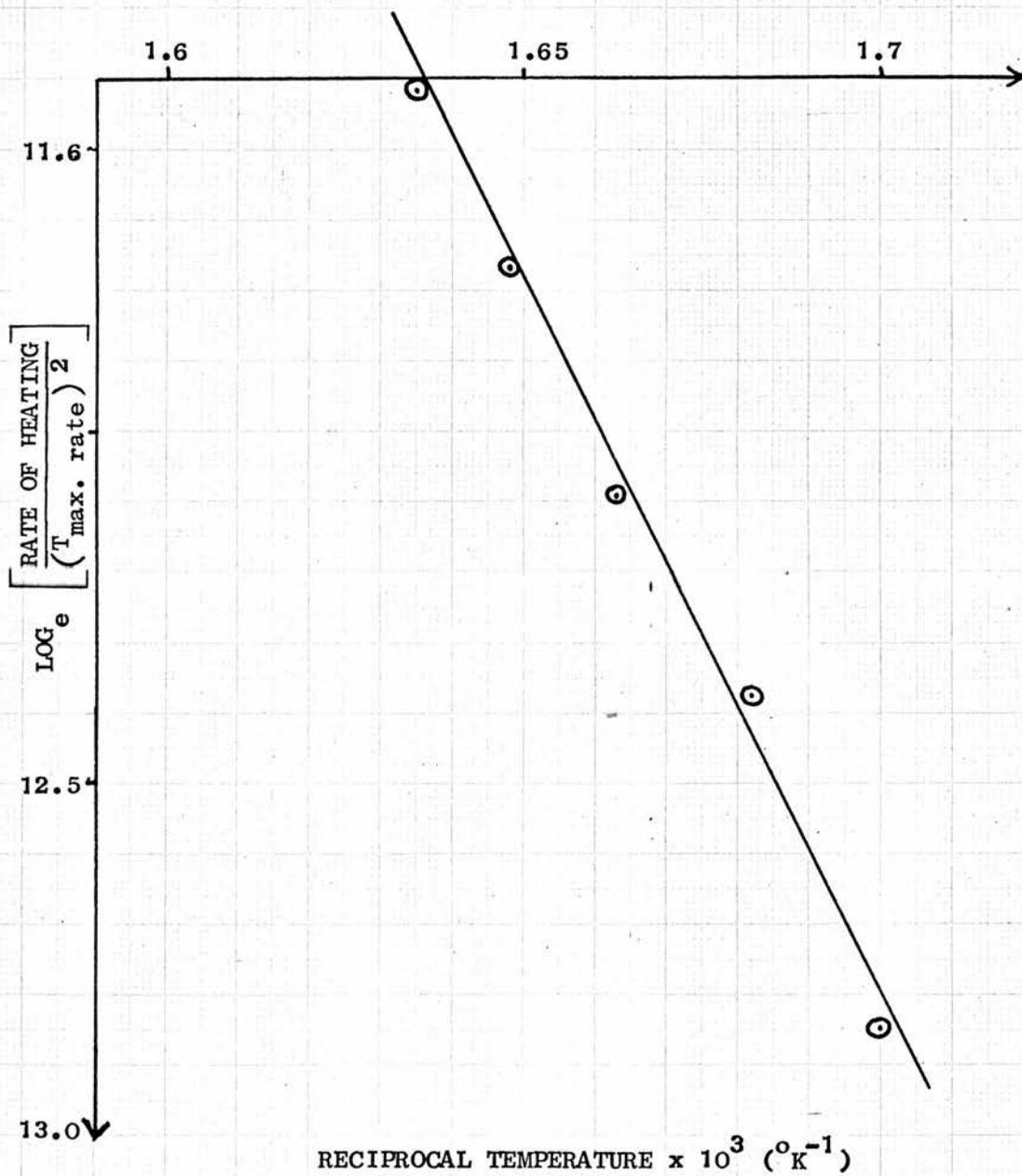
Method 1. Osawa.

It was for a more exact study of this method that compound II was chosen. Unfortunately (see figure 11), it was still not possible to derive linear plots of $\log \beta$ versus I/T for conversions less than 25% or so. The expected increase in the accuracy of data abstraction did not occur for this method.

Method 2. Friedman.

In this case however there was a marked increase in the range of applicability with conversion for the complete range, (see figure 12). For the sake of clarity, curves for conversions 20%, 30% and 40% are not shown since they lie very close to the curves of 10% and 50% conversion which are shown).

FIGURE 13. KISSINGER METHOD OF DETERMINING ACTIVATION ENERGY



Method 3. Fuoss

In this case the maximum rate occurred at about 50% conversion (earlier than in the case of compound I at 75% conversion). The abstraction of data for fast rates was not easy or accurate as is the case for compound I. The values of energy of activation are however surprisingly close to each other.

Method 4. Kissinger.

Using the same data as the Fuoss method the value of E_{\max} obtained turned out to be similar to the value for compound I, possibly suggesting a certain insensitivity of the method. (see figure 13).

Method 5. Isothermal.

No isothermal work was done on this compound. The following values for the energy of activation have been reported in the literature and have all been collected isothermally.

Jellinek ⁽⁷⁷⁾	-	45.1	k.cal/mole
Brown and Wall ⁽⁷⁸⁾	-	65.0	"
Madorsky ⁽⁷⁹⁾	-	55.0	"
Madorsky ⁽⁸⁰⁾	-	55.0	"

TABLE 2

Activation Energy (k.cal.mole⁻¹) for the Thermal Decomposition
of poly(α -Methylstyrene)

(1) Graphical Determination

W/Wo	<u>Friedman</u>	<u>Osawa</u>
0.9	55	-
0.8	47	-
0.7	43	-
0.6	45	43
0.5	51	44
0.4	51	46
0.3	50	45
0.2	43	45
0.1	52	47
Mean value	49.2	44.9

(2) Least mean squares Determination

0.9	45	-
0.8	42	-
0.7	43	-
0.6	46	42
0.5	50	44
0.4	47	44
0.3	47	44
0.2	41	46
0.1	51	47
Mean	45.8	44.2

Fuoss β - 1.0 1.5 2.0 3.0 4.0 °C/min.
E - 51.2 46.5 51.8 51.4 52.1 - Mean 50.6

Kissinger 43.5

Further reference will be made to these methods in chapter 4.

A table of results for poly(α -methylstyrene) faces this on a separate page. (Table 2.)

B. The Copolymer Comparison Study

There were two ranges of copolymers studied, a styrene series and an α -methylstyrene series, (see Chapter 2, Part 4).

They have the following general structures:-



and



For both series (III and IV), R was $\text{---(CH}_2\text{)}_n\text{---}$ where $n = 0, 1, 3, 4, 5, 6$ and 10. For series IV, the α -methylstyrene series only, R was $\text{---Si(CH}_3\text{)}_2\text{---}$, $\text{---}\alpha, \alpha'\text{-orthoxylyene---}$ or $\text{---}\alpha, \alpha'\text{-paraxylyene---}$.

The series of compounds with varying numbers of methylene groups was the most extensively studied.

The work was carried out on the Stanton Massflow Balance described in the previous chapter. As the work was intended to be an exact comparison, very strict standardisation of method was adhered to.

For all cases, the conditions were as follows:-

Heating rate: $3^{\circ}\text{C}/\text{min.}$, the rate being determined graphically.

Sample size : 50mg. in a sample holder of weight 1.82g. and invariant geometry.

Atmosphere : the sample was heated in a high vacuum (pressure better than 10^{-5} torr.)

Chart speed, timing marks etc., were kept constant for all runs. The mullite tube was cleaned after each run and baked in vacuum at 200°C for 30 minutes to remove any absorbed volatiles. In no case were any residues or volatile products characterised. The residue was always less than 0.5%.

FIGURE 14. FRACTIONAL WEIGHT REMAINING vs. TEMPERATURE FOR COPOLYMERS.

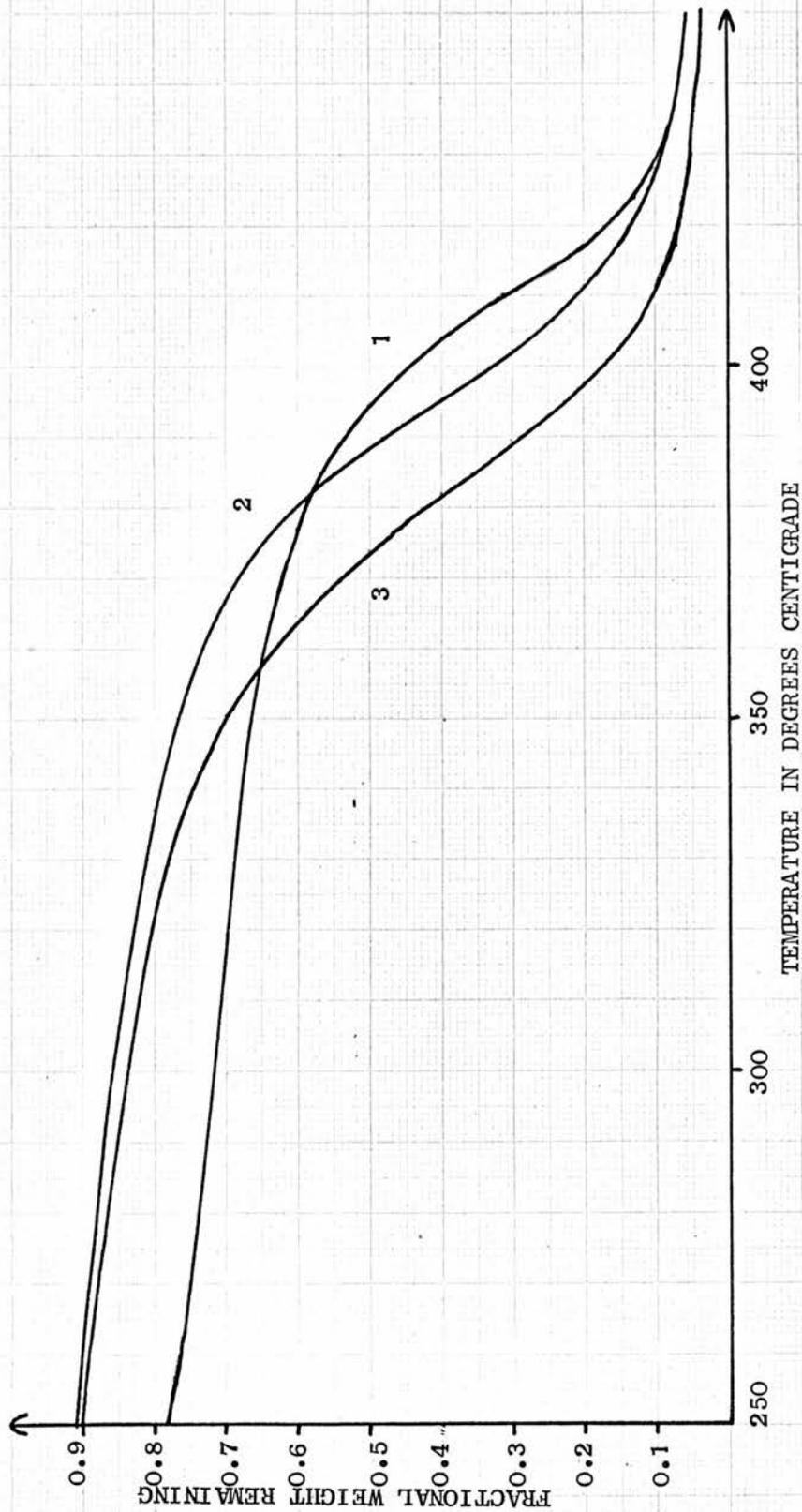


FIGURE 15. FRACTIONAL WEIGHT REMAINING vs. TEMPERATURE FOR COPOLYMERS
 $[C(CH_3, Ph)-CH_2-CH_2-C(CH_3, Ph)-(CH_2)_n]$; 1, $n = 5$; 2, $n = 10$; 3, $n = 0$.

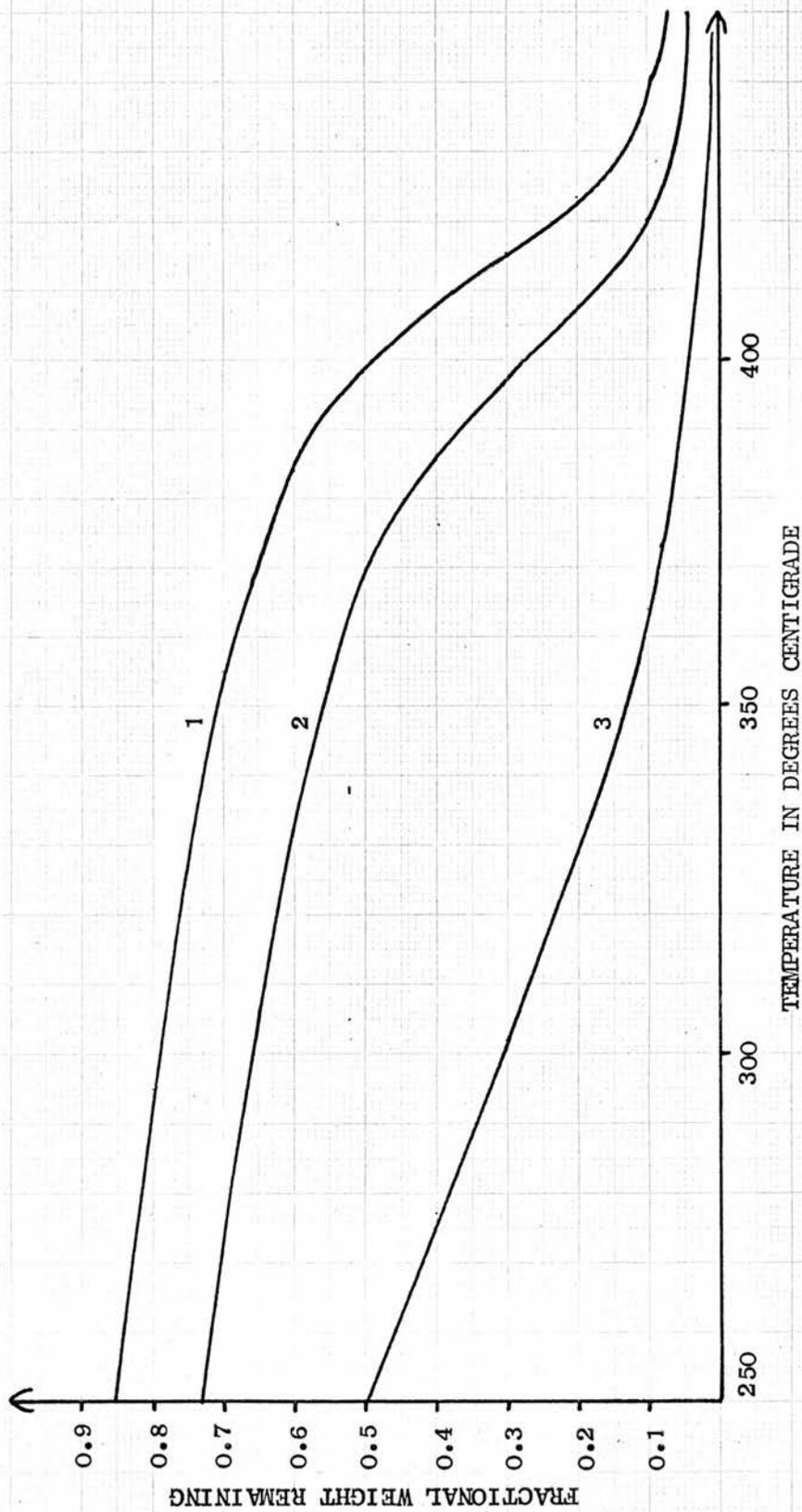
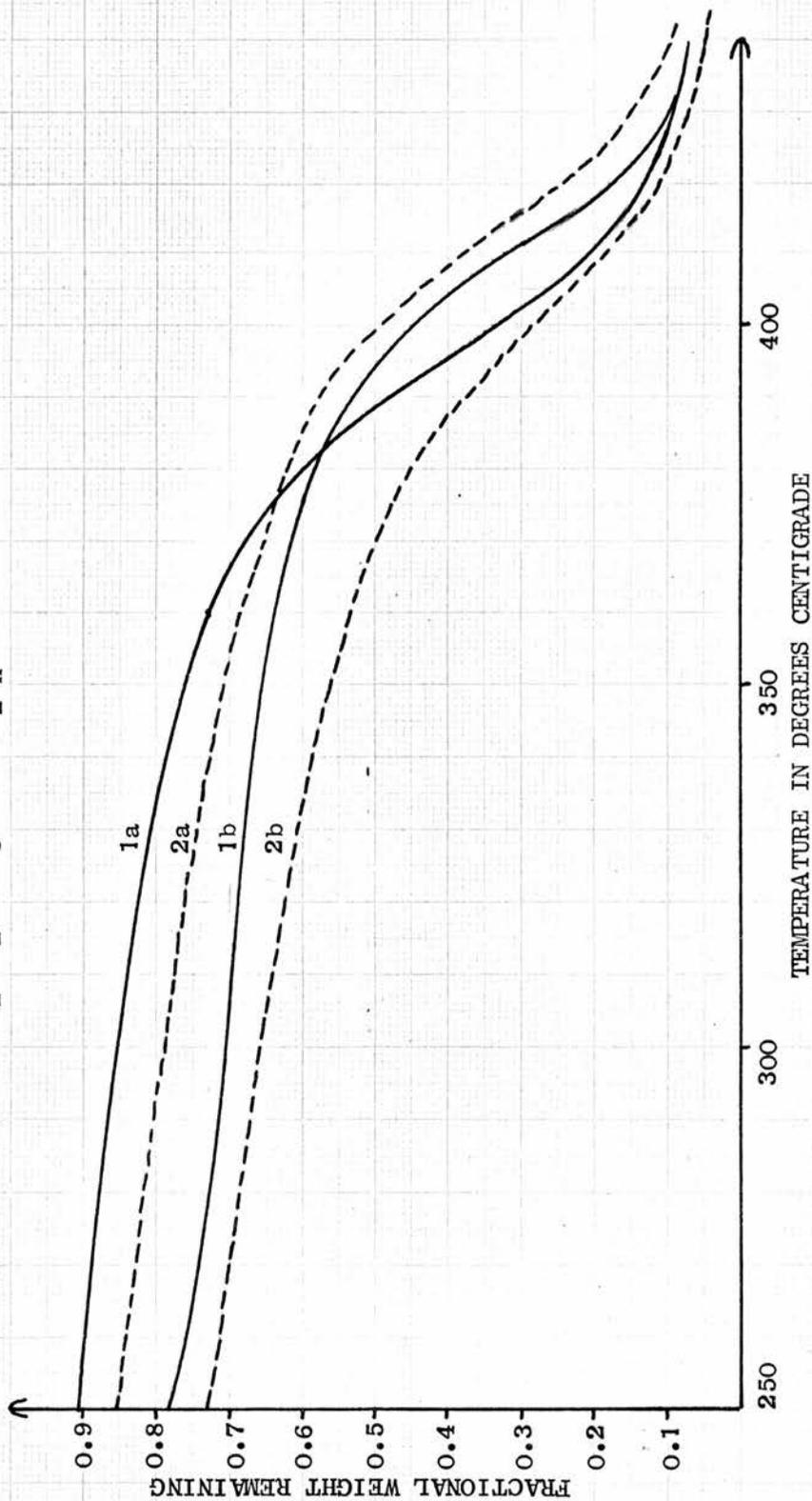
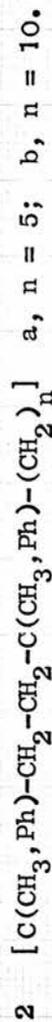
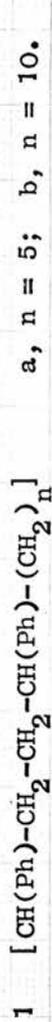


FIGURE 16. FRACTIONAL WEIGHT REMAINING vs. TEMPERATURE FOR COPOLYMERS



The Styrene and α -Methylstyrene/Methylene Copolymers.

Each figure will be considered in turn.

Figure 14.

A plot of fractional weight remaining against temperature for series III copolymers with ten, five and zero (head to head) methylene groups. This has traditionally been the way of representing thermograms in the literature. It will be seen that from about 40% conversion onwards the order of stability is $n = 10 > 5 > 0$.

Figure 15.

The same sort of representation is shown in figure 15 but for series IV, α -methylstyrene. Here, at all conversions the order of stability is $n = 5 > 10 > 0$.

Figure 16.

Just as before, the $n = 10$ and 5 compounds for both series (III and IV) are represented, from which it will be seen that the α -methylstyrene/ $(\text{CH}_2)_5$ compound is the most stable, though there is really no great difference.

Figures 17 and 18.

It was found to be confusing to show all the conversion versus temperature plots for each separate compound in both series on one or two graphs. For this reason figures 17 and 18 were

FIGURE 17. DEGRADATION BEHAVIOUR FOR VARYING COPOLYMER COMPOSITIONS

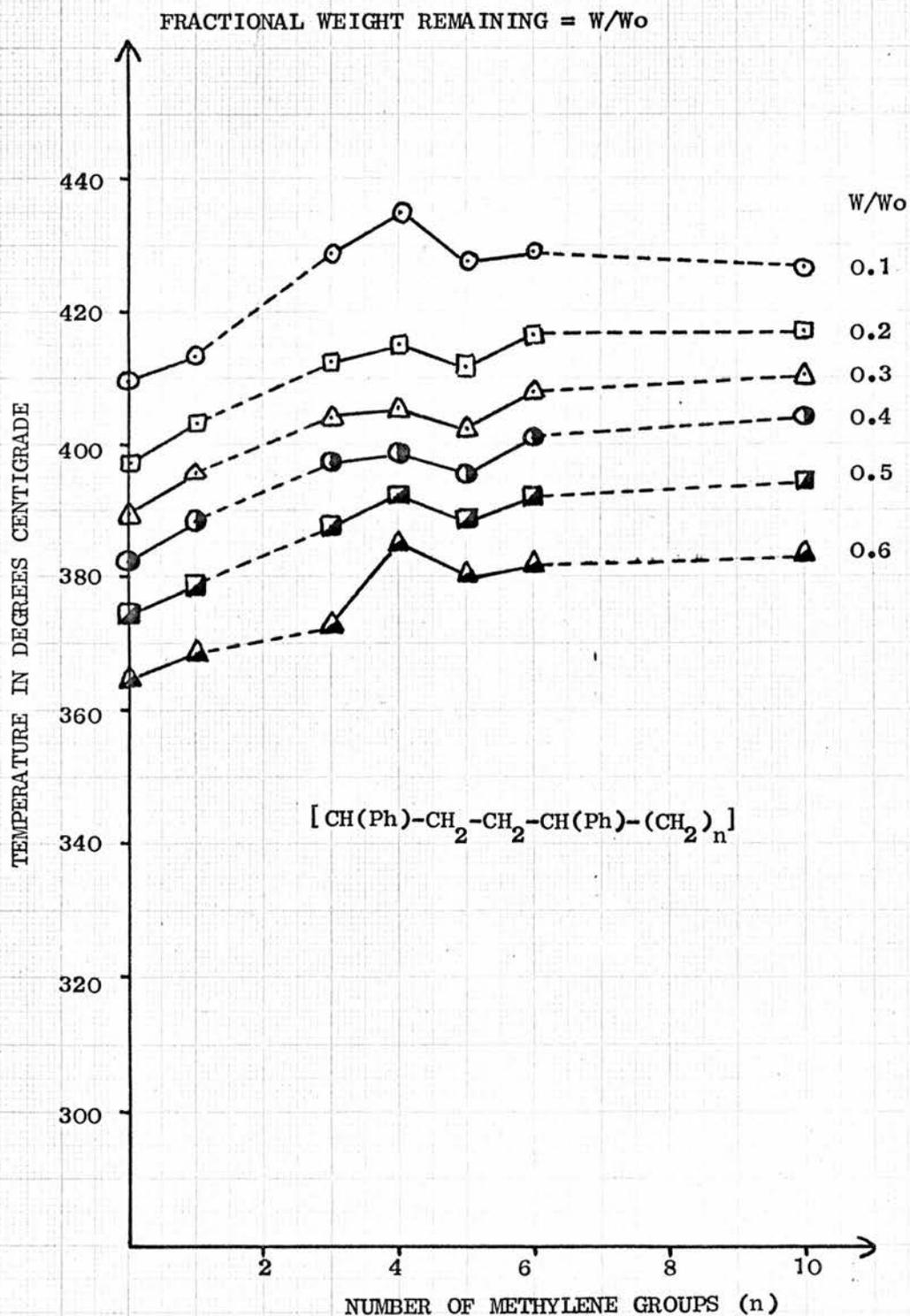
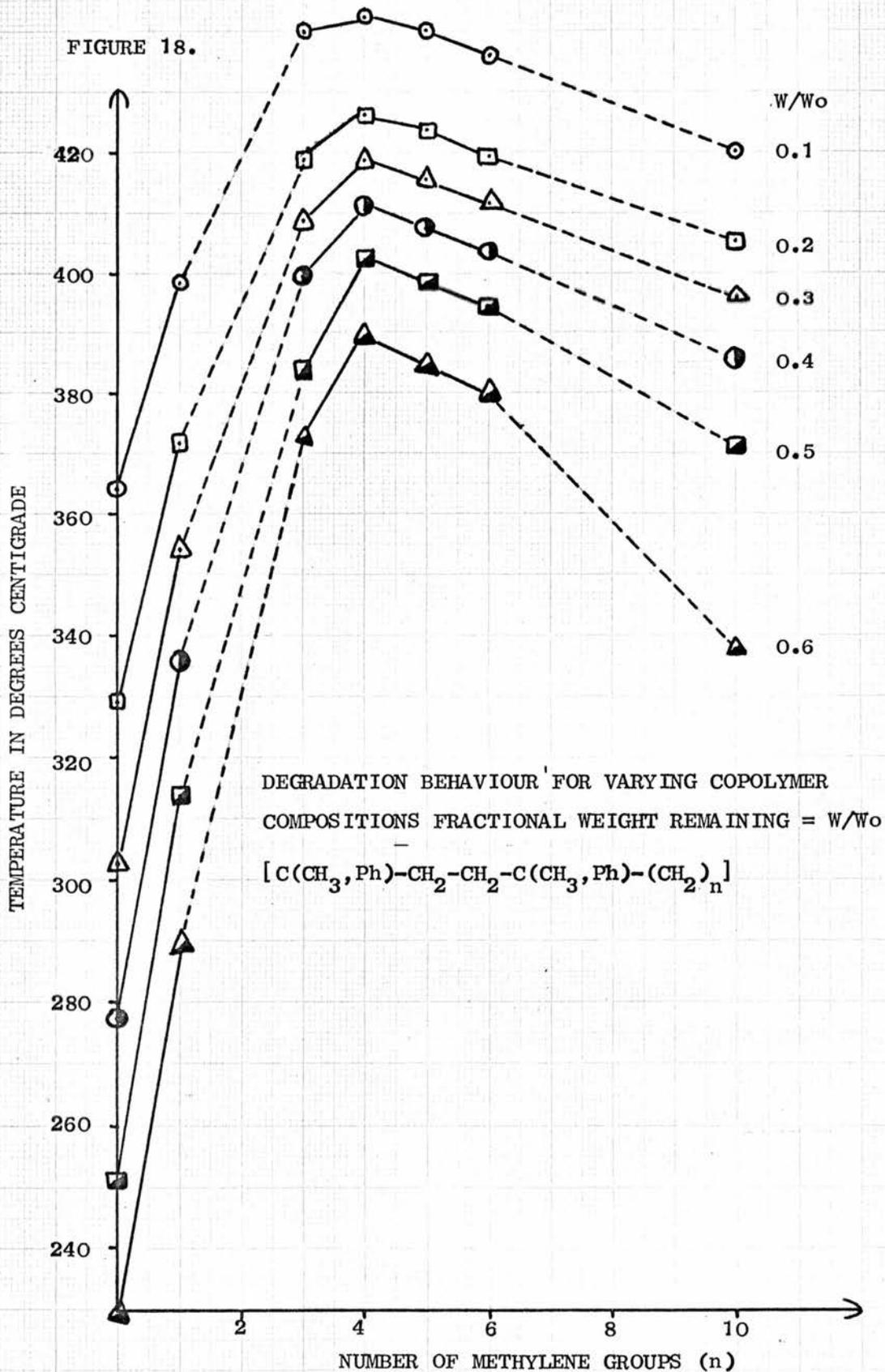


FIGURE 18.



plotted and are a more satisfactory way of presenting data of this type. The degradation temperatures for various conversions were plotted against the number of co-monomer methylene groups in the copolymer repeat unit (n).

It will be seen that, though the general form of the graphs are similar, the two series behave differently in the following ways.

a. In the styrene series (figure 17) there is a much smaller range of temperature variation than in the α -methylstyrene series.

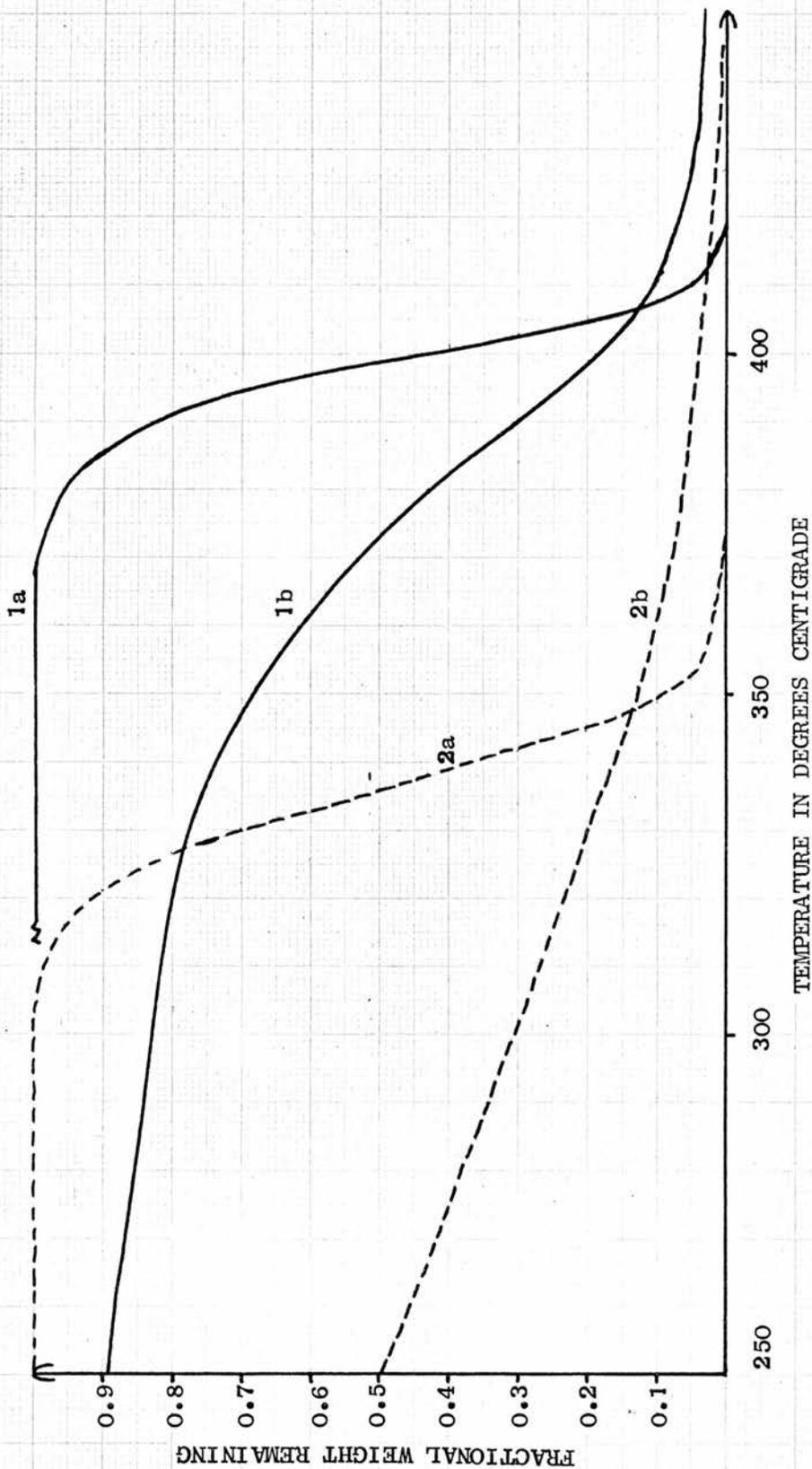
b. The trend of the styrene series is to increase in overall stability up to the n = 10 compound. An exception is for the $\frac{w}{w_0} = 0.1$ value which is slightly anomalous due to experimental scatter. A slight discrepancy also occurs for the n = 5 value which is unexplained but is not due to experimental error.

c. The α -methylstyrene series, however, shows a quite distinct maximum stability for the n = 4 variant with a quite rapid stability increase from the n = 0 compound to this point (n = 4) and a decrease away to the n = 10 compound. (Figure 13.)

It must be pointed out that the dotted lines show an assumed trend only.

FIGURE 19. FRACTIONAL WEIGHT REMAINING vs. TEMPERATURE FOR STYRENE POLYMERS

1. POLYSTYRENE. a. HEAD TO TAIL; b. HEAD TO HEAD.
2. POLY(α METHYL STYRENE). a. HEAD TO TAIL; b. HEAD TO HEAD.



Styrene and α -Methylstyrene Homopolymers.

The styrene and α -methylstyrene head to tail structures were prepared by the anionic method. The head to head polymers were prepared by the vicinal dihalide method.

Figure 19.

This diagram shows the conversion against temperature plot for the four polymers. Broken lines indicate α -methylstyrene polymers, unbroken lines styrene polymers.

Head to head α -methylstyrene (2b) is the least stable and is considerably less stable than its styrene analogue (1b) though the reaction profile of each is roughly similar. The same order of stability occurs for the head to tail polymers but they have a much steeper reaction profile.

α -Methylstyrene Copolymers where R is a group

other than $\langle \text{CH}_2 \rangle_n$.

These compounds were investigated in the hope that they might shed some light on the effect on the degradation of varying the co-monomer group R.

FIGURE 20. FRACTIONAL WEIGHT REMAINING VS. TEMPERATURE

1 POLYETHYLENE. 2,3,4 $[C(CH_3, Ph)-CH_2-CH_2-C(CH_3, Ph)-X]$
2, X = Si(CH₃)₂; 3, X = α, α' -paraxylylene; 4, X = α, α' -orthoxylylene

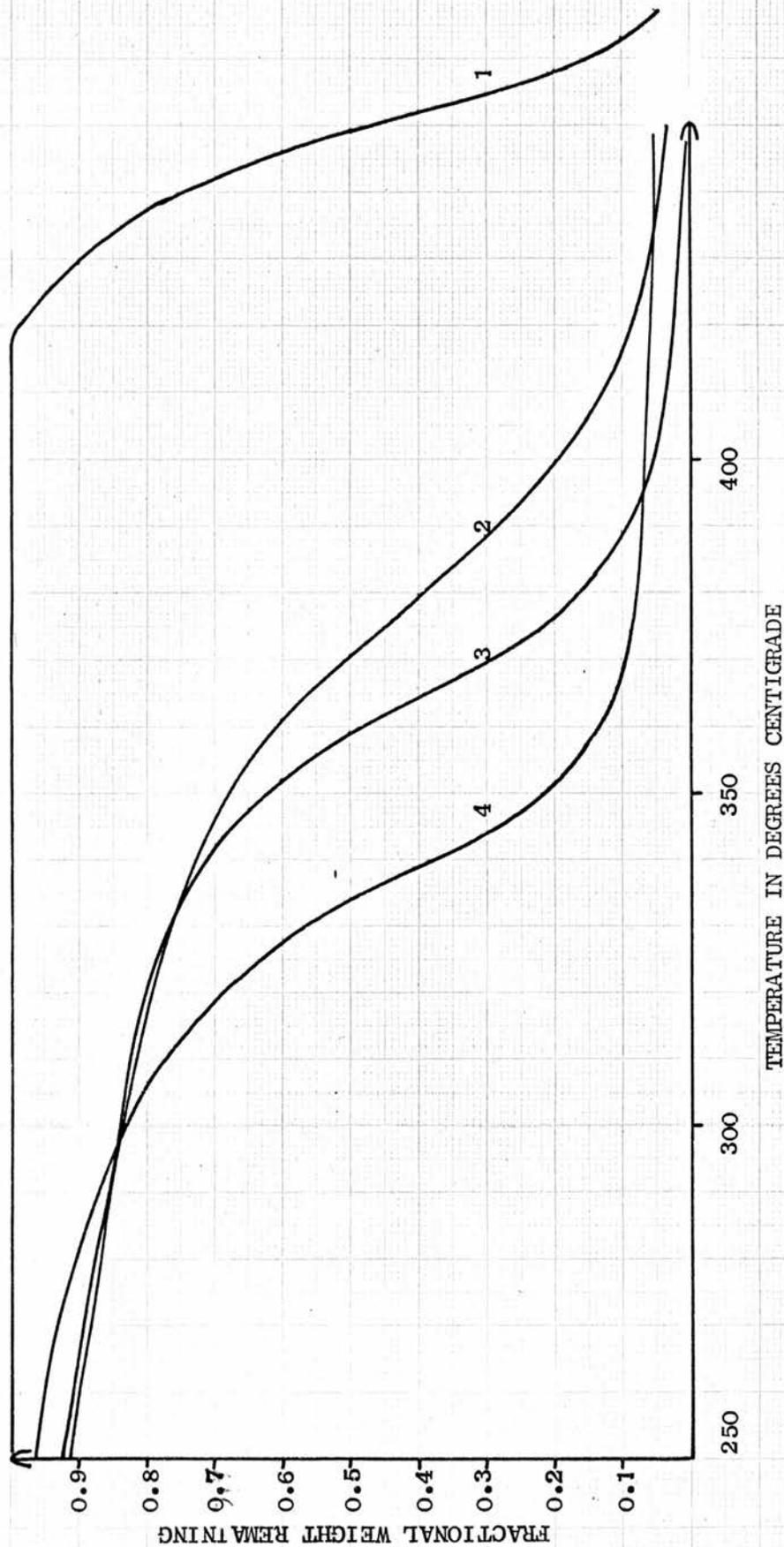


Figure 20.

A comparison is best made between this figure and figure 15.

a. In the cases shown, the inclusion of a group other than methylene lowers the overall stability of the copolymers.

b. The reaction profile generally tends to be slightly steeper for the case where R does not equal $(\text{CH}_2)_n$.

c. The $\text{---Si(CH}_3)_2\text{---}$ group is more stable than either of the xylene groups when used as the co-monomer.

d. The α, α' -paraxylene copolymer is more stable than the α, α' -ortho-xylene compound.

e. The polyethylene compound was added as a "marker" to indicate relative stability.

CHAPTER 4 DISCUSSION

The first part of this thesis was concerned with the thermoanalysis of some polyphosphazenes, particularly their thermogravimetry. It became obvious, partly from this work and partly from a study of the literature, that there were many problems in the performance and analysis of such experiments. Preliminary laboratory work underlined these anomalies and it was then decided, firstly to survey some of the best methods yet published for the analysis of kinetic data and, secondly, to survey various ranges of copolymers to gain some idea of the scope and usefulness of the technique in a comparative study of this nature. In this way it was hoped to build up a picture of the strengths and weaknesses of thermogravimetry as applied to a wide variety of both inorganic and organic polymeric materials. By the nature of this work, it can be argued that the conclusions drawn from the experimental facts are specific to the exact polymers used. However, it is considered that many of these results point to conclusions which hold for most polymeric systems and, indeed, many other types of compound. The work has also suggested (see chapters

1 and 2) modifications to apparatus and techniques which are of general import.

It is intended, in discussing these results, to follow the pattern of the previous chapter and separate this one into two parts, the first dealing with the analysis of the kinetic methods (part A) and the second with the copolymer survey experiments (part B).

Part A. The Kinetic Section

The methods will be considered in turn, outlining the results, their significance and the usefulness of each.

Method 1. Osawa

This method is quickly and easily performed and from the tables of results, it will be seen that there is a very close correspondence between the average values of activation energy for the least mean squares treatment of results and the graphical treatment.

Abstraction of data from the thermograms is simple and since only the heating rate and the temperature at a given

conversion have to be measured, the accuracy of the results should be high, particularly for compounds which have a steep reaction profile. Thus the limiting factor of the technique should be the accuracy of the temperature measuring devices and the linearity of the temperature programmer. However, (see figure 11) the method does not give linear plots for the early and very late parts of the reaction for either compound. There does not seem to be any one simple reason for this and of course the cause may simply be the intrinsic peculiarities of the compounds chosen. However this seems rather unlikely, particularly for the poly(α -methylstyrene) sample. This plot has been used for several other polymers of the Richards copolymer type and always seems to show this anomaly⁽⁸¹⁾. If this limitation in range was caused by inaccurate data abstraction, it would be expected that the poly(α -methylstyrene) with the steep reaction profile would be plotted accurately. In fact there seems little to choose between the two plots, both being non-linear. Thus the conclusion might be that the method is at fault in

its basic theory. It could also be that the method of plotting is too sensitive for the experimental scatter in the low conversion area.

The objections to this method are twofold. Firstly the heating rate must be linear and constant throughout the measured part of the reaction. The effect of a varying heating rate is quite marked (see figure 6) and can cause a considerable error in the results. The programming method used for this work was found to be quite adequate below about 6°C/min. rate. Graphical presentation of the time/temperature data for each run gave the heating rate and also indicated the linearity. Therefore above about 6°C/min. it was easily seen that the linearity worsened with increasing heating rate. The second objection to the method is that the value of the integral $p(x)$ (see Introduction, chapter 1) is an approximation where the "constants" in the equation

$$\log p(x) \cong -2.315 - 0.4567 E/RT$$

are not constants but slowly-changing variables. However

the value 0.4567 changes very little for varying energy of activation (E) and temperature, so, provided that $E/RT > 20$, the equation is accurate to within experimental error. Flynn and Wall⁽⁴⁶⁾ suggest a method of successive approximations for finding the exact constants which would give slightly more accurate answers. However, the constant used (0.4567) changes only by about 1% in the temperature and activation energy range in which this work was carried out, affecting the final value of E by less than 1 k.cal/mole.

The experimental spread from the graphs can be as high as $\pm 5\%$ (from the maximum and minimum slopes) a value which is true for all the graphical methods tried. This is an unnecessarily high error and a more realistic figure would be lower.

Method 2. Friedman

Friedman's method is more time-consuming than the Osawa method though it uses exactly the same thermograms. This is because the first derivatives of the weight loss

versus temperature/time plots must be calculated. In this laboratory these values are collected by hand, a laborious task. It is, however, possible to differentiate the curves electronically though the introduction of such a machine does bring its own errors. It has been shown (chapter 3) that the measurement of fast rates is particularly prone to error. This can, to a certain extent, be minimised by the use of a faster chart speed, but depends, in the final analysis, on the ability of the balance mechanism to accommodate the faster rates of degradation. It should also be pointed out that all differential methods, dealing as they do with small differences tend to magnify experimental scatter.

As with the Osawa method one of the great advantages of Friedman's equation is that there is no assumption made about the value of $f(C)$, the function of the degree of conversion. The point of this is that no significance need be attached to n , the so-called order of the reaction. The other advantage is that, assuming

$f(C)$ is independent of the heating rate, then the method itself will be independent of the heating rate within a run. This factor is important where less linear fast heating rates must be used.

It is noted that, in the case of poly(α -methylstyrene), the full conversion range is plotted on the graph, (see figure 12). This may suggest that the Friedman method is slightly less sensitive to experimental scatter than the Osawa method.

Of these two methods, which are in the author's opinion the best of the dynamic methods of analysis, the Osawa method is marginally superior, mainly because of the ease and accuracy of data extraction.

Method 3. Fuoss

This method is not as good as those others previously mentioned and there are various reasons for this which must be discussed.

The first is that only one value of the activation energy is found, the value at that conversion when the

maximum rate occurs. This makes it impossible to estimate the way in which the activation energy changes throughout the reaction.

Second, and most important, is the great difficulty experienced in abstracting data from the thermograms. The value of the maximum rate $(dC/dT)_{\max}$, its position with respect to temperature (T_{\max}) and conversion $(1-C)_{\max}$, must all be found accurately and are most difficult to abstract, particularly for high heating rates. Thus low rates of heating should be used for the highest accuracy, though it will still be difficult to find the exact point at which the maximum rate of weight loss occurs. It will be seen from the tables that the values of E are fairly consistent for the varying heating rate, though when the heating rate is equal to $1.5^{\circ}\text{C}/\text{min.}$, both polymers show anomalous values of activation energy. In the case of compound I, the mean value of E is lower than the mean values taken from the other methods, whilst for compound II the reverse applies. No particular significance is attached to these facts.

Thirdly and perhaps with some bearing on the remarks immediately preceding, the Fuoss method depends on the assumption that the value of $f(C)$ is $(1-C)^n$ and also that the final equation used should be a function of n . (Fuoss mistakenly reports it not to be a function of n ; see equation [10]). In this work the order has been taken as unity for both compounds since the value of n from isothermal work is one for both of them. (see figure 9 and Madorsky⁽⁸²⁾) Nevertheless, the assumption that the order will be the same for dynamic work is open to some question.

The advantages of the method are that, provided the attendant risks of error are accepted, it is possible to find a value of the activation energy from only one thermogram, (this being one of the original hopes for thermogravimetry). Also the data is fairly quickly, if not easily, abstracted.

Method 4. Kissinger

The Kissinger method, using exactly the same data as the Fuoss method though in a different form, suffers from all the same drawbacks.

However it gives a value of E_{\max} lower in both cases than the mean values of the Fuoss method. The method appears to be rather unusual, in that the value for both compounds is found to be 43-44 k.cal/mole whereas all the other methods give different (mean) values for the two compounds (generally the styrene/decane compound values are about 4-12 k.cals higher than the poly(*o*-methylstyrene) values). This may be chance but seems to indicate the method to be rather insensitive.

This method shows none of the advantages of the Fuoss method and has all its faults. It is not considered to be a particularly good method.

Method 5. Isothermal

This method was not really intended to be under examination as a technique since it has been well tried by many other workers. However, the results provide valuable comparison and lead to some important conclusions.

The results (see tables 1 and 2) show that the activation energy definitely varies with conversion, suggesting that similar

variations found in the dynamic methods are genuine and not a function of data errors or the particular method used. Also the isothermal values, graphically determined, are similar to those determined from least mean squares plots. Readings taken at low conversion, (see figure 9 especially) appear to deviate slightly at the higher isothermal temperatures (400-425°C). This suggests either an anomaly in the reaction for low conversion and high temperatures or, more likely, is a function of the greater difficulty experienced in bringing about isothermal conditions at high temperatures. The rates are slightly low suggesting that the final temperature had not yet been reached.

It is worth pointing out here⁽⁸³⁾ that work carried out very recently in this laboratory has evolved a better technique of performing isothermal runs enabling stable conditions to be reached by about 20-30% degradation or less, instead of 30-40% as in this work. However the balance itself is not very well suited to isothermal work as has been pointed out in the previous chapter.

From figure 9 it will be seen that the order of the reaction for compound I is approximately unity over the whole temperature

and conversion range studied. The value of the initial activation energy (57.5 k.cal/mole) is derived from extrapolated values of the (initial) rate and, as such, is liable to error. However it may be considered to be relevant to the earliest part of the reaction.

The disadvantage of this isothermal method is that once again rates of weight loss must be abstracted from the thermograms. There is also the previously mentioned difficulty of having the sample reach isothermal conditions when it may well be losing weight. This also causes the problem of finding the time at which the reaction started. This time factor is more of a drawback when using the more traditional method of isothermal analysis where the integrated rate equations are employed and some function of the conversion is plotted against time for a given temperature. It is, incidentally, believed that this is the first use of equations [16] and [17] for the analysis of isothermal data. These equations do not require any knowledge of the reaction starting time. The equations are in fact similar

to that of Friedman⁽⁵²⁾ who uses his for dynamic TGA only.

The author considers that, whilst the Osawa and Friedman methods may be able to be extended to the complete conversion range with better techniques and more suitable polymeric systems, those methods offer few, if any, advantages over the isothermal method. Both the best dynamic and the isothermal methods require at least five runs either at varying heating rate in the Osawa and Friedman case, or at different temperatures in the isothermal case and both require the measurement of much the same sort of parameters. In addition the isothermal method does give a value of the order of reaction and a value for the initial activation energy should this be considered of interest.

The Numerical Results

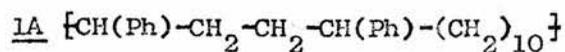
a. of the Activation Energy are given in tables 1 and 2.

Compound I, the styrene/decane copolymer in general shows the higher values of E and also shows greater differences between the mean values. Compound II, on the other hand, has much closer mean values and, as expected, lower E values. It is

very difficult to give any "best value" for E and almost certainly misleading to do so. This author considers that it is really better to look at all the results, particularly the least mean square values of the isothermal and Osawa methods and compare them. From such a treatment, it is obvious that the activation energy for compound I is greater than that of compound II by about 10 k.cal/mole. The literature values for poly(α -methylstyrene) are not consistent but the values obtained by Jellinek⁽⁷⁷⁾, at about 45.1 k.cal/mole, compare well with the dynamic values obtained in this thesis. However Jellinek considers the reaction is zero order whereas Madorsky and Brown and Wall consider the reaction to be first order. It must be noted that the results derived by Jellinek were from a sample of molecular weight 70,000. Brown and Wall used molecular weights of 345,000; 258,000; 155,000 and 79,000 but found no difference in activation energy (65 k.cal/mole) for each sample. The sample used in this work was of low molecular weight - 12,000.

The values of energy of activation derived from the Fuoss and Kissinger approaches are considered to be of less significance than the other results and will not be discussed.

TABLE 3

Pre-Exponential Factors $\log_{10} A$ (min^{-1})

W/W_0	Isothermal	Friedman	Osawa
0.6	12.1	17.4	-
0.5	14.9	17.9	21.4
0.4	16.3	15.6	18.5
0.3	17.3	18.2	15.2
0.2	18.4	15.0	16.7
0.1	<u>17.6</u>	<u>14.1</u>	<u>14.4</u>
Mean Value	16.2	16.4	17.4

Mean Value: $\log_{10} A = 16.7$; $A = 5.0 \times 10^{16} \text{ min}^{-1}$

2A poly(α -methylstyrene)

W/W_0	Friedman	Osawa
0.9	15.3	-
0.8	14.2	-
0.7	14.6	-
0.6	15.9	14.4
0.5	17.3	14.9
0.4	16.1	14.3
0.3	16.2	14.9
0.2	14.2	15.5
0.1	<u>17.3</u>	<u>15.7</u>
Mean	15.3	15.0

Mean Value $\log_{10} A = 15.4$; $A = 2.5 \times 10^{15} \text{ min}^{-1}$

b. of the Pre-exponential Factor. These values have been derived from the least mean square intercepts. They have been calculated as accurately as possible but it must be realised that intercepts are intrinsically less accurate than the slopes of the same lines. These values, given in table 3, are probably best studied as mean values rather than as values for each conversion. They are in themselves of little interest but compare moderately well with other work, for instance Jellinek's⁽⁷⁷⁾ value for poly(α -methylstyrene) of approximately 10^{17} min^{-1} .

c. of the Order of the Reaction. The order of the reaction in the case of compound II was not required for the two best methods used, Osawa and Friedman. However for the Fuoss and Kissinger methods it was needed and a value of unity was assumed. This was the value measured by Brown and Wall⁽⁷⁸⁾ and Madorsky^(79,80).

No work had been carried out previously on Compound I and the reaction was determined isothermally to be first order.

Final Conclusions.

Particularly in the last ten years a great deal of work has been done in an attempt to use dynamic (or programmed) thermogravimetric analysis to deduce kinetic parameters which can be used to aid assessment of polymer stability and degradation mechanism. A great deal of this work, if not all of it, has been controlled in some way by physical factors such as the make of the balance, atmosphere, type of sample holder and so on. These factors, which often vary quite markedly from laboratory to laboratory, can really seriously affect the results obtained from thermobalances. Add to these effects the fact that the degradation behaviour of a given type of polymer, for instance polystyrene, can be radically altered by the method of preparation or pre-treatment and we are left with a series of published results which require very critical examination. In this thesis only the type of compound and the method of analysis have been varied. All other factors have been kept constant and have been discussed at some length elsewhere. Thus it is seen that whilst these results are consistent within themselves they may show some differences from the results taken from other experiments performed

in other laboratories.

The results, then, show quite conclusively that, even using the same thermograms, the method of analysis has a definite effect on the values of the kinetic parameters so obtained, particularly when comparing the results with conversion rather than mean values. This seems to be particularly true for the less steeply profiled compounds. The methods chosen are themselves considered to be representative of the best methods available for analysing thermogravimetric data, particularly the Osawa method. This statement is liable to cause some dissent since doubtless not all workers would agree with the choice. Nevertheless the fact that the methods tried do give widely varying results does require an explanation.

A very facile explanation would be to blame operator error. This is not considered to be the major cause, though it can cause trouble particularly with the abstraction of large amounts of data. Certainly in the case of the Fuoss and Kissinger methods which use exactly the same data throughout, the different results cannot be explained by errors due to data abstraction. Therefore a more fundamental reason for these disparities must be sought.

For this we need to return to the starting point for the derivation of the kinetic equations. That is

$$(dC/dt) = k f.(C), \text{ where } k \text{ is a non-linear function of the temperature such that } k = Ae^{-E/RT}$$

The above equation is usually used incorrectly for the following reason.

If C, the conversion, is considered to be solely a function of time (t) and temperature (T), we may write:-

$$C = f(T,t)$$

Then, differentiating, we have:-

$$dC = \left(\frac{\partial C}{\partial t} \right)_T \cdot dt + \left(\frac{\partial C}{\partial T} \right)_t \cdot dT$$

$$\text{or } \frac{dC}{dt} = \left(\frac{\partial C}{\partial t} \right)_T + \beta \cdot \left(\frac{\partial C}{\partial T} \right)_t$$

where $\beta =$ the heating rate.

Now the original equation should have been written for one temperature or isothermal conditions. When $\beta = 0$, isothermal,

the equation holds since

$$\left(\frac{\partial C}{\partial t} \right)_T = \frac{dC}{dt} = k \cdot f(C)$$

But when the temperature is programmed to rise with time (when $\beta \neq 0$), we cannot write $dC/dt = k f(C)$ since (dC/dt) does not equal $(\partial C / \partial t)_T$

Thus it is impossible to regard the original equation, and therefore each method, except the isothermal method, as being valid.

It was mentioned earlier that the Friedman (dynamic) and this isothermal equation were similar. From the preceding passage it will readily be seen that they are not in fact the same and so it is not surprising that they give different results.

Future Work Suggestions.

1. The effect of various controlled atmospheres on the kinetic parameters derived for a given method would perhaps be illuminating. These effects will almost certainly be quite considerable. (See for instance the recent work of Herring et al.⁽²⁰⁾ who, for the same

compound, note a great difference between the decomposition temperature in air and that in vacuum. In fact, in one example they quote the figures for the temperature of 10% degradation as 475°C in air and 310°C in vacuum).

2. The author considers ~~that~~ it would be interesting to carry out an interlaboratory experiment, where each laboratory use their own balance apparatus but one standard compound. The experiments should then be performed under, say, two atmospheric conditions (nitrogen at a given flow rate and also a high vacuum) and the results collected, analysed and published.

This author considers that the use of thermogravimetry for the measurement of kinetic parameters is not a particularly illuminating or useful exercise. However as he hopes to show in part B of this discussion, TGA is of considerable use in assessing the stability of polymers, relatively if not absolutely.

Part B. The Copolymer Comparison Section

As suggested in part A of this discussion, it is intended to assess the value of thermogravimetry as a technique for studying two ranges of copolymers (see chapter 2 part 4) and comparing relative stabilities. Over and above this study, the results do have some significance in themselves and will be discussed separately.

1. The Technique of Thermogravimetry

It was concluded in part A that the results of using TGA to determine kinetic parameters are, to say the least, open to some doubt. However this is not to say that TGA is pointless. This author believes that thermogravimetry has a great value in studying the stability and mode of degradation of various compounds and that it is in this area that the polymer chemist will derive most benefit.

It is important here to stress the phrase "relative stability". It is perfectly acceptable to take a series of compounds and, using exactly standardised conditions, degrade them and compare the results. Then, such results will be a

measure of relative stability. However this experiment, if repeated in another laboratory, would not necessarily give the same results because of the difficulty of repeating the conditions. Thus such a series of stabilities cannot, unfortunately, be regarded as absolute in nature.

The work done in both parts of this thesis points to some general uses for TGA. (The review by Jen Chiu⁽²⁾ on non-kinetic uses of TGA is a further source of interest).

These uses are:-

1. The shape and position of the weight loss against temperature curve, or the reaction profile as it is called earlier, can indicate some overall breakdown characteristics of the polymer under study. A good example of this is shown in figure 19, when comparing the two poly(α -methylstyrene) curves (2a. and 2b.).

From these curves the following information can be abstracted.

- a. The head to head sample is less stable than the head to tail sample for almost the complete conversion range.

- b. The two reaction profiles are entirely different.

The head to tail sample breaks down at a much more rapid rate than the head to head polymer which begins to break down slowly at about 160°C and continues at a slow rate well beyond 400°C.

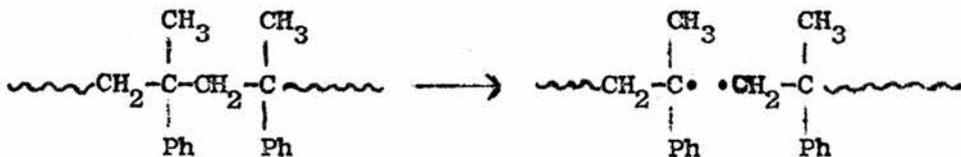
(The remainder of this curve, which is not shown because of scaling difficulties, is as follows:- 10% conversion at 174°C, 20% at 195°C, 30% at 210°C, 40% at 229°C).

c. When product analysis and molecular weight dependence studies have been carried out, it is possible to suggest a breakdown mechanism.

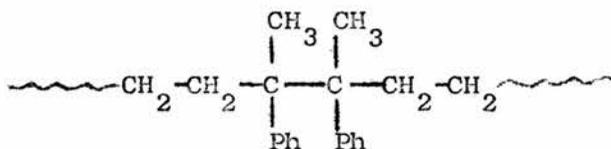
The head to tail polymer is known⁽⁸²⁾ to unzip to monomer but the head to head compound gives less than 1% monomer⁽⁸⁴⁾ at 284°C and gives instead low molecular weight oils.

Thus a reason for the break down behaviour of the head to head polymer may be inferred from the known behaviour of head to tail α -methylstyrene polymer and the foregoing experimental details.

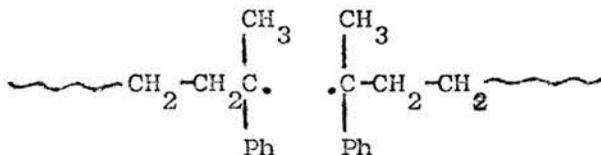
The head to tail polymer decomposes at points along the chain to give two radicals.



The reason for this is that the quaternary carbon atom introduces steric weakness and a relative energy gain due to the delocalisation energy of the free radical product. The radicals may then unzip (length very much greater than 200 monomer units⁽²⁵⁾) as there is an energy gain by producing a monomer unit and a stabilised radical each time a zip takes place. In the case of the head to head sample,



it is, as expected, less stable as there is an even greater carbon steric effect and two highly stabilised radicals are formed.



These radicals do not unzip since they gain no free electron delocalisation energy by so doing. Thus no monomer is formed.

The styrene case is much less simple although many of the above remarks will apply. The chief differences are the presence of more thermally stable main chain bonds and the presence of transferable α -hydrogen atoms.

These are clear-cut examples of various types of degradative mechanism. Other cases, even from this thesis, are much less obvious, but nevertheless some indication of the degradation characteristics can be deduced from thermograms. This must not be over-stated since many other factors must also be known. For instance in the example given above, detailed product analysis would doubtless resolve what does happen to the radicals formed in the thermolysis of the head to head polymer.

2. Another important use is to find the amount and stability of any residue formed in degradation. The organic compounds which have been surveyed in this thesis show little or no residue of any significance, but the inorganic compounds which were looked at in the beginning of the thesis have very significant residues even up to high temperature.

3. Finally, it is possible to compare the relative stabilities of various families or types of compound. This is discussed in the next part.

The foregoing uses are those immediately suggested from this work. There are many other uses to which thermobalances have been and will be put.

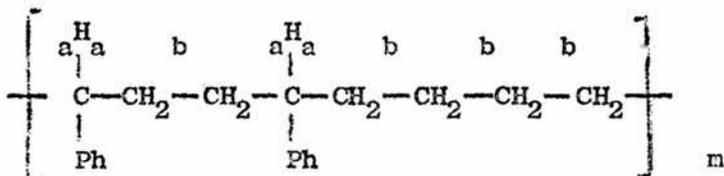
2. The Comparison of Two Series of Copolymers

III and IV

This work was intended as a survey of some ranges of copolymers to assess thermogravimetry as a diagnostic tool, and not as an exhaustive study of their kinetics of degradation. Such a study is at present being carried out in this laboratory. Thus any complete discussion of the results is limited, but certain trends in stability do merit some explanation.

2a. The Styrene Series

The compound shown is the styrene/butane copolymer and will serve as an example.



As a first approximation, there are two types of main-chain bond, a-type between CHPh and CH₂ groups and b-type between adjacent methylene groups. Assuming the relative trend in bond strengths as a basis for argument it is deduced that the b bonds are stronger than a bonds. Thus a possible reason for the situation shown in figure 17 asserts itself. As the number of methylene groups increases, the ratio b:a increases and the main-chain stability should therefore increase. This is the case though some other factor is undoubtedly effective after about n = 4 since the rate of increase of stability does not go on increasing at the same rate as the ratio b:a rises. Thus, while this explanation is only a part of the picture, it may well provide a basis for the mechanism in a more sophisticated argument, when such factors as hydrogen transfer will have to be taken into account.

2b. The α -Methylstyrene Series

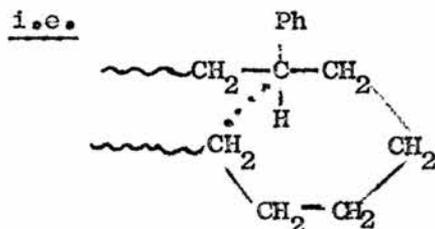
If the above explanation holds it would be expected that

this series should behave in exactly the same way except that the overall relative stability should be diminished. Neither is the case and a maximum appears in the stability curve (see figure 18) at $n = 4$ whilst the overall stability of the more stable styrene copolymers is less than the α -methylstyrene copolymers.

This leads to the conclusion that other factors must play an increasingly important part after about $n = 4$ and should indeed control the degradation.

Other experimental details which must be accounted for are, the wider range of degradation temperatures in the α -methylstyrene series and the anomaly for the $n = 5$ compound of the styrene series.

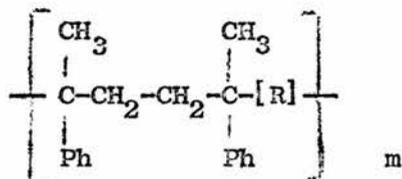
This latter may possibly be due to the formation of a six-membered ring transition state which would facilitate scission.



Product analysis would play an important part in solving this problem.

2c. Other Groups

In the general formula



it was found possible to prepare polymers where [R] was other than a methylene group. The following polymers were degraded, where [R] = $-\text{Si}(\text{CH}_3)_2-$, $-\alpha, \alpha'$ -orthoxylylene $-$ and $-\alpha, \alpha'$ -paraxylylene $-$. As expected (see figure 20), in general, the stability is lower than that of the $\langle \text{CH}_2 \rangle$ group series from about 50% degradation and the curves show a more rapid loss of volatiles resulting in the steeper reaction profiles (compare with figure 15). It is not easy to see the exact reason for this and more work must be done on this problem.

The comparison between the two xylylene polymers is of interest.

The α, α' -paraxylylene compound is more stable than the ortho compound, the difference probably being due to the increase of steric crowding in the molecule and therefore weaker bonding. It is also possible that there may be a stability factor to take into

for the different radicals formed in scission.

The ethylene compound is shown on figure 20 as a "marker" and is high molecular weight unbranched polyethylene from B.P. Chemicals Ltd.

Suggested Work

1. End group effects and molecular weight have not been considered in this thesis and it is quite possible that the "other factors" mentioned earlier in the degradation scheme of the α -methylstyrene series might be of this type. It was hoped that since all the polymers were made at the same place and in the same way by the same person that these factors might be a constant but more work must be done to resolve this point.

2. The dotted lines in figures 17 and 18 indicated an assumed trend. This should be checked by recourse to the appropriate compounds.

3. Product analysis will make a very important contribution to the study of the degradation of these compounds and should be carried out where necessary.

4. The comparison of the head to head and head to tail polymers

is of interest since there is always the possibility of random head to head links in predominantly head to tail polymers, depending on the activation energy difference in the two propagation reactions.

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