RING OPENING REACTIONS OF SOME DIALKYL SUBSTITUTED

1,3,2-DIOXATHIOLAN-4-ONE-2-OXIDES

by

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SUMMARY

The synthesis and polymerisation under various conditions of a series of 1,3,2-dioxathiolan-4-one-2-oxides (∝-hydroxy carboxylic acid anhydrosulphites) derived from disubstituted ∝-hydroxy alkanoic acids has been studied.

In thermal decomposition reactions the length of the n-alkyl group in methyl, n-alkyl substituted compounds of this type was found to primarily affect the rate rather than the mechanism of the reaction. The first-order rate determining ring scission process, leading to the formation of a reactive ∝-lactone intermediate which then undergoes spontaneous polymerisation, is the predominant mechanism even with substituents up to C_8. As the length of the n-alkyl substituent is increased the rate of decomposition and thus polymerisation increases until a plateau value is reached at around C_3. Further increase in substituent length decreases the rate of decomposition, an effect which is attributed to steric hindrance of the leaving group by long (C_6 - C_8) substituents.

The 5,5-dibutyl derivative of the closely related anhydrocarboxylate ring system (1,3-dioxolan-2,4-diones) has been synthesised and its decomposition briefly studied. In the temperature range required for a reasonable rate of decomposition a competitive non-polymer forming reaction is found to be significant.

Of the various initiating systems studied, lithium t-butoxide was found to be particularly successful in inducing the decomposition of anhydrosulphites. A kinetic analysis indicated that, in its early stages, the reaction is first order with respect to monomer and initiator. In the latter stages the reaction becomes slow, possibly due to the onset of heterogeneity and a diffusion controlled situation. Molecular weight studies indicate that the polymer produced by this route has a lower molecular weight and broader molecular weight distribution than that obtained by thermal methods.

Various possible mechanisms for initiated anhydrosulphite decomposition are discussed, and a plausible reaction scheme is suggested.

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LOCATION OF FIGURES

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CHAPTER 1

1.1 INTRODUCTION

Ring-opening reactions as a route to the preparation of higher molecular weight compounds has been known since the middle of the nineteenth century when, in particular, the ring-opening of ethylene oxide by Wurtz[1] and of glycolide the dimer of glycollic acid, by Bischoff and Walden[2] were described. More recently, the production of commercially important plastics such as Nylon 6 and Polyformaldehyde using ring opening methods has resulted in a wider appreciation of this route as a complement to more completely documented addition and condensation methods of high polymer synthesis. In the last decade studies in the field of ring opening polymerisation have expanded greatly but only recently has a comprehensive review of this field been published[3].

The polymerisation reactions of cyclic compounds such as formals, lactones, lactams, epoxides and the N-carboxy anhydrides of α-amino acids (N.C.A.s) have been the subject of many detailed investigations[4,5], but even in systems which have been extensively studied,for example the N.C.A.s, our understanding and knowledge of the many possible polymerisation mechanisms is far from complete. Studies in the mechanisms of polymerisation of the commercially important cyclic monomers have received a significantly greater amount of attention than the other systems for obvious reasons. Of particular note are the polymerisations of epoxides and lactams, the polymers produced from these cyclic monomers being important in the coatings and fibres industries respectively.

Various workers studying the polymerisability of cyclic compounds have noted the effect of ring substituents on the ease of polymerisation of cyclic monomers. In the case of the 1,4-epoxides for example, the unsubstituted ring has been shown to polymerise (albeit with a significant amount of depolymerisation and a resultant ring-chain equilibrium) whereas the successful polymerisation of the substituted ring has not yet been achieved. In contrast to this, the associated four membered ring, the 1,3-epoxide polymerises readily and a large variety of substituents on the ring can be tolerated without adverse effect on the polymerisability of the system[6,7]. The comparative ease of polymerisation of the 1,3 epoxides compared with the 1,4 epoxides is attributable to strain in the ring caused by deviations from ideal bond angles and perhaps repulsion between adjacent hydrogen atoms. This is reflected in the much lower heat of polymerisation of the 1,4 epoxides compared with the 1,3 expoxide series.

The ring opening polymerisation reaction which has achieved the greatest commercial importance is probably the production of nylon 6 from caprolactam. Lactam polymerisation, which may be carried out either by a hydrolytic[8] or by a non-hydrolytic[9] process also demonstrates well the adverse effect of substitution on the ring on the ease of polymerisation. In the water - initiated polymerisation of hexanolactams, the 2-methyl substituted ring will polymerise wherease the 1-methyl substituted or 1-phenyl substituted rings are not regarded as polymerisable in this system. General ring size - polymerisability considerations in lactams show that while most lactams are polymerisable, especially when unsubstituted, the relatively strain free six membered ring is not polymerisable.[8]

The significant factor in most commercially viable ring opening polymerisations is the existence of a ring-chain equilibrium between monomer andpolymer, especially at high conversion. This is of particular importance in the hydrolytic polymerisation of caprolactam to yield Nylon 6. In this process, the ring opening reaction requires the presence of water which must be stripped off again at a later stage in the process. Even so, the ring-chain equilibrium results in the occurrenceof some 10% monomer in the product and this must be removed before the nylon is processed.

The ring opening polymerisation of N.C.A.s, however, is an example of a rather different type of reaction which has, in order to attempt a distinction between it and other ring opening reactions, been called an extrusion polymerisation[10]. Reactions of this type are typified by the loss of a small molecule from each ring at some stage in the polymerisation. In the case of the N.C.A.s the small molecule is carbon dioxide which is evolved as gas and hence removed from the reaction medium. This contrasts with the majority of condensation polymerisations in which a small molecule is also eliminated but where that small molecule is derived from both reactants, for example the water in a conventional dicarboxylic acid - diol polyester polymerisation. Extrusion-type ring opening polymerisations therefore are not generally reversible and a ring-chain equilibrium is not possible.

In recent years, extrusion polymerisations have received a considerable amount of attention. Several comprehensive reviews on the decomposition and polymerisation of the N.C.A.s have been published, and work still continues into methods of their polymerisation, particularly since they may be used as simple building blocks for peptides and polypeptides[11,12]. A series of papers[13-20] has recently appeared on the decomposition of a ring system which is closely related to the N.C.A., the anhydrosulphites of α-hydroxy carboxylic acids. The structure of these compounds which are systematically named as 1, 3, 2-dioxathiolan-4-one-2-oxides is shown diagramatically in Figure Ia. The N.C.A. structure is shown in Figure Ib for comparison. The N.C.A. is prepared by the action of phosgene on the appropriate α-amino acid while the anhydrosulphite is synthesised by the action of thionyl chloride on an α-hydroxy acid. In similar reactions phosgene may be reacted with α-hydroxy acids or α-thio acids to yield compounds Ic[21] and Id[21,22]. Action of thiophosgene on α-hydroxy acids and α-thio acids yields If[23] and Ie[22]. These compounds are known as:-

Ic 1,3-dioxolan-2,4-dione (the anydrocarboxylates of α-hydroxy acids)

Id 1,3-thioxolan-2,4-dione

Ie 2-thioxo-1,3-oxathiolan-5-one

If 2-thioxo-1,3-dioxolan-4-one

Compounds Ia, Ic, If have all been shown to decompose with loss of a small molecule to yield poly α-ester. Id and Ie yield poly α-thioester, Ib yields a poly peptide.

In addition to these compounds the closely related structures Ig[24,25], Ih[35] and Ij[26, 27,28] have also been prepared and yield peptides by extrusion reactions:-

Ig 2,5-thiazolidine-1,3-dione (NTA)

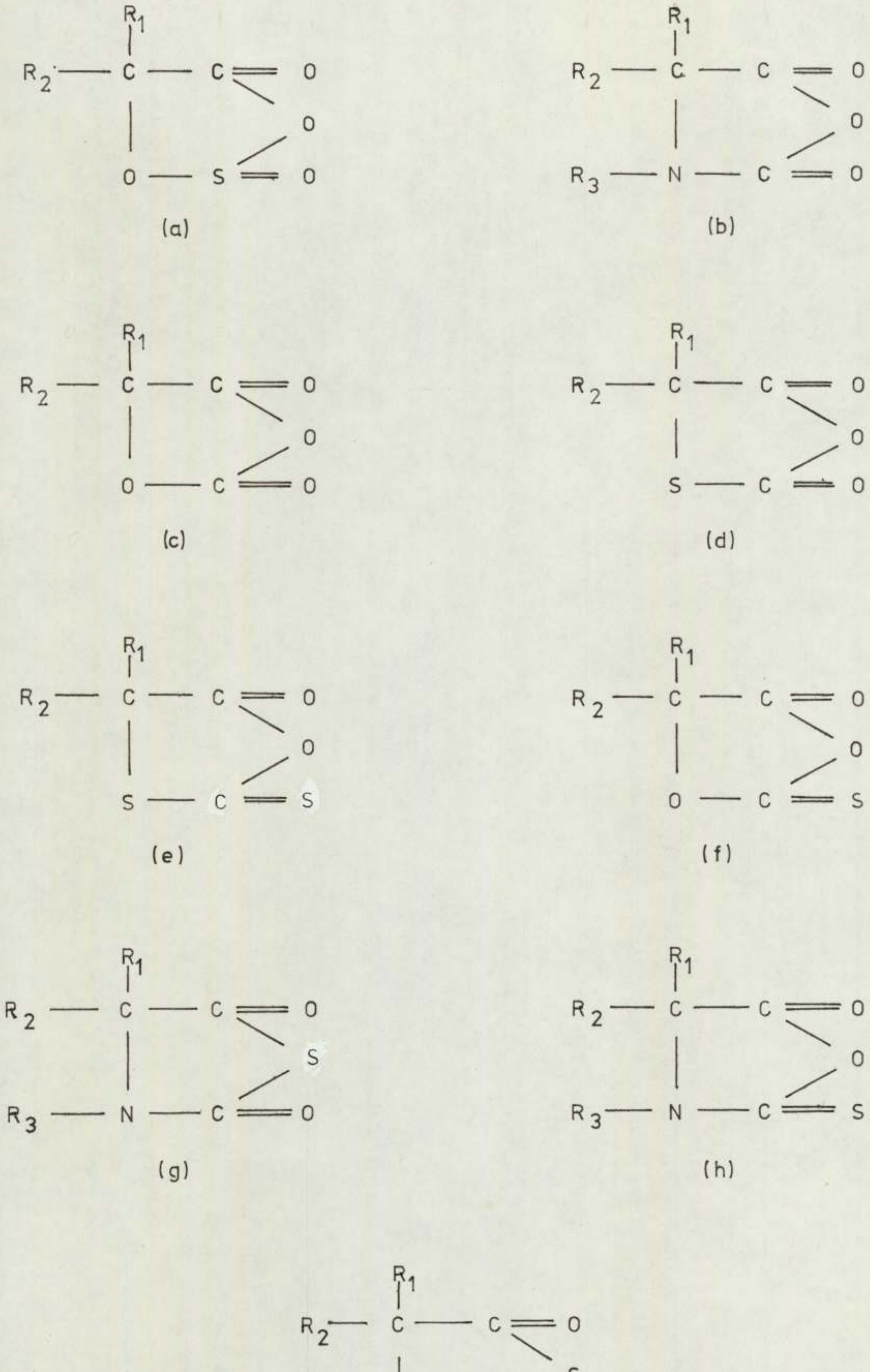
Ih 2-thioxo-5-oxazolidone

Ij 2-thiono-5-thiozolidinone

Only in the case of structures Ia, Ib and Ic has much attention been given to their modes of decomposition, and of these the anhydrosulphites of α-hydroxy acids are of particular interest since they are precursors to high molecular weight poly α-ester.

The poly α-esters are a class of compounds for which no other general method of preparation has yet been discovered. They have been variously prepared by self-condensation of α-hydroxy carboxylic acids using an esterification catalyst, for example orthophosphoric acid[29], by the thermal polymerisation of the silver salts of α-chloro acids, poly(benzilic acid) has been prepared in this way[30] and other polymerisations have been investigated using this method[31]. By decomposition of glycollide in the presence of catalysts, but this route is limited to the unsubstituted poly α-ester, i.e. polyglycollide, or to derivatives having relatively little substitution. Although glycollide itself has been polymerised and is marketed on a commercial basis[41], and 1,4 dimethylglycollide (lactide, the dimer of lactic acid) has also been shown to be polymerisable, 1,1,4,4 -tetramethyl glycollide (the dimer of α-hydroxy isobutyric acid) was considered until

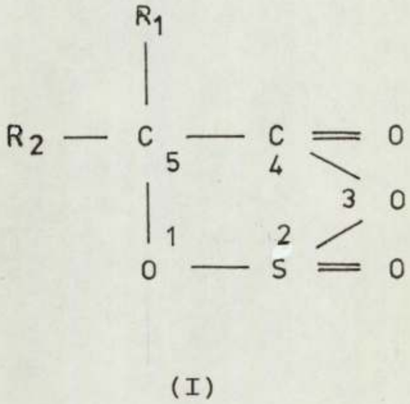
FIGURE I



(a) (b) (c) (d) (e) (f) (g) (h) (j)

recently to be too stable to polymerise[32]. This was another example of the effect of increasing substitution on the polymerisability of cyclic monomers. Recently, however, tetramethyl glycolide has been polymerised thermally in the presence of lithium tert.-butoxide as catalyst[33] to yield high molecular weight poly(isoprop ylidene carboxylate).

A more general route to the poly ∝-esters is the thermal extrusion polymerisation of anhydrosulphites. Alderson investigated this method but failed to produce high molecular weight polymer from any except the ∝-hydroxy isobutyric acid derivative[38]. Rose and Warren[39] extended this work to other members of this class of compounds and also discovered that their decomposition was catalysed by amines,but high molecular weight material was not obtained. Ballard and Tighe[13] later showed that molecular weights in the region of 100,000 are possible using this route provided that rigorous precautions are taken to exclude moisture and to remove chloride containing impurities. Blackbourn and Tighe[20] extended this route to include other dialkyl substituted anhydrosulphites, and some spiro-alkyl substituted anhydrosulphites[19] where both substituents at the C-5 carbon (I) are linked in a methylene chain.



(I)

The mechanism of the thermal decomposition of anhydrosulphites has been studied and shown to take place by two routes. Firstly, a bimolecular attack of nucleophilic species, for example hydroxyl or amine on the C-4 carbonyl of the anhydrosulphite ring with resulting ring cleavage and elimination of sulphur dioxide. A nucleophilic species is regenerated as a terminal hydroxyl group on the growing polymer chain. This process is similar to the amine initiated decomposition of N.C.A.s. Secondly, a unimolecular ring decomposition has been proposed with the subsequent formation of a highly reactive intermediate which can then react rapidly with any available nucleophile. The intermediate proposed is an α-lactone, a species which has recently been isolated[40] and the decomposition of which has been shown to yield the same type of products as those produced by anhydrosulphite decomposition[42-44]. This second mode of decomposition is preferred where steric hindrance to attack at the C-4 carbonyl of the anhydrosulphite is likely to be significant because of bulky groups in the C-5 position.

The anhydrosulphite series is particularly interesting since in contrast to most ring compounds, it becomes more susceptible to decomposition as substitution on the ring increases. This is reflected in an increase in the rate constant for the unimolecular decomposition as the length of n-alkyl substituents at the C-5 position is increased. This kind of behaviour is shown in few other systems, one notable example being the decrease in ring stability of α-substituted butadiene sulphones under hydrolysis, although as compared with unsubstituted sulphones β-substitution tends to stabilise the ring[45]. In contrast to this a ring system which is in some ways similar to the anhydrosulphites, the 2-thioxo-5-oxazolidone shows the usual behaviour associated with substituted ring systems. In this case the unsubstituted or methyl substituted ring is unstable at -20°C while the butyl derivative is rather more stable at this temperature[35].

The decreased thermal stability of highly substituted anhydrosulphites would result in a facile route to highly substituted polyα-esters were it not for a competitive non polymer forming fragmentation reaction which becomes favoured with bulky or electron withdrawing substituents at the C-5 position. This competitive reaction is favoured at higher temperatures for example during the thermal decomposition of bischloromethyl[46] and di n-butyl substituted anhydrosulphites[18]. This leads to difficulties in obtaining pure samples of monomer since the purification procedures tend to result in decomposition of these anhydrosulphites to non-polymeric products. The effectiveness of thermal decomposition of anhydrosulphites as a route to poly α-esters is thus reduced beyond n-propyl substituents in the di n-alkyl series or when the substituents are inductively electron withdrawing.

One of the ring systems most closely related to the anhydrosulphites, the anhydrocarboxylates of α-hydroxy acids (Figure Ic) would appear not to display the desirable characteristic of decreasing stability with increasing ring substitution, since although glycollic acid anhydrocarboxylate (Figure Ic $R_1 = R_2 = H$) will decompose to give polymer at 100°C in eighteen hours[36], the related dimethyl substituted anhydrocarboxylate (Figure $I_c R_1 = R_2 = CH_3$) requires several weeks at this temperature in order to yield a significant amount of polymer[37]. It would also appear that in this case also the presence of increasingly large substituents favours an alternative mode of decomposition, but one which results in a more complex fragmentation of the ring to yield ketone, carbon monoxide and carbon dioxide rather than high molecular weight polymer. The same effect is noted when a higher temperature of decomposition is utilised in order to reduce the lengthy reaction times associated with these monomers.

A more desirable route to polyα-esters having bulky substituents at the single backbone carbon involves the use of an initiated anhydrocarboxylate decomposition. Tighe and Smith, have reported the use of various pyridines as effective initiators in the production of high molecular weight polymer (DP = 100) from the anhydrocarboxylates of mandelic, atrolactic and pentafluorophenyl atrolactic acid[47]. These polymerisations were carried out at room temperature in solution.

Attempts to polymerise the anhydrosulphites of α-hydroxy acids at room temperature using initiators, have met with varying degrees of success, the amine initiated decomposition of anhydrosulphites at room temperature results in only low molecular weight polymer, since the effectiveness of the strongly nucleophilic amine group is lost after the addition of the first monomer unit and replaced by the less nucleophilic hydroxyl group.[68] The polymerisation of methyl chloromethyl substituted anhydrosulphite using an optically active initiator, brucine, is reported to give an optically active polyester[48]. Although few details of the properties of the polymer produced are given. The initiated decomposition of anhydrosulphites using such initiators as sodium methoxide, D.M.F., DMSO, Butyl Lithium, Zinc Chloride/Water has been reported to give polymers. Again little detail is given and no information on molecular weight or molecular weight distribution is provided, the only criterion for polymers being that fraction of product which is insoluble in methanol[49].

Other initiator systems such as organometallic compounds of Magnesium, Zinc and Aluminium etc. were reported to be unsuccessful in polymerising anhydrosulphites[49], although the selection of monomer seemed to be important. For example the chloromethyl substituted anhydrosulphite was polymerised more successfully than the dimethyl substituted ring.

The most successful initiating system appeared to be sodium methoxide in chloroform, this is perhaps not surprising in view of the effectiveness of alkoxides in polymerising many other ring systems. Most notable cases are the polymerisation of lactones by alkoxides[50] wherein there is an acyl oxygen cleavage in the ring resulting from the attack of a nucelophile. However, these polymerisations are very slow at room temperature, and generally temperatures of about 100°C or more are required for reasonable rates of reaction.

The polymerisation of other cyclic monomers with alkoxides has been more extensively studied. 1,2-Epoxides for example polymerise with alkoxides, principally sodium methoxide or phenoxide, at temperatures between 60 and 90°C, the mechanism may be rather more complex than a simple anionic attack of the alkoxide on the ring and in the presence of an alcohol a termolecular transition state is thought to exist.[51] Enhanced rate of decomposition was found with more basic initiators.

The general order being:-

$$tBuOK > tBuONa > KOH > RONa > CH_3ONa > NaOH$$

The polymerisation of 1,2 - epoxides with transition metal alkoxides[52], for example $Zn(OR)_2$, has also been studied and found to depend to a large extent on the crystalline form of the zinc alkoxide; which in turn is dependant on the method of preparation of the alkoxide. In general an amorphous composition is necessary for high polymer to be produced. This catalytic action has been interpreted as a co-ordinate anionic mechanism, and therefore the catalyst in these cases acts primarily as a co-ordination site rather than an initiator in the true anionic mechanism such as is found in the sodium alkoxide initiated polymerisation of 1,2-epoxides.

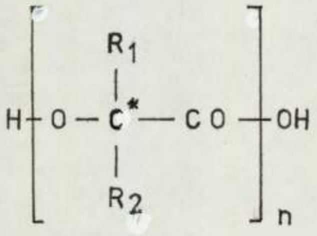
The initiating system most closely allied to the alkoxide initiation of anhydrosulphites is that involving the action of alkoxides on N.C.A.s the mechanism of this decomposition has been well studied[63] and shown to proceed by the attack of the alkoxide on the 5-carbonyl of the N.C.A. ring followed by decarboxylation. This is characterised by an induction period where the reaction is slow, followed by a faster first order reaction. The first order rate constant is about one hundred times faster than the normal primary amine initiated decomposition of N.C.A.s. Very high molecular weights are obtained. An alternative to the attack of alkoxide on the 5-carbonyl is attack at the 2-carbonyl, this has been postulated as a 'termination' reaction but since this kind of wrong addition does not actually destroy the acylate ion which is seen as the propagating species, it cannot be seen as a true termination reaction. Addition via the 2-carbonyl of the N.C.A. ring results only in the introduction of an anhydride linkage in the chain and a carbamate ion as the propogating species for the next addition of N.C.A. Although propogation by addition at the 2-carbonyl with perhaps occasional 'wrong addition' at the 5-carbonyl is a possibility, this is considered unlikely since the 2-carbonyl position is very much less readily attacked than the 5-carbonyl.

Other mechanisms proposed for the 'strong base' polymerisation of N.C.A. include the propogation by means of a terminal amide ion which is the highly reactive species[63]. In this case the polymerisation proceeds by attack of methoxide ions at the C-5 position with generation of terminal amide ion by loss of carbon dioxide from the compound formed. However, other work has demonstrated that this amide ion is unlikely to be present and this mechanism is, therefore, in doubt[64,65].

Other possibilities include the abstraction of a proton from the N.C.A. to yield an "activated monomer". The proton could be removed from the ring Nitrogen where the N-substituted N.C.A.s were not used, or, more improbably, from the α-carbon [64,66]. Alternatively, another activated monomer species is produced by the direct attack of a strong base on the C-5 position to yield a tetrahedral complex in the manner which has been suggested for the tertiary amine initiation of N.C.A.[67]. This is then the initiating species.

The probability of obtaining a very much more highly ordered polymer is considerably increased when a monomer is polymerised at a relatively low temperature. For example styrene is polymerised at temperatures of above 100°C right down to room temperature using various catalysts to yield an atactic product. Whereas polymerisation at -30°C using Zeigler-Natta catalysts yields an isotactic polymer[54]. In this particular case the amorphous atactic product has more desirable properties than the crystalline isotactic product, the former is therefore commercially more important.

The physical properties of a polymer are governed by chain linearity, chain regularity and polarity, and by molecular symmetry especially in relation to side groups. The structure of the poly α-esters produced by anhydrosulphite decomposition is shown below (II).



$$H\left[O-\underset{R_2}{\overset{R_1}{C^*}}-CO\right]_n OH$$

II

Since these polymers contain only one carbon atom between functional groups, the possibility of any side chain propogation is very much reduced and it is in fact very difficult to envisage any side chain initiation mechanism which might take place within the context of the established mechanism of polymerisation of anhydrosulphites. Poly α-ester chains are, therefore, unlikely to have any significant degree of branching.

The regular arrangement of ester linkages must also contribute to a high degree of interchain cohesion. It is notable that the ester linkage in poly α-esters is always aligned in the same direction as opposed to the alternate direction of those polyesters produced by dicarboxylic acid/diol condensation, for example poly(ethylene terephthalate). Ester linkages have sufficient polarity to cause a significant degree of interchain cohesion in polymers as is evidenced by the crystallinity of poly(ethylene terephthalate).

Because poly α-ester backbones have substituents only at each third atomic centre, symmetrical disubstitution lead to a compact molecule, provided that the substituent groups are not exceptionally long or bulky. This leads to a very favourable disposition for high interchain cohesion and hence high crystallinity.The symmetrically disubstituted poly α-esters have been shown to exhibit a high degree of crystallinity and have high melting points[18]. They also exhibit banded spherulites[20] on crystallization from the melt and this has been attributed to the formation of a helical structure which is accepted as an energetically favourable way of accommodating side groups in a backbone of this nature (c.f. the poly peptides).

The use of asymmetrically substituted anhydrosulphites which will have two optically active isomers, leads to a polymer having asymmetric centres in the backbone (C^* in structure II) and since in this case R_1 is not the same as R_2 a considerable degree of disorder can be introduced to the chain. This disorder would be at a maximum when both d- and l- forms of the monomer are incorporated at random into the chain, as is evidenced by the lack of crystallinity of the poly α-ester where $R_1 = CH_3$, $R_2 = C_2H_5$ (II). The use of an optically active anhydrocarboxylate monomer and a catalyst which does not racemize the monomer during polymerisation has been shown to produce an optically active poly α-ester which has a melting point some 15 - 20°C higher than the random polymer[55]. This is still not an ideal situation since groups R_1, R_2 are rotated on alternate substituted centres in the backbone, giving a syndiotactic type of polymer. In order to obtain an isotactic polymer, the alternate addition of d- and l- residues would presumably be required.

An alternative method of producing an optically active polymer has been used by Inoue and co-workers in which an asymmetric-selective polymerisation of dl-β-chloro-α-hydroxy-α-methyl proprionic acid anhydrosulphite (Figure II; $R_1 = CH_3$, $R_2 = CH_2Cl$) with anhydrous brucine[49] appears to give (-) polymer in the early stages and (+) polymer in the latter stages of a solution polymerisation. Although no details of polymer properties are given it may be anticipated that the crystallinity of polymer produced in the early stages of such a reaction would be increased.

It would appear that the crystallinity of symmetrically substituted poly α-esters is high but that this orderliness is easily disrupted by a slight change in size of one of the substituents, probably due to the production of an atactic polymer. This is evidenced by the lack of crystallinity of methyl ethyl substituted anhydrosulphites compared with the symmetrically disubstituted anhydrosulphites. The use of lower temperature catalysed techniques for polymer production from either anhydrosulphites or anhydrocarboxylates can help to restore a significant amount of order. The distinction should, however, be made between the optical activity due to the presence of asymmetric centres in the polymer backbone and that due to the formation of helical structures (right or left handed) in the crystalline solid. It is accepted that the optical activity due to the latter predominates over the former after more than a few turns of the helix[56]. Since regularity of molecular structure appears to be the prime requirement for helix formation, and optical activity and stereo regularity are closely related in the poly α-esters, the optically active polymers should exhibit a large degree of crystallinity and helix formation.

1.2 SCOPE AND OBJECT OF THE PRESENT WORK

The thermal decomposition of anhydrosulphites has been the subject of a number of recent papers. The mechanisms proposed by Ballard and Tighe for the simple members of the series would appear to fulfill the general requirements for the thermal decomposition of this class of compounds, and other workers have extended this investigation to include the symmetrically disubstituted, spiroalkyl substituted as well as some of the aryl substituted members. The work presented in this thesis investigates the effect of a long alkyl chain attached to the anhydrosulphite ring on the polymerisability of the ring, and hence evaluates the limits of this type of ring opening polymerisation as a route to alkyl substituted poly α-esters.

The importance of monomer purity in obtaining high molecular weight poly α-esters product has previously been established and this fact has been appreciated in this work. The level and type of impurities and their effect on the polymers produced will be carefully monitored.

Having thus established the limits of the thermal decomposition of anhydrosulphites as a route to the n-alkyl substituted poly α-esters, it is the further aim of this project to investigate the susceptibility of these monomers to catalytic activity at ambient temperatures. It is intended to establish the general class of initiators or catalysts to which these compounds are sensitive and to attempt to find a catalyst which might be suitable for further investigation.

Anydrosulphites have been shown to yield polymeric products when brought into contact with compounds which, in other monomer/polymer systems, are known to act as catalysts. However, the mechanisms proposed in these studies are not comprehensive, little attempt has been made to distinguish between high polymer and non-polymeric product, and no evaluation of polymeric properties has been documented. This work will therefore carry out a more detailed study into the effect of one particular catalyst on anhydrosulphites decomposition, and hence attempt to propose a feasible reaction mechanism. In particular the effect of impurities in the monomer will be of interest since it may be possible that the inclusion of these impurities in the chain is energetically unfavourable at the lower temperatures. The nature of the product is also of prime importance if a lower temperature polymerisation is to compete with the established thermal route.

CHAPTER 2

EXPERIMENTAL METHODS

EXPERIMENTAL METHODS

Various instrumental techniques were utilised in order to monitor the synthetic route to the monomers. Solvents and other reagents required a very high degree of purity, particularly in terms of freedom from moisture, certain instrumental methods have proved particularly valuable in this respect. Kinetic measurements were made using various methods providing a reliable cross check on the credibility of the kinetic results.

2.1 INSTRUMENTAL TECHNIQUES

Infra red Spectra - For general purpose work a Perkin-Elmer Infra red grating spectrophotometer Model 237 was used. Where investigation of absorptions down to 200 cm^{-1} were required a Model 225 was adequate. Samples were used either as a KBr disc or in solution using a cell with KBr windows, the solvent used is stated at the appropriate point. The reference cell was air unless otherwise stated.

Nuclear Magnetic Resonance Spectra - Proton resonance spectra were recorded using a Perkin-Elmer R14 spectrometer operating at 100 MHz and a temperature of 33.4°C. Tetramethylsilane was used as internal reference. Duterochloroform was found to be a suitable solvent, details of concentrations are given at the appropriate place.

Mass Spectrometry - The instrument used was an AEI MS9. Conditions for use are given at appropriate points in the text. The recordings of spectra are given at three attenuations thus ensuring accurate analysis.

Ultra violet Spectra - These were measured using a Perkin-Elmer 137 UV Spectrophotometer. Tetrahydrofuran purified as in section 2 was used as a solvent with a reference also of THF.

Gas Liquid Chromatography - a Pye Series 10a Gas Chromatograph was used together with a Kathermeter detector. In general a column containing a silicon gum on a fire brick support was found to provide adequate separation with helium as a carrier gas. Other conditions of use are given at the appropriate point in the text.

Carbon Hydrogen Analysis - These determinations were carried out using a Hewlett and Packard, F and M Scientific 185 Carbon, Hydrogen, Nitrogen Analyser operating at a temperature of 1100°C.

Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) - Measurements utilised a Du Pont Differential Thermal Analyser 900 and a Du Pont Thermogravimetric Analyser. Conditions of use are given in the text.

Chlorine Determinations - Assessment of the quantities of chlorine containing impurities present in the monomers were made by the modification of Ingram's[57] technique which has been shown to determine both alkyl and acyl chlorine[58]. Hence the method effectively determines the predominant impurity which has been shown to be an α-chloro acid chloride. The method is essentially a potentrometric titration for determination of chloride ions. Details of the experimental procedure have been described elsewhere[15]. The instrument used was an EIL Model 23A pH meter equipped with a Silver/ Silver-Silver Chloride electrode system.

<u>X-Ray Photographic Data</u> - This was collected by use of a Phillips 11.46 cm diameter powder camera, fitted with a 0.5mm collimator. The samples placed in a lithium beryllium borate tube were subjected to Copper $K\alpha$ radiation using a nickle filter. Exposure time was one and a half hours.

<u>Dry Box Techniques</u> -

a. <u>Removal of Moisture</u> -

Since both the monomers and many of the initiators used were very moisture sensitive, it was found to be convenient to handle them in an essentially dry atmosphere. A glove box manufactured by Slee Ltd. was used. Atmospheric moisture was removed initially by replacement of the air with dry nitrogen and then circulation of the atmosphere in the box through four glass coils immersed in a solid carbon dioxide/acetone mixture at - 78°C. A pumping rate of 4 $1\ \text{min}^{-1}$ through both the glove chamber and access chamber was found to be suitable. In addition, fresh molecular sieve Type 5A supplied by BDH Ltd. was stored in the dry box when the circulation pump was not in use and a visual check on the moisture content of the box was obtained by the use of evaporating dishes containing fresh phosphorous pentoxide. This last drying agent was also effective in the removal of trace moisture.

b. Measurement of Moisture Content -

The dry box atmosphere was continuously monitored with a Shaw Hygrometer fitted with a Red Spot (Sensitive) Type Element, effective over the range 1 - 500 ppm $\frac{v}{v}$ water. This instrument indicated that approximately 90 hours of continuous circulation of the atmosphere through the cold traps was required to bring the moisture content in the box down to 5 ppm $\frac{v}{v}$. Once achieved, this level of dryness was easily maintained by the above system.

Metal Ion Determinations - The concentration of the metal alkoxide solutions and the presence of metal in polymer were detected by means of an EEL Flame Photometer, using the appropriate filters for the metal concerned. The instrument was effective for determination of metal ions down to 10ppm Na^+ or 1 ppm Li^+.

The procedure for determination of the metal ions in solution was as follows:-

A 0.25 ml portion of the non-aqueous solution under investigation was added to 1 litre of water together with 2 drops of 4N hydrochloric acid to ensure complete hydrolysis of the alkoxide. The aqueous solution was then well shaken to ensure that all Li^+ ions had passed into the aqueous phase. The unknown was then determined against standards made up from known lithium sulphate solutions.

A cross check on the validity of lithium sulphate solutions as standards was made using a second set of standards made up from lithium t-butoxide the two sets of standards were found to give identical results over the range 1 - 500 ppm Li^+. No enhancement of the flame due to the presence of the organic solvents used was found in the range 0 - 2.5% $\frac{v}{v}$ (concentration used in actual determinations 0.025% $\frac{v}{v}$).

Vapour Pressure Osmometry - A Mechrolab Model 301A Vapour Pressure Osmometer was used to obtain Number Average molecular weights below 20,000 for poly esters. Additionally, this instrument was used to assess the degree of association of alkoxides in solution.

The method is an isopiestic one measuring the difference in temperature resulting from different rates of mass transfer to a solvent droplet and a solution droplet, in an atmosphere of solvent. Hence the measured property is the number of particles in solution.

Conditions of use are given in the text at the appropriate point. The instrument was calibrated using recrystallised benzil in the relevant solvent.

Techniques used in Kinetic Measurements - The decomposition of anhydrosulphites and anhydrocarboxylates of α-hydroxy acids results in the evolution of one or more gaseous fragments per ring molecule. Hence the rate of decomposition of this type of compound may be followed manometrically, the quantity of gas released may correspond to the quantity of monomer decomposed therefore, and an expression for the rate of decomposition of monomer can be derived from the rate of appearance of gas. This is shown in a later section.

In addition to measurements involving the gaseous fragments, the carbonyl adsorption frequency in the infra-red spectrum of the monomer and products provides an alternative means of monitoring the rate of disappearance of monomer and appearance of product simultaneously.

The well established technique in polymer work of gravimetry, is a rather more laborious method of rate determination but may be used as a cross check, and under some circumstances also to provide additional information to the above techniques.

Gas Evolution Techniques

1. Apparatus

Three designs of apparatus were used to measure the pressure of evolved gas at constant volume. Although a small volume change does occur with both types, it may be shown by simple calculation to be less than 0.01%, hence errors from this source are negligible. To enable a simple kinetic analysis, the evolved gases must behave as an ideal gas. Over the pressure range used, 0-250mm Hg for sulphur dioxide or carbon dioxide this was nearly true.

a. Low Temperature Apparatus Type I, Figure II

This is a modification of the design used by Ballard and Bamford for N.C.A. studies[59]. The apparatus is in two sections; section A is a mercury manometer, section B is a reaction vessel which may be connected to section A by the conical glass joint C. The construction of the apparatus is such that section B may be 'flamed out' or dried in an oven, then

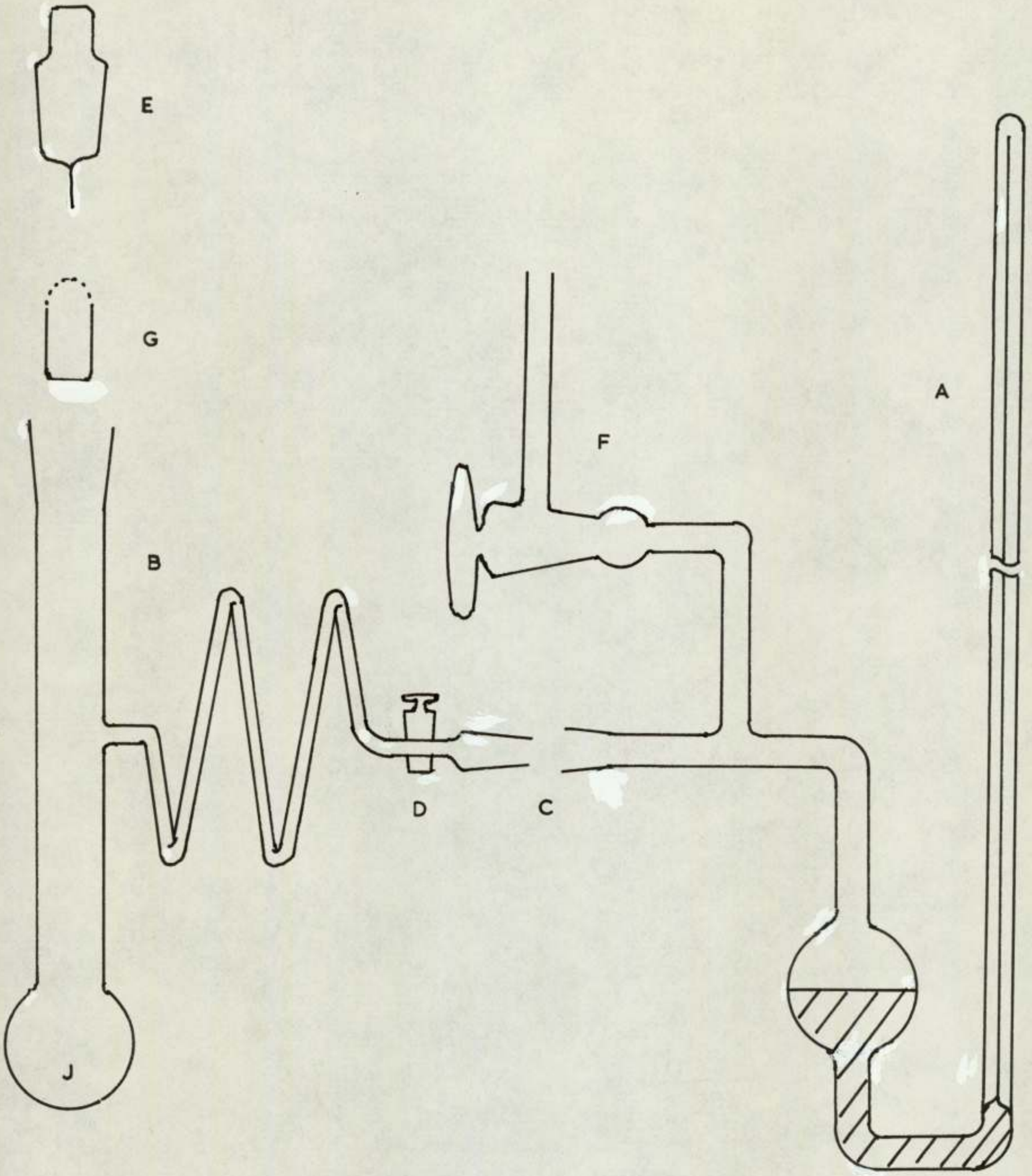


FIGURE II

Low temperature apparatus for gas evolution kinetics - Type I transferred to the dry box with all outlets closed. The reactants could then be introduced in a dry atmosphere before resealing the apparatus by closing tap D and replacing stopper E. Section B was then reconnected to section B, and with tap D still closed section A was evacuated and flamed out to remove all traces of moisture, the coil of section B ensured that the reactants were not affected by this procedure. Tap D was then gently opened to permit evacuation of section B. After sealing the apparatus at tap F, the equipment was ready for use. This type of apparatus was especially useful for following initial rates where two reactants were used, since one of the reactants could be suspended in a bucket G from the stopper E after equilibration in a constant temperature bath, a tap on the stopper E would dislodge the bucket from its host and enable the reactants to mix at the bottom of the apparatus at J.

The low temperature apparatus was only suitable for reactions carried out below 40°C. Above this temperature the grease in the ground glass joints was leached out by the oil of the constant temperature baths, and in consequence leakage occurred.

Manometer rise was followed using a cathetometer or, where reaction was fast, using a glass mirror scale attached to the back of the capilliary.

b. Low Temperature Apparatus - Type II. Figure III

The low temperature apparatus Type I suffered from several limitations. These were, primarily, that the use of

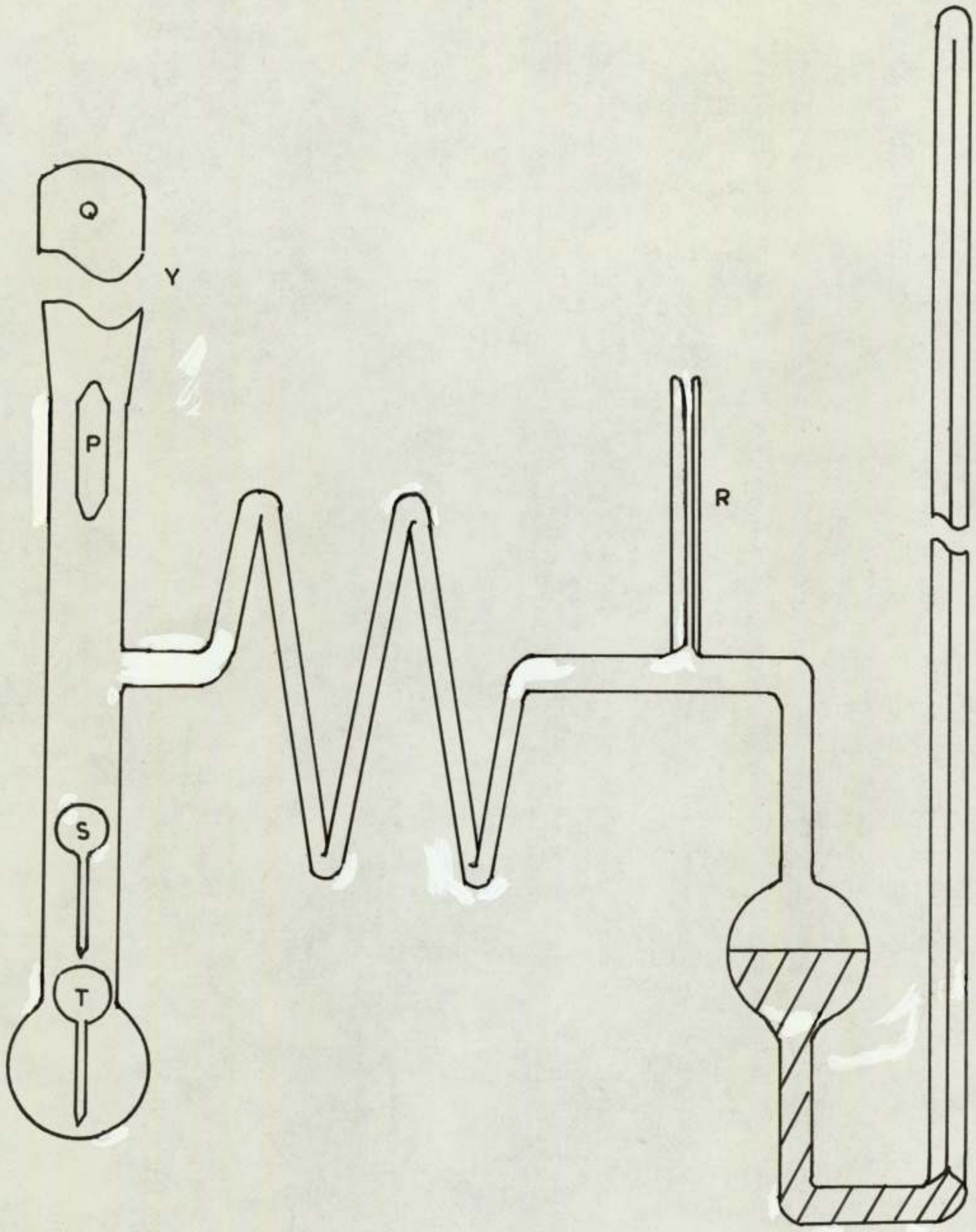


FIGURE III

Low temperature apparatus for gas evolution at constant volume

Type II

ground glass joints sealed by pycene wax or a silicone grease were only resistant to the action of a silicone oil both for a relatively short time, hence leakage frequently occurred during long kinetic runs. Secondly, there is no positive barrier between the monomer solution contained in the bulb of the apparatus, J, and the catalyst in the bucket G. Hence the degassing procedure mentioned above for section B, may, unless the solution contained in the bucket has been previously degassed, result in splashing of the catalyst solution into the monomer thus starting the reaction before the solutions are equilibrated. A further limitation has been discovered in that it is possible for the vapour pressure of a catalyst in the bucket to initiate monomer decomposition before the two are mixed[55]. These difficulties were overcome by the apparatus shown in Figure III.

The apparatus is similar in design to the types shown in Figures II and IV. No ground glass joint or tap is included. This removes the possibility of leakage due to grease being leached out of the joint.

The procedure differs slightly from that followed above; the apparatus was first flamed out while passing a gentle current of dry nitrogen. The apparatus was then allowed to cool still passing dry nitrogen, while the ampules (S and T) containing monomer and initiator solutions were introduced at Y, and then placed in position as shown. The ampules used were made from soda glass, capacity a little greater than the total volume required, the solutions being sealed in them under vacuum. A magnetic breaker (P) was then placed above the ampules and the cap (Q) sealed onto the apparatus using an oxygen/coal gas flame. The apparatus was then evacuated via the capilliary tube R, any further flaming out of the manometer section being carried out at this stage, and sealed by collapsing the capilliary R. The apparatus was then placed in a thermostatted oil bath to equilibrate.

In order to start the reaction the breaker (P) was lifted from the outside of the apparatus with a magnet and allowed to drop onto the ampules. The ampule design shown was found to break easily allowing the breaker to fall to the bottom of the apparatus where it was used as a magnetic stirrer. The coiled section of the apparatus was useful in absorbing vibrations caused by the magnetic follower.

The apparatus was found to be particularly useful where initial rates were required or where a volatile solvent was used and longer times were required to equilibrate the solutions before starting the reaction.

Various modifications of this were possible utilising separate ampules for monomer, initiator and solvent, although it was found to be desirable to use monomer and initiator solutions in order to facilitate rapid mixing of reactants.

c. High Temperature Apparatus. Figure IV

This design, due to Tighe,[68] comprises a completely sealed reaction vessel and mercury manometer. It was found to be more reliable than the low temperature apparatus, where initial rates were not required since it was not possible to equilibrate the reactants before mixing. The procedure for use

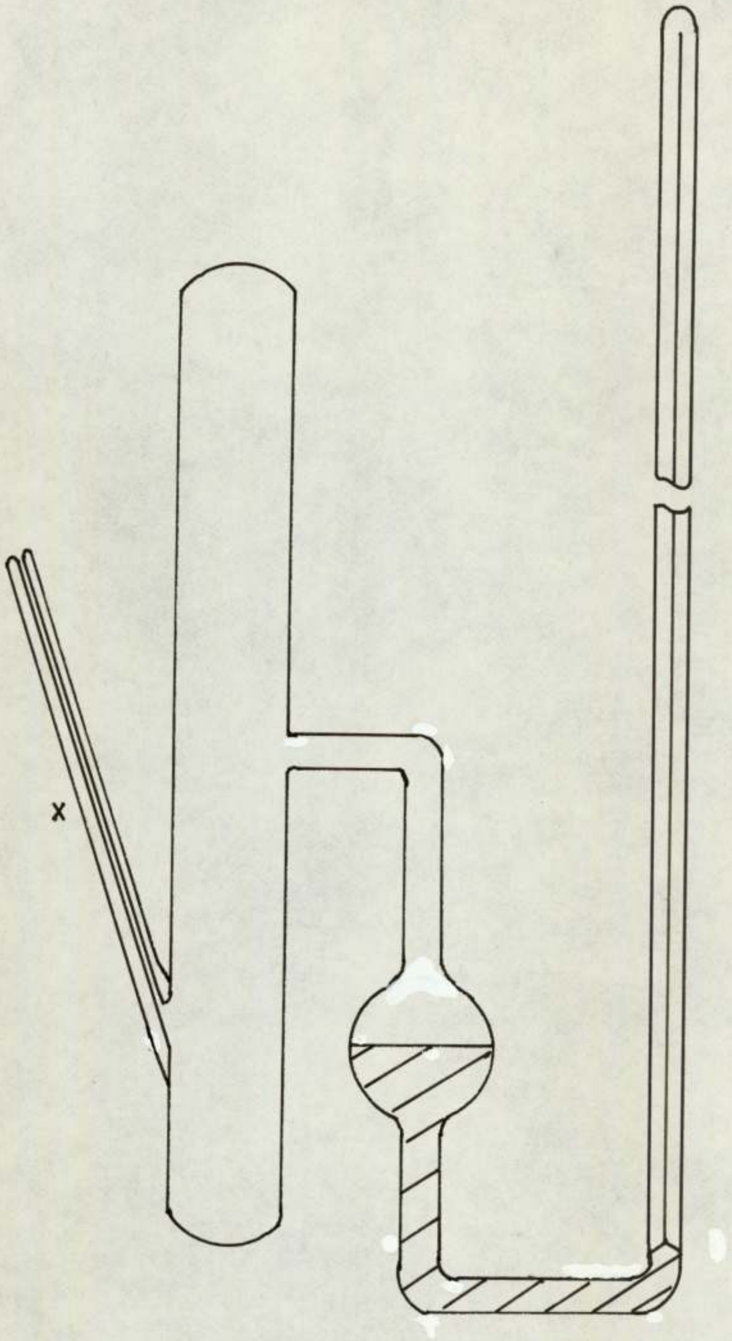


FIGURE IV

High temperature apparatus for measurement of gas evolution at constant volume involved flaming out under reduced pressure followed by cooling to room temperature and bringing the pressure back to atmosphereic by bleeding in dry nitrogen. The reactants were then introduced by syringe via the capilliary X. After degassing by connection to a high vacuum line, the vessel was sealed by collapsing the capilliary X with an oxygen/coal gas flame.

d. Use of Electrical Pressure Measurement Device

Investigations were also made into the use of a pressure transducer to continuously monitor the evolution of gas at constant volume. However, these experiments were limited by attack of the acidic gases evolved on the diaphragm of the transducer, this necessitated the use of a mercury barrier between the reaction vessel and transducer. A further major limitation was found to be the limited range of operation of the transducer, 300 to 1000 mm Hg. This particular limitation was overcome by the use of a dry inert atmosphere over the reactants, which was adjusted to the appropriate pressure. However, this modification introduced problems associated with the time delay necessary to achieve equilibration of the atmosphere, and also with the non-ideal behaviour of the combination of nitrogen atmosphere and gases evolved at the pressure used. This method of following the kinetic of anhydrosulphite decomposition was not therefore pursued.

For all of the above methods it was essential that there was no supersaturation of the solutions by the evolved gas. This condition was prevented by agitation of the solution using a Pifco Vibrator, an equilibrium between the vapour phase and dissolved gas was thus maintained. Reproducible results were only obtained if the solution was agitated immediately prior to taking a manometer reading to achieve equilibrium.

Provided that temperature remains constant, that there is no change in volume and that the gas evolved behaves as near ideal then a simple relationship can be derived between the gas evolved and the concentration of monomer at any given time:-

If $[M]_0$ is initial monomer concentration

$[M]$ is monomer concentration at any given time
$[G]$ is the concentration of evolved gas at a given time

Then if one mole of monomer decomposes to give one mole of evolved gas:-

$[M]_0 = [M] + [G]$ 1
or, when the reaction is complete
$[M]_0 = [G]_\infty$ 2

For an ideal gas at constant volume and constant temperature, the pressure of evolved gas, P, is proportional to the number of moles of gas present

$P \propto [G]$ 3
Hence, $P_\infty \propto [G]_\infty$ 4
and from equation 2:
$\pi P_\infty = [G]_\infty = [M]_0$ 5
where π is a proportionality constant

Let the pressure at any instant be P, then from equation 1:

$$\pi P = [G] = [M]_o - [M] \quad .. \quad .. \quad .. \quad 6$$

Combination of equations 5 and 6 then gives an expression for the fraction of monomer remaining:

$$\frac{[M]}{[M]_o} = \frac{P_\infty - P}{P_\infty} \quad .. \quad .. \quad .. \quad .. \quad .. \quad 7$$

or for the fraction of monomer reacted:

$$\frac{[M]_o - [M]}{[M]_o} = \frac{P}{P_\infty} \quad .. \quad .. \quad .. \quad .. \quad 8$$

where the monomer fragments to give more than one gaseous molecule a similar expression may be derived.
Hence, if two gaseous fragments g_1 and g_2 are evolved equation 7 becomes:

$$\frac{[M]}{[M]_o} = \frac{PT_\infty - PT}{PT_\infty} \quad .. \quad .. \quad .. \quad .. \quad .. \quad 9$$

and equation 8 becomes:

$$\frac{[M]_o - [M]}{[M]_o} = \frac{PT}{PT_\infty} \quad .. \quad .. \quad .. \quad .. \quad 10$$

where $PT = Pg_1 + Pg_2$ at any instant

$PT_\infty = Pg_{1\,\infty} + Pg_{2\,\infty}$ at infinite time

Pg_1 and Pg_2 being the pressures due to gaseous fragments g_1 and g_2 respectively.

Using these expressions the kinetic parameters of the decompositions may be evaluated.

Gravimetric Analysis

The progress of the reactions was also followed by the appearance of polymers. The usual procedure for the isolation of poly α-ester, precipitation in methanol was shown to be ineffective for the isolation of oligomers of some asymmetrically substituted poly α-esters. The technique preferred was the quenching of gravimetry samples in 0.01N hydrochloric acid followed by removal of water and drying under vacuum and in the presence of a drying agent. This procedure rendered inactive any alkaline catalyst and converted monomers to their parent α-hydroxy acid. Washing of the resultant polymer/ α-hydroxy acid mixture with ether removed the ether soluble α-hydroxy acid but dissolved little low molecular weight polymer as evidenced by i.r. analysis of the ether washings.

Infra Red Techniques

The rate of polymerisation of N.C.A.s has been followed by use of the quantitative infra-red analysis utilising the differing carbonyl absorption frequencies of monomer and polymer. A similar technique has been used for both the anhydrosulphites and anhydrocarboxylates of α-hydroxy acids.

The carbonyl absorption frequency of anhydrosulphites is sufficiently far removed from the carbonyl absorption frequencies of any of the products of decomposition investigated in these studies to enable i.r. to be used to investigate rates of decomposition.

The reactions were generally carried out in tetrahydrofuran as solvent and were homogeneous throughout. Although the absorptions due to tetrahydrofuran are minimal in the region of interest a matched solvent blank was used to completely balance out any solvent absorption. Kinetics were followed by the use of a closed cell technique for fast reactions at room temperature and by removal of samples from a reaction mixture where reaction times were longer. Samples were blanketed with dry nitrogen.

The intensity of absorption is given by:-

$$\log\left(\frac{I}{I_o}\right) = ECl \quad \text{.. .. ..} \quad 11$$

where I_o is the intensity of the incident light

I is the intensity of the transmitted light

E is the molar absorptivity coefficient)

) constant

l is the cell path length)

C is the concentration of the absorbing species

now absorbance is given by:-

$$A = \log\left(\frac{I}{I_o}\right) \quad \text{.. .. ..} \quad 12$$

Hence combination of equations 11 and 12 gives:-

$$A = ECl$$

$$\text{or} \quad C = A\,E^{l} \quad \text{.. .. ..} \quad 13$$

$$\text{where} \quad E^{l} = \frac{1}{El}$$

Now let the absorbance of the monomer concentration $[M]$ at any instant be A_t^m then:

$$[M] = A_t^m\,E^{l} \quad \text{.. .. ..} \quad 14$$

at zero time $[M] = [M]_o$, therefore let the absorbance at this time be: A_o^m, then:

$$[M]_o = A_o^m\,E^{l} \quad \text{.. .. ..} \quad 15$$

It follows that the fraction of total monomer decomposed at any given time is:-

$$\frac{[M]_o - [M]}{[M]_o} = \frac{A_o^m - A_t^m}{A_o^m} \quad .. \quad .. \quad 16$$

A similar expression can be derived for the formation of polymer:-

$$\frac{P_t}{P_\infty} = \frac{A_t^p}{A_\infty^p} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad 17$$

where P_t, A_t^p are the concentration and absorbance respectively of polymer at any time t, P_∞ , A_∞^p are the concentration and absorbance respectively of polymer at infinite time.

If the rate of disappearance of monomer is the same as the rate of formation of polymers then:

$$\frac{[M]}{[M]_o} = 1 - \frac{[P]_t}{[P]_\infty} \quad .. \quad .. \quad .. \quad .. \quad .. \quad 18$$

or, using equations 14, 15 and 17:

$$\frac{A_t^m}{A_o^m} = 1 - \frac{A_t^p}{A_\infty^p} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad 19$$

or $$\frac{A_t^m}{A_o^m} = \frac{A_\infty^p - A_t^p}{A_\infty^p} \quad .. \quad .. \quad .. \quad .. \quad .. \quad 20$$

Hence a plot of $\frac{A_t^m}{A_o^m}$ vs $\frac{A_\infty^p - A_t^p}{A_\infty^p}$ will be linear if monomer disappearance occurs at the same rate as polymer formation.

Gel Permeation Chromatography

All gel permeation chromatography was carried out by the Polymer Supply and Characterisation Centre of R.A.P.R.A., Shawbury, Shrewsbury. Molecular weight data as supplied were standardised against polystyrene samples. In order that a reasonably accurate assessment of the molecular weight of poly α-ester samples could be made 'Q factors' were calculated for each poly α-ester.

where 'Q factor' = weight per Å length of the polymer chain assuming planar zig-zag configuration.

Q factor for polystyrene = 41.4

Q factor for poly MEAS = 26.6

Hence, an appropriate conversion factor for poly MEAS is: polystyrene x 0.64.

These analyses are based on the assumption that poly α-esters in the solvent used - T.H.F. - behave in the same manner as polystyrene in the same solvent. The poor solubility of some poly α-esters, especially symmetrically substituted members of the series, may mean that this assumption is not true. The value of these results lies, therefore, not in the absolute magnitudes but their comparative size within the context of poly α-ester studies.

2.2 PURIFICATION OF SOLVENTS AND REAGENTS

In general the methods used were those recommended in Vogel[60] or Weissberger[61]. The prime requisite of these purifications was that moisture should be reduced to a minimum. In consequence solvents were stored in the dry box and always handled therein. Where distillation was to be carried out at atmospheric pressure or under reduced pressure a dry nitrogen atmosphere was used, vented to air through calcium chloride tubes. Materials were redistilled immediately prior to use, the middle fraction only being used.

Dry nitrogen - This was obtained by passing White Spot Nitrogen (B.O.C. Ltd.) through a glass spiral immersed in liquid nitrogen. Trace moisture was thus frozen out.

Nitrobenzene - This solvent was refluxed over phosphorous pentoxide for twenty hours and then fractionally distilled under reduced pressure through a two foot column packed with Dixon gauze rings. The middle fraction, boiling at 70°C/0.5mm Hg was stored over baked barium oxide.

Benzyl Alcohol - This was stored over calcium sulphate for forty-eight hours and then distilled at 60 - 61°C/1.4mm Hg. pressure. It was then stored over baked barium oxide.

Dekalin - Dekalin, B.D.H. S.L.R. standard, was first washed several times with 5% $\frac{w}{v}$ sulphuric acid and then with 10% $\frac{w}{v}$ sodium hydroxide. It was then repeatedly washed with water, and dried overnight with calcium sulphate. The dekalin was then distilled under reduced pressure, the middle fraction boiling at 62 - 63°C/6mm Hg. pressure being collected. Metallic sodium was used to maintain the anhydrous condition of the solvent during storage.

Dimethyl Sulphoxide - This solvent was shaken repeatedly with calcium sulphate to remove its high equilibrium content of water (c.a. 11% at $20^{O}C)^{62}$. It was then refluxed for two hours over baked barium oxide before fractionally distilling under reduced pressure onto fresh baked barium oxide. The fraction boiling at 80^{O}/16mm Hg. as collected.

1,4-Dioxane - This was shaken with calcium sulphate and allowed to stand overnight. It was then distilled from sodium and stored over fresh sodium wire. The middle fraction, B.Pt. $101^{O}C$/760mm Hg. only was collected.

T.H.F. - Tetrahydrofuran was dried over calcium sulphate and then refluxed for four hours over sodium wire. It was then distilled under dry nitrogen at atmospheric pressure from fresh sodium. B.Pt. 76^{O}. T.H.F. was stored over sodium wire, any loss of lustre from the wire was taken to indicate the need for redistillation.

Diethyl Ether - The anhydrous grade supplied by Fisons Scientific Apparatus Ltd. (water content 0.2%) was stored over sodium wire and used as required with no further purification.

Thionyl Chloride - Analytical grade supplied by British Drug Houses Ltd. This was redistilled immediately prior to use. Bpt. $76^{O}C$/760mm Hg.

Phosgene - Supplied by B.D.H. Ltd., (Laboratory Gas Service).

Used as supplied.

Silver Oxide - Supplied by B.D.H. Ltd., dried at 100°C under vacuum in a drying pistol and stored over anhydrous calcium chloride in a dessicator.

1-Bromohexane - Supplied by B.D.H. Ltd. This material was dried over calcium sulphate and distilled at atmospheric pressure just prior to use (boiling point 155°C).

1-Bromobutane - Supplied by B.D.H. Ltd. This reagent treated in the same manner as 1-Bromohexane (boiling point 101°C).

1-Bromooctane - Supplied by B.D.H. Ltd. This reagent treated in the same manner as 1-Bromohexane (boiling point 77-8°C/ 10 mm Hg.).

Pyruvic Acid - Supplied by B.D.H. Ltd. This reagent cyclises slowly to form a mixture of pyruvic acid and α-keto - α-valerolactone-α-carboxylic acid. To minimise formation of this impurity the acid was stored at 0°C.

Diethyl Ketone - This was dried over potassium carbonate and then distilled at atmospheric pressure (boiling point, 102°C/ 760mm Hg) prior to use.

2.3 PREPARATION OF α -HYDROXY ACIDS

The following α-hydroxy acids were commercially available:-

α-hydroxy-α-methyl proprionic acid	-	Cambrian Chemicals Ltd.
α-hydroxy-α-methyl butyric acid	-	Pfaltz and Bauer Inc. New York.
Cyclopentanol-1-carboxylic acid	-	Newton Maine Ltd.

These acids were purified by recrystallisation from benzene /30-40°C petroleum ether mixtures until a sharp melting point was obtained. They were stored in a vacuum dessicator over anhydrous calcium chloride before use.

Other α-hydroxy acids were prepared as follows:-

α-hydroxy-α-ethyl butyric acid - This was prepared by a modified cyanohydrin route, using a tetrahydrofuran/water mixed solvent system instead of water alone. Since all solids are dissolved, reaction takes place at the water/tetrahydrofuran interface. This has been shown to result in better yields than would be obtained with a single solvent system.

Sodium cyanide (80.0g, 1.6 mole) was dissolved in water (300 ml). Tetrahydrofuran (200 ml) was then stirred in and diethyl ketone (86.1g, 1 mole) added. After the addition of six drops of piperidine the reaction mixture was cooled to 5°C in an ice/water bath. Hydrochloric acid (165 ml) was then run into the stirred reaction mixture over a period of two hours. After stirring for a further fifteen hours, the organic and aqueous phases were separated and the aqueous phase washed with 3 x 50 ml portions of diethyl ether. After combination of the organic phases, these were washed with sodium bicarbonate solution and dried over anhydrous sodium sulphate. The volatile components were then removed to yield substantially pure cyanohydrin as shown by g.l.c.

The cyanohydrin was refluxed with hydrochloric acid (225 ml) for 72 hours at 102 - 5°C then anhydrous sodium sulphate added and the reaction mixture cooled and filtered. The filtrate was washed with 3 x 50 ml portions of diethyl ether which were then dried over magnesium sulphate. The ether was then removed to yield a brown solid which was recrystallised from benzene to constant melting point 77-78°C. Yield 26g (19%).

Elemental analysis	found	C,54.3 :H,8.3%
	Required for $C_6H_{12}O_3$	C,54.5: H,9.1%

<u>∝-hydroxy-∝-methyl valeric acid</u> - This acid was prepared in a similar manner to ∝-hydroxy ∝-ethyl hexanoic acid.[53]

Melting point 50-52 °C

<u>∝-hydroxy-∝-methyl carboxylic acids</u> - Preparation of higher members of the ∝-hydroxy acid series, for example among the methyl, n-alkyl ∝-hydroxy acids those members above ∝-hydroxy-∝-methyl butanaic acid, becomes difficult using the conventional or modified cyanohydrin route. This is because of an unfavourable equilibrium between the cyanohydrin and its hydrolysis product, the ∝-hydroxy acid. The resulting yield is poor. An alternative method was therefore selected for the methyl n-alkyl substituted ∝-hydroxy acids, this being the action of pyruvic acid on the appropriate alkyl magnesium bromide and hydrolysis of the product to the

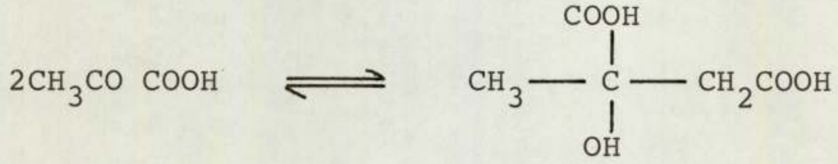
required acid. A similar method has previously been used for the synthesis of 2-pentafluorophenyl-2-hydroxy-carboxylic acids.

α-hydroxy-α-methyl-hexanoic acid

Magnesium turnings	24g	1 mole
1-Bromo hexane	165g	1 mole
Diethyl ether (anhydrous)	400 ml	
Iodine	1 crystal	

The magnesium turnings were slurried with 200 ml of ether and a few mls of the 1-bromo hexane after the addition of the iodine the reaction mixture was warmed until reaction commenced. The rest of the 1-bromo hexane was then mixed with the rest of the ether and run in at a sufficient rate to maintain the reaction at reflux. The reaction mixture was then stirred for a further four hours before reaction with pyruvic acid.

The pyruvic acid used was impure, containing up to 20% of the dimer in equilibrium.



$$2CH_3CO\,COOH \rightleftharpoons CH_3\text{—}C(COOH)(OH)\text{—}CH_2COOH$$

and the reaction of pyruvic acid with an alkyl magnesium bromide is an equilibrium favoured by an excess of the alkyl magnesium bromide. An excess of the grignard reagent was therefore used.

Pyruvic acid	58.8g	0.75 mole
Diethyl ether (anhydrous)	200 ml	

The pyruvic acid dissolved in ether was added dropwise to the grignard reagent, with cooling below 5°C. The white slurry formed was stirred for a further 18 hours allowing to warm to room temperature. On hydrolysis with 300 ml 4N hydrochloric acid the white precipitate was dissolved. The reaction mixture was then stirred for a further four hours then the aqueous layer was separated from the non-aqueous and worked with 3 x 50ml portions of diethyl ether. The etherial solution and washings were combined and dried over anhydrous calcium sulphate. The product on removal of the ether using a rotary evaporator was a brown oil . Glc. showed the major impurities in this oil to be hexanol, the hydrolysis product of the excess grignard reagent, and unreacted pyruvic acid. The α-hydroxy acid was conveniently separated from the oil by conversion to its insoluble copper (II) salt. The acid was isolated by hydrolysis of the copper (II) salt using 2M hydrochloric acid and extraction of the aqueous solution with ether. The etherial solution was dried over calcium sulphate and then the ether removed by evaporation. Recrystallisation of the acid from benzene/pet. ether yielded white crystals of the acid. M.Pt. 69 - 71°C.

Elemental analysis found: C,57.1 : H,9.2%

$C_7H_{14}O_3$ required : C,57.6 : H,9.6%

α-hydroxy-α-methyl octanoic acid

This was prepared by the same route as α-hydroxy-α-methyl octanoic acid, the acid itself was again isolated via the copper salt.

1-bromo octane	193g	1 mole
in diethyl ether	200 ml	
Magnesium turnings	24g	1 mole
slurried in diethyl ether	200 ml	
Iodine	one crystal	

the pyruvic acid was added directly to the grignard reagent

Pyruvic acid	58.5g	0.75 mole
in diethyl ether	200 ml	

The resulting solid was then directly hydrolysed with 4N hydrochloric acid as described above. Separation of the aqueous and non-aqueous phases gave a residual oil containing the required α-hydroxy acid together with unreacted reactants. A sample of the acid was then isolated via the copper (II) salt.

Melting point 43 - 44°C

Elemental analysis found: C,61.8 : H,11.1%

$C_9H_{18}O_3$ requires : C,62.2 : H,10.3%

α-hydroxy-α-methyl decanoic acid

This was prepared in a similar manner to α-hydroxy-α-methyl hexanoic acid. The acid was not isolated from its byproducts.

1-bromo decane	221g	1 mole
in 200 ml anhydrous diethyl ether		
Magnesium turnings	24g	1 mole
slurried in 200 ml anhydrous diethyl ether.		
Iodine	one small crystal	

The grignard reagent was not isolated, pyruvic acid was added directly to the etherial solution

Pyruvic acid	58.5g	0.75 mole

in 200 ml anhydrous ether.

The resulting solid complex was hydrolysed 'in situ' with an excess of 4N hydrochloric acid. Separation of the non aqueous phase yielded the required ∝-hydroxy acid as an impure oil, a sample of which was converted to the pure acid via the copper (II) salt.

Melting Point 40 - 41°C

Elemental Analysis found: C,64.3 : H,8.2%

$C_{11}H_{22}O_3$ requires : C,65.4 : H,10.9%

Characterisation of ∝-hydroxy acids

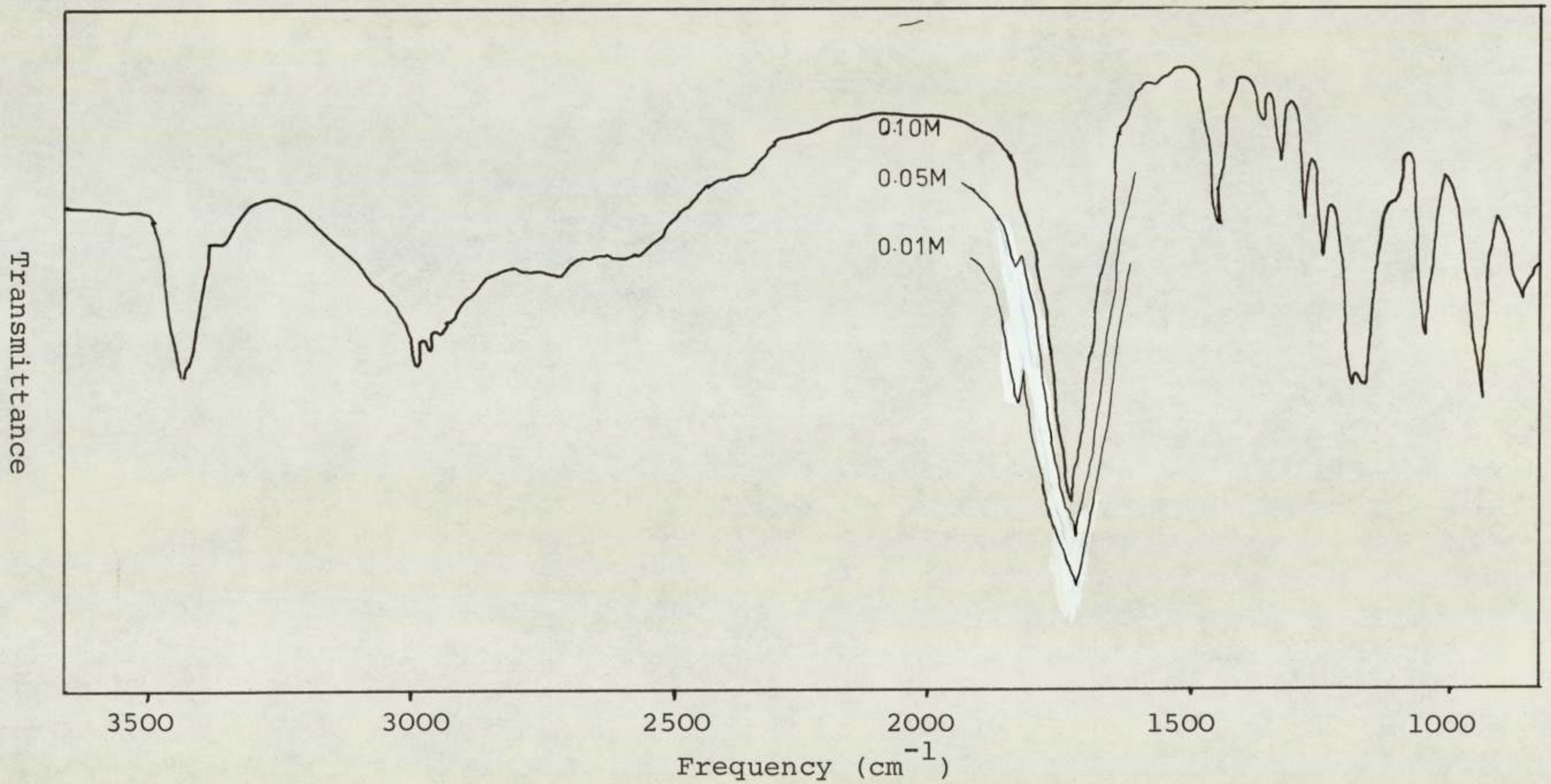
∝-hydroxy acids are easily characterised by their infrared spectra. The spectrum of ∝-hydroxy-∝-methyl hexanoic acid is shown in Figure V as a solution spectrum in carbon tetrachloride at various concentrations. The absorptions due to hydroxylic streaching (3560 cm^{-1}) and carbonyl streaching (1740 cm^{-1}) are clearly shown. At low concentrations, splitting of the carboxyl streaching frequency (1700 cm^{-1} and 1750 cm^{-1}) indicates the presence of monomeric and dimeric species. Other ∝-hydroxy acids are characterised by similar absorptions, systematic variation of the carbonyl absorption is noted as a variation within the series.

2.4 SYNTHESIS OF COPPER (II) SALTS OF ∝-HYDROXY ACIDS

Copper (II) salts of ∝-hydroxy acids provide an alternative precursor to anhydrosulphite and anhydrocarboxylate

FIGURE V

Infra-red spectrum of α-hydroxy-α-methyl hexanoic acid. Spectrum recorded as CCl_4 soln. Reference cell CCl_4.



preparation. In the case of the higher homologues of the methyl n-alkyl anhydrosulphites, the copper (II) salt provides a facile method to the purification of the parent α-hydroxy acid.

A 1.0 molar solution of the α-hydroxy acid was neutralised with ammonium hydroxide and the solution heated to boiling to remove any excess of ammonia, alternatively, neutralisation procedure may be followed using a pH meter with a standard electrode system. Addition of an equal quantity of 0.5 molar copper (II) chloride solution at room temperature gave rapid precipitation of the appropriate α-hydroxy acid copper (II) salt. The salt was washed with warm water and small quantities of acetone.

The product was a green or green blue solid containing large quantities of water. All moisture was removed by heating at 90 - 100°C under vacuum for fifty hours. The absence of water of crystallisation was shown by the use of T.G.A, D.T.A. and infra-red spectrometry.

Blackbourn[58] has recorded the low water solubility of the copper (II) salt of α-hydroxy-α-butyl hexanoic acid and concluded that this is a direct result of the size of the organic radical. All copper (II) salts prepared in this study have a relatively large organic portion and the ease with which they were separated and purified was notable. No further copper salt being precipitated from the aqueous filtrate after holding at 1 - 2°C for several days.

Copper (II) α-hydroxy-α-methyl hexanoate

Elemental analysis found : C,47.0 : H,7.1%

$C_{14}H_{26}O_6Cu$ requires : C,47.6 : H,7.4%

Copper (II) α-hydroxy-α-methyl octanoate

Elemental analysis found : C,51.4 : H,8.0%

$C_{18}H_{34}O_6Cu$ requires : C,52.8 : H,8.3%

Copper (II) α-hydroxy-α-methyl decanoate

Elemental analysis found : C,54.9 : H,8.7%

$C_{22}H_{42}O_6Cu$ requires : C,56.8 : H,9.0%

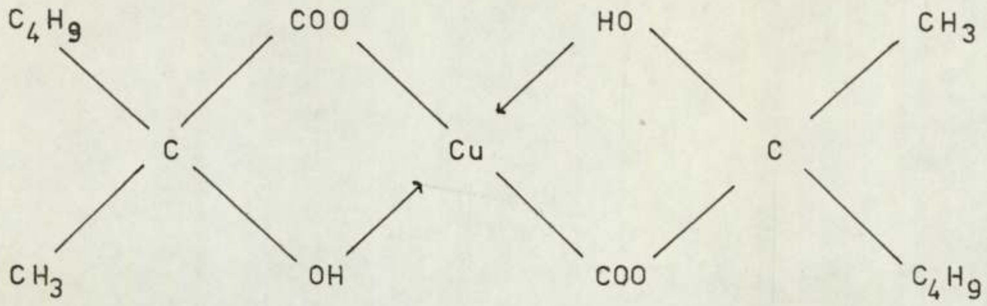
Copper (II) α-hydroxy-α-n-butyl hexanoate

Elemental analysis found : C,53.6 : H,8.8%

$C_{20}H_{38}O_6Cu$ requires : C,54.8 : 8.7%

Characterisation of Copper (II) salts of α-hydroxy acids

The copper (II) salts, as typified by copper (II) α-hydroxy-α-methylhexanoate (III), when completely anhydrous are most easily characterised by their infra-red spectra. The hydroxyl group streaching frequency in the region of 3560 cm^{-1} shown by the free acid is displaced and changed in shape in the copper salt as a result of the co-ordination of the group with the metal atom. The carbonyl streaching frequency, 1740 cm^{-1} in the acid is replaced by an adsorption at 1640 cm^{-1} which is characteristic of the carbonyl streaching frequency of the carboxylate anion. Figure VI shows the infra-red absorption spectrum of copper (II) α-hydroxy-α-methyl hexanoate which may be compared with the free acid Figure V.



(III)

D.T.A. and T.G.A. were used to indicate the presence of moisture in Copper (II) salts of the α -hydroxy acids, and also to indicate the ceiling temperature, for the safe dehydration of the hydrated salts under vacuum. The absence of a peak (D.T.A.) or loss in weight (T.G.A.) between 100° and 150°C indicates that the compound is essentially dry. The temperature of decomposition of the copper (II) salts is indicated by the rapid loss in weight (T.G.A.) or peak (D.T.A.) in the region of 210°. The temperature of decomposition was lowered as the homologous series was ascended. This presumably reflects the larger covalent bonded portion of the molecule.

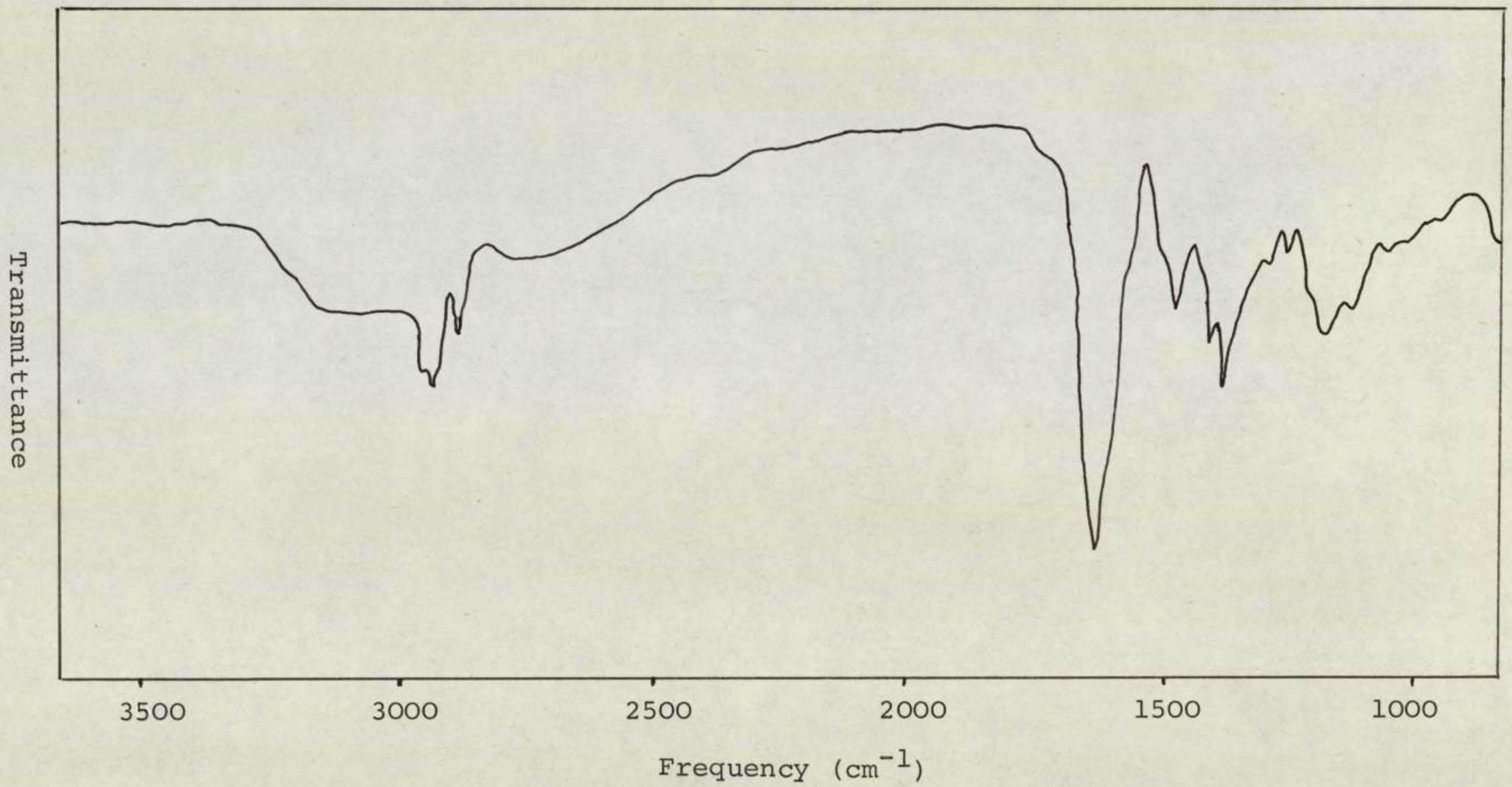
2.5 SYNTHESIS OF ANHYDROSULPHITES AND ANHYDROCARBOXYLATES OF α -HYDROXY ACIDS

Anhydrosulphites

Two methods are now well established for the preparation of α-hydroxy acid anhydrosulphites[18]: the action of thionyl chloride on (a) the free α-hydroxy acid and (b) the anhydrous copper (II) salt of the acid.

FIGURE VI

Infra-red spectrum of copper (II) α-hydroxy-α-methyl hexanoate, spectrum recorded as kBr. disc. Reference cell air.



a. Route via the α-hydroxy acid

The dry α-hydroxy acid (1 mole) was dissolved in 200 ml anhydrous ether, and cooled in an ice bath to below 5°C. Redistilled thionyl chloride (1.5 mole) in 200 ml of anhydrous ether was added dropwise over two hours. The reaction mixture was allowed to warm to room temperature over 18 hours and then placed under partial vacuum (200 - 300 mm Hg) for 6 hours. Ether was then slowly removed under partial vacuum at 15 - 20°C, finally residual ether and thionyl chloride were removed at 10 - 15 mm Hg/20 - 25°C.

b. Route via the copper (II) salt of the α-hydroxy acid

The dry copper salt (1 mole) was slurried in 400 ml anhydrous ether at 0 - 5°C. Redistilled thionyl chloride (3 moles) in 400 ml anhydrous ether was then added dropwise over four hours. The resulting precipitate of copper chloride was then filtered off and washed with anhydrous ether to remove occluded anhydrosulphite. The ether and residual thionyl chloride were then removed under vacuum as in (a).

In all cases, anhydrosulphites were obtained as colourless or pale green oily liquids.

Purification

The major impurities in anhydrosulphite preparation have been shown to be chlorine containing compounds having either acyl or alkyl chlorine or both, and the parent α-hydroxy acid resulting from unreacted starting material or from the ingress of trace moisture.

Chlorine containing impurities have been shown to be effectively and most easily removed by treatment with a 2 molar excess of silver oxide (based on chlorine containing impurity) in ether at $0^{o}C$ for two hours. Parent acid is removed during distillation.

A systematic procedure for anhydrosulphite purification was evolved as follows:

i. Short-path distillation of crude anhydrosulphite under reduced pressure.

ii. Potentiometric chloride determination.

iii. Silver oxide treatment followed by distillation.

iv. Potentiometric chloride determination.

v. Fractional distillation, using either spinning band column or through a 12 inch reflux column packed with Dixon gauze rings.

vi. Final chloride determination.

Steps iii and iv were repeated until a sufficiently low chloride content was obtained. Where required a final distillation through the spinning band column directly into the reaction vessels was carried out also.

Anhydrocarboxylates

The anhydrocarboxylates of α-hydroxy acids may be generally prepared by the action of phosgene on the anhydrous copper (II) salt of the relevant α-hydroxy acid. Pyridine was used to remove hydrogen chloride formed as a byproduct in the reaction, as pyridine hydrochloride.

The anhydrous copper (II) salt (1 mole) was slurried in anhydrous ether (2 litres) and a solution of phosgene (2 moles) dissolved in anhydrous ether (1.0 litre)added. The reaction was stirred for 100 hours at room temperature before the addition of anhydrous pyridine (1.8 mole) in dry ether (500ml). The precipitate of pyridine hydrochloride and copper (II) chloride was removed by filtration and washed to remove adsorbed anhydrocarboxylate. The solvent and any unreacted phosgene were removed by warming to 25°C under vacuum (10 - 20mm Hg).Finally the crude product was subject to a higher vacuum (0.5 - 1.0 mm Hg) for two hours to remove traces of volatiles.

Crude α-hydroxy-α-butyl hexanoic acid anhydrocarboxylate was obtained as a waxy white solid dispersed in a viscous clear liquid.

The impure anhydrocarboxylate was analysed by the modification of Ingrams method used for the anhydrosulphites, for the presence of chlorine containing impurities. The crude product was then redissolved in an excess of anhydrous ether and stirred for 18 hours with a 2 molar excess of baked silver oxide based on chloride content. The silver oxide was then removed by centrifuge and the ether stripped off. The resulting anhydrocarboxylate contained no chlorine as detected by the potentiometric method. The chlorine free anhydrocarboxylate was finally purified by vacuum sublimation.

For the α-hydroxy-α-butyl-hexanoic acid anhydrocarboxylate suitable conditions for sublimation were found to be as follows:-

Crude anhydrocarboxylate	:	25 - 30°C
Cold finger condenser	:	15 - 18°C (water cooled)
Pressure	:	0.5 - 1.0 mm Hg.

The pure anhydrocarboxylate was found to deposit on the cold finger as a viscous colourless liquid. In this respect the final purification was effectively a short path distillation.

Anhydrosulphite and Carboxylate Synthesis and Characterisation

The ring compounds prepared are shown in Table I. These ring compounds may be named systematically as shown or from the parent α-hydroxy acid, for example lactic acid anhydrosulphite. However, both names are cumbersome and it has been general practice in these studies to abbreviate to a set of letters which make the ring compound easily identifiable.

The structures of the ring compounds prepared from α-hydroxy acids, anhydrosulphites and anhydrocarboxylates are shown, the groups R_1 and R_2 are those attached at the C-5 position.

Anhydrosulphite (systematic name)	Abbreviation	R_1	R_2	Parent Acid	Method of preparation	B.Pt. (^{o}C/mm Hg)
5,5-dimethyl-1,3,2 dioxathiolan-4-one-2-oxide	HBAS	CH_3	CH_3	1-hydroxy isobutyric acid	a	56-57/12
5-methyl-5-ethyl-1,3,2-dioxathiolan-4-one-2-oxide	MEAS	CH_3	C_2H_5	1-hydroxy 1 methyl butanic acid	a	29-30/1.4
5,5-dimethyl-1,3,2-dioxathiolan-4-one-2-oxide	DEAS	C_2H_5	C_2H_5	1-hydroxy-1-methyl butanoic acid	a	35-36/0.4
Cyclopentane spiro-5-1,3,2 dioxathiolan-4-one-2-oxide	c'pent AS	$(CH_2)_4$		Cyclobutanol-1-carboxylic acid	a	60-63/0.4
Cyclohexane spiro-5-1,3,2 dioxathiolan-4-one-2-oxide	c'hex AS	$(CH_2)_5$		Cyclohexanol-1-carboxylic acid	a	68-70/0.5
5-methyl-5-propyl-1,3,2 dioxathiolan-4-one-2-oxide	MPAS	CH_3	C_3H_7	1-hydroxy-1-methyl valeric acid	a	73-75/10
5-methyl-5-butyl-1,3,2 dioxathiolan-4-one-2-oxide	MBAS	CH_3	C_4H_9	1-hydroxy-1-methyl hexanoic acid	b	54-56/0.5
5-methyl-5-hexyl-1,3,2 dioxathiolan-4-one-2-oxide	MHAS	CH_3	C_6H_{13}	1-hydroxyl-1-methyl octanoic acid	b	58-60/0.5
5-methyl-5-octyl-1,3,2 dioxathiolan-4-one-2-oxide	MOAS	CH_3	C_8H_{17}	1-hydroxy-1-methyl decanoic acid	b	52-56/0.3
5,5 dibutyl-1,3-dioxolan-2,4-dione	DBAC	C_4H_9	C_4H_9	1-hydroxy-1-butyl hexanoic acid	b	-

TABLE I

Of the compounds shown in Table I the last four have not previously been prepared.

The anhydrosulphites and anhydrocarboxylates of α-hydroxy acids are most easily characterised by their infra-red spectra, shown in Figures VII and VIII respectively. The anhydrosulphite gives rise to a single absorption in the carbonyl region. The frequency of this absorption ($\sim$1820 cm^{-1}) is higher than that due to parent acid, copper (II) salt or the decomposition products of the ring, as a result of the strained nature of this system. The sulphoxide stretching frequency is found as a medium intensity sharp peak in the region of 1240 cm^{-1}. The anhydroxycarboxylates show a splitting of the carbonyl absorption frequency at 1810 cm^{-1} and 1880 cm^{-1} due to the differing environments of the two carbonyl groups.

Only α-chloro acid chlorides give rise to infra red carbonyl absorption frequencies in the same region as the anhydrosulphite ($\sim$ 1820 cm^{-1}), and their presence can be detected by potentiometric titration. Further confirmation of anhydrosulphite and anhydrocarboxylate structure can be provided by U.V. spectra in which two notable absorptions occur at 210 Å (strong) and 290 Å (weaker), N.M.R., and the characteristic fragmentation pattern observed under mass spectral analysis. Elemental analysis gave variable results, probably due to the sensitivity of these compounds to moisture and their fragmentation pattern under the influence of heat.

Mechanism of anhydrosulphite formation

The mechanism involved in the formation of anhydrosulphites

FIGURE VII

Infra-red spectrum of MEAS. Spectrum recorded as carbon tetrachloride solution (10v/v) using KBr plates and 0.025mm spacer. Reference cell air.

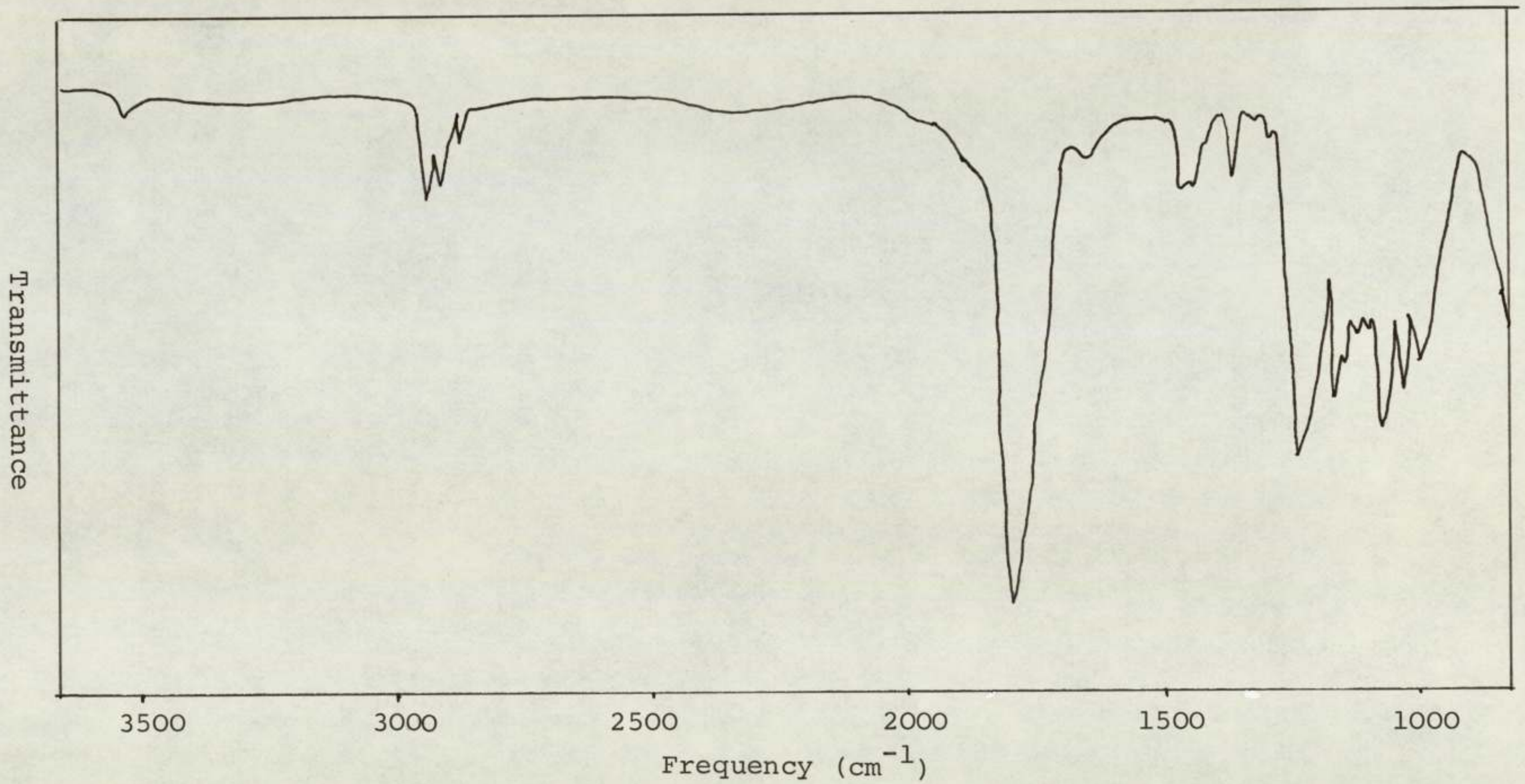
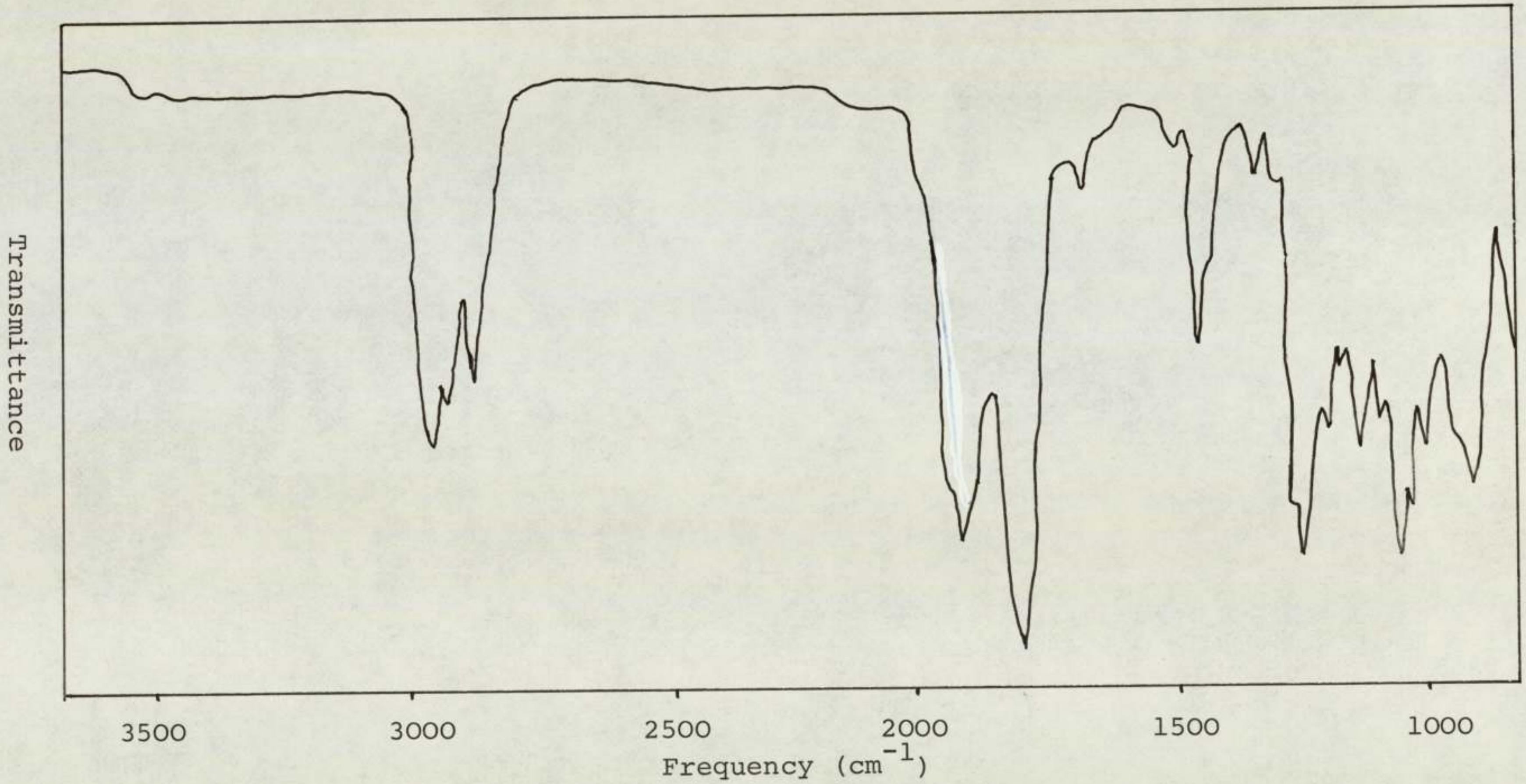


FIGURE VIII

Infra-red spectrum of DBAC. Spectrum recorded as carbon tetrachloride solution (10% v/v) using KBr plates and 0.025mm spacer. Reference cell air.



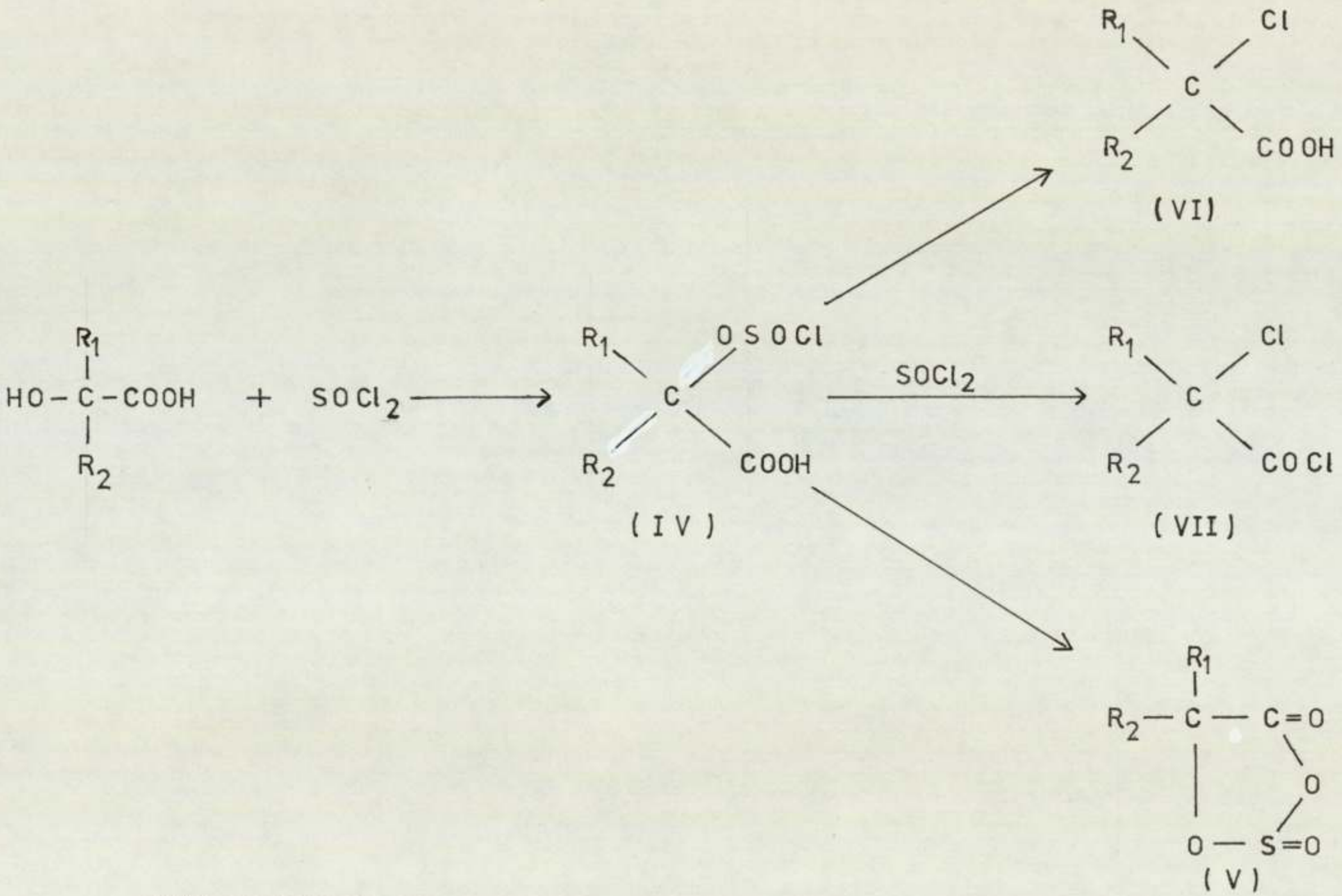
by the reaction of thionyl chloride and an α-hydroxy acid is now well established[18]. However, it is relevant to briefly outline the reactions taking place.

The α-hydroxy carboxylic acid reacts with thionyl chloride to form, initially, an alkyl chlorosulphinate (IV) as an intermediate. This chlorosulphinate may then react intermolecularly with a hydroxyl group, for example another α-hydroxy acid molecule, or by an intramolecular reaction with the carboxylic acid group of the same molecule to yield an anhydrosulphite (V).

Alternatively the alkyl chlorosulphinate may lose sulphur dioxide with the formation of an alkyl chlorine group (VI) or there may be further attack by thionyl chloride on the carboxylic acid grouping to yield, ultimately, an acyl chloride. The possibility therefore exists that both of these last mentioned reactions may take place the product being a α-chloro acid chloride (VII).

This has in fact been shown to be the major impurity in the preparation of most of the anhydrosulphites so far synthesised.[58]

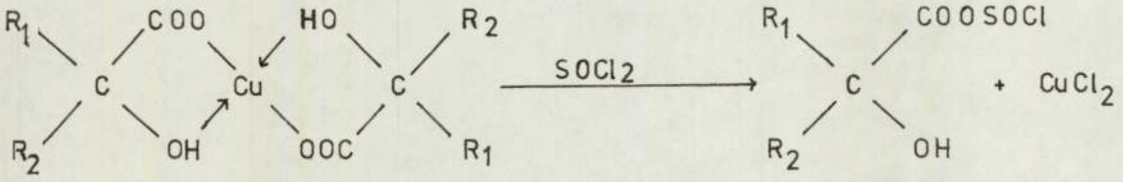
Reaction of thionyl chloride with the copper (II) salt of an α-hydroxy carboxylic acid (VIII) has been shown to have several advantages over direct use of the acid itself. Firstly, the salt may be dried at a higher temperature under vacuum than the parent acid. This results in a reactant which is completely free of water as shown by D.T.A. or i.r. analysis. Traces of water reconvert anhydrosulphites back to



THE REACTION OF THIONYL CHLORIDE WITH ∝-HYDROXY CARBOXYLIC ACIDS the parent acid and hence lower the yield for the reaction.

Secondly, half of the chlorine containing byproduct of the reaction is copper chloride which is precipitated. Removal of this byproduct by filtration or centrifuge is facile.

Thirdly, the suggested mechanism of reaction differs from that of the parent acid and thionyl chloride. It has been suggested that thionyl chloride attacks the carboxylate anion rather than the hydroxylic function of the molecule, with the product intermediate being an acyl chlorosulphinate (IX) as shown below:-

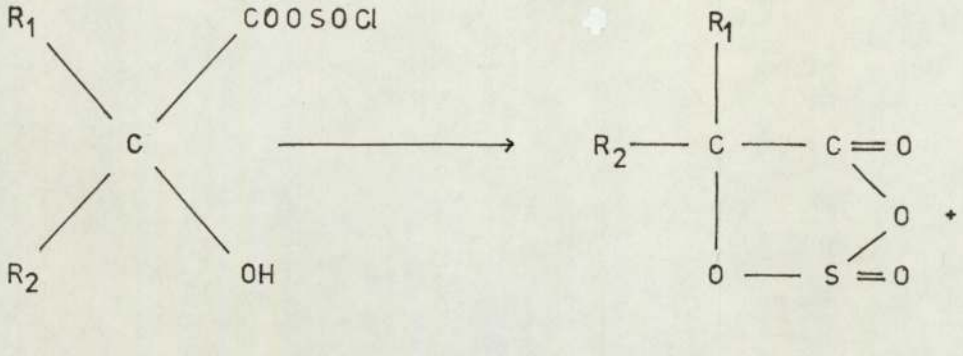


(VIII)

(IX)

Since an acyl chlorosulphinate is expected to be rather more stable than an alkyl chlorosulphinate, the former is less likely to lose sulphur dioxide with the formation of undesirable chlorine containing impurities. The probability of formation of acid chloride or α-chloro acid chloride is, therefore, much reduced.

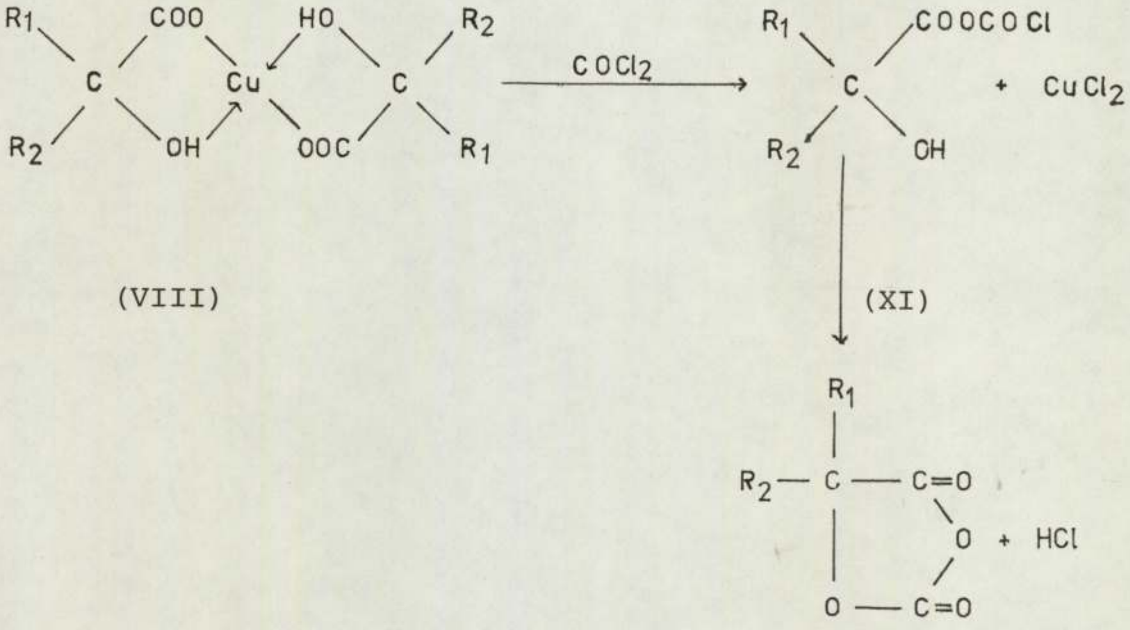
Anhydrosulphite (X) is formed by loss of hydrogen chloride from the acyl chlorosulphinate.



(IX) (X)

Formation of anhydrocarboxylates of α-hydroxy acids

Smith[55] has found that anhydrocarboxylates of α-hydroxy acids (XII) are most conveniently prepared by reaction of phosgene with the copper (II) salt of an α-hydroxy acid (VIII) shown below:



(VIII) (XI) (XII)

In this case the intermediate is an acylchloroformate (XI). The same considerations apply as for the formation of an anhydrosulphite by a similar route (above), the most advantageous feature being the low concentration of chlorine containing byproducts. The use of pyridine to remove hydrogen chloride formed in the cyclisation step provides additional motivation to the cyclisation process by removal of hydrogen chloride from the intermediate.

2.6 PREPARATION OF POLYMERS

Polymer samples were prepared as far as possible under sealed conditions to prevent the ingress of trace moisture etc.

Samples prepared by the thermal decomposition of anhydrosulphites were introduced into carius tubes under anhydrous conditions using a dry box. The closed tubes were then transferred to a vacuum line and evacuated to 0.5 - 1.0 Torr,they were then sealed using an oxygen/coal gas torch and immersed in an oil bath at the appropriate temperature.Where a volatile solvent was to be used, the solution was frozen in liquid nitrogen before evacuation and sealing.

Polymer samples prepared by the catalysed decomposition of anhydrosulphites were prepared in a similar manner to the above except that the freezing of samples was avoided in order that any reaction having an apparent negative activation energy should not be enhanced. Where more volatile solvents were used a dry nitrogen blanket was utilised.

Where the reaction required the periodic removal of samples the build-up of excess pressure by SO_2 evolution was prevented by the use of calcium chloride drying tubes or mercury traps venting to air. Samples were removed by pressurising the reaction vessel with dry nitrogen, and removal of the sample via a tube originating from the bottom of the vessel. Nitrogen was introduced via the moisture traps, see Figure IX, Taps A and B were maintained in the closed position except when opening A to periodically release excess pressure and opening A and B to remove a sample.

Precipitation of polymer samples by mastication with cold methanol has been used as a general procedure for the isolation of poly α-esters in previous anhydrosulphite studies. However, this procedure was found to be unsatisfactory for the isolation of low molecular weight polymers prepared by a catalysed decomposition particularly when decalin was used as solvent. A different procedure was adopted for the isolation of these samples. This was particularly useful where samples were removed before complete conversion.

After removal of the sample the reaction was quenched by addition of water with a drop of 4N hydrochloric acid. This was designed to convert the monomer back to its parent acid and react with the catalyst to produce an inert salt plus an alcohol. Solvent and excess water were then removed by warming under vacuum, and then drying in a vacuum dessicator over phosphorous pentoxide. Where the pure polymer was required, parent acid was first removed by washing with diethyl ether, the polymer being taken up in tetrahydrofuran where possible. Inorganic material was removed by centrifuge

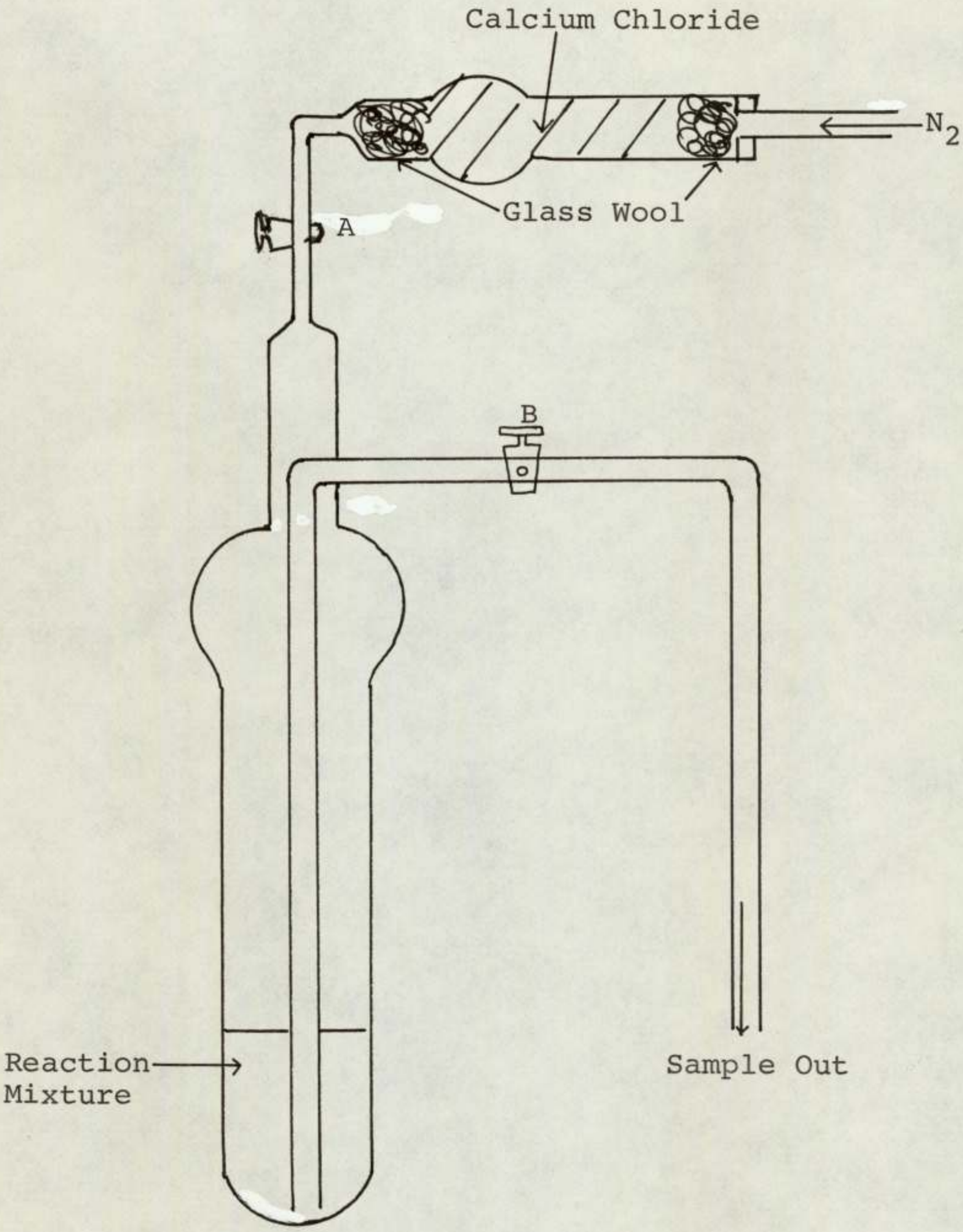


FIGURE IX

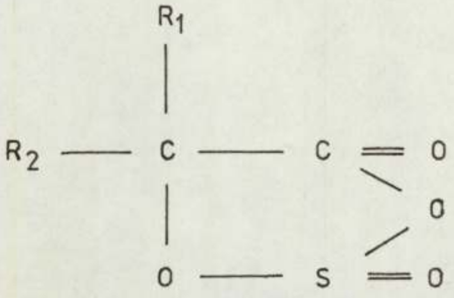
Constant Pressure Polymerisation Vessel

or filtration of the tetrahydrofuran solution.

CHAPTER 3

THE THERMAL DECOMPOSITION OF METHYL, n-ALKYL SUBSTITUTED ANHYDROSULPHITES

The effect of a progressive increase in the chain length of n-alkyl substituents (XIII) ($R^1 = R^2$) on the rate of thermal decomposition of α-hydroxy acid anhydrosulphites has been investigated in some detail[18].



(XIII)

When the C - 5 alkyl groups R_1 , R_2 are methyl or larger it has been demonstrated that the rate of bimolecular hydroxyl attack on the ring becomes insignificant, whereas the rate of unimolecular thermal decomposition of the symmetrically disubstituted ring rises with increasing length of the substituent groups. This effect tends towards a limiting rate when the length of the substituents reachs n-propyl.

The anhydrosulphite ring system has been noted as being particularly unusual in that it becomes thermally less stable as the degree or size of ring substitution increases. This is in contrast to other ring systems which decompose by a unimolecular mechanism. The three membered ring compound 2,2-dimethyl propylene sulphite for example is relatively stable in comparison with the unsubstituted cyclic sulphite. A series of compounds which in a structural sense bear some resemblance to the anhydrosulphites, the 2-thioxo-5-oxazolidones, Figure Ih, do not appear to resemble them in terms of ring stability, but tend to increase in stability with substitution as is described in an earlier chapter.

The peculiar behaviour of the anhydrosulphite series in respect of ring stability has been explained in terms of both the electronic and steric effects of the C - 5 substituents on the ring. In this work, the anhydrosulphite series is further examined in order to ascertain the effect of an increase in length of one of the C - 5 substituents. In this case one of the substituents is maintained as methyl while the other varies from ethyl to n-octyl.

Kinetic Measurements - All measurements were made using the high temperature kinetic apparatus shown in FigureIV , immersed in thermostatted silicon oil baths. Measurement of pressure rise was made using a cathetometer.

RESULTS

In previous studies involving the thermal decomposition of anhydrosulphites, appearance of sulphur dioxide has been shown to coincide with the breakdown of the ring. Assuming that similar processes are involved in the decomposition of methyl,n-alkyl anhydrosulphites, gas evolution studies have been used as the basis for an investigation into patterns of reactivity in this series, although other techniques have also been utilised to provide supporting evidence.

No evidence of catalysis or anticatalysis by sulphur dioxide was indicated as shown by the reproducibility of gas evolution kinetic results at various initial sulphur

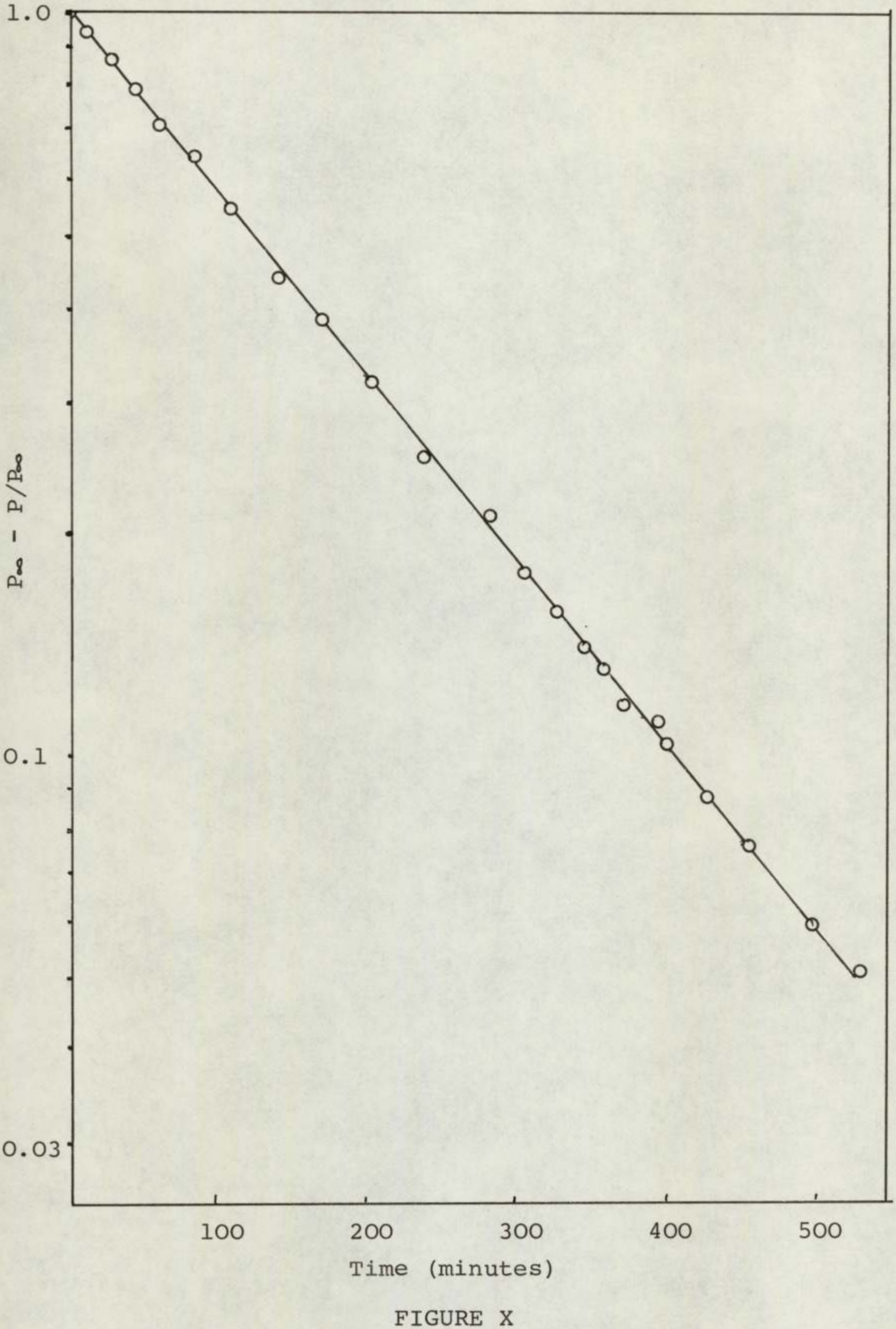


FIGURE X

First order decomposition of MHAS in nitrobenzene at 90°C

$[MHAS]_o = 0.5M$

TABLE II

First order rate constants (k); activation energies (E)- frequency factors (A) and entropies of activation ($\Delta S^{\ddagger}$) for the thermal decomposition of the methyl, n-alkyl anhydrosulphite series at various temperatures

$[\text{anhydrosulphite}]_o = 0.4M$

Temperature °C	$k \times 10^5$ (s^{-1})				
	MEAS	MPAS	MBAS	MHAS	MOAS
70°	0.96	-	-	-	-
80°	2.38[a]	4.00	3.73	-	-
90°	9.70	9.70	10.53	9.33	6.69
100°	-	18.00[b]	29.30	26.70	18.40
110°	-	-	-	53.20	97.50[c]
E (kJ mol^{-1})	125.3	104.9	111.2	110.7	124.3
A (sec^{-1})	1.2×10^{14}	1.8×10^{11}	1.2×10^{12}	7.1×10^{11}	5.3×10^{13}
$\Delta S^{\ddagger}$ (J $deg^{-1} mol^{-1}$)	16.7	37.7	20.9	25.1	8.4

a. at 78.0° b. at 96.0° c. at 114.5o

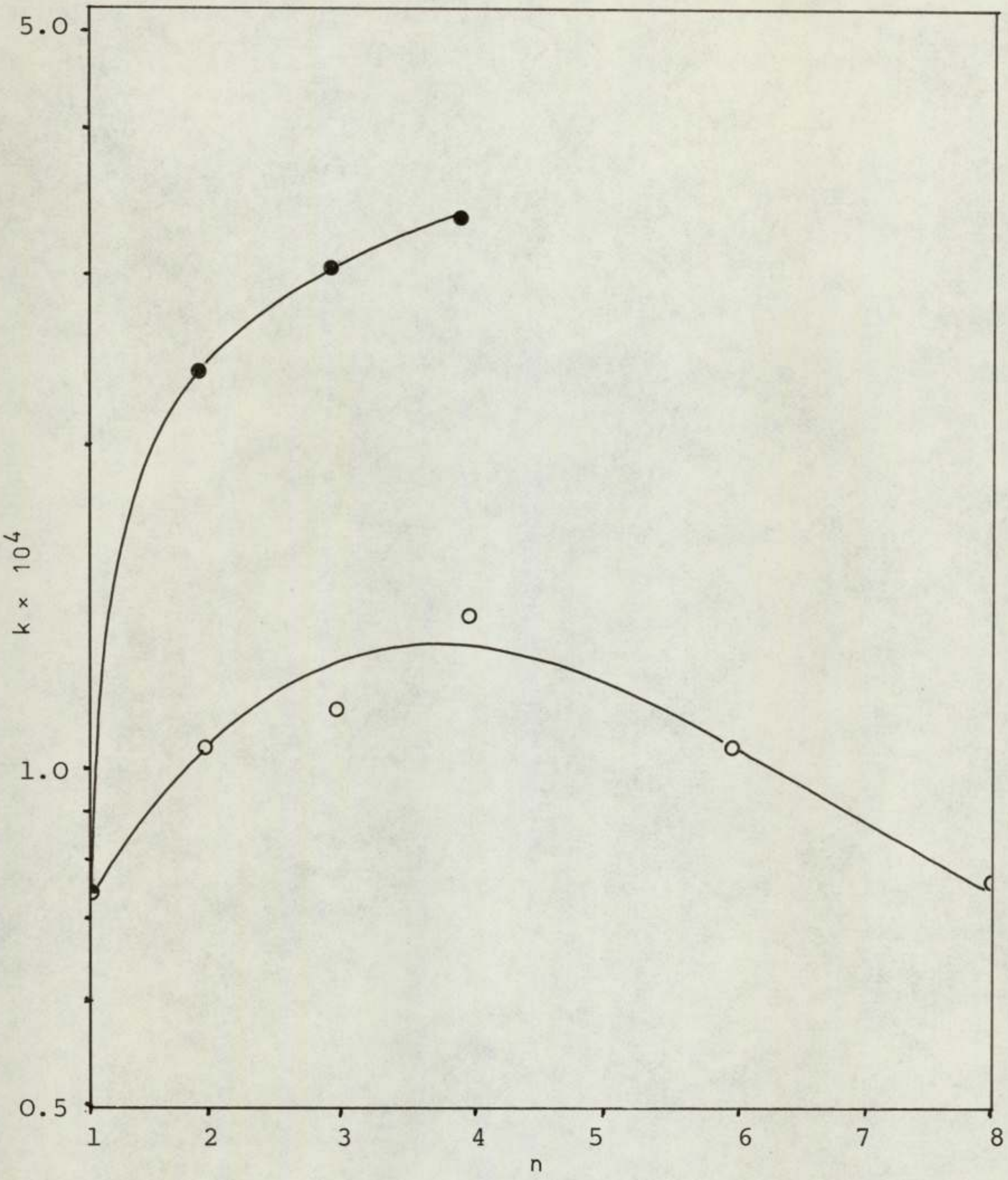


FIGURE XI

Relationship between log k and n for the first order decomposition of symmetrically substituted,●(XIII; $R_1 = R_2 = R$) and unsymmetrically substituted (O, XIII; $R_1 = CH_3$, $R_2 = R$) anhydrosulphites where $R = C_nH_{2n+1}$. Values of k obtained at 90°C in nitrobenzene dioxide pressures. The rate of appearance of product, principally polymer, was also shown to correlate with the decomposition of monomer by the use of infra-red spectroscopy. Figure (X) shows the excellent first order dependance on monomer concentration of MHAS decomposition at 90°C in nitrobenzene and Table II the first order rate constants and derived kinetic paramaters obtained for the methyl, n-alkyl series of anhydrosulphites over the temperature range 80 - 110°C.

It is relevant to compare the trend shown by these results with that observed with the symmetrically di n-alkyl substituted anhydrosulphites. Figure XI shows the results for both series plotted on the same axies. It is apparent that the di n-alkyl series reaches a plateau value greater than the maximum shown by the methyl n-alkyl anhydrosulphites. Additionally, the asymmetrically substituted series shows an inclination towards an increase in relative stability in the higher members.

Distillation of crude anhydrosulphites of this series after removal of chloride containing impurities, gave appreciable quantities of ketone, especially in the higher members. This was amply evidenced by the appearance of a split carbonyl absorption frequency (1720 cm^{-1} - ketone and 1820 cm^{-1} - anhydrosulphite) in the infra-red. The infra-red data was used in order to make a quantitative estimate of the tendency of the methyl, n-alkyl anhydrosulphites to fragment towards ketone formation. The estimate of ketone formed is plotted against the length of the n-alkyl substituent on the anhydrosulphite and is shown in Figure XII. In view of the close boiling points of the anhydrosulphites and their ketonic

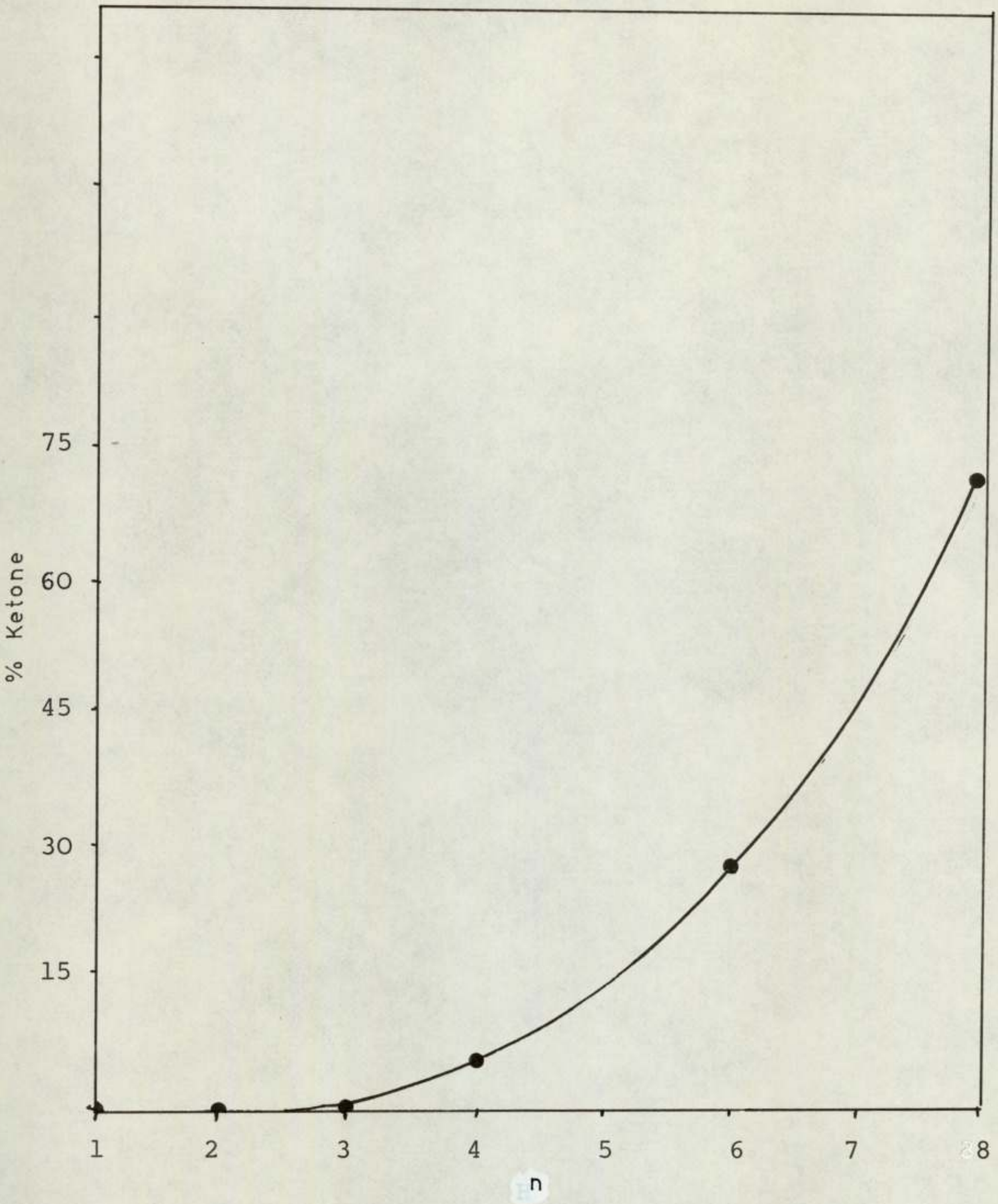


FIGURE XII

Relationship between % ketone formed during distillation at reduced pressure (20mm Hg) and substituent size for unsymmetrically substituted anhydrosulphites (XIII, $R_1 = CH_3$, $R_2 = C_nH_{2n+1}$)

fragments, great care was exercised during the final distillation of the monomers. Samples were removed from monomer used in kinetic work and checked by infra-red for freedom from ketone.

Concentrations of ketone were obtained by g.l.c. study of the completed kinetic runs and comparison with a series of known standards in the same solvent. In the case of the anhydrosulphites studied in this work ketone formation was insignificant under the conditions used for the kinetic studies. With the exception of MOAS where a ketone concentration approaching 10% of total products was found above temperatures of 100°C, the quantity of ketone formed did not exceed 1%.

Effect of Reaction Medium - The effect of hydroxyl groups on the decomposition of the anhydrosulphites was examined. The rate of decomposition of 0.5M solution of anhydrosulphite in nitrobenzene was found to be independent of added hydroxyl group concentration in the range $[OH] = 0.05 - 0.5M$.

A more sensitive test of the susceptibility of anhydrosulphites to bimolecular attack by hydroxy compounds in the manner described earlier, has been shown to be obtained in studies using benzyl alcohol ($[OH] \sim 8.5M$) as solvent. Gas evolution studies in benzyl alcohol showed good first order dependance on monomer concentration and uncomplicated reaction profiles for all of the anhydrosulphites studied. This is illustrated in Figure XIII which, in order to provide a direct comparison with Figure X, relates to the decomposition of MHAS in benzyl alcohol at 90°C. The first order rate constants (k_b) obtained at 90°C in this way are presented in Table III

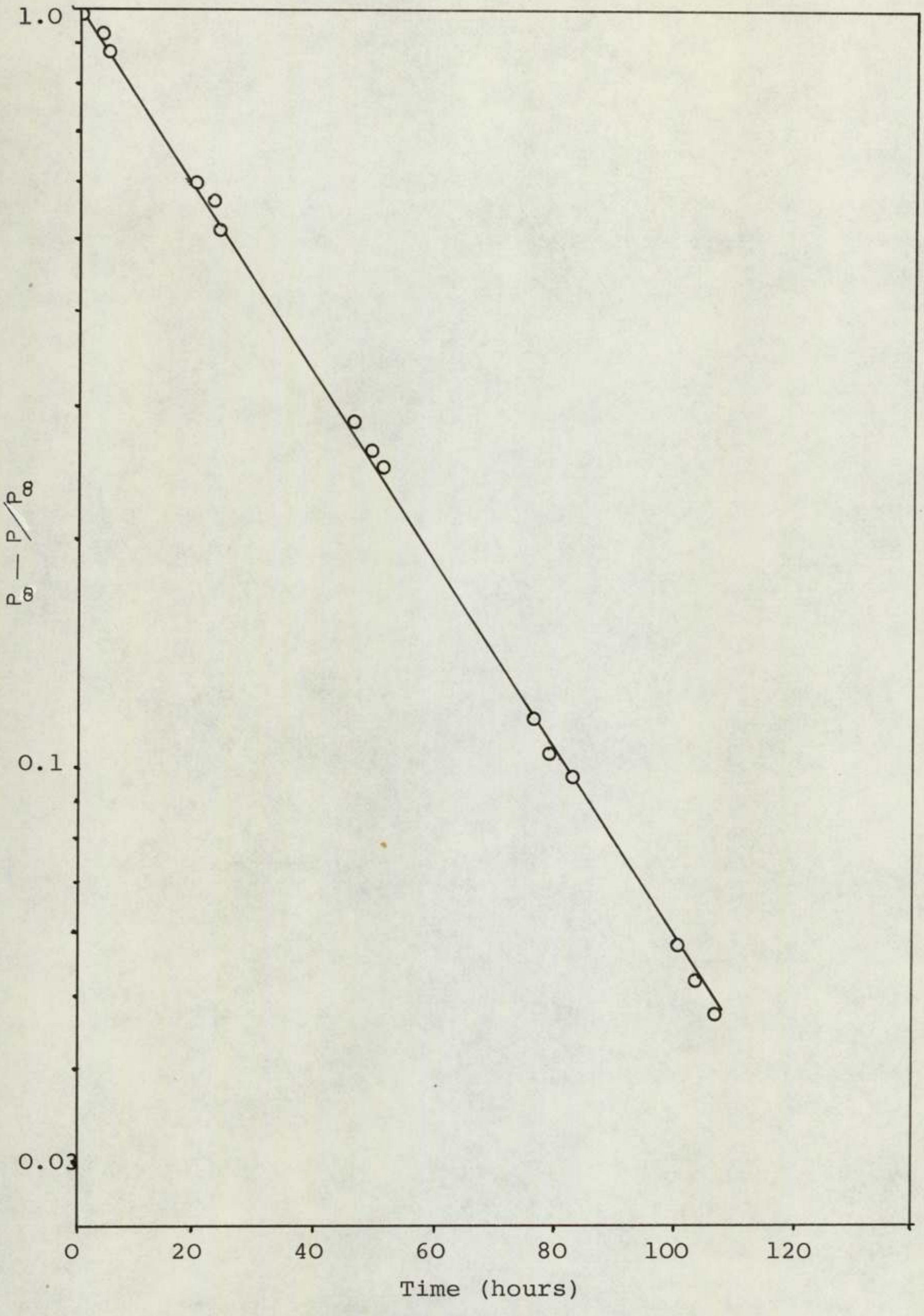


FIGURE XIII

Decomposition of MHAS in benzyl alcohol at 90°C

$[\text{MHAS}]_o = 0.5\text{M}$

together with the value in nitrobenzene (k_n) at the same temperature and the derived ratio ($\frac{k_b}{k_n}$). This ratio has been used to assess the susceptiblity of a given anhydrosulphite to hydroxyl attack and, more particularly, the extent to which bimolecular hydroxyl-initiated propogation will compete with the first order thermal decomposition at that temperature. The bimolecular process is considered to be negiligibly small when the ratio ($\frac{k_b}{k_n}$) is less than 500[16].

TABLE III

First order rate constants (k) for the decomposition of methyl, n-alkyl anhydrosulphites in various solvents at 90°C

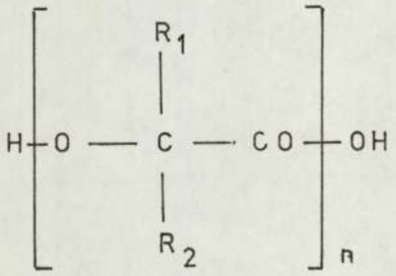
[Anhydrosulphite] = 0.4M

R_2 (structure XIII)	10^5 k (s^{-1})			
	Nitrobenzene	Dekalin	Benzyl Alcohol	$\frac{k_b}{k_n}$
	k_n		k_b	
CH_3	6.5	2.2	5.5	0.8
C_2H_5	9.7	2.3*	3.3	0.3
nC_3H_7	9.7	1.9	0.76	0.08
nC_4H_9	10.5	1.6	0.71	0.07
nC_6H_{13}	9.3	1.4	0.74	0.08

*calculated from other kinetic data

The effect of solvent polarity on thermal decomposition has also been studied. Some variation has been observed amongst the alkyl substituted anhydrosulphites previously studied and a similar but less marked variation has been observed in this work. Within the series the variation is greatest in solvents of high polarity such as nitro benzene and at a minimum with non-polar solvents. Reaction rates are slower in non polar solvents. The first order rate constants relating to the decomposition in decalin (dielectric constant ~ 2.5) at 90°C are included in Table III.

Reaction Products - For reactions in non-hydroxylic solvents the major reaction product was the appropriate poly α-ester.

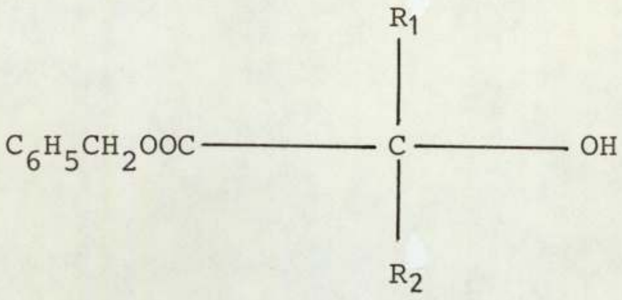


$$H\left[O-\overset{R_1}{\underset{R_2}{C}}-CO\right]_n OH$$

(XIV)

This was isolated from the reaction medium by precipitation at 0°C using an excess of petroleum ether, methanol or ethanol/water mixtures. When washed completely free of solvent and dried the polymers were obtained as white amorphous powders. They were all much more readily soluble in a wide range of organic solvents than their symmetrically substituted counterparts and it was possible to cast them from solution into clear films. These polymers were characterised by the techniques already described and shown to possess hydroxyl and carboxyl end groups which are attributable to the presence of trace moisture during polymerisation.

Reactions carried out in benzyl alcohol were shown to yield products which were identical in nature to those isolated from other anhydrosulphite decompositions in hydroxylic solvents, namely the appropriate benzyl ester (XV) as the major product.



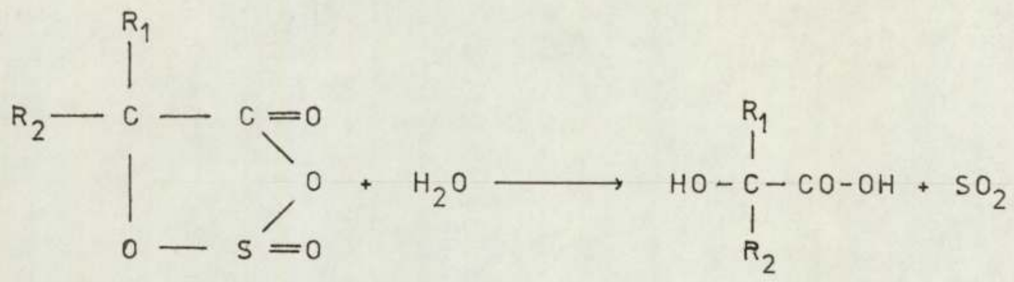
$$C_6H_5CH_2OOC-C(R_1)(R_2)-OH$$

(XV)

In some cases which have been previously referred to traces of ketone were produced in the reaction. These were identified by comparison g.l.c. traces of the reaction products with standards containing the expected ketone. Infra red-spectra showed evidence of a split carbonyl absorption peak and mass spectra which indicated the presence of a parent species corresponding to the ketone in the fragmentation pattern.

DISCUSSION

It is quite apparent from these results that the general kinetic and mechanistic aspects of the thermal decomposition of the methyl, n-alkyl anhydrosulphites follow the general pattern which has been established for other dialkyl substituted anhydrosulphites. The basic scheme is set out below. This consists firstly of reaction of anhydrosulphite with trace moisture to yield the parent α-hydroxy acid, (equation 21), which, together with acid which results from synthesis provides a source of nucleophiles. Secondly, (equation 22)



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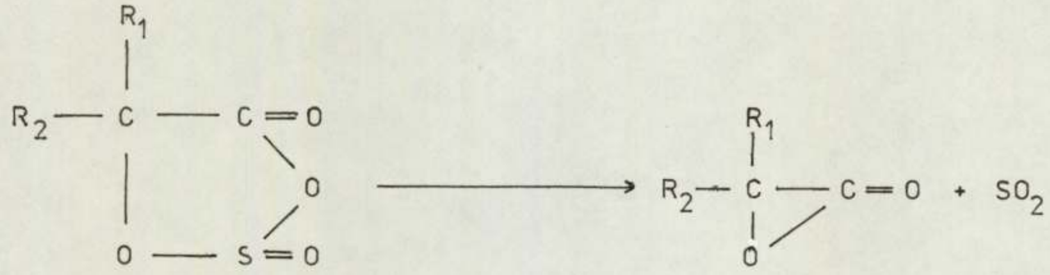

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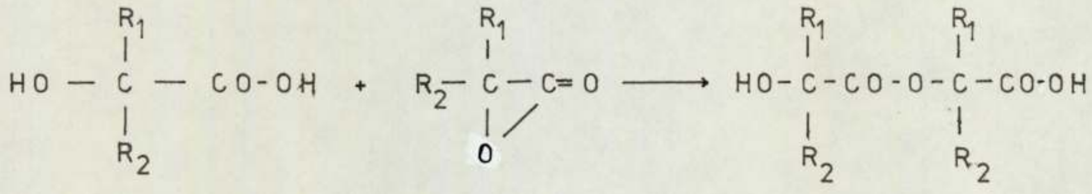

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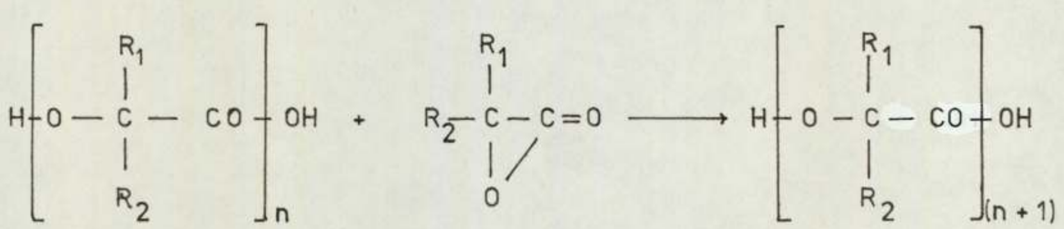

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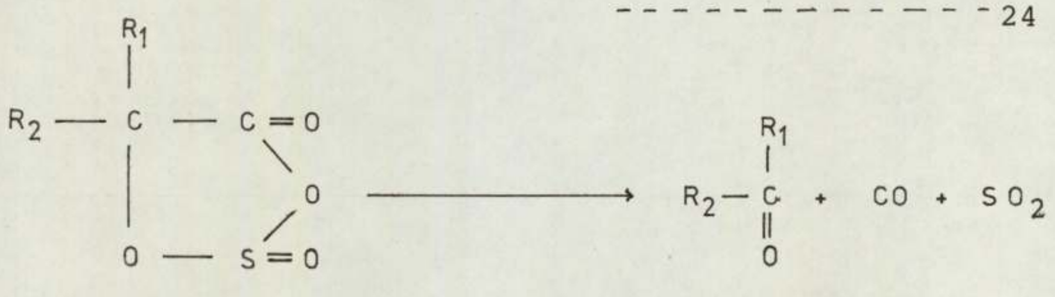

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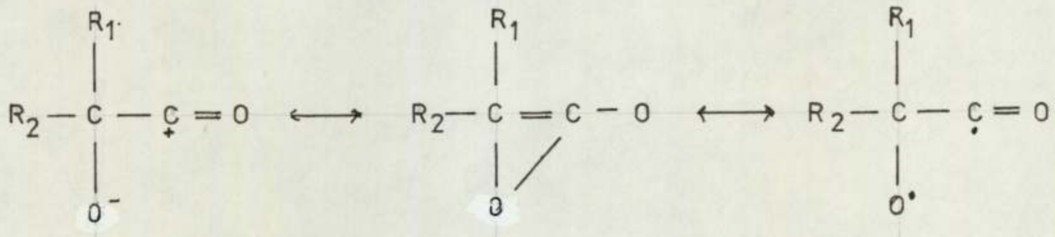
the anhydrosulphite ring breaks down in a unimolecular process under thermal stress to yield a highly reactive intermediate which is shown as the cyclic α-lactone. Thirdly, (equation 23), the intermediate reacts rapidly with any available nucleophile, typically the parent of α-hydroxy acid. The general propogation step involving addition of the α-lactone to the nucleophilic polymer chain end is shown in equation 24. Formation of the α-lactone is, therefore, the rate determining step, and since this step also involves the evolution of sulphur dioxide, gas evolution is a facile method of following the decomposition.

In theory, at least, other forms of the intermediate which is shown on the α-lactone (XVI), are possible. These include a free radical form (XVIa)which has been discounted in other work since the reaction is insensitive to the presence of radical scavengers. And a zwitterionic form (XVIb) which is improbable because of the insensitivity of the reaction rate to solvent polarity. In principle the zwitterionic form may be stabilised by various resonance forms (see Chapter 4) and other work in which a highly substituted α-lactone has been isolated indicates that an energy barrier of several kilocalories exists between the two forms.

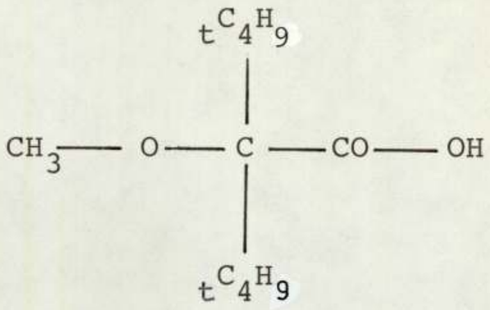


(XVIb) (XVI) (XVIa)

In the field of anhydrosulphite decomposition where the α-lactone is an intermediate with a very limited lifetime the concept of a closed ring with a certain amount of ionic character is most suitable. Those symmetrically substituted anhydrosulphites having fairly large groups at the C - 5 position have been documented as having α-lactone intermediates with rather more polar character. This is supported by work with the methyl, n-alkyl substituted rings where the effect of solvent polarity becomes more marked with those monomers having larger substituents.

The probability of an attack on the ring by a nucleophilic species at the C - 4 carbonyl is not significant, as is shown by the very small $\frac{k_b}{k_n}$ ratios obtained. This process, which is not shown in equations 21 - 24 is effectively excluded on steric grounds when the C - 5 position is disubstituted as in these investigations.

Decomposition in the presence of an excess of benzyl alcohol resulted in attack of the nucleophilic hydroxyl group on the α-lactone and production of the benzyl ester (XV). This process involves attack by the electronegative oxygen of the hydroxyl at the carbonyl of the α-lactone, followed by acyl oxygen scission in the ring and rearrangement of the hydroxylic proton to form a terminal hydroxyl group. In contrast to this, other workers have shown the decomposition of di t-butyl α-lactone in methanol involves attack by the nucleophile at the alkyl substituted carbon followed by scission of the carbon-oxygen bond and the production of a methoxy carboxylic acid (XVII).[42]



$CH_3-O-C(^tC_4H_9)_2-CO-OH$

(XVII)

Although this latter process involves the scission of a carbon-oxygen bond, a process which might be expected to have a higher activation energy than the acyl oxygen scission, presumably the low nucleophilicity of the methanol compared with, for example, benzyl alcohol, coupled with the enhanced electophilicity of the heavily substituted carbon of the ring, favours attack on the carbon rather than the carbonyl. Hence attack of methanol on a highly substituted α-lactone is not comparable to the processes taking place in anhydrosulphite decomposition in this respect.

It is apparent that the limitation in the use of anhydrosulphite decomposition as a synthetic route to poly α-esters is imposed by difficulties of purification rather than any inherent effect of substituent size on polymerisability. Thus, although the competitive fragmentation to ketone (equation 25) does not become dominant in the series studied at the temperatures used for polymerisation, it imposes a severe restriction on the use of distillation as a purification technique.

In addition to the general kinetic pattern of thermal decomposition the actual values of the first-order rate constant (k) and its variation with substituent size presents some interesting features in the methyl, n-alkyl substituted anhydrosulphites. This stems from the ability to synthesise anhydrosulphites with one alkyl group of substantial length, and the role of substituents at the C - 5 position in the ring which is essentially a combination of steric stress, steric hindrance to attacking or leaving groups and electronic effects, all of which may be transmitted to the ring itself.

It has previously been shown that increasing the size of symmetrically introduced di n-alkyl substituents at the C - 5 position decreases the stability of the ring, rapidly at first as the series is ascended, then levelling out to some extent after C_3.[18] Methyl, n-alkyl substitution is shown by these results (Table II) to influence the rate of anhydrosulphite decomposition in essentially the same manner, the results for both series being compared in Figure XI.

However, it is noticeable in the methyl n-alkyl series that as the length of the longest substituent group rises above about C_4, there is a tendency towards greater anhydrosulphite stability. In previous work on anhydrosulphite stability, the rapid increase in the rate of thermal decomposition as the di n-alkyl anhydrosulphite series is ascended has been attributed primarily to the increasing strain transmitted to the ring by the accommodation of increasingly bulky substituents i.e. the Thorp-Ingold effect.[18,69] The slightly greater stability of the methyl n-alkyl series up to C - 5 would agree with this postulate since maintaining one of the substituents as methyl will to some extent reduce problems of accommodation. However, the slight increase in stability noted when the n-alkyl group becomes relatively long would reasonably be associated with a restriction on the leaving group, sulphur dioxide, imposed by a "doubling back" of the long carbon chain over the ring. Courtaulds atomic models demonstrate that an n-octyl group attached at C - 5 can be rotated to such a position so that this type of restriction is entirely feasible. While the number of conformations of an n-octyl carbon chain are large, and the number of these conformations which might affect the leaving group is small, the increase in ring stability for these higher members of the series is correspondingly small. This effect is shown in both nitrobenzene and decalin although the effect is more marked in the more polar solvent.

Further evidence for this comes from n.m.r. studies which show that when C - 5 n-alkyl substituents are not equal, the oxygen substituent bonded to the ring sulphur takes up a conformation away from the larger group.[55] This occurs even with C - 5 ethyl substituents, for example MEAS, and indicates that the presence of such groups influences the conformation of the ring even when the interacting species in question are remote from each other within the accepted limits of covalent radii.

The extent to which steric factors control the stability of anhydrosulphite rings can be compared using steric E_s factors.[70] Figure XIV shows the E_s factor for a number of anhydrosulphites of the symmetrically dialkyl substituted and methyl n-alkyl series plotted against the rate constant (k) for the first order decomposition in nitrobenzene at 90°C. Agreement is reasonable especially since the steric factor as applied to the anhydrosulphite system is a balance of the

KEY FOR FIGURE XIV

anhydrosulphite XIII

	R_1	R_2
A	n-C_4H_9	n-C_4H_9
B	C_3H_7	C_3H_7
C	C_2H_5	C_2H_5
D	CH_3	$_iC_3H_7$
E	CH_3	C_4H_9
F	CH_3	C_6H_{13}
G	CH_3	C_8H_{17}
H	CH_3	CH_3
J	CH_3	H

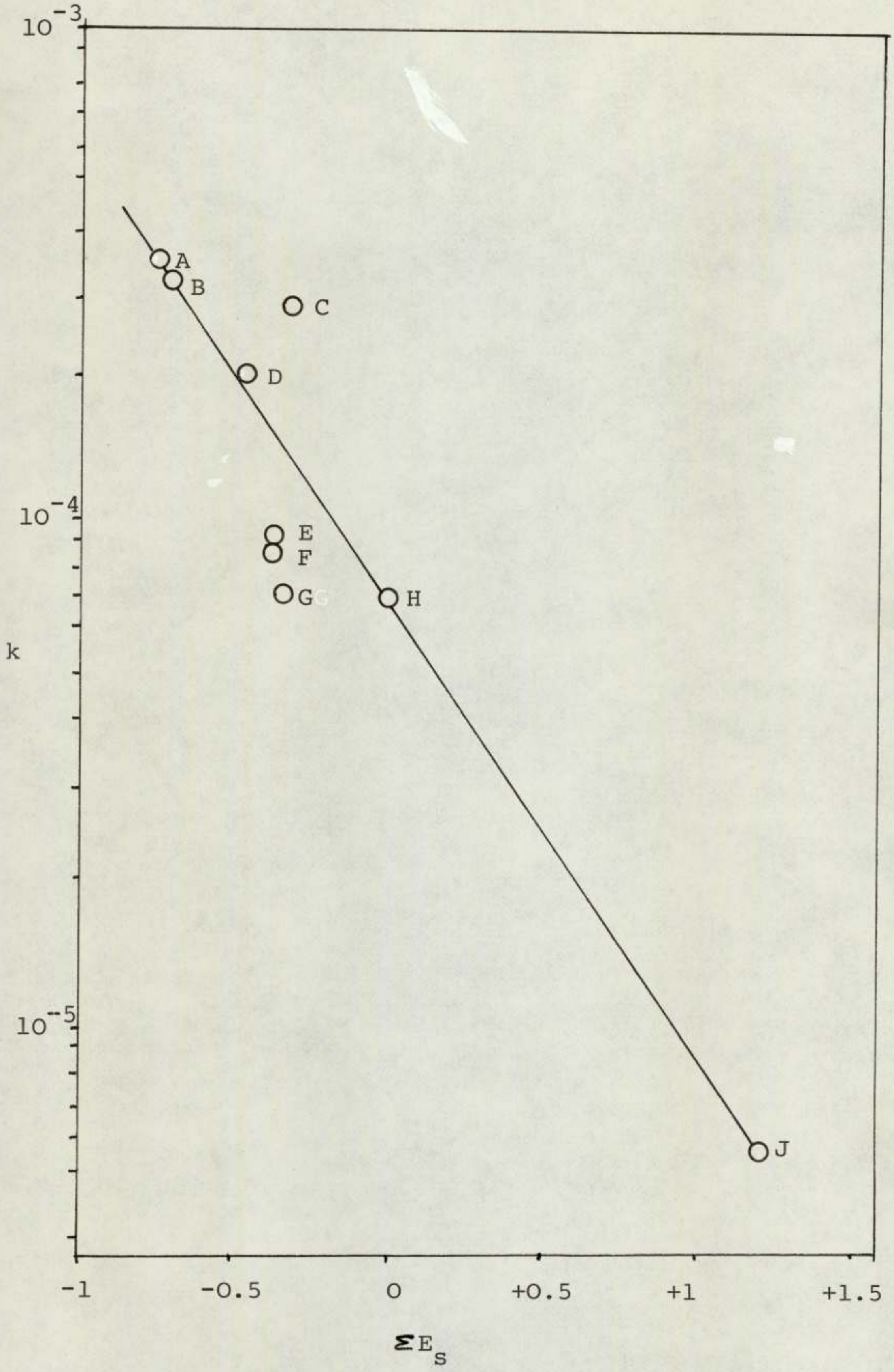


FIGURE XIV

Relationship between steric substituent constant (E_s) and first order rate constant (k) for the decomposition of various anhydrosulphites in nitrobenzene at 90°C.

increasing ring strain due to mutual alkyl group repulsion, and increasing leaving group interference especially with longer alkyl groups. Of these two effects, it would appear that the former is perhaps the more important as best results are obtained with bulky dialkyl substitution. It is useful at this point to compare the chloromethyl substituted anhydrosulphites with their dialkyl substituted analogues.

TABLE IV

First order rate constants (k) for the decomposition of chloromethyl substituted anhydrosulphites in nitrobenzene at 90°C

R_1	R_2	k, nitrobenzene 90°C
CH_3	CH_2Cl	$1.94 \times 10^{-6}\ s^{-1}$
CH_2Cl	CH_2Cl	$2.08 \times 10^{-6}\ s^{-1}$

Although these results are not shown in Figure XIV clearly they do not show good agreement. This demonstrates the effect of electron withdrawing substituents, since on a simple steric basis their size should place them between methyl and ethyl groups.

Attempts have previously been made to assess the extent to which the electronic effects of weakly electron donating substituents affect the purely thermal decomposition of the ring and the sensitivity of this reaction to solvent polarity. The use of Taft σ* substituents have proved helpful in this respect.[18]

The methyl n-alkyl series studied here is suitable for treatment in this way since it contains members which have fairly similar steric characteristcs. The anhydrosulphite (XII) $R_1 = CH_3$, $R_2 = CH_2Cl$ is of particular interest since it lies midway between methyl and ethyl in steric characteristics but it is electronically markedly different. Figure XV shows the relationship between o* and log k for this series with values for the symmetrically di n-alkyl substituted anhydrosulphites included for comparison. This confirms that in the absence of over-riding steric factors (which as shown above can be the major consideration), the electronic properties of the substituent play an important part in determining anhydrosulphite stability. The position of the chloromethyl substituted anhydrosulphite relative to the extended line provides valuable support for this view. The poor agreement obtained with the dichloromethyl substituted anhydrosulphite probably results from problems associated with accommodation of two relatively electro-negitive chloromethyl groups in close proximity to each other. Additionally, the bulkiness of these groups provides further steric repulsion. The net effect of these two factors is a decrease in ring stability which is evidenced by a first-order rate constant higher than that expected from electronic considerations alone.

The anhydrosulphites described in this chapter are of considerable interest in their own right and their preparation in a pure state is of some importance since they provide a potential route to a series of stereoregular poly α-esters. X-ray diffraction studies on the polymers prepared by the thermal techniques described in this chapter indicated that the structures were essentially random. This

KEY FOR FIGURE XV

anhydrosulphite XIII

	R_1	R_2
A	n-C_4H_9	n-C_4H_9
B	C_3H_7	C_3H_7
C	C_2H_5	C_2H_5
D	CH_3	$_iC_3H_7$
E	CH_3	C_2H_5
F	CH_3	C_4H_9
G	CH_3	CH_3
H	H	CH_3
J	CH_3	CH_2Cl
K	CH_2Cl	CH_2Cl

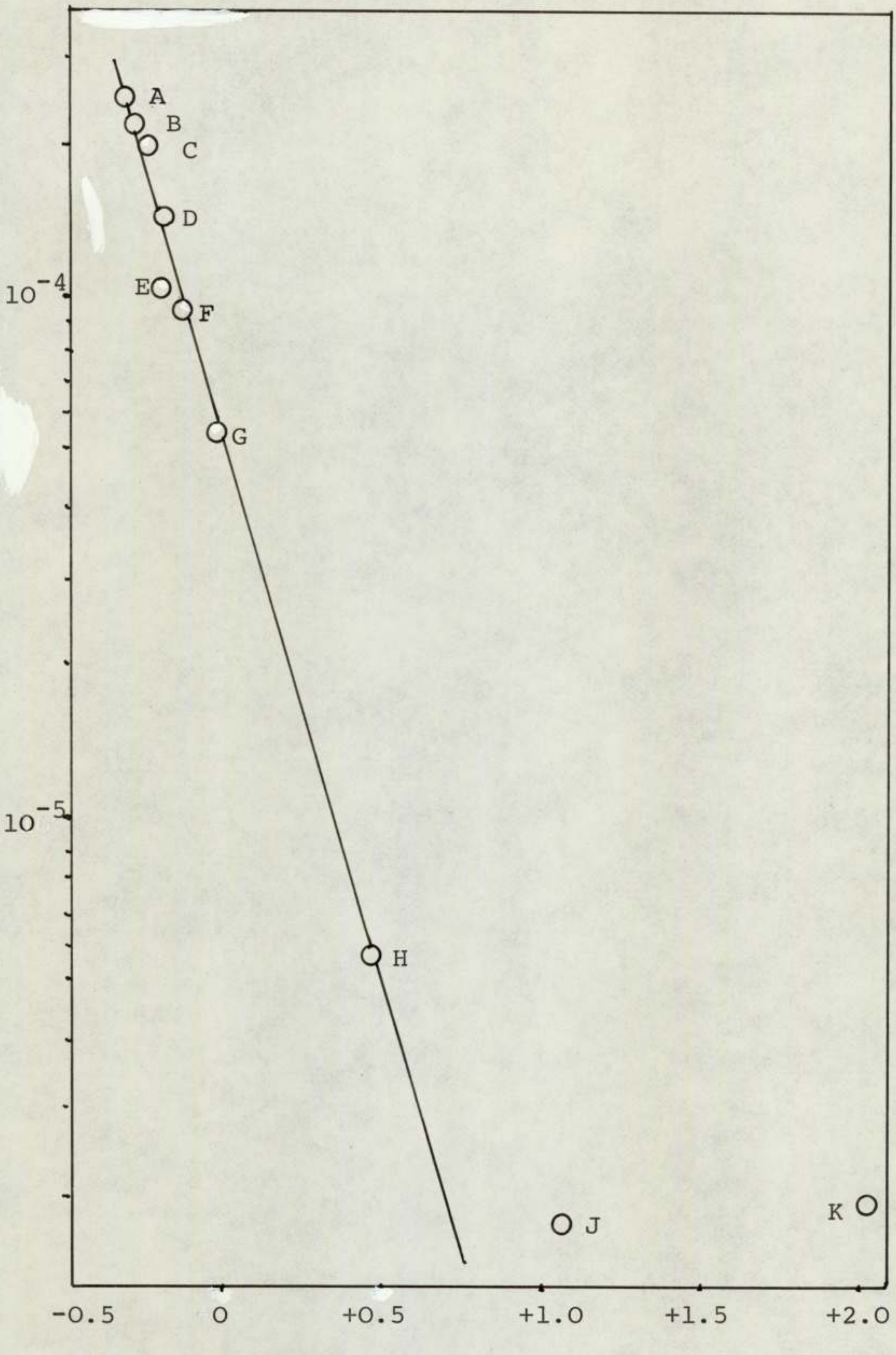
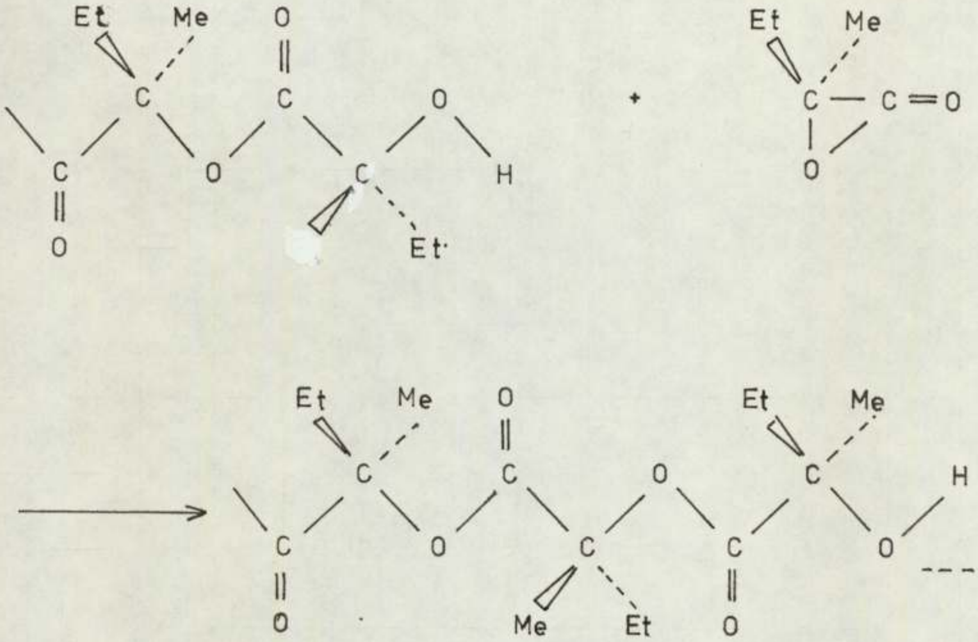


FIGURE XV

Relationship between the first order rate constant (k) and Taft σ* coefficient for the decomposition of various anhydrosulphites in nitrobenzene at 90°C is quite consistent with the small differences in activation energy between syndiotactic and isotactic placement of the α -lactone residue at the growing chain end, and the relatively high temperature ($\sim$ 100°C) used in preparation. Syndiotactic placement in asymmetric anhydrosulphite decomposition results from the addition of a d-α-lactone residue to a chain end which last added an d-residue, or an -l- residue to an l-ended chain. Isotactic placement results from addition of an -l- residue to a -d- ended chain or a -d- residue to an -l-ended chain, equations 26 and 27. This is a direct result of recurrence of the substituted centre every third atomic centre along the polymer backbone.

SYNDIOTACTIC PLACEMENT



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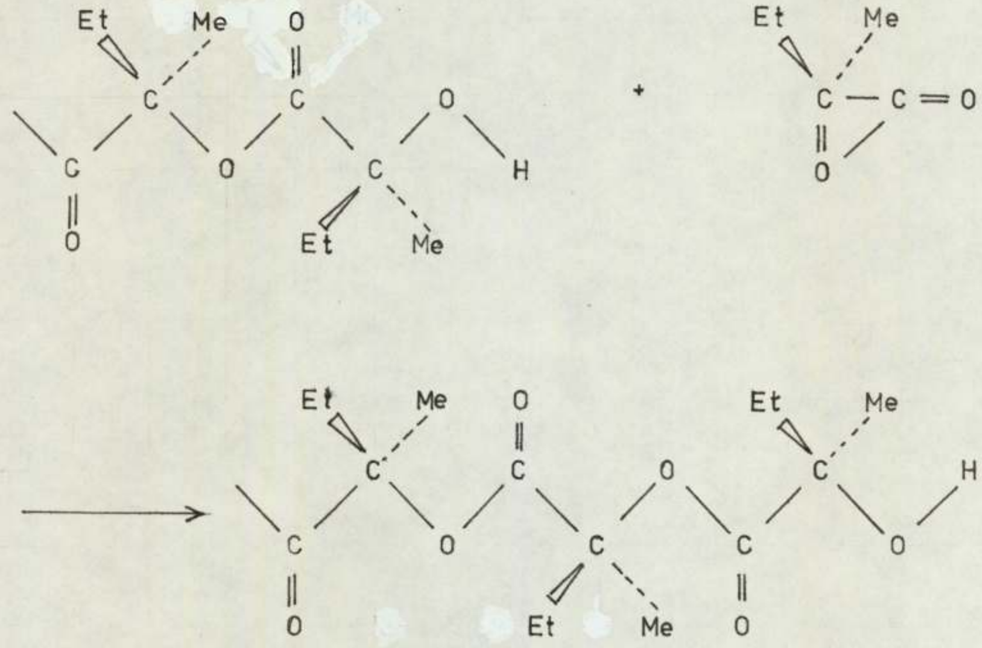
ISOTACTIC PLACEMENT



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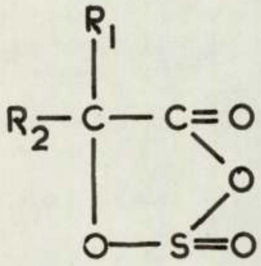
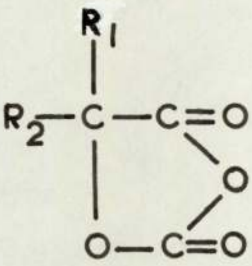
CHAPTER 4

THERMAL DECOMPOSITION OF 5,5-DIBUTYL-1,3-DIOXOLAN-2,4-DIONE

The mode of thermal decomposition of 1,3,2-dioxathiolan-4-one-2-oxides is now well established and the results presented in the previous chapter illustrate the general trend to decreased stability with increased ring substitution. Although 1,3-dioxolan-2,4-diones (XVIII) are structurally similar to the 1,3,2-dioxathiolan-4-one-2-oxides (XIX), their behaviour, as presently understood, is significantly different, thus 5,5-dimethyl 1,3-dioxolan-2,4-dione is a relatively stable solid having a half life at 90°C (nitrobenzene) of over 100 hours in contrast to a value of 3.5 hours for the corresponding 1,3,2-dioxathiolan-4-one-2-oxide.[37]



(XIX)



(XVIII)

It is an obvious extension of the present work to investigate the effect of increased substitution on the stability of the 1,3-dioxolan-2,4-dione ring system. On the basis of work summarised in the previous chapter, introduction of two n-butyl substituents would seem to produce a dramatic effect. It might, therefore, be expected that this increase in degree of substitution would produce markedly different rates of decomposition, although the extent of competitive non-polymer forming fragmentation reactions is a matter for investigation.

In order to clarify the relationship between the more highly substituted anhydrosulphites and anhydrocarboxylates, the 5,5-di n-butyl-1,3-dioxolan-2,4-dione (DBAC) was briefly studied. The investigation was limited to a sufficiently detailed exploration of the rate of decomposition and nature of the products to allow a comparison to be made between this class of compounds and the anhydrosulphites with respect to a general route to the substituted poly α -esters.

RESULTS

The thermal decomposition DBAC was studied in nitrobenzene at various temperatures between 90 and 140°C using the gas evolution techniques described in chapter 2. Pressure of evolved gas was measured as a function of time, and this was used to follow the disappearance of monomer in a manner similar to that used in an earlier chapter for anhydrosulphites.

In the temperature range used, plots of log. monomer concentration versus time showed good straight line behaviour well into the second decade, thus showing the consistent first order behaviour of the process. The profile of Figure XVI is typical of the results obtained in these investigations.

No inhibition or catalysis of the reaction due to evolved gases was found under the conditions used. The overall rate constants derived from the decomposition of DBAC in nitrobenzene are shown in Table V, together with the half life ($t_{\frac{1}{2}}$) for the reaction. A conventional Arrhenius plot, Figure XVII, was used to obtain the activation energy (E), the pre-exponential factor (A), and the entropy of activation ($\Delta S^{\ddagger}$) for

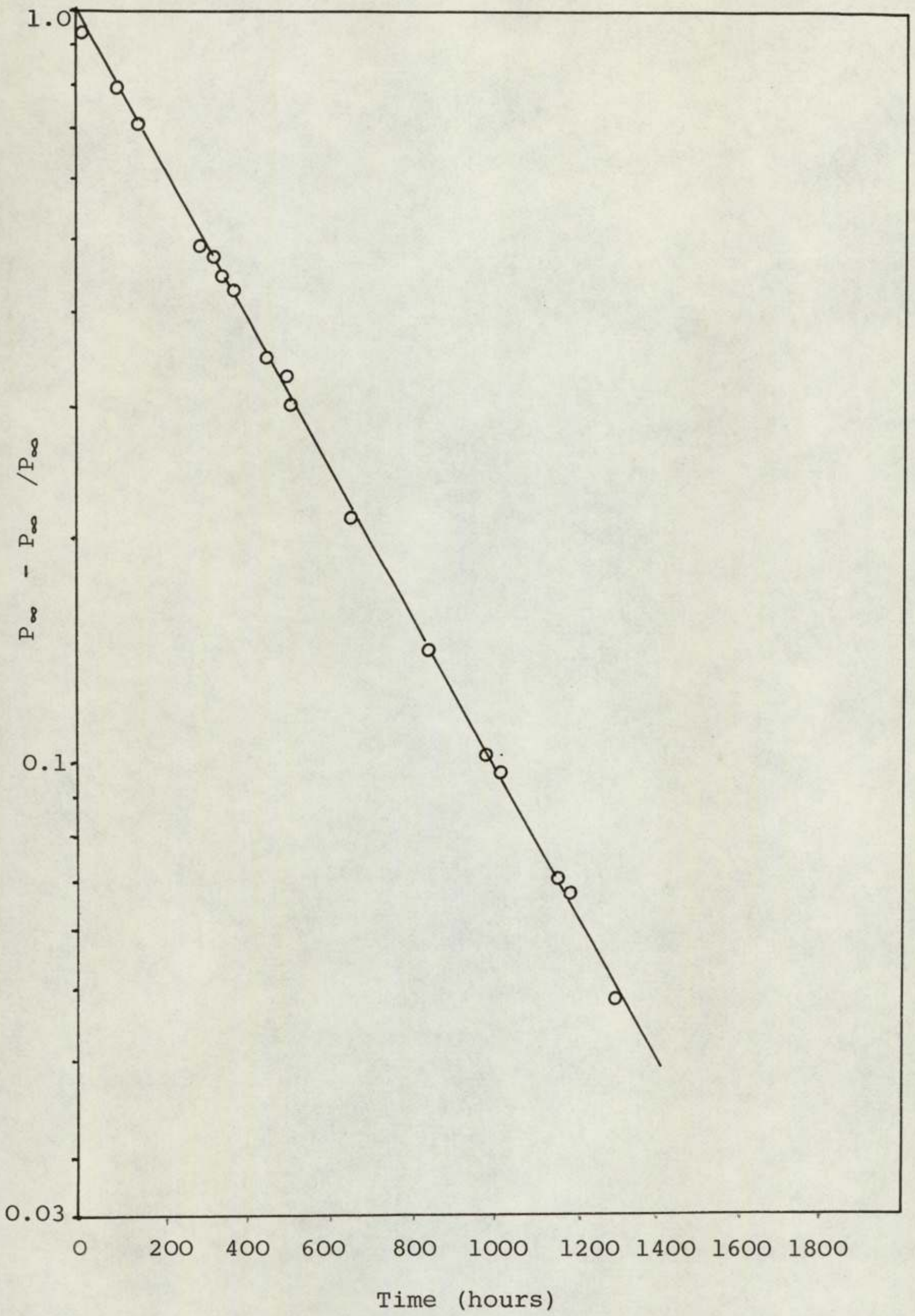


FIGURE XVI

First order decomposition of DBAC in nitrobenzene at 120°C

$[\mathrm{DBAC}]_o = 0.02M$

the reaction. These quantities are also shown in the table.

TABLE V

Overall First-Order Rate Constant, k_1, Activation Energy (E), Pre-exponential factor (A) and Entropy of Activation for the thermal decomposition of DBAC in nitrobenzene

$[DBAC]_0 = 0.020M$

Temperature $^{\circ}C$	$10^7 k_1 (s^{-1})$	$t_{\frac{1}{2}}$ (hours)
97	1.24	1495
120	6.48	300
141	21.4	95
$E (k\ J\ mol^{-1})$	96	
$A\ (sec^{-1})$	6.93×10^6	
$\Delta S^{\ddagger} (J\ K^{-1} mol^{-1})$	39.8	

It was observed, however, that the total pressure rises were greater than could be accounted for by a decomposition process involving carbon dioxide as the only gaseous product. This situation was not entirely unexpected and is analagous to that discussed in chapter 3 for anhydrosulphite decomposition. Examination of the products of completed reactions confirmed the formation of a poly α-ester and carbon dioxide, and, by a combination of g.l.c., infra-red, and mass spectral analysis it was concluded that nonan-5-one and carbon monoxide were the only other products. The good first order profiles of the decomposition indicate that this is again a situation in which two simultaneous first order processes combine to give gas evolution data which is clearly first-order.

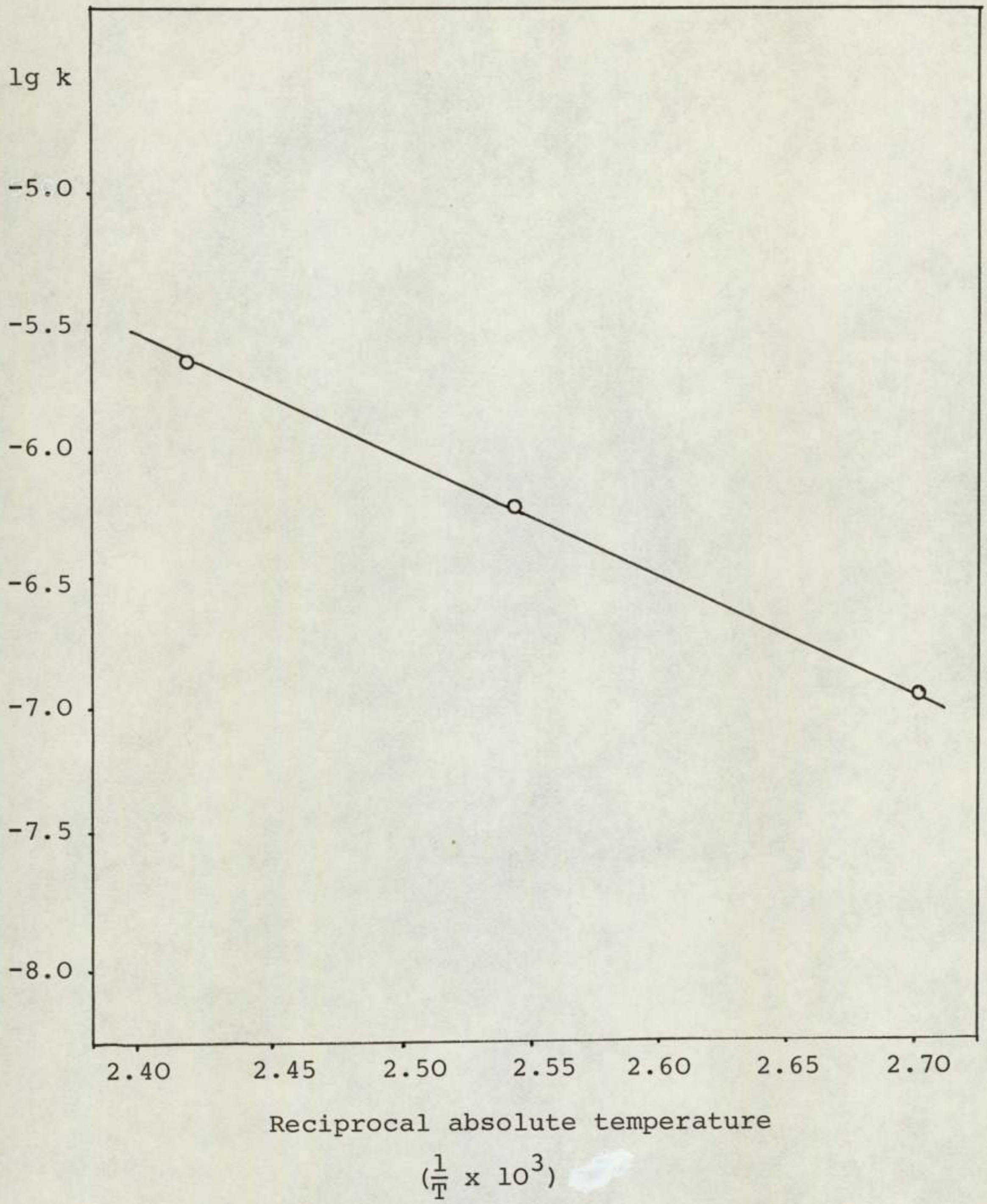


FIGURE XVII

Arrhenius plot for the decomposition of DBAC in nitrobenzene

Comparison of the products of DBAC decomposition in nitrobenzene at various temperatures with standard solutions of nonan-5-one in nitrobenzene using g.l.c., showed that the concentration of ketone present increased with increasing temperature of decomposition. Table VI shows the quantity of nonan-5-one formed expressed as a mole percentage based on polymer plus ketone, at various temperatures. The conditions for g.l.c. analysis are shown below.

TABLE VI

Nonan-5-one formation from the decomposition of DBAC in nitrobenzene at various temperatures

$[\text{DBAC}]_o = 0.02\text{M}$

Temperature ^oC	Mole % Nonan-5-one
97	28.5
120	35.0
141	41.0

Gas-liquid chromatography conditions used in ketone estimation:-

Column :	20M	Carrier	:	Helium
Pressure :	50 psi	Flow rate	:	60 ml min^{-1}
Temperature:	50^{o}C			
Retention times :	Nitrobenzene	17.5 minutes		
	Nonan-5-one	3.3 minutes		

The low molecular weight and small quantity of poly α-ester formed rendered the isolation of the polymeric products difficult, it was not therefore possible to isolate the polymeric products in order to cross check the relative quantity of non-polymeric material formed.

Considerations of the experimental yield of gaseous fragments from this reaction in a vessel of known volume indicated a purity of 94 ± 2% in the DBAC. The appearance of a small absorption peak at 1715 cm^{-1} in the infra-red spectrum of the anhydrocarboxylate indicated that the impurity was the parent acid, the 1715 cm^{-1} absorption corresponding to the principle carbonyl absorption observed in the acid.

DISCUSSION

The overall rate of decomposition of DBAC is rather slower than might have been predicted from studies in the decomposition of the dibutyl substituted anhydrosulphite. Although the rate of decomposition of DBAC in nitrobenzene at 90°C was not examined it may be calculated from the Arrhenius plot Figure XVII. A first order rate constant of 7.5×10^{-8} s^{-1} is obtained. This would at first appear to be unexpected since it means that the rate of decomposition of DBAC is slower than that of dimethyl substituted anhydrocarboxylate,5,5-dimethyl-1,3-dioxolan-2,4-dione.[37] (First order rate constant = $1.0 \times 10^{-7} s^{-1}$ nitrobenzene at 90°C). This contrasts with the behaviour pattern of the structurally similar anhydrosulphites where the rate of decomposition of the dibutyl substituted ring ($k = 26.0 \times 10^{-5} s^{-1}$) is much faster than that of the dimethyl derivative ($k = 6.1 \times 10^{-5} s^{-1}$) at the same temperature.

In the anhydrosulphites this decrease in ring stability is seen as a result of a combination of steric and electronic effects, and it would seem appropriate to apply the same considerations to the anhydrocarboxylates.

The anhydrocarboxylate ring system is, in comparison with the anhydrosulphite ring, relatively strain free. Considerations of bond lengths, bond angles and the use of Courtauld's atomic models show that whereas the anhydrosulphite ring is strained and that only part of the strain is relieved by a "puckering" of the ring, anhydrocarboxylates are planar rings. N.M.R. studies support this view.[55] Thus anhydrosulphites as a group are less stable than the anhydrocarboxylates this is reflected in the first order rate constants for the decomposition of comparable compounds in the two groups, Table VII.

TABLE VII

First order rate constants (k_1) for the decomposition of some ring compounds at 90°Cin nitrobenzene.

Compound abbreviation	Structure (XIX) R_1	R_2	(XVIII) R_1	R_2	First Order Rate Constant x 10^7 (s^{-1})
HBAS	CH_3	CH_3			500
DMAC			CH_3	CH_3	1
DBAS	nC_4H_9	nC_4H_9			2560
DBAC			nC_4H_9	nC_4H_9	0.75

The effect of accommodating two n-butyl groups in the C - 5 position of the anhydrosulphite or anhydrocarboxylate ring is to force a larger angle between the bonds connecting the C - 5 atom to the substituent groups. This results in a compressive effect on the bond angle at this section of the ring system; and is known as the Thorpe-Ingold effect. This effect must transfer an additional strain to the ring and has been cited as part of the reason for the faster rate of decomposition of more highly substituted anhydrosulphites. The same considerations must apply to the anhydrocarboxylate ring although the net effect will probably be reduced since the ring itself is under an appreciably smaller strain. Again, considerations of bond lengths etc. show that there is little more difficulty in accommodating two n-butyl groups at the C - 5 position than in finding room for two methyl groups. Only the free rotation of the n-butyl groups is restricted. It follows, therefore, that the Thorpe-Ingold effect is of limited use in explaining the above variations in rate of decomposition.

Electroniceffects must be an important factor in considerations of ring system stability. Tighe and Blackbourne[18] conclude that the inductive effect may have a significant effect on the rate of anhydrosulphite stability, since a good corrolation is obtained between rate of decomposition of a series of anhydrosulphites under a given set of conditions, and the Taft O* coefficient. However, the change in inductive effect in going from CH_3 to nC_4H_9 is relatively small resulting in only a fourfold change in the first order rate constants in the symmetrically disubtituted anhydrosulphite series. These considerations, when applied to the anhydrocarboxylate ring, which might be expected to possess a rather more symmetrical electron balance,might well prove to be minimal.

A third factor which has been used to explain results obtained with the methyl n-alkyl substituted anhydrosulphites, is the possible effect of the C - 5 substituents on the leaving group (SO_2 for anhydrosulphites, CO_2 for anhydrocarboxylates). When a long n-alkyl chain is present in the C - 5 position it is considered possible to impose a restriction on the leaving group. This effect is also apparent, although to a lesser extent, with a four carbon chain at C - 5. Thus the presence of two n-butyl groups at C - 5 in DBAC could impose a partial restriction on the loss of CO_2, and so result in a slower rate of decomposition. This effect could also be responsible for the slight displacement of DBAS towards a low rate of reaction in the Taft O* plot used to compare the electronic effects of substituents on the rate of decomposition of symmetrically disubstituted anhydrosulphites.

In summary of these effects the rate of anhydrocarboxylate decomposition may, potentially, be increased by:

1. An increase in size of the group at C - 5,
2. An increase in the electronic contribution from these groups,

and decreased by:

3. The leaving group restriction.

The overall effect would appear from the results obtained to be almost zero, a small reduction in rate being apparent indicating that (3) above is most effective for DBAC.

The rate of decomposition of DBAC is appreciably slower than any of the phenyl substituted anhydrocarboxylates[55]; for example in nitrobenzene at 102°C

DBAC $k_1 = 1.78 \times 10^{-7}$

Mandelic acid anhydrocarboxylate $k_1 = 5.0 \times 10^{-7} s^{-1}$

(XVIII $k_1 = H$, $R_2 = C_6H_5$)

Atrolactic acid anhydrocarboxylate $k_1 = 1.5 \times 10^{-6} s^{-1}$

(XVIII $R_1 = CH_3$, $R_2 = C_6H_5$)

This must be considered both in terms of steric and electronic effects. The electronic effects will be difficult to assess but the steric effect of accommodating a relatively bulky phenyl group in the C - 5 position, especially with a methyl group as well, are reflected in the faster rate of decomposition of the phenyl substituted anhydrocarboxylates. This further supports the hypothesis that although n-butyl groups are relatively long, they are not in steric terms bulky, and will not distort the ring structure to any great extent.

Smith[55] has noted that traces of parent α-hydroxy acid enhance the rate of decomposition of mandelic acid anhydrocarboxylate (MAAC, (XVIII), $R_1 = H$, $R_2 = C_6H_5$). The first order rate plots for the decomposition of this anhydrocarboxylate in the presence of trace acid shows a slow initial rate which is attributed to pure thermal scission of the ring, followed by a faster rate the magnitude of which appears to depend on the initial acid concentration. Excess acid gave rise to a comparatively fast first-order decomposition. In contrast to this, the profile of the rate of decomposition of DBAC was always a good straight line, and although a small amount of parent acid was known to be present no enhancement of rate was apparent.

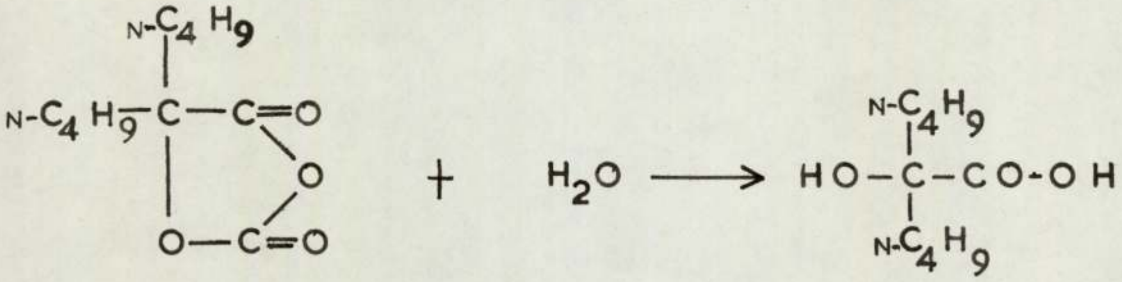
The effect of concentration of monomer on the rate of reaction was not investigated but since the effect of change in concentration of monomer in a given solvent has been shown to have no effect on thermal rate of decomposition of either phenyl substituted anhydrocarboxylates or the dimethyl substituted anhydrocarboxylate, or on the rate of decomposition of the closely related anhydrosulphites, it would seem reasonable to presume that DBAC decomposition is not affected by monomer concentration.

A complete study of the effect of chlorine containing impurities was not carried out since the quantity of chlorine present in the anhydrocarboxylate as measured by potentiometric titration was negligible ($\leq 0.1\%$). The presence of chlorine containing impurities is, therefore, unlikely to be a contributory factor in the very low molecular weight of the product polymer. V.P.O. measurement of the product of decomposition of DBAC at 120°C gave $\bar{M}n = 1200$ which corresponds to poly DBAC at DP of about 7. It would appear much more probable that the presence of parent acid is responsible since this has been shown to have an adverse effect on the molecular weight of poly-α-ester derived from anhydrosulphites although no effect on rate of reaction.

The presence of nonan-5-one among the decomposition products of DBAC indicates a mode of decomposition which is now becoming well established in the reactions of five membered ring compounds derived from α-hydroxy acids. The presence of a ketonic species derived from the fragmentation of the ring has been noted in the decomposition of most anhydrosulphites having large groups situated at the C - 5 position,[18] in addition this competitive non-polymer forming reaction has been well studied where the substituent groups are both chloromethyl[46] and when the substituent is a cyclohexyl ring.[19] The formation of a ketone has been noted during the decomposition of dimethyl and diphenyl substituted anhydrocarboxylates.[37,55]

It would, therefore, seem reasonable to propose a reaction mechanism for DBAC decomposition which is similar to that shown in an earlier chapter for methyl, n-butyl anhydrosulphite:-

Presence of parent ∝-hydroxy acid may be due to the method of synthesis of DBAC or by reaction of DBAC with trace moisture:



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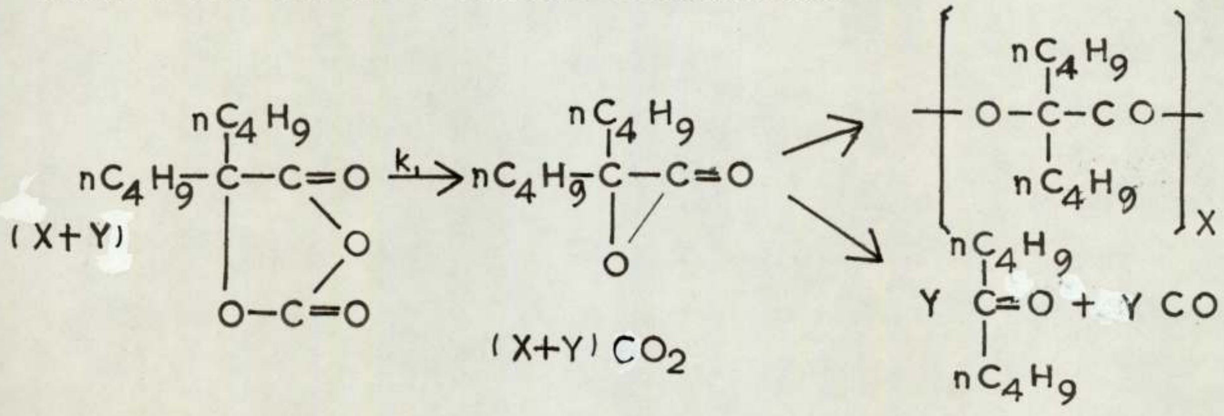
Thermal decomposition of the ring leads to polymer or nonan-5-one via an ∝-lactone intermediate



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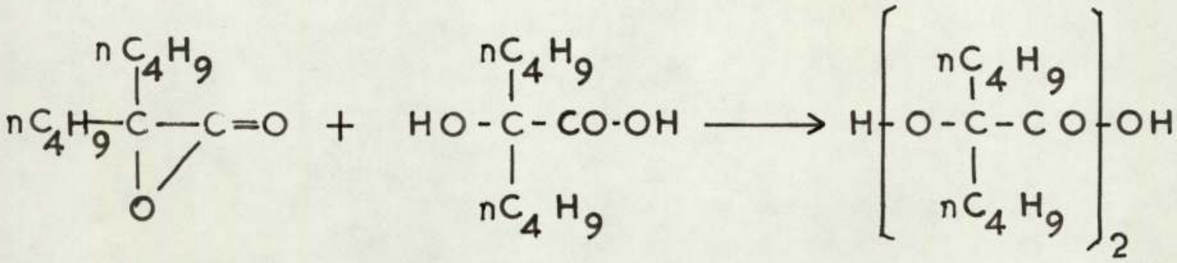
The mechanism of polymer formation is via rapid reaction of the α-lactone with the terminal hydroxy group of α-hydroxy acid



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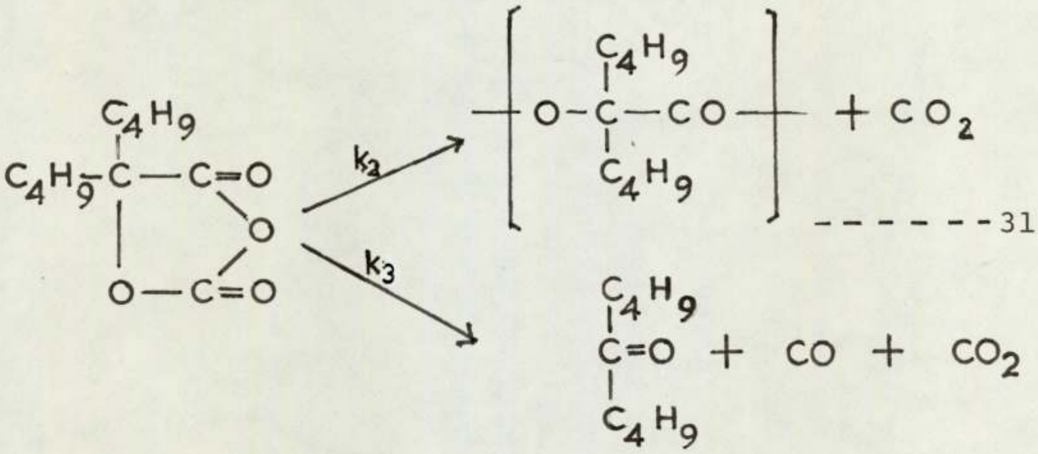
The regeneration of the terminal hydroxyl group enables further reaction with α-lactone. The rate determining step is k_1, formation of the α-lactone which then reacts rapidly to give polymer or ketone.

The overall rate constant k_1 describes the rate of disappearance of DBAC via two routes. Since the overall rate is first order, both of these routes can be described by first order rate constants:-



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where k_2, k_3 are the partial rate constants for the decomposition.

The magnitude of these partial rate constants can be determined, since, for overall first order processes:

$$-\frac{d[M]}{dt} = \frac{d[P]}{dt} + \frac{d[K]}{dt} \quad \ldots\ldots\ldots\ldots\ldots 32$$

where $[M]$, $[P]$, $[K]$ are monomer, polymer and ketone concentrations respectively.

Now:

$$\frac{d[P]}{dt} = k_2 [M] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 33$$

$$\frac{d[K]}{dt} = k_3 [M] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 34$$

Therefore,

$$-\frac{d[M]}{dt} = (k_2 + k_3) [M] \quad \ldots\ldots\ldots\ldots\ldots 35$$

Hence

$$k_2 + k_3 = k_1$$

Further, if the expressions for the appearance of polymer and ketone in equations (33) and (34) are differentiated with respect to time and then combined, then the relative concentrations of ketone and polymer at any given time can be related to the respective rate constants by equation.

$$\frac{[k]}{[P]} = \frac{k_3}{k_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 36$$

For the reaction scheme shown above

$$[M]_o = [P]_\infty + [K]_\infty \quad \ldots\ldots\ldots\ldots 37$$

where

$[M]_o$ = initial monomer concentration

$[P]_\infty$, $[K]_\infty$ = final polymer and ketone concentrations respectively.

$[K]_\infty$ has been determined and is shown for various temperatures in Table VI. $[M]_o$ is known and hence $[P]_\infty$ can be calculated and thus values for k_2 and k_3 determined.

Table VIII shows the individual rate constants for the polymer and ketone forming reactions together with activation energies (E), pre-exponential factors (A) and entropies of activation which were calculated from the Arrhenius plot (Figure XVIII).

TABLE VIII

First Order Rate Constants k_2, k_3, Activation Energies (E), Pre-exponential Factors (A) and Entropies of Activation ($\Delta S^{\ddagger}$) for the formation of ketone and polymer by the thermal decomposition of DBAC in nitrobenzene

$[DBAC]_o$ = 0.02M

Temperature ^oC	$10^7 k_2$ (s^{-1})	$10^7 k_3$ (s^{-1})
97	0.81	0.35
120	4.21	2.27
141	12.60	8.80
E (kJ mol^{-1})	84.3	105
A (s^{-1})	6.30×10^4	1.00×10^7
$\Delta S^{\ddagger}$ (J $K^{-1} mol^{-1}$)	43.5	32.6

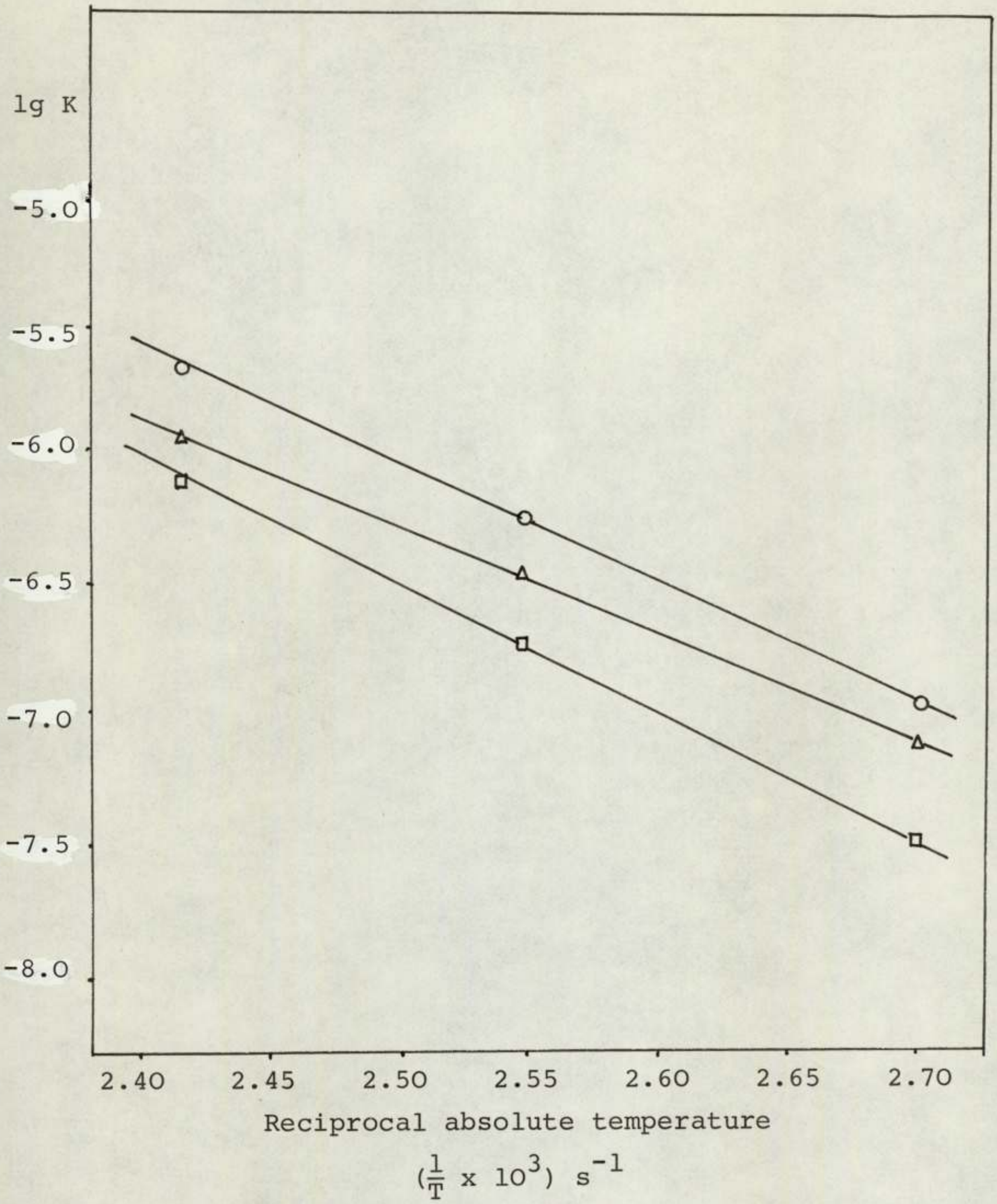


FIGURE XVIII

Arrhenius plots for the competing decomposition reactions of DBAC described by the rate constants k_1, k_2 and k_3 (equation 31)

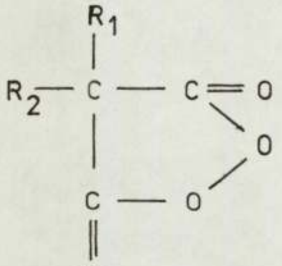
○ $(k_2 + k_3) = k_1$

△ k_2

□ k_3

The activation energies involved in the decomposition of DBAC are of the order required to secure the scission of a covalent bond in a slightly strained ring system. The energies are, however, rather lower than those recorded in the decomposition of the rather more strained anhydrosulphite rings and this in itself is unexpected and may indicate the presence of a more pronounced charge distribution in the transition state. This is further indicated by the relatively low frequency factor A, and fairly high entropy of activation $\Delta S^{\ddagger}$ of the transition state.

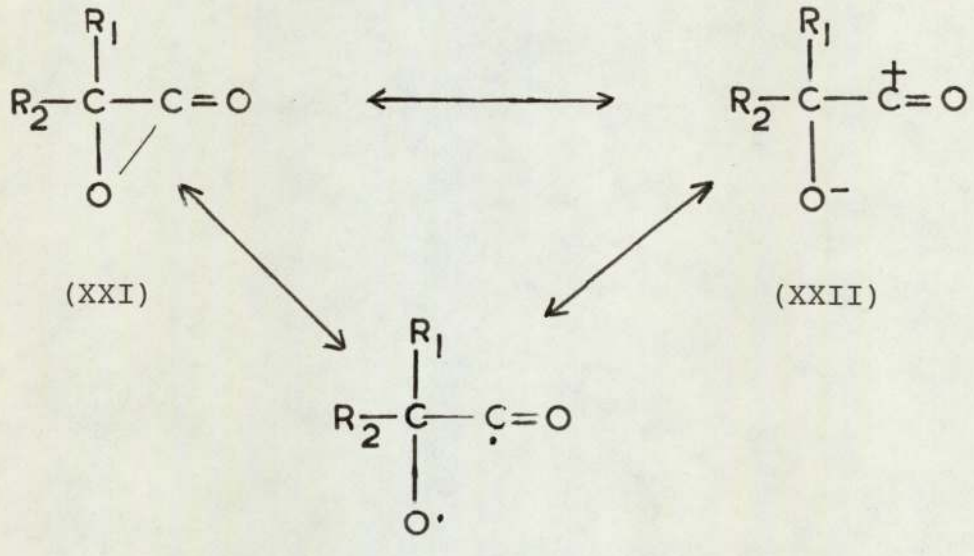
The existence of α-lactones as intermediates has been postulated in many reactions, some of the more notable cases being the hydrolysis of optically active α-bromoproprionic acid[71], nucleophilic substitution and various free radical substitution reactions[73,74]. While many earlier workers postulate the α-lactone as a convenient if hypothetical intermediate in their reactions more recent studies have been concerned with the confirmation of their existence by trapping techniques and product analysis. In particular, the photodecarboxylation of a malonyl peroxide (XX) has been shown to result in the formation of poly α-esters with ketone as one of the byproducts. Although in this case investigations were carried out with di-n-butyl malonyl peroxide the authors concluded that electronic and/or steric stabilisation would be required to stabilise an α-lactone.[42]



(XX)

Irradiation of 4,4-di-n-butyl-1,2-dioxolane-3,5-dione at 77^{o}K, however, has been shown to yield an α-lactone as a primary product[76]. This compound was stable at the temperature used and was characterised by various techniques. On warming above 173^{o}K the α-lactone reacted to yield the appropriate poly α-ester together with some nonan-5-one, thus the decomposition products of di-n-butyl acetolactone are identical to those isolated from DBAC decomposition. The same workers have found that less highly substituted α-lactones tend to produce ketone and carbon monoxide rather than polymer on warming.

There exists in the α-lactone ring system, the possibility of various isomeric forms:-



(XXI)

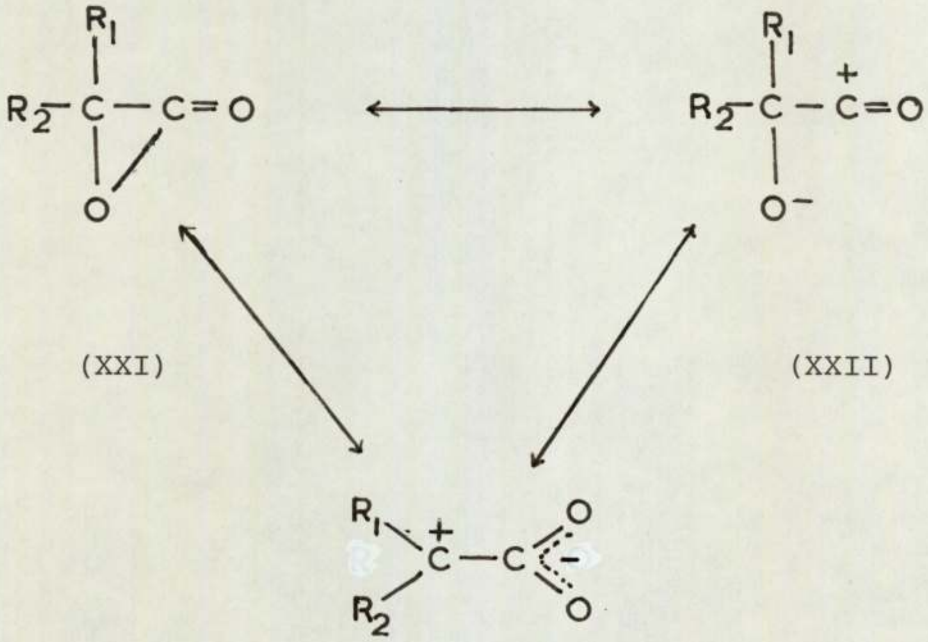
(XXII)

(XXIII)

Previously the extreme polar and radical forms of the α-lactone have been discounted. The radical form because of the inability of an anhydrosulphite to alter the rate of styrene polymerisation, and the inefficiency of a radical scavenger in polymerisation of anhydrosulphites where the α-lactone is again cited as an intermediate. The extreme dipolar form was discounted because the decompositions showed a marked lack of sensitivity to solvent polarity.

However, other work with dibutyl acetolactone indicates that although the closed α-lactone is the predominant form at low temperatures, the open zwitterionic form predominates at temperatures above 100°K.[76] Even the highly stericly hindered di t-butyl acetolactone is apparently in the ionic form above -30°C. Evidence for this comes from the position of the carbonyl absorption frequency in the infra-red.

The pertinant forms of the α-lactone are, therefore:


(XXI)

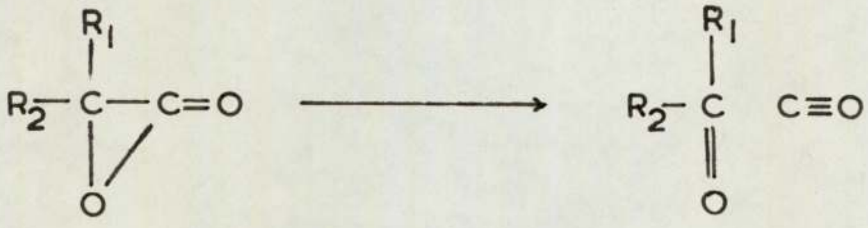
(XXII)

(XXIV)

Now it would appear that the closed ring structure of dibutyl acetolactone (XXI) is improbable at the temperatures used for DBAC decomposition, and the zwitterion structure (XII) or (XXIV) predominates. This situation will obviously lead to very rapid polyester formation.

It has been shown, however, in the mass spectral data of the anhydrosulphites substituted with dimethyl, diethyl, dipropyl and dibutyl groups at the C - 5 position, the incidence of ∝-lactone increases with increasing substitution.[58] It is, therefore, reasonable to suppose that more highly substituted ∝-lactones are more stable. This is supported by the evidence cited earlier and would be a consequence of the closing of the O - C - C bond angle by bulky substituent groups, and the increasing difficulty of charge dispersal at the substituted carbon in order to favour the ionic form of the lactone (XXIV).

Since the various isomeric forms of the ∝-lactone are in resonance, the proportion of ∝-lactone in the closed ring will be increased in dibutyl acetolactone as opposed to, for example, dimethyl acetolactone. It is easier to envisage formation of a ketone (XXXV) and carbon monoxide from the closed ring lactone than the ionic form:-

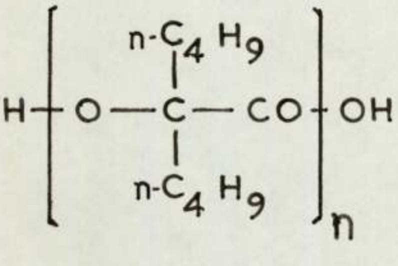


(XXI) (XXV)

This leads to the situation where the more bulky substituent groups on either anhydrosulphites or anhydrocarboxylates lead to more stable ring form α-lactones species and hence to increased opportunity for ketone formation. This is in accordance with the observed facts. This does not, however, extend to the phenyl substituted α-lactone, since in this situation there occurs the possibility of delocalisation of the positive charge in (XXIV), the zwitterion form of the α-lactone is therefore favoured.

The kinetic parameters shown in Table VIII indicate that the rate of formation of ketone increases rather faster than the rate of formation of polymer. Both rates are relatively slow in comparison with other ring decompositions of this type. In order to obtain a reasonable rate of polymerisation an increased temperature is required, but at temperatures above 170°C, extension of Figure XXIV shows that ketone formation will be favoured over polymer formation.

These results indicate that the thermal decomposition of DBAC is not a good route to the di-n-butylglycollic acid polyester (XXVI)



$$H\left[O-\overset{n\text{-}C_4H_9}{\underset{n\text{-}C_4H_9}{C}}-CO\right]_n OH$$

(XXVI)

The rate of polymer formation is slow at lower temperatures and effectively opposed by a non polymer forming reaction at higher temperatures. The di-tert-butyl glycollic acid polyester has been shown to have low thermal stability in comparison with less highly substituted poly-α-esters. A similar lack of thermal stability could also extend to the di-n-butyl substituted polymer and be responsible for some of the unidentified low molecular weight products noted when DBAC had been thermally decomposed.

CHAPTER 5

PRELIMINARY STUDIES IN THE INITIATED DECOMPOSITION OF ANHYDROSULPHITES

The thermal decomposition of α-hydroxy acid anhydrosulphites and anhydrocarboxylates has drawn considerable attention. Polymeric products obtained have a molecular weight range from several thousand to more than one hundred thousand, the actual weight attained depending on monomer purity, conditions of polymerisation, and particular monomer used. The initiated decomposition of these compounds induce by catalytic quantities of materials and at temperatures below those necessary for thermal polymerisation has, however, recieved relatively little attention, although phenyl substituted anhydrocarboxylates in presence of tertiary bases such as pyridine and its derivatives have been shown to give polymeric products at relatively low temperatures.[55]

The structurally similar N-carbonic anhydrides of α-amino acids (N.C.A.s) can be polymerised at room temperatures by primary, secondary and tertiary amines, strong bases and metal salts. The mechanism of these reactions has been extensively reviewed.[12]

Primary and secondary amines are known to react with anhydrosulphites but amides, not polyesters are the products. Tertiary amines (for example pyridine) and tertiary amides (for example N,N-dimethyl formamide) have been reported to catalyse the polymerisation of α-hydroxy isobutyric and α-hydroxy-chloroisobutyic acid anhydrosulphites at room temperature. Similarly, catalytic quantities of diethyl zinc/water, n-butyl lithium and sodium methoxide have been shown to decompose anhydrosulphites to give polymeric products, but in none of these cases have detailed kinetic studies been carried out.[49]

Since the low temperature polymerisation of monomers such as styrene and vinyl chloride has been shown to an enhanced degree of stereoregularity, it is of some considerable interest to prepare poly-α-esters at relatively low temperatures in order to evaluate any change in their physical properties which might be produced by an increase in polymer stereoregularity. In this context a brief investigation was made into the effectiveness of certain types of catalyst which are normally expected to operate in a particular way; anionic, cationic etc.

RESULTS

The initial investigations were carried out on the basis of observed rapidity of reaction and the nature of the products. All reactions were carried out under vacuum as described earlier (Chapter 2), the reaction mixtures were left in a thermostatted bath for a given time after which any useful polymer producing reaction might have been expected to yield an appreciable quantity of product.

Where solid products precipitated out these were separated and washed with ether. Other products were precipitated from solution using ether, petroleum ether or methanol. Table IX shows the catalyst/solvent systems used and the nature of the products obtained.

The reactions which resulted in non-polymeric products were all observed to proceed rapidly when the catalyst system was brought into contact with the anhydrosulphite. This initial reaction was complete within a few minutes and was

TABLE IX

Decomposition of α-ethyl-α-hydroxy butyric acid anhydrosulphite (DEAS) at 25°C catalysed by various systems

$[\mathrm{DEAS}]_o = 0.6M$

Solvent	Catalyst	$m\ l^{-1}$	Polym. time hours	Yield %	Nature of Products
Dekalin	$BF_3(Et_2O)_2$	0.19	72	5	Non polymeric
Dekalin	$TiCl_4/AlEt_3$ ⓐ	0.025	72	15	Non polymeric metal complex
Nitrobenzene	NaOMe ⓐ	0.10	72	20	Polyester
Nitrobenzene	$AlEt_3$	0.05	72	20	Non polymeric
Nitrobenzene	LiOMe ⓐ	0.10	72	55	Polyester
Dekalin	LiO_tBu	0.125	72	60	Polyester
DMSO	LiO_tBu	0.27	24	0	-
Dioxane	LiO_tBu	0.164	72	0	-
THF	LiCl ⓐⓑ	0.280	72	0	-

ⓐ Not a homogeneous catalyst solvent system

ⓑ MEAS

followed by little further gas evolution. In contrast to this those reactions which resulted in polymeric products were characterised by a steady evolution of gas over several hours. In the system sodium methoxide/nitrobenzene, the catalyst was not completely soluble in the solvent at the concentration used, and during the reaction gas was apparently evolved at the surface of the solid phase.

The systems lithium tert-butoxide/DMSO and lithium tert-butoxide/dioxan, produced no decomposition of DEAS within the time scale of the experiment as evidenced by a failure to isolate any products of decomposition and a lack of any evolved gas as measured by manometer rise. The solution of lithium tert-butoxide in DMSO produced a marked visible increase in viscosity of the solution.

Infra-red analysis of the products yielded two very distinct types, polymeric and non-polymeric. The polymeric products were chatacterised by a strong absorption at 1760 cm^{-1} corresponding to the carbonyl streaching frequency in the polymer. In addition a further strong absorption was noted at 1625 - 35 cm^{-1}, the strength of this peak appeared in these initial investigations to be dependant on the quantity of catalyst used. The presence of a weak but broad absorption around 3460 cm^{-1} indicated the presence of hydroxyl groups. The non-polymeric products yielded an infra-red absorption spectrum which was rather different and characterised by a strong broad absorption at 1620 - 1670 cm^{-1} (using $AlEt_3$) and even broader using some other catalysts. Other peaks at 1000 cm^{-1} and 1250 cm^{-1} which are present in the polymeric material do not appear in the non polymeric product. Figures

FIGURE XIX

Infra-red spectrum of polymeric product obtained by the decomposition of DEAS in nitrobenzene as solvent using soldium methoxide. KBr. disc, reference air.

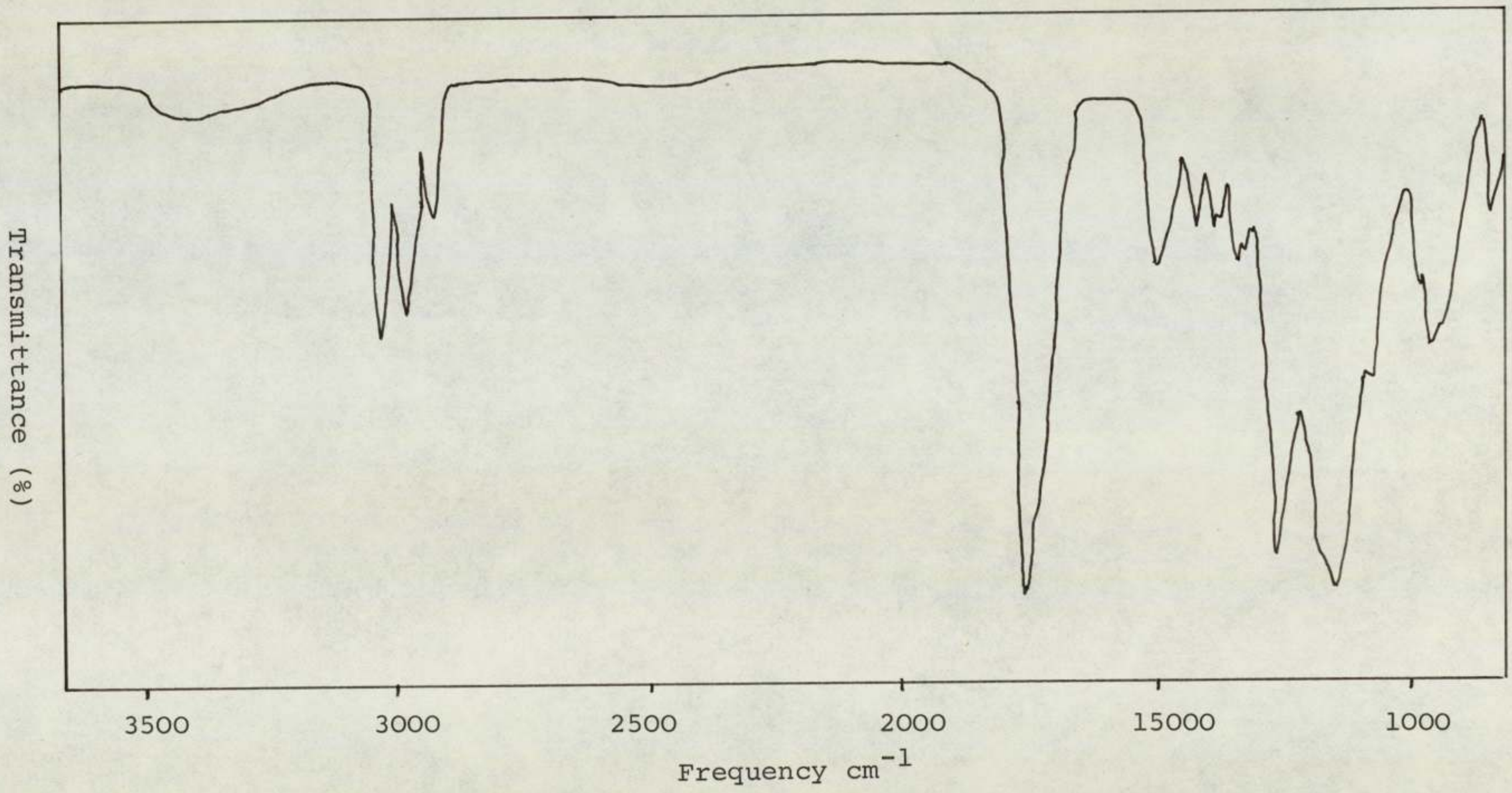
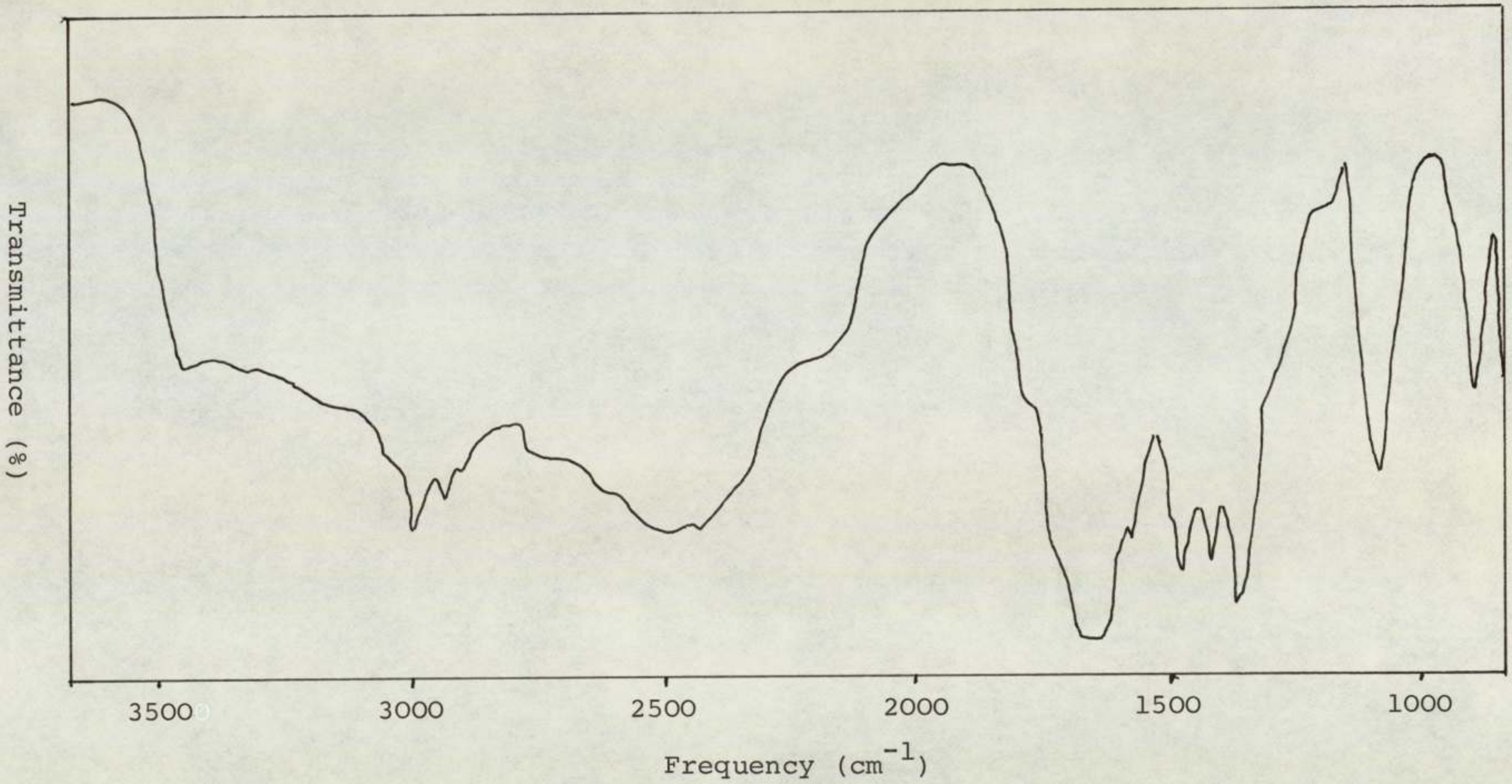


FIGURE XX

Infra-red spectrum of non-polymeric product obtained from the decomposition of DEAS by $AlEt_3$ in nitrobenzene. KBr disc, reference air.



XIX and XX show the infra-red absorption spectra which are characteristic of these two types of product, polymeric and non-polymeric respectively.

T.G.A. and D.T.A. analysis of the product produced by the action of sodium methoxide in nitrobenzene on DEAS indicated that the white solid obtained had melting point 130 - 135°C and decomposition temperature 218°C, whereas the non-polymeric products showed no tendency to melt below their decomposition temperatures (250 - 300°C).

DISCUSSION

The catalysts investigated are typical of the major ionic polymerisation systems in current use, and provide a reasonable indication of the type or types of polymerisation to which anhydrosulphites are susceptible. Cationic polymerisations as represented by the boron trifluoride diethyletherate, anionic systems for example alkoxides, and heterogeneous Ziegler-Natta systems have all been investigated briefly. It must be emphasised that this was intended to be an exploratory rather than comprehensive examination of this point.

The non-polymeric products formed when catalysts such as $AlEt_3$, $TiCl_4/AlEt_3$, and $B7_3(Et_2O)_2$ were used indicate that these compounds react with anhydrosulphites in a manner which renders the production of an effective propogating species improbable. The quantity of product formed shows that the catalyst has reacted with only a small proportion of the available monomer. This is indicative of the formation of a metal complex between the metal atom and a species derived from the anhydrosulphite. Such a compound is perhaps to be expected from the association of a metal ion with a polar molecule such as the anhydrosulphite. Such metal complexes have been recorded in previous studies with anhydrosulphites, where a ratio of 3.4 : 1 of complex product to catalyst used was reported.[13] It would appear from these studies that most compounds containing aluminium yield a similar product with anhydrosulphites.

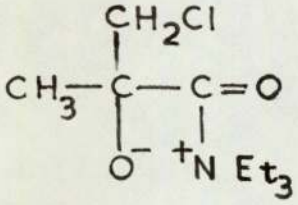
The product of $BF_3(Et_2O)_2$ and anhydrosulphite was a black tar which was highly sensitive to moisture and the analysis of which was impossible without detailed and protracted study. Since the product was not polymeric it was of limited interest and was not further investigated.

It is clear from the results presented in Table IX that anhydrosulphites are susceptible to decomposition by alkoxides and that some of the products of this decomposition are polymeric. The use of alkoxides to induce the decomposition of cyclic compounds of this type has been reported previously. Sodium methoxide has been reported to have no effect on the rate of decomposition of α-hydroxyisobutyric acid anhydrosulphite, HABS, but produced a substantial quantity of polymer with the methyl, chloromethyl analogue.[49] Smith,[55] reports that sodium methoxide catalyses the decomposition of some phenyl substituted anhydrocarboxylates but that this is not a satisfactory route to high molecular weight poly α-ester. Since group I alkoxides are primarily associated with anionic propogation mechanisms it would appear that anhydrosulphites are susceptible to this type of system. This is supported by the fact that they are also reported to be decomposed to polymer by butyl lithium,another anionic initiator.[49]

The inactivity of the system lithium tert-butoxide/DMSO was unexpected since a similar system; sodium methoxide/DMSO, has been reported as effective in the polymerisation of β-propriolactams.[83] However, the basicity of lithium tert-butoxide in DMSO is reduced due to ion pair formation,[75] and this may reduce the activity of this catalyst below the level at which it is effective with this anhydrosulphite.

Product analysis indicates the presence of polymer which is similar to that produced by thermal decomposition of anhydrosulphites. The carbonyl absorption frequency (1760 cm^{-1}) corresponds to that obtained with thermal polymer, and the rest of the infra red spectrum is almost identical. The thermal polymer gives rise to a small absorption at 3400 cm^{-1} due to the presence of hydroxyl groups on the chain ends, comparison of the relative magnitudes of carbonyl and hydroxyl absorptions has been used as a means of assessing molecular weights. The hydroxyl absorption is not clearly defined in the polymer produced by alkoxide induced decomposition, but is replaced by a broader peak. This may be due to the presence of water caused by the hygroscopic alkoxide residues. The absorption at 1625 - 30 cm^{-1} suggests a close association of a positively charged species with the carbonyl, such as would be produced in a carboxylate anion. This presumably indicates the possibility of interaction between the anhydrosulphite and the alkoxide to produce a Group I metal carboxylate species.

Preparation of the lithium salt of α-hydroxy-α-methyl butyric acid yielded a product having an infra-red carbonyl absorption frequency identical to that found in lithium alkoxide decomposed MEAS, thus providing further evidence for the existence of this grouping. In the decomposition of anhydrosulphites at low temperatures initiated by tertiary amines,[49] a species having a carbonyl absorption frequency at 1655 cm^{-1} is formed. This has been attributed to the species(XXVII) which is proposed as the propogating species when the anhydrosulphite is the methyl, chloromethyl derivative and the tertiary amine is triethylamine.



(XXVII)

The low absorption frequency results from the electron withdrawing effect of the triethylamine grouping.

These investigations indicate that anhydrosulphites in general may be polymerised at ambient temperatures by alkoxides. The mechanism shows some of the characteristics of an anionic process. In order to elucidate the reactions taking place a more detailed investigation of the decomposition was undertaken. For these studies, lithium tertiary-butoxide was selected as the alkoxide for several reasons:-

a. Solubility

Lithium compounds show a certain degree of covalency which is not shown with other Group I metals. This results from its high charge/size ratio. This, together with the use of an alkoxide radical having a sizable alkyl portion gives an organometallic compound having a comparatively high solubility in non-polar organic solvents. Lithium alkoxides having smaller alkyl groups, for example lithium methoxide are only sparingly soluble in non-polar organic solvents.

b. Basicity

The high basicity of systems such as potassium tert-butoxide was considered to be undesirable since this might induce undesirable side reactions in the presence of polymer.

c. Stability

Group I alkoxides have a tendency to decompose and disproportionate to produce species such as peroxides. This effect is least apparent with lithium alkoxides and lithium tert-butoxide in particular.

The melting point of polyester prepared by the action of sodium methoxide on DEAS is lower than that given for polymer prepared thermally. The melting and decomposition temperatures for thermally prepared DEAS of DP = 165 are 194 and 240°C respectively. The lower figures for the initiated polymer (135° and 218° respectively) may reflect either a lower degree of polymerisation, or the presence of initiator residues. Since the nature of the end groups is not known in initiated polymer,and the polymer is too insoluble for molecular weight analysis by methods other than end group analysis, comparison of the two polymers cannot accurately be made.

CHAPTER 6

KINETIC STUDIES OF THE ALKOXIDE INITIATED DECOMPOSITION OF ANHYDROSULPHITES

As the preliminary studies indicate, even in the presence of solid undissolved alkoxide, the diethyl substituted anhydrosulphite DEAS is decomposed at an appreciable rate to yield a product which appears to/be a poly-α-ester similar in structure to that obtained by thermal decomposition of the same anhydrosulphite. The products differing only in thermal stability.

In the pursuit of meaningful data to clarify the mechanism of this particular catalysed decomposition, it was necessary to remove as many variables as possible in order to reduce the number of possible influences on the reaction taking place. To this end the maximum solubility was required from the alkoxide since a heterogeneous system is almost invariably more difficult to analyse. Alkoxides derived from Group I elements and having a large alkyl group are comparatively soluble in non-polar organic solvents.

The selection of decalin as a solvent for the majority of these investigations results from the favourable solubility behaviour of alkoxides in this hydrocarbon. Additionally, the high boiling point of decalin allows the process of anhydrosulphite decomposition to be followed by gas evolution since the low volatility of this solvent does not cause any significant interference with the manometric method of following gas evolution at constant volumes. Other work relating to the thermal decomposition of anhydrosulphites in decalin has also been carrried out, and thus comparisons can easily be made.

Methyl ethyl substituted anhydrosulphite MEAS was used as the predominant monomer for these studies for several reasons. Firstly, very high molecular weight polymer has not been prepared from this anhydrosulphite by the thermal route. Reasons given for this include the high percentage of chlorine containing impurities which appear as byproducts during the synthesis. These impurities are difficult to remove except by long and repeated purification procedures.[58] Secondly, MEAS contains an asymmetric carbon atom and the possibility exists, therefore, of separation of optical isomers by an asymmetric selective polymerisation. This could yield a very much more highly ordered polymer, and while this work is not attempted here, the information presented may provide a useful comparison for future work. Thirdly, the polymers so far prepared from asymmetrically substituted anhydrosulphites have all been amorphous. This greatly increases the solubility of an otherwise generally insoluble class of polymers, and assists in the analysis and characterisation of the polymeric products. The symmetrically substituted polymers in contrast are almost insoluble especially when molecular weight is high, and accurate characterisation is, therefore, difficult.

The use of MEAS in decalin is therefore justified as a monomer/solvent system in these initial low temperature investigations, and the advantages of using a comparatively soluble alkoxide are clear.

6.1 REACTION PROFILE AND ORDER OF REACTION

6.1.1. Assessment of Gas Evolution Measurements

Most gas evolution measurements were carried out using apparatus of the type shown in Figure IV and described in Chapter 2. The apparatus was designed for use at temperatures in excess of 40°C but was adapted for use at lower temperatures with certain restrictions. Since this method involves the evacuation and sealing of the apparatus after the introduction of the reactants, the initial stages of the reaction were not studied in some experiments. Hence, where initial rates are quoted in the text these are in fact rates measured after four minutes, since a procedure was adopted in which gas evolution measurements were started four minutes after the mixing of reactants. Adoption of this procedure resulted in a maximum of 4% reaction based on evolved gas, before the reaction was observed in the case of the decomposition of the dimethyl substituted anhydrosulphite HBAS. More commonly the extent of reaction at the time that the 'initial rate' was measured was approximately 0.5% (MEAS).

The error involved in the procedure used can be assessed by plotting the change in rate of reaction with time and extrapolating the curve produced back to four minutes before the start of gas evolution measurements.

In order to confirm these results and to further show the existence of any initial rapid rate of reaction or induction period several experiments were carried out using the apparatus shown in Figure III and described in Chapter 2. In this way the reaction can be observed in its initial stages and the true initial rate measured. Figure XXI shows the rate of evolution of gas as a function of pressure measured in this way for the decomposition of MEAS in the presence of lithium t-butoxide using decalin as solvent. Table X compares the rates of reaction for this decomposition measured in various ways.

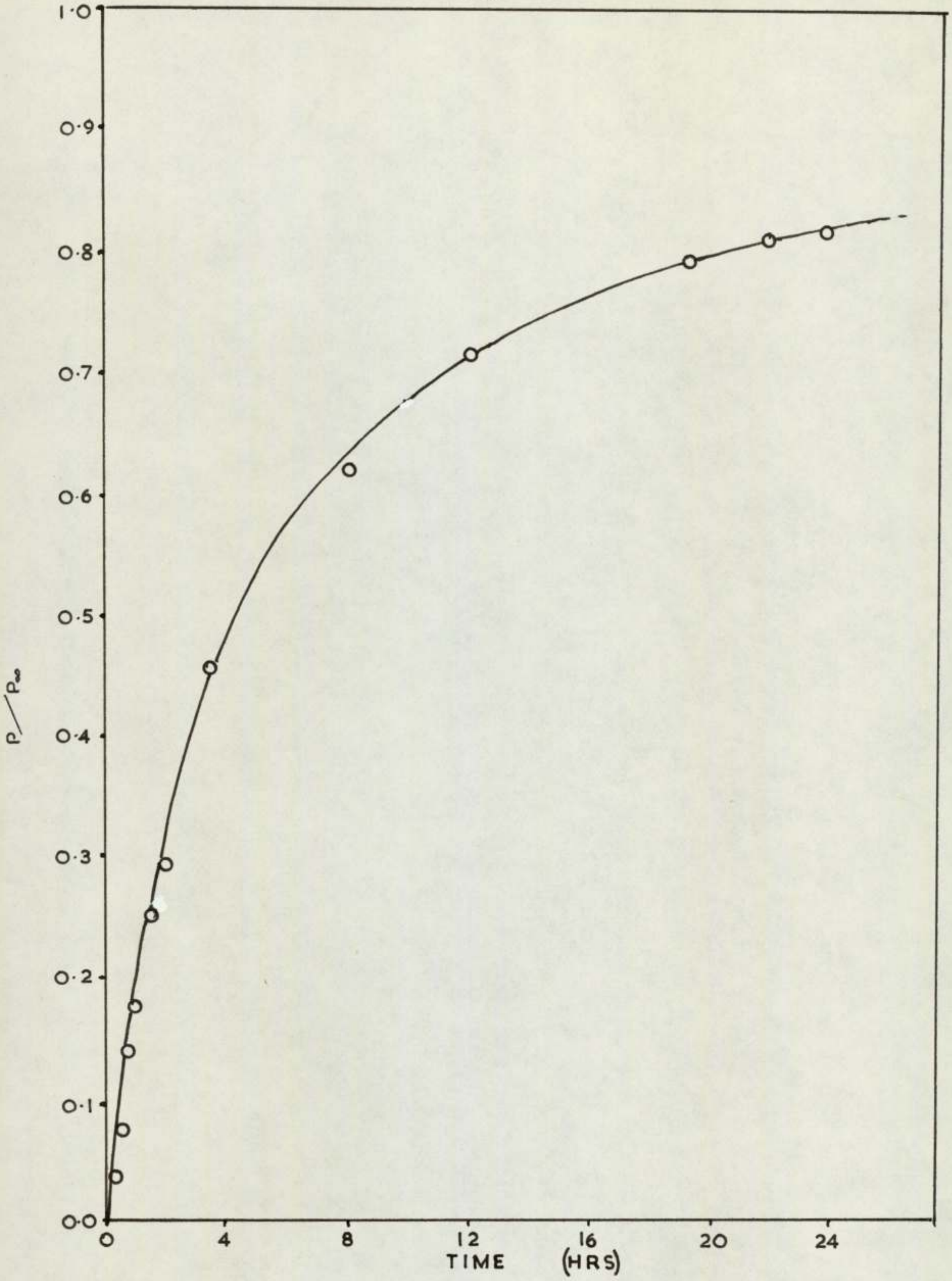


FIGURE XXI

Decomposition of MEAS in the presence of lithium t-butoxide using decalin as solvent at 40°C

$[\text{MEAS}]_0 = 0.75\text{M} \qquad [\text{LiO}_t\text{C}_4\text{H}_9]_0 = 0.0082\text{M}$

TABLE X

Rate of evolution of sulphur dioxide for the decomposition of MEAS in decalin at 40°C using lithium t-butoxide as initiator

$[MEAS]_o = 0.75M \qquad [LiO_tC_4H_9]_o = 0.0082M$

Method of Rate Measurement	Rate ($\times 10^5$) mol $l^{-1}sec^{-1}$
True Initial	3.63
At 4 minutes	3.51
By Extrapolation	3.65

It is apparent from these results that the measurement of rate of gas evolution at 4 minutes involves an error which is within the limits of experimental measurement and is, therefore, negligible. In the investigations where the true initial rate was measured, no rapid evolution of gas or induction period could be measured in the initiator concentration range 0.0082 - 0.1M. Experimental procedure was therefore simplified by measuring the rate after 4 minutes, and this will be quoted as initial rate in the following results.

6.1.2 Results

The rate of evolution of sulphur dioxide at 40°C was measured by observing the manometric pressure rise at constant value. Figure XXII shows a typical plot of pressure rise with time for the system MEAS/decalin/lithium t-butoxide at various initiator concentrations.

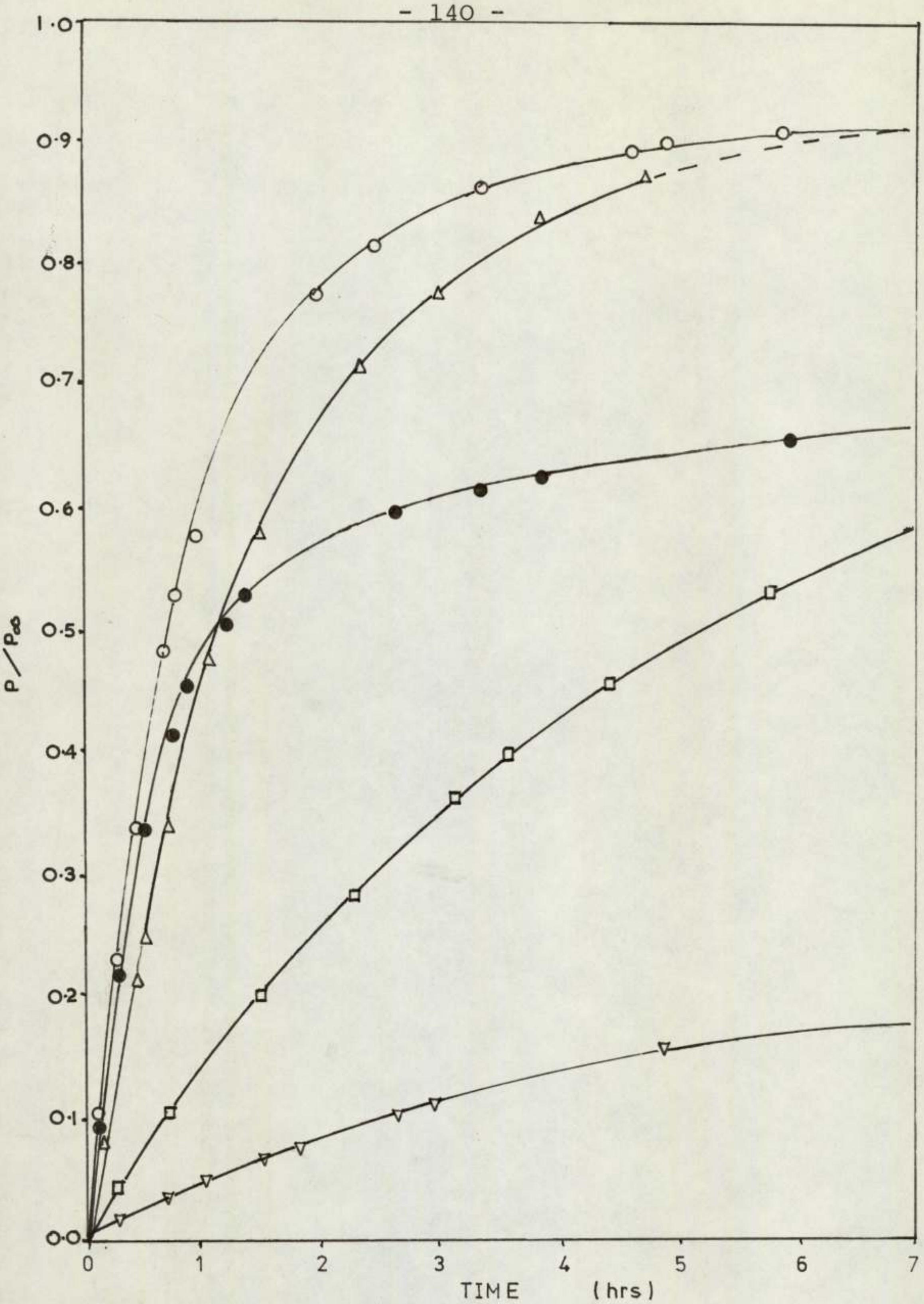


FIGURE XXII

Decomposition of MEAS in the presence of lithium t-butoxide using decalin as solvent at 40°C

$[\text{MEAS}]_o$ = 0.458M

$[\text{LiO}_t\text{C}_4\text{H}_9]$ = 0.0450M ○

" = 0.0349M △

" = 0.0178M ●

" = 0.0089M □

" = 0.0039M ▽

The curves obtained showed an initial relatively rapid rate of reaction extending to some 60 or 70% of the total reaction at higher initiator concentrations, for example 0.035M. This is followed by a slower evolution of gas until all monomer has been consumed, as calculated on total volume of evolved gas. Initial rates show an increase with increasing initiator concentration over the range 0 - 0.1M but at higher initiator concentrations, the initial rate again falls.

The latter stages of the reaction profiles are confused. Where lower initiator concentrations were used, the reaction proceeds at a slower rate initially but in the middle stages the profiles indicate that the reaction using the lower initiator concentration is proceeding at a faster rate and to a higher conversion before the final very slow rate of decomposition takes over. At high initiator concentrations, for example 0.178M, the initial rate is slower than might be expected, and proceeds to smaller extent of reaction before the final slower rate of reaction takes over to go to 100% decomposition.

A conventional first order plot of log $\frac{[M]}{[M]_o}$ Vs time where $[M]_o$ = Initial monomer concentration and $[M]$ = monomer concentration at any given time using evolved gas to indicate the monomer consumed, gave non linear behaviour. A typical first order plot is shown in Figure XXIII. Although a straight line could conceivably be constructed for the first 40 - 50% of the reaction, the reaction thereafter proceeds increasingly slowly and clearly does not proceed with first kinetics with respect to monomer through the complete reaction.

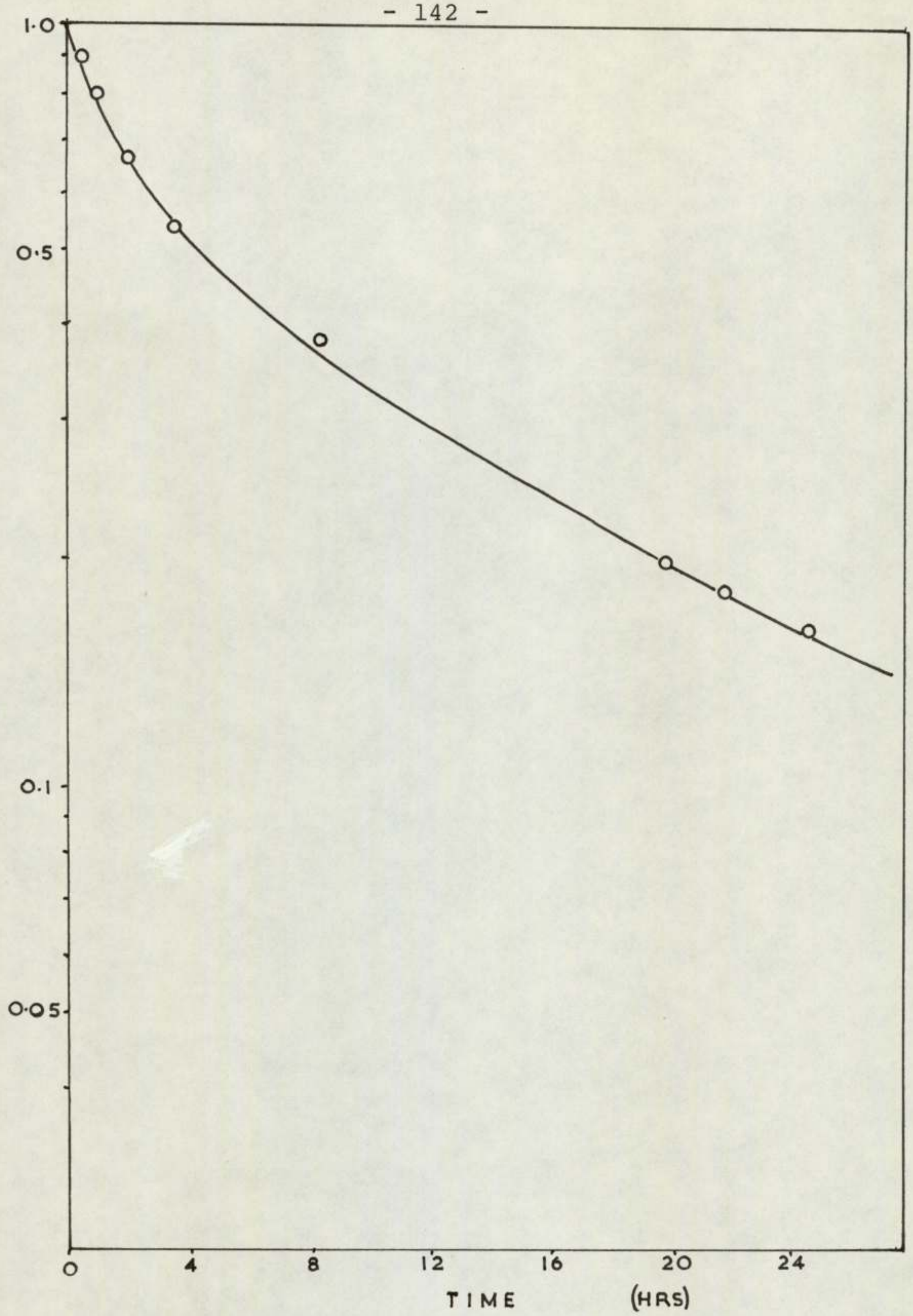


FIGURE XXIII

First-order rate plot of decomposition of MEAS in the presence of lithium t-butoxide in decalin as solvent at 40°C

$[\text{MEAS}]_o = 0.75\text{M} \qquad [\text{LiO}_t\text{C}_4\text{H}_9]_o = 0.0082\text{M}$

When monomer to initiator ratio approaching 1/1 was used, no rapid initial rate of gas evolution was observed although no accurate determination was made using the apparatus shown in Figure III. In all cases the evolved gas corresponded in volume to that calculated on the basis of quantity of monomer used.

In order to obtain consistently repeatable results the reaction mixture required vigorous and repeated agitation. This presumably results from the increased solubility of sulphur dioxide in organic solvents at lower temperatures than those used in thermal decompositions, the reaction solvents being easily supersaturated.

Initial rates of reaction based on the evolved gas were found to be generally reproducible and these were used as the basis for a systematic study of the effect of variation in initiator and monomer concentration on the rate of reaction. Table XI shows the effect of changes in initiator concentration on the initial rate of gas evolution at 40°C at several initial monomer concentrations. These results show how the initial rate of reaction is sensitive to the initial monomer concentration, and the results are shown as a plot of Initial Rate vs Initial Initiator Concentration in Figures XXIIIa and XXIV. These plots show a certain amount of scatter, but a reasonable straight line relationship exists over the range $[I]_0$ = 0 to 0.15M, this section of the plots shown in Figures XXIIIa and XXIV is shown in greater detail in Figure XXV to show the reasonable agreement obtained. At higher initiator concentrations the initial rates of reaction decrease and rather more scatter is indicated.

TABLE XI

Initial rates (k) of MEAS decomposed at 40°C in the presence of lithium tert-butoxide (I) in decalin as solvent

$[\mathrm{MEAS}]_o$ = 0.56M

$[\mathrm{I}]_o$ mol l^{-1}	k ($\times 10^4$) mol $l^{-1}s^{-1}$
0.557	0.914
0.400	4.58
0.250	4.12
0.147	3.85
0.110	3.14
0.0734	1.88
0.0623	2.45
0.0400	0.97

$[\mathrm{MEAS}]_o$ = 0.458M

0.394	0.903
0.291	1.08
0.179	1.49
0.045	1.54
0.0349	0.87
0.0178	0.50
0.0089	0.21
0.0039	0.09

$[\mathrm{MEAS}]_o$ = 0.438M

0.0623	1.06
0.0492	0.88
0.0246	0.39

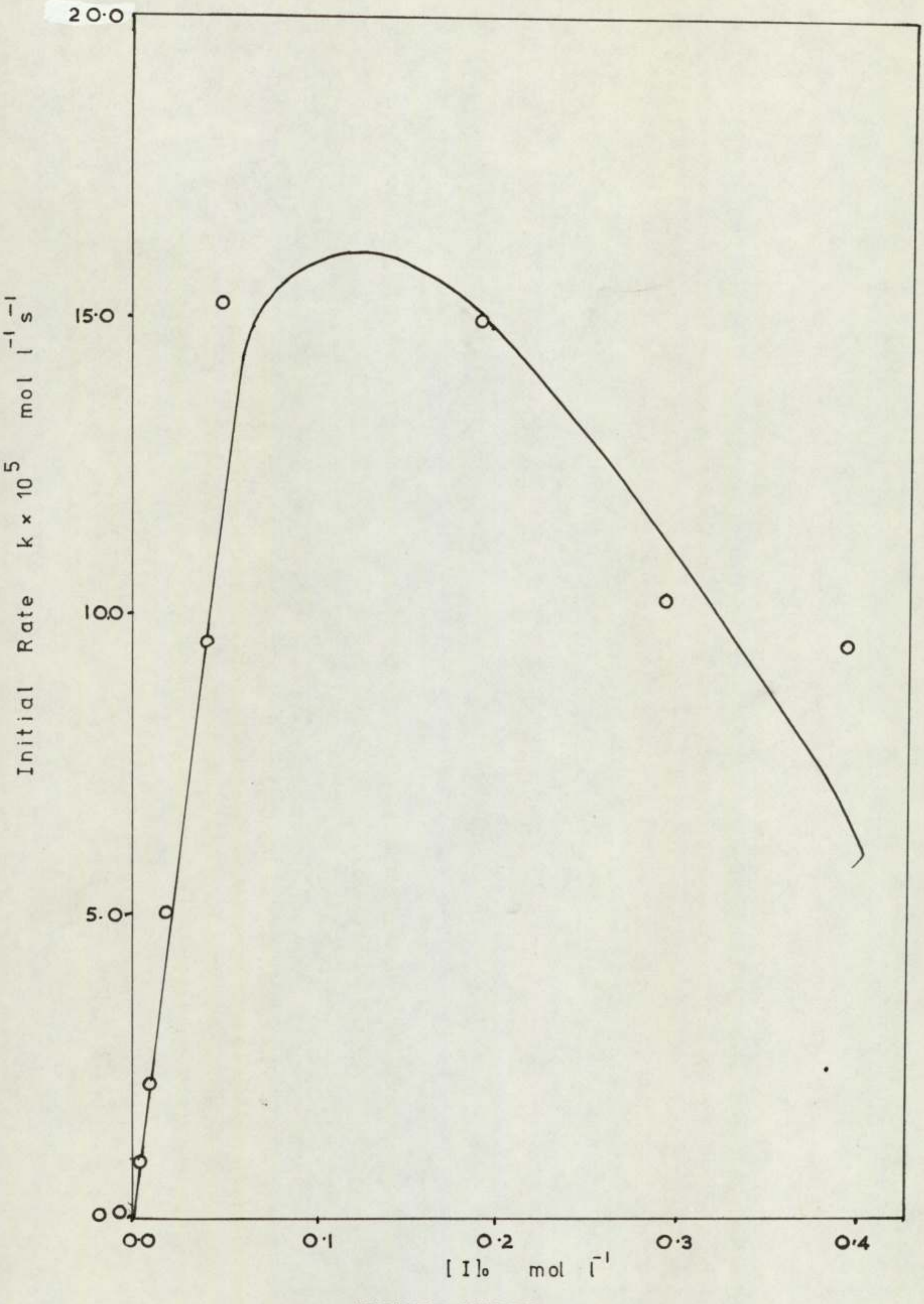


FIGURE XXIIIa

Initial rate (k) Vs initiator concentration for the decomposition of MEAS in decalin at 40°C in the presence of lithium t-butoxide as catalyst

$[MEAS]_o$ = 0.458M

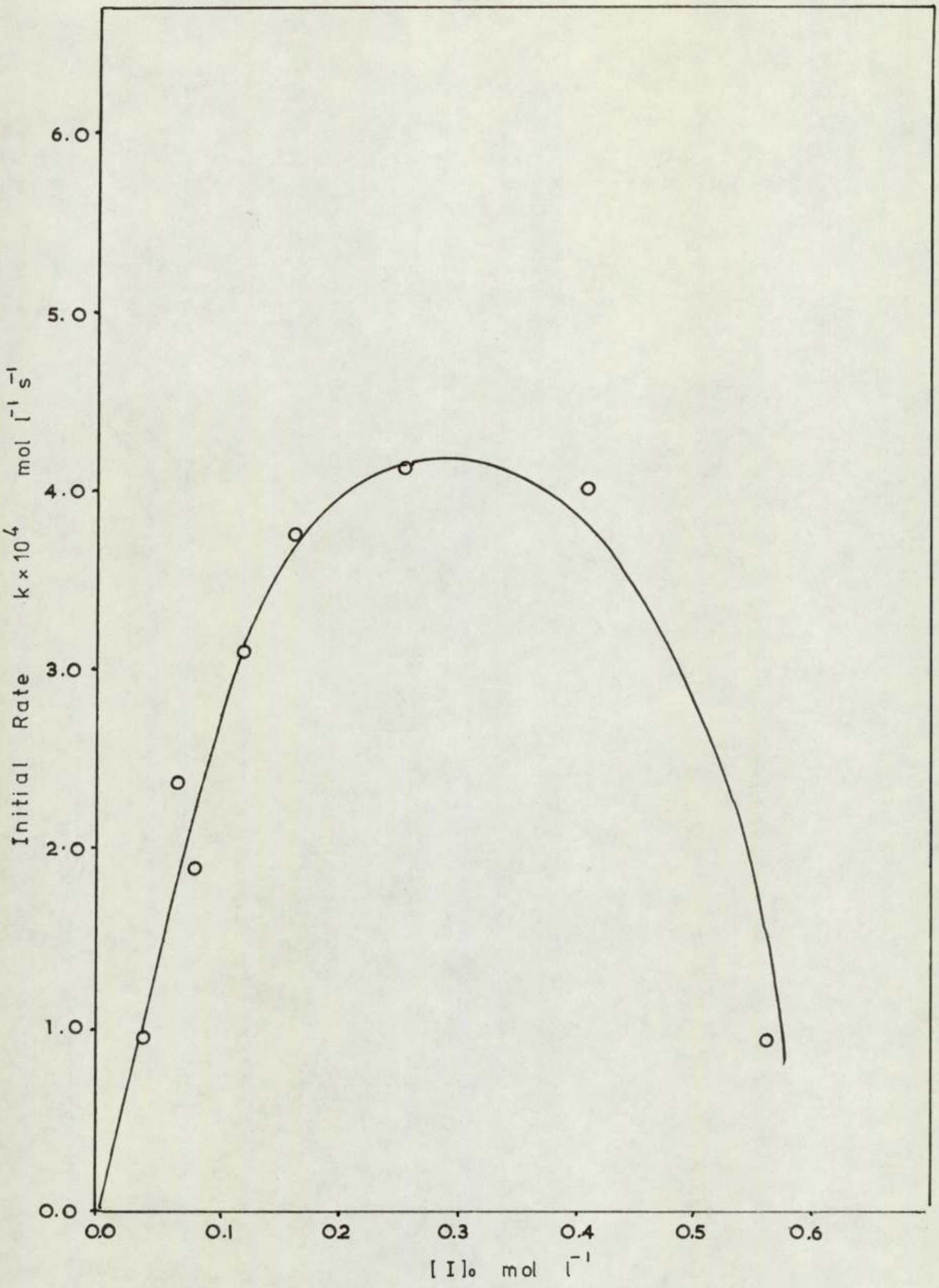


FIGURE XXIV

Initial rate (k) Vs initiator concentration for the decomposition of MEAS in decalin at 40°C in the presence of lithium t-butoxide as initiator

$[MEAS]_o = 0.56M$

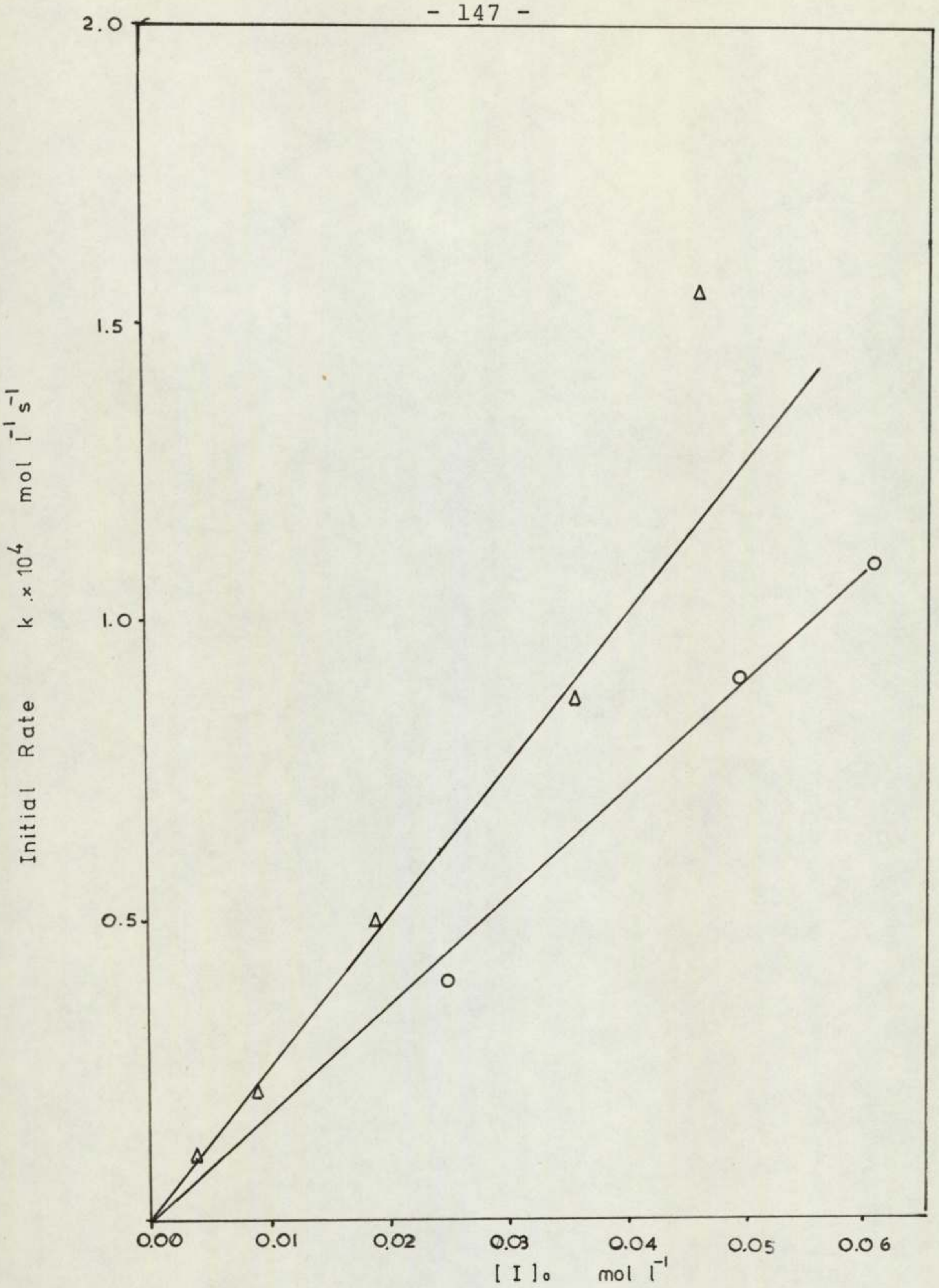


FIGURE XXV

Initial rate (k) Vs initiator concentration for the decomposition of MEAS in decalin at 40°C in the presence of lithium t-butoxide as initiator

$[MEAS]_o$ = 0.458M

$[MEAS]_o$ = 0.438M

Similar studies of the effect on initial rate of monomer decomposition of variation of initial monomer concentration were also carried out. Again gas evolved was measured as a pressure increase at constant volume. Table XII shows the initial rates obtained for these studies at 40°C in decalin. The results are presented graphically in Figure XXVI.

The initial rates of decomposition increase with increasing monomer concentration over the range 0 to 0.8M. At higher concentrations the rate is rather higher than anticipated by the graph by a factor of about 1.4. A reasonable straight line relationship exists in Figure XXVI up to the point at which $[M]_o = 0.82M$.

The existence of a linear relationship between initial rate of decomposition and both initial monomer and initial initiator concentrations implies that rate of reaction, in the early stages at least, is first-order in monomer and initiator,

If the assumption that:

$$-\frac{d[M]}{dt} = \frac{d[SO_2]}{dt} \qquad \ldots\ldots\ldots\ldots 38$$

is true, and this is investigated in the next section, and

$$-\frac{d[M]}{dt} \propto [M]_o \qquad \ldots\ldots\ldots\ldots 39$$

$$-\frac{d[M]}{dt} \propto [I]_o \qquad \ldots\ldots\ldots\ldots 40$$

TABLE XII

Initial rates (k) for MEAS decomposed at 40°C in decalin as solvent at various initial monomer concentrations $[M]_o$

$[\text{Lithium t-butoxide}]_o = 0.062M$

$[M]_o$ mol l^{-1}	k ($\times 10^4$) mol $l^{-1}s^{-1}$
1.12	5.12
0.82	2.83
0.56	2.38
0.53	2.08
0.41	1.06
0.28	0.14
0.15 *	0.41

* $[I]_o = 0.073M$

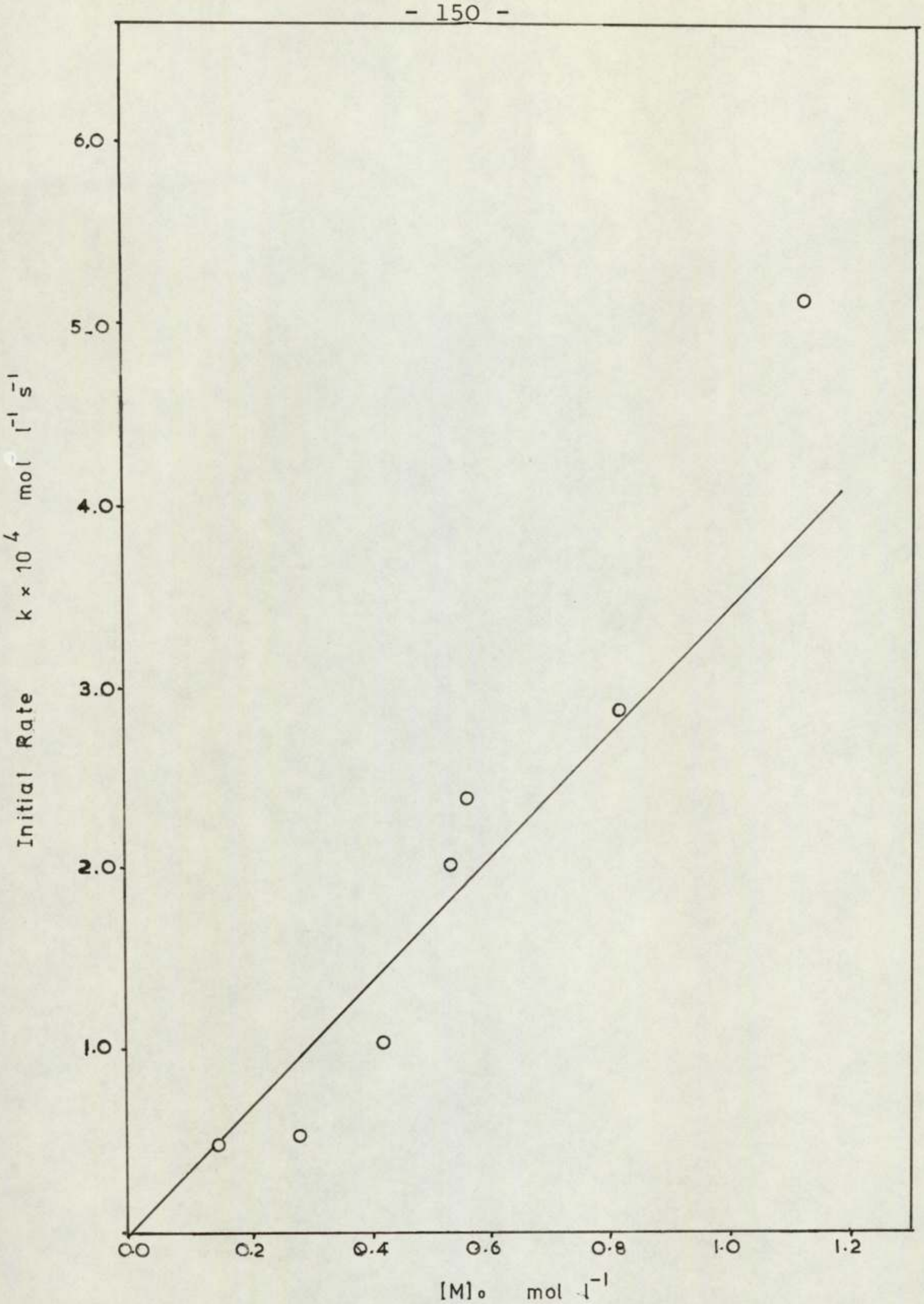


FIGURE XXVI

Initial rate (k) Vs monomer concentration for the decomposition of MEAS in decalin at 40°C in the presence of lithium t-butoxide as initiator

$[I]_o = 0.062$ M

then combining equations 38, 39 and 40:-

$$\frac{d[M]}{dt} = \frac{d[SO_2]}{dt} \propto [M]_o[I]_o \quad \ldots\ldots 41$$

or $$\frac{d[SO_2]}{dt} = k^1 [M]_o[I]_o \quad \ldots\ldots 42$$

where k^1 is a second-order rate constant.

Thus, if the above equation holds for the processes involved here, then

$$k^1 = \frac{d[SO_2]}{dt} / [M]_o[I]_o \quad \ldots\ldots 43$$

So that

$$k^1 \propto \frac{d[SO_2]}{dt} / [M]_o \text{ at constant } [I]_o \quad \cdots 44$$

$$k^1 \propto \frac{d[SO_2]}{dt} / [I]_o \text{ at constant } [M]_o \quad \cdots 45$$

The quantities $\frac{d[SO_2]}{dt} / [M]_o$ and $\frac{d[SO_2]}{dt} / [I]_o$ are given by the slope of the plots in figures XXV and XXVI. The values of k^1 determined in this way are given in Table XIII.

The results shown in Table XIII show reasonably good agreement in the values obtained for k^1. The value which shows greatest deviation $k^1 = 4.18 \times 10^{-4}$ l mol^{-1}sec^{-1} is that which is based on the graph plotted using the smallest number of points, and which is therefore least reliable. The mean is taken by removing the highest and lowest figures and averaging the rest.

TABLE XIII

Second-order rate constants (k^1) obtained from the decomposition of MEAS in decalin at 40°C in the presence of lithium t-butoxide as initiator

$[I]_o$ mol l^{-1}	$[M]_o$ mol l^{-1}	$k^1 \times 10^4$ l $mol^{-1}s^{-1}$
varies	0.560	4.95
varies	0.458	5.74
varies	0.438	4.18
0.073	varies	5.56
Mean	5.25	

No enhancement or reduction in initial rate was observed as a result of variations in sulphur dioxide concentration. Almost identical initial rates were observed at various initial sulphur dioxide concentrations in the range 0 - 200 mm Hg. pressure.

The initial rates obtained in these studies were all faster than the thermal rate of decomposition at the same temperature by several orders of magnitude as indicated in Table XIV.

The thermal rate was estimated by measurement of rates of thermal decomposition at higher temperatures and extrapolation of the results down to 40°C (Chapter 6 section 3).

TABLE XIV

Initial rates of decomposition of MEAS (M) at 40°C in decalin a) in absence of catalyst, b) in presence of lithium t-butoxide (I)

$[I]_o$ mol l^{-1}	$[M]_o$ mol l^{-1}	Initial Rate (x 10^8) mol $l^{-1}s^{-1}$
Thermal	0.56	3.04
0.04	0.56	16500

The results presented in Table XIV indicate that the contribution from thermal decomposition of MEAS at this temperature is insignificant in comparison with the initiated decomposition.

6.2 EFFECT OF TEMPERATURE ON THE ALKOXIDE INITIATED DECOMPOSITION OF MEAS

On the basis that the decomposition, in its initial stages at least, is first order with respect to both monomer and initiator, the second order rate constants (k^1) were determined at several temperatures in the range 35 to 50°C for the decomposition of MEAS in decalin initiated by lithium t-butoxide. These results are shown in Table XV and the standard Arrhenius plot (Figure XXVII) was used to calculate the kinetic parameters.

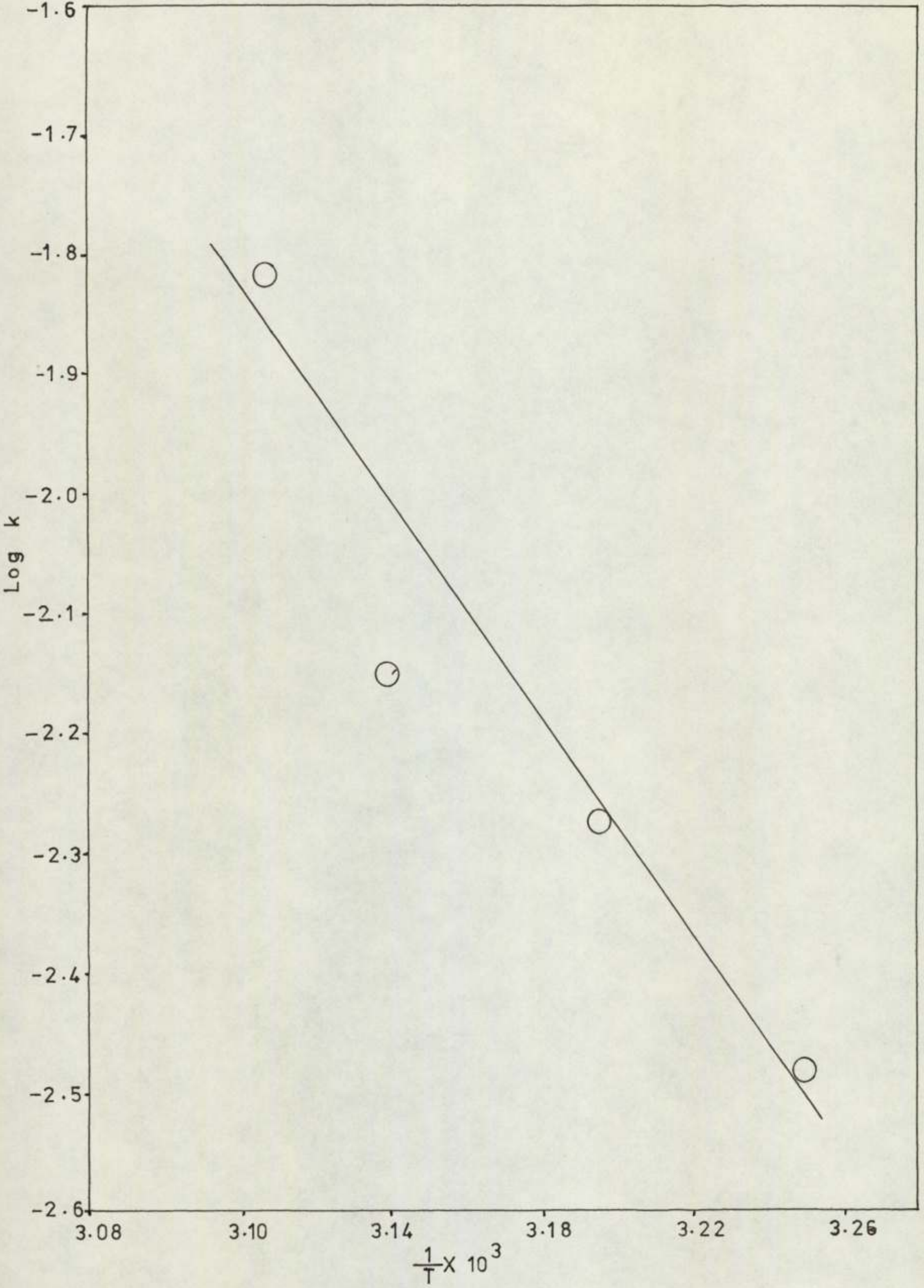


FIGURE XXVII

Arrhenius plot for the decomposition of MEAS with lithium t-butoxide in decalin as solvent

TABLE XV

Second-order rate constants (k^1) and derived activation energy (E) for the decomposition of MEAS initiated by lithium t-butoxide in decalin as solvent at various temperatures

Temperature °C	$k^1 \times 10^3$ l $mol^{-1}s^{-1}$
34.8	3.32
40.0	5.25
45.0	6.95
48.7	14.9
E(kJ mol^{-1})	63.4

Inspection of the Arrhenius plot shows that reasonable straight line agreement is obtained in the temperature range 35 to 45°C, but at temperatures above this the reaction proceeds at a faster rate than expected from the lower temperature data.

The activation energy obtained, 63.4 kJ mol^{-1}, is much lower than those obtained for the thermal decomposition of anhydrosulphites (typically 120 kJ mol^{-1}) and is typical of the formation of a highly charged transition state in which bonds are highly polarised and therefore easily broken, and perhaps the formation of a zwitterion species.

6.3 NON-INITIATED DECOMPOSITION OF MEAS IN DECALIN

Although the general kinetic pattern of the non-

Initiated decomposition of anhydrosulphites in inert solvents is well understood, it is obviously relevant to evaluate the kinetic parameters of the monomer solvent system used in the initiated decompositions, as nearly as possible over the temperature range used for these decompositions. Hence, it can be confirmed that non-initiated reactions play no part in the temperature range used for the initiated decompositions, or the extent of their contributions can be more precisely defined.

RESULTS AND DISCUSSION

MEAS was decomposed thermally in decalin as solvent in the range 95 - 120°C. All reaction profiles showed good first-order behaviour with respect to monomer. First-order rate constants were calculated at several temperatures in the range given, which enabled the kinetic parameters of the reaction to be calculated from a conventional Arrhenius plot as shown in Figure XXVIII. This data is presented in Table XVI.

TABLE XVI

First-order rate constants (k), energy of activation (E) and enthalpy of activation ($\Delta S^{\ddagger}$), and pre-exponential factor for (A) for the decomposition of MEAS in decalin as solvent at several temperatures

$[\text{MEAS}]_0 = 0.56\text{M}$

Temperature (^{o}C)	10^{5}k
95	3.78
105	9.26
121	38.9
E(kJ mol^{-1})	109
A(s^{-1})	7.9×10^{12}
$\Delta S^{\ddagger}$(J mol^{-1}K^{-1})	218

A sample of the product of polymer was prepared for determination of molecular weight and molecular weight distribution. This was carried out by thermal decomposition of MEAS in decalin at 105^{o}C for eight half lives (17 hours). When the reaction was complete, the decalin was removed under vacuum and the polymer sample redissolved in THF for G.P.C. analysis which was carried out under the standard conditions. The results of this analysis are presented in Table XVII.

TABLE XVII

Number average molecular weight ($\bar{M}n$) and molecular weight distribution ($\bar{M}w/\bar{M}n$) for thermally prepared poly MEAS (solvent : decalin at 105^{o}C)

$[MEAS]_o = 0.5M$

Mn	8965
Mw/Mn	1.13

The initial concentration of chlorine containing impurity was 1.87×10^{-2} moles of chlorine per mol of anhydrosulphite, as measured by potentiometric titration. This was present as

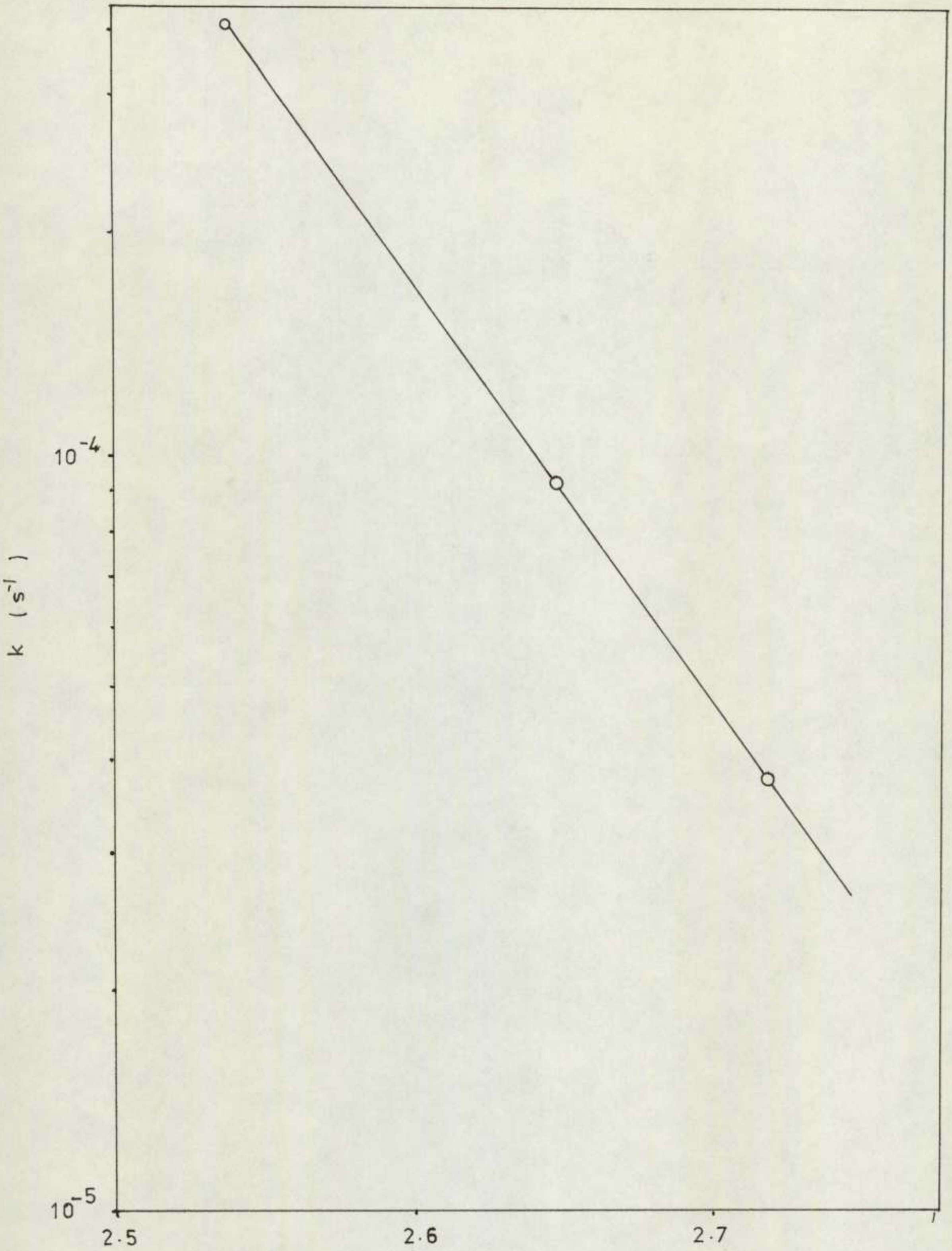


FIGURE XXVIII

Arrhenius plot for the thermal decomposition of MEAS in decalin

α-chloro acid chloride. All reactions were homogeneous throughout.

Standard Arrhenius plots for all of the anhydrosulphites so far studied under conditions of purely thermal decomposition have shown a straight line relationship between log (first-order rate constant) and $\frac{1}{T}$. It can, therefore, reasonably be assumed that extrapolation of the line would lead to derived values for the first-order rate constants at temperatures below those shown in Table XVI. Hence extrapolation to 90°C leads to a rate constant of $2.3 \times 10^{-5}\ s^{-1}$, and this value has been used for comparison in Table III, Chapter 3. The good agreement between this value and other experimentally derived figures indicates the validity of the extrapolation to this temperature.

Further extrapolation of the plot to the temperature range utilised in the initiated decomposition of MEAS provides a useful indication of the thermal stability of this compound at those temperatures. A first order rate constant of $5.4 \times 10^{-8}\ s^{-1}$ at 40°C is obtained which indicates a half life ($t_{\frac{1}{2}}$) of 3560 hours. Hence the constribution of thermal decomposition to loss of MEAS is insignificant at this temperature.

The derived kinetic parameters for decomposition of MEAS in decalin as shown in Table XVI are those associated with unimolecular thermal scission as discussed in Chapter 3. The activation energy is towards the lower end of the range expected for anhydrosulphite decomposition and this reflects the probability of a relatively non-polar intermediate (the α-lactone) in the reaction mechanism. This is to be expected in a non-polar solvent.

The number average molecular weight obtained (Table XVII) in these studies indicates the difficulty in obtaining very high molecular weight polymer from MEAS. Although molecular weights in the region of 100,000 have been obtained from symmetrically disubstituted anhydrosulphites[38], the maximum obtained from MEAS is 18,000. This may well be due to the adverse effect of chlorine containing impurities which are difficult to remove from this monomer. The chlorine impurity level in the monomer used for these molecular weight determinations was rather higher than is desirable for high polymer synthesis from anhydrosulphites.

The molecular weight distribution is narrow and almost poisson. This has been predicted in earlier studies[13], and results from the addition at random of an incoming unit to a fixed number of growing chain ends.

6.4 INFRA-RED STUDIES

In the gas evolution studies documented above, the appearance of sulphur dioxide has been assumed to be coincident with the disappearance of monomer. This assumption, which has been shown to be true for the thermal decomposition of anhydrosulphites, is not necessarily true in the alkoxide induced decompositions. The disappearance of monomer and appearance of products can be conveniently followed by observation of their respective infra-red absorption spectra.

The strained ring system which exists in anhydrosulphites gives rise to a relatively high carbonyl absorption frequency at 1810 cm^{-1} for MEAS. The polymeric products obtained by the thermal decomposition of MEAS are characterised by a lower polyester carbonyl absorption at 1740 cm^{-1}. Both absorptions have been observed in these studies in order to attempt a clarification of the processes taking place.

The infra-red absorption spectrum of the products of MEAS decomposition in the presence of alkoxide catalysts are characterised by the appearance of two strong absorptions at 1740 cm^{-1} and 1620 cm^{-1}. The higher frequency corresponds closely to that which has been shown in thermal decomposition of anhydrosulphites to be characteristic of poly α -ester. The lower frequency (1620 cm^{-1}) absorption which is not shown by the products of thermal decomposition is characterised by a relatively high extinction coefficient and the intensity of this absorption is directly related to the quantity of the alkoxide catalyst used. Figure XXIX shows the relative magnitudes of the two carbonyl absorption frequencies in the products obtained by the decomposition of MEAS in the presence of various quantities of alkoxide. Clearly the quantity of polymeric product as characterised by the 1740 cm^{-1} absorption diminishes as the concentration of alkoxide present increases and the 1620 cm^{-1} absorption increases correspondingly.

Samples taken during the lithium tert-butoxide catalysed decomposition of MEAS were analysed in a qualitative manner in order to assess the changes taking place in the infra-red absorption spectrum of the reaction mixture. Figure XXX shows the spectra at selected times throughout the reaction. Tetra

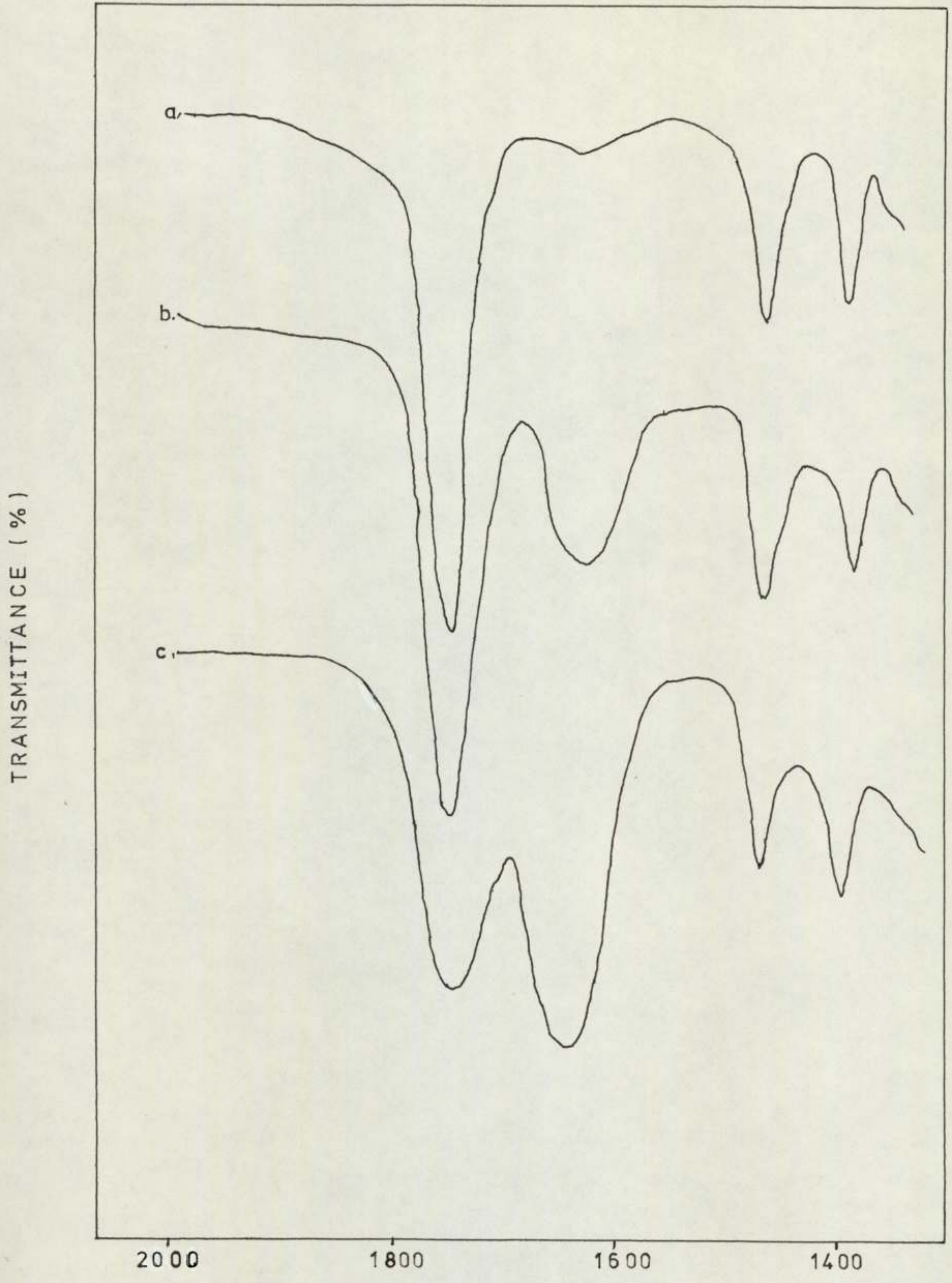


FIGURE XXIX

Infra-red carbonyl absorption frequencies ($\nu_{C=O}$) of products obtained by the decomposition of MEAS in decalin as solvent at 40°C using various concentrations of lithium t-butoxide. Spectra recorded as KBr disc. Reference air.

$[MEAS]_o$ = 0.56M	a.	$[LiO_tC_4H_9]_o$	=	0.021M
	b.	"	=	0.073M
	c.	"	=	0.142M

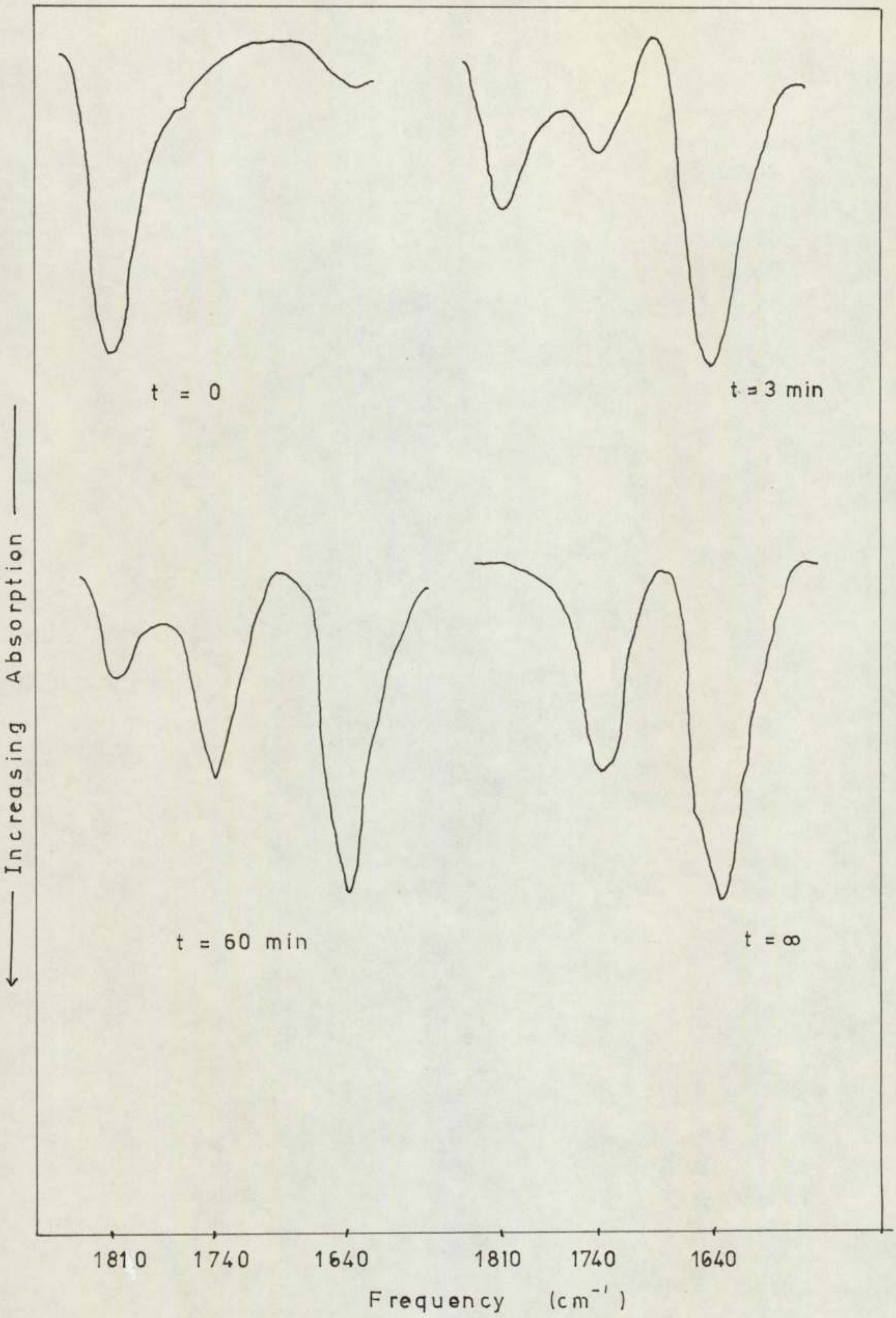


FIGURE XXX

Infra-red spectra of samples taken at time, t, during the decomposition of MEAS at 18^{O}C in THF using lithium tert-butoxide as catalyst. Spectra recorded using NaCl plates and 0.025mm p.t.f.e. spacers hydrofuran (T.H.F.) was used as solvent since the reaction was observed to be homogeneous throughout in this solvent and the alkoxide catalyst was also soluble. As the reaction proceeds, the 1620 cm^{-1} absorption appears rapidly and remains constant throughout. The 1810 cm^{-1} absorption due to monomer decreases steadily and is replaced by the 1740 cm^{-1} absorption due to polymeric products. In this particular investigation the magnitude of the lower frequency absorption is greater than that of higher frequency due to the greater extinction coefficient of the former.

A quantitative study of the disappearance of monomer and appearance of polymer by infra-red methods was also made. Accurate assessment of the concentrations of reactants and products was difficult since the position of the base line showed some variance inspite of the use of a reference cell containing the same solvent. In these studies decalin was used as solvent in order that comparison could be made with gas evolution measurements. Figure XXXI shows the rate of disappearance of monomer and rate of appearance of polymer as evidenced by the magnitude of their carbonyl absorption frequencies. The gas evolution measurements at constant volume are also shown for comparison. A low initial concentration of alkoxide was used so that there should be no large initial decrease in monomer concentration.

The results show that, within the limits of experimental error, the appearance of polymer and disappearance of monomer occur at the same rate. The infra-red results are in good agreement with the gas evolution results over the initial 40% reaction, but thereafter the spectroscopic method indicates

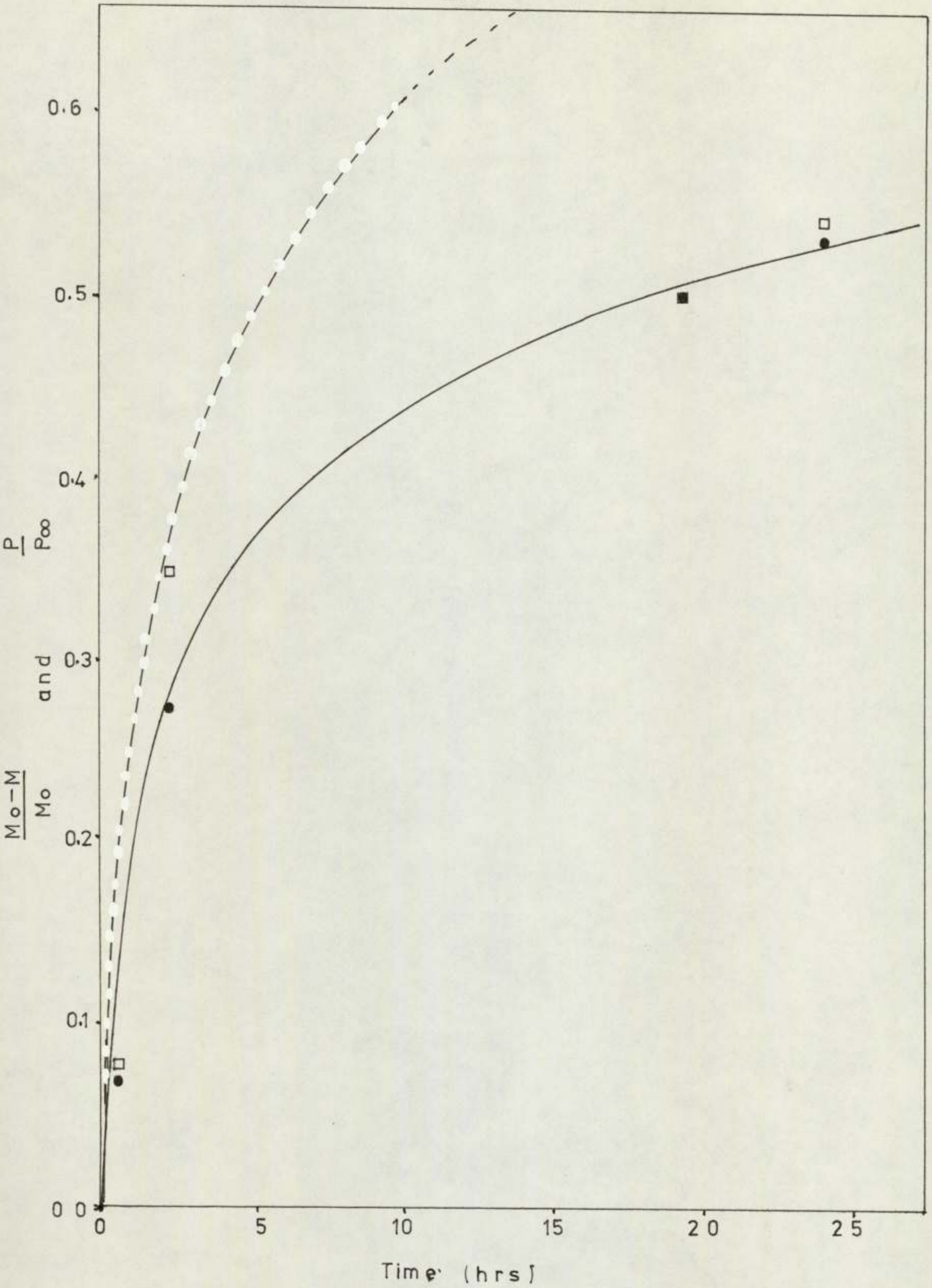


FIGURE XXXI

Disappearance of monomer and appearance of polymer based on infra-red absorptions at 1810 cm^{-1}, ●, (monomer) and 1740 cm^{-1}, □, (polymer) together with evolution of SO_2 (------) for the decomposition of MEAS in decalin at 40°C in the presence of lithium t-butoxide as initiator

$[MEAS]_o$ = 0.75M $[LiO_tC_4H_9]_o$ = 0.0082M a slower rate of reaction. Calculation of initial rates gives the same result for both methods (3.63×10^{-4} mol $l^{-1}s^{-1}$) based on initial monomer concentration. Since the sulphur dioxide cannot be liberated before the monomer decomposes, the failure of the two methods to agree in the latter stages of the reaction probably result from poor agitation with the infra-studies. This factor has been shown to result in variations within the gas evolution studies themselves.

The product of MEAS decomposition using an equivalent quantity of lithium tert-butoxide at 40°C in THF was also examined in order to attempt separation of the various components of the product by selective solvent action. The sample was isolated by removal of THF under vacuum resulting in a white powder. This was washed firstly with diethyl ether and then with chloroform. Infra-red spectra of the initial product before solvent action contained species giving absorption at 1740 and 1620 cm^{-1}. After the diethyl ether washing the spectra showed a substantial decrease in the absorption at 1740 cm^{-1} and after chloroform washing little of this species remained. Little of the species absorbing at 1620 cm^{-1} was removed by either solvent. This indicates that the species having the 1620 cm^{-1} absorption is probably polar and of relatively low molecular weight, probably non-polymeric.

6.5 EFFECT OF SOLVENT POLARITY ON THE ALKOXIDE INITIATED DECOMPOSITION OF MEAS

The effect of an increase in solvent polarity on the rate of decomposition of MEAS in the presence of lithium t-butoxide as initiator,as measured by the change in the second-order rate constant (k^1), was also assessed.

The overall solvent polarity was changed by the use of decalin/nitrobenzene co-solvents in various proportions, the reasons for this co-solvent selection were twofold. Firstly, alkoxides generally have very limited solubility especially in polar solvents such as nitrobenzene. The solubility of lithium t-butoxide in nitrobenzene was assessed as being in the region of 5×10^{-3} mol l^{-1} in initial investigations. The advantages of introducing the alkoxide via a non-polar solvent to this type of cosolvent system is therefore obvious. The concentration of initiator used was low to reduce the probability of precipitation. Secondly, the introduction of a second polar species in addition to the monomer might well show evidence of association with or solvation of the monomer or initiator by the solvent.

RESULTS

The second-order rate constants derived from initial rates of decomposition of MEAS are shown in Table XVIII together with the solvent systems used.

TABLE XVIII

Second-order rate constants (k^1) for the decomposition of MEAS in the presence of lithium t-butoxide using various decalin/nitrobenzene co-solvent mixtures.

$[\text{MEAS}]_o = 0.458\text{M}$ $[\text{LiO}_t\text{C}_4\text{H}_9]_o = 0.034\text{M}$

Solvent Ratio		$k^1 \times 10^4$ $1\ \text{mol}^{-1}\text{s}^{-1}$
Decalin	Nitrobenzene	
4	0	0.87
3	1	0.69
2	2	0.66
3	1	0.70

These results indicate that the initial rate of reaction as represented by the derived second-order rate constant is not greatly affected by the presence of the polar solvent. The reaction profiles were all similar in shape to those obtained using decalin alone as solvent and, although the pressure of evolved gas at the end of the reaction was decreased as the proportion of nitrobenzene used increased, the extent of reaction based on gas evolved approached 100%. The decrease in final gas pressure may be attributed to the increased solubility of sulphur dioxide in nitrobenzene over the solubility in decalin.

These results indicate that interaction between the relatively polar monomer and the initiator has little effect on the rate determining step of this decomposition, since the introduction of a third polar species (nitrobenzene) has little effect on reaction rate.

6.6 EFFECT OF SUCCESSIVE ADDITIONS OF MONOMER TO REACTION MIXTURES

In the decomposition of MEAS and DEAS, the effect of adding a fresh portion of monomer to a reaction mixture in which the reaction had run to completion as measured by gas evolved, was studied.

The procedure involved an initial decomposition using equimolar quantities of monomer and initiator which was continued until all monomer was decomposed (based on sulphur dioxide evolved). The reaction vessel was then opened and a further portion of monomer added equivalent to the initial monomer used. The reaction vessel was then evacuated and sealed, and gas evolution measurements continued. In the case of DEAS this procedure was repeated a third time. Hence initial rates were measured at the same monomer concentration in each case, but the final concentration of decomposed monomer is a multiple of two (MEAS) or three (DEAS) of the initial monomer concentration.

Figure XXXII shows the reaction profiles of DEAS under the conditions described above. The profiles indicate rapid reaction up to some 40% after first addition of monomer, followed by the slower decomposition as the reaction goes to completion. But second and third additions of monomer to the reaction mixture give a faster rate of reaction in the initial stages up to some 60 to 80% reaction, again followed by slow decomposition to complete the reaction. Figure XXXII indicates that successive addition increased both the initial rate of reaction and the extent to which this faster initial rate proceeds. However, the difference in initial rates between second and third additions is marginal.

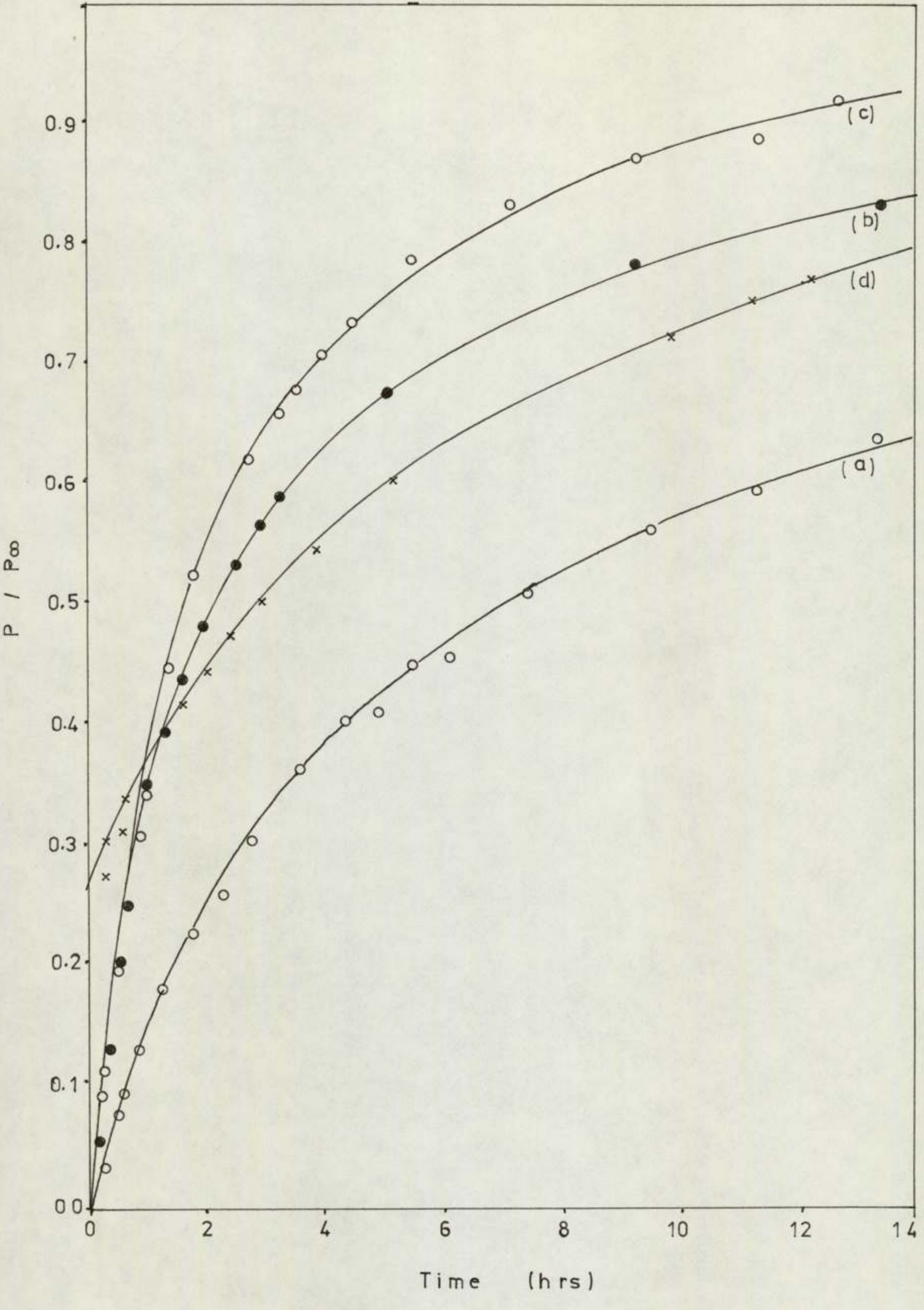


FIGURE XXXII

Effect of addition of successive portions of monomer to completed reactions

$[DEAS]_o$ = 0.56M $[LiO_tC_4H_9]_o$ = 0.56M

a. First Addition b. Second Addition c. Third Addition

d. (1/1) Monomer/initiator under 760 mm Hg SO_2

Addition of only one further quantity of monomer to MEAS indicated that this anhydrosulphite decomposition also shows the same type of behaviour.

Table XIX shows the derived second-order rate constants for the addition of further monomer to anhydrosulphite reaction mixtures in the presence of lithium t-butoxide. DEAS is assumed to be similar to MEAS in that initial rates of decomposition are first order in both monomer and initiator. Since further additions of monomer are made to a completed reaction, the second and third additions are equivalent to addition of monomer to either a polymeric initiator or polymer/initiator mixture.

TABLE XIX

Derived second-order rate constants (k^1) for the addition of successive quantities of anhydrosulphite to completed reactions

$[MEAS]_o = 0.56M \qquad [LiO_tC_4H_9]_o = 0.56M$

Addition of Monomer	$k^1 \times 10^4$ $l\ mol^{-1}s^{-1}$
First	2.98
Second	12.80

$[DEAS]_o = 0.41M \qquad [LiO_tC_4H_9]_o = 0.45M$

Addition of Monomer	$k^1 \times 10^4$ $l\ mol^{-1}s^{-1}$
First	2.98
Second	12.2
Third	12.4

The second-order rate constants reflect the results indicated by the reaction profile. Hence the initial rate of decomposition is faster where the anhydrosulphite is added to a monomer solution which has been previously decomposed in the presence of alkoxide. Further addition of monomer only marginally improves on this faster rate in the case of DEAS.

The derived second-order rate constant for MEAS with first addition of monomer is very much smaller than the same constant derived from the use of lower initiator concentrations (see Table XIII, $k^1 = 5.25 \times 10^{-4}$ l mol^{-1}s^{-1}) and inspection of Figure XXIV shows that the initiator concentration used in this study falls into the uncertain region of the plot.

Decomposition of DEAS using the same monomer and initiator concentrations but under an atmosphere of sulphur dioxide at 760 mm mercury gave a reaction profile identical to that shown in Figure XXXII profile (a), except that the profile is displaced vertically. Evolved gas was in excess of that expected by the same pressure as this displacement. Since the solvent was saturated with sulphur dioxide at a lower temperature than that used for the gas evolution measurement, the displacement can be attributed to equilibration of dissolved gas. Hence the decomposition of DEAS in decalin as solvent in the presence of lithium t-butoxide is not affected by the presence of sulphur dioxide.

CHAPTER 7

THE EFFECT OF MONOMER STRUCTURE ON INITIATED ANHYDROSULPHITE DECOMPOSITION AND RELATED STUDIES

7.1 ALKOXIDE INITIATED DECOMPOSITION OF VARIOUS ANHYDROSULPHITES

The decomposition of a number of disubstituted anhydrosulphites in the presence of lithium t-butoxide using decalin as solvent was briefly studied as a function of sulphur dioxide evolution. All studies in this section were carried out using the apparatus shown in Figure III so that the true initial rate could be observed.

The reaction profiles of four anhydrosulphites are shown in Figure XXXIII. In addition to MEAS, the diethyl, dimethyl and cyclopentyl substituted anhydrosulphites were used (DEAS, HABS, C'pent AS respectively). The initial rates are in the order DEAS $<$ MEAS $<$ C'pentAS $<$ HABS. The rate of decomposition of DEAS is so slow as to be negligible in comparison, under the conditions used. Figure XXXIII shows that the reaction profile of HABS is rather different in shape to that shown by the other anhydrosulphites studied since, although the initial rate is fast, the rate of sulphur dioxide evolution slows rapidly after approximately 50% reaction.

Assuming that all the anhydrosulphites studied behave in the same way as MEAS, i.e. initially the reaction is first-order with respect to both monomer and initiator, the initial rates of decomposition can be converted to their derived second-order rate constants. These are presented in Table XX.

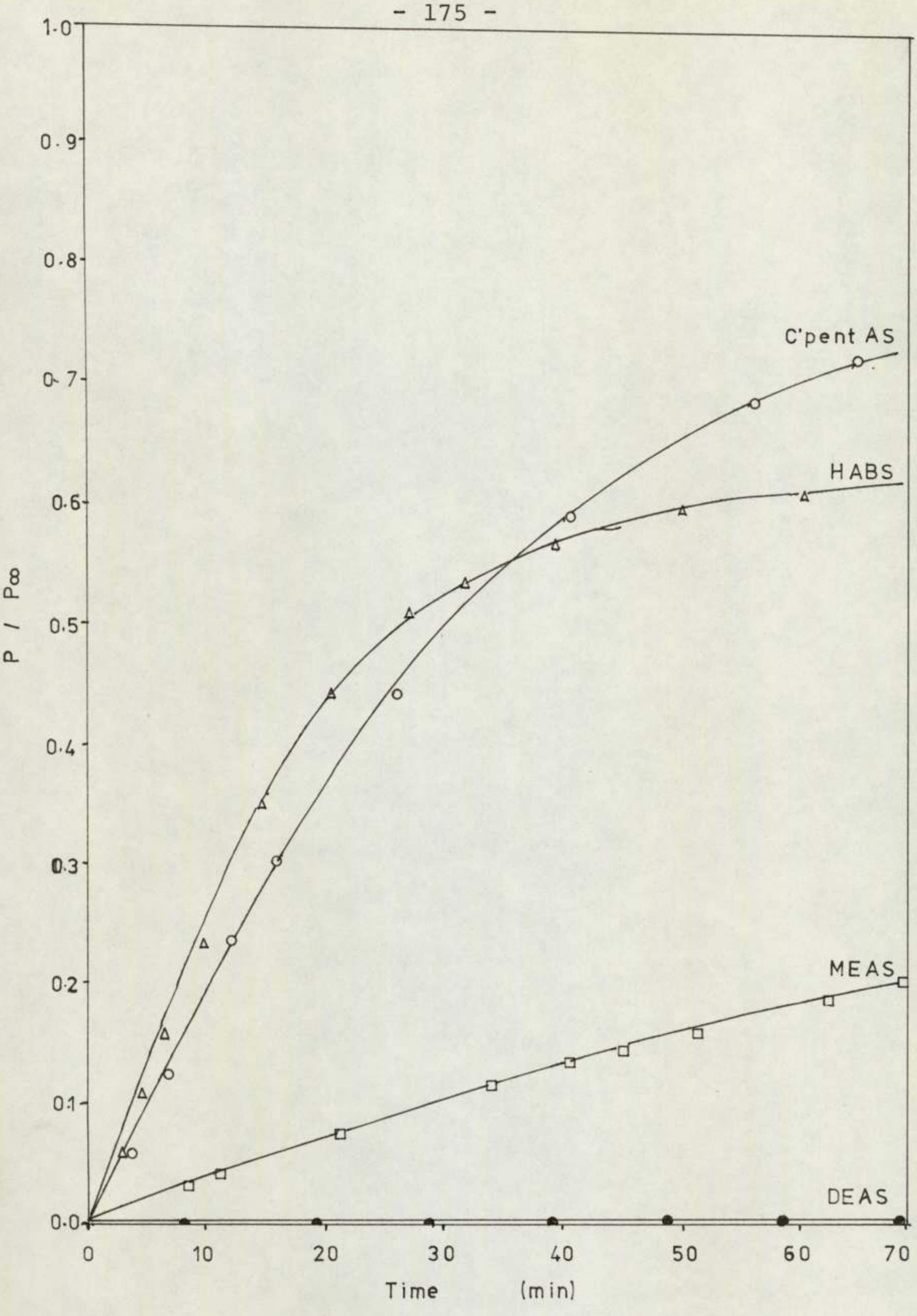


FIGURE XXXIII

Decomposition of various anhydrosulphites in the presence of lithium t-butoxide at 40^{o}C in decalin as solvent

$[\text{anhydrosulphite}]_o$ = 0.75M $[\text{LiO}_t\text{C}_4\text{H}_9]_o$ = 0.0082M

TABLE XX

Derived second-order rate constants (k^1) for the decomposition of some anhydrosulphites in the presence of lithium t-butoxide at 40°C in decalin as solvent

$[\text{Anhydrosulphite}]_o = 0.75M \qquad [\text{LiO}_t\text{C}_4\text{H}_9]_o = 0.0082M$

Anhydrosulphite	$k^1 \times 10^4$ $l\ mol^{-1}s^{-1}$
HABS	482
MEAS	58.0
DEAS	2.98*
C'pentAS	338

* This rate constant derived from decomposition at higher initial initiator concentration.

During the decomposition of both symmetrically disubstituted anhydrosulphites (HABS and DEAS) the system became heterogeneous with the deposition of a small quantity of white solid which was found to be polymeric.

7.2 DECOMPOSITION OF ANHYDROSULPHITES IN THE PRESENCE OF ALCOHOLS

MEAS was decomposed in the presence of lithium t-butoxide as initiator using dry t-butyl alcohol as solvent at 40°C. As a control, a similar concentration of MEAS in t-butanol was decomposed thermally in the absence of alkoxide, at 120°C. A monomer concentration of 0.76 mol l^{-1} was used in both cases and in the initiated system a lithium t-butoxide concentration of 0.016 mol l^{-1} was used.

Infra-red analysis of the two samples was made after the bulk of the solvent had been removed, and the spectra obtained in each case were identical with only minor differences which were attributable to the presence of alkoxide in the lower temperature sample.

The same procedure was carried out with DEAS and again almost identical infra-red spectra were obtained from the products.

The concentrations of reactants used together with the carbonyl absorption frequencies ($\nu_{C=O}$) of the products are listed in Table XXI, also included in this Table are the other relevant absorptions found to occur near the carbonyl absorptions only where alkoxide had been used as initiator. The carbonyl absorption frequencies of the poly α-esters and parent acids obtained from both anhydrosulphites are also included for comparison.

Table XXI indicates that the products obtained by decomposition of both DEAS and MEAS using either thermal or low temperature methods are not the poly α-ester obtained by decomposition in the presence of non-hydroxylic solvents. The possibility of reversion to parent α-hydroxy acid during work up procedures should the anhydrosulphite have failed to decompose is also excluded on the basis of the different infra-red absorptions.

TABLE XXI

Carbonyl absorption frequencies ($\nu_{C=O}$) for the product of decomposition of MEAS and DEAS under both thermal and lithium t-butoxide initiated conditions in the presence of excess t-butanol, with other relevant carbonyl absorptions

$[\text{t-butanol}] = 7.5M$

Anhydrosulphite	$[M]_o$ mol l^{-1}	$[I]_o$ mol l^{-1}	$\nu_{C=O}$ cm^{-1}
MEAS	0.75	Thermal	1730
MEAS	0.75	0.082	1720 and 1650
DEAS	0.76	Thermal	1725
DEAS	0.76	0.016	1725 and 1645
α-hydroxy-α-methyl butyric acid			1730
α-hydroxy-α-ethyl butyric acid			1740
Poly MEAS (thermal)			1755
Poly DEAS (thermal)			1760

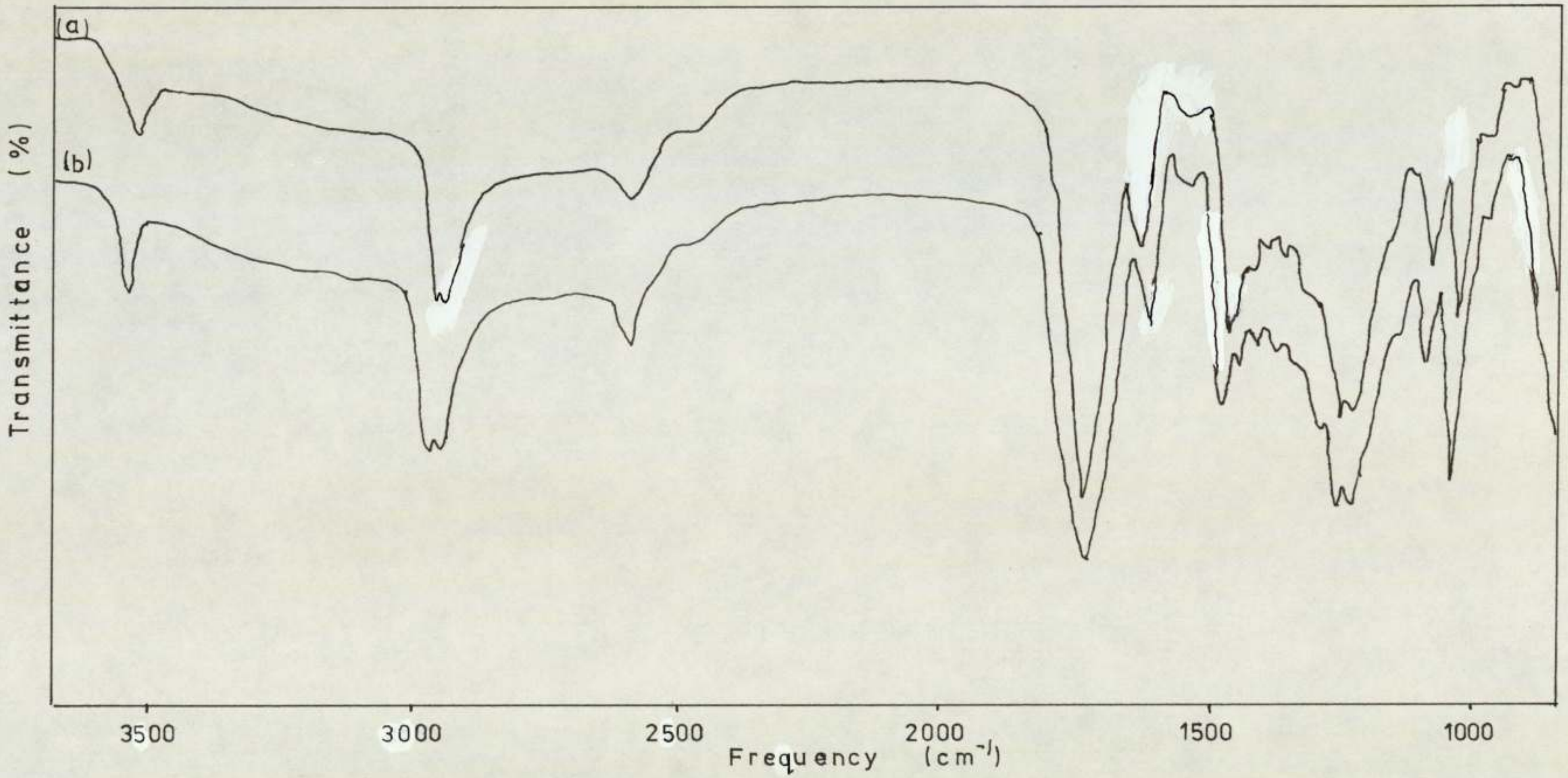
The thermal decomposition of anhydrosulphites in the presence of hydroxylic solvent has been shown to yield the appropriate α-hydroxy ester. The products obtained here for both modes of decomposition have infra-red spectra consistent also with α-hydroxy ester.

The infra-red absorption spectra of the products of DEAS

FIGURE XXXIV

Infra-red absorption spectra of the α-hydroxy esters produced by the decomposition of DEAS in excess t-butanol

a. Thermal b. Lithium t-butoxide initiated decomposition



decomposition in the presence of t-butanol by the two methods are shown in Figure XXXIV.

7.3 DECOMPOSITION OF ANHYDROSULPHITES IN THE PRESENCE OF SODIUM ACETATE

The rate of decomposition of MEAS, as measured by the evolution of sulphur dioxide, in the presence of anhydrous sodium acetate, was studied briefly. A temperature of 30°C was used with THF as solvent.

After the reaction has proceeded to the point of no further evolution of gas, a further equal quantity of monomer was added, and the manometer rise again observed.

Table XXII shows the relevant results. The extent of reaction is based on the final pressure of evolved sulphur dioxide compared with the calculated pressure of gas which should have been evolved. Since the solubility of sulphur dioxide in THF under the conditions used is not accurately known, this calculated values is approximate. Monomer concentration is based on the total monomer present as is the extent of reaction.

Most of the observed reaction after first addition of monomer took place within 30 minutes. Thereafter little reaction was observed. The further 5% reaction after second monomer addition can be attributed to ingress of moisture during handling.

TABLE XXII

Extent of decomposition of MEAS (M) in the presence of sodium acetate (I) at 30°C in THF as solvent

$[I]_o$ mol l^{-1}	$[M]_o$ mol l^{-1}	Extent of Decomposition %
0.56	0.28	~ 30
0.56	0.56	~ 35

Infra-red spectroscopic analysis of the product showed it to contain predominantly unchanged anhydrosulphite and sodium acetate together with parent α-hydroxy acid.

The rapidity of the initial reaction and its limited extent is indicative of the reaction of anhydrosulphite with moisture. Infra-red spectra of the sodium acetate indicated that a certain amount of water of crystallisation had not been removed by the drying process, and the partial decomposition of the anhydrosulphite can be attributed to this.

7.4 LOCATION OF LITHIUM IN POLYMER

A sample of the product of decomposition of MEAS in the presence of lithium t-butoxide was subjected to extraction with various solvents in turn in order to determine the ease with which the lithium present in the product could be removed.

Flame photometry was used as described in Chapter 2, to determine the presence of lithium since this has been shown to be effective for the estimation of lithium down to very low concentrations. The polymer sample used was prepared by MEAS decomposition at 40°C using decalin as solvent and at $[MEAS]_o = 0.75M$, $[LiO_tC_4H_9]_o = 0.0082M$. Solid polymer was washed with solvent then dissolved in THF before adding a sample to water for lithium determination.

Table XXIII shows the residual lithium concentration in the polymer after extraction with each solvent. The lithium concentration is presented as grams of lithium per gram of polymer and is based on the polymer remaining after extraction. Weight loss during extraction was less than 11% total, most of which was lost during the first washing with t-butanol (~8% lost).

TABLE XXIII

Concentration of lithium remaining in polymer after extraction with various solvents

Solvent	Lithium Concentrations gms lithium per 100 gms polymer
before extraction	0.87
t-butanol	0.35
water	0.19
0.4N HCl	0.12

These results show that more than half of the lithium is removed by extraction with a solvent which does not interact chemically with the polymer, i.e. t-butanol, although conceivably some exchange of lithium between alkoxide present in the polymer and the alcohol could have taken place. t-Butanol is a poor solvent for the polymer prepared from MEAS when that polymer has a molecular weight in excess of several hundred.

Washing with water caused a further significant reduction in lithium concentration and this is unusual since poly-α-esters are very insoluble in water. This result indicates the presence of either a very polar non-polymeric species or alkoxides which might be hydrolysed by water to hydroxyl compounds.

Finally, washing with dilute acid resulted in a further reduction of lithium concentration. This might represent the hydrolysis of lithium carboxylates and/or perhaps further removal of those species which were predominantly removed by water. The residual lithium can reasonably be considered as being occluded in the polymer in such a way that the solvents were not able to remove it, a necessary consequence of using washing solid polymer with non-solvent.

7.5 MOLECULAR WEIGHT STUDIES

7.5.1. Gel Permeation Chromatography - G.P.C.

a. Effect of Monomer and Initiator Concentrations

Samples were prepared for gel chromatography analysis as described in Chapter 2 and analysis was carried out under the standard conditions, the results are, therefore, directly comparable.

The analyses showed the molecular weight distribution of the products obtained by the decomposition of anhydrosulphites in the presence of alkoxides to depend to a large extent on the concentration of initiator used. Figure XXXV shows the way in which the molecular weight distribution changes with increasing alkoxide concentration. The high molecular weight portion of the chromatogram moves steadily towards increasingly high molecular weight as the monomer/initiator concentration ratio increases, monomer concentration remaining constant.

The shape of the molecular weight distribution curve is complex and frequently binodel. This has introduced difficulties in ascertaining the point at which high molecular weight material ceases and low molecular weight material begins. The largest molecular weight fraction, which in a more symmetrical distribution is closely represented by $\bar{M}n$, is in these studies frequently a factor of 1.5 higher than $\bar{M}n$.

The chromatograms also show the presence of low molecular weight material which is not included in data used for molecular weight calculations and which is not therefore included in the tables shown below. G.P.C. is not suitable for the separation of very low molecular weight species since these materials may be retained to varying extents on the gel due to differences in polarity as well as size. An additional factor is the effect of these low molecular weight molecules on the refractive index of the eluted solution since this is the property measured in these analyses. This last factor may be responsible for the deviations of the chromatogram below the base line in the area shown in the low molecular weight species.

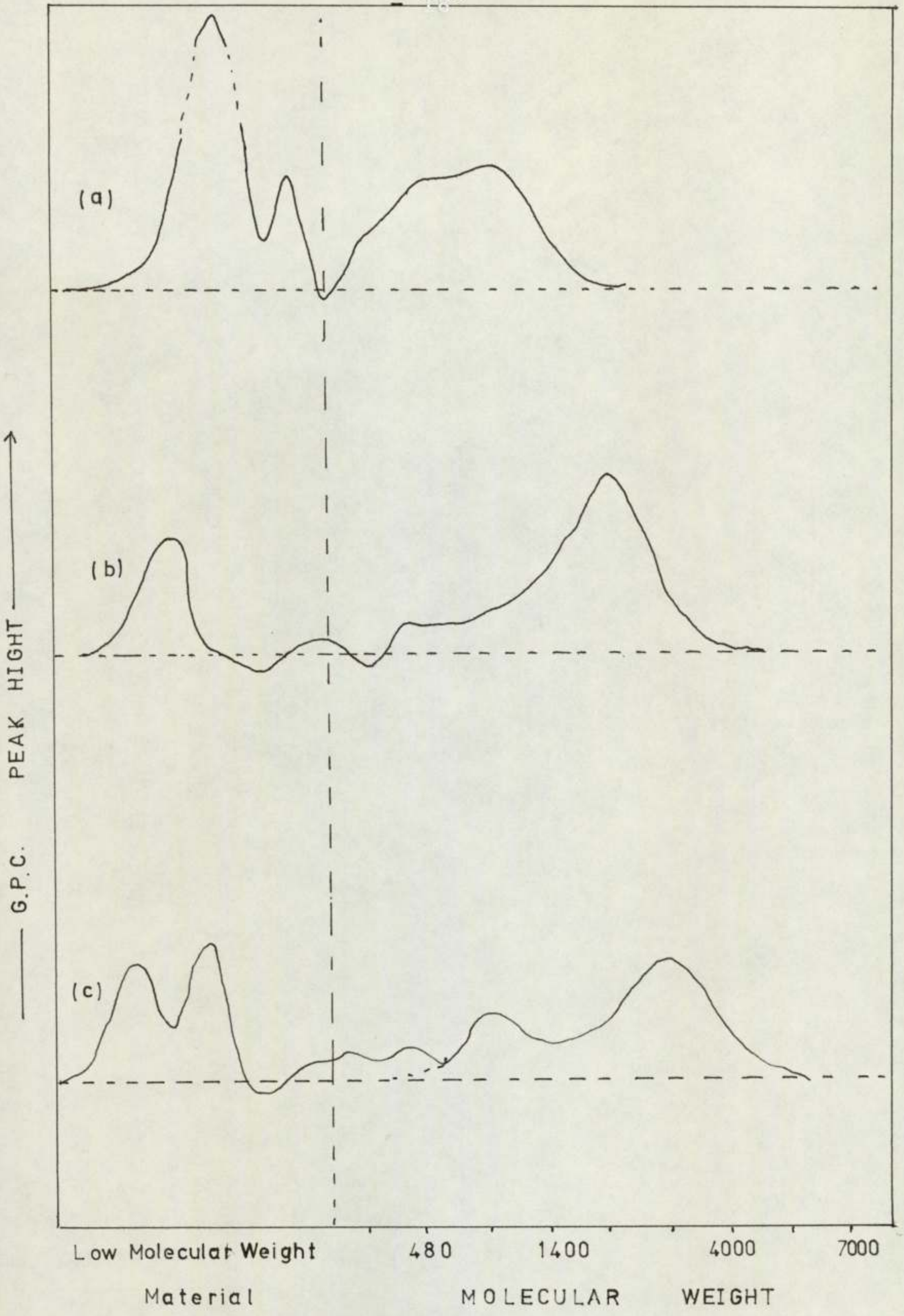


FIGURE XXXV

Variation of molecular weight distribution with initiator concentration

$$[MEAS]_o = 0.56M$$

$$[LiO_tC_4H_9]_o = \text{a. } 0.56M \quad \text{b. } 0.11M \quad \text{c. } 0.056M$$

However, these low molecular weight materials may be considered in a quantitative manner, which, while not suitable for detailed analysis may be used to give an indication of trends. In general, as the amount of initiator used decreases, so does the amount of low molecular weight material.

The effect of a progressive decrease in initiator concentration at constant monomer concentration for the decomposition of MEAS at 40°C in THF is shown in Table XXIV.

TABLE XXIV

Variation of number average molecular weight ($\bar{M}n$) and molecular weight distribution ($\frac{\bar{M}w}{\bar{M}n}$) with lithium t-butoxide concentration $[I]_o$ for the decomposition of MEAS in THF at 40°C

$[I]_o$ mol l^{-1}	$\frac{[M]_o}{[I]_o}$	$\bar{M}n$	$\frac{\bar{M}w}{\bar{M}n}$
0.56	1	700	-
0.112	5	965	1.19
0.056	10	849	1.65
0.0112	50	1040	1.66
0.0056	100	596	1.23
0.0007	800	605	-

$[MEAS]_o = 0.56M$

These results confirm the indications given by the chromatograms (Figure XXXV). As the $\frac{[M]_o}{[I]_o}$ ratio increases the molecular weight also increases up to the ratio $\frac{[M]_o}{[I]_o} = 50$, beyond this the molecular weight decreases again, as shown

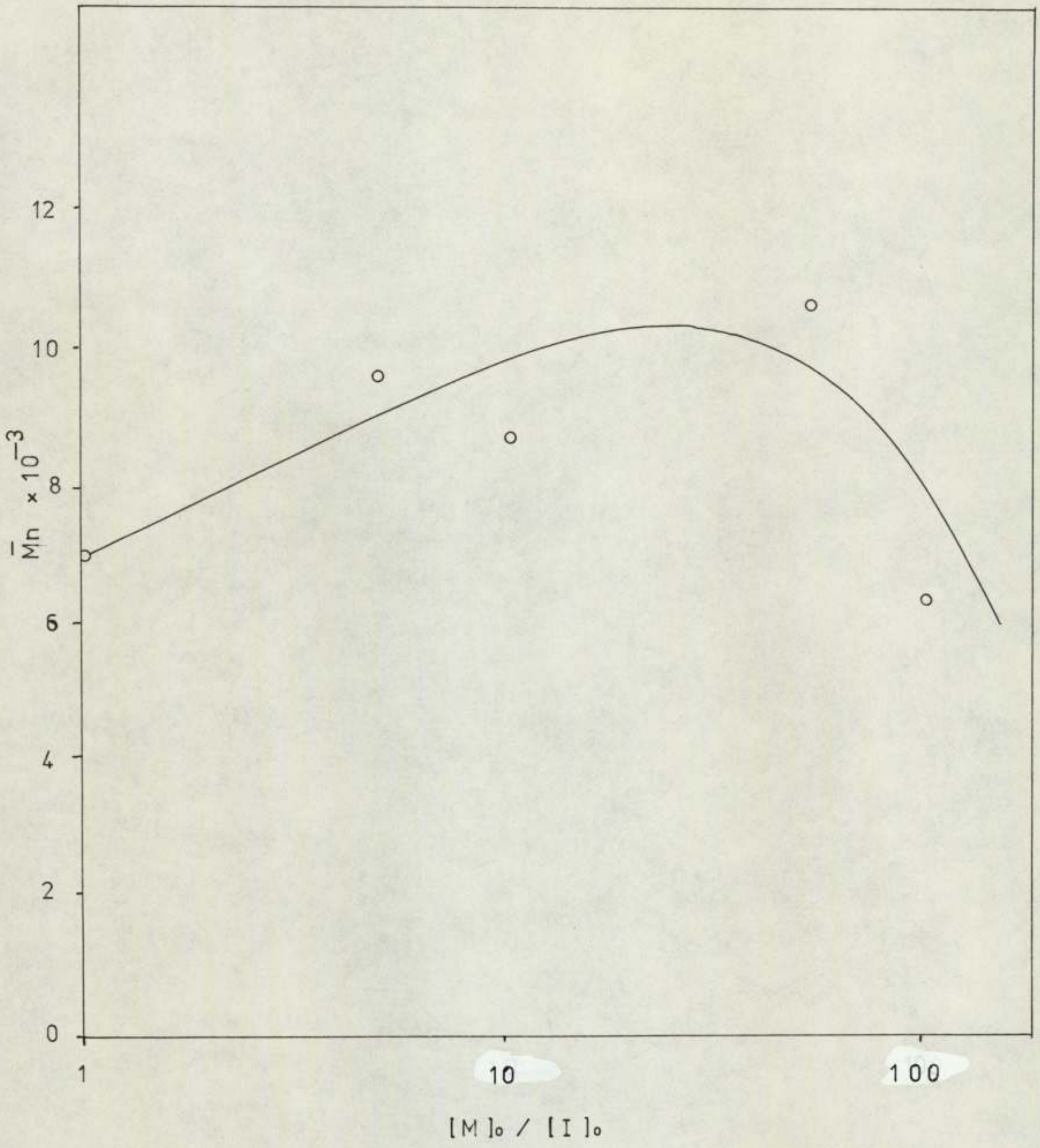


FIGURE XXXVI

Variation of number average molecular weight ($\bar{M}n$) with $[M]_o/[I]_o$ for the lithium t-butoxide initiated decomposition of MEAS in THF at 40°C in Figure XXXVI.

Molecular weight distribution as measured by the ratio of weight to number average molecular weights ($\frac{\bar{M}w}{\bar{M}n}$) also increases with the increase in $\frac{[M]_o}{[I]_o}$ ratio and again decreases at high $\frac{[M]_o}{[I]_o}$ ratio. The molecular weight distribution is wider, approximately 1.6, than that obtained by the thermal decomposition of anhydrosulphites (typically 1.2).

The effect of a change in the $\frac{[M]_o}{[I]_o}$ ratio on the molecular weight was also investigated for the decomposition of MEAS in decalin catalysed by lithium t-butoxide. The ratio can be altered by variation of either $[M]_o$ or $[I]_o$ and the change in number average molecular weight as each of these quantities were varied in turn while maintaining the other constant is shown in Tables XXV A and XXV B. The molecular weight distribution is also shown.

These results show the same trend as those shown for decompositions in THF as solvent using the same catalyst system; molecular weight increases with increasing $\frac{[M]_o}{[I]_o}$ ratio up to the value $\frac{[M]_o}{[I]_o}$ = 90, beyond this point the average molecular weight begins to fall again. This behaviour is shown when both $[M]_o$ and $[I]_o$ are used to vary the $\frac{[M]_o}{[I]_o}$ ratio. The molecular weight distribution tends to become rather more narrow when $\frac{[M]_o}{[I]_o}$ is high in both sets of results.

The results from Tables XXV A and XXV B are presented graphically in Figure XXXVII.

TABLES XXV A and XXV B

Variation of number average molecular weight ($\bar{M}n$) and molecular weight distribution ($\frac{\bar{M}w}{\bar{M}n}$) with monomer to initiator ratio for the decomposition of MEAS in the presence of lithium t-butoxide at 40^{o}C in decalin as solvent

A. Monomer concentration constant, initiator concentration varies

$[MEAS]_o$ = 0.732M

$[I]_o$ mol l^{-1}	$\frac{[M]_o}{[I]_o}$	$\bar{M}n$	$\frac{\bar{M}w}{\bar{M}n}$
0.082	9	1711	1.23
0.041	18	1128	1.43
0.0082	90	2711	1.20
0.0041	180	1315	1.21
0.00082	900	758	1.28

B. Initiator concentration constant, monomer concentration varies

$[LiO_tC_4H_9]_o$ = 0.0082M

$[M]_o$ mol l^{-1}	$\frac{[M]_o}{[I]_o}$	$\bar{M}n$	$\frac{\bar{M}w}{\bar{M}n}$
0.0732	9	2620	1.41
0.1464	18	2340	1.42
0.366	45	2883	1.26
0.732	90	2711	1.20
1.464	180	1430	1.24

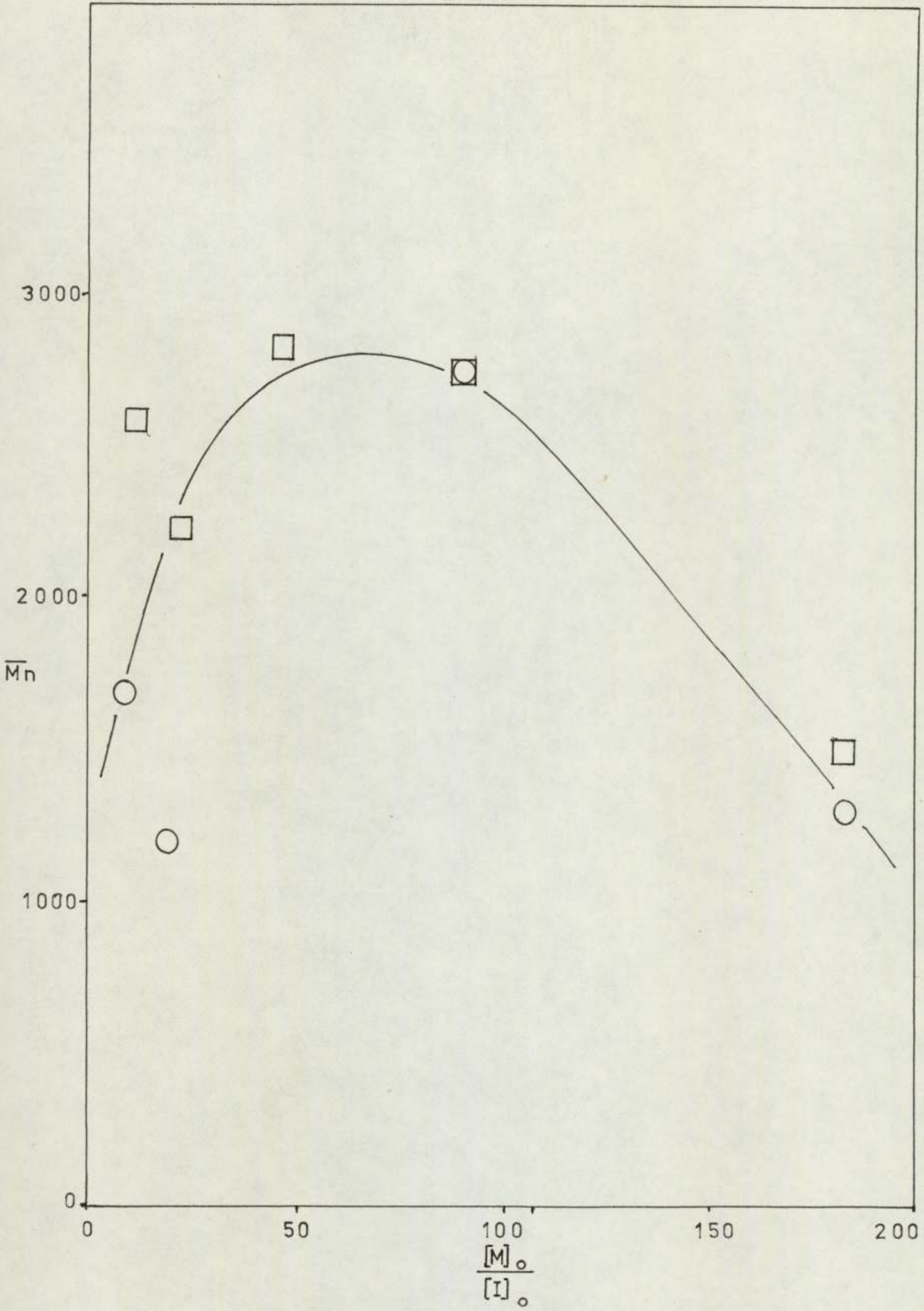


FIGURE XXXVII

Variation of number average molecular weight (Mn) with $[M]_o/[I]_o$ for the decomposition of MEAS in decalin as solvent at 40°C in the presence of lithium t-butoxide

○ $[MEAS]_o$ = 0.732M $[LiO_tC_4H_9]_o$ = varies

□ $[MEAS]_o$ = varies $[LiO_tC_4H_9]_o$ = 0.0082M

The effect of a change in the concentration of both monomer and initiator while maintaining the ratio $[M]_0 / [I]_0$ at a constant value was also investigated; the results are presented in Table XXVI.

TABLE XXVI

Variation of number average molecular weight ($\bar{M}n$) and molecular weight distribution ($\bar{M}w/\bar{M}n$) with concentration of reactants at constant $[M]_0 / [I]_0$ for the decomposition of MEAS in decalin at 40°C in the presence of lithium t-butoxide

$\frac{[M]_0}{mol\ l^{-1}}$	$\frac{[I]_0}{mol\ l^{-1}}$	$[M]_0 / [I]_0$	$\bar{M}n$	$\bar{M}w / \bar{M}n$
0.7320	0.0410	18	1128	1.43
0.3660	0.0205	18	2259	1.44
0.1830	0.0102	18	2876	1.31
0.1464	0.0082	18	2340	1.42
0.0732	0.0041	18	2106	1.48

These results indicate that no significant change in molecular weight of products is obtained by variation in the concentration of reactants used while maintaining constant $[M]_0 / [I]_0$ although the highest molecular weight was obtained with an intermediate concentration of both monomer and polymer in the range studied. The molecular weight distribution changes little with variation in reactant concentration under these conditions.

B. Effect of parent acid and chloride containing impurities

The presence of the parent α-hydroxy acid and chlorine containing impurities, principally α-chloro acid chloride have been shown to be detrimental to the production of high molecular weight material in the thermal decomposition of anhydrosulphites.[58] The effect of these impurities on the molecular weight of the products produced by the alkoxide induced decomposition of MEAS was also studied.

α-chloroacetyl chloride was added to the reaction mixture as the chlorine containing impurity. Polymerisations were carried out at 40°C in tetrahydrofuran as solvent and were analysed in the standard way. The effect of added impurity shown as a molar percent based on monomer is shown in Table XXVII.

TABLE XXVII

Effect of added α-chloro acetyl chloride on molecular weight ($\overline{Mn}$) and molecular weight distribution ($\overline{Mw}/\overline{Mn}$) for the decomposition of MEAS in THF at 40°C using lithium t-butoxide as initiator

$$[\text{MEAS}]_o = 0.70\text{M} \qquad [\text{LiO}_t\text{C}_4\text{H}_9]_o = 0.01\text{M}$$

$$[M]_o / [I]_o = 70$$

α-chloro acetyl chloride mole %	$\overline{Mn}$	$\overline{Mw} / \overline{Mn}$
~ 0.1	2250	1.15
6.0	3170	1.28
25.0	379	1.23

The gel permeation chromatograms indicated a decrease in the proportion of high molecular weight material as the concentration of chloride containing impurity increased, although the number average molecular weight ($\overline{Mn}$) showed an increase for small additions of impurity. The average molecular weight represented by $\overline{Mn}$ = 379 does not accurately reflect the molecular weight of the product, but since no high molecular weight material was produced in this case, the result probably indicates the addition of only one or two monomer residues to the highly reactive acyl chloride.

Added parent α-hydroxy acid was also shown to adversely affect the production of high molecular weight material as shown in Table XXVIII.

TABLE XXVIII

Effect of added α-hydroxy acid on the molecular weight ($\overline{Mn}$) and molecular weight distribution ($\overline{Mw}/\overline{Mn}$) for lithium t-butoxide initiated decomposition of MEAS at 40°C in decalin

α-hydroxy acid mole %	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$
-	960	1.19
10	883	1.32
50	302	1.23

$[MEAS]_o$ = 0.70M $[LiO_tC_4H_9]_o$ = 0.10M

$[M]_o / [I]_o$ = 7

The effect of added parent α-hydroxy acid is to steadily drop the average molecular weight and as in the case of the chlorine containing impurities inspection of the gel permeation chromatograms shows that the quantity of material which can be regarded as polymeric is decreasing with increasing impurity and is essentially non existant at 50% added acid.

C. Variation of molecular weight with conversion

The evolution of gas has been shown to correspond closely to the rates of monomer decomposition and appearance of products. The gas evolution measurements were used to determine the extent of conversion of monomer to products at various times during the reaction. Samples were taken from the reaction mixture and the reaction stopped in these samples by treatment with dilute acid as indicated in the experimental section. The products were transferred to tetrahydrofuran as solvent for G.P.C. analysis.

Table XXIX shows the change in molecular weight and molecular weight distribution with time for the product of MEAS decomposition using an alkoxide initiator. The relevant gas evolution data is presented in Figure XXI.

Figure XXXVIIIshows the results from Table XXIX presented graphically. The stages of the reaction up to approximately 50% conversion show an almost linear increase in average molecular weight with conversion, beyond this point however, the graph becomes confused and a considerable variation in results is apparent. Molecular weight distribution is narrow and does not show any appreciable variation throughout the reaction.

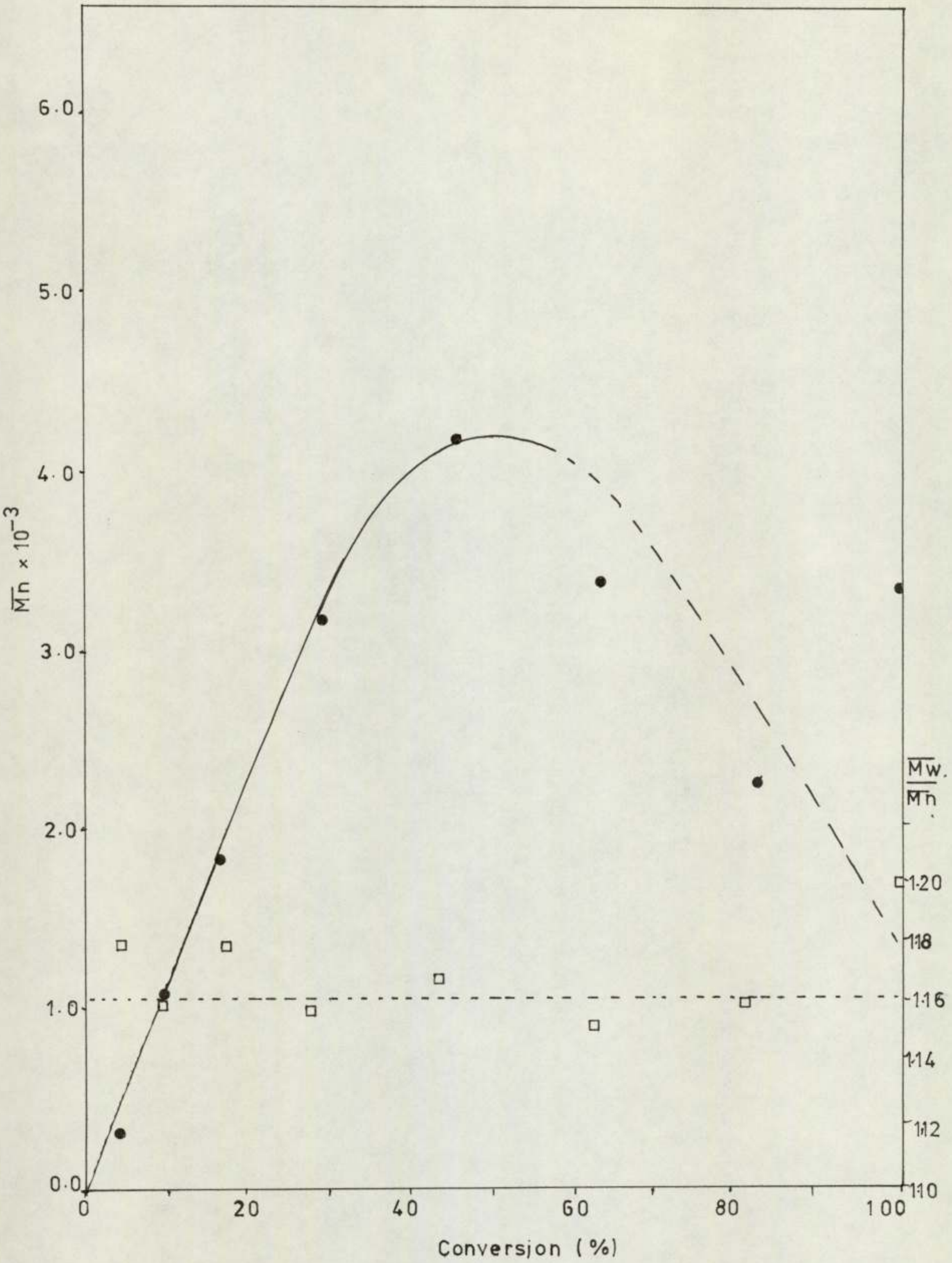


FIGURE XXXVIII

Variation of number average molecular weight*,●, and molecular weight distribution†, □, with conversion for the polymerisation of MEAS in decalin at 40°C in the presence of lithium t-butoxide * ($\bar{M}n$) † ($\frac{\bar{M}w}{\bar{M}n}$)

TABLE XXIX

Variation of molecular weight parameters with conversion for the decomposition of MEAS in decalin at 40°C using lithium t-butoxide as initiator

$[\mathrm{MEAS}]_o = 0.75\mathrm{M} \qquad [\mathrm{LiO}_t\mathrm{C}_4\mathrm{H}_9]_o = 0.0082\mathrm{M}$

$[M]_o / [I]_o = 90$

Conversion %	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$
3	420	1.18
8	983	1.16
17	1816	1.18
30	3186	1.15
47	4179	1.16
63	3272	1.14
82	2281	1.15
100	2111	1.20

D. Molecular weight measurements for other anhydrosulphites

The molecular weight parameters of several other poly α-esters produced by the alkoxide induced decomposition of other anhydrosulphites were also investigated. These are shown in Table XXX.

TABLE XXX

Molecular weight parameters for the products of decomposition of several anhydrosulphites (M) at 40°C in decalin as solvent initiated by lithium t-butoxide (I)

$[M]_o = 0.70M$

Anhydrosulphite	$[I]_o$	$[M]_o$ / $[I]_o$	Mn	Mw/Mn
C'pent AS	0.1	7	1178	1.77
HABS	0.1	7	1390	1.62
*HABS	0.01	70	3996	1.25
MEAS (Thermal)	-	-	8964	1.13

* only THF soluble portion analysed by GPC.

The C'pent AS sample was contaminated with some 2.4% α-chloro acid chloride. This is probably in part responsible for the relatively broad molecular weight distribution which resulted in this case.

The product of the HABS decomposition was characterised by a lack of high molecular weight product at high $[M]_o$ / $[I]_o$ as shown by G.P.C. analysis of the soluble product. A large part of the product deposited from solution during the reaction and was not redissolvable for molecular weight study. Infra-red analysis of this precipitated product showed it to be polymeric, but since end groups were not known, molecular weight was not determined.

The thermal polymer was prepared for comparative purposes and shows the narrow molecular weight distribution expected. The relatively low molecular weight (relative to thermally prepared di n-alkyl substituted polymer) is indicative of the problems experienced with the preparation of high molecular weight asymmetrically substituted poly α-esters.

7.5.2 Vapour Pressure Osmometry

The possibility of association of the initiator lithium alkoxide in the solvents decalin and THF was investigated in the temperature range 25 - 37°C (THF) and 25 - 65°C (decalin). Benzil was used as a standard.

Assuming that benzil itself does not associate in either of these two solvents, and this compound is chosen for its lack of association, then no evidence of alkoxide association was found in decalin. This is somewhat surprising since lithium alkyls frequently have a degree of association of six in hydrocarbon solvents, utilising an inverted micelle structure to lower energy levels.[82]

In THF, however, indications of a degree of association of six were found when measured against benzil. Although this behaviour was shown over the concentration range 0.05 - 0.4M, below 0.05M the degree of association was confused but probably four.

The expected structure in THF is then a micelle containing six, or at lower concentrations four, initiator molecules. This micelle can be expected to be in equilibrium with the single molecule with, in the absence of any reaction which removes initiator, the equilibrium well over to the right.

$$6\mathrm{LiO_tC_4H_9} \rightleftharpoons (\mathrm{LiO_tC_4H_9})_6$$

Vapour pressure osmometry results can best be presented as a plot of R against concentration, where R is a measure of the temperature difference caused by the migration of solvent from a drop of pure solvent to a drop of the alkoxide solution. Since R depends only on the number of particles in solution, a given concentration of a solute in solution should always give the same value of R. Thus, if no association takes place superimposed plots of R against concentration can be expected for standard and alkoxide. Figure XXXIX clearly shows the good agreement obtained between benzil standard and alkoxide in decalin, together with the divergence of the plots for benzil and alkoxide in THF, presumably due to micelle formation.

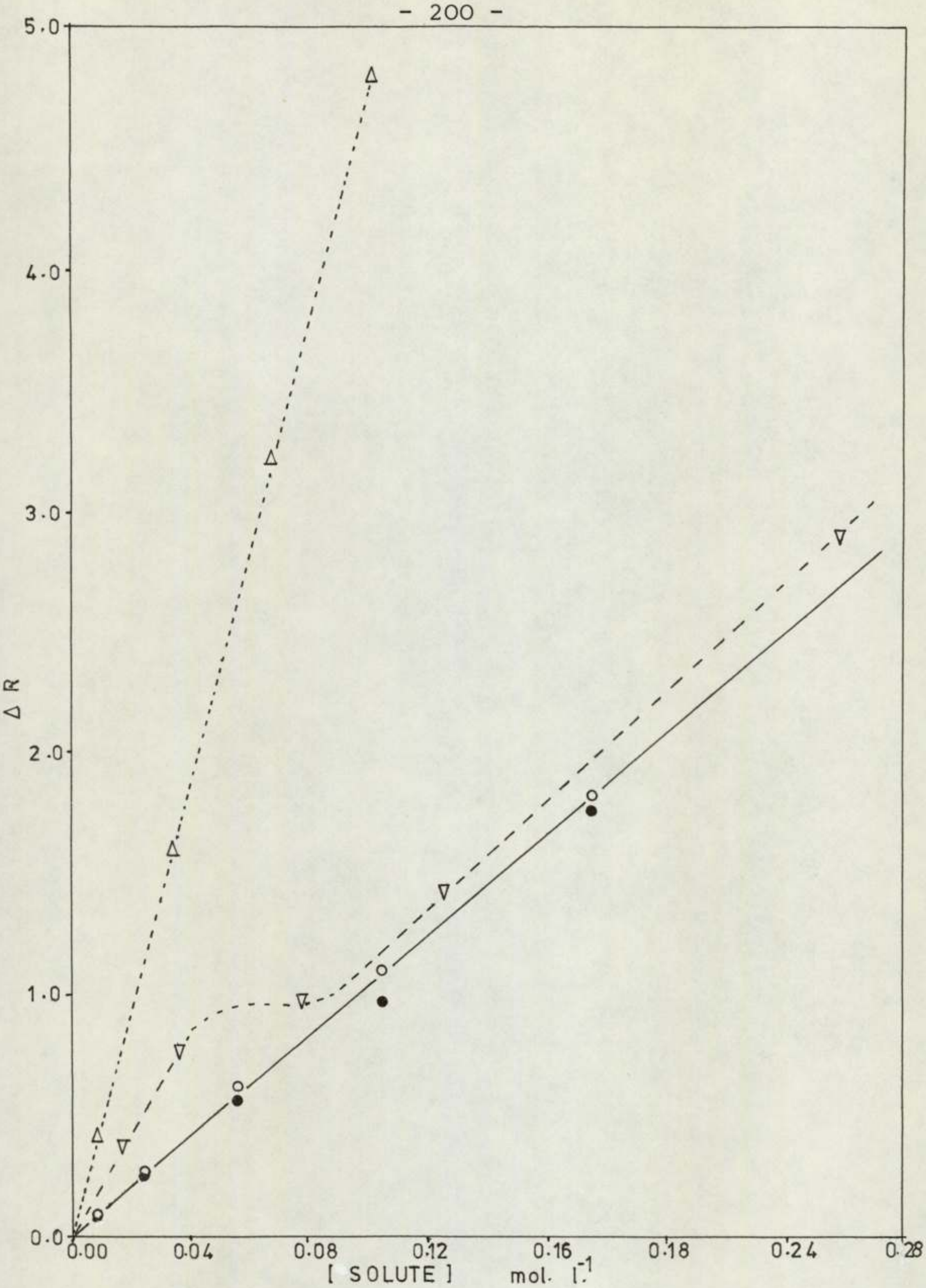


FIGURE XXXIX

Vapour pressure osmometry data for lithium t-butoxide in THF and decalin solvents at 37°C, Benzil Standard.

THF : Benzil △·················△ $LiO_tC_4H_9$ ▽- - - - - -▽

Decalin : Benzil ○————————○ $LiO_tC_4H_9$ ●————————●

CHAPTER 8

DISCUSSION OF ALKOXIDE INITIATED ANHYDROSULPHITE DECOMPOSITION

It is evident from the results presented in the previous two chapters that the mechanisms involved in the decomposition of anhydrosulphites in the presence of alkoxides at ambient temperatures are fundamentally different from those involved in the thermal decomposition of these compounds. The kinetic and analytical results obtained in these studies impose a considerable restriction on the nature of possible mechanisms which may be considered to operate. The characteristic features of the alkoxide initiated reaction may be summarised as follows:

1. The reaction is first-order with respect to both monomer and initiator in the early stages.

2. In the latter stages of the reaction i.e. after some 60% conversion, the rate slows down to a level below that required for first-order behaviour with respect to monomer throughout the reaction.

3. The extent of the initial, relatively rapid portion of the decomposition is reduced as the concentration of initiator is increased, although at very low initiator concentrations the cessation of the rapid decomposition and onset of the slower portion are difficult to separate.

4. Addition of initiator to monomer results in rapid appearance of a product which appears to contain a carboxylate anion, followed by slower appearance of polymeric products.

5. Rate of appearance of polymer is equal to the rate of disappearance of monomer (as judged by infra-red analysis) after the initial rapid reaction.

6. The rate of monomer decomposition is slowed marginally by the addition of a polar cosolvent.

7. The activation energy for the reaction is of the order of 60 kJ mol^{-1}.

8. Reaction in the presence of excess hydroxylic compounds results in the formation of simple mono-esters and very little polyester.

9. Anhydrosulphites are decomposed increasingly slowly as the size of alkyl substituents at the C - 5 position increases.

10. The molecular weight distribution of the polyα-ester produced is more complex than that of thermally prepared polymer and at relatively high initiator concentrations is distinctly binodal. The molecular weight distribution is broader than that obtained by thermal decomposition of anhydrosulphites.

11. The molecular weight of the product polyα-ester is not directly dependant on $\frac{[M]_o}{[I]_o}$ although low $\frac{[M]_o}{[I]_o}$ results in lower overall molecular weight.

12. The molecular weight is little changed by change in both monomer and initiator concentrations whilst

maintaining constant $\frac{[M]_o}{[I]_o}$.

13. Molecular weight increases with conversion in a linear manner, up to some 60% conversion, but molecular weight appears to decrease beyond this point.

14. When lithium alkoxide is used to initiate anhydrosulphite decomposition, the lithium is predominantly associated with low molecular weight product and is easily removed.

15. Simple dialkyl substituted anhydrosulphites are not significantly decomposed by anhydrous sodium acetate.

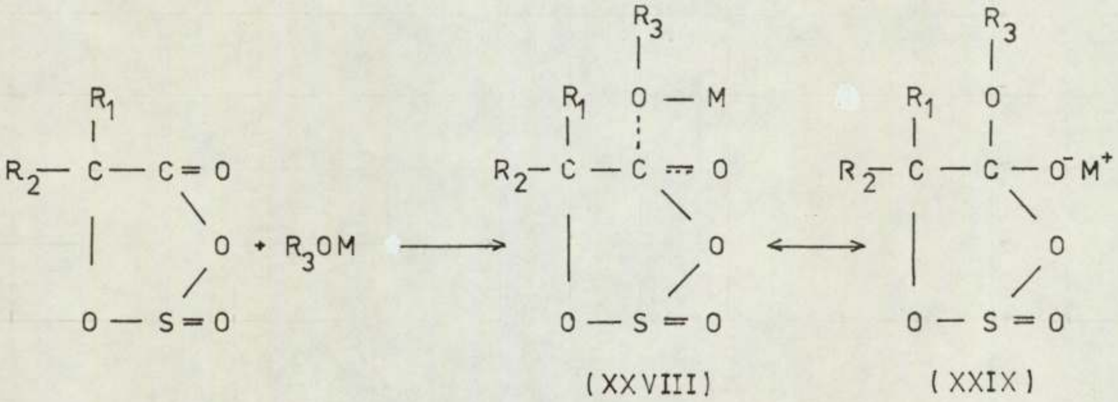
16. Added α-hydroxy acid markedly reduced the molecular weight of the polyester obtained.

17. High concentrations of added α-chloro acid chloride also reduce the molecular weight of the product.

If the experimentally determined energy of activation (approximately 60 kJ mol^{-1}) is a true reflection of the energy required to break bonds in the anhydrosulphite ring, then it would seem probable that the monomer and initiator have reacted together to produce an intermediate in which bonds are highly polarised and, therefore, easily broken. This intermediate is then able to further react to produce polymer. A mechanism can be formulated which might account for these results.

8.1 The simple N.C.A. mechanism

In its most elementary form such a mechanism would be envisaged as an attack at the C - 4 carbonyl of the anhydrosulphite ring by the nucleophilic oxygen atom of the alkoxide and formation of a complex intermediate (XXVIII) similar to the species proposed as an intermediate in the reaction between alkoxides and N.C.A.s[63]. This intermediate could exist either in a non-polar or in an ionic form (XXIX) as is shown in equation 46.



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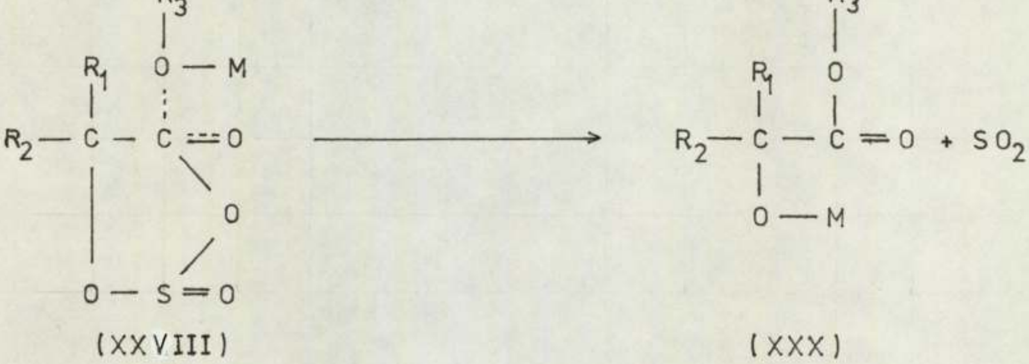
This intermediate then rapidly fragments with the loss of sulphur dioxide and a rearrangement involving the metal ion to regenerate an alkoxide species (XXX), equation 47.



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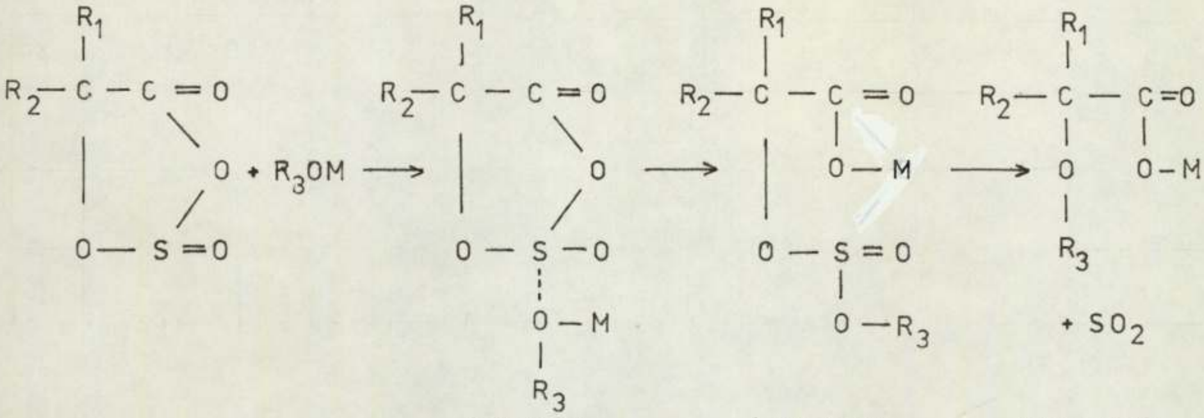
The regenerated alkoxide then attacks further anhydrosulphite molecules in a propogation mechanism.

This reaction scheme, however, lacks certain of the features of the mechanism required by the experimentally determined results. Primarily, no carboxylate anionic species is formed in the course of this mechanism, and secondly, the molecular weight of the resultant polyester should be directly related to the ratio $\frac{[M]_o}{[I]_o}$. Several other features including the observed reaction with hydroxylic species are also difficult to envisage, and the scheme as presented is therefore inadequate.

8.2 The 'wrong addition' N.C.A. mechanism

The occurrence of the carboxylate anion might be possible if the above scheme is modified to include some of the features of sodium methoxide attack on N.C.A.s[63,80]. Such a mechanism would involve attack by the alkoxide on the C-4 position of the ring as the primary polymer producing reaction, in the manner described in equations 46 and 47. However, an alternative attack of the methoxide on the S-2 atom of the ring might be considered if this could then lead to a loss of sulphur dioxide from the intermediate (XXXI) which might reasonably be expected to be unstable. This then leads to formation of a metal carboxylate (XXXIII). Since either the initiator alkoxide R_3OM or the propogating alkoxide (XXX) could undergo this 'wrong addition', the carboxylate anion could be produced at any stage in the reaction. The 'wrong addition' reaction is seen as a termination step, since



(XXXI) (XXXII) (XXXIII)

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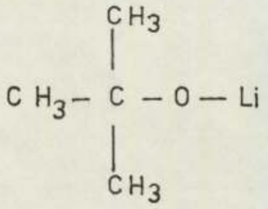
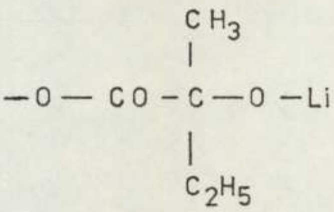
metal carboxylate is not expected to induce decomposition of the anhydrosulphite ring. Evidence for this comes from the failure of anhydrous sodium acetate to decompose anhydrosulphite and at 30°C the failure of the same compound to affect rate or molecular weight distribution in the thermal decomposition of anhydrosulphites[79]. Since initiator is being consumed in this termination, the departure from first order kinetics with respect to monomer during the latter stages of a reaction is explained.

In the case of the initiator lithium t-butoxide used with MEAS, the initial alkoxide (XXXIII) would be more



$CH_3-C(CH_3)_2-O-Li$

(XXXIV)



$-O-CO-C(CH_3)(C_2H_5)-O-Li$

(XXXV)

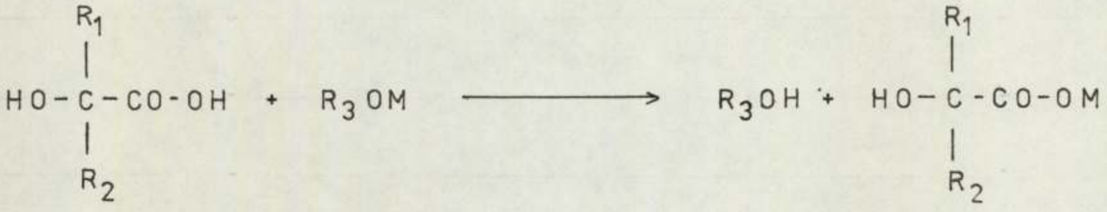
nucleophilic than the propogating alkoxide XXXV and hence the alternative 'wrong addition' could be expected to occur more readily in the initial stages of the reaction (thus producing more low molecular weight material containing the carboxylate anion). This low molecular weight material would be easily extracted, a fact which is in accordance with the observed results. Further, since a termination step is involved, the molecular weight is no longer related directly to $\frac{[M]_o}{[I]_o}$.

This mechanism then is adequate to explain many of the features of the alkoxide initiated decomposition of anhydrosulphites. It is not adequate, however, to explain all of them, notably the occurrence of a simple mono-ester when anhydrosulphite is decomposed by alkoxide in the presence of excess alcoholic species.

Detailed consideration of the probability of alkoxide attack at the sulphur atom of the anhydrosulphite ring reveals that this is unlikely and thus places the credibility of this mechanism in doubt. Even with N.C.A.s the attack of alkoxide on the C-2 carbonyl is considered to occur much more slowly than the attack at the C-4 position[80]. This is presumed to result from the relatively less electrophilic nature of the C-2 carbon as a consequence of its electro-negative situation in the ring. Attack by an alkoxide group on a sulphur atom, itself a reasonably strong nucleophile, in the same environment is therefore highly unlikely. The probability of the 'wrong addition' mechanism as a source of carboxylate anionic species is therefore considered to be remote.

8.3 The 'parent acid' mechanism

An alternative source of carboxylate anions is the direct reaction of alkoxide with trace parent ∝-hydroxy acid as shown in equation 49.



$$HO-\underset{R_2}{\overset{R_1}{C}}-CO\cdot OH + R_3OM \longrightarrow R_3OH + HO-\underset{R_2}{\overset{R_1}{C}}-CO-OM$$

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This mechanism in conjunction with the polyester producing reaction shown in equation 47 would produce the species which have been suggested as the product of alkoxide initiated decomposition of anhydrosulphites. If the reaction above (equation 49) occurred relatively slowly then initiator is gradually consumed and the reaction will not remain first order with respect to monomer. The metal carboxylate is again considered to be inactive for the reason suggested above in the 'wrong addition' mechanism.

However, this mechanism is unlikely to be significant for two reasons in particular. Firstly, in the presence of relatively large concentrations of alkoxide, the concentration of metal salt produced is greater than that which could be accounted for by reaction involving trace quantities of ∝-hydroxy acid. Secondly, the mechanism still involves no process by which the presence of excess hydroxyl containing compound could result in a simple mono-ester.

8.4 The C-5 attack mechanism

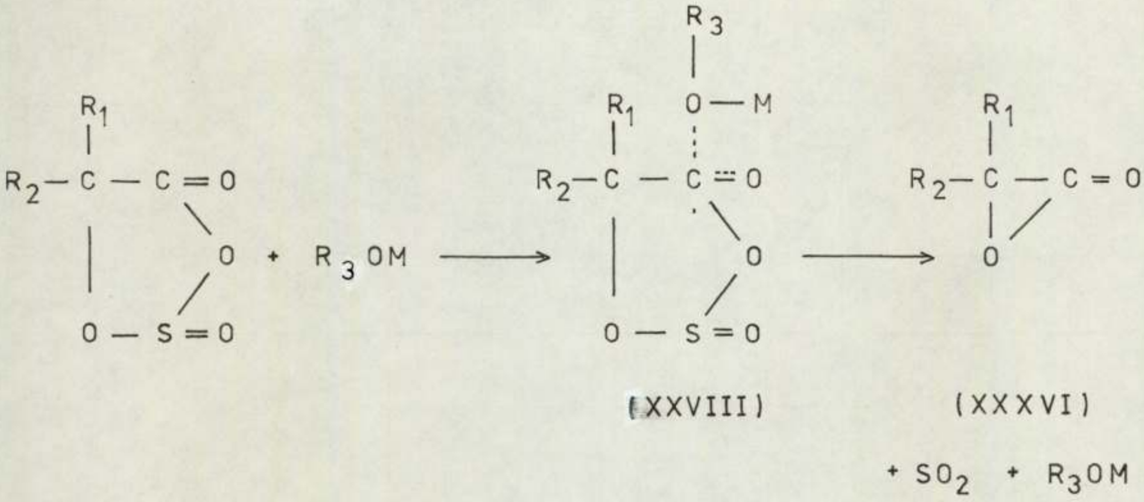
The probability of attack by alkoxide at the C-5 position of the anhydrosulphite as a primary step leading to ring decomposition is extremely unlikely both on steric and electronic grounds since this position is both stericly obstructed to attack and does not have significant nucleophilic character.

8.5 The reactive intermediate mechanism

It is clear from consideration of the above mechanisms that the most difficult factor to accommodate is the formation of the α-hydroxy carboxylic ester when anhydrosulphites are decomposed by alkoxides at low temperatures in the presence of excess alcohol. Formation of these esters during the thermal decomposition of anhydrosulphites in the presence of excess alcohol is adequately explained by the formation of α-lactone intermediates which are then able to react with any available nucleophiles[13]. It would seem reasonable therefore to suppose that a mechanism involving a similar intermediate operates in the low temperature mechanism.

A mechanistic scheme which could be used to describe the processes involved is shown below:

Reaction of alkoxide with anhydrosulphite:

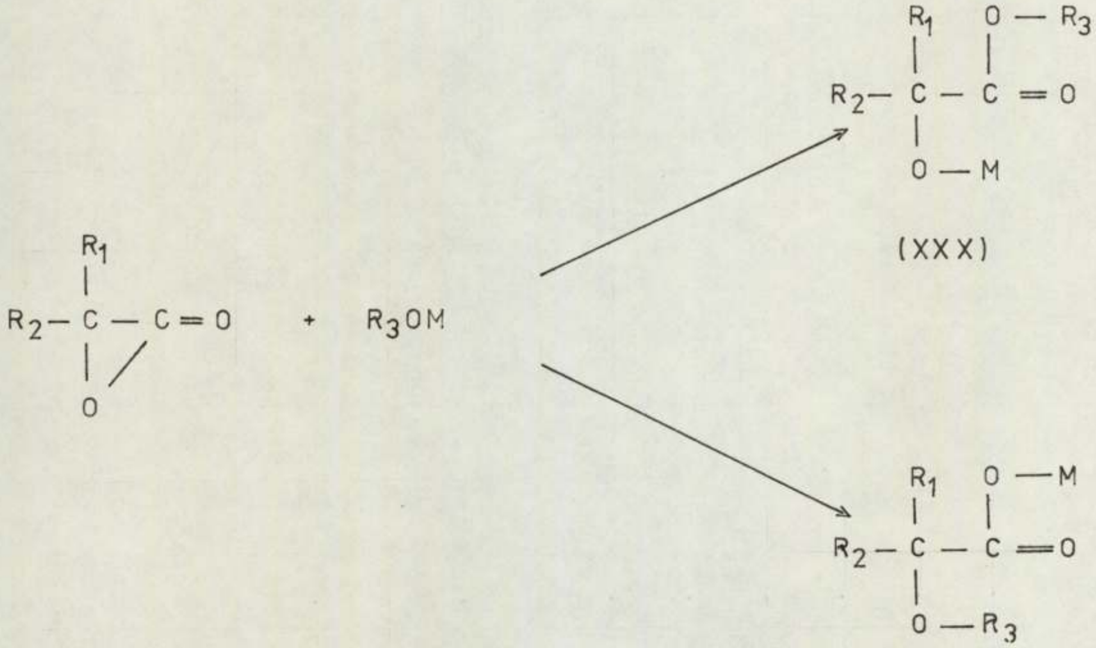


(XXVIII) (XXXVI)

$+ SO_2 + R_3OM$

.... 50

Reaction of α-lactone with alkoxide



(XXX)

(XXXIII)

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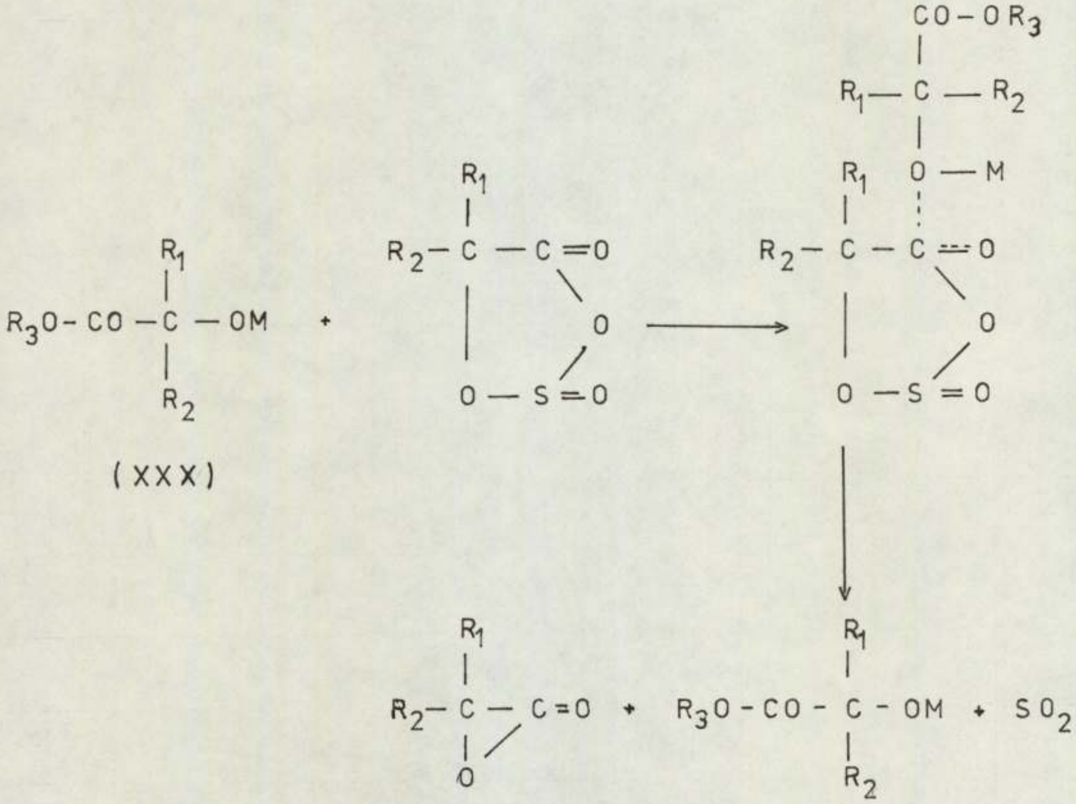
Equation 50 describes the attack of the alkoxide, for example lithium t-butoxide, at the C-4 position on the ring with subsequent formation of the complex (XXVIII) which is then followed by decomposition to give a highly reactive intermediate which is shown here as an α-lactone (XXXVI). Sulphur dioxide is released and the alkoxide regenerated. This is followed by an extremely rapid reaction of the α-lactone with any nucleophile which may be present. The strongest nucleophile available is the alkoxide itself, and, due to this strength, the nucleophile is able to react with the α-lactone in two ways. Firstly, attack again at the carbonyl, regenerating an alkoxide species (XXX), this is in many respects similar to direct production of this alkoxide without the intermediate synthesis of the α-lactone. But secondly, the α-lactone may be attacked at the substituted carbon and the resultant product is the alkoxy ester (XXXIII). Evidence for this type of reaction comes from the decomposition of highly substituted α-lactones in the presence of methanol, where the product is predominantly α-methoxy ester[43].

The first stages of this reaction are therefore seen to take the form of two competitive reactions. The carboxylate anion is produced as a low molecular weight compound in a non-polymer producing reaction, while alkoxide is regenerated in a derived form through a reaction which forms a propogation step.

Infra-red absorption studies indicate that the predominant product in the reaction between equimolar quantities of lithium t-butoxide and MEAS is the alkoxy carboxylate anion (XXXIII). Hence, the larger part of the initiator is removed at a very early stage as inactive metal salt. Infra-red studies also indicate that these reactions are extremely rapid and occur almost instantaneously within the timescale of the rest of the experiment.

Where the initial monomer concentration is much larger than the initial initiator concentration, much monomer remains intact at this stage, although all lithium t-butoxide has been consumed. The remaining monomer is, however, susceptible to attack by the regenerated alkoxide (XXX), equation 52.



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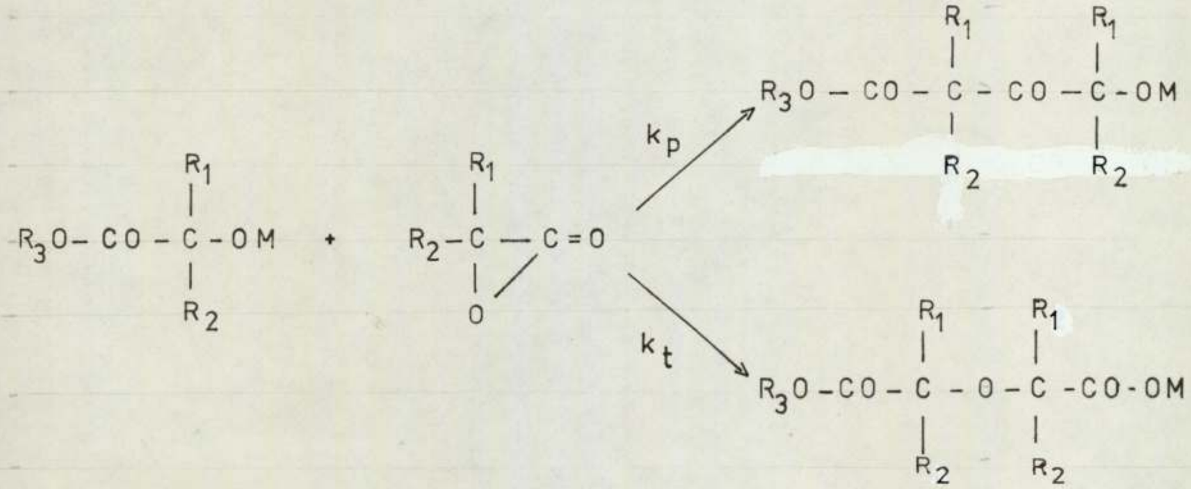
More α-lactone is thus generated, and this may react with nucleophiles in the same way as shown in equation 51, either generating poly-α-ester or terminating via the metal salt.

At this second stage of the reaction the attacking alkoxide is different in two respects from the lithium alkoxide used initially. Firstly, it is a much larger molecule, and secondly since it contains an ester linkage only one carbon removed from the alkoxide linkage it will be much less nucleophilic. These two factors in combination have the effect of slowing down attack at the C-4 position on the ring, and thus the rate of generation of α-lactone, and also of reducing the probability of attack at the substituted carbon of the α-lactone (more bulky less electrophilic species, for example isopropanol, are known not to attack α-lactones at this position[79]). Thus, while the possibility of a termination reaction exists in the later stages of the reaction, this is unlikely to be significant compared with the poly-α-ester producing reaction. If k_p and k_t represent the rate constants for the production of poly-α-ester and carboxylate anion respectively then in the later stages of the reaction $k_p > k_t$, equation 53



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A possible sequence of reactions taking place during the lithium t-butoxide initiated decomposition of anhydrosulphites in a non-polar solvent can be summarised thus:-

1. Reaction of alkoxide with monomer to yield a charge transfer intermediate.

2. Breakdown of the charge transfer complex (XXVIII) to α-lactone, sulphur dioxide and alkoxide.

3. Reaction of α-lactone (XXXVI) with nucleophiles to yield inactive carboxylate containing compound as a major product but also to regenerate 'derived alkoxide' as minor product.

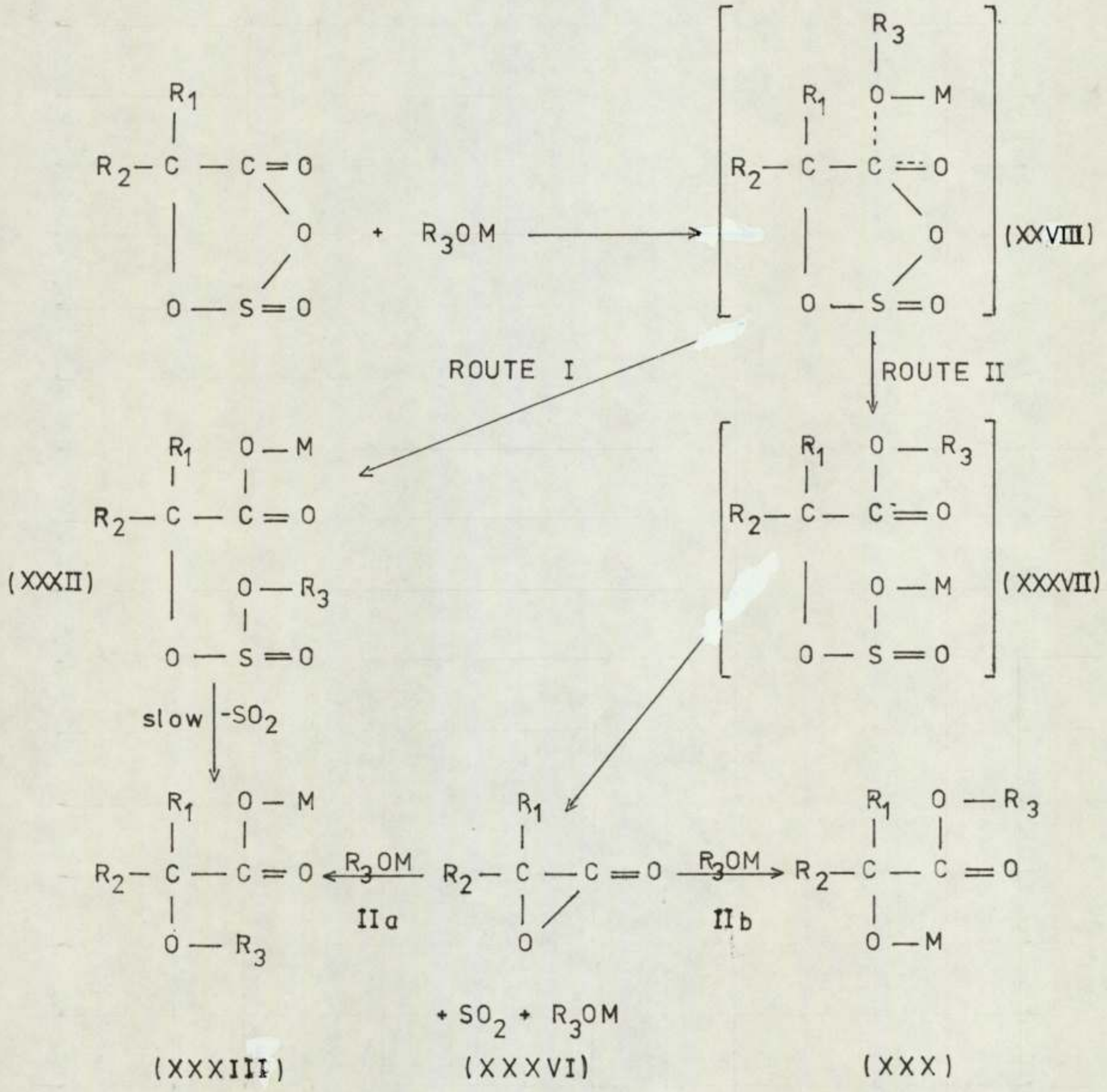
4. Attack by derived alkoxide on more anhydrosulphite, steps 1, 2 and 3 being repeated except that the non-polymer producing reaction is now the minor reaction.

5. Steps 1, 2 and 3 are considered to occur very rapidly on mixing monomer and alkoxide, step 4 is slower and is the sulphur dioxide evolving reaction measured in gas evolution studies.

This reaction scheme has one feature which does not fit observed results however. If equimolar quantities of initiator and monomer are used, then all sulphur dioxide would be released immediately. This is not observed experimentally and this mechanism is, therefore, improbable.

8.6 The modified reactive intermediate mechanism.

Closer examination of the reaction profiles, see Figure XXII, suggests that the evolution of gas is composed of two superimposed gas evolving reactions. Since all the monomer is decomposed and ultimately yields sulphur dioxide, and the extent of the slow latter part of the reaction appears to be closely related to the quantity of initiator used, the following modification to the previous reaction scheme is suggested:



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The α-lactone is permitted to react with any nucleophile as discussed previously.

This reaction scheme involves rapid reaction of the initiator alkoxide to form the charge transfer complex (XXVIII). This complex can then rearrange in two ways. Route I involves the formation of the metal carboxylate (XXXII) which then decomposes slowly in a unimolecular mechanism to yield the carboxylate ester (XXXIII). Route II is fast and may involve formation of the second charge transfer intermediate (XXXVII) which then breaks down to give the α-lactone. The α-lactone will then react with initiator alkoxide in either of two ways; IIa to give the carboxylate ester (XXXIII) by alkoxide attack at the substituted carbon of the lactone, and IIb by attack at the carbonyl of the α-lactone to give the derived alkoxide (XXX). In scheme II all reactions are considered to be too fast to follow by gas evolution.

In the presence of excess monomer, the derived alkoxide (XXX) can further attack the anhydrosulphite ring via Route II except that because of the reduced activity of the alkoxide this will now proceed more slowly. The evolution of gas at, for example a ratio of 5 : 1 monomer to initiator, is therefore that due to slow decomposition of (XXXII) and faster attack of derived alkoxide on anhydrosulphite with subsequent ring decomposition.

Several tests can be applied to this scheme. If equimolar quantities of lithium t-butoxide and monomer are mixed, then the complex (XXVIII) is formed and decomposes by the two

Routes I and II. Route II is not seen except perhaps as rapid evolution of gas during the degassing procedure. All gas evolved will, therefore, be due to the unimolecular decomposition of (XXXII) which will be a first-order decomposition with respect to monomers. In the reaction of equimolar quantities of DEAS and lithium t-butoxide, rapid evolution of gas was noted during degassing and the first–order plot of evolved gas with time is shown in Figure XXXX .

This graph shows fairly good first–order behaviour, with an intercept at 22% reaction. Hence 22% of the monomer decomposed via Route II and the remaining 78% via Route I in a reaction with first-order rate constant = $5.9 \times 10^{-6} s^{-1}$.

Since at the end of the above reaction all of species (XXXII) is decomposed, only the derived alkoxide can decompose any further added monomer, hence addition of further monomer gives the rate of decomposition of monomer by derived alkoxide and this reaction should again be first-order with respect to monomer.

Figure XXXXI shows the first-order plot for the addition of a second portion of monomer to the reaction completed above. Fair agreement is obtained over the first decade but the deviation over the second decade inidcates that the termination reaction, equation IIa equation 54, is operating but is small in comparison with the polymer producing reaction.

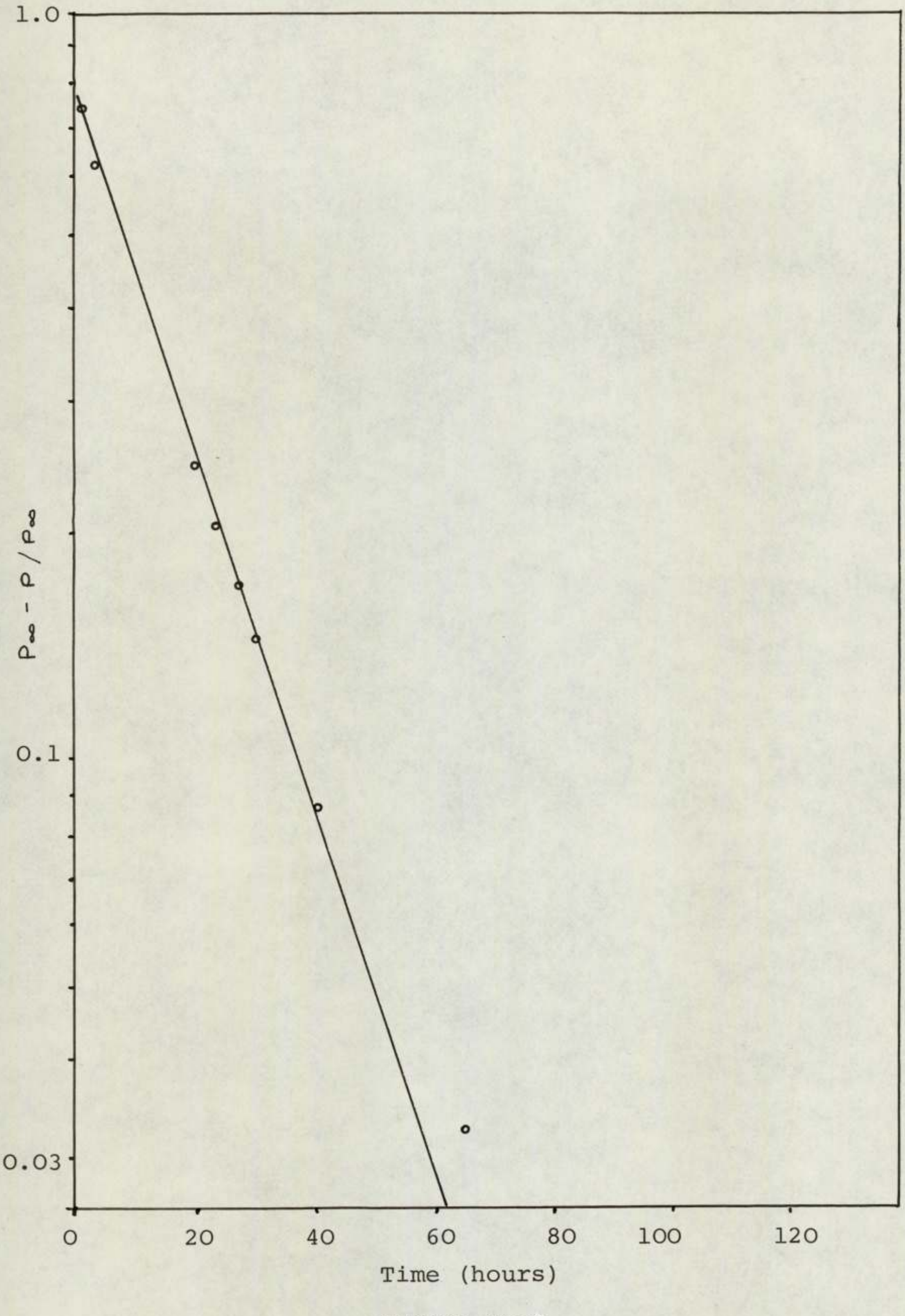


FIGURE XXXX

Decomposition of equimolar DEAS and lithium t-butoxide in decalin at 40°C

$[DEAS]_o$ = 0.56M $[LiO_tC_4H_9]_o$ = 0.56M

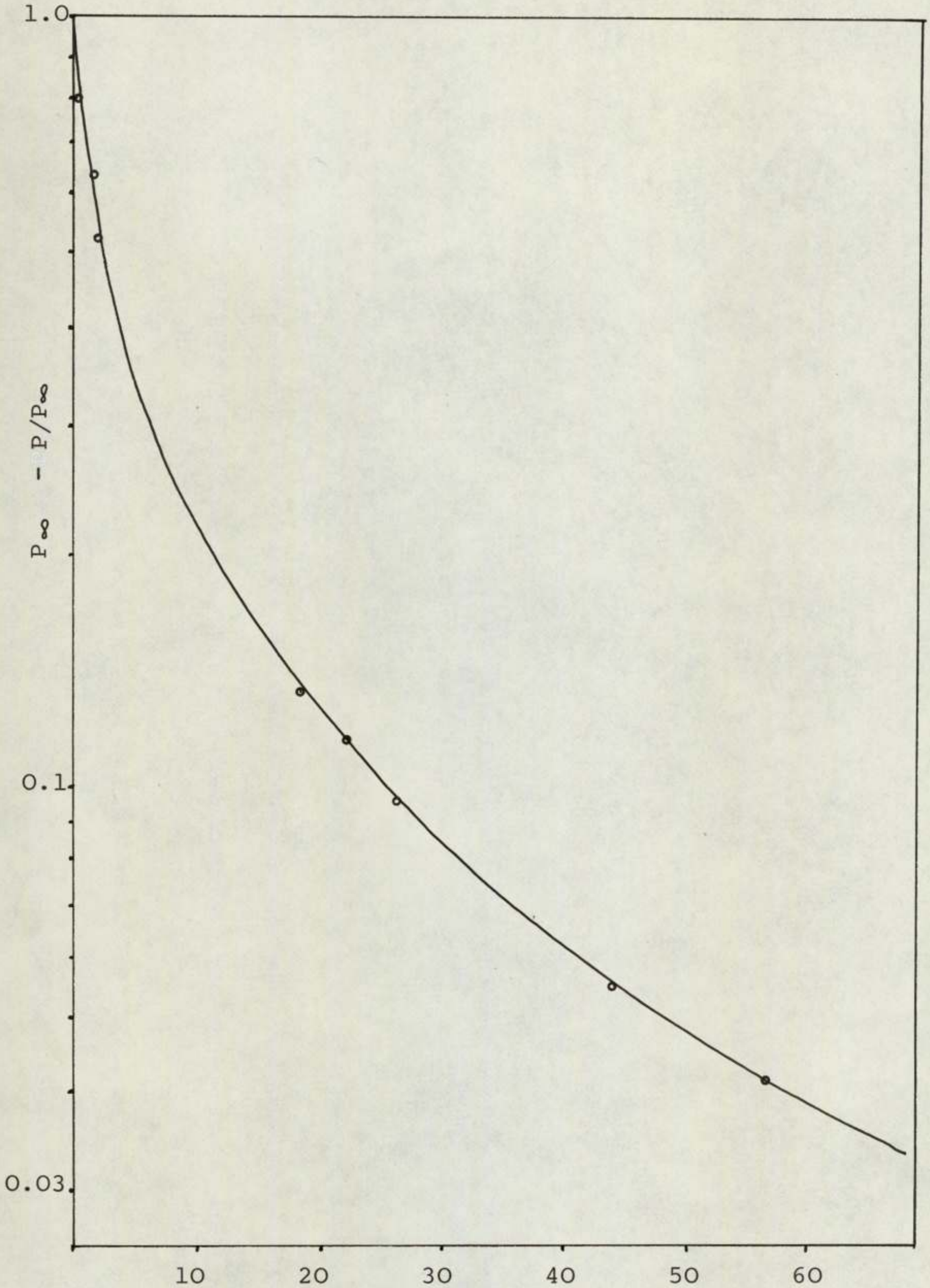
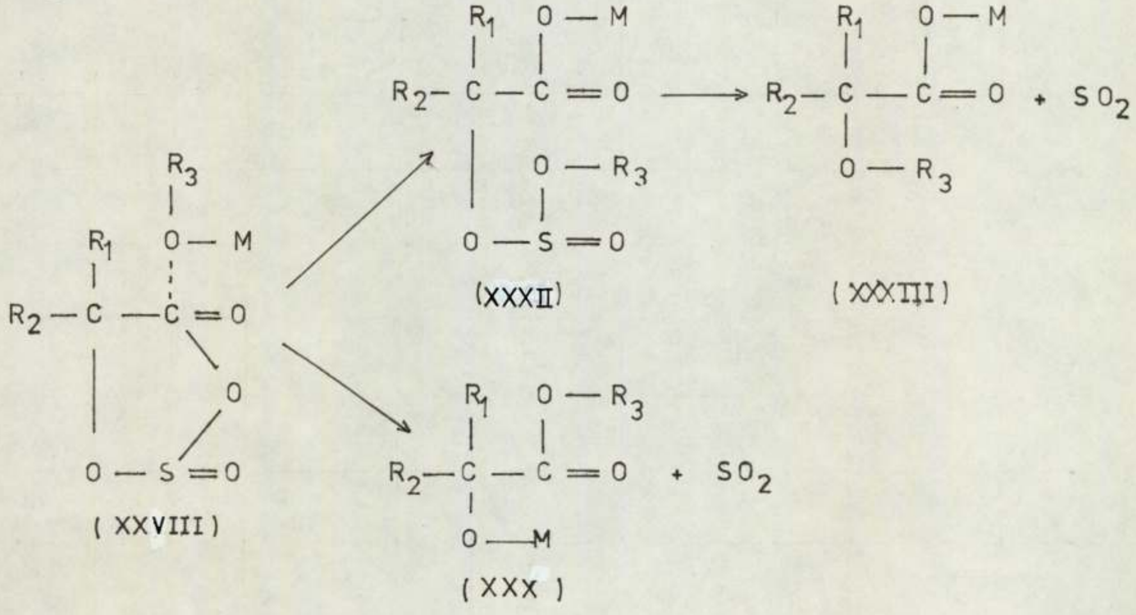


FIGURE XXXXI

Decomposition of second equimolar quantity of DEAS added to fully decomposed equimolar DEAS/lithium t-butoxide

$[DEAS]_0 = 0.56M$

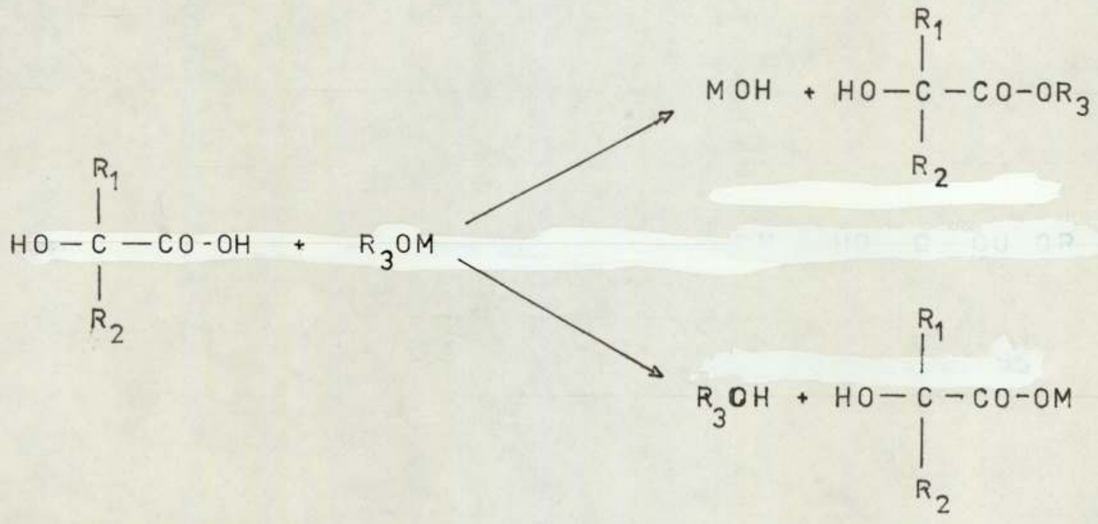
The shape of the reaction profiles shown in Figure XXII is explained using the scheme above. Where a high $[M]_0/[I]_0$ ratio is used decomposition of (XXXII) is unimportant since its concentration is low. At intermediate values of $[M]_0/[I]_0$ for example 10 or 5, then the initial fast reaction is the evolution of sulphur dioxide caused by attack of the derived alkoxide on the monomer remaining after the first rapid formation of the charge transfer complex (XXVIII).- Pertinent structures are presented below for reference. Hence, where $[M]_0/[I]_0 = 10$ the final slow reaction accounts for the last 8% of gas evolution. For a very low ratio of $[M]_0/[I]_0$, for example 2, then half of the monomer is consumed in the initial formation of the charge transfer complex (XXVIII) most of which then decomposes slowly via (XXXII). This leaves a very much reduced monomer concentration for reaction with the derived alkoxide (XXX) hence the abnormally low rates of apparent monomer decomposition at high initiator concentrations. As $[I]_0$ approaches $[M]_0$ we begin to measure the decomposition of (XXXII) as its concentration is increased rather than the decomposition of remaining monomer as its concentration is vastly reduced.



The same analysis can be applied to the decomposition of MEAS when it is decomposed with an equimolar quantity of lithium t-butoxide. In this case, however, straight line behaviour on a conventional first order plot can be seen in the latter part of the reaction, see Figure XXXXII , extrapolation of this portion of the line gives an intercept at some 80% reaction. This can be interpreted in two ways. Firstly, the polymer producing reaction Route IIb equation is the predominant reaction with MEAS, and thus the minor product is the carboxylate. Infra-red absorption studies indicate that this is not so. Alternatively, some of the alkoxide has been lost and the observed reaction is not, therefore, that between equimolar quantities of monomer and initiator.

There are several ways in which initiator can be lost, by reaction with trace impurities:-

a. Reaction with trace parent ∝ -hydroxy acid:



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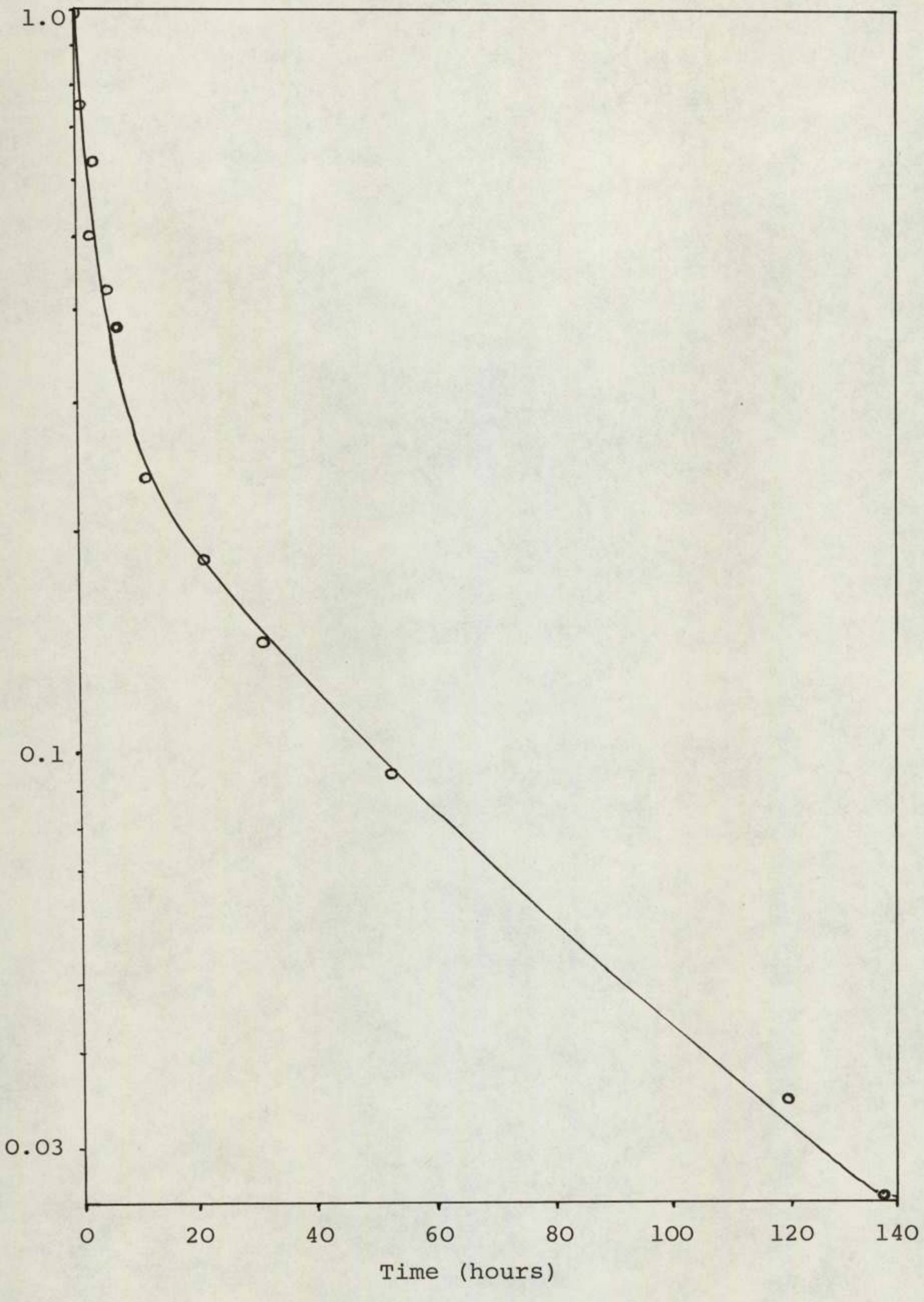
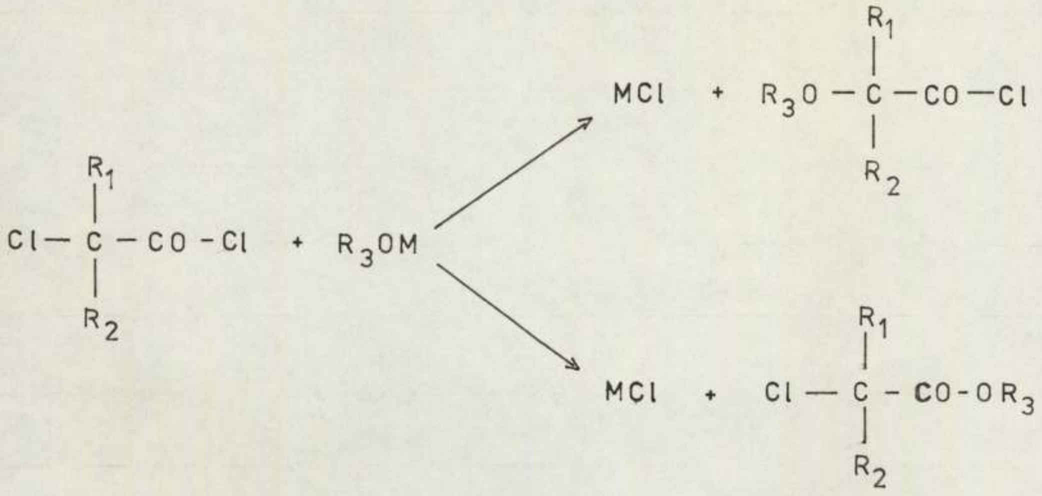


FIGURE XXXXII

Decomposition of equimolar quantities of MEAS and lithium t-butoxide at 40°C in decalin

$[MEAS]_o$ = 0.56M $[LiO_tC_4H_9]_o$ = 0.56M

b. Reaction with chlorine-containing impurities:-



.... 56

c. Reaction with trace moisture:

ROM + H_2O $\longrightarrow$ ROH + MOH 57

MOH is known to be ineffective as a polymerisation initiator . Since the asymmetrically substituted anhydrosulphites are exceptionally difficult to free from the chlorine containing impurity it would seem probable that stage 2 above is responsible for most of the initiator lost.

Completion of the reaction leaves no other active species than the derived alkoxide (XXX) under the preferred reaction scheme IIb, hence addition of more MEAS should give a reaction which is first order with respect to monomer. Figure XXXXIII shows the first order plot for addition of further monomer. Good first order agreement is obtained over more than 80% reaction. The sharp deviation and decrease in rate implies some other process than the termination reaction (equation

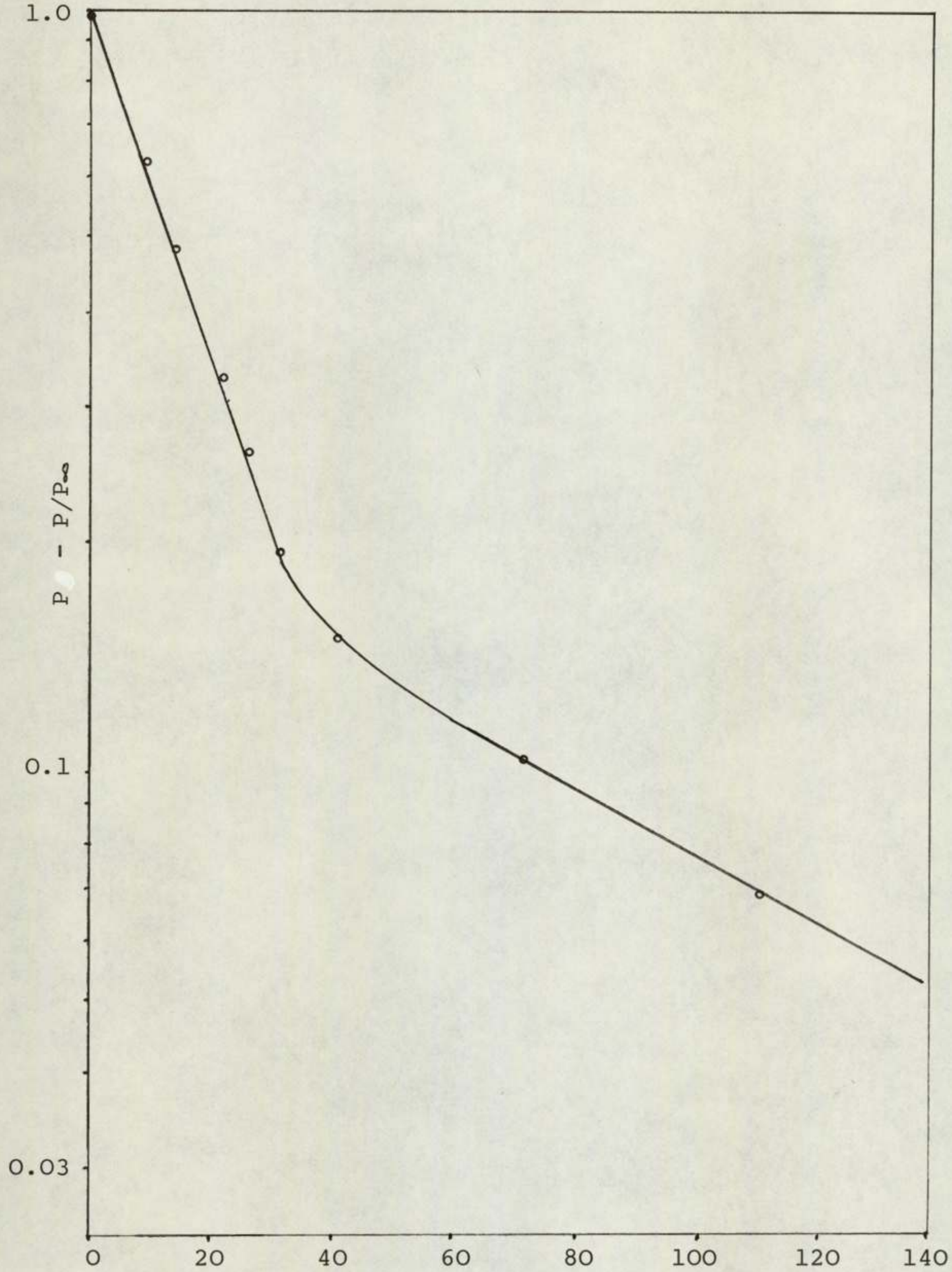


FIGURE XXXXIII

Decomposition of second addition of MEAS to fully decomposed 1:1 MEAS with lithium t-butoxide in decalin at 40°C

$[MEAS]_o = 0.56M$

54 IIa). Since better first-order agreement is obtained with MEAS than DEAS, the deviation is probably associated with the produced polymer and the onset of heterogeneity.

In the absence of quantities of initiator approaching equimolar with monomer, the observed reaction as measured by gas evolution is then predominantly the reaction between the derived alkoxide and the remaining monomer, i.e. equation 52. In the scheme shown in equation 52 this reaction is shown as a simple reaction going from right to left, but this is often not the case where charge transfer complexes of type (XXVIII) are involved. It is perhaps more accurate to indicate the possibility of a reverse reaction in the formation of this intermediate in addition to the decomposition leading to α -lactone. The stages between the charge transfer complex and the α-lactone can be simplified by omission of species (XXXVIII) since this is expected to have only a transitory life. Thus, if I = derived alkoxide, M = monomer, IM* = charge transfer complex, the following reaction scheme can be suggested:

$$I + M \underset{k_b}{\overset{k_f}{\rightleftharpoons}} IM^* \xrightarrow{k_d} \text{Products} + SO_2 + I$$

.... 57a

The rate constants k_f, k_b and k_d describe the forward and reverse reactions in the formation of IM* and the rate of decomposition of the complex to form α-lactone respectively. The reaction of the α-lactone will not be considered here since these are believed to be too fast at these temperatures to interfere with the rate determining step.

If k_f and k_b are represented by the equilibrium constant K, then

$$K = \frac{k_f}{k_b} \qquad \text{.............. 58}$$

Now rate of appearance of products is given by

$$\frac{d\,[prod]}{dt} = k_d\,[IM^*] \qquad \text{.............. 59}$$

and the concentration of IM* can be determined by

$$[IM^*] = K\,[I]\,[M] \qquad \text{.............. 60}$$

Combining equations 59 and 60

$$\frac{d\,[prod]}{dt} = k_d K\,[I]\,[M] \qquad \text{.............. 61}$$

Hence the observed rate constant k_{obs} is a product of the equilibrium constant for the formation of the charge transfer complex, and the rate constant for its decomposition.

$$k_{obs} = k_d K \qquad \text{.............. 62}$$

The concentration of IM* is expected to be small and is not expected to change significantly throughout the reaction.

A similar sequence of reactions could also be expected in the reaction of the initiator alkoxide with monomer, but since these reactions have been shown to be rapid, k_f and k_d are large compared to k_b. The techniques used in these studies are not suitable for the examination of these stages of the reaction.

The nature of the alkoxide, either the initiator or the derived species, has not yet been considered. Organometallic compounds in solution can exist in an infinite variety of forms of which the three structures shown form the simplest examples. In practice all forms between these might reasonably be expected. The structures are the undissociated form (XXXVIII), the associated form (XXXIX) where the anion and the cation are

$$\mathrm{ROM} \qquad\qquad \mathrm{RO}^{\delta-}\text{ ---- }\mathrm{M}^{\delta+} \qquad \mathrm{RO}^{-} \qquad \mathrm{M}+$$

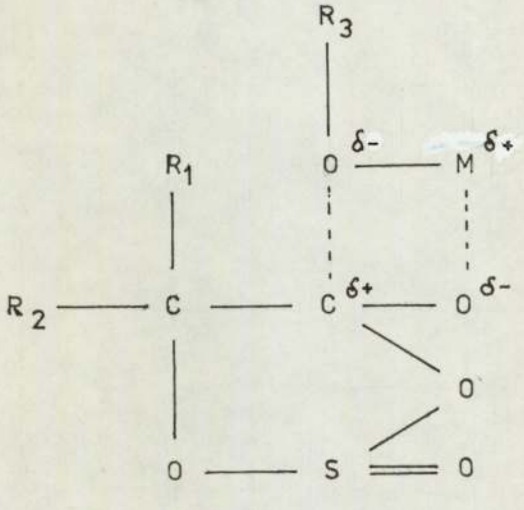
(XXXVIII) (XXXIX) (XXXX)

more distant from each other than in form (XXXVIII) but are still electrostatically held in proximity to each other and form (XXXX) the completely dissociated ions. Structures (XXXIX) and (XXXX) gain the energy required to separate into ions by association with solvent molecules, hence these structures become more probable in polar solvents.

Results indicate that the decomposition of MEAS proceeds more rapidly in THF than in the non-polar solvent decalin. This would be expected where the species responsible for the breakdown of the anhydrosulphite ring is the associated or dissociated form of the alkoxide (XXXIX) or (XXXX). Attack by either the alkoxide anion or the associated ions would be logical since these polarised forms would be attracted by the polar monomer to a greater extent than the undissociated alkoxide. However, if free ions were the active species, then the rate expression with respect to initiator would involve $[I]^{\frac{1}{2}}$ and this has not been observed with these results over the concentration range used.

Additional evidence for the existence of the associated structure (XXXIX) is the information given by vapour pressure osmometry of lithium t-butoxide in THF. This indicated dimerisation and contrasts with solution in decalin where association might reasonably have been expected and was not observed. The association in THF can be reasonably explained as the ion pair association of two or more solvated alkoxide molecules. This type of ion pair dimerisation is known to occur in other metal alkyl/solvent systems[82].

The associated structure is, therefore, preferred as the attacking species. The charge transfer complex which is envisaged as the immediate precursor to the α-lactone can be stabilised as shown below (XXXXI) and the partial ionic character of the alkoxide might be expected to assist formation of this.

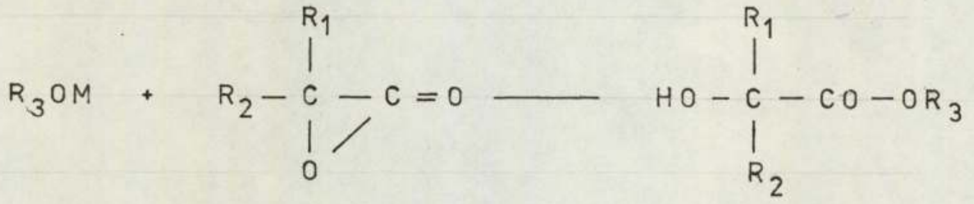


(XXXXI)

The failure of lithium t-butoxide to effect the decomposition of MEAS in dioxan in solvent can be attributed to the increase in energy required for charge separation in the solvent of lower dielectric. The same considerations might be expected with a non-polar solvent, for example decalin, but in this case it is reasonable to expect solvation of the initiator by the monomer itself to occur. Hence the problems of transfer of the "charge separated" initiator from its solvation envelope to the monomer are eliminated. In the presence of a cosolvent mixture such as nitrobenzene, decalin, the initiator and also possibly the monomer would be solvated by the polar component of the cosolvent. This would impose difficulties in the mutual approach of monomer and active initiator and the overall effect is a reduction in rate, as observed. The magnitude of this rate reduction is not large since the energy barriers involved in a change of solvating molecules would be small.

Consideration of the ease of attack of the derived alkoxide species on the C-4 position of the anhydrosulphite ring would indicate that attack is easily obstructed by large groups at the C-5 position. Thus initial rates show that, for the simple dialkyl substituted anhydrosulphites, the propogation step occurs most readily with small alkyl groups and is rapidly slowed by the introduction of larger groups until the diethyl substituted anhydrosulphite DEAS is decomposed at a rate only some ten times faster than the thermal rate at the same temperature. The rate of decomposition of the cyclopentyl derivative C'pent AS is relatively fast in comparison with DEAS. Since these two compounds have almost identical electronic contributions from their C-5 substituents, the faster decomposition of C'pent AS must be due almost entirely to the steric effect of 'pinning back' the alkyl substituents. The marked nature of this increase in rate results from the relatively compact nature of both the attacking and the attacked species.

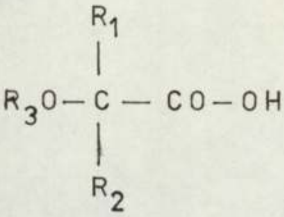
Addition of the ∝-lactone to alkoxide has been considered in some detail, but these compounds are also known to react with other nucleophiles[43]. Hence, in the presence of excess alcohol the predominant reaction will be the addition of the ∝ -lactone to the hydroxyl group, as shown in equation 62, to form an ∝-hydroxy ester (XXXXII).



(XXXII)

.... 63

The isomeric ∝-alkoxy carboxylic acid (XXXXIII) is not found with t-butanol as alcoholic reactant although other studies involving ∝-lactones indicate that the ∝-methoxy carboxylic acid is the major product when methanol is used[43].



$$R_3O-\underset{R_2}{\overset{R_1}{C}}-CO-OH$$

(XXXXIII)

An alternative source of nucleophiles is the presence of trace α-hydroxy carboxylic acid which results from the hydrolysis of the monomer. In thermal polymerisation, the presence of this acid provides a source of addition for α-lactone and is therefore directly linked to molecular weight by the expression,

$$DP = \frac{[M]_o}{[N]} \qquad \ldots\ldots\ldots\ldots\ldots \; 64$$

where:

$[N]$ = concentration of nucelophiles (α-hydroxy acid),

$[M]_o$= monomer concentration,

DP = degree of polymerisation.

Thus, in the thermal polymerisation of MEAS, a number average molecular weight of 20,000 would require a concentration of 0.5 mol% of parent acid. If, as infra-red and gas evolution studies indicate, some 90% of the initial lithium t-butoxide is consumed in a non polymer forming reaction, then at $[M]_0/[I]_0 > 26$, the concentration of α-hydroxy acid becomes equal to or greater than the concentration of derived alkoxide. The α-lactone produced by the decomposition is, therefore, able to add either to derived alkoxide, or to parent acid or to both.

Molecular weight is still controlled by equation 64, but this can now be modified to:

$$\frac{[M]'}{[N] + [I]} \quad \text{..............} \quad 65$$

where:

$[N]$ = concentration of parent acid

$[I]$ = concentration of derived alkoxide

$[M]'$ = monomer not consumed in forming the carboxylate (XXXII).

assuming no termination step involving I.

Since the nucleophilicity of the alkoxide and the hydroxyl group differs, some preferential addition to either species may be expected and this would lead to a difference in molecular weight of the two types of growing chains. A binodal distribution of molecular weight could therefore be expected and this is observed, but only at relatively high initiator concentrations. This binodal distribution disappears as the initiator concentration is reduced and the molecular weight distribution tends towards poisson. Presumably this reflects the very low concentration of alkoxide which is available for addition to α-lactone.

α-Chloro acid chloride is not expected to provide a good source of chain ends to which α-lactone might be expected to react in a polymer producing reaction. Nevertheless, α-lactone is such a reactive species that, in the presence of excess chlorine containing impurity, the product would be a low molecular weight adduct between α-chloro acid chloride and α-lactone. This is in accordance with observed results.

According to the proposed reaction scheme 6, the molecular weight of polymer produced by the alkoxide induced decomposition of anhydrosulphites can never be as high as that produced by the purely thermal route, because the introduction of initiator also introduced more prospective sites for chain growth in addition to α-hydroxy acid. Since most of the initiator introduced becomes involved in a production of an inactive non-polymeric product at an early stage in the reaction, the molecular weight will not be related directly to $[M]_o/[I]_o$ but to $[M]_o/f[I]_o$ where $f[I]_o$ represents that portion of $[I]_o$ which remains as active derived alkoxide. $f[I]_o$ may conceivably change during the reaction depending on the frequency of the termination reaction: equation 56, IIb.

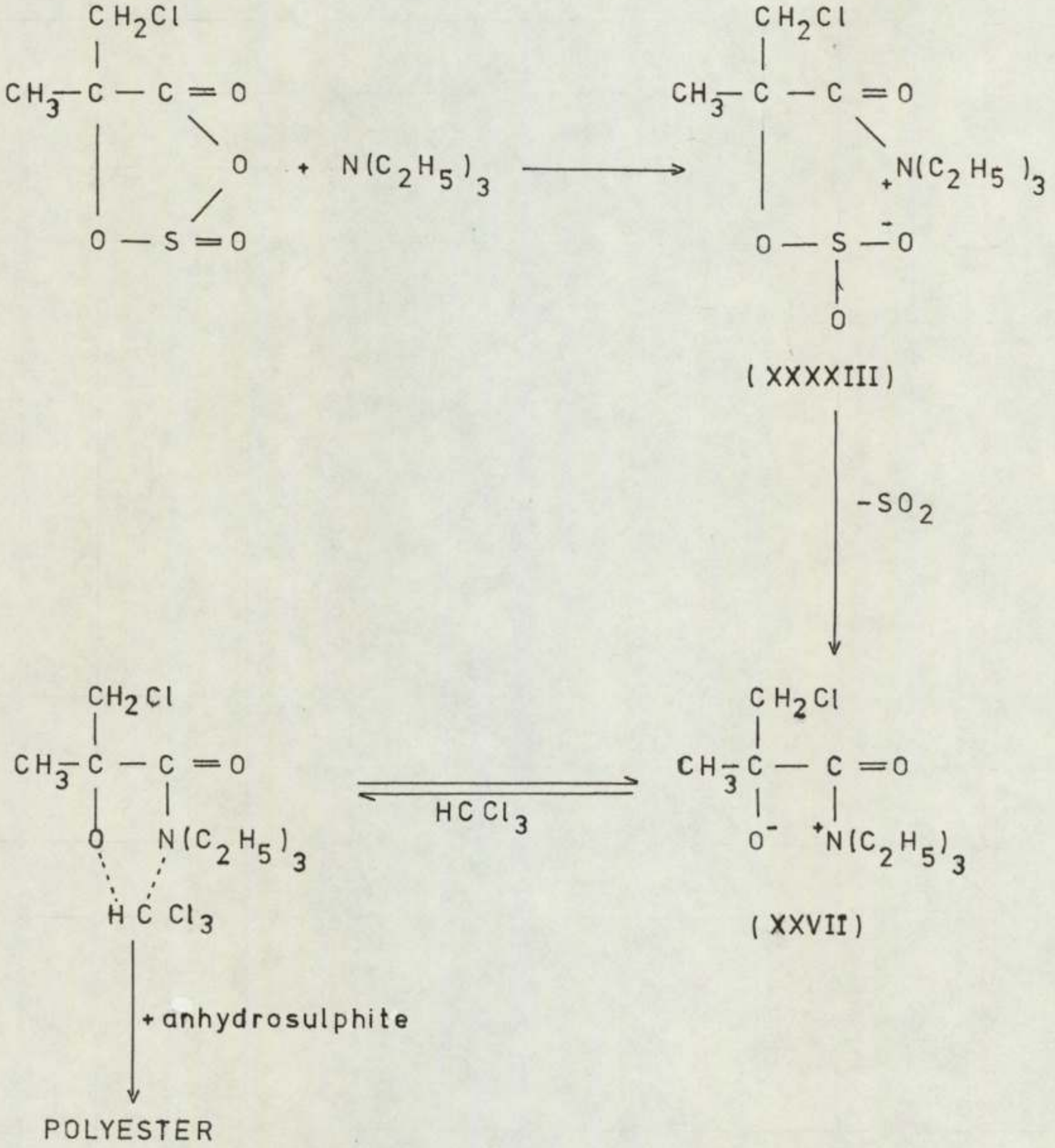
The results obtained for the change in molecular weight and molecular weight distribution as the reaction proceeds are consistent with addition of monomer (or a species derived from the monomer) to a fixed number of growing chain ends. These chain ends would, under the proposed reaction scheme originate from parent α-hydroxy acid, alkoxide etc. The apparent depolymerisation which is indicated above about 60%

conversion may well result from loss of high molecular weight polymer by precipitation from solution during molecular weight analysis. The slight drop in $\bar{M}w/\bar{M}n$ at high conversion is consistent with this theory. The alternative, a base catalysed depolymerisation, perhaps caused by the initiator residues is unlikely since this would lead to an increase in $\bar{M}w/\bar{M}n$.

The deviation of the rate of monomer decomposition from good first-order behaviour during the latter 30% of reaction is perhaps best explained by the appearance of heterogeneity. The reaction profiles indicate a marked and definite point of departure from first order behaviour rather than the gradual departure which could be expected if initiator were consumed at regular intervals, although this would not necessarily be easily detected on a first-order kinetic plot. The slow reaction to completion can, if the polymer is precipitated from solution, be seen as the predominance of a diffusion controlled passage of monomer through heavily solvated polymer to the active chain end, over the earlier concentration dependent reaction.

8.7 Decomposition of anhydrosulphites using other initiator systems

The reported decomposition of the chloromethyl, methyl substituted anhydrosulphite CMAS induced by the action of triethylamine[49] has been cited in a previous chapter. It is relevant to describe the mechanism which has been proposed for this reaction since in some respects it resembles the alkoxide initiated decomposition of anhydrosulphites. The chloromethyl group enhances the nucleophilicity of the C-4 position in an anhydrosulphite ring, and the reactions described were in general faster than the decomposition of the dialkyl substituted rings.



.... 65

In this scheme, the anion is proposed as the initiating species, and the presence of the amide-like carbonyl gives rise to a relatively low infra-red carbonyl absorption frequency. The strength of this absorption remains constant throughout the reaction.

Several features of this reaction are difficult to explain on the basis of the proposed scheme however. For example, using equimolar quantities of initiator and monomer, substantial quantities of polymer are formed in carbon tetrachloride using CMAS/NEt_3 and in chloroform using CMAS/DMF but no polymer is formed in chloroform using CMAS/NEt_3. In all cases the zwitterion (XXVII) is formed. The proposed reaction scheme therefore requires some of the tertiary amine to remain unused in the initial stages. This would seem unlikely since the charge transfer complex (XXVII) is being consumed and would, therefore, disrupt any equilibrium which might exist between (XXXXIII) and the reactants. The concentration of (XXVII) should therefore increase with time. A more likely explanation is that initiator is lost by reaction with chlorine containing impurities so that true equimolar concentrations were not used.

A further feature, the failure of the reactions to go to complete conversion as measured by polymer formation is not explained by this reaction scheme but would be explained as the formation of a low-molecular weight byproduct if a scheme similar to the alkoxide initiated decomposition is used for tertiary amine decomposition.

It is believed, therefore, that the final suggested reaction scheme presented for the alkoxide induced decomposition of anhydrosulphites may be applicable (in part at least) to tertiary amine initiation, and may in fact provide the basis of a general mechanism for the initiated decomposition of anhydrosulphites at temperatures below those required for thermal scission.

CHAPTER 9

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

9.1 CONCLUSIONS

The thermal decomposition of a number of methyl, n-alkyl anhydrosulphites has been studied in order to assess the feasibility of this reaction mechanism as a route to the poly-α-esters.

The ease of preparation of pure samples of the methyl, n-alkyl anhydrosulphites was found to decrease as the length of the n-alkyl chain increased. This results from an increase in the percentage of monomer lost during the purification procedures rather than inherent difficulties associated with synthesis of the ring compound itself. The limits for the preparation of the methyl, n-alkyl anhydrosulphites would, therefore, appear to have been reached when the n-alkyl substitution is greater than about eight or ten carbon atoms. However, this conclusion is reached only in the light of the purification procedures which have previously been used for anhydrosulphites and those described in this thesis. It may well be that different procedures would extent this limit.

All thermal decompositions in the absence of initiator of all of the methyl, n-alkyl anhydrosulphites studied were found to obey good first-order kinetics, and the derived kinetic parameters are those which can reasonably be expected from the unimolecular thermal decomposition of a slightly strained ring system such as the anhydrosulphite. Competitive non-polymer forming reactions were not significant in the temperature range used for kinetic studies although these reactions were responsible for the difficulties experienced in monomer synthesis.

The comparative thermal stability of anhydrosulphites is governed primarily by substituents located at the C-5 position. Any steric interaction between the substituent groups at this position and the ring will necessarily impart some degree of stress to the ring and therefore reduce the stability of the ring. The electronic contribution from these substituent groups is also important; electron donating groups reduce the stability of the ring, although the difference in electronic contribution of two fairly long n-alkyl groups (for example C_6 and C_8) is minimal. Methyl n-alkyl anhydrosulphites have been shown to regain some of their thermal stability as the n-alkyl chain becomes long. This may be due to a restriction on the leaving group (SO_2) caused by doubling back of long n-alkyl chains resulting in a higher energy transition state and, therefore, a more stable monomer.

Since the more highly substituted anhydrosulphites have been shown to be less stable than their simple homologues, the stability of more highly substituted anhydrocarboxylates is of interest. The anhydrocarboxylate ring system is less strained and hence more stable than the closely related anhydrosulphite, and substitution of two n-butyl groups at the C-5 position might reasonably have been expected to produce a decrease in thermal stability of the ring. This was not found to be so, the anhydrocarboxylate DBAC is not only relatively stable, but when it decomposes thermally at significant rates it does so with production of substantial quantities of non-polymeric product. The use of these compounds as precursor to the formation of poly-α-esters would, therefore, appear to be severely limited. Some anhydrosulphites were also subjected to different types of initiator system. It was found that only those initiators of which the normal 'modus operandi' is anionic, were effective in yielding poly-α-ester from anhydrosulphites. These initiators are typified by the alkoxides.

MEAS, which has not produced a very high molecular weight poly-α-ester when decomposed thermally, was decomposed by lithium tert-butoxide at a significant rate at 40°C. The kinetics of the decomposition were not first order with respect to either monomer or initiator throughout the complete reaction, although initial rates indicate an initial first-order dependence on both these quantities in the early stages. These studies together with molecular weight and related studies of the products have enabled a feasible reaction mechanism to be suggested. This mechanism involves, as the polymer producing reaction, the use of the alkoxide as a catalyst to break down the anhydrosulphite and formation of a highly reactive intermediate together with regeneration of the alkoxide with release of a gaseous fragment. This intermediate, which can be regarded as an α-lactone, reacts with any available nucleophile including parent α-hydroxy acid, the initiator alkoxide itself, and polymer chain ends. Chlorine containing compounds can also be incorporated. A second non-polymer forming reaction can also take place between anhydrosulphite and alkoxide and the reaction product, which slowly releases sulphur dioxide, can involve a substantial portion of the alkoxide initiator.

Analysis of the polymeric product of anhydrosulphite decomposition is difficult since these polymers are only sparingly soluble. However, molecular weight studies show that the polymer produced at temperatures in the region of 40°C using alkoxide initiators with anhydrosulphite monomers are of generally lower average molecular weight than those produced by thermal methods. The molecular weight distribution is also broader. This arises as a result of the formation of $\propto$-lactone type intermediates and the use of iniator which can react with an $\propto$-lactone; since this means that the adding monomer residue is presented with a larger number of possible reaction sites than if the initiator was not present.

The situation where the lower temperature initiated decomposition of anhydrosulphites results in a mechanism which excludes the addition of $\propto$-hydroxy acid or chlorine containing impurities on energetic grounds is, therefore, not achieved with alkoxides. It follows, therefore, that the molecular weights of poly-$\propto$-esters produced by alkoxide induced decomposition cannot, if the proposed reaction mechanism is true, exceed those produced by thermal decomposition of the same anhydrosulphite.

9.2 SUGGESTIONS FOR FURTHER WORK

The synthesis of methyl, n-alkyl anhydrosulphites was hampered by decomposition of the monomer during purification procedures. This was a direct result, with higher homologues, of the close approach of the distillation temperature to the temperature at which significant decomposition to ketene occurred. It would be valuable, therefore, to investigate other methods of anhydrosulphite purification. Preparative chromatography would seem to be an obvious choice, since this might also remove chlorine containing impurities.

Provided that suitable purification procedures can be established, the synthesis and decomposition of anhydrosulphites having two long n-alkyl groups (C_6 or C_8) would test the validity of the postulation that leaving group restriction is responsible for an increase in anhydrosulphite stability. More highly branched alkyl groups could also be used. The α-hydroxy acid precursors to these anhydrosulphites may well be more easily prepared by reaction of hydrogen with the lithiated salt of the carboxylic acid[77], than by use of the routes used in this thesis and other anhydrosulphite studies.

The di n-alkyl substituted anhydrocarboxylates warrant further detailed study. The investigations in this work established only that the di n-butyl derivative is not a good precursor to the poly α-ester. The extent to which ketone formation interferes with polymer formation in other members of the series and in other solvents would provide a useful comparison with the anhydrosulphites and other related ring systems.

The tentative mechanism proposed for the alkoxide initiated decomposition of anhydrosulphites can be tested. In particular, the use of equimolar quantities or excess of initiator over monomer should result almost exclusively in formation of the low molecular weight non-polymeric metal salt. This compound could be isolated and analysed, changes in its infra-red absorption spectrum with time should establish that the first formed compound does in fact slowly lose sulphur dioxide if the propose mechanism is true.

Gas evolution techniques have provided a valuable indication of the rate of unimolecular scission of anhydrosulphites under thermal stress, but where initiators are used, the involatile solvents used such as decalin are not very suitable, since they are difficult to remove. Yet a high boiling solvent is necessary if vapour pressure equilibria are not to interfere with gas evolution measurement. Spectroscopic techniques, particularly infra-red and n.m.r. have the advantage that very much smaller quantities of reactants can be used than with gas evolution, and the concentration of all species present at any given time can be evaluated.

Kinetic analysis using either spectroscopy or gas evolution will require a much greater degree of purity than was used in these studies. The use of a high vacuum line system in which monomer, initiator and solvent can be transferred to the reaction vessel while making no contact with any external instrument will be essential. The final gas evolution apparatus developed for these studies in which monomer and initiator were contained in separate sealed vessels within the gas evolution apparatus was a step towards the type of apparatus needed.

Alkoxides are comparatively insoluble in non-polar materials, only highly substituted lithium alkoxides are soluble in non-polar organic solvents. This may, in these studies, have introduced problems associated with the initiator coming out of solution when the polarity of the solvent was changed as the monomer was added. A completely soluble catalyst such as certain titanium aluminium compounds[78] would remove this possible variable in these decompositions.

If the reaction mechanism suggested in this work for initiated decomposition can be further substantiated, then the variation in reactivity between various alkoxides and various anhydrosulphites could be measured in order to assess the contributions made by the steric and electronic effects of the initiators to the overall reactivity. The steric and electronic effects of some anhydrosulphites have already been assessed by their thermal behaviour, therefore, overall reactivity can be related to the properties of the initiator. This could provide further information for the reaction scheme. A similar investigation has been carried out for the reaction between some anhydrocarboxylate and various pyridines[55].

Before any meaningful analysis of the properties of the poly α -esters can be made, a suitable solvent for their molecular weight analysis must be found. Spectroscopic analysis is not sufficiently accurate for high molecular weight material (Mn = +20,000) and end group analysis is uncertain where end groups are unknown as in the initiated decomposition of anhydrosulphites. G.p.c. analysis is more hopeful, perhaps using ortho -dichlorobenzene as solvent, although some symmetrically substituted poly-α-esters appear to be insoluble even in this very good solvent.

When an accurate method of poly-α-ester characterisation has been found it would be useful to compare polymer from anhydrosulphites (decomposed either thermally or by initiators) with polymer from other sources such as the irradiation of malonyl peroxides .

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