STUDIES IN RING OPENING POLYMERISATION

The interactions of some cyclic esters with a bimetallic oxoalkoxide.

A Thesis submitted to the University
of Aston in Birmingham as part
requirement for the degree of Doctor
of Philosophy.

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SUMMARY

The ring opening reactions of some 1,3,2-dioxathiolan-4-one 2-oxide (anhydrosulphites) and 1,3-dioxolan-2,4-diones (anhydrocarboxylates) in the presence of bimetallic oxoalkoxide have been studied.

The synthesis and purification of these cyclic esters have followed established procedures which have been extended to include the use of a lithium salt. Similarly, the synthesis of the catalyst, a mixed metal oxoalkoxide, followed established methods and presented little difficulty.

It has been found that the reactions involving anhydrosulphites yielded very limited amounts of α-ester oligomers, and their reactions were highly sensitive to the degree of substitution on the monomer ring. Reactions involving anhydrocarboxylates were more successful both in terms of α-ester formation and extent of monomer decomposition. In both cases the reactions have been characterised by the separation of the reaction mixture into two layers, one gelatinous, the other liquid. It has been found that the separation of the reaction mixture and decrease in rate of reaction were parallel events.

The kinetics of these reactions have been studied using gas evolution techniques and their products examined by infra red absorption spectroscopy and X-ray diffraction. G.P.C. studies were in general precluded by the lack of solubility of the reaction products in any suitable solvent.

Possible mechanisms for the reactions have been considered. It is thought that reaction proceeds via a four-centred mechanism involving the aluminium-oxygen bond in the catalyst. The mode of addition of the monomer is thought to be sensitive to the degree of substitution on the monomer ring as well as the size and nature of the ring. The present study thus represents the first in which the catalysed decomposition of esters of this kind has not involved an α-lactone intermediate.

The studies involving glycollic acid anhydrocarboxylate have been extended to include decomposition in the presence of catalytic amounts of pyridine and also benzyl alcohol, and the results of the former study have been considered in the light of earlier similar studies involving other anhydrocarboxylates.

Key Words

ANHYDROSULPHITE
ANHYDROCARBOXYLATE
ORGANO-METALLIC
CATALYSED
α-ESTER

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"Knowledge is structured in consciousness"

The Rig Veda

This thesis is dedicated to my mother and father for their encouragement and sacrifice over the years.

CHAPTER 1

1.1 Introduction

The production of high molecular weight organic polymers from cyclic monomers has been an area of increasing interest to both science and technology in recent years. In that time the range of monomers that has been studied has been extensive. No less extensive has been the study of the many factors that affect the polymerisation of these monomers, and the properties of the polymers obtained therefrom.

For obvious reasons, much of this effort has been devoted to the study of those monomers whose polymerisation will yield products of commercial value. Particularly notable monomers in this field are lactams and epoxides whose polymeric products, nylons and polyesters respectively, find wide application.

The polymerisation of cyclic olefins has, in general, not been found rewarding in terms of producing useful polymeric products. The polymerisation of cyclopentene, as described by Amass,(1) is of limited application, and hereinafter the expression 'ring opening polymerisation' will be taken to refer to the production of heterochain polymers from heterocyclic monomers.

The polymerisation of such monomers is critically affected by certain factors. Within the ring, ring strain and the nature and reactivity of the heteroatom or functional group are of great importance, as are the size and nature of the substituents on the ring. External factors, such as reaction temperature, nature of the solvent and presence of any initiating species, are of equal importance.

It is widely recognised that the polymerisability of cyclic monomers is principally controlled by the degree of ring strain in the monomer itself. Ring strain is a thermodynamic property and has two causes. The first is the imposition of constraint on the bond angles between ring members, such that they are unable to adopt their most thermodynamically stable positions. The second is the steric interaction of the substituents on the ring.

Consideration of these factors provides explanation of the variations in the polymerisability of many heterocyclic monomers. For example, it has been found(2) in the polymerisation of lactams, that the five-membered ring will homopolymerise, while the six-membered ring will not. This difference is entirely due to the degree of ring strain in these monomers. In the polymerisation of epoxides, it has been found(3,4) that the 1,3 epoxide will polymerise almost irrespective of the nature of the substituents on the ring, whereas the polymerisation of the 1,4 epoxide is prevented by the presence of any substituent larger than hydrogen.

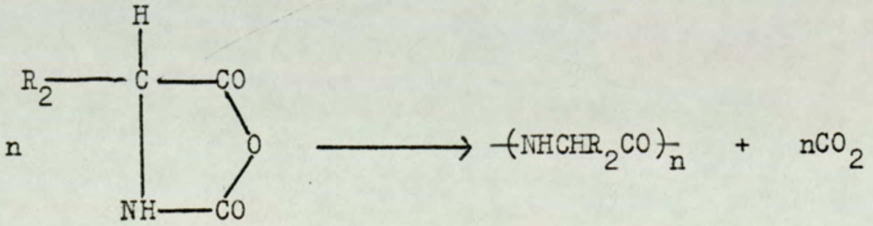
Ring opening reactions may, in certain respects, be classified as both addition and condensation. The polymer formed by such reactions has the structural features of a condensation polymer, and yet it will often have the same composition as the monomer, a characteristic of addition reactions. The mode of polymerisation resembles addition reactions in that it proceeds by successive addition of monomer units, and yet it resembles a condensation reaction in that the molecular weight of the polymer molecules increases throughout the course of the reaction.

Closer examination of ring opening polymerisation reactions shows that they may in fact be divided into two types. The first type is that in which the polymerisation of the heterocycle takes place in such a way that no fragment of the parent molecule splits off during the reaction. The polymeric product therefore contains all elements of the monomer. Typical examples of monomers that polymerise in this way are lactams, lactones and epoxides.

The second type of reaction, which has been called extrusion polymerisation,(5) is one in which part of the monomer is extruded or eliminated during the course of the reaction. In contrast to the first type, there is no evidence of ring-chain equilibrium, and the polymer obtained does not contain all elements found in the parent monomer.

The n-carboxy anhydrides of α-amino acids (NCAs) are an important member of this second class of monomer. The polymerisation of NCAs yields poly-α-amino acids which may be used as simple building blocks for the synthesis of peptides and polypeptides.(6,7,8) For this reason NCAs have been the object of a great deal of attention. The many mechanisms by which they undergo polymerisation, and the factors that control these mechanisms, have been reviewed by Bamford <u>et</u> <u>al</u>.(9) and, more recently, by Szwarc(6) and by Shalitin(10).

The thermal polymerisation of NCAs is accompanied by the evolution of carbon dioxide, always from the C-2 position in the ring, thus



The nature of the end groups of the polymer formed is not known, and the exact mechanism of this superficially straightforward reaction is by no means clear.

The polymerisation of NCAs may also be initiated by substoichiometric amounts of primary and secondary amines via direct attack at the C-5 carbonyl. The effect of substituents on both the NCA and the initiating amine has been studied in detail by Ballard and Bamford.(11) The mechanism proposed is referred to as the 'normal' amine addition, as opposed to attack at the C-2 carbonyl which is non polymer forming and referred to as 'wrong' addition.

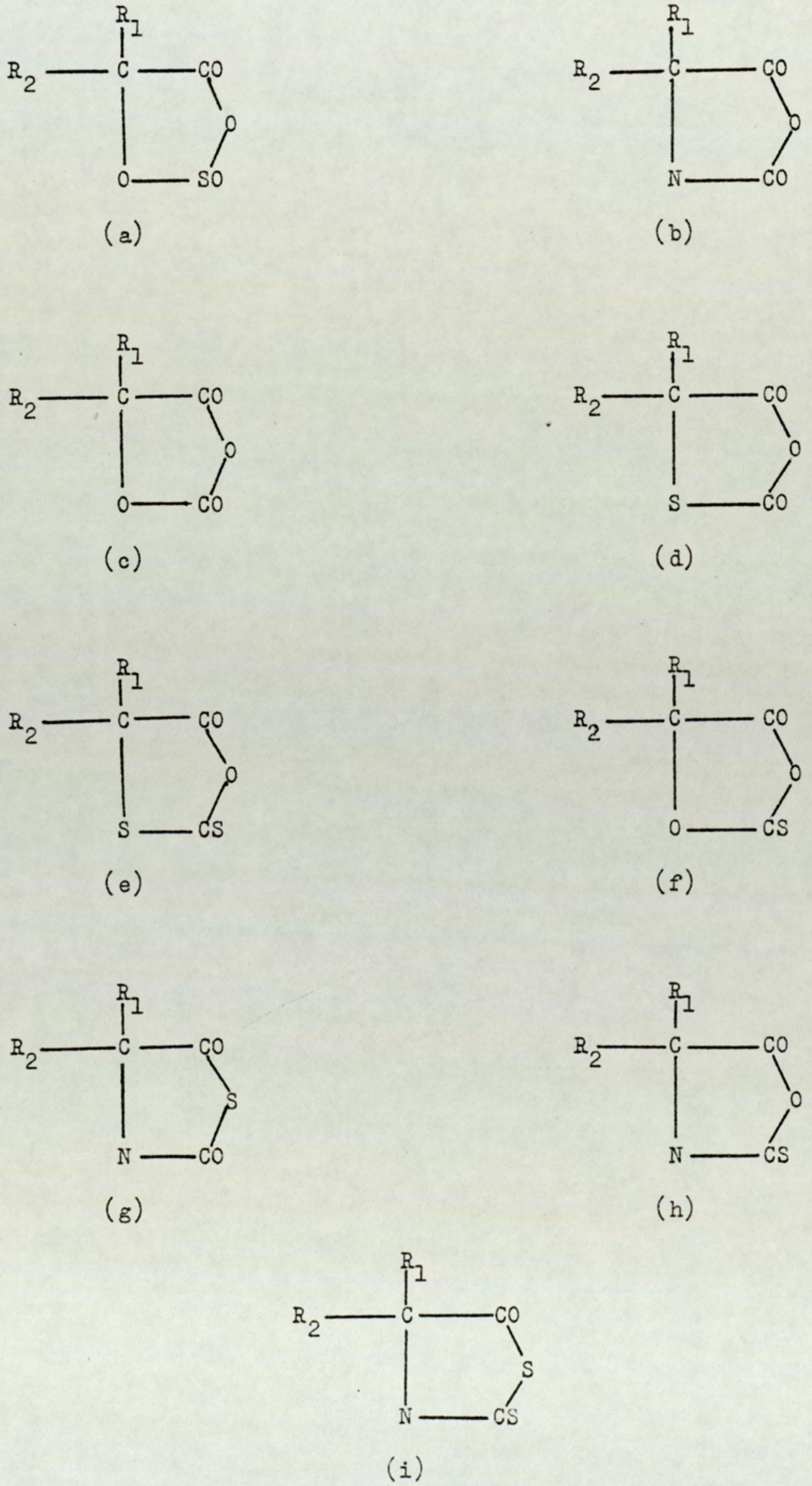
Other initiating species used in an attempt to polymerise NCAs include tertiary amines, strong bases and metal salts. Initiation by tertiary amines results in the abstraction of the nitrogen proton in the ring and subsequent anionic attack by the ring nitrogen on an adjacent NCA molecule. Thus the polymer formed is bifunctional and potentially capable of propagating from both ends. Consequently DP values in excess of the monomer to initiator ratio are found.

Different kinetic behaviour has been observed in the polymerisation of NCAs when initiated by strong bases. Among the various mechanisms proposed, those suggested by Idelson and Blout(12) and Szwarc's(6) modification of the mechanism proposed by Bamford and Block* find widest acceptance.

Extrusion polymerisation is, of course, by no means limited to NCAs. Another class of monomer that polymerises in this way are the 1,3,2-dioxathiolan-4-one-2-oxides, more commonly referred to as anhydrosulphites; a series of papers has recently appeared on their decomposition.(13-20) The structure of these compounds is shown in Figure 1a. The NCA structure is shown in Figure 1b for comparison. Also illustrated in Figure 1 are the structures of several other cyclic compounds all of which undergo extrusion reactions. Their systematic names are as follows:

* J. chem Soc 4989(1961)

Figure 1



Ic	1,3-dioxolan-2,4-dione
Id	1,3-thioxolan-2,4-dione
Ie	2-thioxo-1,3-oxathiolan-5-one
If	2-thioxo-1,3-dioxolan-4-one
Ig	2,5-thiazolidine-1,3-dione
Ih	2-thioxo-5-oxazolidone
Ii	2-thiono-5-thiozolidone

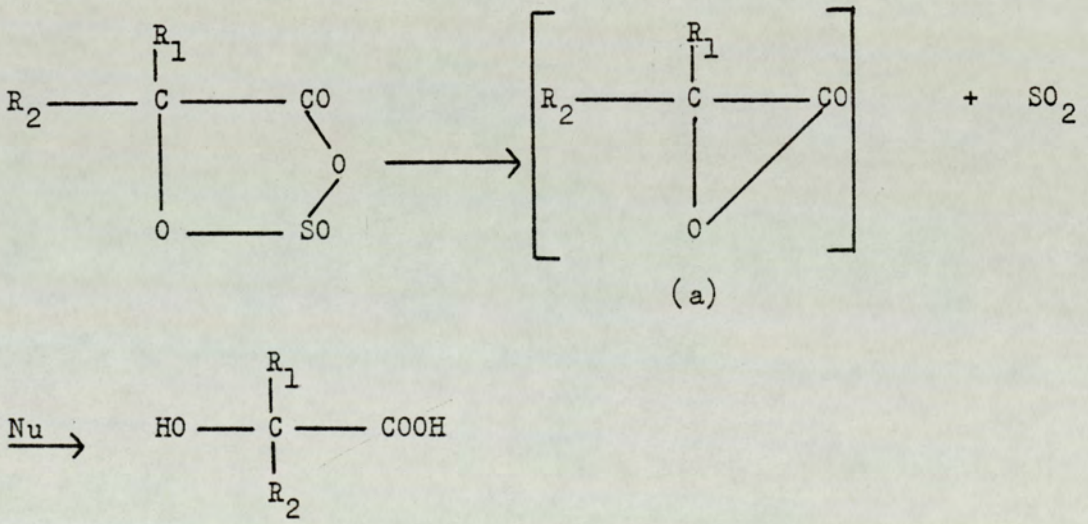
Compounds Ia, Ic(21) and If(23) have all been shown to decompose to yield poly-α-ester, while Id(21,22) and Ie(22) decompose to produce poly-α-thioester. Ig(24,25), Ih(26) and Ii(27,28,29) have been prepared and undergo extrusion reactions to yield polypeptides; as has been shown, Ib also decomposes to yield a polypeptide.

The decomposition of anhydrosulphites (Ia) is of particular significance since it provides a viable means of synthesising high molecular weight poly-α-ester for which no other general method of preparation has yet been discovered. Though poly-α-esters are not used extensively on a commercial scale, they do have certain important specialised applications in surface coatings and have been processed into films and fibres; their potential as surgical sutures has also been examined.(30) Attempted syntheses involving the catalysed self-condensation of α-hydroxy acids,(31) the thermal polymerisation of silver salts of α-chloro acids,(32) and the catalysed decomposition of glycollide,(33) have all been largely unsuccessful. Though glycollide itself has been successfully polymerised on a commercial scale,(30) and recent work by Delbig _et_ _al_.(34) indicates that 1,1,4,4-tetramethyl glycollide may be successfully polymerised in the presence of lithium tertiary butoxide, the thermal extrusion polymerisation of anhydrosulphites has so far been the most rewarding technique for the synthesis of poly-α-esters.

An initial study by Alderson(35) was of limited success, high polymer being obtained only from the dimethyl substituted monomer. Further work by Warren and Rose(36) showed that a range of anhydrosulphites could be polymerised in the presence of an amine catalyst, but the polymer obtained was only of low molecular weight.

A successful polymerisation, to a molecular weight in the region of 100,000, was achieved by Ballard and Tighe(13), whose work showed that for successful polymerisation all traces of moisture must be excluded from the system and all chloride impurities removed.

The mechanism of thermal polymerisation involves the elimination of sulphur dioxide and the formation of a highly active lactone intermediate (a) thus



(a)

The α-lactone subsequently reacts very rapidly with trace nucleophiles or any chain end hydroxyl group present, thus explaining the otherwise puzzling zero order kinetic dependence upon the hydroxyl ion concentration, which does however directly govern the DP of the resultant polymer. The elimination of sulphur dioxide is the rate determining step of this reaction. A second mechanism involving the attack of the chain end hydroxyl group at the C-4 carbonyl can also take place concurrently. This mechanism is not significantly competitive in any case except where at least one of the substituents at the C-5 position is hydrogen and attack is thus not sterically hindered.

The rate of thermal polymerisation of anhydrosulphites increases for the unimolecular decomposition as the size of the substituents at the C-5 carbon increases. The molecule is, in fact, not planar and the ring is strained due to its puckered nature at the position of the sulphur atom. This strain is increased through the transmission of the vibrational and rotational energy of the substituents into the ring. Thus the larger the substituents, the greater the ease of thermal decomposition.

The effect of the increased instability that larger substituents induce in the anhydrosulphite ring is illustrated by the work of Zachariades.(37) In an attempt to produce random copolymers of anhydrosulphites of varying degrees of substitution, it was found that the structure of the polymer produced was not in fact random. The first part of the polymer formed was composed almost entirely of units from the more heavily substituted monomer. Only when the relative concentration of the less substituted monomer increased during the natural course of the reaction did polymer units from this monomer appear in the product. The polymer formed was essentially two separate block polymers linked by a small random copolymer chain.

It might be thought that this decreasing thermal stability would provide a convenient means of preparing highly substituted poly-α-esters, but this is not in fact the case. At higher temperatures a secondary decomposition takes place and a ketone is formed with the evolution of carbon monoxide and sulphur dioxide. This reaction is particularly significant when rings whose substituents are either phenyl or electron withdrawing, such as chloromethyl, are subjected to higher temperatures. Furthermore, the purification of anhydrosulphite rings is hindered by decreased ring stability.

Tighe and Smith(38) have reported the production of high molecular weight poly-α-ester from a heterocyclic monomer closely related to the anhydrosulphites, namely 1,3 dioxolan-2,4-diones (Figure 1b), more commonly referred to as anhydrocarboxylates. Unlike anhydrosulphites, anhydrocarboxylates are planar molecules and increasing the size of the substituents at the C-5 carbon leads to large increases in the time taken to yield high molecular weight polymer. Thus the polymers reported by Tighe and Smith required the use of various pyridines as initiating species.

The initiated polymerisation of anhydrosulphites has recently been the subject of some attention. The amine initiated decomposition is reported(39) to yield only low molecular weight material. Though the strongly nucleophilic amine reacts rapidly with the monomer, the hydroxyl group generated by that reaction is far less nucleophilic and therefore less effective in propagating the reaction.

A paper by Inoue et al.(40) reports attempts to polymerise anhydrosulphites using one of a range of previously untried initiators such as dimethyl formamide, dimethyl sulphoxide, dimethylacetamide and triethylamine. However, since the sole criterion of polymer formation was taken as the solubility of the solid product in methanol, and since no information was given regarding molecular weight or molecular weight distribution, the report must be regarded as inconclusive.

Further work by Inoue et al.(40) expands the range of initiators examined to include several organo-metallic compounds of zinc, aluminium and magnesium. The results relating to systems involving water as a co-catalyst must be questioned, since it is well established that in the presence of moisture the monomer decomposes to yield the parent acid. Again no attempt was made to characterise the solid reaction product other than by examining its solubility in methanol, and no information is given regarding molecular weight or molecular weight distribution.

In further examining the possibilities of initiated polymerisation of anhydrosulphites, Crowe(41) studied a range of organo-metallic initiators including alkoxides, a Zeigler-Natta system and Boron trifluoride diethyletherate. The diethyl substituted monomer was examined, nitrobenzene and dekalin being the principal solvents. The nature of the reaction product was readily characterised as polymeric or non polymeric by infra red analysis. The reactions involving lithium methoxide or sodium methoxide in nitrobenzene were both polymer forming, but the most successful reaction involved the use of lithium tertiary butoxide in dekalin. When lithium tertiary butoxide was used with either dimethyl sulphoxide or dioxane no solid product was obtained, neither was any sulphur dioxide evolved.

A significant factor to emerge from this study was the limited solubility of lithium tertiary butoxide in non polar organic solvents. This proved to be a critical factor. The production of a second non polymeric species was also observed.

In recent years a series of papers(42-46) has appeared in which the reactions between cyclic monomers and bimetallic oxoalkoxide catalysts have been reported. Initial studies were confined to the polymerisation of propylene oxide, and the success achieved in this area has led workers to expand the range of monomers studied to include other oxiranes and lactones.(47,48)

Such reactions are not, of course, classified as extrusion reactions, but the catalysts used to initiate their polymerisation are characterised by their high solubility in a range of organic solvents, both polar and non polar.

1.2 Scope and Object of the Present Work

The susceptibility of anhydrosulphites to polymerisation by an alkoxide has been examined by Crowe,(41) whose work suggests that such reactions may provide a possible route for the low temperature synthesis of high molecular weight poly-α-ester. A major problem reported by Crowe was the extremely low solubility of the catalyst used, lithium tertiary butoxide, in solvents suitable for studies of this kind. Bimetallic oxoalkoxides of the type reported by Tessyie(57,58) are much more soluble than lithium tertiary butoxide.

The work presented in this thesis is primarily concerned with an examination of the feasibility of producing high molecular weight poly-α-ester from the decomposition of anhydrosulphites and anhydrocarboxylates in the presence of a bimetallic oxoalkoxide. It is hoped that by overcoming the problem of catalyst solubility many of the problems encountered by Crowe will be eliminated. The rate and extent of reactions will be examined for a range of monomers, as well as the nature of the reaction products, with a view to assessing the relative importance of steric, electronic effects etc. By examining both anhydrosulphites and anhydrocarboxylates it is hoped that (a) the range of potentially active monomers will be usefully extended and (b) any differences in their behaviour under comparable conditions will prove informative.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 Instrumental Techniques

Infra red Spectra - All infra red spectra were obtained using a Perkin-Elmer infra red grating spectrophotometer Model 237. Samples were used either as a KBr disc or a solution using a cell with KBr windows. The solvent used is stated at the appropriate point. The reference cell was air unless otherwise stated.

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

Thermogravimetric Analysis - Measurements were carried out using a Du Pont Thermogravimetric Analyser. Conditions are given in the text.

X-Ray Photographic Data - This was collected by the use of a Phillips 11.46 cm diameter powder camera, fitted with a 0.5 mm collimator. The samples were placed in lithium beryllium borate tubes and subjected to Copper $K\alpha$ radiation using a nickel filter. Exposure times are as stated, but were generally between 4 and 6 hours.

Dry Box Techniques

a. Removal of Moisture

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 l 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.

2.2 Techniques used in Kinetic Measurements

Gas Evolution Technique

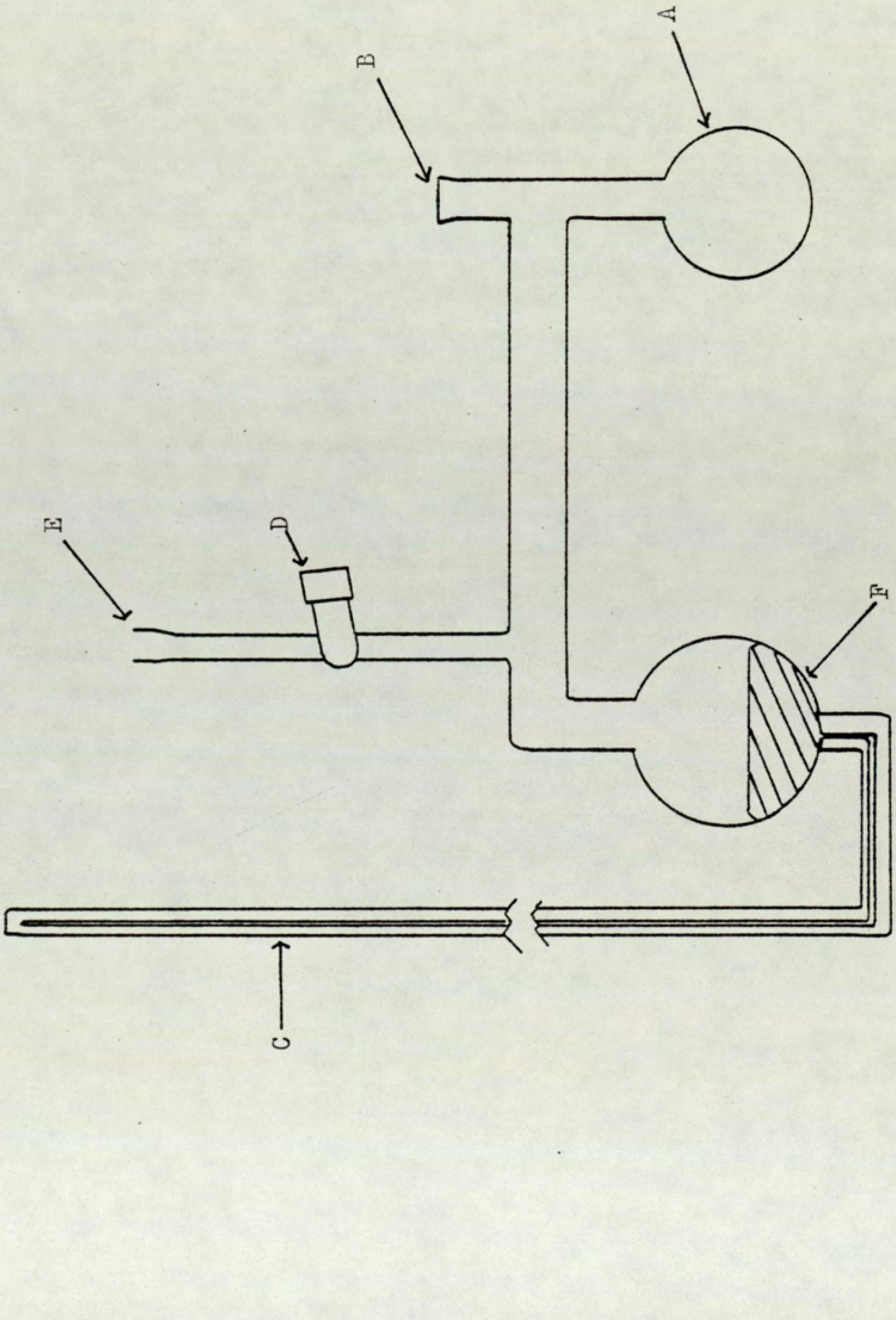
Only one type of kinetic apparatus was used and found to be suitable for all studies over a range of temperatures.

The apparatus is based on a design used by Crowe(41) with certain modifications (see Figure 2). Part F is a mercury manometer, A is the reaction vessel, which is sealed, when appropriate, by placing a 'suba' seal in B. D is a Teflon tap.

The apparatus is attached to a vacuum line via E and 'flamed out' under vacuum with tap D open. After being allowed to cool, still under vacuum, D is closed, and the reactants are introduced into A by

Figure II

Apparatus used for Gas Evolution Kinetics



careful injection, using a hypodermic syringe, through the suba seal at B. Since injection takes place immediately prior to the apparatus being immersed in the constant temperature bath, it is possible to study actual initial rates without the need for extrapolation.

The manometer rise was followed using a cathetometer.

It is essential that no supersaturation of the solutions by the evolved gas be allowed. This was avoided by agitation of the solution using a Pifco vibrator; an equilibrium between the vapour phase and the dissolved gas was thus maintained. Reproducible results are obtained only if the solution is agitated immediately prior to taking a manometer reading. The capillary was also vibrated briefly to prevent mercury sticking to its sides thus giving an erroneous reading.

A useful relationship may be derived between the concentration of monomer and the pressure of the evolved gas at any time during the decomposition. Nominally one mole of monomer will decompose to give one mole of gas (either sulphur dioxide or carbon dioxide). If $[M]_0$ is the initial concentration of monomer, $[M]$ is the concentration of monomer at any time, and $[Gas]$ is the concentration of the gas produced by the decomposition, the following relationship results:

$$[M]_0 = [M] + [Gas] \qquad \text{.... (1)}$$

on completion of the reaction, this equation simplifies to

$$[M]_0 = [Gas]_\infty \qquad \text{.... (2)}$$

At constant temperature and volume for an ideal gas, the number of moles of gas evolved is directly proportional to the pressure of the gas, i.e.

$$P_\infty \propto [Gas]_\infty \qquad \text{.... (3)}$$

therefore

$$\pi P_{\infty} = [\text{Gas}]_{\infty} = [M]_0 \qquad \text{.... (4)}$$

where π is a constant of proportionality. If the pressure at any given time is P, equation (4) may be written as

$$\pi P = [\text{Gas}] = [M]_0 - [M] \qquad \text{.... (5)}$$

Equation (4) and (5) may be combined and rearranged to give the expression

$$\frac{[M]}{[M]_0} = \frac{P_{\infty} - P}{P_{\infty}} \qquad \text{.... (6)}$$

This may be further rearranged to give

$$\frac{[M]_0 - [M]}{[M]_0} = \frac{P}{P_{\infty}} \qquad \text{.... (7)}$$

The use of equations (6) and (7) enables kinetic parameters to be evaluated, and these equations are referred to in the text.

There are three conditions for these equations to function accurately as applied to the system used herein. Constant temperature must be maintained throughout the reaction, the interior volume of the reaction vessel must remain constant throughout the reaction, and the behaviour of the gas evolved must be close to ideal.

The use of a contact thermometer/relay/heater system in controlling the water bath temperature enabled an accurate temperature ($\pm$ 0.03°) to be maintained throughout. The kinetic apparatus used involved the displacement of mercury from a reservoir as the pressure increases. However, this change in volume from initial to final state has been estimated as low as 0.01% of the total volume; the volume, therefore, remains effectively constant, providing the wider bore manometer capillary tubes are not used. Finally, low pressures are involved, up to 25 cm of mercury and the gases evolved, carbon dioxide and sulphur dioxide will exhibit ideal behaviour. The vapour pressure of the solvent is effectively constant throughout the reaction, and no error is introduced if sufficient time is allowed for the reaction vessel and its constituents to attain the working temperature of the water bath before the commencement of manometer readings. There is no evidence recorded, nor indeed was any observed, for catalysis or inhibition of reactions by mercury. The possible interactions between evolved gases and the reagents involved in individual reactions are discussed at a later point and such discussions will not be anticipated here.

2.3 Purification of Solvents and Reagents

The main requirement for solvent purification was the exclusion of trace amounts of water. Solvents and reagents were purified essentially by the methods due to Weissburger(49) and Vogel(50) with adaptations to the choice of internal drying agents for specific solvents. The distillations carried out at atmospheric pressure were vented to the air through a tube containing anhydrous calcium chloride, to prevent entry of atmospheric moisture.

Benzyl Alcohol - The solvent was initially shaken with and allowed to stand over anhydrous magnesium sulphate. It was then fractionally distilled under reduced pressure on to baked barium oxide over which it was stored. The alcohol was redistilled under reduced pressure immediately prior to use.

Dekalin - The solvent was washed several times with a 5% w/v solution of sulphuric acid. It was then shaken with dilute sodium hydroxide solution and finally washed with distilled water. The solvent was dried over anhydrous calcium sulphate and fractionally distilled under reduced pressure.

Pyridine - The anhydrous grade of pyridine as supplied by B.D.H. Laboratory Reagents with a maximum water content of 0.02% was used. All manipulations were carried out under an atmosphere of dry nitrogen.

Diethyl Ether - The anhydrous grade of solvent (0.02% water) as supplied by Fison Scientific Apparatus Ltd was used. The addition of sodium wire maintained the solvent's anhydrous state.

Silver Oxide - Silver oxide was heated in a vacuum drying pistol for twenty-four hours at 100°C.

Anisole - The solvent was dried over anhydrous calcium chloride and fractionally distilled on to baked barium oxide.

α-hydroxy acids - Glycollic, lactic, isobutyric and mandelic acids were all commercially available.

Phosgene - obtained from B.D.H. Laboratory Gas Service Ltd.

Toluene - The solvent was shaken with and allowed to stand over anhydrous calcium chloride. It was then filtered and allowed to stand over sodium wire.

p-Xylene - as for toluene.

n-butyl Lithium - The reagent was supplied by Aldrich Chemicals Co. Inc. as a 1.6M solution in n-hexane under an atmosphere of pure argon. The reagent was supplied in an Aldrich Sure/Seal bottle and could thus be dispensed using standard syringe techniques.

Zinc Acetate - The reagent was supplied by B.D.H. Laboratory Reagents and dried by refluxing with excess acetic anhydride which was subsequently removed by vacuum distillation. Once dried zinc acetate was stored in a sealed container under an atmosphere of dry nitrogen.

Aluminium tertiary-Butoxide - The reagent was supplied by B.D.H. Laboratory Reagents and used as received. All manipulations were carried out in a dry box.

Lithium Lactate - The reagent was supplied by B.D.H. Laboratory Reagents and used as received.

2.4 Synthesis of Copper (II) Salts of α-Hydroxy Acids

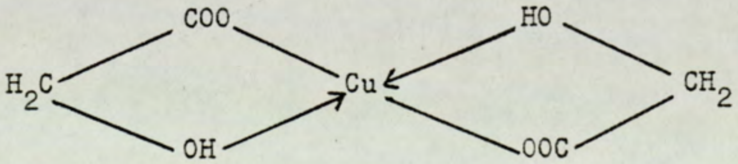
Copper (II) salts of α-hydroxy acids provide a convenient precursor to anhydrosulphite and anhydrocarboxylate preparation. They also provide a simple but effective method to the purification of the parent α-hydroxy acid.

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 ammonia. 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 ether.

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

Characterisation of Copper (II) Salts of α-Hydroxy Acids

The copper (II) salts, as typified by copper (II) glycollate



when completely anhydrous are most easily characterised by their infra red spectra. The hydroxyl group stretching 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 coordination of the group to the metal atom. The carbonyl stretching frequency, 1740 cm^{-1}

in the acid is replaced by an absorption at 1640 cm^{-1} stretching frequency of the carboxylate anion.

2.5 Synthesis of Anhydrosulphites and Anhydrocarboxylates of α-Hydroxy Acids

Anhydrosulphites

(a) Via Copper (II) Salt of α-Hydroxy Acid

The preferred means of synthesising α-hydroxy acid anhydrosulphites involves the action of thionyl chloride on the anhydrous copper (II) salt of the acid rather than on the acid itself. The former technique is simpler, more direct, and generates anhydrosulphites of greater initial purity.

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 a period of four hours. The resulting brown 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 in two stages: (a) Removal under partial vacuum at 15-20°C, then (b) removal at 10-15 mm Hg/20-25°C.

In all cases the anhydrosulphites were obtained as colourless liquids, except in the case of α-hydroxy isobutyric anhydrosulphite, which was a very pale yellow liquid.

(b) Via Lithium Salt

The synthesis of anhydrosulphites from an inorganic salt of the α-hydroxy acid has been confined to the use of copper salts. A synthesis of a lactic acid anhydrosulphite via the corresponding lithium salt was attempted and found to provide a viable alternative.

The dry lithium salt (1 mole, 79 gm) was slurried in 350 ml of anhydrous ether at 0-5°C. Redistilled thionyl chloride (1.5 mole, 178 gm) was then added dropwise over a period of four hours. The resulting white precipitate of lithium chloride was filtered off and washed with anhydrous ether to remove occluded anhydrosulphite. The ether and residual thionyl chloride were removed as in (a). The resultant anhydrosulphite was obtained as a colourless liquid.

(c) 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 six hours. Ether was then slowly removed under partial vacuum at 15-20°C, final residual ether and thionyl chloride were removed at 10-15 mm Hg/20-25°C.

Purification of Anhydrosulphites

The major impurities in the preparation of anhydrosulphites have been shown to be chlorine(14) containing compounds having either acyl or alkyl chlorine or both, together with traces of the parent α-hydroxy acid resulting from unreacted starting material or from the ingress of trace moisture.

Chlorine containing impurities have been shown(14) to be effectively and easily removed by treatment with an excess of silver oxide in ether at 0°C for two hours. The mixture was then fractionally distilled, the anhydrosulphite being the second fraction obtained. The process was repeated, and the purity of the anhydrosulphite confirmed by the absence of the absorption at 1830 cm^{-1} in the infra red, characteristic of such impurities.

Anhydrocarboxylates

The anhydrocarboxylates of α-hydroxy acids may be generally prepared by the action of phosgene on the anhydrous copper (II) of the relevant α-hydroxy acid, or by the action of phosgene on the parent acid itself.

(a) Route Via Copper (II) Salt

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 (500 ml). 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 (10-20 mm Hg). Finally the crude product was subject to a higher vacuum (0.5-1.0 mm Hg) for two hours, to remove final traces of volatiles. The crude anhydrocarboxylate was obtained as a white solid dispersed in a clear viscous liquid.

The main impurities in this crude anhydrocarboxylate are chlorine containing impurities similar to those formed in the synthesis of anhydrosulphites and are removed by a similar technique.

The crude product was dissolved in anhydrous ether and treated with an excess of silver oxide. The silver oxide was removed by centrifuge and the ether stripped off. The anhydrocarboxylate was finally purified by vacuum sublimation. It was found that the pure anhydrocarboxylate would deposit on a cold finger under the following conditions:

Crude anhydrocarboxylate : 10-15°C
Cold finger condenser : 0-5°C (water cooled)
Pressure : 0.5-1 mm Hg

The final product was obtained as a white crystalline solid. The pure anhydrocarboxylate was obtained as a viscous colourless liquid.

(b) Route Via α-Hydroxy Acid

This route is of particular convenience in the synthesis of 5,5-dimethyl-1,3 dioxolan-2,4-dione. The synthesis involves the simultaneous addition of phosgene (1.2 mole, 118 gm) in 500 ml of ether and pyridine (2.0 mole, 158 gm) in 200 ml of ether to a solution of α-hydroxy-isobutyric acid (1.0 mole, 104 gm) in 500 ml of the same solvent. The reaction mixture was maintained at 0-5°C and continuously agitated. After removal of the precipitated pyridine hydrochloride by filtration a clear ethereal solution was obtained. Removal of the ether under vacuum finally resulted in the formation of a strongly lachrymatory crystalline solid which was colourless and proved to be pure α-hydroxy isobutyric anhydrocarboxylate.

The synthetic technique used in the preparation of individual monomers is shown in Table_II. Also presented is the systematic name of each monomer, the more common abbreviation of this name, together with the substituents on the rings. The most widely accepted names of the respective parent acids are also included.

Anhydrosulphite and Anhydrocarboxylate Synthesis and Characterisation

The anhydrosulphites and anhydrocarboxylates of α-hydroxy acids are most easily characterised by their infra red spectra. The anhydrosulphite gives rise to a single absorption in the carbonyl

Table I

Anhydrocarboxylates and Anhydrosulphites

MONOMER (SYSTEMATIC NAME)	ABBREVIATION	R_1	R_2	PARENT ACID	METHOD OF PREPARATION
1,3,2 dioxathiolan-4-one-2-oxide	GAAS	H	H	Glycollic acid	a
5-methyl-1,3,2 dioxathiolan-4-one-2-oxide	LAAS	CH_3	H	Lactic acid	b
5, 5-dimethyl-1,3,2 dioxathiolan-4-one-2-oxide	DMAS	CH_3	CH_3	α-hydroxy isobutyric acid	c
5-phenyl-1,3,2 dioxathiolan-4-one-2-oxide	MAAS	C_6H_5	H	Mandelic acid	a
5-methyl-1,3-thioxolan-2,4-dione	TLAS	CH_3	H	Thiolactic acid	c[22]
1,3-dioxolan 2,4-dione	GAAC	H	H	Glycollic acid	a[1]
5,5-dimethyl-1,3-dioxolan-2,4-dione	DMAC	CH_3	CH_3	α-hydroxy isobutyric acid	b[1]

region. The frequency of this absorption (- 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 anhydrocarboxylates 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.

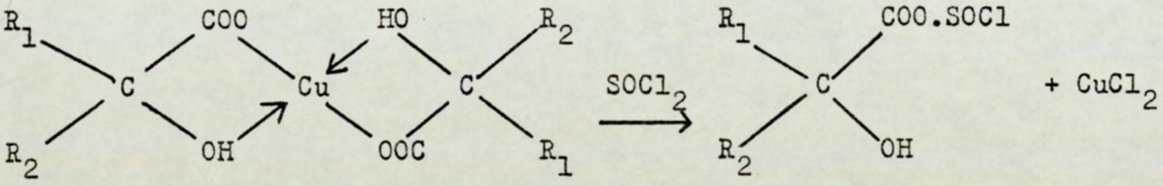
Only α-chloro acid chlorides give rise to infra red carbonyl absorption frequencies in the same region as the anhydrosulphite, and they are removed by treatment with silver oxide. Further confirmation of anhydrosulphite and anhydrocarboxylate structure can be provided by U.V. spectra in which two notable absorptions occur at 210 Å (strong) and 290 Å (weaker), N.M.R., and the characteristic fragment 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 by the reaction of thionyl chloride and the copper (II) salt of the α-hydroxy acid is now well established and has several advantages over the direct use of the acid itself. Firstly the salt may be dried at 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 D.S.C.

Secondly, half the chlorine containing byproduct of the reaction is copper chloride which is precipitated and conveniently removed by subsequent filtration.

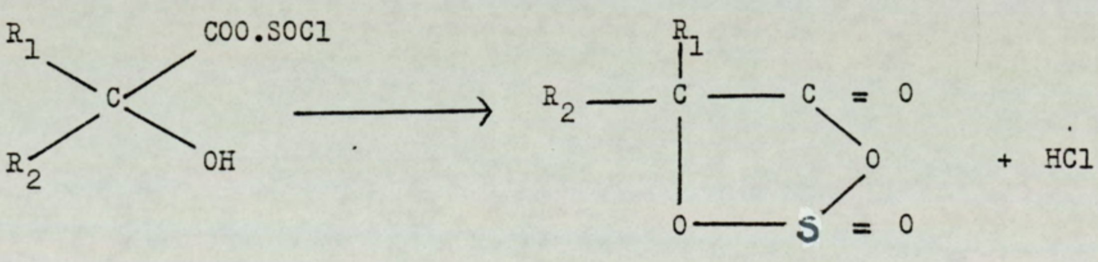
The thionyl chloride attacks the carboxylate anion rather than the hydroxylic function of the molecule, the product being an acyl chlorosulphinate (II).



(I) (II)

The acyl chlorosulphinate is rather more stable than the alkyl chlorosulphinate which would be formed if the thionyl chloride attacked the hydroxylic function of the molecule. In view of this, the former is less likely to lose sulphur dioxide with the formation of undesirable chlorine containing impurities.

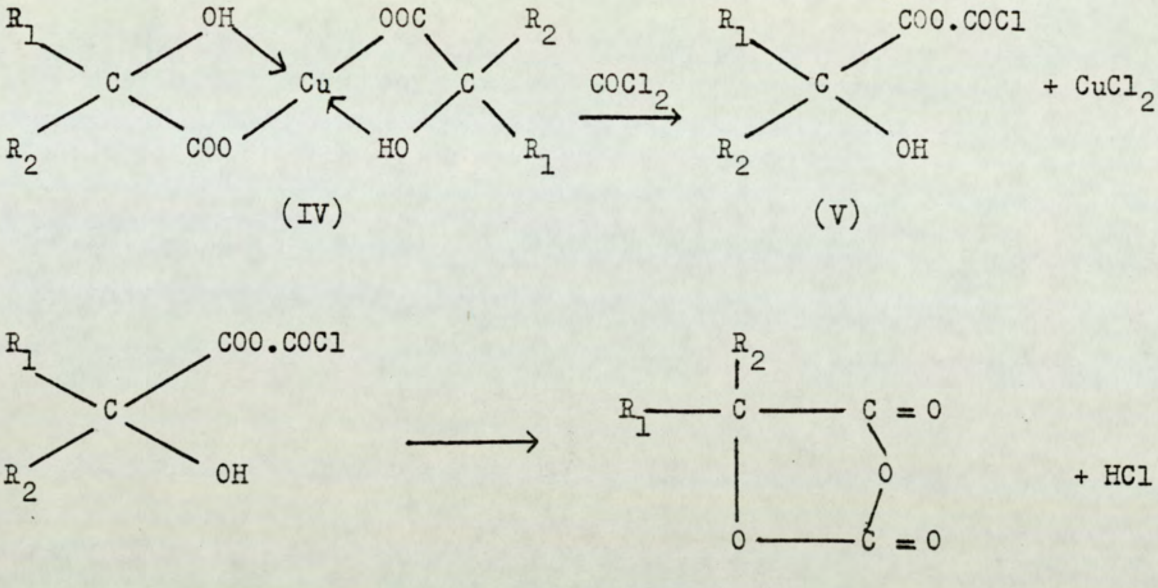
Anhydrosulphite (III) is formed by the loss of hydrogen chloride from the acyl chlorosulphinate



(II) (III)

Formation of Anhydrocarboxylates of α-Hydroxy Acids

Smith has found that anhydrocarboxylates of α-hydroxy acids are most conveniently prepared by the reaction of phosgene with the copper (II) salt of the α-hydroxy acid thus:



(IV) (V) (VI)

In this case the intermediate is an acyl chloroformate (V). As in the synthesis of anhydrosulphites, the main advantages of this method is 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.

Studies relating to the attempted polymerisation of α-hydroxy acid anhydrosulphites using metal alkoxides may be divided into two types: (a) where the alkoxide is added in the form of a previously prepared solution, (b) where the catalyst system used may be expected to generate an alkoxide in situ.

Moue et al.(40) report two examples of reactions which may be placed in the second category. These involve the use of zinc diethyl/water or aluminium triethyl/water as co-catalyst systems. Though such combinations would be expected to generate alkoxide groups, it is well established that in the presence of moisture anhydrosulphites decompose to yield their parent acid, and it is doubtful that solid product of these reactions was polymeric in nature.

Studies belonging to category (a) have proved to be more successful. Certain group I alkoxides have been shown(41) to be active in the polymerisation of α-ethyl-α- hydroxy butyric acid anhydrosulphite, and lithium tertiary butoxide in particular has been shown to be active in the polymerisation of a range of anhydrosulphites.

Until recently lithium tertiary butoxide has been available commercially, but for the present study it was synthesised according to the following method.

Synthesis of Lithium Tertiary Butoxide

The synthesis was carried out in an apparatus typical of that used in reactions involving organolithium compounds or certain Grignard preparations. The apparatus, described by Vogel,(50) allows the synthesis to take place in a dry inert atmosphere, in this case nitrogen.

In the present example, 20 ml of n-butyl lithium (1.6 molar in n-hexane) was added to the reaction vessel together with 3 ml of tertiary butanol in 15 ml of dekalin (molar ratio 1:1). The reaction mixture was allowed to stir slowly over a period of eight hours. During this time n-butane was evolved as a byproduct and was removed by the flow of nitrogen. After eight hours a red/brown solution was obtained.

CHAPTER 3

BIMETALLIC OXOALKOXIDES; SYNTHESIS AND PROPERTIES

All attempts to study the decomposition of anhydrosulphites in the presence of group I alkoxides in general, and lithium tertiary butoxide in particular, have been restricted by their relatively poor solubility in non polar organic solvents which are otherwise well suited to studies of this nature.

Recent developments in the catalysed polymerisation of oxiranes,(42-48, 51, 52) particularly propylene oxide, have led to the discovery of a new family of catalysts which are remarkably soluble in a range of organic solvents, as well as being extremely active in the polymerisation of both oxiranes and lactones. These catalysts are known as Bimetallic Oxoalkoxides (BMOAs) and are of the general formula

$$(RO)_2\, M_1 - O - M_2 - O - M_1\, (OR)_2$$

The properties of such molecules, and in particular their solubility, will be discussed presently. It is convenient at this point to examine their synthesis.

Synthesis of Bimetallic Oxoalkoxides

A patent reporting several straightforward and reproducible syntheses has been presented by Osgan _et_ _al_.(44) The syntheses reported therein are the result of the development of the two-stage condensation reactions first reported by Du Pont scientists.

Studies involving the use of these catalysts where M_1 and M_2 are aluminium and zinc respectively have shown that such molecules are very active in the polymerisation of lactones and oxiranes.(47,48)

Since these studies provide useful background information about both the structure and reactivity of these molecules, it was decided that such a molecule would be suitable for a preliminary study.

The synthesis reported herein, involving aluminium tertiary butoxide and zinc acetate, is based on the method of Osgan et al.(44)

11.25 gm of anhydrous zinc acetate were placed in flask with a mechanical stirrer. Then, 29.65 gm of aluminium tertiary butoxide, dissolved in 40 ml of anhydrous dekalin, was added and the apparatus set for reflux whilst being agitated. The flask was then heated, using an Isomantle, so that the temperature of the mixture was raised to 170-175°C. The heterogeneous mixture first thickens and after 30 minutes all the zinc acetate dissolved. As soon as the zinc acetate had dissolved, the temperature of the reaction mixture was raised to 198-200°C. Heating was continued for a further four hours after which the mixture was allowed to cool and the apparatus adapted for distillation.

The temperature of the mixture was then raised to 98°C and distillation was carried out until approximately 10 ml of distillate had been collected, after which the rate of distillation slowed considerably. Analysis of the distillate both by infra red spectroscopy and refractive index measurements confirmed that it was the tertiary butyl ester of acetic acid, the expected byproduct of this reaction.

The apparatus was then reset for reflux at 198-200°C, and the reaction allowed to continue for a further four hours, to a total of eight and a half hours. After four hours the apparatus was again adapted for distillation at 98°C. This time only 2-3 ml of tertiary butyl acetate were collected.

After further reflux at 198-200°C for one half hour the reaction mixture had acquired a green/brown colour. The dekalin was then distilled under reduced pressure at 180-190°C, leaving in the flask a frothy resinous product which was allowed to cool under dry nitrogen to room temperature. After, cooling, 100 ml of anhydrous toluene was added to the resinous product and a green/brown solution thus obtained. This solution was stored in a sealed flask under a dry nitrogen atmosphere.

Analysis of the final solution of the Bimetallic oxoalkoxide was conducted by Butterworths Microanalytical Consultancy Ltd (B.M.A.C.). The results are expressed as the concentration of each metal in mgml^{-1} as determined by Atomic Absorption Spectroscopy

Zinc	23.8 mgml^{-1}
Aluminium	22.4 mgml^{-1}

Atomic Ratio Al/Zn = 2.28.

The choice of solvent is by no means limited to toluene. Bimetallic oxoalkoxides are highly soluble in many organic solvents, both polar and non polar. Only alcohols, acids, aldehydes and ketones are unsuitable for use.

No great difficulty is experienced with the synthesis providing all solvents and reagents are totally anhydrous. Analysis of both the reaction product and byproduct confirmed that the synthesis had been successful and that the final solution contained the desired Bimetallic oxoalkoxide.

In view of the association exhibited by Bimetallic oxoalkoxides, some difficulty is experienced in selecting meaningful units in which to express the concentration of the catalytic species. Atomic Absorption spectroscopy does, however, allow the determination of the concentration of zinc to be determined with great accuracy, and hereinafter, the concentration of the catalyst will be expressed in molarities with respect to zinc.

No attempt has yet been made to devise a system of nomenclature for bimetallic oxoalkoxides. The catalyst prepared is a metal alkoxide containg zinc as its central atom; in the absence of any I.V.P.A.C. system of nomenclature, it will be referred to as ZMA throughout.

Physical Properties of Bimetallic Oxoalkoxides

It is convenient at this point to recall the more general formula of Bimetallic Oxoalkoxides, i.e.

$$_2(RO) - M_1 - O \cdot M_2 - O - M_1 - (OR)_2$$

The potential range of molecules that may be synthesised is extremely broad as can be seen if one considers the range of metals and alkyl groups that may be used in the type of syntheses reported.

Nature of the Metal M_2

M_2 may be any one of the following metals in their bivalent state, or complexes thereof: Be, Mg, Zn, Cd, Ca, Sr, Ba, Ti, TiO, Cp_2 Ti, V, VO, Cr, Mn, Fe, CO Ni, Cu, ZrO, Mo, Pd, Su, Sn, SnO, R_2Sn, Pt and UO_2, where Cp is a cyclopentadienyl radical and R is a monovalent hydrocarbon radical.

The Nature of M_1

M_1 is a trivalent metal. Trivalent metals that can be used are as follows: Al, Fe, Mo, Cr, V, Ti, Zr, B, Ga, M, Tl and Bi.

The Nature of R

The radicals R may be identical or different, though in practice they are almost always identical. They may be monovalent alkyl, alkenyl, cycloalkyl, cycloalkenyl or aryl hydrocarbon groups, especially those which contain one to twenty carbon atoms.

Whilst the range of potential Bimetallic oxoalkoxides is extremely broad, detailed studies have been confined to a much narrower range. M_2 is most commonly zinc; occasionally molybdenum, iron or cobalt have been studied. M_1 is almost always aluminium and R is most commonly alkyl or alkenyl, containing one to four carbon atoms.

The behaviour of these molecules is governed by many factors, but their association in solution is of particular importance since many of their physical properties are a direct consequence of this association. The nature of this association, together with some of its consequences, will now be considered.

Association of Bimetallic Oxoalkoxides in Solution

The metal atoms contained in an isolated trinuclear bimetallic molecule of the type

$$_2(RO) - M_1 - O - M_2 - O - M_1 - (OR)_2$$

are coordinatively unsaturated. At least two vacancies exist on M_2, and one vacancy exists at each M_1. The molecules accordingly arrange themselves so that these vacant coordination sites are fulfilled. This is done by insertion of the electron pairs available on the oxygen atoms of the OR group, and may be both an inter- and an intramolecular process. Such association has been proven by cryoscopic measurements performed on cyclohexane and benzene solutions. It has been shown that the degree of association is variable and depends mainly on three structural parameters.

(a) The nature of the R group; the less bulky the R group, the greater the degree of association.

(b) The nature of the central metal atom, M_2, and in particular its coordination geometry and coordination number.

(c) The nature of the solvent. It is possible that in the case of certain solvents, the solvent molecules will compete with the OR groups for the vacant sites.

Unless the molecule undergoes any rearrangement, the degree of association is not a function of time.

The consequence of this association is that these molecules, when in solution, exist in clusters containing anything between 6 and 24 metal atoms, depending on the factors already outlined. The distribution of the size of these clusters has not been determined, but it is not expected that cluster size would be monotonous.

One of the most remarkable and potentially useful characteristics of these bimetallic oxoalkoxides is their very high solubility in a broad range of organic solvents. The higher the number of carbon atoms R contains, and the smaller the degree of chain branching in R, the greater the solubility of the molecule, assuming all other factors are held constant.

From consideration of the association of these molecules in solution, we may reasonably infer that the reason for this high solubility is that the compact oxide structure at the centre of these clusters is surrounded by a lipophilic layer of alkoxy groups which maintain the clusters in solution. This view is supported by the fact that in the presence of alcohols, which are known to dissociate such aggregates, there is a marked decrease in solubility.

Colour of Bimetallic Oxoalkoxides in Solution

Another characteristic of these compounds which reveals specific coordination phenomena is their colour, which obviously depends on the nature of M_2, but is also affected, to a remarkable degree, by the nature of the R group.

Two examples illustrate this point. Consider first the molecule $Co\ O_2\ Al_2\ (OR)_2$. When R is n-butyl the solution in benzene is blue, yet when R is isopropyl the solution is red-violet. Similarly, in the case of $Mo\ O_2\ Al_2\ (OR)_2$: when R is n-butyl the solution, again in benzene, is deep green, but when R is isopropyl the solution is brick red.

The variation in colour that results from changing R indicates that as R varies, so does the degree of association of the molecules, and hence the coordination sphere of M_2; this final change is reflected in the dramatic variations in colour that workers have observed.

Summary of Alkoxide Catalysts

The high solubility of oxoalkoxides in non polar organic solvents is in marked contrast to that of the alkoxides examined by Crowe(41) and other workers.(40) As has been pointed out, studies(40,41) involving the use of lithium and sodium alkoxides have been complicated by their limited solubility in such solvents. In some cases the onset of heterogeneity during the course of a reaction has proved to be a further complication.

In view of the high solubility of Bimetallic oxoalkoxides and their proven activity in the ring opening polymerisation of certain heterocyclic monomers, it is a necessary and logical extension of the work already reported that their potential as catalysts for the polymerisation of anhydrosulphites be examined.

The range of potential initiating species studies may be further extended by examining the reactions between n-butyl lithium and certain anhydrosulphites. The only report(40) relating to the use of this compound for this purpose is not conclusive, and the potential of this typically anionic initiating species is also worthy of some consideration.

Table II shows how the degree of association ($\bar{n}$) can vary for bimetallic oxoalkoxides depending on the metals involved, the nature of R and the solvent.

Table II

Mean association degree ($\bar{n}$) of oxoalkoxides as measured cryoscopically

M_1/M_2	R group	Solvent	$\bar{n}$
Al/Zn	n.C_4H_9	C_6H_6	8.0
Al/Co	n.C_4H_9	C_6H_{12}	6.2
Al/Co	n.C_4H_9	C_6H_6	4.1
Al/Fe	n.C_4H_9	C_6H_{12}	8.0
Al/Mo	n.C_4H_9	C_6H_6	3.0

CHAPTER 4

ALKOXIDE INITIATED DECOMPOSITION OF GLYCOLLIC ACID ANHYDROSULPHITE

Glycollic acid anhydrosulphite (GAAS) is a suitable monomer for study in an initial investigation of the susceptibility of anhydrosulphites to decomposition in the presence of ZMA. The absence of any bulky substituents in the C-5 position means that the molecule is the most thermally stable of this family; since purification of the monomer involves repeated distillation, this thermal stability allows the synthesis of a monomer of a high degree of purity without fear of extensive decomposition taking place. Furthermore, the absence of any steric hindrance that might result from the presence of C-5 substituents, minimises the number of variables that must be considered when postulating possible mechanisms of the reaction. Since GAAS is the sterically least hindered anhydrosulphite it will also provide an excellent basis for comparison when considering the behaviour of more highly substituted anhydrosulphite monomers.

In view of the poor solubility of GAAS in dekalin, which is otherwise an excellent solvent for studies of this nature, certain other solvents were examined. Whilst the monomer is soluble in both nitrobenzene and anisole, both solvents proved to be unsuitable for the present study. It was found that when the catalyst solution was injected into a solution of the monomer in either anisole(54) or nitrobenzene, an inert gel was formed, and there was no evidence of any reaction between the monomer and the catalyst. It is thought likely that the solvent molecules compete successfully with the monomer for the available catalytic sites and thus prevent any reaction taking place.

Toluene proved to be a suitable solvent for the present study. The monomer is readily soluble in toluene, which in no discernible way interacts with the available sites on the catalyst molecules, whilst the vapour pressure (2mm Hg) is sufficiently low to allow its use in the experiments conducted. In preliminary experiments the monomer/catalyst mixture showed some tendency to form an inert gel before any reaction could take place. To overcome this tendency, p-xylene was used as a co-solvent. Para-xylene in particular was selected as a co-solvent because of its low vapour pressure and its compatibility with the system already established.

4.1 Kinetic Results and Observations

The rate of evolution of sulphur dioxide at 25°C was measured by observing the manometric pressure rise at constant volume using the apparatus described in section 2.2. Figure III shows a typical plot of pressure rise with time for the system GAAS/p-xylene/catalyst at various catalyst concentrations. The curves obtained show an initial relatively rapid rate of reaction continuing for 50 to 60% of the reaction. This relatively rapid part of the reaction is followed by a more gradual evolution of gas. In no case did the volume of gas evolved during a reaction equal the theoretical volume. The reactions involving the lower catalyst concentrations evolved only a limited quantity of sulphur dioxide.

Table III shows the initial rate of the reaction for the varying catalyst concentration.

Table III

Initial rates (K) of GAAS decomposed at 25°C in the presence of ZMA in dekalin/p-xylene co-solvent.

$[ZMA]_o$ (mol l^{-1})	K X 10^5 (sec^{-1})
0.0728	2.26
0.0364	1.86
0.0182	1.64
0.0091	1.13

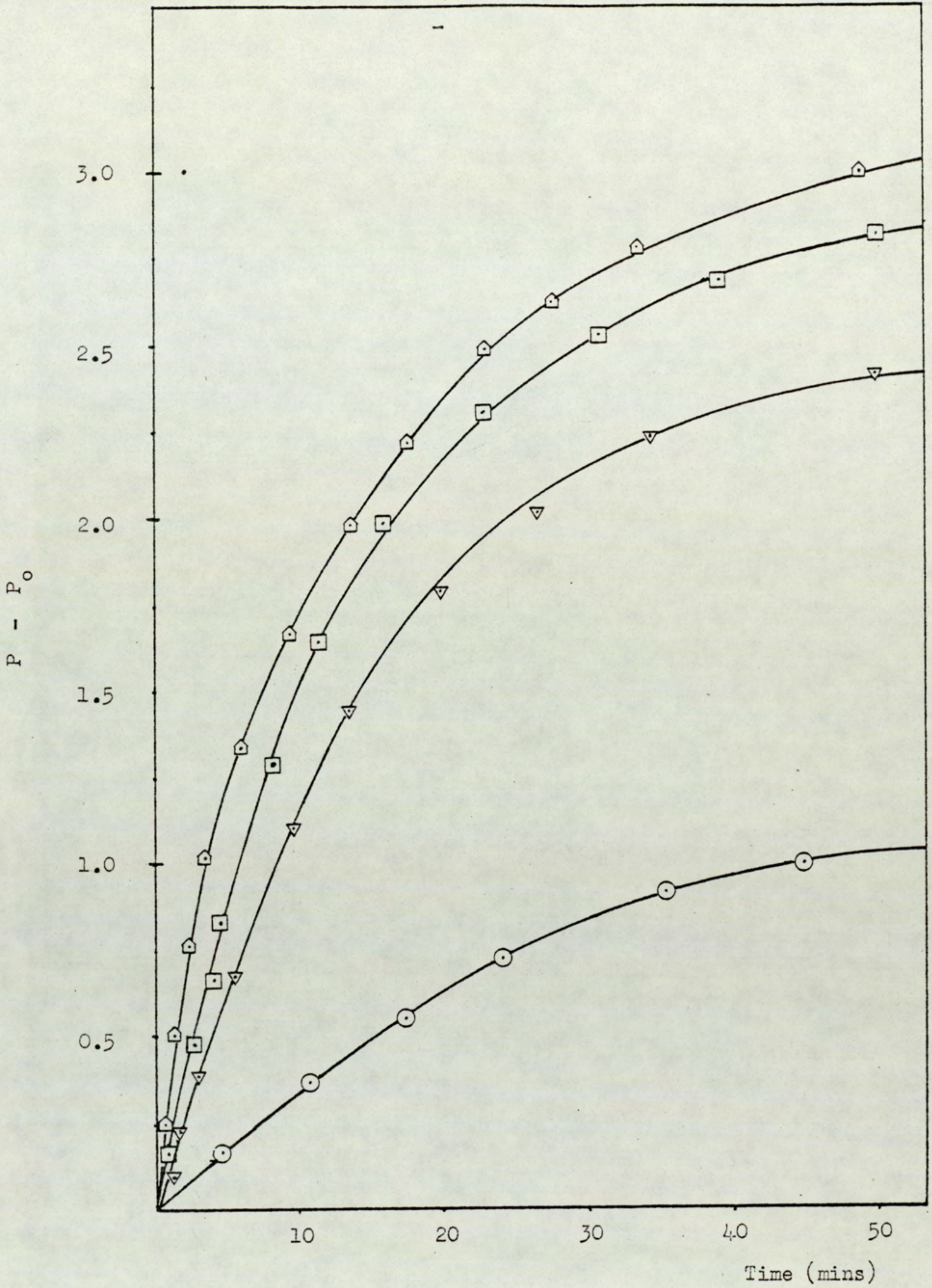


Figure III

Decomposition of GAAS in the presence of ZMA at 25°C.

$GAAS_o$ = 0.75M

ZMA_o = 0.0728M ⌂

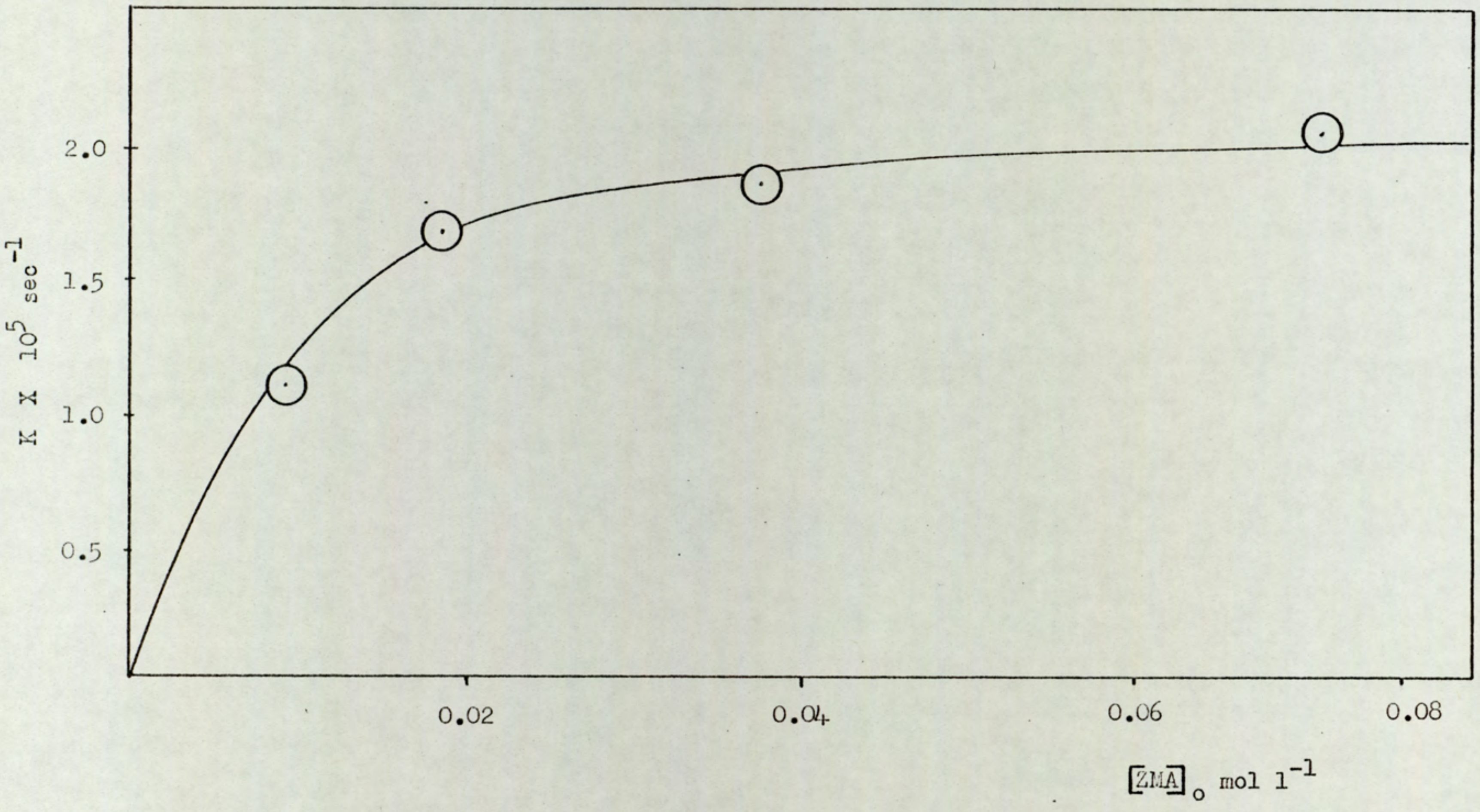
ZMA_o = 0.0364M ⊡

ZMA_o = 0.0182M ▽

ZMA_o = 0.0091M ⊙

Figure IV

Initial rate (K) versus $[\mathrm{ZMA}]_o$ for the decomposition of GAAS at 25°C. $[\mathrm{GAAS}]_o$ = 0.75M.



It can be seen from Figure IV that the relationship between initial rate and catalyst concentration is not linear, but that a maximum catalyst concentration exists, beyond which no marked increase in initial rate is observed.

As the reaction proceeded, it was observed that the reaction mixture separated into two distinct layers. The initial pale green/brown colour of the mixture became more intense in the lower layers, less intense in the higher layers. This difference became more pronounced as the reaction continued until, in the final stages, the reaction mixture was composed of two distinct layers, the upper layer a clear liquid, the lower layer an intensely coloured green/brown gel. The formation of this gel was apparently unaffected by the vibration of the apparatus that always preceded any cathetometer reading. It was also noted that the onset of the visible formation of this gel and the slowing down in the rate of evolution of sulphur dioxide were parallel events.

4.2 The Analysis of the Products

4.2.1 Liquid Layer

Analysis of the reaction products necessarily involved the separate analysis of the two distinct layers. Infra red analysis of the liquid layers showed that in no case did they contain any unreacted monomer or ester of any nature. In fact, the only spectral difference between the liquid layer formed during the course of the reaction and the solvent system used exists in the region 600-800 cm^{-1} and is possibly due to some Friedel-Craft acylation that may occur as a side reaction. The similarity between the various liquid layers formed and the solvent system used was further supported by Refractive Index measurements.

Table IV shows the refractive index of all liquid layers. Each figure represents an average of five readings. The refractive index of the pure solvent mixture and that of the monomer are quoted for the purposes of comparison.

Table IV

Refractive index of liquid layer of reaction product

$[ZMA]_o$ mol l^{-1}	R.I.
0.0728	1.4926
0.0364	1.4932
0.0182	1.4930
0.0091	1.4932
solvent	1.4959
GAAS	1.4715(55)

This confirms the interpretation of the I.R. spectra, that the liquid layer is composed almost totally of solvent.

4.2.2 Solid Products

The gel phase of the reaction product was dried at approximately 70°C under a vacuum of 1 mm, resulting in all cases in a cream/white powder. In the cases of the two lower catalyst concentrations, the limited quantity of solid product proved to be a restriction in the analysis of their respective compositions. As far as the quantity of reaction product allowed, the solid reaction products were examined in the following way.

4.2.2a Gel Permeation Chromatography

Any possibility of data relating to the molecular weight and molecular weight distribution was precluded by the total lack of solubility of the products in any suitable solvent. Tetrahydrofuran (THF), o-dichlorobenzene (ODCB) and o-chlorophenol (OCP) were all tried in an attempt to obtain the 0.2% w/v solution necessary for G.P.C. analysis, all without success. While it is known that polyglycollide is difficult to dissolve due to its closely packed highly crystalline structure, the total lack of solubility of the product was not anticipated and, though in a sense disappointing, is of great interest and will be discussed at a later stage.

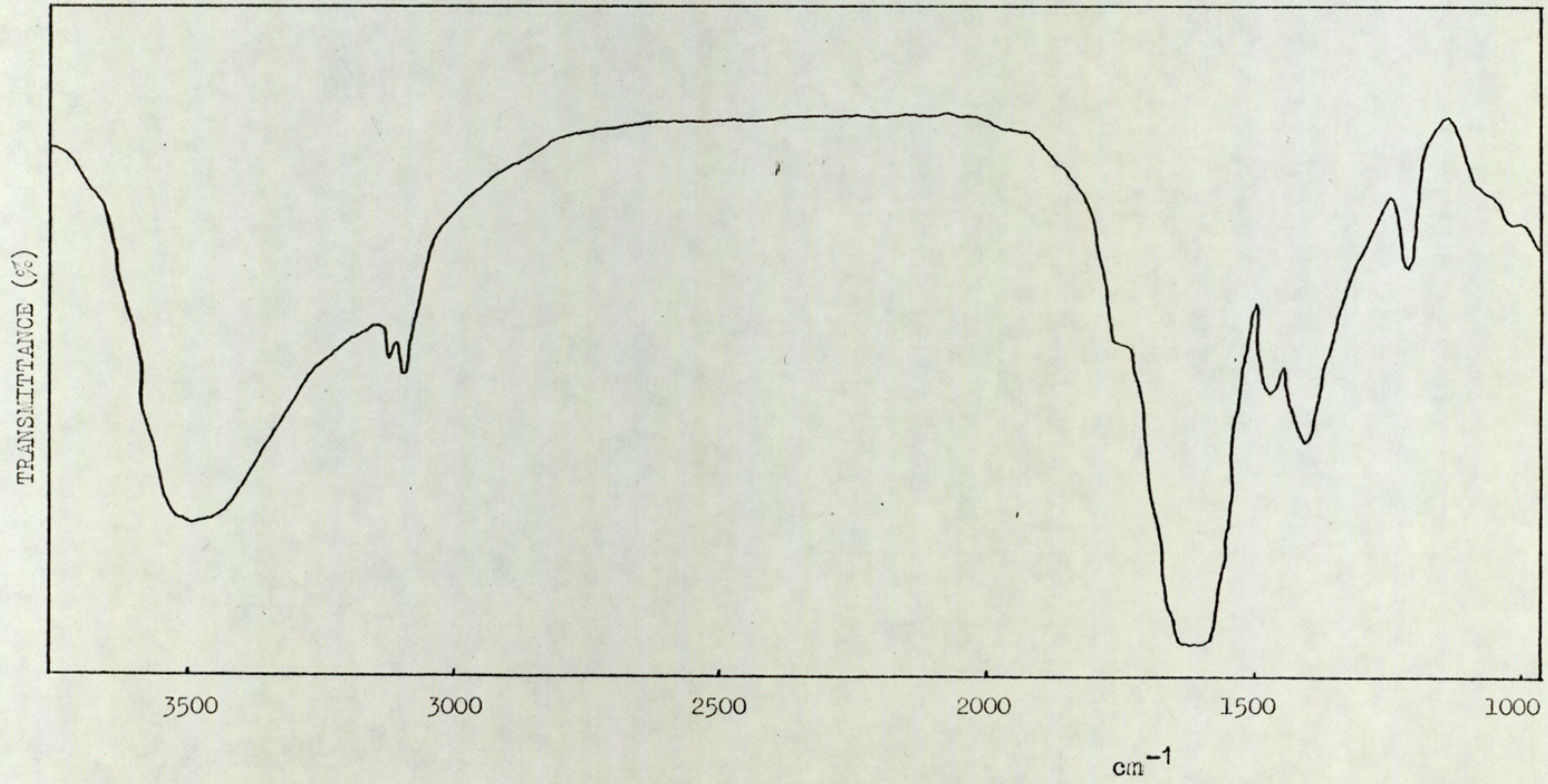
4.2.2b <u>Infra Red Studies</u>

The characteristic absorptions of anhydrosulphite monomers, and the polymers formed therefrom, make I.R. a convenient and highly informative method of analysis. In view of the almost total absence of G.P.C. data it is of added importance in the present study.

The strained ring system which exists in anhydrosulphites gives rise to a relatively high carbonyl absorption frequency, usually at 1810 cm^{-1}. The polymeric products obtained from their thermal decomposition are characterised by a strong absorption at 1740 cm^{-1}; this is due to the carbonyl group now in the relatively unstrained polymer chain environment. The nature of the reaction undergone by the anhydrosulphites studied will be revealed, to some extent at least, by the change in the frequency of the carbonyl absorption. Discussions of the I.R. spectra of the reaction products are therefore principally concerned with the region 1600-1810 cm^{-1} where such absorptions may confidently be expected to occur. The infra red absorption spectra of the solid products of the decomposition of GAAS in the presence of the present catalyst are characterised by a strong absorption (1610 cm^{-1}) and a medium absorption (1740 cm^{-1}). A typical spectrum is shown in Figure V. As the concentration of

Figure V

I.R. spectrum of the solid product of the reaction between GAAS and ZMA. $[\text{GAAS}]_o$ = 01·75M.
$[\text{ZMA}]$ = 0.0728. 25°C. KBr disc reference cell air.



catalyst decreases, the absorption at 1740 cm^{-1} becomes slightly stronger and adopts the form of a more independent peak rather than the shoulder that appears in Figure V. Nevertheless, the relative intensities of the absorptions are, to a very good approximation, the same.

The higher frequency absorption (1740 cm^{-1}) corresponds very closely to that observed in the thermal decomposition of anhydrosulphites and may be confidently attributed to α-ester. The lower frequency absorption (1600 cm^{-1}) is not shown by the products of thermal decomposition, and until recently such absorptions had not been reported in studies relating to anhydrosulphite decomposition. Crowe(41) reports a very similar absorption (1620 cm^{-1}) in the infra red of the product of methyl ethyl anhydrosulphite (MEAS) decomposed by catalytic amounts of lithium tertiary butoxide. As a consequence of a detailed study, Crowe was able to postulate a mechanism for this reaction. The mechanism involves, amongst other things, the formation of a low molecular weight carboxylate ester which is attached to the metal atom of the catalyst and Crowe attributes the absorption at 1620 cm^{-1} to this species. The possibility of the formation of an analogous carboxylate ester in the present reactions merits some consideration, and for the present the absorption at 1620 cm^{-1} is attributed to adduct involving both the catalyst and monomer and will be referred to hereinafter as a metal salt.

4.2.2c Sulphur Determination

In view of the limited quantity of sulphur dioxide evolved during the course of the present reactions, and also taking into account the probability of metal salt formation strongly suggested by I.R. studies, the percentage of sulphur in the solid products of the two reactions involving the higher catalyst concentration was determined. In view of the limited quantity of material available in (2), the figure quoted is only accurate to ± 0.1%.

	Catalyst concentration	% Sulphur
(1)	0.0728	0.6
(2)	0.0364	1.00

4.2.2d X-ray Diffraction

Some guide to the structure of the reaction products was obtained by X-ray diffraction studies using the powder photograph technique. In view of the well-known reciprocal relationship between d-spacings obtained from X-ray diffraction photographs and the length of the repeat unit of the material being examined, it should be possible to differentiate between polymeric and non polymeric materials by inspection of the photographs obtained. For the purposes of the present study the type of scatter observed will be classified as follows:

(1) Repeated clearly defined lines, regularly spaced at small angle to the main beam. These may be attributed to crystalline polymer.

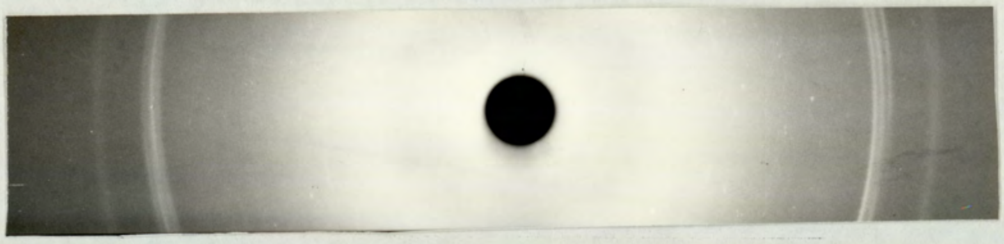
(2) Diffuse scatter at a narrow angle to the main beam, due to amorphous organic material.

(3) Sharp lines at a wide angle of scatter, caused by the metallic content of the product.

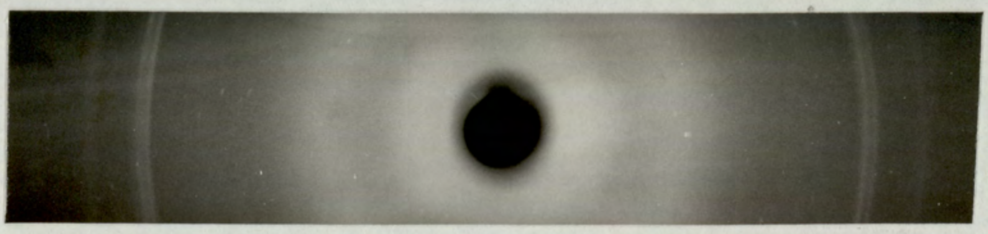
X-ray powder photographs of the products of the reactions involving the two higher catalyst concentrations are shown in Figure VI. The scatter shown on these photographs is classified under the headings

FIGURE VI

Glycollic Acid Anhydrosulphite



$[ZMA]_o$ = 0.0728M



$[ZMA]_o$ = 0.0364M

of (2) and (3). The inner diffuse scatter is typical of that obtained from amorphous organic material, and the fine sharp lines also shown are too widely removed from the central beam to be attributed to anything other than the metal content of the product.

CHAPTER 5

ALKOXIDE INITIATED DECOMPOSITION OF α-HYDROXY ISOBUTYRIC ANHYDROSULPHITE AND MANDELIC ACID ANHYDROSULPHITE

5.1 The Catalysed Decomposition of α-Hydroxy Isobutyric Anhydrosulphite

The anhydrosulphite of α-hydroxy isobutyric acid (DMAS) was prepared by the direct action of thionyl chloride on the parent acid as described in section 2.5c. In view of the work already reported herein, relating to the decomposition of GAAS, a study of the decomposition of DMAS in the presence of ZMA is a logical development.

5.1.1 Observations

In an initial investigation (DMAS - 0.75M / Catalyst 0.0182 mol 1^{-1}) no pressure rise was observed over a period of six hours despite regular agitation to ensure adequate mixing of the reagents. After a further eighteen hours, still no pressure rise had been observed. To eliminate the possibility that the monomer might, in some way, have been hydrolysed during its handling, a small quantity of a known initiator, pyridine, was injected into the reaction mixture. The subsequent pressure rise indicated that at the time of injection the monomer had been intact.

In view of the sensitivity of organo-metallic initiators to trace impurities, two further separate experiments were conducted with increased catalyst concentration, the monomer concentration remaining constant at 0.75M. The catalyst concentrations used, 0.0728 mol 1^{-1} and 0.0364 mol 1^{-1}, can be reasonably presumed to be sufficiently in excess of any trace impurity, thus precluding the possibility that any impurity (trace acid chloride for example) might render the catalyst inert. Once again, no pressure rise was observed for either reaction over a period of twenty-four hours. In the case of the lower catalyst concentration (0.0364 mol l^{-1}) no visible change in appearance of the reaction mixture was observed. However, in the case of the highest catalyst concentration used (0.0728 mol l^{-1}) a barely visible amount of a green/brown gel was seen to have formed at the bottom of the reaction vessel. When dried in the usual manner, this yielded a cream white powder.

5.1.2 Analysis of the Products

I.R. Studies

Analysis of the liquid layer of the final reaction product showed only traces of unreacted monomer. In view of the lack of pressure rise this was predictable. The spectrum of the solid product is presented in Figure VII. It is characterised by a strong absorption at 1610 cm^{-1} and a less intense absorption at 1740 cm^{-1}. These absorptions are attributed to metal salt and poly-α-ester respectively, though in view of the lack of any pressure rise, the presence of any trace of α-ester is unexpected.

The limited quantity of solid reaction product did not allow an attempt to study its nature by X-ray diffraction or G.P.C. In view of the I.R. spectrum of the product, and taking into account the results so far reported, it is not thought likely that the solid product would dissolve in any solvent suitable for G.P.C.

5.2 Decomposition of Mandelic Acid Anhydrosulphite

Mandelic acid anhydrosulphite (MAAS) was prepared by the action of thionyl chloride on the copper salt of the α-hydroxy acid (see section 2.5b). It had been established that DMAS did not react to any appreciable degree with the present catalyst, and that GAAS had shown only limited activity. Whilst MAAS exhibits a degree of steric hindrance comparable in effect to DMAS, the steric hindrance is not symmetrical,

Figure VII

I.R. spectrum of the solid product of the reaction between DMAS and ZMA. $[DMAS]_o = 0.75M$. $[ZMA] = 0.0728M$. $25^{o}C$. KBr disc reference cell air.

so the inactivity of DMAS does not necessarily preclude the possibility that MAAS may prove active. Should the monomer prove active, this asymmetry will be preserved in the polymer formed and so ensure sufficiently high solubility to enable G.P.C. analysis to be conducted.

5.2.1 Observations

An initial study using a relatively low catalyst concentration (0.0091 mol l^{-1}) did not yield any visible pressure rise and a second, concurrent experiment using a much higher catalyst concentration (0.0728 mol l^{-1}) also failed to show any pressure rise over a period of four hours. Both reactions were allowed to stand for a total period of twenty-four hours, after which both reaction vessels contained small quantities of a green/brown gel. This gel once again yielded a cream white powder on drying. Only in the case of the higher catalyst concentration was sufficient material available to allow more than infra red analysis to be conducted.

5.2.2 Analysis of the Reaction Products

I.R. Studies

Analysis of the liquid layers of the reaction mixture revealed only traces of unreacted monomer.

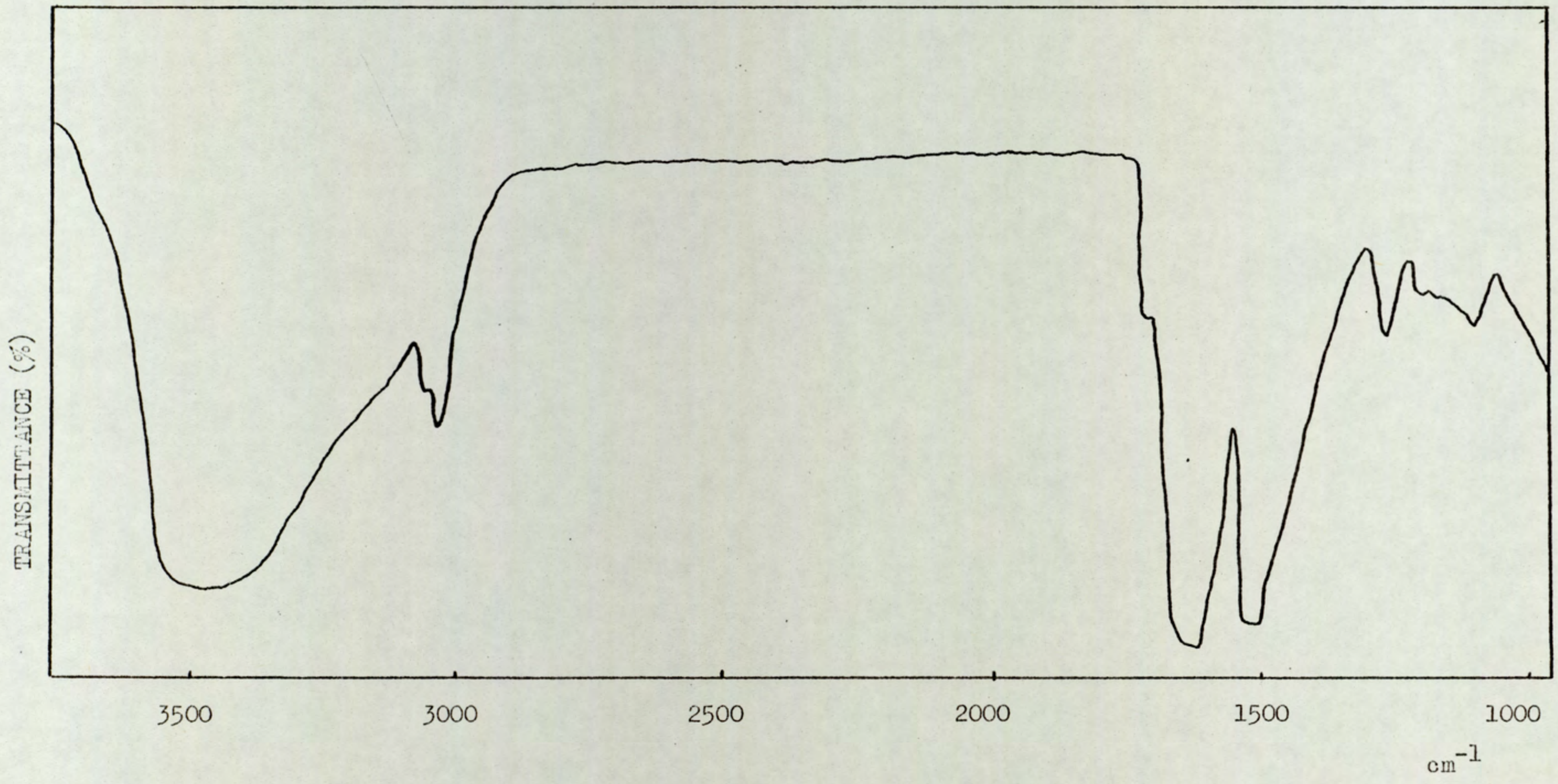
The spectrum of the solid products of one of the reactions is presented in Figure VIII. It shows a strong absorption at 1600 cm^{-1}, and a less intense absorption at 1740 cm^{-1}. The latter absorption is attributed to α-ester, a puzzling feature of the spectra in view of the total lack of evolution of sulphur dioxide.

G.P.C. Studies

Any possibility of analysis of the product of the reaction involving the higher catalyst concentration was precluded by its total lack of solubility in any suitable solvent.

Figure VIII

I.R. spectrum of the solid product of the reaction between ZMA and MAAS. $[ZMA]_o = 0.0728M.$
$[MAAS]_o = 0.75M.$ 25°C. KBr disc reference cell air.



CHAPTER 6

ALKOXIDE INITIATED DECOMPOSITION OF LACTIC ACID ANHYDROSULPHITE

A series of experiments were conducted involving the decomposition of LAAS in the presence of ZMA. It is convenient to present the results obtained in three separate headings: experiments involving p-xylene as a co-solvent, experiments using a single solvent system and further experiments.

All kinetic studies were carried out by gas evolution technique, following the rate of reaction by measurement of the rate of evolution of sulphur dioxide, under the conditions stated.

6.1 Experiments Using P-xylene as Co-solvent

6.1.1 Kinetic Data and Observations

The reaction profiles for the decomposition of LAAS at varying catalyst concentration are shown in Figure IX. It can be seen from Figure IX that for all catalyst concentrations the kinetic profiles do not suggest that reaction taking place is anything other than a smooth continuous process, unlike the reactions involving GAAS/ZMA where some of the profiles suggest the possibility of two consecutive reactions. The initial rates obtained are presented in Table V.

Table V

Initial rate (K) for the Alkoxide initiated decomposition of LAAS.

$[\mathrm{LAAS}]_0 = 0.75\mathrm{M}$ 25°C.

$[\mathrm{ZMA}]_0$ mol l^{-1}	K X $10^4(\sec^{-1})$
0.0607	13.33
0.0304	12.06
0.0152	8.50

Figure IX

Decomposition of LAAS in the presence of ZMA. p-xylene co-solvent. 25°C. $[\text{LAAS}]_o = 0.75\text{M}$.

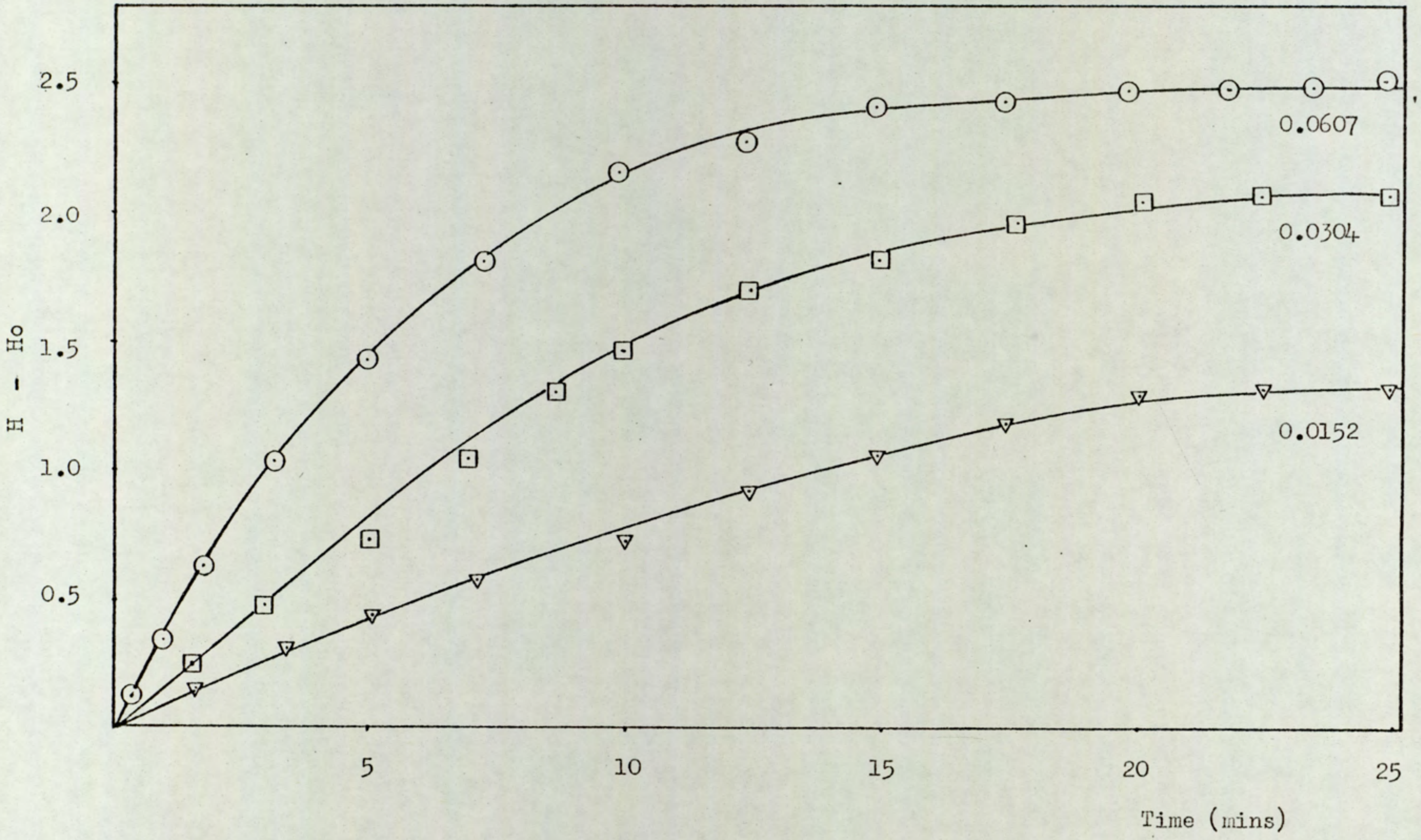


Figure X

Initial rate (K) versus ZMA $_o$ for the decomposition of LAAS at 25°C. p-xylene co-solvent.

$[LAAS]_o$ = 0.75M.

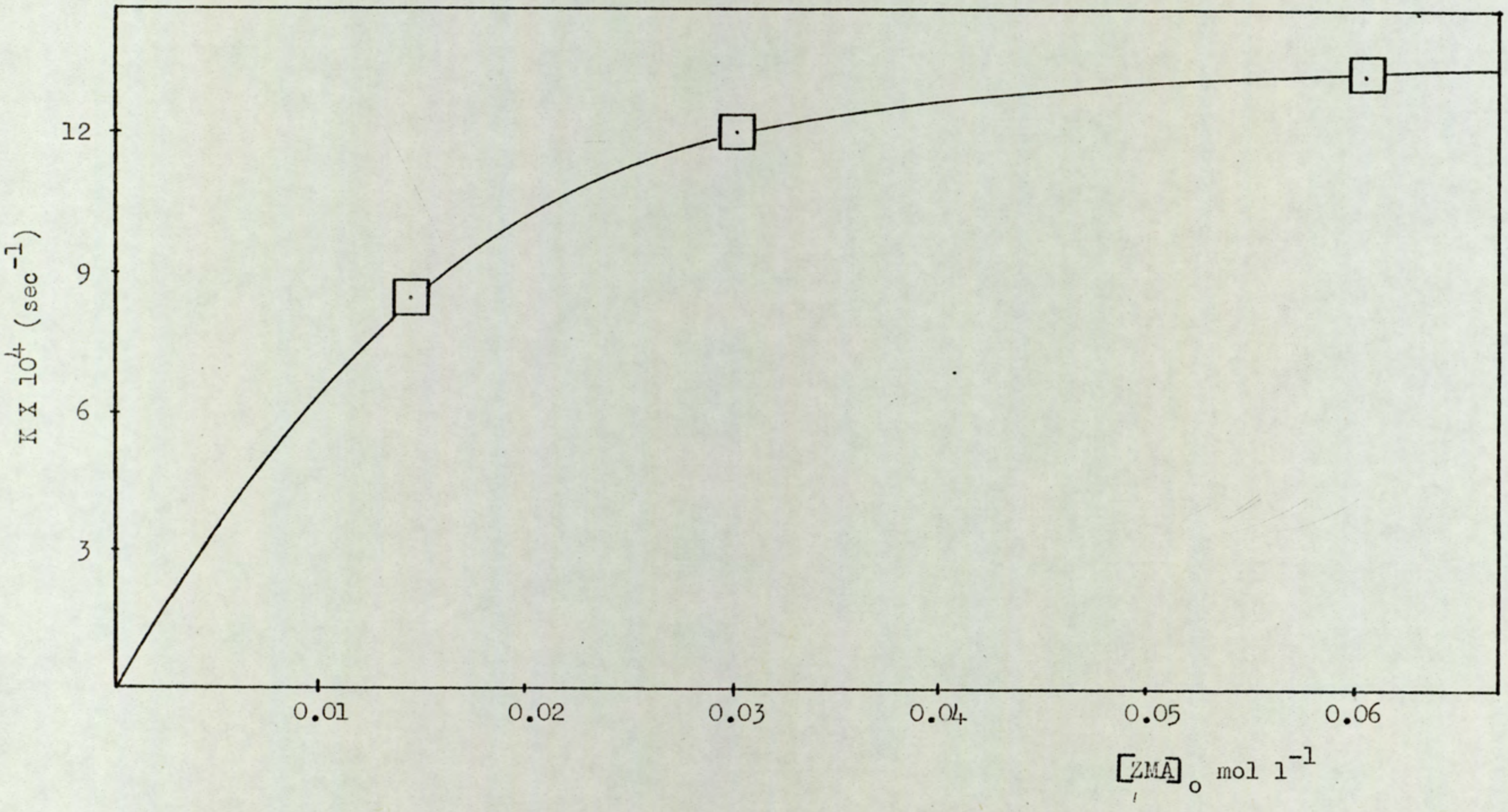


Figure X shows these results as a plot of initial rate vs catalyst concentration.

It is evident that the relationship between initial rate and catalyst concentration is not linear, but that beyond a certain concentration no marked change in initial rate occurs.

It was observed that, as in the decomposition of GAAS, the reaction mixture separated into two layers as the reaction proceeded, and that the beginning of the slower period in the kinetic profile and the onset of this phase separation occurred at approximately the same time.

By the time the reaction was complete, the reaction mixture had separated into two quite distinct layers, one a transparent liquid, the lower layer a dark green/brown gel. It was also observed that the final quantity of solid product obtained was closely linked to the quantity of catalyst used. A result of this was that while reactions involving small amounts of catalyst yielded valuable information, the analysis of their products was necessarily restricted.

6.1.2 Analysis of Reaction Products

(a) Liquid - The upper layer of the reaction mixtures were examined by I.R. In all cases the spectra obtained were identical with that of solvent system being used. There was no evidence of any other reactions having occurred, nor of unreacted monomer.

(b) Solid - In all cases, the green/brown gel formed during the course of the reaction, when dried, yielded a white powder. These solid products were subject to an analysis by the following techniques.

6.1.2a I.R. Studies

The infra red absorption spectra of all the reaction products were initially identical. A typical spectrum is presented in

Figure XI

I.R. spectrum of the solid product for the reaction between ZMA and LAAS, p-xylene co-solvent.

$[ZMA]_o$ = 0.0304M. $[LAAS]_o$ = 0.75M. 25°C. KBr disc reference cell air.

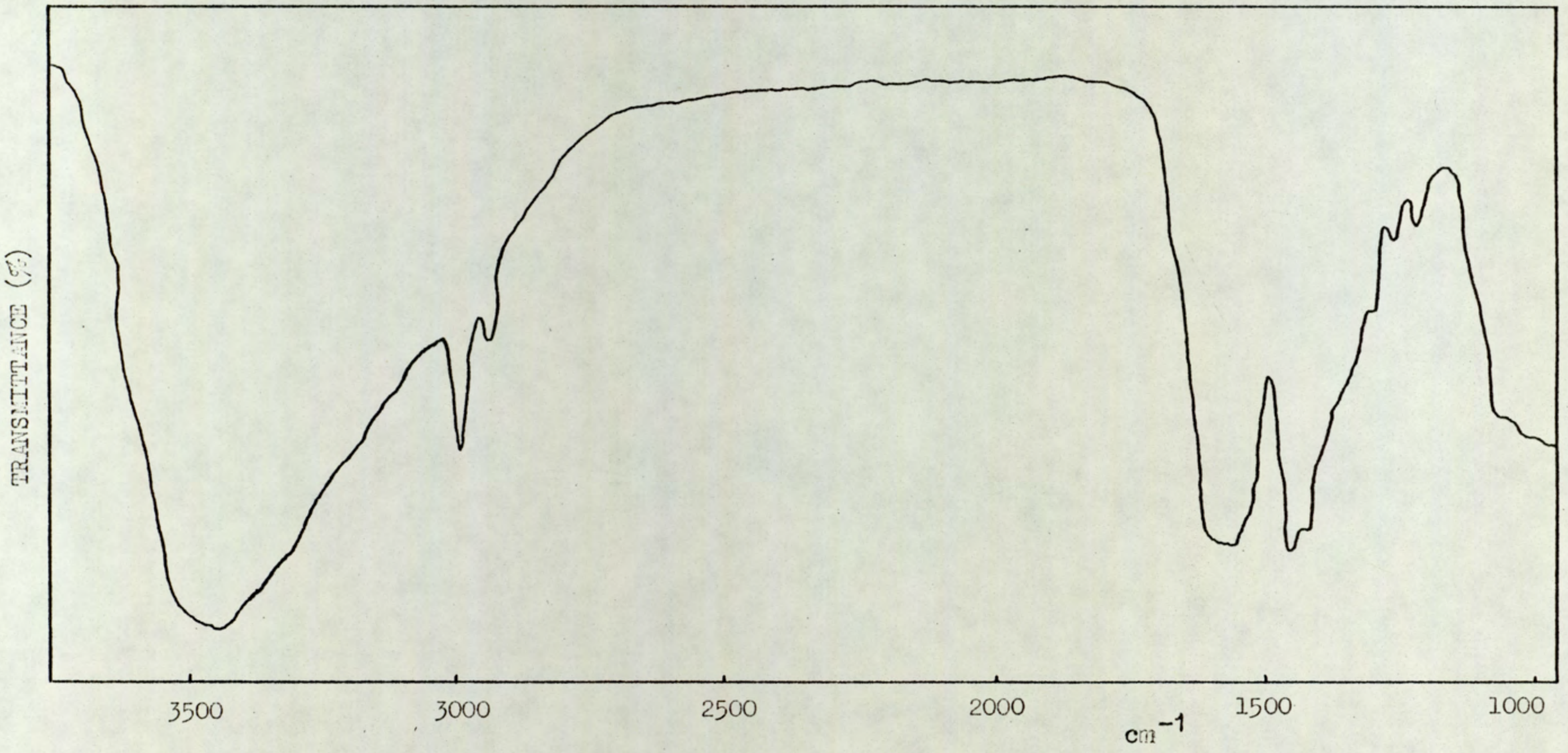


Figure XI. It is characterised by a very strong, fairly broad absorption at 1600 cm^{-1}. Equally important, for the purposes of the present study, is the absence of any absorption at 1740 cm^{-1}. These reactions thus represent the first cases where I.R. analysis shows no evidence of α-ester formation. The spectra obtained indicate that all the monomer that has reacted has formed a metal salt which is in some way attached to the catalyst molecules.

6.1.2b Sulphur Analysis

The solid reaction products were examined for traces of residual sulphur, which was present in all three cases as shown in Table VI.

Table VI

Percentage of sulphur in solid products of the reaction between LAAS and ZMA. $[LAAS]_o$ = 0.75M 25°C.

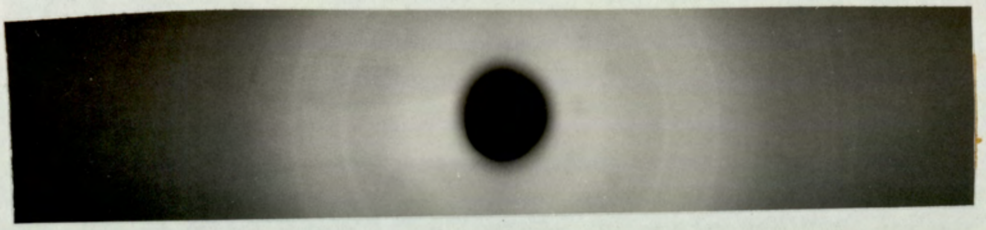
$[ZMA]_o$ mol l^{-1}	% S
0.0607	0.80
0.0304	0.61
0.0152	1.16

6.1.2c X-ray Studies

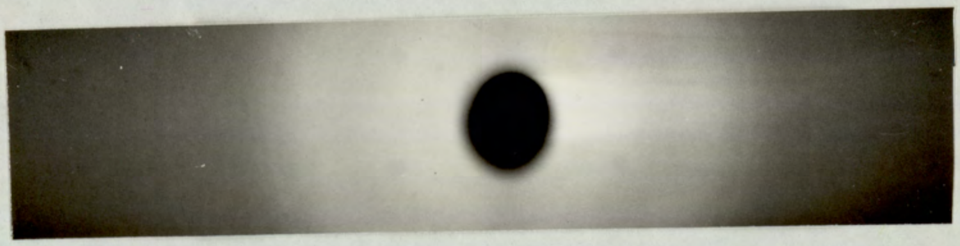
Figure XII shows X-ray diffraction photographs of the products of all three reactions. The principal features of these photographs are the fine, relatively widely spaced lines that appear. There is also a small amount of diffuse scatter at a very narrow angle, due no doubt to the amorphous, low molecular weight organic part of the product, and the absence of any polymeric species, as suggested by the I.R. spectra, is confirmed. The nature and spacing of the fine

FIGURE XII

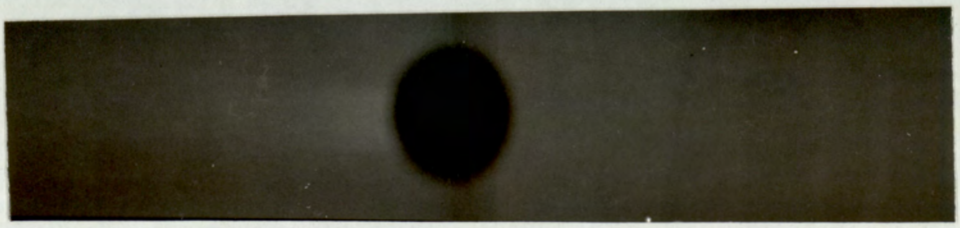
Lactic Acid Anhydrosulphite



$[\mathrm{ZMA}]_0 = 0.0607\mathrm{M}$



$[\mathrm{ZMA}]_0 = 0.0304\mathrm{M}$



$[\mathrm{ZMA}]_0 = 0.0152\mathrm{M}$

lines shown is such that they be confidently attributed to the metal aspect of the organo-metallic salt formed.

6.2 Experiments Using a Single Solvent System

The experiments conducted using toluene also as a diluent enabled the feasibility of using a single solvent system to be assessed. In view of the similarity in the value of the dielectric constants of toluene and p-xylene (2.379, 2.269 respectively) it was not anticipated that any marked change in kinetic behaviour would be observed. However, the higher vapour pressure of toluene must be taken into account.

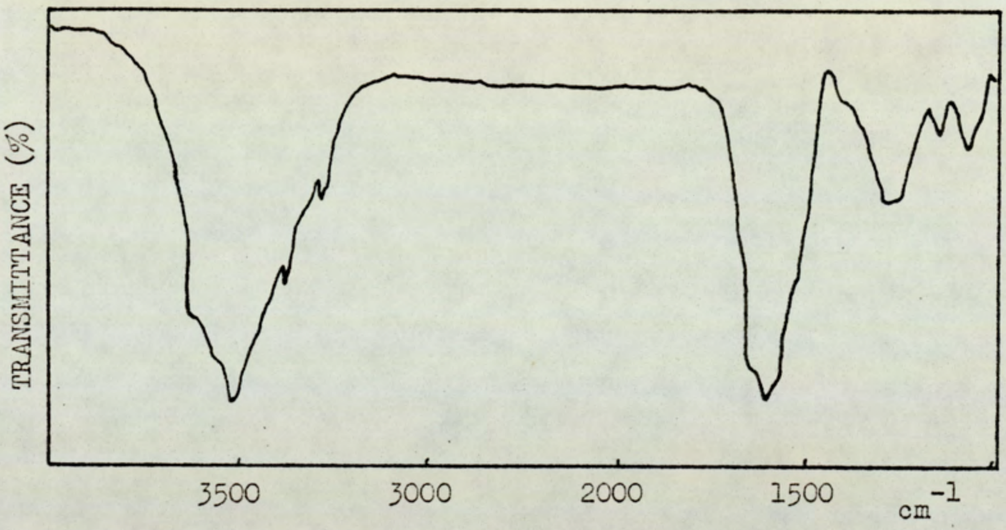
The investigation into the decomposition of LAAS was extended by using very low catalyst concentrations. Furthermore, an experiment was conducted in which no kinetic analysis was attempted; the reaction mixture was placed in a flat-bottomed flask fitted with a glass tube containing calcium chloride to exclude traces of moisture. The reaction mixture was agitated throughout the course of the reaction by means of a magnetic stirrer/teflon follower. Previous experiments had been characterised by the progressive formation of a gel. It was hoped that an analysis of the products of this latter experiment would, by comparison with the products of earlier reactions, permit an assessment of the influence that this gel formation had upon the reaction.

6.2.1 Kinetic Data and Observations

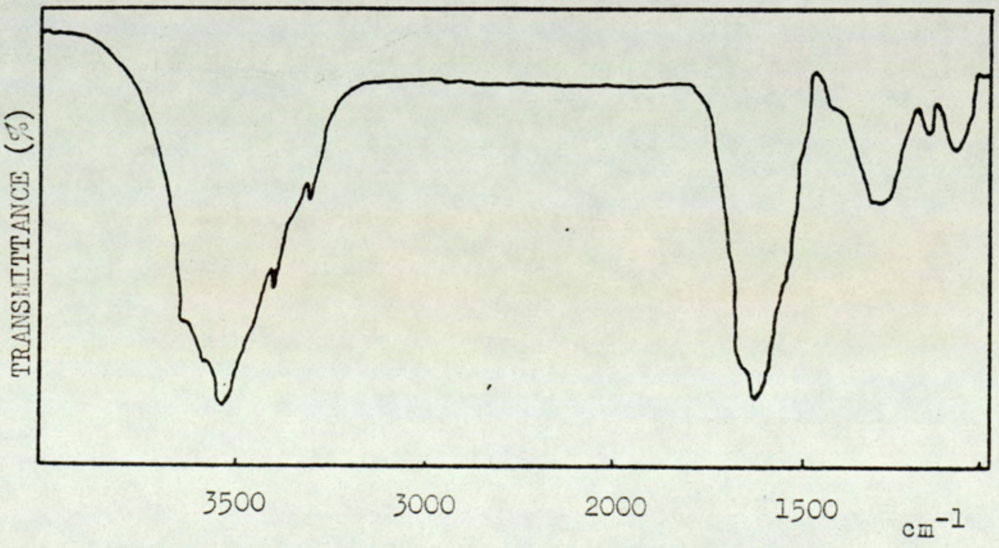
The reaction profiles for the catalysed decomposition of LAAS using a single solvent, toluene, were very similar in overall shape to those obtained using a p-xylene/toluene co-solvent (Figure IX), being smooth and continuous. The total volume of sulphur dioxide evolved was low and once again related directly to the initial

Figures XIII and XIV

I.R. spectra of the products of the reactions between LAAS and ZMA. $[\mathrm{LAAS}]_o = 0.75\mathrm{M}$. $[\mathrm{ZMA}]_o = 0.0067\mathrm{M}$. 25°C. KBr disc reference cell air.



XIII Unstirred reaction



XIV Stirred reaction

catalyst concentration. Once again, the reaction was characterised by the formation of a green/brown gel, and the decrease in the rate of reaction and the formation of this gel were parallel events.

The results obtained are presented in Table VII.

Table VII

Initial rates for the catalysed decomposition of LAAS using a single solvent system. $[\text{LAAS}]_o$ = 0.75M. 25°C.

ZMA_o mol l^{-1}	Initial rate X 10^4 (sec^{-1})
0.0202	0.164
0.0067	0.103

In the reaction which was subject to continual agitation, it was found that whilst the formation of a single gelatinous mass was prevented, the bottom of the reaction vessel was finely coated in a green/brown gelatinous material, the nature of which will now be discussed, together with the nature of the products of the two other experiments involving only one solvent.

6.2.2 Analysis of the Reaction Product

The green/brown gel, when dried under vacuum, yielded a white powder. As a consequence of the very low catalyst concentrations used, the final quantity of solid product was only sufficient to allow analysis by infra red spectroscopy.

6.2.2a I.R. Studies

The I.R. spectra of both the stirred and unstirred reactions were almost identical, the spectrum of the stirred reaction being shown in Figures XIII and XIV. There was no evidence of α-ester formation in any of the reactions, the principal absorption of interest being that at 1610 cm^{-1}, and attributed once again to metal salt formation.

Analysis of the liquid layer showed traces of unreacted monomer, but was otherwise identical with that of the solvent used.

6.3. Experiments Involving both LAAS and GAAS

6.3.1a Kinetic Data and Observations

A comparison of the studies involving LAAS and GAAS, particularly the products of the reactions, shows that whereas the decomposition of GAAS yielded some polymeric product, the decomposition of LAAS did not. Apart from the change of monomer, the conditions of both sets of reactions were identical, and the catalyst concentrations used either identical or directly comparable. The implication of these earlier studies is therefore that the presence of the additional methyl group in the LAAS monomer, exerts a very marked influence on the reaction.

6.3.1b Second Injection Experiments

Two parallel experiments were conducted. (A) involved the catalysed decomposition of LAAS. As soon as the onset of the second, slower phase of the reaction was reached, half a millilitre of undiluted GAAS was injected into the reaction mixture and the subsequent pressure rise studied in the usual way.

The second experiment (B) involved the catalysed decomposition of GAAS under identical conditions to (A). When the second, slower period of the reaction was reached, half a millilitre of 0.75 molar LAAS was injected and the subsequent pressure rise observed.

The reaction profiles of both these reactions are presented

Figure XV

Decomposition of LAAS, subsequent injection of GAAS. 25°C. Toluene solvent. $[ZMA]_o$ = 0.0607M. $[LAAS]$ = 0.75M.

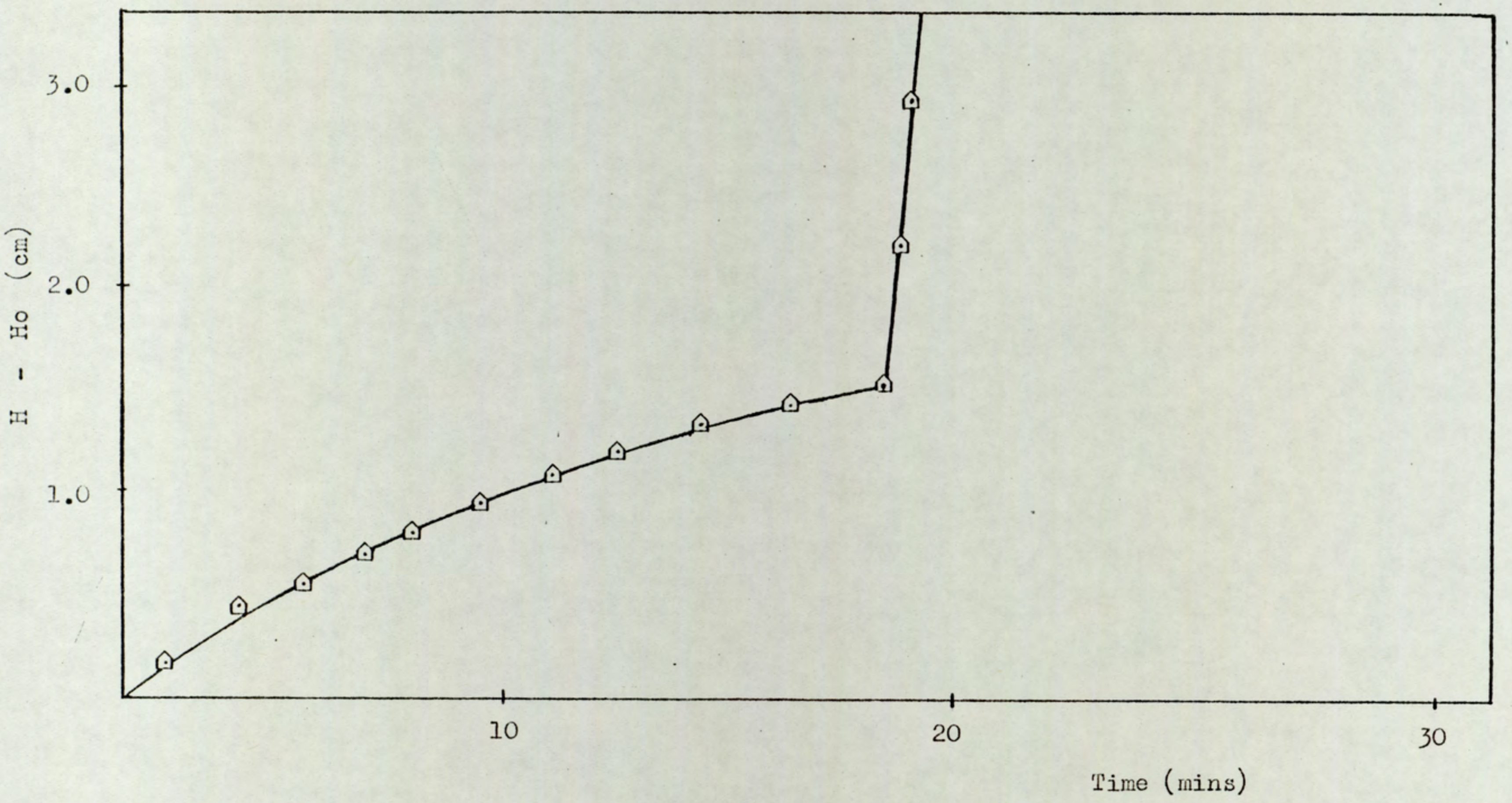
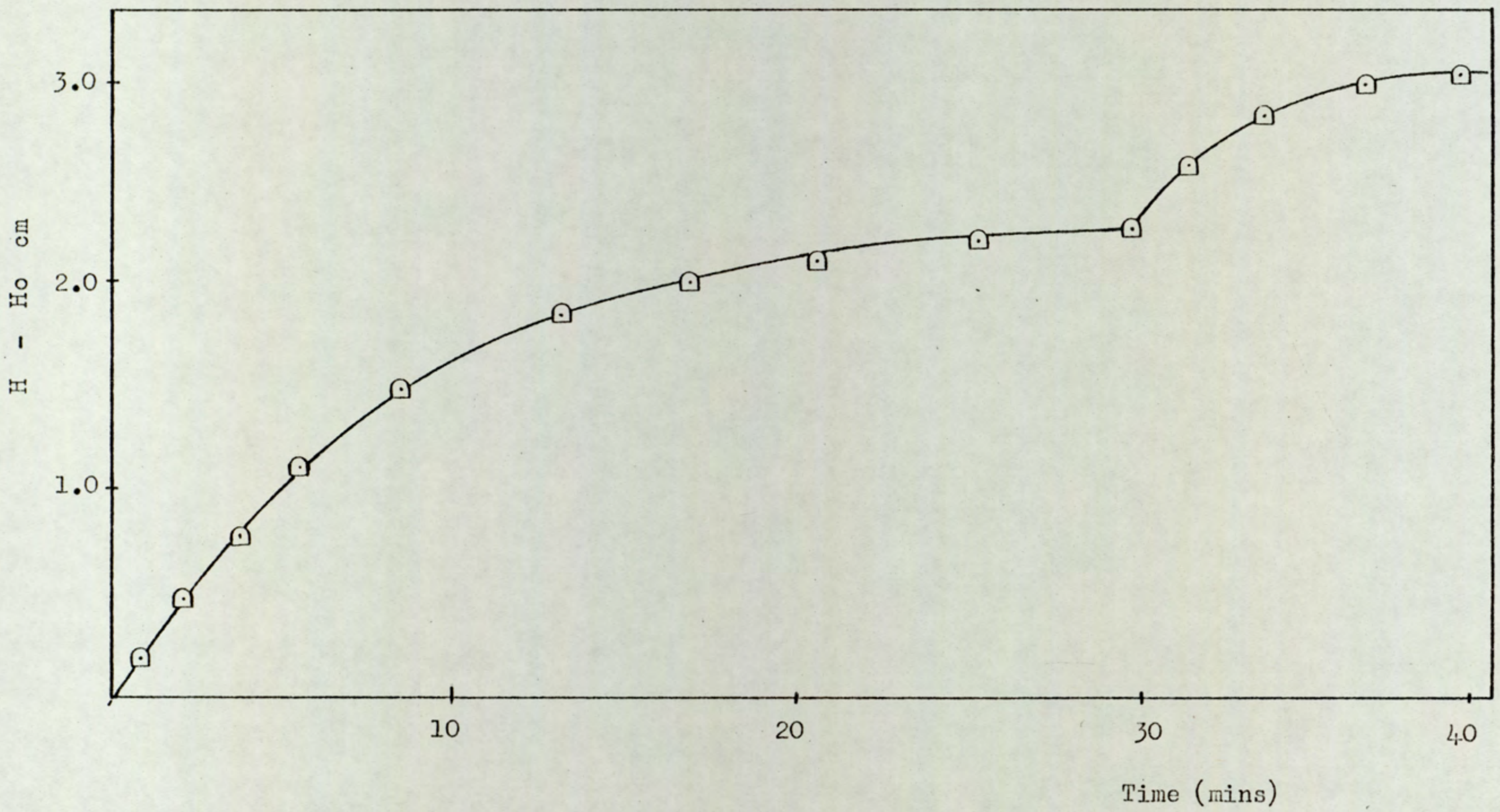


Figure XVI

Decomposition of GAAS, subsequent injection of LAAS. 25°C. Toluene solvent. $[\mathrm{ZMA}]_o$ = 0.0607M. $[\mathrm{GAAS}]_o$ = 0.75M.



in Figures XV and XVI. There is a marked difference between the two profiles. In reaction (A) the injection of GAAS caused such a marked increase in rate that very accurate readings were difficult to obtain. In the case of (B), however, the injection of LAAS caused a short-lived rapid reaction after which the reaction ceased altogether. The contrast in profiles is a clear demonstration of the very marked influence that increased steric hindrance caused by the presence of the extra methyl group in LAAS is having on the reaction. As expected, in both (A) and (B) the reaction mixture became progressively more heterogeneous as the reaction proceeded, until, by the end of the reaction, the characteristic green/brown gel, beneath a clear liquid later, had formed.

6.3.2 Analysis of the Reaction Product

6.3.2a I.R. Studies

Analysis of the liquid layer from reaction (B) revealed traces of residual monomer. No such trace was found in the liquid layer of reaction (A).

The green/brown gel formed during the course of both reactions, when dried under vacuum, gave a white powder. The infra red absorption spectra of the products of both reactions are presented in Figures XVII and XVIII.

The principal feature of the spectrum of the product of reaction (B) is the strong absorption at 1600 cm^{-1}. The slight shoulder at 1740 cm^{-1} indicates the possibility of a very limited amount of polymer formation, probably only to a very low molecular weight. In marked contrast, the spectrum of reaction (A) shows equally strong absorptions at 1740 cm^{-1} and 1600 cm^{-1}, the latter absorption being clear evidence of polymer formation, to a degree hitherto unobserved

Figure XVII

I.R. spectrum of solid product LAAS/ZMA with subsequent injection of GAAS. $[\text{ZMA}]_o = 0.0607$M. $[\text{LAAS}]_o = 0.75$M. 25°C. KBr disc reference cell air.

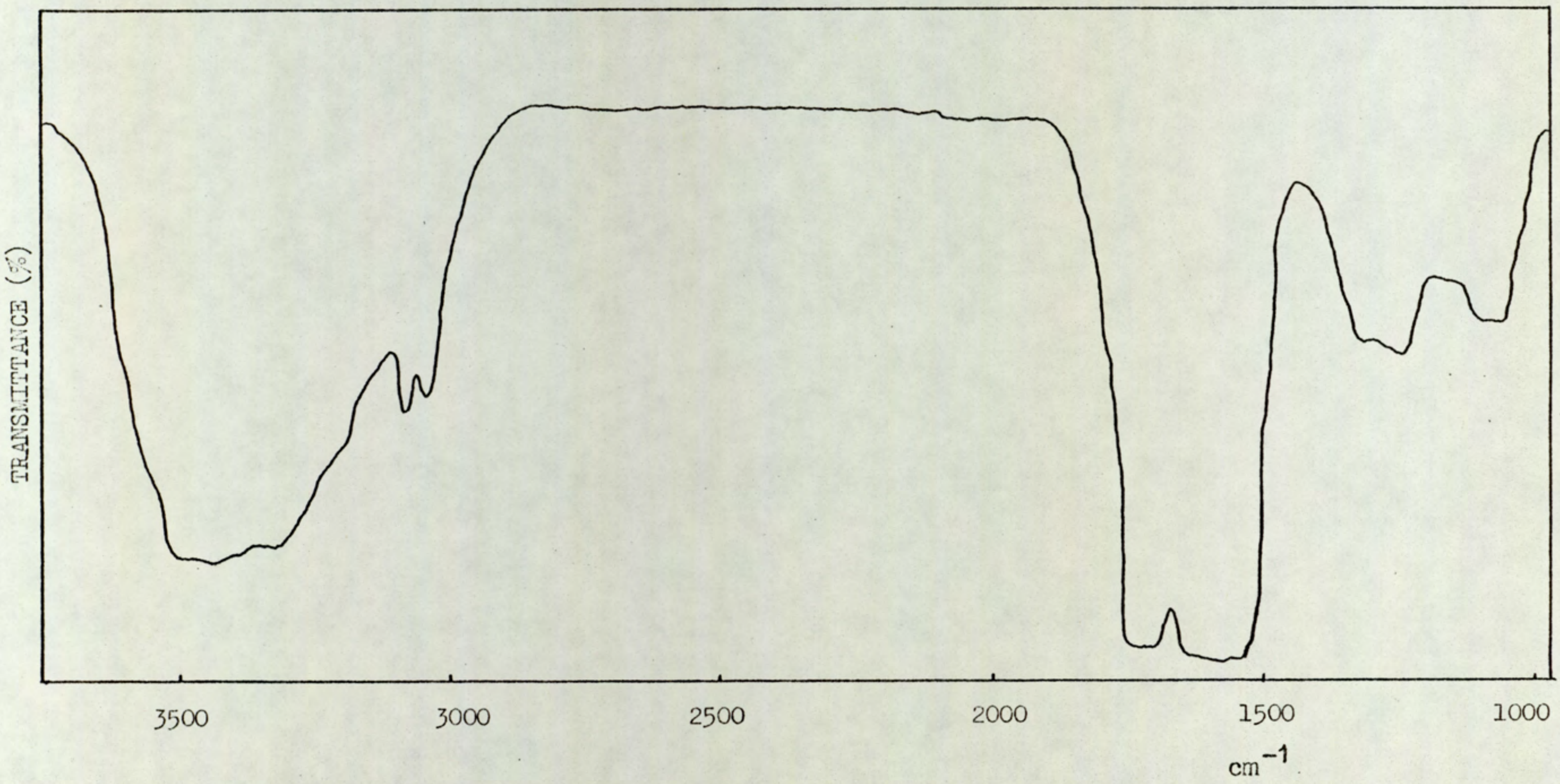
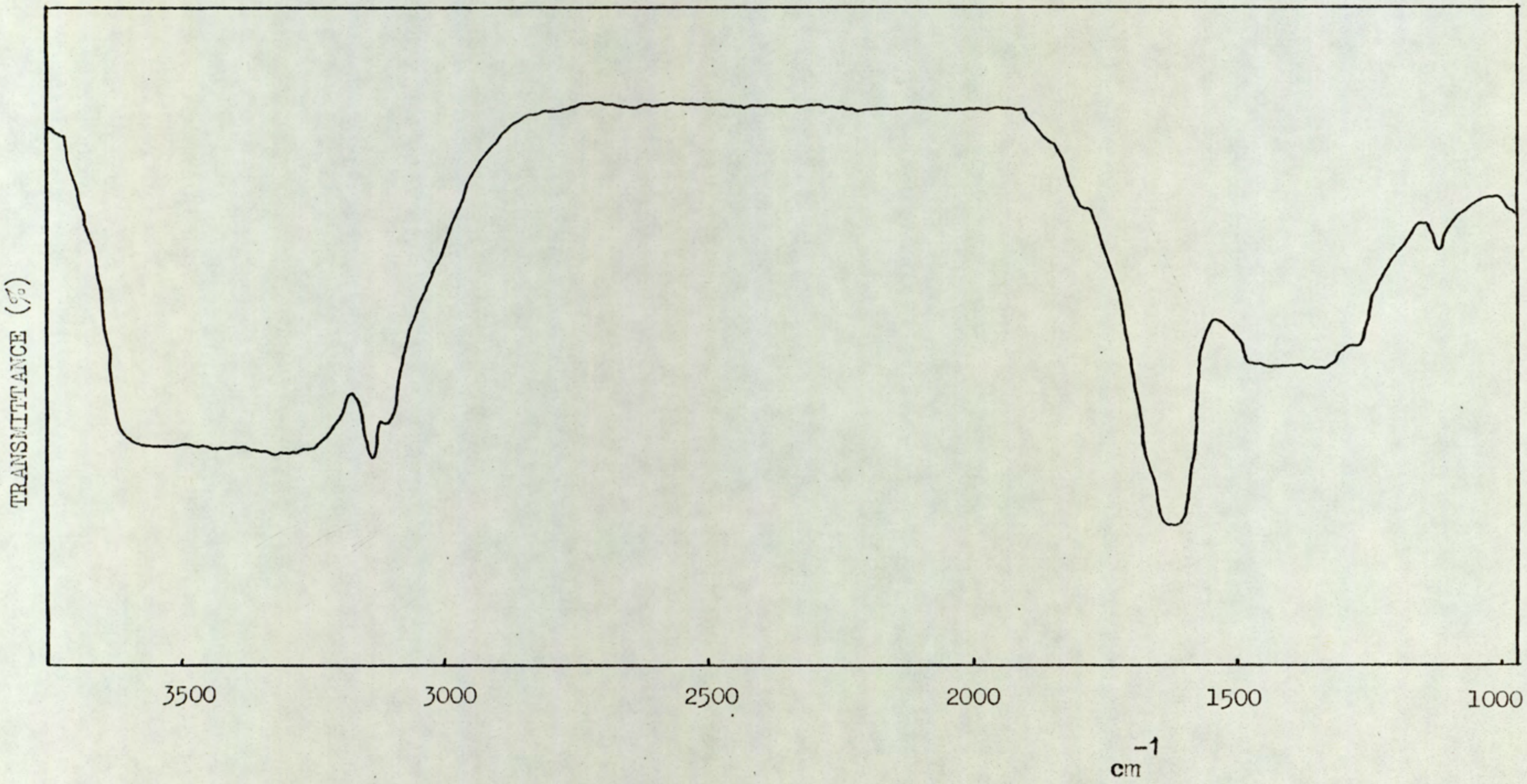


Figure XVIII

I.R. spectrum of solid product GAAS/ZMA with subsequent injection of LAAS. $[ZMA]_o = 0.0607M$. $[LAAS]_o = 0.75M$. 25^oC. KBr disc reference cell air.



in this study. Possible interpretations of this behaviour will be discussed presently.

6.3.2b X-ray Studies

The X-ray powder photographs of both (A) and (B) are presented in Figure XXIII. The diffuse scatter shown by the products of reaction (A) is in the form of an amorphous halo and would seem to indicate the presence of low molecular weight amorphous polymer. The photograph of the products of reaction (B) shows a weak diffuse scatter with fine lines superimposed. The fine lines shown are attributed to the metallic content of the product, and there is no evidence of polymer formation, the diffuse scatter being attributed to the metal salt.

6.3.3 The Use of Hexafluorobenzene as Co-solvent

The range of co-solvents used was extended to include a preliminary experiment involving hexafluorobenzene, a solvent first used by Smith(60) in his studies on the decomposition of anhydrocarboxylates in the presence of pyridine and substituted pyridines.

6.3.4 Kinetic Data and Observations

This preliminary experiment revealed that the change in co-solvent produced very little variation in either the general form of the kinetic profile or the nature of the reaction products as revealed by I.R. and X-ray studies.

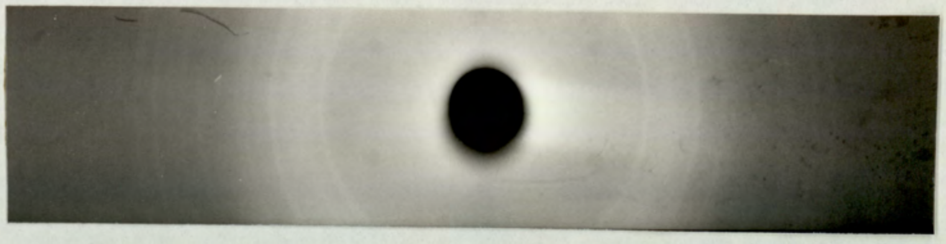
The kinetic profile is shown in Figure XX together with the initial rate. Once again, the profile is a smooth continuous curve, remarkably similar to those obtained when p-xylene was used as a co-solvent (Figure IX).

6.3.4a I.R. Studies

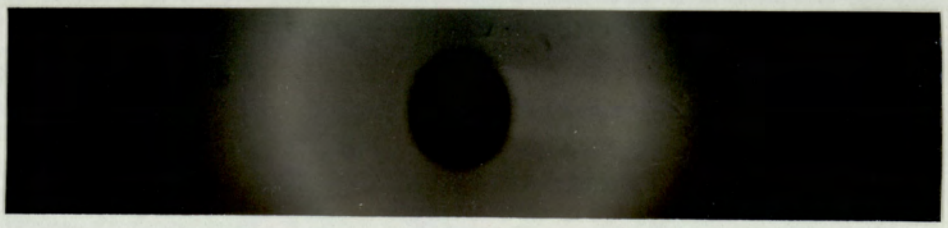
The green/brown gel formed during the course of the reaction

FIGURE XIX

Second Injection Experiments



LAAS: Injection of GAAS

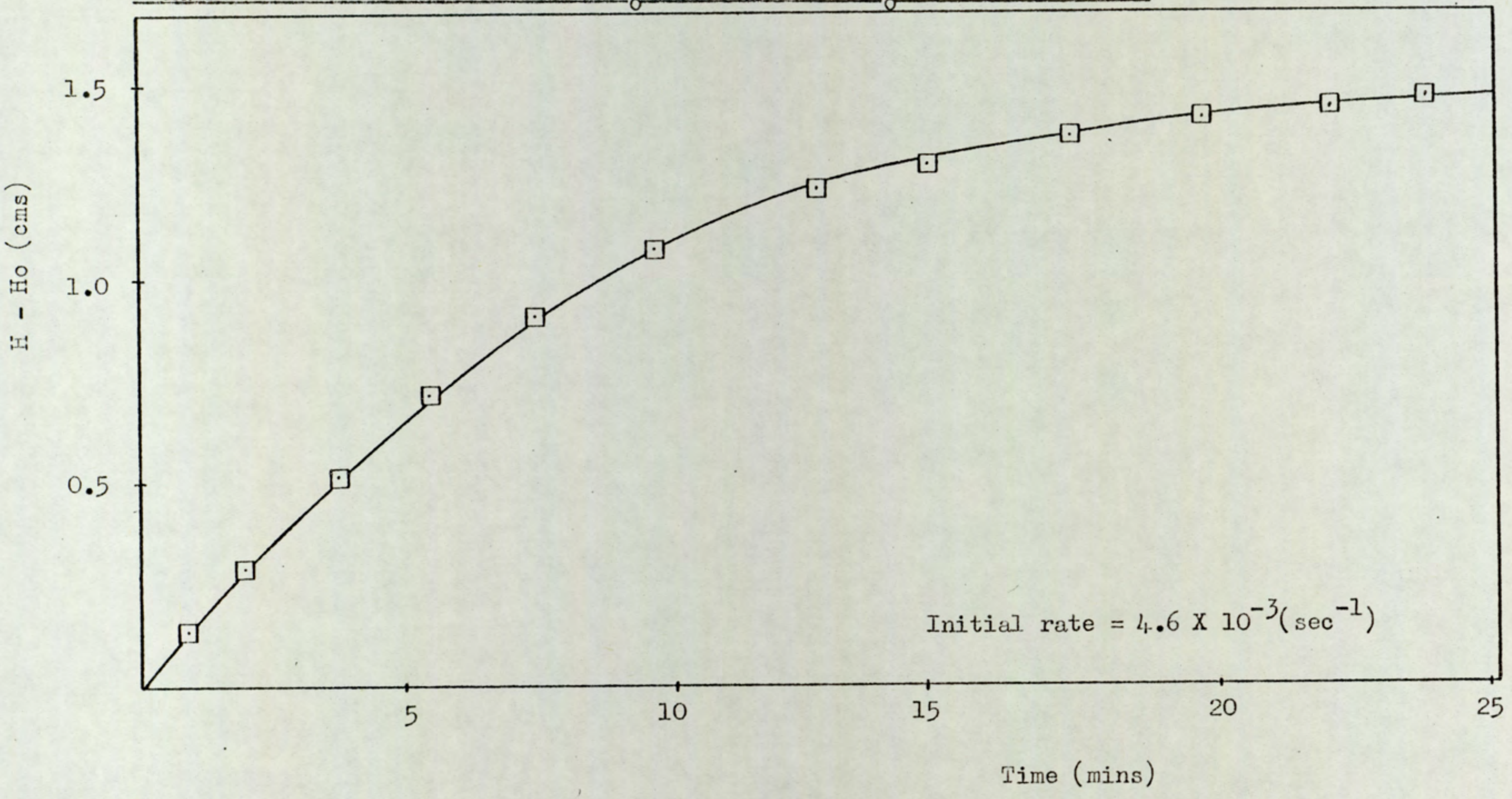


GAAS: Injection of LAAS

Figure XX

Decomposition of LAAS in the presence of ZMA.

Hexafluorobenzene co-solvent LAAS$_o$ = 0.75M ZMA$_o$ = 0.0304M 25°C



Initial rate = 4.6 X 10^{-3}(sec^{-1})

Figure XXI

I.R. spectrum of solid product of decomposition of LAAS in the presence of ZMA.

$LAAS_o = 0.75$ $ZMA_o = 0.0304$. Hexafluorobenzene co-solvent 25°C.

KBr disc reference cell air.

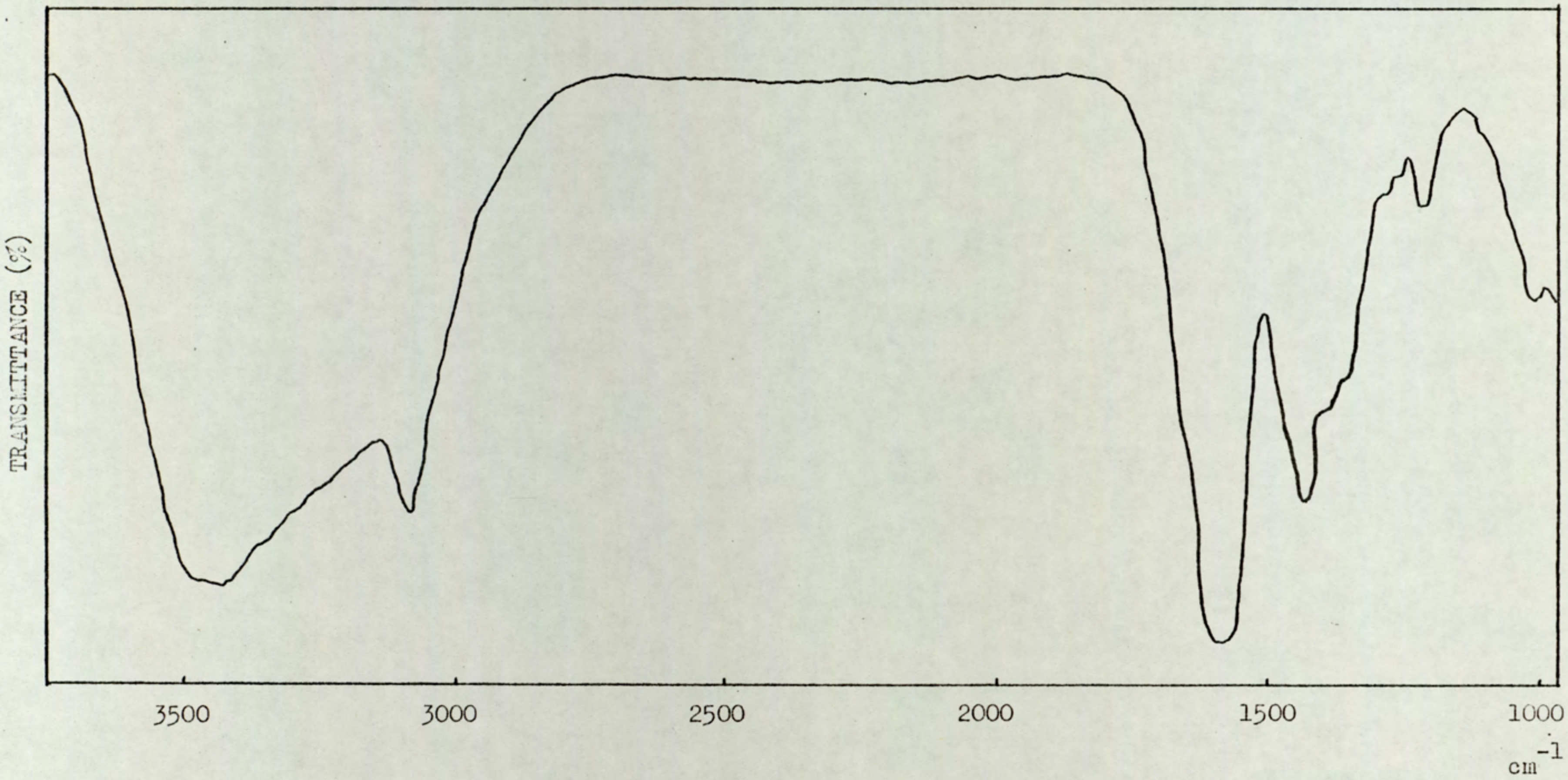
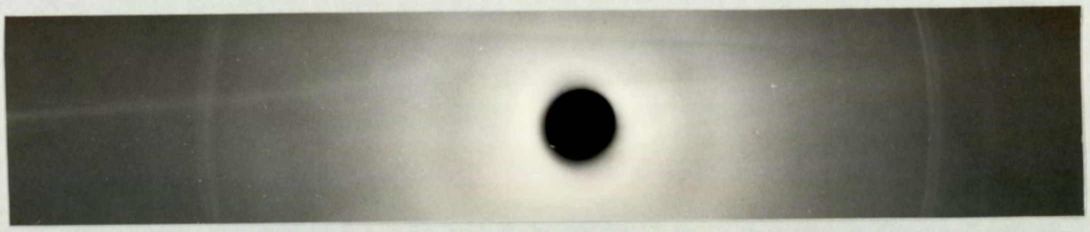


FIGURE XXII



LAAS/C_6F_6/ZMA

$[\text{ZMA}]_0 = 0.0304$

once again dried to yield a white powder. The I.R. absorption spectrum is shown in Figure XXI. The principal feature, as in the products of all experiments so far involving LAAS, is the strong absorption at 1600 cm^{-1}, attributed to a carboxylate ester. Once again, there is a total absence of any absorption at 1740 cm^{-1}, thus indicating that no polymer formation had taken place.

6.3.4b X-ray Studies

The X-ray diffraction powder photograph is shown in Figure XXII. It is characterised by the diffuse scatter at a narrow angle from the beam due to the presence of amorphous material, and several fine, well-defined lines at too wide an angle to be attributed to anything other than the metal in the metal salt whose presence is so clearly indicated by infra red studies (Figure XXI).

CHAPTER 7

THE CATALYSED DECOMPOSITION OF GLYCOLLIC ACID ANHYDROCARBOXYLATE

7.1 Decomposition in the Presence of Pyridine

The pyridine initiated polymerisation of glycollic acid anhydrocarboxylate (GAAC) was studied over a range of temperatures. It has been shown that pyridine may be used to initiate the polymerisation of mandelic acid anhydrocarboxylate(57) (MAAC), 2-pentafluoro-2-hydroxy-propanoic acid anhydrocarboxylate(57) (PFAAC), and atrolactic acid anhydrocarboxylate(54) (AAAC). In all three cases the presence of the bulky substituents at the C-5 carbon sterically hinders the attack by the pyridine molecule, and the degree of substitution at the C-5 molecule has been shown(57) to critically affect the overall rate of the reaction.

In view of the fact that GAAC, the simplest of the anhydrocarboxylates, offers no steric hindrance to the initiating species, it was anticipated that the reactions, even at ambient temperatures, would proceed rapidly and that polyglycollide would be the principal product. This proved to be the case. The evidence for polymer formation will be discussed presently, but an indication of a successful polymerisation reaction, as well as an indication of the high purity of the monomer, was given by the observed precipitation of what proved to be polymeric product during the latter stages of all the reactions studied.

The kinetic characteristics of these reactions have been well established and GAAC conformed to this pattern. The rate of decomposition of GAAC in the presence of pyridine may be expressed thus:

$$-\frac{d[M]}{dt} = \frac{d[CO_2]}{dt} = K_2[M][Pyr] \quad \text{........ (1)}$$

Where M , Pyr and K_2 are the concentration of monomer, pyridine and the second order rate constant respectively. As pyridine is not consumed during the course of the reaction, $[Pyr]$ remains constant and equation (1) may thus be written as

$$-\frac{d[M]}{dt} = K_1[M] \quad \text{........ (2)}$$

where $K_1 = K_2[Pyr]$

and may be considered as a pseudo first order rate constant.

7.1.1 Kinetic Data and Observations

The reaction between GAAC and pyridine was studied in nitrobenzene over the temperature range 18-30°C. Good first order behaviour was observed throughout, and there is no evidence of catalysis or inhibition by carbon dioxide or any reaction products. Typical first order semi-log plots are presented in Figure XXIII.

The derived second order rate constants (K_2) are shown in Table VIII. Also shown are the activation energy (E), as derived from a conventional Arrhenius plot (Figure XXIV), the preexponential factor (A) and the entropy of activation (S).

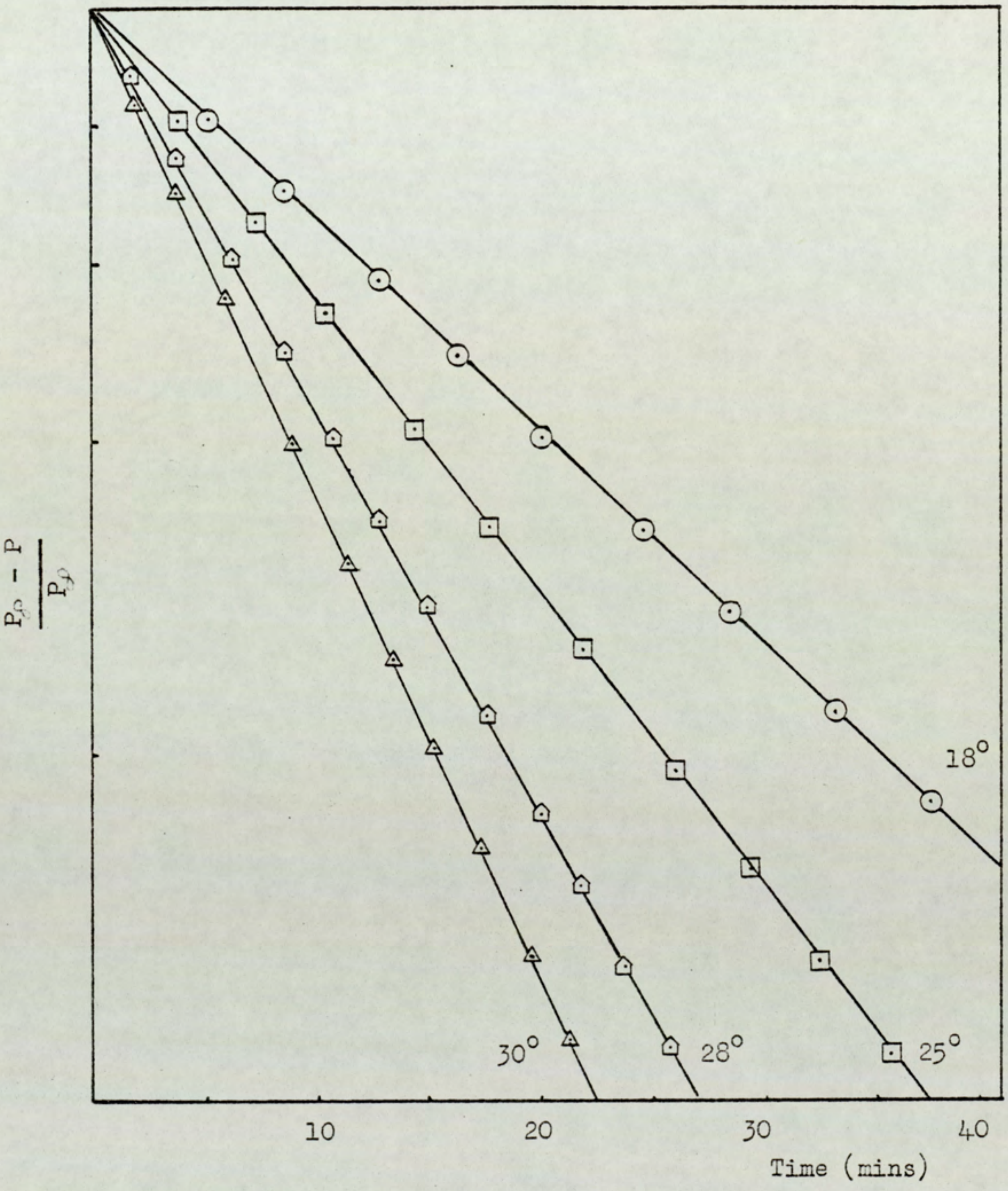


Figure XXIII

Semi logarithmic plot of $(P_\infty - P)/P_\infty$ versus time for the reaction between GAAC and Pyridine over the temperature range 18-30°C.

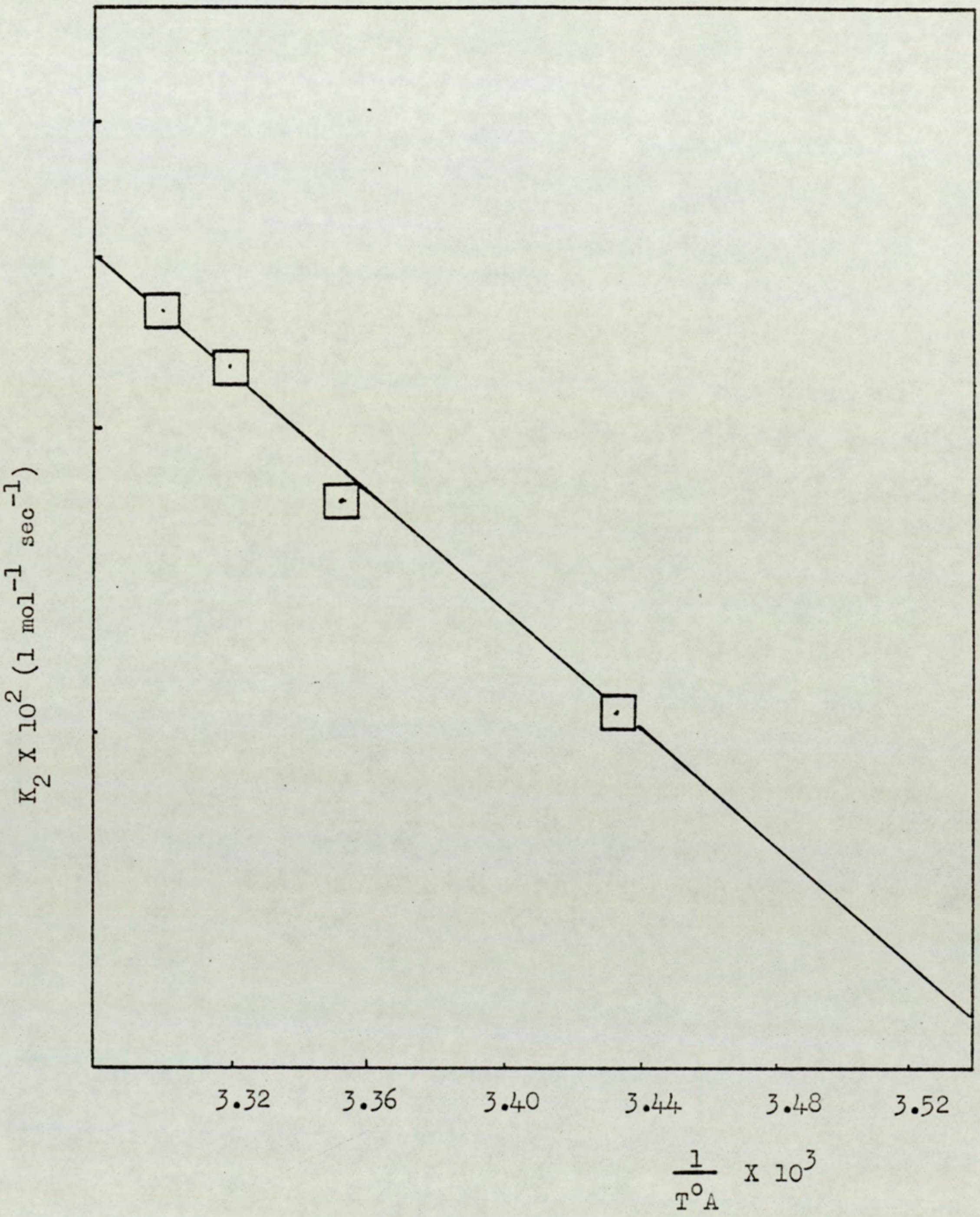


Figure XXIV

Arrhenius plot of second order rate constant K_b versus the reciprocal of absolute temperature for the reaction between GAAC and Pyridine over the temperature range 18-30°C.

Table VIII

Second order rate constants (K_2) and associated kinetic parameters for the decomposition of GAAC in the presence of 10% molar pyridine

[GAAC] = 0.375 mol l^{-1}.

Temperature °C	10^2 K_2 (l mol^{-1} sec^{-1})
18	2.28
25	3.20
28	4.56
30	5.12
E (K.J mol^{-1})	49.07
A (l mol^{-1} sec^{-1})	1.31×10^7
$\Delta S^{\dagger}$ (JK^{-1} mol^{-1})	- 117

Analysis of the Reaction Products

The products of the reactions studied consisted of a solid and liquid phase. Infra red analysis of the liquid phase confirmed that it was a nitrobenzene/pyridine mixture, with no evidence of unreacted monomer or any other species. The white solid precipitate was washed with ether and water, and after drying was examined by I.R. and X-ray diffraction.

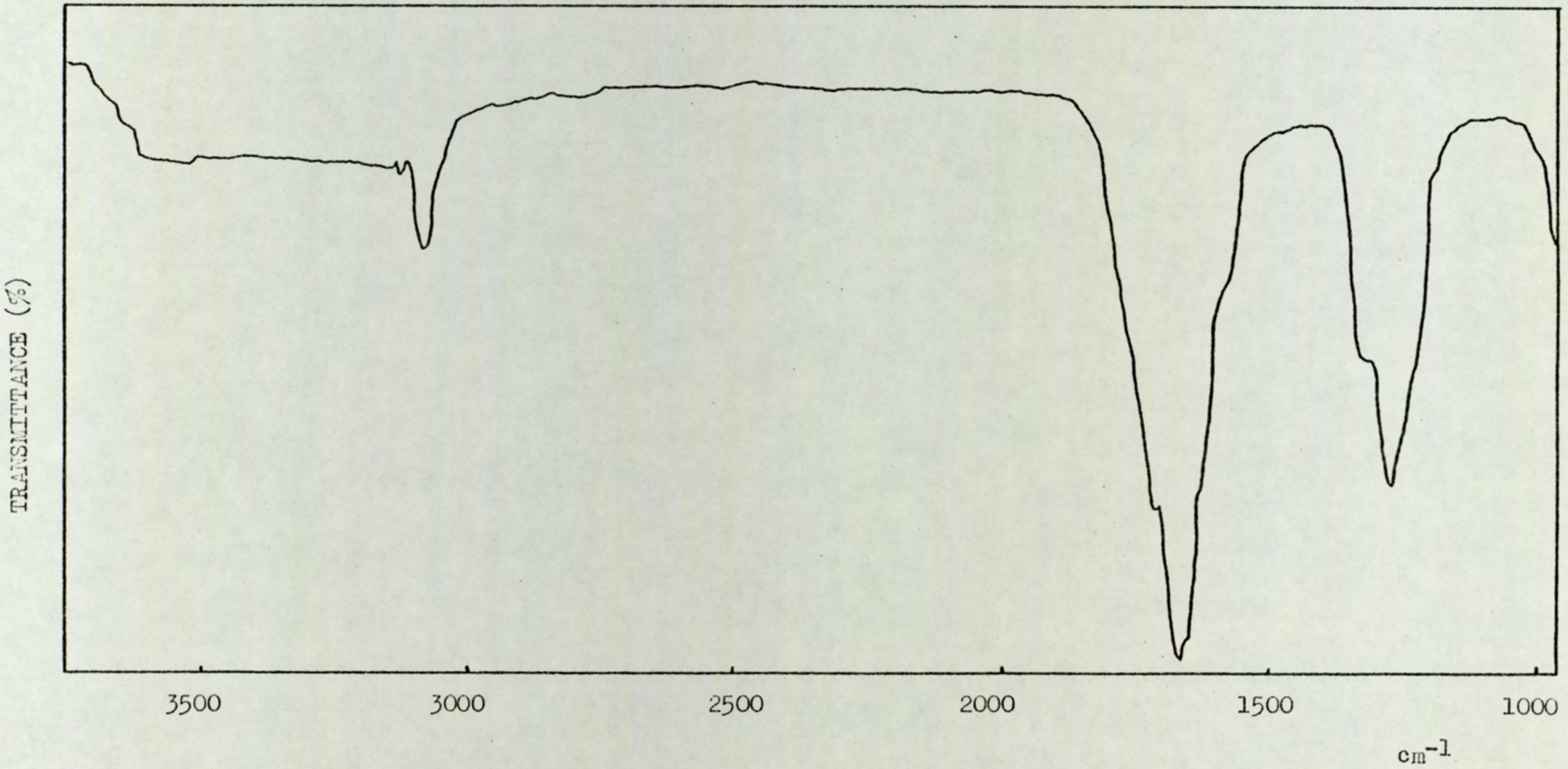
I.R. Studies

The nature of the solid product, as revealed by I. R. studies, proved to be essentially independent of the reaction temperature. A typical spectrum is shown in Figure XXV, and clearly indicates the polymeric nature of the solid product. The strong absorption at 1740 cm^{-1} is characteristic of poly-α-esters, being due to the

Figure XXV

I.R. spectrum of the solid product of the reaction between Pyridine and GAAC, 18°C.

KBr disc reference cell air.



carbonyl present. The presence of hydroxyl end groups is indicated by the absorption at 3500 cm^{-1}. There is no evidence of any non-polymer forming reaction, neither is there any evidence of pyridine being present in any way.

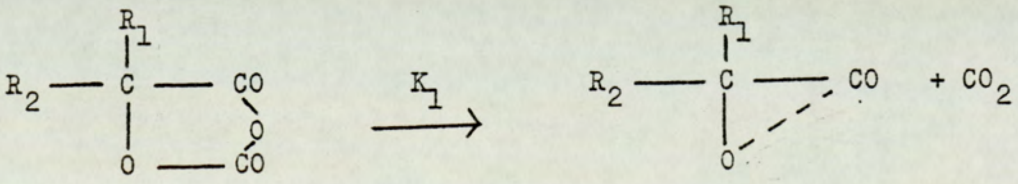
X-ray Diffraction

The ability of poly-∝-esters to adopt a crystalline structure depends, as in all polymers, on the ability of the polymer chains to pack closely. This in turn is related both to the size of the substituents on the chain, and to the symmetry of substitution.

In the case of polyglycollide, substitution is symmetrical, and since both substituents are protons, the conditions for close packing are at an optimum. It would therefore be reasonable to anticipate that the polyglycollide formed during these reactions would be highly crystalline and this proved to be the case, as Figure XXVI clearly indicates.

7.2 Decomposition in the Presence of Benzyl Alcohol

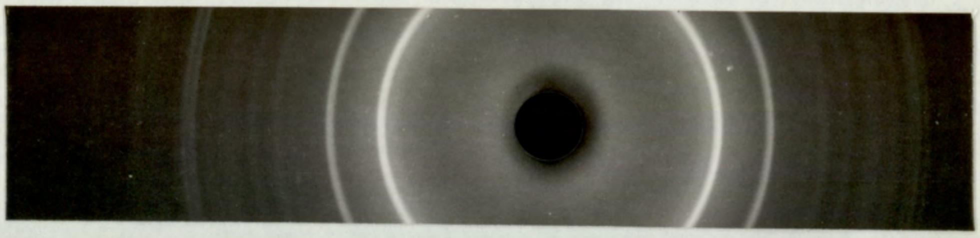
The thermal polymerisation of substituted anhydrocarboxylates occurs essentially by the initial loss of a molecule of carbon dioxide from the monomer ring. The ∝-lactone thus formed takes part in a rapid propagation reaction with a continually regenerated hydroxyl group according to the equations



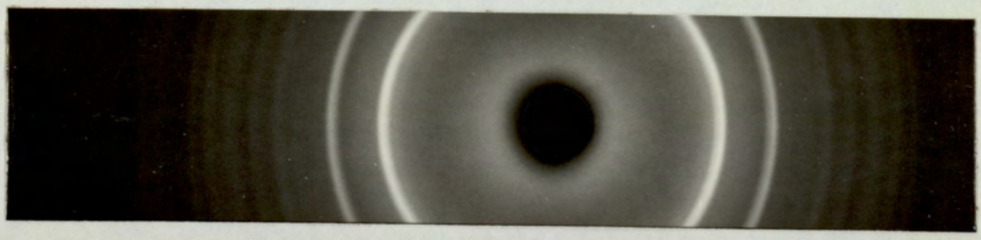
... (3)

FIGURE XXVI

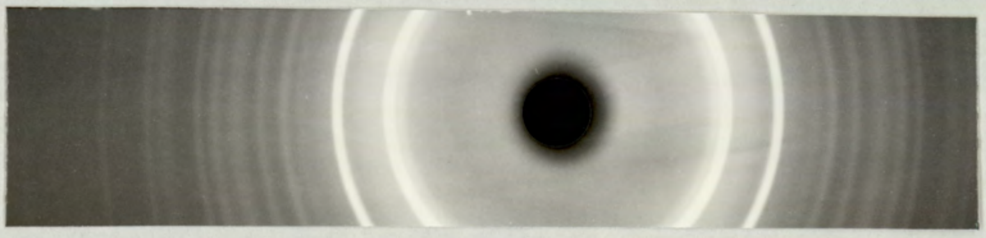
Pyridine/GAAC



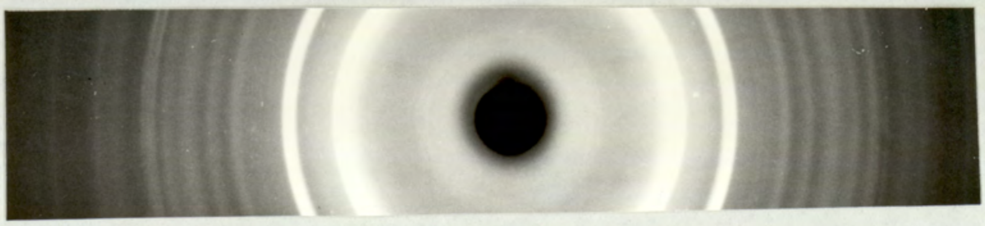
30°C



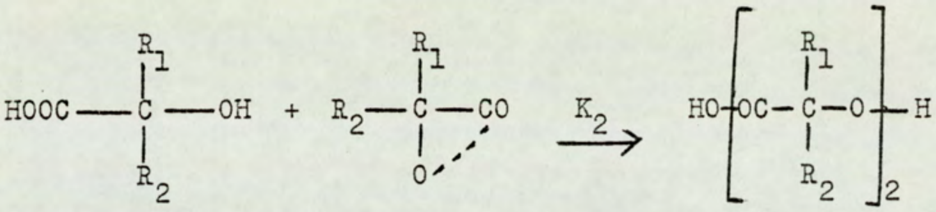
28°C



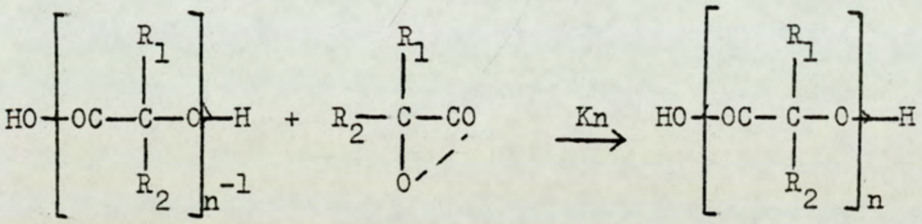
25°C



18°C



...... (4)



...... (5)

It is known that the formation of the α-lactone as described by equation (3) is the rate determining step in this reaction and therefore K_2, K_3 ..... K_n are all very much larger than K_1. The parent acid molecule shown in equation (4) is the product of the reaction between the monomer and adventitious traces of moisture. Despite rigorously anhydrous synthetic conditions, such traces of parent acid are always found in any anhydrocarboxylate prepared, and are known to react extremely rapidly with any α-lactone intermediate present, according to equation (4).

A mode of decomposition of anhydrocarboxylate rings that has been the subject of examination in recent years is that initiated by organic compounds containing one hydroxyl group, typically simple alkyl or aryl alcohols.

In the present study, the work of Smith(57) is extended by the examination of the reaction between benzyl alcohol and glycollic acid anhydrocarboxylate (GAAC) at varying temperature. The monomer is readily prepared to a high degree of purity by the action of phosgene on the copper (II) salt of the parent acid as described in section 2.5b. Nitrobenzene was used as a solvent.

7.2.1 Kinetic Data and Observations

The benzyl alcohol initiated decomposition of GAAC in nitrobenzene was studied over the temperature range 25-40°C. A reaction involving excess benzyl alcohol was also studied at 25°C. Gas evolution techniques were used to study the rate of evolution of carbon dioxide. A graphical presentation of $\log\left[(P_\infty - P)/P_\infty\right]$ against time is shown in Figure XXVII. Good first order behaviour was observed throughout most of the reaction, the only deviation from this being towards the end of the reaction when the initiating species had been consumed. Such deviation was not observed in the reaction involving excess benzyl alcohol, where first order behaviour was observed throughout. No evidence of catalysis or inhibition by CO_2 or any reaction products was detected.

The derived second order rate constants (K_2) for the reactions discussed above are presented in Table IX.

Table IX

Second order rate constants (K_2) and associated kinetic parameters for the reaction between GAAC and benzyl alcohol. $[\text{GAAC}] = 0.375 \text{ mol l}^{-1}$ $[\text{benzyl alcohol}] = 0.047 \text{ mol l}^{-1}$.

Temperature °C	$10^2 K_2$ $(\text{l mol}^{-1} \text{ sec}^{-1})$
25	0.86
30	0.955
39	1.458
45	1.89
25*	1.29
E (KJ mol^{-1})	31.339
A $(\text{l mol}^{-1} \text{ sec}^{-1})$	2.7×10^3
$\Delta S^{\ddagger}$ $(\text{J.K}^{-1} \text{ mol}^{-1})$	- 187

* Reaction with excess Benzyl Alcohol

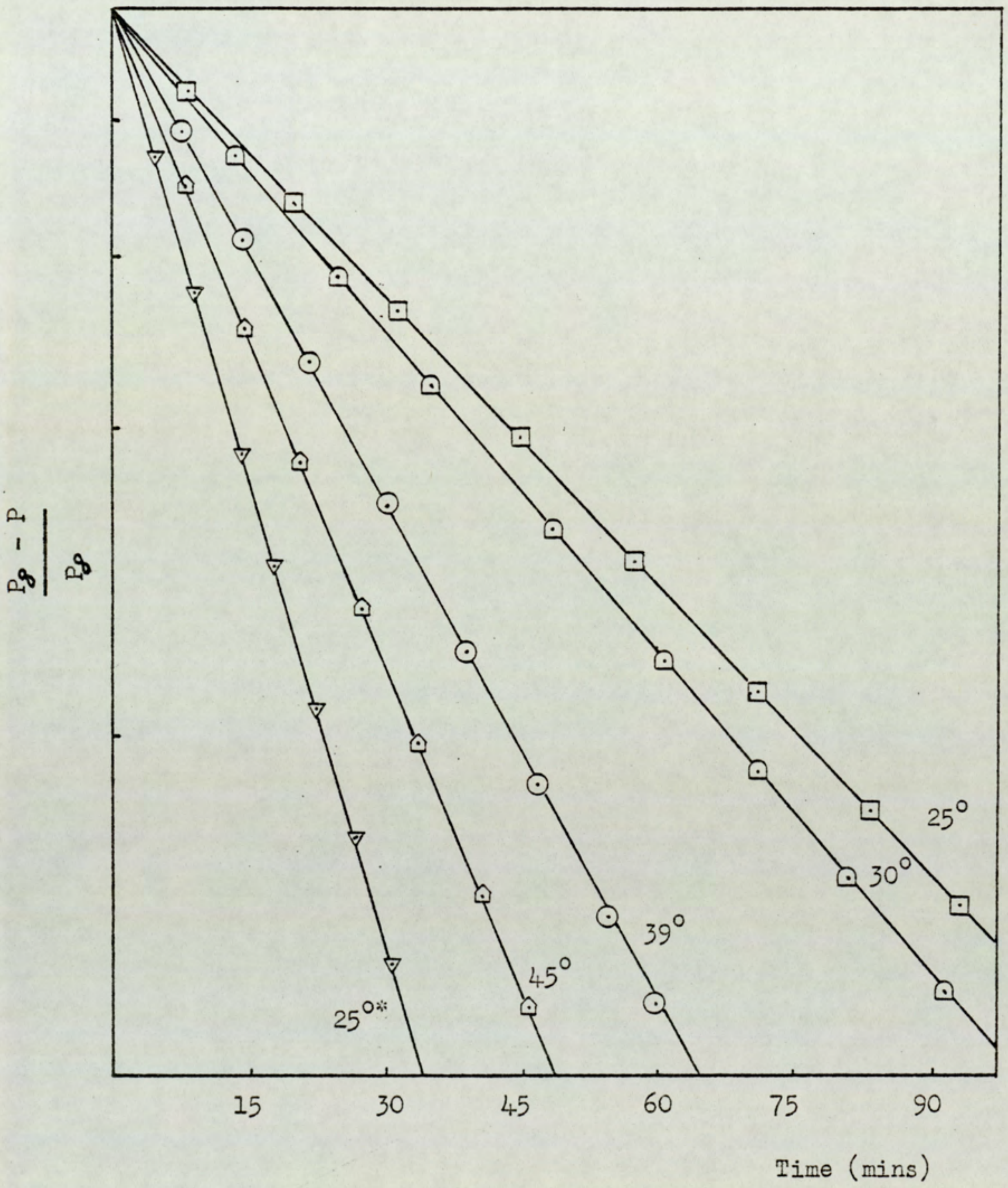


Figure XXVII

Semilogarithmic plot of $(P_{\infty} - P)/P_{\infty}$ versus time for the reaction between GAAC and Benzyl Alcohol over the temperature range 25-45°C.

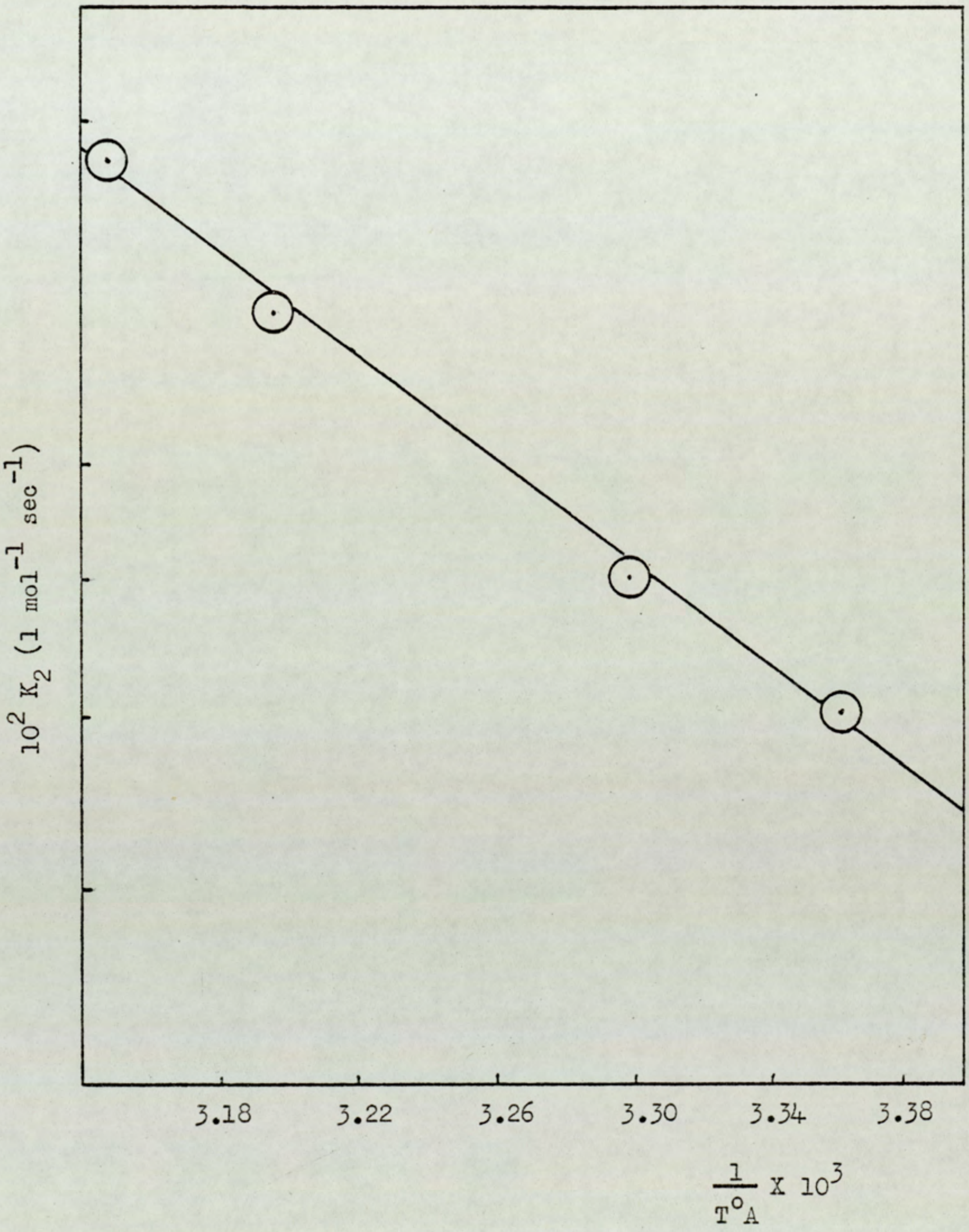


Figure XXVII

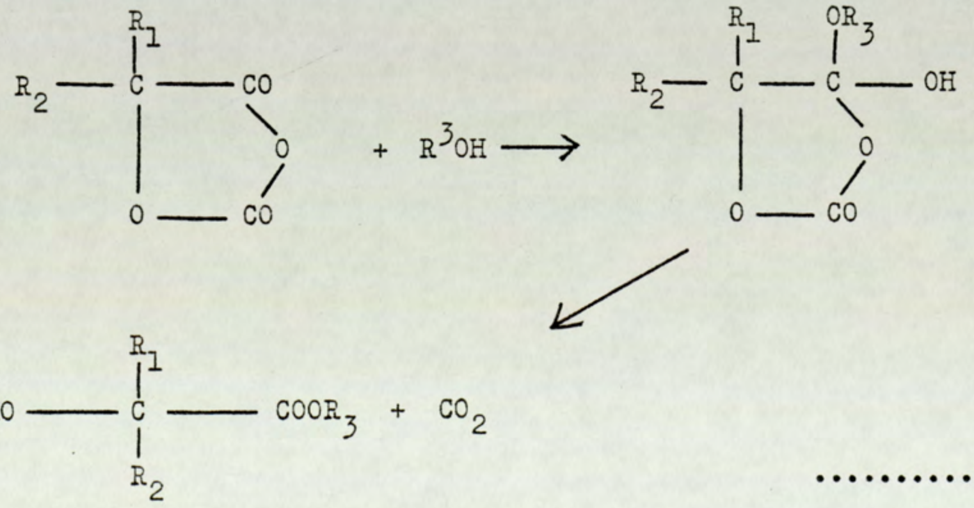
Arrhenius plot of second order rate constant, K_b, versus the reciprocal of absolute temperature for the reaction between GAAC and Benzyl Alcohol over the temperature range 25-45°C.

Also presented in Table IX are the activation energy (E), as derived from a conventional Arrhenius plot (Figure XXVII), the preexponential factor (A) and the entropy of activation ($\Delta S^{\ddagger}$).

7.2.2 Analysis of the Reaction Products

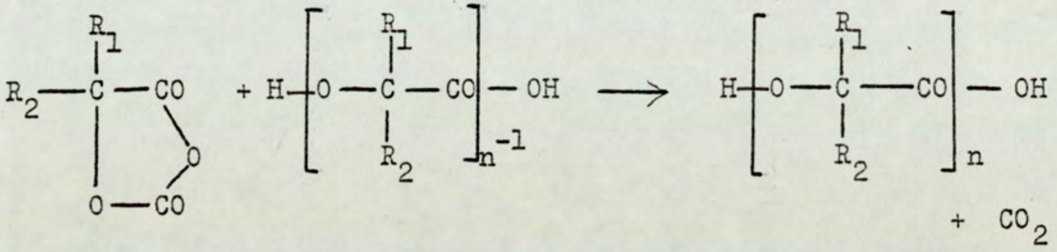
The products of the reactions were all single phase liquids. The analysis of these liquids was confined to infra red spectroscopy, and clearly indicated the presence of ester, characterised by the strong carbonyl absorption at 1740 cm^{-1}. In all cases except that involving excess benzyl alcohol, traces of residual monomer were also found, thus indicating that polymer formation, if any, was extremely limited. The nature of the products, as revealed by I.R., proved to be independent of the reaction temperature, in the range studied.

That this reaction should produce an ester is entirely consistent with the work reported by Smith(60). It is suggested that the rate determining step of the reaction is the addition of the alcohol to the anhydrocarboxylate at the C-4 position. The adduct thus produced decomposes rapidly with the loss of carbon dioxide and proton migration. Thus



.... (6)

Naturally, there will be a bimolecular contribution to ester formation, which involves the attack of a terminal hydroxyl group at the C-4 carbonyl. Thus



.............(7)

7.3 Alkoxide Initiated Decomposition

Glycollic acid anhydrocarboxylate (GAAC) is a suitable monomer for an initial study of the potential of ZMA as a catalyst for the polymerisation of anhydrocarboxylates. The monomer is readily prepared to an acceptable degree of purity by the action of phosgene on the appropriate copper (II) salt, followed by purification as described earlier (see section 2.5c).

The results of the studies reported herein involving the decomposition of GAAC in the presence of pyridine or benzyl alcohol are within the range anticipated and do not suggest any anomalous behaviour at the temperatures involved. In the absence of any bulky substituents in the C-5 position, steric hindrance will be at a minimum, and a study of the decomposition of GAAC in the presence of ZMA should provide a suitable basis for comparison when the reactions of the more substituted anhydrocarboxylates in the presence of ZMA are examined.

In view of the poor solubility of GAAC in toluene, nitrobenzene was selected as a solvent. In view of the difficulties experienced in earlier studies (see section 4.1) the volume of co-solvent used was increased from 1 cm^3 to 1.5 cm^3. This increase proved sufficient to prevent the formation of an inactive solvent/catalyst complex, as the volume of gas evolved during the course of the reactions studied clearly indicated.

7.3.1 Kinetic Data and Observations

The rate of evolution of carbon dioxide at 25°C was measured by observing the manometric pressure rise at constant volume. The corresponding semi-log plot ($\log (P_\infty - P)/P_\infty$) against time presented in Figure XXVIII clearly indicates that the rate of the reaction is dependent on the catalyst concentration, particularly during the latter stages of the reaction. In the two reactions involving the higher catalyst concentrations, there is a marked change in the rates of the reactions after twenty and thirty minutes respectively.

It was observed that as the reaction proceeded, the reaction mixture separated into two quite distinct layers, the upper layer being a clear liquid, the lower layer a green/brown gel whose colour became progressively more intense as the reaction proceeded. The physical appearance of the gel was identical to that of the gel formed in the reaction between ZMA and the corresponding anhydrosulphite, GAAS. However, whereas in this earlier study the formation of this gel and the decrease in the rate of reaction were parallel events, in the study of the present anhydrocarboxylate, this was not always the case.

Table X shows the initial rates of reaction of GAAC at varying catalyst concentration.

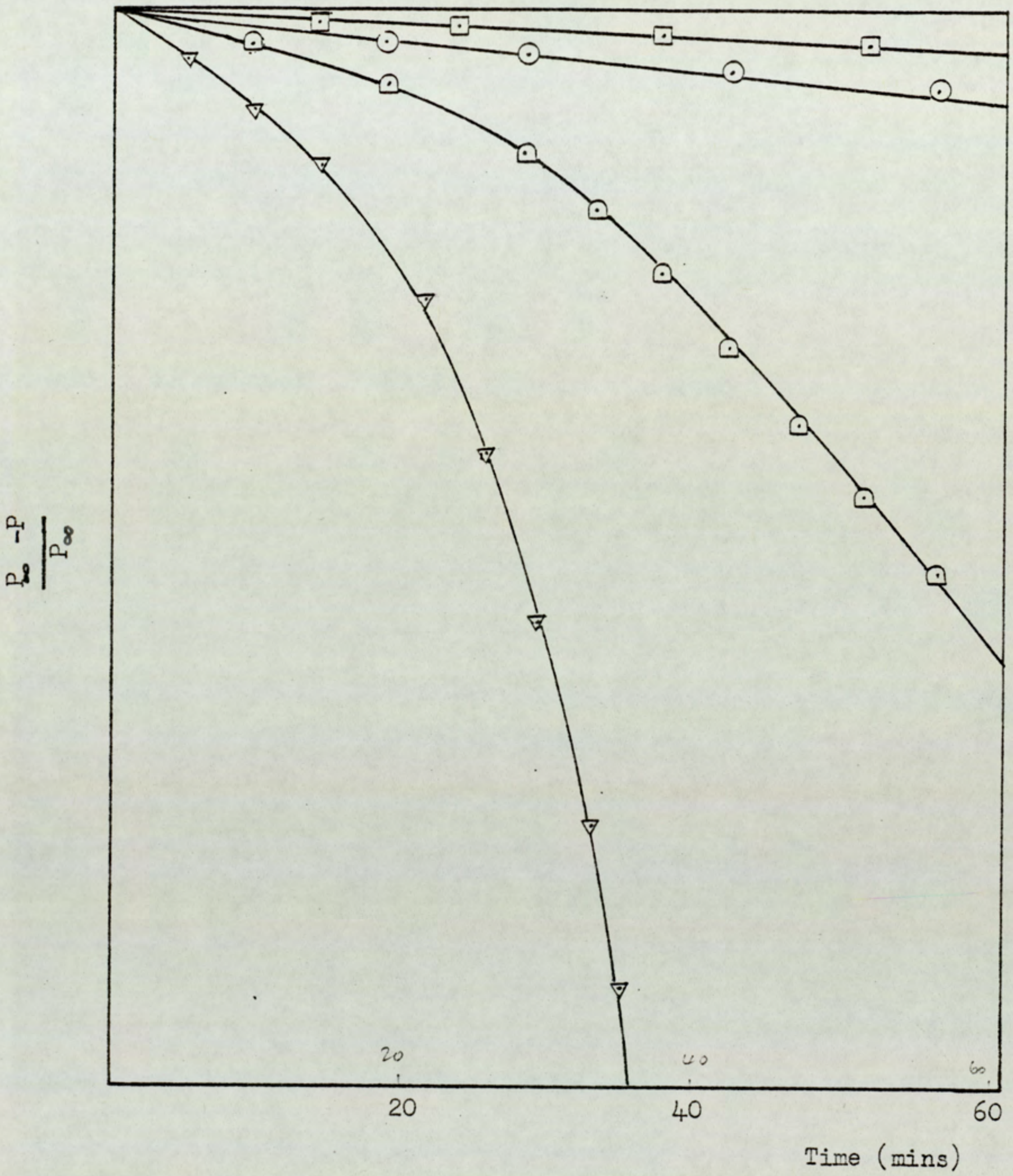


Figure XXVIII

Semilogarithmic plot of $(P_\infty - P)/P_\infty$ versus time for the reaction between GAAC and ZMA. $[GAAC]_o$ = 0.75M.

Figure XXIX

Initial rate (K) versus $[ZMA]_o$ for the decomposition of GAAC in the presence of ZMA at 25°C.

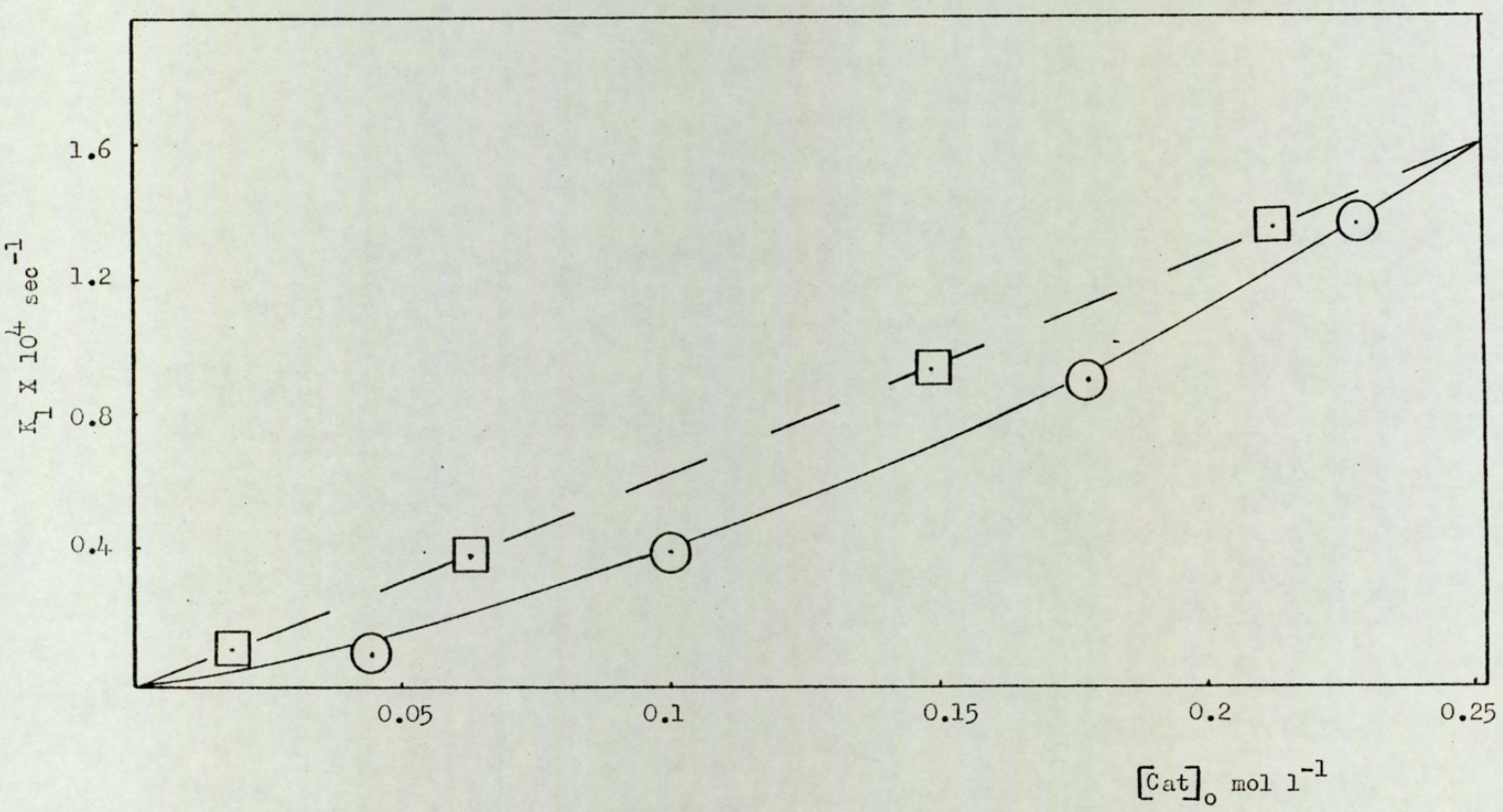


Table X

Initial rates (K) of GAAC decomposed at 25°C in the presence of ZMA, nitrobenzene/p-xylene co-solvent.

Catalyst concentration (mol l^{-1})	Initial rate X 10^4
0.2125	1.266
0.182	1.040
0.0911	0.334
0.0455	0.127

This data is presented graphically in Figure XXIX.

The sensitivity of organo-metallic initiators to trace impurities is widely appreciated. In the case of the present monomer such impurities would be residual acid, traces of moisture or both. Such impurities would render a certain constant percentage of the catalyst inert, so that the effective concentration of catalyst would in fact be lower than that added initially. Such a treatment of the present data would cause the position of the points on the graph presented in Figure XXIX to be moved towards the vertical axis by a small, constant amount. If this operation is performed the relationship arrived at is essentially linear (broken line) as opposed to that obtained by simply considering the actual quantity of catalyst added (unbroken line).

7.3.2 Analysis of the Reaction Products

7.3.2a I.R. Studies

Infra red analysis of the liquid layer formed during the reaction showed no trace of unreacted monomer, as would be expected from the pressure rise observed.

Figure XXX

I.R. spectrum of the solid products of the reaction between ZMA and GAAC. $[\text{ZMA}]_o = 0.0911 \text{ mol } l^{-1}$ $[\text{GAAC}] = 0.75\text{M}$. Temperature 25°C.

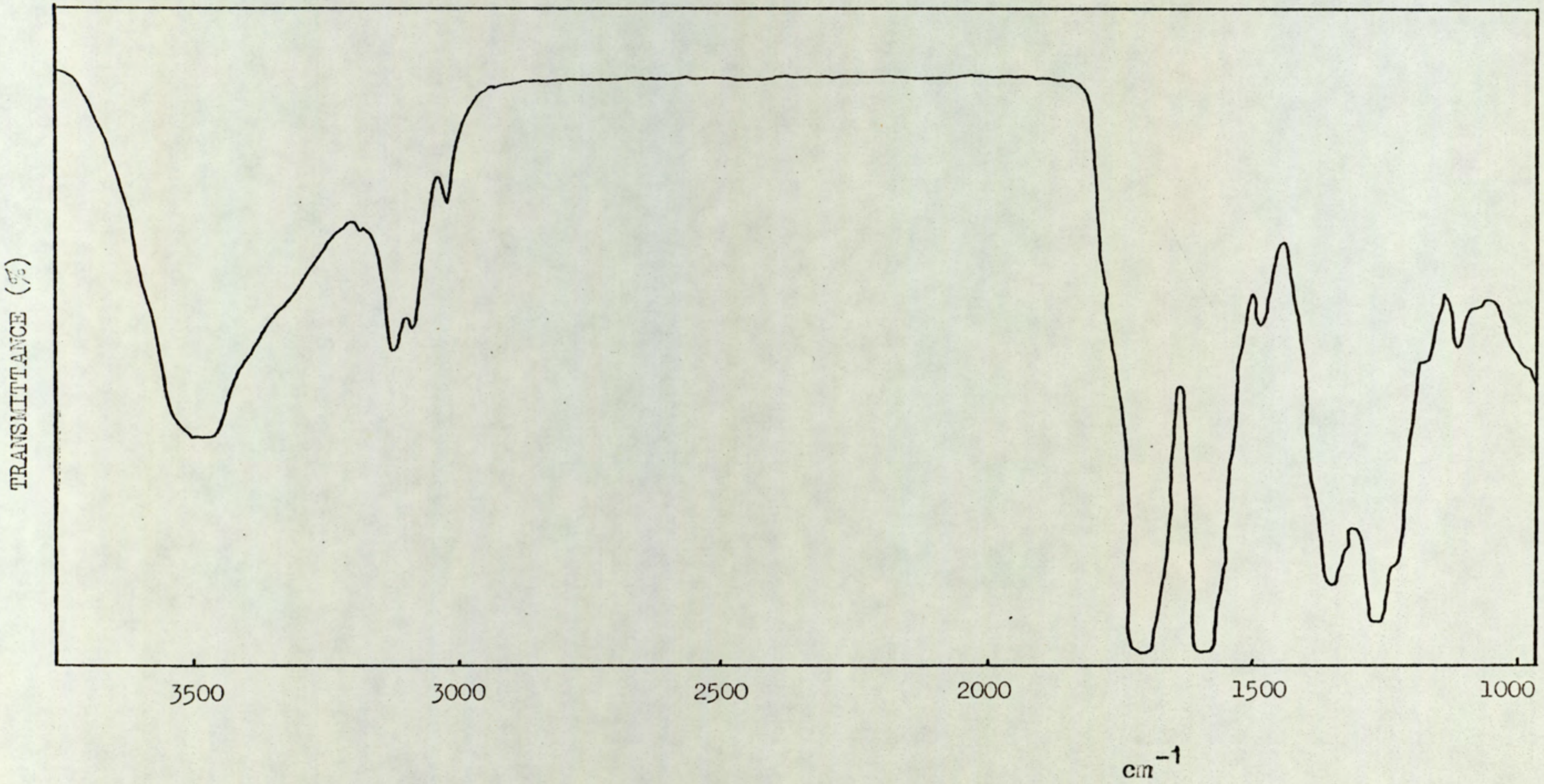
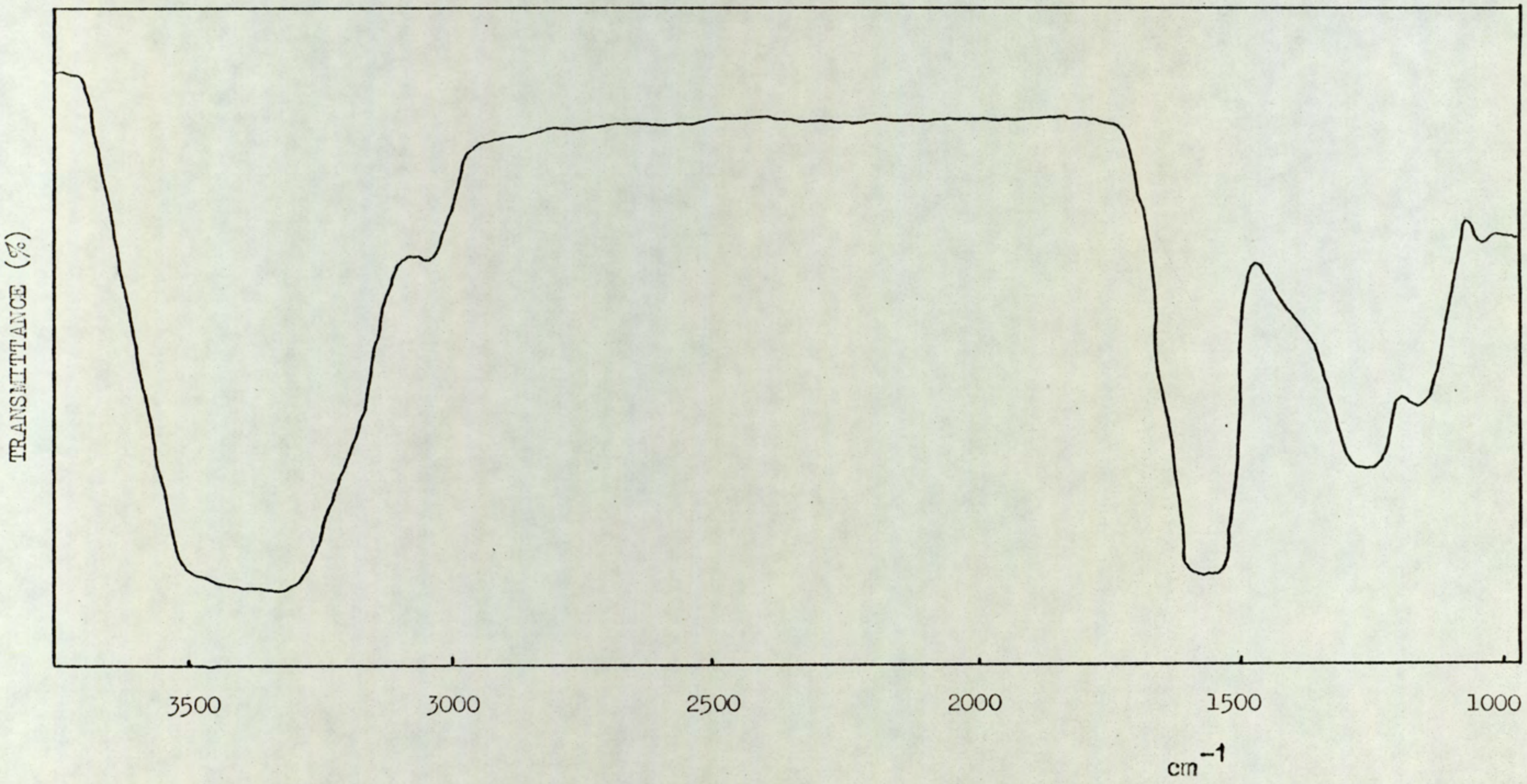


Figure XXXI

I.R. spectrum of the solid product of the reaction between ZMA and GAAC; product treated with Benzyl Alcohol. $[ZMA]_o$ = 0.0911 mol l^{-1}. $[GAAC]_o$ = 0.75M. Temperature 25°C.



In all cases the gel formed during the course of the reaction yielded a white powder on drying. The I.R. spectra of all the reaction products were virtually identical; a typical example is shown in Figure XXX. It is characterised by two equally strong absorptions in the carbonyl region, one at 1740 cm^{-1}, the other at 1600 cm^{-1}. The former is characteristic of poly-α-ester, as the thermal decomposition of anhydrocarboxylates has shown. The equally strong absorption at 1600 cm^{-1} was previously unknown in the catalysed decomposition of anhydrocarboxylates. The relative intensities of the two absorptions appears to be independent of the catalyst concentration used, over the range studied.

The product of one reaction ($[cat] = 0.911$ mol l^{-1}) was treated with hot benzyl alcohol and left to stir for two hours. The undissolved solid was then dried and a second I.R. spectrum taken (Figure XXXI). The spectrum shows that the absorption due to poly-α-ester has totally disappeared. Careful evaporation of the benzyl alcohol did not yield any polymeric product, and there was only a slight decrease in the weight of the reaction product, thus indicating that there was only limited polymer formation. The absorption at 1600 cm^{-1} is identical in both spectra, its source evidently unaffected by treatment with benzyl alcohol.

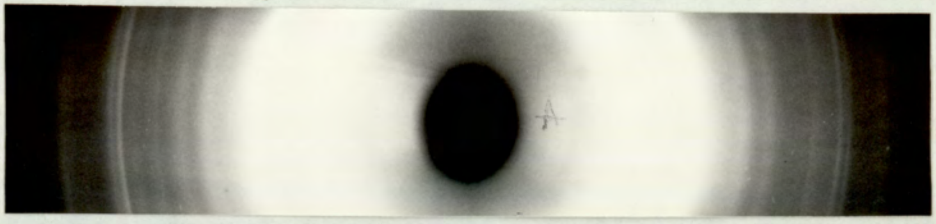
7.3.2b <u>X-ray Diffraction</u>

The X-ray diffraction powder photographs of the products of all reactions are presented in Figure XXXII. The photograph of the reaction product after treatment with benzyl alcohol is also shown.

The photographs of the untreated reaction products show a series of well-defined sharp lines on a diffuse background. The inner fine lines are characteristic of crystalline polymer. In view of

FIGURE XXXII

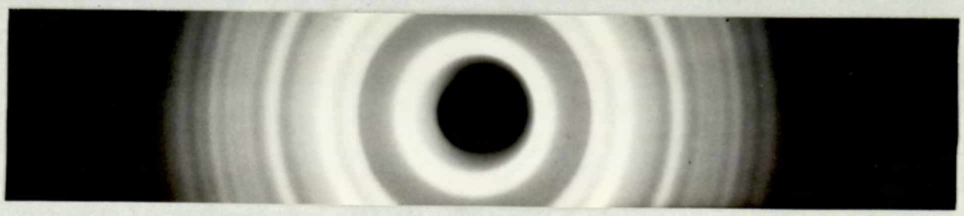
GAAC/ZMA



$[\mathrm{ZMA}]_o = 0.0911\mathrm{M}$ (A)

$[\mathrm{ZMA}]_o = 0.911\mathrm{M}$ (B)
(After treatment with Benzyl Alcohol)

$[\mathrm{ZMA}]_o = 0.182\mathrm{M}$ (C)



$[\mathrm{ZMA}]_o = 0.2125$ (D)

the symmetrical sterically unhindered nature of polyglycollide, this would be expected. The outer fine rings are too far displaced from the central beam to be attributed to polymer. On the basis of previous studies they are though to be caused by the metallic content of the product. The diffuse background scatter is caused by the amorphous organic material in the product.

Comparison of Figures XXXII (a) and XXXII (b) shows the effect of treatment with benzyl alcohol on the product. The sharp inner lines on Figure XXXII (a) are not present in Figure XXXII (b). The fine outer lines, attributed to the metallic content of the product, are unaffected; the diffuse background is, if anything, slightly more intense. The difference between the photographs confirms the change in the nature of product indicated by infra red analysis in the previous section. The benzyl alcohol has dissolved and thus removed the crystalline polymeric part of the product.

CHAPTER 8

ALKOXIDE INITIATED DECOMPOSITION OF α-HYDROXY ISOBUTYRIC ANHYDROCARBOXYLATE

In view of the work already reported herein relating to the decomposition of glycollic acid anhydrocarboxylate (GAAC) in the presence of catalytic amounts of ZMA, a study of the decomposition of α-hydroxy isobutyric anhydrocarboxylate (DMAC) under comparable conditions becomes a logical and necessary development. The monomer is readily prepared by the action of phosgene on the parent acid as described in section 2.5b. DMAC is readily soluble in toluene; thus toluene was used as a solvent for both catalyst and monomer as well as being used as a diluent.

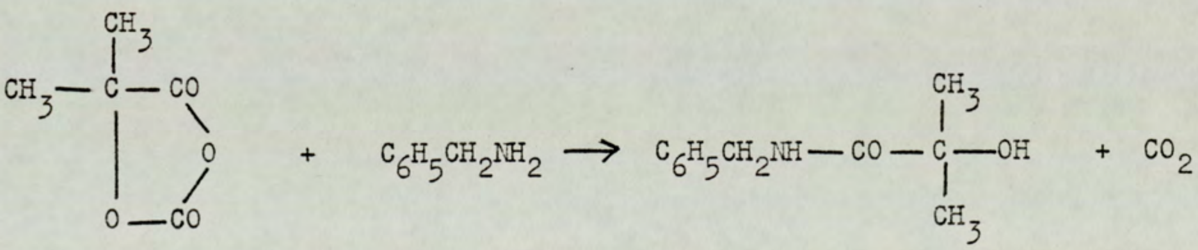
The rate of evolution of carbon dioxide was studied by observing the manometric pressure rise at constant volume. Two sets of experiments were conducted. Firstly the variation in the rate of reaction was studied as a function of catalyst concentration at constant temperature. Subsequently the variation in initial rate of reaction was studied as a function of temperature, both the catalyst and monomer concentrations being constant.

8.1 The Effect of Varying Initial Catalyst Concentration

8.1.1 Kinetic Data and Observations

The decomposition of α-hydroxy isobutyric anhydrocarboxylate (DMAC) in the presence of varying concentrations of ZMA was studied at constant temperature. It was observed that the reaction mixture separated into two distinct layers as the reaction proceeded, and that the slowing down of the reaction and the separation of the reaction mixture were parallel events.

In the case of the lowest catalyst concentration used ($0.0091 \text{ mol } l^{-1}$), no visible pressure rise occurred over a twenty-four hour period; this observation is readily explained. The catalyst, being an alkoxide, will be sensitive to compounds containing hydroxyl groups, such as acids, water etc. In this present case it is thought that the catalyst has been rendered inert by interaction with traces of parent acid produced by the reaction between the monomer and adventitious traces of moisture. Although the amount of acid present would be extremely low, it is evidently present in sufficient quantity to render inert the very limited number of active sites present at very low catalyst concentrations. After twenty-four hours a small quantity of benzylamine was injected into the reaction mixture. Benzylamine is a known reagent for the ring opening of DMAC according to the equation



.... (8)

The pressure rise observed after the injection of benzylamine clearly indicated that the previous inactivity noted was not due to any deficiency in the quantity of potentially active monomer present.

Figure XXXIII shows typical plots of pressure rise with time for DMAC/ZMA in toluene at varying [ZMA]. The initial rates of the reactions are shown in Table XI.

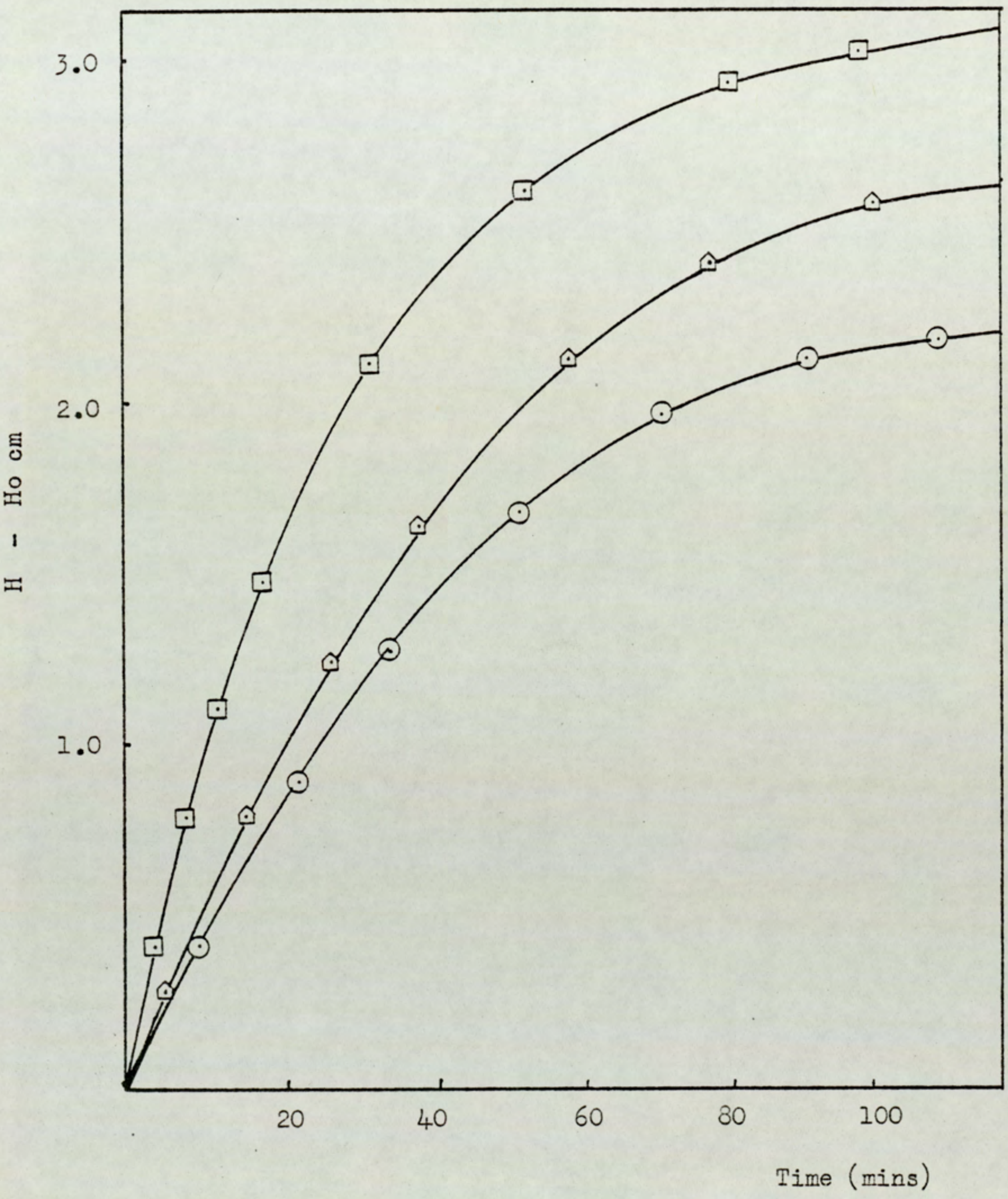


Figure XXXIII

Decomposition of DMAC in the presence of ZMA at 25°C.

Varying catalyst concentration [DMAC] = 0.5M.

Table XI

Initial rates for decomposition of DMAC in toluene in the presence of varying [ZMA] at 25°C. [M] = 0.5m.

Catalyst concentration (mol l^{-1})	Initial rate X 10^5 (sec^{-1})
0.0728	2.97
0.0364	2.82
0.0182	1.91
0.0091	-

These data are presented graphically in Figure XXXIV.

It can be seen from Figure XXXIV that there is a catalyst concentration (approximately 0.056 mol l^{-1}) above which an increase in the catalyst concentration does not cause any marked increase in initial rate. Such behaviour has already been observed in the reactions between GAAS and ZMA, but it is noticeably different from the behaviour of the more directly comparable GAAC.

It is well established that the thermal polymerisation of anhydrocarboxylates proceeds via the formation of an α-lactone intermediate, and that this species will react very rapidly with any hydroxyl group present. Thus a reaction was carried out between ZMA and DMAC in the presence of tertiary butanol; no kinetic analysis was attempted. Examination of the products of this reaction showed them to be almost identical to those of the reactions where tertiary butanol was not present, as their physical appearance had suggested. This is a valuable piece of information, since it effectively eliminates the possibility that the reaction between ZMA and DMAC is

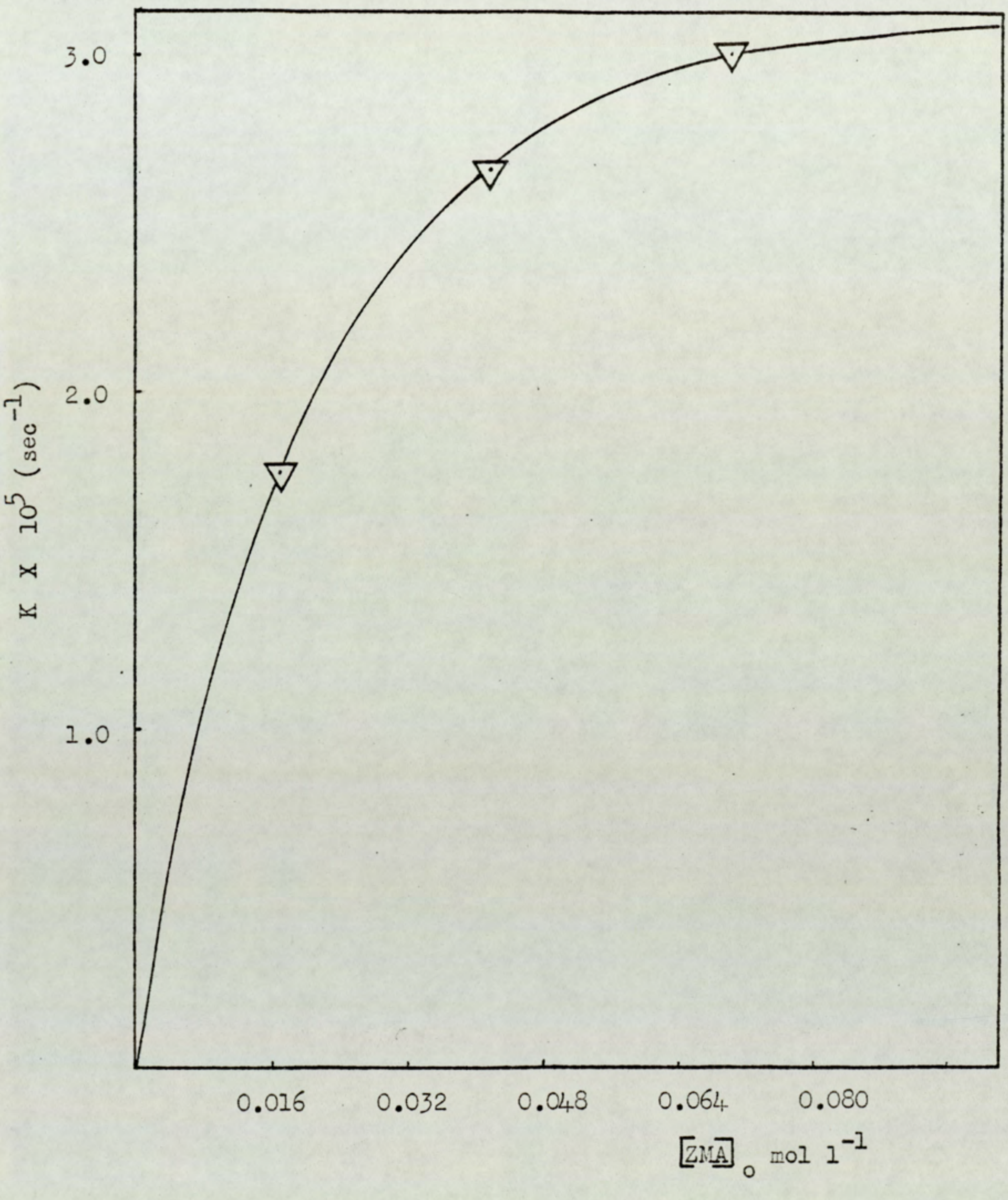


Figure XXXIV

Initial rate (K) versus [ZMA]$_o$ for the decomposition of DMAC in the presence of ZMA at 25°C.

proceeding via an α-lactone intermediate.

8.2 The Effect of Varying Temperature of Reaction

8.2.1 Kinetic Data and Observations

The decomposition of DMAC in the presence of ZMA at fixed concentration was studied as a function of temperature over the temperature range 25-47°C. Once again the reaction was characterised by the formation of two distinct layers, the separation between the two becoming more marked as the reaction proceeded, and apparently unaffected by regular agitation immediately prior to readings being taken.

The pseudo first order rate constants for the reactions studied are presented in Table XII. Also presented are the activation energy (E), preexponential factor (A) and entropy of activation ($\Delta S^{\neq}$) as derived from a conventional Arrhenius plot shown in Figure XXXV.

Table XII

Pseudo first order rate constants and associated kinetic parameters for the reaction of DMAC with ZMA. $[DMAC] = 0.5$ mol litre^{-1}

Temperature °C	10^5 K sec^{-1}
25	2.97
34	5.58
47	14.42
E (K.J. mol^{-1})	60.1
A (l mol^{-1} sec^{-1})	6.404×10^5
$\Delta S^{\neq}$ (J.K^{-1} mol^{-1})	-142.44

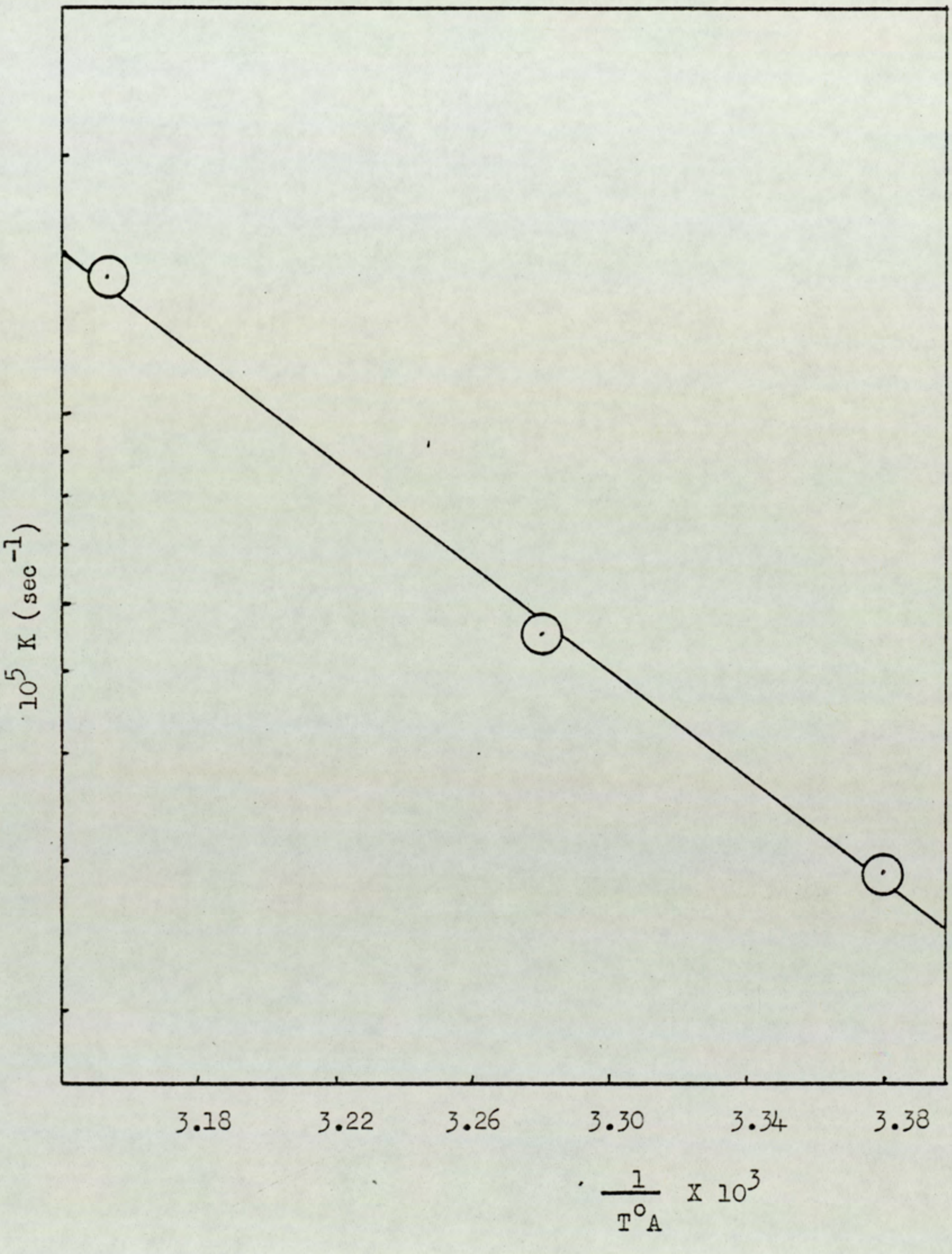


Figure XXXV

Arrhenius plot of the decomposition of DMAC in the presence of ZMA over the temperature range 25-47°C.

8.2.2 Analysis of the Reaction Products

8.2.2a I.R. Studies

The infra red analysis of the liquid layers formed during the reactions showed no unreacted monomer except in the case where no pressure rise was observed.

The I.R. spectra of the solid products proved to be almost identical, irrespective of catalyst concentration or temperature (within the range studied). A typical spectrum is shown in Figure XXXVI. The principal features are the strong absorption at 1600 cm^{-1} and the comparatively less intense absorption at 1740 cm^{-1}. The latter absorption is again attributed to the presence of poly-α-ester, although it is noticeable that the absorption, relative to that at 1600 cm^{-1} is less intense in the present case than it was in the case of the products of the reaction between GAAC/ZMA under the same conditions. The absorption at 1600 cm^{-1} is identical to that observed in the spectra of the products of the GAAC reactions. The general form of this absorption, together with its frequency is very similar to that observed in the spectra of the products of the reactions between the present bimetallic oxoalkoxide and various anhydrosulphites previously reported herein. The similarities between the products of all these reactions will be considered presently; for the moment it is sufficient that they be noted.

Figure XXXVII shows the I.R. spectrum of the solid product of the reaction between DMAC and the present bimetallic oxoalkoxide in the presence of tertiary butanol. Comparison between Figures XXXVI and XXXVII shows what little effect the presence of the tertiary butanol has had on the reaction in terms of the product formed.

Figure XXXVII

I.R. spectrum of the solid product of the reaction between ZMA and DMAC in the presence of tertiary butanol. 25^{o}C. KBr disc reference cell air.

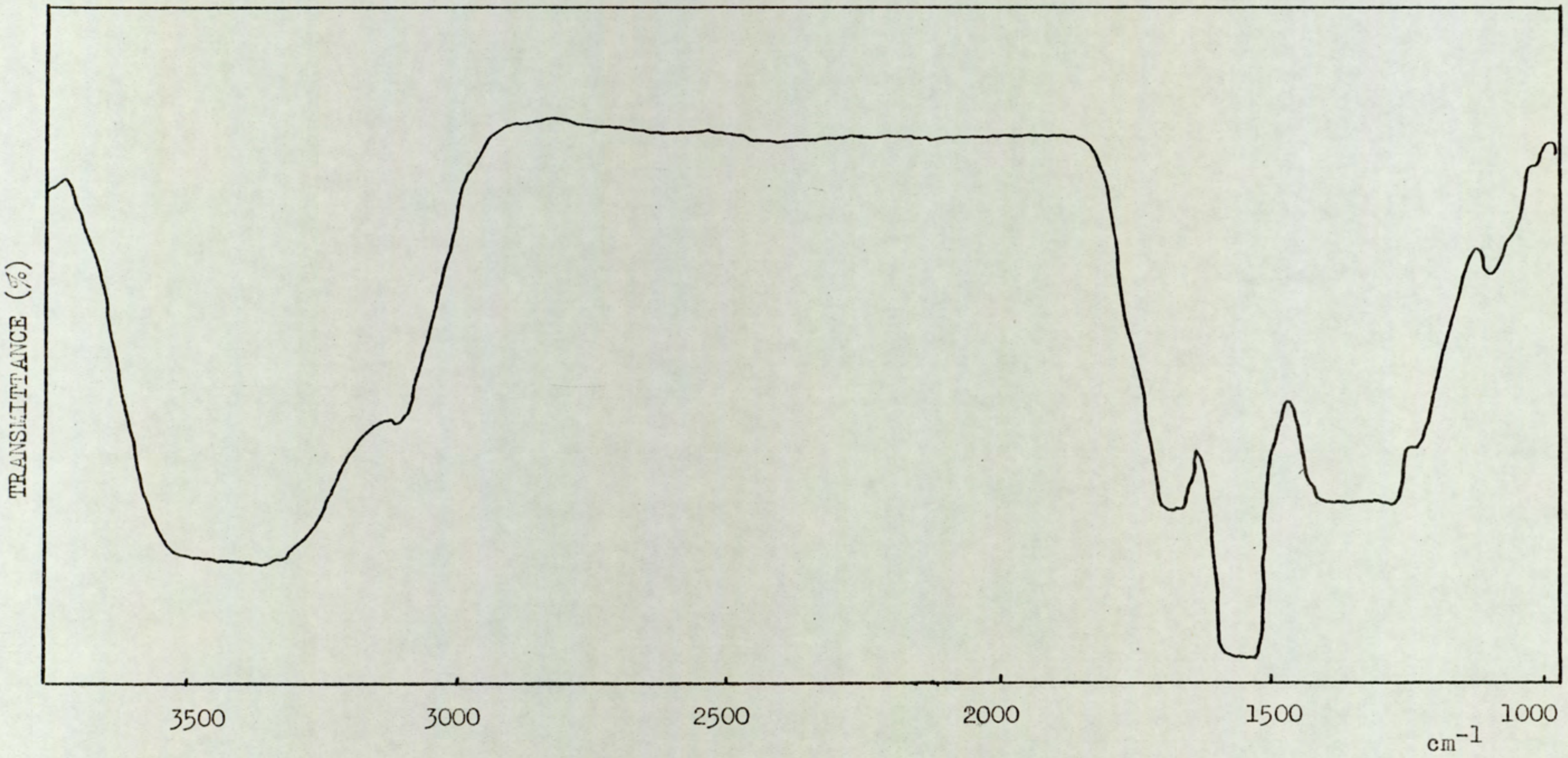
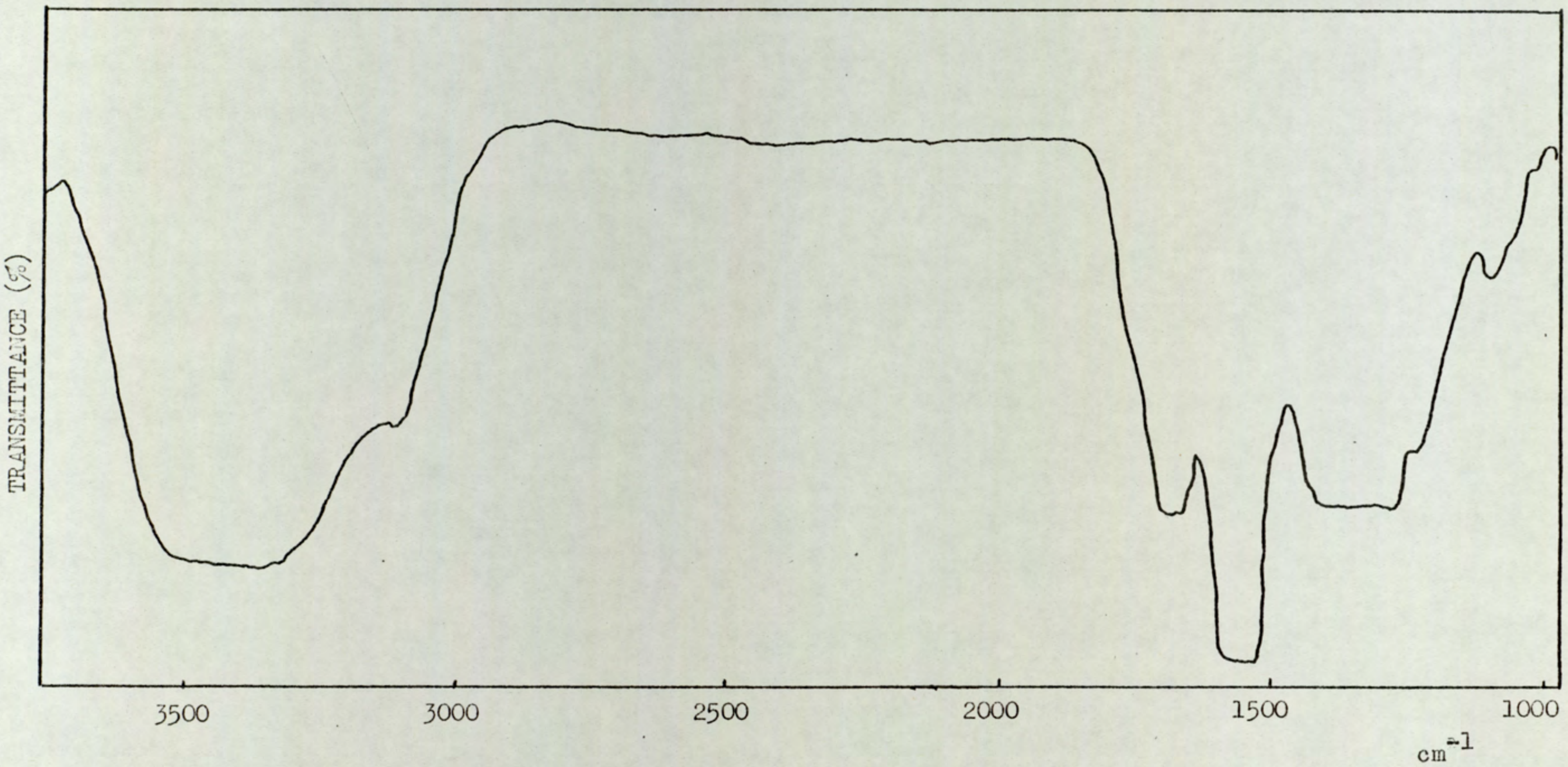


Figure XXXVI

I.R. spectrum of the solid products of the reaction between DMAC and ZMA at 25°C. KBr disc reference cell air.

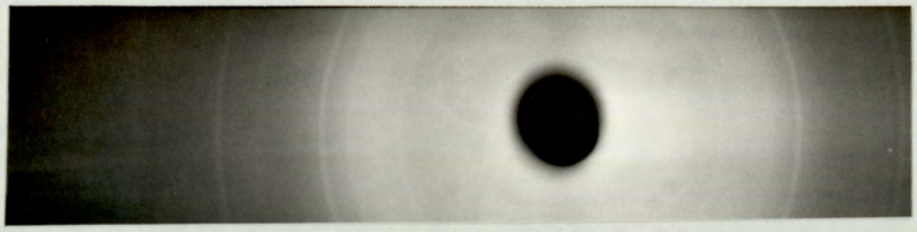


8.2.2b. X-ray Studies

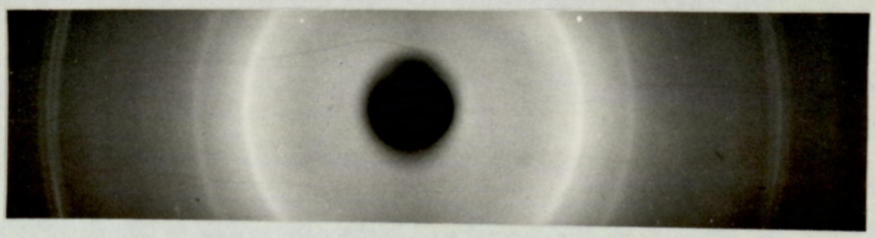
The powder diffraction photographs of the reaction products are shown in Figure XXXIX. The fine lines, well displaced from the central beam are characteristic of the scatter caused by the part of the product. The diffuse background is caused by scatter from the amorphous organic material in the product. Some fine lines close to the central beam are barely visible and indicate the presence of a small amount of crystalline polymer.

FIGURE XXXIX

DMAC/ZMA



Stirred reaction



Unstirred reaction

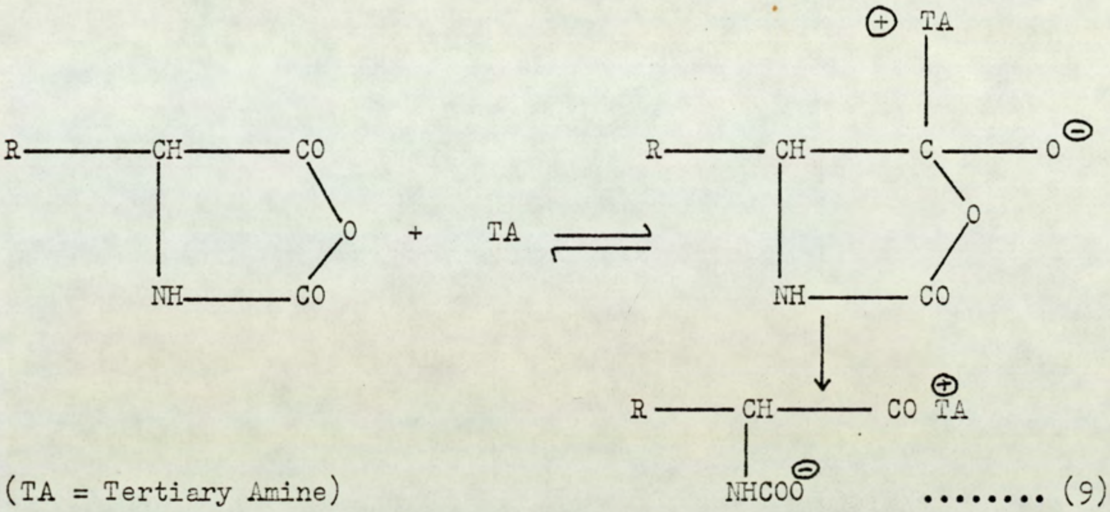
CHAPTER 9

DISCUSSION: PYRIDINE INITIATED DECOMPOSITION

In all cases the decomposition of anhydrocarboxylate in the presence of pyridine produced α-ester with the evolution of gaseous carbon dioxide. No other reaction products were detected; the fact that no pyridine-monomer adduct is formed is explained by the absence of any hydrogen atom attached to the pyridine. It has been shown previously(54,60) that pyridine reacts with anhydrocarboxylates similar to those studied to produce polymer that is hydroxyl/carboxyl terminated, contains no pyridine and possesses number average molecular weights which are independent of the initial concentration of tertiary base. The products of the present reactions are consistent with these reports.

In examining possible mechanisms for the reactions studied, it is interesting and relevant to compare anhydrocarboxylates with N-carbonic anhydrides of α-amino carboxylic acids (NCA) since this latter group of compounds is also susceptible to polymerisation using tertiary amines as initiating species. Although polymerisation occurs with little difficulty, the mechanism of reaction is still not fully understood, though two mechanisms warrant serious consideration.

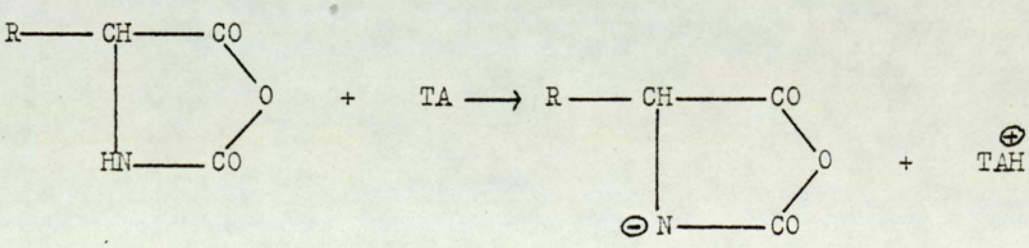
Wieland(61,62) has suggested a mechanism which is analogous to that proposed for the reaction between amines and acid anhydrides. The monomer is attacked at the C(5) carbonyl to form an intermediate which subsequently yields a Zwitterion thus:



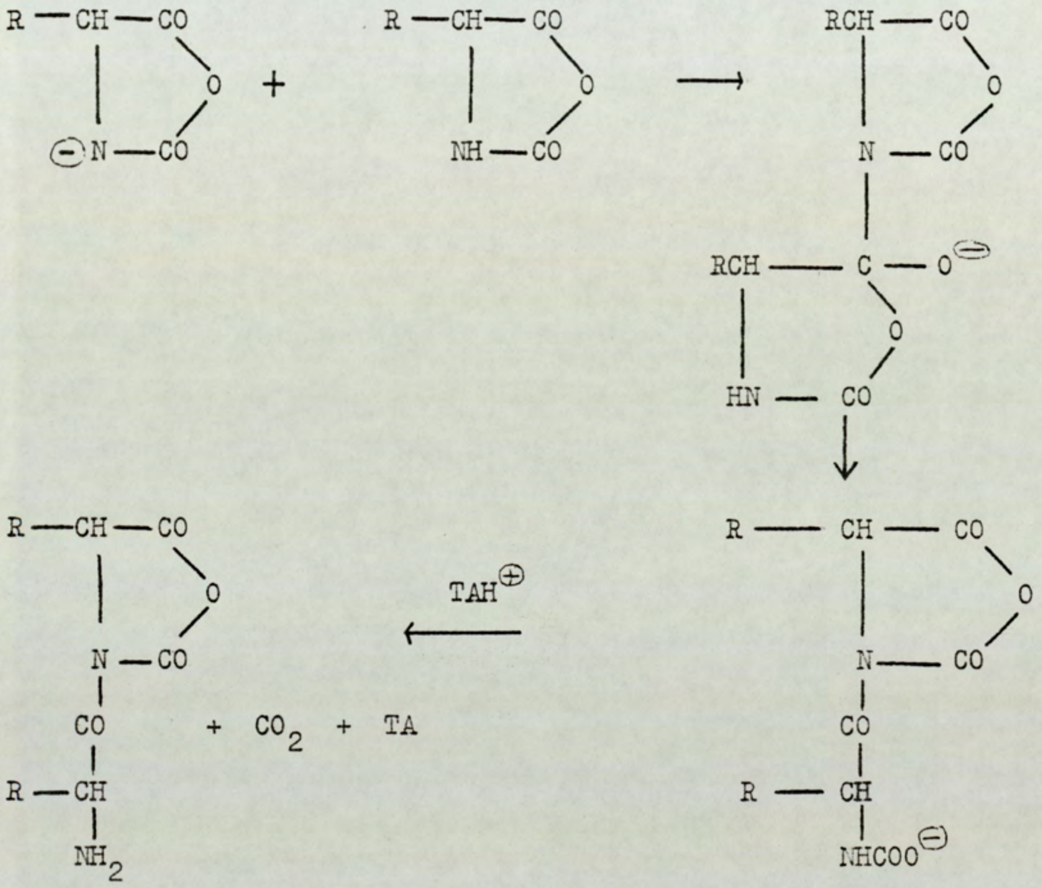
(TA = Tertiary Amine) .... (9)

It was suggested by Wieland that propagation occurred by reaction between the oppositely charged ends of the chain followed by the loss of the tertiary amine. The major flaw in this argument, in terms of its application to the present study, is that one would anticipate the formation of cyclic dimers, but no such species was found. Furthermore, the scheme proposed by Wieland requires that the reaction be second order in monomer and that the base plays a part in the chain growth reaction. Neither of these points is consistent with the experimental observations.

Bamford and Block have proposed a mechanism in which the function of the pyridine is to activate the NCA by proton abstraction from the ring nitrogen. The possibility of nucleophilic attack at the C(5) carbonyl being regarded as being of lesser importance. Thus:



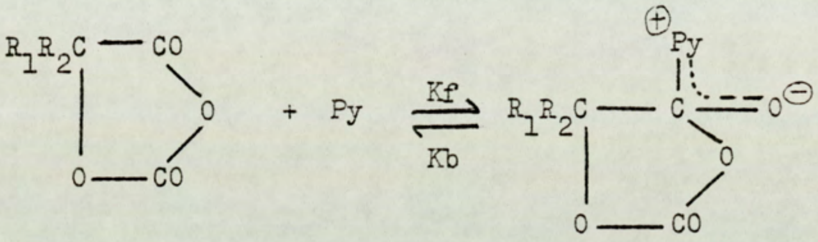
The activated ring now attacks another NCA molecule at the C(5) carbonyl. Thus



................(10)

The final stage involves protonation, the evolution of carbon dioxide and the regeneration of initiator. Whilst this mechanism explains many of the features of NCA polymerisation, its applicability to the anhydrocarboxylate systems must be regarded as very limited. The first stage of the mechanism involves proton abstraction from the monomer. In the case of mandelic acid anhydrocarboxylate, it is thought unlikely that abstraction of the proton at the C(4) carbon would take place. Secondly, successful polymerisations have been carried out in which no such proton was available.

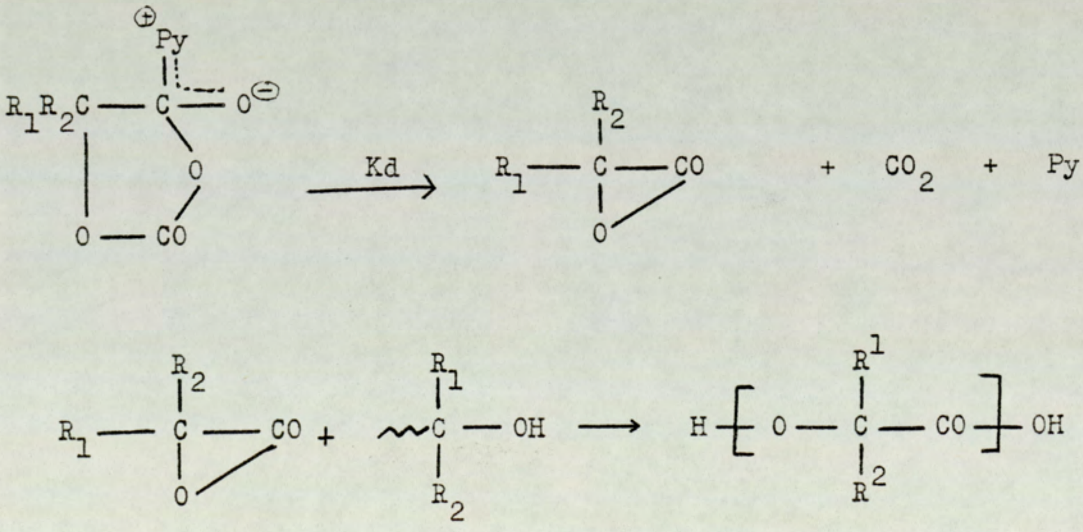
The mechanism proposed involves, firstly, an equilibrium reaction in which the pyridine, acting as a nucleophile, attacks the C(4) carbonyl of the ring to produce an unstable complex, thus



.... (11)

Where Kf and Kb are rate constants.

This complex then either decomposes to produce monomer and pyridine (see above) or decomposes to yield a polymerisable species (α -lactone), carbon dioxide and pyridine, thus



.... (12)

Where Kd is a rate constant.

The α-lactone intermediate is known to be very reactive and it is suggested that it would react immediately with the terminal hydroxyl group of a polymer chain to form α-ester. This step in the reaction makes no contribution to the activation energy and is not rate determining. The presence of α-lactone is readily detected using tertiary butanol which reacts rapidly with α-lactone to produce a low molecular weight ester which takes no further part in the reaction.

If Keq is the equilibrium constant governing the formation of the complex (PyM) between the pyridine (Py) and the monomer (M), then at equilibrium

$$Kf\,[PyM] = Kb\,[M]\,[Py] \qquad \ldots\ldots\ldots (13)$$

and

$$Keq = \frac{Kf}{Kb} = \frac{[PyM]}{[M]\,[Py]} \qquad \ldots\ldots\ldots (14)$$

which, on rearrangement, gives

$$[PyM] = Keq\,[M]\,[Py] \qquad \ldots\ldots\ldots (15)$$

The overall rate equation may be written as

$$\frac{d[CO_2]}{dt} = -\frac{d[M]}{dt} = Kd\,[PyM] \qquad \ldots . (16)$$

hence

$$\frac{d[CO_2]}{dt} = Kd.Keq\,[M]\,[Py] \qquad \ldots\ldots\ldots (17)$$

Since in general

$$\frac{d[CO_2]}{dt} = K_2\,[M]\,[Py] \qquad \ldots\ldots\ldots (18)$$

we can combine (17) and (18) to give

$$K_2 = Kd.Keq \qquad \ldots\ldots\ldots (19)$$

↑
observed
Rate constant

This equation illustrates two very important points. Firstly, the rate of polymerisation of anhydrocarboxylates is governed by both the equilibrium constant for the complex formation and rate of decomposition of the complex to α-lactone. Secondly, as the equation implies, the activation energy of the overall reaction does in fact not refer to a simple single process.

The ability of pyridine to form complexes of the type presented, i.e. charge transfer complexes, has been widely studied. The complex formed by the reaction between pyridine and iodine is of particular interest since the molecule formed contains both n- and aromatic π- electrons. Charge transfer complexes involving purely aromatic π-electron donors have relatively small association constants compared with values obtained for the pyridine-iodine system.(65) Comparison of the values for this latter system with those obtained for aliphatic amine complexes, which are necessarily n-donors, leaves no doubt that the predominant mode of charge transfer complexing in pyridine is by the n-donation of electrons of the tertiary nitrogen atom.

A stable complex has also been reported between dimethylamine and sulphur dioxide.(66) The complex reported is a yellow oil with a melting point of 17°C. This evidence suggests that complexes formed by n-donors are relatively stable and supports the suggestion that the decomposition of anhydrocarboxylates may involve a charge transfer complex.

The mechanism presented involves the nucleophilic attack of the pyridine at the C-4 carbonyl, and one would anticipate that the substituents at the C-5 carbon would play an important role in determining the rate of reaction. When the initiating species is the same, and the solvent system remains constant, the relative reactivities of anhydrocarboxylate rings may be determined by the nature of the substituents on the respective rings and subsequently on the growing polymer chain. The electronic properties of the substituents govern the relative electrophilicity of the C-4 carbonyl, whilst the actual size of the substituents will exert an influence on the rate of reaction since the attack by the pyridine may be sensitive to steric hindrance.

Correlation of the relative magnitude of the electronic (or polar) effect and the steric effect of the substituent with the measured rate of reaction can be achieved by using the Taft equation, i.e.

$$\log \frac{K}{Ko} = \rho^* \sigma^* \qquad \text{..........} (20)$$

This equation correlates a reaction rate, K, with σ^*, a parameter representing the polar (or electronic) effect of the substituent, and ρ^*, an empirical parameter dependent on the nature of the reaction and the reaction conditions.

For the reaction series in which deviation occurred, when using equation (20), due to steric effects associated with the reaction, the equation may be written

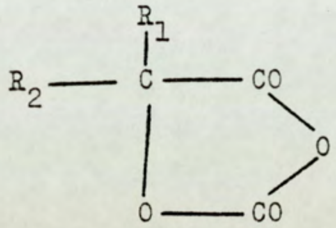
$$\log \frac{K}{Ko} = \rho^* \sigma^* + SE_s \qquad \text{.........} (21)$$

or

$$\log K = \rho^* \sigma^* + SE_s + c \qquad \text{......} (22)$$

Where E_s is considered to be a steric substituent constant governed by an empirical parameter S. Thus the parameters ρ^* and S reflect the relative importance of the polar and steric effects.

In monomers of the general type



the reaction rates at 60°C in the presence of pyridine, using nitrobenzene as a solvent, provide a basis for comparison. The nature of the substituents, the reaction rate constants, together with the combined polar and steric parameter values are presented in Table XIV. The best fit is obtained when a value of two is given to ρ^* and one to E_s, as shown in Figure XXXIX.

It is clear from Figure XXXIX that the aromatic and fluoroaromatic substituents are effective only in terms of their generalised steric and electronic effects, and have no specific activating effect on the polymerisability of anhydrocarboxylates. The rate of polymerisation of GAAC in the presence of pyridine, at 60°C, is, as predicted, greater than for any of the anhydrocarboxylates studied.

The results of the present study are presented in Table together with those of Smith and Kosolsumollamas. It shows that for the pyridine initiated polymerisation of anhydrocarboxylates at almost identical temperatures MAAC with phenyl and hydrogen substituents reacts much more rapidly than AAAC with methyl and phenyl substituents. This strongly suggests that the presence of the methyl group, which is larger than a hydrogen atom, sterically hinders nucleophilic attack at the C-4 carbonyl. PFAAC is directly comparable to AAAC in steric terms and the observed increase in the rate of reaction caused by

TABLE XIII

Substituents on the C-5 carbon of an anhydrocarboxylate ring, second order rate constants for pyridine initiated polymerisation at 60°C in nitrobenzene and the polar and steric parameters

R^1	R^2	K_2 at 60°C mol^{-1} litre sec^{-1}	σ^*(a)	$E_{s(a)}$	$\sigma^* + 2E_s$
C_6H_5	H	1200×10^{-4}	1.09	0.74	2.92
$C_6H_{5(b)}$	CH_3	1.62×10^{-4}	0.6	-0.5	0.7
$C_6F_{6(c)}$	CH_3	14.3×10^{-4}	1.10	-0.5	1.7
C_6H_5	C_6H_5	5.9×10^{-4}	1.2	-1.0	2.2
H	H	2560×10^{-4}	0.98	2.48	4.46

(a) Value obtained from Reference (54)

(b) E_s value was calculated approximately from E_s values of cyclohexyl and cyclopentyl

(c) Value obtained from Reference (60)

the presence of the pentafluorophenyl group is attributed to the increase in susceptibility of the C-4 carbonyl to nucleophilic attack. In the case of BAAC it is apparent that the presence of the two phenyl groups sterically hinders the reaction to the point where an induction period is observed even in the presence of equimolar amounts of pyridine.

In the polymerisation of the monomers presented in Table XIII by pyridine, it is observed that the steric factor exhibits more effect in controlling nucleophilic attack than does the electronic factor as can be seen by their respective energies of activation. PFAAC, although having a faster rate of reaction than that of c'pent AC, also shows a higher free energy of activation; this is the result of a higher energy of the transition state of the highly sterically hindered PFAAC-pyridine adduct.

The relative importance of the steric and electronic factors present is reflected in the Taft plot presented in Figure XXXVIII. The work of Smith and Kosolsumollamas had resulted in the constants ρ and s in the equation

$$\frac{\log K}{\log Ko} = \rho\sigma^{*} + sE_{s} \quad \ldots\ldots\ldots (23)$$

being attributed the values of $\rho = 1.88$ and $s = 1.29$. The results of the present study show that a best fit is obtained, after the inclusion of the data relating to GAAC, by using the values $\rho = 1$ and $s = 2$, again reflecting the much greater importance of the effects of steric hindrance, and that, as predicted, the rate of polymerisation of GAAC by pyridine is greater than for any other anhydrocarboxylate under the same conditions.

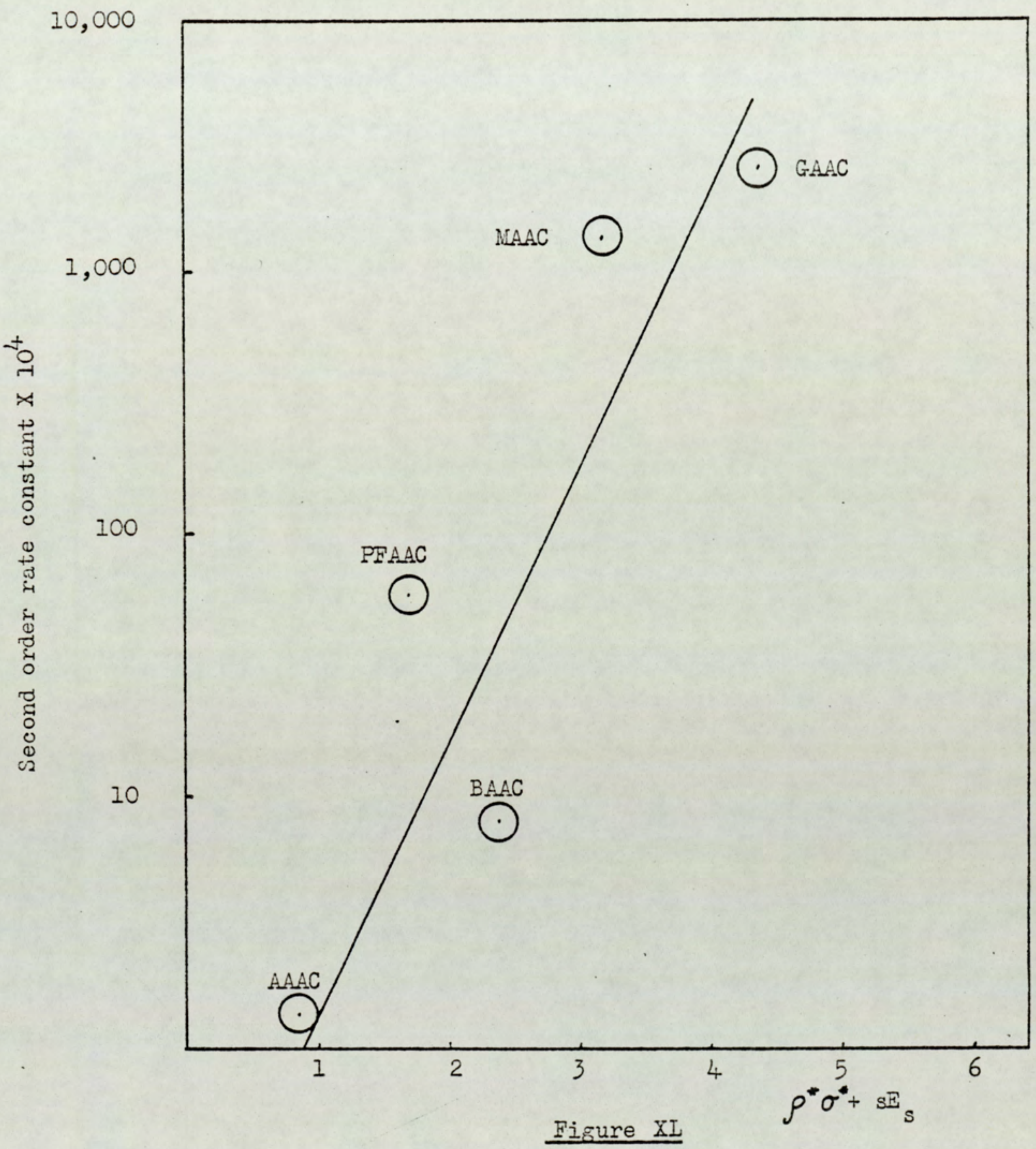


Figure XL

Semilogarithmic plot of second order rate constant against substituent parameters for the reaction between Pyridine and Anhydrocarboxylates.

TABLE XIV

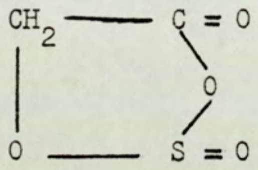
Extrathermodynamic data for the pyridine initiated decomposition of anhydrocarboxylates at 60°C

Monomer	K_2 at $60^{0}C \times 10^{-4}$ mol^{-1} litre sec^{-1}	E_{act} KJ mol^{-1}	A l. $mol^{-1} sec^{-1}$	S J.K^{-1} mol^{-1}
PFAAC	14.3	62.5	6.9×10^{6}	-127
AAAC	1.67	73.3	6.5×10^{7}	-103
C'pent AC	43.5 (at 59.3°C)	55.0	2.5×10^{5}	-149
MAAC	1200	48.3	4.3×10^{6}	-133
BAAC	5.9	87.7	3.8×10^{11}	-67.3
GAAC	2560	49.1	1.31×10^{7}	-117

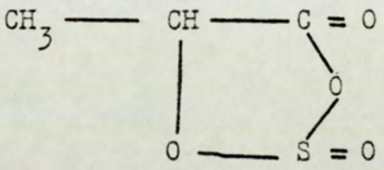
In all cases, the polymerisation of anhydrocarboxylates by pyridine occurs more rapidly and conveniently than the thermal decomposition. The polymer is produced at a much lower temperature and therefore possesses a much greater degree of tacticity, and non polymer forming side reactions are minimised. It is anticipated that with rigorous purification of monomer, initiator and solvent the production of polymer of high molecular weight by this method presents no fundamental problems.

DISCUSSION: ALKOXIDE INITIATED DECOMPOSITIONS

Glycollic acid anhydrosulphite (GAAS) is the least complicated anhydrosulphite monomer studied.



GAAS



LAAS

Since both C-5 substituents are protons, steric hindrance is at a minimum, as are electronic effects. The strain in the anhydrosulphite ring will also be at a minimum. In the case of lactic acid anhydrosulphite (LAAS), the introduction of the methyl group at the C-5 position means that the distribution of electrons in the ring will be disturbed due to the electron releasing inductive effect of the methyl group. The steric hindrance of the monomer is also increased by the presence of the methyl group as is the degree of ring strain. This increase in ring strain with increasing substitution is a characteristic feature of anhydrosulphite rings and is reflected in the decrease in their thermal stability with increasing substitution at the C-5 position.

The decomposition of GAAS in the presence of ZMA occurs at a faster initial rate than that of LAAS under the same conditions. The total volume of SO_2 evolved is greater in the case of GAAS, but in neither case was the final experimental pressure rise equal to the theoretical pressure rise.

The final pressure rises for the reactions between GAAS/ZMA and

LAAS/ZMA were closely and directly related to the initial catalyst concentration, as was the mass of solid reaction product. This would tend to suggest that the addition of the monomer to the catalyst is a fairly straightforward process, but that the subsequent reaction between the monomer and the catalyst-monomer adduct occurs less readily. Thus once all the available catalytic sites have been either occupied by monomer or destroyed by trace impurities, the rate of monomer decomposition is reduced and only limited propagation takes place.

The proposed addition of anhydrosulphite monomer to the catalytic species to form an intermediate is well known for anhydrosulphites. It is an essential feature of the reaction scheme outlined by Crowe(41) in his analysis of the mechanism of reaction of anhydrosulphites and catalytic quantities of lithium tertiary butoxide.

Further evidence for the fact that the initial addition of monomer to the catalyst occurs with greater facility than the subsequent propagation reaction is found by comparing the kinetic profiles for LAAS/ZMA with those of GAAS/ZMA (Figures III and IX). In the latter case, the profile would suggest that the gas evolution is composed of two consecutive gas evolving reactions whereas the kinetic profile of the LAAS/ZMA reactions suggests a single decomposition process.

Comparison of the general nature of the kinetic profiles and spectral evidence for the reactions between LAAS/ZMA shows that, within the range studied, the reaction is not sensitive to the nature of the co-solvent used. The difference in the rates of the reactions is comparatively small and could well be due to a slight change in the size of the catalytic aggregates. The studies reported by

Tessyie(42,57,58) contain no suggestion that a change in the size of catalytic aggregates affects anything other than the actual rate of the reaction, and the results of this particular study support this view. Further evidence to support this suggestion is found in the fact that the nature of the solid products of the reaction between LAAS and ZMA, as revealed by I.R. studies, is the same for both the stirred and the unstirred reactions.

The injection of LAAS into a still active reaction mixture of GAAS/ZMA produced only a limited amount of sulphur dioxide evolution before termination, as Figure XIV indicates. The I.R. spectrum of the solid reaction product shows the formation of a limited amount of α-ester.

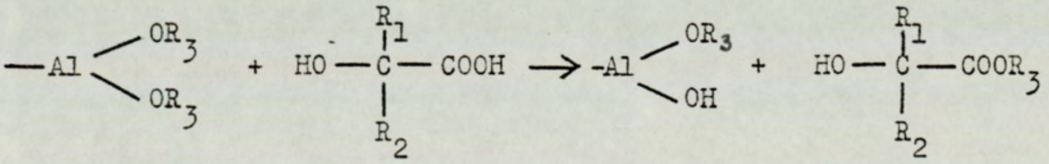
In marked contrast, the injection of GAAS into a still active reaction mixture of LAAS/ZMA produced a larger and more rapid evolution of sulphur dioxide than might have been anticipated from earlier studies (Figure XV). Furthermore, the I.R. spectrum of the solid product (Figure XVII) clearly indicates the formation of an appreciable amount of α-ester, far more than for any previous experiment. Thus there is a marked difference between these two reactions, and a comparison of the monomers involved shows that the major difference between them is the size of one of the C-5 substituents and suggests that the differences observed may be due to the steric factors.

It is of interest that the I.R. spectra of the solid products of the reactions between ZMA/MAAS and ZMA/DMAS should indicate α-ester formation. In neither case was there any evidence of gas evolution, and the quantity of gel formed during the course of the reactions was extremely small. Nevertheless, the absorption at

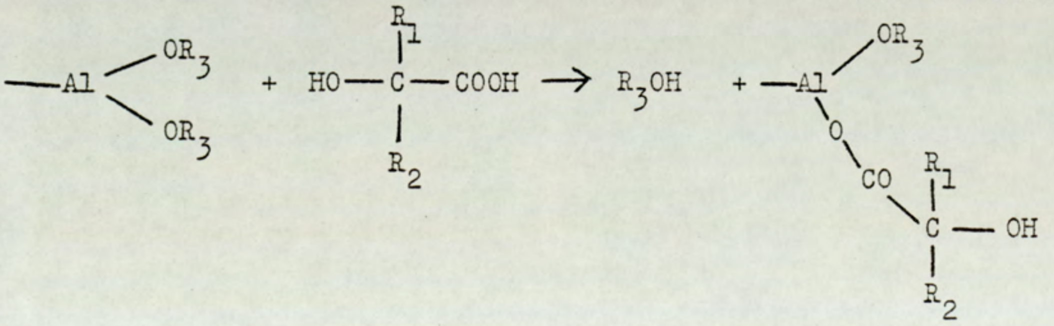
1740 cm^{-1}, present in both spectra, indicates the formation of α-ester, albeit in limited quantities, and possible explanations of these observations will be considered presently.

In view of the sensitive nature of alkoxides, it is to be expected that on mixing of ZMA and anhydrosulphite solutions, certain reactions may take place which would result in the destruction of potentially active catalytic sites. These reactions would involve the alkoxide catalyst and traces of impurities found in all anhydrosulphite monomers to a greater or lesser extent. The nature of these impurities has already been discussed in Chapter 2 (section 2.5). Their interactions with the present catalyst will now be outlined.

The presence of α-hydroxy acid in anhydrosulphite monomers is due to the reaction between the monomer and adventitious traces of moisture. It is anticipated that such acid would react with the present catalyst in two possible ways, as described by equations (24) and (24a). In neither case are the reaction products active ring opening reagents.

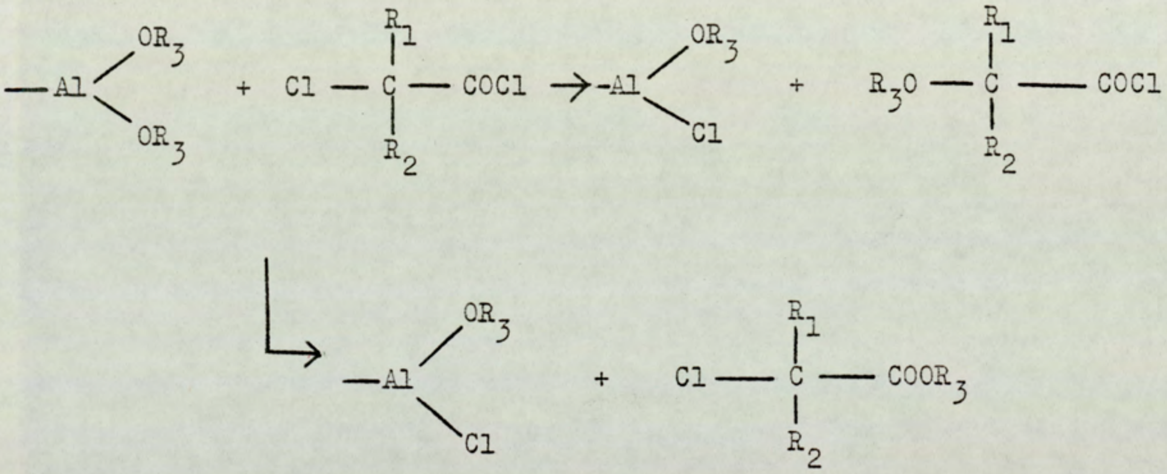


.... (24)



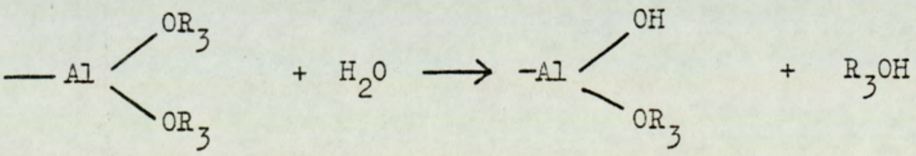
.... (24a)

Despite purification involving the use of silver oxide (section 2.5c) it is inevitable that some traces of acid chloride will still be present in the final monomer solution. Again the reaction between this impurity and the catalyst will result in the destruction of potentially active catalyst sites, thus



.... (25)

The final impurity will be traces of moisture, and in view of the known sensitivity of alkoxides to moisture, such traces will inevitably react rapidly with the catalyst, again resulting in the destruction of potentially active catalytic sites, thus



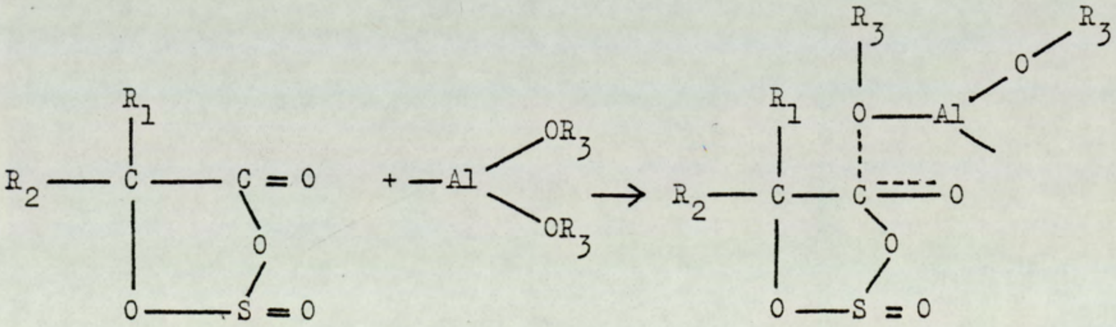
.... (26)

There is no evidence in any of the reported studies of the reactions of anhydrosulphites with metal alkoxides to suggest that any of the reaction products react destructively with the catalytic species. In the present study, the acidity and nucleophilicity of the sulphur dioxide produced by monomer decomposition acquires a new significance in view of the amphoteric nature of the aluminium present in the catalyst and its electronic environment. The possibility of some kind of interaction between the sulphur dioxide produced and the catalyst molecule cannot therefore be rejected.

Consideration of all the information presented suggests certain interpretations and schemes of reaction which are not necessarily mutually exclusive.

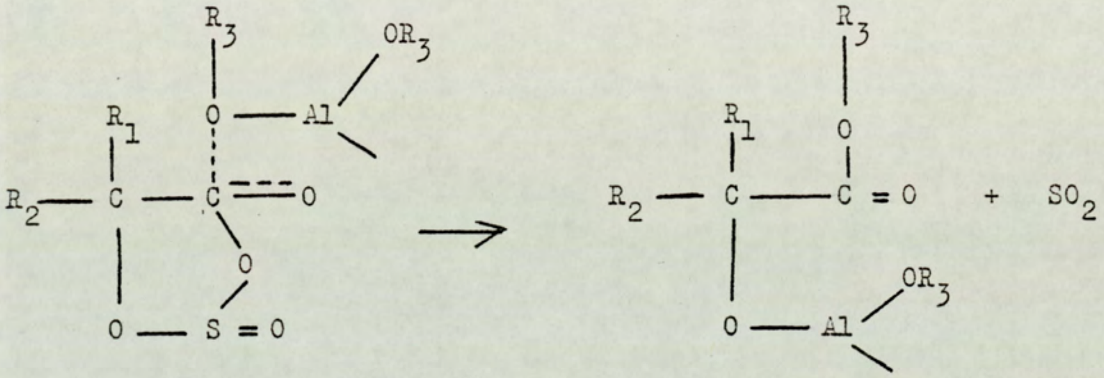
9B1 The NCA Mechanism

The principal feature of this mechanism is the attack by the nucleophilic oxygen of the alkoxide at the C-4 carbonyl position of the anhydrosulphite ring to form a complex intermediate, thus



.... (27)

This intermediate is similar to the species proposed as an intermediate in the reaction between alkoxides and NCAs. It is thought that this intermediate would then fragment rapidly with the loss of SO_2 and rearrangement to regenerate an alkoxide, thus



.... (28)

It is thought that the reaction would then propagate by the reaction between one of the two available alkoxide sites and further monomer molecules.

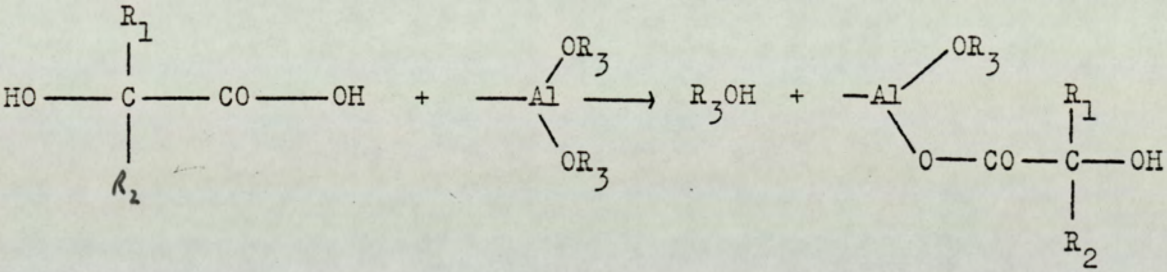
The major limitation of this mechanism, in terms of its applicability to the present study, is that it fails to explain the formation of the carboxylate ester present in the products of all reactions studied. Furthermore, the formation of limited quantities of α-ester for the reactions involving MAAS or DMAS cannot be accounted for, neither can the apparent two-stage nature of the reaction between GAAS and the present alkoxide, and this scheme in itself must therefore be regarded as inadequate although it may contain certain elements that are capable of contributing to a more comprehensive scheme.

9B2 The C-5 Attack Mechanism

The C-5 position in the anhydrosulphite ring is the most sterically crowded position in the ring, as well as having minimal nucleophilic character. It does not therefore present a likely site for attack by the alkoxide, and it is difficult to envisage any mechanism of reaction that would involve attack at this site.

9B3 The Parent Acid Mechanism

A potential source of carboxlate ester is the direct reaction of the alkoxide with traces of α-hydroxy acid, thus



.... (29)

This carboxylate ester is not thought to be capable of inducing decomposition of anhydrosulphite rings. Crowe(41) has found that sodium acetate fails to induce decomposition of anhydrosulphite rings, neither does it affect the rate or molecular weight distribution of the thermal decomposition of anhydrosulphites.

The principal drawback of this mechanism lies in the fact that any parent acid would be present as trace impurities. It has been repeatedly found that carboxylate ester is a major, if not the major, reaction product, and is present in quantities far too great to be accounted for in this way.

The absence of SO_2 in the decomposition of MAAS or DMAS is not accounted for by this mechanism, and this reaction mechanism is not thought to make any significant contribution to effects observed in the present study.

There is a certain amount of evidence to support the view that the catalyst and monomer react to produce an adduct which is less reactive than the original alkoxide, possibly due to steric hindrance. This would, for example, provide some explanation of the relationship between the catalyst concentration and the final yield of solid product, as well as accounting for the limited quantities of SO_2 evolved.

However, such an interpretation fails to explain why there is clear evidence of propagation for the GAAS/ZMA reaction, and, more particularly, why the injection of GAAS into an active LAAS/ZMA reaction should result in a marked increase in the rate of evolution of SO_2. Furthermore, it fails to account for the formation of limited quantities of α-ester in the reactions involving MAAS or DMAS. Therefore this scheme would need substantial modification before it could be accepted.

The precipitation observed during the course of the reaction suggests the possibility that the catalyst and monomer react together to form an adduct which is less soluble than the original catalyst, and that as the reaction proceeds, the number of available active catalyst sites is progressively reduced by precipitation of the adduct.

Some of the principal features of the kinetic data recorded and observations noted certainly lend support to this interpretation. It accounts for the fact that the onset of gel formation and the decrease in the rate of reaction are parallel events, and that the yield of solid product is directly proportional to the amount of catalyst initially present. The decrease in the reactivity of the monomers may to some extent be account for in terms of increasing steric hindrance.

However, closer examination of this general scheme reveals certain important flaws. It fails to account for the absence of any measurable pressure rise, despite α-ester formation, for the reactions involving MAAS and DMAS, neither does it explain the apparent two-stage nature of some of the reactions studied. Furthermore, it offers no explanation of the observed increase in activity when GAAS was injected into an active LAAS/ZMA system. In more fundamental terms there is no <u>a priori</u> reason why the catalyst monomer adduct should be less soluble than the original catalyst itself, particularly when the substituents on the monomer are alkyl or aryl in nature. The failure of this scheme to incorporate these points satisfactorily means that such a scheme must be discarded or at least substantially revised.

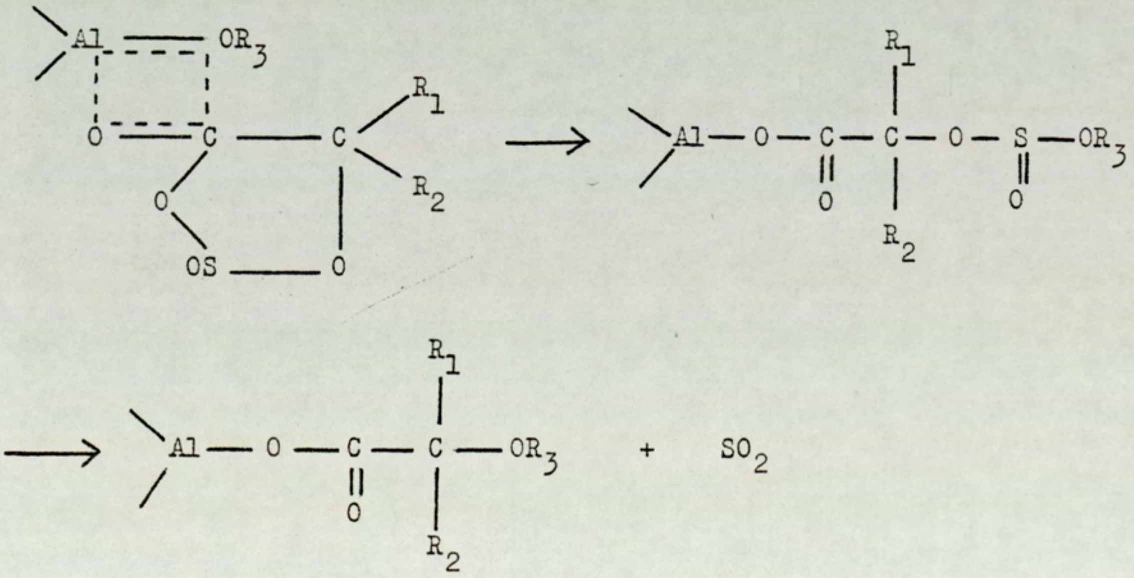
Previous reports relating to the polymerisation of both anhydrosulphites and anhydrocarboxylates have shown that the mechanism of reaction has always involved, at some stage, an α-lactone intermediate. In marked contrast to these reports, particularly that of Crowe(41), the results of the present study show conclusively that no such intermediate is involved.

Consideration of the results of the present study, in the light of work by Tessyie(68), suggests that a more likely scheme of reaction is that involving the aluminium-oxygen bond as part of a four-membered ring. Tessyie(68) has shown in studies of the polymerisation of propriolactone and pivalolactone in the presence of catalysts of the present kind, that the degree of substitution on the ring plays a crucial part in determining the mode of addition of the monomer to the catalyst molecule, and that more than one mode of addition may be involved in any single reaction system.

Thus the possibility that more than one mode of addition may be involved in the present reactions warrants serious consideration. The various possible modes of addition of anhydrosulphite monomers will now be considered. The possible reactions involving anhydrocarboxylates will be discussed at a later stage.

9B4 The C-4 Carbonyl Addition

In the light of earlier work on anhydrosulphites, and by comparison with that reported on lactones, it is thought that the most likely mode of addition of the monomer is that involving the C-4 carbonyl as shown in equation (30):



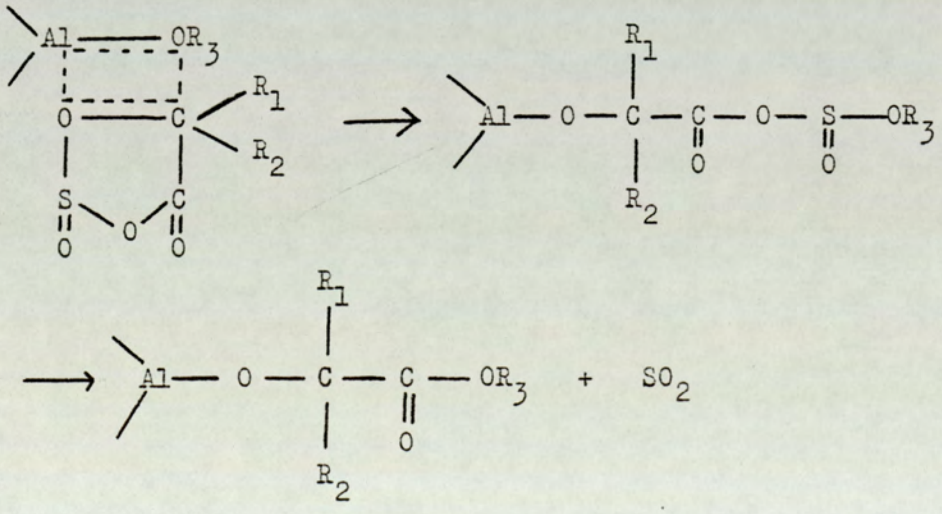
.... (30)

The final reaction products are metal salt and gaseous sulphur dioxide. It has been found that the metal salt is not capable of causing further monomer decomposition. It is thought unlikely that the second aluminium-tertiary butoxide bond would be involved in reactions involving monomer decomposition on steric grounds.

This reaction is similar in some respects to the NCA mechanism discussed earlier (section 9B1). The attack of the nucleophilic oxygen in the alkoxide may well precede the establishment of the four-centred intermediate proposed, though of course this latter intermediate is not found in the NCA mechanism. Of the possible major modes of addition, this is the least sensitive to the steric hindrance offered by the substituents at the C-5 position and accounts for the major component of the solid product being metal salt.

9B5 The One-Five Addition

A second mode of addition is that involving the one-five positions in the ring to form an intermediate which loses sulphur dioxide with the formation of α-ester, thus

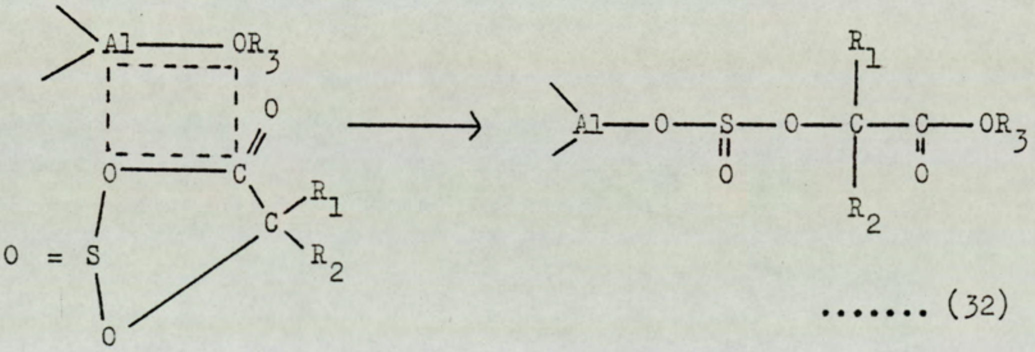


.... (31)

Naturally this mode of addition would be more sensitive to the degree of steric hindrance offered by the substituents attached to the monomer, especially if repeated addition at the aluminium-oxygen bond is involved. This sensitivity is reflected in the fact that there is no evidence of such reaction in the case of LAAS, whereas GAAS is capable of undergoing such a reaction albeit to a limited extent. It is thought that the modes of addition discussed in sections 9B4 and 9B5 represent major reactions. Further possible modes of addition will now be considered.

9B6 The Three-Four Addition

A further mode of addition, again four-centred, involves the C-4 carbon and the O-3 atoms, thus



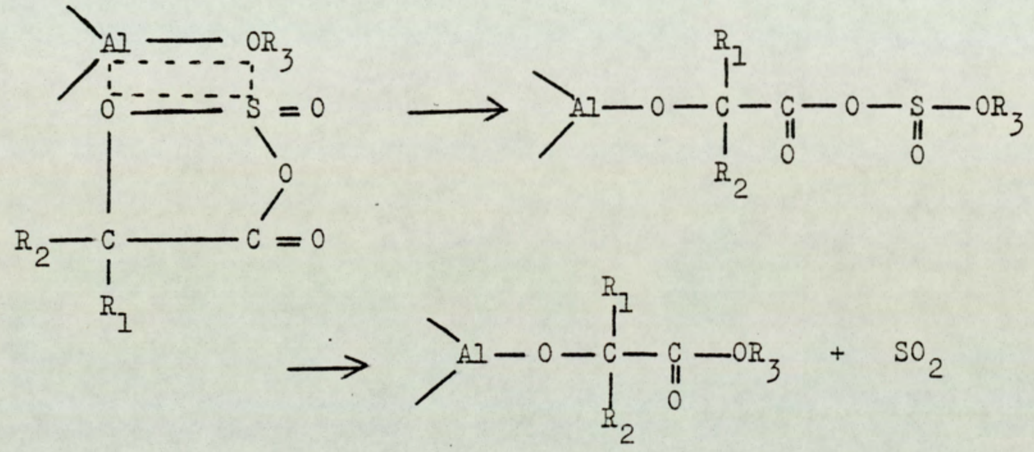
.... (32)

The product of this reaction would of course not be capable of taking part in further ring opening reactions. Whilst such a reaction is feasible, it is thought unlikely that it would make a significant contribution to the present reaction scheme. Any attack involving the C-4 carbon is much more likely, on electronic grounds, alone, to involve the C-4 carbonyl.

9B7 Additions Involving the S-2 Atom

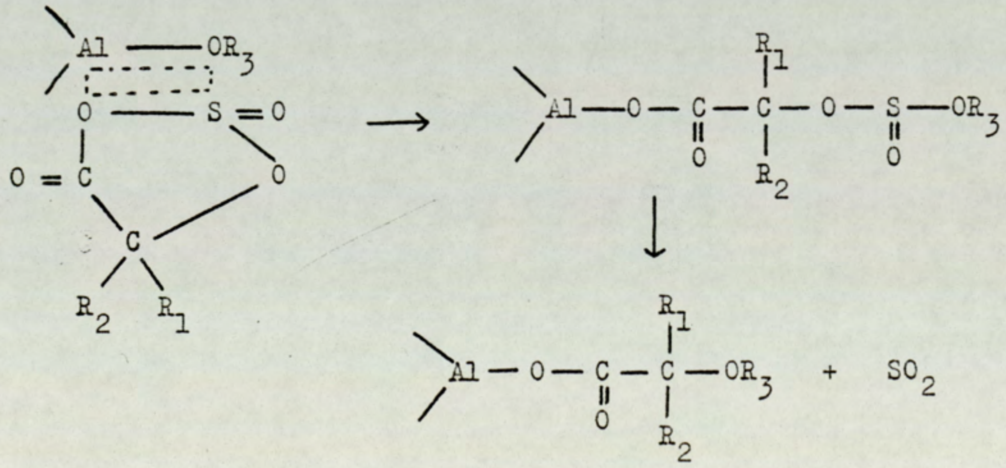
There are three possible modes of addition involving the S-2:

a) The first also involves the O-1 atom and, if correct, would result in the formation of α-ester, thus



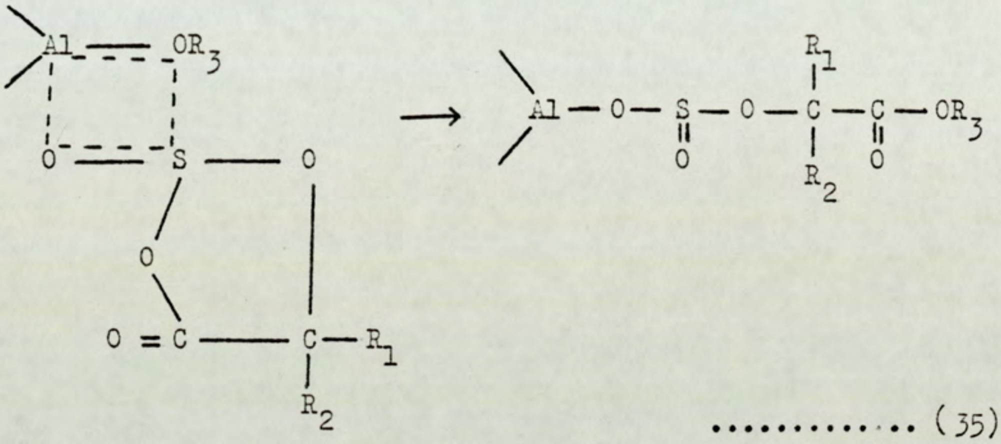
.... (33)

b) A second mode of addition involving the S-2 atom also involves the O-3 atom and, if correct, would result in the formation of metal salt as shown in equation (34)



.... (34)

c) The third and final mode of addition involves the S-2 position alone, thus



.... (35)

These modes of addition, involving the S-2 atom, present at first sight an attractive proposition. The formation of both α-ester and metal salt is accounted for, and the reaction outlined in (35) would result in the destruction of a potentially active catalytic site, and would go some way to accounting for the observed limited extent of the reactions studied.

However, a more careful consideration of the probability of attack involving the sulphur atom of the anhydrosulphite ring shows that this is unlikely and detracts considerably from the credibility of any mechanism in which such attack is involved. The attack of alkoxide on an NCA occurs much more readily at the C-4 carbonyl than at the C-2 carbonyl.(69) This difference is attributed to the less electrophilic nature of the C-2 carbon and hence its electronegative situation in the ring. Attack by an alkoxide group on the sulphur atom, which is itself a fairly strong nucleophile, in a similar environment, is therefore regarded as highly unlikely. The probability that any of the mechanisms outlined in section 9B7 make any contribution to the overall mechanism of reaction is therefore regarded as remote.

It is proposed that the decomposition of anhydrosulphites in the presence of the present catalyst may take place by two possible reactions which are not necessarily mutually exclusive. The mechanisms of these reactions have been outlined in sections 9B4 and 9B5.

It is consistent with the known susceptibility of the C-4 carbonyl in anhydrosulphites to nucleophilic attack that the principal mode of addition of the monomer to the catalyst should involve this site (equation (30)). The metal salt generated by this reaction is the major solid reaction product in all cases and is not thought capable of causing further monomer decomposition. It is very similar to the carboxylate ester first reported by Crowe.(41)

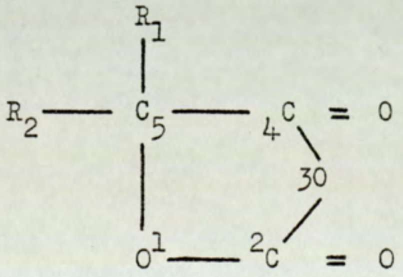
The production of α-ester occurs by the mechanism outlined in equation (31) and is more limited. This is consistent with the known characteristic of anhydrosulphite rings, in that the O-1 atom is not usually involved in the site for catalyst addition. Naturally since the C-5 atom is also involved, this mode of addition is very sensitive to the size of the substituents on the C-5 atom. The sensitivity of this mode of addition to steric factors accounts for the general absence of significant propagation.

The formation of a gel during the course of the reaction means that the reaction system rapidly acquires a three-phase nature. The ease of evolution of sulphur dioxide is thought to be restricted to some extent by the presence of the gel, and the absence of any detectable quantities of sulphur dioxide in the reactions involving MAAS and DMAS is attributed to the failure of the very limited quantities of sulphur dioxide evolved to escape from the gel phase. Naturally it would follow from this that the solid products would contain sulphur, and where such determinations were possible, this theory is supported. Entrapment of sulphur dioxide in this way has not been previously encountered, and was not anticipated when preparing the solid reaction product for infra red analysis; the percentages of sulphur reported must therefore be regarded as indicative rather than quantitative.

Many of the features proposed in the mechanisms for the reactions of anhydrosulphites may be extended to the discussion of the reactions between anhydrocarboxylates and the present catalyst. As in the case of anhydrosulphites several modes of addition warrant serious consideration whilst others, though apparently feasible, are in fact unlikely to make any contribution to the overall reaction scheme. This latter group will be dealt with first.

9B8 Additions Involving the C-2 Atom

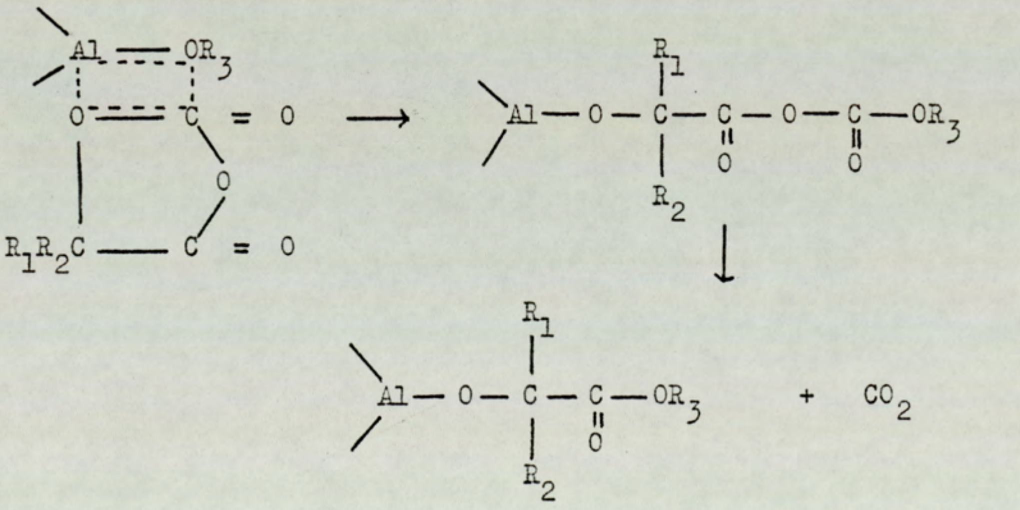
There are three possible modes involving the C-2 atom, those involving O-1 atom and the O-3 atom respectively,



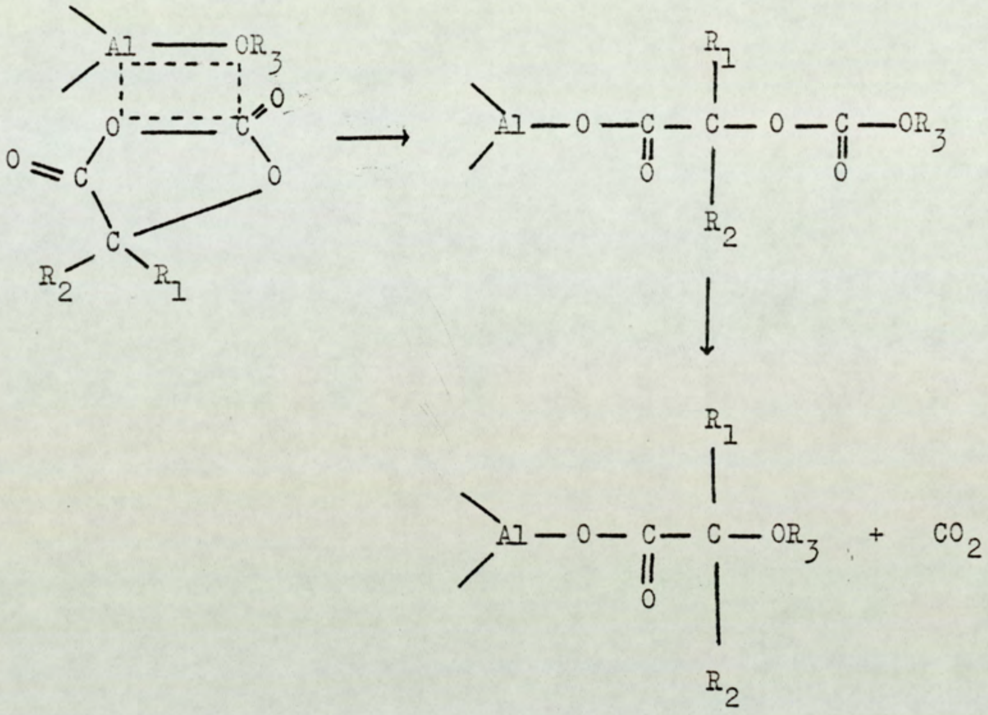
and a third involving the C-2 carbonyl. These modes of addition are analogous to those discussed in section 9B7 relating to additions involving the S-2 atom in anhydrosulphites.

The C-2 carbonyl in the anhydrocarboxylate ring is far less susceptible to nucleophilic attack than the more electropositive C-4 carbonyl. Studies of the initiated polymerisation of anhydrocarboxylates using various alcohols(60) and pyridine and related compounds(54,60) confirm this and in all cases the attack of the initiator at the C-4 carbonyl has been shown to be the first stage in the production of α-ester. It is therefore not anticipated that attack by the present catalyst at the C-4 carbonyl makes any contribution to the overall reaction scheme.

The modes of addition of anhydrocarboxylates involving the C-2 atom and either the O-1 or the O-3 atoms result in the formation of α-ester and metal salt respectively, as shown in equations (36) and (37).



.... (36)

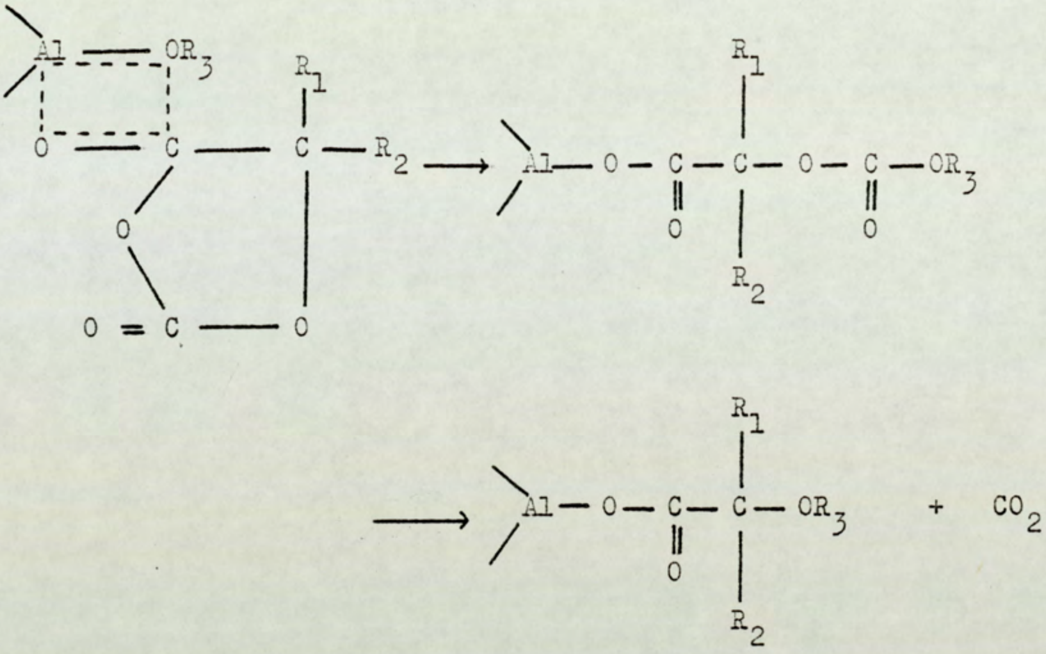


.... (37)

In both cases, however, the C-2 atom is involved, and for the reasons already outlined, it is thought that reactions involving this position are unlikely to make a significant contribution to the overall reaction scheme, though the possibility of such reactions taking place should be excluded altogether.

9 B9: 9B9 The C-4 Carbonyl Addition

All previous studies$^{(54,60)}$ concerning the initiated polymerisation of anhydrocarboxylates have shown that the C-4 carbonyl is the most likely site of attack. It is suggested that the attack of the nucleophilic alkoxide results in the formation of a four-centre intermediate which subsequently yields metal salt and carbon dioxide, thus

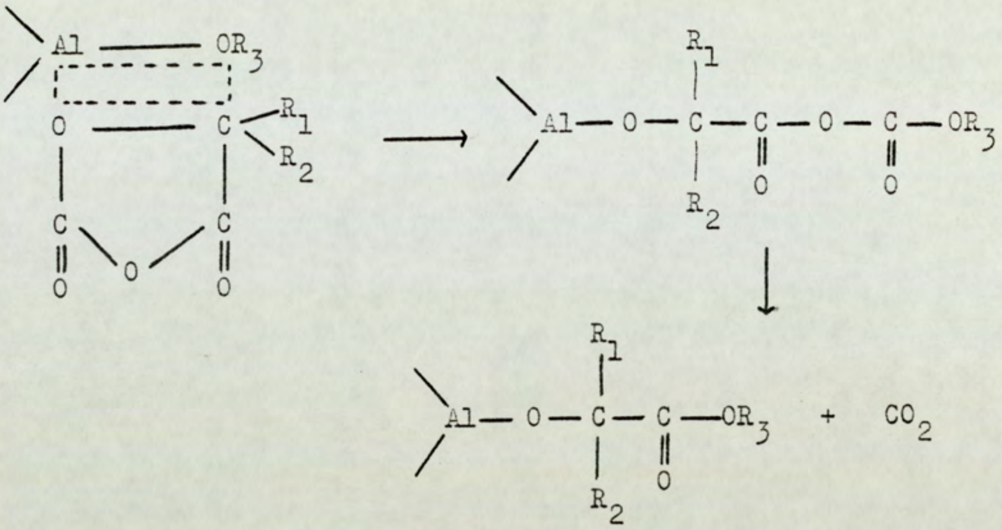


.... (38)

The metal salt thus generated is not thought capable of being involved in the decomposition of further monomer. Support for this mode of addition making a major contribution to the overall reaction scheme is not confined to theoretical considerations or previous experience. Infra red analysis (Figures V and XI) shows this kind of carboxylate ester, first reported by Crowe(41), to be a major reaction product. It is characterised by the broad peak at 1600 cm^{-1}, and is present in the I.R. spectra of the solid products of the reactions between the present catalyst and both anhydrocarboxylates and anhydrosulphites.

9B10 The One-Five Addition

It is thought that a second major mode of addition is that involving the one-five positions to form an intermediate which yields α-ester with the loss of carbon dioxide.



.... (39)

This mode of addition is, of course, more sensitive to the size of the substituents on the C-5 atom than the addition involving the C-4 carbonyl, though the evidence of the present study suggests that this sensitivity is less marked than in the case of anhydrosulphites.

It can now be seen that the reactions of both anhydrosulphites and anhydrocarboxylates have certain major features in common. In both cases the major mode of addition involves the C-4 carbonyl to generate a four-centre intermediate which produces metal salt and the respective gaseous oxides. The production of α-ester occurs by a similar mechanism, this time involving the one-five position in the monomer. The reactions conducted in the presence of tertiary butanol show conclusively that no α-lactone intermediate is involved in any of the reactions involving either class of monomer. All previous reports(41,54,60) relating to the initiated decomposition of both anhydrosulphites and anhydrocarboxylates have emphasised the importance of α-lactone as a reaction intermediate, and the present report represents the first study in which no such species is present.

The comparatively high solubility of bimetallic oxoalkoxides has been attributed to the fact that the aggregated-compact oxide like structure is surrounded by a lipophilic layer of alkoxy groups.(53) It is suggested that the reaction of the catalyst with either class of monomer results in the gradual breakdown of this lipophilic layer to produce an organo-metallic species which is far less soluble than the original catalyst. This idea is supported both by the highly negative entropy of activation reported earlier ($- 142.44$ J.K.$^{-1}$ mol^{-1}) and the progressive formation of an insoluble gel that has become a characteristic of these reactions.

Despite the many similarities in the reactions between ZMA and both anhydrocarboxylates and anhydrosulphites, it is evident that there are also major differences, particularly with regard to α-ester production. In view of the identical modes of addition of the monomers to the original catalyst, the differences must lie in the nature of the monomers themselves and their relative ease of loss of their gaseous oxides.

Studies of the thermal polymerisation of the two types of monomer have shown that anhydrosulphites are considerably less thermally stable than their equivalent anhydrocarboxylates. The data in Table XV illustrates this point.

Table XV

Compound	R_1	R_2	First Order rate constant X 10^7
DMAS	CH_3	CH_3	500
DMAC	CH_3	CH_3	1
DBAS	n-C_4H_9	n-C_4H_9	2560
DBAC	n-C_4H_9	n-C_4H_9	0.75

This marked difference is explained in terms of both electronic and steric factors.

N.M.R. studies on both types of rings have shown(60) that whereas the anhydrocarboxylate ring is a planar molecule, the anhydrosulphite ring is puckered at the position of the S-2 atom. The introduction of a sulphur atom at the two position in place of a carbon atom results in a marked increase in the degree of strain in the cyclic structure and part of this strain is relieved by this ring 'puckering'. Naturally, in view of this comparatively high degree of ring strain, which is amplified by increasing the size of substituents at the C-5 position, the anhydrosulphite monomer is far more susceptible to thermal decomposition.

Tighe and Blackbourn(18) have shown the importance of some electronic effects in anhydrosulphites. The inductive effect due to the presence of n-alkyl groups at the C-5 position was shown to correlate well with the rate of decomposition. However, the change in inductive effect in changing from methyl to n-butyl is small and has only very limited effect on the actual rates of decomposition of anhydrosulphites. In view of the more symmetrical distribution of electrons in anhydrocarboxylates, it is anticipated that they would be even less sensitive to such effects.

It is suggested that as far as the present study is concerned, the crucial difference between the two monomers is that of size. The anhydrocarboxylate is a small, more compact ring, and its comparative ease of addition to the catalyst is shown by the fact that GAAC reacts twice as rapidly as GAAS under the same conditions (initial rate X 10^5 being 3.34 and 1.64 respectively). Indeed, even the more substituted DMAC reacts more rapidly than GAAS (initial rate

X 10^5 = 1.91). Furthermore, infra red analysis shows that α-ester production is far more extensive in anhydrocarboxylates. The ease with which α-ester is formed is a reflection of the ease with which the monomer can undergo one-five addition as outlined in equations (31) and (38). Of the proposed major additions, this mode is the most sensitive to steric factors, and it is thought that the smaller, more compact anhydrocarboxylate is more capable of undergoing such addition.

CHAPTER 10

CONCLUSIONS

The decomposition of anhydrosulphites and anhydrocarboxylates in the presence of a bimetallic oxoalkoxide has been examined for a range of monomers.

The preparation of a range of monomers of both kinds was found to present no fundamental difficulty providing conditions were rigorously anhydrous, and the range of techniques available for monomer synthesis has been extended to include the use of a lithium salt. This method has proved successful in the synthesis of lactic acid anhydrosulphite and there is no a priori reason why it should not be extended to other monomers. The purification of the monomers prepared followed established methods. The problems of monomer decomposition during distillation encountered by Crowe(41) have not been found. This is consistent with the suggestion that the basis of this problem lies in the size of the substituents on the ring.

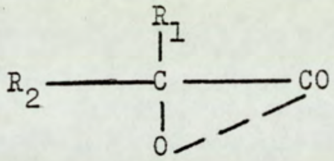
The decomposition of anhydrosulphites in the presence of ZMA proved to be far more complicated than had been anticipated. The formation of a metal salt had previously been encountered by Crowe(41) in his studies involving lithium tertiary butoxide. He also found that the relative proportion of α-ester and metal salt, as indicated by I.R. studies, decreased with increasing catalyst concentration, which is the reverse of the present findings. Furthermore, Crowe found that at very low catalyst concentrations α-ester was formed to the almost total exclusion of metal salt. In the present study, the formation of metal salt has been found to be the major reaction. However, it is now clear that the mechanisms of the present reactions differ fundamentally from those studied by Crowe(41) in that an α-lactone intermediate is not involved.

The possibility that the mechanism involves more than one mode of addition of the monomer to the catalyst molecule, which is of fundamental importance in the interpretation of the findings of the present study, was not thought to make any significant contribution to the mechanism of the reactions studied by Crowe(41). In no case did the reaction involving ZMA and an anhydrosulphite generate significant quantities of α-ester. This fact alone casts doubt over the value of any detailed investigation of the mechanism of these reactions.

In marked contrast, the reactions involving ZMA and the anhydrocarboxylate monomers were far more successful in terms of α-ester formation. The most productive monomer in this area was glycollic acid anhydrocarboxylate, again reflecting the sensitivity of reactions of this type to steric hindrance. The steric limits of anhydrocarboxylate monomers have yet to be defined, but other fundamental features of the mechanism have been established.

In no case was there any evidence of any 'living polymer' behaviour as reported by Tessyie(53) in relation to lactone polymerisation. This would seem to be a result of the separation of the reaction mixture. In no case did injection of further monomer into a reaction where activity had ceased produce any detectable pressure rise.

The four-centred nature of the reaction mechanism is without doubt the most striking feature of the present study. The formation of an α-lactone



∝-lactone

has been a fundamental feature of the polymerisation of monomers of this kind, and in many cases its formation has been the rate determining step of the reaction. The presence of ∝-lactone is readily detected, since any reaction in which it is thought to occur may be carried out in the presence of a reagent such as tertiary butanol. The reaction between an ∝-lactone and such a molecule is extremely rapid and generates low molecular weight ester, which is readily detected. It has been demonstrated quite clearly (Figures XXXVI and XXXVII) that no such product is present. The present study thus represents the very first involving the polymerisation of monomers of this kind in which an ∝-lactone intermediate is not involved.

The results of the study of the decomposition of GAAC in the presence of pyridine further demonstrates the suitability of this method for synthesising poly-∝-ester. Interpretation of the extrathermodynamic data, in the light of the work of Smith(60) and Kosolsummolamus(54), shows that steric rather than electronic considerations are of greater significance in deciding the susceptibility of monomers to decomposition and subsequent polymerisation. The data recorded herein further extends the range of monomers polymerised in this way, and is another step towards establishing a final scale of relative reactivities of anhydrocarboxylates which would enable copolymerisation studies to be conducted.

SUGGESTIONS FOR FURTHER WORK

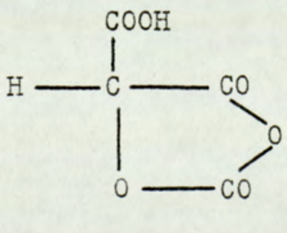
The ring opening polymerisation of either the anhydrocarboxylates or the anhydrosulphites of α-hydroxy carboxylic acids is a proven method of preparing poly-α-ester. Whilst certain methods of polymerisation are established and successful, there are still areas of great potential to be explored.

The decomposition of anhydrocarboxylates in the presence of ZMA has been shown to yield significant quantities of α-ester. The steric limitations of these reactions have yet to be established, though it is clear that the nature of the C-5 substituents exerts a less marked influence than in the case of anhydrosulphites. There is considerable evidence that reactions involving catalysts of this nature are sensitive to the nature of the solvent used. The solvents used in the present experiments, dekalin, p-xylene and toluene, have proven suitable, but there is no evidence to suggest that this range is in any way exclusive. Naturally, the range of potential monomers will be restricted by the sensitivity of the monomers, and it is not anticipated that it would be as broad as in the case of oxiranes or lactones, but its exact limits and influence remain to be established.

In studies of the kind reported herein, the use of vacuum apparatus also imposes restrictions on the nature of the solvents that can be used. A high boiling point is a prerequisite if kinetic measurements are not to be interfered with. The use of high boiling point solvents, however, can increase the difficulty of product isolation. Thus it is relevant to examine the possibility of other means of studying the reactions, and the possibility of using a spectroscopic technique is worthy of serious consideration.

The range of potential catalysts reported by Tessyie(44) is extremely broad. The range of catalysts that have been studied is at present narrow, though constantly expanding in work relating to lactones and oxiranes. Two immediate possibilities arise in relation to the present work. Firstly, the choice of a catalyst in which the alkyl group is linear. This would increase the size of catalytic aggregates quite markedly, and may prevent the separation of the reaction mixture that has been a feature of the present work. Furthermore, it would be of great interest to see if the steric restrictions imposed by the monomer were in any way related to the nature of the alkyl group. A second change that would be of great interest would be the alteration of the central metal atom (zinc) to a transition metal. The range of studies reported by Tessyie(53) relating to lactones in which cobalt was used as a central metal would provide an interesting basis for comparison.

In the area of pyridine initiated decomposition of anhydrocarboxylates, the areas of potential development are perhaps better defined. The establishment of an accurate scale of relative monomer reactivities under identical conditions would be of enormous benefit, since it would allow the development of copolymers of a controlled composition. There is the potential that the copolymers produced could contain reactive side groups. For example, the anhydrocarboxylate of tartronic acid



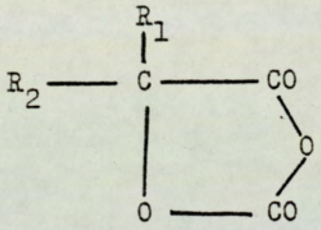
would generate a polymer (or copolymer) with pendant carboxylic acid groups. Such a material would be of enormous interest in the development of polymeric materials for biomedical application and water purification. Its properties could be adapted by copolymerising it with other monomers.

The possibility of polymerising anhydrocarboxylates in the presence of a lithium alkoxide has yet to be examined. The problem of solubility encountered by Crowe has diverted attention to other catalyst systems. In view of the marked difference in reactivity between anhydrosulphites and anhydrocarboxylates encountered in the present study, it is possible that this would be a highly rewarding area of further study. Comparison of the results with the work of Crowe(41) and the studies reported herein would greatly clarify the potential of metal alkoxides in this area of ring opening polymerisation and thus provide a firm basis for further research that would be both relevant and productive.

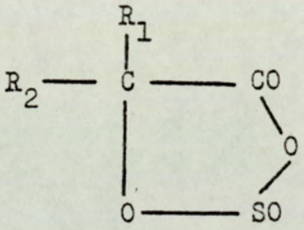
APPENDIX

Nomenclature

The work presented in this thesis has been concerned with the ring opening reaction of cyclic compounds of the following types:



(a)



(b)

Their systematic names are respectively (a) 1,3-dioxolan 2,4-dione and (b) 1,3,2 dioxathiolan-4-one-2-oxide. However, they are more commonly known as (a) α-hydroxy carboxylic acid anhydrocarboxylate and (b) α-hydroxy carboxylic acid anhydrosulphite, for example glycollic acid anhydrocarboxylate and lactic acid anhydrosulphite. For convenience, abbreviations such as LAAS for the latter case have been used throughout the text.

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