THE POLYMERISATION OF SULPHUR

CONTAINING HETEROCYCLES

by

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SUMMARY

A number of α-thio-carboxylic acid anhydrocarboxylates and
α-thio-carboxylic acid anhydrosulphites have been synthesised by
the reaction of the parent α-thio acids with carbonyl chloride
($COCl_2$) and thionyl chloride ($SOCl_2$) respectively.

The base-initiated decomposition of the anhydrocarboxylates
has been studied in some detail using both protic and aprotic bases.
Kinetic studies have been carried out by means of gas evolution
techniques and the reaction products (principally poly-α-thioesters)
characterised.

The characteristics of the reactions of the α-thioacid
anhydrocarboxylates with protic and with aprotic bases are quite
different.   Mechanisms have been proposed that account for these
differences and for the observed effects of ring substituents on
the polymerisability of monomers of this type.

A third type of reaction has been studied, this is the thermal
(non-initiated) decomposition of the anhydrocarboxylate of α-thio
isobutyric acid.   The presence of two methyl substituents makes
this compound relatively stable to attack by bases but has the
opposite effect on its rate of thermal decomposition.   In this
latter reaction a competition was observed between polymerisation
and formation of tetramethyl thioglycollide.   The overall kinetics
of the reaction were studied by both gas evolution and spectroscopic
techniques.

The proposed mechanism involves the primary decomposition of the ring in a first-order rate-controlling process leading to the expulsion of carbon dioxide and the formation of an α-thiolactone intermediate. This highly reactive species then takes part in a non rate-controlling chain addition process leading to polymer formation. The formation of tetramethyl thioglycollide takes place in competition with this latter reaction.

The characterisation of the poly α-thioesters produced in these reactions has been carried out using a variety of techniques. The polymers are highly crystalline but of appreciably lower melting point and thermal stability than their oxygen-containing counterparts.

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1.1 Introduction

Ring opening polymerisation is a mode of polymerisation in which a
cyclic monomer is converted to polymer by a ring opening reaction.
In a few cases such as propiolactone, and bischloromethyl substituted
oxetane it is the only way to synthesize high molecular weight polymers
of a particular structure.   Polymers produced in this way are becoming
commercially important as synthetic fibres, films and surface coatings
on an increasing scale (e.g. nylon 6, polyglycollide and polylactide).
Although many examples of ring opening polymerisations in which the
elements of the rings are completely and quantitatively transferred
to a polymer chain and which are frequently in equilibrium with that
chain are known, there are relatively few in which chain growth takes
place concurrently with the elimination of a small molecule, such as
sulphur dioxide or carbon dioxide.   Lactones, lactams and epoxides
are examples of monomers belonging to the former group whereas N-
carbonic anhydrides (NCAs) of α-amino-acids, anhydrosulphites and
anhydrocarboxylates of α-hydroxy-acids belong to the latter group.
It is the intention of the present study to examine yet another class
of 5-membered hetero-cycles containing sulphur as a hetero-atom.

A recent review on ring opening polymerisation covers many[1]
aspects of the ring opening polymerisation of lactones, lactams,
epoxides, episulphides and NCAs of α-amino acids.   The tendency

towards polymerisation depends upon various factors such as ring strain,
the reactivity of the particular functional group in the ring, the size
and number of substituents and the polarity of the substituents.

Carothers[2] has extensively studied the polymerisability of cyclic
lactones (I) from these points of view.

$$(CH_2)x \text{——————} CO$$
$$O$$
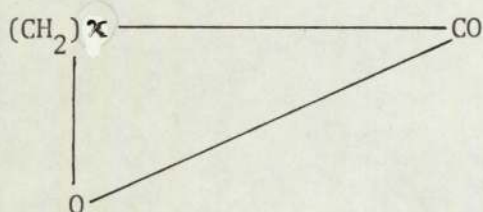
(I)

Thus lactones (I) which are 4, 7 and 8 membered ring compounds in
general tend to polymerise, 5-membered lactones do not polymerise and
6-membered lactones, except for those unsubstituted by at least one-
n-propyl or two methyl groups polymerise readily.

Glycollide, ethylene oxalates and trimethylene carbonates are
considered as modified lactones and they bear some resemblance in
polymerisation behaviour to 6-membered lactones such as δ-valero-
lactone.   Early studies of Bischoff and Walden[3] described the
transformation of glycollide, into a polymer by the action of heat
or zinc chloride catalyst.   They also reported that lactide, the
cyclic dimer of lactic acid polymerised with little difficulty.
Later Hall and Schneider[4] reported that the more highly substituted
tetramethyl glycollide did not polymerise.   High molecular weight

polymers of glycollide $(II; R^1 = R^2 = H)$ and lactide $(R^1 = H, R^2 = CH_3)$ which have fibre and film forming properties have been prepared by the polymerisation of these monomers at high temperatures in the presence of metal oxides and similar catalysts.
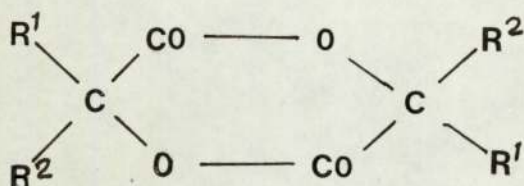
(II)

The structure of lactones (I) is analogous to cyclic amides and yet presents some fundamental differences in polymerisability from these cyclic monomers.

The conversion of lactams (III) to linear polyamides may be accomplished by either hydrolytic or nonhydrolytic processes.
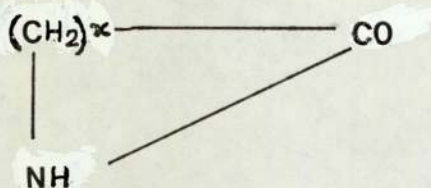
(III)

Here 5 and 6 membered rings undergo polymerisation with difficulty while 7 and 8 membered rings polymerise at high temperatures. Both

alkyl and aryl substituents are found to diminish polymerisability.
Caprolactam[5], which has five methylene units polymerises readily to
give nylon 6, a fibre forming polymer having greater flexibility than
nylon 66.

Among the anhydrides of α-functional acids, N-carboxy α-amino
anhydrides (NCAs),(IV) have been extensively studied:
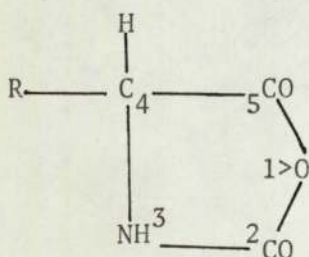
(IV)

These compounds referred to as 'Leuchs[6] anhydrides' were prepared
first by Leuchs in 1906.

Polymerisation of N-carboxy α-amino acid anhydrides to polypeptides
represents an important and interesting process which yields polymers not
easily produced by other techniques.   This reaction which attracted the
attention of many investigators and has been extensively studied during
the last 30 years, proceeds through a chain poly addition i.e. the growth
is determined by the sequence of steps:

$$Pn + M \rightarrow P(n + 1)$$

rather than: $$Pn + Pm \rightarrow P(n+m)$$
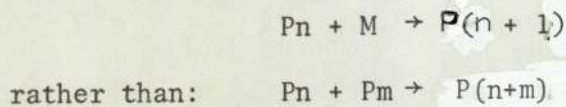
The overall reaction proceeds through initiation and propagation and
often it includes some termination.

More than one hundred NCAs and their corresponding polymers have been synthesized from α-amino acids or from their derivatives. The kinetics of several systems have been thoroughly investigated and much light has been shed on the mechanism of polymerisation. The NCAs undergo polymerisation by a variety of mechanisms, depending on the components of the reacting systems. In some cases the mechanism is quite simple, while some are complex and not clearly understood.

The Leuchs anhydrides are extremely reactive compounds and very sensitive to moisture and requiring storage below -20°C.

NCAs undergo polymerisation thermally but usually initiators such as water, primary, secondary and tertiary amines, salts and strong bases are required.

On heating, NCAs melt sharply with evolution of carbon dioxide and form polyamino-acids.

$$n \quad \begin{array}{c} RCH_4 \underline{\hspace{3cm}} _5CO \\ | \qquad\qquad\qquad \diagdown \\ | \qquad\qquad\qquad 1\ O \\ | \qquad\qquad\qquad \diagup \\ 3 \qquad\qquad 2 \\ NH \underline{\hspace{3cm}} CO \end{array} \xrightarrow{\Delta} [-HNCHRCO-]_n + nCO_2 \qquad (1)$$
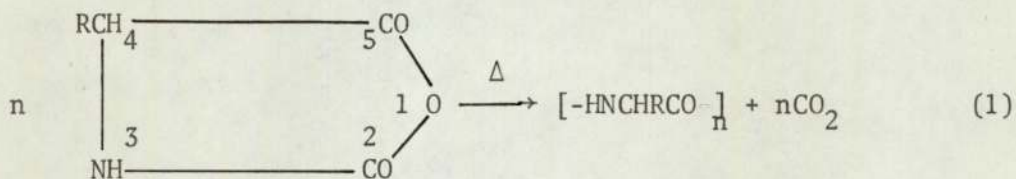
Heyns and Brokmann[7] have demonstrated that the released carbon dioxide is formed exclusively from C-2 atom of the ring. It was suggested that the traces of moisture initiate the reaction.

Another suggestion was that the NCAs reacts via its isomer[8]

$$n \quad \begin{array}{c} \text{RCH} \longrightarrow \text{CO} \\ | \qquad\quad \text{O} \\ \text{NH} \longrightarrow \text{CO} \end{array} \longrightarrow \begin{array}{c} \text{RCH.COOH} \\ | \\ \text{N=C=O} \end{array} \longrightarrow [\text{HNCHRO}]_n + n\text{CO}_2 \qquad (2)$$
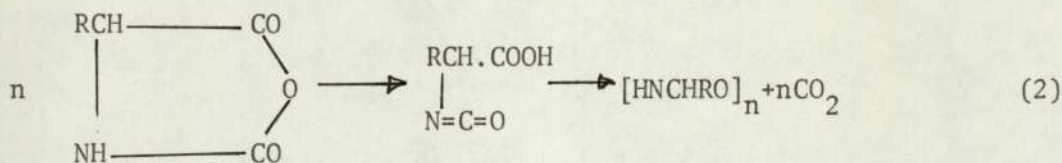
However, the actual reaction mechanism is obscure and the nature of the polymer end group is unknown.

The water catalysed polymerisation of DL-phenyl alanine NCA in benzene was studied at high temperatures by Noma & Tsuchida[9]. The reaction was first order only after a short induction period. Later Woodward & Schram[10] obtained polyamino-acids from NCA dissolved in benzene and it was assumed that traces of water initiate the reaction.

$$\begin{array}{c} \text{RCH} \longrightarrow \text{C} \overset{\text{O}}{\underset{\text{O}}{<}} \\ | \qquad\qquad + \text{H}_2\text{O} \\ \text{HN} \longrightarrow \text{C} \underset{\text{O}}{<} \end{array} \longrightarrow \begin{array}{c} \text{RCH.COOH} \\ | \\ \text{HNCOOH} \end{array} \longrightarrow$$

$$\begin{array}{c} \text{RCH} \longrightarrow \text{COOH} \\ | \\ \text{NH}_2 + \text{CO}_2 \end{array} \qquad (3)$$
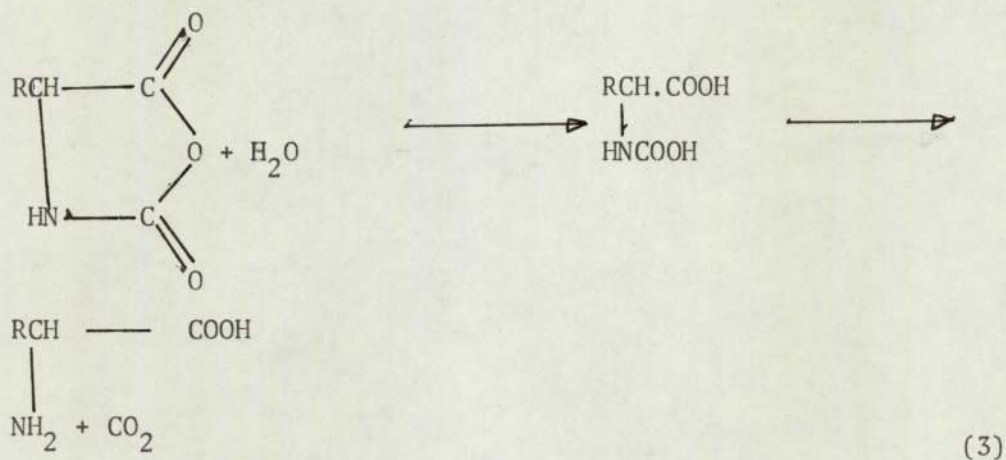
The newly formed terminal amino group reacted with more monomers thus propagating the reaction.

The reaction of NCAs with amines was reported by Fuchs in 1922[11] and by Wessely[12] in 1925.   In an excess of Leuch's anhydride the amine formed from Leuch's anhydride reacts again with a molecule of NCA and produces a dimer possessing a terminal amine group.   Repetitions of these reactions lead to amine terminated polypeptides, hence the normal or simple amine propagated polymerisation of Leuch's anhydride is described by the overall reaction.

$$\sim\!\!\sim COCHR.NH_2 + NCA \longrightarrow COCHRNHCOCHRNH_2 + CO_2 \qquad (4)$$
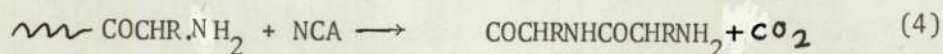
Waley & Watson[13] were the first to report a kinetic study of this process.   They initiated the polymerisation of Sarcosine NCA by a preformed low molecular weight polysarcosine possessing a terminal amine group.   The work of these workers was soon extended by the studies of Ballard & Bamford[14].   They showed that some of the complex kinetic features of sarcosine arose from the catalytic action of carbon dioxide.

Certain apparent anomalies have been observed during the normal amine initiated polymerisation of NCAs.   The NCAs with one or no substituents polymerise easily while NCA with two methyl groups in the α-position (C4) does not yield high molecular weight polymer.   Stereochemical studies have indicated that this is due to the shielding effect of the two methyl groups[15], which sterically hinder the approaching base to react with the carbonyl.

Blout and Karlson[16] have found that tertiary amine served as initiator in the polymerisation of γ-Benzyl-glutamate NCA in dioxane.

The polymer obtained had a very high molecular weight. They found that the molecular weight was independent of $[M]_o/[1]_o$. Weiland[17] suggested a mechanism analogous to that of the reaction between the amine and acid anhydride.

$$\text{(5)}$$

The nucleophilic amine adds to the 5 CO, forming a tetrahedral complex which opens to a Zwitterionic compound. The reaction between the oppositely charged termini of two chains propagates the polymerisation.

Ballard & Bamford[18] suggested a different mechanism. They suggested that the role of the base is to abstract the proton from the -NH-, and the anionic activated NCA thus formed attacks the 5 CO of a non-activated NCA molecule.

$$\text{(6)}$$

More recently, Bamford and Block[19], simplified the previous
mechanism and suggested that the tertiary amine activates the NCA
monomer just by acting as a base and abstracting a proton from the NH.
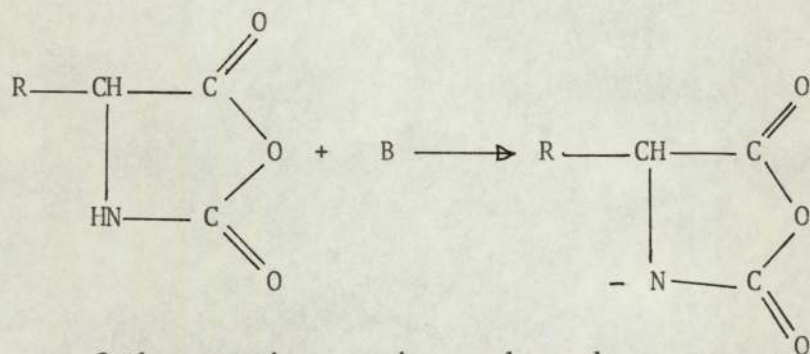
The sequence of the reaction remains unchanged.

(7)
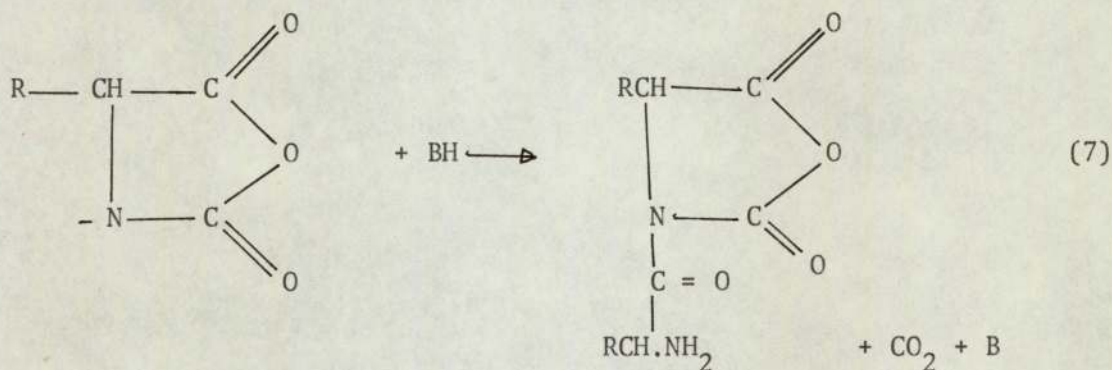
The most suitable method for synthesizing homo and co-polypeptides
from NCAs is by using CH_3ONa and NaOH as initiators in solvents such as
dioxane, benzene, THF etc. The reaction followed a slow induction period
up to 30% conversion and then fast first order reaction. The rate
constant is 100 times faster than that found in the primary and secondary
amine initiated polymerisation, with high molecular weight polymer obtained.
Idelson and Blout [20] suggested a mechanism of reaction between NCA and
methoxide. They depicted two polymerisation pathways. The propa-
gation is via the nucleophilic attack of the 2CO of intact NCA by the

terminal carboxylate ion (mechanism AA) or via the attack on the 5C=O
of an intact NCA by the terminal carbomate ion (mechanism BB).   In
either case, mixed carboxylic-carbamic acid anhydride is formed, which
decarboxylates and forms a peptide bond.   Blout and Idelson assumed a
termination step by wrong addition results in formation of either acid
anhydride or in a urea derivative.

(8)
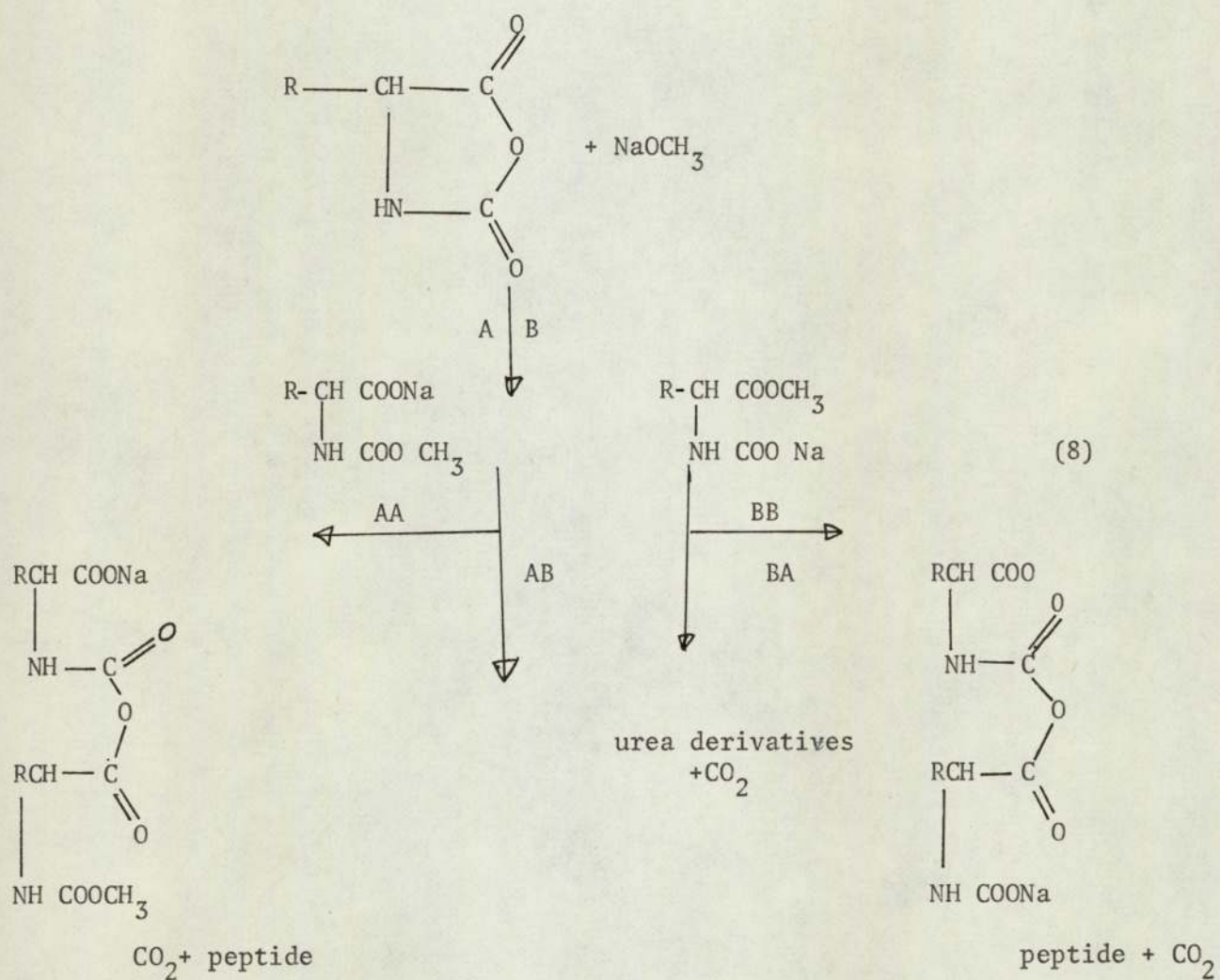
The compounds which share the greatest resemblance to NCAs are
anhydrosulphites and anhydrocarboxylates of α-hydroxy carboxylic acids.
The anhydrides with one or no substituents polymerise very easily.
Whereas for some cases with two substituents in the α-position they
polymerise only thermally or do not polymerise at all.

Among the anhydrides of α-hydroxy carboxylic acids, anhydrosulphites have been comparatively and widely studied.   The cyclic monomer is expressed by the general formula as shown below.

$$R^1 \!\!-\!\! \underset{5}{\overset{\overset{\displaystyle R^2}{|}}{C}} \!-\!\!-\!\! \underset{\underset{2}{|}}{\overset{\overset{4}{}}{}} \!\!-\!\! \underset{SO}{\overset{CO}{\diagdown_{}^{3}O\diagup_{2}}}$$

R¹⸺C₅⸺⸺CO
           4   \
           3   O
   |1   2   /
   O ⸺⸺⸺ SO
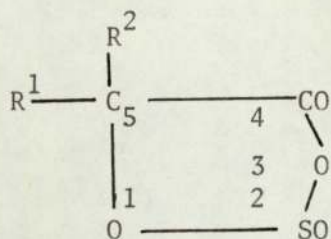
(V)

The synthesis of anhydrosulphite derivatives was first reported by Blaise & Montagne in 1926[21]. They prepared chlorosulphinate of glycollyl chloride by the reaction of glycollic acid with thionyl chloride.   Later, they extended the work to lactic and α-hydroxy isobutyric acid and reached similarly with thionyl chloride.   The products obtained did not contain any chlorine and were designated as anhydro-sulphites of α-hydroxy compounds.   It was also reported that anhydro-sulphites of glycollic, lactic and isobutyric acid decomposed to polymer with liberation of sulphur dioxide when heated at high temperatures.

Further investigations showed that in the presence of nucleo-philic reagents, such as alcohols, amines and water, they liberated sulphur dioxide yielding esters, anilide and parent hydroxy acid respectively.

Alderson[22] developed a method for production of high molecular weight poly α-ester from the α-hydroxy isobutyric acid-anhydrosulphite.

He showed the controlled elimination of sulphur dioxide from
α-hydroxy-isobutyric acid anhydrosulphite in dry inert solvents such
as benzene, chlorobenzene and in absence of initiators gave polymers
of high molecular weight. The temperature of the thermal decomposition
of the anhydrosulphite to polymer was governed by the boiling point of
the solvent. It was observed that the presence of moisture reduced the
molecular weight of the polymers.

Rose and Warren[23] later extended the work of Alderson to a series
of α-hydroxy acids. The anhydrosulphites were prepared by minor
adaptations of Alderson's procedure, and showed that thermal decompo-
sition of these compounds gave sulphur dioxide and the polyesters.

$$R - C(R^1) - CO, O, SO, O \longrightarrow [O.CRR^1CO]_n + nSO_2 \qquad (9)$$

V

	a	b	c	d	e	f	g
R	Me	Me	Et	Me	CH_2Cl	H	$(CH_2)5$
R^1	Me	Et	Et	CH_2Cl	CH_2Cl	H	

Polymers of high molecular weight were readily obtained by
following Alderson's procedure from (V.a) and using chlorobenzene as
the solvent. The other purified anhydrosulphites from (Vb-Vd) gave
polymers of lower molecular weight The impure anhydrosulphites
(Vf and Vg) gave polymers of very low molecular weight. The bis-

chloromethyl derivative (Ve) gave low yields of polymer, the greater portion of it being decomposed to SO_2, CO, and sym-dichloro-acetone. It was found that pyridine increased the rate of polymer formation from (Va) and enabled high yields of polymer to be obtained from (Ve) but the later polymers were of very low molecular weight.

Despite the varying degrees of polymerisations the technique of Alderson to synthesize poly α-esters offers a useful synthetic route. Although linear polyesters are in general well studied, the simplest members of the group, with only one atom between repeat ester units have received comparatively little attention. This is due to lack of general synthetic routes. The direct self esterification of α-hydroxy acids has been successfully applied for forming polyester. Of the many esterification methods commonly used, this type of poly-esterification has got many disadvantages. The reaction is often slow and is carried out in an inert solvent, under reduced pressure, or a flow of nitrogen. The simplest technique uses heat alone although Du Pont have employed this technique for synthesising poly-glycollic ester with an antimonytrichloride as catalyst. Their method is limited only to polyglycollic and polylactic esters however.

A somewhat better method consists in converting the α-hydroxy acid to the corresponding lactide and glycollide by intramolecular cyclisation. The lactides and glycollides may be polymerised at elevated temperatures in the presence of a suitable catalyst. This method has got some structural disadvantages. Hall demonstrated that tetramethyl glycollide inhibits polymerisation. This fact and

the failure of some of the α-hydroxy acids, to cyclise smoothly, limits this method.

Another method consists in reacting a di-halide with a metal salt of the dicarboxylic acid. This method has also proved to be unsuitable for general use.

So in comparison to these methods, Alderson's method proved more versatile.

More recently Ballard and Tighe[24] were successful in obtaining pure samples of anhydrosulphites which was not possible with Alderson's procedure. They developed a technique involving the use of metal salts of the α-hydroxy acids with thionyl chloride. This technique was used to prepare lactic anhydrosulphite which could not be prepared in pure state by reacting thionyl chloride with lactic acid. The lactic acid anhydrosulphite was purified by treatment with triethylamine to remove considerable chlorine impurities. In the same series of experiments, glycollic acid anhydrosulphite and isobutyric acid anhydrosulphite were synthesized by applying the same method and the chlorine impurities were removed by treating the compound with triethylamine in ether.

Ballard and Tighe[25] first investigated the mode of polymerisation of glycollic, lactic and isobutyric acid anhydrosulphites. They concluded that anhydrosulphites thermally decompose to form a highly reactive α-lactone intermediate which takes part in a rapid propagation

$$R^1 \overset{\overset{\displaystyle R^2}{|}}{\underset{\underset{\displaystyle O \rule{1.5em}{0.4pt} SO}{|}}{C^1}} \diagdown \overset{CO}{\underset{O}{\diagup}} \longrightarrow R^1 \overset{\overset{\displaystyle R^2}{|}}{\underset{\underset{\displaystyle O}{|}}{C}} \diagdown \overset{CO}{\diagup} + SO_2$$

α-lactone   (10)

with chain end hydroxyl group.   The anhydrosulphites of lactic and
glycollic acid can be polymerised by initiators such as water, alcohol
and amines.   Ring opening and propagation takes place by direct
nucleophilic attack at the $C_{(4)}$ carbonyl of the anhydrosulphites in a
manner similar to normal amine initiated polymerisation of NCAs.

$$RNH_2 + R^1 \overset{\overset{\displaystyle R^2}{|}}{\underset{\underset{\displaystyle O \rule{1.5em}{0.4pt} SO}{|}}{C}} \diagdown \overset{CO}{\underset{O}{\diagup}} \longrightarrow RNH \rule{1em}{0.4pt} \overset{\overset{\displaystyle O}{\|}}{C} \rule{1em}{0.4pt} \overset{\overset{\displaystyle R^1}{|}}{\underset{\underset{\displaystyle R^2}{|}}{C}} \rule{1em}{0.4pt} OH \quad (11)$$
$$+ \; SO_2$$

The success of these workers in obtaining pure samples of anhydro-
sulphites of glycollic, lactic and isobutyric contrasts with the products
obtained by Rose & Warren, Tighe and co-workers[27] later extended
their work to synthesize a series of α-hydroxy anhydrosulphites.   A
general list of the compounds synthesized, purified and polymerised
are given below

$$R^1 \overset{\overset{\displaystyle R^2}{|}}{\underset{\underset{\displaystyle O \rule{1.5em}{0.4pt} SO}{|}}{C}} \diagdown \overset{CO}{\underset{O}{\diagup}} \longrightarrow [\, O \rule{1em}{0.4pt} \overset{\overset{\displaystyle R^1}{|}}{\underset{\underset{\displaystyle R^2}{|}}{C}} \rule{1em}{0.4pt} CO \,]_n + n\,SO_2$$

(12)

	1	2	3	4	5	6	7	8	9	10	11
R^1	H	H	Me	Me	Et	Pr	Bu	$(CH_2)_3$	$(CH_2)_4$	$(CH_2)_5$	$(CH_2)_6$
R^2	H	Me	Me	Et	Et	Pr	Bu				

The anhydrosulphides synthesized were liquid and contained considerable percentage of impurity.   The percentage of chlorine impurity in the anhydrosulphites were determined by potentiometric titrations and purified by initial treatment with triethylamine or preferably silver oxide and distillation under reduced pressure.

The reaction mechanisms have also been put forward for the poly- merisation of anhydrosulphites which have been synthesized in later studies.   The mechanism is essentially the same as described before. Thus the anhydrosulphite polymerises thermally via the formation of an extremely active α-lactone intermediate which takes part in a rapid propagation step by reaction with a hydroxyl group associated with the growing chain end.   The iniation mechanism involving direct hydroxyl attack at the ring has also been postulated but the latter mechanism seems to be insignificant in comparison to thermal decomposition mechanism except where at least one of the substituents $C(5)$ is a hydrogen.

As the size of the substituents on the anhydrosulphite ring increases, the rate of polymerisation also increases although in obtaining high molecular weight polymers from anhydrosulphites purity of the monomers remains the most important factor.   With large substituents such as phenyl groups, a secondary fragmentation process

becomes appreciable.   This leads to the comparative formation of
ketone and carbon monoxide in addition to sulphurdioxide   and polymers.

From the kinetic studies of the polymerisations of NCAs and
anhydrosulphites two major differences have been observed.   The
terminal group of the resultant polypeptide is of higher nucleo-
philicity than the terminal hydroxyl group of the poly α-ester, thus
rendering direct attack on the ring by the former terminal more
reactive than the latter.   With the increase of the substituents on
the NCA ring, the initiated polymerisation is sterically hindered,
but in cases of anhydrosulphites, an alternative route of polymerisation
is provided by the facile thermal extrusion reaction.

The anhydrocarboxylates of α-hydroxy carboxylic acids (VI) have
been less extensively studied than the corresponding anhydrosulphites.
W. H. Davies[28] first published work on the synthesis of anhydro-
carboxylates of α-hydroxy carboxylic acids including those derived
from glycollic ($R^1=R^2=H$), lactic ($R^1=H_2$ $R^2=CH_3$) and mandelic
($R^1=H$, $R^2=C_6H_5$) acids by direct reaction with phosgene.

$$
\begin{array}{c}
R^2 \\
| \\
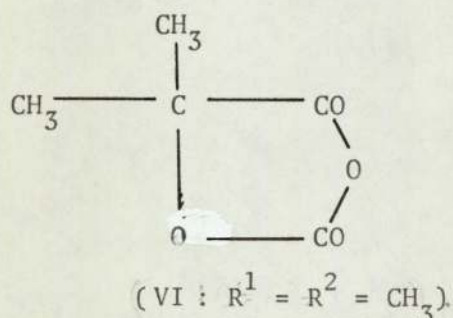R^1 \underline{\qquad} \underset{5}{C} \underline{\qquad}_4 CO \\
\end{array}
$$
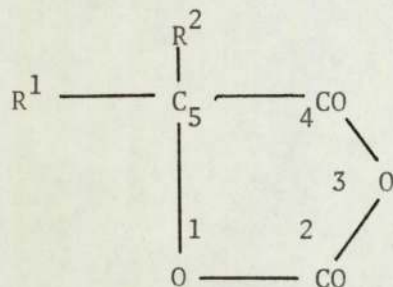
VI

These anhydrocarboxylates were purified by recrystallization from
anhydrous, low boiling solvents such as ether.   Davies mentioned the

formation of polyglycollic ester from the glycollic acid anhydro-
carboxylate when this compound was heated at 100°C for 18 hours,
whereas lactic acid anydrocarboxylate was recovered unchanged when
heated at the same temperature and for the same period.   Both anhydro-
carboxy derivatives decomposed with evolution of carbon dioxide when
treated with amine and water, resulting in a polymeric residue, but
no definite attempt was made to prepare high molecular weight
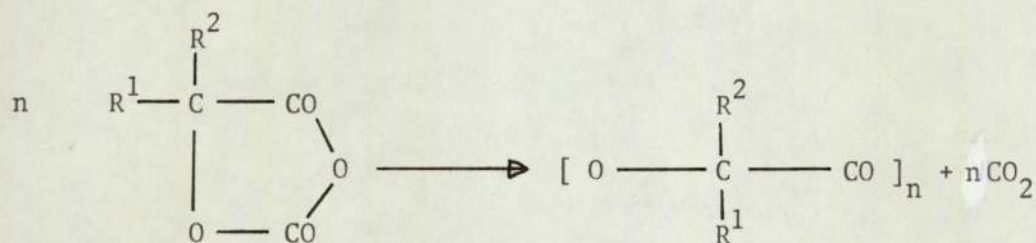polymers.

Later Tighe[29] attempted to synthesize anhydrocarboxylates of
α-hydroxy carboxylic acids based on the work of Davies.   Glycollic
acid anhydrocarboxylate could not be obtained in pure state,   but
the author was successful in synthesizing lactic and mandelic acid
anhydrocarboxylates although the methods for purification described
by Davies such as crystallization or fractional distillation were
found unsatisfactory in the preparation of compounds of high purity.
The technique used by Davies was unsuccessfully applied to the
synthesis of the previously unknown anhydrocarboxylate of α-hydroxy
isobutyric acid.   A successful modification involved simultaneous
addition of phosgene in ether and pyridine in ether to the α-hydroxy
acid in the same solvent at low temperature (< 0°C).   The
anhydrocarboxylate obtained by this method is a lachrimatory solid,
having a melting point of 38°C when pure.

$$
\begin{array}{ccc}
 & CH_3 & \\
 & | & \\
CH_3 \!\!-\!\!\!-\!\!\!-\!\! C \!\!-\!\!\!-\!\!\!-\!\! CO & \\
 & | & \diagdown \\
 & & O \\
 & | & \diagup \\
 & O \!\!-\!\!\!-\!\!\!-\!\! CO &
\end{array}
$$

(VI : R^1 = R^2 = CH_3).

The same author[30] studied the mode of polymerisations of the
anhydroxylate.   Thermal decomposition of isobutyric anhydrocarboxylate
in dry inert solvents was found to obey first order kinetics yielding
principally carbon dioxide and isopropylidene carboxylate oligomers
It was concluded that α-hydroxy isobutyric anhydrocarboxylate was
thermally too stable to polymerise ($t_{\frac{1}{2}}$ = 1050 hours, 90°C) and the
polymerisation of this compound by nucleophilic initiation and bimolecular
propagation involving successive attack of the ring was sterically
hindered by two methyl groups in the α-position.

In the case of other members of the anhydrocarboxylate series such
as glycollic and lactic, polymerisation by nucleophilic initiation is
possible, but thermal polymerisation would of course be very slow in
comparison with the corresponding anhydrosulphites.

More recently Smith and Tighe[31] extended the work of Davies to
a series of anhydrocarboxylates.

$$n \quad R^1\!-\!\underset{\underset{O\,-\,CO}{|}}{\overset{\overset{R^2}{|}}{C}}\!-\!CO \diagdown O \longrightarrow [\,O\!-\!\underset{\underset{R^1}{|}}{\overset{\overset{R^2}{|}}{C}}\!-\!CO\,]_n + n\,CO_2$$

(13)

	a	b	c	d
R^1	H	CH_3	C_6H_5	CH_3
R^2	C_6H_5	C_6H_5	C_6H_5	C_6F_5

In the synthesis of these compounds, copper salts of the corres-
ponding α-hydroxy acids were used instead of the α-hydroxy acids
themselves.   The use of copper salts has two important advantages over
direct use of the α-hydroxy acids.   First it may be obtained in anhydrous
state and secondly it minimises the formation of α-chloro-acid derivatives
as impurities during the reaction.   The purification of the anhydro-
carboxylates by sublimation was reported as preferable to recrystalli-
sation.

The kinetic studies of these and related compounds have shown that
the anhydrocarboxylates of α-hydroxy acids may be polymerised if the
thermal stability of the ring is lowered by the introduction of bulky
C(5) substituents (e.g. VI, $R^1 = R^2 = \phi$).   Alternatively polymerisation
can be achieved if the C(4) carbonyl is activated by an introduction of
an electron withdrawing group at C(5)   In the latter case at least
one side of the ring must be   free from steric hindrance.
$$\text{(i.e. VI, } R^1 = H, R^2 = \phi)$$
Preliminary published work suggests that both thermal and hydroxyl
initiated mechanisms occur in this class of compounds.   In addition,
a new mechanism, involving the use of tertiary (aprotic) bases has
been noted.

$$\text{(14)}$$

A logical extension of these investigations of the relationship
of cyclic monomer structure to polymerisability would be the intro-
duction of sulphur in place of oxygen as in VII.

$$R^1 \!-\!\!\!-\! \underset{\underset{S}{\overset{\overset{R^2}{|}}{\underset{|}{C}}}\!-\!\!\!-\!\!\!-\! \overset{CO}{\underset{CO}{\diagdown\!\!\!\!\diagup}}O$$
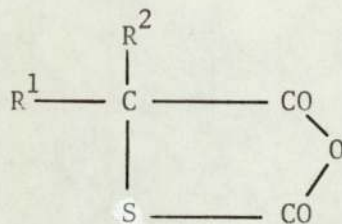
VII

These compounds may in principle be derived from α-thio-acids,
such as thioglycollic ($R^1 = R^2 = H$), thio-lactic ($R^1 = H$, $R^2 = CH_3$)
and thioisobutyric ($R^1 = R^2 = CH_3$) acids.

It is thought that the presence of sulphur in the ring may
considerably affect the reactivity of this type of compound.   The
thioanhydrocarboxylates may be more reactive than the corresponding
anhydrosulphites and anhydrocarboxylates of α-hydroxy carboxylic acids,
as sulphur is a larger molecule causing the ring to become more un-
stable. The studies of these compounds will, however, resolve this
speculation and it is hoped, provide more information on the relative
effects of sulphur and oxygen on polymer properties.

Very little work has been carried out in this field.   In 1959,
Schöberl[32] published results of his studies of polythioglycollide.
The work was mainly limited to the synthesis of the polymers.   In
addition, while the present work was in progress, Bührer and Elius[33,34]
published an account of the synthesis of polythioglycollide and poly-
thiolactide from compounds of type VII. No kinetic studies were carried
out however.

1.2 Scope and object of the present work

Poly α-esters synthesized from cyclic monomers are gradually increasing in number, as are the potential applications especially in the field of speciality polymers. The main object of the present work is to synthesize thioanhydrocarboxylates from α-thio-acids and to study the kinetics and mechanistic aspects of the polymerisation together with some aspects of the properties of the resultant polymers.

The initial aim of the work is to develop a synthetic technique which will give optimum yield and purity. One primary aim of this part of the work is to synthesize thioisobutyric anhydrocarboxylate which has not been previously reported, and which represents an important structure in the study of monomer polymerisability. The reactivity of the later compound will thus be compared with that of α-amino isobutyric acid anhydrocarboxylate and anhydrides of α-hydroxy isobutyric acid.

Subsequent work will involve the assessment of the most suitable route for the polymerisation of the anhydrocarboxylates. Initiated polymerisation is in many ways preferable to thermal polymerisation which generally involves higher temperature and the possibility of competing fragmentation reactions. The major objective of the work is the establishment of the mechanisms for the polymerisation reactions and the rationalisation of the results on a structural basis. It is hoped to compare the properties of the polymers with those of the corresponding poly-α-esters.

CHAPTER II

EXPERIMENTAL METHODS

2.1 Apparatus and Techniques

1. Distillation under reduced pressure: Distillation and fractional distillation were carried out in the apparatus shown in figure 2.1. This consisted of a round-bottomed flask (A) of 250 ml capacity, which was connected with a still-head (B). This again was fitted with a thermometer (C) and water condenser (D) which was connected with a receiver (E) and at this point with a vacuum-line. The temperature of the receiver during distillation was kept by a cold trap. The contents of the flask (A) were agitated by a magnetic follower which was actuated by a magnetic stirrer. The magnetic stirrer was combined with a hot plate (G). The temperature of the water-bath (H) was maintained by the hot plate. Distillation and fractional distillation of solvents, reagents and anhydrosulphites were conveniently carried out in this apparatus. After distillation nitrogen gas was passed through the vacuum line to the distillate, from a nitrogen cylinder. Thus distillates were collected in an atmosphere of nitrogen, immediately stoppered and transferred for storage to a dry box, where appropriate drying agents such as molecular sieve were added. Materials of limited stability such as anhydrosulphites were stored in a refrigerator.
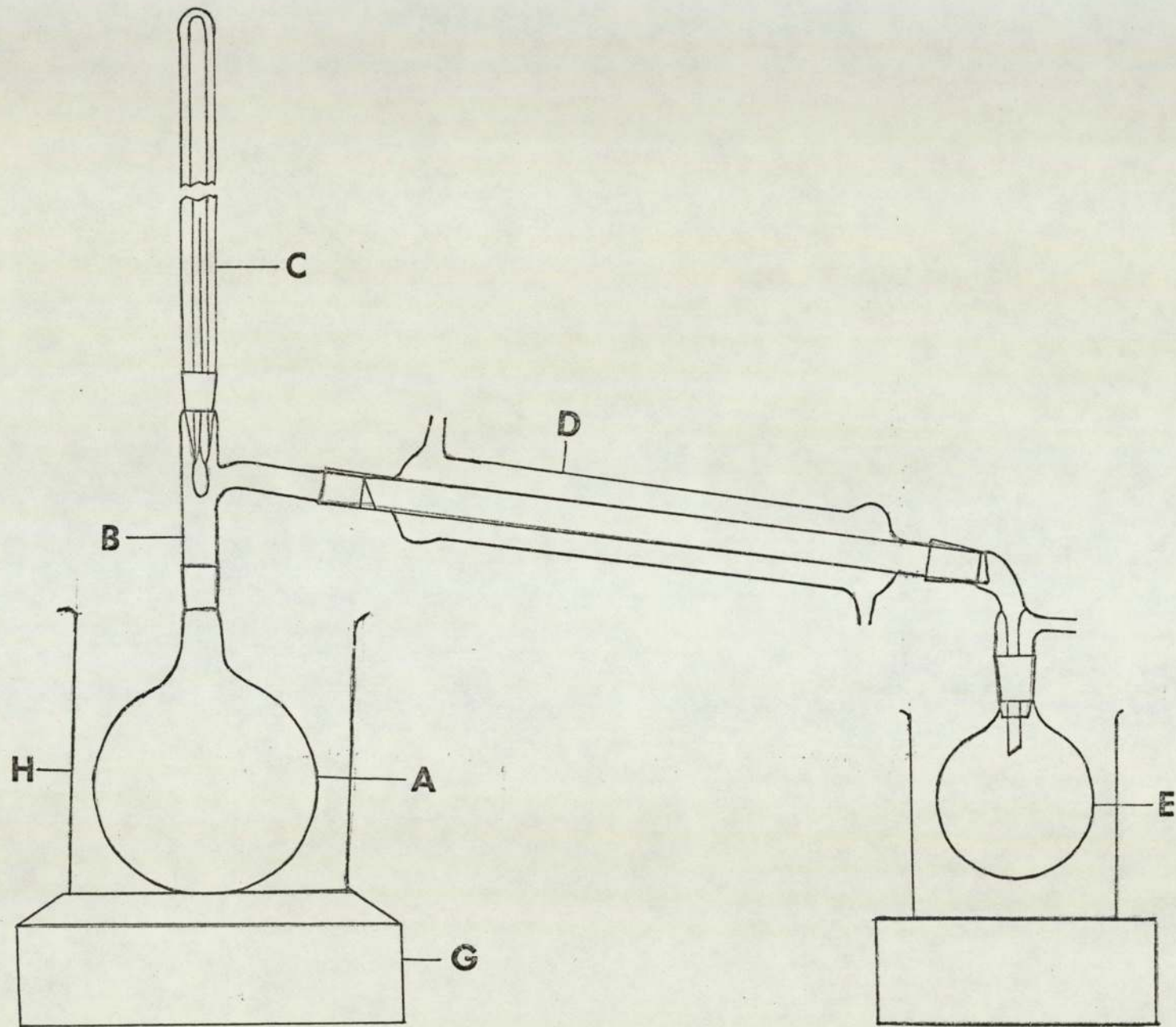
Fig. 2.1   Distillation Apparatus.

2. Dry-Box: Substantially dry or inert atmospheres were needed for handling anhydrides and various solvents and reagents. Two types of dry-boxes were used for this purpose.

(i) Gallenkamp Model X Glove Box: This dry-box was used for manipulation of anhydrides, reagents and solvents in an atmosphere of nitrogen. The moisture was completely removed from the dry-box by means of a vacuum pump, nitrogen was then passed into the dry-box from a cylinder, through one of the glass spirals. The excess nitrogen was passed out through another glass spiral. In addition, drying agents, such as phosphorous pentoxide, silica gel and molecular sieve were kept inside the chambers in small glass beakers to ensure that the atmosphere inside the dry-box was substantially moisture free.

(ii) Gallenkamp Model MA 950 Glove Box: This dry-box was used for manipulations of the anhydrocarboxylates which are very sensitive to moisture and needed a completely dry atmosphere. Thus moisture was removed from the chambers of the dry-box by means of a circulating pump used in conjunction with two glass spirals immersed in cold traps containing solid carbon dioxide/acetone mixture. In addition as before drying agents were kept inside the dry-box. The moisture content was monitored by a Shaw electronic hygrometer and maintained below 20 parts per million.

3. Vacuum Sublimation: This technique was used in the purification of thio-anhydrocarboxylates. Vacuum sublimation was carried out in the apparatus shown in figure 2.2. The apparatus was completely dried in an oven at a temperature of 110-115°C for a few hours and then transferred to a dry-box. All the joints were treated with high vacuum silicon-grease to avoid any leakage during sublimation. The impure anhydro-
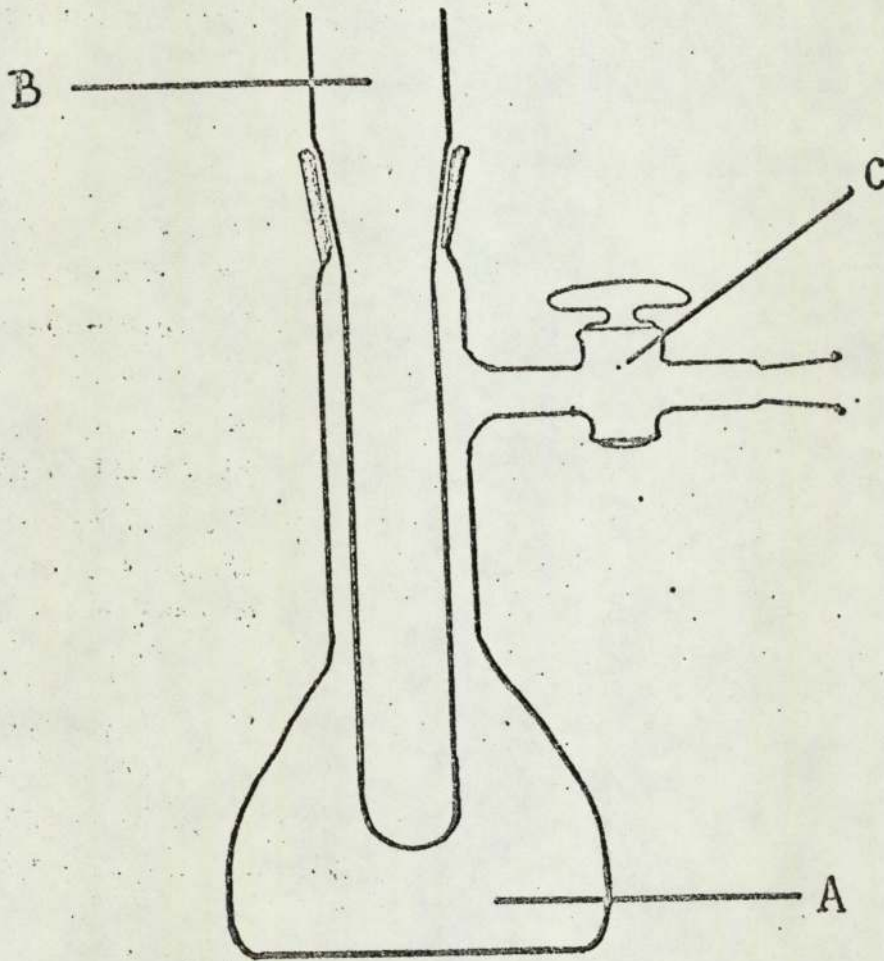
FIGURE 2.2 Vacuum Sublimation Apparatus

carboxylates were placed in the main chamber (A), the cold finger (B) was re-connected to the main chamber and finally the tap (C) was closed before the apparatus was taken out of the dry-box. The vacuum sublimer was placed in a water-bath and connected to the vacuum line through the cone (D). The cold finger (B) was then filled with dry-ice and the vacuum sublimer evacuated by opening the tap (C). Sublimation of the anhydrocarboxylate was carried out at an empirically determined temperature (usually 10°-$20°C$ below the melting point of the compound) for a period depending on the amount of the compound taken. When the sublimation was over the tap (C) was closed, and the apparatus was transferred to the dry-box. The anhydrocarboxylate was removed from the cold finger in a pure state, collected in a sample bottle and stored in dry-ice before use.

4. Infra-Red Spectra: Infra-red spectra were taken in carbon tetrachloride solution or kBr disc, with the Perkin-Elmer infra-red spectrophotomer Model 457. The details of the state of the samples are described where appropriate in the text.

5. Kinetic Measurements: Two types of kinetic apparatus were used for the measurements of rate of decomposition of the thio-anhydrocarboxylates, one for low temperature kinetic measurement and the other for high temperature measurements. Both types of apparatus were dried in an oven at a temperature of 110°C for a few hours before use.

(a) Low temperature kinetic measurement (25°-45°C)

The apparatus which was developed and used by Waley and Watson, and later modified by Ballard and Bamford, and used by many others is shown in figure 2.3. The reaction vessel (A) was connected by means of a

glass spiral to a cone (B). At the top the reaction vessel was provided
with a quickfit socket (C), which was closed by a quickfit cone (D),
having a hook attached to the lower end, enabling a glass bucket (E)
normally used for initiators, to be suspended above the reaction medium
and dropped into the reactants when required. Gas pressure, which
increased during the course of the reaction, was measured by connecting
the vessel to the manometer unit by means of cone (B) via socket (F).
The rise in mercury level in the manometer (G), was measured directly by
reference to the calibrated mirror scale (H). The initiated decompo-
sition of the thio-anhydrocarboxylates was carried out in this apparatus
which was maintained at a constant temperature by means of a water bath.
A hypodermic syringe was used to measure the reactants and injected into
the reaction vessel. The reaction vessel was assembled and sealed inside
the dry-box to avoid moisture, and then joined to the manometer unit out-
side the dry-box, and the whole system was evacuated by opening the
tap (I), by a high vacuum pump through the socket (J). Then the kinetic
apparatus was placed in the thermostat bath and allowed a few minutes to
attain the temperature of the bath. When the system attained the
temperature of the bath, the reaction was started by dropping the bucket
containing the initiator into the reactants and the rise in pressure was
noted at appropriate time-intervals and continued until the decomposition
of the anhydrocarboxylate was complete.

When more reactive initiators such as pyridine and benzylamine
were used to initiate the decomposition of the anhydrocarboxylates,
reaction started as soon as the apparatus was evacuated, even at room
temperature. This was due to the small amount of pyridine or benzylamine
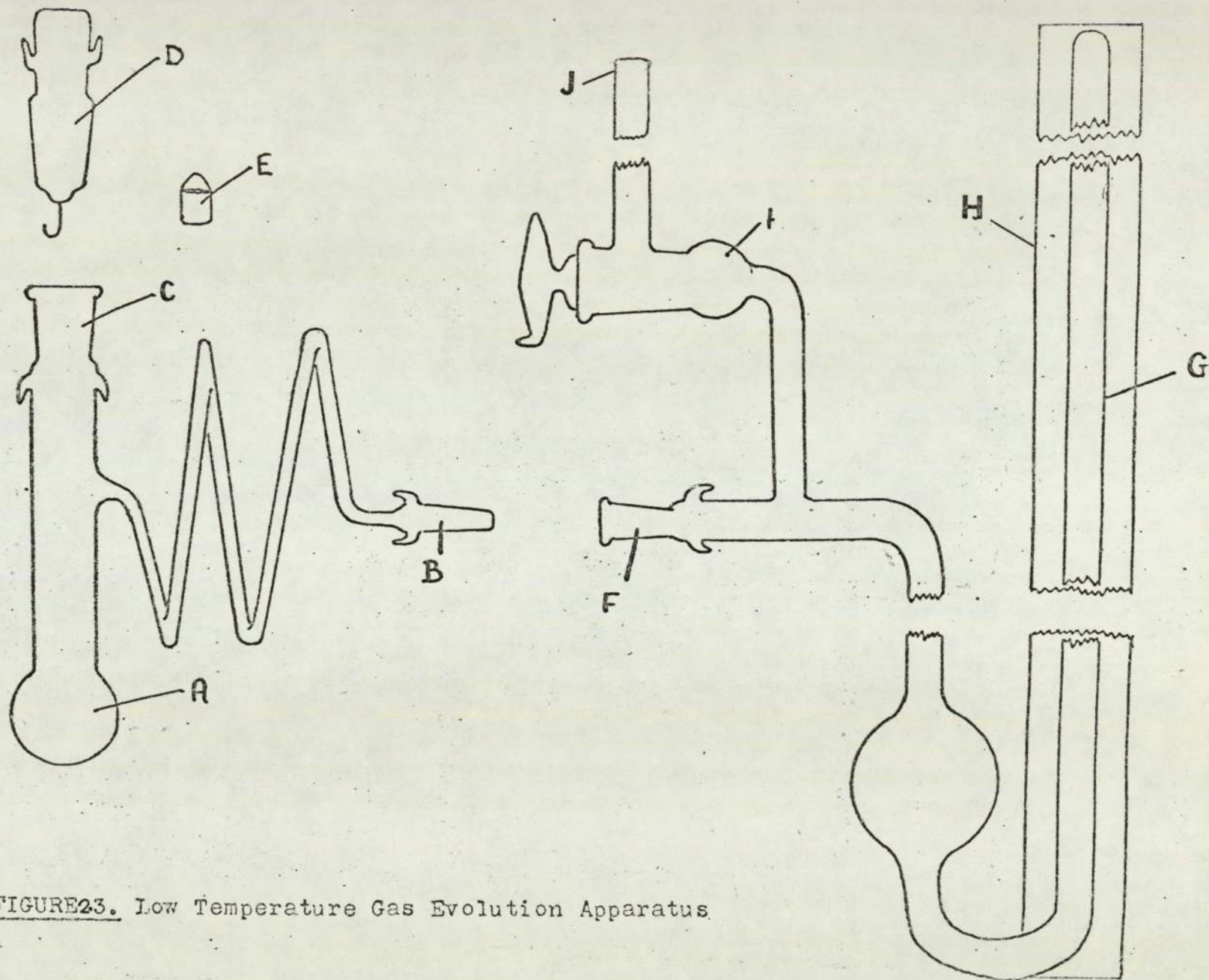
FIGURE 23. Low Temperature Gas Evolution Apparatus

in the vapour phase, reacting with the anhydrocarboxylates before the bucket has been dropped from the hook. In such cases it was not possible to calculate accurately the rise in pressure in the manometer. This was avoided by sealing the socket (C) by means of a suba-seal and injecting the initiatiors directly from a precision hypodermic syringe. This injection marked the start of the reaction.

(b) <u>High temperature kinetic measurements</u> (Temperature range $50°-150°C$)

The previous kinetic apparatus was found unsuitable for high temperature kinetic measurements. The trouble originated from the ground glass joints which tend to leak after a short time at higher temperatures. Tighe modified the apparatus as shown in figure 2.4. This apparatus was mainly used for thermal decomposition of anhydrides at higher temperature. The anhydrocarboxylates in solution were measured by a hypodermic syringe and introduced into the large reaction vessel through the side tube. The whole apparatus was then evacuated by a vacuum pump and the side tube was sealed in an oxygen flame while the entire system was under vacuum. The apparatus was then placed into a thermostat oil-bath. The rate of gas evolution was measured by following the rise of mercury thread in the manometer, using a cathotometer.

(c) <u>Agitation</u>

All types of reaction vessels were agitated by means of a Pifco vibrator. The application of the vibrator to the clamp or stand holding the apparatus was found to provide sufficient agitation for the reaction medium. The apparatus was agitated before taking each pressure reading to ensure that carbon dioxide in the gas phase was in equilibrium with that in the liquid phase.
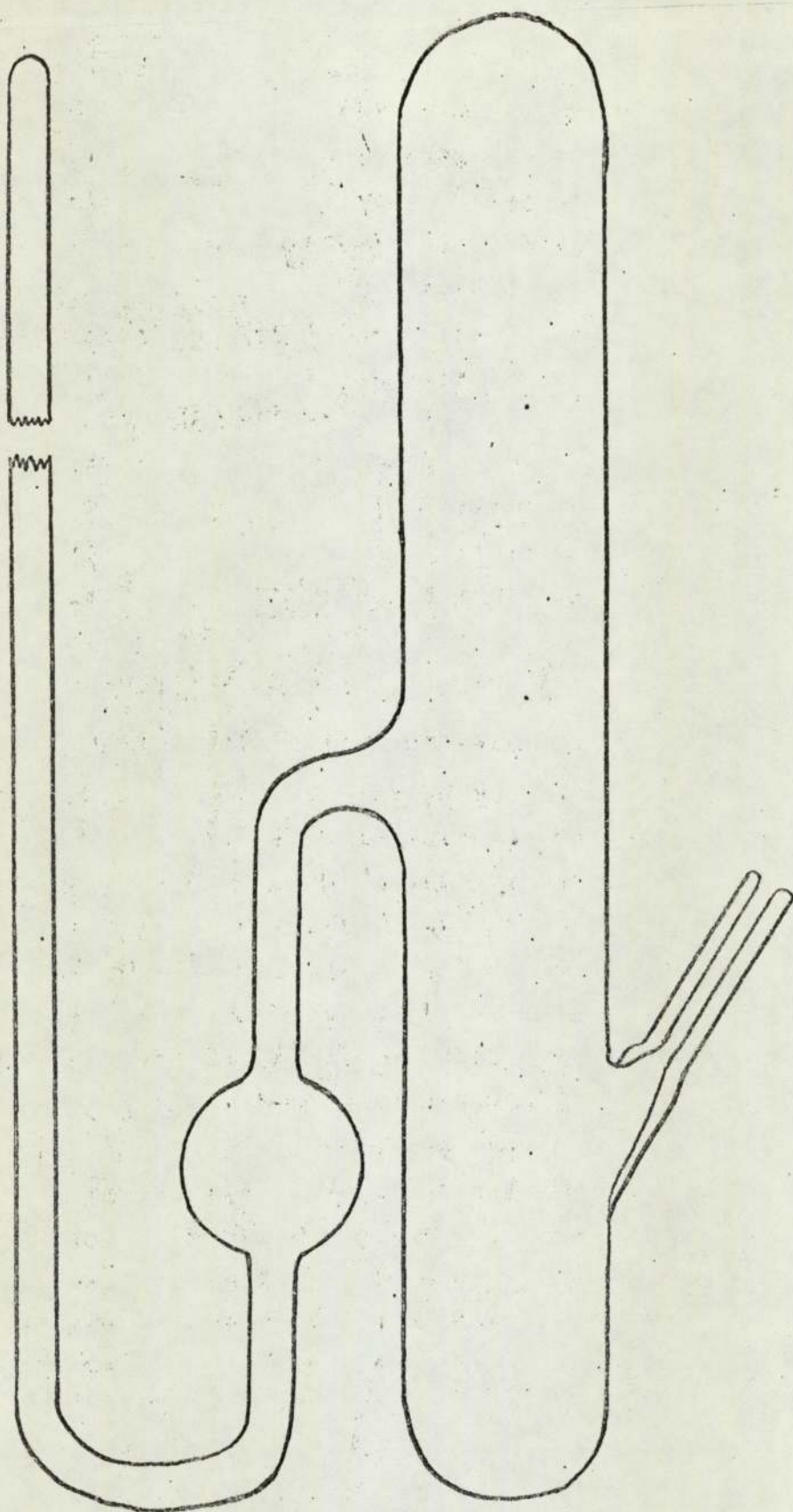
FIGURE2.4.   High Temperature Gas Evolution Apparatus

Measurement of reaction rates by gas evolution techniques:

The use of gas evolution techniques to follow the course of chemical reactions is well established.   Waley and Watson, and Ballard and Bamford followed this technique of measuring rates of evolution of carbon dioxide and related these to the rate of decomposition of N-carboxy-α-amino-acid anhydrides.   Later Tighe and many others extended this technique to study kinetics of anhydrosulphites and anhydrocarboxylates of α-hydroxy acids. A relationship between manomer concentration and the gas pressure has been derived for the general case in which one mole of monomer decomposes to yield a one mole of a gas, the initial monomer concentration $[M]_o$ being related to the monomer concentration at any instant $[M]$ and the concentration of the gas the decomposition has produced $[G]$, by the equation:

$$[M]_o = [M] + [G] \tag{15}$$

If the reaction proceeds to completion,

$$[M]_o = [G]_\infty \tag{16}$$

For an ideal gas in a system at constant volume and temperature the pressure P is directly proportional to the number of moles of gas produced, that is

$$P_\infty \ \alpha [G]_\infty \tag{17}$$

Introducing a proportionality constant π:

$$\pi P_\infty = [G]_\infty = [M]_o \tag{18}$$

If P is the pressure of the gas at any instant, equation gives

$$\pi P = [G] = [M]_o - [M] \tag{19}$$

Equations (4) and (3) now combine to yield

$$\frac{[M]}{[M]_o} = \frac{\pi (P_\infty - P)}{P_\infty} = \frac{P_\infty - P}{P_\infty} \tag{20}$$

Re-arranging

$$\frac{[M]_o - [M]}{[M]_o} = \frac{P}{P_\infty} \tag{21}$$

Eqns. 20 and 21 are used to calculate rate data and kinetic parameters.

There are three requirements for these equations to function properly without modifications. First the temperature of the baths must be maintained at constant temperature throughout the reaction. Secondly, the volume of the reaction vessel should not change and finally the evolved gas must be near to ideal.

These three requirements were maintained during kinetic studies of the α-thio-anhydrocarboxylates by careful experimental technique, and the fact that evolved carbon dioxide gas behaved almost ideally over the pressure range studied (0-40 mm Hg).

6. Temperature Controlled water-bath and oil-bath: A temperature controlled water bath was used for low temperature kinetic apparatus where initiated decompositions of the thioanhydrocarboxylates were carried out. This was fitted with a conventional contact thermometer relay/heater system.

For work at high temperatures (>80°C) an oil bath consisting of a dewar vessel of eight litres capacity was used in conjunction with silicone oil. Risella oil was used as an alternative bath fluid for work at intermediate temperatures (40-90°C).

7. Determination of chloride ion concentration: The method used to determine the ionisable chloride concentration was a modification of Ingram's potentiometric titration method.

To a weighed amount of α-thio-anhydrocarboxylates (approximately 0.1 gm) was added a large excess of 3:1 (V/V) distilled water: acetone

and a few drops of IN nitric acid. The solution was then heated to about 70°C for three minutes, cooled and titrated potentiometrically with 0.IN silver nitrate. The end point was determined graphically. The electrode system used was silver/silver: silver chloride in conjunction with E.I.L. Model 23A PH meter.

This method was used to determine the percentage of acid chloride impurity in thio-anhydrocarboxylates. During potentiometric titrations it was observed that silver nitrate reacted with thio-anhydrocarboxylate in addition to acid chloride thus precipitating silver sulphide. This method was therefore unsuitable for accurate determination of the percentage of acid chloride in thio-anhydrocarboxylates.

8. Thermogravimetric analysis (T.G.A.): T.G.A. of polythioesters were carried out using the Du-pont 950 thermogravimetric analyser.

9. Mass spectrometer: An AEI MS 9 instrument was used for recording mass spectra.

10. Gas liquid chromatograph: Chromatography was carried out with a Pye gas chromatograph series 104. An E 30 column consisting of silicone gum on firebrick was used together with helium carried gas and a Katharometer detector.

11. Gel Permeation Chromatography: Molecular weights and molecular weight distributions were determined by gel permeation chromatography. The work was carried out by the polymer supply and characterisation centre at RAPRA. Solvents used in the work were T.H.F. and ortho-dichlorobenzine (ODCB).

12. Spherulite formation: A Reichert hot stage optical microscope
equipped with cross-polars and a magnification of 150, was used to
observe spherulite formation in polymer films. The temperature of the
hot stage of the microscope was controlled by two variable transformers.
A small quantity of a polymer sample was placed on a glass slide, which
was covered with a cover slip. The sample was heated on a hot plate,
about 10°C above the melting point of the polymer. When the polymer
sample melted, the cover slip was gently pressed onto the glass slide,
making a thin film of a molten polymer. The sample was then heated at
that temperature for about two minutes and then quickly transferred to
the hot stage microscope which was maintained at a steady temperature.
A stop watch was started immediately to note the time. After an
induction period ranging from a minute to an hour, the growth of
spherulites was observed. The diameter of a spherulite and the number
of spherulites in the field of view was measured as a function of time
with the micrometer eye-piece.

The spherulite growth rates were measured at three different
temperatures. Finally, photographs of the spherulites were obtained
with a camera fitted to the microscope.

13. Density Gradient Column: A Davenport density gradient column
containing previously calibrated columns of various ranges was used for
the determination of polymer densities.

2.2 Purification of Solvents and Reagents

1. Nitrobenzene: Nitrobenzene was allowed to stand over phosphorous pentoxide for forty-eight hours and then distilled under reduced pressure (temperature 70°-75°C at 1.5 to 2 mm Hg pressure). The middle fraction was collected and stored over molecular sieve.

2. Ethyl acetate: The anhydrous grade ethyl acetate supplied by BDH Chemicals Limited was used for the extraction of thio-anhydro-carboxylates.

3. Tetrahydrofuran (T.H.F.): The solvent was allowed to stand over calcium-chloride for a few days and then fractionally distilled at atmospheric pressure. The distillate was stored in a dark bottle after collection under nitrogen as described in Section 2.1.1.

4. Diethyl ether (anhydrous): The anhydrous grade of ether supplied by Fison Scientific Apparatus Limited with 0.02% water and by BDH Chemicals Limited with a water content of 0.008%, was used for the synthesis of thio-anhydrocarboxylates and the thio-anhydrosulphites.

5. Decalin: The solvent was washed several times with dilute (7%,w/v) sulphuric acid, once with dilute (10% w/v) sodium hydroxide solution and finally three times with distilled water. The washed material was dried over calcium sulphate, fractionally distilled under reduced pressure and collected over sodium wire.

6. Silver oxide: Analar grade silver oxide supplied by Fisons Scientific Apparatus Limited was used.

7. Pyridine: Pyridine was allowed to stand over sodium hydroxide pellets for a few days and distilled at atmospheric pressure and stored in fresh sodium hydroxide.

Alternatively the anhydrous grade pyridine supplied by B.D.H. Laboratory Reagents Limited with a maximum water content of 0.02% was used.

8. <u>Lithium tertiary butoxide</u>: A saturated solution of the alkoxide in anhydrous decalin was prepared inside the dry box. This was used for the initiated decomposition of thio-anhydrocarboxylates.

9. <u>Thio-acids</u>: α-Thio-glycollic acid, α-thio-lactic acid and α-thio-isobutyric acid, (analar grade), were supplied by Koch-Light Laboratories Limited.

10. <u>Petroleum ether</u>: The solvent was allowed to stand over calcium sulphate before use.

11. <u>Benzene</u>: The re-distilled solvent was dried over calcium chloride for a week, filtered inside a dry box and stored over molecular sieve.

12. <u>Benzyl alcohol</u>: This reagent (analar grade) was supplied by M&B Laboratory Chemicals Limited. It was reldistilled and stored over molecular sieve before use.

13. <u>Benzylamine</u>: The analar grade benzylamine supplied by B.D.H. Chemicals Limited was used to stand over solid potassium hydroxide and re-distilled under reduced pressure before use.

14. <u>Phosgene</u>: This was used directly from cylinders supplied by B.D.H. Laboratory Gas Services Limited.

15. <u>Thionyl chloride</u>: Analar grade thionyl chloride supplied by B.D.H. Chemicals Limited was used for the synthesis of thio-anhydrous-sulphites.

CHAPTER III

3.1 Synthesis, Purification and characterisation of cyclic derivatives of α-thio acids

The copper salts and silver salts of α-thio-acids were synthesized by modifications of the method developed by Tighe for the synthesis of copper salts of α-hydroxy acids.

1.   Synthesis of Copper(II) thioglycollate:

α-thio glycollic acid (46.0 grams) was dissolved in 100 mls of distilled water and neutralised by ammonium salt of the acid.   The solution was heated to boiling to remove excess ammonia and then allowed to cool in an ice bath.   Cupric chloride (43.0 grams) was dissolved in about 50 mls of distilled water and the solution was then added slowly to the ammonium salt of the acid whilst stirring.   The precipitate which appeared immediately was allowed to settle for overnight and then filtered in a Buchner funnel, washed several times distilled water and finally with methanol.   The precipitate was dried at 60°C in an oven under vacuum for twenty four hours and stored in a sample bottle.   The colour of the compound was yellow as formed, but turned into pale grey when dried.

2.   Synthesis of Copper(II) thiolactate:

α-thio-lactic acid (53.0 grams) was diluted with 140 mls of distilled water.   The solution was then neutralised with ammonia solution to form ammonium salt of the acid.   The mixture was then, as before,

heated to boiling to remove excess ammonia and allowed go cool in an
ice bath. Cupric chloride (43.0 grams) was dissolved in 100 mls of
distilled water and then added slowly to the ammonium salt of the acid
with constant stirring. A yellow precipitate of cupric thio-lactate
appeared with the addition of the cupric chloride solution. The
precipitate was left overnight and then filtered and washed with
distilled water and finally methyl-alcohol. The compound was dried
at a low temperature, i.e. at 50°C under vacuum for eighteen hours.
The compound changed colour while drying from yellow to pink.

3.   Synthesis of Copper(II) salt of α-thioisobutyric acid:

Twenty grams of thioisobutyric acid was dissolved in 100 mls of
distilled water. The solution was neutralised with ammonia solution
and heated to boiling to remove excess. Cupric chloride (12 grams)
was dissolved in 50 mls of distilled water and added with stirring to
the previously cooled ammonium salt of the acid. When the addition of
cupric chloride solution was over the colour of the whole mixture turned
violet although only a very little precipitate appeared. The mixture
was then evaporated at 100°C for a longer time. No appreciable amount
of the precipitate was obtained even after complete evaporation of the
liquid.

4.   Synthesis of silver salt of α-thio-glycollic acid:

The silver salt of α-thio-glycollic acid was prepared by the
technique described for copper salt preparation of α-thio acids with
the substitution of silver nitrate for cupric chloride. The silver
salt of α-thio-glycollic acid appeared as a grey precipitate which
was washed, dried and stored in the manner described for copper salts
of α-thio acids. Since the silver salts are light sensitive they were
normally stored in dark coloured vessels.

5.   Synthesis of silver salt of α-thio-lactic acid:

The compound was prepared by the same technique as described for silver salt of α-thio-glycollic acid.   The silver salt of the α-thio-lactic acid appeared as a yellow precipitate which was washed, dried and stored as described before.

6.   Synthesis of silver salt of α-thio isobutyric acid:

The silver salt of α-thio isobutyric acid appeared as a white precipitate from the solution, which was washed, dried and stored in a similar manner to that previously described.

Reactions involved in the synthesis of metal-salts may be summarised as shown below in the general case for copper-salts preparation:

$$R^1 \overset{\overset{\displaystyle R^2}{|}}{\underset{\underset{\displaystyle SH}{|}}{C}} - COOH + NH_4OH \longrightarrow R^1 - \overset{\overset{\displaystyle R^2}{|}}{\underset{\underset{\displaystyle SH}{|}}{C}} - COONH_4 + H_2O$$

$$2R^1 \overset{\overset{\displaystyle R^2}{|}}{\underset{\underset{\displaystyle SH}{|}}{C}} - COONH_4 + CUCl_2 \longrightarrow$$

$$R^1 \overset{\overset{\displaystyle R^2}{|}}{\underset{\underset{\displaystyle SH}{|}}{C}} - COO\text{-}Cu\text{-}OOC - \overset{\overset{\displaystyle R^2}{|}}{\underset{\underset{\displaystyle SH}{|}}{C}} - R^1 \quad + 2NH_4Cl$$

(22)
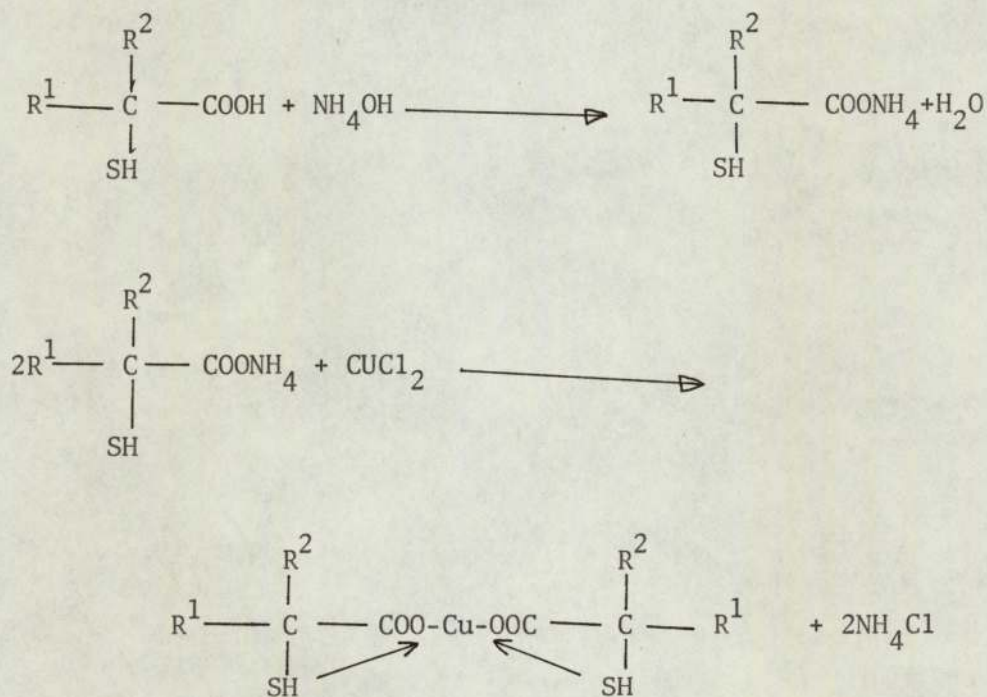
7. Attempted Synthesis of thio-glycollic anhydrocarboxylate from
    Copper(II) thio-glycollate

Carefully dried cupric thio-glycollate (7.00 grams) was slurried
in 100 mls of anhydrous ether and transferred to a 500 ml quickfit
conical flask.   Six (6.0 grams) of carbonyl chloride ($COCl_2$) was
dissolved in 50 mls of anhydrous ether and added to the contents of
the conical flask dropwise by a separating funnel.   The mixture was
continuously agitated by a magnetic follower, actuated by the magnetic
stirrer.   The reaction was allowed to continue for five days at room
temperature.   Then ether and excess phosgene ($COCl_2$) was removed from
the mixture by a suction pump at a temperature of 30°C.   0.2 gram of
silver oxide was suspended in 50 mls of anhydrous ether and added to
the contents of the conical flask.   The purpose of adding silver oxide
was to remove acid chloride impurity as silver chloride.   The reaction
was allowed to continue for twenty four hours during which time white
precipitate appeared.   The mixture was then centrifuged to remove
silver chloride and unreacted silver oxide and the solution was
evacuated at room temperature to remove ether.   After evacuation of
ether, a very small amount of an oily substance remained.   No complete
identification was possible with this compound because of the small
quantity.

8. Synthesis of thio-lactic anhydrocarboxylate from Copper(II)thiolactate

In a typical experiment cupric thio-lactate was dried in an oven
for four hours at 110°C before use following which (9.0 grams) of dried
compound was taken in a conical flask containing 100 mls of anhydrous
ether. Six (6.0 grams) of carbonyl chloride was passed into 50 mls of
anhydrous ether in a narrow-mouthed conical flask and added very slowly

to the quickfit flask by a separating funnel. The temperature of the flask was maintained below 5°C during the addition of phosgene and the reaction was allowed to continue for five days at room temperature. The mixture was then filtered to remove cupric chloride residue and evacuated under suction pump at room temperature to remove ether and unreacted phosgene. Silver oxide (0.25 grams) was suspended in 50 mls of anhydrous ether and added to the flask. After 24 hours the mixture was centrifuged to remove silver chloride and unreacted silver oxide. The solution was then evacuated under vacuum pump at room temperature to remove ether. Only a very small amount of oily substance obtained after complete removal of ether. The compound was insufficient for further work.

With the failure of this method to produce substantial amount of thio-glycollic and thio-lactic anhydrocarboxylates, synthesis of anhydrocarboxylates via metal salts (copper and silver salts of α-thio acids) were abandoned. It was decided to follow an alternative route, that is the synthesis of anhydrocarboxylates of the direct reaction of α-thio acids with carbonyl chloride.

Although no complete analysis of the products of the copper salt reactions was undertaken sufficient information was obtained to demonstrate that in the case of α-thio acids as distinct from α-hydroxy acids formation of the volatile acid chloride is preferred to ring closure to the desired product. The reactions may be summarised as follows.

$$
\underset{R^2}{\overset{R^1}{>}} C \underset{SH}{\overset{COO}{\diagdown}} Cu \underset{OOC}{\overset{SH}{\diagup}} C \underset{R^2}{\overset{R^1}{\diagup}} \quad + \; COCl_2 \quad \longrightarrow \quad \underset{R^2}{\overset{R^1}{>}} C \underset{SH}{\overset{COOCOCl}{\diagdown}} \quad + \; CuCl_2
$$

$$
\underset{R^2}{\overset{R^1}{>}} C \underset{SH}{\overset{CO-O-COCl}{\diagdown}}
\begin{array}{l}
\nearrow \quad \underset{R^2}{\overset{R^1}{>}} C \underset{S-CO}{\overset{CO}{\diagdown}} O \quad + \; HCl \qquad (a) \\[2em]
\searrow \quad \underset{R^2}{\overset{R^1}{>}} C \underset{SH}{\overset{COCl}{\diagdown}} \quad + \; CO_2 \qquad (b)
\end{array}
\qquad (23)
$$
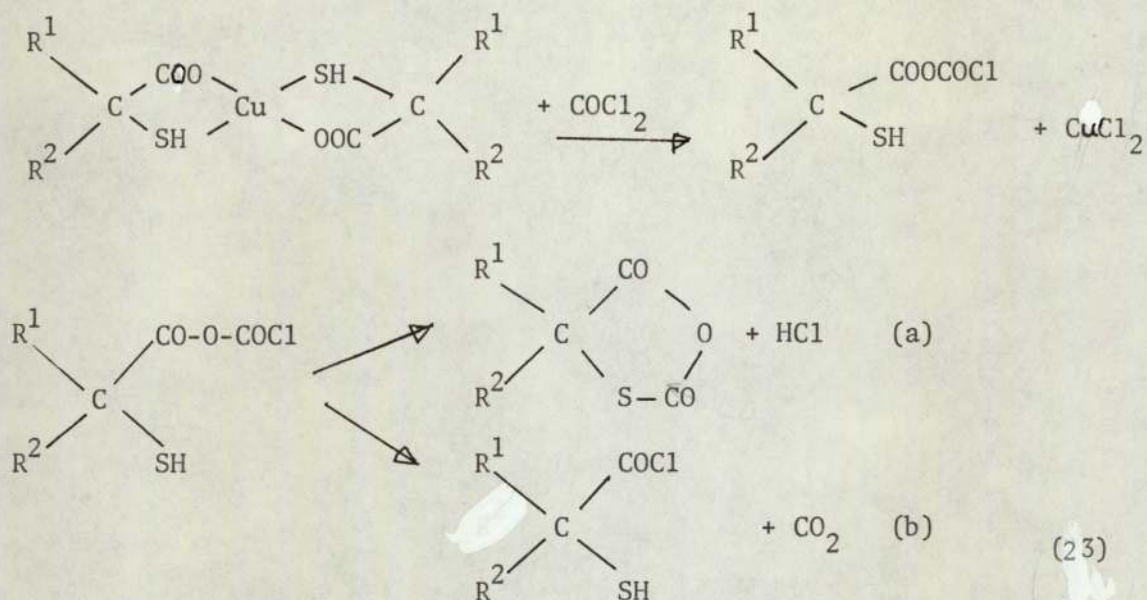
3.2 Synthesis of Thioglycollic anhydrocarboxylate by the direct reaction of α-thio-acid with carbonyl chloride:

In the preferred procedure thio-glycollic acid (46.0 grams) was taken in a 1000 ml quickfit conical flask and dissolved in 300 mls of anhydrous ether. 75.0 grams of phosgene dissolved in 400 mls of anhydrous ether were added to the flask dropwise by a separating funnel whilst the contents of the flask were continuously agitated by a magnetic stirrer. During the addition of phosgene into the acid solution, the temperature of the flask was maintained below 0°C. The reaction was allowed to continue for six days at room temperature, then ether and unreacted phosgene were removed under suction pump at 20°-22°C. The residual oil thus obtained was cyclised by heating at 25°C for three hours under vacuum (1.5 mm Hg pressure). Formation of the crystalline anhydrocarboxy derivative could be observed within fifteen minutes. Within an hour almost the whole of the oil converted into white crystalline solid with a trace amount of liquid (probably unreacted acid).

The chloro-acetyl chloride which was believed to be the major impurity was removed within the first ten minutes of the cyclisation process. The thio-glycollic anhydrocarboxylate thus obtained was extracted with dry benzene inside the dry-box. Melting point of the compound was determined and found to be 67°-68°C. The anhydrocarboxylate was purified by sublimation at a temperature of 64°-65°C under 1.5mm Hg pressure. The compound was stored below -30°C.

Synthesis of thio-lactic anhydrocarboxylate from α-thio-lactic acid:

In the preferred procedure 40.7 mls of thio-lactic acid (53.0 grams) was added to 200 mls of anhydrous ether in a one-litre quickfit conical flask. 76.00 grams of phosgene (1.5 molar ratio) was passed into 500 mls of anhydrous ether and slowly added to the acid solution by a separating funnel. The temperature of the flask was maintained below 0°C while adding the phosgene and the reaction was allowed to continue for five days at room temperature. The contents of the flask were continuously agitated by a magnetic stirrer throughout the reaction. Ether and excess phosgene were removed by a suction pump at 20°-22°C. The remaining oil was then cyclised for three hours at 30°C under vacuum (1.5 mm Hg pressure), during which time approximately 50% of the oil converted into white crystalline solid. The anhydrocarboxylate was extracted from the mixture by analar grade ethyl acetate. The product, which is a white crystalline solid, having a melting point of 44°-45°C was stored in a container surrounded by dry ice.

Synthesis of thio-isobutyric anhydrocarboxylate from α-thio-isobutyric acid

A substantial modification of the previously described technique was found to be necessary in this case. Thus 15.0 grams of thio-

isobutyric acid was taken in a 500 ml quickfit flask and dissolved in
100 mls of anhydrous ether.   20.0 grams of phosgene (1.5 molar ratio)
was passed into 150 mls of anhydrous ether and 18.0 grams of pyridine
(2 molar ratio) was dissolved in 100 mls of the same solvent.   Pyridine
in ether and phosgene in ether were added to the acid solution simult-
aneously at a temperature below 0°C.   The contents of the flask were
continuously agitated by a magnetic follower.   A bulky white precipitate
of pyridine hydrochloride appeared immediately.   The reaction was allowed
to continue at low temperature for four hours and then pyridine hydro-
chloride was filtered off.   The filtrate was taken in a conical flask
and the reaction was allowed to continue for five days at room
temperature.   After twenty four hours a slight precipitate of pyridine
hydrochloride which appeared was filtered off.   Ether and excess
phosgene were finally removed under reduced pressure at room temperature.
The residual oil was cyclised at room temperature under vacuum (1.5 mm
Hg pressure).   The acid chloride which is highly lachrimatory was
removed rapidly and within a few minutes the oil converted into white
crystalline solid.   The anhydrocarboxylate thus obtained is slightly
lachrimatory and melts just at room temperature.   It was stored in a
refrigerator under vacuum.   This compound is not reported in the
literature.

Synthesis of thio-glycollic and thio-lactic anhydrosulphites:

Thio-glycollic and thio-lactic anhydrosulphites were synthesized
principally for comparitive study of both types of anhydrides in
respect of their ease of synthesis and spectral characteristics.

(a) Thio-glycollic acid anhydrosulphites:

α-thio-glycollic acid (46.0 grams) was added to 250 mls of anhydrous ether in a 500 ml quickfit flask.   54.5 mls of thionyl chloride in ether was added slowly by a separating funnel to the acid solution at -10°C.   The system was allowed to warm to room temperature after six hours.   The reaction was allowed to continue for four days.   After twenty four hours of the reaction, almost half of the solvent was removed under reduced pressure at low temperature (20°-22°C) and the rest of the ether and unreacted thionyl chloride after four days under the same conditions.   The red viscous liquid obtained was distilled under reduced pressure (2.0 mm Hg pressure) at about 60°-70°C, yielding a pale yellow mobile liquid (yield 20%)

(b) Thio-lactic acid anhydrosulphite:

α-thio-lactic acid (40.5 mls, 53.0 gms) was dissolved in 250 mls anhydrous ether.   Thionyl chloride (54.5 mls) in ether (150 mls) was added to the acid solution.   The reaction was carried out under the same conditions as described for thio-glycollic anhydrosulphite synthesis.   The residual oil obtained after removal of the solvent wasa distilled under reduced pressure (2 mm Hg) at 60°C.   A middle fraction of the distillate was obtained as a pale yellow liquid.

3.3 Results and Discussion

Although α-thio-glycollic and α-thio-lactic acids anhydrocarboxylates are described in the literature, the compounds prepared in this manner are of too low a standard of purity for kinetic work.   The questions of purification, storage, stability and characterisation are very inadequately dealth with.   The other compounds described herein are novel and not described in the literature.

It is one aim of this project to compare the relative effects of sulphur and oxygen in cyclic esters of α-thio and α-hydroxy carboxylic acids. The first significant difference was encountered in the use of copper(II) salts of the α-functional acids for monomer preparation, whereas copper salt of α-OH carboxylic acids give good yield of anhydrosulphites and anhydrocarboxylates, the yield of the cyclic derivative was negligible for α-thio acids, acid chloride formation being favoured over ring closure to form the cyclic derivative. This difference may be attributed to two major causes. Firstly the greater electro negativity of oxygen provides a more favourable situation for hydrogen removal in ion pair elimination as in (a). Secondly, the results presented in Chapter VI show that the anhydrocarboxylates of α-hydroxy acids are much more stable than the cyclic derivatives of α-thio-acids. Thus the cyclisation to the more stable α-hydroxy anhydro- carboxylate is energetically more favourable process than an equivalent reaction in which α-thio-acid anhydrocarboxylates are formed.

A great deal of work was expended on the direct synthesis of the anhydrocarboxylates of α-thio-acids from the thio-acids themselves. The syntheses presented in this chapter represent preferred conditions.

In the case of α-thio-glycollic and α-thio-lactic this represents 50% molar excess of phosgene over the acid. Since α-chloro-acid chloride impurities produced under these conditions are more easily removed than the unreacted acid which remains when low phosgene excesses are used.

TABLE 3.1

SUMMARY OF THE REACTION PRODUCTS

Parent acid	Unreacted acid %	α-thio-anhy drocarboxylate %	α-chloro acid chloride %	Others %
α-thio glycollic acid	10	70±10	20	-
α-thio lactic acid	30±10	40±10	20	-
α-thio isobutyric acid	-	60±10		30±10

The apparent trend in decreasing reactivities of the α-thio acid
as reflected in the unreacted acid is continued in α-thioisobutyric
acid which is too unreactive for direct formation of thio-anhydro-
carboxylate.   The modified pyridic technique described has provided
an acceptable synthetic route however.

3.4 The purification of thio-anhydrocarboxylates and anhydrosulphites;

The major impurities in the synthesis of thio-anhydrocarboxylates
were therefore found to be α-chloro-acid chloride and the unreacted
α-thio-acids.   The α-chloro-acid chloride may be represented as shown
below:-

$$R^1 \underset{\underset{Cl}{|}}{\overset{\overset{R^2}{|}}{C}} COCl$$
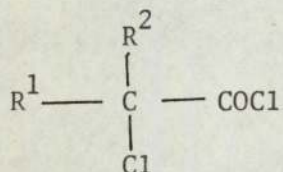
(VIII)

The techniques described in the literature for the purification of thio-anhydrocarboxylates which involved distillation of the thio-anhydrocarboxylate mixture at very low pressures or crystallization from ether could not be achieved with repeated attempts. Attempted removal of α-chloro-acid chloride with silver oxide (which was very successful in the purification of glycollic and lactic acid anhydro-sulphites of α-hydroxy acids)was found to be unsuccessful. It was found by potentiometric titrations (which were used to determine the percentage of ionisable chloride ion concentration in thio-anhydrocarboxylate) that silver oxide reacted with cyclic derivatives of α-thio-acids.

After spending a considerable time on the purification of thio-anhydrocarboxylates a successful technique was developed. This technique involved cyclising the crude anhydrocarboxylate mixture, after removal of the solvent, for two to three hours at room temperature under reduced pressure (1.5 mm Hg pressure) which removed most of the α-chloro-acid chloride. The unreacted α-thio-acids were removed by extracting the thio-anhydrocarboxylates below 0°C by anhydrous benzene, diethyl ether and ethyl acetate. The residual trace amounts of α-chloro-acid chloride and the α-thio-acid were completely removed by vacuum sublimation. The pure thio-anhydro-carboxylates are white crystalline solids and are soluble in most organic solvents.

The purification of thio-anhydrosulphites were carried out by fractional distillation. The principal impurities as before were

α-chloro-acid chloride and unreacted α-thio-acids which were easily removed by this technique. The anhydrosulphites when pure are pale yellow liquid.

It was observed during polymerisation studies described in subsequent chapters, that cyclic thio-glycollides are formed together with polymers. This decomposition occurs slowly even at room temperature under vacuum.

A high level purity of monomers are essential for kinetic studies and to obtain high molecular weight polymers. The presence of impurities such as α-chloro-acid chloride drastically lowers the molecular weight of the polymers

3.5 Characterisation:

The thio-anhydrocarboxylates and thio-anhydrosulphites were characterised by infra red spectra, mass spectra together with other physical and analytical methods. Their reactivity under atmospheric conditions was so great that elemental analysis could not be used.

The yield of carbon dioxide which evolved during the initiated decomposition of thio-anhydrocarboxylates provided a useful means for ascertaining the purity of the thio-anhydrocarboxylates. 2.0 mls of 1 molar solution of thio-anhydrocarboxylate was injected into a low temperature kinetic apparatus through a suba-seal. The apparatus was evacuated under vacuum and transferred to a water bath. 1 ml of 1 molar solution of pyridine injected into the monomer solution.

The amount of carbon dioxide evolved as measured by the pressure rise at room temperature was calculated as a percentage conversion of the monomer to polymer. (Among the thio-anhydrocarboxylates, thio-glycollic anhydrocarboxylate was obtained as almost 98.0% pure.) $98\pm2\%$ of the theoretical amount of CO_2 was obtained consistently with the A/C of thio-glycollic and α-thio-isobutyric. α-thio-lactic was difficult to obtain in the pure form but even so $97\pm\%$ of theoretical were consistently obtained.

The identity and purity of thio-anhydrocarboxylate was also assessed by the conversion of the thio-anhydrocarboxylates to the corresponding parent acids by hydrolysis in a moist atmosphere. The boiling points and melting point determined conformed with the pure acids.

The melting point of thio-glycollic and thio-lactic anhydrocarboxylates were determined by gallenkamp melting point apparatus. The thio-anhydrocarboxylates were filled in the melting point tubes inside the dry box. The thio-isobutyric anhydrocarboxylate melts just at room temperature. The melting points of the thio-anhydrocarboxylates are shown in Table 3.4.

Infra red spectra'

The formation of thio-anhydrocarboxylates and anhydrosulphites was most readily identified by infra red spectra.

The IR spectra for α-thio-acids, their metal salts (copper and silver), acid chlorides, anhydrocarboxylates and anhydrosulphites were obtained with KBr disc and carbon tetrachloride solution.

The characteristic carbonyl peak obtained for all the three α-thio-acids was centered at $1705\pm5\,\text{cm}^{-1}$. Another characteristic peak for thio-acids is the SH group which appeared at $2590\ \text{cm}^{-1}$, $2690\ \text{cm}^{-1}$ (weak). The IR spectra for the copper salts and silver salts (thio-glycollic and thio-lactic) showed a broad carbonyl absorption at $1680\pm5\ \text{cm}^{-1}$. The infra red spectra of copper salts of α-hydroxy carboxylic acids also showed the carboxyl peak at the same region.

The most characteristic absorptions of anhydrocarboxylates of α-thio-acids are observed in the carbonyl region. Two peaks were obtained in this region, one strong absorption at $1770\pm5\ \text{cm}^{-1}$ and a medium strength absorption at $1845\ \text{cm}^{-1}$, which were the same for all the three anhydrocarboxylates. These absorptions for the different carbonyl groups are represented as $C\!-\!C\overset{\displaystyle\nearrow^{O}}{\searrow}$, $1770\ \text{cm}^{-1}$ and $S\!-\!C\underset{\displaystyle O}{\overset{\diagup}{\Longrightarrow}}$, $1845\ \text{cm}^{-1}$.

The reasons for this assignment may be summarised in the following way. The IR spectra for α-hydroxy anhydrocarboxylates were studied by Smith. Two carbonyl peaks were observed in the carbonyl region, one strong absorption at $1810\pm5\,\text{cm}^{-1}$ and a medium strength absorption at $1890\pm10\ \text{cm}^{-1}$. The carbonyl absorption in the corresponding α-hydroxy acid anhydrosulphites occur at $1815\pm5\ \text{cm}^{-1}$. The anhydrosulphites of α-thio acids which were synthesised primarily to enable this comparison to be made same sharp spectra with strong carbonyl absorptions occur at $1800\pm5\ \text{cm}^{-1}$. The relative effects of ring structure on carbonyl absorption frequency together with a clear view of the proposed assignment is shown in
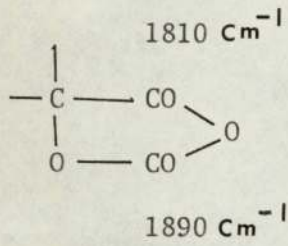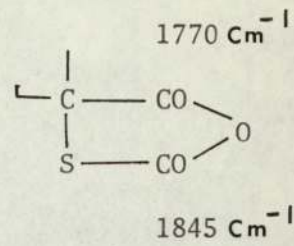
1810 Cm^{-1} 1770 Cm^{-1}

$$
\begin{array}{cc}
\overset{\displaystyle|}{-}\text{C}\underset{\displaystyle|}{}\text{---CO}\diagdown \\
\text{O---CO}\diagup\text{O}
\end{array}
\qquad
\begin{array}{cc}
\overset{\displaystyle|}{\text{---C}}\text{---CO}\diagdown \\
\text{S---CO}\diagup\text{O}
\end{array}
$$

1890 Cm^{-1} 1845 Cm^{-1}

α-hydroxy acid anhydrocarboxylate   α-thio-acid-anhydrocarboxylate

1815 Cm^{-1} 1800 Cm^{-1}

$$
\begin{array}{cc}
-\text{C---CO}\diagdown \\
\text{O --- SO}\diagup\text{O}
\end{array}
\qquad
\begin{array}{cc}
-\text{C --- CO}\diagdown \\
\text{S --- SO}\diagup\text{O}
\end{array}
$$

1215 Cm^{-1} 1170 Cm^{-1} (IX)
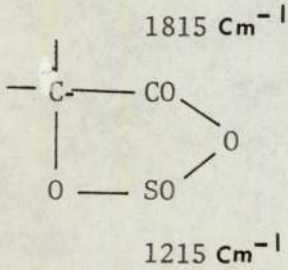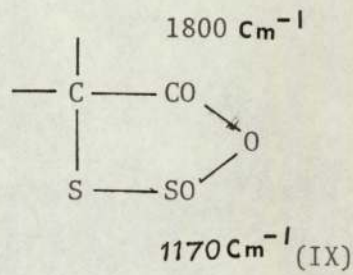
α-hydroxy acid anhydrosulphite   α-thio-acid anhydrosulphite

A further relevant point is the fact that a strong absorption
band occurred at 1805±5 for α-chloro acid chloride impurities
encountered in this work. The model compound chloro-acetylchloride
was studied in carbon tetrachloride where the carbonyl peak appeared at
the same region 1810 cm^{-1}. It is important to note that in these
spectra of the cyclic α-thio acid derivatives the characteristic peaks
for SH-group and carbonyl group associated with α-thio-acids were
completely absent.

The characteristic carbonyl peaks for the parent α-thio-acids,
and the derived silver salts, copper salts, anhydrocarboxylates,
anhydrosulphites and the acid chlorides are summarised in Table 3.2.
It is important to note that no previous published information exists
on the infra red spectra of the cyclic derivation of α-thio-acids.

TABLE 3.2

	α-thio-acids (cm^{-1})	Copper salts & silver salts (cm^{-1})	Anhydrocarboxyl-ates (cm^{-1})	Anhydrosulphites (cm^{-1})	Acid chloride (cm^{-1})
Thio-glycollic acid	1705 ± 5 cm^{-1}	1680 ± 5 cm^{-1} (broad)	1770 ± 5 (S) 1845 (M)	1800 (S)	1805 ± 5(S)
Thio-lactic acid	1705 ± 5 cm^{-1}	1680 ± 5 (broad)	1770 ± 5(S) 1845 (M)	1800 (S)	1805 ± 5(S)
Thio-isobut-yric acid	1705 ± 5 cm^{-1}	1680 ± 5 (broad)	1770 ± 5 (S) 1845 (M)		1805 ± 5(S)

(S) - strong absorption   (M)-medium absorption

A spectrum of thio-glycollic anhydrocarboxylate and another spectrum of thio-glycollic anhydrosulphite are shown in Figs.3.1 and 3.2.   These spectra are of material partially converted to polymer and illustrate the change in carbonyl frequency occurs on polymerisation (Chapter VII)

The Mass Spectra

The mass spectra of α-thio acids, tetramethyl thio-glycollide, thio-anhydrocarboxylates and thio-anhydrosulphites were studied.   The principal fragmentation peaks for these compounds are shown in Table 3.3.   Top mass peaks were observed for α-thio-acids, tetramethyl thio-glycollide, and thio-anhydrocarboxylates, but no top mass peaks were found for thio-anhydrosulphites, thus confirming the fact that thio-anhydrocarboxylates and thio-glycollides are thermally more stable than the corresponding thio-anhydrosulphites.   The relative strength of these top mass peaks however was much lower than that of the α-hydroxy acid anhydrocarboxylates

This agrees with the difference in stability of the two ring systems as discussed in Chapter VI.   In addition a very small peak corresponding formation of a dimer of the thio-lactone in the mass spectrometer was observed.   This has not been reported for other rings of this type.   The principal fragmentation products of thio-anhydrocarboxylates are shown below which corresponds to the principal peaks M̄44, M̄60, M̄72, M̄76, M̄87 and M̄104.
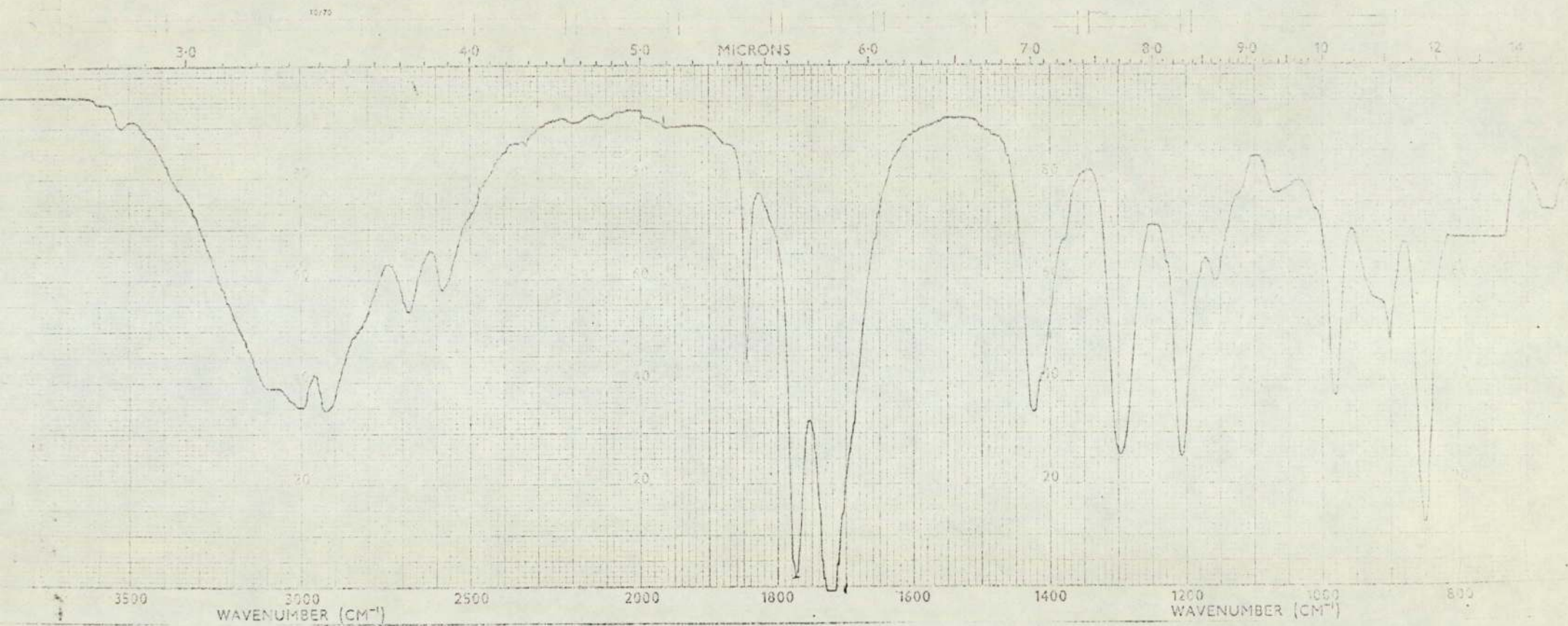
Fig.3.1 Infra red spectrum for Thioglycollic anhydrocarboxylate (partially converted to polymer)
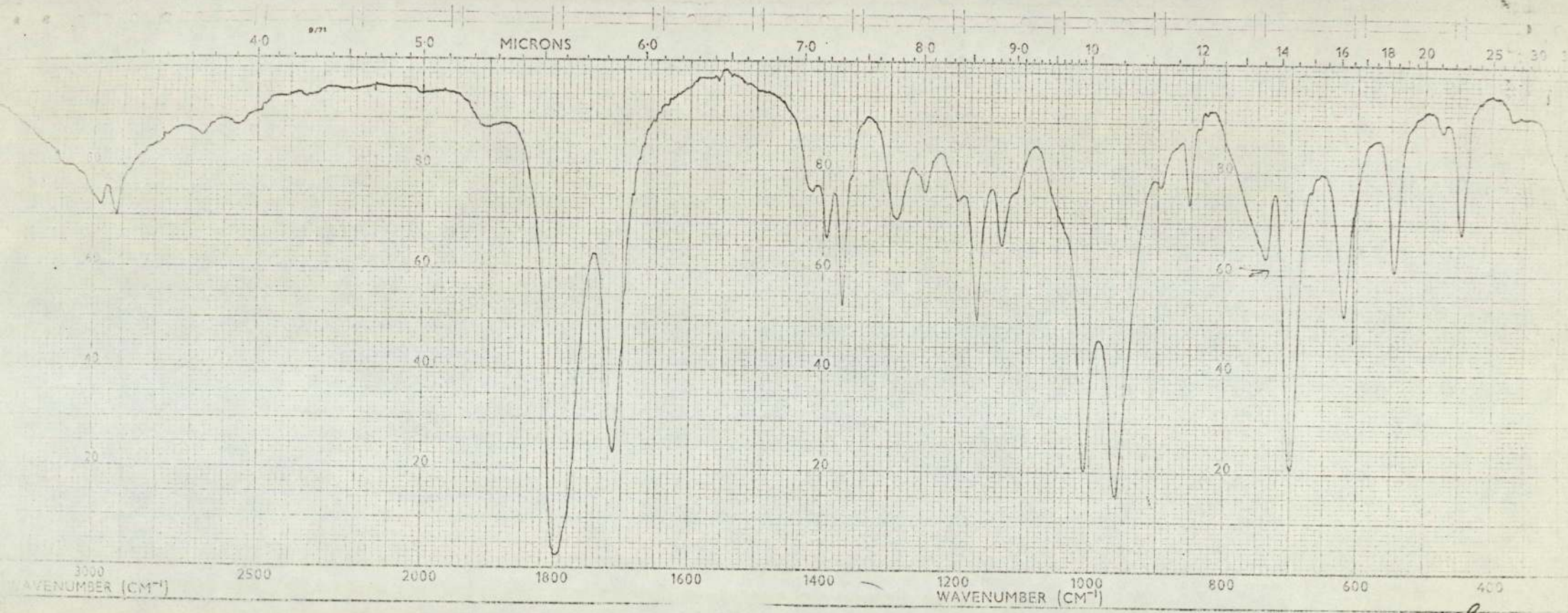
Fig.3.2 Infra red spectrum for Thioglycollic anhydrosulphite (partially converted to polymer)

$$R^1-\underset{\underset{S}{|}}{\overset{\overset{R^2}{|}}{C}}-\underset{\underset{CO}{}}{\overset{CO}{\diagdown}}O$$

$$R^1-\underset{\underset{S}{|}}{\overset{\overset{R^2}{|}}{C}}-CO$$

$$R^1-\underset{\underset{S}{|}}{\overset{\overset{R^2}{|}}{C}}-C$$

$$R^1-\underset{\underset{S}{|}}{\overset{\overset{R^2}{|}}{C}}$$

$$R^1-\underset{}{\overset{\overset{R^2}{|}}{C}}-C=O$$

$$R^1-C=S,$$

$$R^1-\underset{}{\overset{\overset{R^2}{|}}{C}}$$
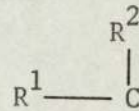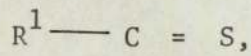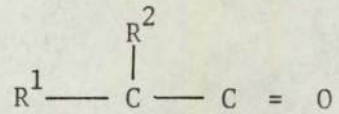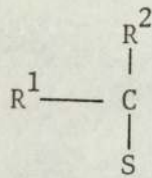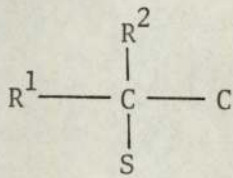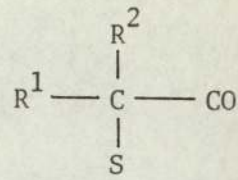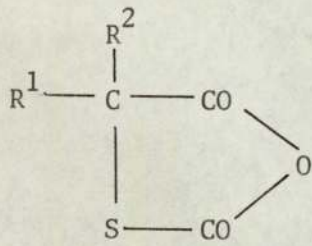
A summary of the major peaks and their relative strength is shown for α-thio-isobutyric acid and thio-anhydrocarboxylates, thio-anhydrosulphites and tetramethyl thio-glycollide in Table 3.3.

TABLE 3.3

α-thio acid (TIBA) M 120	Thio-anhydro carboxylate M 146	Tetramethyl thioglycollide M 204	Thio-anhydro sulphate M 138
M - 18 (M)	M - 44 (S)	M - 102 (W)	M - 64 (S)
CH_3 C—CO CH_3 S	CH_3—C—CO CH_3 S	CH_3—C—CO CH_3 S	H—C—CO H S
M - 33 (S)	M - 60 (S)	M - 118 (S)	M - 80 (S)
CH_3 O C—C CH_3 O—H	CH_3—C—C CH_3 S	CH_3—C—C CH_3 S	H—C—C H S
M - 46 (S)	M - 72 (S)	M - 130 (S)	M - 92 (S)
CH_3 $C = S$ CH_3	CH_3 $C = S$ CH_3	CH_3 $C = S$ CH_3	H—C—H S
M - 61 (S)	M - 76	M - 134 (S)	M - 124
CH_3—$C = S$	CH_3 $C - C = O$ CH_3	CH_3 C—$C = O$ CH_3	H—C H
M - 76 (M)	M - 87 (W)	M - 145 (S)	
$C = S$	CH_3—$C = S$	CH_3—$C = S$	
	M - 104 (M)	M - 162 (M)	
	CH_3 CH_3—C	CH_3 CH_3—C	

(S) - Strong

(M) - Medium

(W) - Weak

TABLE 3.4 Synthesis, purification and characterisation of thio-anhydrocarboxylates

Anhydro-carboxylate	Method of Synthesis	Purification technique	Yield %	M.point ($0°C$)	I.R.spectra $\nu(c=o)$	CO_2 evolved (%)of theory	Mass spectra (Principal peaks)	Hydrolysis product
TGAC (VII; $R^1=H$, $R^2=H$)	a	c	60	67-68	1770 (S) 1845 (M)	98±2	(M-44 (S)	α-thiogly-collic acid
TLAC (VII; $R^1=H$, $R^2=CH_3$)	a	c	30	44-46	1770 (S) 1845 (M)	96±2	(M-60 (S) (M-72 (S)	α-thio lactic acid
TIBAC (VII; $R^1=CH_3$, $R^2=CH_3$)	b	d	55	20-22	1770 (S) 1845 (M)	98±2	(M-76 (M-87 (W) (M-104 (M)	α-thio isobutyric acid

(a) Direct reaction with α-thio-acid

(b) via pyridine route

(c) Extraction with solvents and vacuum sublimation

(d) Evacuation under vacuum.

3.6 General reactivities of thio-anhydrocarboxylates and thio-anhydrosulphites:

It was observed that thio-glycollic anhydrocarboxylate reacts vigorously with amines, comparatively slowly with water and very slowly with alcohols. The reaction of thio-glycollic anhydrocarboxylate with tertiary amine (pyridine) is fast even at room temperature and at high temperatures it is difficult to follow the reaction rates. The reaction of thio-glycollic anhydrocarboxylate with primary amine (benzylamine) was relatively slow, approximately ten times less reactive than the pyridine initiated decomposition of the thio-anhydrocarboxylate. In both cases however polymer was formed when substoichrometric amounts of amine were used. Thio-lactic anhydrocarboxylate reacts with tertiary amine comparatively slowly about three to four times less reactive than the corresponding thio-glycollic anhydrocarboxylate. The same trend is observed with primary amine. Thus from these observations it can be inferred that the rate of reaction is dependent upon the substituent size and number at α-position. Thio-isobutyric anhydrocarboxylate behaved differently from thio-glycollic and thio-lactic anhydrocarboxylates. Thio-isobutyric anhydrocarboxylate reacts quite slowly with pyridine but with primary amine (benzylamine) reacts vigorously yielding principally tetramethyl thio-glycollide as the initial product. During storage under vacuum at room temperature, thio-glycollic and thio-lactic anhydrocarboxylates decompose mainly to oligomers and traces of thio-glycollide and thio-lactide. But thio-isobutyric anhydrocarboxylate under similar conditions at 0°-4°C decomposes principally to tetramethyl thio-glycollide. These reactions will be discussed in more detail in subsequent chapters.

The synthesis of high molecular weight polythio-esters depends mainly upon the purity of the monomers. The reactivities of the thio-anhydrosulphites (thio-glycollic and thio-lactic) have also been qualitatively studied. The indicated decomposition of thio-anhydro-sulphites with amines (pyridine, benzylamine) was found to be vigorous yielding principally polymers. In summary the thio-anhydrocarboxylate and anhydrosulphite rings of α-thio-acids seem to be more unstable than the corresponding rings of the α-hydroxy acids, but to undergo similar types of reactions.

CHAPTER IV

Tertiary Base Initiated decomposition of α-thio acid anhydrocarboxy-
lates [such as thioglycollic anhydrocarboxylate (TGAC), thio-lactic anhy-
drocarboxylate (TLAC) and thioisobutyric anhydrocarboxylate (TIBAC)] and
Related Studies.

It is known that NCA's of α-amino-acids and anhydrocarboxylates of
α-hydroxy acids undergo polymerisation when treated with pyridine. In
some cases (e.g. α-benzyl glutamate NCA), the resulting polymer has a
very high molecular weight which is independent of $[M]_o/[I]_o$. The
kinetic studies of the α-thio acid anhydrocarboxylates with pyridine as
initiators has shown that the decomposition of TGAC with pyridine is rapid,
less so with TLAC and fairly slow with TIBAC under similar conditions. The
results of this study are presented in this chapter.

4.1 Pyridine initiated decomposition of TLAC

The initiated decomposition of TLAC with pyridine occurs at a
comparatively slow rate which is well suited to kinetic work. A
solution of the monomer was prepared in nitrobenzene (desired concen-
tration 1.0 mole/litre). The reaction was carried out at various
concentrations of the monomer and initiator. The rate of decomposition
was measured by gas evolution technique using the conventional low
temperature kinetic apparatus. The rise in pressure in the manometer

due to the evolution of carbon dioxide gas was measured with suitable intervals of time and plots of pressure versus time were drawn. (Fig. 4.1). Conversion of the pressure readings versus time for the decomposition of the α-thio lactic acid anhydrocarboxylate into a conventional first order plot of $\ln(P\infty-P)P\infty$ versus time gave straight lines (Fig.4.2).

This demonstrated that the decomposition of TLAC with pyridine is a first order process with respect to monomer and that pyridine is not consumed during the reaction. The effect of varying the pyridine concentration was studied and within experimental error it was found that monomer decomposition showed a first order dependence upon the initial concentration of pyridine. This is demonstrated in Fig. 4.3. The results may be summarised in the following equation

$$\frac{d[CO_2]}{dt} = \frac{-d[M]}{dt} = k'' [M][Pyr] \qquad (24)$$

This enables the second order rate constant k'' to be calculated at 25°C and shown in Table 4.1.

Table 4.1: Kinetic data for the pyridine initiated decomposition of TLAC

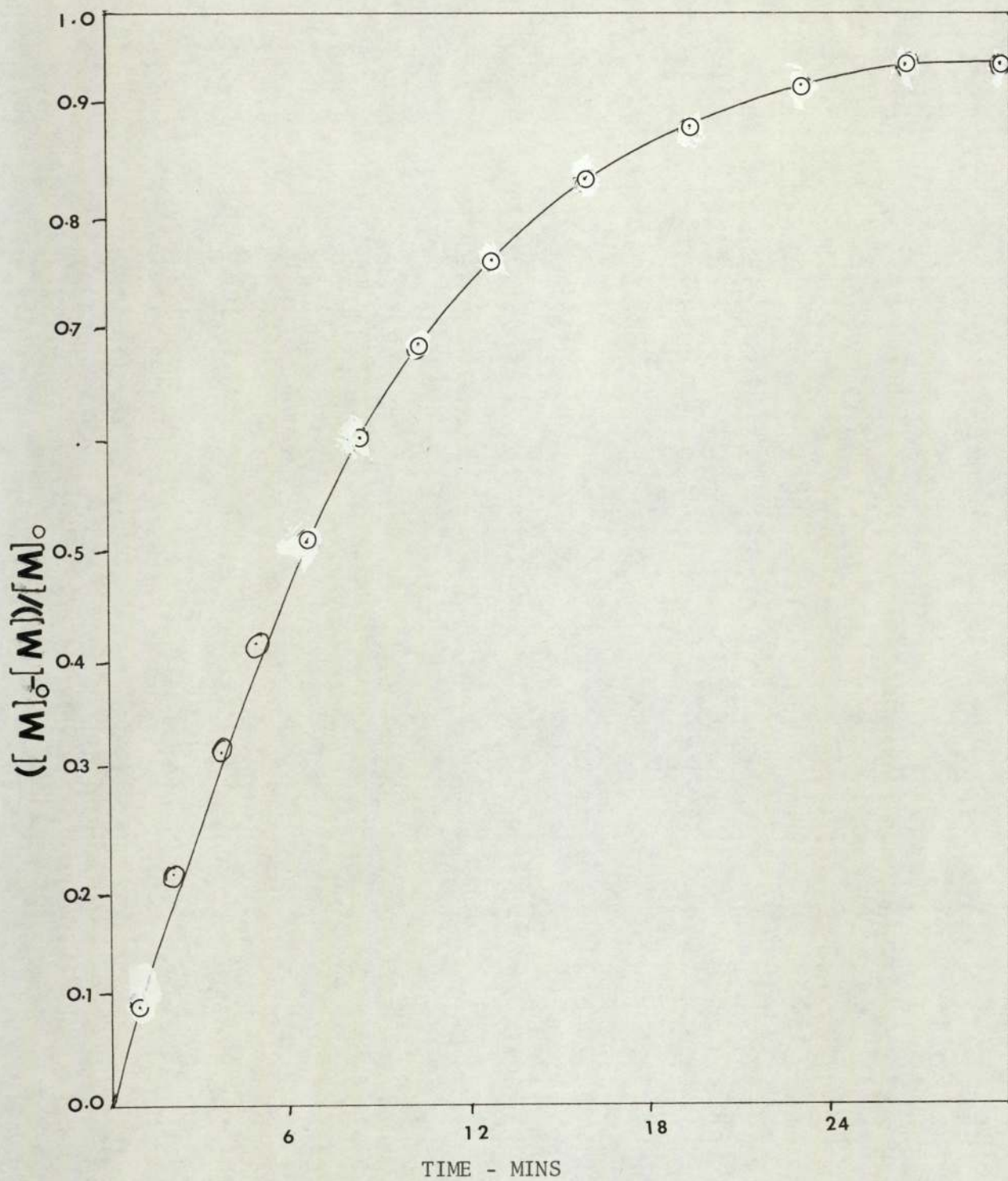| Temperature	Monomer Mol/litre	Pyridine Mol/litre	second order rate constant $k''(l.mol^{-1}s^{-1})$
25°C	1.08	0.19	1.26×10^{-2}
"	0.87	0.08	1.50×10^{-2}
"	0.94	0.06	1.50×10^{-2}

Fig. 4.1   Rate curves for the decomposition of TLAC with pyridine at 25°C.
            [TLAC] = 1.08 Mole/litre
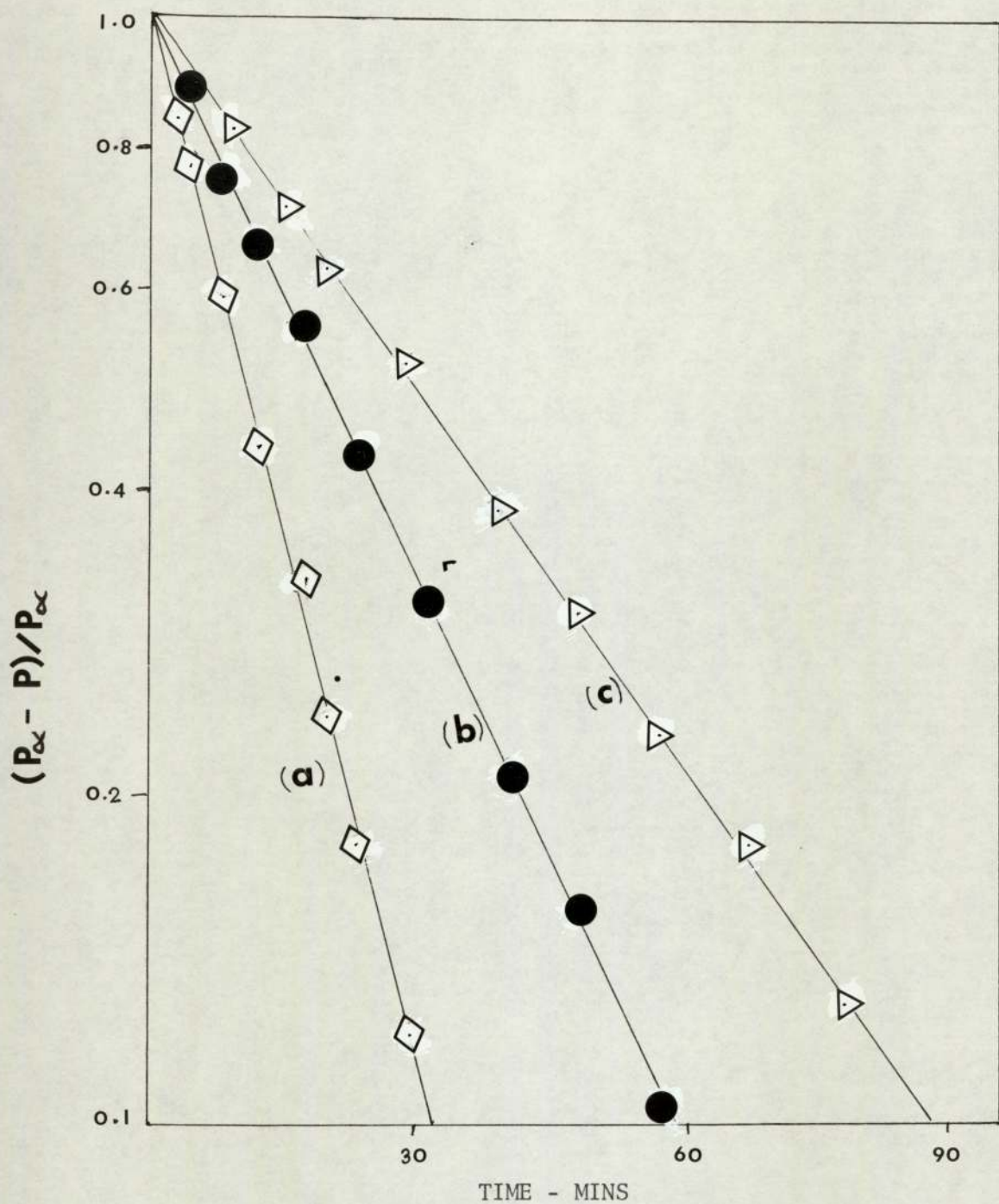   [Pyridine] = 0.19 Mole/litre.

Fig. 4.2   Semi-logarithmic plot of (Pα-P)/Pα versus time for the reaction of
TLAC with pyridine.

   (a) [TLAC] = 1.08 mole/litre, [pyridine] = 0.19 mole/litre
   (b) [TLAC] = 0.87 mole/litre, [Pyridine] = 0.08 mole/litre
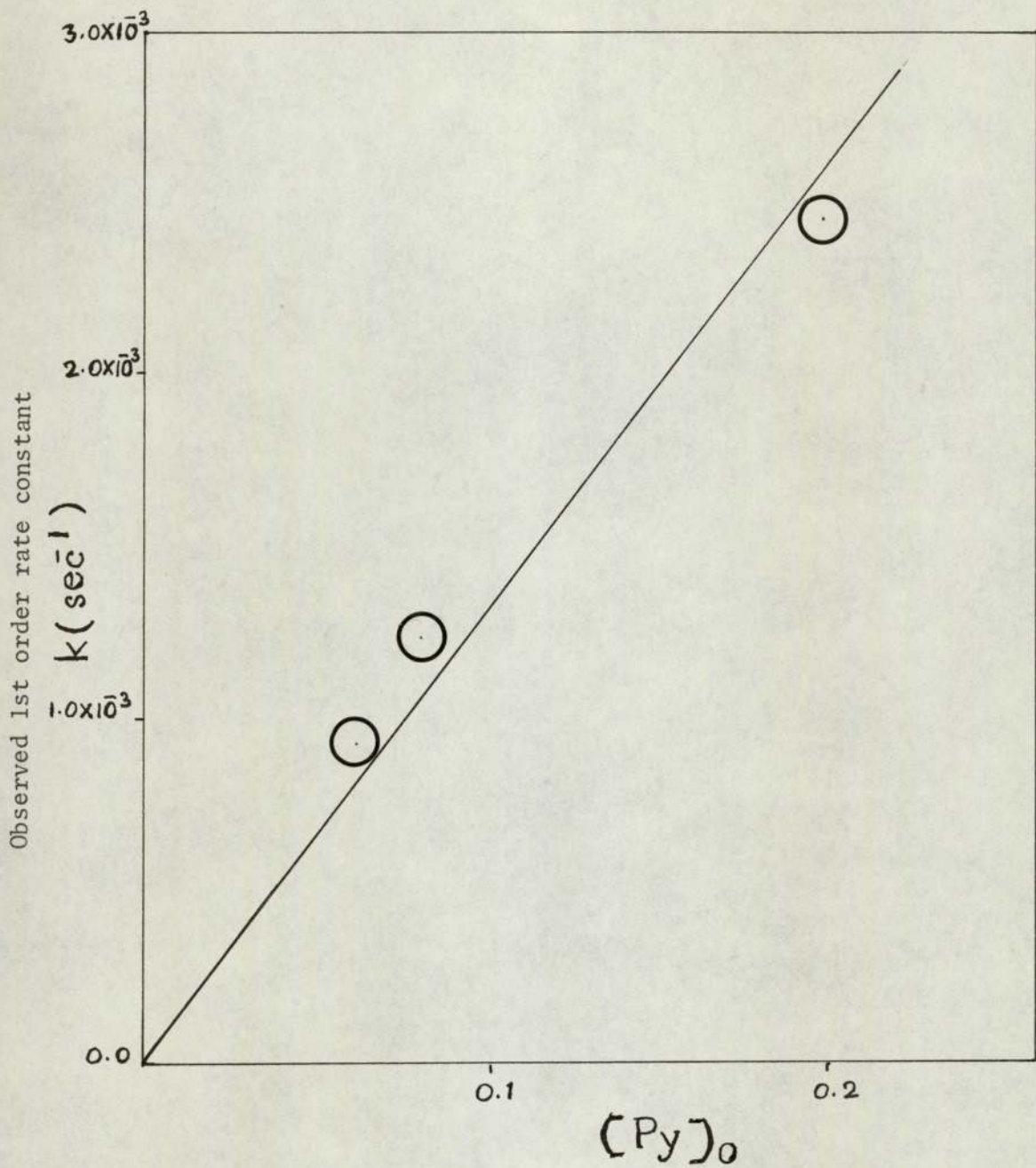   (c) [TLAC] = 0.94 mole/litre, [Pyridine] = 0.06 mole/litre

Fig. 4.3   Initial rate studies of the decomposition of TLAC in
            nitrobenzene at 25°C.   Effect of added pyridine

The products of the decomposition were low molecular weight poly thio-α-esters, the structure and properties of which will be discussed more fully in a subsequent chapter. TLAC was more difficult to prepare in a pure state than other monomers of this group. It is believed that, as in the case of similar compounds, impurities play a major part in controlling the molecular weight of the resultant polymer. For this reason further kinetic studies were concentrated on TGAC and TIBAC

4.2 Pyridine initiated decomposition of TGAC

Preliminary tests indicated that TGAC is highly reactive. A solution of the monomer in nitro-benzene (concentration 1.0 mole/litre) was prepared. The rate of decomposition of the monomer was first measured by gas evolution technique using the low temperature kinetic apparatus as shown in Fig.4.4. In the beginning of the kinetic studies the monomer solution was introduced into the reaction vessel inside the dry box. The initiator was weighed into a small bucket and allowed to suspend from a hook attached to the socket of the reaction vessel. This manipulation was also carried out inside the dry box. The reaction vessel was closed by a tap before it was taken out and joined to the manometer with a vacuum pump at room temperature. It was observed that the reaction started during evacuation before knocking down the bucket containing the initiator and so proper decomposition studies could not be achieved.

In the later kinetic studies the mouth of the reaction vessel was closed with a suba-seal. The monomer solution was introduced

into the reaction vessel by means of a hypodermic syringe. The whole
apparatus was evacuated as described above and placed in the water bath.
A few minutes are allowed to attain the temperature of the water-bath.
As in the case of monomer, a solution of the initiator was prepared
in nitrobenzene (concentration 1.0 mole/litre). When the kinetic
apparatus attained the temperature of the water bath, initiator
solution was injected into the reacting vessel through the suba-seal
by means of a hypodermic syringe. The evolution of carbon dioxide
started immediately. The rise in mercury (Hg) in the manometer due
to the evolution of carbon dioxide gas was followed by reference to
a calibrated mirror scale attached to the manometer. This method of
obtaining pressure readings was preferred over a cathetometer as the
reactions carried out in this apparatus were too fast and did not
allow time for the manipulations of the cathetometer between consecutive
readings.

Conversion of the carbon dioxide pressure data to conventional
first order plots showed a good straight line behaviour. This
indicated that as in the case of TLAC the decomposition of TGAC using
pyridine as an initiator was first order process with respect to
monomer and pyridine and that the effective concentration of the
active initiator remained constant throughout the reaction.

The effect of temperature on the reaction was studied and
the fractional decomposition of TGAC at various temperatures is shown
in Figs. 4.4 and 4.5 shows a typical first order plot for the
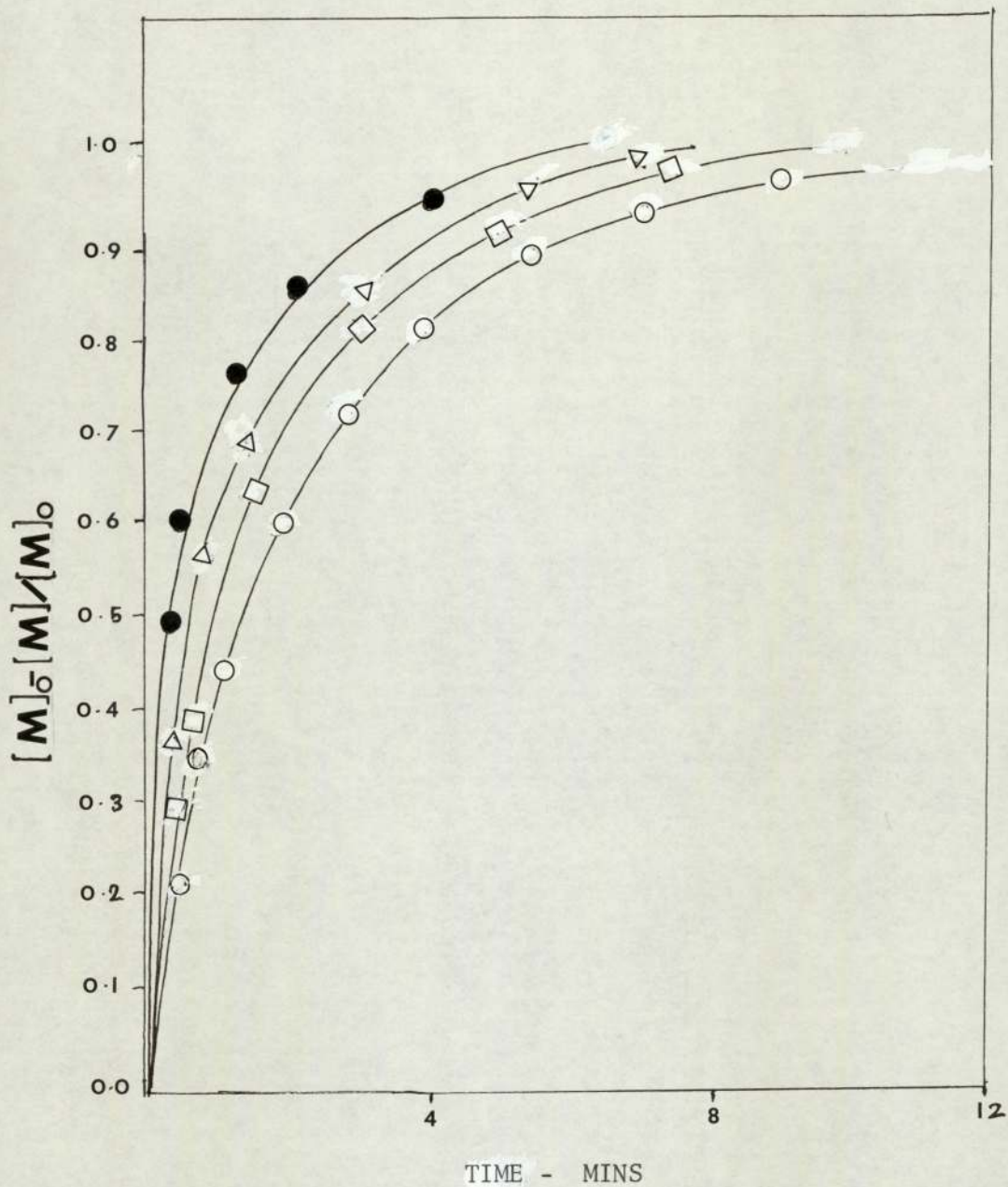decomposition of TGAC at various temperatures. The effect of

Fig. 4.4 Initial rate curves for the decomposition of TGAC with

⊙ 0.139M Pyridine at 22°C

□ 0.128M Pyridine at 25°C

△ 0.128M Pyridine at 30°C

● 0.110M Pyridine at 36°C

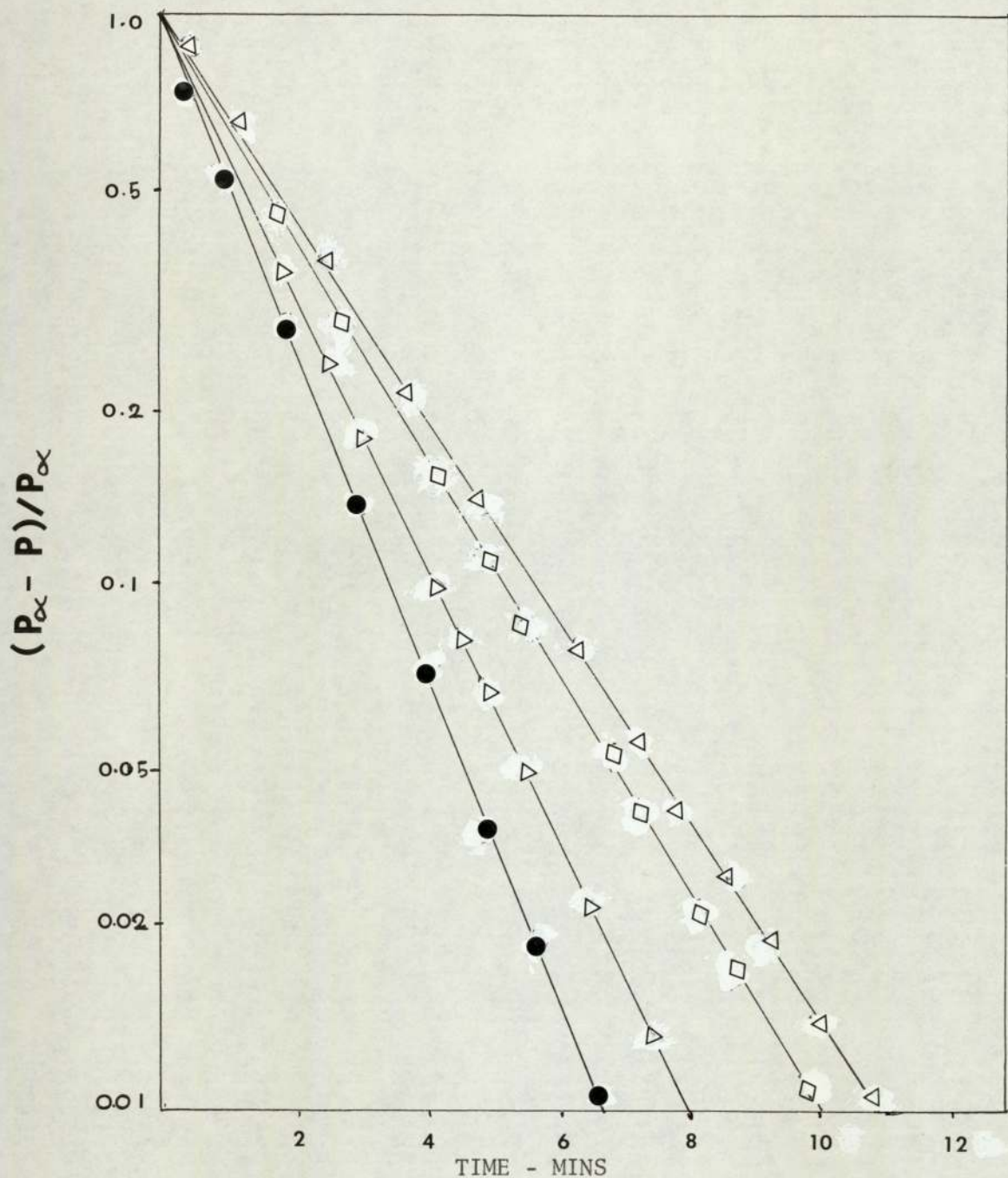$[TGAC] = 1.0$ mole/litre^{-1}

(1M = 1 mole / litre)

Fig. 4.5 First-Order (Semi-logarithmic) Plots for the decomposition of TGAC, with

               $\triangledown$ 0.139M Pyridine at 22°C

               $\Diamond$ 0.128M Pyridine at 25°C

               $\triangle$ 0.128M Pyridine at 30°C

               ● 0.110M Pyridine at 35°C

      1M = 1.0Mole / litre

temperature is quite marked. Reactions of TGAC are much more difficult to study than those of TLAC and the decomposition of the monomer occurs even with a ▨▨▨ trace amount of pyridine. The second order rate constant k'' was calculated from the following equation as shown in Table 4.2.

$$\frac{d[CO_2]}{dt} = \frac{-d[TGAC]}{dt} = k''[TGAC]\,[Pyr] \qquad (25)$$

Table 4.2 Second order rate constant K'', Energy of activation E, pre-exponential factor A and entropy of activation $\Delta S^{\pm}$ for the decomposition of TGAC with pyridine.

TGAC = 1.0 mole/litre

Temperature	Second order rate constant k'' ($L\ mol^{-1}s^{-1}$)
22°C	4.52×10^{-2}
25°C	5.21×10^{-2}
30°C	8.51×10^{-2}
35°C	11.61×10^{-2}
E ($k\ cal\ mol^{-1}$)	11.96
($kJ\ mol^{-1}$)	49.87
A ($\ell mol^{-1}s^{-1}$)	2.9×10^{6}
$\Delta S^{\pm}$ ($cal.deg.^{-1}mol^{-1}$)	-29.4

The energy of activation E, pre-exponential factor A and the entropy of activation $\Delta S^{\pm}$ were calculated from a conventional arrhenius plot. The values obtained are at first sight similar to those expected for nucleo-philic attack at an activated site rather than thermal cleavage of the ring.

The Arrhenius plot used in the calculation is shown in Fig.4.6.

The decomposition of TGAC initiated with pyridine resulted in the formation of a polymer.   The structure of which may be represented as shown below:

$$-\{S - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - CO\}_n$$

(X)
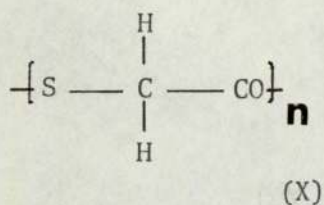
The formation of the polymer was reflected in the infra red spectra, where the carbonyl peaks of the monomer (1845cm^{-1}, 1770cm^{-1}) disappeared and that of the ester appeared at 1690cm^{-1}, which is the characteristic region for poly thio-esters.   X-ray diffraction studies indicate that the polymer is highly crystalline.   The polymer appeared to be of very high molecular weight and low solubility which made routine determination very difficult.

Large changes in initial Pyridine: Monomer ratio had little apparent effect on the molecular weight however.   The nature and properties of the polymer will be discussed in more detail in a subsequent chapter.

The reaction mechanism probably involves the formation of some sort of intermediate between the monomer and base which rapidly decarboxylates to yield a species capable of taking part in a chain propagation process.   The equation below depicts a possible sequence of reactions leading to the formation of polymers

$$TGAC + Pyridine \longrightarrow [TGAC-Py]$$

$$Polymerisable\ species + CO_2 + Pyridine \longrightarrow$$
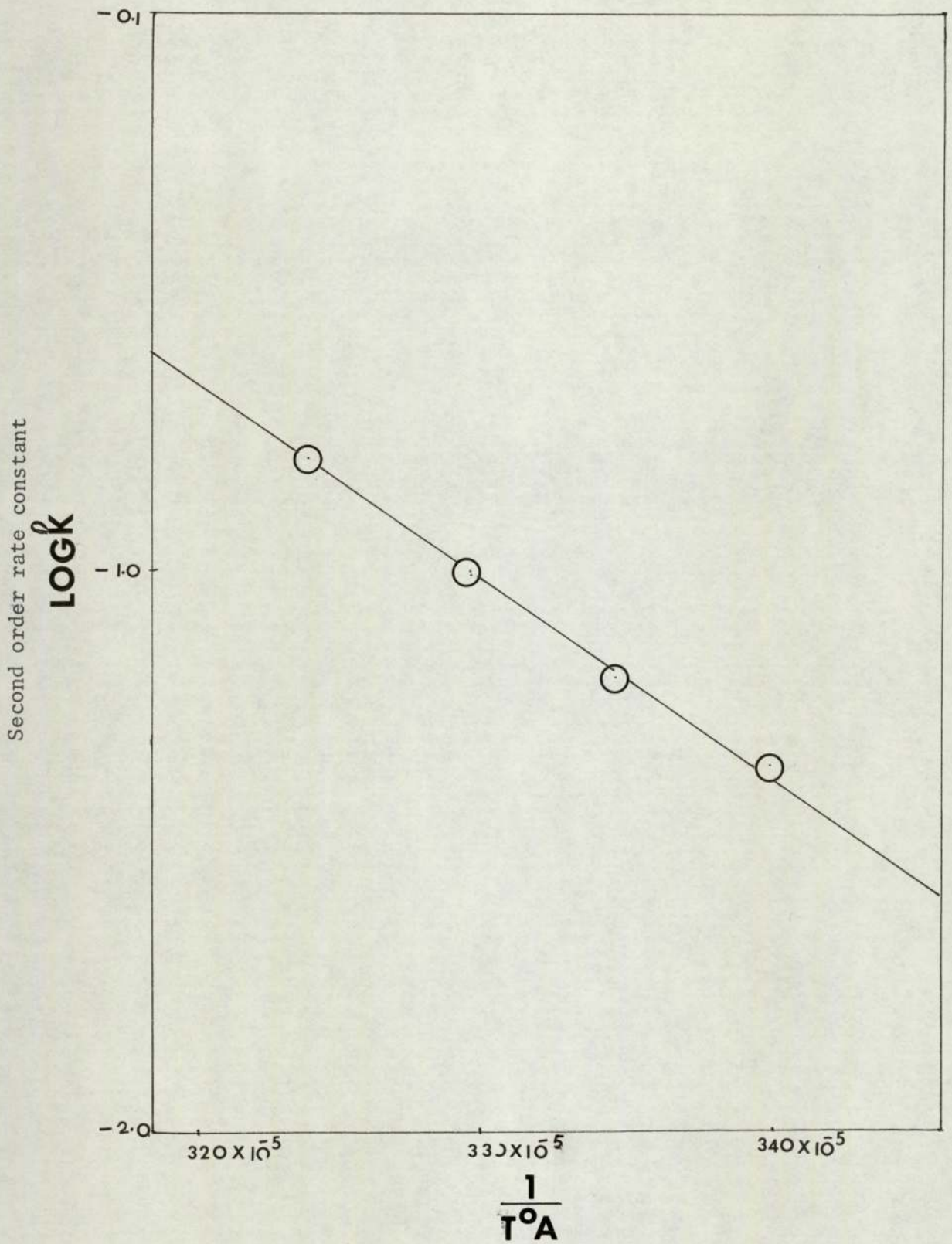
(26)

$$Polymer.$$
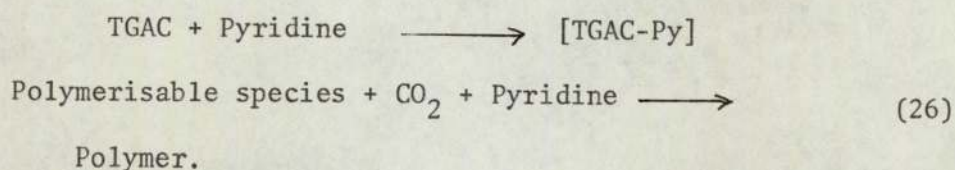
Fig. 4.6   Arrhenius plot of the second order rate constant logk
            versus the reciprocal of absolute temperature for the
            decomposition of TGAC with Pyridine.
            Temperature range 22° - 35°C.

The strength of the change transfer bond will depend essentially upon the nucleophilicity of the initiator, the susceptibility of $C_{(4)}$ carbonyl to this form of attack and the steric hindrence associated with both the initiator and the substituents at $C_{(5)}$ of the α-thio acid anhydrocarboxylates. In the case of TGAC there is no steric hindrence attached to the $C_{(5)}$ carbonyl and so the attacking nucleophile can approach the $C_{(4)}$ carbonyl easily thus resulting a rapid reaction rate. The mechanism of the reaction will be discussed in detail in the later section together with TLAC and TIBAC which seems to be common in all the three α-thio acid-anhydrocarboxylates.

4.3 Pyridine-initiated decomposition of TIBAC

The decomposition of TIBAC with pyridine at various temperatures
was found to be fairly slow in comparisons with TGAC and TLAC.   A
solution of the thioisobutyric anhydrocarboxylate was prepared in
nitrobenzene (concentration 1.0 mole/litre).   The rate of decomposition
of the monomer was studied by gas evolution technique using initiator
type low temperature kinetic apparatus as before.   Reactions were
carried out at several temperatures and various concentrations of
monomer and initiator.

From the preliminary pressure readings plots of pressure versus
time were drawn.   Then converting the pressure data into a conventional
first order plot of $\ln(P\infty-P)/P\infty$ versus time gave reasonable straight
lines.   Fig. 4.7 shows the curves for the percentage conversion of
TIBAC with time at various temperatures and Fig. 4.8 is a typical first
order plot of monomer decomposition versus time at various temperatures.
The effect of temperature can be seen in the pressure curve (Fig.4.7)
where the rate increases steadily with increase in temperature.   The
decomposition of the monomer occurs even with a trace amount of
pyridine as in the case of TGAC and TLAC but more slowly.
In a similar way the rate of decomposition is dependent upon the
initial concentration of pyridine.   This is shown in Fig. 4.9.   Thus
the reaction is first order in monomer and first order in pyridine and
in addition pyridine is not consumed during the reaction.   Second
order rate constants may therefore be derived from the following
expression:

$$\frac{d[CO_2]}{dt} \quad = \quad \frac{-d[TIBAC]}{dt} = k''[TIBAC][Pyr] \qquad (27)$$

Table 4.3 gives the second order rate constant and derived energy of activation E, pre exponential factor A and entropy of activation calculated from Arrhenius equation (Fig.4.10).

Table 4.3   Second order rate constant k'' and derived kinetic parameters for the reaction of TIBAC with pyridine.

Temperature	Monomer mole/litre	Pyridine mole/litre	Second order rate constant k''. (ℓ.mol^{-1}s^{-1})
35°C	0.66	0.33	1.48×10^{-3}
35°C	0.66	0.16	1.50×10^{-3}
45°C	0.50	0.50	3.0×10^{-3}
53°C	0.16	0.08	8.0×10^{-3}

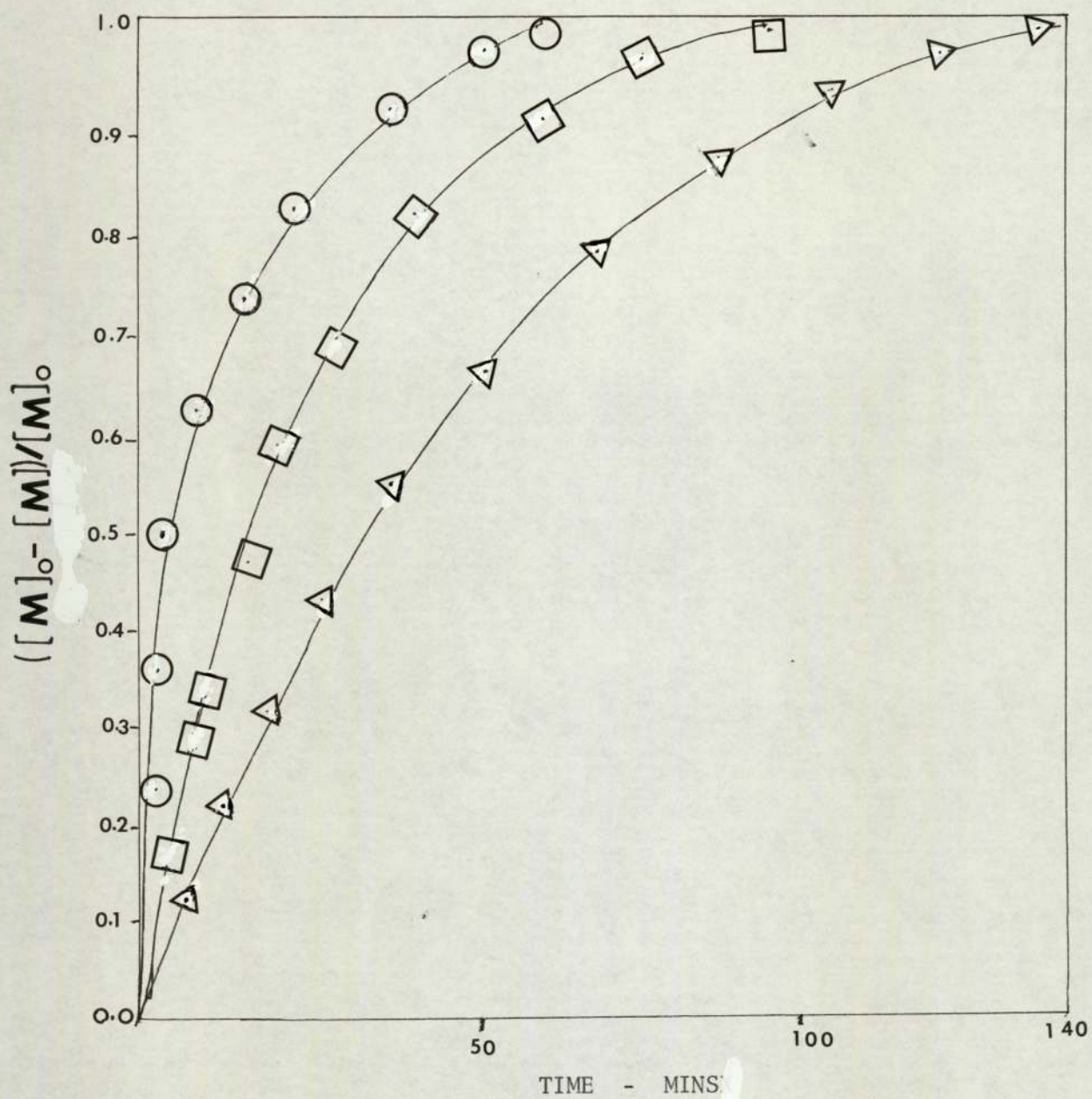|			
Ea	18.0 (k cal mol^{-1}) :	(75.2 (kJ mol^{-1})	
A	6.0×10^{8} (ℓmol^{-1}S^{-1})		
$\Delta S^{\pm}$	-15.7 (cal deg^{-1} mol^{-1})		

Fig. 4.7 Initial rate curves for the decomposition of TIBAC with
⊙ equimolar pyridine at 45°C
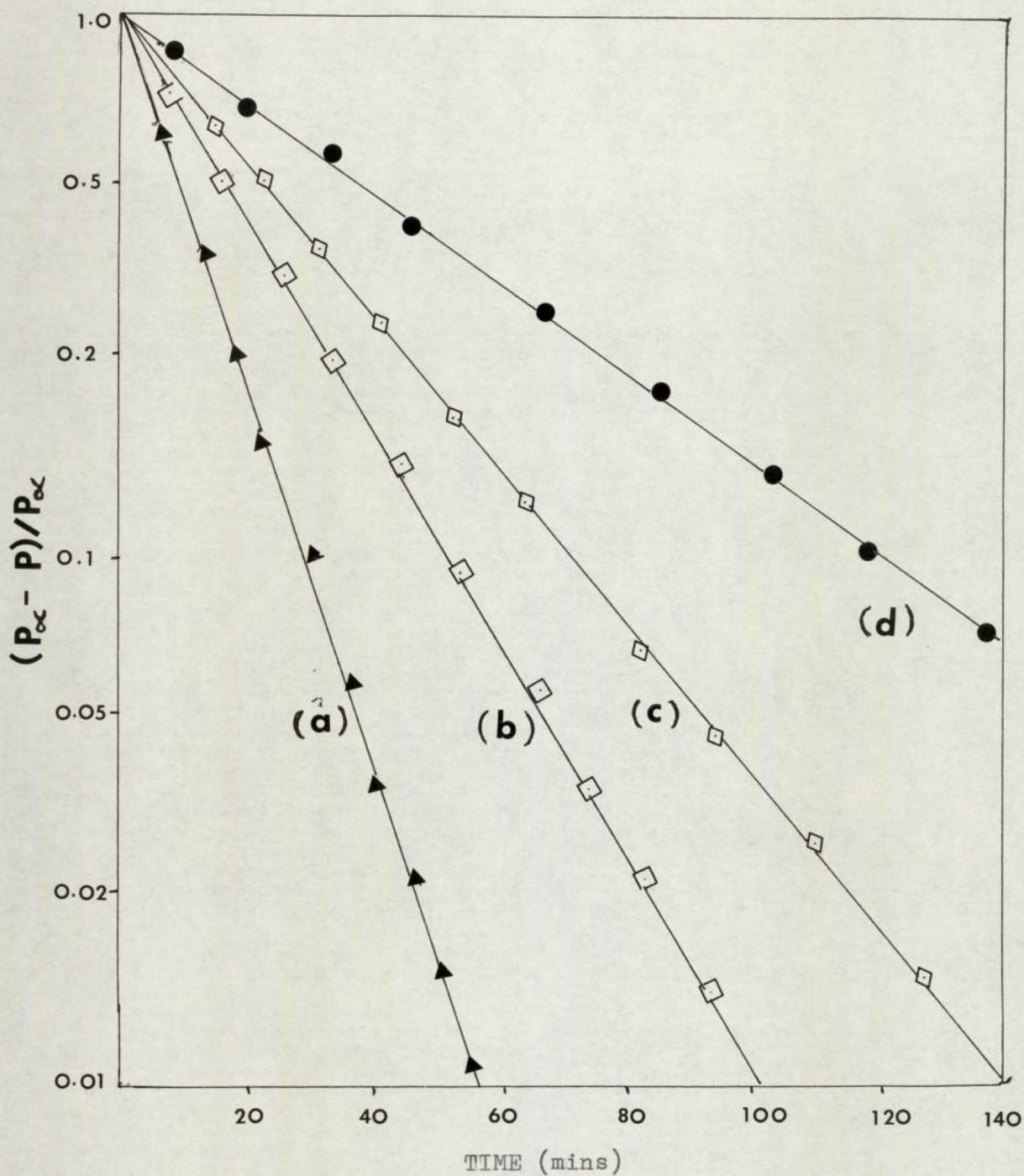▢ 2:1 molar pyridine at 53°C
△ 2:1 molar pyridine at 35°C

Fig. 4.8   First order (semi-logarithmic) plots for the
decomposition of TIBAC with

(a) equimolar pyridine at 45°C
(b) 2:1 molar pyridine at 53°C
(c) 2:1 molar pyridine at 35°C
(d) 4:1 molar pyridine at 35°C
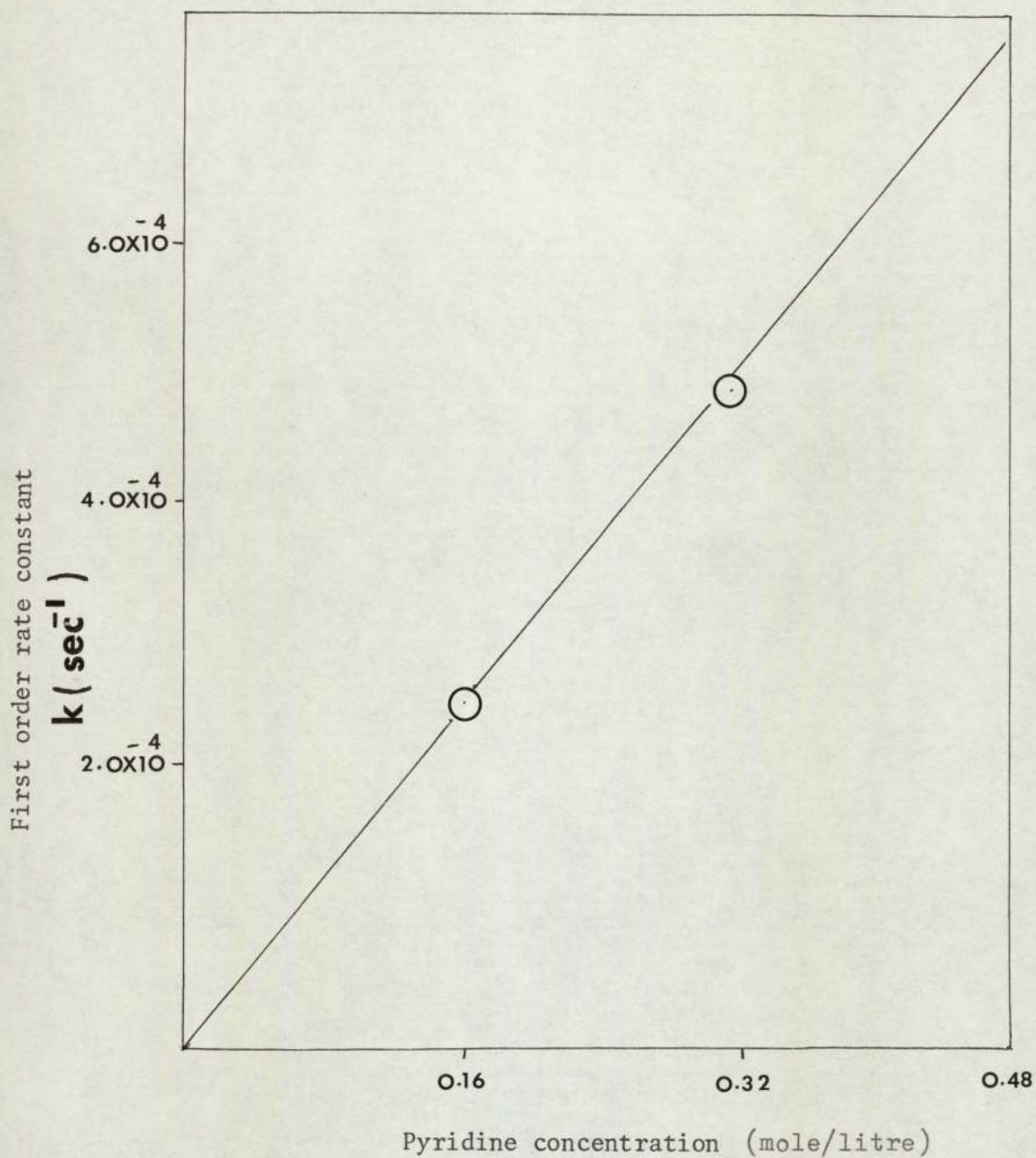
Fig. 4.9   The effect of added pyridine on the observed rate
            constant for the decomposition of TIBAC at 35°C.

    [M] = 0.66 Mole/litre
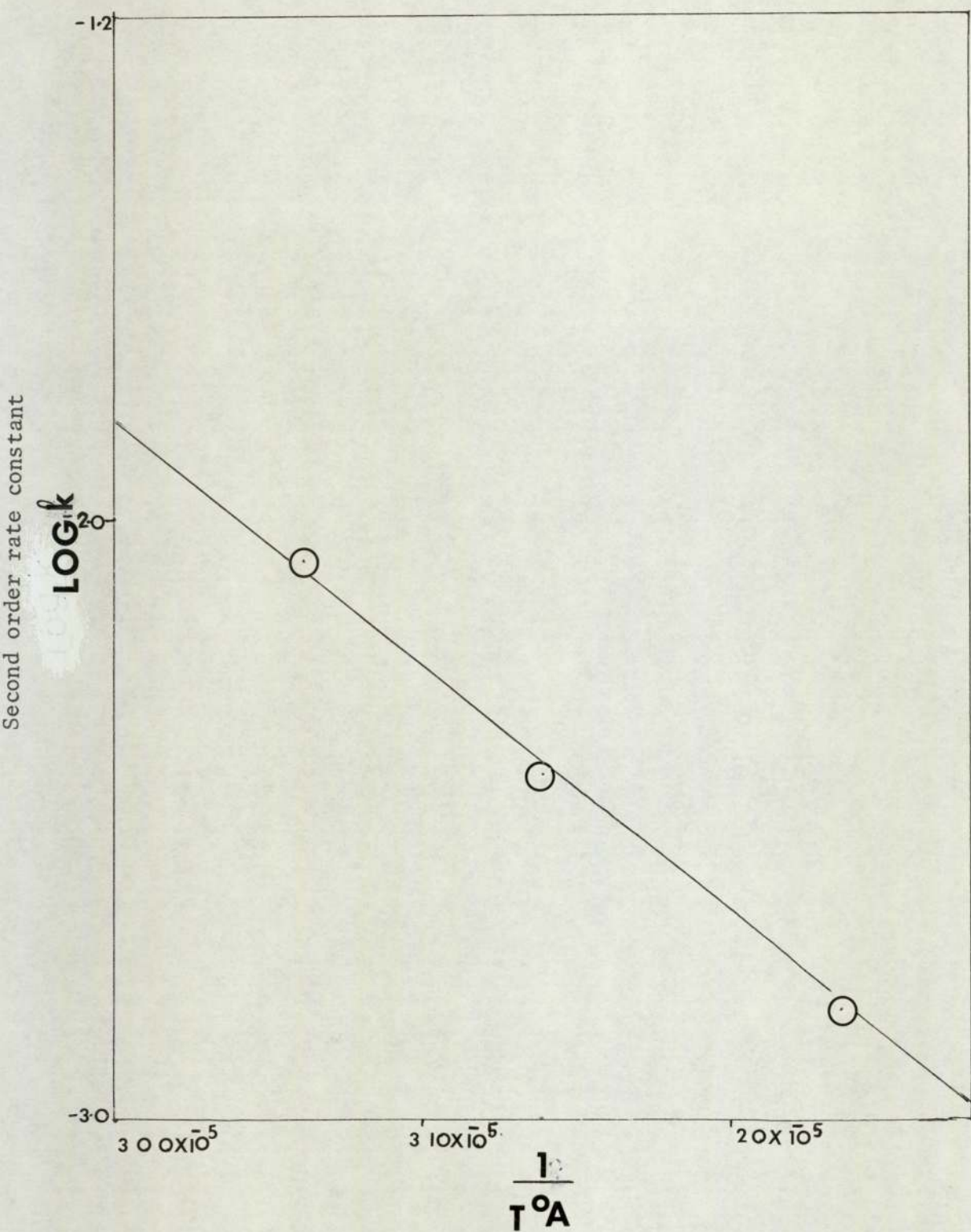
Fig. 4.10   Arrhenius plot of the second order rate constant
             (log k) versus the reciprocal of absolute
             temperature for the reaction of TIBAC with pyridine.
             Temperature range 35°C - 53°C.

One significant difference between TIBAC and the other two anhy-
drocarboxylates is the fact that addition of pyridine to the former
is accompanied by formation of a bulky white precipitate. This is
more noticeable at higher pyridine concentrations when the rate of
decomposition is more rapid. Although TGAC decomposition is faster
than that of TIBAC actual precipitation of polymer from nitrobenzene
only takes place slowly. The precipitate from TIBAC however is of
quite different appearance.

In order to investigate the nature of the precipitate equimolar
concentrations of the monomer and pyridine were reacted at room
temperature. A molar solution of TIBAC and pyridine was prepared
in anhydrous ether and pyridine solution (concentration 1.0 mole/litre)
was introduced into the monomer solution in a flask (mouth of the flask
was closed with a suba-seal) by a hypodermic syringe. A precipitate
appeared immediately on the addition of the pyridine solution. After
the evaporation of ether under vacuum at room temperature a viscous
material was obtained. GPC analysis indicated that the product
consisted of 5-6 monomer units i.e. the molecular weight ranged
between 500-600. The infra red spectra of this polymer showed the
carbonyl ester peak at $1670 cm^{-1}$ which is the characteristic region
for poly-thio-esters. It appears that the product isolated in this
way was

$$[S \text{——} \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} \text{——} CO]_n \qquad (n = 5\text{-}6)$$
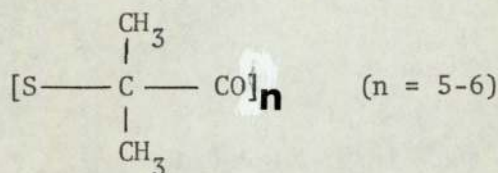
(XI)

Despite further attempts it was not possible to isolate the white precipitate formed early in the reaction. Upon evacuation of the solvent decomposition occurred with the formation of polymer as indicated above. Long reaction times followed by this isolation procedure gave higher molecular weight polymer. It is believed that the initial precipitate is that of an unstable pyridine - TIBAC complex which subsequently polymerises.

The possibility that it was tetra methyl thioglycollide was investigated but no appreciable quantity of this coumpound was detected.
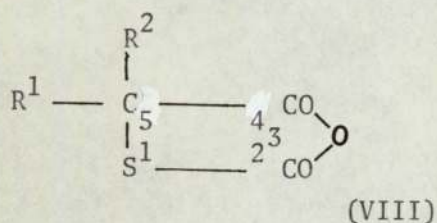
The nature and properties of the polymer are more fully discussed in a subsequent chapter.

4.4 DISCUSSION

The decomposition of α-thio-anhydrocarboxylates with pyridine exhibits reactivity in the order as shown below:

$$TGAC \longrightarrow TLAC \longrightarrow TIBAC$$
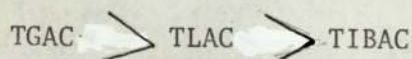
α-thio-glycollic acid anhydrocarboxylate is approximately three and a half times faster than α-thio-lactic acid anhydrocarboxylate and which in turn is some twenty five times faster than α-thioisobutyric acid anhydrocarboxylate. It is therefore observed that with one substituent in C(5) there is a moderate steric effect on the rate but with two substituents at C(5) steric effect has a tremendous effect in reducing the rate. Although the difference could in principle be explained by a change in reaction mechanism, it appears from kinetic studies that the decomposition of these three thioanhydrocarboxylates - TGAC, TLAC and TIBAC is linked with a common mechanism
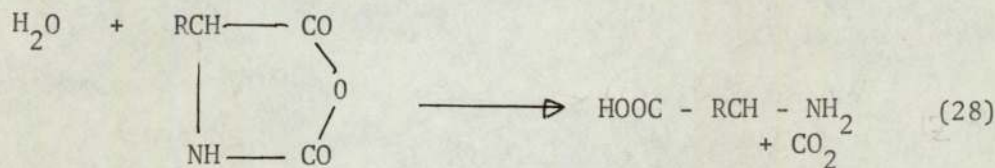
$$R^1 - \underset{\underset{S^1}{|}}{\overset{\overset{R^2}{|}}{C}}_5 \underset{\qquad}{\overset{\qquad}{\underset{2}{\overset{4}{\underset{3}{-}}}}} \begin{matrix} CO \\ CO \end{matrix} O$$

(VIII)

The decomposition of similar ring compounds such as NCAs of α-amino-acids and anhydrocarboxylates of α-hydroxy acids with pyridine have been widely studied. No general mechanism is found but various mechanisms are proposed each being predominant under special conditions. First few mechanisms will be discussed and then the probable mechanism will be proposed for the decomposition of thio-anhydrocarboxylates with pyridine.

Tertiary amines were amongst the first initiators of the NCA polymerisation which had been described in the literature and it seems
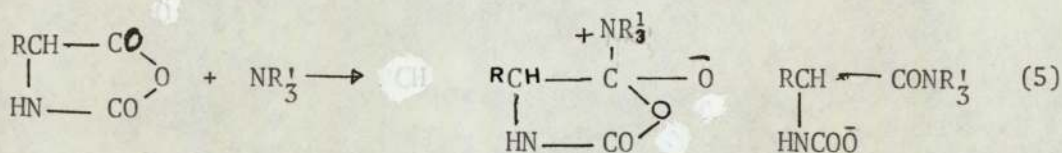
that the polymerisation of all the known NCA's may be accomplished by their action. Wesseley[12] reported in 1925 that glycine and phenyl alamine NCAs are readily polymerised in pyridine at ambient temperatures and later he reported a similar polymerisation of sarcosine NCA.

In the early years of these studies some controversy arose as to whether traces of water are necessary for the initiation induced by tertiary amines. The initiation by primary and secondary amines has been explained by postulating transfer of a labile proton to the monomer.

$$H_2O \quad + \quad \begin{array}{c} RCH \longrightarrow CO \\ | \qquad \qquad O \\ NH \longrightarrow CO \end{array} \longrightarrow HOOC - RCH - NH_2 \quad + CO_2 \qquad (28)$$

Such protons are not available in a tertiary base and therefore Coleman[35] suggested a co-catalysis by traces of water which would supply the protons. However, the elaborated studies of Wessely demonstrated that water is not necessary for the pyridine initiation and more recent studies of Bamford's[19] group have confirmed the fact.

Wieland[17] suggested a mechanism that the nucleophile adds to the $C_{(5)}$ carbonyl forming a tetrahedral complex which opens to a Zwitterionic compound. The reaction between the oppositely charged termini of two chains propagates the polymerisation.

$$\begin{array}{c} RCH \longrightarrow CO \\ | \qquad \qquad O \\ HN \longrightarrow CO \end{array} + NR_3' \longrightarrow \begin{array}{c} ^+NR_3' \\ | \\ RCH \longrightarrow C \longrightarrow \bar{O} \\ | \qquad \qquad O \\ HN \longrightarrow CO \end{array} \quad \begin{array}{c} RCH \longleftarrow CONR_3' \\ | \\ HNCO\bar{O} \end{array} \qquad (5)$$
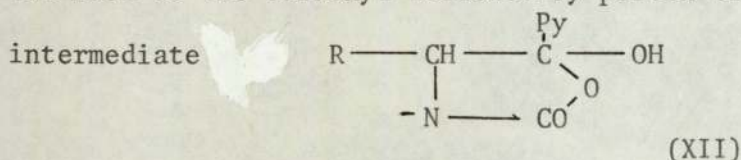
The mechanism   demands concurrent formation of diketopiperazines

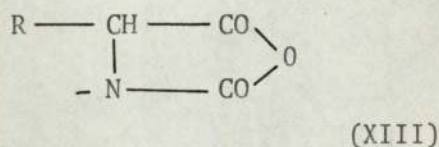which could not be obtained in practice.

    A different mechanism has been suggested by Ballard and Bamford.

According to them the role of the base is to abstract the proton of the

ring nitrogen and the anionic NCA

$$\text{RCH} \underset{|}{\overset{}{\longrightarrow}} \text{CO} \diagdown_{O}$$
$$- \text{N} \longrightarrow \text{CO} \diagup$$
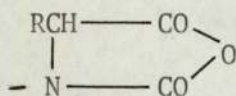
Thus formed attacks the $C_{(5)}$ carbonyl of a non-activated molecule.

This could be achieved either by direct abstraction or by attack of

the base at the carbonyl followed by proton transfer to give the

intermediate

$$R \longrightarrow \underset{|}{\text{CH}} \longrightarrow \overset{Py}{\underset{}{C}} \longrightarrow \text{OH}$$
$$- \text{N} \longrightarrow \text{CO} \diagup^{O}$$

(XII)

which decomposes to

$$R \longrightarrow \underset{|}{\text{CH}} \longrightarrow \text{CO} \diagdown_{O}$$
$$- \text{N} \longrightarrow \text{CO} \diagup$$

(XIII)

    Recently Bamford and Block simplified the previous mechanism.

They assumes that the tertiary amine activates the NCA monomer predom-

inantly by acting as a base and abstracting a proton of the ring

nitrogen. This assumption was supported by examining the capacity

of several tertiary amine compounds to serve as initiators. In the

series, pyridine, 2-picoline (2-methyl pyridine), and 2,6 lutidine

(2,6 dimethyl pyridine), the basicity increases with degree of

methylation of the aromatic rings, on the otherhand, steric hindrance

of the tertiary nitrogen atom decreases its nucleophilic power, hence

lutidine is the least reactive nucleophile and pyridine is the most

reactive (e.g. in the formation of XII)

When these amines were used to polymerise NCA it was found that
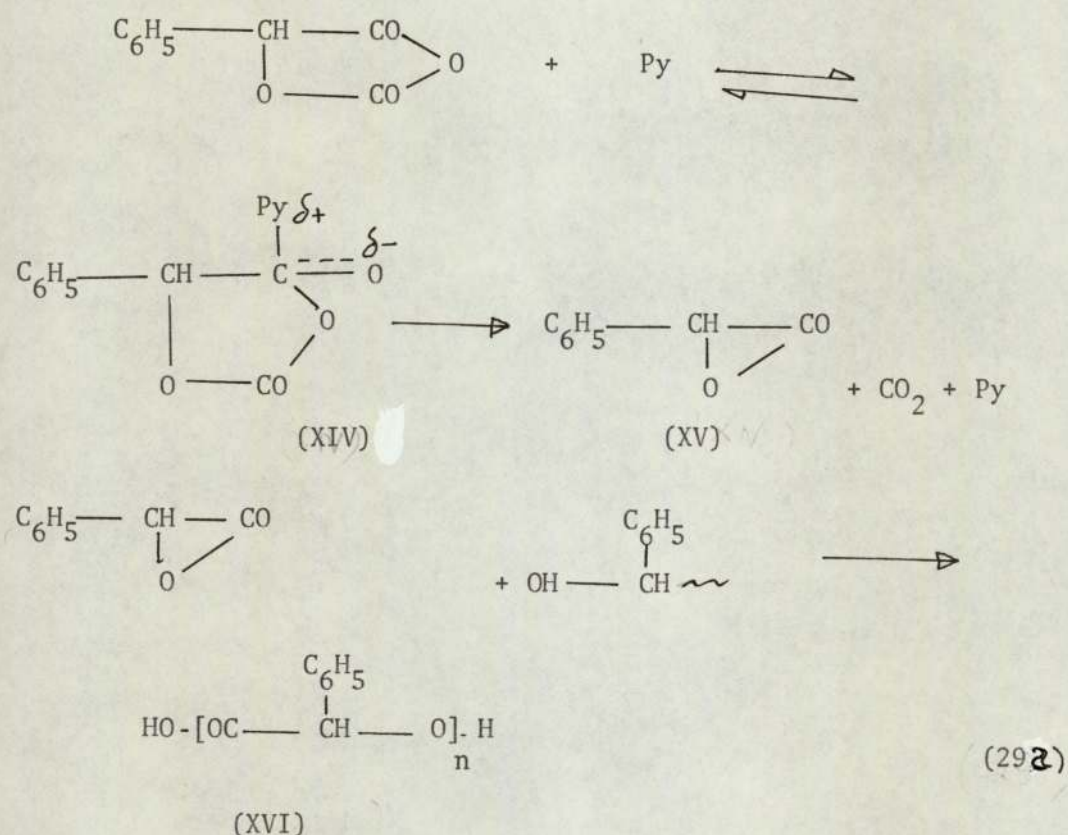lutidine is more reactive than pyridine indicating that (XIII)

must be formed directly.   In the case of anhydride however, Gold and
Jefferson[36] found the reverse, i.e. pyridine is most reactive,
indicating a nucleophilic attack on the anhydride and not proton
abstraction.

More recently Smith and Tighe have put forward a mechanism for
the polymerisation of anhydrocarboxylates of α-hydroxy acids

$$R^1 \underset{\underset{O \longrightarrow CO}{\overset{|}{\underset{C}{|}}}}{\overset{R^2}{\overset{|}{\longrightarrow}}} CO \diagdown_O$$
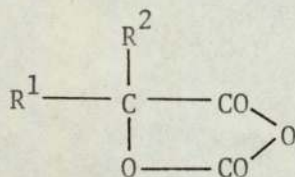
with pyridine.   Since the ring nitrogen atom is absent in these
compounds proton abstraction reaction of the type seen in XIII & XII
must necessarily be absent.   In addition NCA polymerisation with
pyridine is kinetically second order in monomer and first order in
pyridine, an observation which can be accounted for by all previously
discussed mechanisms.   The pyridine initiated polymerisation
of anhydrocarboxylates of α-hydroxy acids on the other hand has been
shown to be first order in both monomer and pyridine.   The proposed
mechanism involves the nucleophilic attack on the $C_{(4)}$ carbonyl by
the initiator and then fragmentation of the anhydrocarboxylates via
a charge transfer complex.   Loss of carbon dioxide involves the
formation of a species which is capable of taking part in a poly-
merisation reaction with trace nucleophile such as the hydroxyl
groups of traces of the parent acid.   The intermediate is believed
to be the α-lactone. The role of pyridine is considered to greatly on hence

the decomposition of the monomer to form a polymerisable intermediate.
Equation(29) indicate the sequence of reactions

$$C_6H_5 - CH - CO{\diagdown}O \quad + \quad Py \; \rightleftharpoons$$
$$O - CO{\diagup}$$

$$C_6H_5 - CH - \overset{\overset{\displaystyle Py\,\delta+}{|}}{C} \underset{\diagdown O \diagup}{=\!=\!=\!\!{}^{\delta-}\!\! O} \longrightarrow C_6H_5 - CH - CO \quad + CO_2 + Py$$
$$| \qquad\qquad\qquad\qquad O \diagup$$
$$O - CO$$

(XIV) \qquad\qquad\qquad (XV)

$$C_6H_5 - CH - CO \qquad\qquad\qquad C_6H_5$$
$$O\diagup \qquad + OH - \overset{|}{CH} \sim \qquad \longrightarrow$$

$$HO-[OC - \overset{\overset{\displaystyle C_6H_5}{|}}{CH} - O]_n H$$

(29 a)

(XVI)

The tertiary base initiated polymerisation of TGAC, TLAC and TIBAC must
now be considered in the light of the kinetic results presented in this
chapter and the mechanisms proposed for related systems.

The first group of mechanisms that can be discounted are those
involving direct proton abstraction.   Since no analogous proton
exists in α-thio-anhydrocarboxylates, mechanisms of this type cannot
occur.   In addition, the second order kinetics not observed with
TGAC and its homologous demanded by this mechanism.

Secondly the Wieland type mechanism cannot be at all representative
of the pyridine initiated decomposition of anhydrocarboxylates of α-thio-
acid.

It is important to spend some time discussing this point however
because while this work was in progress a paper by Elius and Buhrer[33,34]
was published in which the polymerisation of TGAC and TLAC was proposed
to occur by this mechanism. The proposal was only speculative however
as the authors admit since no kinetic work was carried out.

The main experimental work in the paper was the comparison of the
molecular weight and yields of polymer, produced after arbitrary time
periods with various potential initiators. This (the molecular weight)
aspect of the work was most valuable at the present project - a point
which will be discussed in a later chapter.

The first point of objection to the Wieland mechanism is the
absence of substial quantities of the six-membered thio-glycollides
in the reaction products. This point must be taken with caution
however since in subsequent chapters the point will be made that these
compounds apparently polymerise in the presence of benzylamine at a
reasonable rate. It may be inferred therefore that the stability of
glycollides in the polymerising system under discussion would be
limited. It would be wrong therefore to make a judgement about the
polymerisation mechanism solely on the basis of the apparent absence
of glycollides.

The second objection is much more fundamental and lies in the
kinetic studies. The Wieland reaction cannot explain first order
kinetics in both pyridine and monomer since it requires second order
behaviour in monomers. In fact it was to explain this kinetic

phenomenon in NCA polymerisation that the mechanism was first proposed. Elius and Buhrers'[33] suggestion that the Wieland mechanism is able to explain α-thio-acid anhydrocarboxylate polymerisation therefore be rejected (which was made in the absence of kinetic data).

The third mechanism put forward by Smith and Tighe suggests that pyridine is not a conventional initiator but a means of promoting the decomposition of the anhydrocarboxylates to yield a polymerisable species. This may be considered for the decomposition of TGAC, TLAC and TIBAC. Since it appears to satisfy the requirements. A suitable modification of this mechanism is shown in equation (29 b).

(XVII)

(XVIII)

$$+CO_2 + Pyr$$

(29 b)

(XIX)
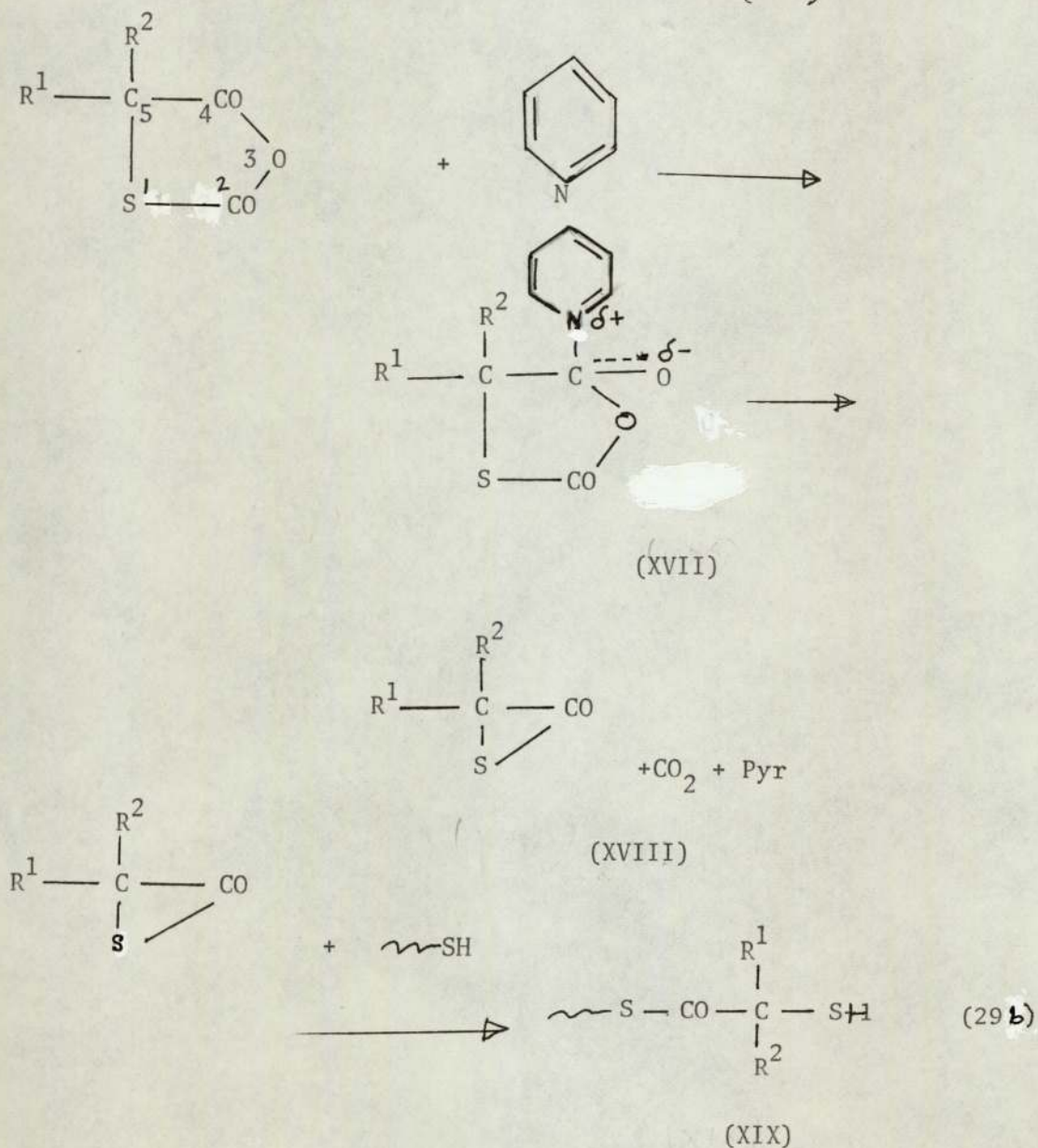
The nucleophile attacks the $C_{(4)}$ carbonyl and forms a charge transfer complex (XVII) which decomposes to form a highly reactive α-thio-lactone (XVIII) which undergoes chain addition poly-merisation by reaction with the terminal SH group of the polymer chain. If a trace of parent αthio-acid initiate the chain growth process the polymer produced will have one SH and one COOH end group. It is relevant to note that the first step in this mechanism is effectively identical to that leading to structure (XII) in NCA polymerisation. It seems probable that this mechanism is not excluded in the NCAS but is simply too slow to compete effectively with direct hydrogen abstraction.

The various available pieces of information must now be compared to test the validity of this mechanism. This can most conveniently be done by constructing a table in which the information for each monomer can be summarised and compared in Table 4.4.

TABLE 4.4

Kinetic parameters	TGAC	TLAC	TIBAC
1. Order in monomer	One	One	One
2. Order in pyridine	One	One	One
3. Pyridine consumed	No	No	No
4. Molecular weight dependence on pyridine	Not apparent	Not apparent	Not apparent
5. k'' ($\ell mol^{-1}s^{-1}$) at 25°C	$5.2 \times 10^{\pm 2}$	1.5×10^{-2}	6.5×10^{-4}
6. Ea ($kcals\ mol^{-1}$)	11.96		18.0
7. A ($\ell mol^{-1}s^{-1}$)	2.90×10^{6}		6.0×10^{8}
8. $\Delta S^{\pm}$ ($cal\ deg^{-1}mol^{-1}$)	-29.4		-15.7

The evidence seems to point clearly to the fact that a single mechanism is operative for all three monomers.

The kinetic parameters are consistent with the proposed mechanism (Equation 29b). The activation energy (12-18 kcals mol^{-1}) is lower than that required for decomposition of the unactivated ring (Chapter 6) and supports the idea of the formation of a transitory activated complex. The frequency factor in the range of 10^{6}-10^{8} $l.mol^{-1}s^{-1}$ is consistent with a mechanism which is sterically difficult such as the attack of pyridine at the $C_{(4)}$ carbonyl. The negative values of entropy of activation require the formation of a polar transition state. In contrast α-thio-lactone formed by thermal decomposition (described in Chapter 6) showed the kinetic parameters very different from the pyridine initiated decomposition although the intermediate α-thio-lactone is the same.

Smith was able to demonstrate the importance of electronic effects at $C_{(5)}$ by comparing phenyl and pentafluorophenyl groups in α-hydroxy anhydrocarboxylates. Although such effects are smaller in alkyl groups, the substituted thio-anhydrocarboxylates studied here must show some electronic effect. The rate of the reaction for TGAC is observed to be three and a half times faster than for TLAC which in turn is twenty-six times faster than TIBAC. The observed kinetic rates clearly demonstrate that not only the steric effect is operative but also the electronic effect plays a prominent role in the rate of the reaction.

On this basis the rates of decomposition of mandelic acid anhydrocarboxylate (MAAC) may be compared with α-thio-lactic acid anhydrocarboxylate (TLAC).

Although the steric effect is almost the same, because of electronic effects the rate of decomposition of MAAC should be several times faster than TLAC but the observed rate is only slightly higher for MAAC. α-hydroxy anhydrosulphites have extensively been studied. The relative electronic effects can be observed if we compare the rates of lactic acid anhydrosulphite (LAAS) with mandelic acid anhydrosulphite (MAAS). The rate for MAAS decomposition is ten times faster than LAAS.

If the $C_{(5)}$ substituents alone affected the rate the same effect should have been observed for MAAC and TLAC. The rate of decomposition of MAAC is 1.92×10^{-2} $\ell\text{mol}^{-1}\text{s}^{-1}$ and observed rate for TLAC decomposition is 1.50×10^{-2} $\ell\text{mol}^{-1}\text{s}^{-1}$ which shows a very little difference in the rates.

From this it is apparent that the sulphur containing ring reacts more rapidly than oxygen containing ring. This may be due to the faster formation of the activated complex (XVII) or its more facile decomposition. This requires information on the relative effects of sulphur and oxygen on the thermal stability of the rings which will be considered in subsequent chapters and finally discussed in Chapter 8.

4.5 Decomposition of TIBAC with alkoxide (Tertiary butyl lithium oxide) Results and Discussion

A very short study of the decomposition of TIBAC with alkoxide was made at 35°C for comparison purpose. The reaction was slow in the beginning and after about 25% decomposition of the monomer, the rate became faster. A solution of the monomer was prepared in decalin (concentration 1.0 mole/litre). A Molar solution of the initiator was prepared in the same solvent. As before decomposition of the monomer was studied in a low temperature kinetic apparatus. The monomer solution was introduced into the reacting vessel by a hypodermic syringe. When the kinetic apparatus attained the temperature of the bath, initiator solution was introduced into the monomer solution by a hypodermic syringe. The rise in pressure in the manometer due to the evolution of carbon dioxide was measured with suitable interval of time. A plot of pressure versus time was drawn. Then converting the pressure data, a first order plot of $\ln(P_\infty P)/P_\infty$ versus time was drawn. Fig. 4.11 is a plot of pressure curve showing the percentage conversion of monomer with time. Fig. 4.12 is a semi-logarithmic plot of $\ln(P_\infty P)/P_\infty$ versus time. The curve showed about 25% slow induction period followed by a fast reaction.

Table 4.5 gives the first order rate constants calculated from the semi-logarithmic plot and the corresponding half lives.

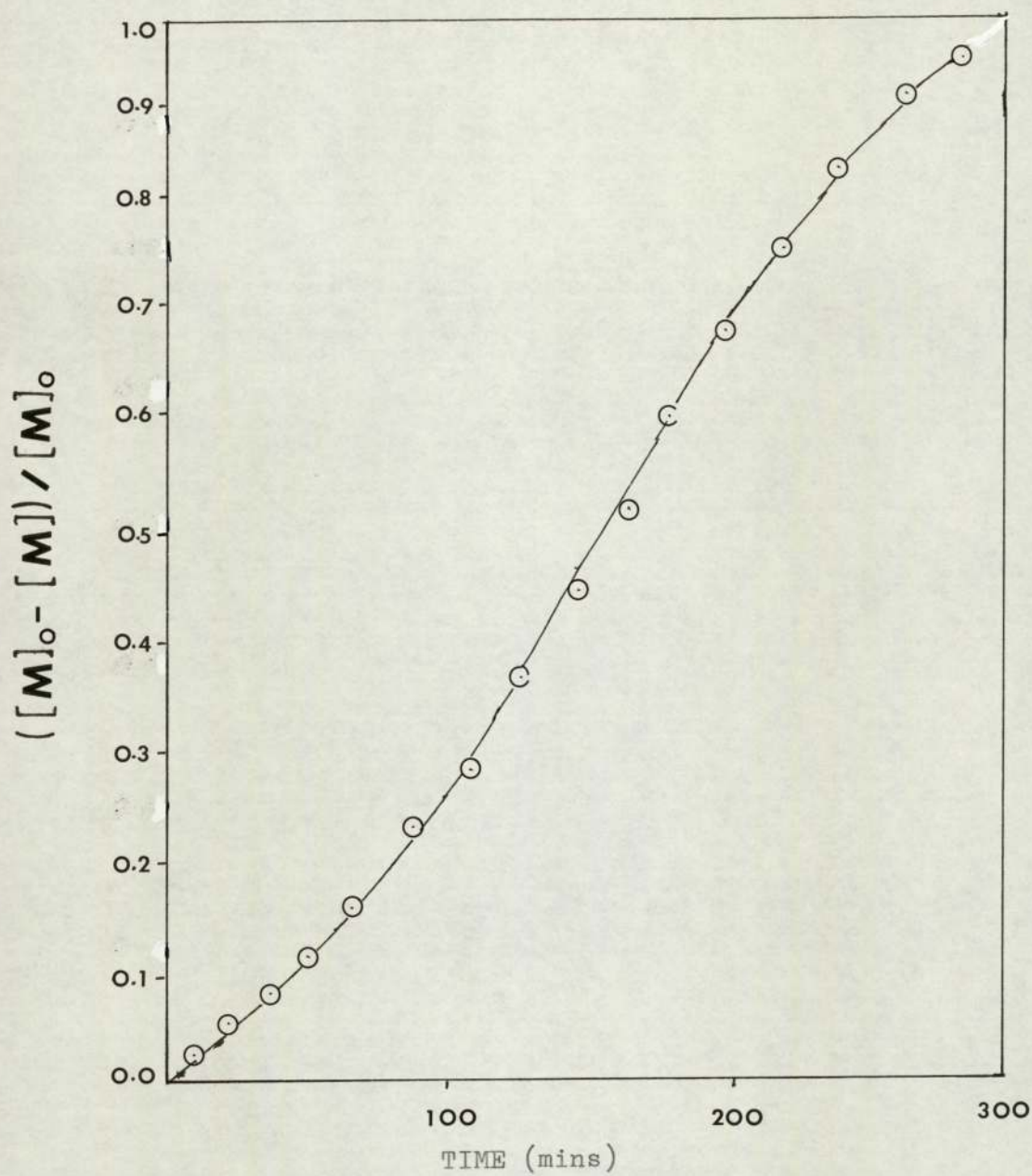| Temperature	Rate const. k.sec^{-1}	Half lives $t_{\frac{1}{2}}$ (minute)
35°C	k_1 7.0×10^{-5}	165.00
35°C	k_2 2.30×10^{-4}	48.00

Fig. 4.11   Rate curves for the decomposition of TIBAC with
             alkoxide at 35°C.

             $[TIBAC]_o$ = 1.0 Mole/litre
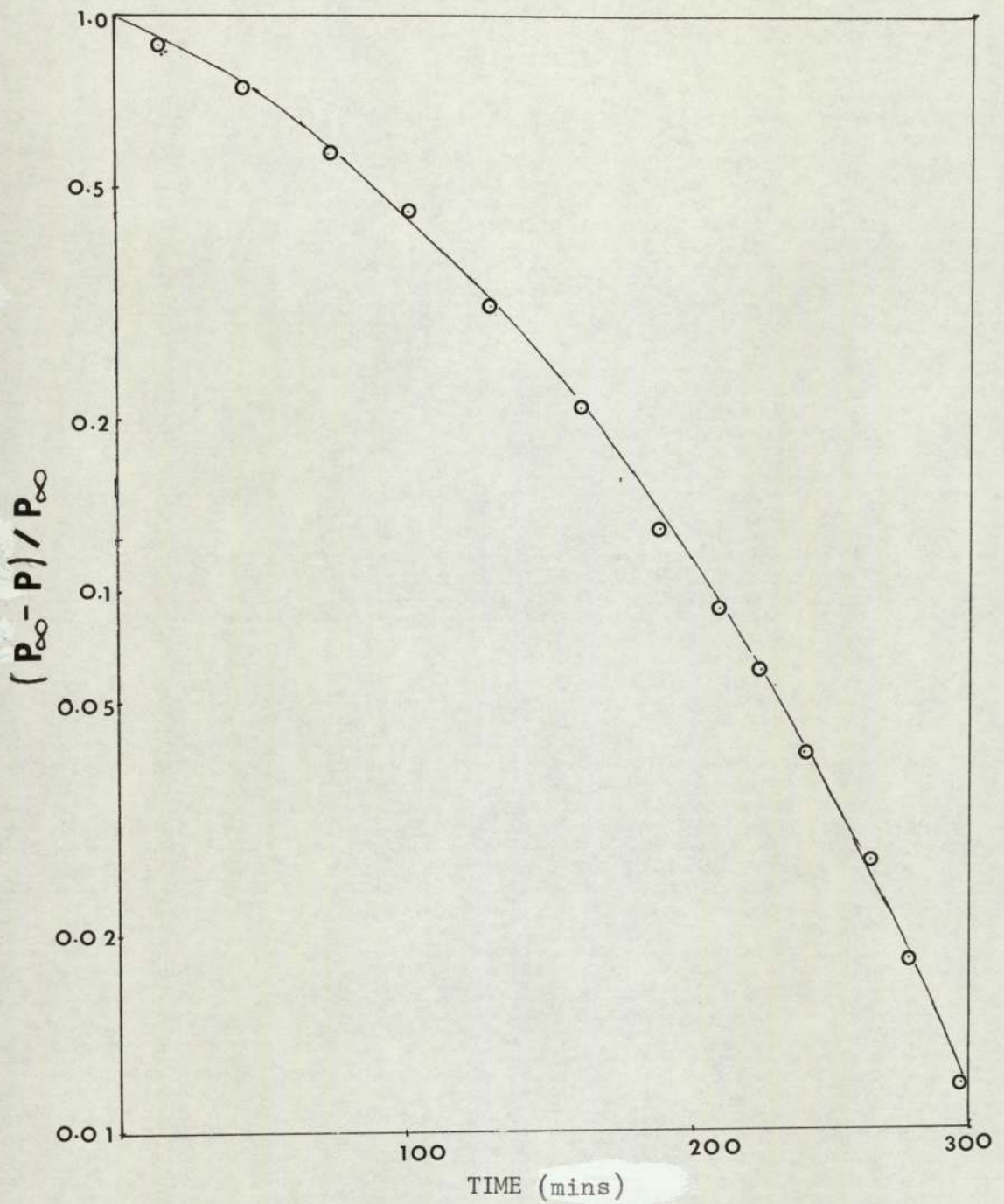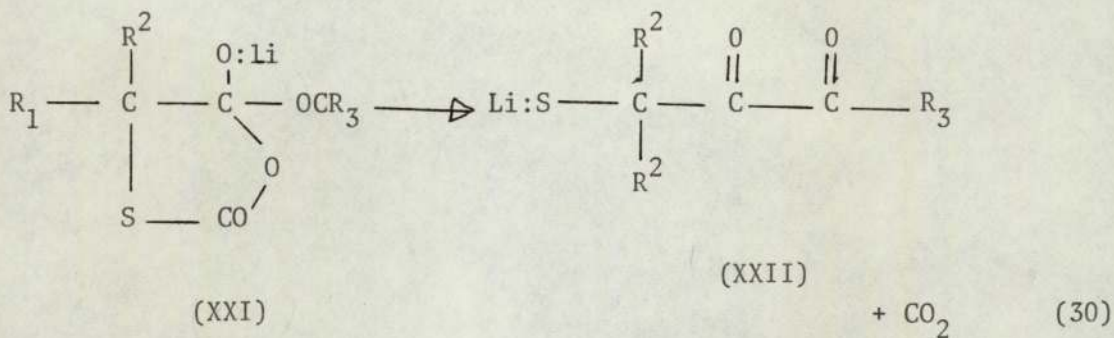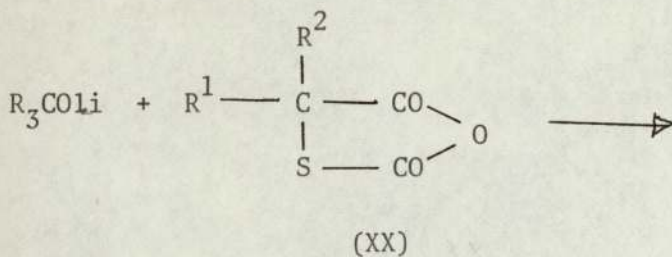 $[INITIATOR]_o$ = 0.2 Mole/litre

Fig. 4.12   First order (semi-logarithmic) plot for the
             decomposition of TIBAC with alkoxide at 35°C.

             [TIBAC]   = 1.0 Mole/litre

The polymerisation reaction is therefore apparently character-
ised by a propagation rate $k_2 > k_1$.

An equimolar amount of the initiator was injected into the
monomer solution. A precipitate appeared fairly quickly. The
solvent was removed under suction pump at room temperature leaving a
white solid. The melting point of the compound was found to be
$120^\circ - 130^\circ C$. The IR-spectra of the compound showed the ester carbonyl
peak at 1630 cm^{-1} which is the characteristic region for polythioester
thus confirming the polymer formed. The molecular weight of the
polymer was determined by GP.C which showed the weight average
molecular weight to be 40,000 but the distribution very broad (>5)

The decomposition of NCA's initiated by strong base was studied.[1]
The main features of the reaction are (1) slow induction period up to
30% conversion, then the reaction proceeds by a first order reaction
(2) The first order reactions is one-hundred times faster than that
found in primary amine initiated polymerisation (3) very high molecular
weights up to $Mw \sim 10^6$. Similar effects were observed in the
polymerisation of TIBAC initiated by alkoxide. One possible
mechanism involves the nucleophilic attack by the alkoxide to the $C_{(4)}$
carbonyl of the thio-anhydrocarboxylate and the liberation of the
carbon dioxide from the anhydride. The terminal S:Li group formed
attacks the second anhydride and the propagation continues by the
terminal S:Li group.

$$R_3COLi \;+\; R^1 \underset{\underset{S \rule[0.5ex]{1em}{0.4pt} CO}{|}}{\overset{\overset{R^2}{|}}{C}} \rule[0.5ex]{1em}{0.4pt} \underset{CO}{\overset{CO}{>}} O \longrightarrow$$

(XX)

$$R_1 \underset{\underset{S \rule[0.5ex]{1em}{0.4pt} CO}{|}}{\overset{\overset{R^2}{|}}{C}} \rule[0.5ex]{1em}{0.4pt} \underset{\overset{|}{O}}{\overset{\overset{O:Li}{|}}{C}} \rule[0.5ex]{1em}{0.4pt} OCR_3 \longrightarrow Li:S \rule[0.5ex]{1em}{0.4pt} \underset{\overset{|}{R^2}}{\overset{\overset{R^2}{|}}{C}} \rule[0.5ex]{1em}{0.4pt} \overset{\overset{O}{\|}}{C} \rule[0.5ex]{1em}{0.4pt} \overset{\overset{O}{\|}}{C} \rule[0.5ex]{1em}{0.4pt} R_3$$

(XXI)   (XXII) $+ \; CO_2$ (30)

Since polymer is formed this must be appreciably more active than the O---Li group of the initiator. Hence the degree of polymerisation is considerably greater than $\dfrac{[M]}{[I]}$ and the distribution very broad.

CHAPTER V

BENZYLAMINE INITIATED DECOMPOSITION OF TGAC,

TLAC AND TIBAC AND RELATED STUDIES

The work presented in this chapter mainly relates to the kinetic
behaviour of TGAC, TLAC and TIBAC during the benzylamine initiated
decomposition of these thio-anhydrocarboxylates.   The kinetic
studies of TGAC with benzyl alcohol are also presented in this
chapter.

5.1 Benzyl Alcohol initiated decomposition of TGAC

The rate of decomposition of TGAC in nitrobenzene (concentration
1 mol/litre) initiated by benzyl alcohol was measured at 25°C in an
initiator-type kinetic apparatus.   Equivalent amounts of TGAC and
benzyl alcohol were used to measure the rate of evolution of CO_2.
The rate was slow in the beginning and increased gradually.   The
rise in pressure as before was measured as a function of time.
Fig. 5.1 is a plot of monomer conversion versus time.   Fig.5.2 is a
conventional first order plot of $\ln(P\infty-P)/P\infty$ versus time.   From the
semi-logarithmic plot, the rate constants and half lives were calcu-
lated.   The initial reaction of TGAC with benzyl alcohol may in all
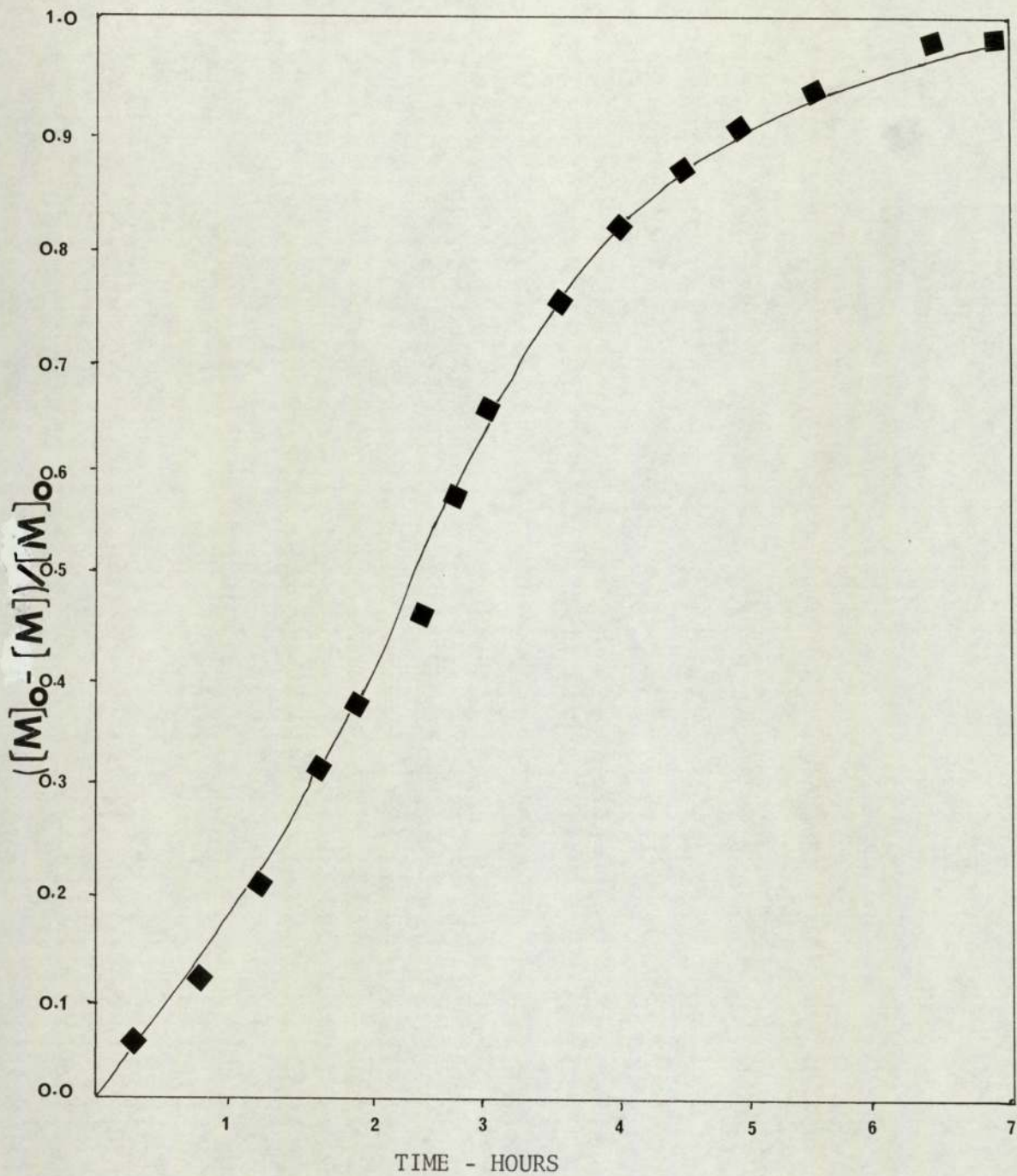probability be expressed by the following equation:

$$\frac{-d[CO_2]}{dt} = \frac{-d[M]}{dt} = K_b [M]_0 [OH]_0 \qquad (31)$$
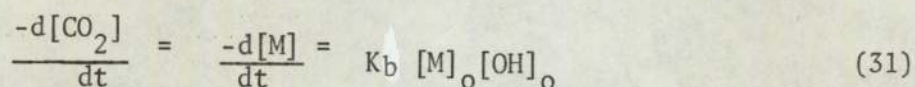
Fig. 5.1   Initial rate curves for the decomposition of TGAC with
            benzyl alcohol at 25°C.

$$[\text{TGAC}] = 1.0 \ \text{mol.l}^{-1}$$
$$(\theta CH_2OH] = 1.0 \ \text{mol.l}^{-1}$$
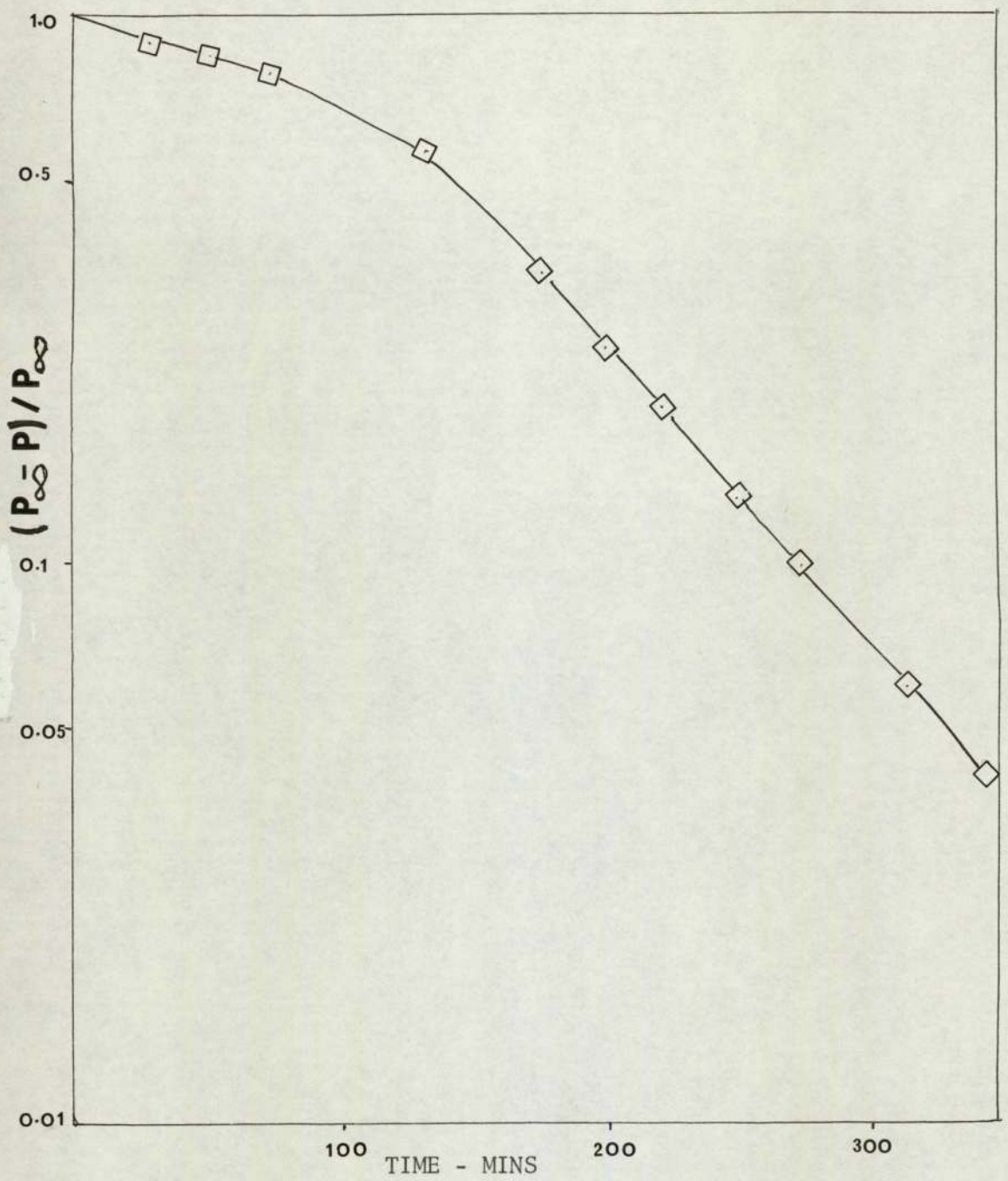
Fig. 5.2   Semi-logarithmic plot of $(P\infty-P)/P\infty$ versus time for the
decomposition of TGAC with benzyl alcohol at 25°C in
nitrobenzene

$$[TGAC] = 1.0 \text{ mol.l}^{-1}$$

$$[\theta CH_2OH] = 1.0 \text{ mol.l}^{-1}$$

where $[CO_2]$, $[M]_o$ and $[OH]_o$ refer to the concentrations of CO_2, monomer and benzyl alcohol. k_b is the second order rate constant, which can be calculated from the following equation

$$k_b = \frac{k_b'}{[OH]} \quad \text{where } k_b' \text{ is the first order rate} \tag{32}$$

constant directly determined from Fig.5.2. Since no experimental justification for equation(32) was obtained however, and some complications occur in this reaction the results will be analysed in terms of the directly observed first order rate constants. Since $[OH]_o = 1$ mol ℓ^{-1}, the initial second order constant k_b would be numerically identical.

Table 5.1 gives the first order rate constants and the corresponding half lives.

$$[TGAC]_o = 1 \text{ mole}/\ell$$

$$[C_6H_5CH_2OH]_o = 1 \text{ mole}/\ell$$

Temperature	First order *rate constant* $k_b'(S^{-1})$	Half lives $t\frac{1}{2}$(in minutes)
25°C	5.3×10^{-5} (Initial)	217.90
25°C	1.3×10^{-4} (Final)	88.50

5.2 Benzylamine initiated decomposition of TGAC: Results

The rate of decomposition of TGAC with benzylamine was measured in nitrobenzene solution at various temperatures in nitrobenzene solution (concentration 1 mole/litre). Gas evolution techniques were used to follow the rate of decomposition. Plots of concentration versus time were drawn, and manipulated as before. Fig.5.3 is a plot of the decomposition of the monomer versus time and Fig.5.4 is a semi-logarithmic plot of $\ln(P_\infty - P)/P_\infty$ versus time at various temperatures.

It is observed that the rate is dependent upon the concentration of the initiator as shown in Fig. 5.5. The reaction of TGAC with benzylamine may be expressed by the following rate equation:

$$\frac{-d[CO_2]}{dt} = \frac{-d[M]}{dt} = k_b[M][\Theta NH_2] \tag{33}$$

where $[CO_2]$, $[M]$ and $[\Theta NH_2]$ refer to the concentrations of CO_2, monomer and benzylamine, and K_b is the second order rate constant. For the present experiments however the above equation after simplification may be written as

$$\frac{-d[M]}{dt} = k'_b[M] \tag{34}$$

where K'_b is a pseudo first order rate constant calculated from the semi-logarithmic plot of $\ln(P_\infty - P)/P_\infty$ versus time.
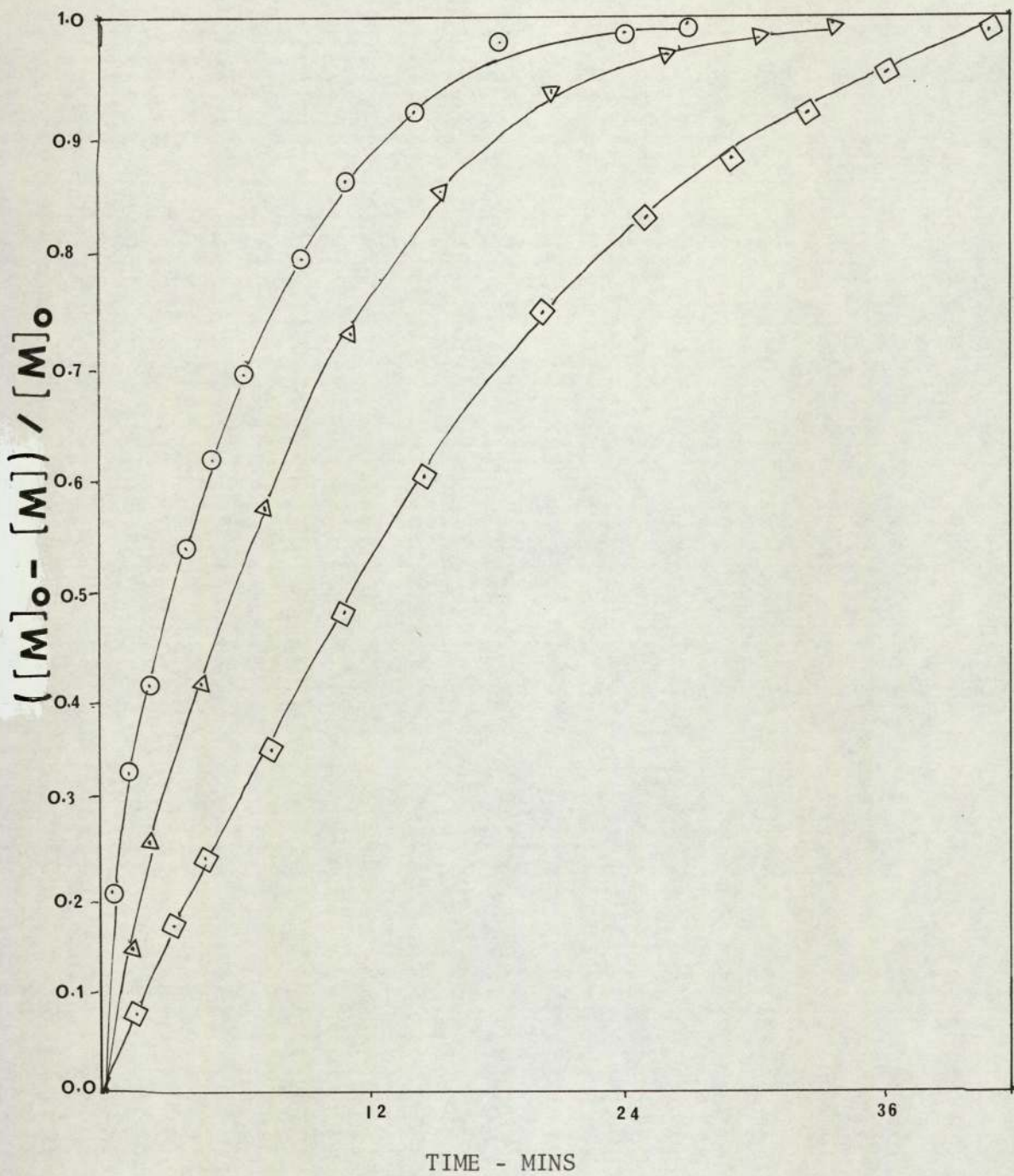
Fig. 5.3   Initial rate curves for the decomposition of TGAC with
            benzyl amine at 25°C - ☐ , 30°C - △ and 40°C - ⊙

            $[TGAC] = 1.0 \text{ mol. } l^{-1}$
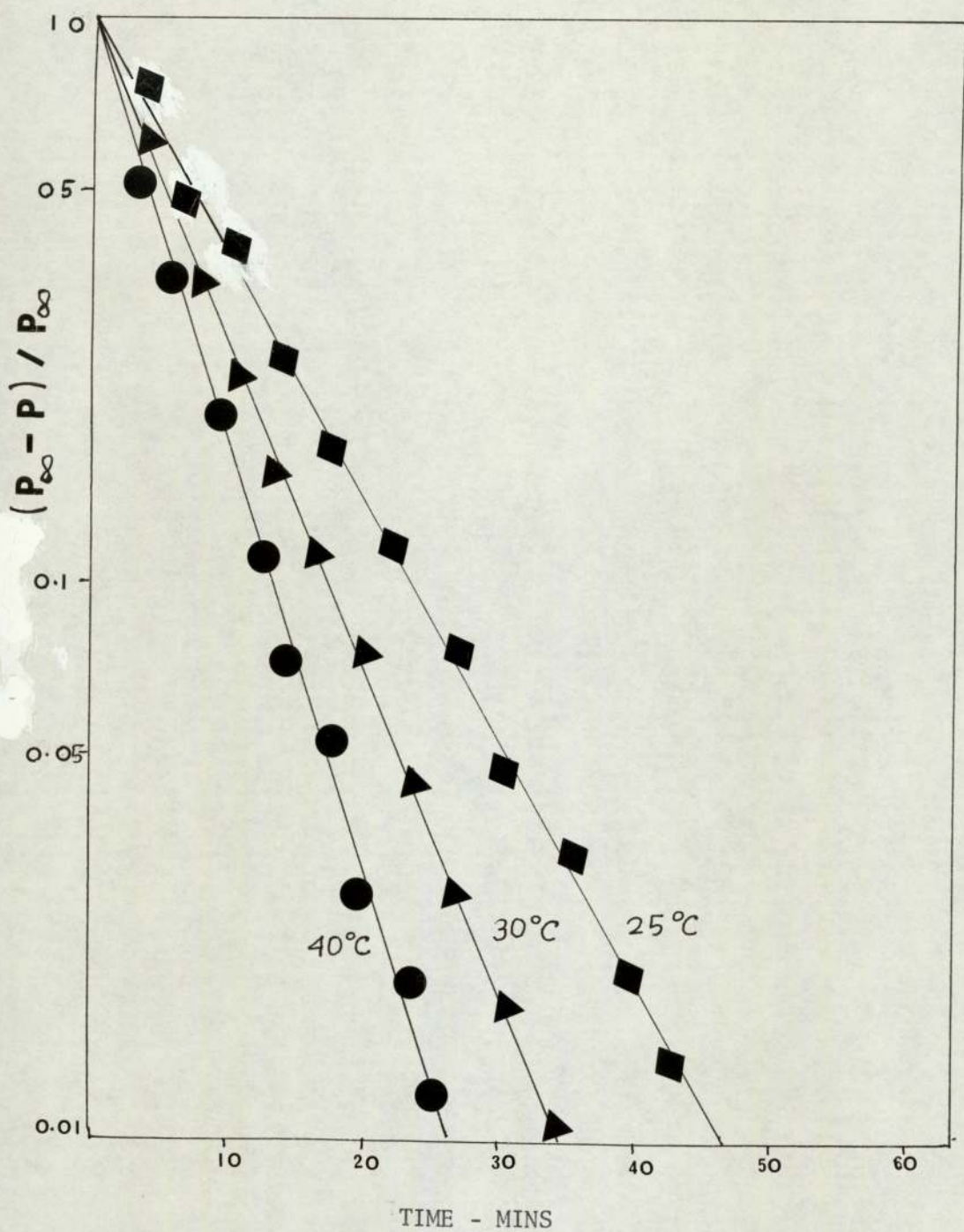
            $[\theta CH_2 NH_2] = 0.25 \text{ mol. } l^{-1}$

Fig. 5.4   Semi-logarithmic plot of (Pα-P)/Pα versus time for the
           decomposition of TGAC at 25°C, 30°C and 40°C.

$[TGAC] = 1.0 \text{ mol.l}^{-1}$
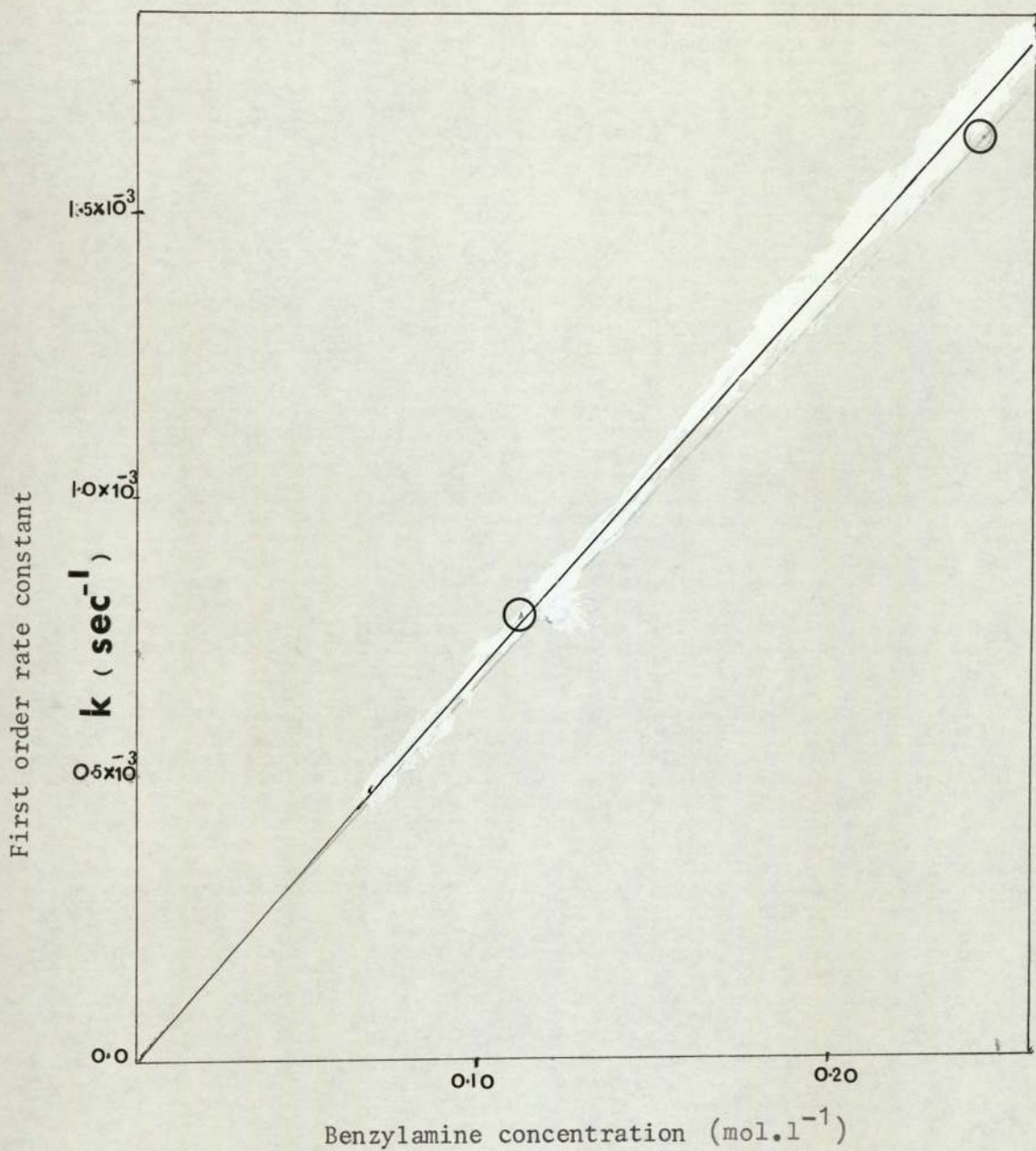
$[\Theta CH_2 NH_2] = 0.25 \text{ mol.l}^{-1}$

Fig. 5.5   Initial rate curves for the decomposition of TGAC with
benzylamine.   The effect of added benzylamine.

$[\Theta NH_2]_0 = 0.25$ mol. 1^{-1}

Table 5.2 gives the first order (pseudo) rate constants calculated from the semi-logarithmic plots and the corresponding half lives at various temperatures for the reaction of TGAC with benzylamine in nitrobenzene.

Table 5.2. First order rate constant, and the associated kinetic parameters for the reaction of TGAC with $\emptyset NH_2$ in nitro-benzine $[TGAC]_o$ = 1 mole/litre.

Temperature	Initiator mole/litre	Rate constant $K'(sec^{-1})$	Half lives $t\frac{1}{2}$ (minute)
25°C	0.12	7.60×10^{-4}	15.20
25°C	0.25	1.65×10^{-3}	7.00
30°C	0.25	1.92×10^{-3}	6.00
35°C	0.25	2.32×10^{-3}	5.00
40°C	0.25	2.74×10^{-3}	4.20

Table 5.3 represents the second order rate constants calculated from
the first order rate constants, energy of activation E, pre-
exponential factor A and entropy of activation $\Delta S\pm$ for the
decomposition of TGAC with benzylamine.

<div align="center">

TGAC = 1 mole/litre, benzylamine

= 0.25 mole/litre.

</div>

Temperature	Second order rate constant k'' (L mole^{-1}sec^{-1})
25°C	6.60×10^{-3}
25°C	6.30×10^{-3}
30°C	7.69×10^{-3}
35°C	9.30×10^{-3}
40°C	10.90×10^{-3}
Ea(kcals mole^{-1})	8.00 [66.80 (kJ mol^{-1})]
A(L mol^{-1}sec^{-1})	1.35×10^{4}
$\Delta S\pm$(cals deg^{-1}mol^{-1})	-18.80

It is important to note that the same value of Ea (activation energy) is obtained from the first order constants (Table 5.2). The Arrhenius plot for the decomposition of TGAC with benzylamine for a temperature range of 25°C-40°C is shown in Fig.5.6.

The products obtained from the above kinetic studies are mainly polymer which have been examined by infra red spectra, mass spectra, gel permeation chromatography and other physical methods. The infra red spectra obtained with KBr disc showed the character-istic ester carbonyl peak at 1690cm^{-1}. The gel permeation chromatography analysis of the polymer in orthodichlorobenzene showed a high molecular weight (>40,000). The characteristic feature of this polymer is that it is insoluble in almost all organic solvents, and highly crystalline. Further information relating to the structure and properties of the polymer are given in Chapter 7. The mechanism of the polymerisation will be discussed together with TLAC and TIBAC.
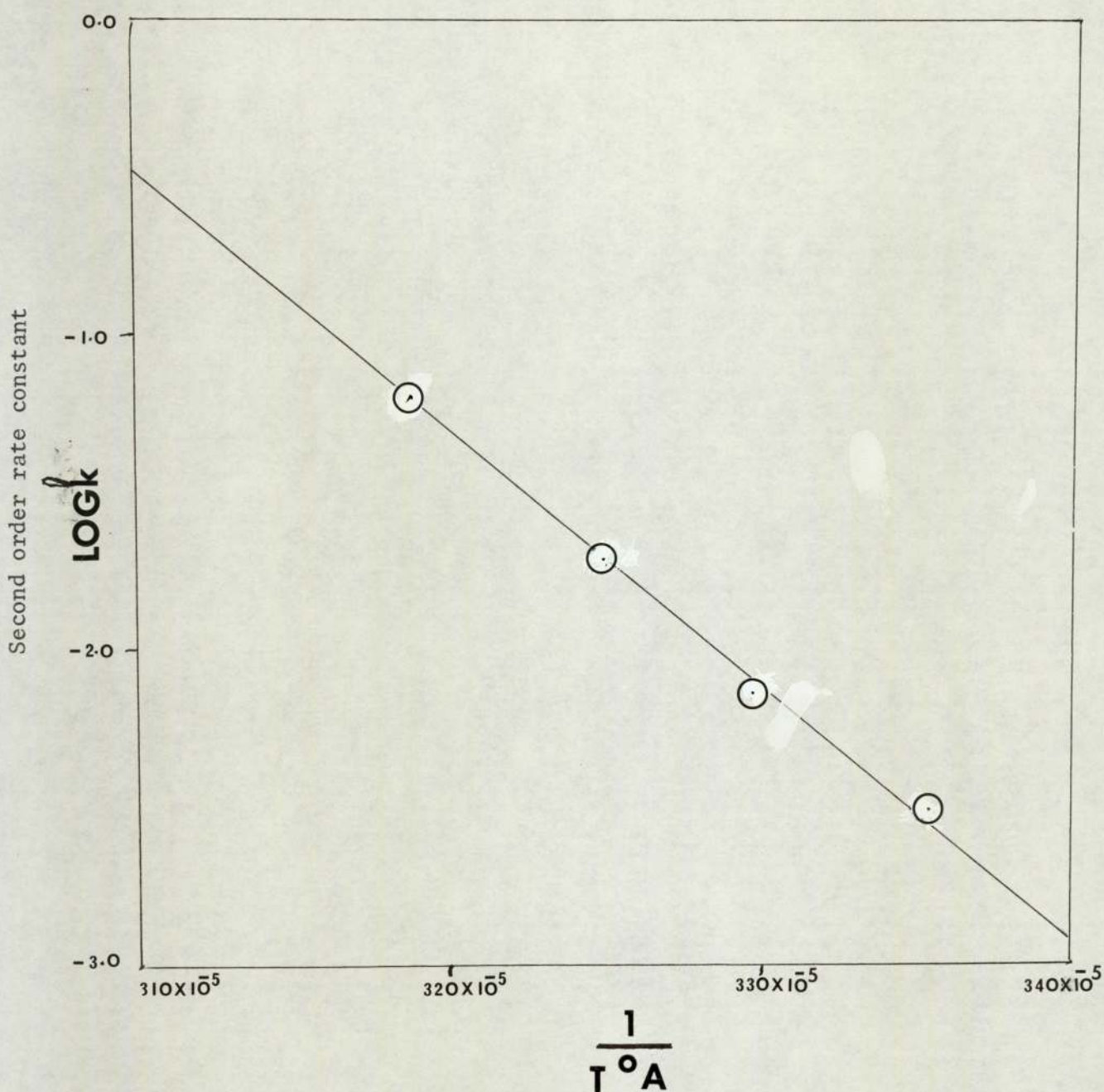
Fig. 5.6   Arrhenius plot of second order rate constant (-log k)
            versus the reciprocal of the absolute temperature $\frac{1}{T°A}$

            for the decomposition of TGAC with benzyl amine.
            Temperature range : 25° - 40°C.

5.3. Initiated decomposition of TLAC with benzylamine

The rate of decomposition of TLAC was also studied in nitro-benzene solution (1 mole/litre) at several temperatures. The low temperature kinetic apparatus was used to measure the rate of evolution of CO_2 gas. The rate was comparatively slow in comparison with TGAC under similar conditions. Fig. 5.7 is a plot of pressure versus time. Fig. 5.8 is a semilogarithmic plot of $\ln(P\infty P)/P\infty$.

By analogy with similar systems it is believed that the reaction of TLAC with benzylamine may again be expressed by the following rate equation.

$$\frac{-d[CO_2]}{dt} = \frac{-d[M]}{dt} = k_b'' [M][NH_2] \tag{35}$$

where $[CO_2]$, $[M]$ and $[NH_2]$ refer to the concentrations of CO_2, monomer and benzylamine and k_b'' is the second order rate constant calculated from the semi-logarithmic plot of $\ln(P\infty P)/P\infty$. Table 5.4 represents pseudo first order rate constants, half lives for the decomposition of TLAC with benzylamine in nitrobenzene.
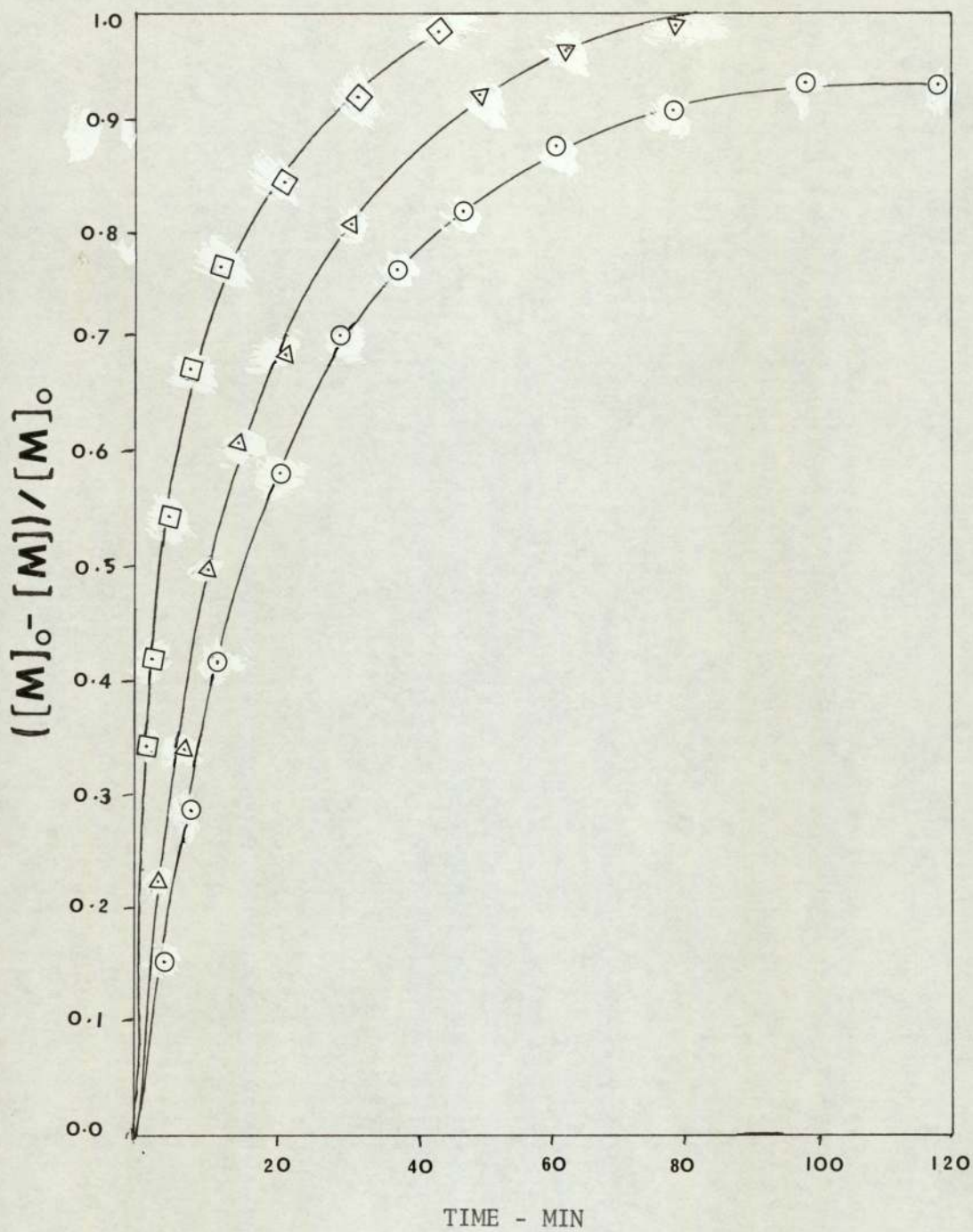
Fig. 5.7   Rate curves for the decomposition of TLAC with
benzylamine at ⊙ 30°C, △ 35°C and ⊡ 40°C

[TLAC] = 1.0 mol. l^{-1}
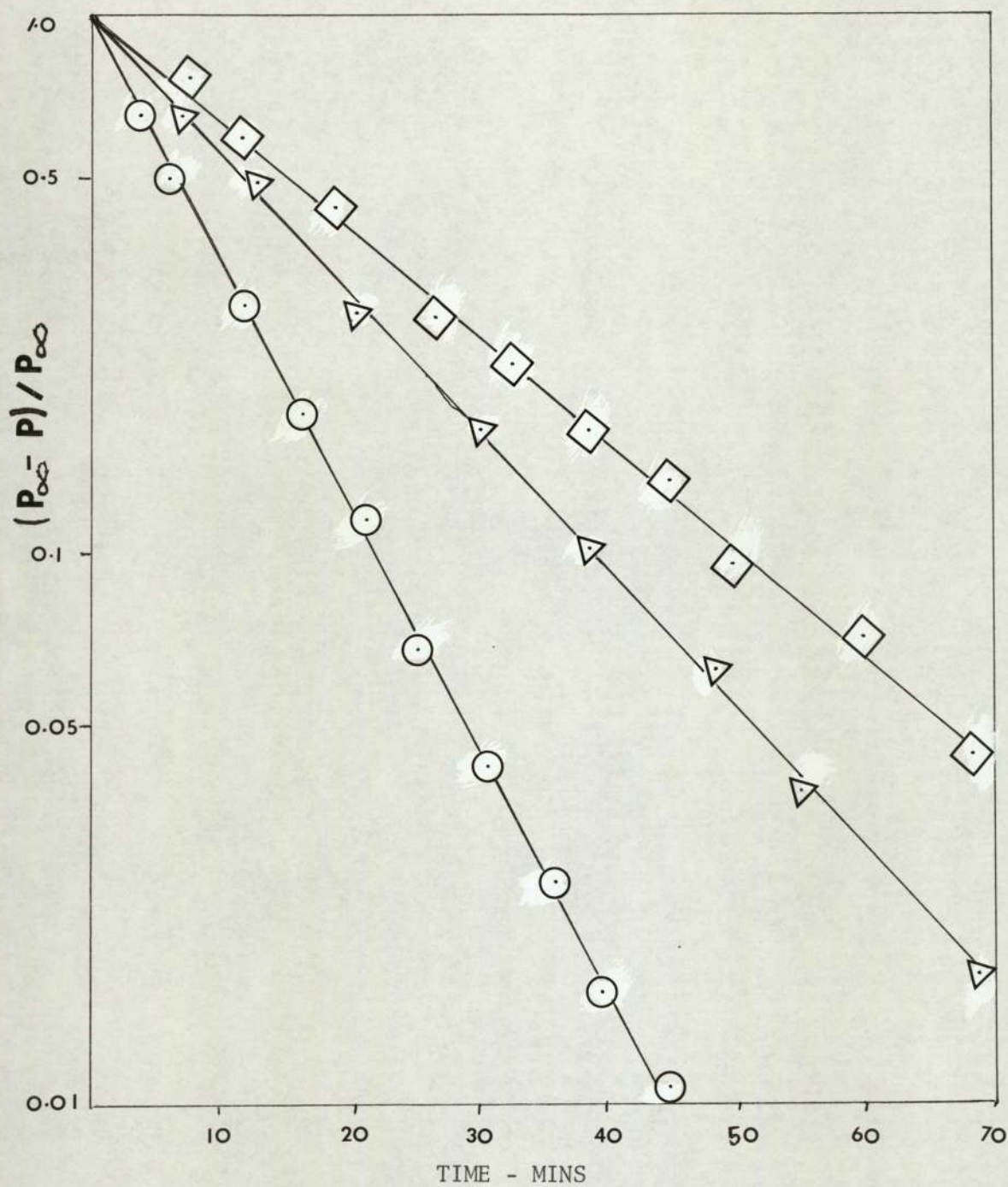
[θCH$_2$NH$_2$] = 0.30 mol.l^{-1}

Fig. 5.8   Semi-logarithmic plot of (P∞-P)/P∞ versus time for the
            reaction of TLAC with benzylamine at
            ⊙ 40°C, △ 35°C   and ⊡ 30°C

            [TLAC] = 1.0 mol.1^{-1}

            [θCH$_2$NH$_2$] = 0.30 mol.1^{-1}

Table 5.4 First order rate constants k_b' and associated kinetic

parameters for the reaction of TLAC with Benzylamine

$[TLAC]_o$ = 1 mole/litre $[\theta NH_2]$ = 0.30 mole/litre.

Temperatures	First order rate constant $k_b'(sec^{-1})$	$t\frac{1}{2}$(minute)
25°C	3.05 x 10^{-4}	36.75
30°C	6.10 x 10^{-4}	18.98
35°C	9.51 x 10^{-4}	12.00
40°C	1.62 x 10^{-3}	7.05

Table 5.5 gives second order rate constants calculated from the first
order rate constants, energy of activation, frequency factor A and
entropy of activation $\Delta S\pm$.   The Arrhenius plot for the decomposition
of TLAC with benzylamine for temperature range of 25°C-40°C is shown
in Fig. 5.9.

Table 5.5 Second order rate constants k_b'' and derived kinetic

parameters for the reaction of TLAC with benzylamine

as shown in Table 5.4.

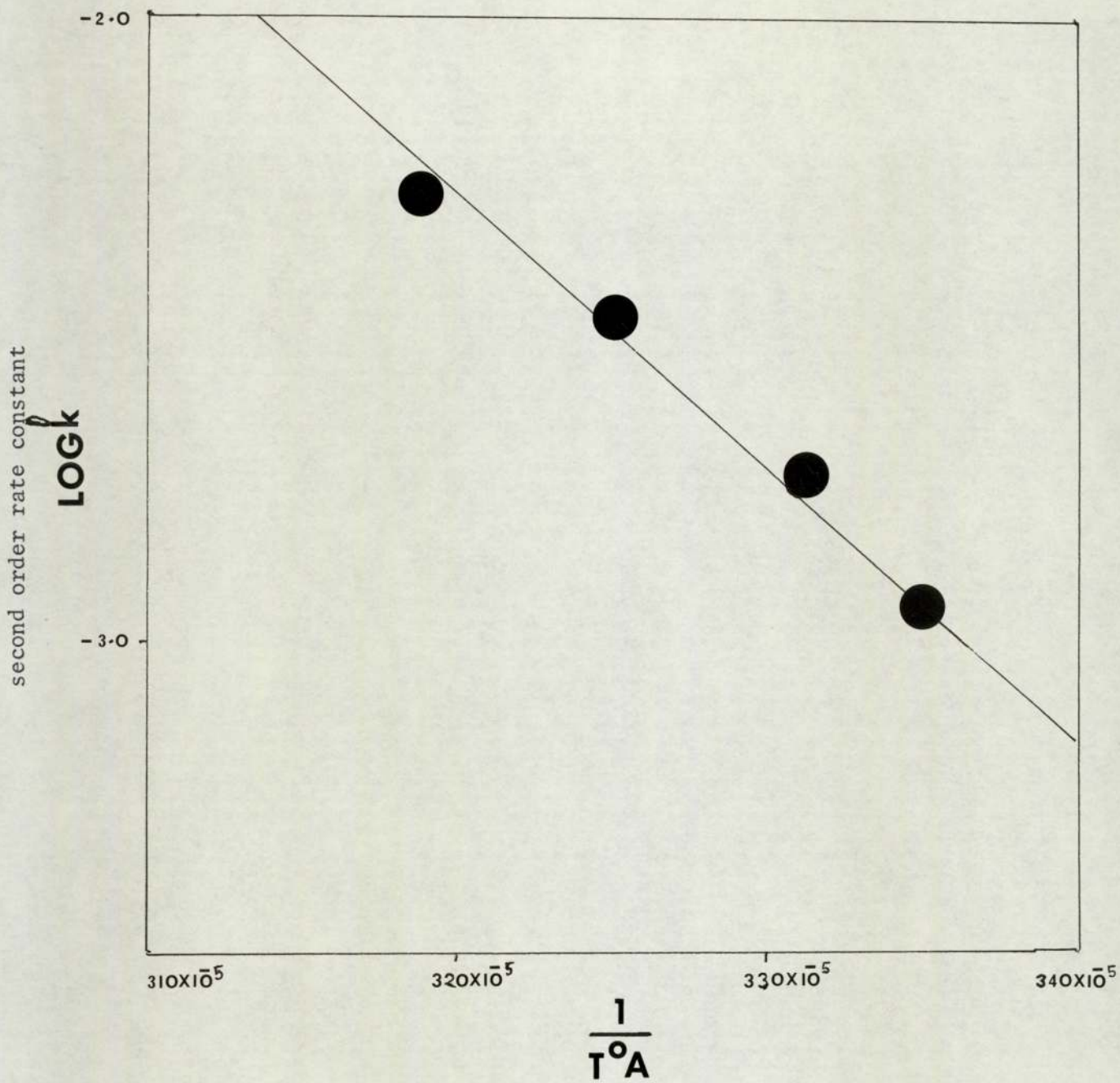| Temperature °C	Second order rate constant $k_b''(\ell \, mol^{-1}sec)^1$
25°C	1.10 x 10^{-3}
30°C	2.04 x 10^{-3}
35°C	3.17 x 10^{-3}
40°C	5.40 x 10^{-3}
Ea (k cals mol^{-1})	17.98 [75.15 ($kJ \, mol^{-1}$)]
A ($\ell \, mols^{-1}sec^{-1}$)	1.58 x 10^9
$\Delta S\pm$ (cals $deg^{-1} \, mol^{-1}$)	-13.92

Fig. 5.9 Arrhenius plot of -log k cersus reciprocal of absolute
temperature for the decomposition of TLAC with benzyl
amine.   Temperature range 25° - 40°C.

The decomposition products obtained were again examined by infra red spectra, mass spectra, gel permeation chromatography etc. The IR spectra in KBr showed the characteristic carbonyl peak at 1700cm^{-1}. The G.PC analysis showed that the polymer mainly consisted of 4-5 monomer units. The reason for low molecular weight polymer may be due to the amount of impurities such as α-chloro-acid chloride which may have terminated the polymer chains. This problem was also encountered with pyridine initiator of TLAC (Chapter 4).

The mechanism of the polymerisation reactions which seems similar to TGAC polymerisation will be described later.
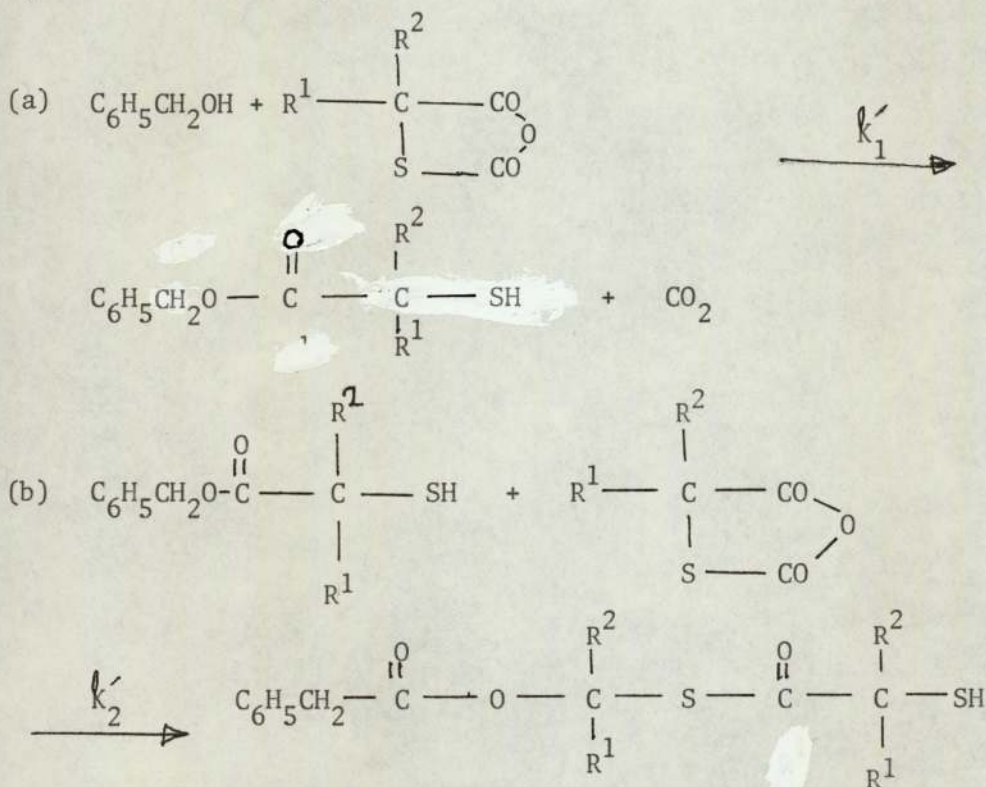
5.4. Initiated decomposition of TIBAC with benzylamine

The decomposition of TIBAC was carried out as before in nitro-benzene solution and the rate of decomposition was measured by gas evolution techniques in low temperature kinetic apparatus. It was observed when the bucket containing the initiator was dropped into the monomer solution, a huge precipitate appeared immediately with sudden rise in pressure in the manometer. The reaction was carried out several times at 25°C but each time the same result was obtained. Due to this difficulty, normal kinetic studies could not be achieved for TIBAC. Later 1 molar solution of the monomer and the initiator were prepared in anhydrous ether. The monomer solution was taken in a conical flask whose mouth was closed by a suba-seal. An equimolar amount of initiator solution was injected into the monomer solution at room temperature. A white precipitate appeared immediately with the evolution of CO_2. The solvent was removed by a suction pump at room temperature. The residue was a white solid, having a melting point ranging from 200°C-250°C. As the compound is insoluble in most organic solvents, characterisation was difficult and the molecular weight of the material could not be determined.
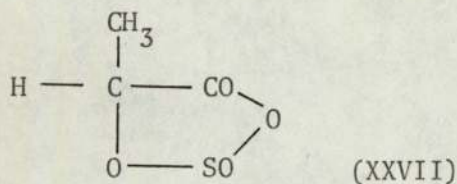
5.5 .Hydroxyl initiated decomposition: Discussion

It was observed during the decomposition of TGAC with benzyl alcohol that the reaction displayed a slow induction period up to 20% conversion of the monomer which gradually increased.   The analysis of the kinetic results (Fig. 5.2-Table 5.1) showed two limiting rate constants and that the propogation or final rate constant (k_2') was about three times faster than the initial constant (k_1').   This can be readily explained.   Benzyl alcohol is a very weak base and nucleophile and therefore it attacks TGAC ring with great difficulty.   When a weak nucleophile is used, the reaction rate increases with conversion, as the newly formed terminal SH group is more basic and a good nucleophile therefore it reacts very much faster with the monomer. k_2'' is faster than k_1'.

(a)
$$ C_6H_5CH_2OH + R^1 \overset{R^2}{\underset{S \longrightarrow CO}{\underset{|}{\overset{|}{C}}} \begin{matrix} CO \\ O \end{matrix}} \qquad \xrightarrow{\quad k_1' \quad} $$

$$ C_6H_5CH_2O - \overset{O}{\overset{\|}{C}} - \overset{R^2}{\underset{\underset{R^1}{|}}{\overset{|}{C}}} - SH \quad + \quad CO_2 $$

(b)
$$ C_6H_5CH_2O-\overset{O}{\overset{\|}{C}} - \overset{R^1}{\underset{\underset{R^1}{|}}{\overset{|}{C}}} - SH \quad + \quad R^1 \overset{R^2}{\underset{S \longrightarrow CO}{\underset{|}{\overset{|}{C}}} \begin{matrix} CO \\ O \end{matrix}} $$

$$ \xrightarrow{\quad k_2' \quad} C_6H_5CH_2 - \overset{O}{\overset{\|}{C}} \longrightarrow O - \overset{R^2}{\underset{\underset{R^1}{|}}{\overset{|}{C}}} - S - \overset{O}{\overset{\|}{C}} - \overset{R^2}{\underset{\underset{R^1}{|}}{\overset{|}{C}}} - SH $$

(36)

The rate constant k_1' for benzyl alcohol initiated decomposition of TGAC is similar to that for the oxygen containing ring LAAS

$$
\begin{array}{c}
\text{CH}_3 \\
|\\
\text{H} \longrightarrow \text{C} \longrightarrow \text{CO} \\
|\qquad\qquad \searrow \text{O} \\
\text{O} \longrightarrow \text{SO} \nearrow
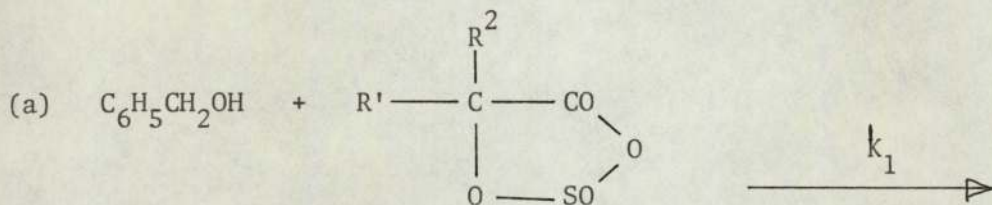\end{array}
\qquad \text{(XXVII)}
$$

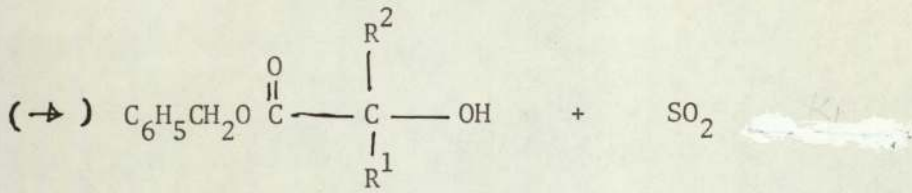but k_2' for TGAC at 25°C is about 26 times faster than LAAS at 65°C.

i.e. $k_2'(\text{TGAC, 25°C}) = 1.3 \times 10^{-4}$ $(\text{L mol}^{-1}\text{s}^{-1})$

$k_2(\text{LAAS, 65°C}) = 4.8 \times 10^{-6}$ $(\text{L mol}^{-1}\text{s}^{-1})$
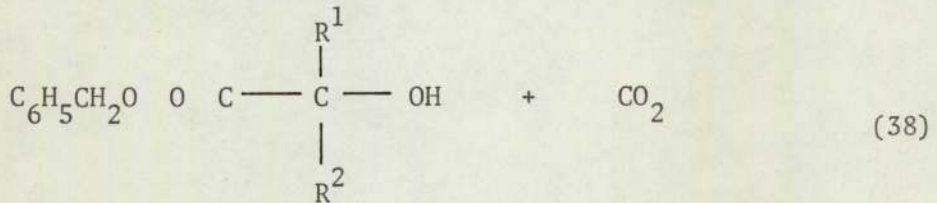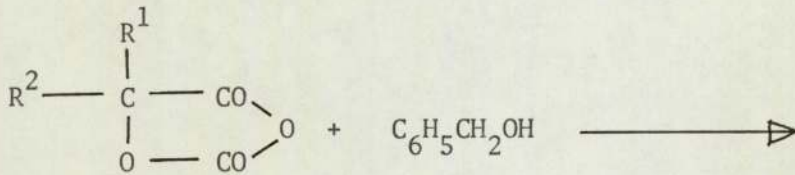
It must be noted also that the value used for $k_2'(\text{TGAC})$ here will be greatly underestimated since not all the available hydroxyl will have been converted to -SH groups.   The value should be identical to that produced by benzylamine initiation (Table 5.6) as will become apparent in the following discussion.

The reason for slow reaction for lactic acid anhydrocarboxylate (LAAS) is obvious.   The benzyl alcohol attacking the α-hydroxy anhydrosulphite ring regenerates OH group, which is a weak and sterically hindered nucleophile and attacks the next ring with difficulty.

$$
\text{(a)} \quad \text{C}_6\text{H}_5\text{CH}_2\text{OH} \quad + \quad
\begin{array}{c}
\text{R}^2 \\
|\\
\text{R}' \longrightarrow \text{C} \longrightarrow \text{CO} \\
|\qquad\qquad \searrow \text{O} \\
\text{O} \longrightarrow \text{SO} \nearrow
\end{array}
\qquad \xrightarrow{\quad k_1 \quad}
$$

$$(\rightarrow) \quad C_6H_5CH_2O-\underset{\underset{}{\overset{O}{\parallel}}}{C}-\underset{\underset{R^1}{\overset{R^2}{|}}}{C}-OH \quad + \quad SO_2$$

$$(b) \quad C_6H_5CH_2O-\underset{\underset{R^1}{\overset{O}{\parallel}}}{C}-\underset{\underset{R^1}{\overset{R^2}{|}}}{C}-OH \quad + \quad \underset{\underset{O-SO}{\overset{R^2}{|}}}{R'-C}-\overset{CO}{\underset{}{}}$$

$$\overset{k_2}{\longrightarrow} \quad C_6H_5CH_2O-\underset{\underset{R^1}{\overset{O}{\parallel}}}{C}-\underset{\underset{R^1}{\overset{R^2}{|}}}{C}-O-\underset{}{\overset{O}{C}}-\underset{\underset{R^1}{\overset{R^2}{|}}}{C}-OH \quad + SO_2 \quad (37)$$
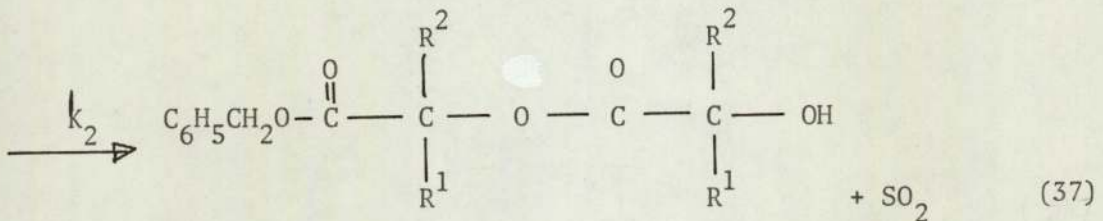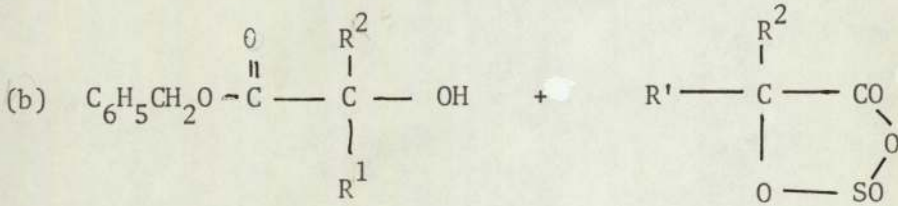
The reaction of benzyl alcohol with α-hydroxy anhydrocarboxylates produces the corresponding α-hydroxy carboxylic esters (Equation 39)

$$R^2-\underset{\underset{O}{\overset{R^1}{|}}}{C}-\overset{CO}{\underset{CO}{}}O \quad + \quad C_6H_5CH_2OH \quad \longrightarrow$$

$$C_6H_5CH_2O \quad O \quad C-\underset{\underset{R^2}{\overset{R^1}{|}}}{C}-OH \quad + \quad CO_2 \quad (38)$$

The regenerated OH group coupled with steric hindrance cannot take part in propagation reaction unless R^1 or R^2 or both = H and then only very slowly. However, the decomposition product of the reaction of TGAC with equimolar benzyl alcohol when isolated and examined by IR spectra and GPC was found to consist of polythioesters. This confirms the fact that the propagation reaction (Eq.36) occur smoothly and readily.

5.6 Amine initiated decomposition: Discussion

The rates of decomposition of TGAC initiated with benzylamine
are quite fast.   The rate of decomposition of TGAC is about 3-4 times
faster than TLAC.   The comparitive slow rate for the latter is
obviously due to the steric and electronic effect of one methyl
group in the α-carbon on attack of the incoming nucleophile.   TIBAC
however, behaved differently: with the addition of initiator, a white
precipitate appeared immediately possibly due to a competing reaction
leading to the formation of tetramethyl thioglycollide which subse-
quently polymerises.   More probably however the precipitate is an
unstable complex.

The rate of decomposition of TGAC, TLAC and TIBAC with benzyl-
amine may be compared with NCA's of α-amino acids and α-hydroxy
anhydrocarboxylates and anhydrosulphites of α-hydroxy acids.

The NCA's with one or no substituents other than hydrogen at $C_{(4)}$
polymerise very easily with benzylamine.   NCA's

$$R^1 \underset{4}{—} C_4 \underset{5}{—} CO$$
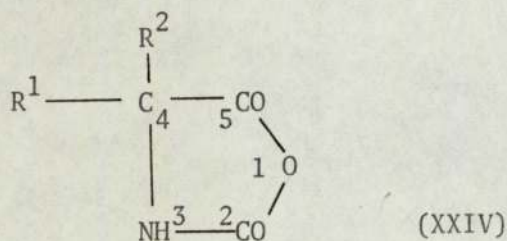
with two methyl groups at $C_{(4)}$ do not polymerise at all
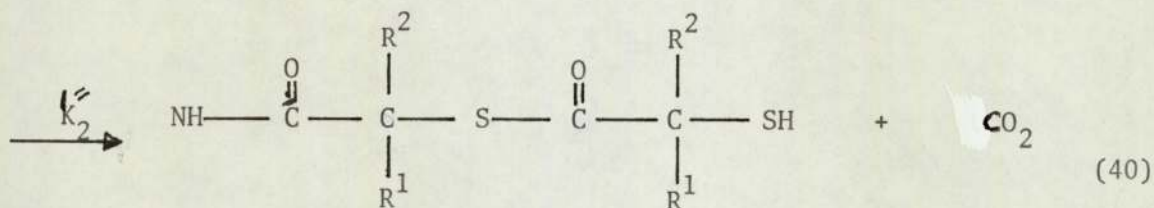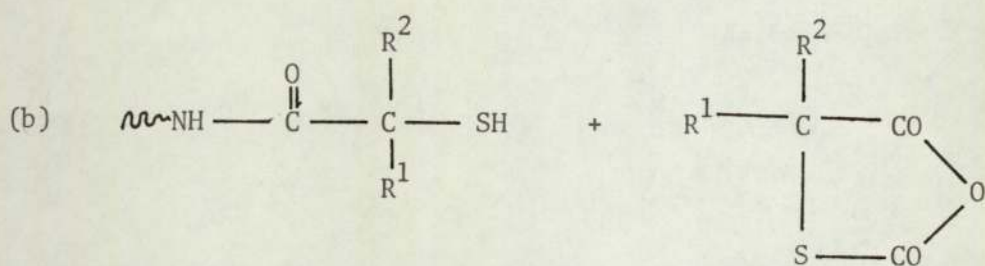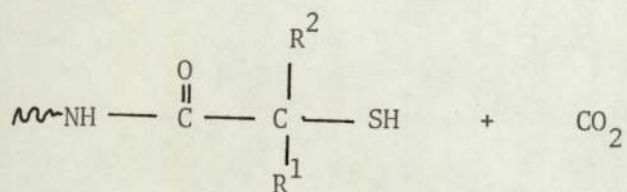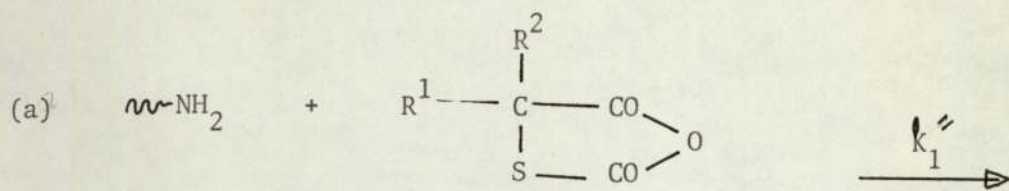
(XXIV)

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† The conventional numbering of the NCA ring is based on the oxazolidine
  system and differs from the IUPAC - based numbering adopted for
  α-hydroxy and α-thio acids derivatives

$$C_6H_5CH_2NH_2 \quad + \quad \begin{array}{c} RCH \text{---} CO \\ | \qquad\qquad O \\ NH \text{---} CO \end{array} \quad \longrightarrow$$

$$C_6H_5CH_2NH \text{---} \underset{\parallel}{\overset{O}{C}} \text{---} \underset{H}{\overset{R}{C}} \text{---} NH_2 \quad + \quad CO_2 \qquad\qquad (39)$$
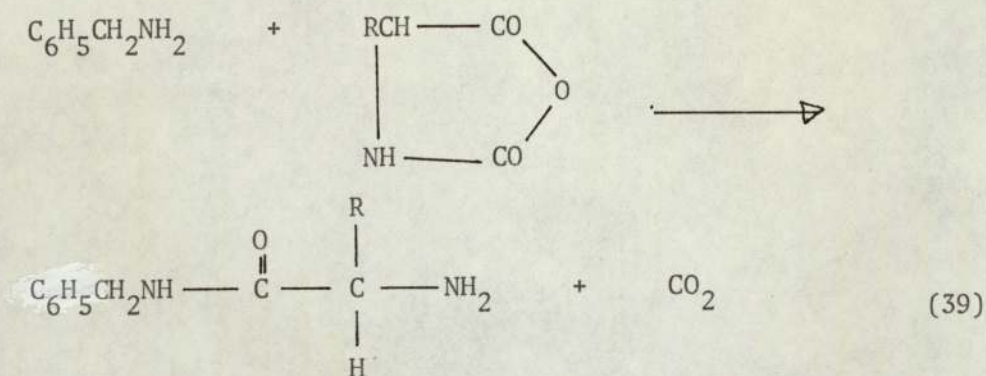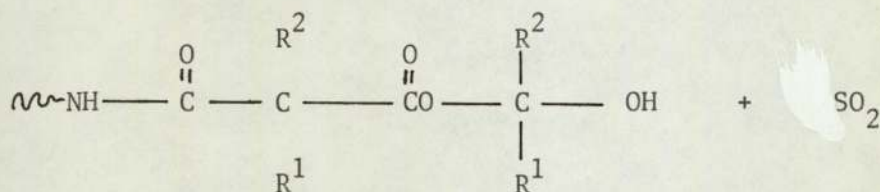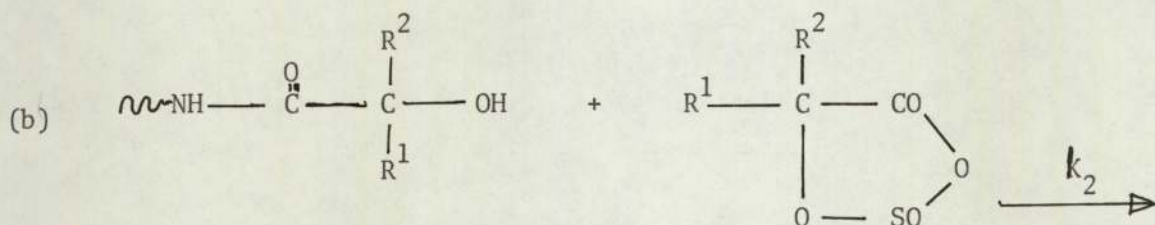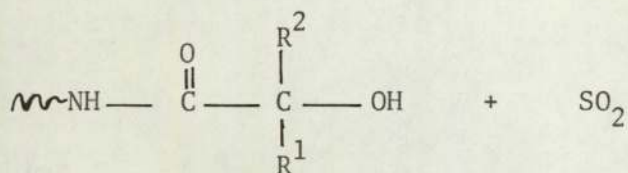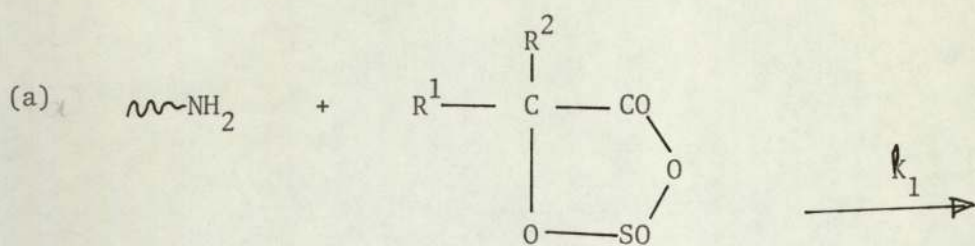
In the subsequent step the terminal amine group attacks the second anhydrocarboxylate and liberates carbon dioxide and regenerates an amine group which acts as a propagating agent.

It appears that amine initiated polymerisation of thio-anhydro-carboxylates involves the attack of the amine nucleophile at the $C_{(4)}$ carbonyl, liberating CO_2 and producing a terminal -SH group which then acts as a propagating agent. The difference between thio-anhydrocarboxylates and NCA's of α-amino acids with amines lies simply in the fact that the former produces terminal -SH group and the latter produces terminal -NH$_2$ group. TIBAC polymerises with primary amine whereas similar ring compounds such as dimethyl substituted NCA does not polymerise. It may be inferred that -SH is a more effective nucleophile than NH$_2$ in this type of reaction.

The proposed mechanism in this reaction of thio-anhydrocarboxy-lates with benzylamine may be represented as shown in equation 40 .

(a) $\sim NH_2$ + structure ($R^1 - \overset{\overset{R^2}{|}}{\underset{\underset{S}{|}}{C}} - \overset{CO}{\underset{CO}{}} O$) $\xrightarrow{k_1''}$

$\sim NH - \overset{\overset{O}{\|}}{C} - \overset{\overset{R^2}{|}}{\underset{\underset{R^1}{|}}{C}} - SH$ + CO_2

(b) $\sim NH - \overset{\overset{O}{\|}}{C} - \overset{\overset{R^2}{|}}{\underset{\underset{R^1}{|}}{C}} - SH$ + $R^1 - \overset{\overset{R^2}{|}}{\underset{\underset{S}{|}}{C}} - \overset{CO}{\underset{CO}{}} O$

$\xrightarrow{k_2''}$ $NH - \overset{\overset{O}{\|}}{C} - \overset{\overset{R^2}{|}}{\underset{\underset{R^1}{|}}{C}} - S - \overset{\overset{O}{\|}}{C} - \overset{\overset{R^2}{|}}{\underset{\underset{R^1}{|}}{C}} - SH$ + CO_2

(40)

Anhydrocarboxylates and anhydrosulphites of α-hydroxy acids react extremely rapidly with primary amine in the first place to give the corresponding amide. The second stage however involves the terminal hydroxyl group which is a weak nucleophile. The reactions are shown in equation (41) for the anhydrosulphite case.
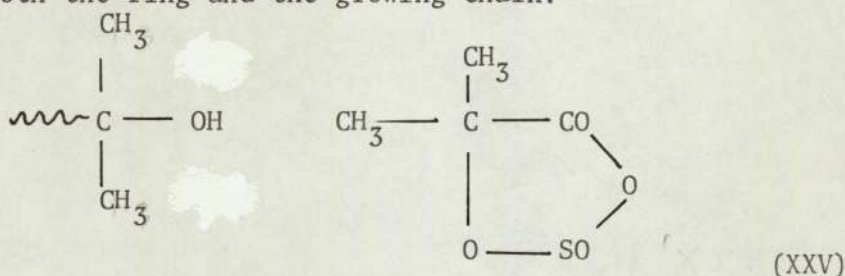
(a) $\sim\text{NH}_2$ +

$$R^1 \!\!-\!\! \overset{\displaystyle R^2}{\underset{\displaystyle O \!-\! SO}{\overset{|}{\underset{|}{C}}}} \!\!-\!\! CO \diagdown\!\!\diagup O \qquad \xrightarrow{\;k_1\;}$$

$$\sim\text{NH} \!-\! \overset{O}{\overset{\|}{C}} \!-\! \overset{\displaystyle R^2}{\underset{\displaystyle R^1}{\overset{|}{\underset{|}{C}}}} \!-\! OH \quad + \quad SO_2$$

(b)

$$\sim\text{NH} \!-\! \overset{O}{\overset{\|}{C}} \!-\! \overset{\displaystyle R^2}{\underset{\displaystyle R^1}{\overset{|}{\underset{|}{C}}}} \!-\! OH \quad + \quad R^1 \!\!-\!\! \overset{\displaystyle R^2}{\underset{\displaystyle O \!-\! SO}{\overset{|}{\underset{|}{C}}}} \!\!-\!\! CO \diagdown\!\!\diagup O \qquad \xrightarrow{\;k_2\;}$$

$$\sim\text{NH} \!-\! \overset{O}{\overset{\|}{C}} \!-\! \overset{\displaystyle R^2}{\underset{\displaystyle R^1}{\overset{|}{\underset{|}{C}}}} \!-\! \overset{O}{\overset{\|}{C}}O \!-\! \overset{\displaystyle R^2}{\underset{\displaystyle R^1}{\overset{|}{\underset{|}{C}}}} \!-\! OH \quad + \quad SO_2 \qquad (41)$$

Although the benzylamine initiated decomposition of α-thio-anhydrocarboxylates has not been studied exhaustively we now have the basis for a reasonable comparison of the α-hydroxy and α-thio-acid derivatives.

In the first place it appears that the reactions corresponding to k_1'' (amine attack) in the α-thio acid anhydrocarboxylates occur too rapidly to enable reasonable measurements to be made. Thus the rate data contained in this chapter is concerned mainly with the reaction corresponding to k_2''.

The most effective comparison to be made therefore is that
between the anhydrocarboxylate of α-thio acids (equation b)
and the anhydrosulphites of α-hydroxy acids (equation b)
Since comparable data exists Table 5.6 compares the relevant infor-
mation.

Here again there is reasonable evidence for a common mechanism
occurring in the case of TGAC and TLAC and again in the case of GAAS
and LAAS - there is also reasonable evidence that the two uniting
mechanism are similar in nature.   HBAS and TIBAC are obviously
anomalous in certain respects.   The fact that the nature of the
product is effected by benzylamine case confirms the belief that the
mechanism discussed in the previous chapter cannot be operating.
On the otherhand all the observations (with the possible exception of
the anomalous behaviour of TIBAC) can be explained on the basis of
the mechanism shown in equation (40).   This is of course well
established in the case of α-hydroxy anhydrosulphites and the failure
of HBAS to polymerise is seen not as anamolous behaviour but simply
the consequence of steric hindrance of two methyl groups since they
affect both the ring and the growing chain.

$$
\begin{array}{ccc}
\text{CH}_3 & & \text{CH}_3 \\
| & & | \\
\sim\sim\text{C}-\text{OH} & & \text{CH}_3-\text{C}-\text{CO} \\
| & & | \quad\quad\;\; \searrow \\
\text{CH}_3 & & \quad\quad\quad\quad\text{O} \\
& & \text{O}-\text{SO} \;\; \nearrow
\end{array}
$$

(XXV)

As the kinetic parameters are consistent for GAAS with -OH
attack on $C_{(4)}$ carbonyl and so those for TGAC are also consistent
with -SH group attack on $C_{(4)}$ carbonyl.   We have seen (K_1 Benzyl alcohol)

TABLE 5.6   Compares the relative information.

Monomer	TGAC	TLAC	TIBAC	GAAS	LaAS	HBAS
R_1/R_2	H/H	H/Me	Me/Me	H/H	H/Me	Me/Me
Order in Monomer	First	First	First	First	First	First
Order in Benzylamine	First	First	First	First	First	First
Effect of Mol.WT.ON [Benz]$_o$	Marked	Marked	Marked	MoLα $\frac{1}{[B]_o}$	MoLα $\frac{1}{[B]_o}$	MoLα $\frac{1}{[B]_o}$
k_2	6.6 x10^{-3} at 25°C(l mol^{-1}s^{-1})	1.10x10^{-3} at 25°C($l$mol^{-1}sec^{-1})	-	2.2x10^{-5} (80°,l.mol^{-1}s^{-1})	0.9 x 10^{-5} (80°l,m^{-1}s^{-1})	<10^{-8} (80°.l,m^{-1}l^{-1})
Polymer Formed	Yes	Yes	Yes	Yes (slowly)	Yes (slowly)	NO
E_a (k cal mol^{-1})	8.0	17.98	-	15	11.9	-
A(l mol^{-1}s^{-1})	1.35x10^4	1.58x10^9	-	6.3x10^4	1.2x10^2	-
ΔS±(Cal.deg^{-1}mol^{-1})	-18.80	-13.92	-	-10	-12approx.	-
k_1(Benzyl alc)	5.3x10^{-5} 25°C (s^{-1})	-	-	10.0x10^{-4} 45° ,l.mol^{-1}s^{-1}	5x10^{-5} 45°l.m^{-1}s^{-1}	<10^{-8} 45° l.m^{-1}s^{-1}

that the intrinsic activities of the $C_{(4)}$ C = O of the rings are not vastly different but the -SH formed by benzyl alcohol attack much faster reflected in rate constants k_2' in Table 5.6.

The greater effectiveness of sulphur is due in part to greater size thus the attacking species is less affected by TGAC and TLAC

i.e.

$$\sim\!\!\!\sim C \underset{\underset{R^2}{|}}{\overset{\overset{R^1}{|}}{|}} SH$$
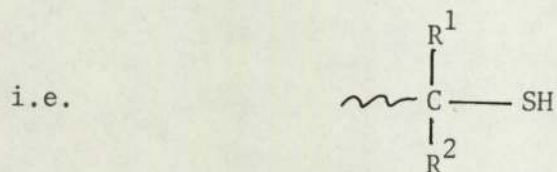
The behaviour of TIBAC with benzylamine is not readily understood. POssibly it forms a monomer - initiator complex in the first place which later undergoes polymerisation slowly. A much more detailed study would be necessary to establish the nature of this reaction.

CHAPTER VI

THE THERMAL DECOMPOSITION OF THIO-ISOBUTYRIC ANHYDROCARBOXYLATE
(TIBAC)

RESULTS AND DISCUSSION:

The work presented in this chapter concerns the thermal decomposition of thioisobutyric anhydrocarboxylate which is discussed and compared with analogous anhydro-sulphites and anhydrocarboxylates of α-hydroxy carboxylic acids. The thermal decomposition of thio-glycollic and thiolatic anhydrocarboxylates could not be studied due to their highly reactive nature to initiators.

6.1 Results:

The rates of thermal decomposition of TIBAC were followed by gas evolution techniques using high temperature kinetic apparatus as shown in Fig. 6.1. The rate of disappearance of monomer was also followed by examining the infra red spectra of the monomer refluxed in carbon tetrachloride solution (80°C).

A solution of thioisobutyric anhydrocarboxylate was prepared in nitrobenzene solution (concentration 1 mol/litre). The thermal decomposition of the monomer solution was studied over a temperature range of 90°C - 112°C. A measured quantity of the monomer solution was transferred to the reacting vessel of the kinetic apparatus through the side-tube by a hypodermic syringe. The whole apparatus

was then evacuated under vacuum at room temperature, sealed and transferred to a constant temperature oil bath. The rate of evolution of carbon dioxide was measured manometrically by a cathéto-meter at suitable time intervals. when the decomposition was complete, the mixture was removed by re-opening the side tube.

A plot of concentration of monomer versus time was drawn for each kinetic run from the pressure readings. Another plot of $\ln(P_\infty P)/P_\infty$ versus time was drawn by converting the pressure data, which showed that monomer decomposition was a first order process. Fig. 6.1 shows a plot of monomer decomposition versus time and Fig. 6.2 shows such a conventional first order plot from which the rate constants were calculated. Successive batches of purified monomer gave consistent results which confirmed the absence of adventitious initiator.

The thermal decomposition of monomer in absence of any initiator may be expressed by the following equation:

$$\frac{d[P]}{dt} = \frac{-d[TIBAC]}{dt} = \frac{d[CO_2]}{dt} = k_0 \, [TIBAC] \tag{42}$$

where [P], [TIBAC] and [CO_2] refer to the concentrations of polymer, TIBAC and carbon dioxide respectively and k_0 is the first order rate constant. Table 6.1 represents the constants observed for the thermal decomposition of TIBAC in nitrobenzene for a temperature range of 80°C - 112°C.
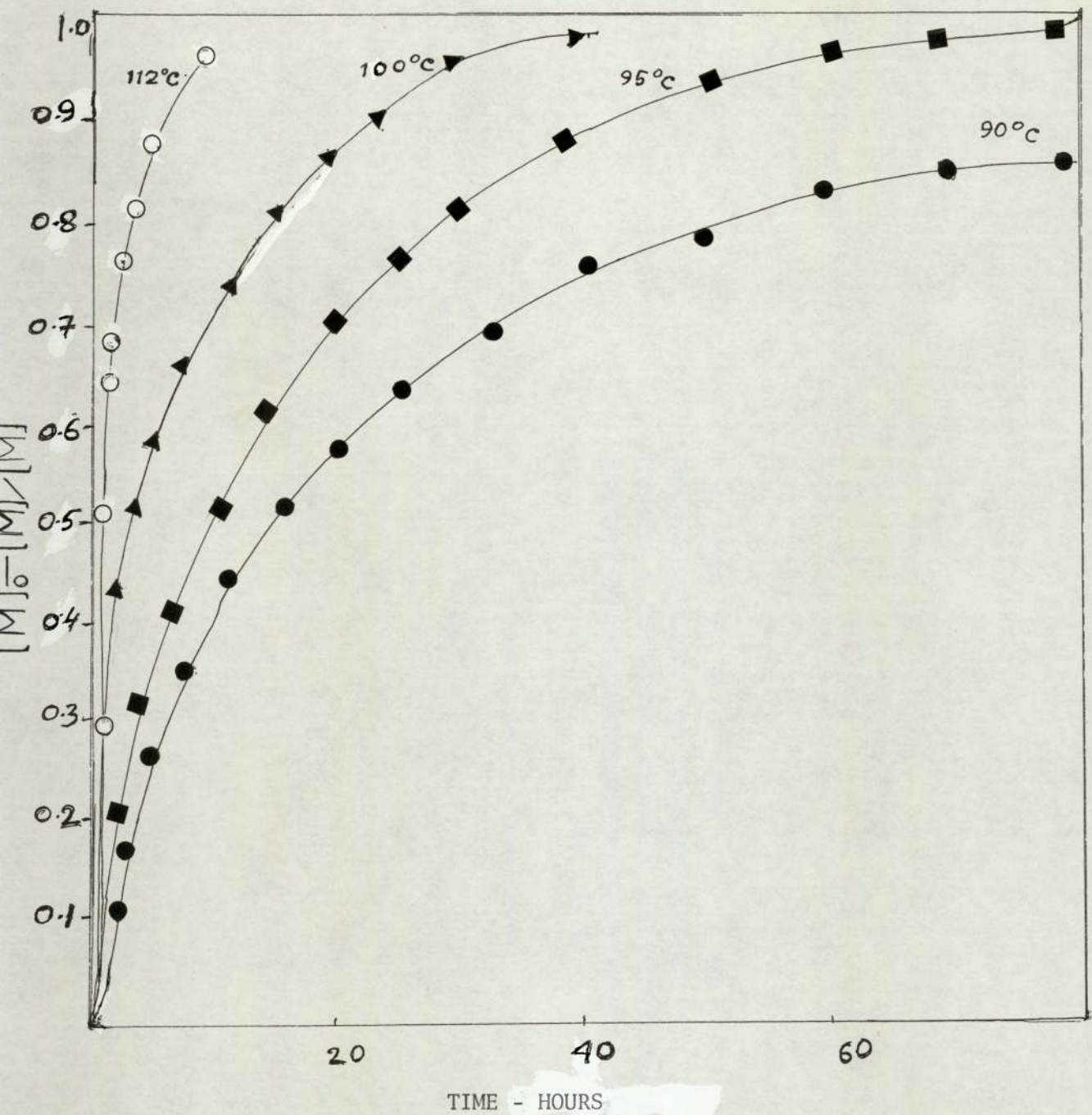
Fig. 6.1   Thermal polymerisation of TIBAC in nitrobenzene at
different temperatures, plotted as percentage
conversion to polymer versus time.
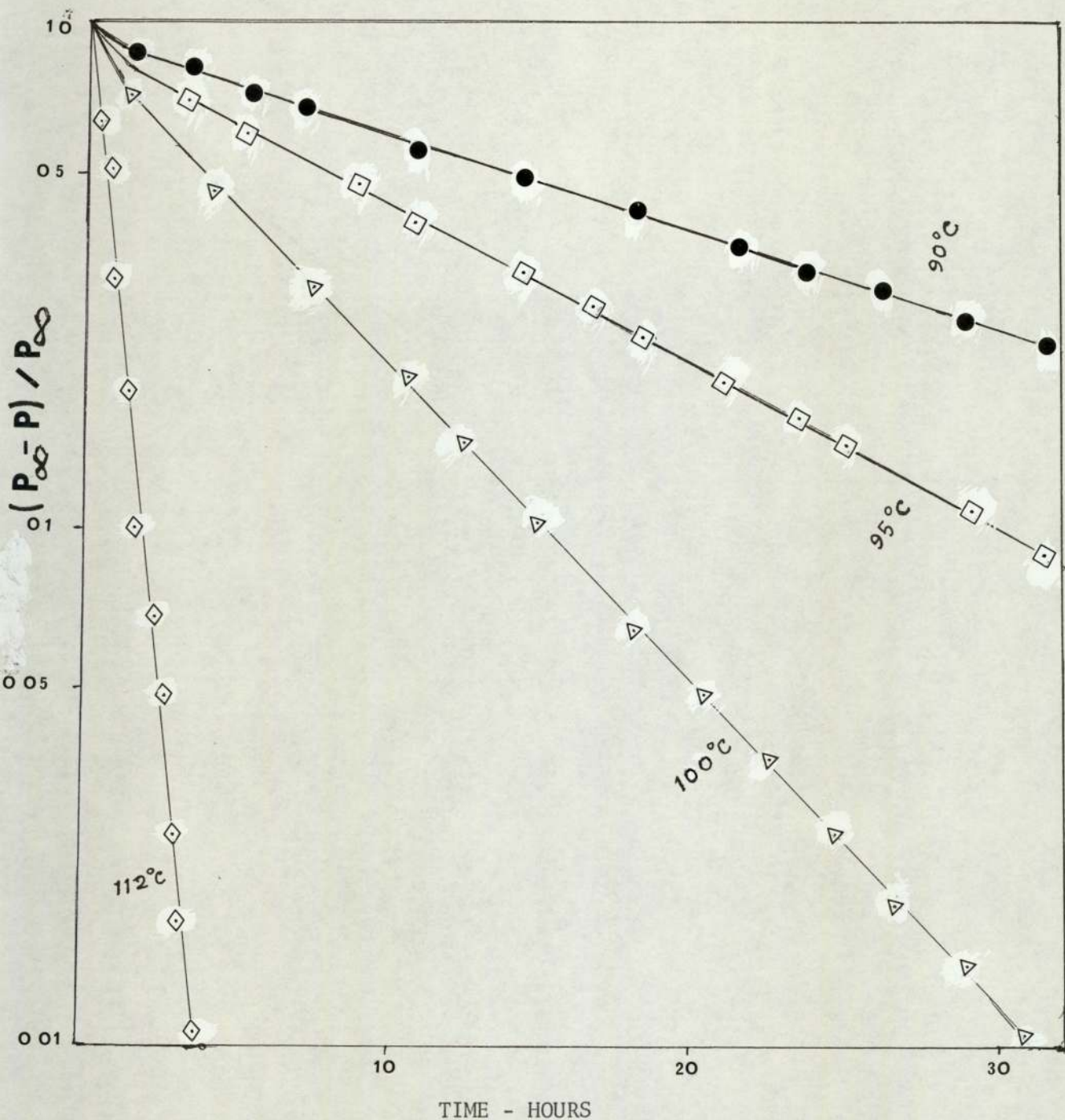
Fig. 6.2   Conventional first order plots of $\ln(P\alpha-P)/P\alpha$ versus time
for the decomposition of TIBAC in nitrobenzene at different
temperatures.

TABLE 6.1

First order rate constants (k_o) calculated from the semi-logarithmic plot of $\ln(P_\infty P)/P_\infty$ versus time together with the corresponding half-lives and derived kinetic parameters. [TIBAC] = 1.0 mol/L^{-1}

Temperature °C	First order rate constants k_o (sec^{-1})	Half-lives $t_{\frac{1}{2}}$ (hours)
80	1.1×10^{-6}	173.00
90	8.0×10^{-6}	23.30
95	1.50×10^{-5}	12.55
100	3.85×10^{-5}	5.00
112	3.00×10^{-4}	(38.00 minutes)
E ($kcals\ mol^{-1}$)	45.0	
($kJ\ mol^{-1}$)	188.1	
A ($L.mol^{-1}sec^{-1}$)	1.69×10^{22}	
$\Delta S \ddagger$ ($cals\ deg^{-1} mol^{-1}$)	36.49	

The energy of activation (E), pre-exponential factor (A) and entropy of activation were calculated from an Arrhenius plot (Fig.6.3)

The product obtained from thermal decomposition which were examined by IR and mass spectra and gel permeation chromatography were not completely consistent with polymer formation. Because of the difficulty in isolating mixed products from non-volatile solvents such as nitrobenzene a modified technique was adopted.
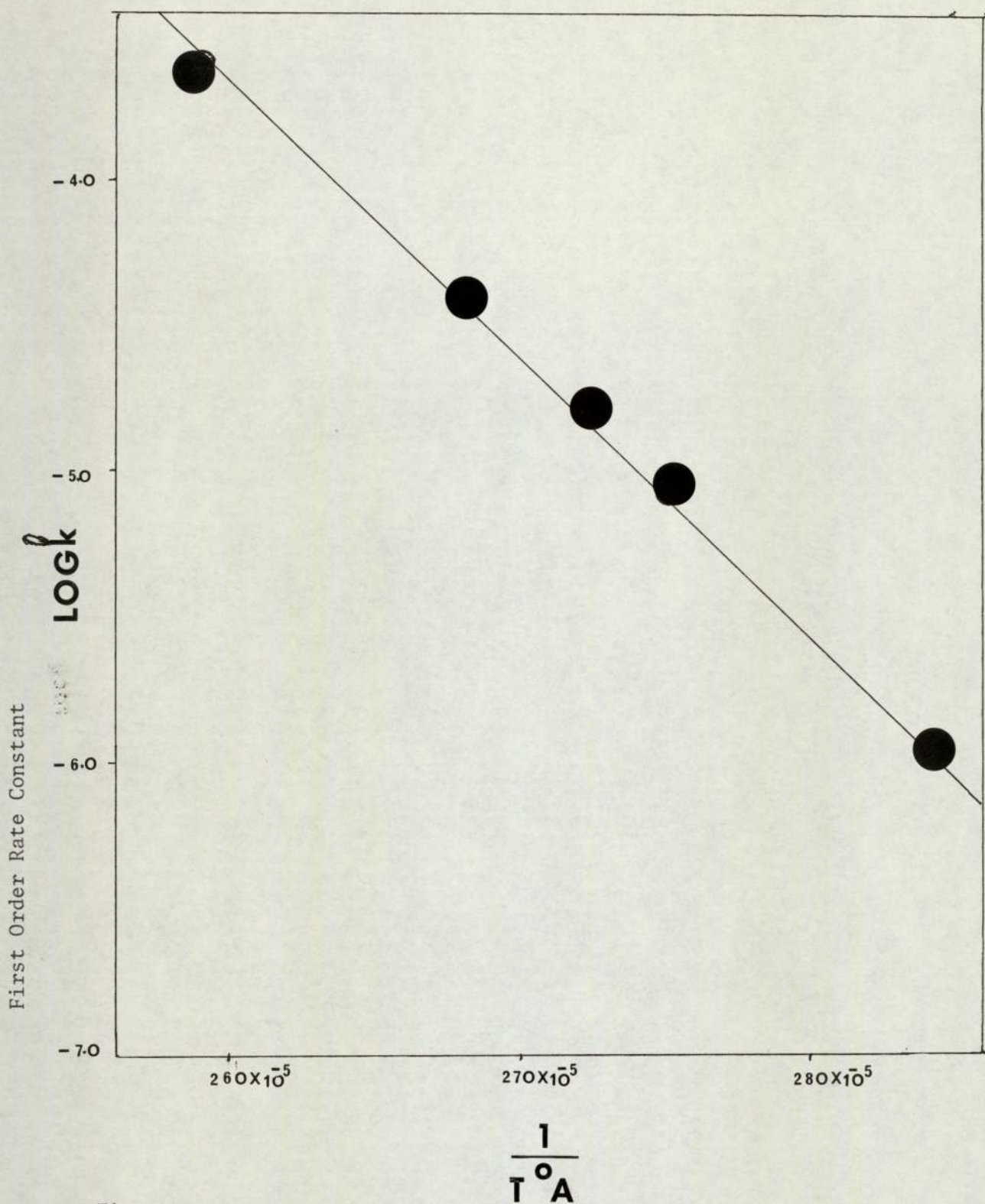
Fig.

Fig. 6.3   Arrhenius plot of log k versus $\frac{1}{T^{\circ}A}$ for the decomposition
of TIBAC in nitrobenzene for temperature range of 80°-112°C.

TIBAC was refluxed in carbon tetrachloride in a constant temperature oil bath at 80°C for a prolonged period, whilst studying the decomposition in this way it was observed that a considerable percentage of TIBAC decomposed to tetramethyl thio-glycollide. Samples were taken from the flask by a hypodermic syringe after one and a half hours, three hours, twenty-four hours and then at frequent intervals for a period of a month. Infra red spectra were taken for each sample. The IR spectra showed the gradual disappearance of carbonyl peaks associated with TIBAC and reappearance of two new peaks.

The magnitude of the peaks was compared by taking one of the methyl stretching peaks (1385 cm^{-1}) as the reference peak. After several days all peaks corresponding to the carbonyls of the TIBAC and impurities disappeared leaving behind two prominant carbonyl peaks which were later examined and identified as tetramethyl thio-collide (1705±5 cm^{-1}) and polymer (1675±5 cm^{-1})

XXVI
($R^1 = R^2 = Me$, TMTG)

The TMTG is soluble in ether and hot carbon tetrachloride and has a melting point of 130°C±2°C. The TMTG was also characterised by mass spectra.   The principal peaks with corresponding fragmentation products are shown in Table 3.3.

The results of the carbon tetrachloride experiment are summarised in Fig. 6.4 and Table 6.2.

Table 6.2 Ratio of magnitudes of Tetramethyl thioglycollide ($1705 cm^{-1}$) and polythio-isobutyric acid ($1680 cm^{-1}$) peaks as a function of time.

Time	$\dfrac{\text{TMTG}}{\text{Polymer}}$
1 day	1.06
10 days	1.07
22 days	1.06
29 days	1.04
35 days	1.04
mixed product heated at 300°C for 2 minutes	1.70

This information demonstrates that although tetramethyl thio-glycollide is formed by degradation of polythioisobutyric acid at high temperature (Chapter 7). This is not the route of its formation from TIBAC under the mild conditions used here. Fig. 6.4 and Table 6.2 fitted together confirm that tetramethyl thioglycollide and polymer are formed concurrently and are paralleled by monomer decomposition. The relative proportions of TMTG and polymer cannot be predicted directly from these results since the relative magnitude of extinction coefficients are not known.
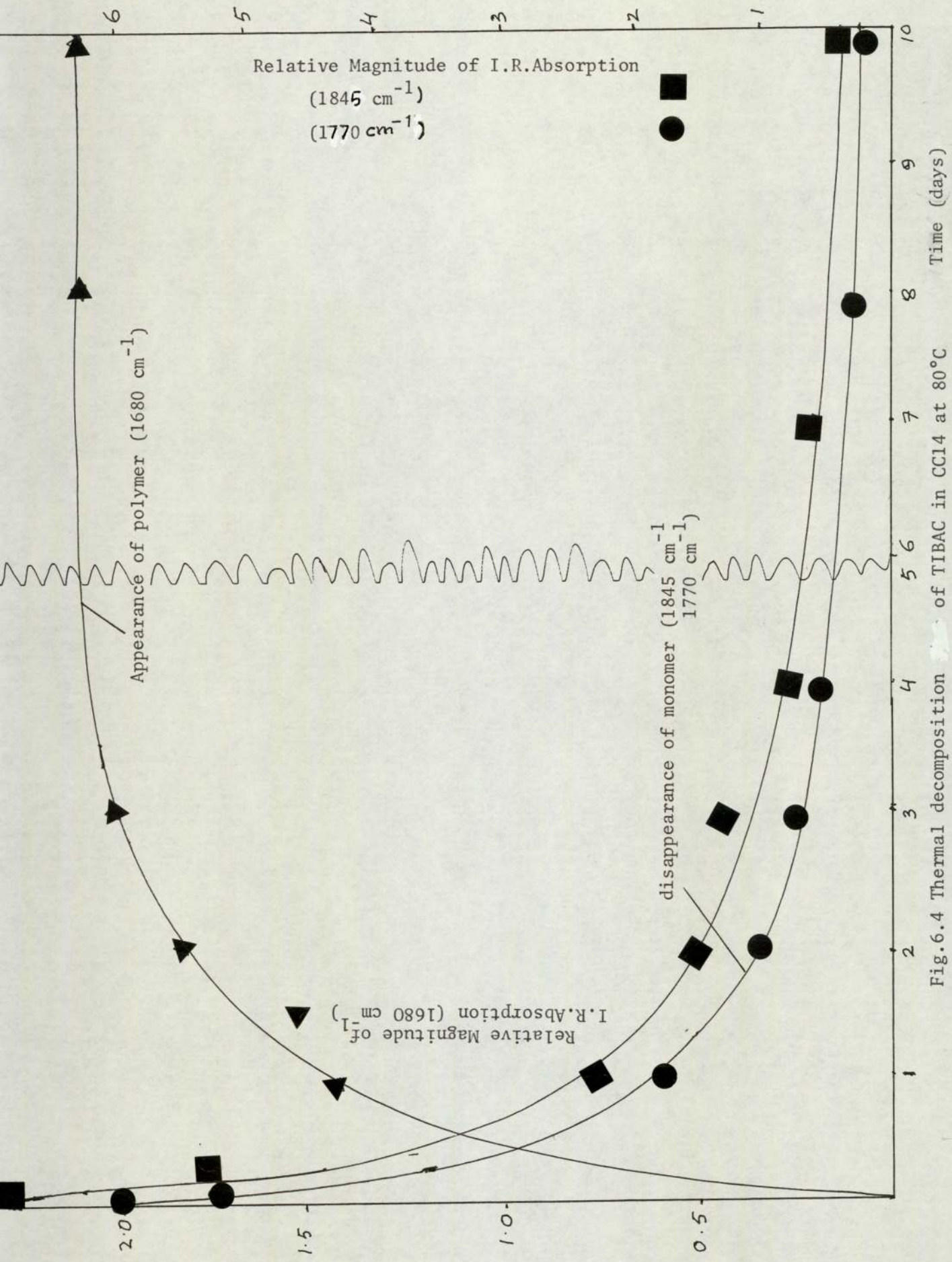
Fig.6.4 Thermal decomposition of TIBAC in CCl4 at 80°C

Relative Magnitude of I.R.Absorption

(1845 cm^{-1}) ■

(1770 cm^{-1}) ●

Appearance of polymer (1680 cm^{-1})

disappearance of monomer (1845 cm^{-1}
1770 cm^{-1})

Relative Magnitude of
I.R.Absorption (1680 cm^{-1}) ▼

Time (days)

Discussion:

The thermal stability of the anhydrosulphites and anhydro-
carboxylates of α-hydroxy carboxylic acids depend mainly upon three
factors which have been established by previous workers in this
field.   These are internal strain in the ring, the nature of the
substituents at the α-carbon and the nature of the reaction medium.

Thus the thermal stability of the rings decreases with
increasing substituents at the α-carbon atom, which can be observed
from the following rate constants.   Glycollic acid anhydrosulphite[24]
(GAAS) has a first order rate constant at 90°C in nitrobenzene of
$5.3 \times 10^{-6} sec^{-1}$ which is very similar to lactic acid anhydrosulphite
(LAAS) at the same temperature and in the same solvent ($5.0 \times 10^{-6} sec^{-1}$).

In the case of the dimethyl substituted anhydrosulphite (HBAS)
however the rate has increased tenfold under similar conditions
($6.0 \times 10^{-5} sec^{-1}$).

A series of rings are illustrated below:

GAAS XXVII   LAAS XXVIII   HBAS XXIX
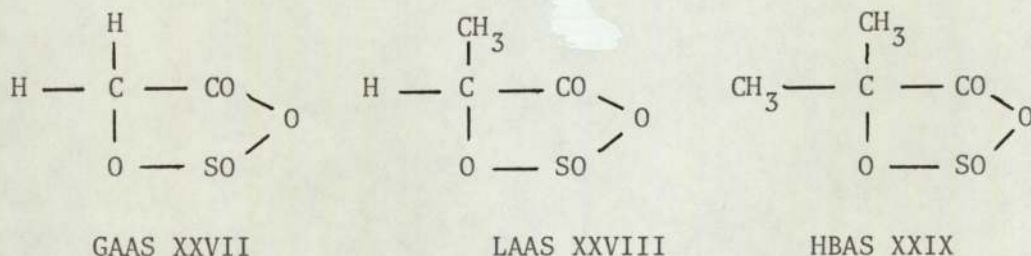
The replacement of single hydrogen atom by a methyl substituent
imparts very little strain to the ring, but accommodation of two
methyl substituents is more difficult and leads to a considerable
decrease in ring stability.

The effect is much larger when bulky groups such as phenyl are
introduced.   The diphenyl substituted anhydrosulphite derived from
                      anhydrosulphite
benzylic acid (BAAS) for example has a first order rate constant of
3.0 x 10^{-3}sec^{-1} at 90°C in nitrobenzene.   The ring opening reactions
of the dimethyl substituted α-hydroxy carboxylic acid anhydrocarboxylate
(DMAC) has been studied by Tighe.   The first order rate constant
obtained for thermal decomposition of DMAC at 90°C in nitrobenzene
was found to be 1.0 x 10^{-7}sec^{-1}.   The difference in stability of
HBAS and DMAC has been explained in terms of the relative size of
carbon and sulphur in the 2-position.   Thus the anhydrocarboxylate
ring is planar whereas the anhydrosulphite ring is puckered and not
stable.   The rate constants obtained with HBAS and DMAC may be
compared with the value obtained for thermal decomposition of TIBAC
in nitrobenzene at 90°C(8.0 x 10^{-6}sec^{-1}).   Thus the rate of
decomposition of TIBAC is (80) eighty times faster than the analogous
dimethyl substituted α-hydroxy acid anhydrocarboxylate (DMAC).   The
faster rate for TIBAC may be simply explained by the fact that
sulphur being a larger molecule than oxygen causes more ring strain.
Although no nmr evidence has been obtained it is probable that the
ring has become puckered to accommodate the sulphur.

It has been established by previous workers that the rate of
decomposition of the rings increases with most solvents as polarity
increases.   Although the changes are not great compared with
reactions involving nucleophilic attack of polymer species for all
comparative kinetic studies nitrobenzene is used as a solvent for
the sake of standardization however.   The following Table 6.3 compares

the first order rate constants for various rings studied at 90°C

in nitrobenzene

Table 6.3. Compares first order rate constants.

Temperature	Solvent	Monomer	First order rate constants
90°C	Nitrobenzene	HBAS	$6.0 \times 10^{-5} (sec^{-1})$
"	"	DMAC	$1.0 \times 10^{-7} (sec^{-1})$
"	"	DEAS	$2.0 \times 10^{-4} (sec^{-1})$
"	"	BAAS	$3.0 \times 10^{-3} (sec^{-1})$
"	"	BAAC	$1.31 \times 10^{-5} (sec^{-1})$
"	"	TIBAC	$8.0 \times 10^{-6} (sec^{-1})$

The structure of DEAS, BAAS and BAAC and TIBAC are shown below.
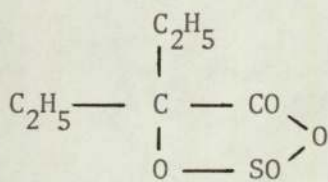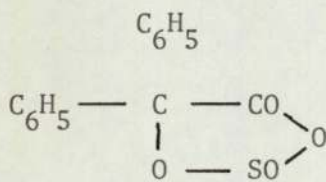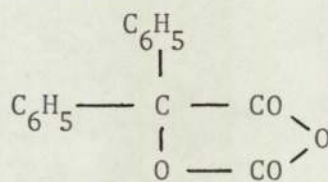
DEAS XXX   BAAS XXXI   BAAC XXXII
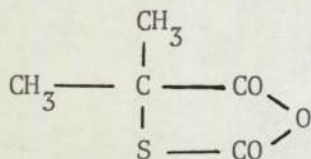
TIBAC XXXIII

It can be seen that changing the ring structure leads to more

marked change than major increases in $C_{(5)}$ substituent size.   Thus

replacing $C_{(5)}$ methylene by phenyls (BAAC) as compared to (DMAC) has

considerably less effect than replacing the oxygen O-(1) by sulphur.

The mechanism of the thermal polymerisation of anhydrosulphites and anhydrocarboxylates of α-hydroxy carboxylic acids have been studied by Tighe and various co-workers. The proposed mechanism involves the formation of a highly   reactive α-lactone which takes part in a polymerisation reaction with the terminal hydroxyl group of the polymer chain. A similar mechanism is also proposed for thermal polymerisation of anhydrocarboxylate of α-hydroxy acids such as BAAC.
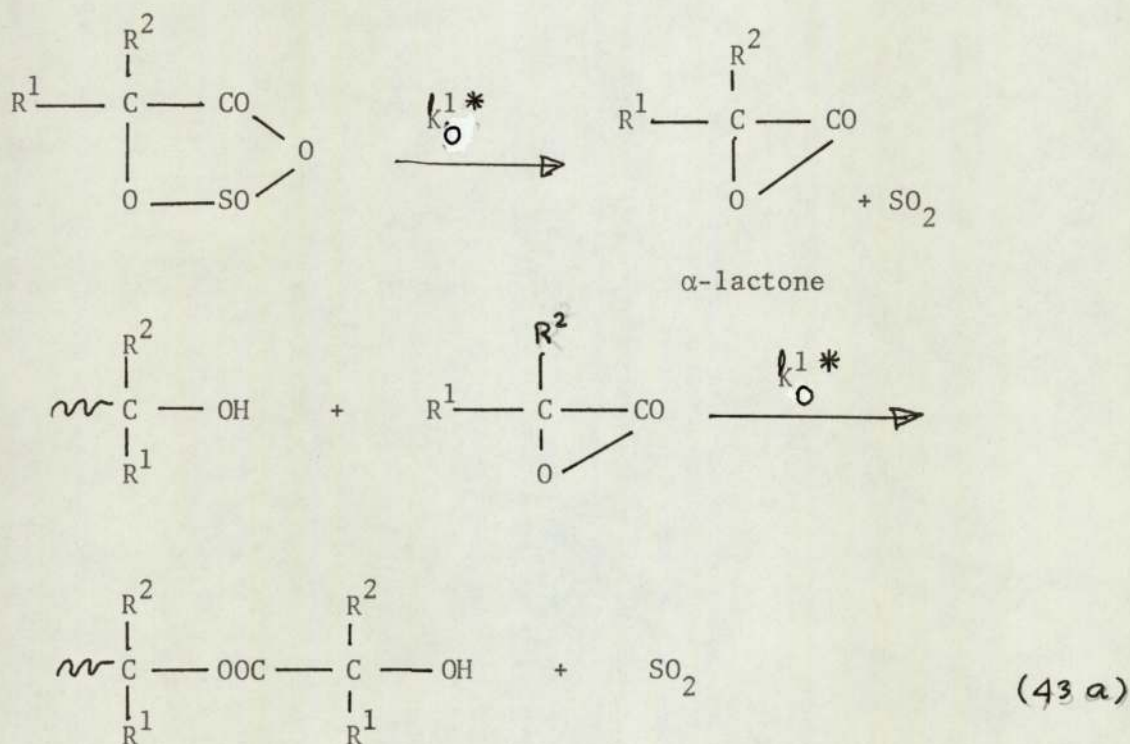
In this sequence of reactions k_0^{1*} is the rate determining step. The products obtained for thermal decomposition of TIBAC at 95°C and above are difficult to characterise. The products obtained at 80°C - 90°C is a mixture of polymer and tetramethylthioglycollide (TMTG). The thermal decomposition of TIBAC probably involves the

initial formation of the α-thio-lactone which can dimerise to form
tetramethyl thio-glycollide (TMTG).   The highly reactive α-lactone
can also polymerise by addition to the terminal -SH group of the
polymer chain.   The role of tetramethyl thio-glycollide in sub-
sequent reactions is obscure.

Thus the proposed mechanism for the thermal polymerisation of
TIBAC may be shown below.

$$(43b)$$
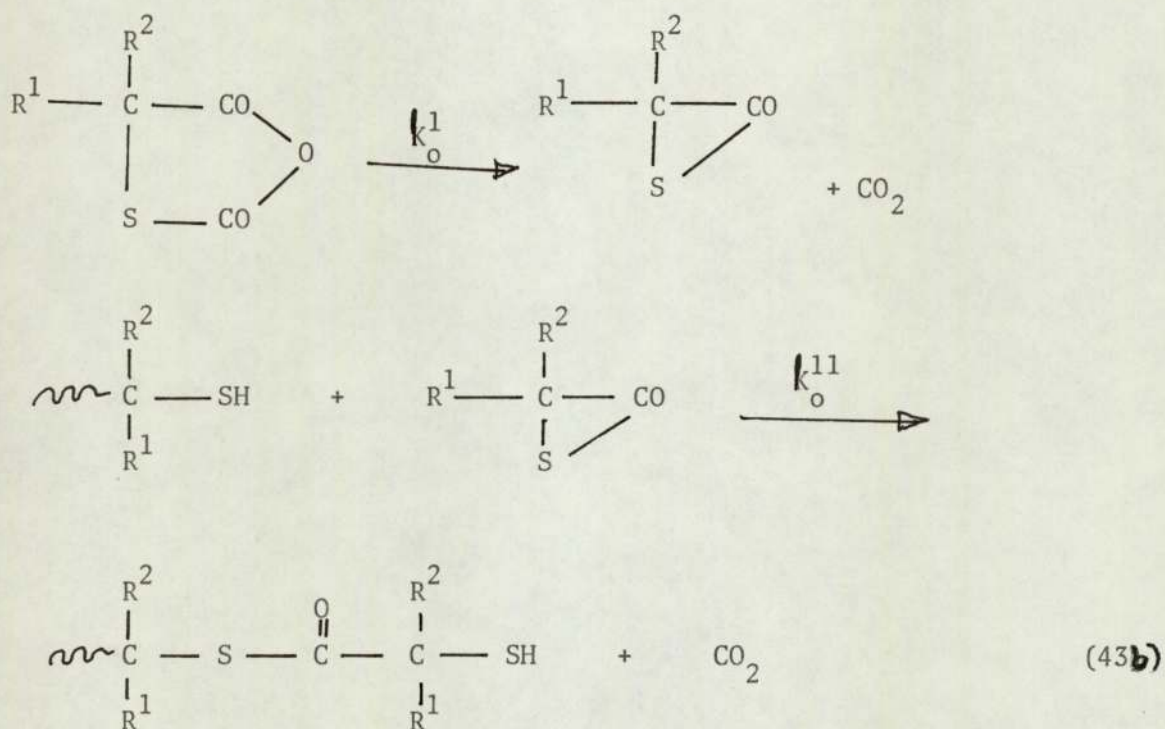
In this sequence of reactions k_o^{1} is again rate determining.
The activated energy and related kinetic parameters (Table 6.1)
determined by experiment are consistent with thermal scission process
and quite different from those obtained with bimolecular reactions
(Chapters IV and V).   The products of pyridine initiated decompo-
sition of TIBAC is a polymer which tends to support this mechanism
since both depend on the α-thio-lactone.

α-thio-glycollic and α-thio-lactic acid anhydrocarboxylates are expected to be more stable thermally than TIBAC. Their rates of thermal decomposition can be estimated approximately at 90°C in nitrobenzene by comparison with the anhydrosulphite series.

$$TIBAC = 8.0 \times 10^{-6} sec^{-1}$$

$$TLAC = 8.0 \times 10^{-7} sec^{-1}$$

$$TGAC = 1.0 \times 10^{-7} sec^{-1}$$

Thus the rate is 80 times less for TGAC than TIBAC. From these theoretical values it appears that TGAC and TLAC are too stable to form polymers by this route. The alternative route to polymerisation is of course by initiations. TGAC and TLAC are reactive to initiation and very easily form polymers in this way.

Thus there is very little hope of establishing experimental conditions under which the thermal decomposition of TGAC and TLAC can be studied without interference from minute but effective traces of initiators.

CHAPTER VII
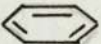
CHARACTERISATION OF REACTION PRODUCTS

7.1 Reactions with Pyridine: Summary

In all cases the molar ratio of the monomer : initiator had no substantial effect on reaction product but only on its rate of formation. Impurities in reaction medium or monomer however led to a substantial lowering in molecular weight of polymer produced. Unfortunately as the molecular weight increased, solubility decreased and no systematic determination of molecular weight could be carried out within the scope of the project. The polymer supply and characterisation centre at RAPRA was able to make some measurements using orthodichlorobenzene at $138°C$.

7.2 Reactions with Benzylamine: Summary

Here the molar ratio of monomer: initiator exerted a marked influence on the nature of the product although the molecular weight produced did not seem to be directly related to $\frac{[M]_o}{[I]_o}$. Polymers produced at moderate high $\frac{[M]_o}{[I]_o}$ ratios (> 20) were substantially identical in behaviour to those produced by pyridine initiation. At $\frac{[M]_o}{[I]_o} \sim 1$ however the amide $\langle\!=\!\rangle CH_2NHCO - \overset{R^2}{\underset{R^1}{C}} - SH$

was produced in quantity.   Its spectral characteristics and melting point (270°C) were quite distinct from those of the polymers.   The most significant parts of the IR spectra is the presence of an amide-like carbonyl at 1590 cm^{-1} and strong terminal -SH at 2560 cm^{-1}, both of which are absent in the polymer.   The enhanced hydrogen bonding in the amide is reflected in the high melting point.

7.3   Thermal Decomposition : Summary

Thermal decomposition studies were only carried out with TIBAC. There was considerable confusion over the behaviour of the monomer at first until it was realised that one of the decomposition products was TMTG, and this product was also formed by decomposition of the monomer under vacuum at low temperatures upon prolonged storage.   The distinctive characteristics of TMTG have been referred to in Chapters III and VI.

7.4   Polymer Characterisation

Poly α-esters are of some interest for making synthetic fibres, films etc. for speciality use.   The polymers which have got high melting points and which are not easily soluble in organic solvents may fairly readily be made into fibres and films.

Although the present work is mainly concerned for the synthesis and to elucidate the mechanisms of polymerisation, the possibility of the use of the polymers and derived polymers was of some interest. The polythioesters synthesised, were characterised by infra red spectra, gel permeation chromatography, x-ray powder photography,

thermo-gravimetric analysis, spherulite growth measurements, solubility, density, melting point and mass spectra etc.

7.4.1. Synthesis and isolation of poly-thio-glycollic acid: Preferred techniques

The general techniques for monomer initiation have been described in Chapters IV to VI. After complete reaction the polymer was filtered, washed several times with diethyl ether and finally with methanol. The polymer was dried at low temperature (60°C) under vacuum. Thioglycollic polymer could be readily prepared by either pyridine, benzylamine or benzylalcohol initiation. This was readily prepared and purified of the monomers and the easiest to polymerise.

7.4.2 Polythio-lactic acid: preferred techniques

Polymers from α-thio-lactic acid anhydrocarboxylate were prepared mainly by benzylamine initiated decomposition of the monomer. The decomposition of the monomer to polymer was carried out in the low temperature kinetic apparatus as described before. The polymer was precipitated out as a white crystalline solid. This was the most difficult monomer to prepare in the pure state and consequently most difficult polymer to prepare in high molecular weight.

7.4.3 Polythioisobutyric acid:

Polythioisobutyric acid was prepared thermally as well as by initiation with benzyl amine, pyridine and lithium t-butoxide. The polymers prepared thermally are in the temperature range of 80°C-112°C

in high temperature kinetic apparatus as described before. Another more convenient method of preparing polymer thermally is in the carius tube in the temperature range of 90°C-100°C. A one molar solution of the monomer in nitrobenzene was introduced into the carius tubes by a hypodermic syringe, which was sealed under vacuum at room temperature and heated in an oil bath for 4-5 days. The tube was then cooled, opened to remove the polymeric mixture, which consists of a mixture of polymer and tetramethylthioglycollide. The TMTG was polymerised from the mixture by adding a few drops of benzylamine. The polymer precipitated out immediately. The mixture was just heated at 45°C for complete reaction.

7.4.4 Solubility:

The low molecular weight polymers (polythioglycollic esters) are soluble in most organic solvents at room temperature. It is stated in the literature that thioglycollic polymer is soluble in dichloro-acetic acid. Although this is true for lower molecular weight materials, high molecular weight polymers are not soluble at room temperature in any available organic solvents. The polymer is however soluble in ortho-dichloro-benzene at high temperature.

The thio-lactic polymer prepared is of low molecular weight ($\sim$ 1000) and soluble in most organic solvents such as methanol, ethanol, THF etc.

Thioisobutyric polymer is insoluble in most organic solvents but soluble in orthodichlorobenzene (ODCB) at high temperature. THF, chloroform and dichloro-acetic acid decompose the polymer after 1 - 2 months at room temperature.

7.4.5. Melting Point

The melting point of the polymers were initially determined by gallenkamp melting point-apparatus. The melting point of thioglycollic polymers ranges from $110°C - 160°C$ depending upon the degree of polymerisation. The melting point of thio-lactic polymers ranges from $145°C - 165°C$ and for thioisobutyric polymer the melting point range is from $110°C-200°C$.

7.4.6 Measurement of density of the polymers
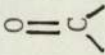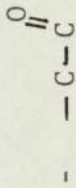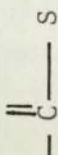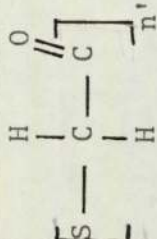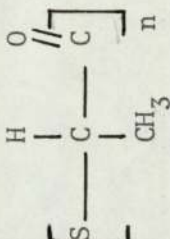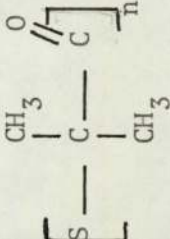
The density of the polymers was measured by density gradient column using carbon tetrachloride (density 1.59 $gmcc^{-1}$) and xylene (density 0.86 $gmcc^{-1}$). The samples were not annealed but measured as prepared.

The density obtained for thioglycollic polymer is 1.58, for thio-lactic polymer is 1.30 and for thioisobutyric polymer is 1.35.
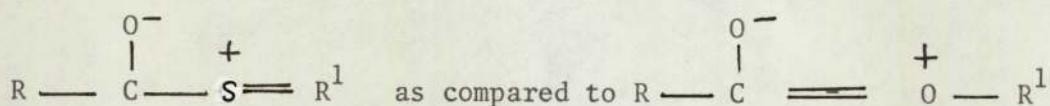
7.4.7 IR Spectra

The infra red spectra of polythioesters were studied in KBr disc. The various characteristic peaks observed for individual polymer are shown in the following Table 7.1.

TABLE 7.1

Polymers	$\equiv C - H$ Asym stretch / $\equiv C-H$ Sym "	$O=C$	$-CH_3$ Asym bending / $-CH_3$ Sym. bending	$-C-C=O$	$-C=C-S$
$[S-CH_2-C(=O)]_{n'}$	2960 cm^{-1} / 2920 cm^{-1}	1680 ± 5 cm^{-1}	1375 ± 5 cm^{-1} / 1270 cm^{-1}	1150 cm^{-1}	990 cm^{-1}
$[S-CH(CH_3)-C(=O)]_{n}$	2980 cm^{-1} / 2900 cm^{-1}	1700 ± 5 cm^{-1}	1440 cm^{-1} / 1390 cm^{-1}	1200 cm^{-1}	920 cm^{-1}
$[S-C(CH_3)_2-C(=O)]_{n}$	2990 cm^{-1} / 2940 cm^{-1}	1690 ± 5 cm^{-1}	1450 cm^{-1} / 1380 cm^{-1}	1130 cm^{-1}	950 cm^{-1}

In a number of simple open chain aliphatic thio esters the carbonyl stretching frequency occurs at 1675 cm^{-1}. The explanation for this low frequency as compared to 1735 cm^{-1} for ordinary aliphatic esters is the greater relative importance of the resonance structure

$$R \underline{\hspace{1cm}} \overset{\overset{\textstyle O^-}{\textstyle |}}{C} \underline{\hspace{1cm}} S \overset{+}{=\!=\!=} R^1 \quad \text{as compared to} \quad R \underline{\hspace{1cm}} \overset{\overset{\textstyle O^-}{\textstyle |}}{C} =\!=\!= \overset{+}{O} \underline{\hspace{1cm}} R^1$$

in ordinary esters.

Comparison of ordinary and thio esters [38].

A series of compounds (thio esters) have an intense absorption at $\sim$ 1690 cm^{-1}. There can be no doubt that this is essentially a carbonyl stretching vibration and has been so assigned by others. Ordinary esters of analogous type have their carbonyl stretching frequency at 1735±5 cm^{-1}. That the difference in C = O stretching frequency between RCO — OR^1 and RCŌSR^1 results from the mass difference between oxygen and sulphur seems most unlikely. Halford has shown if the atoms attached to the C = O group have mass $\geqslant$ 12 (i.e. carbon or heavier) the mass sizes have effectively no influence on the C = O stretching frequency. The great difference of the C = O frequency in CO — S and CO — Cl show that the effects of mass must be small or negligible or are quite coincidentally cancelled by other factors. Nor is it reasonable that this C = O frequency difference be largely dependent upon difference in C - O and C - S bond length, for here again the covalent bond radii of S and O are nearly identical and obviously not related to their effects upon the stretching frequency of a carbonyl group to which each is attached. The difference then between the C = O frequency in — CO — O and — CO — S-must result

principally from the change in the C = O force constant, which results

from replacing O by S.   The factors which affect the force constant

are described below.

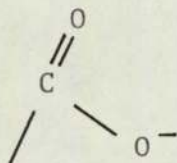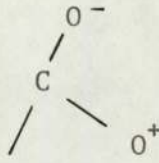Barnes has suggested that of the two resonance forms

$$
\begin{matrix}
O & \qquad\qquad & O^- \\
\| & & / \\
C & & C \\
/\ \backslash & & /\ \backslash\!\backslash^+ \\
\ \ S^- & & \ \ S
\end{matrix}
$$
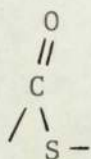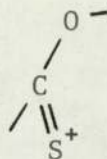
(i)   (ii)

form (ii) is relatively more important in thio esters than form (iv)

of the two resonance forms in ordinary esters.

$$
\begin{matrix}
O & \qquad\qquad & O^- \\
\| & & / \\
C & & C \\
/\quad\searrow & & /\quad\searrow \\
\qquad O^- & & \qquad O^+
\end{matrix}
$$

(iii)   (iv)

Hence if this "resonance effect" were the only one affecting carbonyl

force constants, then ketone carbonyl absorption to be at higher

frequency than ester carbonyl absorption which, of course, is not

the case.   The over compensating effect is the inductive effect

(or electro-negativity).   In terms of modern electronic theory this

effect is the tendency of the α-bond between the O and C atoms

(of the $\overset{O}{\underset{C-O}{\|}}$ bond) to be polarised toward the O atom, with the

result that the other bonds of the carbonyl carbon atom have a

tendency to be polarised more toward that atom, presumably this

results in a stronger carbonyl bond (C = O), and hence an increased

force constant for the C = O stretching vibrations. So as the electronegativity of O is higher than S (O = 3.5, S = 2.6) this inductive effect of O which increases the carbonyl force constant in ordinary esters will be greater than a similar inductive effect of S in thio esters so the difference between ordinary and thiol esters C = O frequencies can result from both resonance and inductive effects. The spectra of poly-thio-glycollic acid and polylthioisobutyric acid in KBr are shown in Figures 7.1 and 7.2.

7.4.8 The molecular weight of the polymers:

The molecular weight of the polythioesters were determined by gel permeation chromatography. The solvent used for low molecular weight polymers was THF. As the high molecular weight polymers are not soluble in THF, the solvent used was ortho-dichlorobenzene at high temperature (138°C). The molecular weights obtained for polythioesters are shown in the Table 7.2. The low molecular weight polythio-glycollic esters are obtained mainly from the hydroxyl initiated decomposition of the impure monomers. The high molecular weight polythioglycollic esters are obtained from the initiated decomposition of the pure monomer. The thio-lactic polymers are obtained mainly from the benzylamine initiated decomposition of the monomers. The polymers obtained are of low molecular weight. The thio-isobutyric polymers are obtained both from thermal and initiated decomposition of the monomers. The polymers obtained ranged from the very low to very high molecular weights.

Fig. 7.1 Infra red spectrum for Polythiocollic acid

Fig. 7.2   Infra red spectrum for Polythioisobutyric acid

TABLE 7.2: Results of GPC analysis of typical polymer samples

Monomer	Initiators	Solvent	$M\bar{n}$	$M\bar{w}$	$M\bar{w}/M\bar{n}$
	Moisture	THF	367.0	427.3	1.76
TGAC	››	THF	490.8	524.3	1.07
	Adventious traces of moisture	ODCB	40487	470.25	1.16
TLAC	Benzylamine	THF	349	406	1.16
	Pyridine	ODCB	424.0	540.0	1.27
TIBAC	Alkoxide	ODCB	39555	464160	11.73
	Benzylamine	ODCB	13859	253440	15.98

NOTE: THF is only suitable for low molecular weight samples.

7.4.9 X-ray powder photographs

X-ray powder photographs of thioglycollic polyester, thio-
lactic polyester and thioisobutyric polyesters are presented in Figures.
The polythioesters are highly crystalline as can be seen from the
photographs. Structural features which favour polymer crystallinity
include chain polarity linearity and regularity. The polythioesters
are crystalline because such requirements are satisfied. As the size
of the substituents is increased, interchain cohesion is reduced and
chain packing becomes difficult resulting amorphous polymers. Previous

studies of polyesters indicated that glycollic, lactic and isobutyric polyesters are crystalline because they satisfy the requirements of the crystallization.poly(MEAS, BAAC, MAAC, AAAC, PFAAC)are amorphous because these compounds are unsymmetrically substituted.

The degree of crystallinity in poly α-esters control the solubility of the polmers. Stonger intermolecular forces within crystalline regions make the polymers insoluble in most of the organic solvents.

The % crystallinity of the polythioesters were calculated from the densitometer graph. The % crystallization obtained for individual polythioesters are shown below:-

|		
Thioglycollic polymer	-	75%
Thio-lactic polymer	-	58%
Thioisobutyric polymer	-	70%

The d-spacing for polythioesters were calculated from the X-ray powder photograph films with the aim to calculate the crystal size of the polymer molecules.

d-spacing for thioglycollic, thio-lactic and thioisobutyric polymers are shown in Table 7.3.

TABLE 7.3

d-spacing	Thio-glycollic polymer	Thio-lactic polymer	Thioisobutyric polymer
R1	5.52	5.75	6.32
R2	4.12	5.05	5.45
R3	3.60	4.65	4.71
R4	3.30	4.31	4.55
R5	2.85	4.02	3.95
R6	2.45	3.75	3.63
R7	2.03	3.34	3.24
R8	1.80	2.80	3.10
R9	1.47	2.56	2.69
R10	1.28	2.36	2.30
R11	-	2.19	2.15

X-ray powder photographs of polythioglycollic acid, polythio-lactic acid and polythioisobutyric acid are shown in Figure 7.3, 7.4 and 7.5.
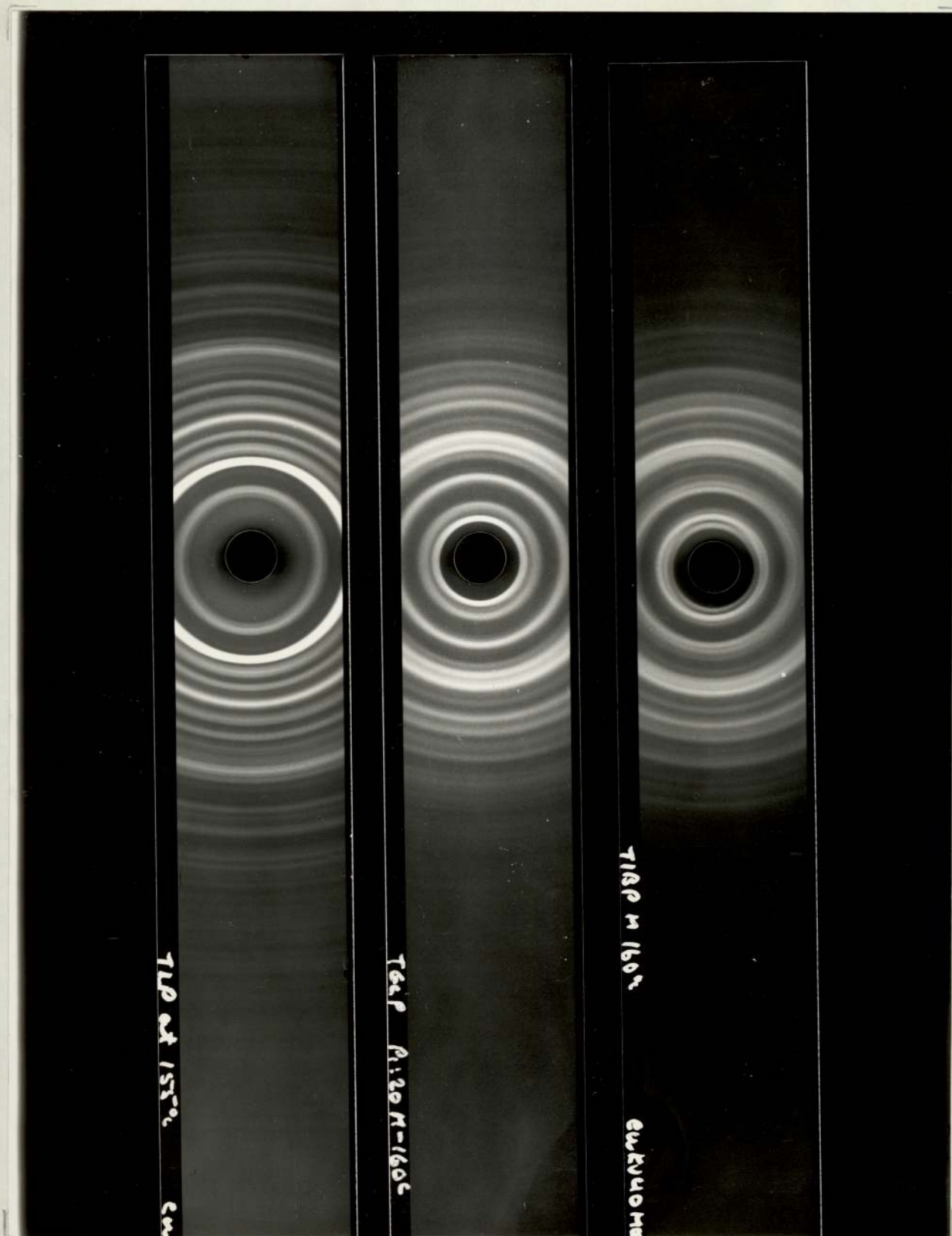
Figures (7.3, 7.4 and 7.5) : x ray powder photographs

of polythioesters

7.4.10 Thermal Decomposition Studies

The thermal stability of polythioesters were assessed by thermo-gravimetric analysis, typical traces are shown in Figure 7.6.(α)

(a) Polythio-glycollic is stable up to 225°C in nitrogen as well as in air. The polymer starts decomposition after that temperature. At 300°C the weight loss is 60%. The decomposition product remained constant almost up to 500°C.

(b) Polythio-lactic acid is stable up to 150°C and starts de-composition after that temperature. At 250°C the weight loss is more than 90%

(c) Polythioisobutyric acid: The polymer is stable up to 160°C. The weight loss at 200°C is almost 50%.

The polymers are appreciably less stable than the corresponding poly-α-esters

$$-\left[O - \underset{\underset{R^1}{|}}{\overset{\overset{R^2}{|}}{C}} - CO \right]_n -$$
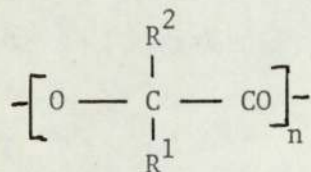
but show the same trend in terms of substituent effects. Some preliminary isothermal decomposition studies were carried out and these together with the fact that the six membered thioglycollide forms the major decomposition product, support the view that a similar decomposition mechanism occurs in the two series. This is a four centred mechanism and is shown in equation (44). This suggestion obviously needs detailed study to prove or disprove this hypothesis.
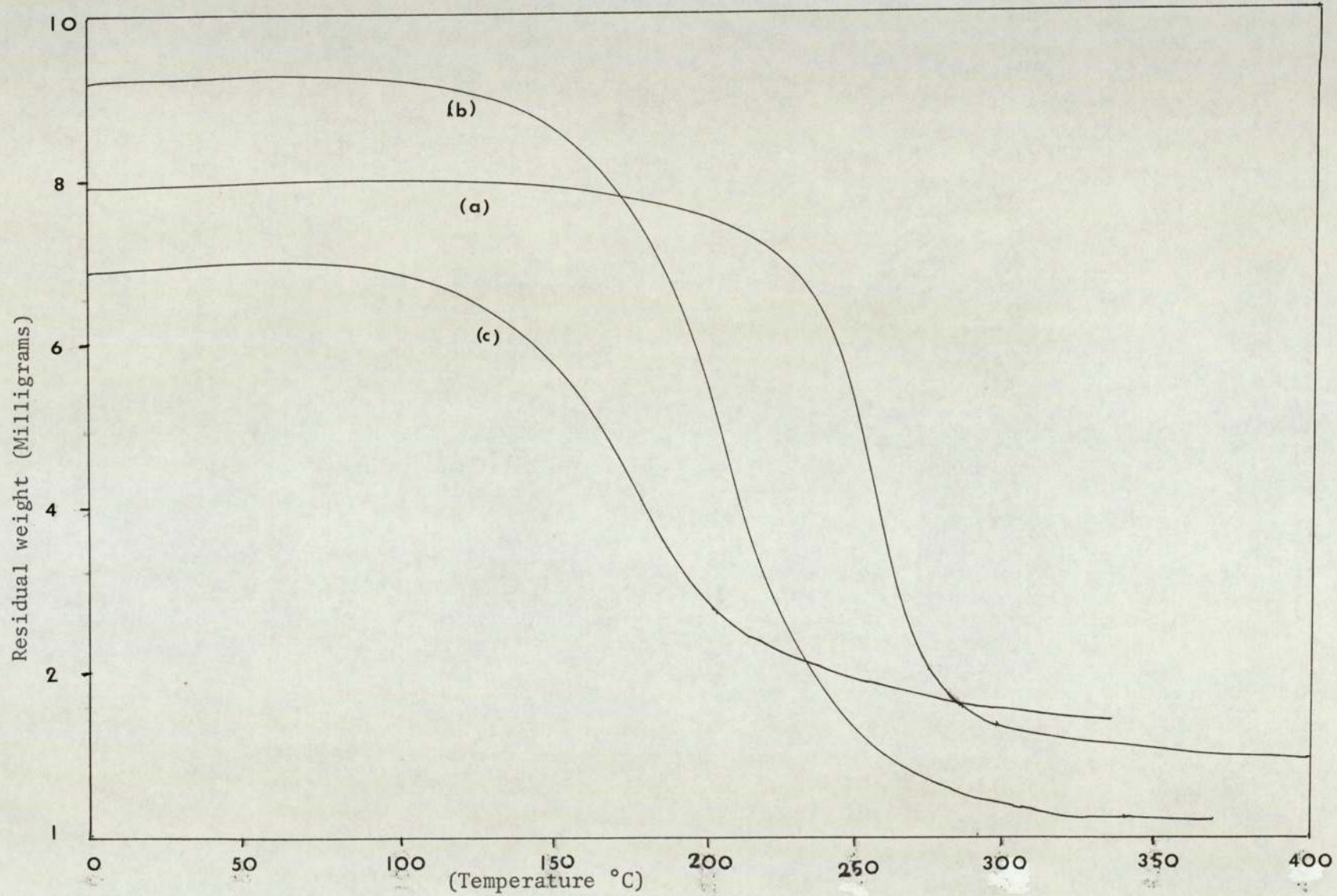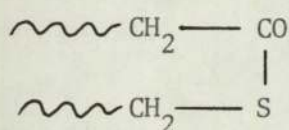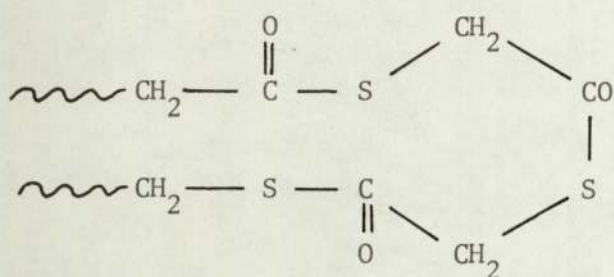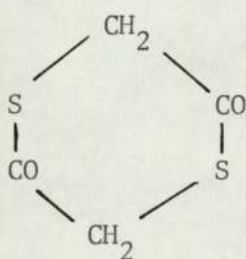
Fig.7.6(a) TGA traces for (a) polythioglycollic acid, (b) Polythiolactic acid and (c) polythioisobutyric acid.

$$\begin{array}{ccc}
\sim\!\!\sim CH_2\!\!-\!\!\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}\!\!-\!\!S & \overset{\displaystyle CH_2}{\diagup\;\diagdown} & CO \\
 & & | \\
\sim\!\!\sim CH_2\!\!-\!\!S\!\!-\!\!\underset{\displaystyle \underset{\displaystyle O}{\|}}{C} & \diagdown\;\diagup & S \\
 & CH_2 &
\end{array}$$

$$\begin{array}{ccccc}
\sim\!\!\sim CH_2\!\!-\!\!CO & & & \overset{\displaystyle CH_2}{\diagup\;\diagdown} & \\
| & + & S & & CO \\
\sim\!\!\sim CH_2\!\!-\!\!S & & | & & | \\
 & & CO & & S \\
 & & \diagdown\;\diagup & & \\
 & & CH_2 & &
\end{array} \qquad (44)$$

XXXIV

7.4.11 Spherulite Growth

In the present study the growth rates of spherulites in poly-thioglycollic ester and poly thioisobutyric ester were measured directly by polarising microscope equipped with an electric hot stage providing good constancy in the required temperature region. Samples were sandwiched between the cover glasses. The thin films of melt crystallised polymers were examined between crossed polars and the photographs were taken with a camera attached to the micro-scope. Figs. 7.6, 7.7 and 7.8 are the optical micrographs of various molecular weight fractions of poly thioisobutyric ester crystallised at $100°$. $110°$ and $150°C$ respectively. All these micrographs exhibit a fibrous spherulitic texture, with crystal growth being predominant in one direction only. This is to be
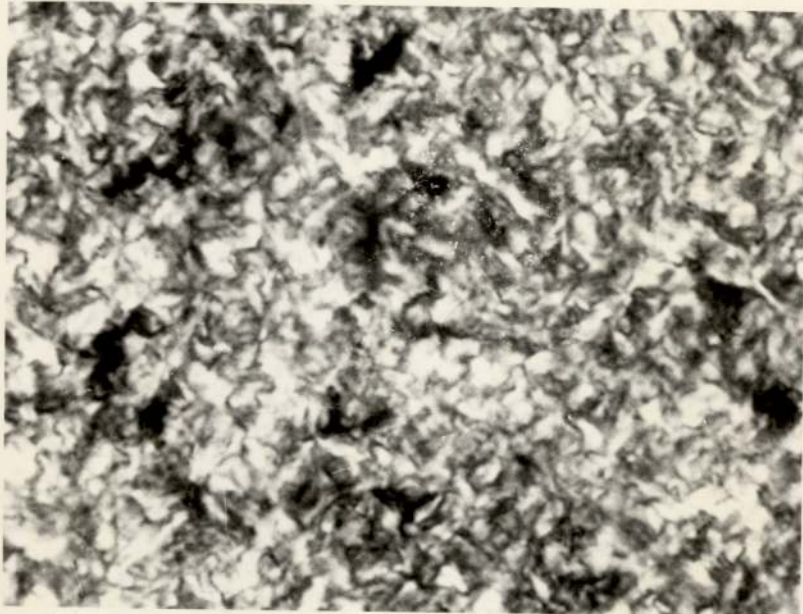
Figures (7.6(b), 7.7)   Growth of Spherulite
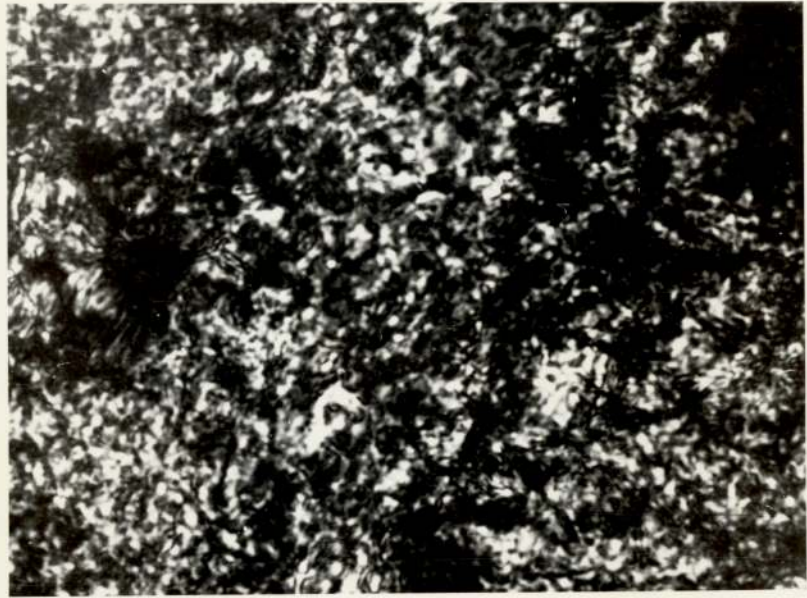
for polythioisobutyric acid

Figure 7.8 :   Growth of Spherulite for
polythioisobutyric acid

expected from a lamellar chain folded structure of homopolymers.
In principal the size of the spherulites is related to the nucleation
density which in turn is determined by temperature of the crystal-
lisation. When a polymer is crystallised close to the melting
point the nucleation density is rather low due to high kinetic
energy of the molecule. Once few critical size nuclei are formed
growth can occur by the addition of more molecule, and the nuclei
can grow into large spherulites before their growth is arrested by
mutual impingement. Consequently polymers crystallised at
temperatures close to the melting point should produce large
spherulites. As the crystallisation temperature is lowered, the
number of nuclei formed per unit time in a given volume increases
and due to high nucleation density spherulites thus formed start
impinging at a very early stage and hardly reach recognisable size.
Figs. 7.6, 7.7 and 7.8 were obtained from poly thio-isobutyric
ester of different molecular weight fractions. The ΔT, degree of
supercooling, $(Tm-Tc)$, for these polymers is 30°C, 50°C and 50°C
respectively. As expected Fig. 7.6 shows some recognisable
spherulite structure but it appears that in Fig.7.7 and Fig. 7.8 ΔT
is too large to produce spherulites of recognisable size.   Molecular
weight influence rate of crystallisation through its effect on ΔT.
However, in addition to that it has been reported by various workers
that lower molecular weight fractions under similar conditions
produce larger spherulites than those with higher molecular weight.
This makes the interpretation of Figs.7.6, 7.7 and 7.8 more difficult
since ΔT values and their molecular weights are not comparable.
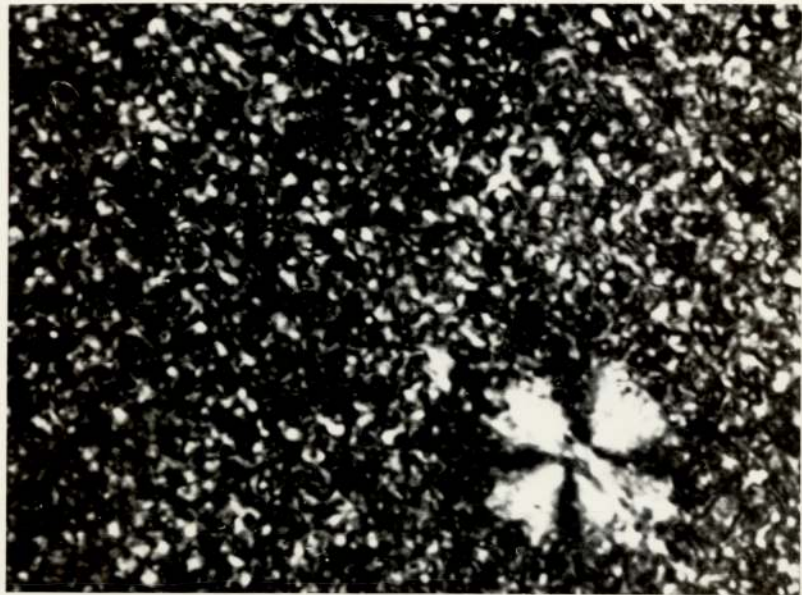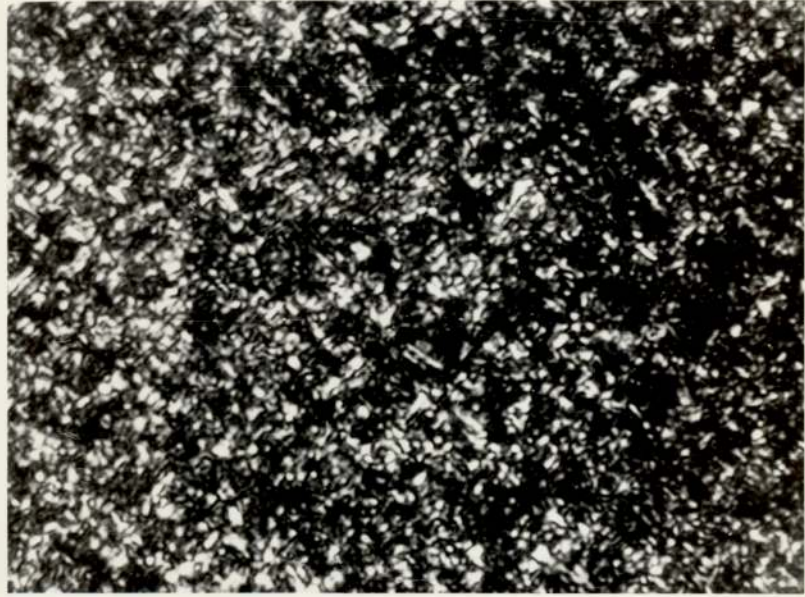
Figures (7.9 and 7.10)   Growth of
Spherulites for polythioglycollic acid

Figure 7.11 :   Growth of Spherulite for

polythioglycollic acid

The temperature effect of crystallisation temperatures on the spherulite size is more clearly demonstrated in Figs. 7.9, 7.10 and 7.11 which are the optical micrographs of polythioglycollic (Tm. 120°C - 130°C) crystallised at 80°C, 86°C and 90°C. Fig.7.9 due to relatively high value of ΔT indicates high nucleation density and so the spherulites are too small to be optically resolved. In Fig.7.10 a single spherulite with characteristic maltese cross can be clearly observed which is still embedded in a matrix of smaller spherulites. At still higher crystallisation temperature (Fig. 7.11) a part of a single spherulite with zig-zag extinction pattern is observable. The spherulite grown at this temperature appears to be more fibrous which is in agreement with studies reported for other polymers. The growth rates of spherulites was also measured on an optical microscope by melting a piece of polymer between two glass slides at a temperature of which was about 20°C above the melting point of the polymer. This ensured complete melting. The sample was then transferred to the hot stage of the optical microscope which was maintained at a predetermined temperature. The induction time in each case was measured as a function of time. In a separate experiment, under similar conditions the increase in the radius of the spherulites was measured as a function of time, Fig.7.12. The radius of a spherulite is plotted against time for polythioglycollic ester which was crystallised at 95°C. A similar plot is made in Fig. 7.13 for the same polymer but of lower molecular weight. The slope of the curve which determines the growth rate indicates the lower molecular weight fraction has higher rate of crystallisation. Since the melting
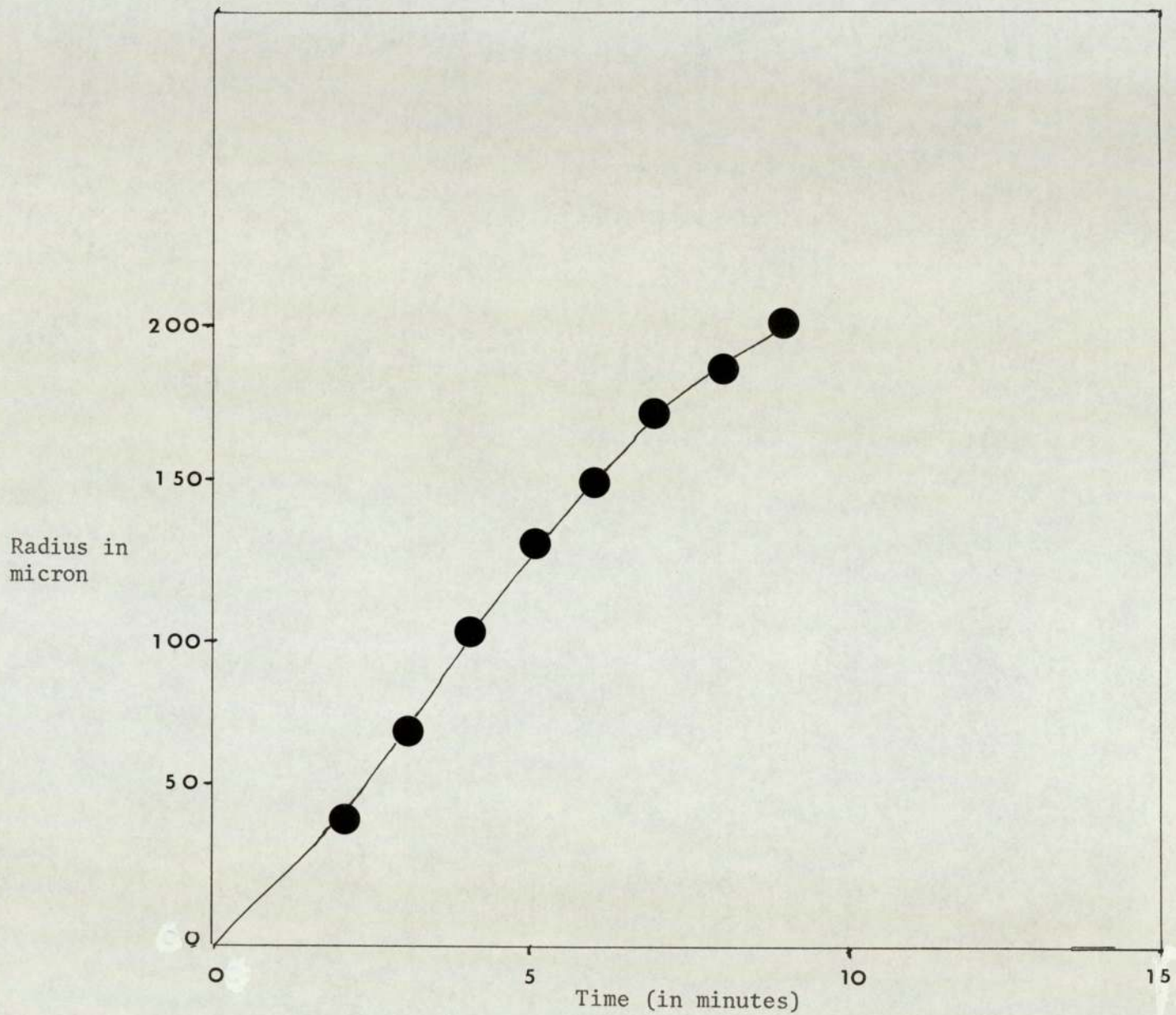
Fig. 7.12   Rate of growth of spherulite at 95°-96°C for polythio-glycollic acid.
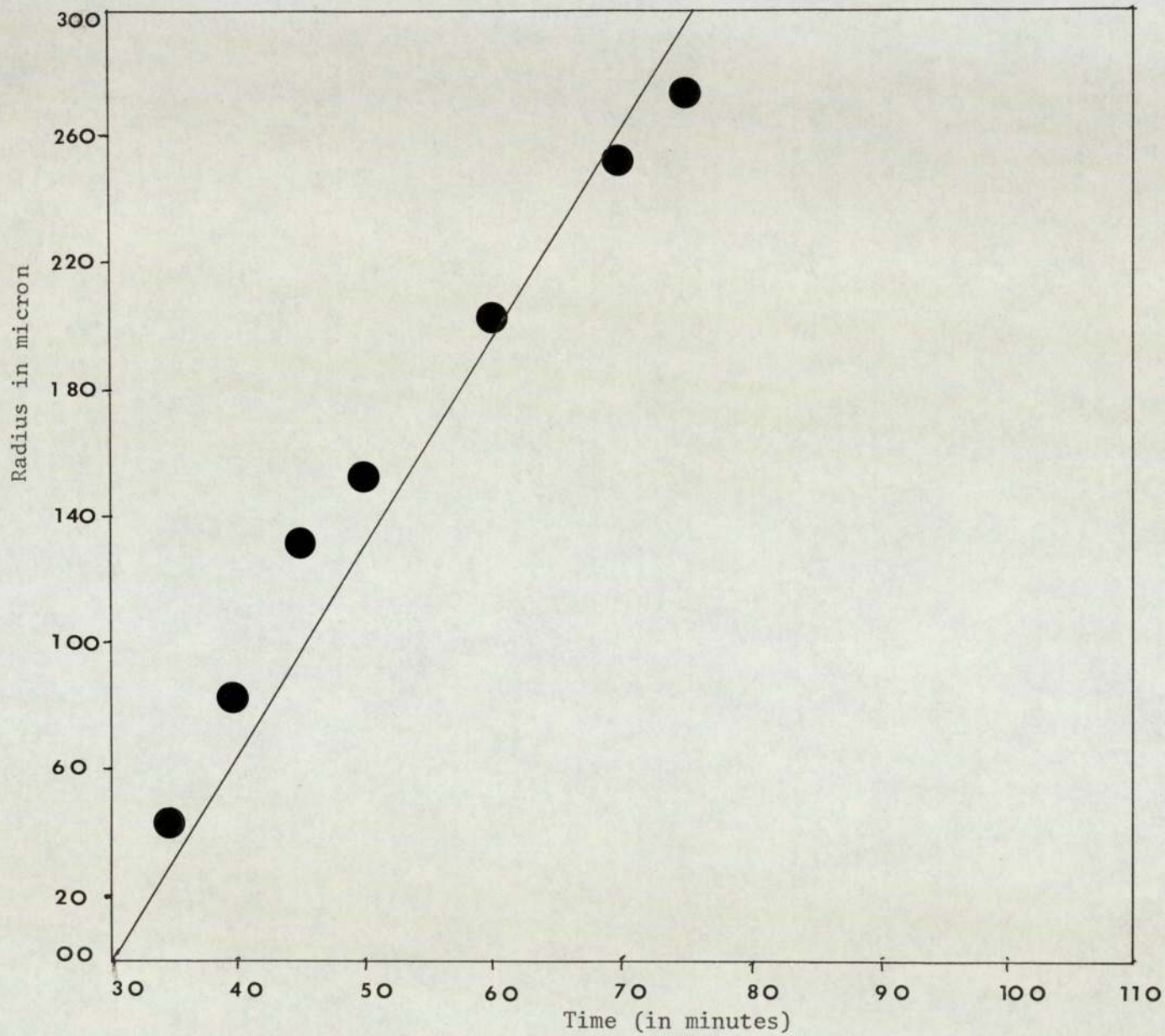   (Higher Molecular weight)

Fig. 7.13 Rate of growth of spherulite 95°C for polythio-glycollic acid

point of the two polymer fractions are comparable the difference in crystallisation rates cannot be attributed to the different values of ΔT but is directly related to molecular weight. Similar observations have been made on several other polymers such as polyethylene, polyethylene terephthalate, poly ethylene adipate and poly carbonates. In addition to molecular weight both the polydispersity and nature of molecular weight distribution have an effect on the course of crystallisation. However, the crystallisation rates for nylon-6 fractions are reported to increase with molecular weight. This is difficult to explain since the increase in viscosity of polymer melt owing to increase in molecular weight would reduce the mobility of crystallising macromolecules and thus the rate of transport of molecules to and from the crystal surface should also decrease.

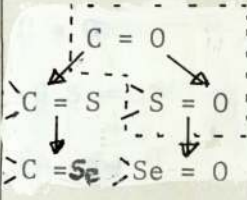### 7.4.12 Crystallisation Rate (Depolarised Light Intensity) Measurements

Some preliminary studies were carried out on the thioglycollic polymer to compare the rate of crystallisation with that of the oxygen containing analogue. The samples were believed to be of comparable molecular weight ($\bar{M}w$ 20,000). The results are presented as crystallisation half-times as a function of degree of supercooling in Table 7.4.

Poly*thio*glycollic Acid (Tm153°C)			Poly glycollic Acid (Tm 220°C)		
Tc	ΔT	$t\frac{1}{2}$(sec)	Tc	ΔT	$t\frac{1}{2}$(sec)
100	53	60			
106	47	70	179	46	390
108.5	44.5	80	183	42	330
110	43.0	80	184	41	450
113	40.0	220	187	38	1080
116	37.0	320	191	34	1960
117	35	340			

Although the figures only enable a partial comparison to be made they do confirm that polythioglycollic and polyglycollic acid both crystallise very rapidly. There is some indication that the process is more rapid in the case of P.T.G. acid.

CHAPTER VIII

8.1 Summary and Conclusions: Suggestions for further work

The work presented in this thesis is an attempt to extend the knowledge of the behaviour of cyclic esters of α-functional acids. It is the first substantial synthetic and kinetic study of TGAC, TLAC and TIBAC (and the first work of any kind on the latter compound).

If the general structure of the cyclic derivatives of α-functional acids is represented by

$$
\begin{array}{c}
R^2 \\
| \\
R^1 \!-\! C_5 \!-\!_4 CO \\
| \qquad \ \ \ _3 \ O \\
_1 \quad _2 \\
X \!-\! YO
\end{array}
$$

(XXXV)

Then the most obvious possibilities for values of R^1, R^2, X and Y in this structure are found together in the periodic table

B	C	N	O	F
	Si	P	S	Cl
		As	Se	Br

TABLE 8.1 Structural effects in cyclic ester monomers

	R^1/R^1	X	Y
	H/H H/Me Alkyl Me/Me C - H (aryl) C - F (Fluoroalkyl) C - F (Fluoroaryl)	= S = NH = O = Se	C = O C = S S = O C = Se Se = O
Size effects	(a) Ring strain (b) Steric hindrance of C(4)	(a) Ring strain (Planarity)	(a) Ring strain (Planarity)
Polarity effects	(a) Ring stability (b) Activity of C(4)	(a) Ring stability (b) Activity of C(4) (c) Nucleophilicity of ⌇SH and ⌇S⁻	(a) Ring stability (b) Activity of C(4)

By using the concepts of changing size and polarity as predicted by relative placings in the periodic table, it is becoming possible to understand and predict the behaviour in terms of rates and mechanisms of the type of monomer used in this work.   This is illustrated in table 8·1 which summarises the various factors referred to previous chapters.   The area of work contained in this thesis is indicated with dotted lines.

Although the methods of synthesis and purification for the various cyclic monomers within the scope of table 8.1 are broadly similar, there are certain aspects which are peculiar to particular groups. The work described in Chapter III illustrates this point in relation to α-thio acid derivatives.

The method of synthesis of thio-anhydrocarboxylates via the metal salt technique was found to be unsuitable. The best method for the synthesis of TGAC and TLAC is by the direct reaction of α-thio acids with carbonyl chloride in the molar ratio of 1:1.5, which minimises the formation of α-chloro-acid chloride whilst ensuring an adequate conversion of acid. The successful synthesis of TIBAC requires the concurrent addition of pyridine which facilitates reaction by assisting hydrogen chloride elimination. The synthesis of thioglycollic anhydro-sulphite (TGAS) and thio-lactic anhydrosulphite (TLAS) by the reaction of α-thio acids with thionyl chloride ($SOCl_2$) is possible under similar conditions to those described for the synthesis of thio anhydrocarboxy-lates.

In general purification by vacuum sublimation and related techniques were found to be most successful. More significant however is the discovery that the monomers tend to decompose slowly to yield thioglycollides even in the region of room temperature. The mechanism of this process has not been studied but the problem is largely avoided by storing monomers at temperatures below -20°C.

The reactivity of the monomers (TGAC, TLAC and TIBAC) after
purification has been studied with various potential initiators
(e.g. pyridine, benzyl alcohol, benzylamine) and in one case (TIBAC)
the thermal decomposition has been examined.

In Chapter IV various aspects of the pyridine-initiated
decomposition of thio-anhydrocarboxylates are presented. On the
basis of the additional information discussed in subsequent chapters
a more complete analysis can now be made.   Because of the apparent
similarity of the behaviour of α-hydroxy acid and α-thio acid
anhydrocarboxylates it can reasonably be assumed that the basic poly-
merisation mechanisms will be similar.

Thus a mechanism for the decomposition of TGAC, TLAC and TIBAC
with pyridine can be based on that proposed for α-hydroxy acid
anhydrocarboxylate.   This involves an initial equilibrium reaction
between monomer and pyridine on one hand and an intermediate
(probably a charge transfer complex) on the other, followed by the
decomposition of this intermediate to yield a polymerisable species.
Equations given below outline the scheme for the reaction.

$$M + Py \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [MPy^*] \xrightarrow{k_d}$$

Product + CO_2 + Py . . . .   (45)
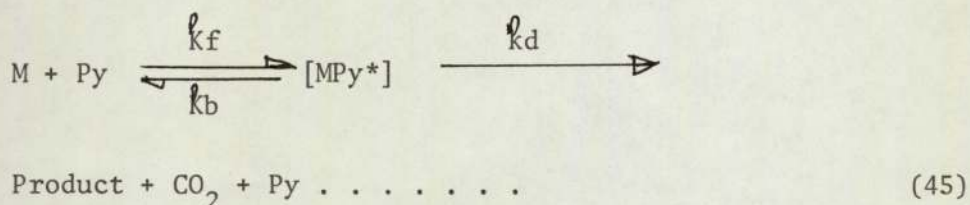
The charge transfer complex is represented by $[MPy^*]$ and k_f, k_b
and k_d are the relevant rate constants for the processes indicated.

The equilibrium constant K is given by

$$K = \frac{kf}{kb} \qquad (46)$$

The rate of formation of the product is given by $\frac{d(Product)}{dt} = kd[MPy^*]$ (47)

The product is considered to be an α-lactone which takes part in a non-rate determining propagation reaction. The concentration of [MPy*] and the reactants are related through the equilibrium constant K, (Equation 48)

$$[MPy^*] = K[M][Py] \qquad (48)$$

assuming that the concentration of [MPy*] is small compared with $[M]_o$ and $[Py]_o$, i.e. [MPy*] is a reactive intermediate.

The measured rate constant k_{obs} is a product of the actual rate constant for the decomposition process and the equilibrium constant. Thus the reaction appears first order in spite of the complexity of the mechanism. The actual step which involves bond breaking is governed by kd, but the measured rate of reaction k_{obs} is the product of kd and the equilibrium constant K.

$$observed\ rate = K. kd[M][Py] \qquad (49)$$

We can now make some comparison of observed rates in the α-hydroxy and α-thio-acid anhydrocarboxylates and attempt to rationalise the differences in terms of contributions to K and kd. The observed rate constant for TGAC (6.0×10^{-2} L mol^{-1} sec^{-1}) is higher than mandelic acid anhydrocarboxylate (MAAC 1.93×10^{-2} L mol^{-1} sec^{-1}) at 25°C in nitrobenzene.
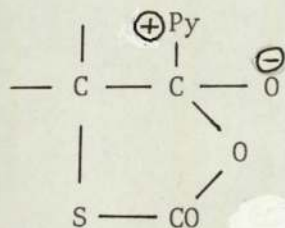
From the work on related systems we can estimate that the effect of introducing a phenyl substituent in place of hydrogen should be a marked (approximately 6 fold) increase in rate.   This assumes that the other structural features of the ring are identical since the observed rates for TGAC and MAAC (mandelic acid anhydrocarboxylate) are in the ratio 3:1 in the opposite sense to that expected.we can conclude that sulphur containing ring is almost twenty (i.e. 6 x 3) times more   reactive to pyridine than its oxygen containing analogue.

i.e.

$$\sim 20\times \;\;>$$

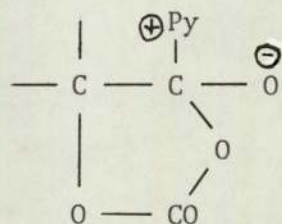(A)   (B)
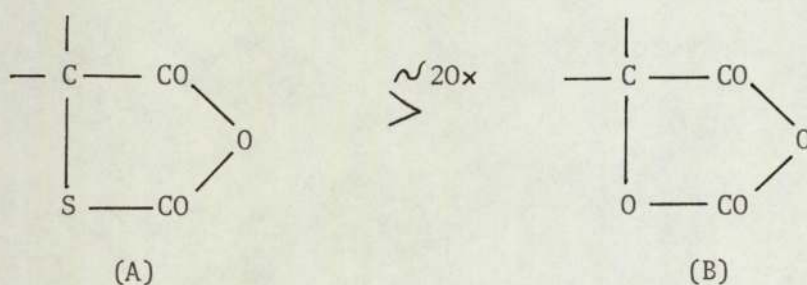
This pyridine reaction is made up of a nucleophilic attack at the $C_{(4)}$ carbonyl and the decomposition of the complex formed by this reaction. From the results presented in Chapter V we have seen that the $C_{(4)}$ carbonyl in rings of type A is only some three times more reactive than that in rings of type B .   It would appear therefore that this factor cannot completely explain the much greater reactivity of rings of type (A) to pyridine.   On the other hand work presented in Chapter VI shows that the thermal decomposition of the sulphur containing ring (A) occurs much more readily than that of type (B). In the specific examples presented in that chapter the first order rate constants for (A) and (B) differed by a factor of one hundred[41] (approximately).

It is well known[77] that as two types of ring (α-hydroxy acid anhydrocarboxylate and anhydrosulphite) are concurrently destabilised by introducing bulky $C_{(5)}$ substituents the rate constants will tend to converge.   It seems reasonable to assume therefore that the complex derived from the reaction of (B) with pyridine will be considerably less than 100 times more stable than the complex derived from the reaction of A with pyridine. On the other hand the complex

$$
\begin{array}{c}
\quad\quad\overset{\displaystyle |}{\quad}\quad\overset{\displaystyle \oplus Py}{\underset{\displaystyle |}{\quad}}\\
-\,C\,-\,C\,-\,\overset{\ominus}{O}\\
\quad\quad\overset{\displaystyle |}{\quad}\quad\quad\diagdown\\
\quad\quad\quad\quad\quad O\\
\quad\quad\quad\quad\diagup\\
S\,-\,CO
\end{array}
$$

must still be affected by the ring sulphur and therefore be considerably less stable than

$$
\begin{array}{c}
\quad\quad\overset{\displaystyle |}{\quad}\quad\overset{\displaystyle \oplus Py}{\underset{\displaystyle |}{\quad}}\\
-\,C\,-\,C\,-\,\overset{\ominus}{O}\\
\quad\quad\overset{\displaystyle |}{\quad}\quad\quad\diagdown\\
\quad\quad\quad\quad\quad O\\
\quad\quad\quad\quad\diagup\\
O\,-\,CO
\end{array}
$$

In the summary then the rate of reaction of A and B with pyridine (Equation 49) seems to be affacted by both $C_{(4)}$ activity (ie k) and ring instability (ie kd).   On balance however it seems reasonable to assume that the latter effect is greater.

One of the most important pieces of information which comes from this kinetic study is that TIBAC initiated with pyridine produces a polymer whereas ring compounds such as DMAC (dimethyl substituted anhydrocarboxylate of α-hydroxy acid) and the dimethyl substituted NCA do not polymerise at reasonably measurable rates.

The work presented in previous chapters makes it obvious that the mechanisms are different.   Those α-hydroxy acid anhydrocarboxylates that do polymerise with pyridine show identical kinetic behaviour to the α-thio acid anhydrocarboxylates (Chapter IV).   These are the only two groups of compounds so far studied that follow this kinetic pattern and the pattern and the work in Chapter IV therefore provides valuable support for the mechanism proposed by Smith and Tighe[37, 77].   The fact that DMAC has not been observed to polymerise is simply because the rate is slow.   In the presence of 0.1 molar pyridine the half life would be almost 150 hours at 25°C (predicted from data in this chapter and Chapter IV).

The kinetics and mechanisms make it clear in this case (equations 45 - 49) that the propagation step itself is not affected but only the formation and decomposition of the monomer-pyridine complex.   The NCA case however is quite different (Chapter IV).   The kinetics are second order and relate to a rate determining propagation step.   This step follows a rapid proton abstraction which leads to the formation of an 'activated' monomer.

$$CH_3 - \underset{\underset{\ominus N - CO}{\overset{|}{\underset{|}{C}}}}{\overset{\overset{CH_3}{\overset{|}{}}}{C}} - CO \diagdown O \diagup$$
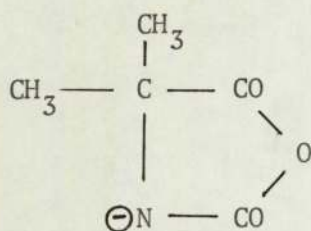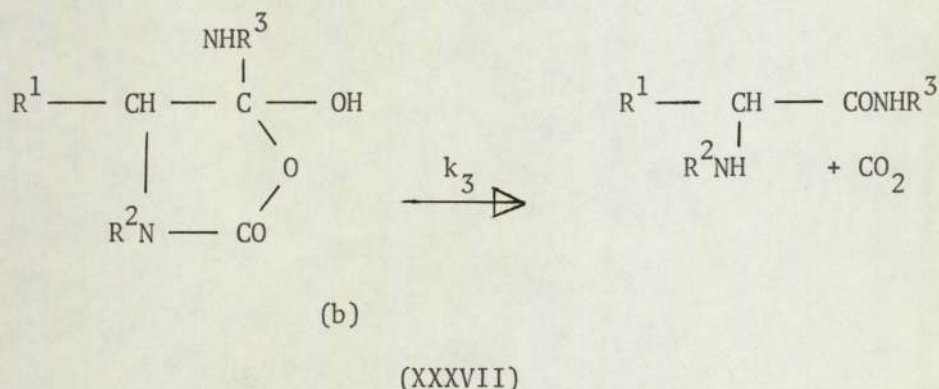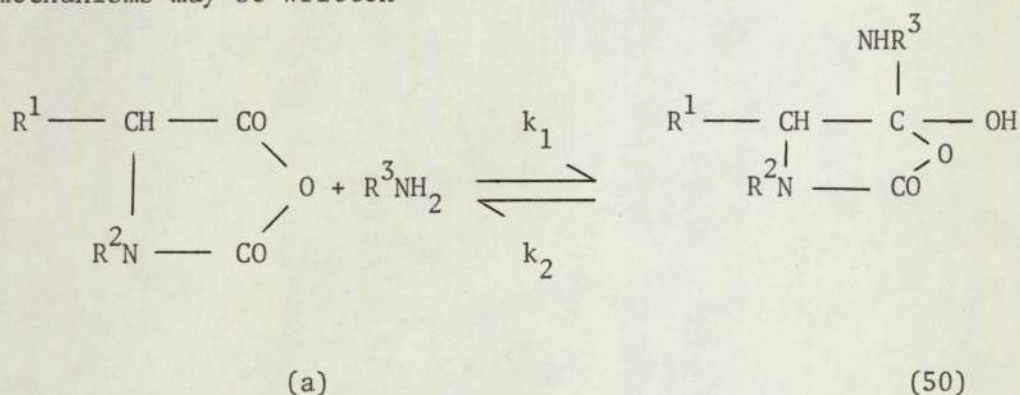
(XXXVI)

It is the reaction of this species with a second monomer unit that is impeded (due to steric hindrance) in the case illustrated.

The benzylamine initiated decomposition of TGAC and TLAC on the other hand follow the mechanism of normal amine initiated decomposition of NCA's very closely although TIBAC behaves differently. Possibly TIBAC forms a monomer-initiator complex in the first place which latter polymerises.

Although we have no evidence to support this point a parallel exists in the NCA series. Ballard and Bamford[15] point out that the mechanisms may be written

$$R^1 - CH - CO \atop \diagdown \atop | \qquad O + R^3NH_2 \atop R^2N - CO \diagup} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R^1 - CH - C \atop | \qquad | \atop R^2N - CO} \overset{NHR^3}{\underset{}{|}} - OH \atop \diagdown O$$

(a)   (50)

$$R^1 - CH - C \atop | \qquad | \atop R^2N - CO} \overset{NHR^3}{\underset{}{|}} - OH \atop \diagdown O \atop \diagup} \overset{k_3}{\longrightarrow} R^1 - CH - CONHR^3 \atop | \atop R^2NH \qquad + CO_2$$

(b)

(XXXVII)

Although 50(a) is usually rate controlling and no equilibrium is seen to exist this is not always the case. Sarcosine NCA(R^1=H, $R^2 = CH_3$) behaves abnormally in that the equilibrium leading to complex formation 50(a) is rapidly established and 50(b) is rate determining.

On the other hand when $R^1 = CH_3$ and $R^2 = H$ and $R^1 = R^2 = CH_3$ normal behaviour is observed. There is, apparently, no obvious fundamental reason for this peculiarity.

In the same way there is no valid reason for expecting TIBAC to take part in an abnormal reaction in which equilibrium formation of benzylamine-TIBAC complex is rapidly established. Such behaviour would however explain the observations.

The benzyl alcohol initiated decomposition of TGAC (Chapter V) shows that the rate of chain propagation is much higher than the rate of hydroxyl initiation. The problems of incomplete incorporation of initiator resulting from this behaviour is not found with benzyl-amine. Propagation rate constants obtained in this way with TGAC are higher than corresponding anhydrosulphites and anhydrocarboxylates of α-hydroxy acids as shown in Table 5.3. This acid derivative after initial attack produces CH_2- SH group which is a strong nucleophile and can attack the next ring quite easily. The hydroxyacid derivatives after initial attack produces -OH group which is a weak nucleophile. Hence the rate is faster for α-thio anhydrocarboxylates. Thus the apparently abnormal behaviour in benzyl alcohol is seen as a natural consequence of the greater effectiveness in these reactions of the thiol group as compared with the hydroxyl group.

One final peculiarity remains. The thermal decomposition of TIBAC produces both polymer and tetra methyl thio-glycollide. TGAC and TLAC were unfortunately too stable for thermal studies but did form thio-glycollide on prolonged storage.

Only two cases of[50] [99] glycollide formation are known in the hydroxy acid series - normally no trace can be detected. The two cases both involve considerable straining of the valence angles at $C_{(5)}$. Normally $C_{(5)}$ substituents

(XXXVIII)   (XXXIX)
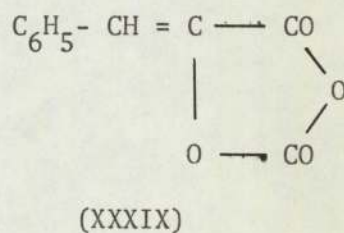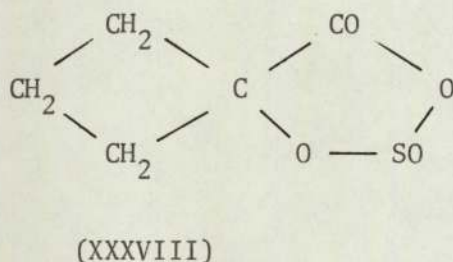
attempt to occupy maximum free volume and transmit a compressive strain to the ring but in these cases the effect is exactly opposite since the external bond angles are compressed. In the case of XXXVIII it is said[101] that the parent α-hydroxy acid has the bond angles that are ideally suited to glycollide formation. Isolation and storage of the free acid is therefore difficult. It is obvious that the different size of sulphur compared to oxygen has a similar effect in facilitating thioglycollide formation. The marked effect of sulphur in this series is confirmed by two observations. Firstly there is the marked difference in the rates of decomposition of TIBAC and the corresponding α-hydroxy acid anhydrocarboxylate (DMAC). Secondly there is the fact that thio-glycollide formation could be observed in the mass spectra of thio anhydrocarboxylate. This phenomena does not occur with α-hydroxy acid derivatives.

Turning now in conclusion to Table 8.1 the effects referred to above can be seen quite clearly. The effect of the size of sulphur

for example should be observed at both X and Y.   This is borne out in
practice
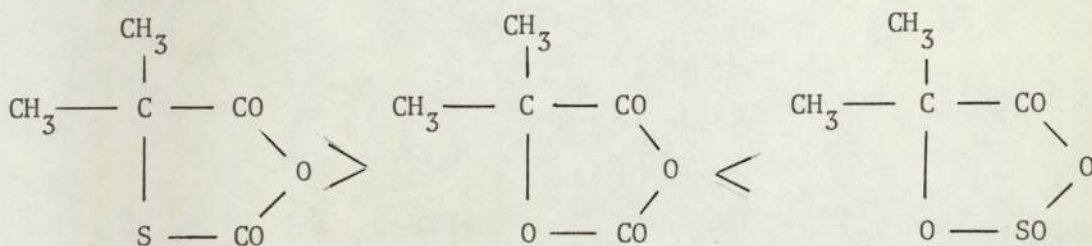
$t\frac{1}{2}$ = **23.3** hours

(90°CØNO$_2$)

$t\frac{1}{2}$ = 1000 hours

(90°CØNO$_2$)

$t\frac{1}{2}$ = 3.5 hours

(90°CØNO$_2$)

Although electronic effects will contribute steric effects are
predominant   here.

On the other hand in nucleophilic propagation reactions of X
(Table 8.1) electronic effects must be predominant.   These points
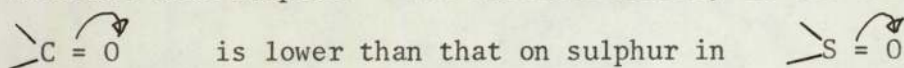have been discussed in Chapter V.

The activity of the $C_{(4)}$ carbonyl is known to be markedly
affected by R^1 and R^2 (Table 8.1) but in addition X and Y have some
effect.   Thus the reactivity of the various unsubstituted rings to
benzyl alcohol may be placed in the following order.
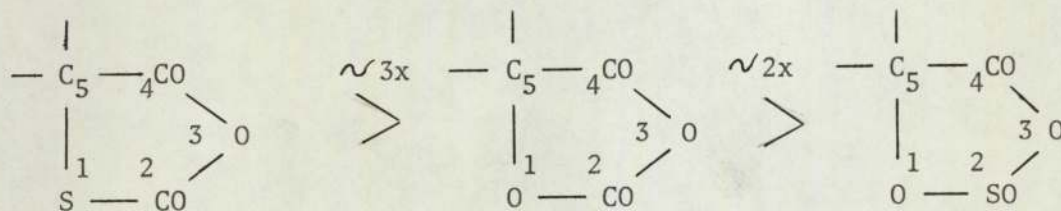
At first sight this may appear difficult to explain but two points
must be borne in mind. Firstly the ring must be regarded as a closed
electronic system. Secondly, the electronegavitity of an atom will
affect $C_{(4)}$ quite differently when that atom is within the ring as
distinct from substituted on a ring atom. Thus a polar or electro-
negative substituent at $C_{(5)}$ will activate the $C_{(4)}$ carbonyl by
withdrawing electrons from the ring. The more polar atom within the
ring will however tend to de-activate $C_{(4)}$ by increasing the available
electron density of the ring.

On this basis the more metallic atoms (in terms of periodic
table nomenclature) will reduce the overall electron density within
the ring and thus activate $C_{(4)}$ to nucleophilic attack. Since sulphur
is more metallic than oxygen the ring with sulphur at positionS(1) has
a more active $C_{(4)}$ carbonyl than the ring with oxygen at position O(1).

In the case of these latter (oxygen containing) rings carbon is
more metallic than sulphur. The electron density on the carbon in
$\underset{\diagdown}{\diagup}C = O$ is lower than that on sulphur in $\underset{\diagdown}{\diagup}S = O$
hence the carbonyl containing ring is more active.

This same argument can be applied to electronic effects of X
and Y on ring stability (Table 8.1). This point was mentioned in a
previous paragraph. It has been established that decreasing the
overall electron density within a ring increases the thermal stability.
Although the major effects of X and Y in effecting thermal stability
will result from the relationship between size and ring strain, there

will be a secondary electronic effect. This will be small in
comparison but will lie in the opposite direction to the electronic
effects on $C_{(4)}$ activity discussed above. Thus the electronic
effect of oxygen within the ring will be to reduce the thermal
stability in comparison to sulphur. It must be emphasised again
however that the greater size of sulphur will swamp this effect.

8.2 Suggestions for further work

Although the objectives of this project have been largely
achieved, one area of the investigation has proved to be dis-
a-pointing. This is the study of the relationship between the
various polymerisation parameters and the molecular weight of the
resultant polymer. Reliance was placed on the G.P.C. technique
and several experiments (including the effect of reaction time
on conversion and product on thermal decomposition presented in
Chapter 6) were designed to give molecular weight information.
In the event of only one of the PSCC services (orthodichlorobenzene
at 130°C) was able to handle the higher molecular weight products
and these were the greatest interest. Unfortunately over-heating
at the dissolution stage caused the degradation of several samples
and this coupled with other local difficulties meant that reliable
information could not be obtained in many cases.

It was felt that in the present project more importance should
be placed on completing the kinetic investigation with purified
monomers. It would now be appropriate however to carry out a short
investigation to confirm the general observations on factors
controlling molecular weight. The easiest way to do this would be to

use g.p.c. but to supervise carefully the dissolution and general handling of samples.

An additional field of interest is that of co-polymerisation of the α-thio acid anhydrocarboxylates and α-hydroxy acid anhydrocarboxylates. This would be a useful and interesting way of obtaining more information about the relative activity of the chain growth species (e.g. α-lactone and α-thio lactone). In addition the co-polymers produced would be of interest in their own right.

The whole field of poly α-thioester characterisation could now be extended. In particular X-ray studies on the crystal structures of the fibres coupled with comparative crystallisation data would be worth pursuing. Similarly the thermal degradation mechanism of the polymers and co-polymers could be studied quite readily using established techniques. In this way, further information on the comparative behaviour of sulphur and oxygen could be obtained.

The synthesis of α-thio acid anhydrosulphites and their polymerisation which have not been properly dealt with would be an interesting field to explore. Preliminary studies indicate that they readily form polymers with initiators such as pyridine and benzylamine etc. Their thermal decomposition would also merit examination. Preliminary observation supports the prediction (Made on the basis of Chapter 3) that two sulphur atoms in the

ring would produce relatively low thermal stability. The thermal polymerisation of the α-thio acid anhydrosulphites would thus give an alternative route for the synthesis of poly α-thio glycollic and α-thio lactic acids which was not possible for the thermally stable α-thio acid anhydrocarboxylates (TGAC and TLAC).

It has been observed that α-thio acid anhydrocarboxylates (mainly TIBAC) decompose to corresponding tetra methyl thioglycollide when stored under vacuum even at low temperatures. The polythio-isobutyric ester prepared so far either by initiation or by thermal decomposition of the monomer are contaminated by this compound. The best method of polymerisation may be to first convert the TIBAC to the corresponding thioglycollide and subsequently polymerise the thioglycollide. The polymerisation of tetramethyl thioglycollide (TMTG) in ether, nitrobenzene appears to be easily carried out by a variety of nucleophiles (e.g. benzylamine, hexylamine etc.) which in itself would make an interesting investigation.

Although it is unlikely that poly α-thio esters will find large scale commercial application recent trends in speciality polymers illustrate the possible uses for materials of this type. In particular certain biomedical applications require highly specific combinations of permeability, permselectivity and surface properties. Cyclic esters are already showing some potential as monomers for grafting onto backbones containing nucleophiles (e.g. OH or NH_2). In this way they modify the properties of the parent polymer by, for example, altering permeability or providing
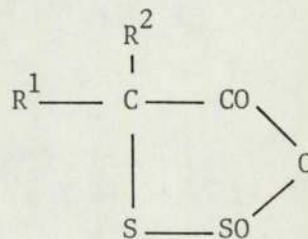
binding sites. Since sulphur plays an important part in some biological systems, it is possible that the ability to incorporate sulphur by grafting techniques may achieve significance in the future.

8.3 Nomenclature

The work presented in this thesis involves the synthesis of the compounds of type (i) and (ii) and their polymerisation
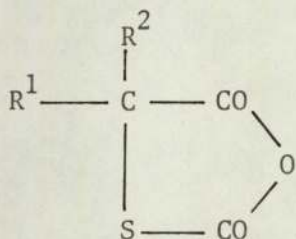
where ($R^1 = R^2 = H$) for thioglycollic, ($R^1 = H$, $R^2 = CH_3$) thiolactic and ($R^1 = R^2 = CH_3$) thioisobutyric anhydrocarboxylates (i) and anhydrosulphites (ii). The parent α-thio acids being used as a prefix to identify individual members and abbreviated as TGAC, TLAC and TIBAC for (i) and TGAS and TLAS for (ii). Although it is possible to name these compounds systematically using IUPAC nomenclature these names have not been used in this thesis. This is simply because they are cumbersome and have not yet been used in the literature, they are

   (i) 1,3 oxathiolan - 2,5-dione
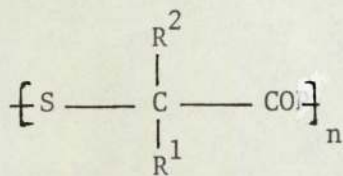
      (i.e. TLAC will be 5 methyl-1,3-oxathiolan-2,5-dione)

   (ii) 3,1,2 oxadithiolan-4-one-2-oxide

      (i.e. TLAS will be

         5 methyl-3,1,2-oxadithiolan-4-one-2-oxide)

It is common practice to refer to poly α esters in terms of the systematic chemical names of the repeat unit.

$$\left[S - \underset{\underset{R^1}{|}}{\overset{\overset{R^2}{|}}{C}} - CO \right]_n$$

(iii)

Simple poly α-esters are known for sometime and often identified in terms of the monomer or derivative acid e.g. glycollide or poly-glycollic acid ($R^1 = R^2 = H$).

So the polymers prepared from TGAC, TLAC and TIBAC are designated as polythioglycollic acid, polythio-lactic acid and polythioisobutyric acid.

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